

a higher vapor pressure. A summary of these estimated intermolecular energy terms is shown in Table II.

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Aggregation of Amphiphiles in Nonaqueous Media

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The physical factors controlling aggregation of surfactants in nonaqueous solutions are identified and their contribution to the standard free energy of formation of the aggregates are calculated. In contrast to aqueous systems, there is no strong tendency (like that due to the hydrophobic bonding) favoring the formation of large aggregates to the formation of small aggregates. The resulting size distribution is such that under all conditions larger amounts of surfactant molecules are contained within the small aggregates than within the larger ones. For these reasons, the size dependent properties, such as the apparent average aggregation numbers, change only gradually with increasing surfactant concentration. Hence, in contrast to the aqueous systems, the nonaqueous systems do not exhibit a critical micelle concentration (cmc). The unique structure of water (which gives rise to the hydrophobic bonding of the amphiphiles) is responsible for the preferential formation of large aggregates at sufficiently large surfactant concentrations and, hence, for the occurrence of the cmc in aqueous systems.

I. Introduction

The aggregation of surfactant molecules in nonaqueous media has, in the past, been described by using concepts borrowed from aggregation in aqueous systems.^{1,2} The aggregates have been visualized as spherical with the polar head groups of the amphiphiles shielded from the solvent by the hydrocarbon tails. Because this structure is the reverse of that occurring in aqueous systems, these aggregates have been called "inverted micelles".

However, the behavior of nonaqueous solutions of surfactant molecules markedly differs from aqueous ones.³⁻⁷ In aqueous systems, as the surfactant concentration is increased, the physical, colligative and spectral properties of the system undergo an abrupt change over a narrow region of concentrations. The concentration at which this sharp transition occurs is called the critical micelle concentration (cmc). In contrast, the physical properties of the nonaqueous surfactant solutions change gradually without any sharp transition^{3,8,9} as the concentration increases. Therefore, the existence of a cmc is questionable for nonaqueous systems. Even though values for the cmc have been reported in literature for some nonaqueous solutions, a critical examination of these results by Kertes³ led to the conclusion that a cmc is absent in these systems as well. Nevertheless, experiment confirms that aggregation occurs in nonaqueous solutions even at low surfactant concentrations. The average aggregation numbers are, however, much smaller than in aqueous systems, seldom exceeding 10.

Although the behaviors of aqueous and nonaqueous systems are very different, they can be described by using

a common thermodynamic approach based on a size distribution of aggregates. The contrasting behavior of the two kinds of systems arises since the small aggregates are unstable in aqueous media but are stable in nonaqueous media. This happens because of the unique structure of water and the consequent hydrophobic bonding of amphiphiles in water.¹⁰ The structural changes induced by nonpolar molecules in water lead to additional ordering of the water molecules and, therefore, give rise to a positive, unfavorable, free energy change. Consequently there is a strong tendency to minimize the contact between water and the hydrocarbon tails of the amphiphiles by forming aggregates in which the hydrocarbon tails are shielded from water by the polar head groups. Obviously this shielding is hardly possible in small aggregates. Whereas the hydrophobic bonding favors the formation of large aggregates, the decrease in the entropy of the system caused by the decrease in the number of particles has the opposite effect. At low amphiphilic concentrations the latter effect is dominant and hence virtually no aggregates form. At higher amphiphilic concentrations both effects become competitive and the concentration of the large aggregates becomes significant. Consequently, aggregates form in significant number only above a certain concentration and they are relatively large in size. This explains the occurrence of a cmc in aqueous systems.

In contrast, the structure of the nonaqueous solvents is largely unaltered by the presence of the surfactant molecules. The interaction of the amphiphilic tails with the solvent molecules is just as favorable as with the other amphiphilic tails. Hence, in this case, no tendency fa-

voring the formation of relatively large aggregates exists. However, the dipole-dipole interactions between the polar head groups, which constitute the main attractive force for aggregation, lead to the formation of relatively small aggregates. For this reason a cmc does not occur in nonaqueous systems.

The goal of the present paper is to develop in more detail and in quantitative terms the qualitative picture suggested above. For this purpose, the physicochemical factors responsible for aggregation in nonaqueous systems are identified and the corresponding free-energy changes are estimated. It is found that, indeed, the resulting size distribution of aggregates is incompatible with the existence of a cmc. This does not imply the total absence of large aggregates, but only that much larger amounts of surfactant molecules are contained within the smaller than within the larger aggregates. Furthermore, the average aggregation numbers in nonaqueous media are calculated as a function of temperature and of some characteristics of the surfactant and solvent.

II. Size Distribution of Aggregates

At equilibrium the system consists of solvent molecules, single amphiphiles, and aggregates. If we consider the aggregates of different sizes as distinct chemical species, the free energy of the system is given by

$$\Phi = N_S \mu_S^\circ + N_1 \mu_1^\circ + \sum_{g=2}^{\infty} N_g \mu_g^\circ + kT \left[N_S \ln \frac{N_S}{F} + N_1 \ln \frac{N_1}{F} + \sum_{g=2}^{\infty} N_g \ln \frac{N_g}{F} \right] \quad (1)$$

In eq 1, N is the number of molecules, μ° is the standard chemical potential, k is the Boltzmann constant, and T is the absolute temperature. The subscripts S, 1, and g refer to the solvent, the singly dispersed amphiphiles, and aggregates of size g , respectively. F is the total number of particles:

$$F = N_S + N_1 + \sum_{g=2}^{\infty} N_g \quad (2)$$

The minimum of the free energy Φ subject to the constraint $N_1 + \sum_{g=2}^{\infty} gN_g = \text{constant}$, provides the equilibrium size distribution of the aggregates:

$$\frac{N_g}{F} = \left(\frac{N_1}{F} \right)^g \exp(-g\Delta G_g^\circ / kT) \quad (3)$$

Here $\Delta G_g^\circ = [(\mu_g^\circ / g) - \mu_1^\circ]$ is the difference between the standard free energies of an amphiphile within an aggregate of size g and a singly dispersed amphiphile in the solvent. Equation 3 contains two factors. One of them, $(N_1/F)^g$, is due to the entropic decrease produced by the reduction through aggregation of the number of particles, whereas the other, $\exp(-g\Delta G_g^\circ / kT)$, is due to the standard free energy change of aggregation, ΔG_g° . Depending upon the relative contributions of these two factors, the size distribution of the aggregates can be (i) a monotone decreasing function, (ii) a monotone increasing function, or (iii) a function possessing one or more extrema.^{11,12} A monotone increasing function or a function with only a minimum and no maximum has to be associated with phase separation. A cmc exists when the concentrations of large aggregates are large compared to those of small aggregates.¹¹⁻¹³ In such cases the size distribution function has a minimum in the range of small aggregation numbers and a maximum at large aggregation numbers. Of course, the concentration at the minimum is small compared to that at the maximum. On the other hand, if the size

distribution is monotone decreasing or if it possesses a minimum and a maximum in comparable concentrations at sufficiently small values of g , then the size dependent properties show only a gradual change. It is shown below that in nonaqueous systems, one obtains only the latter types of size distribution functions which are incompatible with a cmc.

III. Attractive and Repulsive Factors Responsible for Aggregation

As mentioned earlier, in aqueous systems the presence of the surfactant molecule essentially changes the structure of the solvent in the neighborhood of its hydrocarbon tail. In contrast, for nonaqueous systems the structure of the solvent remains largely unaffected by the addition of amphiphiles. Consequently, unlike the aqueous systems, there is no contribution to ΔG_g° caused by changes in the structure of the solvent.

The hydrocarbon tail of the singly dispersed surfactant interacts only with the solvent, whereas if incorporated in an aggregate it interacts with both the solvent and the other neighboring amphiphilic tails within the same aggregate. However, the dispersion forces between organic molecules are almost independent of the nature of the molecules and depend only on the intermolecular distances.¹⁴ Hence the dispersion interactions of a hydrocarbon tail in the aggregate and of a hydrocarbon tail in a singly dispersed amphiphile are practically the same. Therefore these dispersion interactions do not contribute to ΔG_g° .

