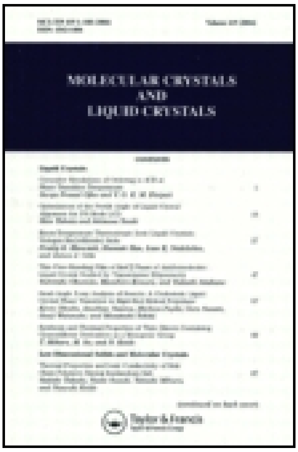

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: V. A. Lobaskin & V. K. Pershin (1995): Pair Interaction Potential for Nonionic Micelles in Aqueous Media, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 585-594

To link to this article: http://dx.doi.org/10.1080/10587259508038731

Mol. Cryst. Liq. Cryst. 1995, Vol. 260, pp. 585–594
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PAIR INTERACTION POTENTIAL FOR NONIONIC MICELLES IN AQUEOUS MEDIA

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Abstract Temperature behaviour of the potential of mean force and the second virial coefficient is studied for nonionic micelles in aqueous medium. The proposed model of intermicellar interaction is then used for the analysis of phase diagrams of nonionic micellar solutions.

INTRODUCTION

The essential role of intermicellar interactions in various processes such as cloudiness or mesophase formation which occur in lyotropic systems was stressed repeatedly for the last years[1-4]. Considerable theoretical attention has already been devoted to developing a theory of forces between amphiphilic surfaces in liquids[5,6]. In our recent work[7] on the basis of the disjoining pressure concept, we have proposed the model of intermicellar interaction in aqueous solutions of nonionic surfactants, which allows one to take into account solute-solute, solute-solvent and solvent-solvent interactions.

The goal of the present work was to study temperature behaviour of intermicellar interaction so as to describe phase separation of nonionic micellar solutions.

VIRIAL EXPANSION FOR A MICELLAR SOLUTION

It is known from experiments, that in some nonionic micellar solutions the micellar mass and size remain fairly constant through a wide concentration range over the critical micellization concentration[8,9]. Therefore, it is reasonable to consider single-phase micellar solution to be a two-component system, where the solvent consists of water plus monomer and the micelles form the solute. Furthermore, it is convenient to assume micelles to be monodisperse with a single aggregation number independent on concentration.

The McMillan-Mayer theory may be applied to nonionic micellar solution if the micellar molar mass is independent on concentration[10]. According to Ref.10, the micelle activity coefficient γ and the osmotic pressure π may be represented as series in micelle number density ρ

$$\ln\gamma = 2B_{22}\rho + 3B_{222}\rho^2 + \ldots \tag{1}$$

$$\pi/(\rho kT) = 1 + B_{22}\rho + B_{222}\rho^2 + \ldots \tag{2}$$

Here, the virial coefficients B_{ii} are related to the solute-solute cluster integrals b_{ii} (for example $B_{22}=-b_{22}$). The second virial coefficient is defined by[10]

$$B_{22}=-2\pi N_A \int_0^\infty (\exp(-\Psi(r)/kT)-1)r^2dr \tag{3}$$

where $\Psi(r)$ is the potential of mean force (PMF) of solute-solute interaction in aqueous medium. To analyse the state equation (1) in explicit form, one needs to calculate the virial coefficient B_{22} (3).

THE POTENTIAL OF MEAN FORCE

For spherical solute particles, the PMF is the work done on two particles to bring them from infinite separation to distance r from each other in the given solvent. In general, this work consists of two parts: the work done against the forces of intermicellar interaction (u(r)) and the work done on the change of the free energy of the solvent. Denoting the work on the last process by W(r) we can write the expression for PMF as[7]

$$\Psi(r) = u(r) + W(r) \tag{4}$$

The potential energy of intermicellar interaction is

$$u(r) = u_0 + u_d + u_s \tag{5}$$

where u_0 is a potential of the steric repulsion between the hard spheres of the radius R, u_d and u_s are the potentials of dispersion and structural interaction, respectively[7]. The energy of the dispersion interaction between spherical particles in liquid is described by the Hamaker formula:

$$u_d(r)=-(A/6)\{2R^2/(r^2-4R^2)+2R^2/r^2+\ln(1-4R^2/r^2)\} \tag{6}$$

where r is a separation between centers of micelles, A is the complex Hamaker constant for the system amphiphile-water-amphiphile.

