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INTERACTIONS OF NEUTRAL MOLECULES WITH IONIC MICELLES

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I. ABSTRACT

The interactions of neutral molecules with ionic micelles are analyzed. The cell and mass action models are presented in order to provide a semi-quantitative description of the solubilization process. Both approaches are

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discussed from a thermodynamic and kinetic point of view and the different definitions of solute incorporation constants are also discussed and compared. An extensive compilation of standard free energies of transfer from water to micelles is provided and the basis of the employed methods to obtain them is presented. Several aspects of the solubilization process such as its dynamics, the effect of additives, the probe microenvironment and its dependence with the solute mean occupation number are reviewed and critically discussed. The effect of solute incorporation upon the micelle shape and size is also briefly reviewed.

II. INTRODUCTION

Ionic micelles can interact with any kind of solute in aqueous solution and, in general, those interactions could be classified in at least four types: 1) interactions with apolar molecules; 2) interactions with polar or amphiphilic molecules; 3) interactions with simple mono- or polivalent ions; and 4) interactions with amphiphilic ions. This classification can be rationalized after considering all the possible locations of a solute in a very crude micellar aggregate such as that depicted in Fig. 1.

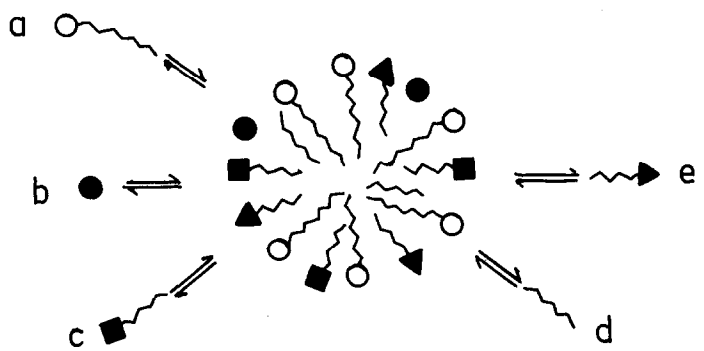

Fig. 1. Schematic representation of the different kinds of association of solutes to ionic micelles. a) surfactant monomer; b) simple counterion; c) amphiphilic molecule; d) amphiphilic counterion; e) hydrophobic molecule.

According to this picture, the chemical potential of any solute incorporated in the micellar aggregate will be strongly dependent, at a given intramicellar concentration, upon its location in the micelle and will be determined by hydrophobic, electrostatic and specific interactions between the solute and the micelle (defined in its more general way). Furthermore, it is evident that if a free energy of transfer from the water phase to the micelle is considered, this value must include the thermodynamic properties of the solutes in the aqueous phase.

The incorporation of neutral molecules in micellar aggregates (a process known as "solubilization") is of practical importance in detergency, oil recovery, catalysis, etc. It can also serve as a basis to understand biological phenomena like those taking place in hydrophobic environments near a water interface such as membranes or enzymes. The fundamental basis of micellar solubilization was established early by McBain and Hutchinson (ref. 1) and by Elworthy (ref. 2).

The solubilization of apolar and polar molecules could in principle be considered as different. Apolar molecules will solubilize in the "micellar core" and polar molecules will be "adsorbed" in the surface (ref. 3). Nevertheless, in terms of the current models discussed below, they can be considered as extremes of a "continuum" and treated within the same framework.

The association of a solute to a micellar assembly (sometimes characterized by the solute properties or by the increase in its solubility in the micellar solution in relation to that measured in pure water) can be treated from a kinetic or a thermodynamic point of view. Furthermore, it has also been treated as a statistical problem by characterizing the type of distribution of solute molecules among the micelles (ref. 4). These three approaches are not independent but are closely related.

Any attempt to develop more general theoretical models for analyzing the incorporation of solutes into micelles should, in principle, take into account: 1) the thermodynamic contributions of all of the components present in the solution (surfactant, counterions, solute, cosolute, electrolyte and solvent); 2) the intermicellar interaction (electrical repulsion and attractive dispersion forces); and 3) the smallness, dispersity and microheterogeneity of the micellear aggregates. Ideally, the model should provide a rigorous framework for treating the individual electrical and non-electrical contributions to the free energy and should predict the most probable site(s) of solute incorporation; the effects of solute incorporation on the aggregation of the surfactant (micellar size, shape and aggregation number) and the effects of cosolutes, electrolyte or other additives on the solubilization equilibrium. In addition, the model should allow quantitative or semi-quantitative prediction of the efficiency of solute incorporation into the micellar aggregate based on an analysis of the structures of the solute and the surfactant. Evidently, no such model is yet available. Among the available alternatives, that which best seems to combine the necessary elements of theoretical rigor with the conceptual clarity and simplicity required for the formulation of meaningful (experimentally verificable!) predictive relationships is the cell model approach of Wennerström and coworkers (ref. 4 - 6).

A. The cell model

In this approach, the micellar solution is subdivided into a set of N_m identical volume elements of cells, each of which contains a single micellar aggregate and its associated aqueous solution with the appropriate quantities of water, aqueous electrolyte, counterions, etc. In comparison with other approaches, this type of cell model provides a particularly convenient formal framework for analyzing electrostatic effects, in particular, intermicellar interactions and local concentration profiles of ionic species in the intermicellar aqueous region. Since each cell contains one micelle, the total number of cells in volume V_t of solution is given by:

$$N_m = [M]V_t \cdot N = [D_m] \cdot N/\bar{N} \cdot Vt \quad , \tag{1}$$

where N is the Avogadro's number, [M] is the molar concentration of micelles, $[D_m]$ is the total concentration of surfactant monomers in micellar form and $\bar{N}$ is the average aggregation number of micelles. Assuming (merely for convenience) a spherical micelle at the center of a spherical symmetric cell, the outer radius or boundary of the cell can be readily known by simple geometry to be: $R = 0{,}735\ ([D_m]/\bar{N})^{1/3}$, where R is expressed in nm. Thus, for example, one liter of 0.025 M solution of a typical ionic detergent with a milimolar CMC and a mean aggregation number of 80 would contain 1.8×10^{20} cells, corresponding to an average intermicellar distance (= 2R) of 22 nm.

The total free energy of a micellar solution containing N_m micelles will be:

$$G_t = N_m G_o + G_{mix} \quad , \tag{2}$$

where G_o is the free energy per cell and G_{mix} is the free energy of mixing of the micelles in the solution. For ideal mixing:

$$G_{mix} = KT \cdot N_m \cdot (\ln X_M - 1) \quad , \tag{3}$$

where X_M is the mole fraction of micelles in the solution. Within each cell, the free energy G_o should depend on (ref. 4 - 6): 1) the quantities and standard chemical potentials of the components present in either the micelle ($n_{i_m} \cdot u^o_{i_m}$) or the aqueous phase ($n_{i_w} \cdot u^o_{i_w}$) 2) a surface free energy contribution (G_s) per cell due to the interface between the micellar components and the aqueous phase; 3) an electrostatic contribution (G_{el}) per cell; and 4) a free energy contribution due to the mixing of the components within the cell. Thus, for G_o we may write:

$$G_o = \Sigma_{i_m} \bar{n}_{i_m} \cdot \bar{u}^o_{i_m} + \Sigma_{i_w} n_{i_w} u^o_{i_w} + G_s + G_{el} + \bar{G}_{mix} \tag{4}$$

Combining Eqs. 2 - 4 to obtain G_t and taking the derivative provides a general relationship for the chemical potential (ref. 6):

$$u_j = \left(\frac{\delta Gt}{\delta nj}\right)_{P,T,ni\neq j} = u_j^o + \left(\frac{\delta Gs}{\delta nj}\right) + \left(\frac{\delta Gel}{\delta nj}\right) + \left(\frac{\delta \bar{G}mix}{\delta nj}\right) + \frac{\delta \bar{G}mix/Nm}{\delta j} \quad . \qquad (5)$$

As shown by Wennerström et al. (ref. 4 - 6), the following set of assumptions permits evaluation of the derivatives on the right-hand side of Eq. 5 and hence of the chemical potential of all species present in the solution:
(1): The Poisson-Boltzmann equation is assumed to provide a valid description of the electrostatic effects within the cell.

If the electrostatic potential, ψ_r, at any point $\underline{r}$ in the aqueous region of the cell is taken to be zero at cell boundary (i.e., if $\psi_{(R)} = 0$) then it can be shown quite generally that the chemical potential of the water is given by:

$$\mu_{H_2O} = \mu^o_{H_2O} - \bar{V}_{H_2O} RT \Sigma Ci_w(R) \ , \qquad (6)$$

where $\bar{V}_{H_2O}$ is the partial molar volume of water and the summation refers to the local concentrations at the cell boundary of all components except water. For all the other components, the chemical potential in the aqueous region can be written as:

$$u_{iw} = u^o_{iw} + kT \ln X_{iw}(R), \qquad (7)$$

where $X_{iw}(R) = C_{iw}(R)/55.5$ is the mole fraction of component i at the cell boundary (activity coefficient corrections can obviously be introduced when necessary).

(2): The interfacial free energy contribution G_s (due largely to residual contact between the apolar micellar core and water) is assumed to be directly proportional to the surface area A of the aggregate via the proportionality constant γ (the effective interfacial tension).

(3): The mixing of the components within the micelle is assumed to be ideal. This implies that the standard chemical potential of a micellar component is not a function of position within the micellar aggregate and implicitly defines a unitary standard state for micellar components in terms of mole fractions X_{im} in a "dry" micelle (water having been treated explicitly, via G_s, as a non-micellar component). Except for cases in which the solute is distinctly amphiphilic, this is potentially a quite bad assumption (correctable, of course, by recourse to empirical activity coefficients). More detailed models would be required to account for intramicellar equilibrium between solubilization sites (e.g., explicit models for intramicellar variation of

$\bar{\mu}^{o}_{im}$) (ref. 7); likewise, other standard states such as volume fractions (ref. 8) or molarities (ref. 9,10) of the solute in the aggregate may prove to be more adequate.

Based on these assumptions and an analysis of the electrostatic free energy in terms of the energy (E_{el}) of the direct ion-ion interactions and the entropy arising from the non-uniform distribution of the ions in the aqueous phase, Jonsson et al. (ref. 5,6) arrived at the following relationship for the chemical potential of the micellar components:

$$\mu_{im} = \bar{\mu}^{o}_{im} + Z_i e_o \psi_o + kT \ln \bar{X}_{im} + (A_i/A)[\gamma_i A - E_{el} - kT\Sigma n_{iw} + RTV_{aq}\Sigma C_{iw}(R)] + kT/\bar{N}_{jo} \cdot \ln XM, \quad (8)$$

where Z_i is the charge of component i, e_o is the electronic charge, ψ_o is the effective micellar surface potential, γ_i is the effective interfacial tension, V_{aq} is the volume of the aqueous region of the cell and Z_i/A is the fraction of the total aggregate surface area attributable to component i.

It should be noted that, within the framework of the present treatment, micelle-associated counterions (or for that matter any micelle-associated solute which fails to penetrate at all into the micellar core, the criterion for penetration being a net reduction in its contact with water) are not considered to be components of the micellar aggregate. Consequently, their binding to the micelles should be treated in terms of an adsorption at the charged interface. In the case of counterions, a Langmuir-Stern isotherm provides a convenient formalism for treating counterion exchange and specific counterion effects on the micellar surface potential.

There is as yet no real consensus as to the best form in which to quantify the association of neutral solutes to micelles. As a result, partitioning coefficients or binding constants for neutral solutes have been expressed in at least four different forms, denoted as: K_m, K_s, K_{MW} and K_x. The preference for a given form has been largely dictated by the nature of the experimental technique used to investigate the solubilization, the concentration units employed, the micelle model assumed or the intended application of the final value.

B. The mass action model

The most realistic model for analyzing solute incorporation is undoubtedly that based on the mass action approach. In its most general form (ref. 7, 11 - 15) the solubilization process can be treated in terms of the stepwise addition of solute molecules S to aggregates MS_i containing i solute molecules. Thus, representing the unperturbed non-solute-containing (empty) micelle by M_o, the sequential solubilization equilibria can be expressed in the form:

$$M_o + S_w \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} MS_1 \quad ; \tag{9}$$

$$MS_1 + S_w \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} MS_2 \quad ; \tag{10}$$

$$MS_{n-1} + S_W \underset{k_{-n}}{\overset{k_{+n}}{\rightleftharpoons}} MS_n \quad . \tag{11}$$

The individual equilibrium constants K_i for the i^{th} association equilibrium is given by:

$$K_i = \frac{k_{+i}}{k_{-i}} = \frac{[MS_i]}{[MS_{i-1}][S_w]} \quad ; \tag{12}$$

where $[S_w]$ is the equilibrium concentration of solute in the intermicellar aqueous phase. From mass balance, the total concentration [M] of micelles present in the solution is:

$$[M] = \sum_{i=0}^{n} [MS_i] \quad , \tag{13}$$

while the total concentration of solute is given by:

$$[S_T] = [S_w] + [S_m] = [S_w] + \sum_{i=0}^{n} i \cdot [MS_i] \quad , \tag{14}$$

where $[S_m]$ is the total analytical concentration of micelle incorporated solute.

The third parameter of interest is the average number of incorporated solute molecules per micelle, usually referred to as the average incorporation number or average occupation number $\bar{n}$ and defined as:

$$\bar{n} = \frac{[S_m]}{[M]} = \frac{\sum_{i=0}^{n} i \cdot [MS_i]}{\sum_{i=0}^{n} [MS_i]} \quad . \tag{15}$$

Further progress requires that one make simplifying assumptions with respect to the maximum number n of solutes which can be incorporated into a given micelle, the effect of solute incorporation on the average aggregation number $\bar{N}$ of the micelle and the relationship between the successive values of the equilibrium constants, K_i. We shall consider here one such set of assumptions which gives rise to a particularly useful limiting model for the solu-

bilization process (ref. 7): 1) the micellar aggregation number is independent of the presence of the solute ($\bar{N}$ constant for all aggregates); 2) the solute entry rate is independent of the number of solute molecules present in the micelle ($k_{+i} = k_+$ for all i); 3) the solute exit rate is directly proportional to the number of solutes present in the micelle (i.e., $k_{-i} = i \cdot k_-$); and 4) the solubilization capacity of the micelle is "infinite" ($n \to \infty$).

Based on these assumptions, the fraction P_i of micelles containing exactly "i" solutes can readily be shown to be (ref. 7):

$$P_i = \frac{[MS_i]}{[M]} = \frac{(\bar{n})^i}{i!} \exp(-\bar{n}) \quad , \tag{16}$$

which corresponds to a Poisson distribution with an average occupation number of:

$$\bar{n} = K_m [S_w] \quad , \tag{17}$$

where:

$$K_m = \frac{k_+}{k_-} \tag{18}$$

is the equilibrium constant for incorporation of the first solute into an empty micelle. Combining Eq. 17 with the definition of $\bar{n}$ (Eq. 15) leads to the extremely interesting relationship (ref. 7):

$$K_m = \frac{\bar{n}}{[S_w]} = \frac{[S_m]}{[S_w][M]} \quad . \tag{19}$$

This last equation implies that, within the limits of this model, solute incorporation can be treated as if it were governed by the following pseudo-equilibrium:

$$S_w + M \underset{\longleftarrow}{\overset{K_m}{\longrightarrow}} S_m \tag{20}$$

with a net solute entry rate of:

$$v_+ = k_+ [M] [S_w] \tag{21}$$

and a net exit rate of:

$$v_- = k_- [S_m] = k_- \bar{n} [M] \quad . \tag{22}$$

Since k_- is a pseudo-first rate constant, $1/k_-$ is in effect the mean life time of a given solute molecule inside a micelle (ref. 7); k_+ is a bimolecular

rate constant which can be expressed as:

$$k_+ = \beta k_{dif} \quad , \tag{23}$$

where k_{dif} is the rate constant for diffusion-controlled encounters between the aqueous solute and the micelles and β is the net efficiency of solute incorporation per encounter.

