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Solubilization as a Separation Process

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ABSTRACT

In this paper a separation process for hydrocarbon molecules is suggested, based on solubilization in aqueous solutions by surfactant micelles. A molecular thermodynamic approach to solubilization is formulated which relates the extent of solubilization and the selectivity to the structure and properties of the surfactant and of the solubilizate molecules. An evaluation of the solubilization characteristics of benzene and hexane in aqueous solutions of non-ionic octyl glucoside, anionic sodium dodecyl sulfate and cationic cetyl pyridinium chloride is made and solubilization phase diagrams for the above systems are constructed. These diagrams indicate the formation of micelles at concentrations which are lower than the critical micelle concentration of the surfactant alone. The calculations predict, for all three surfactants, preferential solubilization of (aromatic) benzene compared to (aliphatic) n-alkanes. The preferential solubilization of benzene is caused by its smaller molecular volume and lower interfacial tension against water. Preliminary experimental results using cetyl pyridinium chloride as surfactant and an equimolar binary mixture of hexane and benzene as solubilizates indicate a selectivity of over 7 for benzene compared to hexane, and a ratio of about one molecule of benzene solubilized for every surfactant molecule in the micelle.

INTRODUCTION

Surface active molecules consisting of a non-polar hydrocarbonaceous part and a polar ionic or non-ionic part self-assemble in aqueous solutions in such a way as to minimize the contact between the non-polar tail of the surfactant and water. Various types of molecular assemblies are generated depending upon the chemical structure of the surfactant molecule and its concentration in solution. In dilute aqueous solutions either micelles or vesicles are formed whereas in more concentrated solutions various liquid crystalline structures are generated [1-3]. The micelles have a non-polar hydrocarbon core which is shielded from water by a polar shell made up of surfactant head groups. In vesicles, two layers of surfactant molecules associate in such a way as to give rise to a hydrocarbon shell surrounded on the interior and the exterior by polar head groups. Therefore, vesicles are spherical surfactant bilayers dispersed in water and containing an encapsulated aqueous phase. Non-polar molecules which are sparingly soluble in water find a compatible environment in the hydrocarbonaceous non-polar interior of the micelles or in the non-polar shell of the vesicles. This results in the solubilization of molecules (which are otherwise insoluble in water) in the hydrocarbonaceous environment of the surfactant aggregates [4,5]. The extent of this solubilization depends upon the chemical features of the surfactant and of the solubilizate molecules, as well as on the conditions of the system, such as temperature, pressure, concentrations and ionic strength. Here by solubilization we understand both (i) the molecular dispersion of the solubilizates between the hydrocarbon tails of the surfactant molecules constituting the micelles (Type I) as well as (ii) the formation of a core of solubilizates surrounded by a layer of surfactant molecules as in microemulsions (Type II) (Figure 1). Because of different molecular interactions, one may expect the micellar solutions to exhibit different solubilizing capacities for different solubilizates. This suggests the possibility of using solubilization for separation purposes.

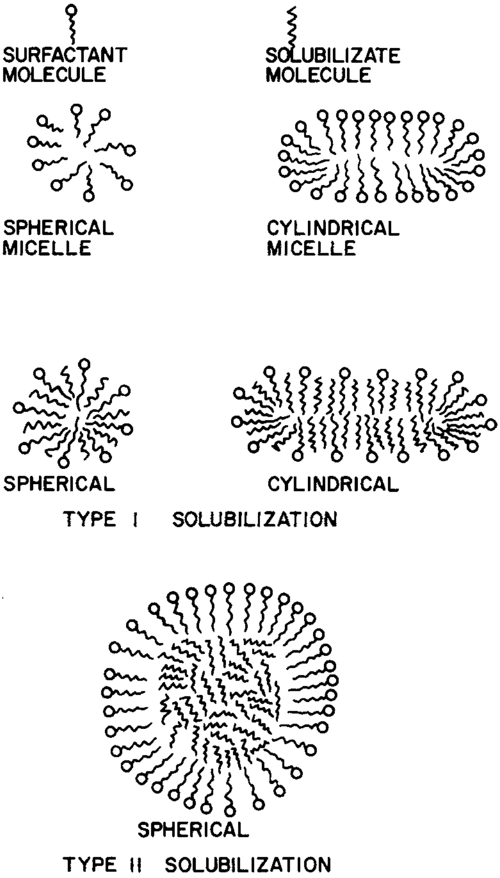

FIGURE 1. Schematic representation of pure micelles and micelles containing solubilizates. For Type I solubilization the solubilizate molecules are located between the surfactant tails in the micelles. For Type II solubilization the solubilizate molecules form a core surrounded by the surfactant molecules as in microemulsions.

The main goal of this paper is to evaluate the solubilization capacities of surfactant solutions as a function of the molecular structures of surfactant and solubilizates. A thermodynamic approach is developed which enables the construction of phase diagrams and hence the identification of the conditions under which solubilization occurs. In addition, it provides the size distribution of the micelles, the relative proportion of solubilizate to surfactant molecules in micelles and, in the case of binary solubilizates, also the extent of preferential solubilization of one component over another. Both Type I and Type II solubilization models mentioned above have been taken into account in the calculations. For the surfactants and conditions examined in this paper, the calculations indicate the occurrence of only Type I solubilization, implying that microemulsions are not generated under these conditions. The main conclusion of the calculations is that (aromatic) benzene molecules are selectively solubilized compared to (aliphatic) hexane molecules in all three (non-ionic, anionic and cationic) surfactant solutions.

