Direct measurement of interactions in supermolecular fluids and liquid crystals

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Abstract - The understanding of the nature of the interactions between amphiphilic aggregates or within the assemblies of the molecular architecture is of fundamental importance. Direct measurement of forces between two unsupported self-assembled aggregates in solution is a formidable task. A new application of the surface force apparatus demonstrates that the interactions operating in micellar solutions or in a stack of membranes, such as a multilamellar mesophase, are not so intractable. For these two illustrating examples, the following features are emerging :
— In aqueous micellar systems, where the electrostatic interactions dominate, the competition between a double-layer repulsion and a depletion attraction has been identified. At large volume micellar fractions, the depletion and oscillatory structural effects are enhanced.
— In lyotropic lamellar mesophases, the compressibility of the stack normal to the layers is related directly to the free energy density of interlayer interactions, so that measurements of layer compressibility allow the nature of the forces to be inferred. The method presented here suffers from none of the difficulties usually encountered in the measurement of elastic properties of smectic phases (combination of several elastic moduli, model-dependence, etc). Moreover structural information about the confined mesophase, such as reticular spacing and the nature and dynamics of packing defects, is obtained.

INTRODUCTION

Surfactant molecules aggregate in solution to form a variety of structures. The type of self-assembled structure depends not only on the nature of the amphiphilic molecule and the composition of the system, but also on the salinity, the nature of the nonpolar liquid, and external conditions such as temperature. Significant progress has been made in predicting and explaining these structures from the geometry of the molecular entities (ref. 1). In addition, surface forces between aggregates significantly affect the phase behaviour and the macroscopic properties of the system. Most of the information about the nature of the inter-aggregate interactions has been inferred from scattering experiments (ref. 2). Direct measurement of forces between unsupported self-assembled entities in solution has remained a formidable task. Through the application of the osmotic stress technique (ref. 3), the interactions between bilayers stacked in a multilayer array have been directly measured (ref. 4), and also between DNA double helices (ref. 5), and both neutral and charged polysaccharides (ref. 6), etc. Using a surface force apparatus (ref. 7), the direct measurement of the force acting between two macroscopic surfaces immersed in such systems can provide some clues as to the nature of the inter-aggregate interactions. Moreover, the influence of the macroscopic surface on the behaviour of the system can also be studied, and one can obtain insight into the behaviour of fluids close to a wall and in thin films confined between two walls and thereby their stabilisation mechanism.

The surface force apparatus has proven itself as a powerful technique for studying the interactions between surfaces in simple liquids and solutions (ref. 7-11). A wide range of experiments with surfactants adsorbed to mica surfaces from solution (ref. 12) or lipids deposited as Langmuir-Blodgett films (ref. 13) has been carried out. The forces measured between monolayers or bilayers attached to the mica surfaces may provide information on the interlamellar interactions in liquid crystalline systems with the same constituent bilayers. They may also give some insight into the diffuse double layer interaction of the electrolyte solution confined between such charged interfaces as was shown for coated surfaces immersed in ionic micellar solutions (ref. 10) and protein solutions (ref. 11) .

However, in the case of surfactant layers attached to macroscopic rigid surfaces, the suppression of membrane undulations and/or lipid head group mobility when compared to unsupported bilayers makes the connection between those measurements to any real interactions between free bilayers or membranes remote. Obviously, with such a device, the advantage of directly measuring the interactions is lost, and one must resort to some more indirect way of studying the inter aggregate interactions.

By application of the surface force apparatus technique we demonstrate that the interactions operating in micellar solutions or in a multilamellar mesophase, are not so intractable. These two illustrating examples investigate the interactions in the most simple association structures encountered for surfactants in solution. No long-range correlation exists for the globular aggregates of micellar systems, while lyotropic lamellar mesophases are planar stacks of membranes that contain surfactant and/or cosurfactant and sometimes a solvent, separated by diluent, arranged in a one-dimensional array.