Slightly different initial assumptions give rise to alternative statistical distributions of the solute among the micelles. Virtually all of these alternative distributions (like the Poisson distribution itself) have a common origin in the binomial distribution (ref. 11 - 16) and hence reduce to a Poisson distribution in the limit of low incorporation number (either $\bar{n} << 1$ or $\bar{n} << m$). Indeed, despite considerations to the contrary (ref. 16), most of the data obtained to date are compatible with a Poisson or Poisson-like distribution for neutral solutes (ref. 7,17). Perhaps the strongest evidence for the applicability of a Poisson distribution is the fact (ref. 7,17) that values of K_m determined from saturation measurements at the solubility limit are generally in reasonable agreement with those determined at very low incorporation numbers (or, alternatively, with those required to simulate kinetic data at low substrate concentrations).

From a practical standpoint, the use of K_m to describe solute incorporation suffers from the inconvenience of requiring a knowledge of the concentration of micelles. Although the micelle concentration $[M]$ can in principle be calculated by dividing the concentration of micellized surfactant ($[D_m]$) by the average aggregation number ($\bar{N}$):

$$[M] = [D_m]/\bar{N} \tag{24}$$

reliable aggregation numbers (in the absence of solutes!) are available for only a few detergents. As a consequence, the more common form of expressing the solute incorporation constant has been as K_s, defined in terms of $[D_m]$ and trivially related to K_m:

$$K_s = \frac{[S_m]}{[S_w]\,[D_m]} = \frac{K_m}{\bar{N}} \quad . \tag{25}$$

This definition of K_s, which in essence reduces the solubilization process to a pseudophase equilibrium of the solute between a micellized surfactant phase and the aqueous phase:

$$S_w + D_m \underset{\longleftarrow}{\xrightarrow{K_s}} S_m \tag{26}$$

has played a central role in more recent pseudophase models for analyzing micellar effects on the kinetics of ground state reactions (ref. 18 - 20).

This same pseudophase equilibrium also serves as the basis for defining two partitioning coefficients, the local concentration scale coefficient K_{MW} and the mole fraction scale coefficient K_x, both of which have been used to obtain thermodynamic parameters associated with the transfer of the solute from the aqueous phase to the micelle. K_{MW} is defined as:

$$K_{MS} = \frac{[\bar{S}_m]}{[\bar{S}_w]} \quad , \tag{27}$$

where $[\bar{S}_m]$ and $[\bar{S}_w]$ refer to the local concentration of the solute in moles per liter of the actual volume of either the micellar or aqueous phase, respectively. If $[S_m]$ and $[S_w]$ are the analytical concentrations of micellar and aqueous substrate (based on the total solution volume), the local molar solute concentrations are given by:

$$[\bar{S}_m] = \frac{[S_m]}{[D_m]\bar{V}} \tag{28}$$

and

$$[\bar{S}_w] = \frac{[S_w]}{1 - D_m \bar{V}} \quad , \tag{29}$$

where $\bar{V}$, the appropriate volume of the micellar phase per mole of micellized detergent, is generally taken to be the partial molar volume of the micellized surfactant. Substituting these into the expression for K_{MW} (Eq. 27) provides the following relationship between K_{MW} and K_s:

$$K_{MW} = \frac{[S_m](1 - [D_m]\bar{V}}{[S_w][D_m]\bar{V}} = (K_s/\bar{V})(1 - [D_m]\bar{V} \quad , \tag{30}$$

or, since the volume fraction of the solution occupied by the micelles ($[D_m]\bar{V}$) is usually quite small relative to unity:

$$K_{MW} \simeq K_s/\bar{V} \quad . \tag{31}$$

Thus, K_{MW} can be calculated from K_s by assuming a value for $\bar{V}$. Alternatively, chromatographic methods for measuring solute partitioning coefficients (ref. 21,22) provide the product $\bar{V}$ ($K_{MW} - 1$) directly, the value of which is approximately equal to ($K_s - \bar{V}$). K_{MW} has been used to describe substrate incorporation in several kinetic models for micellar catalysis, notably that of Berezin et al. (ref. 23,24) (referred to as P by them). Ben Naim (ref. 9,10) has argued that K_{MW}, which assumes a standard state based on local molar concentrations, is the preferred form of the partitioning coefficient for calculating standard free energies of transfer of solutes from water to the micelle.

The dimensionless mole fraction partitioning constant, K_x, is defined as:

$$K_x = \frac{X_m}{X_w} \quad . \tag{32}$$

The expression for the solute mole fraction in the aqueous phase is straightforward:

$$X_w = \frac{[S_w]}{[S_w] + CMC + 55.5} \quad . \tag{33}$$

As for X_m, it has become customary to express the mole fraction of the micelle-incorporated solute in terms of its mole fraction in a "dry" micelle (ref. 25); i.e., to ignore water as a possible third micellar component and simply write:

$$X_m = \frac{[S_m]}{[S_m]+[D_m]} \quad . \tag{34}$$

Combining these equations provides an expression for K_x in terms of the analytical concentrations of the detergent and solute:

$$K_x = \frac{55.5[S_m]}{[S_w]([S_m] + [D_m])} = \frac{55.5\ K_s}{1 + K_s[S_w]} \tag{35}$$

At low degrees of solute incorporation ($K_s[S_w] = [S_m]/[D_m] << 1$), K_x can be interrelated to K_{MW} and K_s via:

$$K_x = 55.5\ K_{MW}\ \bar{V} = 55.5\ K_s \quad . \tag{36}$$

The principal application use of K_x has been in the calculation of standard free energies of transfer of solutes from water to the micelle based on the unitary scale (mole fraction standard state). Implicit in this use of K_x is the supposition that the solute is distributed homogeneously within the micelle, forming an ideal mixture with the detergent (*vide infra*).

In summary, the following relationships can be established between the different binding constants:

$$K_x = 55.5 \cdot K_s \quad ; \tag{37}$$

$$K_x = K_{MW} \cdot \bar{V}_m \cdot 55.5 \ ; \tag{38}$$

$$K_s = K_{MW} \cdot \bar{V}_m \quad ; \tag{39}$$

$$K_M = K_s \cdot \bar{N} \quad . \tag{40}$$

Thus, if the value of the partition coefficient is known on any given scale, the corresponding values on the other scale can be calculated by assigning

values to the parameters $\bar{V}_m$ and $\bar{N}$. For the commonly used detergents SLS and CTAB, the following values of $\bar{V}_m$ and $\bar{N}$ (in the absence of added electrolytes) are recommended: $\bar{V}_m$ (CTAB) = 0.363 dm^3/mole (ref. 26,27); $\bar{V}_m$ (SLS) = 0.25 dm^3/mole (ref. 28 - 30); $\bar{N}$ (CTAB) = 84 (ref. 31); $\bar{N}$ (SLS) = 58 (ref. 32,33).

C. Standard free energies of transfer of solutes from water to micelles

In order to transform experimental solute partitioning constants or incorporation coefficients into thermodynamically meaningful standard free energies of transfer (SFET) of the solute from water to the micellar environment, one must adopt an appropriate reference state for the solute in the micellar pseudophase. In addition, one should be aware of potential limitations inherent in the model on which the partitioning constants or incorporation coefficients themselves are based. At present, the choice of the "best" standard state is a matter of controversy. On the one hand, Ben Naim (ref. 9,10) advocates on the basis of statistical mechanical arguments the use of the molarity scale (total concentrations) for the calculation of the SFET values. On this scale, the SFET would provide a measure of the difference in the solvation properties of the two phases with respect to the solute. On the other hand, Tanford (ref. 34), following Gourney (ref. 35) and Kauzmann (ref. 36) suggests that the SFET be expressed in the unitary system (mole fraction standard state). On this latter scale, the SFET should incorporate all interactions of the solute with the micelle. In this context, however, it should be re-emphasized that the solute mole fraction in the micellar pseudophase is usually expressed in a form which ignores water as a potential component of the micellar pseudophase.

As mentioned before, the mass action law probably provides the most meaningful approach for treating the association of molecules to micelles. From a practical standpoint, however, the two-phase of pseudophase model is a much more convenient approximation, both for analyzing experimental data for solute incorporation and for calculating SFET values. Thus, the respective chemical potentials of the solute in the micellar and aqueous phases can be expressed in the form:

$$\mu_m = \mu_m^o(T,P) + RT\ln X_m\gamma_m \quad ; \tag{41}$$

$$\mu_w = \mu_w^o(T,P) + RT\ln X_w\gamma_w \quad . \tag{42}$$

At equilibrium, the SFET can be written as:

$$\mu_t^o = \mu_m^o - \mu_w^o = -RT\ln \frac{X_m\gamma_m}{X_w\gamma_w} = -RT\ln K_X \quad , \tag{43}$$

where x_m and x_w represent the mole fractions of the solute in the micellar and water phases, respectively, and γ_m and γ_w are the corresponding activity coefficients. For a neutral solute, γ_w can usually be assumed to be unity and, when the partitioning coefficient is independent of the surfactant concentration or average solute incorporation number, γ_m can also safely be taken to be unity. Departures from this ideal behavior can, of course, be treated via inclusion of nonideality of mixing. The simplest approach is probably that based on the so called regular solution theory (ref. 37,38) which was used by Mukerjee (ref. 39) to interpret the non-ideal behavior of the distribution of benzoic acid derivatives betweeen water and micelles of nonionic surfactants. In this approach, the activity coefficient of the component solubilized in the micelle is assumed to be given by:

$$Ln\gamma_m = (1 - x_m)^2 \cdot \sigma/RT \quad , \tag{44}$$

where σ is an adjustable interaction energy parameter which approaches $RTln\gamma_m$ as x_m tends to zero. In the present work, we have assumed the validity of the pseudophase model, ideal behavior and a unitary standard state for all calculations of SFET from experimental partitioning coefficient data.

Having established a basis on which to calculate SFET values from experimental solute incorporation data, it is of interest to analyze these values for trends which might provide insight into the nature of the intermolecular forces which contribute to solute incorporation in the micellar pseudophase. One potentially useful approach is to assumed that $\Delta\mu_t^o$ is an additive-constitutive property of the solute molecule; i.e., that the SFET of a molecule from water to the micelle can be factored into individual group contributions from its hydrophilic and hydrophobic constitutent molecular moieties. This assumption, extensively used for the partitioning of solute in non-miscible solvents (ref. 40) permits one to separate the total free energy ($\Delta\mu_t^o$) for transfer of the molecule from one solvent to another (from water to micelles in this case) into a hydrophilic component ($\Delta\mu_{hy}^o$) and a hydrophobic component ($\Delta\mu_c^o$). If the latter is further assumed to reflect individual contributions from "n_c" hydrophobic groups of the molecule (ref. 41), $\Delta\mu_t^o$ can be written in the form:

$$\Delta\mu_t^o = \Delta\mu_{hy}^o + n_c\Delta\mu_c^o \quad . \tag{45}$$

In agreement with this assumption, $\Delta\mu_t^o$ for a set of related solutes (or related micelle-forming surfactants) is frequently found to be a linear function of the number of homologous hydrophobic groups present in the solute (or surfactant). Similar linear free energy relationships have also been found in virtually all studies of the distribution of solutes between water

and bulk nonaqueous solvents (ref. 40,41). In view of the uncertainties surrounding the choice of the appropriate standard state for expressing $\Delta\mu_t^o$ in micellar systems, it should be noted that the slopes of correlations of $\Delta\mu_t^o$ vs. the number of homologous functional groups, which presumably reflect the contribution of that group to the overall transfer free energy, are independent of the standard state chosen. Thus, it is only the intercept, which incoporates the contributions from the remaining groups of the solute molecule, that is dependent on the choice of the standard state (ref. 42).

Leo et al. (ref. 41) have also considered the case of a family of solute molecules in which the number "n_h" of hydrophilic groups is changed, in which case Eq. 45 takes the form:

$$\Delta\mu_t^o = n_h\Delta\mu_{hy}^o + \Delta\mu_c^o \quad . \tag{46}$$

When the solubilizate is a relatively hydrophobic ion, for example, a carboxylate, alkyl phenoxide or arylsulfonate ion, the total $\Delta\mu_t^o$ also contains an electrostatic contribution, $\Delta\mu_{el}^o$; i.e.:

$$\Delta\mu_t^o = \Delta\mu_{hy}^o + n_c\Delta\mu_c^o + \Delta\mu_{el}^o \quad . \tag{47}$$

However, attempts to interpret the $\Delta\mu_{el}^o$ in terms of a straightforward electrostatic contribution may be complicated by the fact that counterionic organic solutes tend to form ion pairs with the surfactant monomer in the aqueous phase, in which case it is the uncharged (if both solute and detergent are monovalent) ion pair that is transferred from water to micelle (ref. 43,44). In reality, ion pairing of counterionic substrates is probably one out of a variety of potentially unique interactions. The existence of such (often unperceived) interactions merely emphasizes the fact that the solute activity in the intermicellar aqueous phase cannot *a priori* be presumed to be equivalent to that in a bulk micelle-free water phase.

An important extension of the thermodynamic analysis of micellar solubilization is the separation of the free energy of transfer into its constituent enthalpic and entropic components. In principle, the standard enthalpy of transfer (ΔH_t^o) can be obtained from the temperature dependence of $\Delta\mu_t^o$ (ref. 40). In practice, however, this method proves to be rather imprecise because the changes in $\Delta\mu_t^o$ with temperature are usually small. Furthermore, in view of the possibility of temperature-dependent changes in micellar structure, measurements over a wide temperature range are inherently undesirable. Direct calorimetric measurements are therefore preferable whenever possible. Since only very limited data of this type are presently available, comprehensive calorimetric determinations of standard enthalpies (ΔH_t^o) for the

transfer of solutes from water to micelles as a function of the hydrophilic or hydrophobic properties of the solute, the nature of the detergent and the composition of the solution should be of inestimable value. Once the enthalpy of transfer has been determined, the standard entropy of transfer can, of course, be calculated from the relationship:

$$\Delta S_t^o = (\Delta H_t^o - \Delta \mu_t^o)/T \quad . \tag{48}$$

Like $\Delta \mu_t^o$, the magnitude of ΔS_t^o is also a function of the choice of the reference state, the values of ΔS_t^o calculated on the unitary (mole fraction scale) being more positive than those calculated on the molarity scale.

