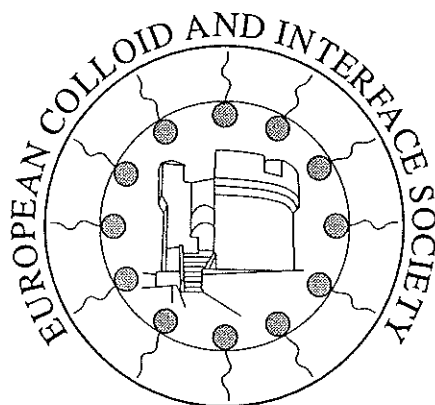


12th Conference of the European
Colloid and Interface Society

BOOK OF ABSTRACTS

LECTURES

POSTERS



Dubrovnik-Cavtat, Croatia
SEPTEMBER 20-25, 1998

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FOREWORD

The Organizing Committee has both the privilege and obligation to welcome in Dubrovnik and Cavtat the delegates from Europe, U.S.A. and Israel at the 12th Conference of the *European Colloid and Interface Society*.

It is our great pleasure to offer you this *Book of Abstracts* which contains 148 abstracts reflecting the work of over 355 contributors from many different countries.

We would like to express our gratitude to the members of the Scientific Committee; they helped us in the difficult task of selecting the contributions for oral or poster presentations. Indeed, their work will continue after the conference is finished, by participation in the refereeing procedure for the scientific works that will be submitted for publication in the book "*Trends in Colloid and Interface Science XIII*" from the series *Progress in Colloid & Polymer Science*.

Special thanks go to all contributors who worked hard to create new scientific approaches. We hope that participants will enjoy all the aspects of the conference: the presented results, lively discussions in the conference room as well as in front of posters, which will be open for discussion all the time, and the "beach talks."

We are glad to be able to grant a very low conference fee to young scientists.

The Organizing Committee gratefully acknowledges the financial support from the European Colloid and Interface Society and from the Croatian organizations listed on the next page.

Durdica Težak

The Organising Committee sincerely thanks the following organizations for their sponsorship of 12th Conference of the European Colloid and Interface Society ECIS98.



Croatian National Tourist Board



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Industry of Building Materials, Jerovec

ORAL COMMUNICATIONS

MONDAY, 21.09.1998

AMPHIPHILIC SYSTEMS

8.30-8.40 OPENING OF THE CONFERENCE

8.40-10.20

*Key-note lecture***L1 Phase Changes in Colloid Science**

Ronald H. Ottewill

*Invited lecture***L2 From perforated vesicles to dispersed reversed phases. A random walk among self-assembled lipid structures**

Mats Almgren, K. Edwards, J. Gustavsson

L3 Structural investigations of biological amphiphiles

Doris Orthaber and Otto Glatter

10.20-10.40 COFFEE BREAK

10.40-13.00

*Invited lecture***L4 Micelle polymorphism in lyotropic-nematic and lyotropic-cholesteric phases**

Hans Dieter Dörfler

L5 Titration calorimetry of DNA-cationic liposomes interactions

Paula C. A. Barreleiro, Paschalis Alexandridis, B. Lindman and G. Olofsson

L6 Single-molecule visualization of the interaction between DNA and oppositely charged mixed liposomes

Yuliya S. Mel'nikova, Sergej M. Mel'nikov and Jan-Erik Löfroth

L7 Structure and stability of DNA - cationic surfactant complexes

Siobhan Morrissey, E. Kudryashov, K. Dawson and W. A. Buckin

L8 Electrostatic correlations fold polyelectrolytes

Malek Kahn, S. Melnikov and Bo Jönsson

L9 Order in phospholipid Langmuir-Blodgett layers and the effect of the electrical potential of the substrate

J. Mieke Kleijn and Junlin Yang

L10 Micellar growth and interaction in the ternary system C12E5/decane/water

Ulrich Menge, P. Lang and G. H. Findenegg

13.00-16.00 LUNCH AND AFTERNOON BREAK

16.00-21.00 DEPARTURE TO DUBROVNIK, CEREMONY IN DUKE'S PALACE, CONCERT OF CAPELLA RAGUSINA, FREE TIME IN DUBROVNIK

TUESDAY, 22.09.1998

8.30-10.00

*Invited lecture***L11 The liquid crystalline properties of colloidal suspensions of vanadium pentoxide**

Patrick Davidson, O. Pelletier, C. Bourgaux and J. Livage

L12 A gel phase of densely packed unilamellar vesicles: structure and kinetics of formation

Michael Gradzielski, M. Müller, M. Bergmeier and H. Hoffmann

L13 Stable and transient states of phospholipid hydration

P. Laggner, K. Pressl, G. Pabst, M. Rappold and H. Amenitsch

L14 Occurrence of two critical points in lamellar phases of ternary systems

Thomas Zemb, L. Belloni, M. Dubois, I. Rico Lattes and F. Ricoul

10.00-10.20 COFFEE BREAK

10.20-12.50

Invited lecture

- L15 Double emulsions - recent developments**
Nissim Garti
- L16 Do lecithin worm-like micelles behave as equilibrium polymers?**
Ger J. M. Koper
- L17 A small-angle neutron scattering (SANS) study of aggregates formed from aqueous mixtures of an anionic and cationic surfactant**
Magnus Bergström, Jan Skov Pedersen, Peter Schurtenberger and Stefan U. Egelhaaf
- L18 Solubilization of silicone oils in flat and curved surfactant monolayers**
B.P. Binks and J. Dong
- L19 Nanodisks with variable structural surface charge: in catanionic systems**
Monique Dubois, Th. Gulik Krzywicki and Th. Zemb
- L20 Non-adsorbing polymer mediated interactions between fluid membranes in lyotropic lamellar phases**
Christian Ligoure and Gérard Bouglet
- L21 Bilayer formation in water from new urea-based double-chain dimethylammonium amphiphile containing perfluorinated moieties**
Stéphane Szönyi, M. A. Jouani, A. Cambon

13-16 LUNCH AND AFTERNOON BREAK

16-18.00

Invited lecture

- L22 Measurements of interfacial curvatures and evidence for morphological transition in semi-fluorinated non-isometric microemulsions**
Sung-Min Choi, Pierandrea LoNostro and Sow Hsin Chen
- Invited lecture*
- L23 Microstructure and interfacial tensions in nonionic microemulsion systems**
Thomas Sottmann and R. Strey
- L24 Size distribution in emulsions**
Luigi Ambrosone, G. Colafemmina, M. Giustini, G. Palazzo and A. Ceglie
- L25 Spectroscopic study of polynucleotides in cationic W/O microemulsions**
Elisabetta Balestrieri, M. Giomini, A.M. Giuliani, M. Giustini, and A. Ceglie
- L26 Controlled micro-sized solid particles formation and matter transfer within emulsions**
Daniele Clausse and Ljepša Komunjer

18.00-20.00 COFFEE BREAK AND POSTER SESSION 1

WEDNESDAY, 23.09.1998

POLYMERS

8.30-10.00

Invited lecture

- L27 Shear induced alignment and textures in a micellar cubic crystals**
Gregoire Porte, F. Molino, J. F. Berret, O. Diat and P. Lindner
- L28 Surface properties of ice studied by atomic force microscope**
Astrid Döppenschmidt, M. Kappl and H-J. Butt
- L29 Adsorption of gelatin and surfactants to polystyrene**
S. Fiona Turner, S. M. Clarke and A. R. Rennie
- L30 Adsorption of ethyl(hydroxyethyl)cellulose on solid surfaces. Effect of hydrophobic modification and surfactant addition to the polymer layer**
Fredrik Joabsson, K. Thuressona and B. Lindman

10.00-10.20 COFFEE BREAK

10.20-12.10

Invited lecture

- L31 Nonionic micelles near the critical point - Micellar growth vs. attractive interactions**
Otto Glatter and R. Strey
- L32 Aggregation dynamics of the block copolymer L64 in aqueous solution**
M. Kositzka, P. Alexandridis, A.T. Hatton and J. F. Holzwarth
- L33 Characterization by fluorescence energy transfer of the core of polyisoprene-poly(methyl methacrylate) diblock copolymer micelles. Strong segregation in acetonitrile**
Karin Schillén, A. Yekta, S. Ni and M.A. Winnik
- L34 Fluidification of concentrated suspensions by adsorbed polymers and copolymers**
Françoise Lafuma, M. Gourmand and C. Poncet
- L35 Experimental characterization of dendrimer solutions**
Francesco Mallamace, P. Liseur, D. Lombardo, N. Micali, A. Romeo and L. M. Scolaro

12.30-19.00 CRUISING BY BOAT, PICNIC ON ISLAND LOPUD

THURSDAY, 24.09.1998

8.30-10.10

Invited lecture

- L36 Hydrogen bonds in organized monolayers**
Dietmar Möbius, O. Félix, C. Drexlerl and M. W. Hosseini
- Invited lecture*
- L37 Associating polymer-surfactant system**
Björn Lindman, L. Piculell, E. Marques, K. Thuresson, S. Nilsson, A. Khan and M. Miguel
- L38 Supramolecular structure of polysaccharide-cationic surfactant complexes**
Niklas Hedin and O. Regev
- L39 Interaction between cationic-anionic surfactant vesicles and oppositely charged polymers**
E. Marques, A. Khan, Maria da Graça M. Miguel and B. Lindman

10.10-10.30 COFFEE BREAK

10.30-11.10

- L40 Adsorption of a random copolymer polyelectrolyte on titanium dioxide**
Annabelle Pina, E. Nakache, B. Feret and P. Depraetere
- L41 Association mechanism of hydrophobically modified polyelectrolytes and interactions with surfactants. A ^{19}F NMR study**
Istvan Furó and I. Illiopoulos

INTERFACES

11.10-13.00

Invited lecture

- L42 Electrostatic and chemical interactions of ions in electrolytes and ionic point charge double layers**
Mirko Mirnik
- L43 Phase equilibria of polydisperse colloids**
Richard M. L. Evans, D. J. Fairhurst, W. C. K. Poon
- L44 Flocculation stability of weakly charged oil-in water emulsion droplets**
R. Aveyard, B. P. Binks, Jordi J. Esquena, P. D. I. Fletcher
- L45 Effect of the lecithin on the properties of b-lactoglobulin stabilized O/W emulsions**
Egle Bylaite, T. Nylander, R. P. Venskutonis
- L46 Surface light scattering from surfactant solutions**
John C. Earnshaw, M. W. D. Grattan, K. Lunkenheimer
- L47 Electrorheological effects in lecithin organogels**
Thomas Dürschmidt, H. Hoffmann, Y. A. Shchipunov

13.00-16.00 LUNCH AND AFTERNOON BREAK

16.00-17.00

Invited lecture

L48 Electrokinetic and rheologic characterization of titania suspensions of high solids fraction and high ionic strength microemulsion systems

Jarl Rosenholm, J. Gustavsson, M. Kosmulski, M. Jokinen and P. Mikkola

Invited lecture

L49 Conformal invariance in two-dimensional cluster-cluster aggregation

John C. Earnshaw and M. B. J. Harrison

17.00-17.20 COFFEE BREAK

17.20-19.00

L50 Silica stabilized multiple emulsions

Brian R. Midmore, T. M. Herrington

L51 Structure, dynamics and formation of the colloidal-liquid and colloidal-gel

Abdellatif Moussaid

L52 On the behaviour of non ionic surfactant in organic solvent: influence of water on the aggregation process and adsorption mechanism onto silica gel prehydrated or not

Serge Lagerge, J. Zajac, S. Partyka

L53 Linear growth and branching of reverse polymer-like micelles of lecithin

Yurii A. Shchipunov, H. Hoffmann

L54 On the mechanism of the solvation forces

L. B. Boinovich and A. M. Emelyanenko

19.00-20.30 POSTER SESSION 2

21.30 GALA DINNER

FRIDAY, 25.09.1998

EXPERIMENTAL TECHNIQUES

9.30-10.10

L55 Novel glycol silicate and their interaction with surfactant for the synthesis of mesoporous silicate

Kerstin K. Sattler, H. Hoffmann

L56 A difusing wave spectroscopy study of the viscoelastic moduli of acidified milk gel

E. O. Arikainen, J. C. Earnshaw

10.10-10.30 COFFEE BREAK

10.30-11.50

L57 Diffusing wave spectroscopy of flowing foam

John C. Earnshaw, J. O. Uhomobhi

L58 Quasi two-dimensional "Bubble method" for surface tension and contact angle measurements

Ljepša Komunjer, D. Clausse, D. Mutaftschiev

L59 Measuring the contact angle of individual colloidal particles

Markus Preuss, Hans-Jürgen Butt

L60 Organo silicon nanoparticles as optical tracers

Wolfgang Schaertl, K. Gohr, C. Graf, C. Roos, M. Schmidt

11.50 CLOSING OF THE CONFERENCE

POSTERS

POSTER SESSION 1

- P_{1,0} In Memoriam: Božo Težak (1907-1980), International Summer Schools/Conferences/Symposia, Croatia, 1969-1990**
Mirko Mirnik
- P_{1,1} Structural investigation on lecithin organogels**
Ruggero Angelico, A. Ceglie, U. Olsson, G. Palazzo
- P_{1,2} The purifying of mine waters from colloidal suspensions by flocculation**
Saule B. Aidarova, K. B. Musabekov, N. K. Tussupbayev, Sh. A. Muzdybayeva
- P_{1,3} Studies of phase behavior in sugar-derived surfactant systems**
N. Azemar, E. Moreno, I. Carrera, R. Pons, P. Bault, P. Godé, G. Goethals, P. Martin, P. Villa, C. Solans
- P_{1,4} Interactions of carboxymethylcelluloses with lamellar liquid crystalline systems**
Iris Bogen, J. Kötz, B. Tiersch
- P_{1,5} Shear induced thickening in aqueous solution of new thermosensitive amphiphilic copolymers**
Georges Bokias, D. Hourdet, I. Iliopoulos
- P_{1,6} Effect of short-range attractive interactions on the low-frequency electrical conductivity of water-in-oil microemulsions**
F. Bordi, C. Cametti, A. Di Biasio
- P_{1,7} Structural transition from catanionic surfactant salt to mixed cationic/anionic vesicles**
Marija Bujan, I. Šmit, N. Filipović-Vinceković
- P_{1,8} Adsorption parameters and selected performance of N-alkyl-N-methylaldonamides**
Bogdan Burczyk, K. A. Wilk, A. Sokolowski, L. Syper
- P_{1,9} Kinetics of ligand substitution at square-planar palladium(II) complexes in heptaneAOT-water microemulsions**
F. Paolo Cavasino, C. Sbriziolo, M. L. Turco Liveri
- P_{1,10} Synthesis and surface activity of polyoxybutylenated higher alcohol sodium sulfates**
Jan Chlebicki
- P_{1,11} Langmuir monolayers formed by a novel group of aromatic amphiphiles**
Patrycja Dynarowicz-Latka, J. Czapkiewicz, K. Kita, P. Milart
- P_{1,12} Physico-chemical properties of asymmetric catanionic surfactants: hexadecyltrimethylammonium alkyl sulfates**
Nada Filipović-Vinceković, V. Tomašić, S. Popović
- P_{1,13} Study of the relation between phase behavior, emulsification and emulsion properties**
A. Forgari, J. Esquena, C. Gonzáles, C. Solans
- P_{1,14} Formation of trichlorofluoromethane hydrate formation in W/O emulsions studied by differential scanning calorimetry**
B. Fouconier, V. Legrand, D. Clausse, L. Bergflodt, J. Sjöblom
- P_{1,15} NMR relaxation and diffusion studies of micelles and micellar components**
Istvan Furó, N. Hedin, R. Sitnikov, U. Henriksson
- P_{1,16} Morphology and structure of cadmium dodecylbenzenesulphonate under the influence of natural sea water**
Mirna Galešić, Đ. Težak, M. Tudja
- P_{1,17} Adsorption of surfactants as a condition of cleansing action**
A. El Ghzaoui, S. Partyka
- P_{1,18} Adsorption of dodecyl ammonium chloride on sea shell conches**
B. Homen, M. Bujan, J. Posavac, D. Grbeša, M. Sikirić
- P_{1,19} Direct analysis of SANS and SAXS measurements of catanionic surfactant mixtures by Fourier transformation**
Daniel J. Ianpietro, L. Brasher, E. W. Kaller, A. Stradner, O. Glatter
- P_{1,20} Structure and dynamics of vesicles from symmetrical double chain alkylbenzenesulphonates**
Nenad Jalšenjak, N. Judaš, I. Štefanić, S. Šegota, S. Haas
- P_{1,21} Properties of cationic surfactants in pure and mixed states**
Nada Filipović-Vinceković, M. Bujan, Iva Juranović

- P₁₂₂ **Experimental studies of two-dimensional foam**
A. Abd el Kader, J. C. Earnshaw
- P₁₂₃ **DMSO-induced dehydration of DPPC membranes studied by X-ray diffraction, calorimetry and small-angle neutron scattering**
Mikael A. Kiselev, P. Lesieur, A. M. Kiselev
- P₁₂₄ **Investigation of polyelectrolyte-surfactant interactions by surfactant selective membranes**
Sabine Kosmella, J. Kötz, K. Shirahama, J. Liu
- P₁₂₅ **Characterization of sea-surface microlayers by monolayer technique and Brewster angle microscopy**
Zlatica Kozarac, D. Möbius, M. T. Martin
- P₁₂₆ **Ionization degree of sodium 4-(4'-alkylphenylazo)benzoates in aqueous solution**
Tomasz Kozlecki, K. A. Wilk, R. Zielinski
- P₁₂₇ **Aggregates of surfactant cage molecules**
Anabelle Laplace, C. Larpent, Th. Zemb, J. Zhu
- P₁₂₈ **Stability of sponge-like fluid membranes**
T. D. Le, U. Olsson, H. Wennerström and P. Schurtenberger
- P₁₂₉ **Polyelectrolytes as stabilizers for colored form (cation) of some natural organic dyes**
A. Lopes, J. Lima, A. Maçanita
- P₁₃₀ **Electric potential near a single conducting ion channel in a charged membrane**
Victor Levadny, V. Aguiléll, M. Belaya
- P₁₃₁ **Ion permeability of a thin membrane with soft polar interfaces**
Victor Levadny, V. Aguiléll, M. Belaya
- P₁₃₂ **Neutron specular and off specular reflection from the Aerosol OT lamellar phase at the solid/solution interface**
Zhi Xin Li, C. C. Dong, J. Penfold, R. K. Thomas
- P₁₃₃ **Mixtures of spherical and rodlike colloids with polymer brush surfaces**
Gudrun Lindenblatt, A. Strack, W. Shaertl
- P₁₃₄ **A study of the behaviour of mixed monolayers of amphotericin B and dipalmitoyl phosphatidic acid from hysteresis experiments**
José Miñones Conde, J. Miñones, O. Conde, R. Seoane
- P₁₃₅ **A study of the stability of Amphotericin B monolayers**
José Miñones Conde, Rey Gómez-Serranillos, R. Seoane, O. Conde and M. Casas
- P₁₃₆ **Complex formation between poly(N-isopropylacrylamide) and ionic surfactants. Influence of the molecular weight of the polymer**
Y. Mylonas, G. Staikos, P. Lianos
- P₁₃₇ **Effects of the surfaces on the phase transition peculiarities in lyotropic nematics: Experimental study and a theoretical approach**
Arif Nesrullajev, F. Buyukkeliq, D. Demirhan, N. Kazanci, T. Yildiz
- P₁₃₈ **Mesomorphic and thermotropic properties of lyotropic nematic N_d and N_c mesophases**
Arif Nesrullajev, N. Kazanci
- P₁₃₉ **Interactions between hydrophobically modified polymers and surfactants. Effect of spacer between polymer backbone and hydrophilic tail**
Susanne Nilsson, Anna-Lena Kjöniksen, B. Nyström, K. Thuresson, B. Lindman
- P₁₄₀ **Characterization of microemulsions based on polymeric surfactant**
Mireia Plaza, C. Solans, K. Stickdorn, Th. F. Tadros, R. Pons
- P₁₄₁ **Polymer adsorption on porous and nonporous adsorbent modified by surfactant**
I. A. Polunina
- P₁₄₂ **Bicontinuous phases in a fluorinated non ionic surfactant - water system**
Marie-Helene Ropers, V. Schmitt, M. J. Stebe
- P₁₄₃ **Pressure-area isotherms. Behaviour of cyclosporin-pyrene-labelled phospholipids**
Isabel Sáñez, A. Suárez, A. G. Gonzales, I. Aristegui, J. Minones Trillo
- P₁₄₄ **Surface properties of stigmastanyl phosphorylcholine monolayers spread at the air/water interface**
R. Seoane, H. Minones Jr., E. Iribarnegaray, M. Casas
- P₁₄₅ **Phenomenon of the effective shear viscosity of thin wetting films**
Vladimir Smorodin

- P₁46 Phase transitions in insoluble monolayers of branched phospholipids**
Stefan Siegel, D. Vollhardt, H. Möhwald
- P₁47 Structure of modified particle aggregates in metal-filled polymer films**
V. I. Roldughin, V. V. Vysotsky
- P₁48 Theoretical studies on structure and molecular properties of N-alkyl-N-methylgluconamides**
Henryk Szymusiak, K. A. Wilk, R. Zielinski
- P₁49 Phase behavior in mixture of cationic and anionic surfactants: hehadecyltrimethylammonium bromide/sodium dodecyl sulfate**
Vlasta Tomašić, I. Štefanić, N. Filipović-Vinceković
- P₁50 Interfacial tensions in heptane-aqueous NaCl systems containing Aerosol OT and a second single-chain ionic surfactant**
Barbara Zielonka, A. Sokolowski
- P₁51 Influence of amphiphiles on the activity of native and immobilized phospholipase D**
N. Yu. Zonova, A. V. Chesnokov, E. V. Shumilina, Yu. A. Shchipunov
- P₁52 Biotransformations using lipases in microemulsion based gels**
Aris Xenakis and H. Stamatis

POSTER SESSION 2

- P₂53 Phase transformation of magnesium hydrogenureate octahydrate**
Vesna Babić-Ivančić, M. Jendric and N. Šoštarić
- P₂54 Measurement of partition coefficient between heptane and water of alkylpyridinium salts**
I. P. Baranova, N. N. Kochurova and V. N. Ivanov
- P₂55 A new methodics of drop edge recognition and its application for surface tension and contact angle measurement**
L. B. Boinovich and A. M. Emelyanenko
- P₂57 Scanning angle null ellipsometry**
René C. van Duijvenbode and Ger J. M. Koper
- P₂58 Contact angles and the transition between a Sessile drop and a wetting film studied by Monte Carlo simulation**
A. M. Emelyanenko and L. B. Boinovich
- P₂59 Characterization of surfactant solutions with density, viscosity and ultrasonic speed**
Gerhard Fritz, G. Sherf and O. Glatter
- P₂60 The effect of polymer adsorption on concentrated colloidal silica dispersions**
Andrea Hawkins, T. M. Herrington
- P₂61 Growth of silver iodide colloids investigated by dynamic light scattering**
Stanka Heimer, S. Šegota, D. Težak
- P₂62 Rheology of bimodal charge-stabilized polymer dispersions**
Frank M. Horn, W. Richtering
- P₂63 Dissolution of anionic surfactants. Effect of cations on the change of heat capacity**
Vesna Hrust, M. Skurić, Z. Šošić, N. Kallay
- P₂64 Spinodal decomposition in the viscous hydrodynamic regime**
Simon Jury
- P₂65 Measuring the temperature-dependence of surface forces**
Michael Kappl, H. Müller, H.-J. Butt, J. Rühle, J. Orth and W. Meyer
- P₂66 Interfacial tension between two binary metallic phases (not absolutely rigid approximation)**
Elena V. Kishtikova, A. A. Shebzukov
- P₂67 Binding of Cd²⁺ at goethite aqueous interface**
D. Kovačević, A. Pohlmeier, G. Özbas and N. Kallay
- P₂68 Effect of the porosity and relative polarity of MCM-41 materials on the adsorption of monomeric and dimeric cationic surfactants at the solid-water interface**
M. J. Meziani, J. Zajac, A. El Ghzaoui and S. Lagerge
- P₂69 Thermodynamic analysis of the surface of high-energy solids at macroscopic and microscopic levels**
V. Médout-Marère, J. M. Douillard, J. C. Giuntini, S. Partyka, S. Lagerge

- P₂70 Long-range interactions in disperse systems**
Tatjana V. Lokotosh, N. P. Malomuzh
- P₂71 Fluctuation effects in emulsions near the percolation threshold**
Nikolay P. Malomuzh, R. R. Stepanjan
- P₂72 Theories of colloid chemistry based on the point charge double layer model and their experimental verification**
Mirko Mirnik
- P₂73 Improvement of SAXS measurements by Göbel mirrors**
Doris Orthaber, A. Bergmann, G. Scherf and O. Glatter
- P₂74 Application of surfactants in emulsifying metalworking fluids**
Ljiljana Pedišić, M. Šviglin-Marasović
- P₂75 Hydrophobically modified polyelectrolytes stabilizing macroemulsions**
Patrick J. Perrin, N. Monfreux, F. Lafuma
- P₂76 Interfacial charge in mixed oxide aqueous suspensions**
T. Preočanin, D. Dodlek, Z. Brzović and N. Kallay
- P₂77 Mixed hydrogenated and fluorinated systems**
S. Rocca, M. J. Stebe
- P₂78 Direct measurement of depletion potentials in mixtures of colloids and non-ionic polymers**
Daniel Rudhardt, C. Bechinger, P. Leiderer
- P₂79 Rupture of aqueous wetting films**
H. J. Schulze, K. W. Stöckelhuber, Ph. Letocart, J. Mahnke and H. Partzsch
- P₂80 Structure factor and thermodynamics of concentrated colloidal dispersions**
Yu. V. Shulepov
- P₂81 Interactions in calcium oxalate hydrate/surfactant systems**
Maja Sikirić, N. Filipović-Vinceković, V. Babić-Ivančić, H. Füredi-Milhofer
- P₂82 Ultrasonic analysis of heat induced milk coagulation in calcium fortified milk**
Cormac Smyth, K. Dawson, V. A. Buckin
- P₂83 Surface migration of colloids adsorbed on mineral surfaces in the presence of organic molecules**
Olivier Spalla
- P₂84 Shape and line tension of water lenses at the dodecan/air interface**
K. W. Stöckelhuber, B. Radoev, H. J. Schulze
- P₂85 Potentiometric and DLS investigation of the precipitation of lanthanum fluoride**
Nada Stubičar
- P₂86 Aggregate structure and percolation properties of metal-filled polymer films**
V. V. Vysotsky, V. I. Roldughin
- P₂87 Dimensionality reduction induced melting**
Qi-huo Wei, Clemens Bechinger, Daniel Rudhardt, Paul Leiderer
- P₂88 Experimental observation of laser induced freezing melting in two-dimensional colloids**
Qi-huo Wei, Clemens Bechinger, Daniel Rudhardt, Paul Leiderer

LECTURES

L1 PHASE CHANGES IN COLLOID SCIENCE

R.H. Ottewill

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Following methods of preparing very monodisperse colloidal spheres at high concentrations it has been found that many molecular states have analogous states in colloidal systems. These can be observed in water as a dispersion medium where the spheres are charged. However, some of the clearest results have come from research with spheres in a nonaqueous environment. Under these conditions the spheres behave as "nearly hard spheres". In addition, the refractive index of the organic medium can be matched with that of the particles enabling light scattering techniques to be used to examine structures.

The gaseous, fluid, crystalline and glassy states can be recognised as well as coexisting states. The transition from fluid to crystalline occurs at a volume fraction of ca 0.5, very close to that theoretically predicted.

There are similarities with the phase changes observed in amphiphilic systems except that in the latter there is much stronger interaction with the medium.

Colloid Science covers a very wide field with many phenomena. Some consideration of these in terms of phase changes, in which entropic changes play a major rôle, can lead to some unification of the subject.

L2 FROM PERFORATED VESICLES TO DISPERSED REVERSED PHASES. A RANDOM WALK AMONG SELF-ASSEMBLED LIPID STRUCTURES

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Perforated vesicles may appear as intermediates when liposomes are solubilized by surfactants, before mixed micelles form at high concentrations. These vesicles are related to a defective region of the lamellar phase in systems of polar lipids with surfactants in water, which often extends in a narrow tongue towards the water corner. The defect bilayer is a compromise structure, between flat bilayers and cylinders. Polar lipids such as glycerolmonooleate form reversed (cubic, hexagonal) structures with water, and by adding a surfactant a succession of structures with increasingly positive curvature (curved towards the hydrophobic region) are created. An interesting aspect of these systems is the possibility to form particles (emulsomes) by dispersing the reversed phases. Hexasomes, dispersed hexagonal phases have been found, as well as cubosomes of both primitive and diamond cubic membranes.

L3 STRUCTURAL INVESTIGATIONS OF BIOLOGICAL AMPHIPHILES

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The functionality of biological amphiphiles strongly depends on the aggregation state of the compound, most likely because of differences in the interaction with all membranes and uptake by target cells. In addition to being relevant for interaction with cells and thus for the potential therapeutic efficiency of for example synthetic phospholipid analogs, their aggregation state and the stability of aggregates in body fluids is of importance. The type of aggregate formed by an amphiphilic molecule in solution depends on several variables, such as concentration, temperature, time, ionic strength, and ionic composition of the buffer. The type of aggregate formed under defined conditions, the size distribution of the particles, phase transitions as well as stability upon storage is examined by dynamic light scattering and small angle X-ray scattering.