INTERACTIONS IN LAMELLAR SYSTEMS

At the simplest level, force measurements between solid surfaces immersed in multilayered systems yield direct information on the interlayer spacing, as shown in ref. 14-18. The presence of macroscopic surfaces may influence dramatically the behaviour of the layered system. In confined geometries, the stack of membranes may adopt a periodicity departing strongly from the bulk layer spacing (ref. 16, 18), and the interactions may be superimposed on an overall repulsive (ref. 14) or attractive (ref. 16-18) background due to the presence of the walls. There is a wealth of additional information to be gained by application of the surface force technique to lamellar systems. Elastic properties of the layered structure can be extracted from the force - distance profile (ref. 14, 17, 18) and thereby the stabilisation mechanism can be inferred.
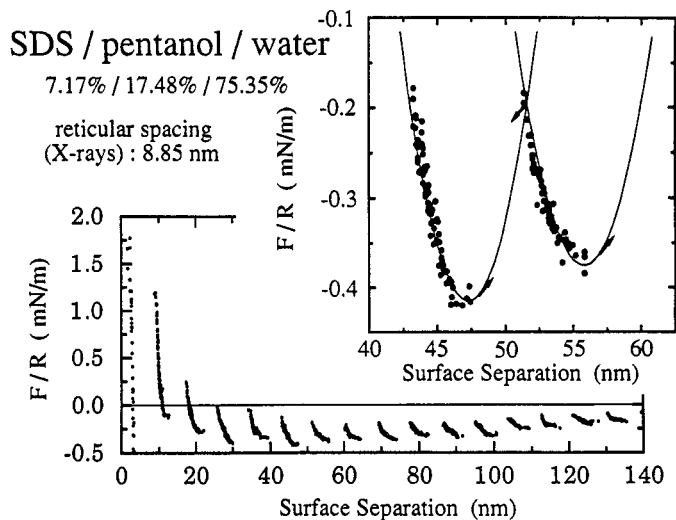

Fig. 1. Force F (normalized by the mean radius of curvature R of the surfaces) as a function of separation between two mica sheets immersed in a water-swollen lamellar mesophase. The first 16 oscillations from contact are shown. Top : enlargement of the forces around the sixth and seventh oscillations. The solid lines are parabolic fits using a layer compressional modulus B = 1.8 x 10⁶ erg/cm³ and converting the measured forces to free energies between parallel flats according to the Derjaguin approximation.

Here the two molecularly smooth mica surfaces of the surface force apparatus (Mark IV, the latest version of the series, ref. 19) are immersed in the water-swollen lamellar mesophase of a lyotropic liquid crystal (sodium dodecylsulphate (SDS) / pentanol / water). The bulk reticular spacing is 8.8 nm, as measured by X-rays, and from the composition it can be calculated that each bilayer constituted of SDS surfactant and pentanol molecules has a thickness of 2 nm, separated by a water layer of 6.8 nm. The layers are aligned on the whole parallel to the walls (homeotropic alignment). No surfactant layer is adsorbed on the mica surfaces, as expected considering the negative charge of the mica when immersed in aqueous solutions combined with the anionic character of the SDS. So firstly a water layer coats each wall, before the periodic bilayers and water layers are alternately stacked. Because of the crossed-cylinder configuration of the walls (ref. 7), equivalent to that of a sphere on a flat (as the surface separation D is much smaller than the radius of curvature R of the surfaces), the lamellae have to contour the slightly curved surfaces. Accordingly, the number of lamellae between the walls increases with distance from the line joining the points of closest approach of the two surfaces, and a network of edge dislocations is formed to accommodate the confinement of the lamellar mesophase in the wedge.