The head groups of ionic amphiphiles are mostly undissociated in solvents of low dielectric constant and behave essentially as dipoles, whereas the head groups of nonionic amphiphiles possess a permanent dipole moment. When the amphiphiles are singly dispersed, the head group interacts with the solvent via dispersion forces, dipole-induced-dipole interactions, and, in aromatic solvents, via charge-transfer interactions. These interactions are also negligible. Indeed, a measure of the solvent-head group interactions is the change in the surface tension of the solvent caused by the addition of the surfactant. This is, however, negligibly small for most nonpolar solvents.³

The polar head groups of amphiphiles within the aggregates interact via dipole-dipole, dipole-induced dipole, dispersion, and closed shell repulsion interactions. The dipole-dipole interactions are the most important (see below).

In systems wherein intermolecular hydrogen bonds or metal coordination bonds exist between surfactant head groups, these bonds make significant contributions to aggregation,^{3-5,15} in addition to those due to the interactions between the polar head groups.

Further, the amphiphiles have greater freedom for translational and rotational motions when they are singly dispersed than when they are incorporated into the aggregates. This reduction in the translational and the rotational freedom of motion provides another contribution to ΔG_g° .

Accounting for all these contributions, we can write ΔG_g° as

$$\Delta G_g^\circ = [\mu_g^\circ / g - \mu_1^\circ] = \Delta G^\circ_{\text{head group interactions}} + \Delta G^\circ_{\text{loss of trans freedom of motion}} + \Delta G^\circ_{\text{loss of rot. freedom of motion}} + \Delta G^\circ_{\text{hydrogen bonding or metal coordination bonding}} \quad \left(\begin{array}{l} \text{when} \\ \text{applicable} \end{array} \right) \quad (4)$$

The contribution to ΔG_g° due to the reduction of rotational

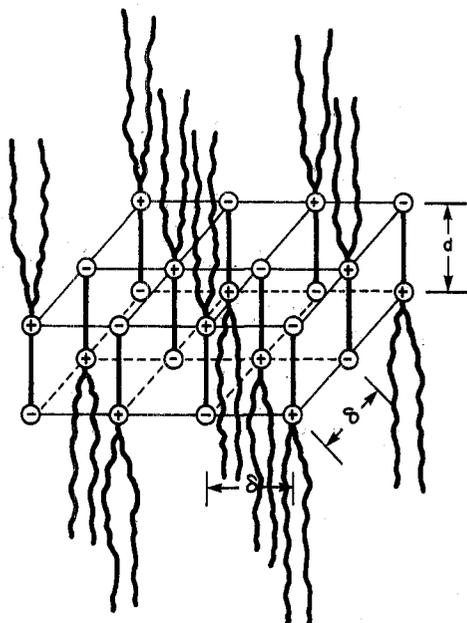


Figure 1. The lamellar aggregates and the compact two-dimensional arrangement of dipoles. The + and - signs denote the two charges of the dipole.

freedom of motion is repulsive (positive), whereas that due to the dipole-dipole interactions between the head groups is attractive (negative). The contribution due to the reduction of translational freedom of motion is generally positive.²³ The presence of hydrogen bonding or of metal coordination bonding between the head groups provide additional attractive contributions.

Interactions between Head Groups. The free energy due to the dipole-dipole interaction depends upon the mutual orientation of the dipoles in the interior of the aggregates. Following Muller^{16,17} and Kertes³ we assume that the aggregates have a compact arrangement in which the head groups are stacked as in a bilayer (Figure 1). The total interaction energy is computed by treating each charged group as a point charge at a specified location and by summing up all the pairwise Coulombic interactions. As suggested by Muller, the pairwise interaction is corrected by a multiplicative factor 0.65. This correction, computed for the dimerization energy, accounts for dipole-induced-dipole interactions, dispersion forces, and closed shell repulsions. The numerical results obtained can satisfactorily be represented in the range $1 \leq \delta/d \leq 1.5$, by the expression

$$\Delta G_{\text{hgi}}^{\circ} = - \left\{ \frac{[0.75/(\delta/d) - 0.33](g-1)}{[0.2(\delta/d) + g]} \right\} \frac{\epsilon^2}{Dd} \quad (5)$$

where the subscript hgi means head group interaction, ϵ is the electronic charge, D is the dielectric constant of the solvent, d is the distance between the point charges of the dipole, and δ is the distance between the neighboring arrays of dipoles (Figure 1). The value of δ is determined by the geometry of the polar head group and also (see below) by the steric restrictions introduced by the hydrocarbon chains. If the two charged groups constituting the dipole are identical in size and symmetry, then $\delta/d = 1.0$ and expression 5 yields, with an average deviation of less than 5%, the numerical results obtained by Muller¹⁷ (we note that the data tabulated by Muller are in units of 0.65). However, due to steric restrictions such as those arising from the unequal size and the asymmetry of the two charged groups, δ/d is somewhat larger than unity for most of the surfactants.

As mentioned above, the hydrocarbon chains of the aggregated amphiphiles can generate in some conditions a steric constraint which affects the distance δ between the arrays of head groups. The considerations which follow will identify these conditions. The volume accessible to the hydrocarbon chain in an aggregate represented by the lattice of Figure 1 corresponds to two dome-shaped regions, one on each face of the aggregate.¹⁷ This accessible volume V_{acc} is composed of three terms: (1) the volume normal to the two surfaces of the lattice (which is twice the product of the lattice area $(g^{1/2} - 1)^2 \delta^2$ and the tail length l_0); (2) the supplementary hemicylindrical volume due to the freedom of motion of the chains located on the circumference of the lattice (which is the product of the circumference $[4(g^{1/2} - 1)\delta]$ and the area of the hemicylinder $\pi l_0^2/2$); and (3) the additional volume due to the freedom of motion of the amphiphiles located at the four corners of the lattice (which is four times the volume of a quarter of a sphere $\pi l_0^3/3$). Consequently, the accessible volume is

$$V_{\text{acc}} = 2(g^{1/2} - 1)^2 \delta^2 l_0 + 2(g^{1/2} - 1) \pi \delta l_0^2 + \frac{4}{3} \pi l_0^3 \quad (6)$$

When the amphiphilar tail is a straight hydrocarbon chain, l_0 is the length of this chain; when the amphiphilar tail is a branched hydrocarbon molecule, l_0 is the length of the principal hydrocarbon chain of the branched molecule. The accessible volume per amphiphile (V_{acc}/g) decreases with increasing aggregation number but, obviously, cannot become smaller than the volume v_0 of the amphiphilar tail. When V_{acc}/g approaches v_0 one can expect, because of some steric restrictions, an increase of the distance δ . However, under these steric restrictions hardly any aggregates form because the repulsion caused by the reduction of translational freedom is very large (see below) and the dipole-dipole attractions between the head groups are very small. Consequently the effect of the mentioned steric restrictions can be neglected.

Besides the two-dimensional arrangement of the head groups from Figure 1, one can also consider a unidimensional open chain structure.¹⁷ For a given aggregation number, if δ/d is close to unity, the dipole-dipole attractions between amphiphiles are considerably smaller in the open chain structure than in the two-dimensional lamellar aggregates. Even though the entropic decrease associated with the open chain structure is somewhat smaller, the free-energy change associated with the dipole-dipole attractions overcomes the above effect and the lamellar structure is thermodynamically favored. However, if the deviation of δ/d from unity is quite large, the dipole-dipole attractions in a lamellar aggregate are not substantially different from those in an open chain structure. Under these conditions the open chain structure may be thermodynamically preferred. However, when δ/d significantly deviates from unity, the aggregates are expected to be quite small.

