

Light scattering from the L_3 (sponge) phase: Evidence against logarithmic corrections to ideal scaling

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(Received 30 May 1995)

We present compressibility data over a broad range of surfactant concentrations from static light scattering experiments on the L_3 phase appearing in the system AOT [sodium bis(2-ethylhexyl) sulfosuccinate]–NaCl–water. The results are seen to support a model for the thermodynamics of this phase recently proposed by the present authors. They also provide strong evidence against logarithmic corrections to the free energy of the sponge phase, previously suggested to arise from renormalization effects.

PACS number(s): 64.70.Ja, 82.65.Dp, 78.35.+c

In a recent paper [1], the present authors proposed a description of the thermodynamics of the L_3 (sponge) phase within the flexible surface model. In brief, this description is based upon the treatment of the midplane of the multiply-connected, disordered bilayer which separates the two solvent domains as a minimal surface. The curvature free energy density is then calculated at the interface with solvent, this interface being modeled as a surface displaced by a fixed distance l , the monolayer thickness, from the midplane. Treating mean curvature as the dominating contribution to the free energy density g , the result that we obtained was

$$g = 2\kappa \left[\frac{H_0}{l^2} \Phi^3 + \frac{1}{4l^3} \Phi^5 \right], \quad (1)$$

where H_0 is the spontaneous curvature and κ the bending modulus of the monolayers constituting the bilayer, and Φ is the volume fraction of surfactant.

The leading-order term scales as Φ^3 , as suggested originally by Porte *et al.* [2] for an ideal fluid bilayer or monolayer system in the approximation of an harmonic local curvature energy. The fact that the monolayers prefer to curve slightly towards the solvent means that the coefficient of this leading-order term is negative, and therefore the phase becomes unstable at low concentrations, and there is a phase separation with dilute solution. At higher concentrations the phase is stabilized by the quintic term, arising from the finite-thickness contribution to the mean curvature at harmonic order. For reasons discussed in Ref. [1] the contribution from fluctuations, Gaussian curvature and entropy were neglected, as were contributions to the quintic term in the free energy density from anharmonic terms in the monolayer local curvature energy. Bending modulus renormalization [3–6] is not invoked, following our belief that it is an artifact of construction rather than a real physical effect [7]. The essential point is that whilst one may in principle cast a mathematical description of the system in terms of renormalized bending moduli and surface areas, it is an entirely different matter as to whether these effects ultimately appear in the free energy of the system. In calculating

the phase equilibria with the commonly observed nearby phases of lamellae and a dilute solution of monomers, we were able to present calculated phase diagrams which showed the characteristically observed sequence of phase transitions as a function of increasing Φ , $L_1 \rightarrow L_3 \rightarrow L_\alpha$, and also the narrowness of the sponge phase in surfactant concentration.

We also presented results from static light scattering (SLS) experiments for the system AOT [sodium bis(2-ethylhexyl) sulfosuccinate]– NaNO_3 –water. SLS is a valuable tool for checking the predictions of a thermodynamic model, as the predicted osmotic compressibility is related to the excess Rayleigh ratio $\Delta R(q)$ extrapolated to $q=0$ via [8,9]

$$\Delta R(0) = \frac{4\pi^2 n_0^2}{\lambda_0^4} \left[\frac{dn}{d\Phi} \right]^2 k_B T \Phi \left[\frac{\partial \Pi}{\partial \Phi} \right]^{-1}, \quad (2)$$

where Π is the osmotic pressure, n_0 is the refractive index of the solvent, n is the refractive index of the solution, and λ_0 is the wavelength of the incident light in vacuum.

The following four important points came out of those experiments.

(1) The forward scattering intensity is very sensitive to the exact position within the phase, and so dilution-line specification is essential if one is to test models of the sponge phase.

(2) We must be sure that we are far from critical points that will influence the compressibility data, and hence systems with as few components as possible should be used.

(3) Over the range of surfactant volume fractions over which we measured $\Phi=0.13$ to 0.38 the results confirmed the predictions of our model, which are, along the phase boundaries:

$$[\Delta R(0)]^{-1} \approx d_3 \Phi^3 + d_2 \Phi^2 + d_1 \Phi. \quad (3)$$

(4) No evidence was seen for the effects of bending modulus or membrane area renormalization, which have been suggested to contribute to the free energy density of

the sponge and like phases so that [5,10,11]

$$g = \Phi^3(a + b \ln \Phi), \quad (4)$$

where a and b are positive coefficients, and thus

$$[\Delta R(0)]^{-1} \sim \Phi \ln(\Phi/\Phi^*), \quad (5)$$

where Φ^* has a small but finite value. The effect of the logarithmic correction term to ideal scaling would be increasingly strong as the system is diluted. The aim of this report is to investigate one important possibility: that the range of surfactant concentrations over which we previously measured terminated at too high a value, and therefore only tested our model's validity in the high concentration regime where the putative logarithmic corrections are not significant. Thus it may have been argued that both the quintic term in our model and the logarithmic renormalization correction term could happily coexist, one dominating the other in the different concentration regimes. The resolution of this point would be of obvious significance to the now vigorous debate on renormalization effects in fluid membrane systems.