It has already been demonstrated (ref. 17) that the modulus of layer compression, B, can be derived directly from force measurements as a function of thickness for a multilamellar stack. The total force across a water-swollen lamellar phase oscillates regularly with surface separations (Fig. 1, where only the first 16 oscillations are shown), with a periodicity equals to the bulk reticular spacing d (here d=8.8 nm). When the separation between the walls changes, the stack experiences an elastic stress induced by the weak normal strain. The free energy density E is a set of parabolic curves centered around l_n, which is an integral multiple of the reticular distance d. Every time two adjacent parabolae intersect, the elastic energy of the system is lowered by the exclusion or introduction of a layer. In other words the stress is released by the creation or annihilation of an elementary edge dislocation (ref. 17). As shown in the top of Fig. 1, the measured forces can be fitted by a parabolic profile. As one surface is moved toward the other, the stack of layers undergoes compression on the left-hand side of the parabola. The parabola is followed until it intersects the adjacent parabola. At this point an inward jump to the compressive part of the next oscillation occurs because of the mechanical instability of the device ($\partial(F/R)/\partial l \geq K/R$ where K is the cantilever spring constant; see ref. 7). When the movement of the surfaces is reversed, the force is measured past the minimum of the nth parabola and the surfaces jump out from the decompression part when again the gradient of the force exceeds K. The solid parabolic lines of Fig. 1 are obtained with B = 1.8×10^6 erg/cm^3, using the Derjaguin approximation (ref. 20) which relates the free energy E between flat surfaces of unit area to the force F normalized by the mean radius R of the surfaces ($E = F/2\pi R$).

The value of the compressibility modulus reflects the nature of the interaction between two membranes. B would be independent of the number of layers n if the smectic phase were a perfect 1D crystal, but for a quasi-ordered system the theory predicts a Landau-Peierls type correction $B_n = B (1 + A \ln(l_n/d))^{4/5}$ (ref. 21). The same theory indicates a correction of only a few percent when the thickness l_n is more than one thousand layers. Our measurements of the second to the sixteenth oscillation show that this effect is negligible. On the other hand, for the first oscillation, a slight increase of the modulus of compressibility from that measured in bulk is observed (ref. 17). This effect arises from the difference in charge density between the mica surfaces and the bilayers, and leads to an effective modulus correcting the preceding value : B = $(1.9\pm0.4) \times 10^6$ erg/cm^3 (ref. 17). The measured value is in close agreement with that inferred from high-resolution X-ray scattering (ref. 22) and also with the theoretical one (ref. 17), demonstrating that the interactions are purely electrostatic in this water swollen lamellar mesophase.

In conclusion, the direct measurement of the layer compressibility modulus, B, in smectic phases is feasible with a surface force apparatus. Knowledge of B as a function of the reticular distance allows the type of interaction to be determined. Insight into the behaviour of these phases in confined geometries can be obtained. In addition information about the structure and the nature of the defects (edge dislocations, Burgers vectors, energy of creation or annihilation, velocity, etc) is accessible.

INTERACTIONS IN MICELLAR SYSTEMS

The force as a function of separation between two mica surfaces immersed in different aqueous micellar solutions of cetyltrimethylammonium bromide (CTAB) at 25 °C (above the Krafft temperature of the surfactant) has been measured. The micellar volume fraction varies from about 0.007 (about twenty times the c.m.c.) to 0.073. Potassium bromide (up to 0.1 M) is used to change the ionic strength of the solutions. Complete details of these experiments can be found in ref. 23.

Cationic surfactant molecules adsorb to the mica surfaces as soon as they are in contact with the aqueous micellar solutions, and at the equilibrium, each surface is coated with an adsorbed CTAB bilayer, the thickness of which is independent of salt concentration (about 3.2 nm, ref. 23) and in direct agreement with previous observations (ref. 10, 12b). The two crossed cylinders (mean radius R, typically 1-2 cm) of molecularly smooth mica surfaces are geometrically equivalent to two spheres of radius 2R approaching each other when the surface separation D is much smaller than the radii (D « R). Each coated with an adsorbed bilayer, these charged surfaces are surrounded by a diffuse double layer, characterized by a "thickness" δ, and behave as soft walls with an effective hard-sphere diameter (ref. 23) $d_1'=d_1+2\delta$ ($d_1=4R$ see above).