The investigated systems are synthetic phospholipid analogs and sugar surfactants. In nature both of them serve several functions. For phospholipids, quantitatively, most important is their role as building blocks of cellular membranes. In addition, phospholipids are known that they are physiologically active by themselves. These new phospholipid analogs show remarkable activities against tumor cells, and they are antiviral, antiinflammatory and antipsoriatic agents. Most of the compounds are structurally related to glycerophospholipids. However, the type of substituents at the glycerol backbone and in the headgroup is quite different from that found in natural phospholipids or known phospholipid analogs, so that the aggregation behavior of the new compounds in an aqueous environment cannot be predicted.

The second group of investigated amphiphiles are sugar surfactants such as glycosphingolipids (gangliosides) or alkylpolyglucosides. Glycosphingolipids are involved in a variety of surface phenomena, such as cell-cell recognition and interaction, signal transduction, and they serve as receptors for toxins and viruses.

In this contribution we show results from dynamic light scattering and small angle X-ray scattering experiments for phospholipid analogs and sugar surfactants and demonstrate the possibility of structural research (structure and interaction) on these systems with scattering methods.

L4

MICELLE POLYMORPHISM IN LYOTROPIC-NEMATIC AND LYOTROPIC-CHOLESTERIC PHASES

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Behavior and properties of lyotropic mesophases in the binary system hexadecyldimethylammonium-bromide/water and the ternary system hexadecyldimethylammoniumbromide/water/n-decanol were studied. The following lyotropic phases were observed by microscopic texture observation: Hexagonal phase (H), lamellar phase (L_α), rodlike nematic phase (N_C) and disklike nematic phase (N_D). The positions of the corresponding regions in the binary and ternary phase diagrams were fixed.

Disklike lyotropic-cholesteric phases were induced in the disklike lyotropic-nematic matrix by adding optically active compounds. We have focused our attention of chiral compounds. When subjected to the influence of a magnetic field, the disklike lyotropic-cholesteric phase Ch_D shows the so-called spaghetti-like texture. This texture have been used to determine the pitch length. A linear relation between reciprocal pitch length and concentration of the optically active component was established and the helix twisted power (HTP) was calculated. The HTP values were dependend on the chemical structure of the optically active component.

The phase behavior and their alignment in magnetic field of the ternary system hexadecyldimethylethy-lammoniumbromide/water/n-decanol were investigated by texture observations and small-angle X-ray scattering in order to determine shape, size and aggregation numbers of micelles. A shape transformation of the micellar aggregates and changes of their aggregation number of chiral compound with asymmetric C-atom are found in the lyotropic-nematic matrix.

The chiral compounds large the micellar asymmetry and induce a chiral shape of micellar aggregates. It seems to us that the chiral elements are located in the head group region of the anisotropic micellare aggregates and diminish their asymmetry. In this case the mechanism of twisting is mainly caused by interaction in pairs of chiral molecules of adjacent micellar aggregates in the lyotropic-cholesteric phase. But details of the twisting mechanism occurring in this transition formation process from the lyotropic nematic into the cholesteric structure are not yet completely elucidated.

L5

TITRATION CALORIMETRY OF DNA-CATIONIC LIPOSOMES INTERACTIONS

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Gene therapy, *in vivo* transfection of cells with foreign nucleic acids, provides a general framework for curing (and not just treating) a great number of diseases [1]. The most efficient gene transfer vectors currently in use are viruses which involve complex technologies and suffer from severe limitations. Cationic liposomes appear promising but they suffer from low efficiency and toxicity at high concentrations, thus further work is necessary. The structure and morphology of these resulting complex has been studied by high resolution synchrotron angle x-ray scattering and cryo-TEM by several authors [2] and a lamellar and hexagonal structures were reported. However is not clear the relationship between system characteristics, structure and transfection efficiencies. Also the interactions between the cationic lipid and DNA and formation mechanism are still unknown.

In this study [3] we report the thermodynamics of the binding of cationic liposomes to DNA using isothermal titration calorimetry (ITC). An increase of the heat uptake was observed close to the charge neutralization point which suggest that the DNA-cationic liposomes interaction is mainly electrostatic. However the role of the hydrophobic domain of the cationic liposomes is also adressed. The enthalpy change and binding isotherm associated with this process were measured as a function of liposome size and composition (type of helper lipid in the liposome), charge ratio and solution conditions (pH, ionic strength) which allows the identification and understanding of some of the key parameters that affect the DNA-cationic liposomes interaction.

Fluorescence spectroscopy were also used to characterize the binding and cryo-TEM was used simply as a visual evidence at the molecular-level. The results were interpreted in terms of a model that allows the determination of the thermodynamic properties. Finally these results were compared with the binding of cationic polymers to DNA.

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L6

SINGLE-MOLECULE VISUALIZATION OF THE INTERACTION BETWEEN DNA AND OPPOSITELY CHARGED MIXED LIPOSOMES

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Medical therapies based on the introduction of genetic material into cells have gained increased interest during the latest years [1]. Specially, liposomes composed of mixtures of cationic and neutral lipids and complexed with negatively charged DNA have been shown to be one candidate delivery system to achieve the transfer of DNA to living cells. However, almost no studies have been carried out to describe the behavior of single DNA molecules in solutions in the presence of such liposomes.

In this work we present results from studies of the conformational behavior of giant single dsDNA in the presence of mixed DODAB/DOPE (dioctadecyldimethylammonium bromide/dioleoyl phosphatidylethanolamine) liposomes. The studies were carried out with a fluorescence microscopy technique, which has been reported earlier [2] in studies of DNA-surfactant interactions at the single-molecule level.

We found that the interaction between DNA chains and mixed liposomes started at very low lipid concentrations, far below the DNA concentration, which emphasized a high cooperativity of the process [2b,c]. Thus, even at the lowest liposome concentrations studied, the DNA molecules exhibited two limiting conformational states of an extended coil and a compact globule. When the liposome concentration reached a critical value, the conformational distribution of DNA chains became unimodal and all DNA molecules were found to be in a collapsed globular conformation. Interestingly, the critical DODAB concentration, corresponding to the transition observed, strongly depended on the liposome composition, i.e., on the molar ratio between cationic and neutral lipids. This effect might be explained both in terms of the surface charge density of the mixed liposomes and by taking into account the interplay between the DODAB-DNA complex formation and the degree of incorporation of the cationic lipid into the mixed liposomes.

In the examined system both reactants (negatively charged DNA and positively charged mixed liposomes) underwent a structural phase transition: DNA compaction and liposome disintegration. This structural reorganization in the system was also followed by cryo-TEM. Finally, the results were compared with results obtained with the dynamic light scattering technique on systems at higher concentrations, then giving the ensemble average results.

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L7

STRUCTURE AND STABILITY OF DNA - CATIONIC SURFACTANT COMPLEXES

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We have used a combination of optical spectroscopy, fluorescence and isothermal titration calorimetry techniques to study the binding of the cationic surfactant, dodecyltrimethylammonium bromide, to short fragments of DNA. The change in UV spectra of DNA on addition of the surfactant indicates conformational rearrangements of DNA helix. The UV melting curves the DNA-surfactant complexes show a biphasic transition at surfactant/phosphate ratio 1.2 and monophasic transition at lower and higher concentrations of surfactant. Overall the melting experiments demonstrate the dual effect of the surfactant acting as a helix stabiliser and destabiliser. The calorimetric titration curves also indicate the presence of two stages of binding of surfactant to DNA. The absolute values and the temperature dependence of the heat of surfactant binding observed is close to that expected for micelle formation on the DNA surface. In addition, the fluorescence of a hydrophobic probe in DNA solution was monitored as the ratio of surfactant to DNA was increased. The fluorescence change can be interpreted as the migration of the probe into the hydrophobic micelle-like environment at surfactant/phosphate ratios more than 1.2. The results are in agreement with previous work, which showed that the compressibility change on the binding of dodecyltrimethylammo-

nium bromide to DNA was similar to the compressibility change on micelle formation. Overall the results indicate a micelle like structure on the DNA surface.

L8 ELECTROSTATIC CORRELATIONS FOLD POLYELECTROLYTES

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DNA condensation and polyelectrolyte aggregation are phenomena indicating an effective attraction between monomers with charges of the same sign. Fluorescence microscopy have been performed showing that single DNA molecules goes through a coil-globule transition when the importance of electrostatic interactions are increased. The electrostatics of the polyelectrolyte system have been changed by altering the counterions, the dielectric constant (i.e. changing the solvent) and by changing the temperature.

Also Monte Carlo simulations have been performed for a single polyelectrolyte in a cell model, showing the same sort of condensation for the macromolecule when the electrostatic contributions to the free energy dominate. We believe that the attractive force is due to electrostatic ion-ion correlations which overcome the normal electrostatic repulsion between the monomers in the macromolecule. A simple free energy analysis, balancing the counterion entropy and the ion-ion correlation energy, can be performed to rationalize the importance of an attractive ion-ion correlation mechanism. This correlation is absent in the traditional mean-field (Poisson-Boltzmann) theory which always predicts an effective repulsive interaction between monomers.

The observed correlation effect is thought to contribute to the compacting, bending and kinking of DNA, and of other similarly highly charged polyelectrolytes.

(1) Malek O. Khan and Bo Jönsson, *Electrostatic Correlations Fold DNA*, Submitted for publication.

(2) S. Melnikov, B. Lindman, M. Khan and B. Jönsson, *Phase Behavior of a Single DNA in Mixed Solvents*, Submitted for publication.

L9 ORDER IN PHOSPHOLIPID LANGMUIR-BLODGETT LAYERS AND THE EFFECT OF THE ELECTRICAL POTENTIAL OF THE SUBSTRATE

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Phospholipid films on solid substrates are increasingly attracting attention as model systems for biological membranes, as well as for their application in electrochemical (bio)sensors. A direct motivation for the present study comes from the work of Nelson, Van Leeuwen and Leermakers [1]. They showed that for a phospholipid monolayer adsorbed on a mercury electrode the permeability for metal ions dramatically depends on the applied potential. Using a theoretical model the potential-dependent behaviour was explained in terms of structural transitions in the monolayers. These transitions might be exploited to detect compounds in low concentrations, since they are very sensitive to additives in the system.

With total internal reflection fluorescence (TIRF) the orientation distribution of fluorophores on an optically transparent substrate can be determined [2]. Recently, we presented the first results of orientation measurements on Langmuir-Blodgett (LB) dipalmitoylphosphatidylcholine (DPPC) monolayers containing fluorescent probes on quartz [3]. Here we report on orientation measurements on DPPC LB layers on a semi-conducting indium tin oxide (ITO) surface as a function of externally applied potentials. The potential effect is small for monolayers and bilayers on unmodified (hydrophilic) ITO; with decreasing potential the ordering changes slightly to more random distributions, possibly due to the onset of hydrogen evolution. For monolayers on hydrophobized ITO, where the phospholipids are initially with their tails directed towards the surface, the changes are more significant. At the highest potential applied nearly all molecules are flat on the surface. This results most likely from enhanced competition between headgroups and tails for access to the surface as it becomes more polarized. The electrochemistry of $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{bipyridyl})_3^{2+/3+}$ was investigated by cyclic voltammetry. On unmodified ITO the redox reactions are hardly hindered by the presence of DPPC monolayers and bilayers. On hydrophobized ITO a DPPC monolayer enhances the reactions.

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(3) X. Zhai and J.M. Kleijn, *Biophys. J.* 72 (1997) 2651-2659.

L10 MICELLAR GROWTH AND INTERACTION IN THE TERNARY SYSTEM C 12E5/DECANE/WATER

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The microstructure of the ternary system pentaethyleneglycol-monododecylether (C12E5)/decane/water has been investigated in the water-rich regime at several temperatures with static and dynamic light scattering. The ratio $A = m(\text{oil})/(m(\text{oil})+m(\text{surfactant}))$ was varied within $0.02 \leq A \leq 0.35$, while the mass fraction of the dispersed phase ranged between $0.0004 \leq \gamma \leq 0.2$, where γ denotes the mass fraction of the dispersed oil-amphiphile mixture at constant A .

Data analysis suggests the existence of giant wormlike flexible micelles at low oil content that grow uniaxially with the concentration of the dispersed phase ($A=\text{const.}$, $T=22^\circ\text{C}$). Combining a power law $M_w \propto c^\alpha$ for the concentration dependence of the mass-average molar weight M_w with the structure factor $S(c,q=0)$ for flexible polymer chains, the apparent molar masses are well described over a wide concentration range. This approach has been successfully applied to ternary reverse microemulsions as well as binary micellar solutions [1]. Contrary to those investigations, we obtain $\alpha \approx 0.5 - 0.6$ as it is predicted from mean field theory [2].

Increasing the oil fraction of the dispersed phase at constant temperature, the molar mass of the micelles reach a maximum at about $A = 0.07$. At higher oil content, the micellar growth decreases, until eventually droplet microemulsion are formed, where spherical oil-swollen micelles interact with each other like hard spheres.

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(2) Cates, M. E. and Candau, S. J.; J. Phys.: Condens. Matter 2 (1990), 6869-6892.

L11 THE LIQUID-CRYSTALLINE PROPERTIES OF COLLOIDAL SUSPENSIONS OF VANADIUM PENTOXIDE

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Vanadium pentoxide (V_2O_5) gels and sols are made of charged semi-flexible V_2O_5 ribbons dispersed in water. These colloidal materials are synthesized via a sol/gel process which is a typical "chimie douce" technique. The V_2O_5 ribbons are 10 Å thick, about 200 Å wide and 3000 Å persistence length. The suspensions form both a lyotropic nematic phase and an isotropic one separated by a biphasic region around a volume fraction $\phi \approx 1\%$ [1]. The nematic domain is further divided by a sol/gel transition at $\phi \approx 2.5\%$. At low volume fractions ($1\% < \phi < 2.5\%$), the nematic sol displays typical Schlieren textures in polarized light microscopy and can be aligned in moderate magnetic fields (≈ 0.3 Tesla) [2]. Small angle X-ray scattering patterns of aligned samples are very similar to those of the suspensions of Tobacco Mosaic Virus. At low ionic strength, the nematic/isotropic phase transition is well described by the Onsager model. However, increasing the ionic strength stabilizes the nematic phase which indicates the appearance of attractive interactions. This behaviour cannot be described by the Onsager model which only assumes excluded volume interactions. At large volume fractions ($\phi \approx 5\%$), in the gel regime, Couette shear cell experiments have recently revealed the existence of a biaxial nematic phase.

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L12 A GEL PHASE OF DENSELY PACKED UNILAMELLAR VESICLES: STRUCTURE AND KINETICS OF FORMATION

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Recently we found a stiff and elastic gel phase in the ternary surfactant system sodium oleate/1-octanol/water at fairly low surfactant concentration (5-10 wt%). The phase behavior of this system has been characterized by means of electric conductivity and rheological measurements, and the rheological moduli are found to be about a factor 100 higher than typically observed in similar systems. The structure of this phase has been investigated by means of freeze-fracture electron microscopy and small-angle neutron scattering (SANS).

The structural investigations showed that the addition of the cosurfactant octanol leads to the formation of small unilamellar vesicles of 250-500 Å diameter. For sufficiently high octanol content the vesicles become

so monodisperse that they can pack densely and highly ordered which explains the high shear modulus. The gel has elastic properties and exhibits the 'ringing phenomenon' typically encountered for cubic phases. Dilution of the gel phase with water leads to a swelling of the vesicles whereas the packing fraction of the system remains constant until a maximum diameter of about 500 Å is reached. The vesicles do not grow further and upon further dilution one enters into a viscous phase.

In our study we determined systematically the conditions necessary for the formation of the monodisperse vesicles. This means also how the formation of the gel phase depends on the structure of surfactant and cosurfactant and the composition of the system.

Another interesting aspect is the formation process of this gel phase. Upon mixing the respective components one first obtains an emulsion that is readily transformed into a transparent solution that becomes more viscous with time and gellifies during the course of 30 mins to 5 hours, depending on the composition of the sample. This self-organizing process has been characterized by us by means of rheological and SANS measurements. Evidently the initially present emulsion is transformed spontaneously into vesicles that change in size and become more monodisperse with time and finally get highly ordered in the gel phase.

L13 STABLE AND TRANSIENT STATES OF PHOSPHOLIPID HYDRATION

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New information on the solvation of the liquid crystalline L_α -phase of phospholipids has been observed by advanced methods of small-angle X-ray scattering. Separation of 2 - 3 coexisting L_α -phases has been observed in the presence of strongly hydrated salts in particular of LiCl with phosphatidylcholines. These discrete phases differ in their lamellar repeat spacing by about 3 Å, roughly equal to the thickness of one water monolayer. Most importantly, the transition between these phases as a function of salt content is stepwise and not continuous with regard to the dimension.

Related observations were made by IR-laser T-jump SAX using synchrotron X-rays. There, the L_α -phase of phosphatidylcholine transiently forms a thin L_α^* -phase within less > 1 msec, again differing from the parent phase by about 3 Å. The L_α^* -phase occurs also as an intermediate component of the $L_\beta' \rightarrow P_\beta'$ and $L_\alpha \rightarrow H_{II}$ transitions, respectively. The results suggest a non-monotonous decay of the interbilayer hydration potential with local minima at spacings of one water monolayer.

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L14 OCCURRENCE OF TWO CRITICAL POINTS IN LAMELLAR PHASES OF TERNARY SYSTEMS

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The Winsor I, Winsor II phase behaviour of microemulsion is well documented since fifty years (1948). In the case off low concentration of surfactant, excess internal phase is expelled from the microemulsion, the so-called emulsification failure is due to an excess of admissible bending radius of microemulsions. At higher surfactant content, liquid-gas transitions are observed: attraction between micelles produce a phase separation. As a result of these phase separation mechanisms in ternary microemulsions, two distinct critical points are observed in ternary phase diagrams at a fixed temperature.

We show in this paper that the same behaviour exists with lamellar phases. Concentrated and diluted lamellar phase are in equilibrium. Upon adding a third component, a critical point between two lamellar phases is observed. In the water rich part of the phase diagram, we observe a lamellar phase in equilibrium with extremely dilute bilayers. When adding a third component, the two phases in equilibrium merge in composition: in the case of lamellar phases also, a second critical point is obtained.

We will demonstrate this behaviour on the ternary system made of water, a double chain cationic surfactant (DDAB) and a synthetic glycolipid (N-lauroyl, N-nonyl lactitol, a synthetic glycolipid with two hydrophobic chains). The equilibrium phase triangle, a phase diagram is determined, as well as the osmotic pressure in the whole domain of stability of the lamellar phase made of mixed surfactant.

We show that this occurrence of two critical points at the same temperature is the of a strong electrostatic repulsion counter-balanced by strong binding of the bromide counter-ion as well as an adhesion energy induced by the hydrophilic headgroups. Only combination of two attractive mechanism are compatible with the equation of state, i.e. the osmotic pressure which varies by six orders of magnitude.

L15 DOUBLE EMULSIONS - RECENT DEVELOPMENTS

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Multiple emulsions are emulsions within emulsions, stabilized traditionally by monomeric emulsifiers both at the inner and outer interface.

Double emulsions are thermodynamically unstable, and fast coalescence, as well as fast release of markers and drugs, have been the main drawbacks of this technology.

Polymeric synthetic emulsifiers, as well as natural macromolecules in combination with monomeric emulsifiers, have recently been studied and evaluated.

The lecture brings new results on the use of amphiphilic proteins such as BSA and casein along with monomeric emulsifiers in relation to improved stability and release properties. Kinetic results are brought to demonstrate the role of BSA as the inner emulsifier and the outer emulsifier. Diffusion controlled mechanisms are suggested.

Synthetic block copolymers, based on silicon backbones and polyethylene oxide side-chains have also been studied. Double emulsions, with relatively small droplets (5 μm) are formed and excellent stability (to storage, shear and dilution) is obtained. Release data indicate that the newly designated double emulsions have longer shelf-life and very slow rates of release of markers. Such emulsions are good candidates for cosmetic, food, pharmaceutical and agricultural applications.

L16 DO LECITHIN WORM-LIKE MICELLES BEHAVE AS EQUILIBRIUM POLYMERS?

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Data collected by means of a number of different experimental techniques on lecithin water-in-oil microemulsions clearly indicate that for water-to-surfactant ratios below 2 and for moderately low concentrations the system is most likely a rod-like micellar solution. For very low concentrations, the micelles are spherulike. The concentration range in which the sphere-like micelles grow towards rodlike micelles has been alternatively interpreted as indicative of the growth of flexible worm-like micelles. Both the fact that the micelles are here found to be rod-like instead of flexible and the fact that the alternative interpretation yields the anomalously large value of 1.2 for the growth exponent, lead to the conclusion that lecithin worm-like micelles do not behave as equilibrium polymers.

L17 A SMALL-ANGLE NEUTRON SCATTERING (SANS) STUDY OF AGGREGATES FORMED FROM AQUEOUS MIXTURES OF AN ANIONIC AND A CATIONIC SURFACTANTMagnus Bergström,¹ Jan Skov Pedersen,¹ Peter Schurtenberger,² Stefan U. Egelhaaf³¹ *Condensed Matter Physics and Chemistry Department, Riso National Laboratory, Roskilde, Denmark*² *Institute for Polymers, ETH, Zürich, Switzerland*³ *Institute Laue-Langevin, Grenoble, France*

Different samples of sodium dodecyl sulphate (SDS, anionic surfactant) and dodecyl trimethylammonium bromide (DTAB, cationic surfactant) in pure D_2O as well as in a 0.1 M NaBr solution, have been studied at 40 °C using small-angle neutron scattering (SANS). The scattering data were fitted by various models for geometrically differently shaped particles using conventional least-squares methods. For the case where no extra salt was added, small unilamellar vesicles ($350 \text{ \AA} < R_v < 650 \text{ \AA}$) were found in the very dilute samples of compositions [SDS]:[DTAB] = 15:85 - 25:75 and 75:25 - 85:15 whereas larger oligolamellar vesicles predominate in the dilute samples nearer equimolar surfactant composition. When the overall surfactant concentration is increased above 0.25 - 1.0 wt %, depending on composition, we observe evident transitions from either small unilamellar vesicles to micellar aggregates or from larger oligolamellar vesicles to lamellar sheets. The data obtained from the samples where micelles were found were best fitted with a model for monodisperse tri-axial ellipsoids and, hence, the micelles appeared to be shaped as tablets, *i.e.* as small rigid elongated bilayer fragments. As the surfactant composition approaches equimolarity at a fixed overall surfactant concentration above the limit where no vesicles form, the micelles grow in both width and length until, at about [SDS]:[DTAB] = 30:70 and 70:30, a transition to large lamellar sheets occur.

As NaBr was added in order to give a total concentration of 0.1 M, the concentration regions where vesicles predominate were reduced so that no vesicles were found above 0.25 wt % overall surfactant. The data obtained from the samples where small micelles appeared were best fitted by either a model for monodisperse tri-axial ellipsoidal particles or a model for polydisperse rigid rods with elliptical cross-sections. The tabletshaped micelles found at higher surfactant concentrations grow rapidly in length, but only slightly in

width, as equimolarity is approached, in striking contrast to the case where no extra salt was added. As a result, elongated flexible ribbon-like micelles as long as several thousands of Angstroms form before a transition to large lamellar sheets occur at about $[\text{SDS}]:[\text{DTAB}] = 25:75 - 30:70$ and $75:25 - 70:30$. The former aggregates were best fitted with a model for self-avoiding worm-like aggregates with elliptical cross-sections.

L18 SOLUBILISATION OF SILICONE OILS IN FLAT AND CURVED SURFACTANT MONOLAYERS

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The behaviour of silicone oils in systems containing surfactant is very important industrially. Thus, these oils are used in commercial antifoams together with dispersed particles, in emulsified form in cosmetic formulations and as lubricants in a variety of products. However, there has been relatively little published concerning their behavior in water-surfactant systems.

We have investigated the *equilibrium phase behaviour* of systems containing anionic surfactant+water+silicone oil, where the oil is the polydimethylsiloxane (PDMS) type. On increasing the salt concentration, 2 phase-3 phase-2 phase equilibria are observed. The distribution of surfactant between phases and the uptake of water into reversed micelles formed at high [salt] has been determined. It is believed that microemulsions exist either in water or oil, with the third phase probably of L_3 structure. These findings have been complemented by turbidity titrations in single phase microemulsions.

In addition, the spreading or *wetting behavior* of these oils on the surfactant monolayers adsorbed at the air-water surface has been studied. We have performed experiments in which the lowering of the surface tension due to oil adsorption is determined following the addition of liquid oil to the surface. This, along with the oil-water tension, enables the calculation of the initial (S_i) and equilibrium (S_e) spreading coefficients. Values of S_i are positive at all salt concentrations consistent with the observation that PDMS spreads on these monolayers. S_e values are all close to zero indicative of thermodynamic equilibrium. For low molecular weight oils, the complete adsorption isotherm of oil at concentrations above the cmc has been measured by adsorption from vapour, as a function of the partial pressure. Without salt, the maximum ratio of oil: surfactant molecules in the film is 3.5. Adding salt causes the surface concentration of oil to fall initially and then increase. Possible causes for this behaviour are suggested.

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L19 NANODISKS WITH VARIABLE STRUCTURAL SURFACE CHARGE: IN CATANIONIC SYSTEMS

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Catanionic systems are usually made by adding anionic and cationic surfactants: these are quaternary systems, because the excess counter-ions are present as added salt. The amount excess counter-ions, proportional to the initial concentration of surfactants, act as screening ions of imposed concentration.

In order to obtain a pure catanionic system, the two initial molecules should have OH^- and H^+ as counter-ions. We use the system myristic acid (C_{13}COOH) and CTAOH ($\text{C}_{16}(\text{CH}_3)\text{NOH}$). The purity of counter-ions was checked with capillary electrophoresis. Preparing an aqueous solution of hydroxide and fatty acid, one obtains water molecules instead of "excess salt". Therefore, the system is a ternary one.

At equimolar concentration, one obtains only concentrated precipitates. However, surprisingly, close to the equimolar point, when one of the two surfactants is in excess, clear solutions are obtained.

We will describe the equilibrium phase diagram of this ternary system. The swelling of a lamellar phase with frozen hydrophobic chains (L_b) up to 1000 Å is observed. In extremely diluted solutions, rigid nanodisks of controllable size are produced. SANS, SAXS and electron microscopy of these rigid charged finite nanodisks will be shown.

L20 NON-ADSORBING-POLYMER-MEDIATED INTERACTIONS BETWEEN FLUID MEMBRANES IN LYOTROPIC LAMELLAR PHASES

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We have investigated a mixed amphiphilic system formed from a brine swollen surfactant lamellar phase in between of which is incorporated a neutral water-soluble non adsorbing polymer: polyvinylpyrrolidone (PVP), with a very large molecular weight. The existence of a critical L_a/L_a phase separation is quantita-

tively explained by a theoretical model, we have developed, which predicts the smectic compressibility of non adsorbing polymer-containing lamellar phases, taking into account the polymer-mediated interactions between the membranes. In the case, where the lamellar phase is electrostatically stabilized, the polymer can be confined in all proportions into the lamellar phase; this allows a systematic experimental study of the different confinement regimes of polymer solutions. The three relevant elastic constants of this mixed lamellar phase (the layer compression modulus and the two bending moduli) have been measured using different experimental techniques (SAXS, SANS, NMR, optical microscopy). The results are compared with theoretical predictions.

L21 **BILAYER FORMATION IN WATER FROM NEW UREA-BASED DOUBLE-CHAIN DIMETHYLAMMONIUM AMPHIPHILE CONTAINING PERFLUORINATED MOIETIES**

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Thanks to their high stability and chemical inertness of their components, the F-alkylated liposomal systems should be able to exhibit a strong power of drugs retention between the administration site and the considered target. Their relative impermeability should also be able to considerably reduce the toxicity of drugs. Therefore our work consisted in finalizing simple strategies of synthesis to obtain easily new double-chain perfluoroalkylated amphiphiles having a modular structure to test their ability to form membrane bilayers.

In the present work we describe the synthesis of new F-alkylated isocyanates: $R_F C_2 H_4 S (CH_2)_p NCO$ (I) and the corresponding F-alkylated ureas: $R_F C_2 H_4 S (CH_2)_p NHC(O)NHC_2 H_4 N(CH_3)_2$ (II) where $R_F = C_4 H_9, C_6 F_{13}, C_8 F_{17}$ and $p = 1, 3$. The quaternization of F-alkylated ureas (II) by 1-bromo alkanes and (2-(F-hexyl)ethyl)bromo acetamide to double-chain dimethylammonium amphiphiles the vesicle-forming ability of which was investigated and discussed according to their molecular structure. The vesicles were produced by sonication of amphiphiles in water and bilayer structures elucidated by Freeze Fracture Electron Micrographs.

L22 **MEASUREMENTS OF INTERFACIAL CURVATURES AND EVIDENCE FOR MORPHOLOGICAL TRANSITION IN SEMIFLUORINATED NON-ISOMETRIC MICROEMULSIONS**

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Fluorinated surfactants have been studied for their ability to form supramolecular aggregates in water and oils (hydrocarbons or fluorocarbons). Because of their capacity to dissolve large amounts of gases (such as oxygen and carbon dioxide), fluorocarbons have also been tested for specific medical purposes, and their microemulsions are among the candidates for the production of suitable blood substitutes and other bio-compatible fluids.