A central question in the thermodynamic analysis of solute incorporation has been (and continues to be) the interpretation of the origin and significance of the incremental hydrophobic contribution ($\Delta \mu_c^o$) per methyl or ethylene group to the overall free energy of transfer of the solute from water to the micelle. Thus, using the unitary system and Wishnia's results (ref. 45), Tanford (ref. 34) found that the SFET values for transfer of alkanes from water to SLS micelles obey the linear expression:

$$\Delta \mu_t^o = -1.934 - 0.771\ n_c \quad , \tag{49}$$

where n_c is the total number of alkyl carbon atoms in the alkane. The slope of -0.771 Kcal/mole which corresponds to the contribution to $\Delta \mu_t^o$ from each of the carbon atoms of the alkane molecule is similar to that found for the transfer of alkanes from water to hydrocarbon solvents (-0.88 Kcal/mole) (ref. 34), suggesting that alkanes are located in a micelle environment similar to that of a nonaqueous hydrocarbon-like solvent. The non-zero value of the constant term has been attributed by Tanford (ref. 34) and by Birdi (ref. 46) to the difference in the contributions of $-CH_3$ and $-CH_2$ groups to the SFET. From the data for transfer to hydrocarbon solvents, Tanford calculated a $\Delta \mu_c^o$ value of -0.88 Kcal/mole for a $-CH_2$ group versus a contribution of ca. -2.1 Kcal/mole for each $-CH_3$ group, the difference being attributed to the greater degree of contact of the $-CH_3$ group with water as compared to a $-CH_2$ group. In addition, it is also necessary to take into account that the calculation attributes most of the differences in translational entropy of the entire molecule to the terminal methyl group. According to Spink and Colgan (ref. 47), the contributions of the methyl and methylene groups to the standard free energies, enthalpies and entropies of transfer of aliphatic molecules from water to micelles and from water to hydrocarbon media (Table 1) are characterized by a more positive enthalpy, a much more positive entropy and consequently, a larger incremental contribution to $\Delta \mu_t^o$ for the methyl group relative to the methylene group.

TABLE 1

Standard thermodynamic parameters for the transfer of methyl and methylene groups from water to nonpolar media (ref. 47).

Group	$-\Delta\mu_t^o$ Kcal/mole	ΔH_t^o Kcal/mole	$T\Delta S_t^o$ Kcal/mole
$-CH_2$ [†]	0.86	-0.67	0.19
$-CH_3$ [†]	2.06	+1.22	3.28
$-CH_2$ [††]	0.76	-0.98	-0.24
$-CH_3$ [††]	1.78	+1.00	2.78

[†]Methyl and methylene contributions for transfer from water to pure hydrocarbons, evaluated by Spink and Colgan (ref. 47) from the data of Amidon and Anik (ref. 56).

[††]The same as in Footnote 1 but based on the transfer of hydrocarbons from water to SLS micelles from the results of Wishinia (ref. 45).

Even more surprising is the fact that the enthalpic contribution to the transfer is positive for the $-CH_3$ group and negative for the $-CH_2$ group, implying that methyl groups are energetically more stabilized in water, while methylene groups are energetically more stable in a hydrocarbon environment. Thus, the net hydrophobic nature of the $-CH_3$ group would appear to derive largely from the entropic contribution. In contrast, the hydrophobicity of the $-CH_2$ group can be attributed mainly to an enthalpic contribution, the entropic term being rather small and even negative in the case of transfer to SLS micelles. The implications of this analysis are of fundamental importance, especially since an explanation for the hydrophobic effect based solely on the water structuring capability of hydrocarbon chains would lead one to expect both positive enthalpic and entropic contributions for transfer of hydrocarbons from aqueous to nonpolar solution. Indeed, the SFET for transfer of any solute from water to micelles or, for that matter, from water to any other phase, will necessarily be a function of both the strength of the interaction between the solute and the micelle and of the peculiarities of the interaction of the solute with water.

The SFET for transfer of a given solute from water to a series of different micelles is also a linear function of the number of carbon atoms of the alkyl chain of the micelle-forming surfactant (ref. 46,48). However, the hydrophobic contribution per $-CH_2$ group of the surfactant alkyl chain (for incorporation of molecules like Orange OT, naphthalene and methylazobenzene) is much smaller (ca. -0.2 Kcal/mole) than the corresponding contribution per $-CH_2$ group of alkyl solubilizated hydrocarbon (-0.8 Kcal;mole, ref. 34).

Of particular interest is the fact that Treiner (ref. 42) has found an excellent correlation between the constants for partitioning of polar solutes between water and ionic micelles and those for partioning between water and n-octanol. The existence of such a correlation implies that solutes of relatively high polarity of the type studied by Treiner exhibit intrinsic differences in hydrophilicity (probably related to the extent and the strength of hydration) in the same manner that the hydrophobicity of a given molecule varies with the number of constituent carbon atoms.

In Table 2, we have collected data for the incorporation of a large number of substrates into a variety of different micelles. Since an extensive analysis of the individual data is beyond the scope of the present work, only the major trends will be considered. In the cases where sufficient data were available, values of $\Delta\mu_c^o$ were determined for families of homologous molecules. These values, together with analogous values for transfer from water to bulk solvents, are collected in Table 3.

Table 2 also includes the corresponding directly measured enthalpies of transfer for those (few) solutes for which data are available, along with calculated values of the entropic contribution ($T\Delta S_t^o$) to the transfer. These data are restricted to the studies by Larsen and Magid (ref. 49) and, more recently, by Spink and coworkers (ref. 47,50). The data of Larsen and Magid for the transfer of benzoic acids from water to the CTAB micelle (Table 2) clearly suggest that both enthalpic and entropic factors contribute to the overall free energy of transfer to the micelle. This is reinforced by the work of Spink et al. (ref. 47,50), in which the thermodynamic functions for transfer of aliphatic alcohols from water to deoxycholate micelles were measured (Table 2). Although the free energy of transfer was found to be a linear function of the number of carbons in the aliphatic chain of the alcohol, neither the entropic nor the enthalpic contributions to the SFET exhibit simple linear relationships when considered separately. Enthalpy-entropy compensation resulting in linear correlations of the free energy may prove to be the rule rather than the exception.

In general terms, the factors which tend to favor the transfer of a solute from the aqueous phase to the micelle can be summarized as follows: 1) an increase in the overall hydrophobicity of the solute; 2) an increase in the length of the hydrocarbon chain of the surfactant; 3) a change in the relative positions of hydrophilic substituents from a para or diametrical orientation to an ortho or adjacent position; and 4) the presence of aryl moieties in the solute.

These latter two factors are apparently indicative of additional contributions which arise from the interaction of certain types of aromatic residues

TABLE 2

Association constants (K_s and K_x), free energies ($\Delta\mu_t^o$), enthalpies (ΔH_t^o) and entropies ($T\Delta S_t^o$) of transfer of molecules from the aqueous to the micellar pseudophase

Surfactant	Substrate	K_s	$K_x \times 10^{-3}$	$-\Delta\mu_t^o$ Kcal/mole	ΔH_t^o Kcal/mole	$T\Delta S_t^o$ Kcal/mole	Ref.	Entries
CTAB[a]	2-naphthol	1390	77.1	6.6			58	1
CTAB	phenol	270	15.0	5.7			57-58	2
CTAB	p-methyl phenol	490	27.2	6.0			57-58	3
CTAB	p-ethyl phenol	790	43.2	6.3			57-58	4
CTAB	p-n-propyl phenol	1400	77.7	6.7			57-58	5
CTAB	p-t-butyl phenol	1700	94.4	6.8			57-58	6
CTAB	p-t-amyl phenol	4300	239	7.3			57-58	7
CTAB	p-sec-butyl phenol	1900	105	6.9			58	8
CTAB	m-t-butyl phenol	1700	94.4	6.8			58	9
CTAB	phenoxide	1800	100	6.8			57-58	10
CTAB	p-methyl phenoxide	3300	183	7.2			57-58	11
CTAB	p-ethyl phenoxide	5300	294	7.5			57-58	12
CTAB	p-n-propyl phenoxide	9600	533	7.8			57-58	13
CTAB	p-t-butyl phenoxide	10000	555	7.9			57-58	14
CTAB	p-t-amyl phenoxide	27000	1500	8.4			57-58	15
CTAB	benzoic acid	378	21.0	5.9			57	16
CTAB	p-methyl benzoic acid	743	41.2	6.3			57	17
CTAB	p-ethyl benzoic acid	1727	95.8	6.8			57	18
CTAB	p-t-butyl benzoic acid	3600	200	7.2			57	19
CTAB	benzoate	2865	159	7.1			57	20
CTAB	p-methyl benzoate	2865	159	7.1			57	21
CTAB	p-ethyl benzoate	4015	223	7.3			57	22
CTAB	p-t-butyl benzoate	5625	313	7.5			57	23
CTAB	aniline	116	6.44	5.5			57	24
CTAB	p-methyl aniline	193	10.7	5.5			57	25
SLS[b]	phenol	50	2.78	4.7			57	26
SLS	p-methyl phenol	83	4.61	5.0			57	27
SLS	p-ethyl phenol	163	9.0	5.4			57	28
SLS	p-n-propyl phenol	270	15.0	5.7			57	29
SLS	p-t-butyl phenol	378	21.0	5.9			57	30
SLS	p-t-amyl phenol	1041	57.8	6.5			57	31
SLS	aniline	83	4.61	5.0			57	32
SLS	aniline H^+	450	25.0	6.0			57	33
SLS	benzoic acid	193	10.7	5.5			57	34
SLS	p-methyl benzoic acid	228	12.7	5.6			57	35
SLS	p-ethyl benzoic acid	448	24.9	6.0			57	36
SLS	p-t-butoxy benzoic acid	880	44.8	6.4			57	37
SLS	p-methyl aniline H^+	628	34.9	6.2			57	38
			ALKYL ALCOHOLS					
Sodium deoxycholate	butanol	0.95	0.053	2.34	6.60	8.94	47	39
Sodium deoxycholate	pentanol	2.20	0.122	2.73	3.78	6.51	47	40
Sodium deoxycholate	hexanol	9.21	0.51	3.68	1.87	5.57	47	41
Sodium deoxycholate	heptanol	36.4	2.02	4.49	1.22	5.72	47	42
SLS	butanol	5.4	0.30	3.38			61	43
SLS	pentanol	13.0	0.72	3.90			61	44
SLS	hexanol	40.5	2.25	4.57			61	45
SLS	heptanol	108.5	6.02	5.16			61	46
SLS	heptanol	111.7	6.20	5.15			62	47
Sodium cholate	heptanol	37.8	2.10	4.51			62	48
Sodium deoxycholate	heptanol	55.9	3.10	4.74			62	49
DTAB[c]	ethanol	0.010	0.18	1.36			42	50
DTAB	propanol	0.033	0.59	2.06			42	51
DTAB	2-propanol	0.027	0.49	1.95			42	52
DTAB	butanol	0.094	1.69	2.68			42	53
DTAB	t-butanol	0.045	0.81	2.25			42	54
DTAB	methanol	0.29	5.19	3.34			42	55
DTAB	hexanol	0.87	15.7	3.99			42	56
			PHENONES					
SLS	acetophenone	35.2	1.95	4.47			84	57
SLS	propiophenone	81.0	4.50	4.86			84	58
SLS	isobutyrophenone	129.3	7.16	5.24			84	59
SLS	p-methoxiacetophenone	51.7	2.87	4.70			84	60
SLS	xanthone	109.0	6.05	5.14			84	61
			BENZOIC ACIDS					
CTAB	o-nitrobenzoic	28.7	1.59	4.35	-2.29	2.06	49	62
CTAB	o-chlorobenzoic	36.3	2.01	4.49	-2.22	2.27	49	63
CTAB	o-aminobenzoic	33.0	1.83	4.43	-5.09	-0.66	49	64
CTAB	p-aminobenzoic	18.9	1.05	4.10	-1.78	2.32	49	65
CTAB	o-hydroxybenzoic	59.2	3.29	4.77	-6.19	-1.42	49	66
CTAB	p-hydroxybenzoic	12.0	0.67	3.83	-9.25	-5.42	49	67
			p-NITRO PHENYL ALKYL CARBOXYLATES					
N-Myristoil-histidine, CTAB mixed micelles	acetate	30.1	1.67	4.38			59	68
N-Myristoil-histidine...	propionate	108	6.0	5.13			59	69
N-Myristoil-histidine...	butyrate	345	19.2	5.82			59	70
N-Myristoil-histidind...	valerate	769	42.7	6.29			59	71
N-Myristoil-histidine...	hexanoate	2000	111	6.85			59	72
CTAB	acetate	54	3.0	4.72			79-80	73
CTAB	acetate	27	1.5	4.31			81	74
CTAB	butyrate	530	29.4	6.07			82	75
CTAB	heptanoate	4500	250	7.33			83	76

TABLE 2 (continued)

Surfactant	Substrate	K_s	$K_x \times 10^{-3}$	$-\Delta\mu_t^o$ Kcal/mole	ΔH_t^o Kcal/mole	$T\Delta S_t^o$ Kcal/mole	Ref.	Entries
			p-NITRO PHENYL ALKANOATES					
CTAB	acetate	27	1.5	4.31			63	77
CTAB	trimethyl acetate	440	24.4	5.96			63	78
CTAB	butyrate	530	29.4	6.07			63	79
CTAB	heptanoate	4500	250	7.33			63	80
CTAB	cinnamate	3800	211	7.23			63	81
CTAB	salicylate	630	35	6.17			63	82
			ALKANES					
SLS	ethane	5.9	0.33	3.42			34	83
SLS	propane	23.0	1.28	4.22			34	84
SLS	butane	108	5.99	5.13			34	85
SLS	pentane	293	16.3	5.72			34	86
			MISCELLANEOUS					
DTAB	dioxane	0.005	0.09	0.95			42	87
DTAB	ethylmethylketone	0.025	0.45	1.90			42	88
DTAB	diethylamine	0.043	0.77	2.22			42	89
DTAB	triethylamine	0.306	5.55	3.38			42	90
DTAB	propylacetate	0.141	2.54	2.94			42	91
DTAB	ethylether	0.041	0.74	2.19			42	92
DTAB	tetrahydrofuran	0.026	0.47	1.92			42	93
DTAB	cyclohexanone	0.098	1.77	2.72			42	94
CTAB	dinitrochlorobenzene	67	3.72	4.85			66	95
CTACl[d]	dinitrochlorobenzene	82	4.55	4.97			66	96
CTAOH[e]	dinitrochlorobenzene	100-250	555-13.9	5.09-5.63			64	97
CTAB	dinitrochloronaphthalene	600	33.3	6.14			66	98
CTACl	dinitrochloronaphthalene	600	33.3	6.14			66	99
CTAB	benzoic anhydride	650	36.1	6.19			67	100
CTAB	N-$C_{12}H_{25}$-3-Cp(k)	20	1.11	4.14			60	101
CTAB	N-$C_{14}H_{29}$-3-Cp(k)	390	21.6	5.90			60	102
CTAB	N-$C_{16}H_{33}$-3-Cp(k)	3500	194	7.18			60	103
CTAB	ethylbenzoate	200	12.2	5.55			68	104
CTAB	ethyl p-amino benzoate	250	13.9	5.63			68	105
CTAB	ethyl p-nitro benzoate	240	13.3	5.60			68	106
CTACl	$C_{12}H_{25}N^+(CH_3)_2COOCH_3$	26	1.44	4.29			69	107
TDTACl[f]	$C_{12}H_{25}N^+(CH_3)_2CH_2COOCH_3$	22	1.22	4.19			69	108
CTAB	5,5'-dithiobis(2-nitro benzoic acid)	20000	1110	8.21			70	109
DDCACl[g]	5.5'-dithiobis(2-nitrobenzoic acid)	40000	2220	8.62			70	110
CTACl	p-nitrophenyldiphenyl phosphate	16000	888	8.08			71-72-73	111
CTAB	p-nitrophenyldiphenyl phosphate	16900	888	8.08			74	112
CTAOH	p-nitrophenyldiphenyl phosphate	10000	555	7.80			64	113
CTAF[h]	p-nitrophenyldiphenyl phosphate	10000	555	7.80			64	114
SLS	2,4-dinitrochlorobenzene	14	0.78	3.93			74	115
CTAB	2,4-dintrofluorobenzene	54	3.0	4.72			74	116
CTAB	malachite green	29	1.61	4.36			75	117
SLS	malachite green	8000	444	7.67			75	118
CTA	$PhCO_2C_6H_3(NO_2)_3$	650	36.1	6.19			66	119
CTAB	$(O_2NC_6H_4O)_2CO$	1000	55.5	6.45			67	120
CTAMES[i]	$PhSO_3Me$	55	3.05	4.73			66	121
SLS	N-trifluoroacetyl-indole	420	23.3	5.93			76	122
SLS	1-benzyldihydronicotinamide	285	15.8	5.70			78	123
SLS	benzyl-3-acetyl-1,4-dihydropridine	405	22.5	5.91			78	124
SLS	benzidine	220	12.2	5.55			77	125
SLS	ferrocene	340	18.9	5.81			85	126
SLS	2,2'-bipyridyl 4,4'-dimethyl	40	2.22	4.55			86	127
CTACl	benzimidazole	43	2.39	4.59			65	128
CTAB	benzimidazole	36	2.0	4.48			65	129
$CTANO_3$[j]	benzimidazole	36	2.0	4.48			65	130
CTAB	naphthimidazole	1100	61.1	6.50			65	131

