

On the Partitioning of Cosurfactant in Mixed Micelles: Size Enhancement and Nematic Stability[†]

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We consider a role for nonionic cosurfactant (e.g., alcohol) in ionic surfactant/water solutions according to which cosurfactant interposes itself between surfactant molecules at the micellar surface, thereby diluting the charge density. This relief of electrostatic strain is most pronounced in regions of low curvature (small head-group area). Accordingly, the cosurfactant can be shown to go preferentially into the body rather than the caps (rim) of finite-size prolate (oblate) aggregates. As a consequence of this partitioning of cosurfactant between different environments in mixed anisotropic micelles, the standard chemical potential per molecule is found to decrease faster with aggregation number (s) than in the pure surfactant/water situation: in the case of rods, for example, $\bar{\mu}_s^\circ = \bar{\mu}_\infty^\circ + (\delta_1/s) + (\delta_2/s^2)$. The presence of the $1/s^2$ term leads to a stronger increase of average size with overall amphiphile concentration and to an enhancement of nematic (vs. isotropic) phase stability. Rough estimates of these effects are made for a wide range of cosurfactant-to-surfactant ratios.

Introduction

The dramatic effects of cosurfactant on surfactant-solution polymorphism and microemulsion stability are widely appreciated.¹ Nevertheless there remains little theoretical understanding of the mechanisms whereby cosurfactants modify the preferred curvature of micellar packing, lower the interfacial tension, etc. Mather,² following up an earlier treatment by Parseghian³ of the hexagonal \rightarrow lamellar transition in ionic surfactant/water systems, has discussed a particularly simple role for added cosurfactant. Basically, the nonionic cosurfactant is assumed to dilute the surface charge by interposing itself between the charged "heads" of the surfactant molecules; the "tails" of the two amphiphilic species are supposed to pack similarly in the micellar interior. In this way the lower-curvature (i.e., smaller head-group area) structures are stabilized by added cosurfactant; e.g., the hexagonal phase gives way to the lamellar. In the present paper we use a kindred idea to treat explicitly the effect of cosurfactant on self-assembly and phase transitions in finite-aggregate solutions. We concentrate on the case of rodlike micelles, treating the partitioning of cosurfactant between the different (i.e., "body" and "cap") local environments. Added alcohol, for example, is shown to go preferentially into the "body" (where it can most effectively relieve the electrostatic "strain" due to the charged surfactant molecules), consistent with recent experimental inferences.⁴ As a consequence of this partitioning, the average micellar size is enhanced, as is the stability of the nematic phase of finite-sized rods.

Free Energies

As discussed elsewhere,⁵ the chemical potential per molecule for an aggregate of size s can be written (in units of kT) as

$$\bar{\mu}_s = \bar{\mu}_s^\circ + \bar{\mu}_s^\theta + \frac{1}{s} \ln \frac{X_s}{s} + \frac{1}{s} \chi_s + \frac{1}{s} \sigma_s \quad (1)$$

The first term is the reversible work (divided by s) necessary to couple the s micelle to the solution ("from vacuum"). The second term includes the contributions from the translational and rotational degrees of freedom of the aggregate:

$$\bar{\mu}_s^\theta \simeq -\frac{A}{s} - \frac{5}{s} \ln s \quad (2)$$

for long rods, with A a constant of order $10 \ln 10$ for typical surfactant molecules in room temperature solutions.^{6a} The third term in (1) is the "entropy of mixing" contribution, with X_s denoting the mole fraction of surfactant plus cosurfactant molecules incorporated into micelles of size s . The final two terms include the corrections to ideal-solution behavior due to *interaggregate* interactions (of the excluded-volume type); they also allow for the possibility of long-range orientational (nematic) order. More explicitly, for long rods,⁵

$$\frac{1}{s} \chi_s \simeq \frac{1}{s} \rho \sum_{s'} \frac{X_{s'}}{s'} \int d\Omega f_s(\Omega) \int d\Omega' f_{s'}(\Omega') v_{ss'}(\Omega, \Omega') \rightarrow \frac{2v}{\alpha^{1/2}} + \frac{v}{s} \quad (3)$$