We have studied the phase behavior and the associated microstructures of microemulsions formed from solution of perfluorooctanoic acid (PFOA) in water and perfluorooctane (PFO). Analysis of small-angle neutron-scattering intensity distributions with clipped random wave model (CRW), having a specific spectral density function, provides a detailed description of the microstructure of one phase, non-isometric microemulsions. Specifically, we are able to deduce from the analysis the average mean, Gaussian, and square mean curvatures of the oil-water interface in a bicontinuous microemulsion. From such curvature information we present evidence for the morphology transformation occurring within the one phase channel as one varies the oil/water volume fraction ratio. The CRW model also gives 3-D views of the interfacial morphologies which substantiate the transition.

L23 **MICROSTRUCTURE AND INTERFACIAL TENSIONS IN NONIONIC MICROEMULSION SYSTEMS**

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In recent years microemulsions were studied intensively. However, a quantitative theoretical description of macro- and microscopic properties of these microstructured systems is still lacking. The systematic investigation of 19 water - *n*-alkane - alkylpolyglykoether ($C_i E_j$) - systems shows striking similarities in the phase behavior, the interfacial tensions and the microstructure [1]. The knowledge of the forms and sizes of the microstructures permits determining the state of curvature of the amphiphilic film, and thus permits ana-

lyzing the interfacial tension measurement an experiment on the bending energy of the amphiphilic film [2]. By this analysis all interfacial tension curves can be scaled on a master curve [3]. The few "critical" parameters needed are the maximal domain size, the temperature sensitivity ($T_u - T_l$) and the mean temperature $(T_u + T_l)/2$ of the three phase body. This results will enable us, to develop in near future a "coresponding states" for microemulsion systems.

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L24 SIZE DISTRIBUTION IN EMULSIONS

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Non-equilibrium etherogeneous systems of one liquid dispersed into another in the form of droplets having radii of the order of micrometers, are known as emulsions. Emulsions play an ubiquitary role in the everyday life. A large portion of foodstuffs, paints, pharmacological preparations are comprised in the above reported definition. The fact that emulsions are, in most cases, opaques and present multiple (light) scattering is a considerable obstacle to the use of optical techniques. Otherwise, the optical appearance of the sample is totally irrelevant for NMR measurements. We present a general method that allows to figure out the size distribution of a collection of droplets of dilute emulsion systems using NMR Pulse Gradient Spin-Echo (PGSE) measurements. We will show that the expression to obtain the volume fraction distribution is equivalent to a Fredholm integral equation of the first kind, proving that a solution of this equation can be easily found if its kernel has a complete bi-orthogonal system of eigenvectors. Two numerical procedures will be discussed. The first, termed indirect, is based on the expansion of the unknown distribution function in the eigenfunctions of the kernel. The second one, called direct, uses the properties of shifted Legendre polynomials to numerically integrate the integral equation and evaluates the unknown distribution by means of a constrained least-squares procedure. Furthermore, we will illustrate a procedure to determine the diffusion coefficient of the dispersed phase (inside the droplets).

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L25 SPECTROSCOPIC STUDY OF POLYNUCLEOTIDES IN CATIONIC W/O MICROEMULSIONS

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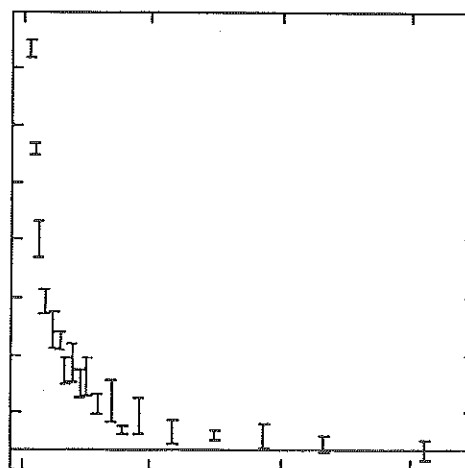
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One of the several questions still open in cellular physiology is the discrepancy among the nucleic acids longitudinal dimensions and the size of the case containing them. Such discrepancy plays a crucial role in regulating the expressions of the DNA and can be rationalized turning to the help of model systems, such as liposomes and W/O microemulsions solubilizing natural and/or synthetic polynucleotides. Both these systems, in fact, can provide a closed inner compartment where the interactions of the guest molecules with the secluding interface can be maximized.

Compared to the liposomes, the W/O microemulsions require milder preparation procedure, leading to a final system generally characterized by an almost spherical shape with very low polydispersity. Taking into account these advantages the behaviour of polynucleotides has been studied after their solubilization in a cationic W/O microemulsion.

A spectroscopic investigation carried out on the quaternary W/O microemulsion CTAB | *n*-pentanol | *n*-hexane | water solubilizing different amount of both natural (calf thymus DNA) and synthetic (poly AT) polynucleotides have been undertaken. Compared to water solutions, both the guest species show hyperchromism, such an effect being much more evident at low concentration of the biopolymer (see figure). This finding suggests the existence of interactions among the phosphoglucidic backbone of the polynucleotides and the



cationic micellar wall which could lead the biopolymer to assume a more relaxed configuration. Such an interpretation is coherent with experiments of alkaline denaturation in W/O microemulsions, which reveal a polymer much more inclined to the denaturation than the parent system in water.

L26 CONTROLLED MICROSIZED SOLID PARTICLES FORMATION AND MATTER TRANSFER WITHIN EMULSIONS

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Different procedures for micro-sized solids formation will be presented.

First, it is shown how to get micro-sized particles by cooling simple emulsions made of liquid droplets dispersed in a bulk immiscible liquid. Solid particles should be obtained by solidification of the droplets during cooling. Due to nucleation phenomena, the droplets solidification temperatures are scattered and lower than the one corresponding to the solid-liquid equilibrium. The solidification conditions will be thoroughly described.

Another means is to cause by chemical reaction, the solid precipitation inside the droplets by coalescence of droplets belonging to two different composition emulsions. Example of colloidal AgI in water droplets obtained by coalescence of (KI + water) droplets and (AgNO₃ + water) droplets is presented.

A third procedure involving matter transfers within emulsions will be described. Such transfers have been observed on simple, mixed and multiple emulsions.

Simple water in oil emulsions W/O regularly agitated show water transfers due to water vapor pressures gradient between the droplets and the atmosphere. Using this procedure, micro-sized NaCl or NH₄Cl solid particles have been obtained from aqueous solutions of these salts dispersed within emulsions.

In mixed and multiple emulsions, the transfers are due to the differences between the compositions of the droplets (mixed emulsion) and of the dispersed droplets in the globules and the bulk phase wherein the globules are themselves dispersed (multiple emulsion).

L27 SHEAR INDUCED ALIGNMENT AND TEXTURES IN A MICELLAR CUBIC CRYSTAL

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We report on X-ray (SAXS) scattering experiments under shear on a micellar cubic crystal. The micelles results from self-assembling of triblock copolymers (EO)₁₂₇(PO)₄₈(EO)₁₂₇ dissolved in water, where EO is for ethylene oxide and PO for propylene oxide. At concentration above typically 20 %, the spherical aggregates (120 Å radius) come to close packing, forming a long range ordered cubic phase. We first show that the solid elastoplastic samples are polycrystalline at rest, with fcc symmetry. Under shear, above the yield stress, and the material flows and the polycrystalline texture shear aligns progressively: the isotropic rings related to the initial powder-average transform into well defined Bragg spots. The intensity and distribution of these Bragg spots in the reciprocal space are consistent with a layering of the cubic crystal into 2D-hexagonal compact layers with the dense directions parallel to the flow velocity. The scattering patterns, as received from SANS and SAXS evolve markedly upon increasing the shear rate applied and the corresponding shear-induced structures are discussed and related to the mechanical response to strain as obtained from rheological measurements.

L28 SURFACE PROPERTIES OF ICE STUDIED BY ATOMIC FORCE MICROSCOPY

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Although the surface of ice has been extensively investigated it is only poorly understood. One example is the yet unexplained low coefficient of friction. We used the atomic force microscope (AFM) to investigate surface properties of ice in a temperature range of -24 to -0.7 °C. An upper limit of the thickness of the liquid-like layer on the surface of ice was found to vary between about 12 nm at -24 °C and 70 nm at -0.7 °C. This was correlated with an increase of the adhesion force. In force-versus-distance measurements the tip penetrated into the ice. This behavior can be interpreted in two ways:

- Either a 'soft' ice layer exists between the liquid-like layer and bulk ice or

- the presence of the solid tip surface causes the ice surface to change its mechanical properties.

Friction was also measured with the AFM, which provides not only the possibility to measure friction on a small scale (500 nm) but also with small contact area (radius of curvature of the AFM tip ≈ 50 nm), and at small sliding velocities (0.2 - 60 $\mu\text{m/sec}$). Friction increased with decreasing velocity, which is probably due to the penetration of the tip into the ice at low velocities.

L29

ADSORPTION OF GELATIN AND SURFACTANTS TO POLYSTYRENE

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Neutron reflection experiments have been performed to investigate the arrangement of gelatin adsorbed from aqueous solution to hydrophobic polystyrene surfaces. Adsorption has been studied as a function of pH and in the presence of the surfactants sodium dodecyl sulphate (SDS) and hexadecyl trimethyl ammonium bromide (CTAB). The results can be understood in conjunction with the knowledge of the amino acid composition of the gelatin.

Neutron reflection offers two main advantages as an experimental technique:

- it provides information about the spatial distribution of adsorbate perpendicular to the interface as well as total mass adsorbed
- it can be used to distinguish between protonated and deuterated material. This means that the mass and distribution of the two components of a mixed gelatin/surfactant layer can be determined separately. Deuterated and protonated surfactant can be used in different contrasts of H_2O and D_2O to highlight each species in turn.

Gelatin is an amphoteric polyelectrolyte with amino groups arranged along a single peptide backbone. Different amino groups are positive or negative depending on pH; the isoelectric point of the gelatin is at pH 5. Fractionated single chain alpha gelatin of known amino acid sequence was used for this study.

Neutron reflection measurements have been used to provide an adsorption isotherm for the alpha gelatin at its isoelectric point. Surface excess, thickness and density of the adsorbed layer are all seen to increase with solution concentration. The adsorbed layers have maximum density at the polystyrene surface, with the density profile decaying into solution. The adsorbed mass of gelatin rises to $\sim 7 \text{ mg m}^{-2}$, with decay lengths rising to $\sim 55 \text{ \AA}$ for 0.1% solution. This is a thin layer considering that the extended length of the gelatin molecule is 2850 \AA . Analysis of the amino group sequence of the gelatin reveals that hydrophilic dissociated groups are few and isolated along the gelatin molecule, which is largely hydrophobic with only short loops penetrating into the solution.

Little change is observed in the surface excess of gelatin as the solution pH is varied, but a thinner more dense gelatin layer is observed at pH 3 and a less dense layer is observed at pH 8. This correlates with changes in the dissociation of the amino groups as the pH is varied. There are fewer hydrophilic dissociated groups at low pH. Preliminary results on the adsorption of gelatin in the presence of surfactants reveal that both the anionic SDS and the cationic CTAB adsorb uniformly with the gelatin rather than directly to the polystyrene surface.

L30

ADSORPTION OF ETHYL(HYDROXYETHYL)CELLULOSE ON SOLID SURFACE. EFFECT OF HYDROPHOBIC MODIFICATION AND SURFACTANT ADDITION TO THE POLYMER LAYER

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The adsorption of ethyl(hydroxyethyl)cellulose (EHEC) and the hydrophobically modified analogue (HM-EHEC) from aqueous solutions on solid surfaces (silica, hydrophobized silica) has been studied by null ellipsometry. At the hydrophilic silica surface, a pseudo-plateau adsorbed amount was reached above approximately 0.01 wt. % polymer. On silica surface, the hydrophobic modification of the polymer has no significant effect on the plateau adsorbed amount, but at low bulk polymer concentration ($<10^{-4}$ wt.%) the HM-EHEC adsorbs less than EHEC. Both polymers show higher affinity to the hydrophobic surface, but HM-EHEC give a substantially higher plateau adsorbed amount compared to EHEC. Similar to the silica surface, HM-EHEC adsorbs less at low bulk polymer concentration ($<10^{-4}$ wt.%).

The effect of addition of various amounts of surfactants to the adsorbed polymer layer was also studied. On silica, large expansions of the polymer layer (up to 5 times thicker than the presorbed layer) was observed with anionic surfactant (SDS), while no expansion effect of the layer thickness was observed with nonionic surfactant (C_{12}E_8). The expansion patterns qualitatively follow the solution binding isotherms. On hydrophobic surface an initial expansion of the HM-EHEC layer was observed on addition of SDS (<2

mmolal), while at higher SDS concentrations the polymer was partially desorbed from the surface. In the case of EHEC, rearrangement effects on the surface was initially observed, followed by desorption of polymer at higher SDS concentrations. Cationic surfactant (CTAC) seemed to have less effect on the polymer layer than the anionic SDS.

L31 NONIONIC MICELLES NEAR THE CRITICAL POINT - MICELLAR GROWTH VS. ATTRACTIVE INTERACTIONS

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Nonionic surfactants (oligo(oxyethylene)-n-alkyl ether, $C_{12}E_6$) show a rich phase behavior in aqueous mixtures. The understanding of the binary phase behavior and structural properties is central for the understanding of ternary mixtures with oil (microemulsions). A common feature of these surfactants in mixtures with water is an upper miscibility gap with a lower critical point in the temperature - composition diagram.

In literature one finds conflicting interpretations of the temperature and concentration dependence of such aqueous solutions of nonionic surfactants. M. Zulauf and colleagues explained their neutron and light scattering data from C_8E_4 and C_8E_5 near the critical point by assuming spherical micelles, constant in shape and size but with increasing attractive interaction when approaching T_c [1,2]. This picture is still used for the interpretation of light scattering data [3], even though it was highly questioned in a comment, based on NMR experiments, by the Lund group some years ago [4]. The assumption of the attractive interaction was based on the fact that the SANS data did not change essentially with temperature at $Q > 0.5 \text{ nm}^{-1}$. It was concluded that the temperature dependent changes can be explained only by a fixed micellar shape and size but increasing attractive interaction.

With a series of SANS experiments assisted by additional depolarized dynamic light scattering experiments and low shear viscosimetry we can show that both effects - temperature induced changes in the micellar structures and critical phenomena - exist, but they were not separated carefully enough in the past. Our high resolution SANS data together with a recently developed evaluation technique, the generalized indirect Fourier transformation, allowed this separation for different concentrations around c_c for a series of different $C_{12}E_j$'s. At low temperatures the micelles are spherical or elongated to rod-like shape, their length grows with concentration and temperature. Approaching T_c the rods start to show attractive interaction.

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L32 AGGREGATION DYNAMICS OF THE BLOCK COPOLYMER L64 IN AQUEOUS SOLUTION

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The aggregation dynamics of aqueous solutions of the amphiphilic triblock copolymer L64 have been investigated using the "iodine Laser Temperature Jump" (ILTJ) or "Stopped-Flow" (SF) with light scattering detection. ILTJN and SF investigations cover the whole range from the Critical Micellization Temperature (CMT) up to the Cloud Point (CP) of commercial and purified L64. Three relaxation times τ belonging to three well defined temperature regions were detected. The first and fastest relaxation time τ_1 occurred in the microsecond time range and was accompanied by an increase in scattered light intensity. The second and third relaxation times τ_2 and τ_3 occur on a longer time scale of 1-100 ms. Relaxation time τ_2 was accompanied by a decrease of scattered light intensity whereas τ_3 shows an increase.

By observing the temperature dependence of the three relaxation processes it was found that τ_1 and τ_2 decrease with increasing temperature while τ_3 increases with increasing L64 concentrations.

From our experimental results we conclude the following:

- τ_1 is associated with unimer insertion into micelles.
- τ_2 reflects the redistribution of the aggregation number of the micelles and the water exchange

between micelles and solution, as can be confirmed by neutron scattering (SANS).

- τ_3 is caused by an increasing interaction between micelles as well as coalescence near the cloud point temperature.

The interaction of L64 with SDS will also be discussed.

L33 CHARACTERIZATION BY FLUORESCENCE ENERGY TRANSFER OF THE CORE OF POLYISOPRENE-POLY(METHYL METHACRYLATE) DIBLOCK COPOLYMER MICELLES. STRONG SEGREGATION IN ACETONITRILE

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Fluorescence decay measurements of the rate of non-radiative direct energy transfer has been employed to characterize the core and the core-corona interface of polyisoprene-poly(methyl methacrylate) (PI-PMMA) diblock copolymer micelles in acetonitrile. The micelle consist of a core of the insoluble PI-blocks and a corona of the soluble PMMA-blocks. The block copolymers are labeled, at the block junction, with a single fluorescent dye, either a donor chromophore (phenanthrene) or an acceptor chromophore (anthracene). Micelles were prepared in which the components are randomly mixed. Because the polymers are junction-labeled, the chromophores are naturally confined to the interface of each micelle. Fluorescence decay measurements show that the donor emission displays a non-exponential decay profile due to energy transfer. Analysis of the data indicate that energy transfer takes place on a surface of a sphere, within a narrow interfacial region, implying strong segregation of PI and PMMA in the micelle. From the data analysis, a micellar core radius of (7.6 ± 0.9) nm and an aggregation number of 98 ± 24 are obtained. The results are compared with those obtained from viscosity, static and dynamic light scattering measurements.

L34 FLUIDIFICATION OF CONCENTRATED SUSPENSIONS BY ADSORBED POLYMERS AND COPOLYMERS

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Applications of highly concentrated suspensions require easy processing and homogeneous dispersion of the particles. Such characteristics imply the lowest possible viscosity for the highest solid charge, a challenge that can only be reached thanks to the use of additives that protect the surfaces against aggregation together with a limited increase of the effective volume of the particles. Because their irreversible adsorption at solid/liquid interfaces deeply modifies interparticle forces, polymers are very efficient for this purpose, but it is very important to adjust their characteristics as a function of the surface properties.

This paper deals, in a rather general way, with the effect of polymers on the rheological behavior of various kinds of concentrated suspensions in which particles display either hydrophilic, or hydrophobic or heterocoagulating surfaces. The richness of possibilities offered by copolymers in this domain will be emphasized and it will be shown with a few experimental examples how to match the main parameters (i.e. chemical composition, architecture, molecular weight, surface coverage etc.) in order to optimize the dispersion level of a given system. These results are systematically correlated with the adsorption and interfacial properties of the polymer and the importance of the balance between electrostatic and steric repulsions is underlined.

L35 EXPERIMENTAL CHARACTERIZATION OF DENDRIMER SOLUTIONS

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"Dendrimers" or "Starburst Polymers" are a new class of regularly branched macromolecules with unique structural and topological features whose properties are attracting the interest of science and technology. By means of new iterative stepwise synthetic methodologies it is possible to grow, through successive generations, highly branched dendritic structures. More precisely, these macromolecules are constructed from various initiator cores on which radially branched layers, termed generations (*g* for short), are covalently attached, thus yielding a three-dimensional highly ordered polymeric compound. The final exterior layer may be further chemically modified to provide a variety of terminal functionalities.

Physics of dendrimers have been studied recently by means of theoretical methods, MD simulation as well as experimental investigations, but although new insight has been gained, much remains to be done.

Their physical properties, in fact, are partly explained, and although a qualitative understanding is proposed, a quantitative interpretation is still lacking.

To have a complete characterization of the polyamidoamine (PAMAM) starburst dendrimers in methanol solution we have carried out a series of SAXS experiments. We have explored the intensity profiles for dendrimers of different generations ($g=1.5, 2, 2.5, 3, 3.5$) at various concentrations. The measured spectra show that the half integer generations are characterized by pronounced interparticle correlations also in the dilute regime indicating a long ranged order. By means of a simple statistical mechanical model, widely used in charged complex fluids we calculate for the $g=3.5$ case the inter-dendrimer structure factor $S(q)$. Obtained results give indication of a partial ionization process which interest the carboxylate (COO^-Na^+) terminal groups.

The investigation is also focused on the study of the density distribution inside the starburst polymer and in particular in determining the scaling law relating the molecular mass M with the giration radius R . We obtain that integer and half-integer generations have different scaling behaviors indicating different internal structures. In particular, the integer generations, bearing terminal amino groups, exhibit a closely compact space filling structure; whereas the half-integer generations, with charged terminal carboxylate groups, display a less compact (fractal) structure. This latter result can be ascribed to a swelling effect of the chains due to charge condensation of the counter-ions.

L36

HYDROGEN BONDS IN ORGANIZED MONOLAYERS

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Non-amphiphilic molecules in the adjacent aqueous phase may bind to the head groups of insoluble monolayers at the air-water interface by electrostatic interactions and hydrogen bonding. Pure hydrogen bonding requires several bonds per molecule. In particular, multisite interactions of a solute with different amphiphiles involving both electrostatic attraction and hydrogen bonds can cause lateral organization of the amphiphiles with formation of systems showing molecular recognition [1]. Formation of associates of two components by H bonds, one being an amphiphilic barbituric acid derivative, the second being triaminopyrimidine, TAP, have been observed in monolayers at the air-water interface after co-spreading of the two compounds. The water soluble TAP is retained in the monolayer and causes hydrolysis of the ABA as deduced from reflection spectroscopy [2] at the air-water interface.

The strategy of combining electrostatic attraction with H bonds has been used to form extended aggregates of two components, that may even crystallize from aqueous solutions [3]. This approach has been adapted for organizing appropriate derivatives in monolayers. An amphiphilic bisamidinium ion, THA, binds dicarboxylic acids like terephthalic acid or nitro-isophthalic acid. As in the case mentioned above, the two components were co-spread, i.e. the spreading solution for formation of the monolayer contained both compounds in the molar ratio 1: 1. Binding of the acids has been established by measuring surface pressure vs. area and surface potential vs. area isotherms as well as by absorption spectroscopy of single monolayers transferred at constant surface pressure from the water surface onto quartz plates [4].

Depending on the number of anionic groups and geometrical organization formation of extended strands (α -network) or of two-dimensional (β -network) structures is expected. Recently, we have investigated the interactions between THA and the water soluble tetrasulfonatophenyl-porphin. From preliminary results we conclude that the porphyrin is kept in the plane of the hydrophilic amidinium moiety of the cationic component, positioned between THA molecules by H bonds that induce a directionality of the organization. The electrostatic interactions alone would lead to binding of the porphyrin below the plane of cationic groups.

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L37 ASSOCIATING POLYMER-SURFACTANT SYSTEMS

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Mixed polymer-surfactant solutions may show segregative or associative phase separation. The latter case will be reviewed and it is found that we can distinguish between three types of surfactant binding to polymers, with different contributions from hydrophobic and electrostatic interactions. For polyelectrolyte-surfactant systems the role of electrolyte and water addition in controlling behaviour is discussed. For hydrophobically modified polymers/polymer-modified surfactants, binding isotherms, and the relation between micelle size and rheology is described. The control of rheology by controlling micelle size is described. Finally, we describe polymer-vesicle association for the case of thermodynamically stable catanionic surfactants.

L38 SUPRAMOLECULAR STRUCTURE OF POLYSACCHARIDE-CATIONIC SURFACTANTS COMPLEXES

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We study the anionic polysaccharide from the capsule of the red microalga *Porphyridum* sp. (Psp) and its interaction with cationic surfactants. We mix cationic surfactant (C_nTAX) in excess with the polysaccharide. This results in a spontaneous precipitation of a charge-neutralized polysaccharide-surfactant complex. The precipitate is redissolved in organic solvents and can form a film. The complex, both as film and powder, is studied with various methods such as SAXS, WAXS, ²H-NMR, light and electron microscopy. We find that the complex has well-defined characteristic lengths both in the 3-4 nm and in the 0.3-0.4 nm scales.

Upon dissolution of the complex in a concentrated electrolyte solution, it forms a viscoelastic solution at low surfactant and polysaccharide concentrations. We investigate the rheological properties of the solution and study the supramolecular structure with cryo-transmission electron microscopy (cryo-TEM). This electrostatically bound complex is compared to a chemically bound polysaccharide-surfactant polymer: a hydrophobically modified polysaccharide.

L39 INTERACTION BETWEEN CATIONIC-ANIONIC SURFACTANT VESICLES AND OPPOSITELY CHARGED POLYMERS

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Mixed solutions of cationic and anionic surfactants are known to form thermodynamically stable vesicles over wide concentration ranges. This phase behaviour is reviewed and the conditions of vesicle formation, and their microstructure is discussed. Vesicles are either rich in cationic or in anionic surfactant.

The present work reports novel studies of the interaction between thermodynamically stable vesicles and water-soluble polymers. In particular, we have investigated the interaction between catanionic vesicles with a net negative charge and cationic water-soluble polymers; one of the cationic polymers is of the hydrophobically modified type. The experimental work included phase diagram determination, rheology and cryo transmission electron microscopy.

With regard to phase behaviour, there is a close analogy with previous studies of polyelectrolyte micelle mixtures and an associative phase separation in a wide range of charge stoichiometries. Interesting novel gels are identified in the homogeneous single phase regions and their structures discussed with reference to the cryo-TEM results. The latter showed different features depending on composition, regular single-walled vesicles, faceted vesicles membrane fragments and disc micelles and small spherical micelles.

L40 ADSORPTION OF A RANDOM COPOLYMER POLYELECTROLYTE ON TITANIUM DIOXIDE

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Polymers adsorption at solid-liquid interfaces is relevant in many industrial applications : painting, cosmetics, wastewater treatment, flotation separation... Homopolymers and block copolymers have been

widely studied [1]. But, a few charged random copolymers have been investigated. The hydrolysed Styrene Maleic Anhydride (hSMA) copolymer studied here is a polyelectrolyte. It presents an apolar part - styrene - and a polar part - two carboxylate functions. In order to predict the behavior of this polyelectrolyte in different applications, it is interesting to study its adsorption at different pH and ionic strength.

At high pH values, adsorption of the negatively charged hSMA on titanium dioxide is observed, although the solid particles are also negatively charged at this pH. The higher the pH, the lower the adsorption. At constant pH, adsorption isotherms are highly dependent on ionic strength. This latter can be varied either by increasing the hSMA concentration itself, or by adding monovalent salt (potassium nitrate) in a solution of given hSMA concentration. At potassium nitrate concentrations higher than 10^{-2} mol/l, the adsorption model is found Langmuirian.

A tentative adsorption mechanism is proposed. It is governed by two kinds of interactions: an electrostatic one between the discrete positive sites of the surface and the hSMA copolymers, and a nonelectrostatic one between the preadsorbed hSMA copolymers and the free hSMA copolymers in solution. This mechanism is confirmed by microelectrophoretic measurements.

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L41

ASSOCIATION MECHANISM OF HYDROPHOBICALLY MODIFIED POLYELECTROLYTES AND INTERACTIONS WITH SURFACTANTS. A ^{19}F NMR STUDY

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The behavior of hydrophobically modified water-soluble polymers in aqueous media has been extensively studied in the past few years. These materials, used as additives in aqueous formulations, are based on a water-soluble backbone to which a low fraction of hydrophobic side groups, usually long alkyl chains, are attached. Nowadays it is well established that the hydrophobic side groups can form micelle-like aggregates acting as crosslinks between the polymer chains and thus providing a pronounced increase of the rheological properties (viscosity, elastic modulus) of the system. However, the detailed structure of the aggregates and their dynamics (such as the exchange of polymer chains between the free and aggregated states) is still a matter of debate.

The present study is on a low-molecular-weight derivative of poly(sodium acrylate) that contains perfluoro-octyl sidechains (C8F). The resulting random copolymer, where 8% of the acrylate units has attached sidechains, has an average polymerization degree ~ 100 . The ^{19}F NMR spectrum of this polymer clearly displays the signature of slow exchange between the free and the aggregated states of the C8F groups, namely two distinct peaks for each fluorine nuclei, one corresponding to the free and the other to the aggregated form. The molecular exchange time between those two locations is longer than 1 s as confirmed by spin relaxation, diffusion, and exchange NMR experiments. Thus it becomes simple (via spectral integrals) to measure the fraction of polymers in the aggregated state and to follow independently the overall and sidechain dynamics in the free and aggregated states by longitudinal and transverse spin relaxation experiments.

Another feature of hydrophobically modified polymers is their ability to form mixed micelles with surfactants. By recording the effect of a hydrogenated surfactant, sodium dodecyl sulfate (SDS), on the ^{19}F NMR spectrum we established that below the cmc only a small fraction of the added SDS is incorporated in the aggregates formed by the C8F chains. Above the cmc, SDS-rich micelles are formed in which some C8F chains are solubilized. The relative fraction of C8F chains that are in the SDS-rich micelles increases with the surfactant concentration. The coexistence of these two types of aggregates is attributed to the non-ideal mixing between the hydrogenated surfactants and the perfluorinated side chains of the polymer.

L42

ELECTROSTATIC AND CHEMICAL INTERACTIONS OF IONS IN ELECTROLYTES AND IN IONIC POINT CHARGE DOUBLE LAYERS

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By the application of the Madelung constant, M , the Debye-Hückel radius, $1/\kappa$, is deduced directly from the definition of the average edge length of the cube, l , which contains one ion of an 1-1 electrolyte. The same edge length is calculated from the electrolyte concentration. It is assumed that two ions of opposite charge are separated for the distance that equals half of the Debye-Hückel radius, $1/(2\kappa)$.