Intermolecular Bonding between Head Groups. In some nonaqueous solutions of surfactants, hydrogen bonding or metal coordination bonding may occur between the head groups.^{3-5,15} These intermolecular bonds are quasichemical in nature. The energy of this quasichemical bond depends on a number of factors such as the nature of the polar head group and of the solvent and can lie anywhere between $(-1kT)$ and $(-5kT)$. The contribution to ΔG_g° of various types of intermolecular bonding (imb) is calculated from

$$\Delta G_{\text{imb}}^{\circ} = \Delta E^{\circ} [B(g)/g] \quad (7)$$

where ΔE° is the energy of the quasichemical bond, and

$B(g)$ is the total number of intermolecular bonds in an aggregate of size g . The number of possible quasichemical bonds between the polar heads depends on the number of bonding sites available in each head group and on the number of nearest neighbor head groups. Head groups such as ammonium halides and metal carboxylates make available a pair of atoms for quasichemical bonding.³ Thus each polar head can bond with only two nearest neighbors irrespective of whether the aggregates have a lamellar structure or an open chain structure. Hence $B(g)$ equals g . For some amphiphiles, the simultaneous formation of two quasichemical bonds in a dimeric aggregate may be hindered because of the stereochemistry of the polar head group. If this occurs, $B(g) = 1$ for $g = 2$ and equals g for $g > 2$. As mentioned earlier, the contributions of these quasichemical bonds between the amphiphilic head groups to ΔG_g° augment those due to the dipole-dipole interactions between the head groups.

Loss of Translational Freedom of Motion. The single amphiphiles have free translation in the free volume of the solvent. The corresponding partition function is given by

$$Q_1^{\text{trans}} = (2\pi mkT/h^2)^{3/2} V f_1 \quad (8)$$

where m is the mass of the amphiphile, h is Planck's constant, V is the total volume of the system, and f_1 is the free volume fraction of the solvent. For nonpolar liquids, f_1 can be estimated by using the following expression given by Bondi:^{18,19}

$$f_1 = (1/v_s)(4\pi/3) \left(\frac{v_s - v_{\text{VWS}}}{A_{\text{VWS}}} \right)^3 \quad (9)$$

where v_s is the molecular volume of the solvent, v_{VWS} is the van der Waals volume, and A_{VWS} is the van der Waals area of the solvent molecule.

Similarly for the external translational partition function of an aggregate of size g in the solvent, one can write

$$Q_g^{\text{ext trans}} = (2\pi mgkT/h^2)^{3/2} V f_1 \quad (10)$$

The amphiphiles constituting the aggregate have translational motion within the free volume of the aggregate. This internal translation of the amphiphiles within the aggregate has an additional constraint because the head groups are confined to the interior of the aggregate. A measure of the allowed internal translation of the tails subject to this constraint on the head groups is the ratio $(V_{\text{acc}}^* - gv_0^*)/V_{\text{acc}}^*$, where V_{acc}^* is the local accessible volume in the immediate neighborhood of the head groups (within a distance L^* from the polar head-hydrocarbon tail interface), and v_0^* is the volume of the portion of the amphiphilic tail contained within this distance of L^* from the head group. The local accessible volume V_{acc}^* can be calculated by using eq 6 and replacing, however, the tail length l_0 by the distance L^* . There is, however, no unique way to define the location of L^* .¹⁷ Of course, an upper bound of this local ratio is given by the global ratio $(V_{\text{acc}} - gv_0)/V_{\text{acc}}$, where V_{acc} is the volume accessible to the entire tail length and not simply to the portion adjacent to the polar head group. The present calculations are carried out by using this global ratio $(V_{\text{acc}} - gv_0)/V_{\text{acc}}$ as a measure of the constrained internal translation. For all $L^* < l_0$, corresponding to any alternate measure of the translational constraint, both the constraint on translation and the repulsive contribution to the standard free-energy change will be larger and hence more unfavorable to aggregation. On this basis, one can write for the partition function corresponding to internal translation within an aggregate of size g the expression

$$Q_g^{\text{int trans}} = \frac{1}{g!} \left[(2\pi mkT/h^2)^{3/2} (V_{\text{acc}f_2}) \left(\frac{V_{\text{acc}} - gv_0}{V_{\text{acc}}} \right) \right]^{g-1} \quad (11)$$

where f_2 is the free volume fraction of the solvent penetrated hydrocarbon tail region of the aggregate. f_2 is approximated as equal to the free volume fraction of a liquid composed only of the hydrocarbon tails of the amphiphile and is estimated by using an equation similar to eq 9 used for f_1 . In eq 11 the exponent g is reduced by unity because three degrees of freedom have already been considered for the translation of the entire aggregate. As already mentioned, v_0 cannot become larger than (V_{acc}/g) .

On the basis of eq 8, 10, and 11, the contribution of the reduction in the translational freedom of motion to ΔG_g° can be written as

$$\begin{aligned} \Delta G_g^{\circ \text{ tdf}} = & \frac{1}{g} \left[\left(-kT \ln \frac{Q_g^{\text{trans}}}{F} \right) - \left(-gkT \ln \frac{Q_1^{\text{trans}}}{F} \right) \right] \\ = & -\frac{kT}{g} \left\{ \ln \left[\left(\frac{2\pi mgkT}{h^2} \right)^{3/2} v_s f_1 \right] \right\} + \left[(g - \right. \\ & \left. 1) \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V_{\text{acc}f_2} \left(\frac{V_{\text{acc}} - gv_0}{V_{\text{acc}}} \right) \right] - \right. \\ & \left. \ln g! \right] - \left[g \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} v_s f_1 \right] \right] \end{aligned} \quad (12)$$

where the volume v_s of the solvent molecule has been substituted for the factor (V/F) and the subscript *tdf* means loss of translational freedom.

Loss of Rotational Freedom of Motion. The aggregate as a whole and the singly dispersed amphiphile rotate freely about their long axis in the solvent because their own volume provides the volume required for free rotation. However, their rotation around the short axes requires a larger volume and therefore is severely restricted; the greater the length/diameter ratio, the larger the restriction. The free energy of restricted rotation is calculated by subtracting from the free energy of the completely free rotation an entropic part which accounts for the restriction. This entropic part is evaluated by using the correlation proposed by Bondi for saturated hydrocarbons.¹⁸ For the amphiphiles within the aggregates, the rotation about their short axes is assumed completely frozen since the polar heads are constrained to remain inside the aggregates; further, their rotation about the long axis is also considered to be frozen, since otherwise the compact arrangement of the head groups cannot be kept intact. The free-energy change due to the reduction of the rotational freedom of motion (*lrdf*) can be therefore calculated from

$$\Delta G_g^{\circ \text{ lrdf}} = -\frac{kT}{g} \left\{ \ln \left[\left(\frac{2\pi \bar{I}_g kT}{h^2} \right)^{3/2} 8\pi^2 \right] - \frac{\Delta S_g}{k} \right\} - g \left\{ \ln \left[\left(\frac{2\pi \bar{I}_1 kT}{h^2} \right)^{3/2} 8\pi^2 \right] - \frac{\Delta S_1}{k} \right\} \quad (13)$$

where the first bracketed $\{\}$ term represents the rotational contribution of the aggregate as a whole, and the second, the rotational contribution of single amphiphiles in the solvent. \bar{I}_g and \bar{I}_1 are the average moments of inertia of the aggregate and of the single amphiphile, respectively. ΔS_g and ΔS_1 are the entropic contributions accounting for the constraint on rotation about the short axes for the