With this as a principle aim, we here describe new experiments on the system AOT–NaCl–water, the same system used in Refs. [12,13] by Porte and co-workers to confirm Eq. (5). This allows access to concentrations down to $\Phi \approx 0.05$ and should therefore allow us to test definitively whether the logarithmic term appears or not, and whether our proposed model remains successful in the dilute regime. Where we differ from the previous work in Refs. [12,13] is that we stipulate the dilution lines used in the experiments, and all the results are placed on an absolute scale.

A partial phase diagram at 23 °C is shown in Fig. 1. The dilution lines we use are as close as possible to the phase boundaries, which we have determined to within 0.05 wt % of salt. Samples were equilibrated over (at least) several days. The range of surfactant concentrations is $\Phi = 0.05$ to 0.38. Details of the experimental set-up at the Polymer Institute, ETH Zürich, where the measurements were performed, may be found in Ref. [1].

For the more dilute samples, the range of angles that were measured over was $15^\circ \leq \theta \leq 140^\circ$; for the others a range of $30^\circ \leq \theta \leq 140^\circ$ sufficed to perform the necessary extrapolation to forward scattering with good accuracy.

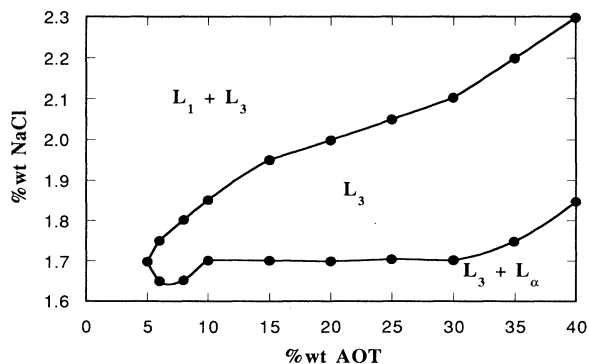


FIG. 1. Partial phase diagram of the AOT–NaCl–water system at 23 °C.

For the dilute samples, non-Ornstein-Zernike (OZ) behavior was found in the high- q regime, as shown in Fig. 2 for two samples, both of surfactant volume fraction $\Phi = 0.053$, but with different salt concentrations: 1.65 wt % NaCl (lower phase boundary) and 1.75 wt % NaCl (upper phase boundary). The difference in moving from one phase boundary to the other is evident.

The behavior for the q dependence of the dilute samples has been previously fitted [10,11] by the functional form

$$\Delta R(q) = A + B \frac{\arctan(q\xi/2)}{(q\xi/2)}, \quad (6)$$

where ξ is a correlation length. We have shown best fits using this expression in Fig. 2(a). For these more dilute samples the extrapolation to forward scattering was done as follows: the data is plotted as shown in Fig. 2(b) and then a linear fit made to the points at low q within the Guinier approximation, thus using only the initial decay of the scattering intensity as a function of wave vector. This then gives the extrapolated value to good accuracy (to within about 5%). Using the specific functional form of Eq. (6) leads to the same values within the given accuracy. At the higher concentrations, the behavior becomes OZ-like over all q values measured, and the extrapolation is thus straightforward. Measurements were made at 23.0 ± 0.1 °C.

The results of the scattering experiments are shown in Fig. 3, where we have also plotted our previous data for