In absence of added salt (or at low ionic strength), the CTAB micelles can be considered as spherical and monodisperse (diameter d_2). They are surrounded by a diffuse outer region of ions and solvent, characterized by another "thickness" ϵ. These highly charged micelles (effective diameter $d_2'=d_2+2\epsilon$) between the two charged walls behave as co-ions expelled from the region of close double-layer overlap. The resulting depletion mechanism (attractive force) is in competition with the repulsive double layer interaction. From this competition emerges a secondary minimum in the interaction potential as shown in Fig. 2.
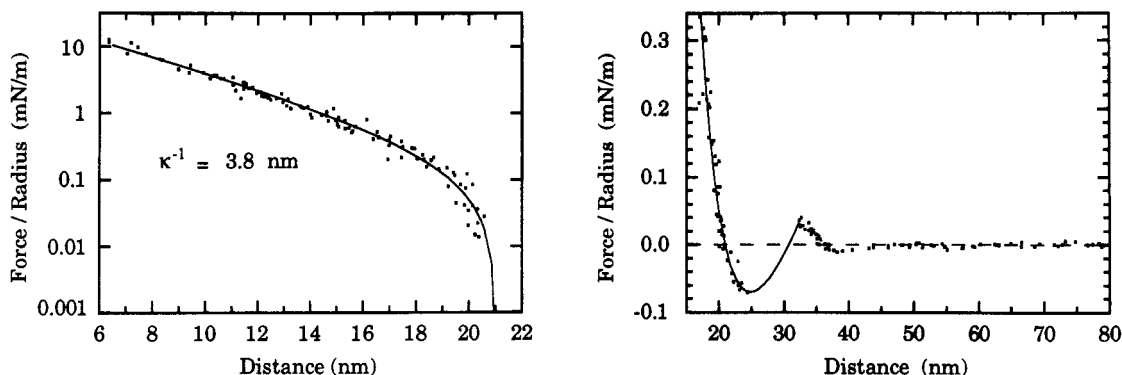
Fig. 2. Normalized force as a function of separation between crossed mica cylinders, each coated with an adsorbed bilayer of CTAB (thickness about 3.2 nm), and immersed in a micellar solution of CTAB (volume fraction about 0.018). The attractive minimum around 25 nm is due to depletion of micelles, while the exponential repulsion at smaller separations arises from double-layer forces due to dissociated counterions and free CTA$^+$ ions only. The solid line is the best-fit numerical solution to a force-distance profile sum of a decaying exponential and a linear function of the separation over the range 6.3 nm (bilayer-bilayer contact) and 32 nm (end of the secondary minimum).

This competition is treated as additive in a similar fashion that DLVO theory considers the summation of electrostatic and dispersion forces :

The attractive depletion contribution to the total interaction is proportional to the osmotic pressure P_{osm} and is also linear with respect to separation D, in the limit where $d_1=4R \gg d_2$, δ, and ε (ref. 23) :

$$f(D)/R = -2\pi \, (d_2'+2\delta-D) \, P_{osm} = -2\pi \, (d_2'+2\delta-D) \, \alpha n_2 k_B T \qquad (1)$$

where n_2 is the number density of micelles and $\alpha(\Phi_2)$ is the osmotic coefficient introduced to account for the interactions between the micelles (volume fraction Φ_2). Eqn.1 is like an Asakura-Oosawa (ref. 24) approximation whose validity has already been discussed in detail (ref. 23, 25). The use of this approximation is reasonable as long as the structural effects are weak, otherwise a coefficient dependent on the concentration must be added to eqn.1. Indeed, the free energy is no longer necessarily zero when the depletion attraction first occurs at $D = d_2' + 2\delta$. Note that this surface separation defines the new range of the interaction for the soft system (micelles between charged walls) compared to a situation of hard-sphere particles between hard walls.