and

(1) (a) For the effects of, for example, added alcohol on micellar properties in simple surfactant solutions, see the recent series of papers by Zana and co-workers: Zana, R.; Picot, C.; Duplessix, R. *J. Colloid Interface Sci.* 1983, 93, 43 and references cited therein. Also: Benton, W. J.; Miller, C. A. *J. Phys. Chem.* 1983, 87, 4981. Almgren, M.; Swarup, S. *J. Phys. Chem.* 1983, 87, 876 and earlier papers in this series. (b) Effects of cosurfactant on microemulsion structures are discussed recently by: Stilbs, P.; Rapacki, K.; Lindman, B. *J. Colloid Interface Sci.* 1983, 95, 583. Mukerjee, S.; Miller, C. A.; Fort, T. *J. Colloid Interface Sci.* 1983, 91, 223. Dorshow, R.; de Buzzoccarini, F.; Buntion, C. A.; Nicoli, D. F. *Phys. Rev. Lett.* 1981, 47, 1336.

(2) Mather, D. E. *J. Colloid Interface Sci.* 1976, 57, 240.

(3) Parseghian, V. A. *Trans. Faraday Soc.* 1966, 62, 848.

(4) Hendrikx, Y.; Charvolin, J.; Rawiso, M. *J. Colloid Interface Sci.*, in press.

(5) (a) McMullen, W. E.; Gelbart, W. M.; Ben-Shaul, A. *J. Phys. Chem.*, in press. (b) Gelbart, W. M.; Ben-Shaul, A.; McMullen, W. E.; Masters, A. *J. Phys. Chem.* 1984, 88, 861. (c) McMullen, W. E.; Ben-Shaul, A.; Gelbart, W. M. *J. Colloid Interface Sci.* 1984, 98, 523. (d) McMullen, W. E.; Gelbart, W. M.; Ben-Shaul, A. *J. Chem. Phys.*, in press.

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$$\frac{1}{s}\sigma_s = \frac{1}{s} \int d\Omega f_s(\Omega) \ln 4\pi f_s(\Omega) \rightarrow \frac{\ln \alpha - 1}{s} \quad (4)$$

Here $f_s(\Omega)$ is the fraction of s rods per unit solid angle having orientation Ω , and $v_{s\Omega}(\Omega, \Omega')$ is the volume excluded to an s, Ω -rod by an s', Ω' -rod; ρ is the total number density of molecules (surfactant + cosurfactant + water). The heavy arrows in eq 3 and 4 point to the simplifications that result for *nematic* $(1/s)\chi_s$ and $(1/s)\sigma$ in the case where only one size (s) is allowed and where Onsager's choice $f_s(\Omega) \sim \cosh(\alpha_s \cos \theta)$ is used to describe the distribution of micellar orientations. Accordingly, α is the effective nematic order parameter, and v is the volume fraction of surfactant plus cosurfactant material: $v \equiv \rho v X$, where v is the volume of a (surfactant or cosurfactant) molecule and X ($\leftrightarrow X_s$) is the fraction of amphiphile species. Note that, for the *isotropic* phase, $f_s(\Omega) = 1/(4\pi)$ and

$$\frac{1}{s}\chi_s \rightarrow v + \frac{v}{s} \quad (3')$$

and

$$\frac{1}{s}\sigma_s \rightarrow 0 \quad (4')$$

Cosurfactant Mechanism

As outlined above, the only free energy term whose *form* is affected by the presence of cosurfactant is $\tilde{\mu}_s^\circ$. In a binary ionic surfactant/water system of rod-shaped micelles, for example, $\tilde{\mu}_s^\circ = \tilde{\mu}_\infty^\circ + (\delta/s)$. With added cosurfactant, on the other hand, $\tilde{\mu}_s^\circ$ depends in a more complicated way on size because of the different head-group behavior. More explicitly, recall that the free energy of an ionic surfactant molecule can be argued to vary with its head-group area according to⁶

$$\mu_i(a) = \gamma a_i + (C/a_i) + g \quad (5)$$

Here γ is the interfacial tension, C a phenomenological constant related to the charging of an ionic double layer, and g the "tail" contribution to overall chemical potential. a_i , the area per head group, depends on local curvature: e.g.,

$$a_{\text{cylindrical body}} = 2\frac{v}{l} \quad a_{\text{spherical cap}} = 3\frac{v}{l} \quad (6)$$

with l the length of the "tail" (and v , as before, its volume).

