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Cluster partition function for the micellar phase of an amphiphile–solvent mixture in a lattice model

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Abstract. The cluster partition function for a lattice model of an amphiphile–solvent mixture is derived for small amphiphile concentration using a piecewise linear approximation for the cluster statistics and in the absence of head–head interactions. The partition function depends upon the lattice dimensionality, the lattice coordination number, the number of segments in the amphiphile chain, the temperature and the nature of the head–solvent and tail–solvent interactions. No prior assumptions are made about the presence or geometry of micelles. It is shown that for this partition function, with suitable choice of temperature and amphiphile concentration, the cluster size distribution shows a micellar phase for sufficiently solvophilic head–solvent interactions.

The micelle size is limited by entropy alone and the dominant clusters are compact but not necessarily spherical. The model exhibits a critical micelle concentration which depends upon amphiphile chain length in a way which agrees with experiment. However, the model fails to give the correct temperature dependence of the critical micelle concentration. The micellar phase is also more limited, and the critical micelle concentration smaller, than is observed for real amphiphilic materials.

1. Introduction

The formation of micelles in dilute solutions of amphiphilic materials is well established experimentally but the theoretical understanding of the process is more restricted (e.g. Mittal 1984). In the majority of theoretical studies the micelles are explicitly introduced either by making assumptions about the form of the free energy or assuming a particular cluster geometry.

In this paper we derive the cluster partition function for a lattice model of an amphiphile–solvent mixture without any prior assumptions about the presence or form of the micelles. The arguments are related to those used by Fisher (1967) in his droplet model of condensation. It is shown that the model exhibits a micellar phase and that the micelle size is limited by entropy alone. It is assumed (Wennerstrom 1979) that a micellar phase is associated with a cluster size distribution which shows both a minimum and a maximum.

We consider a lattice model of an amphiphile and solvent mixture (Care 1987a, b). The model represents an incompressible solution of N_A amphiphile molecules and N_S solvent molecules. The molecules occupy the sites of a regular lattice with coordination number c . Each amphiphile is represented by a flexible chain of s adjacent sites with one

site on the end of the chain representing the solvophilic head and the remaining $(s - 1)$ sites representing the flexible solvophobic tail. The remaining sites in the lattice each represent solvent molecule. There are no unoccupied sites. The total number of sites on the lattice, M , is equal to $sN_A + N_S$. The nearest-neighbour potential energy for fully flexible amphiphiles is given by

$$U/kT = \beta(n_{TS} + \gamma n_{HS} + \eta n_{HH}) \quad (1)$$

where n_{HS} , n_{TS} , n_{HH} are the total number of head-solvent, tail-solvent and head-head bonds. The parameter β is the ratio of the tail-solvent bond energy to kT , γ the ratio of the head-solvent bond energy to the tail-solvent bond energy and η the ratio of the head-head bond energy to the tail-solvent bond energy. Care (1987a) showed that the lattice imposes constraints on the number of each type of possible bond and that for nearest neighbour interactions there are only three independent bond parameters.

In order to represent normal amphiphilic behaviour, the tail-solvent interaction is chosen to be solvophobic ($\beta > 0$) and the head-solvent interaction is chosen to be solvophilic ($\gamma < 0$). We also set $\eta = 0$ and hence ignore head-head interactions.

2. The cluster partition function

The grand partition function for the binary mixture may be written with standard notation (Hill 1960) as

$$\Xi(M, T, \mu_A, \mu_S) = \sum_{N_A \geq 0} \sum_{N_S \geq 0} Q(M, T, N_A, N_S) \exp\left(\frac{\mu_S N_S}{kT}\right) \exp\left(\frac{\mu_A N_A}{kT}\right) \quad (2)$$

where μ_A and μ_S are the chemical potentials for the amphiphiles and the solvent respectively, and $Q(M, T, N_A, N_S)$ is the canonical partition function for a two component system given by

$$Q(M, T, N_A, N_S) = [q_S]^{N_S} [q_A]^{N_A} \sum_i \exp\left(-\frac{U_i}{kT}\right) \quad (3)$$

q_A and q_S being the non-configurational partition functions for the amphiphile molecules and solvent molecules, respectively.