(a) cetyltrimethylammonium bromide
(b) sodium lauryl sulfate
(c) dodecyltrimethylammonium bromide
(d) cetyltrimethylammonium chloride
(e) cetyltrimethylammonium hydroxide
(f) tetradecyltrimethylammonium chloride
(g) dioctadecyldimethylammonium chloride
(h) cetyltrimethylammonium fluoride
(i) cetyltrimethylammonium mesylate
(j) cetyltrimethylammonium nitrate
(k) N-alkyl-3-carbamoyl pyridinium ions

TABLE 3

Hydrophobic ($\Delta\mu_c^o$), hydrophilic ($\Delta\mu_{hy}^o$) and electrostatic ($\Delta\mu_e^o$) contributions to the free energies of transfer of molecular moieties from water to micelles or to hydrophobic solvents

Surfactant or Solvent	Family of Molecules	$-\Delta\mu_c^{o(d)}$ Kcal/mole	$-\Delta\mu_{hy}^{o\,(d)}$ Kcal/mole	$-\Delta\mu_e^{o(e)}$ Kcal/mole	Ref.
CTAB[a]	p-alkyl phenols	0.32	5.7 >	1.2	57-58
CTAB	p-alkyl phenoxides	0.31	6.9		
CTAB	p-alkyl benzoic acids	0.34	6.0		57-58
CTAB	p-alkyl benzoates	0.12	7.0 >	1.0	
CTAB	p.alkyl anilines	0.27	5.2	-	57
CTAB	aromatic hydrocarbons	0.83	4.3	-	57
CTAB	p-nitrophenyl alkyl carboxylates	0.63	3.4	-	59
CTAB	N-alkyl-3-carbamoyl-pyridinium ions	0.75	3.3	-	60
SLS[b]	alkyl phenols	0.36	4.66	-	57-58
SLS	p-alkyl benzoic acids	0.29	5.4	-	57
SLS	p-alkyl anilines	0.39	4.8		57
SLS	p-alkyl anilines x H^+	0.17	6.0 >	1.2	57
SLS	aromatic hydrocarbons	0.55	4.2	-	57
SLS	aliphatic alcohols	0.60	0.95	-	61
SLS	aliphatic alcohols	0.60	0.95	-	42
DTAB[c]	aliphatic alcohols	0.66	0.068	-	42
Lecithin	aliphatic alcohols	0.55	-	-	42
Octanol	aliphatic alcohols	0.79	-	-	42
Octane	aliphatic alcohols	0.81	-	-	42
SLS	aliphatic hycrocarbons	0.77	-	-	34
n-heptane	alkyl phenols	0.78	0.00	-	57
n-heptane	p-alkyl benzoic acids	0.90	0.22	-	57
n-heptane	p-alkyl anilines	0.98	0.59	-	57
n-heptane	p-alkyl benzenes	0.80	4.3	-	57
p-alkyl benzenes	p-alkyl benzenes	0.75	4.6	-	34
n-heptane	carboxilic acids	0.825	-3.9	-	34
aliphatic alcohols	aliphatic alcohols	0.821	-1.34	-	34
aliphatic hydrocarbons	aliphatic hydrocarbons	0.884	-	-	34
p-alkyl benzenes	p-alkyl benzenes	1.00	-	-	34

(a), (b) and (c) as defined in Table 2.

(d) In terms of unitary system; i.e., using the molar fraction scale and from Eq. 45.

(e) Neglecting ion paring formation (Eq. 47).

with the micellar microenvironment. Thus, substitution of one of the protons of benzene by a hydrophilic substituent (-OH, -COOH, $-NH_2$) gives rise to a much stronger interaction with both CTAB and SDS micelles. Due to its hydration, the hydrophilic group would tend to remain near the micelle surface, enhancing the interaction of the π electron cloud of the benzene ring with the electric field produced by the charged surfactant head groups at the micelle surface. This explanation is consistent with the heats of solubilization of phenol and p-nitrophenol in CTAB as compared with other solvents (ref. 49) and with the SFET data for transfer of phenols, benzoic acids, anilines and benzene from water to n-heptane (Table 3). In fact, the transfer of benzene

from water to n-heptane is more favorable relative to the other solutes, a trend which is opposite to that observed for transfer from water to CTAB micelles. Finally, the presence of an aryl group in the solute seems to favor a stronger interaction with cationic micelles than with anionic micelles, suggesting the existence of a specific interaction between the cationic head groups of the micelles and the aromatic ring of the solute molecule. Both NMR and absorption spectroscopy (ref. 51 - 55), as well as enthalpies for transfer of phenols from water to 0.1 M CTAB (ref. 49) provide corroborative evidence for this type of interaction.

III. EXPERIMENTAL METHODS

The experimental methods used to investigate the association of solutes to micelles may be classified into three principal groups: solubilization, separation and spectroscopic methods. Other miscellaneous methods (e.g., kinetic analysis of ground state reactions) will also be briefly considered. In general, the method itself will be emphasized since the results obtained with any of the different methods can be treated in a similar fashion to obtain the required association constant. For nonionic substrates, this constant is usually expressed as K_s (Eq. 25) which can in turn be transformed into K_M, K_{MW} or K_x (Eqs. 37 - 40).

A. Solubilization methods

The simplest and oldest of the methods are the solubilization methods, which are based on the enhancement of the solubility of solutes in the presence of a surfactant at concentrations above its CMC. Excess pure solute, in either its solid, liquid or vapor form (in the last case, the procedure is known as the isopiestic method), must be in equilibrium with both the micelle-associated solute and the free solute in the aqueous phase. In essence, one determines the total amount of dissolved substrate in the presence ($[S_t]$) and absence ($[S_0]$) of micelles. Assuming that the solubility in the aqueous phase is unaffected by the presence of micelles, K_s can be written as:

$$K_s = \frac{[S_t] - [S_0]}{[S_0]([D_t] - CMC)} \quad . \tag{50}$$

Rearranging this equation, a plot of the saturation solubility ratio $[S_t]/[S_0]$ versus the total detergent concentration $[D_t]$ should be linear with slope K_s:

$$\frac{[S_t]}{[S_0]} = K_s[D_t] + 1 - K_s CMC \quad . \tag{51}$$

In spite of its experimental simplicity, the solubilization method has the disadvantage that the concentration of solid or liquid solutes cannot be controlled (being automatically determined by the solubility of the solute in water). Highly soluble substrates can thus profoundly perturb the micellar structure, making the intepretation of the experimental results difficult. On the other hand, the method is extremely versatile when applied to just about any type of gaseous solute. Thus, by equilibrating the micellar solution at different solute partial pressures, the intramicellar solubility can be measured from very low occupation numbers up to those equivalent to saturation with the liquid (or solid) solute. This isopiestic method, originally employed by Wishnia (ref. 45) to measure the solubility of hydrocarbons in SLS micelles, has recently been employed by several groups. The amount of solute present in the solution phase can be measured by gas-liquid chromatography (ref. 47,61,62,87), from the pressure drop in a calibrated volume (ref. 45,47, 61,87 - 89), from the amount of gas released from a supersaturated solution previously equilibrated with the gas at an elevated pressure (ref. 90 - 93), or from the final equilibrium pressure over a solution containing a precisely known amount of liquid (ref. 94,95). The isopiestic method typically provides data of high precision over a wide range of solute activities, allowing determination of thermodynamic parameters with a high degree of confidence. Indeed, the data for solubilization of cyclohexane by sodium octyl sulphate micelles (ref. 94) and for solubilization of benzene and cyclohexane by sodium deoxycholate micelles obtained by this method probably represent the most precise measurements currently available of solute incorporation over a wide range of solute activities. Similarly, the work of Bolden et al. (ref. 93) furnishes the most precise values for the solubility of gases (O_2, CH_4, ethane and propane) in sodium alkyl sulfate micelles. Finally, it should be noted that by simply increasing the solute pressure, one can estimate partitioning coefficients even for solutes that have very low incorporation numbers under normal experimental conditions.

B. Separation methods

A true physical separation of micelles from the aqueous phase is, of course, impossible since removal of the solvent would in itself imply destruction of the micelle. However, there are two methods, ultrafiltration and gel filtration, which in effect permit a separation or isolation of part of the aqueous phase from the remainder of the solution containing the micelles.

The ultrafiltration method was first used by McBain et al. (ref. 96,97) and Hutchinsin et al. (ref. 98,99). More recently, Dougherty and Berg (ref. 25), Bunton et al. (ref. 74) and Sepúlveda et al. (ref. 57,100) have used this

method to determine partitioning coefficients for a wide variety of solute types. In a recent paper, Schechter et al. (ref. 101) have established the conditions under which ultrafiltration experiments in micellar solution provide the most reliable results. The method is based on the capacity of certain membrane filters to retain species with molecular weights similar to, or greater than, those of micelles. The technique requires a special stirrable and pressurizable filter cell fitted with an adequate (molecular weight retention, solvent compatibility, solute adsorption) membrane filter. A small part of the micellar solution (pre-equilibrated with the solute) is passed through the membrane, the solute concentrations C, in the filtrate and filtrand solutions measured and the fraction of micellar solute calculated from the equation:

$$\frac{[S_m]}{[S_t]} = \frac{C_{filtrand} - C_{filtrate}}{C_{filtrand}} \quad . \tag{52}$$

The method requires constant stirring of the solution and only a small amount of filtrate should be collected for analysis in order to avoid a change in the overall composition of the filtrand. Other problems may arise from adsorption of surfactant or solute on to the membrane, from differences in the rate of filtration of water relative to free monomer or solute and to streaming potential effects. The principal advantages of the method are its range of applicability, relative simplicity and the fact that the micelle and substrate concentrations can be varied over a wide range.

In the gel filtration method, the portion of the aqueous phase containing the free solute is "separated" from the remainder of the solution by the use of a cross-linked dextran gel (usually Sephadex) which excludes from its interior species with molecular weights above a certain limit determined by the characteristics of the gel (ref. 102). As long as the micelle has a molecular weight larger than this exclusion limit of the gel, upon passage of a micelle-containing mobile phase through a column of the gel the composition of the solute within the gel phase should correspond to that of the aqueous phase and hence contain only free surfactant monomers, non-micelle-bound solute molecules and any low molecular weight electrolyte present. At surfactant concentrations well above the CMC, the relative rate of migration (retention volume) of an added low molecular weight solute will be a function of the partitioning coefficient of the solute between the micellar and aqueous phases. Thus, given the parameters of the gel column, the degree of adsorption of the solute in the gel matrix, the partial specific volume of the surfactant molecule in the micelle and the molecular sieving constant, K_{MW} can be evaluated experimentally from the retention volume data.

The gel filtration method seems to be suitable for the detemination of partitioning coefficients in the range of 10 - 1000. Although measurement of

values up to perhaps 10,000 may be possible, the method is less useful when the partitioning coefficient is close to or less than unity because of the small volume fraction occupied by the micelles.

In related work, Armstrong et al. (ref. 21,22,23) have shown in detail how both high pressure liquid chromtagraphy (HPLC) and thin layer chromatography (TLC) can be employed to determine partitioning coefficients using micellar solutions as the mobile phase. The technique is based on the concept that a solute which incorporates into the micelle must chromatograph at a different rate in the presence of a micellar mobile phase than it would in the absence of micelles. From the effect of the surfactant on the solute elution volume, it is possible to obtain the solute partitioning coefficient, K_{MW}, from HPLC via the formula:

$$V_s/(V_e - V_m) = \frac{\bar{V}(K_{MW}-1)}{K_{SW}} [D_m] + \frac{1}{K_{SW}} \quad . \tag{53}$$

In TLC, the relative solute migration (R_f) can be related to K_{MW} via:

$$R_f/(1 - R_f) = \frac{V_m}{V_s} \cdot \frac{\bar{V}(K_{MW} - 1)}{K_{SW}} [D_m] + \frac{V_m}{V_s} \cdot \frac{1}{K_{SW}} \quad . \tag{54}$$

In these equation, V_s is the volume of the stationary phase, V_m is the volume of the mobile phase, V_e is the elution volume of the solute, $[D_m]$ is the concentration of micellized surfactant in the mobile phase, $\bar{V}$ is the partial molar volume of the surfactant in the micelle and K_{SW} is the coefficient for partitioning of the solute between water and the stationary phase.

A plot of the term on the left-hand side of the equation against $[D_m]$ permits the evaluation of K_{MW} from the slope/intercept ratio. The method is general, requires a minimum of equipment and, when applied with due care, seems to be one of the potentially more useful methods for determining K_{MW}. One problem, for which corrections can be applied, is that even at moderate detergent concentrations, binding of the surfactant to the stationary phase may reduce $[D_m]$ significantly; such binding may, however, also cause variations in K_{SW}. In addition, the method (in particular TLC) cannot be applied to solutes that bind strongly to the stationary phase.

C. Spectroscopic methods

The spectroscopic methods take advantage of differences in the absorption or emission of electromagnetic radiation between solute molecules bound to micelles and those free in the aqueous phase. The discrimination between molecules in the two solubilization environments permits quantification of the amount of solute that is either free or micelle-bound. Some of these methods

also provide additional information as to the nature of the local solubilization environment sensed by the micelle-incorporated substrate.

Shifts in the absorption spectrum of chromophore-containing molecules upon solubilization in micelles are often observed, especially in cationic micelles. Thus, addition of detergent (above the CMC) to an aqueous solution of the solute of interest typically results in a shift of the absorption spectrum. At high surfactant concentrations, however, no further shift is observed upon addition of more detergent, indicating that the solute is fully incorporated in the micellar pseudophase. At the intermediate detergent concentrations, the net absorbance (A) of the solute at a given wavelength is the sum of contributions from micelle-bound and free solute:

$$A = A_w \cdot \frac{[S_w]}{[S_t]} + A_m \cdot \frac{[S_m]}{[S_t]} \quad , \tag{55}$$

where A_w and A_m are, respectively, the corresponding absorbances of the solute in water and in a concentrated surfactant solution in which all of the solute is incorporated into the micelles. The experimental error can be diminished by choosing a wavelength at which the change in absorbance is large and by using appropriate detergent containing reference solutions. If the absorbance measurements are made on solutions containing a constant concentration of the solute and increasing concentrations of the surfactant, the fraction $\underline{f}$ of micelle-bound solute is given by:

$$f = \frac{[S_m]}{[S_t]} = (A - A_a)/(A_m - A_a). \tag{56}$$

When K_s is small, A_m cannot be measured directly and alternative procedures are required. Thus, for example, if the conditions required by Eq. 55 are fulfilled, the combination of Eqs. 25, 55 and 56 gives:

$$(A - A_o)/[S_T] = K_s \cdot A_m - K_s \cdot A \tag{57}$$

and K_s can be obtained from the slope of a plot of the first term of Eq. 57 vs. A with no prior knowledge of A_m. Other more general plotting procedures have also been described (ref. 104).