According to Ref.7, we write down the potential of structural forces between hydrated surfaces of the radius R

$$u_s(r) = KR\exp(-(r-2R)/l) \tag{7}$$

where l is a correlation length of the molecular ordering, K is a state-dependent coefficient which is proportional to the degree of hydration. In the previous work[7] we represented K in the form $K=K'\exp(Q/kT)$, where K' is a temperature-independent factor and Q plays a role of an activation energy for solvent molecules.

solution) the coefficient cannot be correctly determined in experiment because of increase in the collective character of intermicellar interactions. That is why the large negative values of the second virial coefficient and its derivative ($\partial B_{22}/\partial T$) seem doubtful. Therefore, we can consider the meanings of the fit 1 to be more realistic.

THE PHENOMENOLOGICAL STATE EQUATION AT FINITE DILUTION

In our previous work we have considered the second virial coefficient at finite dilution. We have used a concentration-dependent micellar PMF instead of the McMillan-Mayer PMF $\Psi(r)$ in Eq.(8). We assumed that the potential u(r) does not depend on the micelle concentration. Moreover, we have supposed W(r) to be a small negative value decreasing with concentration that corresponds to the weak hydrophobic attraction between dehydrated micelles. Basing on these suppositions, we have suggested a state equation for a micellar solution

$$\pi/(\rho kT) = 1 + B^*(T)\rho + W\rho^{q-1} \qquad (8)$$

and the expression for the micelle activity coefficient

$$\ln\gamma = 2B^*(T)\rho + 2W\rho^{q-1} \qquad (9)$$

where $1<q<2$, $B^*(T)=1+K^*\exp(Q^*/kT)-A^*$ (q, K^*, Q^* and A^* are positive fitting parameters) and W is a negative constant, determined by the values of K^*, Q^*, A^* and q. This four-parameter model provides full coincidence of the calculated results with the experimental consolution curves[9] for the solutions of nonionic surfactant $C_{12}E_8$ in water[7,14].

The preceding analysis shows that phase behaviour of nonionic micellar solutions is determined by the temperature dependence of the micellar PMF. The increase in the hydrophobic character of the micelles is due to the intensification of thermal motion of the solvent molecules and

TEMPERATURE BEHAVIOUR OF THE MICELLAR INTERACTION POTENTIAL

For the further analysis, we assume W(r) to be independent on temperature. Figure 1 shows the qualitative form of the normalized potential u(r)/kT (5) for $A/6 \approx KRl^2$. There are two qualitative types of intermicellar potentials depending on whether the dispersion or the structural term dominates at the short distances. The curve 1 corresponds to the short-range structural forces ($l=0.1R$). There exists a potential barrier near the point $r=2R$ in this case. Its width and the R value add up to the radius of a hydrated micelle. In the case of "long-range" structural effects $l=0.5R$ (curve 2), there appears a deep potential well near the point of contact of the micelles, followed by an energy barrier and a secondary minimum. Both the shapes of the potential are typical for those observed in charged colloids according to the DLVO theory[11,12].

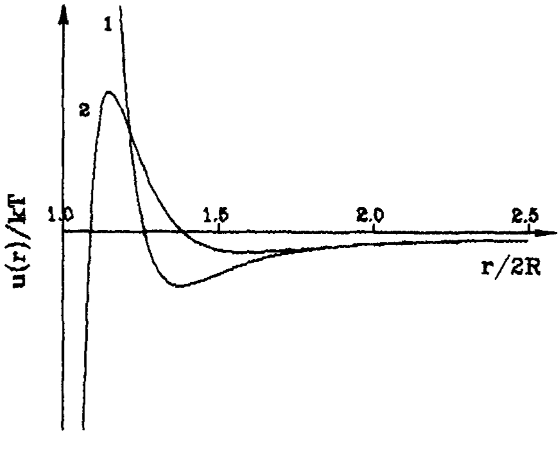

FIGURE 1 Qualitative form of the normalized potential u(r)/kT for $l=0.1R$(1) and $l=0.5R$(2)