THERMODYNAMICS OF SOLUBILIZATION

A. Size Distribution of Micelles Containing Solubilizates

A thermodynamic description of solubilization in micellar solutions can be developed in a manner analogous to that for micelle formation in the absence of solubilizates [6-9]. At equilibrium, the aqueous solution is composed of N_W water molecules, N_1 singly dispersed surfactant molecules, N_{1S} singly dispersed solubilizate molecules and N_{gj} micelles (composed of g surfactant and j solubilizate molecules). The aqueous solution is assumed to be dilute. Micelles of different sizes containing different amounts of solubilizate molecules are considered as distinct species, each characterized by its standard chemical potential. The standard chemical potential of a micelle containing g surfactant and j solubilizate molecules is denoted by μ°_{gj}.

The standard chemical potential of the solvent molecule and of the singly dispersed surfactant and solubilizate molecules are denoted by μ°_s; μ°_1, and μ°_{1S}, respectively. Pure water constitutes the standard state for the solvent, whereas the infinitely dilute solution is the standard state of all the other components. Because we assume a dilute system, the mutual interactions among micelles, single surfactant and solubilizate are negligible and the free energy of the aqueous solution is given by

$$G = N_w\mu^\circ_w + N_1\,\mu^\circ_1 + N_{1S}\mu^\circ_{1S} + \sum_g\sum_j N_{gj}\,\mu^\circ_{gj} + kT\,[N_w\,\ell n\,(N_w/F) + N_1\,\ell n\,(N_1/F) + N_{1S}\,\ell n\,(N_{1S}/F) + \sum_g\sum_j N_{gj}\,\ell n\,(N_{gj}/F)]\quad . \tag{1}$$

In equation (1), k is the Boltzmann constant, T is the absolute temperature and F is the total number of particles in the system,

$$F = N_w + N_1 + N_{1S} + \sum_g\sum_j N_{gj}\quad . \tag{2}$$

For given amounts of surfactant and solubilizate molecules,

$$N_1 + \sum_g\sum_j g\,N_{gj} = \text{constant}, \tag{3}$$

and

$$N_{1S} + \sum_g\sum_j j\,N_{gj} = \text{constant}. \tag{4}$$

The equilibrium state of the system corresponds to a minimum of the total free energy G. This condition, along with the constraints (3) and (4) provide the following size distribution for the micelles:

$$(N_{gj}/F) = (N_1/F)^g\,(N_{1S}/F)^j\,\exp[-(\mu^\circ_{gj}-g\mu^\circ_1-j\mu^\circ_{1S})/kT)\quad . \tag{5}$$

The argument in the exponential term represents the difference in standard free energy between a micelle with g surfactant and j solubilizate molecules and a system of g surfactant and j solubilizate molecules which are singly dispersed in solution. For Type I solubilization, the micelles are assumed to be spherical at small aggregation numbers and cylindrical with hemispherical ends at large aggregation numbers. The transition from spheres to cylinders is assumed to occur when the radius of the micelle becomes equal to the extended length of the surfactant molecule. For Type II solubilization, the micelles are assumed to be spherical and to contain a core of solubilizate molecules.

Equation (5) can be extended to micelles containing two solubilizate species. One obtains:

$$(N_{gj'j''}/F) = (N_1/F)^g (N_{1S'}/F)^{j'} (N_{1S''}/F)^{j''}$$

$$\exp\,[-(\mu^\circ_{gj'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''})/kT] \ . \qquad (5')$$

In the above equation, the superscripts ' and " refer to the two solubilizate species. The micelle is now composed of g surfactant molecules, j' solubilizate molecules of type S' and j" solubilizate molecules of type S".

When micelles containing solubilizates form, the hydrocarbon tails of the surfactant molecules and the hydrocarbonaceous solubilizate molecules are displaced from the aqueous environment to the hydrocarbon environment of the interior of the micelles. Of course, the micellar interior of Type I solubilization differs from a bulk hydrocarbon liquid because of the additional constraints on molecular motion experienced within the organized molecular assemblies [1,8-10]. In earlier papers, a thermodynamic model for micelle formation in the absence of solubilizates has been developed [8,9]. Here, a more simple but equivalent approach is used. In this approach, the standard free energy of transfer of the surfactant tail and of the solubilizate from an aqueous to a bulk hydrocarbon phase are taken from experimental data instead of being calculated from partition functions. The additional constraints imposed by the molecular organization in the hydrocarbon like interior of the micelles are treated as corrections to the above free energies. The corrections could be estimated either from experimental critical micelle concentration (CMC) data or from the theoretical model developed in References [7-9].