The electrostatic repulsion can be treated by a linearized Poisson-Boltzmann contribution for surface separations sufficiently large with a Debye screening length κ_0^{-1} given by (ref. 10, 23) :

$$\kappa_0^{\,2} = \frac{4\pi q^2}{\varepsilon k_B T} \left\{ 2\rho_{cmc} + \frac{(\rho_S - \rho_{cmc})}{N}(N-Q) + \rho_{K^+} + \rho_{Br^-} \right\} \qquad (2)$$

where ρ_S is the surfactant concentration, ρ_{cmc} that at the critical micellar concentration (c.m.c.), N the mean micellar aggregation number, Q the mean net effective charge of the micelle, ρ_{K^+} the concentration of potassium ions and ρ_{Br^-} that of bromide brought in excess by the external salt. In these highly asymmetric electrolytes the measured double-layer decay lengths κ_0^{-1} appear to be due entirely to the free surfactant ions CTA$^+$, and both added salt plus dissociated counterions (bromide) released by the surfactant and the micelles, with no apparent contribution from charged micelles.

The ever-present van der Waals interaction does not pose an experimental limitation to the interpretation of the attractive contribution in this charged micellar system. Indeed, a typical Hamaker constant of about 1.5×10^{-20} J for the interaction between mica surfaces coated with adsorbed bilayers across the aqueous micellar solutions (ref. 10, 12b, 23) indicates that the attractive dispersion forces cannot account for the occurence of a secondary minimum in the interaction potential at least at low ionic strength ([KBr] < 0.02 M). On the other hand, at high salt concentration (Fig. 3) the same contribution would be about one third of the depth of the minimum.

CTAB

$\Phi = 0.030$

[KBr] = 0.1 M

[KBr] = 0.02 M

no added salt

Force / Radius (mN/m)

0.5
0.4
0.3
0.2
0.1
0.0
-0.1

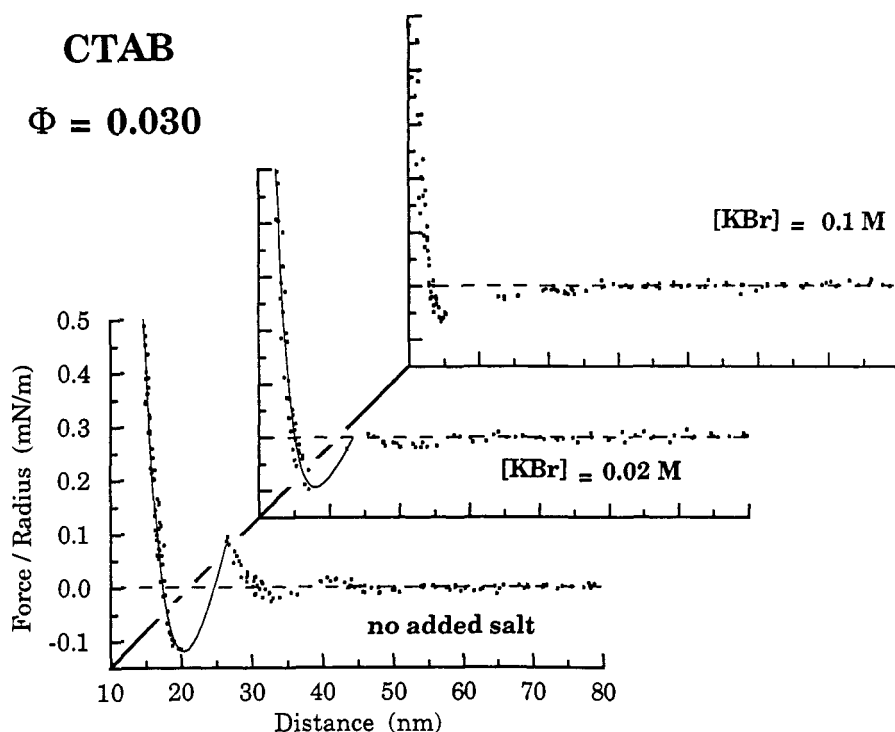10   20   30   40   50   60   70   80

Distance (nm)

Fig. 3. Same as in Fig. 2 but for a volume fraction of about 0.030 and in presence of potassium bromide. Note the disappearance of the structural oscillation and the shift of the secondary minimum towards smaller surface separation as the ionic strength is increased. At [KBr] = 0.1 M, no fit has been attempted as the micelles are highly anisotropic and polydisperse.