The theoretical function of activity coefficient with concentration, $m/(mol/kg)$,

$$\gamma_m = 1/[F_m + F_+(m^{E_+} - 1) + F_-(m^{E_-} - 1)]$$

is deduced considering that the ion interactions are, along with the electrostatic free energy change, also under the influence of the chemical potential of cations and anions. Two constant parameters, $E_+ = 1/2$ and $E_- = 1$, are theoretical. The parameters F_m , F_+ and F_- can be estimated by fitting the function to experimental sets of points of any electrolyte. The parameter F_m is determined by the electrostatic free energy changes, F_+ , E_+ , F_- , E_- , by chemical potentials of cations and anions. Five Figures demonstrate that the same function can be fitted with a high degree of precision to experimental activity coefficient plots of the alkali halides. In this way the theory is supported experimentally.

The theoretical function of electrokinetic quotient, q , is proposed, measured as electrophoretic mobility, or electroosmotic transport across membranes, or streaming current, or streaming potential on ionic strength or concentration, I_c , which reads

$$q = q_m - s |\log(I_{cm}/I_c)|$$

It has a positive slope in the low logarithm of ionic strength and a negative slope in the high logarithm of ionic strength. Experimental plots have equal linear functions with a positive and a negative slope.

The theoretical function is defined by three constant parameters q_m , s , I_{cm} , one independent variable, I_c , and one dependent variable q . Constant parameters can be estimated by fitting the theoretical function to experimental sets of electrokinetic points. The electrostatic potentials κ_p and κ_{pm} , which replace the classical Smoluchowski's and Henry's ξ -potentials, can be calculated from the experimental s , q_m and q obtained by fitting by

$$\kappa_p/\kappa_{pm} = 10^{[(q_m - q)/(2s)]}$$

Smoluchowski's or Henry's ξ -potentials are calculated by multiplying of the experimental mobility or transport data by theoretical constants that are valid for hypothetical long and narrow colloidal particles of $l \gg r \gg 1/\kappa$ or capillaries in membranes of $r \gg 1/\kappa$. Such particles and membranes do not exist in real colloidal systems. This is the reason that the hypothetical theoretical constants cannot be valid for real colloidal particles or real membranes in various systems and in variable ionic strength. The values of Smoluchowski's or Henry's ξ -potentials are of no significance but the shape of the plots remains unchanged. However, the correct result of Smoluchowski's and Henry's theories is that the ξ -potentials are of electrostatic origin.

L43 PHASE EQUILIBRIA OF POLYDISPERSE COLLOIDS

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The methods of statistical mechanics, which were developed to treat systems of indistinguishable atoms, have been widely successful when applied to colloidal suspensions. However, colloidal particles are almost inevitably not identical, and certainly not indistinguishable. They are, to some extent, polydisperse in some characteristic, such as radius, charge, oblateness, etc. Thus, the parallel commonly drawn between colloidal and atomic systems is clearly inadequate for a full appreciation of their behaviour. Polydispersity should not be regarded as an inconvenient complication to thermodynamics, as it brings a rich variety of physics not seen in pure systems. For instance, when polydisperse systems phase-separate, they generically fractionate, ending up with different distributions of particles in each phase, e.g. a denser phase favouring larger particles.

A truly polydisperse system in the thermodynamic limit contains infinitely many species. Therefore, calculations of phase equilibria involve infinitely many coexistence constraints (a difficulty not encountered when determining single-phase properties such as structure factors). This hampers the mathematics. Such calculations have been attempted using various, often arbitrary, approximations. The results they yield tend to be cumbersome and system-specific and therefore do not educate the intuition.

By perturbing about monodisperse systems, we provide a complete description of two-phase equilibria in ANY system which is slightly polydisperse in some property. The resulting universal law of fractionation is surprisingly concise. The predictions apply to all systems whose distribution of polydisperse property (such as size) is sufficiently narrow. For quantitative comparison with a real system, we performed measurements on a colloid-polymer mixture, using both light scattering and extensive counting of TEM micrographs to obtain particle size distributions in coexisting phases. We furthermore show that phase separation is an effective method of reducing polydispersity only for systems with a skewed distribution.

L44 FLOCCULATION STABILITY OF WEAKLY CHARGED OIL-IN-WATER EMULSION DROPLETS

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We have investigated the stability with respect to flocculation of oil-in-water emulsions stabilised by different nonionic surfactants containing a few mole% of ionic surfactants. All the systems are stable with respect to coalescence and Ostwald ripening but show a well defined transition from a non-flocculated to a flocculated state. The flocculation transition depends on the concentration of added electrolyte and on the mole% of added ionic surfactant which controls the surface charge density of the droplets. Flocculation may be induced either by increasing the salt concentration or by decreasing the ionic surfactant concentration. For the different emulsion systems we have determined the locus of the flocculation transition as functions of the salt and ionic surfactant concentrations - the "stability map". In addition, the energy of interaction in the flocculated state when the droplets are mutually adhesive has been determined from microscopic measurements of the contact angle between the thin film separating adhering emulsion droplets and the adjoining meniscus.

The results have been *quantitatively* modelled using DLVO theory appropriate to the case of the deformable emulsion drops. Three types of colloidal forces have been considered; attractive dispersion forces, repulsive electrostatic forces and short range repulsive forces. All the necessary input parameters for the model are obtained from independent measurements or are derived from the emulsion compositions. Good, quantitative agreement is observed with the experimental results.

We will describe results for emulsions where the main nonionic stabilising surfactant is either an alkyl glucoside (with a compact, globular hydrophilic headgroup) or an alkyl ethoxylate surfactant for which the headgroup is in an extended conformation and gives a "hairy" layer. Ethoxylate headgroups of different chain lengths have been examined.

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L45 EFFECT OF THE LECITHIN ON THE PROPERTIES OF β -LACTOGLOBULIN STABILIZED O/W EMULSIONS

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Whey proteins are widely used as a functional ingredients in food systems. Their physicochemical and emulsification properties have been studied, but most of the reported studies have used vegetable oils or model compounds as the dispersed phase. One novel application for whey proteins that is currently being studied is their use as microencapsulating agents. The key to a successful microencapsulation process is the formation of a stable emulsion in which the encapsulated material (the core) is dispersed in a solution of the encapsulating (wall) agent. The formation of whey protein stabilized films at the core/wall interfaces is thus important. The composition and structure of stabilizing layers in o/w emulsions are affected by the competitive displacement of protein from the interface by surfactant and by the nature and strength of protein-surfactant interactions in the aqueous phase and the oil-water interface.

Since there is a lack of information regarding the microstructural features of whey proteins based emulsions, this research has been undertaken in order to determine the microstructural properties of β -lactoglobulin stabilized emulsions consisting of olive and caraway oil which is used as the flavoring agent for spray-dried products. The objective was to investigate how the β -Lg stabilized emulsions were affected by the lecithin and to compare the properties of mixed films protein+lecithin at the interfaces of 2 oils: olive oil-water and caraway oil-water. The evaluation of the physico-chemical characteristics of emulsions were carried out: particle size distribution, creaming ratio, content of adsorbed proteins on the oil-water interface and protein surface concentration.

L46 SURFACE LIGHT SCATTERING FROM SURFACTANT SOLUTIONS

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The scattering of light by thermally excited capillary waves provides a powerful probe of the dynamics of liquid surfaces. Attention has turned in recent years to studies of adsorbed monolayers of amphiphilic molecules, which have revealed various novel phenomena, some quite unexpected. These include the detection

of step-wise changes in the dilatational elastic properties of the adsorbed film [1] which were correlated with previously postulated changes in adsorption state [2]. These transitional effects in the adsorbed films were associated with changes in the dynamics of molecular reorientation within the film [3]; subsequent studies revealed the expected viscoelastic relaxation of the dilatational modulus in such films [4].

Surfactants having molecular geometries which do not permit such reorientation should not exhibit such viscoelastic phenomena. We have tested this proposition in a surface light scattering study of adsorbed films of phosphine oxide [5]. We report the behaviour of the high frequency capillary waves and the surface viscoelastic properties which we deduce from these observations. Comparisons with other amphiphiles, such as decanoic acid and CTAB suggest that the reorientational model is appropriate.

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L47 **ELECTORHEOLOGICAL EFFECTS IN LECITHIN ORGANOGELS**

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The effects of an external electric field on ternary mixtures consisting of lecithin, *n*-decane and water or glycerol have been studied by means of oscillating rheology, polarizing microscopy and electric birefringence. The polar additives (water and glycerol) introduced in trace amounts into a nonaqueous solution induce a transformation of initially spherical reverse micelles into extended tubular (polymer-like) ones. Their entanglement results in the formation of a temporal threedimensional network bringing about viscoelastic properties of jelly-like phases (organogels). When a critical concentration of a polar additive is exceeded, the homogeneous organogel undergoes a phase separation into a nonviscous solution and a compact jelly-like phase. With further increasing concentration, a solid precipitate is formed. The effects of an electric field have been studied on both the homogeneous organogels and the two-phase systems.

It has been shown that a voltage applied causes an increase in the rheological parameters of all the examined mixtures. A critical voltage inducing the response is about 40 and 100 V/mm for water- and glycerol-containing organogels, respectively. In the latter case, a region of the reproducible and stable electrorheological (ER) effect is extended up to 1700 V/mm that is 3-4 times greater than that observed in the jelly-like phases with water. The ER response depends on the molar ratio of the polar additives to lecithin. Diagrams describing the behavior of ternary mixtures under the electric field have been constructed. They differ for water- and glycerol-containing organogels. A dependence of the stable ER effects on the molar ratio of glycerol to lecithin has a maximum in the vicinity of the phase separation of the homogeneous organogel, whereas for water-containing systems there is gradually ascending trajectory up to and including mixtures with the solid precipitate.

A new rheological regime has been established when the frequency-sweep measurements were performed on the homogeneous lecithin organogels under an electric field. This feature is the square-root scaling of the dynamic moduli with the frequency. Previously this has not been observed in systems consisting of the polymer-like micelles. The established scaling is inherent in polymers. By analogy, the rheological behavior is related to the ordering of cylindrical micelles under the action of an external electric field.

L48 **ELECTROKINETIC AND RHEOLOGIC CHARACTERIZATION OF TITANIA SUSPENSIONS OF HIGH SOLIDS FRACTION AND HIGH IONIC STRENGTH MICROEMULSION SYSTEMS**

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The stability against sedimentation and the viscoelastic properties of a high solids fraction titania suspension is related to the zeta potential and the particle size. Both the pH and the ionic strength is varied over wide ranges. It is found that the indifferent electrolyte added shifts the isoelectric point towards the alkaline range until no charge reversal is found. An enhanced ionic strength shifts the maximum viscosity and the point of maximum resistance against flow as a function of pH in a characteristic way. The dependency of the flow properties on the electrolyte concentration at high and low pH are partly opposite to each other. However, the point of maximum resistance against flow is found to be linearly dependent on the square of the zeta potential of the suspension. The slope of these curves increase with an increased electrolyte concentration. The results are discussed with reference to recent theories explaining this effect.

L49 CONFORMAL INVARIANCE IN TWO-DIMENSIONAL CLUSTER-CLUSTER AGGREGATION

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Cluster-cluster aggregation has been extensively studied as a paradigm for random colloidal growth. In the diffusion-limited case it is found that the system self-organizes into a stationary scaling state dominated by a single length scale: the inter-cluster separation [1, 2]. On the other hand the reaction limited case finally reaches a state lacking any characteristic length scale [3]: it has been suggested that this is a case of self-organization to the critical state.

It is conjectured that reaction-limited cluster-cluster aggregation in two dimensions displays conformal invariance [4]. In support of this hypothesis, it is found that structure functions computed for on-lattice aggregation are asymptotically invariant under conformal transformation as $t \rightarrow \infty$. Further, the fractal dimension determined for 2D RLCA is in good accord with predictions based on conformal invariance [5, 6]. This conjecture provides, for the first time, a theoretical framework for RLCA.

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L50 SILICA STABILISED MULTIPLE EMULSIONS

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Colloidal silica has been used to prepare both o/w/o and w/o/w multiple emulsions. Because the destabilisation caused by surfactant diffusion has been eliminated, the multiple emulsions described are highly stable and show no variation in secondary emulsion droplet size over a six month period. The rheology of the multiple emulsions also indicated high stability. The 1° o/w emulsion was prepared using hydrophilic silica (Ludox™ HS-40) and NP30 as a costabiliser. The secondary emulsification to prepare the o/w/o emulsion was effected using a hydrophobic silica (Wacker HDK H2000). In a similar way the 1° w/o emulsion was prepared with HDK H2000 silica. Hydroxypropyl cellulose was added to the dispersed aqueous phase to reduce the droplet size. Ludox™ HS-40 was then used in the secondary emulsification to prepare the w/o/w emulsion. A mixture of NP30 and NP6 was used as the costabiliser the latter surfactant added to reduce the interfacial tension.

L51 STRUCTURE, DYNAMICS AND FORMATION OF THE COLLOIDAL-LIQUID AND COLLOIDAL-GEL

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The effect of adding non-adsorbing polymer (Polystyrene) induces phase separation in a suspension of colloidal particles (PMMA) due to the depletion mechanism [1]. The range of the potential is determined by the size of the polymer and its depth increases with polymer concentration. The topology of the phase diagram depends on the ratio of the radius of gyration of the polymer to the radius of the colloidal particles. At high size ratio, a three-phase coexistence of colloidal gas, liquid and crystal is observed.

We studied, using two colour dynamic light scattering (TCDLS) [2], the development of structure and dynamics of the liquid phase as the size ratio is reduced from 0.57 (a "well-developed" liquid) to 0.25 (a "marginal" liquid). We find that while the local structure remains almost unchanged, long-ranged fluctuations appear as the size ratio is reduced [3]. Particle diffusion is found largely to reflect these structural developments.

At higher polymer concentration, three regimes of non-equilibrium aggregation behaviour are observed. One of these regimes is "transient gelation". Using TCDLS, the variation of structure and dynamics during the lifetime of the colloidal-gel is studied [4].

The implications of these findings for our understanding of the liquid state and non-equilibrium gelation will be discussed.

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**L52 ON THE BEHAVIOUR OF NON IONIC SURFACTANT IN ORGANIC SOLVENT:
 INFLUENCE OF WATER ON THE AGGREGATION PROCESS AND ADSORPTION MECHANISM
 ONTO SILICA GEL PREHYDRATED OR NOT**

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The behaviour of two non ionic surfactants, poly(oxyethylene) glycol alkylphenyl ether TX-35 and TX-100, in solution in n-heptane and at the silica gel-n-heptane interface has been carefully examined.

In a first part, we were interested in the aggregation process of the poly(oxyethylene) glycol alkylphenyl ether in n-heptane and in the solubilization of water in the reverse micelle of the surfactant (micellar solubilization). The results of microcalorimetric, viscosimetric and quasi elastic light scattering studies on dilution and hydration of TX-35 non ionic surfactant in n-heptane, in the presence and in the absence of water in the apolar medium, respectively, are reported. The amount of water which can be introduced in the system is followed in a very wide range of surfactant concentration allowing a critical aggregation concentration to be determined. The differential molar enthalpies of dilution and hydration of TX-35 determined by microcalorimetry and the mean diameters of the aggregates obtained from the quasi elastic light scattering experiments are discussed in details allowing some important conclusions to be drawn concerning the occurrence of a gradual aggregation process on a very wide range of concentration.

In a second part, the results at 298 K of isotherms and microcalorimetric studies (differential molar enthalpy of adsorption) on the two non ionic surfactants (TX-35 and TX-100) adsorption onto silica gel prehydrated or not are compared. In the case of adsorption experiments performed onto prehydrated support, the amount of water remaining or released in the bulk phase after the attainment of the surfactant adsorption equilibrium was also determined in the whole range of the isotherm. The effect of the interfacial water on the mechanism of non ionic surfactant adsorption is discussed. Moreover an HPLC study allowed to show a selective adsorption of the polydisperse Triton non ionic surfactants onto silica gel according the length of their oxyethylene chains.

L53 LINEAR GROWTH AND BRANCHING OF REVERSE POLYMER-LIKE MICELLES OF LECITHIN

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The viscoelastic properties of jelly-like phases (organogels) of lecithin produced by addition of trace amounts of water into a n-decane solution have been studied by an oscillation rheology. The polar additive induces the transformation of initial spherical micelles into flexible cylindrical ones called polymer-like micelles. Their entanglement results in the formation of a transient three-dimensional network responsible for the viscoelastic properties of the lecithin organogels.

It has been shown that the rheological behavior of jelly-like phases is primarily determined by molar ratio of water to lecithin (n_w) in the ternary mixtures. When n_w is varied between 1.5 and 2.7, the scaling dependencies of the zero shear viscosity, plateau modulus and terminal relaxation time obey a model by Cates that was developed for linear flexible polymer-like micelles. With increasing molar ratio of water to lecithin in ternary mixtures ($n_w > 2.7$), deviations from the Cates' model has been established. The power law exponents are close to those expected from a model of connected (branched) micellar aggregates. This result enables us to conclude that the growth of reverse lecithin micelles after the water addition includes at least two stages. In an early stage, there is a transformation of spherical micelles into cylindrical aggregates owing to the uniaxial elongation. The linear polymer-like micelles present in a solution. In the second stage, the micellar branching occurs.

The influence of various surfactants on the viscoelastic properties of the lecithin organogels and the growth of the polymer-like micelles has been examined. It is shown that some of additives occurs pronounced effects when they are introduced in minor amounts. A change of the micellar growth mechanism has been also established.

L54 A NEW METHODICS OF DROP EDGE RECOGNITION AND ITS APPLICATION FOR SURFACE TENSION AND CONTACT ANGLE MEASUREMENT

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The investigation of parameters of sessile drops is the essential part in the study of wetting. The conjunction of digital image processing and method of sessile drop provides the efficiency of interfacial tension and contact angle measurement.

We have developed a new method of recognition the drop borders. It is based on the physical idea that the object on the image can be recognized if a gray level gradient on the edge of object exceeds the level of noise in the field of image. The special procedures were developed to exclude the influence of illumination nonuniformity and diffraction phenomena.

Using of image collection allows to improve the signal to noise ratio and thus the resolution capacity of the experimental technique.

Above procedures have been realized in the experimental setup and have shown the reproducible results being in good agreement with the literature data.

The work was performed with financial support by Russian Foundation for Fundamental Research (grant # 98-03-32732).

L55 NOVEL GLYCOL SILICATE AND THEIR INTERACTION WITH SURFACTANT FOR THE SYNTHESIS OF MESOPOROUS SILICATE

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Silica gels can be prepared in the presence of micelles by hydrolysis and condensation of appropriate precursor molecules. After removing the surfactant by high temperature calcination a mesoporous silicate remains, which can be used as a catalyst or a molecular sieve.

The most used precursors are tetraethoxy silicate (TEOS) and tetramethoxy silicate (TMOS). During the hydrolysis of these compounds ethanol or methanol is formed which affects the surfactant mesophases.

It is shown that novel glycol and esters of the ortho silicic acid show two main advantages compared with common precursor molecules. First, they are water soluble and be dissolved in the surfactant phase. Second, no ethanol or methanol with its structure destroying properties is released during hydrolysis.

The formation of porous materials can therefore be better controlled from the time dependent changes during hydrolysis and condensation. An important question thereby is the influence on the surfactant on the silicate structure and vice versa. The gel building process of our new systems was investigated by time dependent small angle neutron scattering (SANS). Contrast variation makes it possible to show the scattering part of the single components (silicate or surfactant) separated from each other.

The formation of a fractal silicate structure results in an increase of the scattering intensity at low q -values. The fractal dimension D of a particle can be determined from its scattering profile: $S(q) \propto q^{-D}$. It is shown that both the surfactant concentration and solvent have an influence on this fractal dimension and the time of gelation. Measurements after gelation demonstrate the unchanged presence of surfactant micelles.

L56 A DIFFUSING WAVE SPECTROSCOPY STUDY OF THE VISCOELASTIC MODULI OF ACIDIFIED MILK GEL

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It has recently been shown that it is possible to extract the frequency-dependent linear viscoelastic moduli of certain dense colloidal systems by interpretation of data obtained by diffusing-wave spectroscopy [1]. For a variety of monodisperse colloidal system this approach yields experimental data which show good accord with the results of conventional mechanical rheometry. The method thus holds out the prospect of non-invasive determination of viscoelastic properties of dense colloidal systems. It is not, however, clear how far this approach may be applicable to complex, polydisperse colloidal systems which are liable to be encountered in practice.

We have applied a technically similar approach to the very much more complex colloidal system provided by acidified skimmed milk gel [2]. We will present details of our approach, and compare the light scattering results for $G'(\omega)$ and $G''(\omega)$ with those obtained from conventional rheometry.

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L57 DIFFUSING WAVE SPECTROSCOPY OF FLOWING FOAM

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Diffusing-wave spectroscopy has been used to study the effects of strain upon the dynamics of a model foam (shaving cream). The observed data are consistent with the hypothesis that the dynamic process reflected in the light scattering involves local rearrangement events in the foam [1]. The rate of such events is increased in strained foam [2]. Above a threshold strain the rate at which elementary strain-induced rearrangements occur in the foam is proportional to strain rate [3]. These results are in accord with the findings of recent computer simulations [4, 5, 6]. However, below a threshold strain rate the rate at which elementary strain-induced rearrangements occur depends only on the strain, whereas it is above this threshold that the rate is proportional to strain rate. No such phenomenon is found for foam subject to shear strain. A possible mechanism for the unexpected behaviour at low strain rates is outlined.

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L58 QUASI TWO-DIMENSIONAL "BUBBLE METHOD" FOR SURFACE TENSION AND CONTACT ANGLE MEASUREMENTS

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We propose a method for simultaneous determination of surface tension of a liquid and of the contact angle between a liquid and a solid, based on the shape of a gas bubble captured at the solid-liquid interface in a thin cell with plane-parallel walls.

The quasi two-dimensional geometry simplifies the theoretical treatment of the bubble profile, compared to that of the three-dimensional sessile drop performed by Bashforth and Adams.

We focused this study on the measurement of contact angles between a crystal and its own melt, which meets great difficulties due to the necessity of maintaining simultaneously capillary and thermodynamic equilibria between the phases. For these reasons, the experimental glass cell (wall to wall distance 0.5 mm) was pressed against a furnace composed of two independently regulated copper block, allowing small temperature gradient across a dividing 0.3 mm slot. This configuration permits to set-up a stationary solid-melt interface at a temperature only few tenths of degree away from the melting point. High purity argon bubble is introduced through a 0.24 mm syringe needle.

The micrographs of bubbles 2-4 mm of diameter give direct access to both surface tension and contact angle. Surface tension is determined by comparison of the experimental and theoretical profiles.

Additional advantages of the method, with respect to that of the sessile drop, are absence of contamination and of evaporation of the liquid during measurement. It can be applied also to non transparent substances.

L59 MEASURING THE CONTACT ANGLE OF INDIVIDUAL COLLOIDAL PARTICLES

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In sphere tensiometry the surface tension of a liquid is determined by measuring the force required to pull a sphere out of a liquid. We constructed an experimental set-up for "microsphere" tensiometry. The aim was to measure the contact angle of individual colloidal particles. Therefore particles are attached to atomic force microscope cantilevers which serve as force sensors. The particle is placed into a cuvette filled with the liquid. A gas bubble is placed onto the bottom of the cuvette. Then the particle is moved into the gas-liquid interface. The position of the particle is adjusted with a calibrated piezo translator. From the equilib-

rium position of the particle in the gas-liquid interface the contact angle can be determined. Since force and distance can be measured with a high precision (resolutions were 0.1 nN and 1 nm at full dynamic ranges of 1 μ N and 15 μ m, respectively) the random error of the contact angle is less than 1 %. This allows to study the influence of line tension, curved interfaces or surface forces. First results obtained with spherical particles of roughly 5 μ m diameter are presented.

L60

ORGANO SILICON NANOPARTICLES AS OPTICAL TRACERS

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Organo silicon microgels have been prepared by polycondensation in microemulsion of trimethoxysilanes. Highly crosslinked rather monodisperse particles of radius about 10 nm are obtained. Using silanes with special functional groups as comonomers, model particles suitable for studies in colloid physics are available: photoreactive and fluorescent dyes have been chemically incorporated into the microgels to prepare tracers for diffusion studies using Forced Rayleigh Scattering and Fluorescence Correlation Spectroscopy. To avoid effects of dye labels on interparticle interactions, the tracers have been designed as core-shell systems: a functionalized core, used for chemically binding dye labels into the colloidal particles, is surrounded by a thin non-functional shell of trimethoxymethylsilane. Influence of shell thickness in the range 0 - 2 nm on labeling efficiency has been probed by uv/vis-absorption spectroscopy.

Microgels containing small gold clusters have been developed as tracers for Dynamic Light Scattering. Using laser light of wavelength 514 nm, light absorption of those tracers causes convectional flux which can be probed by distinct oscillations in the DLS signals. Using laser light at 647 nm far from the absorption band of the gold-containing colloids, at low light intensity convection ceases and particle self diffusion can be measured in concentrated dispersions. By mixing a small amount of strongly scattering gold tracers into a matrix of refractive index matched colloidal particles, particle mobility has been probed as a function of particle concentration.

POSTERS

P₁₀**IN MEMORIAM: BOŽO TEŽAK (1907-1980),
INTERNATIONAL SUMMER SCHOOLS/CONFERENCES/SYMPOSIA, CROATIA, 1969-1990**

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In 1969, the first SUMMER SCHOOL, SOLID/LIQUID INTERFACES was initiated and organized in Dubrovnik-Cavtat by Professor Božo Težak, Faculty of Science, University of Zagreb, Zagreb, Croatia. His primary intention was to initiate discussions on the solid/liquid interfaces in colloid chemistry. Six international summer schools, conferences or symposia followed and new topics were included.

The Proceedings of the meetings were published in *Croatica Chemica Acta*, 42 (1970) No 2, 1-300; 45 (1973) 1-307; 48 (1976), No. 4, 391-686; 56 (1983), No. 3, 315-551; 60 (1987), No. 3, 357-294.

Till his premature passing away in 1980, Professor Božo Težak was the Chairman of the Scientific and Organizing Committees and Editor in Chief of the Proceedings.

One hundred and forty contributions, from twenty one countries, were presented at all meetings. Seventy three contributions by authors from fifteen countries dealt with the solid/liquid interfaces in colloids. Papers discussing double layers on colloidal solid/liquid interfaces were not separated from the papers treating "electrochemical" and "electrical" double layers with homogeneously spread electronic charges on electrode surface. The interfaces on colloidal particles are ionic and the "point charge double layer" model is only correct for them. All theories were based on the incorrect "homogeneous charge double layer model" which holds for electrodes of Galvanic cells only. The postulates of the theories were not checked experimentally.

Professor Božo Težak practiced, fought for and believed in the following main principles of science: (1) the right to publish theoretical and experimental results, (2) the freedom to choose what to publish, (3) the responsibility for what is published, and (4) the duty to study and apply the published results. He hoped that in this way science would acquire an adequate position in contemporary society and that it would best serve the benefit of mankind.

Many Editors of many journals and their referees do not act in accordance with the ethically and scientifically correct Težak's principles. The present author's contradicting experiences are described in his "Open Letter" (available on request from the Author!).

The said meetings fulfilled the tremendous task in unifying the scientists from all over the world in the search for scientific truth.

We, the scientists should agree with Professor Božo Težak's principles and should follow them. All of us who knew him, or were familiar his activities, owe him profound thankfulness and immense gratitude.

(Remark: The present author is confident that all B. Težak's principles are in full accord with "Ethical Guidelines to Publication of Chemical Research", 12A *Langmuir*, Vol. 14, No. 1, 1998.)

P₁₁**STRUCTURAL INVESTIGATION ON LECITHIN ORGANOGELS**R. Angelico,^{1,3} A. Ceglie,² U. Olsson,³ G. Palazzo¹¹ *Dipartimento di Chimica, Università di Bari, Bari, Italy*² *DISTAAM, Università del Molise, Campobasso, Italy*³ *Physical Chemistry 1, University of Lund, Lund, Sweden*

Self-diffusion and phase equilibria studies have been carried out on the three-components system lecithin/water/cyclohexane. The overall phase diagram was determined by means of small angle X ray measurements, optical microscopy under polarized light and ³¹P and ²H NMR spectra. Water and lecithin self-diffusion measurements in a wide range of the L₂ phase were performed using pulsed gradient NMR methods (both PGSE and stimulated echo). The lecithin diffusion was rationalized in terms of curvilinear diffusion along wormlike micelles, while the water experience also inter-micellar exchange. As a whole the results obtained exclude the presence of branched micelles, and show the presence of a transition towards spherical reverse micelles with increasing the water content.

P₁₂**THE PURIFYING OF MINE WATERS FROM COLLOIDAL SUSPENSIONS BY FLOCCULATION**

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The mine and size-damp waters of lead-zink deposits (sidles) is palliated by suspended substances (particle of rock, clays), mineral salts (chlorides, sulfates, silicates) also cations of hard metals (copper, zink,

ferrum, nickel, cobalt, molly). The concentration of suspended substances not subjected to purifying and processing on the special apparatus reaches to 2000 mg/l excelling the (30 mg/l) and pollute water reservoirs and rivers. It makes loss on water flora and fauna and also has effect on the population's health.

