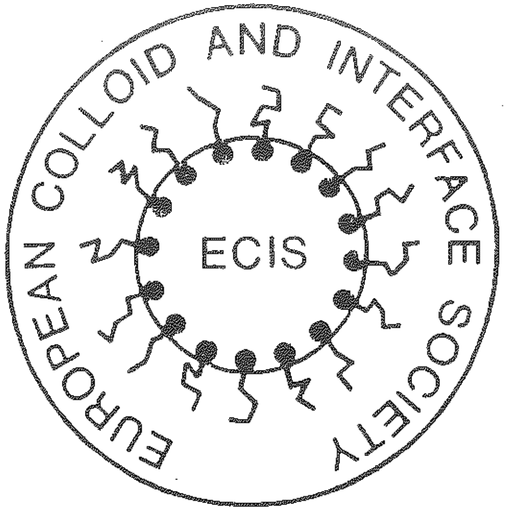

PROGRAM
AND
ABSTRACTS

ARCACHON (FRANCE)

19-22 September 1988

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11:10 F. HESLOT, A.M. CAZABAT, P. LEVINSON
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15:15 *CLOSING WORDS*

LECTURES

INDUCED ADHESION
OF DIGALACTOSYL DIGLYCERIDE (DGDG) MEMBRANES

M. Mutz and W. Helfrich

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DGDG is as abundant in plant membranes as is lecithin in animal membranes. We have found that it swells in pure water and in salt solution, forming many large single membranes. Their mutual adhesion caused by lateral tension is similar but stronger than that of lecithins, the contact angle of symmetric adhesion of two single membranes being 60 GRAD instead of 45 GRAD.

Multivalent Ions and Flexible Polyelectrolytes as Counterions in an Electric Double Layer.

Bo Jönsson, Clifford E. Woodward, Bo Svensson and Torbjön Åkesson
Physical Chemistry 2, Chemical Centre, POB 124
S-22100 Lund, SWEDEN

Recent investigations of the Poisson-Boltzmann theory using simulation techniques have shown it to be a good approximation for electric double layers with monovalent point counterions and in the absence of added salt. Under the same conditions but with divalent ions the Poisson-Boltzmann equation fails completely in the description of the force between two overlapping double layers. The failure is due to neglect of ion-ion correlations and becomes progressively more severe at high coupling strength, as for example with divalent ions.

These conclusions are also valid in the presence of salt, although the ion size also plays a role and in general tend to counteract correlation effects. Additional mechanisms appear at very high salt concentration and again the simulations predict qualitatively different force curves from the Poisson-Boltzmann theory.

It is of both theoretical and practical interest to further explore systems where ionic correlations play a role. However, small multivalent ions are scarce in nature and in order to find such of practical use we have found it necessary to work with flexible polyelectrolytes. Hence, we have, guided by Monte Carlo simulations developed an approximate theory for flexible polyelectrolytes in an electric double layer. Both Monte Carlo simulations and the theory predicts a strong decrease of the entropic double layer repulsion in presence of polyelectrolytic counterions. Under certain realistic conditions the repulsion will be smaller than the attractive correlation force *between* two double layers. Thus the addition of polyelectrolytes can dramatically modulate the force between charged aggregates and the present theoretical approach provides a framework for understanding these effects. In all systems studied so far the magnitude of this force component is (much) larger than of the usual van der Waals attraction.

A Poisson-Boltzmann Approximation for Strongly Interacting Macroionic Solutions.

by

Clifford E. Woodward and Bo Jönsson.
Physical Chemistry 2
Chemical Centre, POB 124
S-221 00 Lund, SWEDEN

Disregarding many(≥ 3)-body interactions, the effective pair potential between macroions is derived as the difference in free energy between adding two macroions at fixed separation and at infinite separation to the dispersion, assuming other macroions do not respond to the added particles. The free energy difference is obtained using the overlap approximation, within the framework of a free energy functional, obtained by simplyfying a full Poisson-Boltzmann treatment of the dispersion. The resulting pair potential has a screened Coulombic form, but with an apparently renormalised macroion charge and renormalised screening length. The model thus gives the appearance of ion binding, but no binding is assumed. The theory gives excellent agreement with experimental structure factors for dilute dispersions of micelles and colloids, where the usual DLVO potential fails, provided the surface charge density and volume fraction are not too large.

NON-AQUEOUS SILICA DISPERSIONS. CHARGED PARTICLE INTERACTIONS STUDIED BY SCATTERING OF LIGHT.

by A.P. Philipse and A. Vrij

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A novel type of stable colloidal dispersions in weakly polar organic solvents will be described. The particles consist of a charged, spherical silica core, coated with 3-methacryloxypropyl trimethoxysilane, and are nearly uniform in size.

An important feature of this silica is that it can be optically matched up to high particle volume fractions.

It provides therefore a very appropriate model dispersion for light scattering studies of the combined effect of charged and high content of dispersed materials.

Static and dynamic interactions were measured between the charged silica spheres suspended in an optically-matching, salt-free mixture of ethanol and toluene up to volume fractions of ten per cent.

The static structure factor, S(K), is compared with theoretical calculations based on the RMSA approximation for a single-component fluid of charged marcro-particles.

Also an effective diffusion coefficient $D_e(K)$ was determined and combined with S(K) to obtain the function H(K), which represents the hydrodynamic interactions.

From H(K), obtained for the first time for charged particles, we conclude that the long-range electrostatic repulsion between the spheres has a pronounced influence on the hydrodynamics of large-scale, collective particle motions, whereas small-scale single-particle diffusion is relatively unaffected.

At higher silica concentrations colloidal crystallization is observed in these dispersions, as well as the formation of a glass-like phase.

INFLUENCE OF THE STERIC STABILIZATION LAYER ON THE CRYSTALLIZATION OF COLLOIDAL SILICA PARTICLES

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Colloidal silica spheres were coated with stearylalcohol and polyisobutylene, thus forming uncharged sterically stabilized particles. By increasing the thickness of the stabilization layer (by changing the molecular weight of polyisobutylene), the short-range interaction between the particles was varied from a nearly hard sphere potential to a somewhat softer potential.

Study of the crystallization phenomena of these systems revealed that the rate of crystallization increased dramatically as the thickness of the organic stabilization layer was increased. Light scattering experiments of the ordering phenomena that lead to the formation of colloidal crystals will be presented.

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Experimental and Theoretical Aspects on Cluster Size Distribution of Latex Particles Flocculating in presence of Water Soluble Polymers

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SUMMARY. The size distribution of latex particles flocculating in the presence of poly(4-vinylpyridine) was measured using an automatic particle counter. The distribution and its time evolution were determined as a function of the polymer concentration and the pH of the aqueous suspension. In any case the cluster size distribution c(g,t) are well described at large time by the formula:

$$c(g,t)-t^{-2\omega}\psi(gt^{-\omega}) \tag{1}$$

were the function ψ does not depend explicitely on time. The first moment of the distribution scales like $t^{-\omega}$. Eq.(1) is interpreted on the basis of a dynamic scaling argument (renormalization of the scale of time and size)

At a polymer concentration were the flocculation efficiency is maximum, ω is equal to unity. This simple behavour is interpreted on the basis of the generalized Smoluchowski's equations:

$$\frac{\partial c(g,t)}{\partial t} - \int_0^g K(g-n,n)c(g-n,t)c(n,t)dn$$
$$-2c(g,t)\int_0^{\infty} c(n,t)K(g,n)dn \tag{2}$$

The r.h.s. first term represents the increase in g-fold particles due to represents the decrease of g-fold particles.The collision frequency K(g,n) can be expressed as:

$$K(g,n)-\frac{kT}{3\eta}(R_g+R_n)(D_g+D_n) \tag{3}$$

R_g,R_n and D_g,D_n are respectively the radius of gyration and the diffusion coefficients. If R_g-g^{ν} and $D_\eta-g^{\gamma}$,and when $\nu-\gamma$, it can be shown that $\omega-1$. However, for small and large polymer concentrations, ω becomes negative. This point is explained by taking into account the probability p of efficient collisions between g and n-fold clusters when electrostatic repulsions and polymer-polymer repulsions are dominant at respectively small and large polymer concentrations. The probability p can be expressed by:

$$p \propto \int_0^L \exp-[\Delta G_e(x)+\Delta G_p(x)]/kT\, dx$$

$\Delta G_e(x)$ is the electrostatic free-energy of the charged colloid at the distance x, whereas $\Delta G_p(x)$ is the free-energy of polymer-polymer interactions.

FRACTAL STRUCTURE OF ULTRAFINE FERROUS COLLOIDS OBTAINED IN MICROEMULSIONS

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J.Rivas
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There has been great interest recently in both the formation dynamics and the properties of ultrafine colloidal particles[1]. It has been found that the structure of colloidal aggregates depends heavily on the kinetic processes involved in the aggregation phenomena. Also, in various cases, it has been shown that the aggregates exhibit scale invariance which can be described by the fractal geometry[2].

We have obtained different kinds of monodisperse ferrous colloids in various types of microemulsions. The ultrafine particles obtained (radius ≈ 2nm) have been characterized by small-angle X-ray scattering, electron microscopy, magnetization measurements and differential scanning calorimetry.

The experiments performed clearly reveal the fractal nature of the ferrous colloids, with a fractal dimension D=2.2±0.1 which indicates that the particles are formed via reaction-limited cluster-cluster aggregation phenomena.

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AGGREGATION IN INTERFACIAL COLLOIDAL SYSTEMS

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Recent computer simulations have demonstrated the fractal nature of structures arising in aggregation processes (1). Experiments on various aggregating systems have qualitatively confirmed this picture (2,3). Quantitative comparison of experimental results with data from computer experiments provides a certain amount of information concerning the processes involved.

Studies of aggregation in two dimensions offer the possibility of further testing current theories, as the fractal dimension of the aggregates depends strongly on the spatial dimensionality involved. We have studied a two-dimensional system: polystyrene latex microspheres trapped at the air-water interface (4,5). The basic interaction between the particles is a long-ranged electrostatic repulsion, but this can be screened to permit aggregation driven by short-range attractive forces. Careful choice of experimental conditions permits the inter-particle forces to be modified.

The aggregation in this system has been followed by direct microscope observation. Video-micrographs taken at various times during the aggregation process have been digitised for image analysis. Pair correlation functions, structure functions and radii of gyration as functions of mass have been computed. The fractal dimensions (D_f) extracted from these various approaches will be compared. The various mechanisms of aggregation operative under various experimental conditions will be discussed, based on the D_f values.

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REVERSIBLE FLOCCULATION OF COLLOIDAL SUSPENSIONS BY WATER-SOLUBLE POLYMERS

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The possibility to concentrate, then redisperse colloidal suspensions is not only of great theoretical interest, but do affect the industrial process of solid-liquid separation, which must be often followed by a redispersion stage.

Up to now, these consecutive operations are unrealizable in presence of polymers, since flocculation and adsorption are generally considered as irreversible in this case.

Previous studies have pointed out the occurrence of two main flocculation mechanisms : charge neutralization and interparticle bridging. The use of copolymers makes it possible to take into account these two different mechanisms together.

Based on this idea, new copolymers of acrylamide with N-vinylimidazole were prepared, via radical polymerization and characterized by light scattering, viscometry, potentiometric titrations and UV studies. One peculiarity of the chosen system is its dependence on pH : actually the degree of neutralization of such cationic polyelectrolytes, does vary with pH, especially near the pK value. It is shown, that these copolymers may induce reversible flocculation of negatively charged suspensions, like silica ones, by simple pH adjustment. Performances of the systems were followed by some physico-chemical methods such as adsorption isotherms, light scattering, hydrodynamic layer thickness and zeta potential measurements.

The observed results are explained in terms of flocculation mechanisms as a function of pH.

STABILITY OF SILICA COLLOIDS AND WETTING TRANSITIONS

par: V.Gurfein, F.Perrot and D.Beysens

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When Silica colloids (diameter 500-2000 Å) are immersed in a binary fluid (water+2-6 lutidine) the stability of the solution is affected by capillary interactions. For particular values of the composition and the temperature of the fluid, a flocculation of the colloids can be observed. This process is reversible, and is analogous to a solid-gas transition for the colloids. It is due to the sudden increase of an adsorbed layer of lutidine (or water, according to the different surface characteristics). This phenomenon, which is expected to be universal, can be related to the wetting and adsorption properties of solids in contact with fluid mixtures.

STEP-WISE THINNING OF FOAM FILMS CONTAINING COLLOID PARTICLES

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The phenomenon of stratification (step-wise thinning) of liquid films was observed long ago by Johnnot and Perrin with foam films. We observed similar phenomenon with films from latex suspension in water. Then it is possible to explain the stratification as a layer-by-layer thinning of ordered structures of colloid particles (micelles or latex particles) inside the film. These structures and the ordering in bulk latex suspensions have similar physical nature. The thickness of the metastable states of a stratifying film are calculated by means of a new expression for the disjoining pressure of a film containing micel
The calculated and the measured values of the film thickness are in good agreement. The driving force of the step-wise thinning of the film is attributed to the gradient of the chemical potential of the micelles at the film periphery. The appearance and expansion of spot in the film can be explained by the micellar self-diffusion. This ex- planation is supported by the experimental data. The phenomenon of stratification gives a method for investigating the ordering in coll dal systems and their stability.

Microemulsion gels in the ternary system Tetradecylaminoxide, water, hydrocarbon.

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Tetradecylaminoxide is a zwitterionic surfactant with a behaviour which is in between the typical behaviour of a nonionic and a cationic surfactant. In the isotropic solution it forms small rodlike micelles at room temperature which become larger with increasing temperature up to about 40°C. For even higher temperatures the size of the rods decreases again. The system forms a nematic phase between 32 - 35% by weight which is then followed by a hexagonal phase.

When a few percent hydrocarbon is solubilized into the isotropic or liquid crystalline surfactant systems which contain between 30 - 40% of surfactant the rodlike micelles undergo a rod-sphere transition and the highly viscous solutions turn to low viscous solutions. For a somewhat higher hydrocarbon content the systems solidifie and form a single phase which is highly transparent, optically isotropic and solid.

The position of the microemulsion gels in the ternary phase diagram was established for a homologues series of hydrocarbons between Tetradecane and Heptane and also for Cyclohexane. With the smaller Alkanes the Gelphases move to a higher hydrocarbon content. The properties of the investigated systems are very similar as the properties of Microemulsion gels which have been reported for the ternary systems oleylpolyglycol-ether, paraffinoil and water.

We have carried out SANS and SAXS measurements on these phases to determine their structure. We have some evidence for a cubic phase. Most of our samples give however only a single correlation peak which is due to a nearest neighbour order. It seems therefore that the phases can sometimes exist as a cubic phase and sometimes as a kind of glassy state which has the same macroscopic properties. For the characterisation of the system we also carried out rheological, nmr and electric birefringence measurements. Of particular interest of the systems is their extraordinary high shear modulus and yield value.

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QUASI ELASTIC LIGHT SCATTERING STUDY OF SWOLLEN LAMELLAR PHASES

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We study the Rayleigh-Brillouin spectrum of swollen lamellar phases. The samples are multicomponent systems made of water, surfactant and alkane. The phase diagram features a lamellar (smectic A) phase which ranges from concentrated to extremely swollen surfactant structures. The anisotropic dispersion relations of the hydrodynamic modes are investigated in oriented samples : the behaviour of elastic constants and transport coefficients as a function of dilution is shown and discussed.

C14

BICONTINUOUS STRUCTURE IN THE "ANOMALOUS ISOTROPIC PHASE" L_3

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The "anomalous isotropic phase" is a fluid phase that appears in many surfactant systems and presents unusual streaming birefringence. Its physical properties differ from those of the classical micellar solutions and its position in the phase diagrams is close to the domain of stability of the swollen lamellar phase.

Its structure is here investigated using small angle neutron scattering. At local scale it consists of bilayers very similar to those of the neighbouring swollen lamellar phase. Its swelling behavior upon dilution differs from the lamellar phase and rather indicates a bicontinuous topology of the large scale arrangement comparable to the so called "Scriven molten cubic structure".

A rough modelization is proposed for the free energy of such structures which allows to derive the evolution of the osmotic compressibility as function of the dilution. It is found in good agreement with additional light scattering data.

STRUCTURAL ASPECTS OF THREE–COMPONENT MICROEMULSIONS

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The phase behavior of ternary systems water–oil–ionic amphiphile has been studied in detail[1a]. As for nonionic amphiphiles described previously [1b], the phase behavior follows general patterns. The important difference being the reversed temperature dependence of the phase sequences. Moving along well–defined paths in the phase diagrams the one–phase region is traced by changing water–to–oil ratio, amphiphile concentration and temperature. We study by small–angle neutron scattering, freeze fracture electron microscopy, electrical conductivity etc. the inversion from water–in–oil to bicontinous to oil–in water microemulsions. The interpretation of the results is facilitated by avoiding the use of cosurfactants as an unnecessary complication. Including literature results on related systems the microstructure of microemulsions made of either ionic[2,3] or nonionic[4–6] amphiphiles is found to follow general patterns.

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SANS of micellar solutions under shear.

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Viscoelastic surfactant systems consist of entangled rodlike micelles. If the rods are charged and the solutions contain no excess salt the SANS pattern is dominated by a strong correlation peak. Measurements on single chain surfactants under shear by us and by others have shown that the position of the correlation peak is not effected by shear, even when the shear is high enough to align the rodlike micelles completely [1,2]. With increasing shear rate the scattering intensity of the isotropic scattering ring is however more and more concentrated into two scattering peaks perpendicular to the flow direction. The fall-off of the intensity of the scattering peak in the direction of flow permits the evaluation of the length distribution of the micellar rods.

New measurements on the double chain surfactant systems Hexadecyloctyl-dimethylammoniumbromide ($C_{16}C_{8}$-DMABr) show a second correlation peak which develops with increasing shear. The aligned rods show a hexagonal order.

Besides the two prominent scattering peaks the scattering patterns consist of an isotropic ring at the position of the first peak. This ring indicates the presence of smaller rods which are not aligned under shear and that two types of structures exist in the solution, which are in thermodynamic equilibrium. With increasing shear the equilibrium between the small and large structures is shifted to the large structures which are aligned by the shear.

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COMPARISON OF ADSORPTION AND AGGREGATION OF IONIC AND NONIONIC SURFACTANTS IN OIL + WATER SYSTEMS

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We report the effects of various additives (salt, alcohols, alkanes, aromatic hydrocarbons and ionic surfactants) on the cloud points of aqueous solutions of nonionic surfactants of the alkyl polyoxyethylene type. The cloud point is very sensitive to the nature of the additive. For example, short chain alkanes cause an initial decrease in cloud point after which it rises and, at saturation with alkane it may or may not reach the cloud point in the absence of alkane. For a given surfactant the cloud point at saturation with alkane is greater for larger chain alkanes. The effects of the additives on the structure of the surfactant aggregates have been measured using a time-resolved fluorescence technique and viscometry. In general, additives which reduce the cloud point increase the viscosity and vice versa. The results are discussed in terms of the different solubilisation sites of the additives and the resulting changes in aggregate size and shape and inter-aggregate interactions. For the example of added alkane, the initial decrease in cloud point is thought to correspond to penetration of the alkyl region of the surfactant monolayer. Further addition of alkane corresponds to core solubilisation producing, at saturation, spherical oil-in-water microemulsion droplets.

The one-phase oil-in-water microemulsion region is bounded by the cloud point curve at higher temperatures and by the phase boundary at which an excess oil phase separates (Winsor I) at low temperatures. The Winsor I phase boundary (solubilisation curve), together with the Winsor II boundary, have been determined as a function of temperature by titration. These data allow the microemulsion droplet sizes at the Winsor I and Winsor II phase boundaries to be determined and related to the measured values of the oil/water interfacial tension. The intersection of the cloud point curve with the Winsor I curve corresponds to the onset of the three phase region where oil, water and surfactant-rich phases coexist. This occurs at a temperature close to the phase inversion temperature (PIT) where a minimum, ultralow interfacial tension is observed. The behaviour of these nonionic systems will be compared with that of systems containing ionic surfactants.

VISCOELASTIC PROPERTIES OF CONCENTRATED SUSPENSIONS

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The viscoelastic properties of concentrated suspensions will be discussed in terms of the interaction forces between the particles. Three main systems will be described: (i) those in which double layer repulsion predominates the interaction; (ii) those in which steric repulsion dominates the interaction, and (iii) those where the net interaction is attractive. Both weak and strong flocculation cases will be considered.

For measurement of viscoelasticity, oscillatory measurements are required over a wide frequency range (in the linear viscoelastic region). By fixing the frequency range and changing parameters such as volume fraction, electrolyte concentration and temperature, it is possible to obtain information in particle-particle interaction. With electrostatically stabilised dispersions, the double layer extension (which is determined by electrolyte concentration) plays a major role. With sterically stabilised dispersions, the adsorbed layer thickness determines the range of interaction. Such sterically stabilised dispersions may be weakly flocculated by addition of free (non-adsorbing) polymer, and such flocculation can be followed using viscoelastic measurements. Electrostatically stabilised suspensions can be strongly flocculated by addition of electrolyte, whereas sterically stabilised systems undergo incipient flocculation at high electrolyte concentration and/or increasing the temperature. Examples will be given to illustrate the use of viscoelastic measurements for following such flocculation.

SOME NEW RESULTS on RHEOLOGY of CONCENTRATED COLLOIDAL DISPERSIONS

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From some data for well-characterized systems (as latex or silica sphere suspensions), some recent results on rheological properties of concentrated colloidal dispersions will be discussed. These properties have been related to the changes in some **microstructure**, which depends on the concentration, size and shape of particles and the type and magnitude of particule interactions, including strong effects due to the presence of polymer molecules in the suspending fluid.

Up to now, exact theories, either failed in accounting for all these interactions, excepted in the dilute limit, or took them only partly into account. On the other hand, phenomenological theories for shear viscosity dependences in both the volume fraction Φ and the reduced shear rate $\dot{\gamma}_r$ have been developped. For $\eta(\Phi)$, special mention must be made of the Krieger's equation, as a mean field result, which involves a packing volume fraction of particle, Φ_m. Alternatively, considering the dispersion as a microscopically inhomogeneous binary mixture, Effective Medium Theories have been recently revisited, but they still remain limited to small Φ-values, since they give a too small packing fraction ($\Phi_m \simeq .40$) . Such a discrepancy can be seen as resulting from the presence of clusters, the size of which increases as Φ increases, and for equilibrium conditions, could reach some macroscopic scale (especially close to the percolation threshold). For steady shear, dynamic equilibrium between rupture and formation of clusters leads to a shear-rate dependent mean cluster size.

Some improvement in rheological description of colloidal dispersions can be, expected from considering (i) the system as a suspension of clusters, (ii) the internal (micro)-structure of a typical cluster (may be a fractal) - especially the type of packing, i.e. the solid fraction within a cluster - as mirroring the properties of the system at the microscale, especially those of primary particles (size distribution, shape, nature of interactions ...).

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Detergency: A Problem of Surfactant Adsorption and Molecular Packing.

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By means of a previously developed *in situ* ellipsometric method(1,2) the removal of triglycerides from hard surfaces by surfactants is investigated for different classes of surfactants. In addition the fat removal efficiency of different surfactants is investigated as a function of temperature, salinity, added cosurfactant or hydrocarbon etc.

Different surfactants show a very different cleaning efficiency and even more striking is the strong influence of the parameters mentioned. In a number of cases a nonmonotonic variation is observed. These different findings are discussed in relation to phase diagrams and microemulsion structure.

While the cleaning is a complex process, it is suggested that cleaning efficiency can mainly be referred to the optimal packing of the surfactants under the conditions given. It is postulated that maximal removal is related to the optimal surfactant packing into planar layers, i e zero curvature towards water and soil. For all systems investigated this simple model is shown to give a good ratinalization of the experimental observations.

Paricular emphasis is put on nonionic oligo(ethyleneoxide) surfactants where a nonmonotonic behaviour with respect to both temperature, hydrocarbon concentration and EO chain length is observed. These findings are discussed in relation to other phenomena exhibited by these surfactants and in particular in relation to recent work concerned with a temperature dependent head-group conformation leading to a decreased polarity at higher temperature(3,4).

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PREPARATION OF MONODISPERSE, MAGNETIZABLE, COMPOSITE METAL/POLYMER MICROSPHERES

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Colloidal microparticles are becoming ingreasingly used as microcarriers in bioengeneering , immunodiagnostics,also for "in vivo" uses for example in drug targeting or contrast aids in imaging systems. The advantages of microspheres over traditionnal supports are mainly related to the high specific surface and the absence of porosity which enhance reaction kinetics.Magnetic particles are even more attractive since they can be collected very simply using a single magnet. Among the different characteristics of the particles , the magnetic properties internal morphologies and size distribution are the most important.