The number of lattice sites M is fixed and hence (2) may be rewritten in the form

$$\Xi(M, T, \mu_A, \mu_S) = (e^{\beta\mu_S})^M \Phi(M, T, \mu'_A) \quad (4)$$

where

$$\Phi(M, T, \mu'_A) = \sum_{N_A \geq 0} Q(M, T, N_A) \exp\left(\frac{\mu'_A N_A}{kT}\right). \quad (5)$$

Here Φ is the grand partition function for a one-component system with N_A objects on a lattice of M sites, each with chemical potential $\mu'_A = \mu_A - s\mu_S$. $Q(M, T, N_A)$ is a canonical partition function for a one-component system with a definition analogous to that given in equation (3).

The grand partition function of the form (5) may be expanded in terms of physical clusters (Hill 1956). At low concentrations, near the critical micelle concentration, we

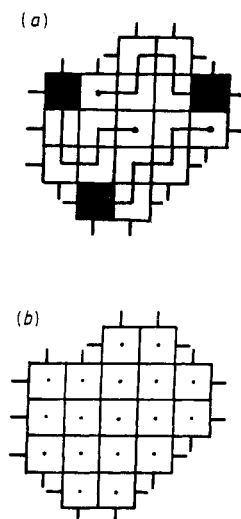


Figure 1. (a) n -cluster with $n = 3$; (b) (x, p) -cluster with $x = 18$ and $p = 20$.

may ignore cluster-cluster interactions and the mole fraction of monomers in clusters containing n monomers, X_n , is given by

$$X_n = [nQ_n(T)/(Q_1(T))^n]X_1^n \quad (6)$$

where $Q_n(T)$ is the cluster partition function for n monomers

$$Q_n(T) = (q(T))^n \sum_{p=p^-}^{p^+} \sum_{n_{\text{HS}}=0}^{n^+_{\text{HS}}} g_n(p, n_{\text{HS}}) \exp[-\beta(p - n_{\text{HS}})] \exp[-\beta\gamma n_{\text{HS}}]. \quad (7)$$

In equation (7), $g_n(p, n_{\text{HS}})$ is the total number of n -clusters with p surface bonds and n_{HS} head-solvent bonds. $q(T)$ is the non-configurational partition function for each monomer.

A monomer is assumed to be connected to a cluster if it shares at least one nearest-neighbour bond with the cluster. In the following we describe a connected cluster of n monomers as an n -cluster and this occupies ns sites. We describe a connected cluster of x lattice sites with p surface bonds as an (x, p) -cluster. These clusters are illustrated in figure 1.

The minimum number of surface bonds on a n -cluster, p^- , is related to the perimeter of the most compact n -cluster. We assume that in a lattice of dimensionality d this is of the form

$$p^- = \text{int}(\xi_d(ns)^{(d-1)/d}) \quad (8)$$

where

$$\xi_2 = 2(\pi)^{1/2}$$

$$\xi_3 = 4\pi(3/4\pi)^{2/3}.$$

The maximum number of surface bonds on an n -cluster, p^+ , is obtained when the monomers are arranged linearly. This suggests

$$p^+ = (c - 2)ns + 1 + \delta \quad (9)$$

where for future convenience $\delta = 1$ or 0 in order to ensure $(p^+ + p^-)$ is even.

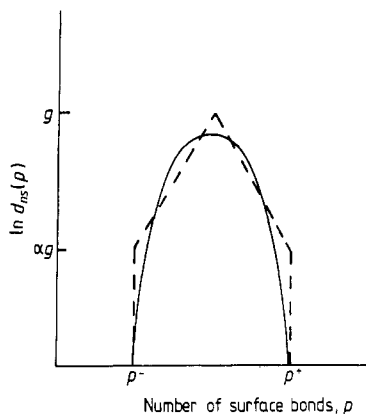


Figure 2. Full curve, exact form of $\ln d_{ns}(p)$ for small ns ; broken lines, piecewise linear approximation for $\ln d_{ns}(p)$.