In this work complex researches on influences of polyacrylamid (PAA), polyethylenimine (PEI) on the degree of brightening of mine water of Belous undertaking of the East-Kazakstan region is results. It has been shown that PAA and PEI flocculate at determined concentrations of colloidal suspensions of mine waters. At the same time we should point that PAA is more effective flocculating agent than PEI. The flocculating capable is intensified of PEI and PAA at the determined relatives ($n = [\text{PEI}]/[\text{PAA}] = 0,3-0,7$) in comparison with individual components. The investigation of the kinetics of the flocculation showed the removal of the colloidal suspensions reaches to the zero during 10 min. at the presence of the mixtures of PEI and PAA. The strengthening of flocculating capable of the PEI and PAA mixture is explained by polycomplex between hem at the surface of the particle units at the expense of electrostatical binding which leads to the fast-sedimenting flake like flocules.

P₁₃

STUDIES OF PHASE BEHAVIOR IN SUGAR-DERIVED SURFACTANT SYSTEMS

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Phase behavior of new surfactant molecules derived from D-glucose and D-galactose has been studied. These molecules consist of an alkyl chain R ($\text{C}_n\text{H}_{2n+1}$) linked to galactose or glucose by an ether group. The influence of the alkyl chain length and its position in the molecule has been determined by means of phase diagram determinations and microscopic observations of water/surfactant systems as a function of temperature and surfactant concentration. The results obtained have shown that solubility of these compounds is not significantly modified with the change in one OH group orientation. However, the position of the alkyl chain length has an influence in the hydrophilic-lipophilic properties of these molecules. Surfactants with alkyl chain lengths, n higher than 8, form lamellar liquid crystalline phases while at lower n values hexagonal structures are observed. Micellar solutions and liquid crystalline phases of these binary water/surfactant systems have been characterized by light scattering and small angle X-ray scattering (SAXS) techniques.

P₁₄

INTERACTIONS OF CARBOXYMETHYLCELLULOSES WITH LAMELLAR LIQUID CRYSTALLINE SYSTEMS

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The influence of polyelectrolytes on structure formation in the liquid crystalline system Na-dodecylsulfate (SDS)/decanol/water has been investigated by means of SAXS, rheology and electron microscopy. It is known [1,2], that a cationic polyelectrolyte can be incorporated into the SDS/decanol/water system without phenomena of macroscopic phase separation. It can be concluded from our investigations, that the polymer is directly attached on the sulfate head groups of the lamella because of electrostatic interactions. Contrary to the incorporation of a cationic polyelectrolyte a penetration of an anionic polyelectrolyte into the hydrophilic part of the bilayer will get some more problems and phenomena of macroscopic phase separation were observed.

Our investigations are focused to mixtures of the preformed lamellar system, mentioned above, with the anionic polyelectrolyte Na-polyacrylate (PAA) and Na-carboxymethylcellulose (CMC). The CMC's used here differ with regard to the substitution along the backbone chain. The degrees of substitution (DS) of these cellulose derivatives are between 0.7 - 1.7.

The cellulose derivatives themselves show typical textures under polarized light in dependence on the content of water and the DS. SAXS-measurements show a general decrease of the interlayer spacing in comparison to the SDS/decanol/water system, but a linear slope with increasing water content in contrast to mixtures containing PAA.

Rheological investigations show that carboxymethylcelluloses can be used successful as rheologic modifiers of the liquid crystal. That means, at a water content of 40-60% microfibrilles are macroscopically incorporated into the lamellar system without phase separation. The resulting system shows a thixotropic behaviour and a significant higher shear stability.

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P₁₅

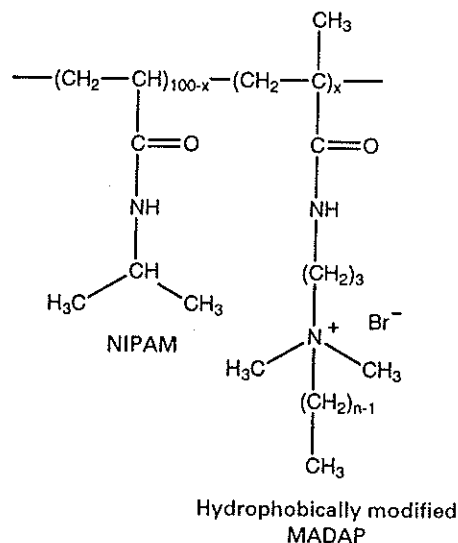
SHEAR INDUCED THICKENING IN AQUEOUS SOLUTION OF NEW THERMOSENSITIVE AMPHIPHILIC COPOLYMERS

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We report the synthesis and study of new amphiphilic copolymers, which combine in aqueous solution both associating and thermosensitive properties. The backbone of these polymers, prepared by radical copolymerisation in water, is consisted mainly of a thermosensitive monomer, the N-isopropylacrylamide (NIPAM), and, in a lower content, of a second monomer bearing amine groups, the [(N,N-dimethylaminopropyl)methacrylamide] (MADAP). These groups are in a second step alkylated in chloroform by an alkylbromide, to give the final cationically charged and hydrophobically modified copolymers of NIPAM (x is the alkylation degree and n is the number of carbon atoms of the pendant alkyl groups).

The original rheological properties, ranging from the usual associating behaviour at low temperature to the shear induced thickening (or gelation) at higher temperature, is closely related to the phase behaviour of these materials. The influence on this behaviour of several parameters, such as the temperature, the polymer concentration, the degree of alkylation and the alkyl chain length, is discussed.

P₁₆

EFFECT OF SHORT-RANGE ATTRACTIVE INTERACTIONS ON THE LOW-FREQUENCY ELECTRICAL CONDUCTIVITY OF WATER-IN-OIL MICROEMULSIONS

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Microemulsions composed of water and oil phases separated by a monomolecular layer of amphiphilic molecules exhibit a large variety of structural rearrangements, including clustering, percolation and critical phenomena. Within certain ranges of composition and temperature, a water-in-oil microemulsion can be effectively considered as a heterogeneous two-component system, made up of conducting spherical droplets of water, coated by a monolayer of surfactant molecules and uniformly dispersed in a continuous, non-conducting, oil medium.

The electrical conductivity is caused by a charge fluctuation mechanism, i.e., the transient fusion of two adjacent droplets to form a short-lived "dimer droplet", where ions (counterions) can randomly redistribute.

In this note, we report on low-frequency electrical conductivity measurements of water-in-oil microemulsion systems, formed by using four different organic solvents (*n*-pentane, *n*-heptane, *n*-decane and carbon tetrachloride) at different water-to-surfactant molar ratio *W*, in the temperature range from 5 to 60 °C (up to the stability limit of the single phase system). To evaluate the effect of short-range attractive interactions between surfactant coated water droplets, the microemulsion composition has been appropriately varied by maintaining constant the distance between two adjacent droplets. The experimental data have been analyzed in the light of the currently stated charge fluctuation theories and the parameters characterizing the tail interpenetration evaluated for the different solvents investigated. The results presented here give further support to the identification of the interdroplet interaction as due to the penetration of the surfactant tails of water droplets.

P₁₇

STRUCTURAL TRANSITIONS FROM CATIONIC SURFACTANT SALT TO MIXED CATIONIC/ANIONIC VESICLES

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Structural transitions from crystalline cationic salt to mixed cationic/anionic vesicles were investigated in the mixtures of alkylammonium chlorides and sodium alkyl sulfates of the same chain length. The excess

of one of the surfactants in the cationic lamellar structure led to disruption of the planar bilayer and formation of the closed bilayer vesicle through a series of equilibria. The composition of mixed cationic/anionic vesicles depended on the molar ratio between cationic and anionic surfactant. Molecular scale rearrangements occurred most probably due to the electrostatic interactions between headgroups located at the bilayer/solution interface.

P₁₈

ADSORPTION PARAMETERS AND SELECTED PERFORMANCE PROPERTIES OF N-ALKYL-N-METHYLLACTONAMIDES

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N-Alkylgluconamides constitute a new group of nonionic surfactants. They are recently used in new-developed surfactant systems which show improved performance [1] and reduced environmental impact [2]. In our previous paper [3] we have shown that the presence in N-alkylgluconamides of an amide methyl group and two glucose segment (as in lactobionamides) instead of one glucose unit both increase significantly the surfactant solubility. On the other hand the introduction of an additional CHOH group into the glucose moiety (as in glucoheptonamides) causes an hydrophobic effect.

In the present contribution we report our results on adsorption at the aqueous solution-air interface of two series of amides: N-alkyl-N-methylgluconamides and N-alkyl-N-methylgluconamides, both containing C₁₀, C₁₂, C₁₄, C₁₆, and C₁₈ (oleyl) alkyl groups. Surface properties of these surfactants, i.e., surface excess concentration, Γ , surface area demand per molecule, A, effectiveness of surface tension reduction, π , and critical micelle concentration, cmc, were determined from surface tension isotherms. Foaming and wetting abilities were measured as well. The obtained results were discussed and compared with those reported for commercial alkylpolyglycosides.

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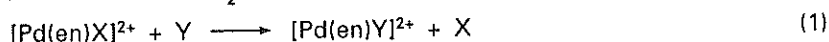
P₁₉

KINETICS OF LIGAND SUBSTITUTION AT SQUARE-PLANAR PALLADIUM(II) COMPLEXES IN HEPTANE-AOT-WATER MICROEMULSIONS

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The kinetics of the substitution reactions (1) of the coordinated ligand X (= 2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine) of the palladium(II) complex [Pd(en)X]²⁺, where en = ethylenediamine, by en or N,N-dimethylethylenediamine (Y) have been studied at 25.0 °C in heptane-AOT-water microemulsions as a function of the AOT concentration at the constant R (= [H₂O]/[AOT]) values of 3, 8, and 20 or 30.



The overall second-order rate constants are higher in microemulsions than in bulk water and decrease significantly as both the AOT concentration (at constant R) and the molar ratio R (at a given [AOT]) increase. Moreover, the reaction rates depend to a significant extent on the nature of both the incoming and leaving ligand.

The least-squares analysis of the kinetic data, made by applying the pseudophase model, leads to the suggestion that two reactions contribute significantly to the overall rate of the substitution process (1), i.e., the reactions of the palladium complex bound to the negatively charged AOT/water interface with the nucleophile Y present in both the water pool and the interfacial region.

Evidence is obtained that the same rate effects of the incoming and leaving ligands are operative in both bulk water and the AOT interface and that the substitution reactions proceed by the same rates and mechanism in the two different media.

The present findings lead to the conclusion that the "effective" AOT pseudophase volume (per mole of surfactant) in which reaction occurs is not a constant parameter when the molar ratio R is changed and increases as the interfacial AOT layer curvature (i.e., the droplet size) becomes larger. This result is of particular interest in kinetic studies of chemical reactions performed in these microheterogeneous media.

P₁₁₀ SYNTHESIS AND SURFACE ACTIVITY OF POLYOXYBUTYLENATED HIGHER ALCOHOL SODIUM SULFATES

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Some polyoxybutylene glycol alkyl monoethers were obtained from C₈ - C₁₄ aliphatic alcohols and α -butylene oxide in the presence of basic catalyst. These compounds were used to synthesize a series of sulfate-type anionic surfactants RO[CH₂CH(C₂H₅)O]_mSO₃Na where R=C₈H₁₇, C₁₀H₂₁, C₁₂H₂₅, C₁₄H₂₉; m=1, 2, 3, and 4.

Surface activity of these compounds in aqueous solutions, i.e. critical micelle concentration, CMC, surface tension at CMC, γ_{cmc} , surface excess concentration, Γ , surface area demand per molecule, A, and standard free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$ have been determined.

The surface tension and critical micelle concentration of the aqueous solution of these surfactants are presented as the function of oxybutylene units number in a sulfate-bearing molecule m_{BO}. It has been found that the presence of oxybutylene units in a molecule of the compounds enhances the surface activity and increases γ_{cmc} of these surfactants. The slopes of function: $\log \text{CMC} = f(m_{\text{BO}})$ are identical for all homologous series studied and, in practice, do not depend on the oxybutylene chain length.

The relation between the CMC and the number of C atoms in the alkyl group and the number of oxybutylene units of anionic surfactants can be expressed by the following equation:

$$\ln [\text{CMC}] = - \frac{nW_{\text{CH}_2}}{(1 + K_g)kT} - \frac{nW_{\text{BO}}}{(1 + K_g)kT} + \text{const}$$

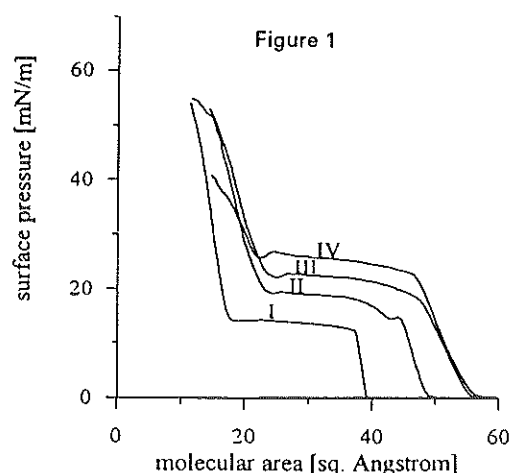
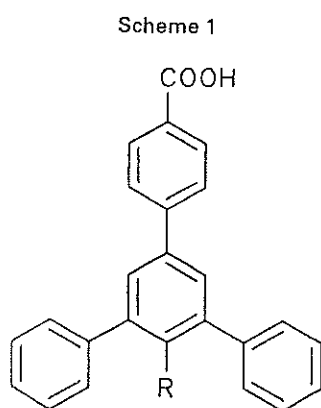
where m is the number of BO units in the ionic surfactant; W_{BO} is a van der Waals energy of interaction per BO unit similar to W_{CH₂}. Since the relationships of $\log[\text{CMC}]$ vs n and $\log[\text{CMC}]$ vs m are linear, it is possible to calculate W_{BO} for a given n and W_{CH₂} for a given m.

From the ratio of the CMC change per methylene and oxybutylene unit the cohesive energy change during transition from molecular to the micellar state was determined and the CH₂ unit equivalent was calculated to be approx. 0.6 oxybutylene units in these anionic surfactants.

P₁₁₁ LANGMUIR MONOLAYERS FORMED BY A NOVEL GROUP OF AROMATIC AMPHIPHILES

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Our investigations on the surface pressure/area (π/A) isotherms for Langmuir monolayers formed by a series of aromatic carboxylic acids have been supplemented by Brewster angle microscopy (BAM) results. The compounds studied constitute a novel group of amphiphilic molecules which are characterized by an uncondensed polyphenyl ring system. They have the structure of symmetrical triphenylbenzene, as illustrated in the Scheme below:



The results have shown that the parent compound (I), for which R = -H, as well as its derivatives, with R = -CH₃ (II); -C₆H₅ (III) and -C₆H₄CH₃ (IV), when spread at the air/water interface form stable monolayers which exhibit a characteristic broad "plateau" (see Fig. 1). The lift-off areas (ranging from 40 - Å²) as well as the surface pressures at which collapse of the condensed liquid state of the monolayers occurs, increase with the bulkiness of the R substituent. Interestingly, the plateau spans in all cases over a region corresponding to a decrease of the molecular area by a factor of about 2. Subsequently, the compressibility of the film drops markedly and eventually an irreversible collapse appears at pressures just below 60 mN/m. BAM results

indicate that homogeneous films exist in the liquid-condensed pre-plateau region. When the middle part of the plateau is reached, characteristic stripes are being observed. 3D domains occur only in the post-plateau part of the isotherms.

P₁₁₂ PHYSICO-CHEMICAL PROPERTIES OF ASYMMETRIC CATIONIC SURFACTANTS: HEXADECYLTRIMETHYLAMMONIUM ALKYL SULFATES

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A series of novel cationic surfactants was prepared by mixing equimolar solutions of cationic (hexadecyltrimethylammonium bromide) and anionic (sodium alkyl sulfate, with the chain length C₁₀, C₁₂ and C₁₄) surfactants. New compounds were characterized by optical microscopy, X-ray diffraction, IR spectroscopy, ¹H NMR, and chemical analyses. The asymmetric cationic surfactants exhibited a complex thermal behavior. Several successive phase transitions in the solid state were detected as shown by calorimetric, thermogravimetric and X-ray diffraction data and polarizing microscopy observation. On heating, several solid crystalline-solid crystalline, solid crystalline-liquid crystalline, and liquid crystalline-isotropic liquid phase transitions were observed. On cooling, however, all hexadecyl-trimethylammonium alkyl sulfates underwent reversible changes, exhibited a temperature hysteresis and an advanced ordering in the crystal lattice.

P₁₁₃ STUDY OF THE RELATION BETWEEN PHASE BEHAVIOR, EMULSIFICATION AND EMULSION PROPERTIES.

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The main aim of this work was to study the relationship between the type of phases present during the emulsification process, the order of addition of the components during emulsification and droplet size distribution of the resulting emulsions. In this study, an appropriate ternary water/ethoxylated nonionic surfactant/aliphatic hydrocarbon system was chosen as a model system to form water in oil emulsions at 25°C. Phase behavior of the model system was determined at constant temperature in order to know the phases at equilibrium and also those involved in the emulsification process. The emulsification methods studied were: (A) addition of oil to an aqueous surfactant dispersion, (B) addition of water to a surfactant solution in oil, and (C) emulsification of pre-equilibrated samples. Emulsion droplet size distributions were obtained by means of laser diffraction and scattering methods. Emulsions obtained with methods A and C were poly-disperse. In contrast, emulsions with narrow size distribution were obtained with method B. In addition, with method B very small droplet sizes (50 nm approximately) could be obtained at certain water/oil ratios. This type of emulsions are considered to be nanoemulsions (also referred in the literature as miniemulsions and ultrafine emulsions). The results have been interpreted according to the changes in the natural curvature of the surfactant during the emulsification process.

P₁₁₄ FORMATION OF TRICHLOROFUOROMETHANE HYDRATE IN W/O EMULSIONS STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY

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At low temperature and high pressure conditions, present in off-shore oil and gas exploitation and processing, water incorporate some natural gases and form crystalline ice-like compounds, called clathrate hydrates.

During crude oil transport, the conditions can be gathered together for observing clathrate hydrates formation, in such a way leading serious problems such as plugs in pipelines. The interest of oil industry for these hydrates has, consequently, given rise to some extensive studies.

The formation of the trichlorofluoromethane (CCl₃F) hydrate has been studied in water in oil emulsions stabilized by non-ionic surfactant. This model system allows to get near some actual situations observed in drill-hole. For handling simplifications, the CCl₃F has been used as substitute for gases because this compound forms a hydrate under mild conditions, that is 3-7 °C at 1 bar. This model system was proposed and studied initially by J. Sjöblom and al. by means of time-domain dielectric spectroscopy. This present work,

initiated afterwards as a complementary approach of the precedent one, deals with the study of the hydrate formation by differential scanning calorimetry. This technique, suitable for detecting the phase transitions, is adapted also to quantify these phenomena.

The calorimetry plots obtained with emulsions containing CCl_3F and compared with those obtained with CCl_3F free emulsions reveal, during the heating scanning, the existence of an endothermic peak ascribed to the hydrate melting. The hydrate appearance has been related to the parameters such as the lowest temperature limit, cooling and heating rates, the value of a steady temperature plateau and the time elapsed at chosen temperature. Our data indicate the existence of two hydrate polymorphs with melting points at approximately 3 °C and 10 °C respectively. Moreover, according to our results, it appears that the ice formation induces a synergy for the hydrate formation.

P₁15 **NMR RELAXATION AND DIFFUSION STUDIES OF MICELLES AND MICELLAR COMPONENTS**

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While most aspects of micellar structure are well characterized nowadays, here we illustrate how NMR can help to clarify a few of the remaining problems. The first two studies are on cetyltrimethylammonium bromide (CTAB) micelles with or without aromatic solubilizers while the third one has been performed on cesium perfluorooctanoate micelles.

The first example concerns with the surface diffusion of Br^- ions. While this counterion is often described or imagined as "strongly bound" to the micellar surface, ^{81}Br NMR relaxation experiments reveal that it diffuses almost as fast as the Br^- ion in an isotropic solution and its hydration shell is only marginally disturbed by the vicinity of the positively charged headgroups.

The second example concerns with measuring the effect of solubilizers on micellar size. When micelles grow from spherical into another shape their translational diffusion just as well their tumbling becomes slower. A slowing-down of translational diffusion can be directly detected by pulse-field-gradient spin-echo (PGSE) NMR experiments; an accurate measurement of the micellar axial ratio requires rather accurate experimental data. A slower tumbling becomes reflected in the frequency dependence of the NMR relaxation rates that can be revealed by NMR measurements performed at multiple fields.

The third example is about the state of perfluoro-alkyl chains in micelles. As one important characteristic, the variation of the order parameter of the C-H bond along the alkyl chain has been measured in many different protonated surfactants and yielded rather similar order parameter profiles independent, for example, of the phase structure. Here we present the order parameter profile for perfluoro-alkyl chains as revealed by ^{19}F -decoupled ^{13}C relaxation experiments.

P₁16 **MORPHOLOGY AND STRUCTURE OF CADMIUM DODECYLBENZENESULPHONATE UNDER THE INFLUENCE OF NATURAL SEA WATER**

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Cadmium dodecylbenzenesulphonate [$\text{Cd}(\text{DBS})_2$] precipitates from water solutions both in the crystal form and as liquid crystalline phase. In the sea water of different salinity the precipitation synergistic effect takes place. The precipitation reactions include the anionic and cationic macro constituents of the sea water and dodecylbenzenesulphonic acid.

The chemical composition and the structure of mixed crystals and liquid crystalline phases have been determined in the solution of the sea water by using the qualitative and quantitative analysis of chemical elements on scanning electron microscope. The concentration of sea water is expressed by the chlorine ion $[\text{Cl}^-] = 10^{-2} \text{ mol dm}^{-3}$. A good agreement of the results achieved by the complexometric analysis, atomic absorption, X-ray diffraction, as well as, thermogravimetric analysis, was found. These methods showed that cadmium partly was included into the lamellar bilayers, and it was partly crystallized within the liquid crystal matrix in the form of $\text{Cd}(\text{DBS})_2$ and CdCl_2 . It can be assumed that some amount of cadmium has been adsorbed at negatively charged surface of the surfactant micelles.

These investigations present an approach to the extraction of heavy metals from waste waters and from natural ecosystems with surface-active agents.

P₁17 ADSORPTION OF SURFACTANTS AS A CONDITION OF CLEANSING ACTION

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The cleansing action of a surfactant is a consequence of his adsorption on the dirt which adheres to objects. At first, we have defined the dirt-surface system as the the diesel engine soot particles deposit on polymeric surface. Then, we analysed the cleaning effectiveness of several surfactants and we tried to correlate this efficiency with the adsorption phenomena. The force of adhesion between the soot particles and the surface are greatly diminished when the system is immersed in surfactants solution. The cleansing action increase with the length of the alkyl moiety of the surfactant and decrease with the number of oxide groups of the nonionic surfactants. This action can be related to the variation of the interfacial potentiel of the dirt particles and to the spreading pressure of the adsorbed film on dirt surface.

P₁18 ADSORPTION OF DODECYL AMMONIUM CHLORIDE ON SEA SHELL CONCHES

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It is well known that surfactants may control crystallization processes through retardation or enhancement of nucleation, crystal growth and/or aggregation. The quantity of surfactants in environment is getting bigger every day. Therefore, we investigated the adsorption of dodecyl ammonium chloride (DDACL) on sea shell conches in model system.

The adsorption of DDACL on sea shell conches was studied as a function of surfactant concentration. Composition of conches was determined by RTG and FTIR analysis. The initial conditions were: pH 6.5, ionic strength 0.3 mol dm⁻³ and 298 K.

The adsorption isothermes were analyzed by general adsorption isotherm equation for surfactants [1]. The equilibrium constants, aggregation number, amount of adsorbed monomer and saturated adsorption were calculated.

(1) B-Y. Zhu, T. Gu (1991) Adv. Colloid. Interface Sci. 37:1-32

P₁19 DIRECT ANALYSIS OF SANS AND SAXS MEASUREMENTS OF CATIONIC SURFACTANT MIXTURES BY FOURIER TRANSFORMATION

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Vesicle and micellar structures formed by mixtures of the oppositely charged surfactants cetyltrimethylammonium bromide (CTAB) and sodium octylsulfate (SOS) with and without added sodium bromide (NaBr) have been examined by small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) techniques. The resulting spectra have been evaluated using Fourier transform/deconvolution technique. Through indirect Fourier transformation of the scattering intensity and subsequent deconvolution of the resulting cross-sectional pair distance distribution function, detailed contrast density profiles of the aggregate cross-section are obtained. Since SAXS and SANS are sensitive to different physical properties of the scattering particle, these techniques can be used in parallel to obtain a rich variety of information. The electron density of the hydrocarbon chains is lower than the solvent while the electron density of the head groups is higher than the solvent and the advantage of using SAXS is that the point where the contrast changes can clearly be identified. On the other hand addition of NaBr inhibits the analysis of the SAXS data because of the increased overall solvent electron density and the counterions. The effect on the neutron scattering length density of the solvent is much less pronounced and therefore in this case SANS is much more favourable.

The SAXS and SANS analysis, when compared with theoretical calculations from a thermodynamic cell model, indicate that the surfactant head groups occupy a diffuse region near the core/water interface.

P₁₂₀ STRUCTURE AND DYNAMICS OF VESICLES FROM SYMMETRICAL DOUBLE CHAIN ALKYL BENZENESULPHONATES

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Symmetrical double-chain sodium 1'-(7)-tridecylbenzenesulphonate (7STBS) (C₁₃-compound) was prepared by conventional methods from reagent-grade starting materials. Appropriate symmetrical ketone reacts with phenylmagnesium bromide in Grignard reaction, giving tertiary alcohol A. Hydrogenation of A over palladium in cold acetic acid gives alkyl-substituted benzene, which, upon sulphonation by Doe's procedure, and neutralization of resulting sulphonic acid, yields sodium salt.

Using conductometric titration and surface tension measurements two critical concentrations, (c.m.c.)₁ and (c.m.c.)₂, have been determined in the binary surfactant/water system.

The samples were observed at room temperature using an Axiovert 35 Zeiss polarized light microscope operated with differential interference contrast optics (DIC LM). In the dilute regime the formation of either lamellar bilayers and multilayers or vesicles were found. It was shown that the particles belong to a multilamellar vesicle phase. The texture observed in the polarization microscope without using the I plate showed the sparkling particles. Particles' diameters of freshly prepared systems were found to be 75 - 220 nm relating to the surfactant 0.5 - 7 %, and 150 - 310 nm by aged systems with the surfactant 0.5 - 1.5 %, respectively. The time dependent shift in the vesicle/lamellar phase transition of the macroscopically equilibrated systems could be supposed to be a low energy transition. In addition, dynamic light scattering determination showed that some structural changes occurred by aging the samples. The transition between the vesicles and lamellae was governed also by the concentration and temperature change.

P₁₂₁ PROPERTIES OF CATIONIC SURFACTANTS IN PURE AND MIXED STATES

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The solution properties of the cationic surfactants dodecyl-, tetradecyl-, and hexadecylammonium chloride as well as hexadecyltrimethylammonium bromide in pure and mixed states have been studied. Their adsorption at the air/solution interface and micellar properties (the critical micelle concentration, counterion binding, thermodynamic of micellization, hydrodynamic radius, etc.) were evaluated by surface tension, conductance and light scattering measurements. The surfactant mixed non-ideally in both the mixed films and in mixed micelles. A change of counterion binding was observed compared to the pure states. The composition of mixed films and mixed micelles, the corresponding activity coefficients, and the interaction parameters were determined using the regular solution theory.

P₁₂₂ EXPERIMENTAL STUDIES OF TWO-DIMENSIONAL FOAM

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Foam is an example of a disordered physical system, of widespread practical significance, which remains rather poorly understood [1]. Two-dimensional foam retains many of the characteristics of the 3D case but offers many advantages for study, notably that the system is readily visualized. Two-dimensional arrays of bubbles on the surface of soap solutions, which have been used as model systems for condensed matter physics, and have recently been adopted as examples of two-dimensional foam [2, 3].

We have adapted methods of creating bubble rafts to produce perfect triangular foam lattices, as well as ones containing isolated defects. We find that introducing one defect into a perfectly 6-coordinated 2D foam significantly enhances its stability and completely alters its temporal evolution [3]. We have studied the evolution about various kinds of isolated point defects in two-dimensional liquid foam [4, 5]. As the foam about the defect coarsens it becomes disordered, the degree of disorder growing with time broadly in line with recent simulations [6, 7] and not as suggested by earlier work [8].

This work is being extended to study grain boundaries, and the bubble-level response of 2D foam to applied shear stress.

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P₁₂₃ DMSO-INDUCED DEHYDRATION OF DPPC MEMBRANES STUDIED BY X-RAY DIFFRACTION, CALORIMETRY AND SMALL-ANGLE NEUTRON SCATTERING

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The cryoprotection properties of dimethyl sulfoxide (DMSO), a substance well known for its biological and therapeutic applications, were investigated on lipid membranes by X-ray diffraction, differential scanning calorimetry and small-angle neutron scattering. The experimental study of water freezing and melting of ice was performed in the ternary system which consists of 1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine (DPPC), DMSO and water. The influence of DMSO on the DPPC membrane structure was established in the excess of solvent in the region of DMSO molar fraction from 0.0 to 1.0. The methods applied demonstrated the differences in the membrane structure in three sub-regions of DMSO molar fraction (X_{DMSO}): from 0.0 to 0.3 for the first, from 0.3 to 0.9 for the second, and from 0.9 to 1.0 for the third subregion. The results for $0.0 \leq X_{\text{DMSO}} \leq 0.3$ can be explained in the framework of DMSO-induced dehydration of intermembrane space.