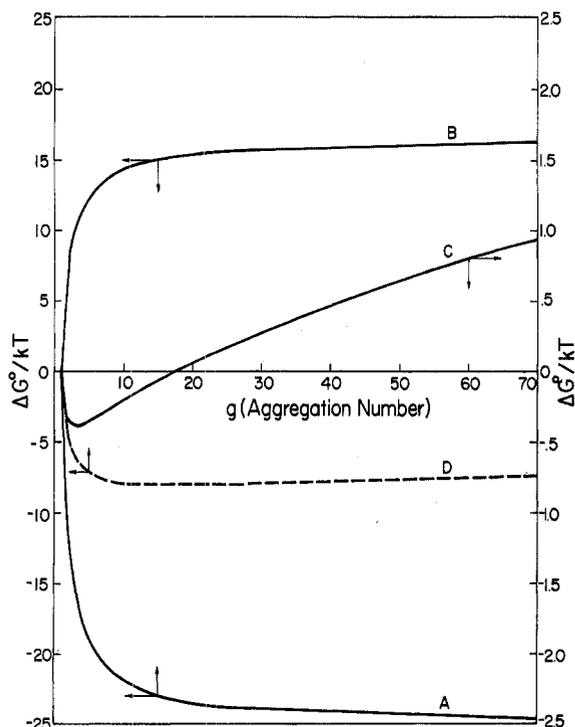


Figure 2. The standard free-energy difference ΔG_g^0 and its components in nonaqueous solutions of amphiphiles. $d = 4 \text{ \AA}$, $\delta/d = 1.0$, $D = 2.3$, $n = 6$, $z = 2$, $T = 298 \text{ K}$, $l_0 = 7.7 \text{ \AA}$. (A) Dipole-dipole interactions; (B) reduction of rotational freedom of motion; (C) reduction of translational freedom of motion; (D) ΔG_g^0 .

aggregate and the single amphiphile, respectively. Following Bondi's suggestion,¹⁸ one assumes that ΔS_g and ΔS_1 depend on the degree of restriction R which is defined as the ratio between the volume required for free rotation and the empty volume available for rotation. The degree of restriction R is calculated from

$$R = \frac{\pi \left(\frac{2g\nu_0}{\pi l_c} \right)^{1/2} \left(l_c^2 + \frac{g\nu_0}{2\pi l_c} \right) - g\nu_{vw}}{g\nu_0 - g\nu_{vw}} \quad (14)$$

for the aggregate, and from

$$R = \frac{\pi \left(\frac{4\nu_0}{\pi l_c} \right)^{1/2} (l_c^2/4 + \nu_0/\pi l_c) - \nu_{vw}}{\nu_0 - \nu_{vw}} \quad (15)$$

for the single amphiphile. Here ν_{vw} is the van der Waals volume of the hydrocarbon tail, ν_0 its molecular volume, and l_c the length of the amphiphilic tail in its coiled configuration. l_c is computed as indicated by Taylor.²⁰ In eq 14, the factor $(2g\nu_0/\pi l_c)^{1/2}$ is the width and $(l_c^2 + g\nu_0/2\pi l_c)^{1/2}$ is the radius of the volume swept by an aggregate rotating about its short axis. The corresponding quantities in eq 15 for a single amphiphile are $(4\nu_0/\pi l_c)^{1/2}$ and $(l_c^2/4 + \nu_0/\pi l_c)^{1/2}$, respectively. The reduction of the rotational freedom of motion provides a repulsive contribution to ΔG_g^0 .

IV. Results and Discussion

Free Energy Change, Size Distribution, and Cmc. The free energy difference ΔG_g^0 and its components are plotted in Figure 2 for a surfactant with two hexyl hydrocarbon tails in a nonaqueous solvent of low dielectric constant. This figure shows that $(-\Delta G_g^0)$ is quite large even for $g = 2$ and remains almost constant for $g > 12$. Therefore, the concentration of the smaller aggregates, $g < 15$, is larger than that of the higher oligomers, $g > 15$.

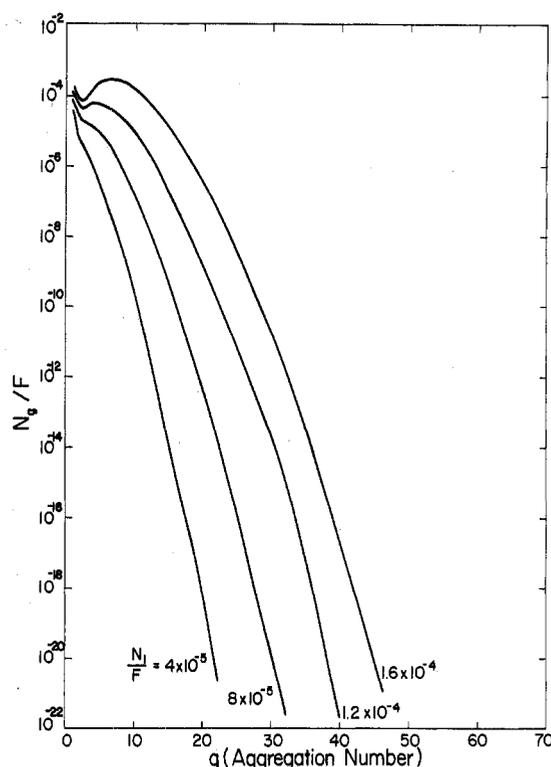


Figure 3. The size distribution of aggregates in nonaqueous solutions of amphiphiles. The values of the parameters are as for Figure 2.

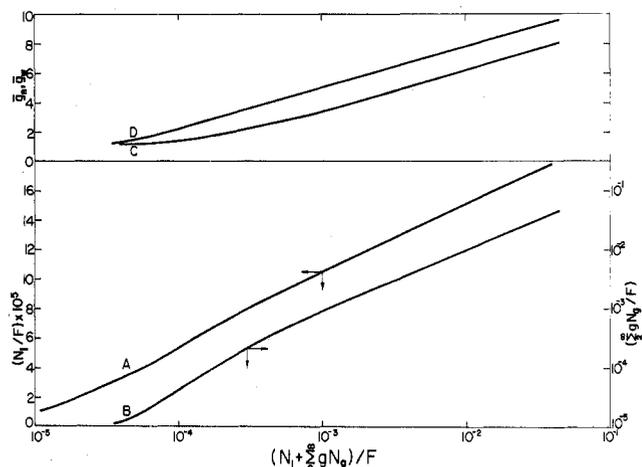


Figure 4. The variation of size-dependent quantities with total amphiphilic concentration in nonaqueous solutions of amphiphiles. The values of the parameters are as for Figure 2. (A) N_1/F ; (B) $\sum_{g=2}^{\infty} gN_g/F$; (C) $[N_1/F + \sum_{g=2}^{\infty} gN_g/F] / [N_1/F + \sum_{g=2}^{\infty} N_g/F] \equiv \bar{g}_n$; (D) $[N_1/F + \sum_{g=2}^{\infty} g^2 N_g/F] / [N_1/F + \sum_{g=2}^{\infty} gN_g/F] \equiv \bar{g}_w$.

Calculated size distribution curves in nonaqueous systems are plotted in Figure 3 for various single amphiphile concentrations. The total mole fraction of the amphiphiles is varied up to 5×10^{-2} , which constitutes an upper bound of the solubility limit of most surfactants in nonpolar solvents.³ The figure shows that the size distribution is either monotonically decreasing or possesses a minimum and a maximum in the range of relatively small aggregates. It is worth observing that, in the above example, most of the amphiphiles are present in aggregates with $g < 15$. The number n of CH_2 and CH_3 groups per hydrocarbon chain of the amphiphilic tail was, however, 6. In general for most common surfactants, n is larger and, therefore, the bulk of the amphiphiles present are incorporated within aggregates of sizes smaller than $g = 10$.