The maximum number of head solvent bonds on an n -cluster, n_{HS}^+ is given by

$$n_{\text{HS}}^+ = \text{Min}(p, n(c-1)). \quad (10)$$

The central problem is the determination of $g_n(p, n_{\text{HS}})$. In order to make progress we write

$$g_n(p, n_{\text{HS}}) = d_{ns}(p)c_n(p, n_{\text{HS}}) \quad (11)$$

where $d_{ns}(p)$ is the number of possible (ns, p) -clusters, and $c_n(p, n_{\text{HS}})$ is the number of ways of arranging n monomers on an (ns, p) -cluster to give n_{HS} head-solvent bonds. From standard lattice statistics we identify $d_{ns}(p)$ as a coefficient in the appropriate cluster perimeter polynomial (Sykes and Glen 1976) and note that the number of connected clusters of ns lattice sites, D_{ns} , is given asymptotically by (Domb 1976)

$$D_{ns} = A\lambda^{ns}/(ns)^\theta \quad (12)$$

where λ , θ and A are constants which are determined by the nature of the lattice and its dimensionality. It is evident that

$$\sum_{p=p^-}^{p^+} d_{ns}(p) = D_{ns}. \quad (13)$$

Unfortunately the $d_{ns}(p)$ are only tabulated for small n and hence we make a piecewise linear approximation in equation (7) as follows

$$\begin{aligned} \ln d_{ns}(p) &= -\infty & p < p^- \\ &= \alpha g + 2g(1-\alpha)(p-p^-)/(p^+-p^-) & p^- \leq p \leq p^- + (p^+-p^-)/2 \\ &= \alpha g + 2g(1-\alpha)(p^+-p)/(p^+-p^-) & p^- + (p^+-p^-)/2 \leq p \leq p^+ \\ &= -\infty & p > p^+ \end{aligned} \quad (14)$$

where g is determined by the condition (13). An approximate expression for g in terms of λ , θ and A is given later in the paper. α is a free parameter in the range $0 < \alpha < 1$.

The exact form of $\ln d_{ns}(p)$ is known for small ns for some lattices (e.g., Sykes and Glen 1976) and it is reasonable to assume it will have a similar form for large ns . This is shown schematically in figure 2, together with the piecewise linear approximation for $\ln d_{ns}(p)$.

α is included in equation (14) in order to improve the fit of the piecewise linear approximation to the expected curve of $\ln d_{ns}(p)$ and is typically set at 0.5. The results obtained below are not affected qualitatively by the choice of this parameter. An improved form for $\ln d_{ns}(p)$ can be obtained by a quadratic fit but this unfortunately makes the summation intractable.

The combinatorial term $c_n(p, n_{HS})$ may be estimated by assuming that the bonds within an n -cluster are independent. This approximation is similar in philosophy to the quasi-chemical approximation and ignores the connectivity of each amphiphile. Inclusion of this connectivity in an improved approximation would enhance the micellisation of the model by inhibiting large clusters in which amphiphile heads were unable to reach the surface. There are a total of nsc bonds associated with an n -cluster, of which $n(c - 1)$ are head bonds. The term $c_n(p, n_{HS})$ is then the product of the number of ways of arranging n_{HS} head-solvent bonds among p surface sites and the remaining $(n(c - 1) - n_{HS})$ head bonds among $nsc - p$ internal bonds. Thus

$$c_n(p, n_{HS}) = [p!/(n_{HS})!(p - n_{HS})!] \times (nsc - p)!/[n(c - 1) - n_{HS}]![nsc - p - n(c - 1) + n_{HS}]! \tag{15}$$

We use Stirling's approximation and the assumption that the important clusters have many more internal bonds than surface bonds to rewrite (15) as

$$c_n(p, n_{HS}) = [p!/(n_{HS})!(p - n_{HS})!][sc/(c - 1)]^{n(c-1)-n_{HS}} \tag{16}$$

If we substitute equations (11), (14) and (16) into equation (7) and rearrange, we find that the cluster partition function is given by

$$Q_n(T) = \{q(T)[sc/(c - 1)]^{c-1}\}^n e^{\alpha g} \left\{ \exp\left(-\frac{2gp^-(1 - \alpha)}{(p^+ - p^-)}\right) \times \sum_{p=p^-}^{(p^+ + p^-)/2} \left[\exp\left(-\beta + \frac{2g(1 - \alpha)}{p^+ - p^-}\right) \right]^p \sum_{n_{HS}=0}^{n_{HS}} \frac{p!}{(n_{HS})!(p - n_{HS})!} \times \left(\frac{(c - 1) e^{\beta(1 - \gamma)}}{sc} \right)^{n_{HS}} + \exp\left(\frac{2gp^+(1 - \alpha)}{p^+ - p^-}\right) \times \sum_{p=(p^+ + p^-)/2+1}^{p^+} \left[\exp\left(-\beta - \frac{2g(1 - \alpha)}{p^+ - p^-}\right) \right]^p \times \sum_{n_{HS}=0}^{n_{HS}} \frac{p!}{(n_{HS})!(p - n_{HS})!} \left[\frac{(c - 1) e^{\beta(1 - \gamma)}}{sc} \right]^{n_{HS}} \right\} \tag{17}$$