B. Standard Free Energy Change Associated with the Transfer of a Hydrocarbon Molecule from an Aqueous to a Hydrocarbon Medium

The partition function for a solution of hydrocarbon in water may be written, in terms of partition functions for (i) the hydrocarbon molecule in water, Q_{HW}, (ii) the water molecules adjacent to the hydrocarbon molecule, Q_{W*}, and (iii) the water molecules in the bulk water, Q_W, as:

$$Q_{solution} = [Q_{HW}^{N_H}/N_H!][Q_{W*}^{aN_H}/(aN_H)!][Q_W^{(N_W-aN_H)}/(N_W-aN_H)!] . \quad (6)$$

In equation (6), N_H is the number of hydrocarbon molecules, N_W is the total number of water molecules and 'aN_H' is that part of the water molecules surrounding the N_H hydrocarbon molecules as 'a' adjacent water molecules for each hydrocarbon molecule. From equation (6), one obtains for the standard chemical potential of the hydrocarbon molecule in water, the following expression:

$$\mu_{HW}^{\circ} = -kT \, \ell n \, [Q_{HW} \, (Q_{W*}/Q_W)^a] \quad . \quad (7)$$

If the molecular partition function of the hydrocarbon molecule in bulk hydrocarbon phase is Q_{HH}, then the standard chemical potential of the hydrocarbon molecule in its bulk phase is

$$\mu_{HH}^{\circ} = -kT \, \ell n \, Q_{HH} \quad . \quad (8)$$

The difference in standard chemical potentials when the hydrocarbon molecule is transferred from water to a bulk hydrocarbon phase is therefore given by:

$$(\mu_{HH}^{\circ}-\mu_{HW}^{\circ})/kT = \ell n \, [(Q_{HW}/Q_{HH})(Q_{W*}/Q_W)^a] \quad . \quad (9)$$

The partition function of a hydrocarbon molecule in the bulk hydrocarbon phase can be written as:

$$Q_{HH} = [(2\pi mkT/h^2)^{3/2} v_H][(2\pi \bar{I}_1 kT/h^2)^{3/2} 8\pi^2]$$
$$[\exp -(\Phi_{HH}/kT)] , \qquad (10)$$

where the three factors represent the translational, rotational and configurational partition functions, respectively. In equation (10), h is Planck's constant, m is the mass of the hydrocarbon molecule, v_H is its molecular volume and $\bar{I}_1$ is its average moment of inertia. An explicit equation to calculate $\bar{I}_1$ is given in the Appendix. The configurational factor accounts for all the attractive and repulsive interactions. The constraints imposed on the free rotation of the molecule by the close packing and by the orientation of the hydrocarbon chains in the bulk liquid, as well as the hindered internal rotation around the C-C bonds are also a result of these interactions.

Similarly, the partition function of a hydrocarbon molecule in water can be written as:

$$Q_{HW} = [(2\pi mkT/h^2)^{3/2} v_W][(2\pi \bar{I}_1 kT/h^2)^{3/2} 8\pi^2]$$
$$[\exp -(\Phi_{HW}/kT)] , \qquad (11)$$

where V_W is the molecular volume of water. Here again, the three terms represent the translational, rotational and configurational partition functions, respectively.

Combining equations (9) to (11), one obtains

$$[(\mu^\circ_{HH}-\mu^\circ_{HW})/kT] = - \ln [v_H/v_W] + [(\Phi_{HH}/kT) -(\Phi_{HW}/kT)$$
$$+ \ln (Q_{W*}/Q_W)^a] . \qquad (12)$$

Denoting by (ψ/kT) the second term on the right hand side of equation (12), the standard free energy for transfer of a hydrocarbon molecule from water to bulk hydrocarbon is given by

$$[(\mu^\circ_{HH}-\mu^\circ_{HW})/kT] = - \ln [v_H/v_W] + [\psi/kT] . \qquad (13)$$

The standard free energy of transfer has been determined experimentally for a number of hydrocarbon molecules, at various temperatures [11,12]. These experimental data allow one to determine the value of (ψ/kT) for various hydrocarbon groups. On the basis of a group contribution approach, one can then calculate the value of (ψ/kT) for any hydrocarbon molecule of interest encountered either as surfactant tail or as solubilizate molecule. This approach obviates the need to write down detailed expressions for Φ_{HH}, Φ_{HW} and the partition functions Q_{W*} and Q_W. The values of (ψ/kT), estimated from experimental hydrocarbon solubility data at 25°C, are as follows: -1.35 for the CH_2 group in n-alkanes, -2.50 for the CH_3 group in n-alkanes and -1.00 for the CH group in aromatics.

C. Standard Free Energy Change Associated with the Formation of Micelles Containing Solubilizates

The standard chemical potential of a singly dispersed amphiphile in water differs from that of a hydrocarbon in water due to the presence of polar headgroup-water interactions. Therefore, comparing with equation (7), one can write

$$\mu_1^\circ = - kT \ln [Q_{HW}(Q_{W*}/Q_W)^a \, Q_{PW}] \quad , \tag{14}$$

where Q_{PW} is the partition function of the polar head group of the surfactant in water. Combining with equation (11), one obtains

$$(\mu_1^\circ/kT) = - \ln [(2\pi mkT/h^2)^{3/2} v_W] - \ln [(2\pi \bar{I}_1 kT/h^2)^{3/2} 8\pi^2] + (\Phi_{HW}/kT) - \ln (Q_{W*}/Q_W)^a - \ln Q_{PW} \quad . \tag{15}$$

The standard chemical potential of a singly dispersed molecule of solubilizate in water can be obtained from the above equation by ignoring the polar head group-water interactions. One thus obtains

$$(\mu^\circ_{1S}/kT) = -\ln\,[(2\pi m_S kT/h^2)^{3/2}\, v_W] - \ln\,[(2\pi \bar{I}_{1S} kT/h^2)^{3/2}\, 8\pi^2] + (\Phi_{HW,S}/kT) - \ln\,(Q_{W*}/Q_W)^{a_S} \quad . \tag{16}$$

Here the subscript S denotes the solubilizate molecule, and all the quantities have the same meaning as before, except that they refer to the solubilizate.