The solid lines in Figs. 2 and 3 represent the numerical fit to the experimental measured data for a force-distance profile described by a law : $f(D)/R = A_1\exp(-\kappa D) + A_2D + A_3$ for $D \leq d_2' + 2\delta$, where the electrostatics treated by a linearized Poisson-Boltzmann contribution is in competition with the depletion attraction which is spatially linear (eqn.1), and the van der Waals contribution is neglected at these separations.

The modelled force is in remarkable agreement with the measured profile for micellar systems at low ionic strength ([KBr] < 0.02 M) where the aggregates can be considered as spherical with a low polydispersity in size. More precisely, the decay-lengths extracted from the fits agree well with the values calculated by eqn.2. For instance, for the data reported in Fig. 2 ($\Phi_2 \approx 0.018$, in absence of salt), the fit gives $\kappa^{-1} = 3.8$ nm compared to the expected $\kappa_0^{-1} = 3.6$ nm calculated by eqn.2 using an aggregation number of 90 (ref. 26) and a fractional ionization of the micelles $Q/N \approx 0.22$ (ref. 27). Furthermore, when the structural effects are weak, the fits give a ratio $-A_3/A_2 \approx d_2'+2\delta$ in close agreement with the measured values (31.5 nm compared to the measured 32.3 nm in Fig. 2). Finally, from $A_2 = -2\pi\alpha n_2 k_B T$ and using a micelle diameter around 4.7 nm (ref. 28), the osmotic coefficient α can be estimated. Thus an effective volume fraction Φ_2' is derived from $\alpha(\Phi)=P_{osm}/nk_B T=(1+\Phi+\Phi^2-\Phi^3)/(1-\Phi)^3$ according to the Carnahan-Starling approximation (ref. 29), and by use of the geometric limit of planar walls (since $d_1=4R \gg d_2$). The effective concentration can also be extracted from the period of the oscillatory profile which arises due to structural effects. As an illustration, the results shown in Fig. 2 give an effective volume $\Phi_2' \approx 0.25$ (osmotic cofficient 3.01 obtained from the fit) in very good agreement with the value 0.23 calculated with an effective diameter $d_2' \approx 11.1$ nm, as indicated by the oscillation in the force profile occuring between 43.5 and 32.4 nm.

At high surfactant concentration and/or high ionic strength ([KBr] > 0.02 M), the polydispersity of the size of the micelles as well as the anisotropy of their shape increase, which means that the quantitative analysis described above can no longer be utilized. Firstly, at high volume fraction, the observation of large structural effects (ref. 23a), makes the Asakura-Oosawa approximation a poor one (ref. 25). Secondly, any

polydispersity of the aggregates may reduce the net interaction between the walls. Finally, at high ionic strength, the aggregates are no longer spherical but large, elongated, and probably flexible (ref. 30). At electrolyte concentrations well below the threshold of the reported sphere-rod transition for the micelles (ref. 27) the structural oscillations in the force-distance profile disappear (Fig. 3). This effect is a complementary manifestation of the reduction of the osmotic coefficient and conversely of the effective hard-sphere volume fraction (α decreases from 4.7 in absence of salt down to about 2-3 at [KBr] = 0.02 M (Fig. 3; ref. 23b). At higher electrolyte concentrations, the aggregates are so anisotropic that they should overlap forming a transient network similar to an entangled polymer solution (semi-dilute range). As mentioned above, the van der Waals interaction is not solely responsible for the secondary minimum (Fig. 3). Despite the absence of a quantitative analysis of the data, our results suggest that even in this particular situation with elongated micelles, an important depletion contribution remains.