The absorption method is simple, does not perturb the system and can be employed over a wide range of concentration of both surfactant and solute. The method is, of course, restricted to systems in which micellar incorporation of the solute is accompanied by an appropriate spectral shift.

Fast absorption spectroscopic techniques (flash photolysis and transient excited state spectroscopy) can also be employed to obtain partitioning coefficients. The technique has been applied to photoactive probes (such as aromatic

ketones) in SLS micelles (ref. 84) and to a variety of compounds which quench excited triplet states (such as mono- and diolefins) (ref. 105). An advantage of this method is that it provides not only the partitioning constant K_s, but also the rates of micellar entry and exit of the probe. On the other hand, it requires sophisticated instrumentation unavailable in most research centers. Moreover, when the method is applied to the excited probe itself, rather than a quencher species, one obtains the partitioning coefficient of the excited triplet state rather than that of the ground state.

Luminescence measurements can also be employed to study the partitioning of solutes between the micellar pseudophase and the surrounding aqueous phase.

The partitioning coefficient of a luminescent compound can be determined either from modifications in its luminescence characteristics upon incorporation into the micelle or by selectively quenching its emission in either of the pseudophases. Various modifications in the fluorescence characteristics of the probe, including changes in the fluorescence intensity (resulting from changes in the fluorescence quantum yield), changes in the excited probe lifetime, shifts in the position of the emission and changes in the fine structure of the fluorescence spectra, have been employed to evaluate the micellar solubility of probes (ref. 7, 105 - 110) ranging from aromatic compounds to singlet oxygen. In most cases, the experimental approach is similar to that employed in the absorbance method, the change in fluorescence characteristics being monitored as a function of the surfactant concentration. The main advantage of fluorescence is the sensitivity of the technique, which, for suitable solutes, permits measurements down to ~10^{-8} M. On the other hand, it is somewhat limited in that it can only be applied to fluorescent solutes or to solutes that are efficient quenchers of the emission of an appropriate fluorescent probe.

Time-resolved fluorescence permits the determination of K_s from a single fluorescence decay curve at a known surfactant concentration if the lifetimes in both the micellar psuedophase and the aqueous phase can be adequately resolved (ref. 110). The fraction of solute incorporated into the micelles may then be calculated from the relationship:

$$\frac{[S_m]}{[S_r]} = 1 + \frac{F_w \cdot \varepsilon_{mic} \cdot \phi^F_{mic} \cdot \tau_w}{F_m \cdot \varepsilon_{water} \cdot \phi^F_{water} \cdot \tau_w} , \qquad (58)$$

where F_w and F_m are the amplitudes of the fluorescence signals from the aqueous and micellar phases, ε_{water} and ε_{mic} are the respective extinction coefficients, ϕ^F represents the fluorescence yield under steady-state illumination and τ is the probe lifetime in each pseudophase.

The partitioning of a fluorescent probe can also be determined from selective quenching of its luminescence in one of the pseudophases. This has usually been done by selective quenching of the aqueous luminescence, using small hydrophilic coions as quenchers (ref. 7,104,111,112). The method assumes that the quencher is excluded from the micelle and that the excited probe does not enter or leave the micelle during its lifetime. Since singlet lifetimes are typically short (usually less than 20 nsec), this latter requirement is not particularly serious; both conditions can be verified experimentally, for example, by showing that the lifetime of the micellar probe is unaffected upon addition of the quencher (ref. 104). The data treatment initially proposed by Quina and Toscano (ref. 104) leads to the following relationship for the fluorescence yields in the presence (ϕ_{F_1}) and absence ($\phi^o_{F_1}$) of the quencher Q (when the solution is excited at an isosbestic point for absorption by the aqueous and micellar probe):

$$\frac{\phi_{F_1}}{\phi^o_{F_1} - \phi_{F_1}} = \left[\frac{[S_m]}{[S_w]} \cdot \frac{(\phi_{F_1})_{Mic}}{(\phi^o_{F_1})_w} + 1\right] \cdot \left[1 + \frac{1}{k_Q \cdot \tau^o_w} \cdot \frac{1}{[Q]}\right] \quad . \tag{59}$$

A plot of the left-hand side of Eq. 59 against $1/[Q]$ gives the ratio $[S_m]/[S_w]$; division by the corresponding value of $[D_m]$ provides K_s. A slightly modified version of this equation, which takes into account the possibility of different absorptivities in the two phases, has been employed by Lissi and Abuin (ref. 111,112).

The partitioning coefficient of certain types of additives can be determined on the basis of the effect their addition provokes on the fluorescence of a micelle-incorporated probe. The method has generally been applied to fluorescence quenchers (ref. 113 - 118). Encinas and Lissi (ref. 113) have developed a method which can also be applied to solutes that do not interact directly with the excited molecule (ref. 119). Their method, based on the assumption that the quenching of the probe fluorescence is determined only by the mean quencher occupation number, does not require knowledge of the quenching mechanism (which may be either static of dynamic) or of the relationship between the probe lifetime and the quencher exit rate. Furthermore, one can measure variations in the solute partitioning coefficient with increasing mean occupation number. In essence, one measures the probe fluorescence intensity ratio I^o_F/I_F in the absence and presence of quencher as a function of quencher concentration at several surfactant concentrations. The quencher concentration $[Q]_i$ required to produce a given common value of $I^o_{F_1}/I_{F_1}$ at each surfactant concentration is determined and the data are plotted according to the relationship:

$$[Q]_i/f_{aq} = \tilde{n}/K + \tilde{n}[Dm]_i/f_{aq} \quad , \tag{60}$$

where $[Dm]_i$ is the concentration of micellized detergent, $\tilde{n}$ is the mean occupation number and f_{aq} is the volume fraction of the solution occudpied by the aqueous phase. This method has been applied to a wide variety of solutes as structurally diverse as hydrogen peroxide and aliphatic diolefins and with K_s values in micellar SLS ranging from 50 up to 10^4 (ref. 117).

The partitioning of a probe can be deduced, as in other spectroscopic methods, by relating the chemical shift and/or line width of a NMR resonance of the probe to the corresponding values in water and in an "infinitely" concentrated surfactant solution. Except for pratical limitations such as relatively low sensitivity, NMR spectroscopy is potentially a universal tool for measuring partitioning coefficients. Thus, for example, partitioning coefficients for several aromatic alcohols have been determined at saturation in micellar SLS using ^1H NMR spectroscopy (ref. 120).

A similar approach can be employed to obtain K_s values from epr measurements, as exemplified by studies of the partitioning of di-tert-butyl nitroxide radicals between water and SLS micelles (ref. 121 - 123). Although epr spectroscopy is, by comparison with NMR, a quite sensitive technique, its use is restricted to paramagnetic species.

Stilbs (ref. 124) has employed the Fourier Transform NMR pulsed-gradient spin echo (FT-PGSE) self-diffusion technique to study solubilization of several species in SLS micelles. The method is of general validity and provides a direct estimate of the amounts of micellar and aqueous solute. The method monitors the Brownian displacement of individual molecules on a time scale of about 300 nsec, during which time a typical micelle diffuses roughly 1000 times its own diameter. Solubilizate diffusion within the micelle is therefore unimportant and the solute self-diffusion coefficient (D_A^{app}) can be written as:

$$D_A^{app} = f \cdot D_A^{mic} + (1 - f) \cdot D_A^{free} \quad , \tag{61}$$

where $f = [S_m]/[S_t]$ is the fraction of the solute associated with the micelles. The micellar self-diffusion coefficient D_A^{mic} can be determined by monitoring D^{app} of a very hydrophobic compound such as tetramethylsilane, while D_A^{free} can be obtained from the solute diffusion coefficient in pure water by applying a small correction to take into account micellar obstruction effects. The method apparently gives precise values of $\underline{f}$ in the range from ~0.05 to 0.95 and hence permits estimation of K_s values over a range of at least three orders of magnitude. The method has the additional advantage that it can be applied

to almost any solute-surfactant pair, as well as to mixtures of solubilizates, since each compound can be determined independently.

D. Miscellaneous methods

Kaneshina et al. (ref. 125) have employed the depression of the Krafft point of the surfactant to quantify the incorporation of anesthetics and alcohols into ionic surfactant micelles. Thus, if the Krafft point is considered to be the melting temperature of the hydrated solid surfactant (ref. 126), the depression of the Krafft point in the presence of additives can be treated as a colligative property. At low mole fractions of the additive in the micellar pseudophase, simple thermodynamic considerations then lead to the relationship (ref. 125):

$$K_{MW} = \frac{(-\Delta T) \cdot \Delta H_f}{(RT_o)^2} \cdot \frac{1}{X_w} \quad , \tag{62}$$

where $-\Delta T$ is the Krafft point depression, T_o is the unperturbed Krafft point, ΔH_f is the change in enthalpy upon going from the hydrated solid to the micellar state and X_w is the mole fraction of the solute in the aqueous phase. The method gives values similar to those obtained by other techniques, but its general validity may be limited to systems in which free energy contributions due to changes in counterion binding accompanying solute incorporation are relatively unimportant.

Partitioning constants have also been evaluated from CMC depressions induced by the solute (ref. 125). Thus, Shirahama and Kashiwabara (ref. 127) proposed that:

$$(-\theta)K_{MW} = \frac{d \ln CMC}{d X_w} \tag{63}$$

The $(-\theta)$ has been referred to as the ISA (interaction of surfactant and additive) coefficient by Hayase and Hayano (ref. 128) and its physical meaning has been discussed by Manabe et al. (ref. 129). The ISA coefficient seems to be constant for a series of related compounds; e.g., -0.69 for alcohols (ref. 129) and -0.52 for anesthetics (ref. 126) in SLS. Treiner (ref. 42) employed this approach to calculate partitioning coefficients for several polar molecules in aqueous DTAB after correction of the CMC change for the contribution from the Setchenov salting out constant. Although it gives results similar to those obtained in other systems, this method depends heavily on the use of empirically calculated Setchenov constants and "assumed" ISA coefficients.

De Lissi et al. (ref. 130) have recently proposed a method for obtaining K_s for association of alcohols to micelles on the basis of partial molar volume measurements.

A number of substrate incorporation coefficients (K_s values) have been extracted from analysis of the effect of the surfactant on the kinetics of ground-state reactions. The validity of the parameters derived from such an analysis is, of course, a direct function of the validity of the assumed kinetic model. Much of the available data of this type refers to bimolecular reactions in ionic micellar solution and were obtained using the enzyme model (ref. 19,41,42,131 - 133). This kinetic model is now recognized to be strictly applicable to certain special limiting types of pseudounimolecular reactions, namely pseudophase limit reactions in which one of the participating reagents is excluded from the micellar phase (ref. 134,135).

An interesting example of this last kinetic situation is the use of pulse radiolysis to study solute incorporation in micellar SLS (ref. 136 - 139). The method takes advantage of the fact that only the aqueous solute or probe reacts with hydrated electrons, the micellar probe being unreactive due to electrostatic shielding by the anionic micelle. The method is limited to probes whose solubility in water is relatively high ($>10^{-5}$ M). By monitoring the effect of naphthalene in water, SLS in water and mixtures of naphthalene and SLS on the rate of decay of the hydrated electron at 650 nm, Evers et al. (ref. 139) obtained data for the partitioning of naphthalene as a function of SLS concentration. In addition, it was also possible to estimate the partitioning coefficient of the neutral radicals produced upon protonation of the intially-formed naphthalene radical anion.

Finally, we note that other experimental techniques such as potentiometry (ref. 140), polarography (ref. 141) and quasi-elastic light scattering (ref. 141) have also been occasionally employed to evaluate K_s. Due to the limited extent of their application, however, these will not be considered in detail.

IV. SOLUBILIZATION DYNAMICS

The first attempt to measure the rates of exchange for solutes between micelles appears to be that of Nakagawa and Tori (ref. 142), who were able to establish an upper limit for the exit rate of anthracene molecules from CTAB micelles. In the interval since this pioneering work, a reasonable body of data has been obtained on the exchange of solubilizates between the micelles and the surrounding media. Of course, the dynamic nature of the micelle in itself provides a "trivial" mechanism of solute exchange; i.e., complete micelle disruption on a time scale of the order of milliseconds. Of interest here, however, are the dynamics of stepwise exchange of the solute via entry and exit rates according to:

$$S_w + MS_{n-1} \underset{k_{-n}}{\overset{k_{+n}}{\rightleftharpoons}} MS_n \qquad (64)$$

with $n \geq 1$.

Under normal experimental conditions, this exchange of the probe takes place on a time scale of between 10^{-3} and 10^{-8} sec and hence fast detection techniques (stopped flow, relaxation and fast spectroscopic techniques) are required to evaluate the individual rate constants.

Stopped flow techniques, being rather slow, are of utility only in select cases (ref. 87). Although extensively exploited to study the dynamics of monomer-micelle exchange, ultrasonic relaxation has been only sparingly applied to solute exchange. Wyn-Jones et al. (ref. 143,144) did, however, use ultrasonic relaxation to evaluate exchange rates of n-alcohols in micellar CTAB. The values of the entry and exit rate constants listed in Table 1 were obtained by combining the single relaxation time observed for the exchange process with partitioning constants determined by the saturation method and thus refer to exchange in a strongly perturbed micelle.

Spectroscopic techniques such as electron paramagnetic resonance (ref. 145) and transient time-resolved absorption (ref. 146 - 149) and emission spectroscopy (ref. 7,116,150,151) are particularly suitable for measuring exchange rates on the time scale considered. A time-resolved flash CIDNP (chemically induced dynamic nuclear polarization) method has also been used to evaluate the rate of exit of benzyl radicals from SLS micelles (ref. 148). In at least one system (ref. 149), exchange rate constants were extracted from steady state photolysis data.