Now consider how a cosurfactant (like an alcohol with $l \simeq l_{\text{soap}}$, $v \simeq v_{\text{soap}}$) affects each of the above μ_i 's. In diluting the charge density at the micellar surface, the cosurfactant lowers the electrostatic "strain" associated with the C/a_i term in (5). Suppose a rod contains n_1 surfactant and m_1 cosurfactant molecules in its cylindrical "body" and n_2 and m_2 in its spherical "caps". Then C/a_i is reduced by a factor of $n_1/(n_1 + m_1)$ in the body and $n_2/(n_2 + m_2)$ in the caps. As for the interfacial energy term, γa_i , we assume that surfactant and cosurfactant make equal contributions. (Similarly for g .) It follows that (here i runs over both species and both micellar environments)

$$s\tilde{\mu}_s^\circ = \sum_i \mu_i = (n_1 + m_1)\gamma \left(\frac{2v}{l}\right) + n_1 \frac{C}{\left(\frac{2v}{l}\right)} \frac{n_1}{n_1 + m_1} + (n_2 + m_2)\gamma \left(\frac{3v}{l}\right) + n_2 \frac{C}{\left(\frac{3v}{l}\right)} \frac{n_2}{n_2 + m_2} + sg \quad (7)$$

It remains only to determine the partitioning of surfactant and alcohol (i.e., n_1, n_2, m_1 , and m_2) which allows the free energy $\mu_s^\circ = s\tilde{\mu}_s^\circ$ of an s -aggregate to be a minimum. Thus we need to minimize the right-hand side of eq 7 with respect to n_1, n_2, m_1 , and m_2 , subject to the constraints

$$n_1 + n_2 + m_1 + m_2 = s \quad (8a)$$

$$n_2 + m_2 = m \quad (8b)$$

and

$$\frac{m_1 + m_2}{s} = \lambda \quad (8c)$$

Here $m = (4\pi l^3)/(3v)$ is the total number of amphiphilic species in the caps (recall that l and v are common to both species), and λ is the mole fraction of cosurfactant. (We assume for simplicity that the "global"—experimentally fixed—value of λ is respected at the individual micelle level, i.e., that every aggregate has the same alcohol-to-surfactant ratio independent of s . Note, however, that the *partitioning* of cosurfactant between body and cap still depends strongly on size.)

Results for Partitioning

Optimizing the partitioning as described above leads directly to

$$\tilde{\mu}_s^\circ \simeq \tilde{\mu}_\infty^\circ + (\delta_1/s) + (\delta_2/s^2) \quad (9)$$

with each of the coefficients on the right-hand side being explicit functions of g, γ, v, l, C , and λ . For small values of λ (i.e., $\lambda \leq 1/3$), we find that $m_2 \equiv 0$; i.e., all of the alcohol goes into the cylindrical body.⁷ In this case, for $0 \leq \lambda \leq 1/3$,

$$\tilde{\mu}_\infty^\circ = \frac{2\gamma v}{l} + \frac{Cl}{2v} + g + \lambda(\lambda - 2)$$

$$\delta_1 = m \left[\frac{\gamma v}{l} - \frac{Cl}{6v} + \lambda^2 \frac{Cl}{2v} \right]$$

and

$$\delta_2 = m^2 \lambda^2 \frac{Cl}{2v} \quad (10a)$$

Note that in the limit of no cosurfactant (i.e., $\lambda \rightarrow 0$), $\delta_2 \rightarrow 0$ and $\tilde{\mu}_s^\circ$ given by eq 9 and 10a reduces to $\tilde{\mu}_s^\circ(\lambda \rightarrow 0) = \tilde{\mu}_\infty^\circ + (\delta/s)$ with each of the right-hand-side coefficients taking on their "usual" values:^{5,6} $\tilde{\mu}_\infty^\circ = \tilde{\mu}_{\text{cyl}}^\circ = \gamma(2v)/l$

$[C/(2v/l)] + g$ and $\sigma = m[\tilde{\mu}_{\text{cap}}^\circ - \tilde{\mu}_{\text{cyl}}^\circ]$.