The concentration of single amphiphiles and that of amphiphiles incorporated within the aggregates are plotted

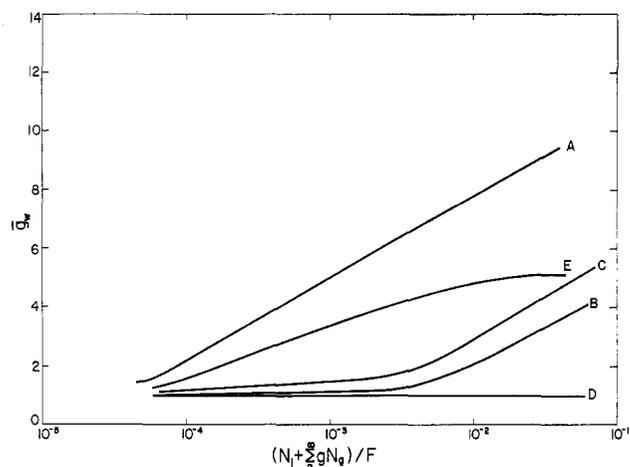


Figure 5. The effect of dipole-dipole interactions on the apparent weight average aggregation numbers. $d = 4 \text{ \AA}$, $\delta/d = 1.0$, $D = 2.3$, $n = 6$, $z = 2$, $T = 298 \text{ K}$, $l_0 = 7.7 \text{ \AA}$. In each of the curves one of the above values is replaced as shown below: (A) none; (B) $d = 5 \text{ \AA}$; (C) $\delta/d = 1.1$; (D) $\delta/d = 1.3$; (E) $l_0 = 5.7 \text{ \AA}$.

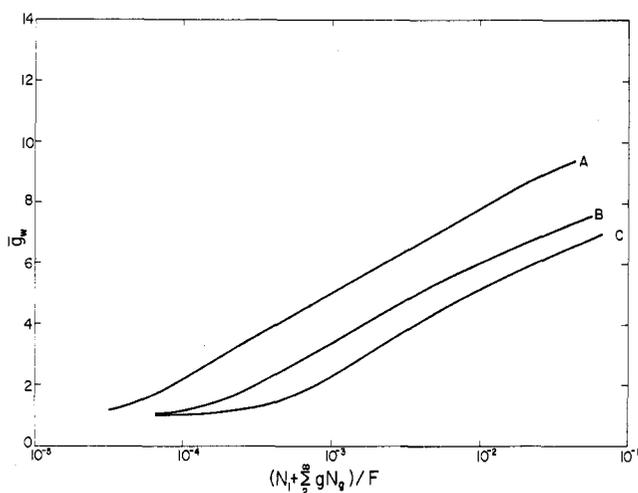


Figure 6. The dependence of the apparent weight average aggregation numbers on the chain length of amphiphile. $d = 4 \text{ \AA}$, $\delta/d = 1.0$, $D = 2.3$, $z = 2$, $T = 298 \text{ K}$. (A) $n = 6$, $l_0 = 7.7 \text{ \AA}$; (B) $n = 12$, $l_0 = 15.4 \text{ \AA}$; (C) $n = 18$, $l_0 = 23.1 \text{ \AA}$.

in Figure 4 against the total amphiphilic concentration. The plot also includes the change of the apparent number average aggregation numbers and of the apparent weight average aggregation numbers with the total amphiphilic concentration. Most of the physical, colligative, or spectral properties are proportional to one or the other of the above quantities. Consequently, one can consider that these plots represent those physical properties vs. concentration. The curves show a gradual change as the total amphiphilic concentration is increased. Because a sharp transition cannot be identified, one may conclude that a cmc does not exist for nonaqueous solutions of amphiphiles. The gradual change in Figure 4 of various size-dependent quantities is a result of the fact that there is no preferential formation of large aggregates. Nevertheless, one may notice from Figures 3 and 4 that, even though a cmc is absent in the nonaqueous systems, large aggregates are also formed and the concentrations of aggregates are quite large. Numerous methods of measurement (including very sensitive spectral methods³) are in agreement with the above conclusions. Only the experiments based on solubilization appear to suggest a cmc. The latter experiments are, however, inappropriate to reach a conclusion as to the existence of a cmc, because the solubilized molecules (water or ions) change essentially the interaction forces.

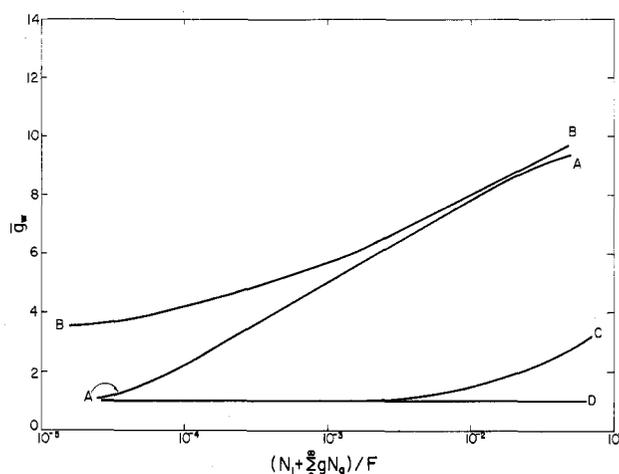


Figure 7. The dependence of apparent weight average aggregation numbers on intermolecular bonding and on the dielectric constant of the solvent. $d = 4 \text{ \AA}$, $\delta/d = 1.0$, $n = 6$, $z = 2$, $T = 298 \text{ K}$, $l_0 = 7.7 \text{ \AA}$. (A) $D = 2.3$, $\Delta E^\circ = 0$; (B) $D = 2.3$, $\Delta E^\circ = -5kT$; (C) $D = 3.0$, $\Delta E^\circ = 0$; (D) $D = 5$, $\Delta E^\circ = 0$.

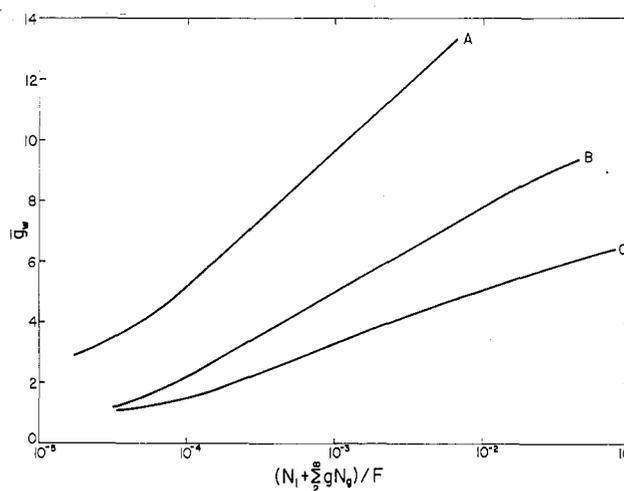


Figure 8. The effect of the number of hydrocarbon chains per amphiphilic tail on the apparent weight average aggregation number. $d = 4 \text{ \AA}$, $\delta/d = 1.0$, $D = 2.3$, $n = 6$, $T = 298 \text{ K}$, $l_0 = 7.7 \text{ \AA}$. (A) $z = 1$; (B) $z = 2$; (C) $z = 3$.

Effect of the Solvent and of the Characteristics of the Surfactant. The apparent average aggregation number is plotted vs. the total amphiphilic concentration in Figures 5–8 for different characteristics of the surfactant and of the solvent. Of course, the average aggregation numbers have upper bounds determined by the limited solubility of the surfactant in the solvent. Figure 5 shows that for $\delta/d = 1$, if the size d of the head group is increased, the average aggregation numbers decrease. Even though the size of the head group affects all the components of the free energy difference ΔG_g° , the dominant effect is the decrease in the attractive dipole-dipole interactions. The experimental observations concerning the effect of the size of the head group^{3,6,7} are consistent with the present theory. The effect of δ/d on the average aggregation number is also plotted in Figure 5. The deviation of this ratio from unity accounts for the unequal sizes and asymmetry of the charged groups constituting the dipoles. It is found that the average aggregation numbers decrease with increasing δ/d . This happens because the dipole-dipole attractions are the largest when the charged groups constituting the dipole are equal in size and symmetric.