An expression for the standard chemical potential of the micelle (composed of g surfactant and j solubilizate molecules) is now written in terms of translational, rotational and configurational partition functions. For Type I solubilization, the surfactant tails are assumed to mix ideally with the solubilizate molecules. Therefore, the translational part of the standard chemical potential is given by

$$(\mu^\circ_{gj}/kT)_{\text{Translation}} = -\ln\,[\{2\pi(mg+m_S j)kT/h^2\}^{3/2}\, v_W] - \ln\,[1/g!\{(2\pi mkT/h^2)^{3/2}\,(gv + jv_S)\}^{g-1}] - \ln\,[1/j!\{(2\pi m_S kT/h^2)^{3/2}\,(gv + jv_S)\}^{j}] \quad . \tag{17}$$

In equation (17), the first term on the right hand side accounts for the translation of the micelle as a whole; the second and third terms represent the translation within the micelle of the surfactant molecules and of the solubilizate molecules, respectively. The quantities v and v_S are the volumes of the surfactant and solubilizate molecules.

For Type II solubilization, the solubilizate molecules form a core and do not mix with the surrounding layer of the surfactant molecules. In this case the translational part is given by the expression

$$[\mu^\circ_{gj}/kT]_{\text{Translation}} = -\ln\,[\{2\pi(mg+m_S j)kT/h^2\}^{3/2}\, v_W] - \ln[1/g!\{(2\pi mkT/h^2)^{3/2}\, gv\}^{g-1}] - \ln[1/j!\{(2\pi m_S kT/h^2)^{3/2}\, jv_S\}^{j}] \quad . \tag{17'}$$

The difference between equations (17) and (17') gives the contribution of the entropy of mixing inside the micelles in Type I solubilization.

The rotational part of the standard chemical potential of the micelle is

$$(\mu^\circ_{gj}/kT)_{\text{Rotation}} = -\ln[\{2\pi\bar{I}_{gj}kT/h^2\}^{3/2}\;8\pi^2]$$
$$-\ln[\{2\pi\bar{I}_1kT/h^2\}^{3/2}\;8\pi^2]^{g-1}$$
$$-\ln[\{2\pi\bar{I}_{1S}kT/h^2\}^{3/2}\;8\pi^2]^{j}\quad. \tag{18}$$

The first term on the right hand side refers to the rotation of the aggregate as a whole. The second and third terms refer to the rotation of the surfactant and solubilizate molecules inside the aggregates. These terms are written as for a hydrocarbon molecule in a bulk hydrocarbon medium. While the surfactant and the solubilizate molecules are more constrained within the aggregate, this constraint is incorporated within the configurational partition function because it is caused by the interaction forces.

The configuration partition function of the micelle accounts for the interactions in the micellar interior, for the interactions of the polar head group of surfactant with water, for the interfacial free energy between water and hydrocarbonaceous micellar surface exposed to water and for the steric and electrostatic interactions of the polar head groups:

$$(\mu^\circ_{gj}/kT)_{\text{Configurational}} = [g\Phi^*_{HH}/kT] + [j\Phi^*_{HH,S}/kT]$$
$$-\ln\,(Q_{PW})^{g} + (\mu^\circ_{gj}/kT)_{\substack{\text{Steric}\\ \text{Interactions}}} + (\mu^\circ_{gj}/kT)_{\substack{\text{Interfacial}\\ \text{Free Energy}}}$$
$$+\,(\mu^\circ_{gj}/kT)_{\substack{\text{Electrostatic}\\ \text{Interactions}}} \tag{19}$$

In the above equation the interaction potentials Φ^*_{HH} and $\Phi^*_{HH,S}$ of the hydrocarbon tail of surfactant and solubilizate (hydrocarbon) molecule in the interior of the micelle are somewhat different from their values Φ_{HH} and $\Phi_{HH,S}$ in a bulk hydrocarbon environment. This difference is not large and can be viewed as a correction factor on the interaction potential Φ_{HH} in a bulk hydrocarbon medium (see below).