For larger values of λ (i.e., $1/3 < \lambda \leq 1$), we find

$$\tilde{\mu}_\infty^\circ = \frac{2\gamma v}{l} + g + \frac{Cl}{2v}(1 - \lambda)^2$$

$$\delta_1 = m \left[\frac{\gamma v}{l} - \frac{Cl}{4v}(1 - \lambda)^2 \right]$$

and

$$\delta_2 = m^2(1 - \lambda)^2 \frac{Cl}{8v} \quad (10b)$$

Note that δ_2 vanishes in the $\lambda \rightarrow 1$ (*pure* cosurfactant) limit

(6) (a) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* 1976, 72, 1525. (b) Israelachvili, J. N.; Marcelja, S.; Horn, R. G. *Q. Rev. Biophys.* 1980, 13, 121. (c) Tanford, C. "The Hydrophobic Effect", 2nd ed.; Wiley: New York, 1980.

(7) Actually, for $\lambda \leq 1/3$, minimization of eq 7 subject to eq 8a-c leads to $m_2 < 0$; accordingly, to restore physical reason we set $m_2 \equiv 0$ and evaluate $\tilde{\mu}_s^\circ$ directly to give eq 9 and 10a. [More precisely, the "critical" value of λ corresponds to $1/3(1 - (m/s))$.]

Table I. Effect of Cosurfactant on the I \rightarrow N Transition^a

λ	δ_1	δ_2	s_N	s_I	α	ν
0	45.3	0	58	43	17.5	0.072
0.1	46.1	16.3	69	52	16.9	0.059
0.2	48.5	65.3	108	85	16.1	0.037
0.3	52.6	147	200	159	15.9	0.020
0.4	57.8	147	382	294	16.5	0.011
0.5	62.3	102	682	510	17.1	0.0061
0.6	66.0	65.2	1125	832	17.3	0.0037
0.7	68.8	36.7	1676	1233	17.4	0.0025
0.8	70.8	16.3	2235	1640	17.5	0.0019
0.9	72.1	4.08	2657	1949	17.5	0.0016
1.0	72.5	0	2816	2064	17.5	0.0015

^a Columns 2 and 3 give the coefficients of the "1/s" and "1/s²" contributions to $\bar{\mu}_s^\circ$ for values of alcohol mole fraction (λ) ranging from 0 to 1—see eq 9 and discussion in text. The remaining columns specify the volume fraction (ν) and the order parameters (s_N , α , and s_I) for the coexisting isotropic and nematic phases.

as well as in the $\lambda \rightarrow 0$ (*no* cosurfactant) case described above. This is consistent with $\bar{\mu}_s^\circ$ decreasing as 1/s for any rodlike aggregate of a *single* amphiphilic species—vs. "(1/s) + (1/s²)" for the *mixed* situation. But the $\lambda \rightarrow 1$ limit must be interpreted with caution in the case of cosurfactants (e.g., alcohols) that do not form micelles by themselves.

Phase Behaviors and the I \rightarrow N Transition

By substitution of eq 9 and 10a,b for $\bar{\mu}_s^\circ$, eq 3,3' and 4,4' for (1/s) χ_s and (1/s) σ_s , and eq 2 for $\bar{\mu}_s^\theta$, the chemical potential $\bar{\mu}_s$ in (1) can be expressed as an explicit function of s and α (and the self-assembly parameters γ , C , l , and ν). Recall that s and α are the "order parameters" characterizing the isotropic (I) and nematic (N) phases of the micellar solution: " s " describes the size and " α " the alignment of the rodlike aggregates. Thus, minimizing $\bar{\mu}_s^{(I)}$ and $\bar{\mu}_s^{(N)}$ with respect to s and α determines the thermodynamic states of interest for arbitrary volume fraction ν and alcohol-to-surfactant ratio λ . We find