In summary, at low ionic strength, the observed deviation from the pure double-layer repulsion is due to the depletion of the micelles in the double-layer overlap. The modelled force, which is in fair agreement with the measured profile, is based on the simple assumption that all the contributions to the interaction are purely additive. Direct force measurements between charged CTAB bilayers in micellar solutions at large volume fractions indicate that depletion and structural contributions superimpose on top of classical double-layer interactions. At high ionic strength, the situation is more complicated, as the micelles can no longer be considered as spherical with a low polydispersity. The force profile has thus only been interpreted qualitatively. Nevertheless, the case of very anisotropic micelles is of most interest. The analogy between a solution of giant one-dimensional micelles and a polymer solution could be used in order to measure directly depletion interactions both in dilute and semi-dilute regimes. A direct comparison with non adsorbing polymer solutions would then be possible. Finally, our results underline the consequences that the addition of surfactant micelles to a colloid suspension can have. They confirm the depletion mechanism proposed by different authors both in the creaming of oil-in-water emulsions (ref. 31) and to account for flocculation of polystyrene latex by surfactant (ref. 32). Thus, just as addition of salt may destabilize a charged suspension, addition of charged micelles may induce flocculation, reflecting the occurence of a secondary minimum in the interaction potential between two colloids. The addition of an oscillatory potential to the depletion minimum confirms the interpretation of ordered micelle structuring in thin films formed from surfactant solutions (ref. 33). As it turns out that the main parameter governing the oscillatory potential is the effective volume of the particles, one can suggest (ref. 23) the possibility of several metastable states for a dispersion of particles in relatively low concentrated micellar solutions at different surfactant concentration and ionic strength, leading to the presence of reentrant phase transitions.

REFERENCES

1. J.N. Israelachvili, D.J. Mitchell, and B.W. Ninham, J. Chem. Soc. Faraday Trans. 2 72, 1525-1568 (1976) ; D.J. Mitchell and B.W. Ninham, J. Chem. Soc. Faraday Trans. 2 77, 601-629 (1981) ; S.T. Hyde, J. Physique (France) 51, supplément n° 23, C7-209-C7-228 (1990) .
2. J.B. Hayter and J. Penfold, Mol. Phys. 42, 109-118 (1981) ; J. Chem. Soc. Faraday Trans. 1 77, 1851-1863 (1981) .
3. V.A. Parsegian, N. Fuller, and R.P. Rand, Proc. Natl. Acad. Sci. U.S.A. 76, 2750-2754 (1979) ; V.A. Parsegian, R.P. Rand, and D.C. Rau, Methods Enzymol. 127, 400-416 (1986) .
4. D.M. LeNeveu, R.P. Rand, and V.A. Parsegian, Nature (London) 259, 601-603 (1976) ; see also the review : R.P. Rand, and V.A. Parsegian, Biochim. Biophys. Acta 988, 351-376 (1989) .
5. D.C. Rau, B.K. Lee, and V.A. Parsegian, Proc. Natl. Acad. Sci. U.S.A. 81, 2621-2625 (1984) .
6. D.C. Rau and V.A. Parsegian, Science 249, 1278-1281 (1990) .
7. J.N. Israelachvili and G.E. Adams, J. Chem. Soc. Faraday Trans. 1 74, 975-1001 (1978) .
8. R.M. Pashley, J. Colloid Interface Sci. 80, 153-162 (1981) ; 83, 531-546 (1981) ; 102, 23-35 (1984); J.N. Israelachvili and R.M. Pashley, Nature (London) 306, 249-250 (1983) .
9. R.G. Horn and J.N. Israelachvili, J. Chem. Phys. 75, 1400-1411 (1981) ; H.K. Christenson, J. Chem. Phys. 78, 6906-6913 (1983) ; H.K. Christenson and R.G. Horn, Chem. Phys. Lett. 98, 45-48 (1983) ; R.G. Horn, D.F. Evans, and B.W. Ninham, J. Phys. Chem. 92, 3531-3537 (1988) .
10. R.M. Pashley and B.W. Ninham, J. Phys. Chem. 91, 2902-2903 (1987) .
11. P. Kékicheff and B.W. Ninham, Europhys. Lett. 12, 471-477 (1990) .
12. R.M. Pashley, P.M. McGuiggan, B.W. Ninham, J. Brady, and D.F. Evans, J. Phys.Chem. 90, 1637-1642 (1986) ; P. Kékicheff, H.K. Christenson, and B.W. Ninham, Colloids Surf. 40, 31-41 (1989) .
13. J. Marra and J.N. Israelachvili, Biochemistry 24, 4608-4618 (1985) ; J. Marra, J. Phys.Chem. 90, 2145-2150 (1986) .