We can perform these summations by noting the following results

$$\sum_{s=0}^{\text{Min}(n,p)} \frac{p!}{s!(p - s)!} x^s = (1 + x)^p [1 - H(p - n - \frac{1}{2})I_{x/(1+x)}(n + 1, p - n)] \tag{18}$$

where n and p are positive integers, $I_z = (a, b)$ is the incomplete beta function (e.g. Abramowitz and Stegun 1965) and $H(x)$ is the Heaviside step function. We define

$$q(t, z, a, b, n) = \sum_{p=a}^b t^p (1 - H(p - n - \frac{1}{2})I_z(n + 1, p - n)) \tag{19}$$

where $0 \leq z \leq 1$, $-\infty < t < \infty$ and $n < b$.

Using results in appendix 1 it can be shown that

$$\begin{aligned}
 q(t, z, a, b, n) &= \frac{t^a - t^{n+1}}{(1-t)} + t^{n+1}(1-z^{n+1}) + s(t, z, n+2, b, n) & n \geq a \\
 &= t^{n+1}(1-z^{n+1}) + s(t, z, n+2, b, n) & n = a - 1 \\
 &= s(t, z, a, b, n) & n < a - 1
 \end{aligned}
 \tag{20}$$

where

$$\begin{aligned}
 s(t, z, a, b, n) &= [1/(1-t)] \{ [zt/[1-t(1-z)]]^{n+1} [\hat{I}_{t(1-z)}(b-n, n+2) \\
 &\quad - \hat{I}_{t(1-z)}(a-n-1, n+2)] \\
 &\quad + t^a \hat{I}_{1-z}(a-n-1, n+2) - t^{b+1} \hat{I}_{1-z}(b-n, n+2) \}.
 \end{aligned}
 \tag{21}$$

$\hat{I}_z = (p, q)$ is the extended incomplete beta function defined in appendix 1.

Using results (7) to (21) we may finally write the cluster partition function as

$$\begin{aligned}
 Q_n(T) &= \{q(T)[sc/(c-1)]^{c-1}\}^n \left\{ \exp\left(\alpha g - \frac{2gp^-(1-\alpha)}{p^+ - p^-}\right) q\left[1 + (c-1)e^{\beta(1-\gamma)}/sc\right] \right. \\
 &\quad \times \exp\left(-\beta + \frac{2g(1-\alpha)}{p^+ - p^-}\right), \frac{(c-1)e^{\beta(1-\gamma)}}{sc + (c-1)e^{\beta(1-\gamma)}}, p^-, \frac{p^+ + p^-}{2}, n(c-1) \left. \right] \\
 &\quad + \exp\left(\alpha g + \frac{2gp^+(1-\alpha)}{p^+ - p^-}\right) q\left[1 + (c-1)e^{\beta(1-\gamma)}/sc\right] \\
 &\quad \times \exp\left(-\beta - \frac{2g(1-\alpha)}{p^+ - p^-}\right), \frac{(c-1)e^{\beta(1-\gamma)}}{sc + (c-1)e^{\beta(1-\gamma)}}, \frac{p^+ + p^-}{2} + 1, p^+, n(c-1) \left. \right\}.
 \end{aligned}
 \tag{22}$$

The terms p^+ and p^- are defined in equations (8) and (9) and it can be shown to a good approximation that

$$g = \ln D_{ns} - \ln \left[(D_{ns}^{2(1-\alpha)/(p^+ - p^-)} + 1) / (D_{ns}^{2(1-\alpha)/(p^+ - p^-)} - 1) \right]
 \tag{23}$$

where D_{ns} is defined by equation (12).