$$[s^{(I)}]^6 \simeq \left(\frac{e^{A+6}}{\nu\rho} \right) \nu e^\nu e^{(\delta_1+2(\delta_2/s^{(I)}))} \quad (11a)$$

and

$$[s^{(N)}]^4 \simeq \left(\frac{e^{A+5}}{\nu\rho} \right) \nu^3 e^\nu e^{(\delta_1+2(\delta_2/s^{(N)}))} \quad (11b)$$

where

$$\alpha \simeq [s^{(N)}\nu]^2 \quad (11c)$$

The corresponding difference $\bar{\mu}^{(I)} - \bar{\mu}^{(N)}$ changes sign at $\nu = \nu_{I/N}$. Table I gives the value of $\nu_{I/N}$, plus $s^{(I)}$ and $s^{(N)}$ for the coexisting phases, as a function of alcohol-to-surfactant ratio (λ).

Note that in both the $\lambda \rightarrow 0$ and $\lambda \rightarrow 1$ limits, $\alpha \rightarrow 17.5$ and $(s^{(N)}/s^{(I)}) \rightarrow 1.37$. These values agree with the "universal" transition properties calculated earlier^{5d} by us,

including polydispersity—indeed, α and the ratio of average rod sizes in the coexisting phases are found to be independent of δ (δ_1). Furthermore, as expected from eq 11c [$s^{(N)}\nu \simeq \alpha^{1/2} \simeq \text{constant}$], $\nu_{I/N}$ varies inversely with $s^{(N)}$ ($\sim s^{(I)}$) as δ is varied in the $\delta_2 \equiv 0$ limits ($\lambda = 0$ or 1). In general (i.e., $\delta_2 \neq 0$), however, both α and $s^{(N)}/s^{(I)}$ depend on δ_2 , and ν does not decrease precisely as $1/s^{(N)}$ (Table I).

Discussion

We have considered a physically reasonable, commonly accepted role for nonionic cosurfactant in ionic surfactant/water systems. According to this mechanism, added cosurfactant serves to lower the charge density on the micellar surface. By expressing the surface free energy as an explicit function of the self-assembly parameters (e.g., interfacial tension, double-layer strength, and the volume and length of an amphiphilic molecule), we determine directly the partitioning of cosurfactant among the high- and low-curvature regions of an anisotropic micelle. In the case of rodlike aggregates, for example, we show that nonionic cosurfactant (e.g.; alkanol) will be found disproportionately in the cylindrical body rather than in the spherical caps. Similar results prevail for disklike micelles:⁸ the cosurfactant partitions preferentially into the lower curvature (smaller head group) environment where it can most effectively relieve the strain of electrostatic interactions. This conclusion is borne out in preliminary contrast-variation, neutron scattering studies by Charvolin et al.⁴

As a consequence of the partitioning behavior of cosurfactant, we argue that the free energy per molecule in mixed micelles will decrease faster with aggregation number than in the pure surfactant/water situation. This leads to a stronger dependence of average micellar size on overall amphiphile concentration. It is important to note, however, that we have only considered here the effects of added cosurfactant on *intra*aggregate free energies. The dilution of surface charge affects also the interactions *between* micelles. Thus, in applying the above ideas to concentrated solutions, it will be necessary to treat explicitly the contributions to (1/s) χ_s (see eq 1) from the *charges* on the rodlike aggregates (*as well as* from their excluded volumes). In this connection, we are not aware of experiments on rodlike micelles, *at low added salt*, in which their average size is correlated with amount of added cosurfactant. Data of this kind, in conjunction with theoretical analyses of interaggregate electrostatic contributions to micellar free energy, will allow for a more complete understanding of cosurfactant behaviors in isotropic solutions. The effect of surface charge dilution on the forces between micellar rods must of course be included as well in treating the transition to nematic states.^{9,10}

(8) McMullen, W. E., unpublished notes.

(9) Deutsch, J. M.; Goldenfeld, N. D. *J. Phys. (Orsay, Fr.)* 1982, 43, 651.

(10) Rosenfeld, Y.; Gelbart, W. M. *J. Chem. Phys.*, in press.