Figure 2 demonstrates a set of u(r) curves calculated according to Eq. (7) for $l=0.1R$ at different temperatures. Since the equilibrium $u_s(r)$ value decreases as

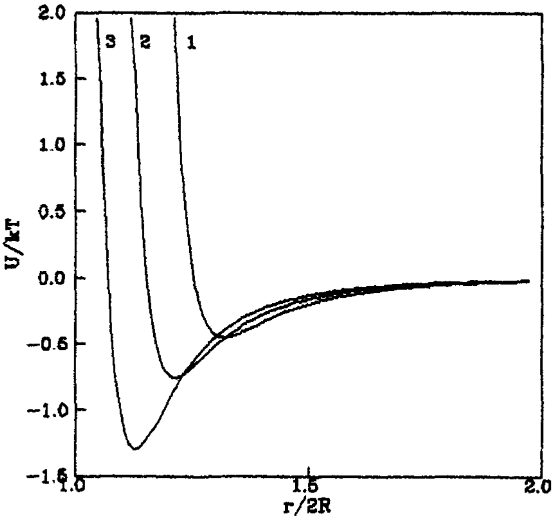

FIGURE 2 The normalized potential $u(r)/kT$ at different temperatures: $T_1<T_2<T_3$

the temperature is raised, the potential barrier retarding the coacervation of micelles lowers and concurrently potential minimum depth increases. It is seen from the pictures that the effective micelle radius also decreases with temperature.

TEMPERATURE DEPENDENCE OF THE SECOND VIRIAL COEFFICIENT

Using Eqs. (4-7) we obtain the second virial coefficient in the form

$$B_{22}=-2\pi N_A\{(2R)^3/3-\int_{2R}^{\infty}(\exp(-\Psi(r)/kT)-1)r^2dr\} \qquad (8)$$

N_A is the Avogadro's number. Temperature dependence of the B_{22} value is caused by the thermal motion of micelles themselves and solvent molecules. In the limit of $T\to\infty$ the integral in Eq. (8) tends to zero. In this limit the virial coefficient equals to the volume excluded by a micelle. At the low temperatures the exponential function $\exp(-\Psi(r)/kT)$

rapidly increases due to the increase in the structural potential and, hence, the integral diverges, $B_{22} \to \infty$.

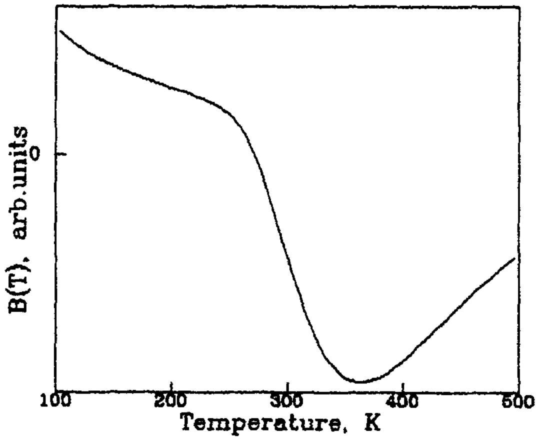

FIGURE 3 Temperature dependence of the second virial coefficient $B_{22}(T)$.

Considering formally the behaviour of function $B_{22}(T)$ (8) over a wide temperature range ($T=100 \div 500K$), we find that it is non-monotonic. There exists a minimum on the plot of B_{22} versus T (Fig.4). One can divide the $B_{22}(T)$ curve into three regions corresponding to different types of effective intermicellar interaction:

1) At the temperatures lower than T~300K the second virial coefficient is positive because of significant contribution of the structural component to PMF ($u_s \propto \exp(Q/kT)$). The effective intermicellar interaction is repulsive.

2) At the temperatures between 300K and 350K the value of $B_{22}(T)$ gradually decreases and eventually becomes negative. In this temperature range micelles are attracted to each other due to the dispersion interaction.