For Type I solubilization, the hydrocarbon-water interface consists of part of the tails of the surfactant as well as of some solubilizate molecules. The interfacial free energy term is therefore written as the product of the interfacial tension of the surfactant tail-solubilizate mixture against water (σ_{mix}) and the hydrocarbon surface area exposed to water.

$$(\mu^\circ_{gj}/kT)_{\substack{\text{Interfacial}\\ \text{Free Energy}}} = (\sigma_{mix}/kT)[A_{gj} - ga_o] \quad . \tag{20}$$

In the above equation A_{gj} is the surface area of the micelle and a_o is the area per surfactant molecule shielded by the head group from the contact with water. σ_{mix} can be estimated, as shown in the Appendix, using empirical correlations of the type suggested by Fowkes [13] and Good [14]. For Type II solubilization, the interface consists of the hydrocarbon tails of the surfactant only, since all the solubilizate molecules are assumed to be contained within a core. The interfacial free energy term, in this case, is analogous to that given by equation (20), except that σ_{mix} is replaced by σ, the interfacial tension of the surfactant tails against water.

For the steric interactions between the polar head groups the following contribution to the standard chemical potential of the micelle [8,9],

$$(\mu^\circ_{gj}/kT)_{\substack{\text{Steric}\\ \text{Interactions}}} = - \ell n \; [(A_{gj}-ga_p)/A_{gj}]^g \quad , \tag{21}$$

is used. Here A_{gj} is the surface area of the micelle and a_p is the cross-sectional area of the polar head group. The area $(A_{gj}-ga_p)$ is the surface area available for the free movement of surfactant molecules and the ratio of this surface area to the total surface area of the micelle measures the probability of non-occurrence of steric hindrance to molecular motion within micelles. The expression in equation (21) is analogous to that used for hard particle repulsions.

Finally, the contribution of the mutual electrostatic interactions between the surfactant head groups located at the micellar surface can be written, in the framework of the Debye-Hückel approximation, for spherical micelles and for both Type I and Type II solubilization, as

$$(\mu^\circ_{gj}/kT)_{\substack{\text{Electrostatic}\\ \text{Interactions}}} = [\varepsilon^2\beta^2 g^2/\{2D(r_{gj}+\delta)kT\}] [(1+\kappa a_i)/\{1+\kappa a_i+\kappa(r_{gj}+\delta)\}] \quad . \qquad (22)$$

For cylindrical micelles (Type I solubilization)

$$(\mu^\circ_{gj}/kT)_{\substack{\text{Electrostatic}\\ \text{Interactions}}} = [\varepsilon^2\beta^2 g^2/(DLkT)] [K_0(\kappa\{r_{gj}+\delta\})/[\kappa\{r_{gj}+\delta\}K_1(\kappa\{r_{gj}+\delta\})] + \ln(\{r_{gj}+\delta+a_i\}/\{r_{gj}+\delta\})] \quad . \qquad (23)$$

In the above expressions, ε is the electronic charge, β is the degree of dissociation of the ionic head groups, D is the dielectric constant of water, κ is the reciprocal Debye length, a_i is the radius of the counterion, δ is the distance of separation between the hydrophobic surface and the location of the charge on the polar head group, r_{gj} is the radius of the spherical (or, cylindrical) hydrophobic surface of the micelle, L is the length of the cylindrical micelle and K_0 and K_1 are the modified Bessel functions of order 0 and 1, respectively. Combining equations (14) to (23), the following expression can be obtained for the standard free energy change associated with the formation of micelles:

$$[(\mu^\circ_{gj}-g\mu^\circ_1-j\mu^\circ_{1S})/kT]_{\text{Translation}} = \{-1/2\ \ell n\ g-g-(g-1)\ \ell n$$

$$[(V+\{j/g\}V_S)/V_W]\} + \{-j-j\ \ln[(\{g/j\}V+V_S)/V_W]\}$$

$$-\ 3/2\ \ln[1+\{jm_S/gm\}],\ \text{for Type I solubilization,} \qquad (24)$$

$$[\mu^\circ_{gj}-g\mu^\circ_1-j\mu^\circ_{1S}/kT]_{\text{Translation}} = [-1/2\ \ln g-g-(g-1)\ \ln(V/V_W)]$$

$$+\ [-j-j\ \ln(V_S/V_W)] - 3/2\ \ln[1+(jm_S/gm)]\ ,$$

$$\text{for Type II solubilization}\ , \qquad (24')$$

$$(\mu^\circ_{gj}-g\mu^\circ_1\ -j\mu^\circ_{1S}/kT)_{\text{Rotation}} = -3/2\ \ln(\bar{I}_{gj}/\bar{I}_1)\ , \qquad (25)$$

and

$$(\mu^\circ_{gj}-g\mu^\circ_1-j\mu^\circ_{1S}/kT)_{\text{Configuration}} = (g\psi^*/kT)$$

$$+\ (j\psi^*_S/kT) + (\mu^\circ_{gj}/kT)_{\substack{\text{Interfacial}\\ \text{Free Energy}}}\ .$$

$$+\ (\mu^\circ_{gj}/kT)_{\substack{\text{Steric}\\ \text{Interactions}}} + (\mu^\circ_{gj}/kT)_{\substack{\text{Electrostatic}\\ \text{Interactions}}}\ . \qquad (26)$$