Various aspects of the use of photophysical techniques to investigate micellar entry and exit of solutes and statistics of solute incorporation have been reviewed (ref. 17,152). Of particular note are two key papers by Tachiya (ref. 14,15) in which general closed form solutions are obtained for the rate of decay of an excited micelle localized fluorescence probe in the presence of a quencher species that distributes statistically among the available micelles in accord with either a Poisson (ref. 14) or a binomial (ref. 15) distribution. In principle, the Tachiya equations permit determination of all of the relevant kinetic parameters associated with solubilization of the quencher and/or detergent concentration. Frequently, by judicious choice of the system and experimental conditions, it is often possible to measure micellar entry and exit rates directly from the probe decay. Thus, the entry rate of an excited water-soluble probe can be determined by measuring its lifetime under conditions such that it is quenched upon entry into a micelle. This method has been used by Ligh and Scaiano (ref. 153) to measure the rate of entry of acetone into SLS and CTAC micelles. Conversely, the exit rate of a micelle-incorporated chromophore can be determined directly by measuring the lifetime of the excited species under conditions in which it is quenched

only upon exit into the aqueous phase. The following simple kinetic scheme is appropriate for this latter situation:

$$MS + h\nu \longrightarrow MS^* \quad (65)$$

$$MS^* \xrightarrow{k_d} MS + h\nu \quad (66)$$

$$MS^* \xrightarrow{k_-} M + S^* \quad (67)$$

$$S^* + Q_w \xrightarrow{k_Q} \text{quenching} \quad (68)$$

$$S^* + M \xrightarrow{k_+} MS^* \quad (69)$$

where Q_w is a micelle-excluded water-soluble quencher; i.e., a quencher coion. If the following condition holds:

$$k_- \gg k_d \quad (70)$$

$$k_Q[Q_w] \gg k_+ \cdot M \quad (71)$$

$$k_Q[Q_w] \gg k_- \quad (72)$$

the lifetime of S* is then equal to $1/k_-$. This lifetime can be measured directly by time resolved fluorescence, by phosphorescence decay, or by transient absorption spectroscopy. The first condition ($k_- \gg k_d$) is the most restrictive and is usually fulfilled only by the long-lived triplet states.

This method has been applied to triplet anthracene in CTAB micelles, using Cu^{++} ions as the quencher (ref. 150) and to several aromatic triplets in SLS, employing NO_2^- as quencher (ref. 7); triplet concentrations were monitored by time-resolved emission spectroscopy. A similar approach, using transient absorption spectroscopy and NO_2^- as quencher, was employed by Scaiano and Selwyn (ref. 84) to measure the lifetime of several micelle-incorporated ketones. One point which merits emphasis is that in all these systems, the exit rate is that of the excited triplet state rather than that of the ground state species; consequently, calculation of k_+ values using the partitioning coefficient of the ground state species (ref. 7,150) may lead to significant errors. The approach of Scaiano and Selwyn (ref. 84) has the advantage that it permits direct evaluation of both K_M and k_-, and hence of k_+ (see Eq. 83) for the excited triplet. Values of k_- and k_+ evaluated in this manner are collected in Table 4.

A slightly modified approach can be employed to determine the micellar entrance rate of neutral water-soluble quenchers using a micelle-localized fluorescence probe. The reaction scheme can, by appropriate choice of the experimental conditions, be reduced to:

$$MS + h\nu \longrightarrow MS^* \tag{73}$$

$$MS^* + Q_w \xrightarrow{k_+} QMS^* \tag{74}$$

$$QMS^* \xrightarrow{k_Q} \text{intramicellar quenching} \tag{75}$$

If the intramicellar quenching occurs with unit efficiency, the probe lifetime can be directly related to the quencher entry rate:

$$k_+[Q_w] = 1/\tau(MS^*) \quad . \tag{76}$$

This method was originally applied to the quenching of the fluorescence of solubilized pyrene by methylene iodide (ref. 150) and subsequently to the quenching of 1,5-dimethylnaphthalene by oxygen at high pressure (ref. 115). Experimental values of k_+, as well as the corresponding k_- values calculated from the partitioning constant K_M are given in Table 4.

Selwyn and Scaiano (ref. 146) measured the triplet lifetime of phenanthrene in SLS micelles as a function of the concentration of conjugated dienes. For the dienes that are almost exclusively incorporated into the micelles, the phenanthrene lifetime is determined by the exit rate of the quencher. From dienes that partition between the aqueous and micellar phases, the values of k_+ and k_- (Table 4) can be derived from a study of the kinetics of triplet decay as a function of quencher and surfactant concentration.

The rate at which a photochemically produced free radical leaves a micelle can be determined using the following reaction scheme:

$$h\nu + MS \longrightarrow MS_1^* \tag{77}$$

$$MS_1^* \longrightarrow MS_3^* \tag{78}$$

$$MS_3^* \longrightarrow M_3(R\text{---}R') \tag{79}$$

$$M_3(R\text{---}R') \begin{cases} \xrightarrow{k_{isc}} M_1(R\text{---}R') \longrightarrow \text{Products} \\ \xrightarrow{k_-} R_w + MR' \\ \xrightarrow{k'_-} R'_w + MR \end{cases} \tag{80}$$

where M(R---R') is a micelle-caged free radical pair. If the radical in the aqueous phase (R_w and R'_w) and in single occupied micelles (MR' and MR) are sufficiently stable on the time scale of the experiments, this simple scheme leads to the following expression for the radical lifetime and the net stable free radical yield:

TABLE 4

Exit (k_-) and entry (k_+) rates of molecules from and to micelles

Compound	Surfactant	k_+ 10^{-9} $M^{-1}s^{-1}$	k_- 10^{-6} s^{-1}	Ref.
Propanol	CTAB	3.8	81	144
Butanol	CTAB	4.4	58	144
Pentanol	CTAB	6.8	26	144
Hexanol	CTAB	4.2	9	144
Anthracene	CTAB	--	<10	264
1-bromonaphthalene	SLS	5 - 8	0.025	264
Naphthalene	SLS	--	>0.05	264
Acetophenone	SLS	15.6	7.8	84
Propiophenone	SLS	14.1	3.0	84
Isobutyrophenone	SLS	12	1.6	84
Xanthone	SLS	17	2.7	84
di-terbutylnitroxide	SLS	1.4	--	145
CH_2I_2	SLS	25	10	264
O_2	SLS	14	350	115
O_2	CTAB	13	--	115
Cis-1,3-pentadiene	SLS	1.2	8.9	146
Trans-1,3-pentadiene	SLS	0.95	6.9	146
1,3-hexadiene	SLS	0.83	2.3	146
Cis-2-trans-4-hexadiene	SLS	--	1.0	146
1,3-cyclohexadiene	SLS	1.3	5.6	146
2,4-dimethylpentadiene	SLS	--	0.37	146
1,3-cycloheptadiene	SLS	--	1.3	146
1,3-octadiene	SLS	--	0.13	146
2,5-dimethyl-2,4-hexadiene	SLS	--	0.19	146
1,3-cyclooctadiene	SLS	--	0.35	146
Acetone	SLS	10	--	146
Acetone	CTAC	34	--	146
Cyclohexadienyl radical	SLS	--	4.4×10^6	148
Benzyl radical	SLS	--	1.4×10^6	148
$^1O_2$	SLS	1.5	37×10^7	149

$$\tau_R = \tau_{R'} = (k_{isc} + k_- + k'_-) \tag{81}$$

and

$$\frac{[R_\infty]}{[R_0]} = \frac{[R'_\infty]}{[R'_0]} = \frac{k_- + k'_-}{k_- + k'_+ + k_{isc}} \quad . \tag{82}$$

Measurement of τ_R and $R_{t=\infty}/R_{t=0}$ permits evaluation of k_{isc} and of the sum of the exit rates $k_- + k'_-$. Scaiano et al. (ref. 147) have applied this scheme to the photolysis of benzophenone in CTACl and SLS in the presence of 1,4-cyclohexadiene, which gives benzydrol and cyclohexadienyl radicals. In CTACl and SLS the values of $k_- + k'_-$ are 1.6×10^6 s^{-1} and 4.4×10^6 s^{-1}, respectively. These exit rates undoubtedly correspond to those of the cyclohexadienyl radicals. By a similar method, Turro et al. (ref. 148) estimated a rate of 1.4×10^6 s^{-1} for the exit of benzyl radicals from SLS micelles.

In considering the trends for the entry and exit rate constants collected in Table 4, several major shortcomings of the data obtained from quenching experiments should be noted. First, if the excited probe is located at the micelle-water interface (as is probably the case for most of the aromatic probes employed), it can be quenched by a water-soluble quencher that has not yet become "micelle bound". Thus, k_+ measures the time required for the quencher to approach the excited molecule (within the effective quenching radius) rather than the true entry rate associated with the partitioning constant, $K_M = k_+/k_-$. Second, one must be extremely wary about the neglect of intramicellar quenching by water-soluble quenchers, even when the potential quencher is a hydrophilic ionic species of the same charge as the micelle (ref. 154). Finally, all of the above approaches assume, either implicitly or explicitly, that the exchange process is controlled by a simple bimolecular encounter involving the aqueous probe and micelles. Microscopic reversibility then implies that the exit rate corresponds to a true unimolecular process of the micelle-incorporated probe. These assumptions have been questioned, at least for the singlet oxygen ($^1O_2$) by Matheson and Massoudi (ref. 149), who concluded that, at high O_2 pressures, the entrance (and exit) of the excited molecules is "assisted" by the ground state species; these apparently anomalous results warrant further verification.

These factors may contribute to some of the peculiarities evident in the entry rate data in Table 1.

From simple considerations of relative mobility, the rate constant for bimolecular encounter between a small molecule solubilized in the aqueous phase and a micelle of radius R_{mic} should be approximately give by (ref. 155):

$$k_{dif} = 4\pi \cdot N' \cdot R_{mic} \cdot D_{probe} \quad , \tag{83}$$

where $N' = N_{avog}/1000$ and D_{probe} is the probe diffusion coefficient. The values of k_{dif} for typical solutes should then be of the order of 5×10^{10} to 10^{11} $M^{-1}s^{-1}$ depending upon the probe diffusion coefficient and micellar size. The k_+ values collected in Table 4 ranges from 0.8×10^9 to 34×10^9 $M^{-1}s^{-1}$ with no clear relationship to either micellar size of solute properties. In this

regard, it is noteworthy that acetone, one of the more hydrophobic solutes, has the fastest rate of entry. This result is just the opposite of that expected from simple "thermodynamic" considerations. To what extent these entry rate data reflect experimental errors and/or faulty assumptions is difficult to evaluate, although they do, as a whole, tend to indicate that solute "incorporation" is considerably slower than "solute-micelle" collisions. A hypothetical, though nonetheless appealing explanation is that a "salting out" of the probe results in a significant reduction of the local concentration of the probe in the immediate vicinity of the micelle surface.

In contrast to the entry rate data, micellar exit rates vary over an enormous range, from $\approx 10^8$ s^{-1} down to less than $\approx 10^3$ s^{-1} (Table 4). Furthermore, families of compounds exhibit a clear trend; i.e., k_- decreases as the solute hydrophobicity increases. The dependence of K_m on solute hydrophobicity thus appears to be principally a function of k_- rather than of k_+.

V. SOLUBILIZATION ENVIRONMENTS OF NEUTRAL MOLECULES INCORPORATED INTO MICELLES

Lawrence (ref. 156) was the first to point out that the site of incorporation of a solubilized molecule should depend on its relative hydrophobic and hydrophilic tendencies. The first direct physical evidence regarding the solubilization environment of hydrocarbon derivatives in micellar systems was obtained by Hughes et al. (ref. 157), who found that the region of solubilization had a low electron density, similar to that of liquid paraffins. In the intervening years, the nature of the microenvironment sensed by the solute has been investigated by a variety of methods and several reviews are available (ref. 158 - 161).

A neutral molecule incorporated into (or solubilized in) a micelle can be located in a variety of microenvironments, ranging (at least in principle) between the two extremes of a hydrocarbon like solvent (the micellar "core") and a completely aqueous medium (or at least a water-rich interface with a high charge density). Indeed, the distinctive feature of the micelle as a solvent is that it can provide not only different microenvironments for different molecules, but also different environments for the different parts of the same molecule. Thus, polar molecules encounter a polar environment, hydrophobic molecules have available a "hydrocarbon-like" medium and amphiphatic molecules should be able to orient themselves at the micelle-water interface with their hydrophobic portion extending into the "hydrocarbon-like core". "Oriented" solubilization of this type has in fact been demonstrated conclusively by proton nuclear magnetic resonance spectroscopy (ref. 55,158,162). Based on these considerations alone, one can readily understand

why micelles are capable of dissolving such a wide variety of solutes (including amphiphilic molecules) and exhibit solvent capacities larger than those of either polar or nonpolar solvents (ref. 1).

Additional aspects which should be considered in studies designed to probe the micellar microenvironment are the dynamic nature of the solubilization process and the fact that, even at very low occupation numbers, the presence of the solute can significantly modify the micellar structure. The dynamics of solute incorporation includes micellar entry and exit of the solute or probe as well as the rotational and translational motion of the solute within the micellar aggregate itself. As discussed above, the rate of solute entry into the micelle is nearly diffusion controlled while the time scale for micellar exit is determined mainly by the hydrophobicity (ref. 163,164). Typical values of the pseudo-unimolecular exit rate constants fall in the range of 10^3 to 10^8 sec^{-1} (see Table 4). The solute molecule can rapidly migrate between different regions of the micelle and hence between different microenvironments. Thus, a property such as the λ_{max} of the absorption spectrum of a probe will, in reality, be a weighted average over the accessible solubilization environments. Other features of the absorption band, such as the band width, may also be indicative of a multiplicity of environments. Simmilarly, the relative slow time scale of NMR spectroscopy ($\sim 10^{-4}$ sec) implies that the observed signals will be averaged over all possible intramicellar displacements of the solute. On the other hand, the fast time scale of fluorescence spectroscopy (down to less <1 nanosecond) or deuterium magnetic resonance and spin relaxation techniques (ref. 167), makes these methods particularly suitable for experiments on intermicellar migration and on reorientation of probes. Thus, time correlated fluorescence measurements could be employed to follow changes in the average microenvironments sensed by an excited probe during its lifetime, either by measuring the fluorescence spectrum at different times after excitation or by tuning the excited probe lifetime, through addition of appropriate quenchers. As in all studies which use probe molecules to infer properties of the system, one cannot overlook the possibility that the observed behavior reflects primarily probe-induced perturbations. Incorporation of even a single solute molecule must perturb the original system to some extent. Moreover, the microenvironment sensed by the probe necessarily corresponds to that at the site of perturbation. The question of perturbation is particularly relevant in micellar systems since the aggregates tend to be rather small (<100 monomers) and the probes employed tend to be rather large (e.g., polycyclic aromatic hydrocarbons). In one of the early quantitative studies of solubilization sites, Erikson and Gilbert (ref. 55) showed that addition of benzene to micellar CTAB shifts the CTAB proton NMR

resonances. At low incorporation of benzene, there is a rapid shift of the $N\text{-}CH_3$ and the $\alpha\text{-}CH_2$ hydrogen resonances to higher fields, implying preferential adsorption close to the $\alpha\text{-}CH_2$ groups. Since this process presumably involves at least some rearrangement of water molecules at the adsorption sites, the resultant solute-induced perturbation of the "solvent" properties of the micelle should be magnified at even higher occupation numbers. Several of the discrepancies between results obtained by different techniques or by the same technique in different laboratories can be attributed to differences in the degree of solute incorporation (ref. 165,166).

A. The "model dependence" of the solubilization site

The validity of attempts to draw definitive conclusions as to the nature and location of an intramicellar solubilization site is seriously compromised by the necessity of assuming (or presuming) a model for the micellar aggregate itself. Thus, if the probe under investigation senses a polar microenvironment, adepts of a tightly packed micelle model would infer that the probe must reside at the micelle surface. On the other hand, proponents of an "open" micelle could argue that the apparent polarity of the microenvironment is a consequence of penetration of water down to a site in the micellar interior. The truth is probably somewhere between these extremes. Thus, these are compelling evidences for substantial residual water-hydrocarbon contact even at the terminus of the hydrophobic moiety of the surfactant and several well designed experiments (e.g., photo-abstraction of hydrogen atoms from the surfactant alkyl chain by benzophenone derivatives) have failed to reveal the presence of dramatic reactivity gradients along the surfactant chain (ref. 167). Indeed, this is precisely what one might expect in retrospect on the basis of random intertwining and doubling back of the surfactant hydrophobic chains in a dynamic micellar aggregate, independent of the degree of "openness" of the micellar structure.