In this paper we describe the preparation of monosized magnetic particles made up of a crosslinked polystyrene entrapping finely divided cobalt crystallites. The metal is introduced within preformed polymer particles,by thermolysis of metal carbonyl complexes. It is shown that nucleophilic pyridine units present in the polymer promote the thermolysis selectively inside the particles. The distribution of cobalt is discussed in relation with the chemical composition and crosslinking level of the microspheres.

EXPERIMENTAL STUDY OF PHASE SEPARATION IN IONIC FERROFLUIDS

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A ferrofluid is a colloïdal suspension of magnetic particles the diameter of which is typically 10 nm. For an ionic ferrofluid, particles bear superficial charges. Aggregation due to van der Waals and magnetic forces is then prevented by screened electrostatic repulsive forces.

A reversible phase separation may be induced by an appropriate modification of any interaction parameter (magnetic field, temperature or ionic strength). Such a phase transition has been predicted by theory and descripted as a liquid-gas transition.

We present here an experimental study of the phase separation induced by increasing ionic strength in alkaline ferrofluids. The both co-existing phases are liquid, one dilute in magnetic grain, the other one very concentrated (ca. 18% in volume). Phase diagrams versus ionic strength are built up for various ferrofluids in zero magnetic field and at room temperature. The operating variables are the ionic strength, the magnetic grain concentration, and the size caracteristics of the sols. It appears that such a phase separation may also be a way to control the particle-size distribution.

Measurement of the Curvature Rigidity Constant of a Monolayer

Ellipsometry and Reflectivity

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Interfacial properties play a prominent part in determining the properties of systems containing amphiphilic molecules. The curvature rigidity K and the spontaneous curvature of a surfactant monolayer are two essential parameters to determine the phase structures of microemulsions.

The energy of a transverse wave at an interface is dominated by the rigidity at short wavelength and capillarity at larger wavelength. The study of short wavelength thermal fluctuations is consequently a means to measure K.

Two optical techniques are sensitive to the roughness of an interface : reflectivity measurements and ellipsometry. The reflectivity gives informations on $<\xi^2>$ where ξ is the vertical deplacement of the interface. It is a summation over all the wavelengths of the fluctuations, so it is not very sensitive to the rigidity but can give some information on the rigidity of monolayers at a liquid free interface using X rays (large rigidity : $K \sim 100\ k_BT$). The other technique is ellipsometry which probes the quantity ,$\Sigma q <\xi_q{}^2>$, where ξ_q is the amplitude of a mode of wave vector q. It is a method very sensitive to the short wavelengths fluctuations and well adapted to measurements of very low rigidities ($K \sim k_BT$) on a monolayer of ultra low surface tension [1] ($\gamma \leq 10^{-2}$ dynes/cm).

The approximation of independent thermal modes commonly adopted is insuffisant in this case. The amplitude of each mode is very small but the number of modes of high q is very large. We must take into account the coupling between modes of an interface with microscopic surface tension and rigidity.

The theory we have developed avoids any divergence of the thermal fluctuations at high q. It agrees with the results of optical measurements at critical interfaces (K = 0) without introducing microscopic parameters and allows one to deduce the rigidity of monolayers at oil-water interfaces from ellipsometric measurements [2].

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THE SURFACE VISCOELASTICITY OF SURFACTANT SOLUTIONS AND HIGH FREQUENCY CAPILLARY WAVES

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Capillary waves have long been used to investigate the viscoelastic properties of fluid surfaces (1). The values of these properties may depend upon the wave frequency, reflecting relaxation processes within the system. One particular case, exchange of surfactant molecules between surface and bulk solution, has been analysed theoretically. Various processes may dominate this exchange, leading to very different predictions for the behaviour of the surface dilational elastic modulus and the corresponding surface viscosity (2). For concentrations below the CMC the dominant process is diffusive exchange between the adsorbed surface film and solution, determined by the diffusion constant of the surfactant molecule. The changes in the capillary wave propagation can be analysed in terms of this diffusion constant. For medium chain-length surfactants, experiments at widely different wave frequencies (3, 4, 5) yield values for the diffusion constant which differ by several orders of magnitude. This is not readily comprehensible in terms of the theoretical treatment.

We have systematically studied solutions of a homologous series of normal alcohols, in light scattering experiments involving thermally excited capillary waves of high frequency (> 10^5Hz). Unlike previous studies (eg, 5), our experiments were designed to maximise the sensitivity of the capillary waves to the dilational modulus. The data from these experiments are consistent with Lucassen's theory of diffusional interchange, using the bulk values of diffusion constant.

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RELATIONSHIP BETWEEN THE FILM RIGIDITY, INTERFACIAL TENSIONS AND MICROSCOPIC STRUCTURE IN SEVERAL MICROEMULSION SYSTEMS

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Systems containing oil, water, surfactant and cosurfactant may form microemulsions which undergo the Winsor I- III- II transitions upon increasing electrolyte concentration. The oil-water interfacial tension exhibits a minimum, ultralow value when a third, middle phase containing most of the surfactant and comparable amounts of water and oil is formed. The middle phase may be either a lamellar liquid crystal or a bicontinuous microemulsion in which the spontaneous curvature of the surfactant monolayer is close to zero. Thermal fluctuations of the layers are then dominated by the rigidity or bending elasticity of the film.

We have measured the interfacial tensions using surface laser light scattering equipment and the rigidity via ellipsometry experiments in a variety of anionic and cationic surfactant systems. Information concerning the microstructure has been deduced from light and X-ray scattering experiments. These data are discussed in terms of existing theories describing microemulsion phase stability. Particular interest has been devoted towards bicontinuous microemulsions.

SPREADING OF A POLYMER LIQUID ON SOLID SURFACES : ROLE OF LONG RANGE FORCES.

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A theoretical description of the spreading of a liquid on a solid surface has recently been proposed by de Gennes and coworkers[1], pointing out the role of long range forces on both the spreading kinetics, and the final state of spreading : a thin precursor film should progressively develop in front of the macroscopic liquid edge, with a structure conditioned by long range forces. This approach allows to solve both the delicate problem of the moving contact line and the paradox of the apparent independence of the macroscopic spreading kinetics versus the spreading parameter S (i.e. the surface energy gained by covering one unit area of solid by the liquid). We shall present an experimental study of the spreading behaviour of a model system : polydimethylsiloxane droplets deposited on smooth horizontal silicon wafers for which grafting procedures have been developed in order to get different positive values of the spreading parameter S. The drops indeed decompose into a macroscopic part (thicknesses larger than 100 nm) and a precursor film. The spreading kinetics of the macroscopic part, characterized by simultaneous size R(t) and apparent contact angle $\theta_a(t)$ measurements, appears independent of S. R and θ_a follow universal scaling laws over more than three decades, in very good agreement with Tanner's laws[2]. The profile and the time evolution of the precursor film, characterized by reflectometry in polarized light and spatially resolved ellipsometry, appear to strongly depend on S. The results will be compared with theoretical predictions, and special polymeric features will be pointed out, and discussed in terms of slippage at the solid wall, or coils desentanglement. A particular emphasis will be paid to the final stages of spreading which give particularly illustrative tests of the models.

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PRECURSORS FILMS IN WETTING

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Thin and ultrathin films, whose properties are controlled by long range and short range microscopic forces, respectively, play a major role in wetting processes, especially in the case of complete wetting$^{(1,2)}$.

We have studied precursor films of silicone oils (polydimethylsiloxanes - PDMS - methyl terminated). They are convenient systems being non volatile wetting liquids with a wide range of viscosities, from 0.02 Pa.s (simple liquid) to more than 20 Pa.s (polymeric liquid).

The long range forces are pure Van der Waals interactions and some information on short range forces has been recently obtained by force measurements$^{(3)}$.

We have studied the films growing at the edge of a static or dynamic liquid front of PDMS on a silicon wafer.

The technique is real time, single wavelength ellipsometry, with a high acquisition rate (1 ms per point). The spatial resolution is 0.5 mm, the relative precision on thickness is better than 0.2 Å. The absolute precision is 10 % in the range 0 - 200 Å. The setup allows to obtain a cartography of 4 × 4 cm^2 samples. Significant measurements require a neutral atmosphere (nitrogen U) as the rate of growth of a contaminant layer in the atmosphere is 0.5 Å/day.

Detailed thickness measurements in the range 0 - 200 Å for low viscosity oils will be presented and discussed.

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DYNAMICS OF WETTING

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The dynamics of wetting are important for coating processes. At a moving contactline at the fluid/solid interface, the contact angle, under static conditions given by the equation of Young, changes. Here, the equation of Young has to be extended. Using some approximations concerning the hydronamical penatration depth at the moving meniscus in a capillary it is shown that:

$$\cos\vartheta = \cos\vartheta_o - \gamma \, Ca^{1/2} \qquad (1)$$

with ϑ: the dynamic advancing contact angle
ϑ_o: the static contact angle
Ca: the capillary number
γ: a proportionallity factor considered later.

This equation was verified experimentally by plunging a sheet of a solid substrate with a velocity v into a pool of liquid. It is found that $\cos\vartheta$ changes linearly with $v^{1/2}$. Using liquids with various viscosities (η) and surface tensions (σ) equation 1 is proven. These results are also correlated with published data from other investigators. It turns out that the proportionallity factor γ depends on the nature of the solid substrate and equation 1 is finally written as:

$$\cos\vartheta = \cos\vartheta_o - 2(1 + \cos\vartheta_o)Ca^{1/2} \qquad (2)$$

From this equation it follows that the maximum speed of wetting, v_{max}, at which air entrainment sets in is given by:

$$v_{max} = 0.25\,\sigma/\eta \qquad (3)$$

Hence this maximum velocity does not depend on the nature of the solid substrate! This is verified experimentally, also using published data from other investigators.
Following the same reasoning, the kinetics for a Wilhelmy plate are considered.

STRUCTURAL STUDIES OF MONOLAYERS OF AMPHIPHILES ADSORBED AT THE AIR-WATER INTERFACE : AN EXPERIMENTAL APPROACH OF PHASE TRANSITIONS USING FLUORESCENCE MICROSCOPY

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Mc CONNELL and MOHWALD have demonstrated that fluorescence microscopy (sometimes also called epifluorescence), when coupled with low-light level camera detection, is sensitive enough to observe the structure of monomolecular films a few Å thick deposited on solid or liquid substrates. We have applied this technique to the study of Langmuir films of pentadecanoic acid and myristic acid mixed with small concentrations of fluorescent probes (0.1-1% by mole) and spread at the air-water interface at 20°C. The surface density can be continuously changed by a movable barrier and the corresponding surface pressure is simultaneously measured by the Wilhelmy hanging plate method. A wide variety of structures is observed : uniform dark or bright backgrounds, spherical islands, irregularly-shaped objects, white foams and dark foams. All these structures can be related to the various states of the two-dimensional layer. At very low densities, probably higher than 2000 $Å^2$ per molecule, only the gaseous phases exists. However, as the monolayer is gradually compressed, the liquid expanded-gas two-phase region is entered. The transition is first-order, as evidenced by the coexistence of liquid and gaseous phases. At densities between 70 and 45$Å^2$ per molecule, the monolayer is in the liquid expanded state and looks homogeneous. Below 45$Å^2$ and down to 22 $Å^2$, a coexistence between liquid expanded and liquid condensed domains is observed. As the molecular surface density is gradually increased by compression, the denser phase becomes prominent over the other until the entire monolayer is converted to the liquid condensed state. The reverse situation is observed on expansion. These observations ascertain that the liquid expanded-liquid condensed transitions in pentadecanoic acid and in myristic acid are definitely first-order. In the latter compound, a new type of metastable pattern is sometimes observed at elevated temperatures and rapid compression. The shape of the liquid condensed domains can actually be changed continuously from self-similar fingering structures to circular platelets over a 5°C temperature range below the estimated critical temperature of 31± 0.5°C. We explain the pattern changes in terms of a diffusion-driven instability, taking into account the damping effect of line tension, which vanishes at T_c but gets large at lower temperatures. It is further shown that noise-reduced diffusion limited aggregation models can provide a satisfactory simulation of the observed structures.

ON SOME SOLVED AND UNSOLVED PROBLEMS ON WATER/PDMS/SURFACTANT SYSTEMS

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Most of the properties of the polydimethylsiloxane (PDMS) oils can be deduced from the structure of the linear polymeric chain of the macromolecule :

- flexibility and stability of the Si-O-Si backbone
- hydrophobicity of the methyl substituents of the silicum atom.

But in fact, the advantages of pure PDMS for industrial applications are limited. For the major uses, it is always necessary :

- either to disperse variable amounts of silice in PDMS
- or to emulsify PDMS in water.

The interfacial properties of the water/PDMS/surfactant system were therefore investigated :

- phase diagrams, surface tension and ellipsometric measurements (carried out at CNRS Montpellier)
- X-Ray and RPE measurements (carried out at Collège de France) ,

and wil be reported.

The relationship between the ampliphilic behaviour of the PDMS chain and the pratical advantages of the PDMS/water system will be discussed.

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LIQUID CRYSTALS IN LIVING MATERIALS: HOW NATURE MAKES USE OF LIQUID CRYSTALLINE PROPERTIES OF BIOMEMBRANES

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The liquid crystalline state plays an important role in living materials: Two cases have been extensively studied: the DNA-organization in a virus and the biological membrane. Our contribution deals mainly with the second case. First we discuss the role of lipid bilayer for the molecular organization and dynamics of membranes where it is essential that the lipid bilayer can exist in two states: the quasi-crystalline smetic B and a smetic A state.
The low dimensionality of the smetic phase is essential for two reasons: first the logarithmic dependence of the lateral mobility on the molecular diameter allows for fast reorganization even of very large membrane proteins. Secondly, the molecular organization of the membrane may be effectively controlled by macromolecular adsorption. Thirdly, signal transmission across the membrane is possible.

As a further subject we discuss the dynamic properties of membranes, such as the local molecular motions (as studied by dynamic neutron scattering) and thermally excited (undulatory) membrane excitations as well as shape fluctuations and shape transitions of vesicles and cells.

Finally, elastic and viscoelastic properties of lipid bilayers and cell plasma membranes are discussed in context with their role for cellular shapes and motions.

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Thermal Fluctuations of Giant Vesicles and Elastic Properties of Bilayer Lipid Membranes. The Role of the Excess Surface

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The elastic modulus, K_c, of lipid bilayers can be measured, in principle, by observation of the thermal fluctuations of giant vesicles under an optical microscope. Two methods have been recently proposed: the first (Engelhart et al., J. Physique Lett. **46**(1985)395) is based on Fourier series decomposition of the vesicle contours, the elastic modulus, K_c, being inversely proportional to the mean square amplitude of fluctuations of different harmonics; the second developped in the laboratory (I. Bivas et al., J. Physique **48**(1987)855) is based on a mean square fit of angular autocorrelation function of the fluctuations. The obtained values of the elastic modulus, K_c, are close to $0.4\ 10^{-19} J$ in the first case and close to $1.28\ 10^{-19} J$ in the second.

A study has been started whose aim is to reveal the origin of this important discrepancy. A series of lipid vesicles has been studied and analysed according to both methods already mentioned. The conditions of image acquisition as well as image processing have been optimised for: first, improving the contour sharpness and second, obtaining a larger number of images (as many as possible). The first results lead to the conclusion that both methods give values of K_c that varied from one vesicle to another. Therefore the models used are not suitably well adapted to the experimental conditions. In fact both approaches suppose an equipartition of the energy among the different harmonics, e.g. an independence of different modes of fluctuations. But in fact the vesicle surface as well as the vesicle volume must be considered as constant, and this conditions can be satisfied only in the case when the excess surface of the vesicle is just enough for the fluctuations. In the opposit case, e.g. in the general case, the value of K_c obtained by these methods is only an apparent value that depends on the curvature elasticity of bilayer as well as on the excess of the surface, i.e. the vesicle ellipticity.

An extensive theoretical study of the influence of this parameter on the interpretation of the experimental results has been made. A suitable theoretical model of thermal fluctuations must extract the same value of the elastic modulus, K_c, from different vesicles, a value that is a true measure of bilayer elasticity, or at least, it must be able to define the ideal conditions for a good experiment.

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ELECTROFUSION OF CELL-SIZE LIPOSOMES WITH PROTOPLASTS

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Liposomes from Egg lecithin can fuse with pea protoplasts after dielectrophoretic alignment and membrane destabilization by DC pulses of high intensity. We showed that such liposomes can be collected dielectrophoretically on circular electrodes. They form pearls chains and sometimes fuse. The liposomes were formed by swelling at high temperatures to get thin-walled liposomes, in some caseseven unilamellar. The medium was 0.5 M mannitol solution . The pea protoplasts were obtained in the same medium. Ficoll was additionally added to improve the visualization of the liposomes. Its concentration was 2.5 % by weight. Both solutions were mixed and placed in a standard chamber, which has two platinum wires. The electrofusion of the liposomes with the protoplasts was observed on the very electrode. The optimal conditions for electrofusion depend on the lipid composition and the field parameters. By adding different positively charged lipids and cholesterol one can improve the probability for fusion. Possible mechanisms of electrofusion in this case can be based on instability of fluctuation-waves and reversible pore formation. These results may have applications for transfer of genes and other biologically active substances into cells as well as to basic research in the field of membranology.

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FAST TIME-RESOLVED X-RAY DIFFRACTION ON PHOSPHOLIPID PHASE TRANSITIONS

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The extreme X-ray flux offered by synchrotron radiation sources opens the field for X-ray diffraction on the millisecond time-scale. The kinetics and molecular mechanisms of structural rearrangements during phase transitions of phospholipids can thus be studied in real time during temperature scanning experiments (1). The transitions between different lamellar phases of hydrated phosphatidylcholines (lecithins) as well as between lamellar and inverted hexagonal phases of phosphatidylethanolamines have been studied. These studies, performed by conduction heating were limited in their time-resolution to about 1 s, through the heat conduction properties of the aqueous samples. In order to fully capitalize on the available X-ray flux an enhancement of the heating rates has to be achieved by a principally different method. In the present study, temperature jumps were achieved by infrared absorption from a pulsed Erbium laser (1,54 µ; 2-3 joules / pulse of 1 ms). This leads to direct and more homogeneous temperature jumps of the samples. This should allow more detailed insight into the rapid transition processes. First results on the main gel-to-liquid crystalline transition will be described.

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Structures Formed in the Lecithin/Triton X-100-system

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The effects of Triton X-100 on structure and size of sonicated lecithin vesicles was studied by means of quasielastic light scattering and cryo-transmission electron microscopy. Low concentrations of Triton have little effect on the vesicle size and structure. Very high surfactant concentrations gives rise to the formation of mixed micelles. Upon addition of intermediate concentrations of Triton, very large vesicles, having a radii of as much as 1000 Å, are formed. The two methods give aggregate sizes in good agreement. In cryo-TEM pictures of the samples, discoid bilayer fragments can be seen in coexistence with the vesicles. Close to the concentration range where mixed micelles are formed, the vesicles become distorted and membrane defects can be detected. Cryo-TEM was used to follow the formation of the large vesicles as function of time. Addition of Triton seems to disrupt the vesicles quickly (<30 s) and completely to form micelles that merge into the large structures within 2 minutes.

Organogels from lecithin water-in-oil microemulsions

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Solutions of lecithin in a variety of organic solvents can be transformed into transparent gels by addition of a small amount of water[1]. The molar ration of water to lecithin (w_o) is in the range of 1-12, depending upon the solvent, and for each organic solvent only a defined $w_{o(gel)}$ is able to produce a gel. The gels are thermoreversible, isotropic and not birefingent. Dynamic shear viscosity measurements have been carried out. Upon addition of water the viscosity η increases by as much as a factor of 10^4 poise, and passes through a distinct maximum of $w_o(_{gel})$. Upon further addition of water, η decreases sharply, and a separation into 2 macroscopic phases can be observed.

We are currently investigating the structure and phase behaviour of these lecithin gels by a combination of viscosity measurements, quasielastic light scattering, NMR (^1H, ^2H, ^{31}P, ^{13}C), ESR and FTIR. The results are analyzed in terms of a recent equilibrium thermodynamics model for microemulsions[2], and analogies with the formation of viscoelastic solutions by giant rod-like micelles and with semidilute polymer solutions are investigated[3].

These novel gels are not only interesting because of their structural properties and their phase behaviour, but also in view of their capability of solubilizing and immobilizing guest molecules such as drugs, dyes and enzymes. This makes them potentially useful for a variety of chemical, pharmaceutical and medical applications.

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NEUTRON SCATTERING INVESTIGATION OF ISOTROPIC SOLUTIONS OF NONIONIC AMPHIPHILES AT HIGH CONCENTRATION

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The structure of aqueous solutions of a nonionic amphiphile, $C_{12}E_8$, was studied by small-angle neutron scattering measurements performed along an isothermal path which crosses the isotropic single-phase region from 0 to 100% amphiphile volume fraction. The aim of the experiment is to investigate how the system evolves from a micellar structure at low amphiphile volume fraction ϕ to a amphiphile-continuous structure at high ϕ. The scattered intensity shows a peak in the whole range $0.25<\phi<0.85$. At intermediate values of ϕ the structure is probably bicontinuous, in analogy to what happens for the transition from water-in-oil to oil-in-water microemulsions.

ELECTROCHEMISTRY OF PROTEIN PARTITIONING IN TWO-PHASE SYSTEMS

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Generally valid thermodynamic relations between the partition coefficient of the protein and the extent of the concomitant co-partition of small ions are presented. The method of analysis is illustrated by some examples, including ion exchange chromatography, adsorption on colloidal particles and solubilization in reverse micelles.

A theory which allows for the prediction and molecular interpretation of the charge regulations introduces the notion of the electrochemical adaptibility of a charged colloidal particle, as measured by its intrinsic capacitance.

Finally, some experimental results are discussed in more detail. The system consists of crystals of the insoluble salt silver iodide as the adsorbent and the protein Bovine Serum Albumin as the adsorbate. Opposed to intuitive expectation we find that when the protein is maximally positive, its adsorption renders the silver iodide surface less negative.

Two thermodynamic relations are succesfully verified, indicating the internal consistency of the various experiments. Application of the model gives two independent estimates of the size of the adsorbed protein. It is concluded that the protein does not substantially modify its native structure upon adsorption.

Binary liquid phase separation and critical phenomena in a protein/water solution.

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We have recently demonstrated the existence of binary liquid phase separation and critical phenomena in aqueous solutions of the bovine lens protein γ_{II}-crystallin[2]. We observed reversible coexistence between two macroscopic, isotropic and optically clear liquid phases which differ in protein concentration. We were able to characterize the coexistence curve consistently by determining the cloud point temperature as a function of protein concentration and by directly measuring the equilibrium protein concentration in both phases as a function of temperature.

Here we report our measurements of the osmotic compressibility and the static correlation range near the critical point of aqueous bovine γ_{II}-crystallin solutions. We have been able to consistently determine the absolute magnitude and the critical exponents γ and ν, by measuring both the intensity of the scattered light and the optical turbidity. We obtain values for γ and ν which are consistent with the three dimensional Ising model.

Our data suggest that selected protein-water solutions can serve as excellent model systems for the study of phase transitions and critical phenomena.

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POSTER CONTRIBUTIONS

P1

ISOTROPIC BICONTINUOUS SOLUTIONS IN SURFACTANT-SOLVENT SYSTEMS: THE L_3 PHASE

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The structure of the isotropic L_3 phase observed in many surfactant-water or surfactant-water-oil systems is analyzed. It is pointed out that the L_3 occurs in equilibrium with a dilute solvent phase on one hand and a lamellar liquid crystalline phase on the other. Furthermore, irrespective of the detailed chemical nature of the system the one phase region is remarkably narrow in one direction indicating that the thermodynamic degrees of freedom is effectively reduced by one due to an internal constraint in the phase. In accordance with previous work it is argued that the basic structural unit in the L_3 phase is a surfactant bilayer. Furthermore we conclude that the L_3 phase occurs when there is a spontaneous curvature towards the solvent at the polar/apolar interface, *i.e.* the interface wants to curve towards the solvent. It is shown that for a system that has such a curvature towards the solvent the surface formed by the bilayer midplane has a negative average Gaussian curvature <K>. By virtue of the Gauss-Bonnet theorem the bilayer under such circumstances has a highly-connected structure. The conclusion is then that under conditions when there is a spontaneous curvature towards the solvent it is possible to reach a low free energy state by forming highly connected bilayer structures rather than planar bilayers. When interbilayer forces are weak the structure tends to be disordered leading to an isotropic solution (L_3) rather than an ordered cubic structure.

To minimize local variations in curvature at the bilayer surface, we demonstrate that the midplane surface should be close to a minimal surface. We then show that a certain dimensionless group associated with a given periodic minimal surface has approximately the same value for all of the well-known isotropic minimal surfaces. Assuming a minimal midplane surface, we can then show that for a given thickness, a bilayer structure with a prescribed area-averaged mean curvature can only exist at a single volume fraction. This explains the internal constraint in the L_3 phase, which is manifested in the narrow character of the L_3 phase. Applying the equations which express this constraint, and using results from a theory due to Cantor to account for the effect of water / head group interactions on bilayer composition, we present fits of these narrow phase-existence regions to the theory, and rationalize the temperature dependence of the L_3 phases in a variety of nonionic surfactant systems.