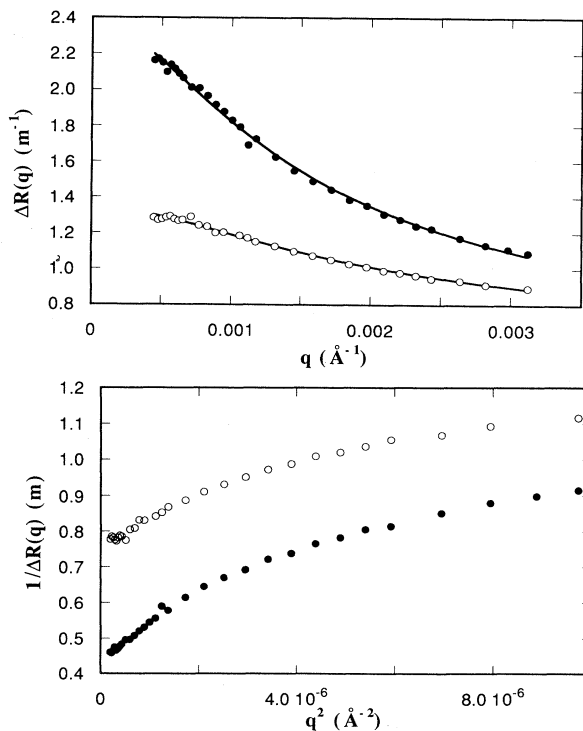


FIG. 2. (a) Plot of the q dependence of $\Delta R(q)$ for two samples of volume fraction $\Phi = 0.053$. Filled circles: 1.75 wt % NaCl; unfilled circles: 1.65 wt % NaCl. The curves are best fits using Eq. (6). (b) The same data plotted as $1/\Delta R(q)$ vs q^2 . The linear behavior at low q values is indicative of the OZ regime; a deviation is clear at higher values of q .

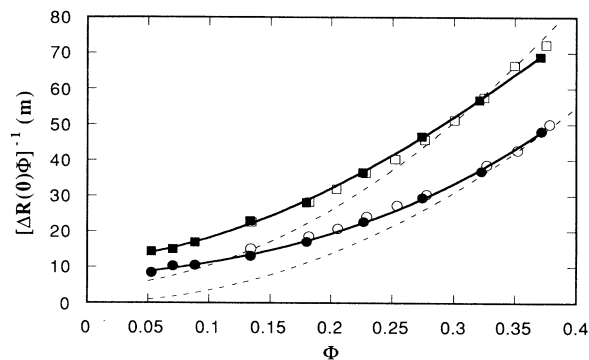


FIG. 3. Results of the light scattering experiments. Solid squares are data for the AOT–NaCl–water system on the lower phase boundary, solid circles are for the same system on the upper phase boundary, unfilled symbols are the corresponding data from Ref. [1] for the system AOT–NaNO₃–water. Solid curves are quadratics of best fit to the data from the chloride system. Dashed curves are predictions from the model, with parameters as given in the main text.

the measurements on the AOT–NaNO₃–water system, all on an absolute scale following the standard procedure described in Ref. [1]. The dashed curves are predictions from the model for a monolayer bending rigidity of $\kappa = 1.8k_B T$ and a value of the difference of the surfactant standard chemical potential in solution and in the bilayer of $\Delta\mu_s^0 = 20k_B T$ [14]. In the regime where they overlap, the results from the two systems agree extremely well when plotted on this absolute scale, confirming the validity and reproducibility of the measurements, and also of our previous estimate for the bilayer rigidity $\kappa_{\text{bil}} \approx 3.6k_B T$ [1].

We turn our attention to the additional data in the dilute regime. All of the data in the full range of $\Phi = 0.05$ to 0.38 for a given dilution line lie on a smooth curve. All experimental curves and theoretical predictions from the model are excellently fitted by quadratics, as suggested by Eq. (3), and these fits are shown. This indicates that the true behavior over all regimes is in fact one of ideal scaling modified by finite-thickness effects which become more significant with increasing concentration. Importantly, *no systematic logarithmic corrections are seen at low concentrations*. We do, however, recognize the discrepancy between our theoretical predictions and the data at low concentrations, this essentially being a difference in the offset of the curves in Fig. 3. It seems that the most likely cause for this is that experimentally we are dealing with, in reality, a ternary system, which we treat here in a pseudobinary approximation (brine being a pseudocomponent). Work is currently in progress to investigate if the inclusion of salt as a true component in our thermodynamic description can explain the difference in this offset between theory and experiment. It is important to note, however, that logarithmic corrections cannot explain the discrepancy as they, if present, would predict that the data would slope more strongly in the dilute regime than even our theoretical curves, asymptotically cutting the horizontal axis at a finite sur-

factant concentration Φ^* on extrapolation [10,12,13], and this is not the case. Figure 4, where we plot $[\Delta R(0)\Phi]^{-1}$ vs $\log_{10}\Phi$ clearly confirms this. In these coordinates, Eq. (5) would predict a straight line of finite slope, but this is not seen in any regime. The fact that at low concentrations the data becomes asymptotically flat is precisely as predicted by our model, where the ideal scaling law of Porte *et al.* [2] is the result at infinite dilution, so that

$$\lim_{\Phi \rightarrow 0} [\Delta R(0)] \sim \Phi^{-1}. \quad (7)$$

Of course the limit cannot be reached experimentally, as the sponge has a finite swelling, that is, there is a phase separation with solvent at some finite value of Φ (see Fig. 1). However, our results indicate clearly that Eq. (7), not Eq. (5), gives the correct asymptotic behavior.