Figure 5 compares two amphiphilic systems differing in the accessible volume V_{acc} . The value of V_{acc} for $l_0 = 5.7 \text{ \AA}$ is for amphiphiles with branched hydrocarbon chains;

the value of V_{acc} for $l_0 = 7.7 \text{ \AA}$ is for amphiphiles with straight hydrocarbon chains, but with the same total number of CH_2 and CH_3 groups. The decrease of V_{acc} decreases the volume available for the translational motion of the amphiphile within the aggregates and thus increases the repulsion due to the loss of translational freedom of motion. This results in a decrease of the average aggregation numbers, a conclusion consistent with experimental data.^{3,7} Also in agreement with experiment,^{3,7} computations show that an increase of the hydrocarbon chain length of the amphiphile decreases the average aggregation number (Figure 6). This happens because, for longer tail lengths, (a) the internal translation of the amphiphiles within the aggregates is more restricted due to the decreased free volume and (b) the rotational freedom decreases due to the increase of the degree of restriction R .

Figure 7 reveals that the presence of hydrogen bonds or metal coordination bonds between the head groups leads to an increase in the average aggregation numbers especially at very low amphiphilic concentrations. This is consistent with the experimental observations on systems containing α -monoglycerol alkanolates, aluminum dicarboxylates, or alkyl ammonium salts in benzene.^{3-5,15}

The nature of the solvent determines the value of the free volume f_1v_S and, more importantly, the dielectric constant D of the solvent. The values of free volume f_1v_S for a wide range of solvents are within a factor of 5. A change of this parameter has the same effect as a change of the concentration of singly dispersed amphiphiles. However, the dielectric constant D of the solvent significantly influences the dipole-dipole attractions and hence the size distribution of the aggregates and the average aggregation numbers (Figure 7). If the polarity of the solvent is large, then the surfactant remains mostly as singly dispersed amphiphiles. Indeed, this happens in polar nonaqueous solvents such as alcohols.³ Figure 8 shows that the average aggregation number decreases when the number of hydrocarbon chains per amphiphile increases. This can be explained by the fact that a larger number of chains increases the repulsive free energy contributions caused by the reduction of translational and rotational freedom of motion.

Small differences have been observed³ concerning the aggregation behavior in aliphatic and aromatic solvents. They may be caused by the charge transfer interactions which occur between the polar head groups of the singly dispersed amphiphiles and the aromatic molecules. The strength of the charge transfer interactions depends on the nature of the electron donor and the electron acceptor. When benzene is the electron donor and an amine is the electron acceptor, the energy involved per molecule is indeed small, less than kT .²¹

Experiments show that, for some systems, the average aggregation number tapers off or even slightly decreases as the concentration of amphiphiles increases.^{3,7,22} This may be due to either the restriction caused by the inequality $V_{acc}/g > v_0$ (see the example given in Figure 5) and/or the fact that the polarity of the solvent increases somewhat with increasing concentration of single amphiphiles. The latter effect is particularly important when the equilibrium concentration of singly dispersed amphiphiles is large.

Effect of Temperature. Figure 9 shows that an increase in the temperature decreases the average aggregation numbers. The free-energy contributions due to the reduction of translational and rotational freedom of motion are affected by temperature. An increase in temperature increases the repulsive component of the free-energy

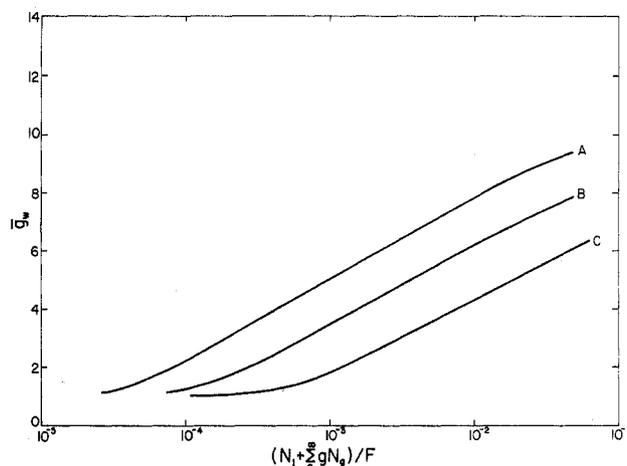


Figure 9. Effect of temperature on the apparent weight average aggregation number. $d = 4 \text{ \AA}$, $\delta/d = 1.0$, $D = 2.3$, $n = 6$, $z = 2$, $l_0 = 7.7 \text{ \AA}$. (A) $T = 298 \text{ K}$; (B) $T = 313 \text{ K}$; (C) $T = 333 \text{ K}$.

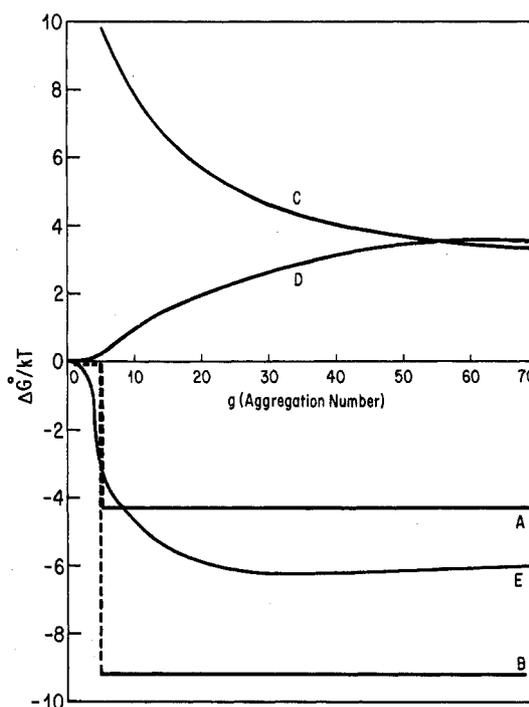


Figure 10. The standard free-energy difference ΔG_g^0 and its components for an aqueous solution of octyl glucoside. The computations are based on eq 4-12 and the data and the expressions contained in Tables I-III of ref 11. (A) Contribution of structural changes in water; (B) cohesive interactions between the hydrocarbon tails; (C) contribution due to formation of hydrocarbon core-water interface; (D) reduction of translational and rotational freedom of motion; (E) ΔG_g^0 .

change ΔG_g^0 and thus decreases the concentration of aggregates and the average aggregation numbers. In addition, the dipole-dipole interactions are probably affected in some measure by changes in temperature because the orientation of the dipoles in the aggregates may change. Figure 9 accounts for the former effect only. Available experimental information on the effect of temperature³ is consistent with the above conclusions.

Aggregation of Amphiphiles in Aqueous Media. In order to compare the aqueous and nonaqueous systems, the free-energy difference ΔG_g^0 and its components are plotted in Figure 10 for a typical aqueous system. Octyl glucoside is chosen because (a) it is nonionic and therefore the electrostatic interactions are absent, (b) it has a short chain and hence forms small micelles, and (c) it is a single chain amphiphile and hence does not form vesicles.

The free-energy difference ΔG_g° in aqueous systems markedly differs from that in nonaqueous systems due to the unique structure of water. For most liquids, the structure is a consequence of the hard-core repulsive part of the intermolecular potential; the attractive part which ensures cohesion can be treated as a perturbation. Water is an exception because of the presence of strong quasi-chemical hydrogen bonding. Nonpolar molecules, if present in water, induce in their immediate vicinity additional ordering of the water molecules favoring increased hydrogen bonding in this region. The increase in the degree of hydrogen bonding gives rise to a negative enthalpy change whereas the increased ordering of water molecules results in a negative entropy change. Since the negative entropy change more than counterbalances the negative enthalpy change, the interaction of nonpolar groups with water are unfavorable. Aggregation involves a large reduction in these unfavorable interactions between water and hydrocarbon and hence the contribution to ΔG_g° of the structural changes in water associated with aggregation is negative (i.e., attractive). For small aggregates in which the shielding of the hydrocarbon tails from water is only partial, this attractive contribution to ΔG_g° is small. This contribution increases for larger aggregates in which the shielding of the hydrocarbon core from water is more effective.