The emerging picture of the L_3 phase is that the solution structure is characterized by a highly- connected bilayer, extending in three dimensions, thus appearing bicontinous in, *e.g.*, NMR self-diffusion experiments, and having an average mean curvature at the polar/apolar interface towards the solvent. The basic driving force for going from a lamellar to an L_3 phase is thus not an entropy increase associated with forming finite lamellar patches, as previously suggested, but rather the opportunity to obtain an optimal curvature of the surfactant monolayer.

P2

INTERFACIAL STUDIES OF ESSENTIAL OILS USED IN GELATIN COMPLEX COACERVATE SYSTEMS

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Complex coacervation is the spontaneous liquid/liquid phase separation that can occur when oppositely charged polyelectrolytes are mixed in aqueous media. The interfacial tension (γ_{IT}) of essential oils against aqueous coacervate and supernatant phases issued from gelatin/gum arabic, gelatin/phosphate and gelatin/alginate coacervate systems were measured in order to gain more insight into the interfacial phenomena involved in the encapsulation procedure of these oils.

The Wilhelmy plate technique was used to follow the effect of temperature (30 to 50°C) and interface age on γ_{IT}. Values of γ_{IT} for all systems were below 8 mN/m. Values of γ_{IT} at 40 to 50°C became too low within 6 hours to be measured by the Wilhelmy plate method. The rate of aging decreases markedly as temperature decreases.

Separate interfacial studies of simple essential oil-water systems reveal high lowerings at orange oil and lemon oil/water interfaces observed on heating of these interfaces. They are attributed to the interfacial adsorption of 8-p-menthene-1-2-diol result of limonene oxidation and present in waters equilibrated with orange and lemon oils.

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P3

X.RAY DIFFRACTION OF MESOPHASES IN THE CTAB-NON AQUEOUS POLAR SOLVENT SYSTEMS

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Many studies have been realized on the liquid crystal phases in aqueous surfactant systems. Recently many intermediate mesophases have been identified in the SDS-water system (1). But water is not the only polar solvent necessary to form these liquid crystal phases (2).

This study, using small-angle X-ray scattering techniques (SAXS), enables to compare the sequence of mesophases obtained with CTAB in different polar solvents-water, formamide, glycerol.- These mesophases are very similar :

Hexagonal phase, p6m → cubic phase Ia3d → lamellar phase (2-3).

Yet we observe some differences :

- a shift of 25°/30°C of the equilibrium temperatures CTAB crystal $\rightleftarrows$ mesophase $\rightleftarrows$ solvent when formamide or glycerol is replacing water.
- an existence area of the p6m phase larger in the water than in the other solvents.
- smaller parameters in the non aqueous solvents.
- a monoclinic phase -2D- only existing in water between hexagonal and cubic phases (4).

These results obtained with a cationic surfactant such as CTAB cannot generalized. Some surfactant exhibit different 3D mesophases of different symetry in water and formamide. The sequence of ordered phases can be more simple in formamide than in water.

These first results show even though the geometrical strengths play an important part on the existence of different mesophases, the nature of solvent - amphiphile interactions driving self-assembly, can also influence the symetry of 3D phases. Binary diagrams seem similar or more simple in formamide than in water.

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DETERGENT EFFICIENCY AND PHASE CHANGES IN NONIONIC SURFACTANT SYSTEMS

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ABSTRACT

The study of detergent properties of surfactant systems is a subject of interest both from a practical and theoretical viewpoints. The elucidation of the mechanisms of detergency has been intensively studied since long ago and the trends observed in the last years towards lower wash temperatures has foccussed a renewed attention towards this aspect.

Oily soil removal has been traditionally interpreted in terms of roll-up mechanism. However other mechanisms such as solubilization, emulsification, and/or intermediate phase formation may also play an important role or under certain circumstances be the predominant one.

In an attempt to contribute to a better understanding of the mechanisms of oil soil removal, the relationship between detergent efficiency and solution properties of nonionic surfactant systems have been studied. In order to avoid the competition of two many factors in the detergency process, which could lead to a misleading interpretation of the results, the number of variables was reduced and the process was simplified.

An oily soil and the washing solution constitute a ternary water/nonionic surfactant/hydrocarbon system. It is well known that the properties of these systems are highly dependent on temperature and that a maximum solubilization of oil in aqueous phase or viceversa occurs at the HLB temperature of the corresponding system.

The detergency tests were carried out at the HLB temperature as well as at higher and lower temperatures. Previous to the determination of the washing efficiency of surfactant/water mixtures their solution properties at the concentrations used in the detergency process were studied.

EVOLUTION OVER A LARGE RANGE OF DILUTION OF A LYOTROPIC LAMELLAR PHASE

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The oil swollen lamellar phase of the system decane-pentanol-sodium octylbenzene sulfonate-water has been investigated using X-rays and light scattering for interlamellar spacing ranging from 40 to 15000Å.

One Bragg singularity is observed in the very low dilution range ($40 < d < 200$Å). It disappears up to roughly 700Å. It can then be followed up to extremely high dilution where higher orders (2 to 3) singularities are observed.

This puzzling behavior will be discussed.

Abstract proposed to the 2nd European
Colloid and Interface Society
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SMALL ANGLE X-RAY SCATTERING OF REVERSE MICELLES USED FOR LIQUID-LIQUID EXTRACTION

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The reverse micelles used are made only from an extractant,the sodium di-2-ethylhexylphosphate(NaDEHP),water and xylene .

The structure of this solution was analysed by small angle X-ray scattering (S.A.X.S.). This method is a very sensitive one to point out aggregated structures,thanks to a large contrast between the polar core and the other compounds . This technique allows to see only the polar part of the structure .

The analysis of our experiments by Guinier or Porod approach allow us to show that :

_ on one hand particles gyration radius is low (below 10 A) and proportionnal to the water quantity but seems to remain constant with the variation of the particles volume fraction ;

_ on the other hand,particles sizes distribution is relatively large and greatly affected by temperature.We studied this effect in order to determine the optimal temperature as well as the water quantity for which the system is nearly monodisperse .

This system has been used to extract a metal from a water phase (liquid-liquid extraction) . We studied the evolution of its structure by sampling the extracted phase, and analysing it by S.A.X.S. .The experiments show that the diffused intensity decreases exponentially with time and that the particle radius does not change during extraction . A correlation between the structure of the solution and its reactivity is attempted .

EXPERIMENTAL STUDY
and
THEORETICAL INTERPRETATION
of
THE INFLUENCE OF SALINITY ON THE MICROEMULSION PHASE BEHAVIOUR

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The experimental system is made of brine, dodecane, n-pentanol, and sodium dodecylsulfate (S.D.S.). The experimental study deals with:

-phase diagram determination in a relevant representation: actice blend (surfactant and cosurfactant) percentage versus salinity (for a given WOR [water/oil ratio] = 1 and a surfactant/cosurfactant ratio = 1/6).

-phase composition analyses and oil and water solubilization parameters determination for a number of Winsor III systems, at different salinities.

The theoretical analysis has been performed within the frame of the thermodynamical stability model recently proposed by our group consistently with the pseudophase assumption.

This study allows us to get a good fit between experimental and calculated solubilization parameters when the composition of the interface is varied and this for all the salinities under study. An interpretation of the salt effect can be proposed.

SPATIAL CORRELATIONS IN BIMODAL COLLOIDAL SYSTEMS
APPLICATION TO THE STABILITY EMULSION

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Polydisperse charged colloidal solutions containing large spheres (diameter ~ 0.5 μm) and small micelles (diameter ~ 40 A) are investigated. The pair distribution function between the large colloidal particles is measured by microscopy and image analysis. The experiments reveal an effective short range attraction between the large particles in presence of added micelles. This attraction increases with increasing the direct colloid-micelle electrostatic repulsion. As for the depletion phenomenon in polymer solution, the origin of this effect is entropic and is related to the expulsion of micelles from the intersticial space between approaching spheres. The theoretical prediction, based on the resolution of integral equations for highly asymetrical two-component charged system, are in good agreement with the experimental data. A consequence of this effective attractive potential is a destabilisation of emulsion by micelles of surfactant. We present an experimental study of this phase diagram for a wide range of ionic strenghts, which is in agreement with theoretical predictions.

CORRELATIONS BETWEEN THE FLUCTUATION MODES OF THE FORM OF FLACCID QUASISPHERICAL LIPID VESICLES AND THEIR ROLE IN CALCULATING THE CURVATURE ELASTIC MODULUS OF THE MEMBRANE. A MONTE-CARLO STUDY

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The thermally induced fluctuations of the form of quasi-spherical lipid vesicles depend on the curvature elastic modulus of their membranes. This modulus can be obtained from the experimentally measured values of the amplitudes of the fluctuations (1-3).

Until now the procedure that has been applied is the following. The fluctuations of the form of the vesicle have been developed in a series of spherical harmonics, and the fluctuation modes have been considered as not correlated. In the present work we show, that this assumption is not quite reasonable, because the energy due to the fluctuations of the area of the membrane would then be thousands of kT (k - Boltzmann constant, T - absolute temperature). Consequently the restriction that the area of the membrane be constant imposes correlations between the fluctuations of the modes. Here we determine the multitude of modes for which the correlations are essential. These are the modes with the largest wave-lengths.

A computer program was done for Monte-Carlo simulations of the fluctuations of the different modes, keeping the membrane area of the vesicle constant. The results gave us the dependence of the quantities, connected with the fluctuations, on the curvature elastic modulus of the membrane and its excess area (the excess area being the difference between the actual area of the vesicle membrane and the area of the sphere with a volume equal to the volume of the vesicle). This permits the determining of the curvature elastic modulus on the base of the experimentally measured fluctuations of the form of the vesicle.

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REASONS FOR THE SLOPING OF THE PLATEAU OF THE Π-A ISOTHERMS OF INSOLUBLE MONOLAYERS ON LIQUID SUBSTRATA IN THE AREA OF THE FIRST ORDER PHASE TRANSITION FROM LIQUID EXTENDED (LIQUID CRYSTAL) TO LIQUID CONDENSED (GEL) PHASE

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At the phase transition from liquid expanded (liquid crystal) to liquid condensed (gel) state of an insoluble monolayer on liquid substratum, the lateral pressure could be not constant in the Π-A isotherm of the process. In the present work one theoretical explanation is proposed of the inclined plateau of the dependence Π(A) at the phase transition.

The reason for the phenomenon could be the fact that when decreasing the mean area per molecule at the beginning of the phase transition the new liquid condensed phase does not exist as a monodomain but in the form of little aggregates, dispersed in the continuous liquid expanded phase. When the mean area per molecule is further decreased,both the number of molecules per aggregate and the number of aggregates change. The dimensions of the aggregates and the slope of the plateau are determined by the edge energy γ of the (one-dimensional) interface between the two phases. The results obtained by us show that the above mentioned plateau is inclined if $\gamma<10^{-6}$ dyn. Some experimental data for monolayers of hexadecoxipropanol on water were analyzed on the basis of the theory proposed by us. The value of the edge energy calculated for this system is $\gamma\sim 2\text{-}4\times 10^{-8}$ dyn.

CRITICAL MICELLAR CONCENTRATION OF SURFACTANT SOLUTIONS WHEN ADDITIVES WITH DIFFERENT SOLUBILITY ARE PRESENT IN THE SOLVENT

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In our earlier theoretical investigations (1,2) we have shown that the critical micellar concentration (CMC) of any surfactant always decreases when there is some additive in the solvent. In the present work we study in more details the dependence of the CMC on the concentration of the additive. The results obtained by us show that for the surfactant solutions the CMC is a simple function of the concentration of the additive if the additive dissolves well in the solvent and a multiple valued function in the opposite case.

The results of the present work could be useful for the determination of the nearest to the solvent vertex part of the phase boundary of the microemulsion phase in the phase diagram water - surfactant - additive.

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P12

FLUID MICROSTRUCTURE TRANSITION FROM GLOBULAR TO BICONTINUOUS IN MID-RANGE MICROEMULSION

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ABSTRACT

Spin-echo pulsed-field gradient nuclear magnetic resonance (SEPFG NMR), quasielastic light scattering (QLS) and freeze-fracture transmission electron microscopy (FFTEM) were used to study surfactant fluid microstructure and dynamics of microemulsions of pentaethylene glycol dodecyl ether ($C_{12}E_5$), water, and octane (C_8) having compositions in the plane $\alpha \equiv C_8/(C_8 + H_2O) = 40$ wt% of the phase diagram. NMR determined translational self diffusion coefficients of oil, water and surfactant, QLS translational diffusion coefficients and FFTEM micrographs are reported along a one-phase corridor around the lamellar region in a temperature-surfactant composition phase diagram. Just below the lamellar region, water continuous microemulsions consisting of oil-rich globules (swollen micelles) in water exhibit small, time-dependent self diffusion coefficients (over times of the order of 0.1 sec) and a biexponential QLS correlation function characteristic of concentrated, polydisperse suspensions of repulsive globules. At temperatures just above the lamellar region, bicontinuous microemulsions exhibit relatively high self diffusion and a monoexponential QLS correlation function. An apparently rather abrupt transition from discontinuous oil-in-water to bicontinuous microstructure, visualized for the first time by electron microscopy, occurs at low surfactant concentration, close to a three-phase region.

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P13

Interfacial Tensions in and near Three-phase Regions in Ternary Hydrocarbon + Water + Nonionic Surfactant Systems

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Three-component systems consisting of a hydrocarbon oil, water and an alkyl polyoxyethylene surfactant, $C_nH_{2n+1}O(CH_2CH_2O)_mH$ (abbreviated C_nE_m), exhibit a phase inversion which commonly involves the formation of a surfactant-rich middle-phase microemulsion. This three-phase region extends from a lower critical end-point temperature T_1 (at which the middle phase and the aqueous phase become identical) to an upper critical end-point temperature T_u (at which the middle phase and oil-rich phase become identical). We have found a second three-phase region in such ternary systems at temperatures below the phase inversion. This lower three-phase region is due to the appearance of a hydrocarbon-rich one-phase region (within the central miscibility gap of oil and water) which is stable over a wide temperature range up to a temperature T_{max}, at which it decomposes into two phases. Below T_{max} the one-phase region is linked to two narrow three-phase triangles. One of these (on the water-rich side of the one-phase region) extends only over a small temperature range and disappears at a lower critical end point. The other three-phase triangle (on the oil-rich side) persists down to low temperatures like the one-phase region. These findings have some similarity with the phase behaviour of four-component systems (oil + water + alcohol + anionic surfactant), when the surfactant-to-water ratio is varied instead of temperature.

We have measured the equilibrium interfacial tensions between neighbouring phases in and near the three-phase regions, using capillary wave dynamic light scattering. For the three-phase region connected with the phase inversion we find deviations from Antonow's rule even for a simple amphiphilic component (C_4E_1). In the new (lower) three-phase region (with C_8E_4 as the surfactant), the minor branch (extending from T_{max} down to a lower critical end point) is dominated by the proximity to this critical point. In the major branch, however, low interfacial tensions (ca. 1 µN m^{-1}) are found over a wide temperature range. Interfacial tensions, densities and viscosities of the two systems studied will be presented.

P14

ADSORPTION OF ACIDS ON MAGHEMITE PARTICLES FOLLOWED BY CONDUCTIMETRY

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Small maghemite particles, which diameter is about 10 nm are obtained by chemical oxidation of freshly precipitated colloidal magnetite. These particles can be peptized in alkaline or in acidic media, when counterions are well choosen. For such synthetized ionic ferrofluids, the point of zero charge is located at about pH 6. The superficial charges are created by specific adsorption of H^+ or OH^- ions. This adsorption has been studied by conductimetry.

Acid (or base) is added to a precipitate constituted only by uncharged maghemite particles. The quantity of acid fixed by the particles is established from conductimetric measurements.

The distribution amoung free acid and acid fixed by particles is governed by two equilibria: an adsorption equilibrium, that lead to acidic superficial sites, and a partition equilibrium between acid in the bulk and acid in bound water.

The exploitation of the experimental results concerning the adsorption equilibrium show that the number of superficial sites is a constant, caracteristic of the particles, unlike the equilibrium constant, which is very dependent on the nature of the added acid: it's value is small for acids which allows solubilization of the particles and almost unlimited for acids leading to flocculates. The partition equilibrium exists only for acids allowing solubilization. It has not been established in the case of base addition.

P15

ADSORPTION OF POLYMERS CONTAINING AROMATIC GROUPS AT LIQUID-AIR AND LIQUID-SOLID INTERFACES

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The adsorption behaviour of a series of oligomers of sulfonic salts containing naphtalenic units and polystyrensulfonates with different molecular weight has been studied both at water-air and water-solid interface.

Surface tension measurements as a function of oligomer concentration showed that the molecules lie flat at water-air interface ; moreover surface activity decreased as the number of monomeric units in the molecule increased. The mechanism of adsorption of the naphtalenic oligomers from their aqueous solution at solid-liquid interface was studied using graphitized carbon black (graphon) as a homogeneous hydrophobic surface with high specific area.

The experimental results showed that all the substances give adsorption isotherms of the Langmuir type. Oligomers surface areas were calculated from the values of saturation adsorption in the plateau region of the isotherms. The values obtained in this way agreed with those previously obtained for a naphtalene molecule adsorbed on graphite from L.E.E.D. experiments.

The distribution at water-air and water-graphon interface were compared for the sodium polystyrensulfonates ; for these systems the kinetic of adsorption and its fundamental parameters were determined.

STRUCTURAL PROPERTIES OF W/O POLYMERIZABLE MICROEMULSIONS IN RELATION WITH THE NATURE OF THE MONOMER.

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One of the most interesting characteristics of polymerization in colloidal dispersions is the production of high molecular weight polymers at high rates in a low viscosity medium. In the case of polymerization in inverse dispersions, the liquid polymers formed, which consist of water-swollen polymer particles dispersed in oil and referred to as inverse latices, present many advantages for applications as compared to solid polymer powders. They are indeed widely used in water treatment, flocculation, paper manufacture, mining and oil recovery. Nevertheless, some instability inherent to inverse latices when prepared in a conventional way and their large particle size distribution led us to investigate more thorougly the polymerization of water-soluble monomers in water/oil microemulsions. The conditions for the formation of thermodynamically stable latex particles have been established and the process has been extended to various monomers (neutral and ionic ones). Particuler emphasis has been given to the role played by the monomers on the structural characteristics of the microemulsions prior to polymerization. The main properties of the final latices are discussed in light of both fundamental and applied research.

DYNAMIC PROPERTIES OF POLYELECTROLYTE GELS

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ABSTRACT

Networks composed of covalently linked polymer chains are of great interest, not only for their unique physical and chemical behaviour, but also for their possible technological application, switches, actuaters for robots, artificial muscles, water reservoirs. For all these applications, the understanding of the equilibrium, and dynamic properties of water-swellable networks is of fundamental importance. Recent results obtained by dynamic light scattering and kinetics of swelling on polyacrylamide and polyacrylic acid gels are presented. The cooperative diffusion of the gels is investigated as a function of the ionization degree and the salt content of the diluent.

SPREADING OF MACROSCOPIC DROPLETS

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We have studied the spreading of non volatile wetting liquids on smooth surfaces. We have chosen silicone oils (polydimethylsiloxanes - PDMS - trimethylterminated) because they wet most surfaces and are available in a wide range of viscosities. Thus they are convenient models for simple, non volatile liquids (viscosity η between 2×10^{-2} and 1 Pa.s) as well for polymers (η larger than 20 Pa.s). Moreover, the long range interactions are pure Van der Waals forces.

A systematic study of the size of the wetted spot versus time has been performed both for sessile and hanging drops of various volumes (0.3 → 40 μl). The oil viscosity was 0.5 Pa.s for hanging drops and has been varied between 2×10^{-2} and 100 Pa.s for sessile drops.

The results for sessile drops compare satisfactorily with the self-similar theory of de Gennes and Joanny in the limits of very small or very extended drops.

A numerical study has been performed, with accounts quantitatively for the whole results, both for sessile and hanging drops.

No polymeric effect (slipping) has been observed in the experiments.

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MARANGONI EFFECTS IN SPREADING

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Concentration or temperature gradients produce changes in the interfacial tension of liquids. Strong hydrodynamic effects result, which are referred to as "Marangoni effects".

The spreading dynamics is greatly affected by these phenomena, usually studied in mixtures of liquids of different volatilities(1) .

Atmospheric contamination by volatile molecules soluble in the liquid during a spreading experiment will have similar effects.

Preliminary results on spreading of silicone oils in an atmosphere containing good solvents of the silicone will be presented. They show a strong acceleration of the spreading process, then the apparition and growth of scallop-like structures at the drop's edge.

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P20

DIFFERENT SPIN PROBE POSITIONS RELATED TO STRUCTURAL CHANGES OF NONIONIC MICROEMULSIONS.

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The ESR spectra of Iodoacetamide, FDNB and 5-Doxyl stearic acid spin labels in nonionic microemulsion systems, formulated with tetraethyleneglycoldodecylether ($C_{12}EO_4$) in decane), show the existence of different spin states, depending on the hydrophobicity of the spin-label and the composition of the microemulsions.

More specifically:

i) when iodoacetamide spin label, a rather small and hydrophilic molecule, was used, one spin state was observed over the entire range of compositions;

ii) in the case of FDNB spin-labelled analogue two distinct spin states were observed (the high field line splits into a doublet) for water contents exceeding certain values, i.e. between R=8 and 15 where $R=[H_2O]/[C_{12}EO_4]$.

iii) finally, the spectral characteristics of the lipophilic 5-doxyl stearic acid spin-label could suggest three spin probe positions corresponding to the water core, the micromembrane and the continuous oil phase of these systems.

The possibility of observing the different number of spin probe positions depends on the rate of exchange of the particular spin label between the different microphases of the system used. Thus iodoacetamide is characterized by fast exchange, whereas, FDNB and 5-doxyl stearic acid spin labels have slow rate of exchange. For the latter probe this behavior is more pronounced than for the FDNB analogue.

Furthermore, the R values above which the distinct spin probe positions appear, correspond to the onset and completion of the structural transition from shapeless aggregates to reversed micelles.

P21

STATIC AND DYNAMIC LIGHT SCATTERING STUDIES OF WATER/AOT/DECANE MICROEMULSIONS IN THE CRITICAL REGION - BACKGROUND AND SIZE EFFECTS.

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ABSTRACT

An extensive light scattering experiment, including the intensity, turbidity and linewidth measurements has been made on a three-component microemulsion system consisting of mixtures of water, decane, and a surfactant AOT at molar ratio ω=[water]/[AOT]=40. The critical and several off-critical solutions have been studied along constant microemulsion droplet volume fraction ϕ lines in the one-phase region over a very large temperature range. Due to the availability of an extensive set of measurements of shear viscosity over a wide range of iso-ϕ lines and temperatures, performed by Berg, Moldover and Huang$^{(1)}$, we are able to perform a complete analysis of light scattering data using the methods developed in ref. (2). The most important result of this analysis is to identify a crossover temperature T_x such that $\xi(T_x)=2R_H$ where ξ is the long range correlation lenght of the order parameter fluctuations and $2R_H$ is the average diameter of the microemulsion droplets. This is a crossover phenomenon from a critical regime dominated by the existence of a diverging correlation length ξ, to a non-critical regime characterized by having interacting droplets whose size $2R_H$ gives the scale of length.

In the vicinity of the lower phase separation temperature T_p the intensity data are very well accounted for by the standard theory of critical binary fluids using a single value for the short range correlation length, $\xi_0=(13.5\pm1.5)$Å, but renormalized critical indices $\gamma^*=\gamma/(1-\alpha)=1.40$ and $\nu^*=\nu/(1-\alpha)=0.70$. For T around and below T_x the scattered intensity is governed by the single-particle scattering of interacting droplets. It is necessary to correct for this background non-critical scattering in order to obtain the renormalized critical exponents.

For the dynamic light scattering the most important feature is the existence of a Debye cutoff wavelength q_D^{-1}, which is identified to be equal to $2R_H$. In agreement with a recent conjecture of Fisher[3]. By combining a mode-coupling theory including the background effects and a linear model equation of state, applicable in the critical region, we are able to fit the dynamic light scattering data using a single Debye cutoff length for both critical and off-critical lines. The linear model scaling equation of state allows us to compute $\xi(\phi,T)$ along the off-critical lines. Owing to the large dimension of the droplets, the background correction to the transport coefficients is very large and amounts to 20% of the order parameter relaxation rate even in the deep critical regime. The background subtracted linewidth Γ_c can be scaled into a universal quantity $\Gamma^*=\Gamma_c 6\pi\eta/[q^3 Rk_B T]$ and plotted as a function of a scaled variables $x=q\xi$. All the experimental data fall on a single line, in good agreement with a universal function given by Kawasaki, with a choice of the correct universal amplitude factor R=1.027, in contrast to the earlier analysyis performed by Kim and Huang[4] on the same system using R=1.2. Analyses of the dynamic light scattering data show that q_D, which in practice can only be measured in the non-critical regime, in fact plays a decisive role in controlling the critical dynamics in the whole temperature range. Further experiments at different at different w values between 20 and 60 are currently under way. For a more complete report see ref.(5) and (6).