3. Results

The expression (22) is plotted in figures 3 to 6 for some parameters chosen to illustrate the behaviour of X_n in the region where the model exhibits micellar behaviour. It is anticipated that each chain segment in the model may be taken to represent several repeat units in real amphiphilic materials. The range of micellar behaviour within the model is more limited than for real amphiphilic materials with the critical micelle concentration (CMC) having a very small value, particularly for longer chain lengths. This latter effect arises because for long chains the effect of the single head segment becomes less important. A similar effect was noted in the quasi-chemical analysis of this model (Care 1987a). It is hoped that the inclusion of a more realistic potential in future

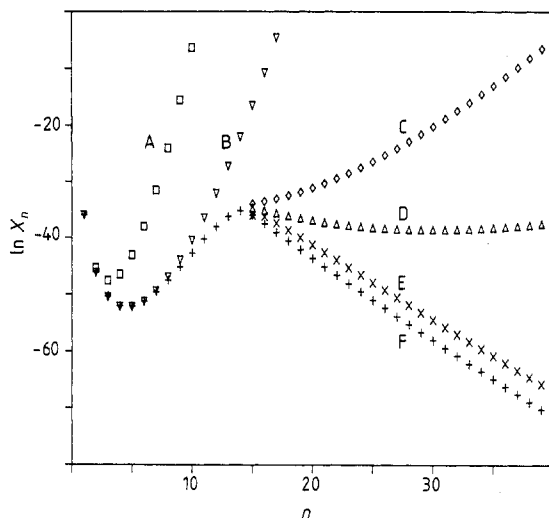


Figure 3. Variation with n of mole fraction of monomers in clusters of size n , X_n . Numbers of segments, $s = 4$. Mole fraction of monomers, $X_1 = 2.58 \times 10^{-16}$. Reduced temperature $\beta^{-1} = 0.18$. Dimensions, $d = 3$. Co-ordination number, $c = 6$. $\alpha = 0.5$. Micellar behaviour only occurs in curves E and F. Curve A, $\gamma = 1.0$; curve B, $\gamma = 0.5$; curve C, $\gamma = 0.0$; curve D, $\gamma = -0.1$; curve E, $\gamma = -0.2$; curve F, $\gamma = -1.0$.

work may improve the correspondence between the CMC predicted by the model and the experimentally observed CMC.

For all figures, the values chosen for the parameters in D_{ns} were $A = 1$, $\theta = 1$ and $\lambda = 4$. It should be noted that plots of the expression (22) show slight irregularities which arise because of the discrete nature of p^- as defined in equation (8). The results presented in the figures show a value for X_n which is obtained by using (22) to interpolate between two integer values of p^- , and effectively set $p^- = \xi_d(ns)^{(d-1)/d}$ rather than $\text{int}(\xi_d(ns)^{(d-1)/d})$.

When interpreting the figures it should be noted that the system undergoes a normal phase separation at low temperature if X_1 exceeds a value X_{cond} , for which an expression is derived in appendix 2.

In figure 3 it can be seen that normal phase separation occurs until γ becomes sufficiently negative. For the temperature and chain length in figure 3, the value of γ at which micelles appear lies in the range $-0.1 > \gamma > -0.2$. It can be seen that for small γ a cluster peak occurs around $n = 14$. This corresponds to the smallest cluster size for which it is possible to have the perimeter entirely composed of head-solvent bonds. Future changes to the model will involve improving the approximation for $c_n(p, n_{\text{HS}})$ to properly allow for surface texture. However it should be noted that the clusters with minimum perimeter are those which dominate the results in the micellar region. It can also be seen that the effect of the solvophobic head-solvent interaction saturates when $\gamma \approx -\beta^{-1}$.

Figure 4 shows how the cluster concentration varies with monomer concentration. It can be seen that at some monomer concentration, X_1 , the concentration of monomers in clusters of size n is equal to X_1 . This value of X_1 may be identified approximately with the critical micelle concentration. It is important to note that as X_1 increases towards