3) When the temperature is raised over 350K, the virial coefficient reaches its minimum and then increases up to positive values. This effective repulsion is caused by the thermal motion of the micelles and the packing effects.

Different parts of the $B_{22}(T)$ curve correspond to the liquid state of the solution depending on the ratio A/K'.

The case when minimum of the $B_{22}(T)$ curve falls into the temperature range of water is of the most interest. In this case reentrant phase transitions in mesophases and closed consolution regions can appear.

The second virial coefficient for nonionic micellar solutions C_iE_j- water has been measured by Herrington and Sahi[13]. The virial coefficient has been found to be positive at t~0°C and negative near the cloud point for all the studied systems. The existence of the minimum on the curve $B_{22}(T)$ is established for the solution $C_{12}E_6$ - H_2O. The temperature of clouding increases in the series of homologs $C_{12}E_j$ when j being increased. The increase in the number of hydrophilic units (ethylene oxide) is reflected by the negative value of $B_{22}(T)$ at higher temperatures.

Figure 4 demonstrates coincidence of our theoretical calculation with the experimental data of Ref 13. For the solution $C_{12}E_8$-H_2O we put $A=1,8 \cdot 10^{-13}$erg, $K'=6,8 \cdot 10^6$dyne/cm^2 $l=3$Å, $R=20$Å, $Q=1600$K (curve 1) and $A=1,7 \cdot 10^{-14}$ erg, $K'=3,68 \cdot 10^5$ dyne/cm^2, $l=3$Å, $R=20$Å, $Q=1600$K (curve 2). The virial coefficient at low temperatures. The curve 1 fits the dramatic decrease of $B_{22}(T)$ on heating. It should be noted, however, that near the cloud point (T=348K for this

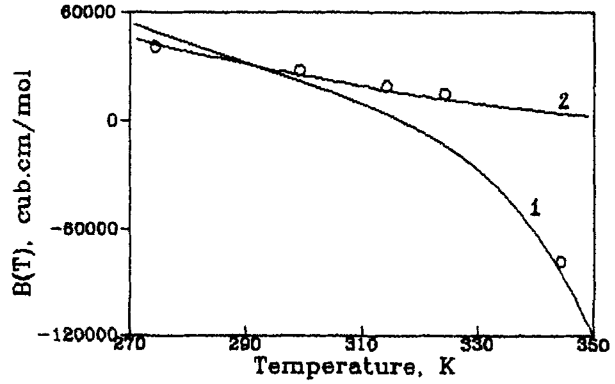

FIGURE 4 Calculated curves $B_{22}(T)$ in comparison with the experimental data of Ref. 13.

dehydration of polar heads of the surfactant particles. It should be noted that both attractive and repulsive forces between micelles fall off with temperature but the attractive forces becomes dominant at the higher temperatures.

In the recent work[6], Israelashvili and Wennerström have suggested quite different treatment of the repulsive force between amphiphilic surfaces. It is considered that the amphiphile headgroup protrusion into the solvent interlayer gives the dominant contribution to the repulsive force and there is no reason to invoke the special hydration (structural) force for an explanation of the stability of colloids. According to Ref.6, we may suppose that decrease in the repulsive component is caused by change of flexibility of the protruding headgroups as a result of the dehydration. Our value of $K=4\cdot10^7$dyne/cm^2 used for the approximation of the experimental data[13] coincide with the estimates of the characteristic value $K=1.4\cdot10^7$dyne/cm^2 for protrusion force between amphiphilic bilayers[6]. It should be remarked, however, that the overlap repulsion should increase with temperature that is in contrast with experimentally observed tendency for decreasing the second virial coefficient.

CONCLUSION

In the present work the temperature behaviour of the second virial coefficient has been studied. It has been found that effective intermicellar interaction is predominantly repulsive at the temperatures close to 0°C becomes attractive as the cloud point is approached. It has been shown that the molecular mechanism of phase separation of micellar solution at the lower critical point involves the dispersion and the hydrophobic attraction between micelles.

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