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ZWITTERIONIC AMPHIPHILES: SYNTHESIS AND PHYSICAL PROPERTIES

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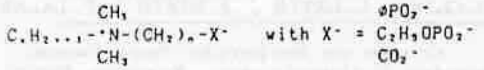
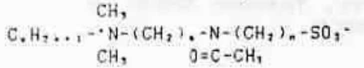
New series of zwitterionic surfactants have been synthesized and physical properties of their aqueous solutions, mesophases and microemulsions studied. These new surfactants can be described by two general chemical formulae:



$$C_xH_{2x+1}-{}^{+}\overset{CH_3}{\underset{CH_3}{N}}-(CH_2)_n-X^- \quad \text{with } X^- = \begin{matrix}\phi PO_3^- \\ C_2H_5OPO_3^- \\ CO_2^-\end{matrix}$$



$$C_xH_{2x+1}-{}^{+}\overset{CH_3}{\underset{CH_3}{N}}-(CH_2)_n-\underset{O=C-CH_3}{N}-(CH_2)_m-SO_3^-$$

with n = 2 or 3 and m = 3 or 4

The synthesis procedures allow their preparative obtention as pure salt free compounds. Krafft temperature of these compounds are low, even with an octadecyl alkyl chain (x=18). Cmc are intermediate between those of ionic and nonionic surfactants. The cmc variation with the number of intercharge methylenes (n) shows a maximum for n = 3 or 4, which is explained by the competition in the free energy of micellization of two opposite contributions which depend on n: the negative free energy of transfer of hydrophobic methylenes from water to micelles which strengthens with n, and a positive and increasing with n term due to dipole-dipole electrostatic repulsions between headgroups at the interface. Large dipole-dipole repulsions cannot occur however, since the intercharge polymethylene brigde is flexible, as evidenced by NMR relaxation experiments, and folds into some loop conformations at the micellar interface, which explains the cmc decrease for n values larger than 4. It is observed that the micellar size decreases as the cmc increases for low n values, but micelles remain small for large intercharge methylene numbers n in spite of a drastic cmc decrease. The same kind of conclusions may be drawn from X-ray structural studies of mesophases and measurements of molecular area per molecule at the air-water interface: area per molecule increases with n, and reaches a plateau for n values above 4. These observations suggest some steric contribution in the head-head repulsions for large n compounds.

The influence of added electrolyte on cmc is little and is explained by electrostatic screening of dipole-dipole interactions at the interface. A peculair behavior is however observed with the second series of surfactants, which is assigned to the complexation power towards cations of the dialkylacetamide group.

Phase diagrams of microemulsions for quaternary mixtures (brine, oil, surfactant and pentanol as a cosurfactant) show the same variation as that of the cmc. The higher the cmc, the larger the Winsor I domain and the smaller the Winsor II domain (the more hydrophilic the surfactant looks like in the microemulsion). These variations are however restricted in amplitude, as compared to variations obtained with ionic surfactants and salt or nonionic ones and temperature. All phase diagrams are rather similar: they all contain Winsor I, II and III domains together with a microemulsion monophasic one. This type of phase diagram remains when temperature or ionic strength (even with divalent cations) are changed, so that the emerging picture of zwitterionic microemulsions is stability against external conditions changes. The main trends observed in the cmc variation upon electrolyte addition for the second surfactant series are also observed in the microemulsion phase diagrams.

DIRECT STUDY OF MICROEMULSION MEMBRANE PSEUDOPHASES VIA DEUTERIUM N. M. R.

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We have performed the experimental study of the S.D.S./Hexanol/D_2O system via Deuterium N.M.R. on a Bruker WH270 and a Bruker MSL200 spectrometer.

The evolution of the experimental quadrupolar coupling constant observed for D_2O allowed us to claim that:
-the lamellar systems encountered are swelling ones
-there are two kinds of relevant sites for water (one is a bounded type, the other one corresponds to "free" water)
-the numbers of "bounded" water molecules are 8 to S.D.S. and 5 to alcohol.

Moreover, our study dealt with the observation of the alcohol signal, to get a better insight of the membrane structure:
To vindicate the evolution of $\Delta\nu_q^{OD}$ versus the ratio n_A/n_S where n_A and n_S hold for the numbers of molecules of alcohol and of surfactant, it was necessary to introduce a two-sites model, the alcohol being supposed to exchange between both at high rate:
-one is characterized by a low quadrupolar splitting and corresponds to a "free" site
-the other is associated to a higher splitting and corresponds to surfactant-complexed molecules of alcohol.

Up to now, we have not been able to determine the thermodynamical constants characterizing this last complexation equilibrium, but we are developping specific experiments to tempt solving this problem.

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- XANTHAN GUM - RELATIONSHIPS BETWEEN RHEOLOGICAL PROPERTIES AND STABILIZING PROPERTIES

Xanthan gum is a high molecular weight polysaccharide that presents several conformations in solution : two different ordered conformations and one disordered conformation. These conformations are characterised by different intrinsic viscosities, and depend on the temperature and the ionic strength of the solvent.

We have used several hydrocolloid samples having significantly different intrinsic viscosities in NaCl O.1 M.

The aim of the present study is first to correlate the intrinsic viscosity values with the rheological behaviour of xanthan gum at higher concentrations (apparent viscosity and visco-elasticity).

Furthermore, we have used the same samples to stabilize colloidal suspension models, and we have found good correlation between rheological properties and the ability to stabilize the dispersions.

This work shows that rheological measurements may be used for the evaluation of xanthan efficiency to stabilize dispersions like particle suspensions or emulsions.

P25

NEW AQUEOUS COLLOIDAL SOLUTIONS OF CERIUM - PROPERTIES AND CHARACTERISTIC

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The chemistry of cerium is quite complex. By using highly sophisticated methods to investigate these complexities, various aqueous sols of cerium have been discovered.

These sols can be used in new catalysis or ceramic techniques, such as sol-gels impregnation or wash coating.

They serve also as raw materials for the synthesis of improved oxides. High surface area cerium oxides with controlled porous volume and pore size distribution are thus prepared by coagulating well-defined sols. Such oxides are choice materials in the catalysis field.

A large range of sols is obtainable. The size of colloïds ranges from 50 A° to 1000 A°, pH is adjustable from 0.5 to 4. Sol stability exists up to a concentration of 600 g/l CeO_2 depending on the sol. A set of analytical techniques have been developed to describe colloïdal solutions. Ultracentrifugation separates colloïds from the liquor. Light scattering allows the average density ol colloïds to be evaluated by taking hydrodynamic diameter (photon correlation spectroscopy) and particular molecular weight (Rayleigh scattering) together. Neutron diffusion reveals how density is distributed within the colloïd. X-Ray diffraction and E.X.A.F.S. compare the colloïd structure with that of CeO_2. Neutron diffraction indicates the presence of hydroxyl groups in the lattice.

Accoustophoresis determines the nature of the surface sites of the colloïds.

These techniques are helpful as an approach to the modelization of cerium colloïds.

P26

COMPARATIVE STUDIES BETWEEN MERCURY COMPOUNDS AND DIFFERENT PHOSPHOLIPID BILAYERS. A FLUORESCENCE POLARIZATION STUDY.

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Mercury compounds and their interactions with the cellular membrane have been investigated mainly from a biochemical point of view because of their thioloprive properties ensuring metal binding on membrane proteins. A more limited number of works are devoted to study the role of phospholipids (PL) in this mechanism. We have analyzed the transmembrane fluxes of mercury derivatives using black lipid membrane (BLM) technic [1] and their accessibility to the hydrophobic core of the bilayer by measuring the quenching of pyrene fluorescence [2]. In the present work we report on the effects of HgC12 and CH3HgCl on the fluidity of various PL by fluorescence polarization, using Diphenylhexatriene (DPH) as a probe, and also point out the differences with the behavior of other cations (Ca2+, Al3+,..). For both derivatives, no significant action is detected with zwitterionic PL. In contrast, changes in the thermotropic properties of negatively charged PL (DPPG, PS, DPPS, DMPS, DMPE) are observed, depending on the polar head of the lipid, the length and the degree of saturation of the aliphatic chains, and the pH (range from 4.0 to 8.0). With DPPG, a weak effect is observed and only for low pH (5.0), corresponding to an increase of the transition temperature (+2°C). A strong perturbation is induced by HgC12 on PL with a serine headgroup. The disappearance of the transition is dose dependent and the transition is completely abolished at 0.5 mM HgC12 and pH=5.8. The inorganic derivative perturbates also the thermotropic properties of PL with ethanolamine headgroup. These results are in agreement with NMR studies previously performed on HgC12-glycine interactions [3], showing that two types of binding could occur:

- electrostatic interactions between negative charges carried on by PL polar heads and mercury chemical species.
- involvement of the amino nitrogen in the formation of the complex PL-HgC12.

These could have important implications on interactions between mercury compounds and biological membranes.

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P27

NEW METHODS FOR MEASURING SIMULTANEOUSLY DIELECTROPHORETIC MOBILITIES AND DENSITIES OF INDIVIDUAL PARTICLES AND CELLS. EXPERIMENTAL RESULTS FOR PEA PROTOPLASTS

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We constructed a new multifunctional chamber. It consists of four electrodes. Two identical platinum wires (electrodes 2 and 3) of radius 0.25 mm are placed symmetrically between two flat metal nickelized electrodes (1 and 3). By switching, the electrodes one can change the direction of the field intensity. Usualy the cells are placed between the cylindrical electrodes 2 and 3. The field is applied between the electrodes 1 and 2.

The dielectrophoretic mobilities D and the relative densities ρ were found by a dynamic and a static method. The dynamic method is based on measuring the rate of cell motion between two pairs of electrodes The static method is based on finding the appropriate voltage to stop the cell motion caused by gravitation. Both methods give the possibility to measure the whole dielectrophoretic spectrum for one and the same cell just by changing the frequency of the field f and measuring the respective rates or voltages.

The values for the dielectrophoretic mobilities are of the same order of magnitude as previosly reported (2,3). Individual pea protoplasts differ in dielectrophoretic mobilities and densities.

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P28

FAST DRAINAGE OF A LIQUID FILM : CASE OF A BUBBLE APPROACHING A FREE SURFACE

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One of the process occuring in coalescence of two bubbles is the drainage of the intervening liquid film. For this stage, most of theoretical analysis are based on the Reynolds lubrication approximation. From our experimental measurements of the film thickness at the apex of a bubble approaching a free surface, we show that the rate of thinning is much higher than predicted by these models for distilled water and aqueous solutions of ethanol. The rest times of the bubbles at the surface are short (few milliseconds) compared with the case of foaming liquid.

In the Reynolds' equation, often used for foams, the drainage rate varies with the 3-th power of the thickness. In our experiments, the power is 3/2 during the first stage of the drainage. The hypothesis of a plug flow in the film, instead of a creeping flow, gives this dependance.

AGGREGATION OF SODIUM DODECYLSULFATE IN MIXTURES OF WATER AND 1,2-ETHANEDIOL.

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The aggregation of surfactants in non-aqueous polar solvents has become a field of increased interest during the last few years. In this work the formation of surfactant aggregates of sodium dodecylsulfate in mixtures of water and 1,2-ethanediol has been studied by density, speed of sound and conductivity meaasurements at 298.2 K.

The surfactant molality at the critical micelle concentration (c.m.c.) increases with increasing mass fraction of 1,2-ethanediol in water. At higher mass fractions of 1,2-ethanediol breakpoints in e.g. the conductivity versus molality curves do occur, but they become less distinct. From the density measurements the partial molar volume of the surfactant was obtained. The difference in the partial molar volume above and below the c.m.c., ΔV_m, decreases with increasing mass fraction of 1,2-ethanediol. The same result was obtained for the difference in the partial molar isentropic compressibility. The phenomen is discussed in terms of the lowered solvophobic interactions, which is indicated from decreased interfacial tension between water-1,2-ethanediol mixtures and alkanes.

STRUCTURE AND STABILITY OF MEMBRANE-PEPTIDE COMPLEXES DRIVEN BY LIPID ACYL CHAIN LENGTH

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Melittin is known to induce membrane lysis and death of biological cells. Deuterium (^2H) and Phosphorus-31 (^{31}P) NMR have been used to investigate both at the molecular and supramolecular levels the mode of action of this 26 amino-acid amphipatic peptide on model and real membranes.

Dramatic NMR lineshape changes as a function of melittin content, temperature and acyl chain length of phosphatidylcholine model membranes have been correlated by means of Quasi Elastic Light Scattering and Electron Microscopy to changes in membrane morphology. Action of this toxin on model membranes thus resides in a macroscopic restructuration of the bilayer leading to new supramolecular entities (lipid-toxin complexes) whose size depend on acyl chain length and physical state of the membranes (gel or fluid).

For lipid-to-peptide molar ratios, R_i, greater than 15 very large spherical vesicles (several thousand Angström diameter) are detected. These vesicles are converted into very small discs (few hundred Angström diameter) by cooling down the system in the gel phase.

This macroscopic membrane restructuration is proposed as a mechanism for membrane lysis.

Mechanisms leading to the formation of these new structures as well as their long term stability have been followed by ^2H- and ^{31}P-NMR. The structural and dynamical behaviour of these lipid-peptide complexes can be accounted for by making use of the shape concept of both components.

Action of Melittin on erythrocyte membranes can be accounted for, at least in part, by results on model membranes.

P31

ADSORPTION OF HYDROLYZED POLYACRYLAMIDES ON TiO_2 and $CaCO_3$ and INFLUENCE OF PHOSPHATE IONS.

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Hydrolyzed polyacrylamides (HPAM) are currently used as thickners in enhanced oil recovery. Adsorption of the polyelectrolyte on the reservoir rocks determines however the feasibility and economical interest of the technique.

In a previous work we have studied the Influence of pH, ionic strength and experimental mixing procedure on the amount adsorbed for a 16 % hydrolyzed Polyacrylamide ($Mw = 2.10^6$) on $CaCO_3$. Results show that maximum surface Coverage by the polymer depends more on interactions between polymer molecules than between the surface and the polymer.

Further studies have been made of the dependence of adsorption on calcium and phosphate ions (10^{-4} to 10^{-1} M/l.).

In the case of calcium Ions at the higher concentration, no difference is measured in the amount adsorbed between the 0 %, 16 % and 100 % hydrolyzed polymers. No more influence of the molecular weight is measured. An interesting result is that a similar surface coverage is obtained on TiO_2 and $CaCO_3$. All these results lead again to the conclusion that overlap of the molecules is the determining factor for surface coverage.

Phosphate Ions decrease dramatically the adsorption of 0 % and 16 % hydrolyzed polymers on both TiO_2 and $CaCO_3$. As the decrease occurs as well with charged and uncharged surfaces and polymers, its origin might be a strong and fast adsorption of the phosphate, which leaves no available sites for the polymer binding. As expected the phosphate Influence is dependent on the experimental procedure : Results are different wether the polymer or the phosphate ions are introduced first.

(This wort is supported by CNRS - ARTEP, FRANCE).

P32

A THEORY OF LONG-RANGE HYDROPHOBIC ATTRACTION FORCES BASED ON A SQUARE GRADIENT VARIATIONAL APPROACH

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It has been demonstrated recently that the attraction forces which act between neutral, hydrophobic surfaces immersed in water are surprisingly strong and long-range[1,2]. Upon separating the two surfaces from molecular contact a vapour/gas cavity forms when the contact angle exceeds 90°. However, when gradually diminishing the surface separation no cavity formation occurs and it is in this regime that comparatively strong attractive forces have been monitored.

In order to account for this phenomenon we have developed a mean-field theory which is based on the notion that molecular ordering effects are causing the hydrophobic attraction. The increased degree of ordering in the contact layer of water molecules next to the hydrophobic surfaces is supposed to be benefici from the free energy point of view whereas the concomitant ordering of the wat molecules in the core of the water film is assumed to increase the free energy

The resulting variational problem generates a surfaces force vs. distance function which is quite similar in shape to the corresponding experimental functio determined by Claesson and Christenson[1]. The implications of our theory (whi is conceptually rather closely related to the earlier theory of Cevc et al[3] o repulsive hydration forces) will be discussed in some detail.

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P33

INTERACTIONS BETWEEN SURFACTANT IONS OF OPPOSITE CHARGE

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Recently a significant attention has been paid to modeling and understanding mixed micelles containing ionic surfactant of opposite charge. In order to gain further insight into the mechanism of interactions between oppositely charged ionic surfactants and counter ion binding, the systems with constant anionic and varying cationic surfactant concentrations were investigated in details. The interactions in mixtures anionic/cationic surfactants were studied by several methods (conductivity, surface tension, turbidity, electrophoretic mobility and emf measurements). The results revealed that the composition of mixed micelles and mixed monolayer at air/water interface changes with solution composition. A model for the interface between mixed micelles and surrounding electrolyte is supposed to incorporate the headgroups of both surfactants and pair of headgroups/counter ions of surfactant in excess.

P34

A comparative study of the adsorption of two fluidifying agents of Cement pastes on TiO_2 and $CaCO_3$

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Formaldehyde condensate of Naphtalene Sulfonate and Melamine Sulfonate are polymeric compounds widely used as fluidifying agents in cement pastes.

Using Titanium dioxide and calcium carbonate as adsorbents, we analyze the influence of some pratical parameters, namely pH, Ionic strength, Molecular weight and ionic nature (Na^+, Ca^{++}, PO_4^{---}).

The influence of electrostatic Interactions on the amount adsorbed is discussed.

Experimental results are very similar for both polymers, owing probably to their common sulfonic functional group.

For a given solution composition (pH, ionic strength, Ca^{++} concentration) the amount adsorbed at surface saturation is the same for both solids, in spite of their different chemical natures.

Maximum adsorption is essentially determined by the overlapping capacity of the molecules. The overlap is dependent on the parameters that modify the polymers charge (pH, Ionic strength and Ca^{++}).

Phosphate ions are more strongly adsorbed than polymer functionnal groups on surface sites. The decrease in polymers adsorption is shown to be proportional to the surface phosphate ions density even in acidic media where the phosphate species are uncharged.

P35

Analysis of the colloïdal properties of a dispersion for the fabrication of a composite Nickel Deposit.

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The Electro and Chemical Depositions of Composite Layers of a metal matrix containing non conductive particles ask for an accurate control of the powders' Dispersion in the working Bath. Specific Requirements are that the particles do not settle and, in the case of a multi-particle system, that they do, or do not give heterocoagulation phenomena, depending on the final properties of the Deposit.

The codeposition of Nickel and hardening particles (SiC) is being studied in our laboratory to establish the relations betwee the properties of the colloïdal suspension (coagulation, floculation settling etc ...) and the Deposits' characteristics (amount of particles embedded, dispersion, homogeneity ...).

Between pH 4 and 5 the Surface's electrical charge is slightl negative. Nickel Ions adsorb on the particles, which may facilitate their binding to the Nickel matrix. The Ionic strength, however, is high and tends to induce some coagulation.

Several organic additives have been used to improve the particles' dispersion and the sedimentation rate. Adsorption of thes compounds is measured as a function of their concentration and of the Bath composition. The dispersing efficiency is measured by sedimentation rate, settled volumes and microscopie Analysis of the Deposits.

In the case of a multi-particles system (SiC + other Mineral each type of mineral having its own charge and surface properties, the use of organic agents proves to be a flexible way to monitor the Colloïdal properties of the Bath. Results will be shown for a system containing SiC and positively charged particles.

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P36

INSTABILITIES IN WETTING PHENOMENA

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When a liquid edge avances on a solid surface , irregularities in the contact line motion are usually observed. They are referred to as stick-slip phenomena.

Chemical or geometrical inhomogeneities at the solid interface are the origin of this behaviour.

Chemical inhomogeneities may occur in liquids containing tensio-active molecules and spreading on high energy surfaces : the molecules will diffuse in front of the contact line and adsorb on the surface, building an hydrophobic barrier to spreading.

Mixed situations (both chemical and geometrical) may be artificially obtained by direct deposition of hydrophobic barriers on the substrate.

We have studied in both cases the amplitude and the periodicity of the instabilities which appear as "waves" travelling along the contact line.

In the first case we have used trioctylamine, or hexadecane with traces of hexadecanol.

In the second case we have used silicone oils (polydimethylsiloxanes).

AQUEOUS FERROFLUIDS BASED ON MANGANESE AND ON COBALT FERRITES ELABORATION AND MAGNETIC BEHAVIOUR

by

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Two new ferrofluids based on manganese and on cobalt ferrites have been synthesized in aqueous solution by using Massart's procedure previously described on colloidal magnetite.

Synthesis of manganese and cobalt ferrites has been performed in order to get magnetic particles of suitable size and stability able to give colloidal solutions. Stable aqueous solutions of such ferrofluids are available in acidic or in basic medium : their molar concentration can reach 17 mol . l^{-1} (i.e. a volumic fraction of 0,27).

Magnetization curves of ferrofluids, at room temperature and for a suitable concentration range, obey the Langevin law. Saturation magnetization for basic or for acidic ferrofluids differs, involving a structural difference between particles which have been treated or not by ferric nitrate to insure acidic solution stability.

When frozen or trapped in a gelatine matrix, ferrofluids based on manganese or on cobalt ferrites behave differently : manganese ferrite keeps the superparamagnetic behaviour of the liquid. On the contrary, magnetization curves of trapped cobalt ferrite, at room temperature, exhibit an hysteresis. Remanent magnetization vary with the particle size. Magnetocristalline anisotropy constants of $MnFe_2O_4$ and $CoFe_2O_4$, i. e. $4 . 10^4$ erg/cm^3 and $2 . 10^6$ erg/cm^3 respectively, differ significantly and are assumed to generate different behaviour of the two compounds.

EMULSIFYING PROPERTIES OF AMPHIPHILIC LIPOPEPTIDES

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Amphiphilic lipopeptides $C_n(AA)_p$ consist of a hydrophobic paraffinic chain C_n containing from 12 to 18 carbon atoms linked through an amide bond to a hydrophilic peptidic chain $(AA)_p$ where AA is one of the following amino-acids : sarcosine, lysine, glutamic acid, hydroxyethylglutamine, hydroxypropylglutamine and serine.

The emulsifying properties of lipopeptides $C_n(AA)_p$ with p smaller than 20 were tested versus numerous pairs of immiscible liquids such as water/hydrocarbons and water/base products of the cosmetic industry. Three types of emulsions were prepared with small amounts of lipopeptides : emulsions, miniemulsions and microemulsions. All the emulsions were found of the oil in water type and the size of the particles was measured by freeze fracture and electron microscopy.

In the case of simple emulsions, formed by ternary systems oil/water/lipopeptide, the respective influence of the nature of the oil (toluene, styrene, dodecane, butylstearate, isopropylmyristate, cosbiol, migliol) the length of the hydrophobic paraffinic chains and the length and the nature of the hydrophilic peptidic chains of the lipopeptides were established.

In the case of miniemulsions, formed by quaternary systems oil/water/ionic lipopeptide/cetylalcohol, the respective influence of the nature of the oil, the length and the nature of the peptidic chains of the lipopeptides and the method of preparation of miniemulsions were established.

In the case of microemulsions formed by quaternary systems oil/water/lipopeptide/aliphatic alcohol or amine with less than 7 carbon atoms, the respective influence of the nature of the coemulsifier and of the molecular characteristics of the lipopeptides were established.

As lipopeptides give easily stable emulsions with base products of the cosmetic industry, the biocompatibility of lipopeptides was studied. For all lipopeptides a biocompatibility by far better than that of sodium dodecylsulfate, and in some cases as good as that of bicatenary emulsifiers was found.

EXPERIMENTAL EVIDENCE FOR A CONNECTED RANDOM SURFACE STRUCTURE FOR AQUEOUS OR OILY ANOMALOUS ISOTROPIC SURFACTANT PHASES

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Anomalous flow birefringent phases, sometimes designated as L_3, have been identified in both the water-rich and the oil-rich parts of the phase diagram of the water(NaCl)-dodecane-pentanol-SDS system. The presence of these phases appear to be associated with that of swollen lamellar phases. Conductivity, light and neutron scattering results provide evidence that the structure of these phases consists of a highly connected, sponge-like, random bilayer-continuous surface. The surfactant surface separates, depending upon the system, either two water-continuous domains or two oil-continuous domains. The data are consistent with the theoretical model proposed by Cates et al (1).

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RHEOLOGICAL PROPERTIES CHARACTERIZATION OF GELATIN GELS FILLED WITH PHOSPHOLIPID VESICLES.

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Small unilamellar vesicles (SUV) or large multilamellar vesicles (MLV) of egg phosphatidylcholine (e-PC) and synthetic dipalmitoyl phosphatidylcholine (DPPC) were added to gelatin gels (5% w/w ; dry gelatin/water).