This is definitive experimental evidence that the renormalization effects, so often invoked as an important thermodynamic feature of fluid membrane phases, do not in fact appear. Two of us have argued previously [7] on a theoretical basis that they are not present, as the renormalized bending moduli refer to a base surface about which the membrane fluctuates. Hence, if renormalization is to be invoked, there must be a clear specification of this base surface, and concomitant area corrections made [15]. In our model [1], there is no such need to identify a base surface, and as we deal with the real interface then the monolayer bending modulus has a concentration-independent physical value, the so-called “bare modulus.”

The results are in clear contradiction to those previously published in Refs. 12, 13 for the same system of AOT–NaCl–water, and in Refs. [10,11] for a quaternary system of surfactant, cosurfactant, water and oil. In the former case, the reason for the discrepancy seems clear: the previous work has suffered from not specifying the trajectory within the phase. Without this specification, the functional form deduced from the data for the compressibility is highly unreliable: a change in the position and nature (e.g., from straight to curved) of the dilution line within the phase will almost certainly lead to a different scaling for the forward scattering intensity being extracted from the data. Hence we have here and in Ref. [1] taken considerable care with this

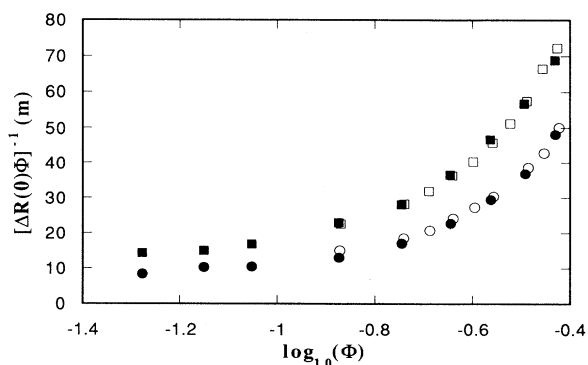


FIG. 4. The results of Fig. 3 presented in the coordinates $[\Delta R(0)\Phi]^{-1}$ vs $\log_{10}\Phi$.

stipulation of the trajectory. Since the phase is narrow, one may think *ab initio* that dilution-line specification is not essential, simply being within the phase is enough. However, this is fallacious, as seen immediately from the data and predictions shown in Fig. 3. Thermodynamically, a generically narrow phase must have a rapidly changing free energy density and osmotic pressure as a function of the control parameters (in this case surfactant and salt concentrations); with the particular form for the free energy density of Eq. (1), this characteristic behavior is also held by the compressibility [which is proportional to $\Phi(\partial\Pi/\partial\Phi)^{-1}$]. Our underlining of this point is not pedantry but indicates the crucial difference between our measurements and those made previously. We also strongly emphasize that our predictions and the data have been compared *on an absolute scale*, this being a strong test of our model, and one which (apart from our work in Ref. [1]) has not been applied to any previous compressibility measurements on the sponge phase.

The above also applies when comparing our results to those obtained for the quaternary system by Roux *et al.* [10,11]. However, there the picture may also be complicated by the fact that such a system may well feature critical behavior; indeed such behavior has been observed and reported in similar systems [11,16]. This would lead to a large increase in the scattering intensity in the vicinity of the critical point, and thus obscure the conclusions

that are drawn from the compressibility data. So again care is needed. It is our view that this particular problem is overcome by the use of pseudobinary systems such as we have done in these experiments, where critical behavior in the regime of the measurements is absent.

In conclusion, we have seen that the results from the new measurements are consistent with previous data presented in Ref. [1] in the overlap region and indicate that the model we have proposed covers not only this more concentrated regime but also makes successful predictions at high dilution, and on an absolute scale. Finite-thickness effects manifest themselves by determining the nature of the coefficient of the ideal scaling term, and as a quintic correction to it in the free energy density, this becoming more significant as the surfactant concentration is increased. Finally, we have shown that if appropriate care is taken when making and testing predictions, compressibility data gives strong experimental evidence that there is no basis in the belief that renormalization effects play a role in the thermodynamics of fluid membrane systems.

We thank Ingegerd Lind for technical assistance. This work was supported by the Swedish Natural Science Research Council (NFR) and the Grdan Gustafsson Foundation.

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