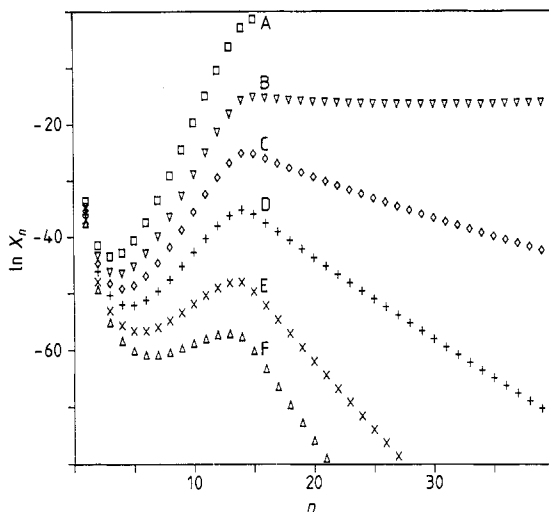


Figure 4. As in figure 3, except for the following: number of segments, $s = 4$. Head-solvent interaction $\gamma = -1$. Reduced temperature $\beta^{-1} = 0.18$. Dimensions, $d = 3$. Coordination number, $c = 6$. $\alpha = 0.5$. $X_{\text{cond}} = 5.27 \times 10^{-16}$ (curve C). Curve A, $X_1 = 2.58 \times 10^{-15}$; curve B, $X_1 = 1.03 \times 10^{-15}$; curve C, $X_1 = 5.27 \times 10^{-16}$; curve D, $X_1 = 2.58 \times 10^{-16}$; curve E, $X_1 = 1.03 \times 10^{-16}$; curve F, $X_1 = 5.16 \times 10^{-17}$.

X_{cond} , the total amphiphile mole fraction, X_A increases much more rapidly. X_A is given by

$$X_A = \sum_{n=1}^{\infty} X_n. \quad (24)$$

A detailed analysis would require evaluation of the summation in equation (24). However, from the peak value of X_n for $X_1 = X_{\text{cond}}$ it can be estimated that the micellar phase shown in figure 4 is stable for at least four orders of magnitude of X_A . Although this range is less than real micellar systems it still represents a significant region of the phase diagram.

Figure 5 shows that the dependence of the critical micelle concentration on chain length is similar to that observed experimentally (Tanford 1980). However the temperature dependence of the CMC in the model (figure 6) is much stronger than that observed experimentally (Tanford 1980, Mittal and Lindman 1984).

4. Conclusion

In conclusion we have used a piecewise linear approximation for the cluster statistics to derive a closed analytic expression for the cluster partition function in a lattice model of an amphiphile-solvent mixture. The partition function depends upon the lattice dimensionality, the lattice coordination number, the number of segments in the amphiphile chain, the temperature and the nature of the head-solvent and tail-solvent interactions. Depending upon the choice of head-solvent interaction, the partition function leads to either normal phase separation or micellar behaviour. In the micellar phase the size of the micelles appears to be limited by entropy alone.

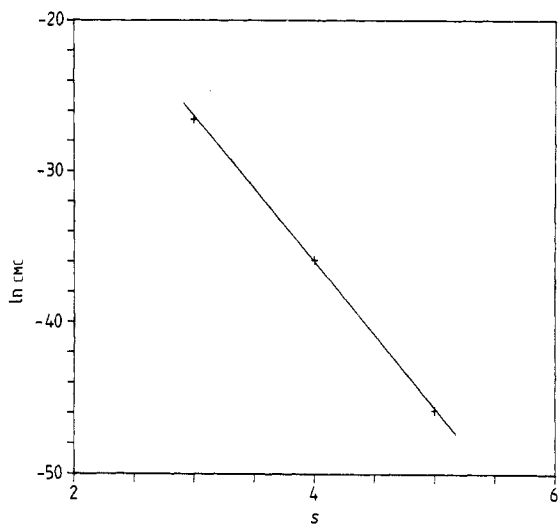


Figure 5. Variation of critical micelle concentration (CMC) with number of segments, s . Head-solvent interaction, $\gamma = -1$. Reduced temperature, $\beta^{-1} = 0.18$. Dimensions, $d = 3$. Coordination number, $c = 6$. $\alpha = 0.5$.

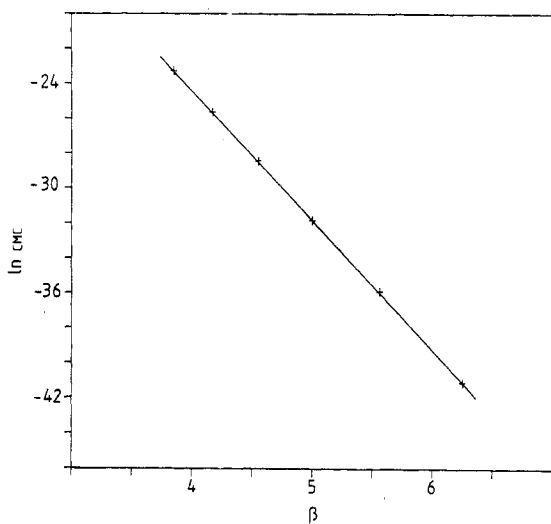


Figure 6. Variation of CMC with β (inverse reduced temperature). Head-solvent interaction, $\gamma = -1$. Number of segments, $s = 4$. Dimensions, $d = 3$. Coordination number $c = 6$. $\alpha = 0.5$.