The small and large deformation behaviours of these "filled" gels were characterized from uniaxial compression experiments. Dynamic measurements in cone-plan geometry were carried out to determine the variation in loss and storage moduli (G" and G') during gelification.

The results will be compared to the rheological behaviour of pure gelatin gels.

ADSORPTION - DESORPTION IN CELESTITE FLOTATION WITH DODECYLAMMONIUM CHLORIDE

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ABSTRACT

Strontium is increasingly consumed for industrial purposes. The main source of strontium is the celestite ore. Only several countries supplies the mineral, and among them Spain is one of the main producers. Celestite ore could be benefitted by flotation using both, cationic and anionic collectors, if suitable conditions are attained. We examined dodecylammonium chloride (DDACl) as the collector. The adsorption equilibrium of DDACl on celestite is achieved after 20 mins. of equilibration in 2 x 10^{-4} M solution. The maximum flotability of celestite, up to 95 % in 10^{-4} M DDACl, appears at pH around 8, and on both sides from this value on the pH scale the floatability decreases. It has been also found that good floatability (above 80 %) occurred when adsorbed DDACl amounts more than 2 calculated monolayers. This situation is probably met in DDACl solutions at concentrations above 10^{-4} M. If the celestite surface is precovered with DDACl, then desorption of this collector takes plce during the flotation. Thus, the desorption was observed even at the 0.5 monolayer precoverage, and only *ca.* 5 monolayers remain on the surface if the initial amount of DDACl was 10 monolayers.

THEORETICAL PREDICTIONS OF THE ELECTROKINETIC AND STABILITY PROPERTIES OF CHOLESTEROL IN AQUEOUS NaCl AND NaCl + BILE SALT SOLUTIONS.

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ABSTRACT

Experimental data on the electrophoretic mobility of cholesterol particles in aqueous NaCl and NaCl + bile salt solutions are employed for the estimation of the zeta potential (ζ) of the particles in these media. The results obtained through the use of the well known Smoluchowski formula are compared with those deduced from the more elaborated treatment (R.W.O'Brien and L.R.White, J.Chem.Soc. Faraday Trans.II., **74**, 1607, (1978)) of electrophoresis considering two particle radius: 1.4 μmm and 5.4 μm. Thus we can determine the relative influence of the relaxation and electrophoretic effect for each experimental condition tested, including the particle size.
The use of the parameter $\zeta\cdot k^{-1}$ (k being the inverse of the length of Debye) allows to correlate the electrokinetic properties of the cholesterol dispersion with its tendency to coagulate. Thus, the influence of pH and NaCl concentration on this parameter has been first discussed. Further, the zeta potential of cholesterol in the presence of a series of bile salts, glicine and taurine conjugated, is used to study the stability conditions of such suspensions, the results being discussed in terms of the different characteristics of bile salts in solution. Application to bile stone formation mechanisms is also discussed.

IN SITU DETERMINATION OF ADSORPTION LAYERS ON COLLOIDS BY LIGHT SCATTERING AND INTERFEROMETRY

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The adsorption properties of colloids (e.g. silica) immersed in a mixture of liquids (e.g.water and lutidine) can be studied directly in the experimental cell by sensitive optical means: light scattering and interferometry. The first technique is applicable to dispersed colloids. It is based on the variations of form and magnitude of the structure factor when compared to the case of the "bare" colloids. The second technique is suitable for flocculated colloids. It consists in measuring the characteristics of the desorption front (or possibly the adsorption front) by laser interferometry in the clear solvent close to the flocculated phase. Both of these techniques provide high sensitivity. It is thus possible to detect the formation of a 10 Å layer of one of the components.

A STUDY BY QUASIELASTIC LIGHT SCATTERING OF THE EFFECT OF SOME POLYCATIONS ON PHOSPHOLIPID LARGE UNILAMELLAR VESICLES

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We have investigated by light scattering techniques the aggregation-fusion effect of poly-L-lysine, Mg^{++}, Ca^{++} on large unilamellar vesicles prepared by the reverse phase evaporation method from DLPE and from mixtures of DMPC-PS at various ratios. The aggregation-fusion has been followed by both static and dynamic light scattering, in particular with the latter , the variation of the average size versus time and therefore the kinetics of the fusion can be studied.

With PC-PS LUV in buffers containing Tris-HCl and NaCl, pH8, the increase of the average volume showed a quasi-constant rate. Effects on the aggregation-fusion rate induced by the concentration expressed by the ratio (lysine/PS) or by the length (or molecular weight MW) of the polylysine have been observed. With high MW polylysine, the aggregation-fusion rate showed a maximum value when the concentration varied, whereas with low MW polylysine, this rate was only increased. The effect of trypsine after addition of polylysine gave insights into the mechanism of the aggregation and the fusion induced by the polylysine .Moreover, the competitivity of the effect of Ca^{++} and Mg^{++} and that of polylysine has been also studied.

In DLPE LUV prepared at pH9 and trace of EDTA, above the transition temperature, on the contrary to the case with PC-PS LUV, the fusion induced by Mg^{++} and Ca^{++} showed the same characteristics. The effect of polylysine (MW 78000) was similar with a much lower molar concentration in lysine .

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MAGNETIC PARTICULATE THIN FILMS ON BILAYER LIPID MEMBRANES (BLMs)

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ABSTRACT:

Cationic magnetic Fe_3O_4 particles have been shown to be strongly attracted onto one or both surfaces of glyceryl monooleate (GMO) bilayer lipid membranes (BLMs). The absence of capacitance changes across the GMO BLM during deposition have been interpreted to imply that the Fe_3O_4 particles did not penetrate beyond the headgroup region (headgroup distance, d_p = 6-8 Å; hydrocarbon bilayer distance, d_h = 48 Å; BLM thickness, $d_b = 2d_p + d_h = 62 \pm 2$ Å) of the surfactants constituting the BLM. Incident-angle-dependent reflectance measurements led to a model for the Fe_3O_4-particle-coated GMO BLM with the following parameters: refractive index of the magnetic particles, n_m = 1.96; thickness of the magnetic particles on the BLM, D_m = 55.1 Å ($D_m = d_m + d_p$); and center-to-center distance between the magnetic particles, S_m = 57.6 Å. Fe_3O_4 particles attracted to the BLM so strongly that they could not be pulled away by a magnet even as strong as 400 Oe. This strong attraction overcame the electrostatic repulsions between neighboring particles and permitted the coverage of the BLM to the extent that it tantamounted to the formation of a monolayer of particulate film. Formation of a second layer of particulate film was proposed to be precluded by particle-particle repulsions which prevailed in the absence of the attractive forces of the BLM. Longitudinal Faraday and Kerr effects as functions of the angle of incident light have been calculated and experimentally determined for GMO BLMs coated on one and both sides of particulate Fe_3O_4 thin films. Magnetic domains have been visualized by polarized videomicroscopy of the Kerr rotation. Support of this work by the National Science Foundation is gratefully acknowledged.

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MACROSTRUCTURE OF ASPHALTENE DISPERSION BY SMALL ANGLE X RAY SCATTERING

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Safaniya asphaltene dispersions have been studied by Small Angle X-ray Scattering samples are petroleum asphaltene from vacuum residues dispersed in several organic solvants (benzene, tetrahydrofurane, pyridine, toluene, orthoxylene). The sample concentration are 0.5 and 1 %.

The experiments were carried out using the synchrotron X-ray radiation of the D.C.I. storage ring at L.U.R.E. (Université d'Orsay, France). The spectra were recorded during 1 h. The wave length was 1.608 Å. The focal distance was 2 m, with 1m between the sample and the linear sensitive detector. Taking into account the sizes of the beam stop and the detector windows which are actually used, the accessible particle range of size was 40-1000 Å.

As a result of spot collimation of the incident beam, the only correction necessary was the sample absorption correction . The petroleum solution was contained in cells with parallel mica windows or in thin capillars.

The experimental data analysis was performed first by direct observation of characteristic laws on the experimental intensity . The experimental curves were then compared with theoretical ones which were computed from different models.

The scattering data present a characteristic profile : at high scattering angles, for all the samples the scattering curves vary with q^{-2}(where $q = 4\pi \sin \theta$, and θ is the half scattering angle) . This behaviour could be produced by a membrane shape of the particule.

We used two different models :

- a thin disc,
- a size distribution of thin discs with the same thickness and a radius distributed

The second model gives a better simulation and seems to be more realistic. The results obtained are in good agreement with various data from the litterature.

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NEW ABSORPTION AND FLUORESCENCE PROBES TO FOLLOW THE DYNAMICS IN LIPID BILAYER SYSTEMS

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The investigation of the main phase transition dynamics in lipid bilayers is now possible between 10^{-9} s and 10^{0} s using our Iodine-Laser Temperature-Jump (ILTJ) technique.

Because of the complexity of molecular changes during phase transitions in lipid membranes detection techniques which are specific for the environment of a single molecule are desired.

We have therefore developed two new lipid probe molecules, the absorption probe acridine orange lecithine (AOL) and the fluorescence probe diphenylhexatrienphosphatidylcholin (DPHPC), which contain only small structural differences compared with the lipid molecule dipalmitoylphosphatidylcholine (DPPC).

The probe AOL differs in the headgroup where $-N(CH_3)_3$ is replaced by acridine orange. When AOL aggregates in lipid layers of DPPC, a change in the absorption spectrum of the AO headgroup around 484 nm can be monitored; this aggregation process reports about the lateral diffusion of single molecules. The wavelength of observation at 484 nm is long enough, so that scattering phenomena from the whole lipid vesicles are negligible.

The probe DPHPC is different to DPPC in the γ-hydrocarbon chain, where the terminal $-C_{13}H_{27}$ is substituted by the fluorescing molecule DPH. The steady state fluorescence anisotropy $r_{ss} = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2\,I_{\perp})$ of DPHPC is a measure for the wobbling space available to the probe. If kinetic measurements are performed starting at least 100 times after the lifetime of the excited state of DPH, r_{ss} can be time resolved from 10^{-6} s to 10^{0} s.

We used both probes AOL and DPHPC to monitor the dynamics of the main phase transition in pure DPPC bilayers as well as in lipid preparations containing cholesterol or polypeptides.

The vesicles were characterized by electron microscopy, turbidity-temperature dependences as well as microcalorimetry (MC). The results from the sum of the amplitudes of the kinetic experiments at a single temperature were compared with the corresponding enthalpy changes (ΔH) from MC measurements. Using the kinetic information it became possible to reconstruct the static equilibrium changes which represent the whole main phase transition like turbidity-temperature, r_{ss}-temperature, or ΔH-temperature dependences. The application of our new probes DPHPC and AOL allowed us to refine our model of the main phase transition in PL-bilayer systems and justifies our hope to achieve detailed information about lipid-protein interactions.

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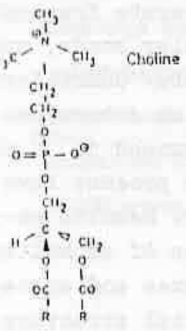
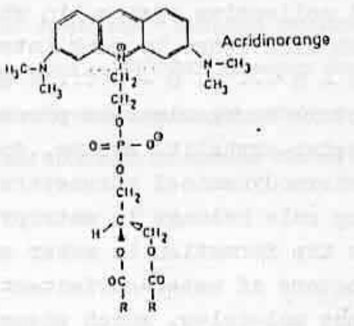
LECITHIN



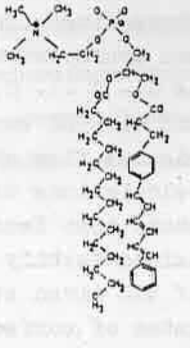
Turbidity

AO-LECITHIN



Absorption

THE DPHPC MOLECULE



Fluorescence

P48

DYNAMIC PROPERTIES INVESTIGATION OF WATER SOLUTIONS OF BIS-QUATERNARY AMMONIUM AMPHOLITES

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Dynamic properties and mechanism of viscous flow of water solutions of ampholite - ethylene-1,2-bis(dimethylcarbdecyloxymethyl)ammonium chloride - were studied by acoustic spectroscopy and viscosimetry. Concentrations of solutions studied were 0,025 - 0,100 M (CMC of ampholite determined by standard technics was about $3\cdot10^{-3}$ M).

Investigations were carried out in frequency range f = 10 - 3000 MHz and in temperature interval from 283 to 353 K. In all range of frequencies and temperatures sound absorption coefficient was directly proportional to f^2. Temperature dependence of sound absorption for ampholite solutions was just the same as for pure water, i.e. excessive absorbance is determined by irreversible reorganization of solution structure.

Obviously, ampholite solution can be modelled as dynamic three-dimensional collective system, in which separate fragments are connected with each other by weak intermolecular bonds, such as O - H ... O, C - H ... O, O - H ... N and others. Characteristic time of structure reorganization process, which determines viscous flow of water-ampholite system, doesn't exceed 10^{-11} s. Calculations of thermodynamical parameters of the process have shown that leading role belongs to entropy factor. Results obtained testify to the formation in water solutions of ampholites of the given structure of water-surfactant complexes and aggregates of surfactant molecules, which possess spatial structure and orientation.

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Phase Diagrams and self - diffusion of Aqueous Lecithin with Decanol and Triton X-100.

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The phase diagrams of two isothermal ternary systems soybean lechithin - water with triton X-100 and with decanol have been determined by ^{2}H NMR and polarising microscopy methods at 293 K. The lamellar liquid crystalline phase of the aqueous lecithin is found to swell and take up more water by the addition of both triton X-100 and decanol and the swelling is more pronounced with the former additive. The stability of the lamellar phase also extends more to the triton X-100 content at low lecithin concentration and by cooling the system to 278 K, the liquid crystalline phase extends from lecithin - water axis to triton X-100 - water axis. The temperature effect on the phase stabilitry with decanol is negligible. Hydration force plays a dominant role for the stability of the lamellar phase formed by the zwitterionic lipids like lecithin and it can be shown qualitatively that the addition of polar cosurfactants like triton X-100 and decanol will lead to the swelling of the lamellar phase as observed experimentally. Lecithin (60%) dissolves easily in decanol giving a clear isotropic solution which can also incorporate about 20% water.The solubility of lecithin in triton X-100 is limited but the aqueous triton X-100 can solubilize a maximum of about 10% lecithin with high water content. NMR self - diffusion measured by Fourier transform pulsed-gradient spin-echo method and ^{1}H NMR linewidths data indicate the formation of (a) small water droplets in the decanolic solution, (b) probably small aggregates of lecithin in decanol and (c) small mixed micelles in the isotropic solution of lecithin - water - Triton X-100 system.

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SIMPLE TECHNIQUE TO DETERMINE THE INTRINSIC VISCOSITY OF XANTHAN GUM AND OF ANOTHER POLYSACCHARIDE

Xanthan gum is a polysaccharide obtained through fermentation.

In the manufacturing process, in addition to the bacterium itself, many parameters can bring about a variation in the molecular mass of the product.

Determining the intrinsic viscosity, which characterizes the applications of the polymer, is not easy, as it is necessary to operate in a dilute medium with appropriate and highly sensitive equipment.

A correlation between the specific viscosity and overlap has thus been established, leading directly to the intrinsic viscosity.

The originality of the research lies in laving varied both concentration and intrinsic viscosity within the overlap parameter. While it is easy to vary concentration, (η) is another matter. The techniques described in the literature start with a reference xanthan gum from which lower masses are obtained either by an enzymatic degradation or by physical degradation (as with ultra-sound). In our procedure the different gums have been obtained by altering the manufacturing process.

This simple technique for evaluating intrinsic viscosity has been extrapolated to another polysaccharide. A similar correlation has been found which gives results that are as satisfactory as for xanthan gum.

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SOLUBILIZATION OF AROMATICS IN AQUEOUS BILE SALTS BENZODIAZEPINES IN SODIUM CHOLATE. ^{1}H NMR STUDY

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The solubilization of water insoluble or slightly soluble drugs such as benzodiazepines in aqueous bile salts is of great importance for their medical use, biological uptake and transport in living organisms. Due to the aromatic moieties included in the molecular structure of benzodiazepines, they induce clear aromatic ring current effects on the ^{1}H NMR chemical shifts of the cholate anion. Based on these effects the solubilization sites of two different benzodiazepines, diazepam and temazepam, in aqueous sodium cholate are estimated. A comparison with the behavior of some simple aromatic model compounds as well as with some other aromatic drugs is included. Both benzodiazepines studied show similar behavior in respect to the induced chemical shifts, in spite of different heptane/water partition coefficients and pK$_a$-values. According to an other study, indomethacine possesses very similar properties compared with benzodiazepines, in contrast to phenylbutazone, which shows negligible chemical shift effects on the bile salt anion.

FRACTAL STRUCTURE OF PORTLAND CEMENT PASTE DURING AGE HARDENING ANALYZED BY X-RAY SMALL-ANGLE SCATTERING

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The changes in inner structure of Portland cement paste during the process of hardening were studied by X-ray small-angle scattering. The scattering curves taken at different intervals between 1 and 28 days after preparation showed asymptotic changes in the exponential decay towards large angles which relates to the inner surface structure. Most significantly it was found that the decay exponent obtained from the slopes in a log-log plot never reached the theoretical value of 4 expected from Porod's law for ideally smooth inner surfaces. Therefore, it is not permitted to define a specific inner surface by this approach. However, the numerical values of the decay exponent, after correction for X-ray beam geometry, can be directly related to the fractal dimension D, of the inner structure. The time course of D, changing from an initial value of 2.1 (day 1) asymptotically to 2.8 (day 28), indicates the progression from a highly ramified and porous structure to a more compact and homogeneous one. This process might be related to the growth of a bulky calcium hydroxide moiety at the account of the ramified calcium silicate and aluminate hydrates gel structure.

REFLECTOMETRY MEASUREMENT OF THE DECREASE OF THE LIQUID FILM AREA IN FOAMS

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The decay of foams with time, whether caused solely by gas diffusion through foam liquid films, or by a combination of that effect and occasional concomitant ruptures, is given most fundamentally by the rate decrease of the liquid film area. So any technique allowing to measure this parameter is useful to determine the stability of these systems.

The decrease of the liquid film area cannot be deduced from optical transparence measurements as suggested about forty years ago by CLARK and BLACKMAN. Indeed, these measurements depend mainly on the drainage of the liquid in the films, a phenomenon very indirectly related to the decrease of the liquid area.

It cannot either be deduced from the increase of the pressure which appears in a closed vessel in which the foam is decaying, as claimed more recently by NISHIOKA and ROSS. In this case, we have observed that measurements are very perturbed by the presence of an hydrostatic pressure, at least as important as the pressure to be measured, so that the results issued from this method seem to be doubtful.

We show that the relative liquid interfacial area can easily be deduced from reflectometry measurements performed at the free surface of the foam. The validity of this method has been proved on foams exempted from liquid film ruptures. It allows to find evolutions in very fine agreement with the more recent theoretical estimates : the decrease of the liquid film area is entirely governed by the gas transfert theory of LEMLICH and, at the end of the evolution, according to a rule recently expressed by MARKWORTH, it is prooortional to the -1/2 power of the time.

So, we think that reflectometry opens new perspectives for a correct determination of foam stability.

Two new granulometry technics used in order to measure emulsions stability.

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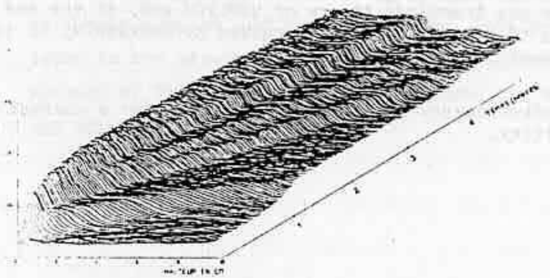
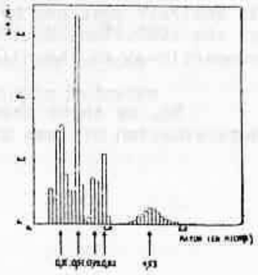
The study of emulsions shows that, in a first way, it is absolutely necessary to know with precision the granulometry of the studied systems. In fact, the explanation of the kinetic stability of these systems, must be illustrated by good granulometry technics. We know several methods such as, light scattering and its correlation, coulter counters, etc... but,all these methods give only an order of the mean size and not the exact repartition of the sizes of the droplets dispersed in the continuous phase.

We have developped two new technics giving much more precise results in this domain.

1-<u>Microscopy</u>: A microscopic view of the sample is obtained by the Nomarsky Interferencial Differencial Contrast (C.I.D.) The method gives an excellent contrast, a definition very close the theoretical value and a small field depth. A video camera gives the picture on a video tape and, this picture is digitalised in 8 bits 512x512 pixels digital picture. Then the numerical picture is mathematicaly treated and we obtain easily the positions and the diameters of the droplets under observation. This method gives a very good result in the range of .3 to 50. µm, with a definition of .05 µm by observing a large number of pictures (about 700 droplets).

2-<u>Centrifugal sedimentation</u>: This method allows the observation of ligth transmition trough a parallelepipedic cell containing the emulsion. The cell is placed in a large diameter rotating disk (diameter about 1.5 m) in order to get about 100g as centrifuge acceleration. Then we have built a system wich measure this transition at each point of the cell for different times; so, we obtain automaticaly an area wich represents the transmitted ligth as a function of time and position in the cell. The deconvolution of this area is programmed and gives directly the granulometry of the emulsion. We have to say that this method allows us to measure sizes going from .2 to 50. µm in 3 hours when the density difference between the two phases is .05 g/cm^3.





For the two methods, it is necessary to use diluted emulsions (say between .1 to 2 % of dispersed phase) to have good results; so, as the other methods , they need a good measurement of the continuous phase to obtain a correct dilution. The figure gives an example of the results of the second method in the case of a mixture of several calibrated latex droplets.

Structure and Dynamics of Water in Oil Microemulsions

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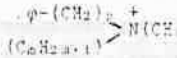
The structure of water in oil microemulsions stabilized either by an anionic surfactant : the sodium bis (2-ethylhexyl) sulfosuccinate (AOT) or by a series of cationic surfactants of the type :



$$\begin{matrix}\varphi\text{-}(CH_2)_p \\ (C_nH_{2n+1})\end{matrix} > \overset{+}{N}(CH_3)_2Cl^-$$

with various chain lengths (n = 10,12,14,16,18) and head groups (p=0,1,2), have been studied by a time-resolved fluorescence method. In the case of AOT-inverted micelles it has been shown that the increase of the length of the oil (alkanes from hexane to dodecane) and of the temperature (between 10°C and 60°C) produce a large increase of the size of the micelles. On the other hand the increase of the main chain length of the cationic surfactant (n from 10 to 18) leads to a large decrease of the size of the micelles for a given oil (chlorobenzene). Besides the size of the micelles the time-resolved fluorescence method allows also to study fast intermicellar exchanges. Such exchanges have been shown to occurs with both the anionic and cationic surfactants. These exchanges increase as the size of the micelles increases. The variations of the rate constant which characterize these exchanges have been correlated with electric percolation phenomena measured in these systems.

Study of the effect of Ca^{2+} and Poly-L-lysine on dimyristoylphosphatidic acid bilayers by Raman and Deuterium NMR spectroscopies.

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Multivalent cations and polycationic species are known to induce drastic structural changes in model membranes composed of acidic phospholipids. In order to elucidate this behavior, we studied the effect of Ca^{2+} and Poly-L-lysines (PLL) of different lengths on dimyristoylphosphatidic acid (DMPA) by Raman and NMR spectroscopies. Raman results clearly show that Ca^{2+} and PLL of high molecular weight (M_w = 200 000) have a great ordering effect on the DMPA acyl chains. On the other hand, short PLL ($M_w \approx 4000$) has an opposite effect since the conformations adopted by the long and short polypeptides in the complex are different. Measurement of orientational ordering via Deuterium solid state NMR allows to quantitate the Raman results and brings light on membrane-peptide interactions at the interface.

RHEOLOGICAL ANALYSIS OF PHARMACEUTICAL SUSPENSIONS WITH A HIGH PERCENTAGE OF SOLID MATTERS

(N.Chr. Larsen (1), K. Eberth (2))

In pharmaceutical suspensions it is vital for the practical use of the preparation that the system can be redispersed by simple shaking. When formulating such systems it is consequently disirable to employ a tool showing the stability of the preparation.

For this purpose knowledge of vehicles as well as dispersed particles is necessary.

Rheological analysis of various Penicillin G Procain suspensions are mentioned with a view to evaluate the effect of protective colloids, strength of ions etc. The results are compared with the redispersability.

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MICELLAR ENHANCED ULTRAFILTRATION OF METAL IONS

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Micellar enhanced ultrafiltration (MEUF) has been shown to be an effective method for removing dissolved organic polluants from aqueous streams (1) and especially water soluble dyes from textile effluents (2,3). There have been a few reports of the use of MEUF in separating divalent or trivalent metal cations or polyvalent anions from aqueous micellar solution (3,4).