P₁₂₄ INVESTIGATION OF POLYELECTROLYTE-SURFACTANT INTERACTIONS BY SURFACTANT SELECTIVE MEMBRANES

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The binding of the cationic surfactant dodecylpyridinium chloride (DoPyCl) to different anionic co-polymers of N-methylvinylacetamide as well as preformed anionic charged polyelectrolyte complexes has been investigated by using a potentiometric technique based on a surfactant ion solid-state electrode.

The polyelectrolyte complexes were "synthesized" by a polyelectrolyte titration experiment which was stopped at a certain degree of conversion, where the anionic component is still in excess. The solid membrane used in the electrode consists of poly(vinyl chloride) plasticized by (bis(2-ethylhexyl) phthalate).

Binding isotherms are analyzed in terms of the nearest neighbor interaction model by Zimm and Bragg and for systems of reduced polyanion-availability of the Scatchard plot, which indicates cooperative interactions already at very low surfactant concentrations ($6 \cdot 10^{-3}$ mM dm⁻³). The binding constants decrease by decreasing the charge density of the cationic copolymer in the preformed polyelectrolyte complexes used.

Static light scattering measurements show simultaneously a decrease of the particle packing density. Consequently, it can be concluded, that in "loose packed" polyelectrolyte complex aggregates the accessibility for cooperative polyelectrolyte-surfactant interactions is decreased significantly [1].

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P₁₂₅ CHARACTERIZATION OF SEA-SURFACE MICROLAYERS BY MONOLAYER TECHNIQUES AND BREWSTER ANGLE MICROSCOPY

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The sea-surface microlayer has been defined as the top 1 to 1000 μm of the sea surface.

Sea-surface microlayers are sites of the adverse biological effects and a medium for the transfer of energy and material between the sea and the atmosphere, representing thus the interfacial region where many important bio-physical-chemical processes and flux of gases are taking place.

Natural samples of sea-surface microlayer and samples which have been previously extracted by organic solvent and then reconstructed on the water surface were studied by monolayer techniques and Brewster angle microscopy (BAM). Surface pressure - area (p - A) and surface potential - area (DV - A) isotherms have been measured. Simultaneously BAM video images have been recorded. From p - A isotherms, thermodynamic parameters describing the states of monolayers, namely compressional modulus C_s -1 and compressibility have been calculated.

Monolayer techniques and BAM are proved to be very efficient analytical tools for a physico-chemical characterization of natural films improving thus our understanding of the mechanisms and physicochemical processes at natural phase boundaries.

It was found that both natural sample of sea-surface microlayer and ex-situ reconstructed film exhibit the characteristics of a liquid expanded phase without undergoing a phase transition. The BAM images taken from these films depend on surface pressure. At lower surface pressures liquid condensed domains are surrounded by liquid expanded phase and by compressing the domains become smaller and densely packed.

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P₁₂₆ IONIZATION DEGREE OF SODIUM 4-(4'-ALKYLPHENYLAZO)BENZOATES IN AQUEOUS SOLUTION

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Sodium 4-(4'-alkylphenylazo)benzoates (C_n AzoCOONa) represent an interesting class of photochromic amphiphiles which contains a rigid azobenzene moiety in the hydrophobic part of the molecule [1,2]. The aggregation behavior of C_n AzoCOONa in the solutions depends mainly on structure, concentration, temperature and method of preparation.

In this work we discuss an effect of the additional electrolyte (sodium chloride and sodium hydroxide at the concentration up to 40 mM) on the micellar ionization degree, α , of C_n AzoCOONa amphiphiles, having alkyl chains of butyl, hexyl and octyl. For the determination of α , and CMC we have performed potentiometric measurements at 25 °C, using Na^+ ionselective electrode. The values of α , and CMC were obtained from the electromotive force data, using known procedures.

It was found that log CMC decreases linearly with increasing number of carbon atoms. The value of CMC in water varies from 9.7 mM to 2.7 mM and 0.72 mM for the butyl, hexyl and octyl derivatives, respectively. For the butyl derivative the value of CMC varies from 9.7 mM in water to 4.7 mM in 40 mM NaCl or 5.3 mM in 40 mM NaOH. Variation of the CMC with the added electrolyte concentrations was described by the empirical Corrin-Harkins equation. The observed decrease in α due to increasing alkyl chain length can be ascribed to the increased surface charge density of micelles. In aqueous NaCl or NaOH solutions a much more pronounced decrease in α observed. It can be attributed to the increase in aggregation number of the micelles with increasing concentration of the added electrolytes.

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P₁₂₇ AGGREGATES OF SURFACTANT CAGE MOLECULES

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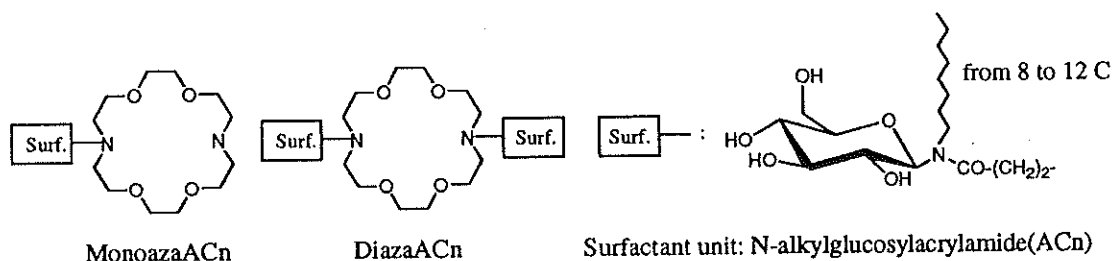
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For applications in selective extraction chemistry, new surfactant cage molecules have been developed and their micellar aqueous solutions studied. With the objective of separating the surfactant properties from the complexing ones, the molecules have been designed with a diblock structure and have been obtained by linking one (or more) surfactant unit [1] to an azacrown molecule which is able to selectively complex cations. We have changed the alkyl chain length (8 to 12 carbon atoms) and the number of linked surfactant (1 or 2) on the aza type cage (see figure).

In order to investigate the relation between complexation and micellisation, the first step is to determine basic thermodynamical parameters with and without complexed ions, in the adsorbed layer (from surface

tension measurements) and in the micellar state. The shape and aggregation number of the micelles are determined by fitting a molecular constrained model of the small angle X-Ray and neutron scattering data simultaneously. The ACn precursors display slightly extended to cylindrical micelles while increasing the alkyl chain length. The measured molecular data of the mono and diazaACn molecules show that their molecular volumes vary linearly with their hydrophobic part and CMCs depend on the chain volumes. The formed micelles are short cylinders whose structure is quite independent of the charge of the molecule and is mostly controlled by the nature and the number of linked surfactants via the steric hindrance of their hydrophobic chains. We have demonstrated experimentally that the molecular volume of the ACn precursor rather than the charge imposes its surfactancy properties on the resulting molecule.



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P₁₂₈ STABILITY OF SPONGE-LIKE FLUID MEMBRANES

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Different viewpoints on the stabilizing mechanism of the characteristically narrow L_3 (sponge) phases have lead to a series of debates in recent years. Several models have been developed to describe such mechanism via thermodynamics. To date, experimental data are insufficient to captiously test present theories; hence this matter rests on analytical grounds. In the present study we investigate two fluid membrane systems, $C_{12}E_5$ -*n*-dec- H_2O and $C_{10}E_3$ - H_2O , to provide additional experimental data for an in-depth examination of models based on the flexible surface approach. System specific parameters, such as the coefficient characterizing the spontaneous curvature temperature-dependence (β) and the two bending moduli (κ and $\bar{\kappa}$), will be critically examined for their roles in stabilizing sponge-like membranes.

P₁₂₉ POLYELECTROLYTES AS STABILIZERS FOR COLORED FORM (CATION) OF SOME NATURAL ORGANIC DYES

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Anthocyanins (mono or di-glucosides) are water-soluble natural pigments, belonging to the group of polyphenols, which play an important role in the coloring of fruits and flower petals. These compounds are potentially very interesting as natural colorant additives in foods, but this application requires improvement of their chemical and photochemical stability [1].

The structural changes occurring in aqueous solutions in the pH range 2-5 have been investigated by Brouillard [2, 3]. In general at pH lower than 3 the only presented form is the flavylium cation (AH^+) (colored form), but at pH greater than 3 there is a complex equilibrium where both quinoidal bases (A), hemiacetal (B) and chalcones (C) (all colorless) can occur. Thus, at moderately acidic pH values where additives can be used the color is lost, unless a mechanism for color stabilization exists. Several mechanisms for color stabilization, involving formation of molecular complexes, have been proposed, namely self-association [4, 5] and copigmentation with other polyphenols [5, 6], which are belived to be the most efficient processes allowing color stabilization *in vivo*.

In this work, we study the effects of pH and ionic strength on the color stabilization of an anthocyanine (oenin) with sulphate derivatized dextran polymers (linear and cross-linked polymers). In order to cover the entire range of aggregate's charge density we have used various degrees of substitution (sulphate) as well as some surfactants (SDS and $C_{12}E_{10}$).

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P₁30 ELECTRIC POTENTIAL NEAR A SINGLE CONDUCTING ION CHANNEL IN A CHARGED MEMBRANE

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It is considered the movement of ions in an aqueous solution converging from bulk towards the entrance of a single conducting channel placed in a charged membrane. The aim of the study is to determine the electric potential distribution and the ion concentration profiles in the vicinity of the channel under steady-state conditions. Moreover, specific attention has been paid to the effect of the membrane surface charge on these profiles. The 3D Poisson equation has been used for the description of the electric potential profile in the solution. The dependence of the ion concentration profiles on the electric potential has been obtained on the basis of Nernst-Planck (NP) equation. We have obtained an approximate solution, which is valid in the solution outside some hemisphere centered in the mouth of the channel. Our solution transforms to Gouy-Chapman's theory at a large distance from the channel entrance. In the nearest vicinity of the channel the above mentioned profiles are almost radially symmetrical. For a neutral membrane they transform into expressions earlier obtained (Peskoff and Bers, 1988). We have analyzed the electric potential ion concentration profiles for the case when the contribution of the lipid charges and ion fluxes to the electric potential profile are of the same order. We have shown these profiles strongly depend on the direction of the ion fluxes, and hence the potential and concentration distributions on both sides of the membrane are significantly different. As a result of the complicated interplay between all electrical sources in the considered system there is a potential minimum in the nearest vicinity ($\sim 2\kappa^{-1}$) and a maximum relatively far from the membrane ($\sim 6\kappa^{-1}$).

P₁31 ION PERMEABILITY OF A THIN MEMBRANE WITH SOFT POLAR INTERFACES.

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We have analysed the ion transport across a structured film with extended soft permeable interfaces (polar zones), placed in an aqueous solution, under short-circuit conditions. We have taken into account the existence of fixed charges and dipoles in these membrane interfaces. The membrane has been modelled as composed of three layers: an inner hydrophobic layer and two polar zones. Nernst-Planck's equation has been used for describing the ion transport and Goldman's approximation has been assumed to be valid for the hydrophobic layer. In the present study we have considered two limit cases, i) the inner hydrophobic layer as the rate determining step; ii) the polar zones as the rate determining step. Mathematical criteria for them has been obtained. The main transport characteristics of the considered system (permeability, permselectivity, etc.) have turned out to be essentially differ in each case. The influence of the electrolyte concentration, the surface dipole density and thickness of the polar zone on the total ion flux and permselectivity has been analysed. It has been shown that the permselectivity of such system depends significantly on all these parameters. Particularly, the permselectivity of the same structured film changes with bulk electrolyte concentration. A general expression for cation selectivity has been obtained. The connection of the developed theory with experimental results has been discussed.

P₁32 NEUTRON SPECULAR AND OFF SPECULAR REFLECTION FROM THE AEROSOL OT LAMELLAR PHASE AT THE SOLID/SOLUTION INTERFACE

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The lamellar structure of sodium bis(2-ethylhexyl) sulfosuccinate (AOT)-water at concentrations in the range 1.5% w/v, well above the critical micelle concentration of 0.11%, has been studied at the solid/solution

interface and in the bulk by means of neutron reflection and small angle neutron scattering (SANS). At 2% and above Bragg peaks are observed in the specular reflectivity that correspond to a multilayer structure with a repeat distance of 160-350 Angstrom depending on temperatures. This is most probably caused by preferential adsorption of the lamellar phase, which in this concentration range coexists with solution. Strong peaks in the off specular reflection are arise from fluctuations in the surface plane and are attributed to large amplitude 'Helfrich' undulations. The separations of the lamellae adsorbed at the interface are found to be consistently lower than in the bulk.

P₁₃₃

MIXTURES OF SPHERICAL AND RODLIKE COLLOIDS WITH POLYMER BRUSH SURFACES

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Colloidal suspensions are interesting model systems to study phase phenomena in condensed matter. So far suspensions consisting of spherical nanoparticles are well understood. However, there is still a lack in experimental investigation of more complex systems like mixtures of spherical and rodlike particles. This is mainly caused by entropic demixing of particles having different topologies, like spheres and polymer coils (depletion demixing) or spheres and cylinders. A possible strategem to overcome this immiscibility is the creation of identical polymeric brush surfaces, like proved, for example, by mixtures of block copolymer micelles with polymer coils. We therefore expect rods and spheres having identical polymer brush surfaces also to be miscible.

The spherical particles are synthesized by grafting linear polymer chains onto the surface of nanosized polyorganosiloxane microgels: the cores have been prepared by polycondensation of trimethoxysilanes, using hydridosilane to introduce a functional shell. The SiH-groups are used for chemically attaching styrene macromonomers onto the colloidal surface by hydrosilylation.

The rodlike particles are obtained by radicalic polymerization of (anionically prepared) macromonomers, resulting in polymacromonomers, which can be seen as molecular bottle-brushes. The radicalic polymerization mechanism leads to cylindrical particles of large length polydispersity. Therefore, materials had to be fractionated by Continous Polymer Fractionation (CPF) to obtain suitable model rodlike particles.

Due to the polymeric surfaces demixing of spherical particles and polymer coils as well as spheres and rodlike particles has been suppressed over a wide range of concentrations. Surface structure of composite films has been probed by Atomic Force Microscopy (AFM), the internal bulk structure by Transmission Electron Microscopy (TEM). Also, optical transparency gives a further indication of homogeneous miscibility. In addition, we investigated dynamical behaviour of composite materials by rheological measurements.

P₁₃₄

A STUDY OF THE BEHAVIOUR OF MIXED MONOLAYERS OF AMPHOTERICIN B AND DIPALMITOYL PHOSPHATIDIC ACID FROM HYSTERESIS EXPERIMENTS

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Amphotericin B (AmB) is a polyene antibiotic used in the treatment of mycoses such as candidiasis, histoplasmosis and cryptococcosis [1], but which unfortunately is also toxic to human cells. In the search for more selective pharmaceutical formulations of this drug, promising results have been obtained, both in vitro and in clinical trials, for formulations that deliver the antibiotic from phospholipid-based liposomes [2], unilamellar vesicles [3] or lipid emulsions [3]. The aim of the present work was to investigate how the phospholipids in these systems reduce the toxicity of AmB. To this end, a monolayer technique was used to determine the behaviour of AmB in the presence of dipalmitoyl phosphatidic acid (DPPA), which is commonly used in the formulations described above. The results obtained confirm the existence of a certain interaction between AmB and DPPC which is confirmed by the plots of mean molecular area versus mole fraction of AmB, which showed significant positive deviations from ideal behaviour. In addition, the stability of the AmB-DPPA "complex" was investigated by means of hysteresis experiments performed on mixed monolayers containing 0.5 mole fraction of AmB and DPPA, which were spread separately or as a mixture; and by experiments in which the time elapsing between spreading of the monolayer and measurement of the π -A isotherm was varied.

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P₁₃₅ A STUDY OF THE STABILITY OF AMPHOTERICIN B MONOLAYERS

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Amphotericin B (AmB) - a polyene antibiotic used as an antimycotic - forms relatively stable monolayers at the air/water interface at low surface pressures [1,2]. At higher surface pressures (π), the monolayer structure rearranges, which is manifest as a constant-pressure plateau in the corresponding π -A plot; and at π beyond this plateau, when the monolayer presents a condensed state, the area occupied by the molecules in the film is so small that this suggests that AmB molecules dissolve in the subphase.

To confirm whether this is the case, in the present work the behaviour of AmB spread on various sub-phases was examined under different experimental conditions, varying the number of AmB molecules spread, the rate of compression of the surface film, the temperature and ionic strength of the subphase. In addition, relaxation studies were carried out for each of the physical states of AmB monolayers spread on water or sodium chloride solutions, by measuring the rate of decrease in their molecular area at constant pressure. The results obtained confirm that AmB molecules can dissolve in the aqueous subphase when the monolayer is in the condensed liquid state, probably because in this state the AmB molecules are oriented vertically with respect to the air/water interface, with their aminodeoxyhexose and carboxylic acid groups anchored in the water.

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P₁₃₆ COMPLEX FORMATION BETWEEN POLY(N-ISOPROPYLACRYLAMIDE) AND IONIC SURFACTANTS. INFLUENCE OF THE MOLECULAR WEIGHT OF THE POLYMER

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Complexation of Poly(N-isopropylacrylamide) (PNIPAAm) with sodium dodecylsulfate has been studied through viscosity, static fluorescence and time resolved fluorescence measurements. The influence of the molecular weight of PNIPAAm on the formation of the polymer-surfactant complexes has been investigated.

P₁₃₇ EFFECTS OF THE SURFACES ON THE PHASE TRANSITION ECULIARI S IN LYOTROPIC NEMATICS: EXPERIMENTAL STUDY AND A THEORETICAL APPROACH

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The investigation of the phase transition peculiarities in the liquid crystals especially the variation of the physical properties with temperature and concentration and the determination of the effect of the external factors on the phase transitions are very important from the fundamental and applied problems point of view. In this study, the effects of different surfaces on the nematic-isotropic liquid (N-I) phase transition in the lyotropic systems, particularly the N-I phase transition temperatures, the width of the heterophase region and the texture transformations are investigated. The phase transition temperatures and the temperature width of the heterophase regions are determined within 10^{-4} accuracy with the capillar temperature wedge setup. The shift of the N-I phase transition temperatures with the effect of the surfaces and changes of the width of the heterophase regions have been found.

Theoretical aspect of the phase transition peculiarities due to surface effects in lyotropic nematics is also mentioned.

P₁₃₈ MESOMORPHIC AND THERMOOPTICAL PROPERTIES OF LYOTROPIC NEMATIC N_d AND N_c MESOPHASES

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In this study, the results of the investigation of macroscopic and microscopic properties of one axis lyotropic-nematic N_d and N_c mesophases are given. The texture transformation dynamics in the N_d and N_c mesophases and the properties of the schlieren-textures occurring in this transformation are investigated. The optical sign of disclinations and the disclination of strength are determined. The variation of index of

refraction with concentration and temperature have examined. The temperature of the nematic-isotropic liquid phase transition and the temperature widths of the heterophase regions of these transition are determined with high accuracy.

For investigations of the texture-transformation dynamic and the peculiarities of schlieren-textures, politermical microscopy technique with crystallooptic method have been used. The determination of the, optical sign of disclinations and the disclination of strength are made with optical mapping technique.

The temperatures of nematic-isotropic liquid phase transitions and the temperature widths of the heterophase regions are determined with using the capillare temperature wedge method. With this method, the temperatures are determined within $\pm 10^{-4}$ °C accuracy. The hysteresis event is found in the investigated N_d and N_c mesophases nematic-isotropic liquid and isotropic liquid-nematic temperatures of phase transition and the amplitudes of the heterophase areas.

In this study, the obtained results are presented and discussed.

P₁₃₉ **INTERACTIONS BETWEEN HYDROPHOBICALLY MODIFIED POLYMERS AND SURFACTANTS. EFFECT OF SPACER BETWEEN POLYMER BACKBONE AND HYDROPHOBIC TAIL.**

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The last decade interactions between hydrophobically modified polymers and surfactants have been widely studied. Typically, concentration or type of surfactant or polymer has been varied. Regarding the polymer hydrophobic tails, interest has been on parameters such as alkyl chain length, substitution degree and nearby ionic groups in order to enhance the hydrophobic interaction. Not much attention has been paid to the effect of flexible spacers between the polymer backbone and the hydrophobic tail. In this investigation we have therefore varied the length of the spacer on a hydrophobically modified ethyl (hydroxyethyl) cellulose (HM-EHEC).

It was found that in aqueous solutions of HM-EHEC and sodium dodecyl sulfate (SDS), the viscosity at low SDS concentrations is modulated by the length of the spacer, whereas at high SDS concentration the viscosity was found to be the same for all different spacer-lengths investigated. However, independent of the length of the spacer group the same general trend was found as a function of SDS concentration with the viscosity first increasing and later decreasing. In order to obtain additional static and dynamic information, the aqueous solutions of the different polymers and SDS have also been investigated by means of pulse field gradient spin echo NMR (PFGSE NMR), time resolved fluorescence quenching and dynamic and static light scattering.

P₁₄₀ **CHARACTERIZATION OF MICROEMULSIONS BASED ON POLYMERIC SURFACTANT**

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Microemulsions formed with water, isopropyl myristate, polymeric surfactant and alkanediol have been investigated using static light scattering, small angle X-Ray scattering (SAXS) and conductivity measurements at 25° C. The light scattering absolute intensity at 90° was analyzed using a procedure based on a hard sphere model. Using this approach, water core droplet radius of about 10nm was calculated. On the other hand, the radius was also obtained through the Guinier's law. The high values thus obtained, about 70nm, could be attributed to aggregate formation. The X-Ray scattering spectra are compatible with spherical droplets of about 5nm of radius. The conductivity showed an increase as a function of water volume fraction that could be attributed to percolation phenomena. All of these results could be interpreted in terms of the possible aggregate units formed.

P₁₄₁ **POLYMER ADSORPTION ON POROUS AND NONPOROUS ADSORBENT MODIFIED BY SURFACTANTS**

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The adsorption of two polymers on the porous aluminosilicagel (trademark ASK, S = 300 m²/g, average pore size 6-8 nm) and nonporous TiO₂ (rutile modification, trademark R-1, S = 7 m²/g) modified by different surfactants has been investigated.

At first, it was studied the individual adsorption of the surfactants (stearic acid - SA; octadecylamine - ODA) and the polymers (polystyrene - PS; copolymer of vinylchloride, vinylacetate and maleinic acid - VMCH) from toluene solution. The adsorption was determined by gravimetric method. Both the surfactants chemically and physically reacted with surface active sites of TiO_2 and ASK. After removing the physically adsorbed surfactants (by boiling toluene) it has been used the solid phase thus modified for polymer adsorption experiences.

The VMCH adsorption on TiO_2 and ASK was partially irreversible owing to the interaction of polymer carboxylic groups with basic OH-groups and sites on the surfaces. The PS adsorption on the fillers was completely reversible, and it was equal 5.5 and - 9 mg/g for TiO_2 and ASK, respectively. Its negative magnitude for ASK, as it was found, is due to the preferable penetration of toluene molecules into the pore space.

It was found that the increasing degree of surface modification of nonporous rutile by surfactants ($\alpha = 1$) leads to the decreasing of the polymer adsorption due to the absence of the free adsorption sites on the surface and sterical hamperings at the interfaces. But the polymer adsorption remarkably increased owing to the dispersity rise of TiO_2 particles in the hydrophobic medium when the surfactant adsorption layers were nonsaturated ($\alpha = 0.2$). ODA molecules hinders the polymer adsorption much less than SA molecules blocking the basic OH⁻ groups and aprotic sites of both adsorbents.

Adsorption of VMCH on porous ASK partially and fully modified by surfactants ($\alpha = 0.2 - 1$) was almost the same. The PS adsorption on ASK modified by SA and ODA became positive one. Probably, the surfactant molecules penetrate into the pore space and activate the hydrophilic surface of the ASK particles with respect to hydrophobic medium.

P₁42 BICONTINUOUS PHASES IN A FLUORINATED NON IONIC SURFACTANT - WATER SYSTEM

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The phase behaviour of a fluorinated non ionic surfactant in water is determined and compared with that of the hydrogenated analogue. It demonstrates its hydrophobic nature. A reverse micellar phase forms at low water content whatever the temperature. Increasing the water amount, the phase diagram exhibits a lamellar phase that transforms into a cubic phase at higher temperature. Finally, adding more water leads to a sponge phase. It only exists for a thin temperature domain and can incorporate until 0.7 water volume fraction. The comparison with the homologue hydrogenated systems reveals that the cubic phase domain is larger for the fluorinated surfactant.

We investigate by SAXS the structures of three phases based on the bilayer arrangement, *i.e.* the bicontinuous cubic, sponge and lamellar phases. First, the peculiar feature of the lamellar phase is the vanishing of the second order peak which permits to determine some structural parameters such as the conformation of the hydrophilic chains.

Secondly this study shows that the cubic phase is described in its upper region, *i.e.* at high temperature, by the Pn3m space group and by Ia3d elsewhere. They are described using both the Inter Connected Rod (ICR) and the Infinite Periodic Minimal Surfaces (IPMS) models. The structural parameters (area per polar head, hydrophobic thickness) determined according those two models are in a good agreement, showing hence their equivalence. The radius of the rods of the two cubic structures are almost the same for a given composition while their lengths are very different.

After reporting the results we discuss them in order to deduce any correlation between the different phases. The surface per polar group and the conformation of the fluorinated chains are equal whatever the phase. Moreover the sponge phase appears as a disordered bicontinuous cubic phase. The structural parameters confirm this feature, proving the major role of the surfactant bilayer (conformation of the hydrophobic and hydrophilic chains and penetration of water) in the phase transitions.

P₁43 PRESSURE-AREA ISOTHERMS. BEHAVIOUR OF CYCLOSPORIN-PYRENE-LABELLED PHOSPHOLIPIDS

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Cyclosporin (CsA) is a cyclic peptide with outstanding immunosuppressive properties, which make it one of the most useful drugs to avoid rejection in organ transplants [1]. The fact that repeated administration of this drug causes important secondary effects, most importantly nephrotoxicity [2] makes it necessary to study new methods of administration which could make it harmless for health. It has been demonstrated that its inclusion in liposomes makes it considerably less toxic [3,4] but it is not known why.

To understand this mechanism, in the present work the possible interaction between CsA and the Dipalmitoylphosphatidylcholine (DPPC), a typical constituent of liposomes, is studied using two techniques: monolayers, in which we obtain the molecular orientation similar to that of liposomes, and fluorescence, using pyrene-labelled phospholipids because these compounds are not fluorescent *"per se"*.

Despite the fact that pyrene does not form stable monolayers as its behaviour is hydrophobic when it is mixed with DPPC it gives a mixed system which when spread at the air/water interface, leads to the formation of monolayers which behave differently from DPPC. Negative deviance from ideal values is significant and demonstrates the existence of forces of attraction between the molecules of the mixture. On the other hand, the mixed monolayers of CsA and DPPC, as well as those formed by CsA and pyrene labelled phospholipids, one in the hydrocarbon chain (1-hexadecanoyl-2-(1-pyrenedecanoyl)-sn-glycero-3-phosphocholine) and the other in the polar head (N-(1-pyrenesulfonyl)-1,2-dihexadecanoyl-sn-glycero-3-phosphoethanolamine, triethylammonium salt) revealed superficial behaviour that shows no interaction between the components, probably due to their immiscibility at the interface.

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P₁₄₄ SURFACE PROPERTIES OF STIGMASTANYL PHOSPHORYLCHOLINE MONOLAYERS SPREAD AT THE AIR/WATER INTERFACE

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Stigmastanyl phosphorylcholine (S-PC) decreases cholesterol absorption in the intestine, lowers cholesterol levels in plasma and also reduces atheroma formation [1]. *In vitro* studies [2] suggest that these effects may be due to the structural changes induced by S-PC in lecithin-taurocholate-cholesterol micelles present in the intestine. This could result in a decrease in cholesterol uptake by the enterocytes and thereby explain the *in vivo* inhibition of cholesterol absorption which has been observed. To investigate this possibility, we are systematically studying the *in vitro* behaviour of SPC in the presence of cholesterol and phospholipids, using the monolayer technique as a model of the behaviour of these systems *in vivo*. The present work describes a preliminary study of S-PC spread at the air/water interface under experimental conditions that differ as regards the number of molecules deposited, the rate of compression of the monolayer, and the temperature, pH and ionic strength of the subphase. The results show that the surface properties of S-PC monolayers are determined mainly by the phosphorylcholine group, while the stigmastanol moiety of S-PC plays only a secondary role in the decrease of their molecular area at constant pressure.

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P₁₄₅ PHENOMENON OF THE EFFECTIVE SHEAR VISCOSITY OF THIN WETTING FILMS

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A phenomenon of an "abnormal" shear viscosity of thin wetting films have been established in a series of different experiments is analyzed theoretically. An exponential law of a dependence of the shear viscosity on a film thickness is derived on a basis of a "topologic" concept of wetting films, as a result of changing of the film topology. Theoretical results are well verified with experimental data on different capillary processes: electroosmosis, microfiltration etc.