Mukerjee and Cardinal (ref. 3,168) have described the solubilization process in terms of a simple model consisting of two distinct, but arbitrarily (or "operationally") defined solubilization sites: the micellar "core" and the "surface". Even assuming only two distinct solubilization sites, however, the proportion of solubilizate in each zone will be determined by a variety of factors, including the probe hydrophobicity (or surface activity), the surface-to-volume ratio (determined by the micelle size and shape) and the characteristics of the "core" and the "surface" (complex functions of the surfactant employed, its concentration, the counterions, other additive present and the mean solute occupation number). The strong preference for the micellar surface as a region of solubilization is in part a consequence of smallness

of the micellar aggregate. For a SLS micelle, at least half of the probe would be within 4 - 5 Å of the surface at any given time. Thus, even if the solute has no affinity for the surface, it is capable of being strongly influenced by the surface and should be accessible to water and encounters with water-soluble molecules. As a first approximation, Mukerjee and Cardinal (ref. 3,168) assume that the solubility in the micellar core can be equated to that in a hydrocarbon solvent if one corrects for effects (the Laplace pressure) due to the small radius of the core. The solubilization in the surface is treated as a surface adsorption obeying a Langmuir type adsorption isotherm, for which the mean driving force is the capacity of the solute to reduce the interfacial (hydrocarbon-water) tension.

With due consideration of the above factors, the simple two-site model can rationalize, at least qualitatively, the results of most solubilization studies. Nonetheless, it whould be emphasized that this model is at best an oversimplification which divides a "continuum" of environments into two extreme types of sites. Thus, a change in the hydrophobicity of the probe (e.g., upon addition of alkyl groups to benzene) which alters the net probe-water contact will be described by the two-site model as a change in the intramicellar distribution of the solute between the two sites, regardless of the actual mechanism. Finally, it should be reemphasized that the time scale for intramicellar migration of a solute is relatively short (10^{-7} to 10^{-9} sec), requiring careful distinction between energetically accessible or "instantaneous" solubilization sites (which may determine chemical or photophysical reactivity) and the time-weighted average solubilization site.

To date, the principal methods employed to investigate the nature of the solute microenvironment are NMR spectroscopy and absorption and emission spectroscopy; several other spectroscopic techniques have also been used, but the results tend to be less readily interpretable; e.g., X-ray diffraction (ref. 158) or restricted to a limited number of solutes; e.g. epr technicques which can be used only with free radicals or spin-labelled surfactants (ref. 158,169 - 171). In addition to the spectroscopic methods, several kinetic techniques provide information regarding the solute environment and/or its accessibility to co-reactants which reside only in the aqueous phase (such as simple ions) or are restricted to the micelle surface (such as ions with hydrophobic groups). These kinetic techniques include: positron annihilation, information related to the hydrophobicity of the probe location (ref. 172); reactions of hydrated electrons, a function of the relative position of the probe with respect to the micelle-water interface (ref. 173); quenching of electronically excited micelle-incorporated solutes by counterions (ref. 106, 174,177) or by highly hydrophobic quenchers such as hydrogen peroxide (ref.

117); measurements of the rates of diffusion controlled processes such as inter- or intramolecular excimer formation (ref. 152), sensitive to the microviscosity of the medium; measurement of the rates of solvent-sensitive unimolecular reactions such as the thermal cis-trans isomerization of p-nitro-p'-dialkylaminoazobenzenes (ref. 178); measurements of rate constants for bimolecular reactions between micelle-localized and water-soluble co-reactants; e.g., reduction of steroids by borohydride (ref. 179) or oxidation of undecanol by chromic acid (ref. 180); measurement of quantum yields and/or product distributions of photoreactions, type II photoelimination of ketones (ref. 181 - 182) or trans-cis photoisomerization of stilbene derivatives (ref. 183); and measurements of the apparent bimolecular rate constants for intramicellar reactions related to the average mutual positions of the reactants inside the aggregate (ref. 184).

The nature of the medium sensed by the solute(s) has also been deduced from thermodynamic measurements of equilibrium constants for complex formation; e.g., between hydrophobic compounds and viologen derivatives (ref. 185-186) and from free energies and/or enthalpies of solubilization (ref. 49,57) by comparison with the corresponding values for solubilization of the solute in polar and nonpolar solvents.

Micelles influence the wavelength of maximum absorption and/or the vibrational fine structure of the ultraviolet absorption band of many organic molecules. Such changes have been extensively exploited to investigate the local microenvironment of the solubilizate in the micelle (ref. 158,165,188-197). Experimentally, one compares a spectral parameter of the solute which exhibits a net solvent-sensitive variation (e.g., the λ_{max}) upon incorporation into the micelle with values obtained in a series of homogeneous solvents. On the basis of this calculation, the solubilization environment in the micelle may be said to correspond to that of an "equivalent solvent" or "equivalent solvent mixture". This calibration approach has several important and potentially severe limitations (ref. 192). Thus, when the spectral variation (e.g., λ_{max}) is plotted against a parameter related to the "polarity" of the homogeneous solvent, protic and aprotic solvents frequently give two distinctly different correlations. Furthermore, the spectral variations for different probes may not correlate with the same solvent property (dielectric constant, concentration of OH groups, the Kosower Z parameter, etc.) of may give rise to a new empirical scale of solvent "polarity" (ref. 198,199). The same considerations apply to the evaluation of micropolarities from fluorescence measurements (ref. 200).

Solvent effects in the excited state can alter the vibrational fine structure and position of the fluorescence band, the lifetime of the excited state,

the fluorescence quantum yield and the fluorescence polarization (ref. 201). These solvent effects, generally attributable to "polar" (in a broad sense) effects and/or to "viscosity" effects, can be used to infer the solute microenvironment in micelles. Pyrene and its derivatives (ref. 109 - 202,203) have probably been the most widely investigated of all fluorescent solutes, though several studies have also been carried out with other polycyclic aromatic hydrocarbons, stilbenes (ref. 204), heterocycles (ref. 109,205), biphenyl derivatives (ref. 206) and dyes (ref. 195,267 - 269). The fine structure of pyrene fluorescence is quite solvent-dependent, due primarily to an increase in the intensity of the forbidden 0-0 vibronic transition in polar solvents. In particular, the ratio between the intensities of the first and third vibronic bands (I_I/I_{III}) provides a sensitive measure of the pyrene microenvironment (see Table 5). This ratio has been used to characterize the microenvironment of pyrene in micelles and the effect of additives (ref. 119,209,210). The variation of I_I/I_{III} with added salt and surfactant concentration indicates a decreased polarity of the solute at high salt and surfactant concentrations. These results have been rationalized in terms of a decrease in net micelle-water contact when the micelle undergoes a sphere-to- rod transition (ref. 210). One drawback of the method is that I_I/I_{III} values do not correlate with any conventional solvent parameter and hence define their own unique "polarity" scale (ref. 200).

TABLE 5

Fluoresence emission spectra of pyrene in different microphases[†] and homogeneous solvents (from ref. 210).

Media	I_I/I_{III}
Dodecane	0.59
n-pentanol	0.92
ethanol	1.10
methanol	1.35
water	1.74
SLS (50 mM)	1.06
SLS (50 mM) + n-hexanol (0.13 M)	0.88
SLS (50 mM) + n-heptane (saturated)	1.09
SLS (70 mM) + NaCl (0.6 M)	0.96
SLS (0.6 M)	0.98
CTAC (20 mM)	1.25
CTAC (0.2 M)	1.12
CTAB (10 mM)	1.20

[†]Abbreviations for surfactants as in Table 2.

Several aromatic compounds have fluorescence bands which exhibit solvent-dependent wavelength shifts. A clear example of such a dependence is provided by pyrenecarboxyaldehyde whose fluorescence exhibits a marked red shift with increasing solvent polarity (ref. 158); thus, in homogeneous solvents, the maximum wavelength of the fluorescence spectrum correlates with the bulk dielectric constant of the solvent, providing an estimate of the effective dielectric constant of the micellar environment at the solutilibization site. From this type of study, it has been concluded that several pyrene derivatives (pyrenecarboxyaldehyde aminopyrene) are located at the micellar surface (ref. 160). Exciplex emission, which is sensitive to the polarity of the medium, has been used to investigate the intramicellar location of the pyrene-triethylamine (ref. 211).

The net fluorescence polarization of a probe depends on the extent of rotation and relaxation during its excited state lifetime, which is in turn related to the viscosity of the medium (ref. 212). Several probes have been employed to estimate the intramicellar viscosity by this method (ref. 201,213,214). Other solvent-dependent properties of excited states (e.g., the solute lifetime) have also been used to infer the nature of the solute microenvironment (ref. 210,215).

Incorporation sites of solutes in micellar systems have been extensively investigated by proton (ref. 158) and ^{13}C (ref. 115,216) NMR spectroscopy. Several features of this technique make it particularly attractive for the evaluation of the intramicellar location of the solute. Thus, both nuclear magnetic resonance frequencies (chemical shifts) and line widths are dependent on the molecular environment of the nuclei; hence, comparison of the values in a micellar system with those in polar and nonpolar solvents provides information on the relative position of the solubilizate. Furthermore, since the average environment of each nucleus can be evaluated independently (ref. 162,120,187,191,217,218), additional valuable information can be obtained regarding the relative position and orientation of the solute in the micelle at different occupation numbers. Finally, it should be noted that the signals of the surfactant are also affected by incorporation of the solute. The changes induced in the resonances of the surfactant provide information on the average solute localization, the manner in which the surfactant environment is modified by solute incorporation (ref. 187,219 - 221) and effects arising from changes in the solute mean occupation number.

B. General data trends

Although simple considerations might suggest that a highly hydrophobic molecule such as a hydrocarbon would prefer to solubilize the micellar core, there is no direct evidence to support this "prejudice"; in fact, the available data

would apparently tend to contradict it. The solubility of hydrocarbons in micelles is considerably lower than that which would be expected from a consideration of the micellar volume and the solubility in typical hydrocarbon solvents (ref. 45,222). This diminished solubility can potentially be explained in terms of: 1) intrinsic differences between the solubilizing properties of the micelle core and a bulk hydrocarbon solvent, either as a result of hydrocarbon-water contact or of more compact packing and reduced mobility of the solute (ref. 3,159,168); 2) a manifestation of the Laplace pressure; or 3) overestimation of the size of the hydrocarbon-like core. Attempts have also been made to deduce information about the solubilization environment of hydrocarbons from thermodynamic measurements, in particular from direct calorimetric measurements of enthalpies of solubilization and temperature dependences of the free energy of transfer (i.e., of the partitioning coefficient). The former approach may be biased by heat effects arising from changes in the nature of the micellar aggregate upon incorporation of the solute (e.g., in the mean aggregation number or in the degree of counterion association); the latter approach also includes any additional temperature-dependent processes associated with changes in the micelle structure. For n-hexane and cyclohexane, two hydrocarbons with positive heats of solubilization in water and positive enthalpies of 0.75 and 0.54 kcal/mol, respectively, were found for transfer from the pure state to 0.2 M CTAB solution at 25^{o}C (ref. 49), suggesting that the solubilization site is distinct from a hydrocarbon solvent.

Similar ambiguities arise in the interpretation of data for the solubilization of aromatic hydrocarbons.

Indeed, an excellent example of the problem of defining a unique solubilization site is provided by the conflicting evidence regarding the location of benzene in micelles. On the basis of the efficiency of electron capture, Fendler and Patterson (ref. 166) concluded that benzene is exposed to water in CTAB, but located outside the SLS micelle. A greater preference of benzene for the surface of CTAB micelles relative to SLS micelles has also been inferred from solubility measurements (ref. 7) and NMR data (ref. 223). This difference can be rationalized in terms of a specific interaction between the aromatic ring and the quaternary ammonium head group. On the other hand, Cardinal and Mukerjee (ref. 168) concluded from UV absorption spectroscopic measurements that the average environment of benzene is very similar in SLS and CTAC micelles, both environments being quite polar (effective average dielectric constant of 46). These results were explained in terms of the surface activity of benzene (ref. 159,178). On the basis of partitioning coefficients, however, Simon et al. (ref. 192) concluded that benzene is, on the average, situated in a nonpolar environment and criticized UV spectroscopy as

a method for determining solute location because of its dependence on the choice of the "calibration scale". Free energies of transfer of benzene to SLS and CTAB micelles (ref. 57) are also suggestive of a nonpolar environment (at low occupation number).

Several works further indicate that the average location of benzene is a function of the incorporation number. From ultrasonic spectroscopy measurements on sodium octyl sulphate micelles, Jobe et al. (ref. 224) concluded that benzene prefers the surface at low occupation numbers; however, once a few solute molecules have been added per micelle, it tends to prefer the micellar core. Similarly, using NMR spectroscopy, Eriksson and Gillberg (ref. 218) found that benzene (as well as several more polar derivatives) resides mainly at the surface of the CTAB micelle at low and intermediate concentrations; above a benzene mole fraction of 0.45, however, solubilization in the core becomes significant. These data have since been confirmed by Matsuo et al. (ref. 187), who found that the terminal methyl signal of CTAB is unaffected by incorporation of benzene at low occupation numbers, while the N-methyl protons are significantly affected. Furthermore, the chemical shift of benzene, extrapolated to zero concentration, was found to be -164.2 Hz, a value close to that in water (-166 Hz). Above a molar ratio of 0.6, benzene solubilized in the hydrocarbon core; however, the size and/or shape of the micelle is so altered from its original state that the concept of a "change in solubilization site" becomes meaningless (ref. 218,221,225). Despite these differences, the bulk of the data are compatible with an initial "adsorption" of benzene, at least in CTA micelles. The conflicting interpretations appear to be associated with data obtained at high occupation numbers (ref. 165,190,225) and attempts to deduce solute locations from thermodynamic measurements (ref. 49,57).

Since the average position of a probe should depend (at least in part) on its hydrophobicity, the degree of penetration of an aromatic derivative into the micelle should be related to the number and polarity of the ring substituents. Indeed, UV spectroscopic measurements (ref. 159) indicate that the polarity sensed by the aromatic rings of n-butyl benzene and p-di-ter-butyl benzene is considerably lower than that sensed by benzene in the same micellar system. The proximity of the aromatic ring to the surface and/or its net exposure to water can also be deduced from quenching experiments with water-soluble quenchers (ref. 95,10,106,117,174,175,176). Thus, González et al. (ref. 106) found that the ratio between the apparent rate constants for quenching of a series of naphthalene derivatives by bromide ion in CTAB micelles and in water correlates with the probe surface activity, as measured by the micelle hydrocarbon solvent partitioning coefficient. The ratio of quenching rate constants increases by a factor of nearly twenty in going from

the most hydrophobic solute considered (2,3-dimethylnaphthalene) to more polar naphthalene derivatives (e.g., 1-naphthalene methanol or 1-cyanonaphthalene), indicating increasing proximity to the surface. Proton NMR studies (ref. 226) provide a similar picture for pyrene derivatives in CTAB micelles. Pyrene itself causes a large shift of the CTAB methylene protons, while pyrene sulfonic acid affects mainly the $N\text{-}CH_3$ protons. In agreement with these NMR results, fluorescence measurements imply that pyrene senses a polar environment in micelles, somewhat more so in SLS micelles than in CTAB micelles (Table 1). This is opposite to what one would expect on the basis of solubility measurements (ref. 7), indicating that care must be exercised in drawing conclusions about the intramicellar location of a solute from solubility data alone.