In order to determine the optimum conditions for the phase separation, the interaction between the metal ions and the micellar surface in the retentate have to be investigated. Further, the interaction of the micellar aggregates with the organic ultrafiltration membranes is to be considered.

Ultrafiltration through polysulfone membranes in batch cell of pure or salt containing surfactant solutions have first been investigated. The relation between the c.m.c. and the concentration of the surfactant in the permeate and the influence of the cut-off point of the membrane have been examined.

Ultrafiltration experiments show that large univalent ions as Cs^+, or multivalents metal ions as Cu^{2+}, Cr^{3+} or $(CrO_4)^{2-}$ are readily adsorbed on the micellar surface. The resulting Na^+/M^{n+} (or $Br^-/(CrO_4)^{2-}$ ion exchange has been studied by the use of specific electrodes (Cu, Na) and by MEUF separation as a function of the surfactant concentration and the initial Na^+/M^{n+} ratio.

By analysis of the UF results, an empirical relation between the metal ions concentrations in the permeate has been found. Ionic activities measurements in the retentate show that activities of metal ions in the retentate (bulk phase) and concentration in the ultrafiltrate may not be identified.

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Polymerization of cetyl trimethyl ammonium methacrylate aqueous micellar solution

by

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In this paper the investigation of a new surfactant characterized by its polymerisable counterion is presented.

In aqueous solution , this surfactant forms spherical micelles closed to the sphericity limit. The C.M.C is equal to 9.810^{-4} M, its aggregation number is about 107 and hydrodynamic radius equal to 30A.

The polymerisation of these micelles followed by NMR technique induces formation of polymeric aggregates. The polymerized solution is investigated by physico-chemical techniques and reactivity reactions. From fluorescence data and from photoelectron transfer reaction it is observed that the diluted polymerized micelles conserve interfaces the hydrophobic character. This is an indirect proof of the existence of polymerized aggregates. These polymerized aggregates are large with an hydrodynamic radius equal to 540 A and an aggregation number equal to 12000 . The size and the shape of these aggregates remain unchanged upon dilution

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DETERMINATION OF VESICLE SIZE DISTRIBUTION BY HPLC

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The ability to measure size polydispersity of vesicles by using a multi-wavelength U.V.-visible detector coupled with a previously described HPLC gel exclusion analyser (M. OLLIVON, A. WALTER, R. BLUMENTHAL, Anal. Biochem. 152,1986) is reported and discussed.

Turbidity spectra are recorded at regular time intervals during the HPLC elution of vesicles. The optical range is chosen such as both the incident wavelengths interfer with the size of the particles and no specific absorption occurs.

Vesicle sizes corresponding to the different elution volumes of the chromatogram are calculated from the turbidity spectra according to the Rayleigh-Gans and the Mie theories of the light-scattering.

Vesicle size distributions are determined by means of statistical lows commonly used in the interpretation of GPC elution profiles.

This HPLC method using a multi-wavelength detector presents the particularity to be absolute in the sense that the data give directly the particle size distributions without the need of an external calibration of the column.

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FRACTAL MODELING OF ORGANIZED ASSEMBLIES. A LUMINESCENCE PROBE STUDY

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Micelles, microemulsions, and lipid vesicles are modeled as fractal objects i.e. systems possessing dilatation symmetry. Analysis of luminescence decay profiles in these systems is done with new equations involving the fractal or the spectral dimension of the reaction medium, allowing their calculation. In this way, the stucture and the dynamics of microheterogeneous systems are treated more realistically. Microemulsions are studied below and at the percolation threshold and lipid vesicles in their gel and liquid crystalline phase.

SYNTHESIS OF LC-POLYSURFACTANTS BY POLYMERIZATION AND POLYCONDENSATION

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We investigated the synthesis of polysurfactants by using different polymerization methods. Amphiphilic molecules with polymerizable endgroups have been synthesized and polymerized by anionic and radical polyreactions.

The cocondensation of hydrophilic and hydrophobic monomers also provides a simple method to obtain amphiphilic polymers.

The phase behavior of the monomeric and polymeric surfactant in aqueous solution was analysed. In case of a suitable hydrophilic/hydrophobic balance of the amphiphiles, lyotropic liquid crystalline phases were observed in defined temperature and concentration regimes.

LIPID MIXTURES IN MONOLAYER AND BLM

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In the context of study of biological membranes models, monolayers and BLMs (Black Lipid Membranes) of monoolein (GMO), monostearin (GMS), ceramide (Cer), galacto- and glucocerebroside (Gal, Glc) have been examined.

In fact GMO and GMS are considered the precursors of phospholipids in biological membranes, and the cerebrosides show very important functions in the same natural membranes.

The spreading isotherms recorded at different temperatures, the surface potentials, and thicknesses determined by ellipsometric measurements of films transferred on solid surface, have allowed to establish the surface phases and single components orientation in monolayers.

The BLM's specific resistance and specific capacitance determinations allowed to find the stability and thickness for the membranes, constituted by the same components.

For the mixtures, the compatibility in monolayers was recognized to be an important factor for the BLM's stability, containing the same lipids.

The effect of non-electrolyte additives on the formation of ionic micelles

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Abstract

Depending on their influence upon the micellization process, additives are classified as either electrolytes or non-electrolytes. Salt-like additives are known to facilitate formation of ionic micelles, mainly by lowering the electrostatic part of the interfacial free energy. As a consequence the CMC decreases while the mean micellar aggregation number increases to the extend that at high ionic strength huge surfactant aggregates are formed. The situation becomes more complicated when the electrolyte additive is also a micelle-forming surfactant, in which case mixed micelles, with composition dependent CMC and aggregation number, are formed. On the other hand, non-electrolyte additives, which are further classified as polar and non-polar, affect micellization in a quite different way depending on the hydrophobicity as well as the quantity of the added non-electrolyte.

In this study we have examined the influence of additives on a number of micelle-forming ionic surfactants, mostly from the point of view of their effect on CMC, aggregation number, micellar composition, etc. It was found that the micellar aggregation number increases with increasing additive mole fraction, when the additive is non-polar, but it decreases when it is polar. The number of additive molecules per micelle increases for both types of additives. Finally, the interfacial charge density remains practically constant with increasing additive concentration for non-polar additives, whereas it increases when the additive is polar.

PREPARATION AND CHARACTERIZATION OF SMALL LIPID VESICLES

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SUMMARY

Small lipid vesicles are suitable for studying model membranes and drug delivery systems. Numerous applications of liposomes are found in the domain of cosmetics and dermatology. Also in the food industry, liposomes have now been introduced for nano-encapsulation of enzymes.

Classical methods for preparation and characterization of liposomes have been well documented for a long time. In this study, the recent technique of microfluidization has been used for the production of small unilamellar vesicles.

The major convenience of this procedure lies in the fact that all use of organic solvents or detergents can be avoided. High lipid concentrations can be utilized and significant encapsulation efficiency may be achieved.

The particular properties of the vesicles produced depend very highly on the pressure used and on the number of passages of the preparation through the microfluidizer.

Small unilamellar vesicles have been characterized in shape and size by electron photomicrography, and their size distribution has been measured by photon correlation spectroscopy.

THE STRUCTURE OF SHEARED COLLOIDAL SUSPENSIONS : BIREFRINGENCE EXPERIMENTS

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The structure of a colloïdal suspension is investigated by light scattering methods. The suspension made of submicronic spheres in water is deionised in order exhibit a liquid-like state at zero-shear. It experiments a shear-stress in a cylindrical Couette cell. The flow is characterized by the Peclet number, $Pe = 6 \pi \mu \gamma a^3 / kT$, which measures the relative importance of Brownian and convective motions.

In previous papers $^{(1,2,3)}$, we had evidenced the deformation of the structure factor S(**k**) - with **k** in the plane of shear - when Pe is in the range $1.4\ 10^{-2} < Pe < 5.7\ 10^{-2}$. A comparison between the experimental results, a linear approximation and numerical results had shown some discrepancy and led us to do some different experiments.

In such a system, we don't have, of course, alignment birefringence; but structural birefringence is induced by the shear flow. Here, we present the first results obtained by birefringence and dichroism in a modified apparatus : the incident beam is normal to the plane of shear and its linear polarisation can be rotated ; the photo detector is measuring the intensity of the direct transmitted light. The main interest in these two methods is to allow us to get an access to the structure deformation (position of compressional and dilatational lines) in the *whole* plane of shear. Birefringence experiments show the shear-induced ellipticity of the transmitted light and we can connect the state of the polarisation with the structure of the suspension. Dichroism experiments confirm these results and, moreover, appear to be an easy method to determine the state of the suspension (solid,ordered liquid or gaseous-like state).

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PRE-NUCLEATION IN BIOMACROMOLECULE CRYSTALLIZATION STUDIED BY QUASI-ELASTIC LIGHT SCATTERING

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As crystallization limits the number of biological macromolecule structures accessible by X-ray crystallography, there is a growing need to better understand biomacromolecule crystallization and to replace trial-and-error methods by rational ones which could be routinely applied as diagnostic tests. In a given solvent (the precipitant agent in the terminology of biological crystal growth) the main point, never known at the present state of the field, is whether an ordered crystalline aggregate or a disordered amorphous precipitate is favored. To approach this problem, two easily crystallizable proteins, hen egg-white lysosyme (Mr 14000) and concanavaline A (Mr 25000) were chosen as model systems to investigate the crystallization process and quasi-elastic light scattering as the experimental probe.
The diffusion coefficient and the size of the scatterers were followed on 80 µl samples at 20 °C ; the concentrations of the macromolecules were in the range of 1 to 20 mg/ml and those of the precipitant agents (various salts) 50 mM to 2 M. Sets of experiments were performed under conditions in which proteins form crystals or amorphous precipitates. Different behaviors were observed in solutions leading to crystallization or to precipitation. In undersaturated solutions favoring crystallization (in the pre-nucleation state) the macromolecules remain in the native state, whereas in conditions leading to precipitation aggregation can be observed. The application of this method to macromolecules which have never been crystallized will be discussed.

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SURFACTANT ADSORPTION LEADING TO INTERFACIAL CONVECTION APPLICATION TO LIQUID LIQUID EXTRACTION

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Surfactant adsorption at liquid-liquid interfaces may induce interfacial convection if the characteristic parameters of the surfactant, the phases and the concentration range are conveniently selected.

The effect of this interfacial instability on liquid-liquid extraction, i.e. the transfer of a compound from one phase into another non miscible one is examined.

Two kinds of extraction are investigated:

-The first one is a transfer of a surfactant between oil and water. We show that the spontaneous convection is ruled by transfer processes (adsorption-desorption, diffusion, convection) as well as thermodynamic properties of the surfactant (desorption energy, partition coefficient). The experimental results are discussed in terms of Marangoni numbers, taking into account the diffusion /convection ratio and the adsorbability of the surfactant.

-The second is a transfer of a metallic ion from water to oil phase by means of a complexation chemical reaction with an extractant which is also a strong surfactant. The interfacial convection obtained is interpreted using a previously described model. The kinetics of the extraction for extractant concentrations below the c.m.c. is discussed according to the different transfer processes involved.

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THE MICELLE-VESICLE TRANSITION OF EGG PC AND OCTYLGLUCOSIDE: APPLICATION TO MEMBRANE PROTEIN RECONSTITUTION.

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The dissolution and formation of egg phosphatidylcholine (PC) vesicles by the detergent octylglucoside were examined systematically by using resonance energy transfer (RET) between fluorescent probes, turbidity, gel exclusion chromatography. Resonance energy transfer was exquisitely sensitive to the intermolecular distance when the lipid were in the lamellar phase and to the transitions leading to mixed micelles. Turbidity and gel exclusion measurements provided information about the aggregation of lipid and detergent. Several reversible discrete transitions between states of the PC-octylglucoside system were observed by RET and turbidity methods during dissolution and vesicle formation. These states could be described as a series of equilibrium structures that took the form of vesicles, open lamellar sheets, and mixed micelles. As detergent was added to an aqueous suspension of vesicles, the octylglucoside partitioned into the vesicles with a partition coefficient of 63. This was accompanied by leakage of small molecules and vesicle swelling until the detergent/lipid ratio reaches 1, for which turbidity increase as well as release of large molecules like inulin has been interpreted as stabilization of lamellar sheet size and vesicle opening. Turbidity maximum and sharp decrease of energy transfer corresponding to the saturation of lamellar sheets by detergent, are related to the lower boundary of a two phase domain where these aggregates coexists with micelles. Complete solubilization over the upper boundary occurs through a progressive micelle size reduction process. Occurence of an isotropic and viscous phase at detergent concentration close to the upper boundary limit for [PC]>2mM and relation between equilibrium and vesicle sizes are also discussed.

INTERFACIAL CHARGES MANIFESTATIONS : KERR AND DIELECTRIC CONSTANTS RELAXATIONS STUDIES IN A MICROEMULSION SYSTEM

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The interfacial charges behaviour of the individual droplets and the processes, at the early stage, of the pairwise aggregation remains not yet understood.

The original conjugation of the dielectric permittivity and the Kerr constant relaxation spectrocopies, in the range from 100 hz to 50 Mhz, have been investigated in a water/oil ternary microemulsion system, at low volume fractions with a special attention to the effect of the water to surfactant ratio contents.

After removing the d.c conductivity and the electrode polarization effects, the experimental dielectric dispersion shows the existence of three relaxations characterizing the Maxwell-Wagner polarization. They are thought to be due successively to the dielectric heterogeneity of the dispersive system, to the polarization of the counterions inside the water core and to the presence of a conductivite layer on the surface of the water droplets. Possible effects from the entrapped water, the water traces in the hydrocarbon shell and the transient dimer aggregates are discussed.

The complementary phase electric birefringence measurements yield the module and the phase spectrums of the Kerr constants in the same systems. They show two dispersions attributed to the presence of dimers and large anisotropic aggregates. Moreover a continuous sign reversal of the Kerr constant, as the droplet size decreases, suggests a collision-induced electric moment associated to a sign change of the polarizability anisotropy. In this two-body effect a local deformation of the interfaces associated to a charge redistribution is discussed.

These simultaneous experimental approaches should be extend to colloïdal dispersions offering a new quantitative picture to the aggregation mechanism.

BEHAVIOUR OF ARTIFICIAL LUNG SURFACTANT LIPOSOMES SPREAD AT THE AIR - WATER INTERFACE

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The L-α dipalmitoyl-lecithin - DPPC : L-α distearoyl - lecithin - DSPC : lecithin of soybean - Epikuron 200 (4:4:2) liposomes are spread at the air-physiological solution interface. The kinetics of spreading is studied by means of surface pressure, surface potential, rheological and electron microscopic measurements. A theoretical approach of the mechanism of the slow transformation of the closed bilayered structure into a surface film has been developed. The properties of the surface films formed after the spreading of the freshly prepared or aged liposomes are compared with the properties of the mixed DPPC:DSPC:Epikuron 200 (4:4:2) monolayers.

The obtained results are related to the exogenous surfactant therapy of the respiratory distress syndrome and the conditions of the administration of artificial lung surfactant liposomes.

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STRUCTURE AND DYNAMICS OF OIL-IN-WATER, WATER-IN-OIL AND "BICONTINUOUS" MICROEMULSION PHASES STABILISED BY DODECYLTRIMETHYLAMMONIUM CHLORIDE.

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Mixtures of cyclohexane and water containing the cationic surfactant dodecyltrimethylammonium chloride (DTAC) undergo the Winsor I - III - II phase progression on addition of increasing amounts of butanol. In this paper we describe the partitioning of the various components between the phases and derive the interfacial compositions of the different microstructures (ie. O/W, W/O and "bicontinuous") present in the microemulsion phases. The number of molecules of butanol per molecule of DTAC in the interface varies from 0.44 (for the O/W droplets) to approximately 13 (for the W/O droplets) when the NaCl concentration is 1.0 mol dm^{-3}. These values increase when the salt concentration is decreased.

We describe results obtained in the different phases using a time-resolved fluorescence (TRF) technique. This method allows the determination of the aggregation number of the colloidal particles and also provides information on the dynamics of solute transport within and between the aggregates. The measured aggregation numbers are in good agreement with those predicted using a simple geometrical model. The transfer of fluorescent probe molecules between W/O droplets is thought to occur via a process of droplet fusion and re-separation. The second-order rate constant for this process is found to be 5.5×10^9 dm^3 mol^{-1} s^{-1} at 50°C dropping to 3.5×10^9 dm^3 mol^{-1} s^{-1} at 30°C. The value at the higher temperature (close to the upper temperature phase limit) is close to the diffusion controlled limit.

The process of droplet fusion involves the formation of a "dumbell" shaped, partially fused intermediate with a region of highly curved surfactant monolayer in the connection between the two droplets. A simple method of modelling the fusion process in terms of the spontaneous curvature and rigidity of the surfactant monolayer will be outlined and the resultant predictions compared with experimental data. Understanding the kinetic phenomena in these systems in terms of measurable parameters of the surfactant monolayer (the spontaneous curvature and rigidity) is relevant to attempts to model the collapse of thermodynamically-unstable macro-emulsion systems.

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SMALL ANGLE NEUTRON SCATTERING STUDIES OF DILUTE MICELLAR SOLUTIONS UNDERGOING SHEAR

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ABSTRACT

A wide range of dilute anisotropically shaped micelles, aligned by couette shear flow have been investigated by small angle neutron scattering. The data is interpreted, using a recently developed theoretical description, in terms of particle size, size distribution, structure and confirmation. At high shear gradients we have observed the effects of polydispersity, and the onset of turbulence. At lower shear gradients we have observed effects due to hindered rotation of the rodlike micelles. Observations in the anisotropic scattering pattern attributable to varying degrees of rod flexibility are presented.

Emphasis will be placed on recent measurements on nonionic and mixed surfactant systems. The shear gradient and temperature dependence of scattering of nonionic micelles near the cloud point have been investigated. The data is consistent with a concomitant reduciton in rod length as the cloud point is approached. Measurements in the presence of electrolyte show changes over a wider range of the phase diagram. The scattering from a mixed cationic and nonionic surfactant system shows direct evidence for the coexistence of two differently shaped moieties. This observation of an equilibrium distributionof rodlike micelles and Lamellar droplets is only possible by virtue of the difference in the orientated coupling to a shear field of the differently shaped species.

Hydrocarbon gels formed from AOT reverse micelles: structure and reactivity

by

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As it has been descrisbed previously, macromolecules are solubilized in reverse micelles (1).

In the present case, gelatine is used as a guest molecule. At low gelatine concentration, a transparent solution is obtained.The data obtained from small angle x rays scattering and from kinetic measurements using hydrated electron as a probe show that the reverse micelles remains spherical and the protein is located at the interface. By increasing gelatine concentration , the micelles are more viscous and finally form a transparent gel as it has been previously described (2). From data obtained by pulseradiolysis and NMR experiments in hydrocarbon gels, it is concluded that bulk water is included in the gels and isooctane does not interact with the other components. From the phase digramm at various gelatine concentrations, it seems reasonable to conclude that water droplets are bounded by several gelatine chains. The syntesis "in situ" of CdS semiconductor shows the formation of " Q particles" with a very narrow distribution in size. The yield of reduction of viologen included in the gel is almost one order of magnitude higher than that observed in aqueous solution.

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PERCOLATION PHENOMENON IN WATER-FREE MICROEMULSIONS

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A water-free microemulsion (glycerol/AOT/isooctane ; molar ratio [glycerol]/[AOT] = 3.2) has been studied at T = 25°C as a function of the (glycerol + AOT) ϕ volume fraction. The measured properties are electric conductivity, dynamic viscosity and dielectric relaxation (Time Domain Spectroscopy).

An increase of conductivity σ and dynamic viscosity η are observed as the volume fraction ϕ increases. The quantities $d(\log \sigma)/d\phi$ and $d(\log \eta)/d\phi$ go through a maximum, as well as static permittivity ε_s. In the same time, the frequency ν_R of maximum loss go through a minimum. The dielectric relaxation may be fitted by a Davidson-Cole distribution of relaxation times.

The results are discussed within the framework of the theory of percolation. The minimum of ν_R at the percolation threshold (associated to the maximum of ε_s) confirms more specifically the theoretical prediction in the (poorly studied) domain of dielectric relaxation. The analogies with microemulsions of the water/AOT/oil type are also discussed.

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ELECTRIC BIREFRINGENCE STUDY OF DISPERSIONS OF PTFE RODS

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We have measured the static and dynamic birefringence induced by an electric-field pulse on a dispersion of PTFE rods having length of about 0.3 μm and diameter of about 0.15 μm. The rods are electrically charged. By using a pulse consisting of a train of square waves of variable frequency, we have been able to separate the contribution of the counterion cloud from that due only to form and intrinsic anisotropy of the rods. We have derived the Kerr constant as a function of the volume fraction of dispersed particles: the effect of electrostatic interactions is already important at volume fractions of 0.1%. By adding a few mM NaCl the counterion contribution is found to disappear.

The dynamics of electric birefringence appears to be controlled by the rotational diffusion constant of the individual rod, irrespective of the volume fraction and the added salt concentration.

COLLOIDAL CHARACTERISTICS OF POLYSTYRENE LATEXES PREPARED IN THE PRESENCE OF AMPHOTERIC SULFOBETAINE SURFACTANTS

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Although some of their physicochemical properties have been well described (particularly as a function of pH and ionic strength), a few studies dealt with the use of amphoteric surfactants in emulsion polymerization. Very recently, Kato et al reported on the emulsion polymerization of styrene using an amphoteric emulsifier of betaine type, and the relations between the properties of the emulsifier solutions versus and the properties of the corresponding latex particles. This work aims at giving information on some colloidal properties of polystyrene latexes prepared in the presence of three various amphoteric sulfobetaine surfactants (dodecyldimethylammoniopropane sulfonate (NC12), 3-N-acetyl-N- (dodecyl (or octadecyl) dimethylammoniomethyl) aminopropane sulfonate (respectively OXC12 and OXC18) in comparison with those obtained using sodium dodecyl sulfate (SDS) or in the absence of surfactants.

The micellar properties of all the emulsifiers have been first well characterized as a function of temperature, ionic strenght and pH. Emulsion polymerization of styrene at 70° C with $K_2S_2O_8$ as an initiator provides narrow size distribution latexes (Dw/Dn 1.05) with a large range of particle size (40 to 800 nm) depending upon the nature and critical micelle concentration of the emulsifier. Such a result was ascribed to the particle formation mechanism (and particularly the nuclation stage duration) as well as to the dynamics of the emulsifier adsorption on the latex particles. Recent data on this adsorption behavior are in favor of a strong interaction between those amphoteric sulfobetaine surfactants and particle surface.

It is noteworthy that such polystyrene colloids exhibit good stability behavior against monovalent and divalent electrolytes ($CaCl_2$ or $MgCl_2$) (as measured by a turbidimetric method). It is found that NC12-stabilized latexes are not stable at acidic or neutral pH, but very stable at high pH, whereas OXC18 provides an excellent stability in the whole range of pH (especially under acidic conditions). Rheological studies in a large range of shear rate showed that the OXC18-stabilized latexes display, at high solids (50 %), a lower viscosity than the other latexes, notably in the low particle size domain (200 nm) ; moreover stability against mechanical shear is also definitively better.

Electrophoretic mobility measurements have been carried out on cleaned-monodispersed polystyrene latexes covered to saturation with SDS, NC12, OXC12 and OXC18 so as to determine the variation of the zeta-potential as a function of pH and electrolyte concentration. Preliminary results seem to show that the potential of the amphoteric-stabilized latexes is lower than that of SDS ones, an indication that the good stabilization confered by these surfactants is not essentially ionic-type.

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ASPHALT EMULSIONS: KINETICS AND THERMODYNAMICS OF THE ADSORPTION OF CATIONIC SURFACTANT AT THE ASPHALT-WATER INTERFACE

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Cationic Asphalt in water emulsions are widely used for road construction and surfacing. The process optimization requires the emulsions to have, at first sight, opposite properties. High stability under storage conditions and either fast or slow, but in any case well controlled breaking behavior under application conditions. Besides, these systems are an interesting model for the basic study of emulsions because the high asphalt viscosity allows the system to afford some perturbations without readily producing coalescence.

In the present work the adsorption of cationic surfactants at the asphalt-water interface (A/W) is investigated. A number of emulsions have been prepared using a laboratory colloid mill. The shear rate, surfactant nature and initial concentration have been varied to obtain emulsions exhibiting different characteristics. The surfactants used were mono- and di- fatty amines, and quaternary ammonium salts in order to examine the effect of the surfactant stucture on the adsorption mechanisms.

Time dependence of adsorption has been studied through electrokinetic property changes entailed by surfactant bulk concentration variations. The typical characteristic time for adsorption is on the order of 2 hours, as compared to 40 hours for desorption. The adsorption process is reversible, and for a given surfactant, the adsorbed amount thus depends only on the equilibrium cocentration in the bulk. The adsorption isotherm exhibits a plateau which appears at an equilibrium value slightly below the C.M.C. This observation support the following conclusions. The surfactant affinity for the A/W interface is relatively low. The plateau values have been used to calculate the molecular packing area of adsorbed surfactants. The values are in the same order of magnitude as those determined from surface tension measurements. Electrokinetic potentials of asphalt droplets are related to the surfactant adsorbed at A/W interfaces through electrical double layer calculations.