Hence for a suitable range of concentrations and temperature, the monomers aggregate into clusters ordered in such a way as to minimise tail-solvent interactions, but so as to maximise head-solvent interactions. However entropy is maximised if many small clusters are formed rather than a limited number of large clusters. The precise cluster size is consequently determined by the competition between these two opposing effects.

The results also show that head-head repulsions are not essential in order to form a micellar phase. The clusters which make the greatest contribution to the partition function are those which are compact but not necessarily spherical. The model gives the correct chain length dependence for the CMC but fails to give the correct temperature dependence for the CMC.

The current work does not correctly predict the surface texture of the clusters. It is possible to define the surface texture of a cluster, τ , as

$$\tau = \text{number of head-solvent bonds/cluster perimeter.} \quad (25)$$

τ will be in the range $0 < \tau < \tau_{\max}$, where τ_{\max} must be less than one from geometrical considerations. Assumptions made in deriving $c_n(p, n_{\text{HS}})$ in equation (15) allow values of $\tau = 1$ in the work presented in this paper. In future work it is hoped to modify the form of $c_n(p, n_{\text{HS}})$ in order to improve the way in which the model deals with surface texture and also to take account of the chain length more carefully.

It is also intended to evaluate the summation (24) and hence determine $X_n(X_A, T)$ rather than $X_n(X_1, T)$ as has been determined in this paper. This will allow comparison with the theory of Israelachvili *et al* (1976) and may also allow the identification of other liquid-crystal phases within the model. The work would be further improved by the inclusion of head-head interactions and longer range interactions, but these changes may render the model intractable. Monte Carlo simulations of the lattice model are currently being undertaken in order to test the validity of the approximations used in this paper.

Appendix 1

We wish to evaluate summations of the form

$$R(t, z, a, b, n) = \sum_{p=a}^b t^p I_z(n+1, p-n) \quad (A1.1)$$

$$= \sum_{p=a}^b t^p \left(\sum_{s=n+1}^p \frac{p!}{s!(p-s)!} z^s (1-z)^{p-s} \right) \quad (A1.2)$$

where a, b, n are positive integers with $b \geq a > (n+1)$, $0 \leq z \leq 1$, $-\infty < t < \infty$ and $I_z(p, q)$ is the incomplete beta function (Abramowitz and Stegun 1965) defined by

$$I_z(p, q) = \frac{1}{B(p, q)} \int_0^z u^{p-1} (1-u)^{q-1} du \quad 0 \leq z \leq 1. \quad (A1.3)$$

Here $B(p, q)$ is the beta function.

We differentiate equation (A1.1) with respect to z , finding after some manipulation that

$$dR/dz = [z^n t^{n+1} / (1-u)^{n+2}] T(u, a, b, n) \quad u = t(1-z) \quad (A1.4)$$

where

$$T(u, a, b, n) = \sum_{p=a}^b \frac{p!}{n!(p-n-1)!} u^{p-n-1} (1-u)^{n+2}. \quad (A1.5)$$

The expression (A1.3) is valid for $-\infty < t < \infty$ and $0 \leq z \leq 1$ except at the point $u = 1$. $T(u, a, b, n)$ has been chosen in such a way that only two terms remain in the summation when it is differentiated with respect to u . An analogous technique is suggested by

Pfeiffer and Schum (1987) for evaluating summations involving the incomplete beta function. Hence we find

$$dT/du = [a!/n!(a-n-2)!](1-u)^{n+1}u^{a-n-2} - [(b+1)!/n!(b-n-1)!](1-u)^{n+1}u^{b-n-1}. \quad (\text{A1.6})$$

We define the 'extended' incomplete beta function, $\hat{I}_z(p, q)$ as

$$\hat{I}_z(p, q) = \frac{1}{B(p, q)} \int_0^z t^{p-1}(1-t)^{q-1} dt \quad (\text{A1.7})$$

where $-\infty < z < \infty$ and p, q are positive integers.