In addition, the hydrocarbon tails within large aggregates are closely packed and hence the attractive van der Waals interactions between the tails are stronger. Such close packing is hindered in the small aggregates by the presence of water molecules in the proximity of the hydrocarbon tails. Hence the attractive contribution to ΔG_g° due to mutual interactions between hydrocarbon tails increases with the aggregation number. Further, the area per amphiphile, of the aggregate, hence the positive (i.e., repulsive) free energy of formation of the interfacial area per amphiphile between the hydrocarbon core and water, decreases with increasing aggregation number. The loss of translational and rotational freedom of motion provides another positive contribution to ΔG_g° which increases with g . However, computations showed¹¹ that the total repulsive free energy decreases with increasing aggregation numbers. Hence, in aqueous systems the attractive component of ΔG_g° increases and the repulsive component of ΔG_g° decreases with increasing aggregation numbers before reaching almost constant values at sufficiently large aggregation numbers. $(-\Delta G_g^\circ)$ is quite small for the small aggregates and only when the aggregation number becomes sufficiently large ($g > 15$, in the present example) the attractive component becomes appreciably larger than the repulsive component.

As already mentioned in section II, the relative balance between the standard free-energy difference ($-g\Delta G_g^\circ$) and the decrease in the entropy associated with the reduction of the number of particles through aggregation determines the size distribution of aggregates. At low concentrations of amphiphiles, the latter entropic factor dominates the former over the entire range of aggregation numbers and virtually no aggregates form. For sufficiently large amphiphilic concentrations, the entropic factor remains dominant for small values of g , and dominates once again for very large values of g . The factor containing the standard free energy is comparable to the entropic factor for intermediate values of g . Consequently, large aggregates form in aqueous systems if the concentration of surfactant is sufficiently large, and small aggregates are practically absent at all concentrations higher than the cmc.

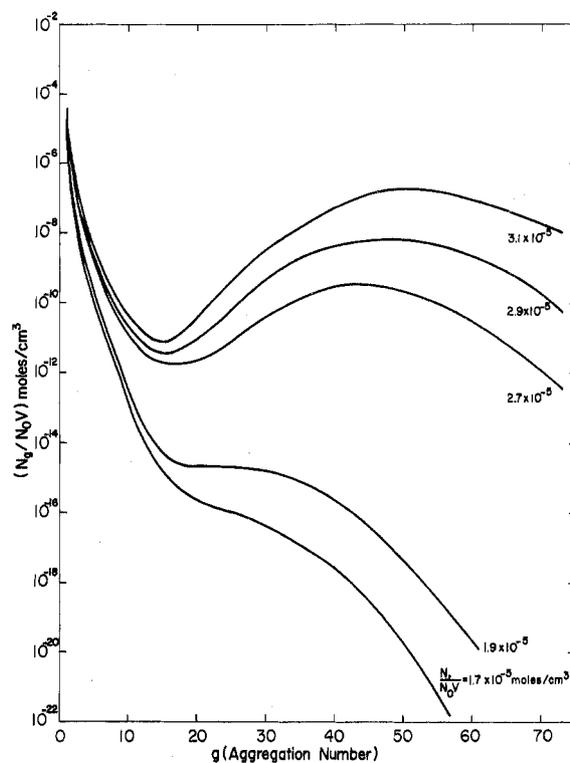


Figure 11. The size distribution of aggregates in aqueous solution of octyl glucoside. The values of the parameters are as for Figure 10.

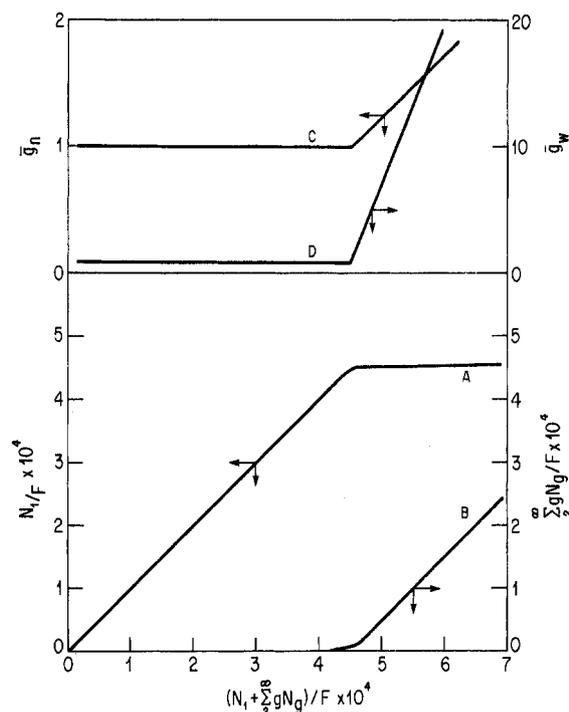


Figure 12. The dependence of size-dependent quantities on the total amphiphilic concentration in aqueous solution of octyl glucoside. The values of the parameters are as for Figure 10. (A) N_1/F ; (B) $\sum_{g=2}^{\infty} gN_g/F$; (C) $(N_1/F + \sum_{g=2}^{\infty} gN_g/F)/(N_1/F + \sum_{g=2}^{\infty} N_g/F)$; (D) $(N_1/F + \sum_{g=2}^{\infty} g^2 N_g/F)/(N_1/F + \sum_{g=2}^{\infty} gN_g/F)$.

In Figure 11 the size distribution is plotted for octyl glucoside in water. This plot shows that for concentrations larger than the cmc (in this case $\text{cmc} \approx 3 \times 10^{-5} \text{ mol/cm}^3$), the number of amphiphiles within the smaller aggregates ($g < 30$) is small compared to those within the larger aggregates. This is in contrast with the nonaqueous systems in which the small aggregates are always present in significant concentrations.

Some size-dependent quantities are plotted in Figure 12 as a function of the total amphiphilic concentration for aqueous solutions of octyl glucoside. In contrast to nonaqueous systems (see Figure 4), these quantities exhibit sharp transitions in a narrow region of concentrations and a cmc can be thus identified.

A cmc can also occur in polar solvents other than water, although the contribution of the structural changes in these solvents to ΔG_g° are probably less important than that in water. This occurs if the attractive interactions between the amphiphilic tails are sufficiently stronger than the interaction of the amphiphilic tail with the solvent.

V. Conclusions

Amphiphiles in nonaqueous media do not possess a critical micelle concentration even though aggregates are formed in significant concentrations. In contrast one can always determine a cmc for aqueous surfactant systems. The unique structure of water (which gives rise to the hydrophobic bonding of the amphiphiles) is largely responsible for the preferential formation at sufficiently high surfactant concentrations of large aggregates and, therefore, for the occurrence of the cmc in aqueous systems.

In contrast to aqueous systems, in nonaqueous systems, the structure of the solvent remains essentially unaffected by the amphiphiles. The dipole-dipole interactions between the head groups constitute, in this case, the principal factor favoring aggregation. In some systems these attractive interactions are augmented by intermolecular hydrogen bonding or metal coordination bonds. The reduction of the translational and the rotational freedom of motion associated with aggregation is the main repulsive factor limiting aggregation. Unlike the aqueous systems, small aggregates form in appreciable number under all conditions. For these reasons the size-dependent properties change only gradually with the concentration of the amphiphiles and a cmc does not exist.

The average aggregation numbers in nonaqueous systems have been calculated as a function of the total amphiphilic concentration for different characteristics of the surfactant and of the solvent. The most influential parameters are found to be those which affect the dipole-dipole interactions, such as the dielectric constant of the solvent, the distance between the charges constituting the dipoles, and their relative size and symmetry. An increase in the dipole-dipole attractions or the occurrence of intermolecular bonding between polar head groups increase the average aggregation numbers. In highly polar solvents virtually no aggregation occurs. The average aggregation number decreases with an increase in (1) the number of alkyl chains per amphiphile, (2) the length of the amphiphilic tail, (3) the steric requirements of the tail close to the polar head group, and (4) the temperature. These conclusions are consistent with available experimental information.