14. R.G. Horn, J.N. Israelachvili, and E. Perez, <u>J. Physique (Paris)</u> <u>42</u>, 39-52 (1981) .
15. L. Ter-Minassian-Saraga and E. Perez, <u>Colloids Surf.</u> <u>12</u>, 213-225 (1984) ;
    O. Abillon and E. Perez, <u>J. Physique (France)</u> <u>51</u>, 2543-2556 (1990) .
16. P. Kékicheff and H.K. Christenson, <u>Phys. Rev. Lett.</u> <u>63</u>, 2823-2826 (1989) .
17. P. Richetti, P. Kékicheff, J.L. Parker, and B.W. Ninham, <u>Nature (London)</u> <u>346</u>, 252-254 (1990) .
18. P. Kékicheff, P. Richetti, and H.K. Christenson, <u>Langmuir</u> <u>7</u>, 1874-1879 (1991) .
19. J.L. Parker, H.K. Christenson, and B.W. Ninham, <u>Rev. Sci. Instrum.</u> <u>60</u>, 3135-3138 (1989) .
20. B.V. Derjaguin, <u>Kolloid Z.</u> <u>69</u>, 155-164 (1934) .
21. P.G. de Gennes, <u>The Physics of Liquid Crystals</u>, Clarendon, Oxford (1974) .
22. D. Roux and C.R. Safinya, <u>J. Phys. France</u> <u>49</u>, 307-318 (1988) .
23. P. Richetti and P. Kékicheff, <u>Phys. Rev. Lett.</u> , submitted .
    P. Kékicheff and P. Richetti, <u>Prog. Coll. Polym. Sci.</u> , submitted .
24. S. Asakura and F. Oosawa, <u>J. Chem. Phys.</u> <u>22</u>, 1255-1256 (1954) .
25. P. Attard, <u>J. Chem. Phys.</u> <u>91</u>, 3072-3082, 3083-3089 (1989) .
26. P. Lianos and R. Zana, <u>J. Colloid Interface Sci.</u> <u>84</u>, 100-107 (1981) .
27. R. Dorshow, J. Briggs, C.A. Bunton, and D.F.Nicoli, <u>J. Phys.Chem.</u> <u>86</u>, 2388-2395 (1982) ;
    R.B. Dorshow, C.A. Bunton, and D.F. Nicoli, <u>J. Phys.Chem.</u> <u>87</u>, 1409-1416 (1983) .
28. P. Ekwall, L. Mandell, P. Solyom, <u>J. Colloid Interface Sci.</u> <u>35</u>, 519-528 (1974) .
29. N.F. Carnahan and K.F. Starling, <u>J. Chem. Phys.</u> <u>53</u>, 600-603 (1970) .
30. S.J. Candau, E. Hirsch, and R. Zana, <u>J. Physique (Paris)</u> <u>45</u>, 1263-1270 (1984) ;
    T. Imae, R. Kamiya, and S. Ikeda, <u>J. Colloid Interface Sci.</u> <u>108</u>, 215-225 (1985) .
31. D. Fairhurst, M.P. Aronson, M.L. Gum, and E.D. Goddard, <u>Colloids Surf.</u> <u>7</u>, 153-159 (1983) ;
    M.P. Aronson, <u>Langmuir</u> <u>5</u>, 494-501 (1989) ;
    J. Bibette, D. Roux, and F. Nallet, <u>Phys. Rev. Lett.</u> <u>65</u>, 2470-2473 (1990) .
32. C. Ma, <u>Colloids Surf.</u> <u>28</u>, 1-7 (1987) .
33. A.D. Nikolov and D.T. Wasan, <u>J. Colloid Interface Sci.</u> <u>133</u>, 1-12 (1989) ;
    A.D. Nikolov, P.A. Kralchevsky, I.B. Ivanov, and D.T. Wasan, <u>J. Colloid Interface Sci.</u> <u>133</u>, 13-22 (1989) .