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P₁₄₆ PHASE TRANSITIONS IN INSOLUBLE MONOLAYERS OF BRANCHED PHOSPHOLIPIDS

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The introduction of side-chains into amphiphilic molecules allows systematic changes in the intermolecular interactions. Dipalmitoyl-phosphatidyl-ethanolamin (DPPE) is modified by side-chains with the length (n) of 1 to 14 at the position 2. The influence of these modifications on the surface pressure area isotherms

and on the structure of the condensed monolayer phase is investigated on a film balance. The domain structures during the main phase transition to a condensed phase are studied by Brewster Angle Microscopy (BAM). Additionally, grazing Incidence X-ray Diffraction measurements deliver information on the lattice.

The branched-chain compounds form stable monolayers on the air/water interface. The influence of short side-chains ($n = 1, 2$) on the domain structures is small. The less dense lateral packing shifts the critical temperature for the phase transition T_c to lower values. The ethyl branched PE shows some peculiarities in the temperature dependence of the phase transition. Longer side chains ($n = 4, 5$) need more space, the disturbance of the lattice is strong and no phase transition takes place ($T_c < 0^\circ\text{C}$).

A side chain with $n = 14$ fits into the lattice as a third chain. This triple-chain PE compound has a hexagonal lattice of untilted molecules. The isotherms indicate, that a phase transition takes place between 15 and 40°C .

P₁₄₇ STRUCTURE OF MODIFIED PARTICLE AGGREGATES IN METAL-FILLED POLYMER FILMS

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The modification of particle surface is one of the main methods to controlling the structure processes in colloidal systems. This method has been tested on numerous objects using versatile surface modifiers. Such experiments have made it possible to study mechanisms of modification affecting the structuring processes and properties of the composites in detail. At the same time, there are a number of cases (occurring, as a rule, in complex systems) where the nature of the modifying effect is not well understood.

In this work we studied the effect of modification of the particle surface on the regularities of aggregation in curing systems and conductivity of the final composite. Composition based on ED-20 epoxy resin with 2 vol % of nickel powder modified with stearic acid were chosen as objects for this study. Two types of modified powders were used in these experiments: (1) a powder with adsorbed (both physically and chemically) molecules of stearic acid, and (2) a powder with only chemisorbed molecules of stearic acid at the surface. Using the cured films, micrographs were obtained with a microscope, on which the morphological parameters of aggregates (average size, anisotropy, bulkiness, structural factor) and their fractal dimension were determined.

The degree of modification of the particle surface with stearic acid was controlled by the measurement of contact angles of epoxy resin on tablets pressed from the powders obtained. Values of the contact angles vary from 30° (for initial unmodified powder) to 130° (for modified powder). After high-temperature washing of the modified powder in toluene, the contact angle was reduced to 90° .

Comparison of the parameters of the aggregates of modified and unmodified particles has shown they to be close. The essential difference was found out only in the aggregate size distributions, and it has not only quantitative but also qualitative character. First of all, the difference concerns with the average size of aggregates, which for modified particles has appeared to be in order more, than for unmodified. In the second place, the difference consists in that the aggregate size distribution of modified particles has clearly defined bimodal character, while for aggregates of unmodified particles it is lognormal.

The change of the average size of aggregates is obviously connected to an increase of particle mobility in polymer matrix, stipulated by their surface modification.

The nature of bimodality cannot be explained by the assumption that two groups of particles (modified and unmodified) are present in a system because (i) particles of different groups exhibit similar mobility, and (ii) particles are easily aggregated with each other, resulting in the formation of aggregates composed of particles of both types (i.e., aggregates actually represent a certain "intermediate" formation).

The probable explanation of the bimodal nature of the size distribution of modified particle aggregates, on our sight, is connected to the deterioration of their compatibility with polymer matrix. It results, on the one hand, in accelerated growth of aggregates, with other - in squeezing out of modified particles from the film bulk to its surface. As a result, the aggregation will proceed in the surface layer, where its rate differs from the aggregation rate in the film bulk, as far as the particle mobilities in the bulk and on the surface of a film are different. Hence, two groups of aggregates, the surface and the bulk ones, will be formed, which are characterized by their own average sizes. That predetermines the bimodal distribution of aggregates.

P₁48 THEORETICAL STUDIES ON STRUCTURE AND MOLECULAR PROPERTIES OF N-ALKYL-N-METHYLGLUCONAMIDES

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N-alkyl-N-methylgluconamides (AMGA) are well known environmentally friendly nonionic surfactants. They show a good stability in aqueous solutions which can be attributed to the presence of amide group and glucose moiety regarded.

In this work we present results of our quantitative estimations of relative basicity and acidity for various potential hydrophilic centers of AMGA molecules using the PM3 method. These values can be regarded as a measure of the hydrogen-bond strength both of H-donating and H-accepting properties of single OH, C=O and N centers within AMGA structure. The calculated gas-acidities (GA) (in kcal/mol) for OH groups are as follows: at C-2 (331.7), C-3 (341.8), C-4 (330.0), C-5 (331.2) and C-6 (338.3) and gas-basicities (GB): at N (196.5), C=O (209.9), C-2 (182.4), C-3 (179.7), C-4 (178.8), C-5 (181.1) and C-6 (179.1). Calculated enthalpies of monohydration for various centers vary from 1.3 (N atom) to 5.3 kcal/mol (OH at C-3) and they roughly correspond to acid-basic properties of OH and N centers. Our results show a strong H-bonding ability of amide group with surrounding water molecules when incremental association enthalpies for AMGA-(H₂O)₄ clusters are computed. Although the competition between different H-bonding networks gives rise to more than one possible isomer we have identified few stable clusters that form interior and surface states. This indicates that association of AMGA with water clusters (H₂O)_n n=3-5 due to formation of H-bonds and border-line H-bonds can enhance the hydrophilic interactions to the vicinal CH₂ or/and CH₃ groups, especially for protonated species. This can be related to high viscosity of the solutions.

In conclusion, we can state that the increase in the alkyl chain length has no effect on hydration state of the glucose moiety of the AMGA molecule, but it shows some effects on the hydration of the nitrogen atom attributable to the increase in hydrophilicity (basicity) of the amide group with elongation of the alkyl chain. The presence of the amide residuum enhances the hydrophilicity of the polar head in extension to the part of alkyl chains due to interior states of AMGA-water clusters. Structures of these stable clusters was also confirmed by *ab initio* calculations in small basis set at the HF level.

P₁49 PHASE BEHAVIOR IN MIXTURE OF CATIONIC AND ANIONIC SURFACTANTS: HEXADECYLTRIMETHYLAMMONIUM BROMIDE/SODIUM DODECYL SULFATE

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The phase equilibria of catanionic surfactant aqueous mixtures, hexadecyltrimethylammonium bromide and sodium dodecyl sulfate have been studied by combined polarizing microscopy, light scattering, conductivity, potentiometric, electrophoretic, and surface tension measurements. The phase behavior, formation of variety of microstructures and the properties of the air/solution interface strongly depended on the molar ratio and actual concentration of surfactants. Lamellar catanionic surfactant salt was formed from equimolar mixtures of the reactants. Stable polydispersed vesicles coexisted with crystalline catanionic salt and transformed to the mixed micelles as mixtures shifted from the equimolar range. The amount of catanionic salt was reduced and the amount of vesicles increased as the surfactants molar ratio increase. The formation and stability of different phases are discussed in terms of surfactant molecular packing constraints and electrostatic effects.

P₁50 INTERFACIAL TENSIONS IN HEPTANE-AQUEOUS NaCl SYSTEMS CONTAINING AEROSOL OT AND A SECOND SINGLE-CHAIN IONIC SURFACTANT

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Water-in-oil microemulsions (Winsor II) can be made to pass to oil-in-water ones (Winsor I) by addition of a second single-chain ionic surfactant (SDS) to the system consisting of a non-polar oil in contact with aqueous solution of Aerosol OT and sufficient amount of NaCl ($m_s > 0.05$ M). Physicochemistry of Winsor transitions determine multicomponent surfactant mixtures composition and furthermore their practical applications.

We have decided to undertake a systematic study concerning effects of sodium sulfates (alkyl: n-C₈H₁₇; n-C₁₀H₂₁; n-C₁₂H₂₅; n-C₁₄H₂₉), sodium sulfonates (alkyl: n-C₈H₁₇; n-C₉H₁₉; n-C₁₀H₂₁; n-C₁₁H₂₃; n-C₁₂H₂₅), sodium carboxylates (alkyl: n-C₇H₁₅; n-C₉H₁₉; n-C₁₁H₂₃; n-C₁₃H₂₇; n-C₁₅H₃₁) in heptan - aqueous 0.1 M NaCl containing

$4.6 \cdot 10^{-4}$ M AOT at 25 °C upon the surfactant film curvature. The results have been discussed in terms of the type, molecular geometry of the ionic surfactant, composition of interfacial monolayers and thermodynamics of transition from Winsor II to Winsor I. For homologous amphiphiles the minima in interfacial tension γ_c , brought about by addition of ionic surfactant were achieved at different concentration of the last one (c_{min}) depending of the alkyl chain. We have shown that there is a linear correlation between the standard free energy change of transition from Winsor II to Winsor I system ($\Delta G^0_{tr} = RT \ln x_{min}$) and the carbon number (n) in alkyl chain for various homologous series of amphiphiles. We have calculated contribution of CH_2 group and ionic head group in ΔG^0_{tr} . The first parameter is almost equal for sulfates and sulfonates and differ a little from carboxylates, but head group contribution decreases in order $COONa$, SO_3Na , SO_4Na , which is adequate to the volume of hydrophilic group. Our studies can provide some information about molecular interactions and can help in understanding and explaining interfacial phenomena.

P₁₅₁ INFLUENCE OF AMPHIPHILES ON THE ACTIVITY OF NATIVE AND IMMOBILIZED PHOSPHOLIPASE D

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The phospholipase *D* promotes the hydrolysis of lecithin, breaking a bond between the phosphate group and the choline residue. It falls into a group of the surface enzymes that are active at the interfacial boundaries and the enzymatic activity of which is strongly dependent on the presence of surface-active agents [1].

The effects of various surfactants on cabbage phospholipase *D* have been studied to gain a better insight into their role in the enzyme functioning. It has been established that anionic substances occur a more pronounced influence than cationic ones. The enzyme activation correlates with the surfactant polar group size and denaturation ability. It has been shown that the effects of surfactants are also evident through a change of the aggregate state of lecithin. When vesicles transformed into micelles, a decrease in the phospholipase activity has been usually observed.

It has been shown that the phospholipase *D* persists in functioning at a restricted number of solid surfaces. Successful immobilization has been realized when carbon fibers or macropore glass have been coated with titanium oxides. The main characteristics and conditions for functioning of the enzyme have been estimated. It has been found out that the phospholipase *D* immobilized on the modified carbon fibers demonstrates larger activity than that of the native enzyme in a solution. The aggregated state of lecithin has also occurred an effect on the enzyme functioning.

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P₁₅₂ BIOTRANSFORMATIONS USING LIPASES IN MICROEMULSION BASED GELS

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Biotransformations in apolar media involving lipases have been widely studied over the last decade. Several methods have been developed for carrying out enzymatic catalysis in such media. The most intensively studied one has been the technique of solubilizing enzymes in reverse micelles or water-in-oil (w/o) microemulsions. These systems provide ideal milieus for the solubilization of hydrophilic enzymes (aqueous dispersed phase), surface-active enzymes (interface), and hydrophobic substrates or products (continuous organic phase). The enzymes are therefore, active as regards the conversion of both hydrophilic and hydrophobic compounds [1,2].

An interesting alternative for biotransformations in apolar organic solvents, that can simplify product isolation and enzyme reuse, is provided by the use of immobilized enzymes in microemulsion-based organogels (MBGs) [3]. The preparation of MBGs was firstly based on the gelation of w/o microemulsions formed with AOT or lecithin, into monophasic optically transparent rigid systems by mixing with an aqueous gelatin solution above the gelling temperature. By cooling at room temperature a transparent gel is formed which has reproducible physical properties.

In this work, several natural gelling agents such as gelatin, agar, -carrageenan and pectin have been tested for the formation of lecithin or AOT microemulsion-based gels. The results presented in this work provide information concerning the utility of these solid gels as a lipase immobilization matrix. It was found that lipase from *Pseudomonas cepacia* keep its catalytic function after entrapment in the gels, catalysing various esterification reactions in non-polar hydrocarbons with 6-12 carbon atoms at room temperature. Various parameters which affect the lipase catalytic behaviour such as the nature and the concentration of

the gelling agent, the concentration of water as well as the concentration of the biocatalyst and the substrates have been examined. The conversions, as well as the initial reaction rates, were higher using gels based on lecithin-stabilized microemulsions and formed with agar as gelling agent. Under operational conditions, high product yields (80-90%) are achievable in repeated syntheses.

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P₂53 PHASE TRANSFORMATION OF MAGNESIUM HYDROGENURATE OCTAHYDRATE

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Magnesium hydrogenurate octahydrate, $\text{Mg}(\text{C}_5\text{H}_3\text{N}_4\text{O}_3)_2 \cdot 8\text{H}_2\text{O}$ was precipitated from aqueous solution at room temperature. The crystals were characterised by RTG, FTIR, TG and optical microscopy. Results revealed the formation of two morphologically different phases named as phase I and phase II. Phase I appeared as long needle-like agglomerates, while phase II appeared as plate-like crystals. Transformation of metastable phase I into thermodynamically stable phase II was completed after 3 month. Crystals of magnesium superscript octahydrate while agginig in water, magnesium chloride or uric acid solutions at 37°C, partially transformed into uric acid even after one day. Solubility product of phase I was determined in water solutions, while of phase II was determined in water, uric acid and magnesium chloride solution, respectively. The influence of small ions and macromolecules (citrate, phytate, hexaammonium tetrapolyphosphate and polyaspartate) on phase transformation was studied, too.

P₂54 MEASUREMENT OF PARTITION COEFFICIENT BETWEEN HEPTANE AND WATER OF ALKYLPIRIDINIUM SALTS

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The partition of mixtures between water and hydrocarbons is important in practical applications such as their use as gasoline additives and corrosion inhibitors; it is also a measure of their "hydrophile-lipophile balans" (HLB) value and thus of their general problem such as emulsifying power. In a typical the partition coefficients of homologous series of surfactant between water and hydrocarbon are calculated by means of Eq:

$$K_p = C_s/C_w$$

C_s = concentration of surfactant in organic phases

C_w = concentration of surfactant in aqueous phases

In practice the measure of concentration surfactant in water is more easy than one in organic phases.

$$K_p = C_s/C_w = C_{1w} - C_{2w}/C_{1w}$$

C_{1w} = concentration surfactant in aqueous phases

C_{2w} = concentration of surfactant in aqueous phases after separated

This equation is couldn't be used in this case, because of salts of alkylpyridine are badly dissolved in heptane (theory of mistakes).

We propose a new method of determination of the partition coefficient in system, where mixture of heptanol : heptane (in ratio 1:0; 3:1; 1:1; 1:3) is used as organic phases. Under these conditions the $V_s/V_w = 1$ is retained. In heptane the partition coefficient is determined by extrapolation of $f(\lg k_p) = V_h$ (V_h - volume of heptanol) to the $V_h = 0$. The three methods are used by us for determination of C_w : Surfactant Ion Electrodes, Photo Electric Calorimetric Method, Method of Second-Phase Titration. Surfactant Ion Electrode method is more simple and accessible, because authors give preference for it.

P₂55 A NEW METHODICS OF DROP EDGE RECOGNITION AND ITS APPLICATION FOR SURFACE TENSION AND CONTACT ANGLE MEASUREMENT

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The investigation of parameters of sessile drops is the essential part in the study of wetting. The conjunction of digital image processing and method of sessile drop provides the efficiency of interfacial tension

and contact angle measurement.

We have developed a new method of recognition the drop borders. It is based on the physical idea that the object on the image can be recognized if a gray level gradient on the edge of object exceeds the level of noise in the field of image. The special procedures were developed to exclude the influence of illumination nonuniformity and diffraction phenomena.

Using of image collection allows to improve the signal to noise ratio and thus the resolution capacity of the experimental technique.

Above procedures have been realized in the experimental setup and have shown the reproducible results being in good agreement with the literature data.

The work was performed with financial support by Russian Foundation for Fundamental Research (grant # 98-03-32732).

ON THE MECHANISM OF SOLVATION FORCES

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Different possible mechanisms of solvation forces have been considered. We have analysed various approaches explaining an oscillatory part of surface forces acting in liquid interlayers. It was shown that the phonon mechanism of long-range surface forces can be applied directly for the explanation of above phenomena. In the frames of this mechanism the oscillations of interaction forces arise due to spatial dispersion resulting in oscillations of density of collective vibration states with film thickness. The peculiarities of solvation forces revealing in different systems and correlation between oscillations parameters and characteristics of interacting media have been discussed.

The work was performed with financial support by Russian Foundation for Fundamental Research (grant # 98-03-32732).

P₂₅₇ SCANNING ANGLE NULL ELLIPSOMETRY

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Scanning angle null ellipsometry around the brewster angle has been used to investigate the optical properties of particles with radii ranging from 5 to 50 nm, that are deposited on a glass-water interface. This is the range of particles where the optical effects are smaller than or within the resolution of simple reflectometry.

The self-built motorized ellipsometer makes use of the null principle with a PCSA-setup: only for one combination of polarizer (P) and retarder (C) the product of polarization state and phase of polarizer, retarder and the substrate (S) results in linear polarized light. The last polarizer (A) serves to find the polarization state of the substrate by finding the null condition: the polarizer crosses out the intensity signal coming from the substrate. The combination of the angles of the polarizers and the retarder lead to the ellipsometry coefficient. In this setup the retarder angle is fixed and the two polarizers varied to find the nulling condition.

With the present setup the ellipsometry coefficient can be obtained with an accuracy of 10^{-5} , a factor 100 more accurate than commercially available ellipsometers like rotating analyzer, or polarization modulation ellipsometers. Next to the fact that with this setup it is possible to measure at different angles with an increment of 0.005° , minute deviations from the ideal interface may be studied. It is no longer necessary to use metal coatings on glass to enhance the differences between the layers and therefore the ellipsometry signal and the information about the adsorption is not confined to the adsorbed mass only. With a simple Abeles-model for thin films, it is possible to extract the particle size, and a combination of refractive index and coverage of adsorbed mass from the ellipsometry coefficient.

P₂₅₈ CONTACT ANGLES AND THE TRANSITION ZONE BETWEEN A SESSILE DROP AND A WETTING FILM STUDIED BY MONTE CARLO SIMULATION

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The equilibrium in the system sessile drop - wetting film for uniformly and nonuniformly wetted substrates has been studied by means of Monte Carlo experiment in frames of two-dimensional SOS model with Kawasaki dynamics. For drops, having the same value of a macroscopic contact angle, the influence of long-range surface forces on the shape of transition zone has been investigated. The conditions of stability

or instability of the transition zone profile are discussed. The influence of a single surface defect on the equilibrium shape of the drop is considered.

The work was performed with financial support by Russian Foundation for Fundamental Research (grant # 98-03-32721).

P₂₅₉ CHARACTERIZATION OF SURFACTANT SOLUTIONS WITH DENSITY, VISCOSITY AND ULTRASONIC SPEED

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We present the possibilities for characterization of surfactant solutions with density, viscosity, and ultrasonic speed using a modified version of a commercially available laboratory instrument (DMA 5000, Anton Paar GesmbH, Graz). This instrument is a new generation of the well established oscillating tube technique for density measurements. The most important modifications to older systems are the addition of an ultrasonic speed cell and the correction of viscosity effects in density measurements. For this purpose the DMA 5000 determines the damping of the oscillating tube by comparing the normal oscillation period to the period that can be observed when using a phase shifted excitation force, giving a method for ultra low shear viscosimetry. Viscosities up to 350 mPa s can be calculated from the damping data with an accuracy of about 10%. So the DMA 5000 gives three results for each measurement: density, sound velocity and viscosity. Thereby the sample is thermostated to about 0.01 K in absolute scale.

We have established methods to measure temperature scans and time dependencies of solutions in a temperature range from 3°C to 75°C.

We have used these possibilities to determine the phase boundaries of aqueous solutions of the EO₂₁-PO₄₇-EO₂₁ triblock copolymer P94. Density and sound velocity show the formation of micelles out of unimers, viscosity and sound velocity allow the determination of the transition from spherical to cylindrical micelles. Viscosity gives also the boundaries of gel-regions in the phase diagram.

Other examples for applications are to follow the aggregation of casein micelles after addition of chymosin and the determination of the critical temperature of C₆E₇ diblock copolymers using viscosity.

P₂₆₀ THE EFFECT OF POLYMER ADSORPTION ON CONCENTRATED COLLOIDAL SILICA DISPERSIONS

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The adsorption of poly(vinylpyrrolidone) (PVP) and Poly(acrylic acid) (sodium salt) (PAA) on silica has been investigated as a function of polymer concentration. Results are reported for a range of molar masses for both polymers.

Rheological techniques have been employed to study the interparticle interactions of the dispersions. Viscometry measurements, at a constant volume fraction, reveal the dispersions to show a change from Newtonian to non-Newtonian flow at a critical polymer concentration thus indicating a flocculated structure. Oscillatory experiments have been carried out to measure the elastic moduli and hence the strength of the flocculated networks as a function of polymer concentration, polymer surface coverage, molar mass and silica volume fraction. The results show weak bridging flocculation occurs at low concentrations for high PAA molar masses, with stronger flocculation as the polymer concentration is increased. Results for PVP show a decrease in measured G' values as molar mass increases (for molar mass range 10,000-40,000).

P₂₆₁ GROWTH OF SILVER IODIDE COLLOIDS INVESTIGATED BY DYNAMIC LIGHT SCATTERING

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The aggregation kinetics of polydispersed colloidal silver iodide particles was investigated by light scattering. The new model of the formation of solid phase from homogeneous solution was established, considering these processes as consecutive ones. The spatial and temporal extents were normalized, so, that the particle sizes showed the same values within the wide scale of the concentration gradient and the time variation. The measurements were performed at room temperature using Brice Phoenix DU2000 SLS, and Otsuka 700 DLS photometer.

Approach to the colloidal stability in this investigation has its justification in the presumption that the stable colloidal structure is established in some determined concentration and time interval. The normalization of the constituent ion's concentration was applied within the wide region from $KI = 2.5 \cdot 10^{-1}$ to $4.0 \cdot 10^{-3}$

mol dm⁻³ and the related time of measurement.

Polydispersity of silver iodide colloids was confirmed by dynamic light scattering, showing bimodal and trimodal distribution of particle sizes. Average hydrodynamic diameter of aggregates as measured ten minutes, one hour, and one day after the preparation of colloid, amounted to $\langle d_h \rangle = (88.4 \pm 24.3)$ nm, $\langle d_h \rangle = (94.8 \pm 13.8)$ nm, and $\langle d_h \rangle = (190.4 \pm 67.4)$ nm, respectively, while its value for normalized conditions amounted to $\langle d_h \rangle = (68.3 \pm 8.0)$ nm. After 1 day the size of particles is observed to be (100 ± 13.2) nm within the low concentration region, since the related sizes occurred to be between 240 and 540 nm within the high concentration region.

P₂62 RHEOLOGY OF BIMODAL CHARGE-STABILIZED POLYMER DISPERSIONS

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Rheological properties of bimodal charge-stabilized polymer latices were determined as a function of salt content, ratio of particle radii and ratio of volume fraction in the mixture.

In the dilute regime viscosities were measured by capillary viscometry. The higher concentrated samples (up to 50%) were rheologically characterized by a controlled stress rheometer using cone/plane and Couette geometry. Diffusion processes in the concentrated latices were detected by fibre optical quasilastic light scattering (FOQELS).

Monodisperse highly charged PS-latices were synthesized by soap free emulsion polymerization using styrene-sulfonate as ionic comonomer. Particle sizes and monodispersity were controlled by using different kinds of cations in synthesis. Binary mixtures were prepared in a defined way by mixing monodisperse samples of known salt content.

Before mixing, the monodisperse components were characterized extensively by electron microscopy, dynamic light scattering, electrophoresis and titration of acidic surface groups. Rheological properties were also determined for each monodisperse latex. These data are used for comparison with data obtained from the bimodal mixtures.

The concentrated bidisperse latices were also characterized by means of fibre optical quasilastic light scattering (FOQELS). For mixtures of large particles (304 nm) with small particles (64 nm), probe diffusion resembling long time self diffusion could be measured. The probe diffusion coefficient and zero shear viscosity showed the same dependence on the volume fraction of particles.

Results for bimodal, charged latex systems are discussed with respect to results from hard sphere like systems and to theoretical models for bidisperse latices.

P₂63 DISSOLUTION OF ANIONIC SURFACTANTS. EFFECT OF CATIONS ON THE CHANGE OF HEAT CAPACITY.

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Dissolution of surface active agents in water usually results in significant heat capacity change ΔC_p which is due to water structuring around the nonpolar "tails". For most of the surfactants ΔC_p is proportional to the chain length.

Heat of dissolution of various salts of anionic surfactants was measured by the reaction calorimeter. Heat capacity change was evaluated from the temperature dependency of the enthalpy.

The effect of cations on ΔC_p of dissolution of fatty and sulphonic acid salts was investigated. All of the examined cations showed the similar effect. However, for copper dodecyl and tetradecyl sulphonates the value of ΔC_p was found to be unusually high.

P₂64 SPINODAL DECOMPOSITION IN THE VISCOUS HYDRODYNAMIC REGIME

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The separation of a binary fluid mixture into its constituent phases involves the interaction of numerous physical phenomena. Studying such a transition gives insight into the underlying mechanisms, their respective strengths and at what stage in the separation each becomes important or dominant. Large scale simulations of three dimensional spinodal decomposition in a binary fluid using Dissipative Particle Dynamics show the approach to a linear time dependence in domain coarsening. We present interface and velocity maps which clearly demonstrate the Siggia mechanism for domain growth.

P₂65 MEASURING THE TEMPERATURE-DEPENDENCE OF SURFACE FORCES

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For the understanding of surface forces the temperature-dependence is important, for instance to separate entropic and enthalpic contributions. Technical reasons, however, prevented an appropriate investigation of surface forces at different, adjustable temperatures. We developed a heat stage for an atomic force microscope which allows stable measurements of force-versus-distance curves in liquids from room temperature up to 65 °C. With this instrument we studied the temperature dependence of the hydrophobic force. In addition, steric forces caused by different polymers in different solvents were investigated.

P₂66 INTERFACIAL TENSION BETWEEN TWO BINARY METALLIC PHASES (NOT ABSOLUTELY RIGID APPROXIMATION)

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Using the finite thickness method (Van-der-Vaals - Guggenheim - Rusanov formalism) and requiring the system to be not absolutely rigid an isotherm of the interfacial tension between two binary condensed phases is derived. The dependence of partial molar volumes and surface areas on concentration, temperature and pressure is taken into consideration. The method of calculating the thermodynamic activities of the interfacial layer is suggested.

The calculations were made for ten binary metallic systems. A difference between the interfacial tension calculated for absolutely rigid model and our results for a number of systems goes up to 10%.

P₂67 BINDING OF Cd²⁺ AT GOETHITE AQUEOUS INTERFACE

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Adsorption of Cd²⁺ at goethite aqueous interface was measured as a function of pH. Electrokinetic properties of the system were also investigated. For the interpretation the Surface Complexation Model was used and the association of cadmium species with negative surface sites was considered. The electrostatic potential affecting the state of surface species was calculated from the electrokinetic potential by the Gouy-Chapman theory introducing the electrokinetic plane separation as an adjustable parameter.

It was found that, in the investigated pH region, practically only singly charged species (CdOH⁺) are bound to the negative surface sites. The equilibrium constant of the corresponding surface reaction was also determined.

P₂68 EFFECT OF THE POROSITY AND RELATIVE POLARITY OF MCM-41 MATERIALS ON THE ADSORPTION OF MONOMERIC AND DIMERIC CATIONIC SURFACTANTS AT THE SOLID-WATER INTERFACE

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Broad principles governing adsorption of ionised surface-active agents on oppositely charged oxide surfaces are well understood. The driving force of adsorption mainly derives from the combination of (a) Coulombic attractions between the ionised surfactant headgroups and the charged surface leading irrevocably to the formation of an electric double layer; (b) specific (i.e., non-Coulombic) interactions of the surfactant headgroups and/or tails with the surface; (c) attractions between the hydrophobic tails and their tendency to escape from an aqueous environment inducing the formation of interfacial aggregates; (d) repulsions between the hydrated headgroups mediated by their ionic atmospheres (adsorption of counterions). Nevertheless, the majority of hitherto effort has been devoted to adsorption on flat surfaces. On account of the high degree of uniformity of the mesopore structure, silicoaluminates of the MCM-41 type can be regarded as model mesoporous adsorbents and so they may play an essential role in the development of adsorption theory and practice.

In the present work, the results of isotherm, electrophoretic and calorimetric studies on surfactant adsorption onto MCM-41 silicoaluminates are reported.

Two series of solid sample were synthesised making use of alkyltrimethyl-ammonium bromides with different chain length as surfactant templates and of aluminium iso-propoxide as source of aluminium with different framework Si/Al ratios. The as-synthesised and calcined samples were characterised by powder X-ray diffraction (XRD), ^{27}Al MAS NMR, nitrogen gas adsorption, flow microcalorimetry of *n*-butanol adsorption from *n*-heptane and water, batch calorimetry of NH_3 chemisorption from the gas phase, calorimetry of immersion in water, *n*-heptane and formamide, as well as potentiometric titrations of the net surface proton balance.