Notation and Expressions Used in the Calculation of the Standard Free-Energy Change

A_{vw}	van der Waals area of the hydrocarbon tail of the amphiphile (values in ref 19)
A_{vws}	van der Waals area of the solvent molecule
d	distance between the charges constituting the dipole
D	dielectric constant of the solvent
f_1	ratio between the free volume per mole and the molar volume of the solvent = 1.63×10^{-2} (in this paper)
f_2	ratio between the free volume per mole and the

	molar volume of the hydrocarbon tail of the amphiphile
F	total number of particles in the system
\bar{g}_n	apparent number average aggregation number = $\sum_{g=1}^{\infty} g N_g / \sum_{g=1}^{\infty} N_g$
\bar{g}_w	apparent weight average aggregation number = $\sum_{g=1}^{\infty} g^2 N_g / \sum_{g=1}^{\infty} g N_g$
h	Planck's constant = 6.625×10^{-27} erg s
I_1	average moment of inertia of a single amphiphile = $[I_{1x} I_{1y} I_{1z}]^{1/3}$
I_{1x}, I_{1y}	moment of inertia of a single amphiphile treated as a cylinder about its short axis = $m[(v/4\pi l) + (l^2/12)]$
I_{1z}	moment of inertia of a single amphiphile treated as a cylinder about its long axis = $mv/(2\pi l)$
I_{gx}, I_{gy}	moment of inertia of the aggregate treated as a cylinder about its short axis = $mg[(gv/8\pi l) + (l^2/3)]$
I_{gz}	moment of inertia of the aggregate treated as a cylinder about its long axis = $mg[gv/(4\pi l)]$
\bar{I}_g	average moment of inertia of the aggregate = $[I_{gx} I_{gy} I_{gz}]^{1/3}$
k	Boltzmann constant = 1.38×10^{-16} erg/K
l_0	extended length of the amphiphilic tail = $(1.50 + 1.269n) \times 10^{-8}$ cm
l_c	length of the amphiphilic tail in its coiled configuration over the temperature range (0–50 °C) = $(5.4/n)^{1/2} l_0$ (ref 20)
l_p	length of the polar head group = $2d$
l	length of a single amphiphile = $l_0 + l_p$
M	molecular weight of the polar head group = 218 (in this paper)
m	mass of a single amphiphile = $[M + z(14n + 1)] \times 1.66 \times 10^{-24}$ g
n	number of CH_3 and CH_2 groups per hydrocarbon chain of the amphiphilic tail
N_0	Avogadro's number = 6.023×10^{23}
T	absolute temperature in K
v_0	volume of amphiphilic tail = $z[27.4 + 26.9n] \times 10^{-24}$ cm ³
v_p	volume of the polar head group = 150×10^{-24} cm ³ (in this paper)
v	volume of a single amphiphile = $v_0 + v_p$
v_{vw}	van der Waals volume of the hydrocarbon tail = $z[5.5 + 17n] \times 10^{-24}$ cm ³
v_{vws}	van der Waals volume of the solvent molecule
v_s	volume of a solvent molecule = 150×10^{-24} cm ³ (in this paper)
V	total volume of the system = Fv_s
V_{acc}	volume accessible for the hydrocarbon tails within an aggregate (defined by eq 6)
z	number of hydrocarbon chains per amphiphilic tail
Greek Symbols	
ϵ	electronic charge = 4.8×10^{-10} esu
δ	distance between arrays of dipoles in the arrangement shown in Figure 1

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- (23) The reduction of the translational freedom of motion always provides a positive contribution to the total free-energy change associated with aggregation. However, a large positive quantity representing a part of the above contribution is already included in the entropy term of eq 3. Consequently, the remaining part which represents the contribution to the standard free-energy change ΔG_p° may be either positive or negative.

Acid-Site Distribution on Faujasite-Type Zeolites Determined by *n*-Butylamine Titration.

1. Comparison of the Use of Hammett and Arylmethanol Indicators on Zeolites X

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Publication costs assisted by the University of Newcastle

The determination of the acidity of the cation-exchanged forms of zeolite X (Na^+ , Ca^{2+} , La^{3+} , H^+) was undertaken by the nonaqueous *n*-butylamine titration method, the endpoint being determined visually by using a series of Hammett indicators for the combined Bronsted and Lewis acidity and a series of arylmethanol indicators to distinguish the Bronsted acidity. Comparison of the visual results from the two types of indicators shows that the arylmethanol indicators were unsatisfactory for visual use, probably because of unreliable color changes due to physical adsorption on the zeolite surface. The distributions of the acid sites found from the recommended visual Hammett indicators were reliable and showed a greater heterogeneity of acid strengths than previous studies. The number and strength of acid sites were increased with a high exchange of sodium ions by multivalent cations, especially for the more highly polarizing La^{3+} cation. The acidity of the H form was slightly less than the La form and was not thermally stable.

Introduction

It is important to be able to determine the nature, strength, and distribution of acid sites on the surface of solid catalysts in order to be able to tailor a catalyst to a specific reaction. The catalytic activity of many surfaces, for example, in petroleum refining has been linked strongly with the presence of acid sites. These may be Bronsted sites (proton donors), such as acidic structural hydroxyl groups, or Lewis sites (electron acceptors), such as the tricoordinated aluminum atoms of a zeolite surface. Not only the number of acid sites but also their strength is important in many catalytic conversions. For example, in the cracking of aromatic molecules, sites of high strength are required whereas the isomerization of alkenes is catalyzed by weaker sites.^{1,2} Emphasis in zeolite catalytic studies has been placed on the role of Bronsted-acid sites in the production of carbocations by proton addition to the adsorbed hydrocarbons. Many correlations between known maximum Bronsted acidity of a surface and maximum conversion of hydrocarbons have been made. The roles of Lewis-acid sites and cation sites are not very clear. Lewis-acid sites have been reported to have a modifying effect on the strength of Bronsted-acid sites that are present^{3,4} or may act directly by forming charge-transfer complexes. The framework cations may be involved in the catalysis of such reactions as the high-temperature cracking of alkanes over alkali-metal forms of zeolites X and Y,^{5,6} and it has been postulated that a free-radical mechanism applies on these surfaces which do not possess Bronsted acidity.

Zeolites are finding rapidly increasing use as catalysts because of their many possible structures and hence acidity modifications. This investigation was undertaken to de-

termine the acidity of a series of cation-exchanged zeolites: Na-X, Ca-X, La-X, H-X, dehydrated at 400 °C. The procedure chosen was that of *n*-butylamine titration in benzene, the endpoints being found for the distribution of Bronsted- and Lewis-acid sites by using a series of increasingly basic Hammett indicators and for the distribution of Bronsted-acid sites only by a series of increasingly basic arylmethanol indicators.

Experimental Section

Na-X zeolite was obtained from Union Carbide (Type 13X) and purified by repeated exchange with 1 M NaCl solution. The composition of the zeolite was $(\text{Na}_2\text{O})_{0.95}(\text{Al}_2\text{O}_3)(\text{SiO}_2)_{2.5} \cdot 5.7\text{H}_2\text{O}$. The cation-exchanged forms were prepared by repeated exchange of a pH 5 buffered suspension of the Na form with a solution of the appropriate chloride salt to give the percentage exchange shown in the parentheses.



The ammonium-exchanged form was heated at 400 °C for 2 h to convert it into the decationated form H-X. All samples were dried overnight at 140 °C and then calcined in air at 400 °C for 2 h.

The acidity of the surface was determined by following the procedure described by Benesi⁷ with visible Hammett indicators as recommended by Drushel and Sommers⁸ and arylmethanol indicators as introduced by Hirschler.⁹

The indicators used and their visible color changes are given in Table I. Samples (200-mg) of the zeolites were transferred in a drybox to each of 25 preweighed screwcap vials of approximately 15-cm³ volume. The solid was