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Interfacial Activity of 1-(2'-Hydroxy-5'-methylphenyl)-octane-1-one Oxime and the Interfacial Mechanism of Copper Extraction

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Interfacial tension isotherms were determined for model pure 1-(2'-hydroxy-5'-methylphenyl)-octane-1-one oxime at toluene/water and octane/water interfaces and used to discuss the kinetic data and the mechanism of copper extraction. Appropriate kinetic equations were derived for different versions of the interfacial process, in which the adsorption of the hydroxyoxime and the intermediate 1:1 complex was considered. Various adsorption isotherms, i.e. Gibbs, Szyszkowski, Frumkin, Temkin and polynomial, were used to determine the interfacial hydroxyoxime concentration. The association of the hydroxyoxime in the organic phase was considered.

The considered adsorption isotherms can be well matched to the experimental data. However, when used for the estimation of the hydroxyoxime interfacial concentration somewhat different results are obtained. This significantly effects the predicted values of the reaction order against hydroxyoxime concentration. The best agreement between predicted reaction orders and those determined experimentally are obtained for the interfacial process in which the slowest step is the reaction between adsorbed intermediate 1:1 complex and the hydroxyoxime molecule present at the sublayer from the water side. Moreover, the differences between reaction orders calculated from various adsorption isotherms are the smallest ones.

MIXED MONOLAYERS OF POLYPEPTIDES AT WATER/AIR INTERFACE

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Mixed monolayers of two polypeptides, poly γ poly γ methyl-L-glutamate (P γ MG) and poly-L-alanine (PLA) in the same α-helix surface conformation, are studied at the water air interface.

From a comparison of the experimental π-A isotherms with Huggins' theory and from the examination of the MIR spectra of PLA and PγMG, it is possible to deduce their interfacial disposition and their α-helix conformation.

The study of mixed monolayers allows to deduce the complete miscibility and the presence of α-helices of both the two polymers and their mixtures.

The hydrophobic nature of the attractive interactions in the PLA and PγMG mixtures has been demonstrated by applying the Joos' theory to the collapse pressures determined at the equilibrium conditions.

The kinetic study of collapse mechanism either of the two separate components or of their mixtures allows to conclude that the process consists essentially in nucleation and growth of a tridimensional phase and that also in the collapsed phase the two polypeptides are compatible.

ENZYME ACTIVITY AND CATION EXCHANGE AS TOOLS FOR THE STUDY OF THE CONFORMATION OF PROTEINS ADSORBED ONTO MINERAL SURFACES

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The maximum of adsorption of proteins at a pH near their i.e.p. is generally interpreted as an effect of a spreading of the protein onto the surface due to increasing intramolecular electrostatic repulsions at either side of the i.e.p., even at electrically charged interfaces. Against this interpretation we present experimental results showing that direct coulombic interactions between an electrically charged surface and a protein play a major role in the adsorption and the modification of conformation of the protein.

Two experimental approaches have been followed.

(a) A study of the effect of the pH and the ionic strength, and of different mineral surfaces (montmorillonite, talc, goethite) chosen for their electrical charge and hydrophobicity/hydrophilicity on enzyme activity of two β-D-glucosidases, a diminished activity indicating a departure from the active conformation.

(b) A NMR study of the exchange of paramagnetic charge compensating cations of montmorillonite on adsorption of bovine serum albumin which permits the measurement of the specific interfacial area occupied by the protein onto the clay mineral surface.

The results show that (i) below the i.e.p. the protein is adsorbed until saturation of the montmorillonite surface, the specific interfacial area increases and the adsorbed enzyme activity decreases with the decrease of pH ; (ii) above the i.e.p., when the pH increases, the surface coverage of the clay by the protein decreases but the specific interfacial area remains constant (bovine serum albumin) and the adsorbed enzyme reaches the same activity than the enzyme in solution (Aspergillus niger β-D-glucosidase) or decreases again after a maximum, but much less than below the i.e.p. (sweet almond β-D-glucosidase).

FLUORINATED AND HYDROGENATED NONIONICS IN AQUEOUS MIXED SYSTEMS

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Parallel investigations are currently performed on fluorinated and hydrogenated nonionics for which the hydrophilic chains are identical or similar (oxyethylene chains). But a further point of interest is then whether such hydrogenated and fluorinated compounds can combine to form mixed micelles, or mixed liquids crystals, etc... or whether each species prefers to remain in its own environment, as generally do hydrocarbons and fluorocarbons. This property depends on the chain length of both the hydrophobic and hydrophilic chains. In order to obtain information on this subject, we have combined several types of measurements : ternary phase diagram determinations, surface tension, X-ray and small angle neutron scattering measurements. Although not yet comprehensive interesting results show that, according to length of the chains of the fluorinated surfactants ($C_{12}EO_6$ was always chosen as the hydrogenated nonionic), the temperature and the ternary composition, many types of structures may be obtained, exhibiting phase behaviours roughly similar to those of ternary oil/water/nonionic surfactant. The precise structure of some micellar and crystalline mixed systems will be presented, as obtained from neutron and X-ray scattering investigations. For example, we have found that in the mixed lamellar crystals, the mean area per polar is a linear function of the overall composition of these systems. As a general rule, at a given temperature, mixed micelles are less ansisometric than pure $C_{12}EO_6$ micelles.

ADHESIVE SPHERE MODEL AND STRUCTURE OF COLLOIDAL SUSPENSIONS

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In a number of non-ionic surfactant-water systems, as well as in inverted micelles, the intermicellar interactions are presumably modelled by a hard sphere potential plus a very short range attractive tail. An idealisation of this potential model is obtained by defining an equivalent adhesive sphere (AS) potential. This equivalence is defined by the equality of the second virial coefficient of the two systems. Baxter has early shown that the main advantage of the AS model is its algebraical simplicity for the calculation of the fluid structure and pressure in the Percus Yevick (PY) approximation. Therefore it is appealing to consider the ASPY as a tool for the analysis of the data of the previous colloïdal systems. The present work is an analysis of the ASPY in order to check its validity with respect to the potential model. Two points are examined: the limitations implied by the equivalence between the potential model and the AS potential and the accuracy of the PY approximation with respect to the quasi-exact approximation MHNC. The potential models considered here are square well potentials of variable depth and width, with or without a repulsive barrier, so as to mimic chain interpenetration effects, hydration and/or water shell effects.

In this work we focus on the intermicellar distributions functions and on the small angle behaviour of the structure factor. The calculations are done at various volume concentration in the range 0-40%. The principal conclusions are: i) The PY theory agrees reasonably with the MHNC theory for the class of potentials considered. ii) The ASPY model leads to structure factors which are in good agreement with those calculated from the previous models if the width of the potential well and barrier does not exceed 10-15% of the hard core diameter of the micelles. Since the calculation of the structure factor of the ASPY is straightforward, this model can be useful for the analysis of x rays and neutron scattering data.

VISCOELASTIC SURFACTANT SOLUTIONS
-KINETICALLY CONTROLLED VISCOSITIES-

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KEYWORDS: surfactant, viscoelasticity, stress relaxation, kinetics

ABSTRACT: *Aqueous solutions of cationic surfactants with strongly binding counterions exhibit viscoelastic properties during flow. The rheological behavior of these gels can be described by only three parameters : the zero shear viscosity , the shear modulus and the stress relaxation time.*

The shear modulus increases monotonously with the square of the reduced surfactant concentration, which is in excellent agreement with theoretical predictions of percolation models.

The stress relaxation time is mainly controlled by kinetic processes, which are responsible for the aggregation behavior of the micellar particles.

The zero shear viscosity can be interpreted in the framework of simple mechanical models, which describe the dynamic properties of viscoelastic fluids.

RHEOLOGICAL PROPERTIES OF TWO-DIMENSIONAL MODEL NETWORKS

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KEYWORDS: percolation, elasticity, network, membrane, adsorption

ABSTRACT: *The tensio-active properties of acrylate and methacrylate diesters can be used to synthesize two-dimensional networks at the interface between oil and water. On irradiation with UV-light , a photopolymerization reaction occurs. We have studied the kinetics of surface gelation by measuring the two-dimensional shear modulus as a function of the reaction time. A two-dimensional sol-gel transition was observed which is in excellent agreement with theoretical predictions of percolation theories . The kinetics of polymerization and cross-linking can completely be interpreted in the framework of simple reaction schemes. The shear modulus of the two-dimensional films depends strongly on the surface concentration of cross-linking agent, which is a typical feature of rubber-elastic systems.*

IONS DISTRIBUTION AROUND CTAB/ALCOHOL MIXED MICELLES ACCORDING THE NONLINEARIZED PB EQUATION AND ITS RELATION WITH MICELLAR CATALYSIS

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It is already known that alcohols influence the micellar ionization degree and the aggregation number of CTAB micelles. These effects are different depending on the kind of alcohols.

In this communication we show the ionization degree and aggregation number results for the systems: CTAB simple micelles and CTAB/Alcohol mixed micelles (Alcohol: 1-butanol, 1-hexanol, 1-octanol, benzyl alcohol). Ions distribution around all of these systems micelles are studied on the basis of the nonlinearized PB equation with the cell model, using the values of ionization degree and aggregation number determined, and by considering the specific interactions of bromide ions with the micellar surface.

The kinetic results obtained for the basic hydrolysis of crystal violet in these system are studied on the basis of this treatment.

The micellar ionization degree has been obtained from conductimetric measurements and the micellar aggregation number from fluorescence spectra studies, using pyrene as a probe and cetylpyridinium chloride as a static quencher.

Description of Aisorption Equilibria on Type A Zeolites with Use of the Polanyi - Dubinin Potential Theory.

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Adsorption of water and methanol on type A zeolites was studied in the dependence on degree of sodium exchange for different cations and the adsorption isotherms were plotted. The isotherms were described initially with Dubinin-Astakhov /DA/ equation. Analysis of the adsorption data points out some limitations for studying the above adsorption systems with the DA equation. Correct descriptions were obtained using the modified Dubinin-Radushkevich-Stoeckli /DRS/ equation as well as equations of isotherms with the distribution function f/B/ other than Gaussian one. As it was stated, the parameter n in the DA equation has values within the range from 2 to 4. The determined equations parameters allowed to plot functions characterising the adsorption potentials of zeolites studied.

This work was supported in part by Polish Ministry of Education within Project CPBP 01.06.

A MONOLAYER STUDY OF THE INTERACTIONS OF AMPHOTERICIN B AND AMPHOTERICIN B METHYLESTER WITH STEROLS AND THEIR SELECTIVE TOXICITY

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The selective toxicity of polyene macrolide antibiotics for fungal cells is attributed to the greater sensitivity of membranes containing ergosterol than those containing cholesterol. To elucide the toxicity effects of polyene macrolide antibiotics more conclusively, the nature of the interactions of amphotericin B with cholesterol or ergosterol in monolayer were systematicaly studied. From the determination of the pressure versus area per molecule two principal results are obtained. The present data (1) suggest first the existence an amphotericin B : sterol complex of 2:1 stoichiometry, which have been speculated to form membranes pores increasing the permeability of the membrane, second the interaction between amphotericin B and ergosterol is larger than the interaction amphotericin B and cholesterol.It has been shown (2) that the sterol groups form with amphotericin B hydrogen bond. Using amphotericin B- methylester (the carbonyl group is esterified) the ability of forming hydrogen bond decreases. The results presented in this paper show an overall decrease of the magnitude of the interactions. However the interaction between amphotericin B- methylester/ergosterol is larger to that obtained using amphotericin B- methylester/cholesterol . These effects are probably due to hydrophobic interactions between sterol and polyene antibiotics in agreement with the previous 31P-NMR studies (3). The results of the studies elucidate more precisely the respective roles of the carboxyl- and amino groups of the polyenes as well as the role of the sterol structure.

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Monolayer of a water soluble protein such as cytochrome c

by

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Cytochrome C is a water soluble protein containing an heme group. Previously (1), it has been concluded from small angle x rays scattering and from kinetics treatments that , in reverse micelles cytochrome c is located at the interface of the micelles and act as the surfactant.

In this paper evidences are presentedshowing that cytochrome c, a water soluble protein, forms monolayers. The number of protein molecules forming the monolayer is time depend. For a given pressure, the number of molecules, at the water-air interface, remains constant . At relatively high pressure cytochrome c is redissolved in the bulk aqueous phase.

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SOME THERMODYNAMIC MODELS OF PROGRESSIVE MICELLIZATION SHAPE OF THE SURFACE PRESSURE CURVES AND PREDICTIONS ON THE DISTRIBUTION OF INTERMEDIATE AGGREGATES

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Several models of progressive micellization based on assumptions on the variation with the intermediate aggregation numbers of the equilibrium constants K_S for monomer inclusion reactions have been recently proposed. These models can explain variations of some experimental properties. However, some fail to predict the presence of a minimum and maximum in the distribution curve $c_S = f(s)$ which is largely accepted from the success fof the Aniansson et al's theory for explaining the behaviours observed in kinetic studies. Others cannot explain the shape of the surface pressure curves ($\Delta\gamma$ vs log c, c being the surfactant concentration, showing a sharp transition at the c.m.c., even the Kegeles' model which assumes a weak increase of K_S for the first values of K_S (for taking into account cooperativity) followed by a strong decrease up to s = N, N being the limiting aggregation number of micelles.

Several new models are presented. A sharp transition in the surface pressure curves is found when a strong increase of K_S is assumed. The limiting value of the surface pressure and the corresponding c.m.c. are strongly dependent on the limiting aggregation number. However, the only assumption of strongly accelerated aggregation cannot predict the accepted shape of the distribution curve. This is allowed in generalizing the Kegeles' model including the assumption of a strong increase of K_S.

This model predicts that the maximum surface excess of adsorbed surfactant deduced from the slope of the $\Delta\gamma$ vs log c curves before c.m.c. may be erroneous. The influence of the nature and concentration of the supporting electrolyte on these curves shown in another communication suggests that the accelerating effect is due to electrostatic interactions. The position of the extrema in the c_S vs s curves is strongly dependent on c, N and on the parameter characterizing the accelerating effect. This can be related to the conditions allowing rodlike micelle formation. The variation of c.m.c. with chain length is mainly explained by those of the activity coefficient of monomers in the solution bulk. A definitive model based on exact variations of K_S vs s should be probably based on evaluation of electrostatic interactions between intermediate aggregates and monomers.

ADSORPTION OF CETYLTRIMETHYLAMMONIUM AT THE FREE SURFACE AND AT THE MERCURY ELECTRODE

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Adsorption at the free surface from aqueous solutions containing a large excess of supporting electrolyte (KCl or KBr) was studied by measuring the surface tension γ. In the presence of KCl (0.5, 1 or 2 M), the surface tension curves (γ vs log c, c being the surfactant concentration) exhibit the usual behaviour with a sharp transition at the c.m.c. and log (c.m.c.) decreases in proportion with c_S, c_S being the salt concentration. This suggests that the adsorption energy as well as c.m.c. are affected by a salting out effect in the bulk. The decrease is smaller in the presence of KBr and the transition between the asymptotic behaviours at low and high concentrations is not so sharp (one decade). Given the widely accepted formation of rodlike micelles even at c.m.c. for C.T.A.B., the shape of the surface tension curves with KBr may be explained by the constancy of the stepwise aggregation equilibrium constant in a large range of aggregation numbers.

At the mercury electrode, at negative and weakly positive surface changes, the surfactant is not adsorbed at c smaller than c.m.c. but for higher concentrations bilayers are formed from adsorption of micelles. However, for concentrations higher than 50 c.m.c., γ tends to become constant, the transition being sharp with 0.5 M KBr and in a range of one decade with 1 M KCl. This transition may be ascribed neither to the spherical-rodlike micelle transformation nor to intermicellar interactions but to some stepwise process in the state of both kinds of micelles inhibiting their adsorption. This process is probably electrostatic in nature and could be due to a change in the degree of neutralization. Such an effect could not have been observed with other kinds of surfactants where monomers are similarly adsorbable at the free surface and at the uncharged mercury electrode.

CHARACTERIZATION OF W/O MICROEMULSIONS BY DSC

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In the present paper the attention is devoted mainly to the study of the etiology of the different thermal events recorded by Differential Scanning Calorimetry (DSC) of w/o microemulsion samples consisting of Hexadecane, K.Oleate, Hexanol and water in the proportions, by weight, K.Oleate/hexanol= 0.6 and (K.Oleate+Hexanol/Hexadecane)=0.68. To this aim, for given and fixed surfactant-to-cosurfactant mass ratios, (binary phase diagram), samples taken from the isotropic, transparent monophasic region of the ternary phase diagram (Hexanol-K.Oleate-Water), were studied. The DSC analysis was carried out on samples of well known composition and structure. The thermal events occurring in the lowest temperature range were investigated in detail.

Purpose of the study: to identify some specific DSC-characteristics that could be assumed as a thermal fingerprint of the w/o microemulsion.

Title: Adsorption of mixed micelles, surfactant and alcohol, on kaolinite and alumina.

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ABSTRACT

Solid-liquid adsorption from mixed micelle solutions have been studied by measurements of adsorption isotherms and electrophoretic mobilities. The influence of both type and concentration of alcohol on the adsorption of sodium dodecylsulfate and alcohol are investgated. The alcohols included are tert-, iso-, sec-, and n-butanol and tert-, sec-, and n-pentanol.

The paper discuss compative adsorption in mixtures of surfactant and alcohol. From aqueous solution these alcohols are not found to adsorb on kaolinite and alumina, as least within the accurancy of the applied analytical detection methods, but still the alcohols coadsorbs in the presence of surfactant. The extent of alcohol adsorption may far exceed the surfactant adsorption density. The alcohol adsorption density is found to reach a maximum near the surfactant cmc.

The plateau level surfactant adsorption density is measured as function of the alcohol concentration. By comparison of different alcohol isomers, the more water soluble alcohols have the strongest effect on the reduction of the surfactant adsorption density at plateau level (above cmc). At a given surfactant concentration below cmc, the adsorption density of surfactant is increased by increase in alcohol to surfactant ratio. The opposite trend is observed in the micellar region.

The electrophoretic mobility data show a complex variation with surfactant and alcohol concentration. The adsorption on the solid phase and also change in electrophoretic mobility is discussed in relation to change in thermodynamic properties and orientation of the molecules in the adsorbed layer.

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ON THE SPECIFIC INTERACTIONS BETWEEN SODIUM DODECYL SULPHATE AND CALCIUN OXALATE PARTICLES. CONTROL MECHANISMS OF THE CRYSTAL GROWTH IN THE PRESENCE OF ANIONIC SURFACTANT.

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Earlier investigations of the spontaneous precipitation of calcium oxalate monohydrate (COM) performed in the presence of sodium dodecyl sulphate (NaDS) /1/ have shown pronounced inhibitory effect of NaDS on the overall crystallization process. NaDS acted as a nucleation modifier also, by favouring the formation of calcium oxalate dihydrate (COD) in a systems where without additive COM was normally found.

In this work further analysis of the kinetic precipitation data with the aim to distinguish between the possible crystal growth controlling mechanisms (surface adsorption, diffusion and/or integration in a crystal laticce) is given. Calculations are carried out according to the theory of crystal growth mechanisms proposed by A.E. Nielsen /2,3/.

The results of the NaDS adsorption on COM particles are discussed too.

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Clay chemistry - an essential aspect in understanding landslides

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Investigations in recent years have shown that many of the processes at work in nature and leading to unstable areas are of chemical character. In order to avoid unexpected catastrophes originating through such causes, it is necessary to be completely familiar with the kind of reactions involved. To the author's knowledge, very few studies have been made to examine natural chemical processes. Although it is well-known that clear-cutting of woods on slopes leads to erosion and slides, very little is known about the chemical changes that such interference implies. Rain dripping from trees has a very complex composition, containing amino acids and polyphenols which interact with the double layers of soil particles. The author has studied different aspects of the colloid-chemical reactions at work in nature, such as electrical conductivity and capacity, self-potentials and rheology. Areas exposed to slides are often of a special chemical character. The clay is affected by dispersing agents and surfactants which make it more fluent. The clay in areas where slides are likely to occur is often dilatant and subjected to rheopexy. The soil may be attacked either by infiltrated natural substances or by man-made substances such as detergents. The kinetics of the active reactions are practically unknown and it is usually believed that reactions affecting stability take place over thousands of years. However, the literature indicates that at least heavy rainstorms accompanied by electrical discharges can cause dangerous changes almost instantly. This work describes a study to follow up changes observed under different climatological conditions. In particular, the influence of infiltrated detergents from leaking sewage lines is treated.

PHASE BEHAVIOUR OF CATIONIC LIPOAMINOACID SURFACTANT SYSTEMS

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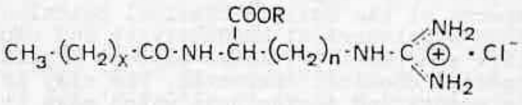
ABSTRACT

Alkyl esters of long chain basic aminoacids are known as cationic surfactants which have a very good solubility in water, many of them possess antimicrobial properties and are generally considered milder and less irritant than other surfactants.

Long chain N^{α}-acyl-L-α-amino-ω-guanidine alkyl acid derivatives with the general formula:



$$CH_3\cdot(CH_2)_x\cdot CO\cdot NH\cdot \overset{COOR}{\overset{|}{C}}H\cdot(CH_2)_n\cdot NH\cdot C\begin{smallmatrix}\nearrow NH_2\\ \oplus\\ \searrow NH_2\end{smallmatrix}\cdot Cl^-$$

have recently been synthesized (1). Physico-chemical and antimicrobial studies of these compounds as a function of the alkyl ester or sodium salt (R), the straight chain length of the fatty acid residue (x) and the number of carbons between the ω-guanidine and α-carboxyl group (n) were carried out (1). Among the different aminoacid surfactant derivatives synthesized, the methyl ester of N^{α}-Lauroyl Arginine (LAM) showed higher activity on both surface and antimicrobial properties.

In addition, some fundamental studies on their phase behaviour in binary and multicomponent systems have been undertaken. The phase equilibria has been determined by optical microscopy, X-Ray diffraction, and NMR in the binary water/LAM and ternary water/LAM/alkanol systems. Solubilization of nonpolar compounds such as hydrocarbons has also been investigated.

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CRYSTAL GROWTH OF LEAD FLUORIDE FROM CONSTANT COMPOSITION SUPERSATURATED SOLUTION. II.THE EFFECT OF Pb/F ACTIVITY RATIO ON THE KINETICS OF CRYSTAL GROWTH

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The rate of crystal growth of lead fluoride has been studied as a function of the activity ratio $(a_{Pb^{2+}}/a_{F^-})$, pH (from 4.0 to 7.0) and ionic strength (as determined by the concentrations of constitutive ions, as well as by the electrolyte addition, KNO_3). Using a potentiometric constant composition method[1] to maintain the level of supersaturation during the course of reaction, the rate of growth of seed crystals (orthorombic α-PbF_2) in aqueous solution at 25°C, has been determined both by analysis the potentiometric data and by analysis the kinetic particle size distribution data (PSD, Coulter Counter technique) as well. Two quite different mechanisms of growth have been revealed depending on which of the component is in excess in supersaturated solution used for growth, either lead nitrate (at a given pH = 4.0 - 5.0) or potassium fluoride (pH = 5.0 -7.0). As it has been established previously, the composition of the supersaturated solution influences the shape, size and PSD of crystals[2], as well as the kinetics of crystal growth, what will be presented in this communication.

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INFLUENCE OF WATER-SOLUBLE POLYMERS - NEW FLUOROCHEMICAL SURFACTANTS INTERACTION UPON EXTINGUISHING EFFICIENCY OF MULTI-PURPOSE FOAM COMPOUNDS.

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The addition of natural, semi-synthetic or synthetic water-soluble polymers in the formulations of fire-fighting foams allows to increase the retention power of water inside foam bubbles but particularly to obtain multi-purpose extinguishing foams, that is, efficient foams just as well on polar liquids (alcohols, ethers, esters, acetone, aldehyde...) than on hydrocarbons fire.

For a long time, the multi purpose foam compounds have been considered as avant-garde products regard to other existing foams : protein, fluoroprotein, synthetic or AFFF which are used only on hydrocarbons fire. But now the multi-purpose foam compounds know a rapid development for two main reasons : the first reason is that the number of various chemical products increases everyday a little more and that their stocking represents a real danger because generally it is difficult to extinguish these products. The second reason is that the new fuels which appeared on the market contain a certain percentage of polar compounds like for example methyl tertiobutyl ether or tertiobutyl alcohol or are completely substituted by alcohols.

Until now, for resisting sufficiently against polar liquid fires, the foam concentrates had to contain a high polymer concentration, but unfortunately this resulted in a considerable decrease of the viscosity, leading to a difficulty of using in the ordinary installations.