All adsorption experiments were carried out from deionised water at 298 K, in the absence of background electrolyte and at free pH. The existence of an excess of negative charge in the sample surfaces was revealed under the experimental conditions employed. Adsorption of alkanediyl- α,ω -bis(dodecyldimethylammonium bromide) dimeric surface-active cations with the alkanediyl spacer groups C_2H_4 , C_6H_{12} , and $\text{C}_{12}\text{H}_{20}$ was compared to that of monomeric tetradecyltrimethylammonium bromide. The surfactant isotherm data were supplemented by measuring the sodium, bromide and hydrogen ion concentrations in the supernatant solution, the electrophoretic mobility of the sample particles, and the differential molar enthalpy of adsorption over the whole adsorption range.

The effect of the pore size and relative polarity of the MCM-41 materials on the mechanism of cationic surfactant adsorption is discussed here.

P₂69 THERMODYNAMIC ANALYSIS OF THE SURFACE OF HIGH-ENERGY SOLIDS AT MACROSCOPIC AND MICROSCOPIC LEVELS

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With a view to understanding both macroscopic and microscopic aspects of solid surface energy, the surfaces of a variety of high-energy solids, including zeolites, clays and silicas, both natural and synthetic have been studied using two different techniques: immersion microcalorimetry and dielectric relaxation. These experiments have been analysed using a hopping model combined with adsorption thermodynamics.

P₂70 LONG-RANGE INTERACTIONS IN DISPERSE SYSTEMS

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To describe the interparticle interactions in micellar and colloid solutions, emulsions and so on, the Derjaguin-Landau-Fervey-Overbeek potential is usually used. On great spacing the last, having an exponential decay, is completed by the power Van-der-Waals potential. Such modeling of the potential allows to give satisfactory qualitative explanation of many characteristic details of phase diagrams in considered solutions. But their quantitative description faces the essential difficulties.

In proposed work the new mechanism of long-range interactions in disperse systems is discussed. The physical origin of it is caused by fluctuation phenomena. The most simple manifestation of such interactions takes place in micellar nonionic solutions with particles of spherical shape. Here the thermal fluctuations of the shape violates the symmetry of disposition of dipole moments on the surface layer of particle. As a result, a micelle acquires the fluctuation multipole moments, which, in their turn, are responsible for additional long-range interactions in solutions. In dependence on relative value of dielectric permittivity of a particle about the solvent the multipole interparticle interactions can be attractive or repulsive. This fact explains the wide spread in interaction constants in different solutions.

In colloid and micellar ionic solutions, emulsions with addition of dissociating surfactants it is necessary additionally to take into account the charge fluctuations in diffusive electric layer. It is shown, that the fluctuation-multipole interactions for the distant particle, the sizes of which do not exceed some characteristic value, are dominating. The analysis of some concrete situations is made. The interrelation of phase diagram peculiarities with specificity of interactions in definite solutions is considered.

P₂71 FLUCTUATION EFFECTS IN EMULSIONS NEAR THE PERCOLATION THRESHOLD

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The fluctuation effects near the percolation threshold display themselves in numerous phenomena: the peculiarities of integral intensity and spectra of molecular light scattering, the frequency dispersion of dielectric permittivity and electroconductivity (in emulsions with an addition of dissociating surfactants) and

so on. To explain the observed regularities the different approaches with limited applicability regions are attracted. Their main defect is insufficient account of collective processes in a system.

The present work is devoted to the development of the general theory of the fluctuations near the percolation threshold. The thermodynamic and statistical versions of the fluctuation theory are given. The central object in the statistical approach is the cluster. The equation, describing the time evolution of clusters, is proposed. The dielectric permittivity and the conductivity of the system are represented as functionals of cluster polarizabilities. The exact form of one- and two- particle polarizabilities is established, the estimations for ones of higher orders are made. The peculiarities of the frequency dispersion of the dielectric permittivity and electroconductivity are investigated. To describe the temperature dependence of the relaxation time the formalism of the frequency moments is attracted. The application of the proposed theory for the description of the molecular light scattering is given.

The considerable attention is paid to the investigation of clusters interaction with the fluctuational hydrodynamic flows. The influence of the lasts on the time decay of the intensities correlation functions, scanned by the photon correlation spectroscopy, is considered in detail. The collective nature of diffusion processes in emulsions is analyzed.

P₂⁷² THEORIES OF COLLOID CHEMISTRY BASED ON THE POINT CHARGE DOUBLE LAYER MODEL AND THEIR EXPERIMENTAL VERIFICATION

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The most important and fundamental processes in colloid chemistry and in physical chemistry of electrolytes are theoretically explained on the basis of the point charge model for ions in double layer and in electrolyte solutions. The same theories are supported by relevant experiments from prominent laboratories from all over the world. They explain the following processes: variation of activity coefficients with electrolyte concentration, (an extension and replacement of the Debye-Hückel theory (to be published, see the oral contribution), electrokinetic phenomena on colloidal particles and in membranes, stability conditions of colloidal particles, counter and constituent ion adsorption on silver iodide, counter ion coagulation kinetics of silver iodide aggregates of hundreds of singlets observed by light scattering, "isoelectric" coagulation kinetics, *i.e.*, coagulation of silver iodide with silver ions, peptization of aged and coagulated silver iodide, ion exchange in coagulation, counter ion coagulation kinetics of latex aggregates of up to six singlets aproof that coagulation is a second order reaction, criticism of Smoluchowski's coagulation theory, heterogeneous exchange of precipitates and amalgams and formation of colloidal crystals.

The present poster demonstrates graphically that all theoretical functions deduced on the basis of the point charge double layer models are supported quantitatively by the corresponding experiments published by scientists from all over the world and cited as references in the following three review papers by the author.

- (1) Ion Exchange Theory of Coagulation and its Experimental Verification, *Croat. Chem. Acta*, 42(1970)161-142.
- (2) Experimental Electrokinetic Systems and the Point Charge Double Layer Model, *Ibid.*, 67(1994)493-508.
- (3) Theories of Colloid Chemistry Based on the Point Charge Double Layer Model, *Ibid.*, 69(1996)125-175.

The main experimental techniques applied are: potentiometric determination of adsorption of constituent ions on precipitates, potentiometry of electrodes of first and second order, counter ion exchange and adsorption by the radioactive tracer technique, counter ion and isoelectric coagulation kinetics observed by light scattering and counter ion coagulation of latices observed by the single light scattering technique, heterogeneous exchange of precipitates and amalgams, electrokinetic studies and studies of the impedance of electrodes.

Theoretical and experimental arguments are offered that as a rule all conventional theories in colloid chemistry must be rejected because not a single of their postulates has ever been supported by experiments. The conventional theories are based on the homogeneous electrical charge double layer model. The same model cannot be valid for colloidal particles because it has been developed exclusively for processes on polarized metallic electrodes of Galvanic cells. Although colloidal particles are isolators as organic latices, semiconductors as ionic solids and exceptionally metallic conductors they are all charged with fixed ions, *i. e.*, adsorbed ions and chemically bound ionic radicals. The best model for them is the point charge double layer model.

P₂₇₃ IMPROVEMENT OF SAXS MEASUREMENTS BY GÖBEL MIRRORS

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Small angle X-ray scattering (SAXS) is a very important and well established method to investigate surfactant aggregates in water or oil. Many surfactants have in aqueous or oily solution a low overall contrast or scattering cross-section for X-rays. Therefore it is important that the intensity of the primary beam is as high as possible. Contrary to the bright synchrotron radiation sources, laboratory X-ray sources emit a highly divergent beam. The Kratky compact camera is constructed to maximize the intensity in the sample using a slit collimation system. The performance of this camera could be further increased if the primary beam is collimated from a divergent into a parallel beam.

A recently developed device for this purpose is the so called, "Göbel mirror". This mirror is made of parabolically bent multilayers. They are designed to convert divergent X-rays from laboratory X-ray sources into a parallel beam of high brilliance. 50 non-parallel layerpairs of alternating tungsten and silicon layers are used to separate CuK α radiation from CuK β radiation and, most importantly, from the bulk of hard X-rays. The function of this kind of X-ray mirrors is based on the high integral reflectivity for the combination of two materials (e.g. W and Si) with a large contrast in electron density. The Göbel mirrors have a parabolic shape and are located in such a way that the anode constitutes the near focus of the parabola.

Another aspect that is worth mentioning is the good separation of the CuK α radiation. The exclusive use of the CuK α is very important when using a position sensitive detector (PSD) because the PSD is not able to distinguish between CuK α radiation and hard X-ray background and these hard X-rays cannot be resolved in position. The quality of the SAXS data with the Göbel mirror is therefore higher because of the higher intensity and the much lower background.

We present all these advantages such as intensity gain, low background, better quality etc. in our experimental results. Another important point is that the good quality of our data will allow to use water as a standard for absolute intensity calibration which is important for the determination of aggregation numbers, molecular weight etc.

P₂₇₄ APPLICATION OF SURFACTANTS IN EMULSIFYING METALWORKING FLUIDS

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Emulsifiable metalworking fluids are subordinate to continuous evolution in order to increase economy and satisfy growing ecological and safety requirements. Therefore, the composition of modern formulations are becoming more and more sophisticated so that the great deal of usual components are changing with new less harmful components. During selection of new components it should be taken into account the satisfying of application properties working emulsions such as cooling of cutting zone, chip flushing, lubrication, corrosion protection, stability, resistance to micro-organisms and others.

In application as emulsifiants have been widely used alkylbenzene sulfonates, then different ethoxilates and nowadays in modern formulation are used fatty acid esters for example succinic acid esters.

Recently, application of carboxilates has gained increasing importance in emulsifiable metalworking fluids. These are mild surfactants showing both nonionic and anionic properties, they are mild to the skin and readily biodegradable. Ether carboxilates increase the dispersity of the emulsions and thus their stability and service life. In contrast to conventional nonionics they also contribute to corrosion properties.

The system of metalworking fluid must be properly optimised in order to obtain the required emulsion properties. In this paper are shown properties of emulsifying metalworking fluids depending on type and quantity of applied emulsifiant.

P₂₇₅ HYDROPHOBICALLY MODIFIED POLYELECTROLYTES STABILIZING MACROEMULSIONS

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Hydrophobically modified poly(sodium acrylate)s are used as emulsifiers of the *n*-dodecane-water system. Weakly modified polyelectrolytes combine both electrosteric and viscosifying stabilization of oil droplets in water. The extended diversity of parameters that exist to modify the polymer behavior in bulk water and at the interface is used to control both the stability and viscosity of oil in water emulsions. Furthermore, it is shown that only 4% of a suitable copolymer (40% with conventional surfactants) is required to form ordered monodisperse emulsions using a simple technique. This unique experiment provides striking evidence of the high emulsifying potential of these copolymers. Finally, external field variables (salt) are

used to tune the type of emulsions containing highly modified well-balanced polymers. From a comparison with surfactants of similar chemical structure, a HLB scale for polymers is established.

P₂76 INTERFACIAL CHARGE IN MIXED OXIDE AQUEOUS SUSPENSIONS

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Surface charge in the aqueous silica and hematite mixed dispersion was determined as a function of pH and mixture composition. In the case of independent charging, surface charge is a sum of surface charges of each oxides. The point of zero charge (p.z.c.) of metal oxide mixture corresponds to the pH where the net surface charge is zero, while one oxide bears positive charge and the other one negative. The p.z.c. of mixed oxides was found to lie between the p.z.c. of pure oxides and depends on specific surface area, mass fraction and point of zero charge of both oxides in the mixture.

The surface charge and the point of zero charge were determined by "mass titration" and acid-base titration of aqueous silica and hematite mixed dispersion. It is shown that "mass titration" could be used as a method for determination of the point of zero charge and surface charge of pure oxides and also applied to their mixtures.

P₂77 MIXED HYDROGENATED AND FLUORINATED SYSTEMS

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Structure of highly concentrated reverse emulsions with hydrophobic surfactant, oil and water is well-known. These systems can be prepared with hydrogenated or fluorinated compounds, with a high water content (more than 97% w/w). Recently, mixed emulsions have been formulated from the mixture of the two kinds of emulsion (hydrogenated and fluorinated) [1]. Surprisingly these systems are stable despite the strong lipophilicity of fluorocarbons.

In order to elucidate the structure of such peculiar emulsions, we have investigated the phase behaviour of the two surfactants in presence of fluorocarbon, hydrocarbon and water. The both surfactants, with the same polar head, are miscible in any proportion and lead to inverse micelles by incorporating water. These mixed micelles can be diluted into an hydrogenated oil, decane for example. Nevertheless, the solubilisation of such micelles in fluorocarbons is limited (particular conditions of temperature and concentrations). Presence of mixed micelles has been demonstrated by small angle scattering techniques.

(1) G. Caldero, M.J. Garcia-Celma, C. Solans, M.J. Stébé, J.C. Ravey, S. Rocca, and R. Pons, *Langmuir* 1998, 14, 1580-1585.

P₂78 DIRECT MEASUREMENT OF DEPLETION POTENTIALS IN MIXTURES OF COLLOIDS AND NON-IONIC POLYMERS

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In colloidal suspensions containing a binary mixture of hard spheres depletion forces occur which substantially contribute to the interaction of the larger spheres among themselves and a wall, respectively. We investigated the depletion force acting on a large colloidal polystyrene sphere immersed in a solution of small non-charged polymer coils close to a flat glass surface by means of total internal reflection microscopy (TIRM) [1]. When the distance between the polystyrene sphere and the wall is smaller than the diameter of the polymer coils, an attractive potential acting on the sphere is observed which depends strongly on the polymer concentration. We present systematic measurements of the interaction potentials between single particles and a fused silica surface for different polymer concentrations. The obtained depletion potentials are in good agreement with theoretical predictions.

(1) D.C. Prieve, F. Luo, F. Lanni, *Faraday Discuss. Chem. Soc.* 83, 297 (1987).

P₂79 RUPTURE OF AQUEOUS WETTING FILMS

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The stability of wetting films with microscopic dimensions formed between interacting particles and gas bubbles in liquids is of fundamental significance for coalescence processes like flotation. By means of the investigation of the stability on model-adsorption layers, produced with help of structured Langmuir-Blodgett layers and surfaces modified by self assembly reactions, we are able to distinguish two possible rupture mechanisms of such thin liquid films:

- *spinodal dewetting* due to growing capillary waves under the action of attractive forces between interfaces and
- *heterogeneous nucleation* inside the wetting films (formation of embryonic gas nuclei), which increases with increasing of surface heterogeneity.

The mechanism of hole formation itself has been investigated by high-speed video technique. We found out for the first time differences between the three phase contact expansion mechanism on homogeneous and non-homogeneous adsorption layers (fig. 1 and 2).

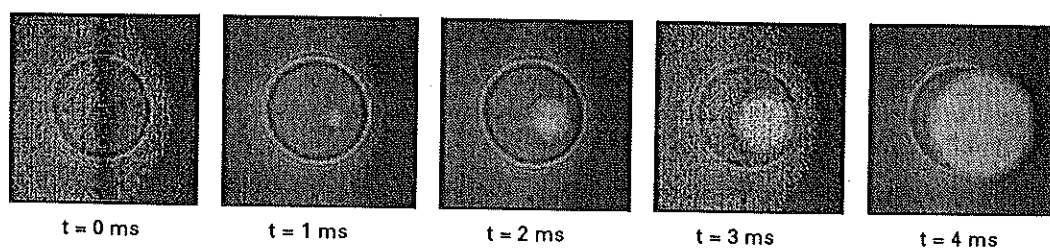


Fig. 1: video sequence of the rupture of a thin water film on a homogeneous methylated glass surface

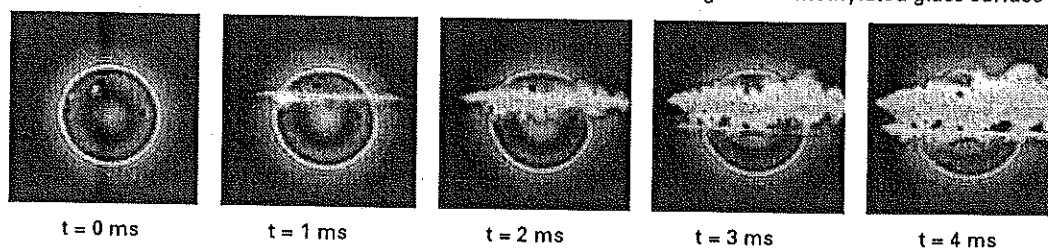


Fig. 2: video sequence of the rupture of a thin water film on a heterogeneous skeletonized LB-layer

P₂80 STRUCTURE FACTOR AND THERMODYNAMICS OF CONCENTRATED COLLOIDAL DISPERSIONS

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In statistical theory of concentrated colloids the microscopic nature of the particle ordering and thermodynamic functions of the system are determined by calculation of the pair correlation function.

Here we propose a simple approach to calculation of the correlation function, utilizing a random phase approximation [1,2]. According to this method, the general correlation function is obtained as a superposition of the correlation function for hard spheres, and a "tail", which represents a long-range interaction in the system.

We determine the total interaction potential of identical colloid particles immersed into an electrolyte solution as the sum of attractive (van der Waals) and repulsive (screened Coulomb) potentials. The latter is calculated for the cases of equilibrium regime (charge regulation) [3], constant electric potential and constant charge at the surface of colloidal particles. All these analytical expressions are derived for a low surface electrostatic potential, and we assume that condition $\kappa_d \gg 1$ is satisfied (κ is the modified Debye-Hückel screening parameter, and d is the particle diameter).

The behavior of the static structure factor and osmotic pressure has been investigated varying different parameters: density of particles, temperature, Hamaker's constant, and electrical characteristics of particle's surface.

Two types of phase transitions were observed in the system: i) gas-liquid phase transition caused by the van der Waals attraction between particles, ii) disorder-order phase transitions driven by repulsive inter-particle interactions. The latter is revealed when comparing behavior of osmotic pressure for continual (fluid), and lattice gas models of a dispersion [4].

- (1) Shulepov, Yu.V., Shulepov S.Yu., *Progr. Colloid Polym. Sci.*, 1996, 100, 148.
- (2) Yukhnovski I.R., Shulepov Yu.V., *J. Stat. Phys.* 1985, 38, 541.
- (3) Shulepov Yu.V., Koopal L.K., Lyklema., Dukhin S.S., *Colloid J.*, 1997, 59, 658.
- (4) Shulepov Yu.V., Aksenenko E.V., *Lattice Gas*, Kiev, Naukova Dumke, 1981.

P₂81

INTERACTIONS IN CALCIUM OXALATE HYDRATE/SURFACTANT SYSTEMS

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Phase transformation of calcium oxalate dihydrate (COD) into the thermodynamically stable monohydrate (COM) has been studied in anionic (sodium dodecyl sulfate (SDS)) and cationic (dodecylammonium chloride (DDACl)) surfactant solutions. Both surfactants inhibited, but did not completely blocked COD to COM transformation: SDS acts as a stronger transformation inhibitor. The inhibition of the transformation process is attributed to the preferential adsorption of surfactant molecules at different crystal faces. Adsorption isotherms for both surfactants followed the two-step (LS) type adsorption model, although some differences in the adsorption behavior were detected. They originated from different ionic and molecular structures of crystal surfaces and the interactions between the surfactant headgroups and crystal surface.

P₂82

ULTRASONIC ANALYSIS OF HEAT INDUCED COAGULATION IN CALCIUM FORTIFIED MILK

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Milk is a complicated colloidal system, the key component of which is casein micelles. Heat induced coagulation of casein micelles is one of the major problems in the design of new milk based products in the food industry. Many of food additives reduce the stability of casein micelles in milk leading to coagulation during heat treatment. Up to now there was a lack of experimental methods allowing fast, non-expensive and technically non-complicated analysis of the heat stability of milk colloids. In the present work we used a new high precision ultrasonic resonator method to monitor the coagulation of calcium fortified low fat milks. The technique provides a relatively cheap, rapid and non-destructive analysis and requires small volumes of material. Calcium fortified milk was developed to improve the mineral intake in the human diet. However addition of calcium leads to a reduction of stability of the casein micelles, resulting in aggregation of these micelles and coagulation in milk when it is heated or added to hot coffee or tee. In the present work we measured the dependence of coagulation temperature of milk on the concentration of calcium added. We also evaluated the effects of potential stabilisers on the coagulation temperature. Two independent parameters, ultrasonic velocity and ultrasonic attenuation in milk were measured as a function of temperature. We observed a sudden increase in the ultrasonic absorption and decrease in ultrasonic velocity at coagulation. Both parameters give the same value of coagulation temperature with the resolution better than 0.3 °C. The results allowed us to evaluate the concentrations of stabilisers required to prevent the coagulation of calcium fortified milk at the temperatures below 100 °C.

P₂83

SURFACE MIGRATION OF COLLOIDS ADSORBED ON MINERAL SURFACES IN THE PRESENCE OF ORGANIC MOLECULES

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Small inorganic particles dispersed in water can adsorb onto a mineral surface when the charges of the two components are opposite. The process can be reversible if the energy of adsorption is small (less than a few kT per particle) or nearly irreversible when the energy is high. In the irreversible case, a common assumption is to consider the particles as blocked at a given position on the surface. We have built a system where the assumption is no more valid. A submonolayer of positive particles can be spontaneously formed on mica (negative surface) from a dilute aqueous dispersion of α -alumina particles (150 nm in size). This pristine layer does not desorb with time in pure water and the particles are blocked at their position of adsorption. Nevertheless, when this layer is incubated in a diluted solution of citrates (pH 7) the particles are allowed to **migrate along the surface without any desorption**. This fundamental process has been demonstrated by analysing the morphology of the layer with an Atomic Force Microscope before and after the incubation stage. In particular, the surface diffusion is demonstrated by the occurrence of two dimensionnal fractal aggregates onto the surface. The structure of the aggregates and the effects of time of incubation, ionic conditions and temperature have studied and the results are discussed in terms of potential of inter-

action between the particles and the mica. The role of the citrate molecules in this process is essential because they modify the interaction potential in two ways: (i) they inverse the sign of the particles (from positive to negative) which nevertheless remain trapped in the vicinity of the mica due to the Van der Waals attraction; (ii) they act as a lubricant between the surfaces to allow the lateral diffusion of the particles.

P₂₈₄ SHAPE AND LINE TENSION OF WATER LENSES AT THE DODECANE/AIR INTERFACE

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Microscopic water lenses were produced by condensation of the moisture of air from the vapor phase on a dodecane surface. These lenses are observed under a reflecting microscope in monochromatic light. Determination of radius of the three phase contact line r_c and the contact angle dodecane/water of the lens $\theta_{d/w}$ by interference fringes allows to calculate the shape of the lens.

Using the modified Neumann-Young equation

$$\sigma_{a/d} - \sigma_{a/w} \cos \theta_{d/w} - \sigma_{d/w} \cos \theta_{a/w} = \frac{\kappa}{r_c}$$

enables the determination of the line tension κ , which has for this system the value of $5 \cdot 10^{-9}$ J/m.

According to a paper of Aveyard and Clint [1] the influence of line tension on the shape of a water lens resting in a dodecane surface was studied. It is remarkable that for positive line tensions two coexisting possible drop shapes appear. If the line tension exceeds a certain value (here: $\kappa_m = 5,59 \cdot 10^{-9}$ J/m), the lens cannot have a stable configuration in the interface and will be expelled into the oil phase.

- (1) R. Aveyard and J. Clint, J.Chem.Soc., Faraday Trans., 93(7) (1997) 1397.

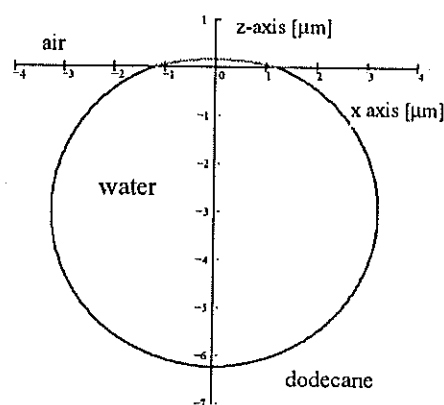


Fig. 1: Typical shape of a water droplet resting in the dodecane/air interface

P₂₈₅ POTENTIOMETRIC AND DLS INVESTIGATION OF THE PRECIPITATION OF LANTHANUM FLUORIDE

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The precipitation processes were characterised in aqueous solution of $\text{La}(\text{NO}_3)_3$ -KF at 25 °C using light scattering method and potentiometric titration with fluoride ion selective electrode. Two processes are taking place: I) neutralisation process at large concentrations of precipitation components in the ratio 1/3 and with the attained pH in the range 4.0 ± 0.3 , leading to the formation of pure LaF_3 (s); II) ionic solubility at $\text{La}(\text{NO}_3)_3$ concentrations below about 10^{-3} mol/dm³ with large hydrated lanthanum ions in solution having pH in the range 6.0 ± 0.3 and fresh precipitated lanthanum fluoride-hydroxide containing large amount of water, which is hard to filter and to dry, and is not suitable for preparation of pure LaF_3 . The size of particles (dynamic light scattering measurements) at the solid/solution concentration limit is much greater (at least for an order of magnitude) in the case II as compared to those in the former case I; where pF-stat crystal growth led to the formation of pure hexagonal LaF_3 (s), as was determined by powder diffraction analysis (XRD).

The activity solubility products in water at 25°C $K_{so}^\circ(\text{LaF}_3) = 1.3 \cdot 10^{-17}$ (lit. value $7 \cdot 10^{-17}$), and in 50 % ethanol solution $3.7 \cdot 10^{-27}$, were determined potentiometrically.

The investigation of micellar medium of non-ionic surfactant on the growth pattern is in progress.

The author is thankful to undergraduate chemistry students Jordanka Semren and Maja Fabulić who contributed to this work at different times.

P₂₈₆ AGGREGATE STRUCTURE AND PERCOLATION PROPERTIES OF METAL-FILLED POLYMER FILMS

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The structure characteristics of nickel particle aggregates, formed in polymer films (epoxy resin) at various curried regimes, and influence on them of particle surface modification were studied. It was shown, that

in all cases under investigation the aggregates have fractal geometry, and their fractal dimension corresponds to the regime of diffusion-controlled aggregation. The increase of curing temperature and the modification of particle surfaces with stearic acid, at given film thickness, do not change the fractal dimension of aggregates, but result in a significant increase of their average size. The conductivity of film composites near the percolation threshold was also investigated.

The comparison of percolation critical indexes and fractal dimensions, determined in these experiments, with known scaling relationships has allowed to conclude that fractal geometries of percolation clusters and clusters, formed at early stages of particle aggregation coincide. As a result, the independence of the fractal dimension of curing regime and of particle modification provides the conductivity critical index independence of them. This fact is confirmed by experimental data.

It is from here possible to generalize, that the percolation characteristics of investigated composition do not depend on the average size of aggregates.

On the other hand, it is experimentally established, that the composite film conductivity and the percolation threshold significantly depend on the curing temperature and the thickness of a film. The analysis has shown, that this is connected as to change of internal stresses, arising in the film during the curing, and its subsequent contraction, as to insulated polymer and oxide interlayers between particles. At an increase of the film thickness and the curing temperatures the internal stresses grow. It, in turn, promotes the insulated interlayers breaking, increase of the film conductivity and decrease of the percolation threshold.

Two percolation transitions in metal-filled polymer films were detected. The first corresponds to the transition from non-conducting state to the state with tunnel conductivity, which is determined by the polymer or oxide layers between the particles and aggregates. The second is related to transition to the metal conductivity.

The existence of two percolation transition can be explained as follows. At low conducting particle concentration $p_c^{(1)} < p < p_c^{(2)}$ ($p_c^{(1)}$ and $p_c^{(2)}$ are the first and the second thresholds, respectively) the infinite conducting cluster has got a small elastic modulus. Thus, the internal stresses are transferred to the infinite conducting cluster to only a small extent, and the particle oxide layers are not ruptured. The composite conductivity is, thus, determined by the layer resistance. As the particle concentration increases both the elastic modulus of infinite conducting cluster and the number of ruptured oxide layers increase too. When the particle concentration passes over a critical value, which is equal to $p_c^{(2)}$ in our case, the charge transfer proceeds only through the ruptured contacts, and the second percolation transition takes place.

P₂₈₇ DIMENSIONALITY REDUCTION INDUCED MELTING

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We study the phase transition of two-dimensional colloids subject to a modulated laser field (interfering fringes). The colloidal particles, which show a liquidlike order under zero light field, are shown to crystallize with a hexagonal order when the fringe spacing is nearly commensurate with a hexagonal lattice and the light intensity is sufficiently strong. However, when the light field is increased further, the induced crystal is observed for the first time to melt to a re-entrant modulated liquid. The re-entrant melting transition is interpreted as a reduction of dimensionality.

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P₂₈₈ EXPERIMENTAL OBSERVATION OF LASER INDUCED FREEZING MELTING IN TWO-DIMENSIONAL COLLOIDS

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We study the phase transition of two-dimensional colloids subject to a modulated laser field. The colloidal particles, which show a liquid-like order in the absence of a light field, start to crystallize when the light intensity reaches a critical value. This phenomenon is known as light-induced freezing (LIF) and has been already observed by other authors [1]. If the light intensity, however, is increased further, the crystal is observed to remelt into a modulated liquid. This was already predicted theoretically as a consequence of the reduction of dimensionality [2] and is now experimentally observed for the first time.

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