The general features of the solubilization of moderately polar compounds such as carbonyl compounds are nicely represented by the work of Fendler et al. (ref. 191) on the microenvironment of acetophenone and benzophenone in several different micellar solutions. Both absorption and proton magnetic resonance spectroscopy were employed to determine the influences of the surfactant head group, the surfactant hydrophobic moiety and the substrate structure on the intramicellar environment. Absorption spectroscopy showed that ketones sensed an environment of high polarity in all of the ionic micelles studied. Proton NMR spectroscopy provided information as to the position and orientation of the solutes. At acetophenone mole fractions of about 0.3 in CTAB and about 0.2 in SLS, the surfactant methylene signals resolve into well defined peaks of approximately equal area, suggesting that the aromatic ring is effectively shielding about half the surfactant protons. In contrast, at lower occupation numbers, only the methylene protons closest to the Stern layer are efficiently shielded, pointing to a change in average solute location (or micellar structure) at the higher solute concentrations. From the methyl group resonance of acetophenone, it was concluded that the acetophenone solubilization site (at low occupation number) is most likely at or near the surface, with the aromatic ring and methyl group oriented toward the interior and the carbonyl oxygen toward the surface of the micelle. Comparison of the surfactant head group, methylene chain and terminal methyl proton resonances also suggested that the phenyl rings of benzophenone are located, on the average, in the region between the Stern layer and the core of CTAB and SLS micelles. These results were confirmed by Ganesh et al. (ref. 219), who showed that the γCH_2 group of the detergent undergoes the largest benzophenone-induced shift in both CTAB and SLS micelles.

Highly polar molecules can *a priori* be expected to be "adsorbed" at the micelle-water interface (ref. 159,168) and indeed in most studies of the properties of the micellar "surface", charged species have been employed in order

to avoid penetration inside the micelle. Even in this case, however, one cannot completely exclude the possibility that the uncharged portion of the probe molecule penetrates to some extent into the micelle and thus suffers an influence from factors not directly related to the micelle-water interface.

One of the most comprehensive studies of the nature of the micellar microenvironment sensed by adsorbed polar probes was carried out by Fernández and Fromherz (ref. 227). Employing coumarin dyes anchored into the micelle by a long alkyl chain, the micropolarity was inferred indirectly from the shift in the pK_a of the probe relative to that in dioxane-water mixtures. In this manner, they arrived at an effective dielectric constant of 32 for nonionic, anionic and cationic micelles, irrespective of the charge of the head group.

Using the E_T (30) of phenolbetaine as a measure of the polarity of the micellar environment, Zachariasse et al. (ref. 195) concluded that the probe molecule is invariably solubilized in the aqueous interface. The values obtained for the effective dielectric constant were dependent on the solvent system chosen to calibrate the polarity scale. Thus, for dodecyl-trimethylammonium chloride, the values ranged from 30 (on a scale calibrated vs. n-alcohols) to 40 (on a scale vs. ethanol-water mixtures). Their values obtained with water-dioxane mixtures as reference solvents are collected in Table 6.

TABLE 6

Effective dielectric constants from E_T (30) values (ref. 145)

Surfactant	Conc. (M)	E_{ef}
DTAC	0.05	36
DTAB	0.05	33
TTAF	0.05	39
TTAC	0.05	33
TTAB	0.05	31
CTAF	0.05	32
CTAC	0.05	31
CTAB	0.05	30
BDHAC[†]	0.05	26
SDeS[††]	0.1	55
SDS	0.1	55

[†]Benzildimethylhexadecylammonium chloride

[††]Sodiumdecyl sulphate; the rest as in Table 2

The results shown in Table 6 indicate that the probe senses a region of higher average micropolarity in anionic surfactant solutions than in trimethylammonium detergent micelles and further suggest a dependence on the counterion type and the surfactant chain length. A greater polarity (or a greater degree

of exposure to water) was also suggested by Wolff (ref. 207) for the SLS surface relative to the CTAC or CTAB micellar surface on the basis of the water-sensitive fluorescence yield of acridine

The solubilization of n-alkanols in micellar solution is typical of that of neutral amphiphilic molecules. The solubilization environment of n-alkanols has been studied using a variety of experimental techniques (ref. 61,119,124, 175,228 - 231). The solubility of the alcohol is considerably larger in ionic micelles than in hydrocarbon solvents, a fact usually attributed to the interfacial location of the alkanol. Indeed, several independent observations support the view that (at least at low occupation numbers) the alcohol intercalates between the detergent monomers at the micelle-water interface. These observations include a decrease in counterion binding upon incorporation of the alcohol (ref. 232,233), a marked decrease in the micellar solubility at high occupation numbers (ref. 119,209,234) and a change in the fluorescence of pyrene upon addition of alcohol. Similarly, Russell and Whitten (ref. 235) found that addition of n-heptanol to micellar SLS affects the formation of a ground state complex between a hydrophilic quencher and several hydrophobic fluorescence probes, such as surfactant stilbenes and 1,4 diphenylbutadiene. The interaction between the probes decreases with increasing n-heptanol concentration, suggesting that the alcohol is interposed between the components which form the complex.

The conformation of a flexible molecule with two polar (or polarizable) groups (and consequently its solubilization environment) depends on the balance of hydrophobic and hydrophilic interactions. Thus, for the first members of the homologous phenyl alkanol series, the addition of a $-CH_2$ group in the chain increases the hydrocarbon-water partitioning coefficient but decreases the values of K_s (ref. 112). This difference is similar to that observed for the ion exchange constants of carboxylic (ref. 236) and dicarboxylic acid anions (ref. 237) in CTAB and can be explained in terms of localization of the polar head (and hence the initial $-CH_2$ group) in a water-rich environment.

Finally, in contrast to the large number of studies of the microenvironment sensed by the probe in otherwise unperturbed micelles, very few studies have been focused on effects due to modification of the micellar microenvironment by cosolutes or water-solute additives. A particularly suitable probe for such studies is pyrene for which the ratio of the intensities of the first and third vibronic bands (I_I/I_{III}) can be used as a sensitive measure of the probe microenvironment (*vide infra*). Values of I_I/I_{III}) in different unperturbed and modified micelles are given in Table 5, together with values in several representative homogeneous solvents.

The effects of cosolutes can be rationalized in terms of a "naive" model in which additives with similar characteristics compete for the same type of "solubilization sites", while solutes of different hydrophobicities prefer to occupy (or create) distinct solubilization sites. Other cosolute data can also be interpreted in terms of this model. Thus, n-heptanol significantly reduces the solubility of naphthalenemethanol and naphthaleneethanol in SLS micelles with very little effect on the solubility of methyl-substituted naphthalenes (ref. 106). Similarly, the addition of n-heptanol decreases the solubility of chloroform in SLS micelles, yet significantly increases the solubilization of n-pentane (ref. 238).

VI. EFFECT OF NEUTRAL SOLUTES ON MICELLAR PROPERTIES

The properties of micelles are very sensitive to additives. Both water-soluble and lipid-soluble additives can modify the shape and size of the micelle, the degree of counterion binding and the nature of the intramicellar microenvironment (e.g., the micellar microviscosity). The effect of an additive can be the result of an indirect effect on the structure of water or a direct consequence of its solubilization in the micelle; in the latter case, the site of intramicellar solubilization plays a determining role. Neutral substrates that incorporate efficiently into micelles are usually either hydrophobic or amphiphatic species (e.g., n-hexanol). Ionic additives can be either small hydrophilic species (e.g., Na^+) or ions with a hydrophobic moiety (e.g., the n-hexyl ammonium ion). These last species are similar to the amphiphatic neutral molecules in that they orient themselves with the polar (or charged) group at the surface and the hydrophobic group directed toward the micellar core (in the "palisade" layer).

Changes in the size and/or shape of the micelles can be determined directly (e.g., by light scattering) or inferred from changes in the macroscopic viscosity of the solution. The size of the micellar aggregate can also be determined by "compartment counting" techniques such as fluorescence quenching (ref. 33) or intramicellar excimer formation (ref. 239).

One of the most comprehensive studies of the effect of nonpolar additives on micellar properties is that of Almgren and Swarup (ref. 24), who determined the effect of addition of n-hexane, n-heptane and toluene on the aggregation number of SLS. They found that solubilization of the hydrocarbon causes the micelle to grow in such a manner as to maintain the surface area per head group the same as in the unperturbed micelles. This constancy holds up to a hydrocarbon/surfactant ratio of 0.5. The same behavior is observed if the hydrocarbon is added to a micelle containing incorporated n-pentanol. Other studies have also provided evidence for micellar growth (ref. 241,243) upon addition

of relatively nonpolar solutes. In general, the data lend support to the proposal of Mukerjee (ref. 244) that solutes which penetrate into the core should preferentially increase the size of the micelle without significantly changing its shape.

In comparison with nonpolar solutes, the behavior of polar or amphiphatic solutes is quite different in the sense that the latter tend to change the micellar shape by promoting the sphere-to-rod transition.

In a series of papers (ref. 229,234,245-258), Zana and co-workers have used a variety of experimental techniques to study the effect of n-alcohols on the micellar properties.

The system most thoroughly investigated was the pentanol-tetradecyl-trimethylammonium bromide system to which methods including conductivity and bromide ion activity, elastic and quasi-elastic light scattering, osmometry, fluorescence decay of micelle-solubilized pyrene, chemical relaxation and small neutron scattering were applied to obtain information about the CMC, molecular weights (M_w) and surfactant aggregation numbers, dynamics of micellar solutions and overall radius of the hydrophobic core. In the initial paper of the series (ref. 145), it was concluded that the addition of n-pentanol noticeably decreased the surfactant aggregation number and increased the bromide ion activity. At any given alcohol concentration, the micelle molecular weight increased with increasing surfactant concentration. The results, obtained both in the absence and presence of added salt, were explained in terms of the effect of the micelle-solubilized alcohol on the surface charge density and the local dielectric constant in the micelle palisade layer. Subsequent work (ref. 246 - 248) showed that the apparent radius of gyration of the micelle increases with increasing alcohol concentration. At low surfactant concentration, the micelles apparently remain spherical in the presence of 1-pentanol; at large pentanol/surfactant ratios, however, they may develop an inner core of 1-pentanol in addition to the 1-pentanol already present in the palisade layer. As the surfactant concentration is increased, the micelles grow, becoming ellipsoidal (or perhaps rodlike).

The effect of a series of different alcohols on anionic SLS micelles has been studied in detail by Almgren and Swarup (ref. 249). These authors found that the radius of the micellar aggregate remains roughly constant upon addition of the alcohols, resulting in an increase in the surface area per detergent headgroup. The aggregation number typically decreased upon the initial addition of the alcohols; further addition of the solute tended, however, to produce an increase in micellar size. The general picture that emerges from their data is that incorporation of an amphiphilic solute into the palisade layer of the micelle causes a separation of the charges (an increase in the

area per charge), implying a decrease in the primary surface charge density. The resulting decrease electrostatic repulsion between the headgroups outweighs any change in the hydrocarbon-water contact at the interface, favoring micellar growth.

As pointed out by Manabe et al. (ref. 129), however, the release of counterions from the micellar surface may conpensate for this decrease in surface charge density, maintaining the electrical surface potential roughly constant.

The effect of both neutral and ionic amphiphiles on micellar properties evidences itself in several systems as a change in the macroscopic viscosity of the solute (ref. 250,251). In some cases, the viscosity of the solution becomes so high that it acquires the properties of a gel (ref. 252,253).

The viscosity effect produced by solutes seems to be related to a change in the micellar shape from spherical to rodlike (ref. 254 - 257). The association of the solute to the micelle may facilitate the formation of large rod-shaped micelles by decreasing the repulsion between the charged headgroups.

The increase in viscosity of a micellar solution is apparently quite solute-specific. For example, Wan (ref. 252), investigating the effects of a variety of substituted benzoic acids on the viscosity of some cationic micellar solutions, found that salicyclic acid and its salts increased the viscosity of dodecyl, tetradecyl and hexadecyl-trimethylammonium bromide solutions. In contrast, m-hydroxybenzoic acid and p-hydroxybenzoic acid, as well as o-, m- and p-amino, chloro- and nitrobenzoic acids caused no viscosity change. Larsen et al. (ref. 260) and Bunton et al. (ref. 261) reported similar results. These latter authors reported very high viscosities for CTAB solutions containing sodium tosylate but not for those containing benzene-sulfonate; disodium phenyl phosphate also has no effect on the viscosity of CTAB micelles (ref. 251). The work of Wan (ref. 252) further indicates that the nature of the micelle contributes to the specificity of the viscosity effect. Thus, the same solutes that greatly increase the viscosity of cationic micelles are without effect when added to anionic or nonionic micelles.

In all of the cases studied, the solutes that produce enhanced viscosity of the micellar solution are aromatic molecules known to be strongly associated to micelles and in particular to cationic micelles. This peculiar interaction between positively charged micelles and aromatic molecules might reflect an increased polarization of the π electron cloud of the aromatic ring under the influence of the positive electric field at the micellar surface. However, association of the solute to the micelle is not in itself a sufficient condition for producing the viscosity effect; the presence of a methyl group, an alkyl chain, or some other appropriate functional group on the aromatic ring is apparently also necessary. Likewise, there seems to be no clear correlation between the magnitude of the solute incorporation coefficient and the viscosity effect.

Finally, in many cases, the addition of the solute initially causes a sharp increase in viscosity (ref. 261), followed by a sharp decrease at higher solute concentrations (ref. 262). We believe that this behavior is a reflection of the strong non-Newtonicity typical of very viscous solutions at finite flow rates (ref. 253). Thus, the CTAB-sodium tosylate system exhibits a pronounced maximum (ref. 261) when the apparent viscosities are plotted against tosylate concentration. However, the maximum disappears if the viscosity data are determined at various flow rates and extrapolated to zero rate of flow (ref. 253).

Although the increase in viscosity is undoubtedly due to a solute-induced change in the micellar shape from spherical to rodlike, the high solute specificity is far from understood and more work is required to identify the structural features of the solute responsible for the manifestation of these interesting effects.

Using the $Ru(bpy)_3^{+2}$/methyl anthracene fluorescence quenching method, Almgren and Swarup (ref. 249) measured the size of SLS micelles in the presence of hydrophobic counterions and of nonionic surfactants. Hydrophobic counterions of these kinds were tested: 1) cationic surfactants with one long alkyl chain (from octylammonium chloride to CTAB); 2) symmetrical tetraalkylammonium (R= C_2H_5, C_4H_9, C_5H_{11}) ions; and 4) tetraphenylphosphonium salts. The first induce a micelle growth (n increases from 67.5 to 87.9 at an octylammonium chloride mole fraction of 0.2, which would leave the surface area per SLS headgroup nearly constant if the micelle were spherical (the large viscosity increase observed when these surfactant counterions are incorporated suggests, however, the occurence of a sphere-to-rod transition). In contrast, tetraalkylammonium ions reduce the surfactant aggregation number (n_{SLS} = 51.5 at a tetraalkylammonium chloride mole fraction of 0.37); the micellar volume remains almost constant with the hydrophobic counterions acting as a spacer between the SLS headgroups. Nonionic surfactants (tetra-, penta-, and octaethyleneglycol mono-n-dodecyl ether) were also found to produce a decrease in the SLS aggregation number, again consistent with a role as a spacer.

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