As already mentioned, ψ^* in equation (26), (corresponding to the surfactant molecule), differs somewhat from the quantity ψ defined in equation (13) for the transfer of a hydrocarbon molecule from water to bulk hydrocarbon. In our earlier theory of micellization [8,9], the interaction forces which impose constraints within the micelles were approximately modelled by considering that the rotational motions of the molecules about their short axes are frozen. The constraints imposed within the bulk hydrocarbon phase by the interaction forces were modelled in terms of restricted rotation for the hydrocarbon molecules; a quantitative estimate was obtained using a correlation of experimental data proposed by Bondi [15]. The free energy difference between the restricted rotational state in the bulk hydrocarbon and the completely frozen rotational state in the micelle provides the value of the difference between ψ and ψ^*. Based on this picture, discussed in more details in reference [16], an estimate of ψ^* can be made. The following group contributions to ψ^*/kT are thus obtained: -1.15 for each CH_2 group in n-alkanes, -2.30 for each CH_3 group in n-alkanes, and -1.00 for each CH group in aromatics. To estimate the values of ψ_S^* associated with the transfer of the solubilizate molecules from water to micelles, the following considerations are relevant. For Type I solubilization, the solubilizate molecules are likely to be more constrained in the micelles than in the bulk solubilizate phase. However, these constraints should be less severe than those experienced by the surfactant molecules whose head groups are anchored to the interface. Therefore, for Type I solubilization, calculations are performed for two limiting situations: (i) the solubilizate inside the micelle is constrained as in the bulk phase, i.e. the group contributions to ψ_S^* and ψ are the same, and (ii) the solubilizate inside the micelle is as constrained as the surfactant tail, i.e. the group contributions to ψ_S^* and ψ^* are the same. For Type II solubilization, the solubilizate molecules constitute a core by themselves and are in an environment similar to their bulk phase. Therefore, the calculations in this case are carried out assuming that contributions to ψ_S^* and ψ are the same.

The above equations can be extended to a binary solubilizate mixture to obtain the following relations:

$$[(\mu^\circ_{gj'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''})/kT]_{\text{Translation}} =$$

$$\{-1/2\ \ell n\ g - g - (g-1)\ \ell n\ [\{V + (j'/g)V_{S'} + (j''/g)V_{S''}\}/V_W]\}$$

$$+ \{-j' - j'\ \ell n\ [\{(g/j')V + V_{S'} + (j''/j')V_{S''}\}/V_W]\}$$

$$+ \{-j'' - j''\ \ell n\ [\{(g/j'')V + V_{S''} + (j'/j'')V_{S'}\}/V_W]\}$$

$$-3/2\ \ell n\ [1 + (j'm_{S'}/gm) + (j''m_{S''}/gm)],$$

for Type I solubilization, (27)

$$[(\mu^\circ_{gj'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''})/kT]_{\text{Translation}} =$$

$$\{-1/2\ \ell n\ g - g - (g-1)\ \ell n\ [V/V_W]\}$$

$$+ \{-j' - j'\ \ell n\ [\{V_{S'} + (j''/j')V_{S''}\}/V_W]\}$$

$$+ \{-j'' - j''\ \ell n\ [\{V_{S''} + (j'/j'')V_{S'}\}/V_W]\}$$

$$- 3/2\ \ell n\ [1 + (j'm_{S'}/gm) + (j''m_{S''}/gm)],$$

for Type II solubilization, (27')

$$[(\mu^\circ_{gj'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''})/kT]_{\text{Rotation}} =$$

$$-3/2\ \ell n\ (\bar{I}_{gj'j''}/\bar{I}_1), \qquad (28)$$

and,

$$[(\mu^\circ_{gj'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''})/kT]_{\text{Configuration}} =$$

$$(g\psi^*/kT) + (j'\psi^*_{S'}/kT) + (j''\psi^*_{S''}/kT)$$

$$+ (\mu^\circ_{gj'j''}/kT)_{\substack{\text{Interfacial}\\ \text{Free Energy}}} + (\mu^\circ_{gj'j''}/kT)_{\substack{\text{Steric}\\ \text{Interactions}}}$$

$$+ (\mu^\circ_{gj'j''}/kT)_{\substack{\text{Electrostatic}\\ \text{Interactions}}} . \qquad (29)$$

The interfacial free energy, the steric and the electrostatic interaction components of the above configuration term are computed using equations (20) to (23), substituting, however, in those equations expressions for $A_{gj'j''}$ and $r_{gj'j''}$ given in the Appendix for the binary solubilizate systems.

Using equations (5), (5') and (24) to (29), one can compute the size distribution of the micelles for Type I solubilization and of the globules of microemulsions for Type II solubilization.

In the next section results based on such computations for the solubilization of hexane and benzene both as single components and as binary mixtures are presented for three different surfactants.