The structural modification of polymers by a synthetic fluoroalkylating agent like for example a perfluoro-alkylated polyamine allowed at once to decrease considerably the polymer content and so the viscosity of concentrate, and to obtain an excellent extinguishing power for the multi-purpose foam compounds.

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Polynomial Approximation of Interfacial Tension Isotherms and its Use for Kinetic Data Interpretation of Metal Extraction

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It is now assumed that the reaction between metal ions and hydrophobic extractants proceeds at the interface and depends upon the surface concentration of extractant molecules. Hydrophobic extractants adsorb at the organic solvent/ water interface and decrease effectively the interfacial tension.

The relationship between the interfacial tension (Y) and the extractant concentration (x) can be presented in form of the polynomial:

$$Y = a_1 + a_2x + a_3x^2 + \dots, \tag{1}$$

where a_1, a_2, a_3 are appropriate constants and x can be either the surfactant concentration (c) or log c.
The surface excess (Γ) equals thus:

$$-RT\Gamma = a_2 + 2a_3x + 3a_4x^2 + \dots . \tag{2}$$

The interfacial extraction process can be described as follows i.e. for M^{2+}:

$$2BH_o = (BH)_{2\,o} \tag{3}$$

$$BH_o = BH_{ad} = BH_{int} \tag{4}$$

$$M^{2+}_{int\,w} + BH_{ad\ or\ int} = MB^{+}_{ad\ or\ int} + H^{+}_{int\,w} \tag{5}$$

$$MB^{+}_{ad\ or\ int} + BH_{ad\ or\ int} = MB_{2\ ad\ or\ int} + H^{+}_{intw} \tag{6}$$

$$BH_{2\ ad\ or\ int} = BH_{2\,o} \tag{7}$$

where BH is the extractant molecule, M^{2+} stands for the metal ion, subscripts o and w denote the molecules in the organic and water phases, respectively, and subscripts ad and int denote the molecules in the adsorption layer and sublayer, respectively.

If diffusion is neglected various kinetic equations are obtained for different reactions assumed as the slowest steps. For $[M^{2+}]_w$=const and $[H^+]_w$=const they can be rearrange to simple expontional equations of the following type:

$$\vec{r} = \vec{k}\,[BH]_o^n\,\Gamma^m \tag{8}$$

where $\vec{r}$ and $\vec{k}$ are the reaction rate and rate constant for the forward extraction, and n and m are appropriate coefficients, different for various mechanism versions.

Appropriate program was written for IBM PC microcomputer and used to simulate extraction rates and reaction orders against extractant concentration for different hydroxyoxime extractants.
An agreement with experimental kinetic data is observed as interfacial process with the formation of the stable 2:1 complex from the intermediate complex 1:1 and the extractant molecule present at the sublayer is considered as the slowest one.

Fast collapse respreading of phosphatidylcholines monolayers. Model of pulmonary surfactant.

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Several superficial compositions of disaturated and unsaturated phosphatidylcholines are studied on compression-expansion cycles with a Langmuir trough.

The past collapse respreading characteristics of the monolayers , compaired with the behaviour of the natural bovine lung surfactant are changed with the ratio of the unsaturated lecithins and with the transition temperature of the mixtures .

Structures of Hydroxy-aluminum / silica flocs : relationship with hydroxy-aluminum flocculant structure .

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The flocs studied were obtained by rapid-mixing , at pH 4.5-5.0 or 7.0-7.5 range , silica colloids suspension (0.8% w/w) with 1) Al_{13} polymers in isolated or aggregated state following the initial hydrolysis ratio $X = (OH)_{added} / (Al)$, 2) an industrial hydroxy aluminium chloro - sulfate : WAC (ATOCHEM).The flocs obtained versus Al/Si ratio were studied through Electrophoretic mobility (E.M) , settling velocity , turbidity and Small - Angle X-Ray Scattering (S.A.X.S) .

The mechanisms of flocculation essentially depend on pH of the mixing reaction .In acidic pH range , charge neutralization mechanism is involved : the optimum flocculation concentrations (o.f.c) correspond to E.M = 0. At neutral pH range , charge neutralization and bridging take place : o.f.c correspond to E.M < 0.

At these different pH , the organization and density of flocs were determined using S.A.X.S technique .The experimental power laws (one decade) were interpreted from the fractal theory and the fractal dimensions (D_f) calculated from the slope of LogI(Q) vs Log(Q) plots. The density of flocs was determined from the distance distribution function P(r) vs r yielding the silica colloids number in flocs per experimental unit volume .The largest D_f and density are obtained with $Al(OH)_{2.5}$ flocculant (small open aggregates of Al_{13} in fractal assembly with $D_f = 1.43$). The $Al(OH)_{2.6}$ flocculant (big and close aggregates of Al_{13} in fractal assembly with $D_f = 1.8$) yielded loosest flocs formed by aggregating small 2-4 silica particles aggregates . The large scale structure of these last flocs was not accessible . Settling velocity (~floc size) and density oppositely vary and depend on the structure of the flocculants . WAC flocculant yields the largest flocs with the lowest density and fractal dimension .

Aluminum flocculants act as organic cationic polyelectrolytes .Highly prehydrolyzed flocculants are not extensively hydrolyzed during dilution or pH variation and the initial structure and size are conserved .

STRUCTURE OF COLLOID SPECIES IN PARTIALLY HYDROLIZED IRON NITRATE AND CHLORITESOLUTIONS

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The hydrolysis by NaOH of Iron (III) in dilute acid solutions is studied through the structure of colloid species by using Small Angle X-Ray Scattering. These structures are studied as a function of hydrolysis ratio : $R = [OH]/[Fe]$

Owing to the fact that the solutions are typically far for equilibrium, the experiments were performed in kinetic conditions.

Samples:

In the first series the polycations have the composition $Fe(OH)_R(NO_3)_{3-R}$ with $R = 1.0 ; 1.5; 2.0; 2.2; 2.5$ and 3.0.

In the second series the composition is given by $Fe(OH)_R Cl_{3-R}$ with $R = 1.0; 2.0$ and 2.5.

The S.A.X.S. data analysis was performed by fitting the experimental curves with computed ones which are based upon aggregation models.

Results:

In both types of solutions the evolution of species as function of R can be defined in 3 steps :

1. Growing of polymeric clusters until $R = 2$,
2. Cluster-cluster type aggregation forming poorly ramified chains. These aggregates are typically more linear than the ones observed for hydrolysis of Al-chloride (Axelos *et al.*, 1986).The Fe species are similar to the aggregates which were theoretically built by (Mors *et al.*, 1987) taking into account high dipolar interactions.
3. The third step consists in cluster-cluster aggregation of the chains.

The local structures of the species and their evolution as a function of R are discussed from calorimetry measurements, U.V. absorption and X-Ray absorption spectroscopy results (Combes *et al.*, 1988).

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INTERACTION OF METALLIC CATIONS WITH THE HYDROUS

(α - FeOOH) SURFACE

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The roles of pH and surface charge in affecting metallic cation behaviour (adsorption-desorption) at the oxide-water interface was studied with complementary methods allowing comparison among the results.

The model systems studied included a well-known synthesized iron oxide (goethite) and Cd, Cu and Pb used in the same form as the background electrolyte (NO_3^- or ClO_4^-).

Measures of the interfacial electrical properties of the goethite, in absence and in presence of metallic cation were obtained from microelectrophoretic mobilities and compared with the ones derived from potentiometric titrations. The more classical solution depletion method was used to calculate the adsorbed and desorbed amounts of heavy metals at the adsorption equilibrium in function of pH ; furthermore the total number of -OH sites was determined by conductometric titrations in absence of background electrolyte.

The main results showed that

- the isoelectric point (iep) of the goethite (microelectrophoresis) was comparable to the point of zero charge (pzc) (potentiometry) in absence of specific ion adsorption

- the shift of the iep towards higher pH values in presence of each metallic cation was confirmed by the shift of the pzc towards lower pH values, indicating a specific adsorption ; desorption experiments showing the same trends, irrespective of the metallic cation the desorption is not entirely reversible

- the adsorption of metallic cation increased with the increase in pH of the suspension and took place even when the surface charge is positive.

ORIENTATION OF ROD-LIKE SURFACTANT AGGREGATES IN A NON AQUEOUS PHYSICAL GEL

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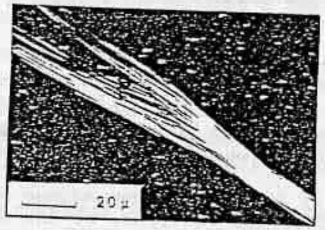
We study the physical gels obtained by aggregation of a steroid derivative in cyclohexane. The amphiphilic steroid molecule can give infinite rod-like aggregates by a multiple hydrogen bonding process. At a critical filamentary concentration viscoelastic gels are obtained through a sharp sol-gel threshold. We present here some preliminary results concerning rod orientation effects in this system.

Long range orientation order is observed in concentrated gel samples as a consequence of excluded volume effects. Typical Schlieren optical textures characterize nematic-like domains in the samples. Anisotropic small angle neutron scattering patterns are observed. The solid xerogel, limit case of highly concentrated systems, is found to be a new mesomorphic state which can be obtained only from the solution gelation route as demonstrated by a calorimetric analysis.

The use of strong magnetic fields during the steroid aggregation kinetics can give strikingly higher order parameters. The initial state of these experiments is always a diluted sol phase. A slow steroid aggregation reaction gives rise to a slow viscosity increase of the sol phase and allows the reorientational motion of the rod-like aggregates. The cooperativity of the steroid aggregation reaction and the additivity property of the diamagnetic susceptibility tensor can balance thermal motion to give highly oriented bundles of fibres.



An oriented xerogel is obtained from demixion of the unstable gel phase. This behaviour is in qualitative agreement with theoretical prediction concerning rigid rod-like polymers in solution. Polarizing optical microscopy, magnetically induced optical birefringence and two dimensional small angle neutron scattering patterns are used to detect the highly anisotropic states.

Besides the thermodynamical and structural interests of the nematic gels, the feasibility of such alignment experiments is correlated with structural features of the molecule and the surfactant aggregate.

LIQUID CRYSTALLINITY IN METAL ION - DODECYLBENZENESULPHONATE SYSTEMS. X-RAY DIFFRACTION CHARACTERIZATION

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Phase behaviour and liquid crystal structure of alkaline earth and transition metal dodecylbenzenesulphonates have been investigated by polarization microscopy and X-ray diffraction. Interplanar distances in the smectics exhibited the differences (D/Å between 35 and 18). It can be assumed that the structures of the lamellar layers have been influenced by the different possible reasons, i.e. the hydration of individual metal ions within the water layers, the depression of water layers, the depression of paraffin layers, the tilting of paraffin layers. The types of lamellar organization in the crystalline phases, crystallized from ether or from water solutions, remain smectics with the rigid structure of smaller interplanar distances than that in liquid crystal state.

STRUCTURE-FUNCTION STUDY FOR HEMOLYTIC AMPHIPHILIC PEPTIDES: PHYSICAL PROPERTIES OF ANALOGUES OF DELTA-TOXIN FROM STAPHYLOCOCCUS AUREUS.

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Several analogues of delta-toxin have been synthesized in order to study thoroughly the relation existing between its amphiphilicity and its biological activity. On one hand, two fragments of natural delta-toxin were available: the 1-11 segment (which displays no hemolytic activity) and the 11-26 segment (hemolytic); on the other hand, hexacosapeptides whose sequences had been rationalized, exhibiting their single tryptophan residues at different positions (Trp5, Trp15 and Trp16). Moreover, a fmoc 1 (fluoren-9-ylmethoxy carbonyl) Trp5 peptide has been synthesized, allowing to investigate what could occur at the N-terminal position. The amphiphilic balance of the natural toxin, as calculated using Eisenberg's method [1], has been conserved for all the analogues.
The interaction between peptides and lipid vesicles, or micelles has been followed by fluorescence changes in the quantum yields and the maximum emission wavelength of Trp, due to the variation of the position of the reporter group. A simple two-state (free/bound) binding model with an association constant and a defined number of lipids per binding site cannot account for the observed results. Analysis of the data is made assuming partition into the membrane and a different peptide autoassociation both in solution and bound to lipids.
Circular dichroism experiments afforded to control the alpha-helix structure of some analogues.
Quenching experiments were carried out with fatty acids and phosphatidylcholine lipids labeled with nitroxide group at different positions in order to investigate the topology of bound peptides as a function of bilayer depth.
Our results are discussed within a model of an amphiphilic alpha-helix, whose hydrophobic groups face the apolar core of bilayers whereas the hydrophilic ones face a more hydrophilic environment.

[1] D.Eisenberg, R.M.Weiss and T.C.Terwilliger (1982), Nature, vol.299, pp. 371-374.

A surfactant system with irredescent colours.

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Swollen lamellar phases with very large spacings have been of considerable interest very recently. [1] It was possible to increase the interlamellar spacing by swelling with water up to 1000A. [2] We report on a system for which the spacings can be expanded to several thousand A. As a consequence the solutions show bright irredescent colours when solutions are illuminated with white light against a dark background. The system consists of the zwitterionic surfactant Tetradecyldimethylaminoxide in the presence of some cosurfactant and smallamounts of hydrocarbon.

The system can be swollen with water up to a water content of 0.99 without loss of the liquid crystallinity. The systems are thermodynamically stable and the irredescent colours reappears after the order has been destroyed by shaking the solutions. It is believed that the large spacings are due to electrostatic forces between the surfactant layers. The charges on the layers are due to protonation of the aminoxide groups by water. The existence region of the irredescent phase as a function of surfactant, hydrocarbon and cosurfactant will be reported. The spacings for the phases were determined from light transmission measurements.

1. F.C. Larche, J. Appell, G. Porte, P. Bassereau, J. Marignan
Physical Review Letters 56, 1700, 1986

2. G. Porte, J. Marignan, P. Bassereau and R. May
J. Physique 49, 1988

ADSORPTION-INDUCED ELECTRON TRANSFERS IN SPINEL IRON OXIDE COLLOIDS

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Phenomena involved in acid-base reactions at the surface of metal oxide colloids are usually independent of the bulk and remain confined into the particle periphery. Modulation by the bulk may however be expected in the case of mixed valency. We show that close interplay of bulk and surface properties actually occurs in colloidal spinel iron oxide (10nm): electron delocalization in the bulk makes surface reactions able to drive redox phenomena over the whole particle.

The colloid behaviour was investigated in various anaerobic aqueous conditions by protometry and kinetically. The evolution of the particle structure, size and surface state was characterized by Mössbauer spectroscopy as well as X-ray diffraction and electron microscopy.

Surface protonation or Fe^{3+} adsorption in weakly acidic medium (pH 2) leads to the conversion $Fe_3O_4 \rightarrow \gamma Fe_2O_3$. That can also be produced by adsorption of non constitutive species such as Ag^+ (pH 4). The mobile electrons are driven out of the particle as released Fe^{2+} ions, or transferred to Ag^+ leading to colloidal metallic silver. The oxide particle becomes similarly iron deficient, but the surface evolves distinctly, with leaching, strong disordering or slight extension.

With adsorption of $Fe(OH)_3$ (pH 9), Fe^{2+} is not desorbed. The mobile electrons remain trapped in the colloid and induce the growth of a spinel layer.

Electrons can be reinjected by readsorbing Fe^{2+} (pH 5) onto the γFe_2O_3 colloid. However, conversion back to Fe_3O_4 is not obtained, the structure remaining largely understoichiometric. Instead, a Fe_3O_4 layer grows epitaxially on the particle while extra electrons are pumped in, probably with simultaneous diffusion of protons to keep the electroneutrality.

The results clearly demonstrate that spinel iron oxide colloids can be used as an electron exchanger.

STRUCTURAL CHANGES INDUCED BY TRITON X-100 ON SONICATED PHOSPHATIDYLCHOLINE LIPOSOMES

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The study of surfactant effects on model and biomembranes is important from the point of view of molecular interactions as well as for biochemical technology. We have recently examined the consequences of adding the non-ionic detergent triton X-100, both at sublytic and lytic concentrations, to multilamellar vesicles phosphatidylcholine liposomes. In the present work we intend to described the complex structural changes of sonicated phosphatidylcholine liposomes in the presence of Triton X-100. We have combined ultrastructural and light-scattering observations with studies on the liberation of vesicle contents, and evaluated the incorporation of radioactive Triton X-100 to phospholipid bilayers and mixed micelles. As a result we can get a more detailed picture of the interaction of detergents with unilamellar liposomes. This may have important implications in view of the potential use of sonicated phospholipid vesicles as drug carriers, since the extracellular body fluids contain natural amphiphile that may act in a similar way as synthetic surfactants.

Solubilization of sonicated unilamellar vesicles starts at low detergent concentration, as compared to the case of large vesicles, and is accompanied by the simultaneous repid formation of large multilamellar liposomes. Measurements of lipid and detergent distribution indicate that, at a 1:1 lipid:detergent mole ratio, about one-third of the lipid, with most of the detergent, is solubilized in the form of mixed micelles. The remaining two-thirds are in the form of multilamellar liposomes, virtually free of detergent. Higher detergent concentrations also bring about the solubilization of these liposomes.

PERFLUOROPOLYETHER MICROEMULSIONS

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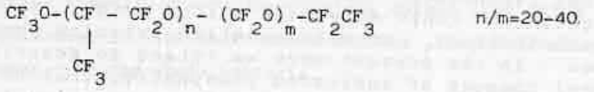
Perfluoropolyethers (PFPE) are fluorinated polymeric fluids having the general formula:



$$CF_3O-(\underset{CF_3}{CF}-CF_2O)_n-(CF_2O)_m-CF_2CF_3 \qquad n/m=20\text{-}40$$

The ethereal bonds in the polymer chain have a strong influence on the conformational freedom of the molecules without significantly affecting the typical hydrophobic properties of the fluorocarbons.

Unlike the other perfluorocarbons, PFPE compounds remain in the liquid state in a very broad range of average molecular weights and temperatures.

Binary, ternary and quaternary phase diagrams have been investigated in the thermal range (283-353)K, for several proportions of the components: PFPE surfactants, PFPE oils, PFPE or hydrocarbon alcohols, and water.

Surface tension and interfacial tension measurements have been performed to investigate the role of both surfactant and alcohol.

Isotropic, transparent systems have been obtained both in the oil and in the water rich regions of the quaternary phase diagrams. The formation of the latter systems was found to be spontaneous, independent of the order of addition of the components and reversible with respect to phase-separation induced by temperature changes.

The above results support the hypothesys of the existence of PFPE microemulsions. Structural investigations are in progress to characterize the system.

NEUTRALIZED SURFACTANT PAIR DOMAINS IN POSITIVELY CHARGED VESICLES. MODELING OF MOSAIC MEMBRANE ORGANIZATION §

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Cosonication of dioctadecyldimethylammonium bromide (DODAB) and $[CH_2{=}CHC_6H_4CONH(CH_2)_{11}O][n\text{-}C_{16}H_{33}O]PO_2^-$ (VBAP) led to the formation of long-lasting, closed-bilayer vesicles. The results obtained from quasi-elastic light-scattering, freeze-fracture electronmicrographs, and ^{31}P-NMR supported the existence of vesicles containing VBAP-DODAB surfactant ion pairs in the matrix of the positively charged bilayer membrane. The observed data, supported by absorption spectroscopy, as well as the phase transition behavior were best accommodated in terms of a model which required aggregation of the VBAP-DODAB ion pairs in rippled phase domains of the membrane. The domain formation was found to depend on the amount of neutralized ion pairs. Investigation of the electrokinetic behavior by electrophoretic light-scattering revealed cooperative ion binding onto the neutralized surfactant pair domains. Such model structures can be linked to the "mosaic" organizations prevailing in biological membranes.

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§ Support of this work by the National Science Foundation and the Army Research Office is gratefully acknowledged.

INFLUENCE OF HYDROGEN/DEUTERIUM ISOTOPE EFFECT ON THE CRITICAL PARAMETERS OF POLYSTYRENE/CYCLOHEXANE

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Experiments with poly(protostyrene) (molar mass 3 105 g mol^{-1})/cyclohexane and poly(protostyrene)/cyclohexane-d12 mixtures are carried out to determine the critical parameter of these systems. It is found that the value of the critical composition and the value of the critical amplitude of local concentration fluctuations determined by static light scattering experiments is not influenced by the H/D exchange. However, the critical temperature of the system poly(protostyrene)/C_6H_{12} is higher by about 4 K than that of the system poly(protostyrene)/C_6H_{12}. These findings will be compared with results of studies of the hydrogen/deuterium isotope effect in binary critical mixtures of small molecules.

INFLUENCE OF HYDROGEN/DEUTERIUM SUBSTITUTION ON THE CRITICAL PARAMETERS OF BINARY MIXTURES

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A review will be given about the influence of a hydrogen/deuterium substitution on the critical parameters (critical composition, critical temperature, correlation length of local concentration fluctuation) of binary mixtures with miscibility gap (binary mixtures of small molecules, polymer solution and polymer blends).

The Ionic Correlation Contribution to the Free Energy of Spherical Double Layers.

by

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and
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Abstract.

An estimate of the ion fluctuation contribution to the free energy for a dispersion of spherical macroions, without additional salt, is made using the Cell Model. The Poisson-Boltzmann approximation is used to estimate the linear response in a given cell, which together with second order perturbation theory allow us to calculate the free energy of interaction between a pair of cells. As well, an infinite order theory is developed. We find excellent agreement with simulations for monovalent counterions, the comparison becoming poorer for more strongly coupled systems. A cubic lattice of cells is studied, modelling a macroionic dispersion. The fluctuation contribution is shown to be several orders of magnitude larger than the usual quantum dispersion forces. However it plays a minor role in the thermodynamics of the lattice.

USE OF MICROEMULSION SYSTEMS AS MEDIA IN HETEROGENEOUS ENZYMIC CATALYSIS

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Lipases catalyze specifically the cleavage of triglycerides to free fatty acids and glycerol. Depending on the reaction media, these enzymes can also be used to catalyze the synthesis or the trans-esterification of some specific triglycerides. These reactions are heterogeneous, taking place at interfaces and they can be performed in water-in-oil microemulsion systems under mild conditions. This approach can provide informations about the interactions between protein molecules and the surfactant membrane separating the oil/water phases. These interactions can have dramatic influence on the enzymic activity.

The nature of the microemulsion used is crucial i) in controlling the equilibrium of the reaction from hydrolysis to condensation, depending on the water content; ii) for differencies of the solubilization site and catalytic action of the enzyme hosted in the dispersed aqueous phase, the structure of which depends on the surfactant used.

In the present work we have studied the catalytic behavior of lipase from *Rhizopous delemar* in the direction of hydrolysis by using AOT anionic, CTAB cationic and $C_{12}EO_4$ nonionic microemulsion systems. Various parameters of the enzymic reaction (such as K_m, pH optimum, T-optimum, water content) were studied in these different systems. The results show that in the AOT system the activity of the enzyme is higher compared to the other systems.

In relation to the enzyme activity the conformational state of the protein molecule in the microemulsion system was also studied by using various spectroscopic probes.

INSTABILITY OF BILAYER MEMBRANES IN EXTERNAL ELECTRIC FIELDS.

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Instability criteria for bilayer membranes are found. The membranes are modeled as transversely isotropic continuous media. Two mechanisms of membrane instability are considered. 1. Membrane instability can be a result of an increasing of area per lipid molecule when isotropic tension along membrane surface is applied, or when there is a compression in transverse direction. 2. Destabilization of membrane following the fluctuation-wave mechanism. In this case membrane instability is due to increasing of a compression in local regions, when membrane thickness changes.

The results are applied to find membrane instability criteria in external electric field. It is shown that critical voltage for second mechanism is lower than that for the first one. Hence membrane instability for low voltages follows fluctuationwave mechanism. Membrane destabilization mechanism for high voltages depends on its viscosities.

Membrane elastic and viscous properties are characterized for membranes with biological interest (red blood cell and pea protoplast membranes).

This work was supported through Grant No 189 from the Ministry of Culture, Science and Education.

PHASE BEHAVIOUR OF CONCENTRATED BINARY DISPERSIONS

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It is well known that suspensions of monodisperse colloidal particles exhibit a fluid-solid transition at sufficiently high concentrations. We have investigated the phase behaviour of concentrated suspensions of sterically stabilised poly(methyl-methacrylate) spheres. In non-polar solvents, these particles interact with a 'nearly hard sphere' repulsive potential and show the phase transitions: Colloidal fluid → colloidal crystal → colloidal glass predicted for a hard sphere system. Furthermore by using a suspension medium chosen to nearly match the particle refractive index, the particle arrangement and dynamics in the bulk of each of these phases can be inferred from light scattering measurements.

In recent work we have investigated the phase behaviour of concentrated binary dispersions. Each particle fraction has a significantly different mean radius combined with a low value of radius polydispersity. Direct observation has provided phase diagrams and the crystal structures have been determined by light diffractometry. In the poster we shall compare these experimental results with recent calculations on the freezing of hard sphere mixtures.

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