We note that in the range $0 \leq z \leq 1$ this function is simply the incomplete beta function. We may now integrate equation (A1.6) to find

$$T(u, a, b, n) = (n+1)[\hat{I}_u(a-n-1, n+2) - \hat{I}_u(b-n, n+2)]. \quad (\text{A1.8})$$

Hence, from equation (A1.4)

$$dR/dz = [1/(1-t)](dG/dz)[\hat{I}_u(a-n-1, n+2) - \hat{I}_u(b-n, n+2)] \quad (\text{A1.9})$$

where

$$dG/dz = t^{n+1}z^{n+1}/(1-t(1-z))^{n+1}. \quad (\text{A1.10})$$

Integrating by parts we find

$$R(t, z, a, b, n) = [1/(1-t)]\{zt/[1-t(1-z)]\}^{n+1}[\hat{I}_{t(1-z)}(a-n-1, n+2) - \hat{I}_{t(1-z)}(b-n, n+2)] + t^a I_z(n+2, a-n-1) - t^{b+1} I_z(n+2, b-n)]. \quad (\text{A1.11})$$

In obtaining equation (A1.11), the integration around the point $u = 1$ is achieved by taking suitable limits.

The extended incomplete beta function obeys relations which are analogous to those for the incomplete beta function (Abramowitz and Stegun 1965). Hence it can be shown that

$$\hat{I}_z(p, q) = 1 - \hat{I}_{1-z}(p, q) \quad (\text{A1.12})$$

$$\hat{I}_z(p, q) = [1/(p+q)][p\hat{I}_z(p+1, q) + q\hat{I}_z(p, q+1)] \quad (\text{A1.13})$$

$$\hat{I}_z(p, q) = (1-z)\hat{I}_z(p, q-1) + z\hat{I}_z(p-1, q) \quad (\text{A1.14})$$

$$\hat{I}_z(p, q) = [\Gamma(p+q)/\Gamma(p+1)\Gamma(q)] z^p(1-z)^{q-1} + \hat{I}_z(p+1, q-1) \quad (\text{A1.15})$$

$$\hat{I}_z(p, q) = [\Gamma(p+q)/\Gamma(p+1)\Gamma(q)] z^p(1-z)^q + \hat{I}_z(p+1, q) \quad (\text{A1.16})$$

$$\hat{I}_z(p, 1) = z^p \quad (\text{A1.17})$$

$$\hat{I}_z(p, q) = \frac{z^p(1-z)^q}{pB(p, q)} \left[1 + \sum_{n=0}^{\infty} \frac{B(p+1, n+1)}{B(p+q, n+1)} z^{n+1} \right] \quad -1 < z < 1. \quad (\text{A1.18})$$

In equations (A1.12) to (A1.18) p and q are assumed to be positive integers and except for equation (A1.18), z is assumed to lie in the range $-\infty < z < \infty$.

In the summation R , defined in equation (A1.1), it is assumed that $a > n + 1$ because the result (A1.11) is not well defined when $a = n + 1$. However, the summation may be extended to include $a = n + 1$ by noting that

$$R(t, z, n + 1, b, n) = (tz)^{n+1} + R(t, z, n + 2, b, n) \quad (\text{A1.19})$$

where we have used a form of the result (A1.17). The second term on the right of (A1.19) may be expanded using result (A1.11).

The extension of the incomplete beta function allows the summation defined in equations (A1.1) and (A1.2) to be found in integral form. For large a and b this result is more readily amenable to numerical evaluation than the original summation.

Appendix 2

The asymptotic form of $Q_n(T)$ can be found most readily from equation (17). After some manipulation it can be shown that

$$\lim_{n \rightarrow \infty} (X_n) = n \exp(-\chi n^{2/3}) y^n \quad (\text{A2.1})$$

where

$$y = \frac{\lambda^{\alpha s} [u(1+v)]^{c-1} X_1}{Q_1(T)} \quad \chi = [2\xi_d(1-\alpha)s^{(d-1)/d} \ln \lambda]/(c-2)$$

$$u = e^{-\beta} \lambda^{2(1-\alpha)/(c-2)} \quad v = (c-1) e^{\beta(1-\gamma)/sc}$$

The equation (A2.1) is valid provided $|u| \ll 1$, $v \gg 1$ and $uv > 1$. These conditions are satisfied for the cases of interest in this paper. Hence the system will exhibit phase separation if X_1 exceeds X_{cond} where X_{cond} is given by

$$X_{\text{cond}} = Q_1(T)/\lambda^{\alpha s} [u(1+v)]^{c-1} \quad (\text{A2.2})$$

The arguments of Israelachvili suggest that a system with X_n given by an equation of the form (A2.1) will make a transition from a micellar phase (if it exists) to infinite bilayers, when X_1 exceeds X_{cond} .

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