RESULTS AND DISCUSSION

For illustrative purposes, the solubilization characteristics of benzene and hexane in non-ionic octyl glucoside, anionic sodium dodecyl sulfate and cationic cetyl pyridinium chloride solutions are calculated. Values of various molecular properties [8,9] which appear in equations (24) to (29) are listed in Table 1 and in the Appendix. It may be noted that the calculations are based on the

Table 1

Properties of Surfactant and Solubilizate Molecules

	Cetyl Pyridinium Chloride	Sodium Dodecyl Sulphate	Octyl Glucoside	Benzene	Hexane
m (or m_s) daltons	339	288	292	78	86
v_H (or v_s) $Å^3$	460	352	243	162	216
a_p $Å^2$	30	17	40	---	---
δ Å	1.5	2.3	---	---	---
a_i Å	1.9	1.0	---	---	---
K litres/mole	0.5	1.0	---	---	---
β^*	0.8	0.7	---	---	---
γ (or γ_s) $\frac{\text{ergs}}{\text{cm}^2}$	27.3	25.1	21.4	28.9	18.0
ξ (or ξ_s)	1.1	1.1	1.1	1.48	1.1
ψ^*/kT (or ψ_s^*/kT)	-18.4	-13.8	-9.2	-6.0	-9.2

[While estimating ψ^*/kT for the surfactant molecules, the contribution of the CH_2 group adjacent to the polar head of the surfactant is considered to be negligible.]

assumption that the degree of dissociation of the ionic head groups at the micellar surface is unaffected by the extent of solubilization. The concentration of the singly dispersed solubilizate molecules has an upper bound given by its solubility in water in the absence of any surfactant molecules. For hexane, this limiting value is 4.24×10^{-6} and for benzene 4.6×10^{-4} (both in mole fraction units)[11,12]. For binary solubilizate systems the limiting concentrations in water of the singly dispersed solubilizate molecules are taken proportional to their mole fractions in the hydrocarbon phase.

For the surfactants and conditions used in the present computations only Type I solubilization (solubilization between the surfactant tails) appears to occur.

A. Phase Diagrams for Single Solubilizates

The phase diagrams representing the solubilization behavior of hexane or benzene in the three surfactant solutions are shown in Figures 2 through 7. In these figures the total concentration of surfactant is plotted against the molar ratio of the total solubilizate to total solubilizate plus total surfactants, λ_{TS}. Four distinct regions can be identified. In region I, a single aqueous phase exists which consists of water and singly dispersed surfactant and solubilizate molecules. For a given λ_{TS}, as the total surfactant concentration is increased, micelles begin to form beyond the critical micelle concentration. In region II, again a single aqueous solution phase is present which includes micelles in addition to singly dispersed surfactant and solubilizate molecules. At low concentrations of surfactants and as the relative proportion of the solubilizate is increased, phase separation of the solubilizate occurs. This is shown in region III where a solubilizate phase is in equilibrium with an aqueous phase which contains singly dispersed surfactant and solubilizate molecules. At high concentration of surfactants, as λ_{TS} is increased, a separation of the solubilizate phase occurs (region IV). Here the solubilizate phase is in equilibrium with an aqueous

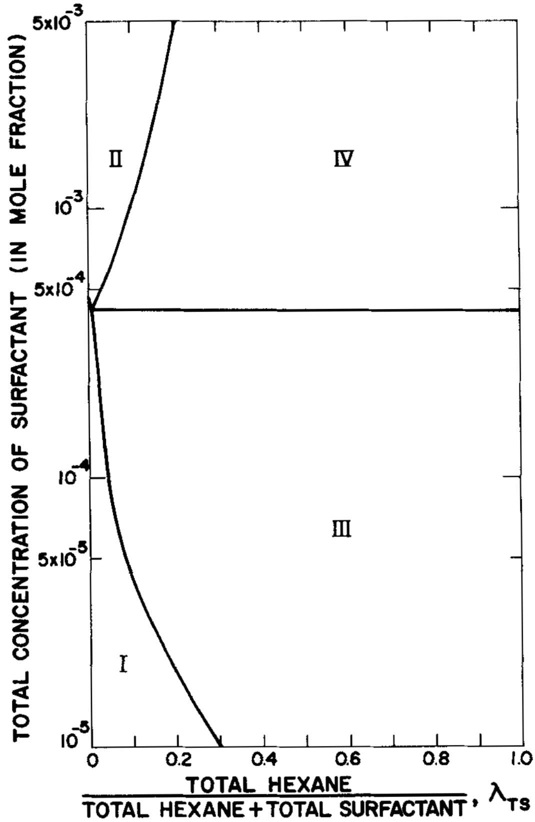

FIGURE 2. Phase diagram for the solubilization of hexane in octyl glucoside micelles. I and II refer to aqueous one-phase regions. III and IV refer to two-phase regions composed of aqueous and hydrocarbon phases. In regions I and III, the aqueous phase is composed of singly dispersed surfactant and solubilizate molecules, but not micelles. In regions II and IV, the aqueous phase includes micelles in addition to singly dispersed surfactant and solubilizate. In regions III and IV the non-aqueous phase is that of solubilizate. This description of the four regions is common to Figures 2 to 7.

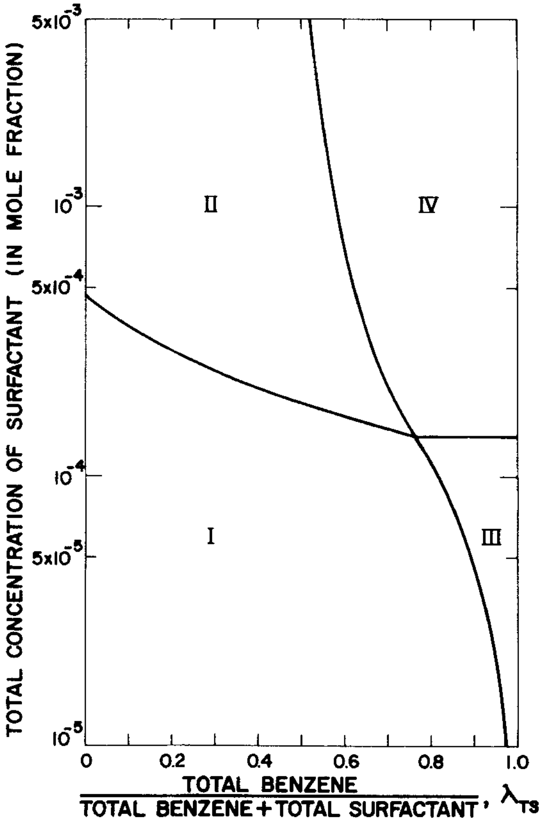

FIGURE 3. Phase diagram for the solubilization of benzene in octyl glucoside micelles.

phase consisting of micelles, singly dispersed surfactant and solubilizate molecules. The boundary between regions I and II is defined by the critical micelle concentration (CMC) curve. One may note the decrease in CMC caused by the presence of the solubilizate. The boundary between regions I and III is defined by the solubility curve of the solubilizate. From these phase diagrams, one can calculate the amount of solubilization and the phase comp-

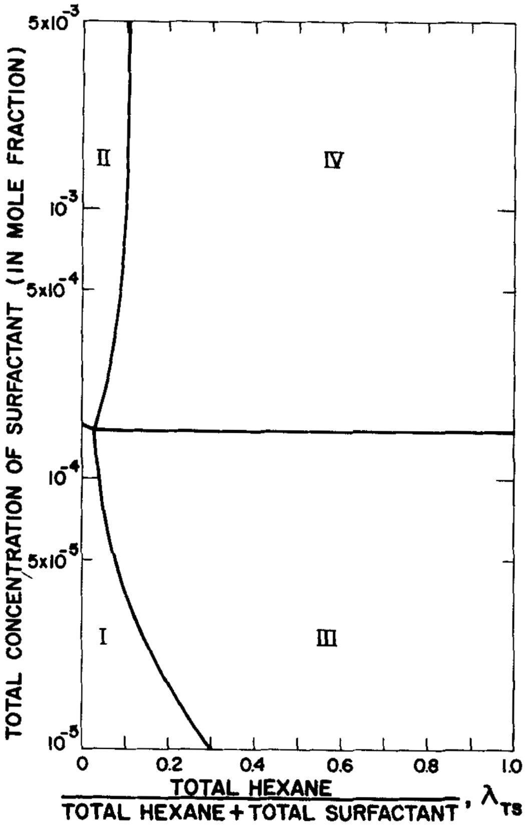

FIGURE 4. Phase diagram for the solubilization of hexane in sodium dodecyl sulfate micelles.

ositions for any given total concentrations of surfactant and solubilizate molecules. These phase diagrams have been calculated assuming that the solubilizate molecules and the surfactant tails are equally constrained in the micelles. No essential change results when the above assumption is replaced by equal constraints for the solubilizate in the micelle and in the bulk solubilizate phase.

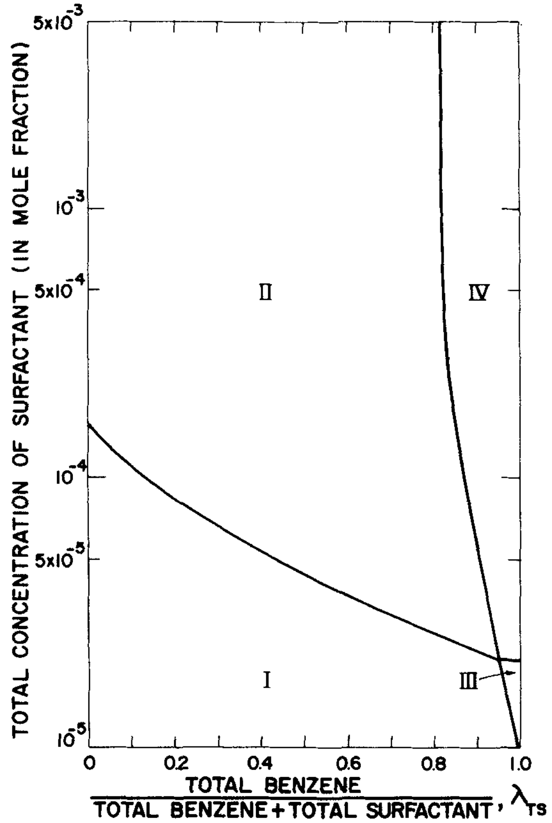

FIGURE 5. Phase diagram for the solubilization of benzene in sodium dodecyl sulfate micelles.

B. Distributions of Micellar Sizes and of Solubilizate/Surfactant Ratio for Single Solubilizates

Figures 8 to 10 provide the values predicted for both the average number of surfactant molecules and the average ratio of solubilizate to surfactant molecules in a micelle, as a function of the total surfactant concentration. The results shown in Figures 8 to 10 correspond to the maximum solubilization, represented in the phase diagram (Figures 2 to 7) by the boundary

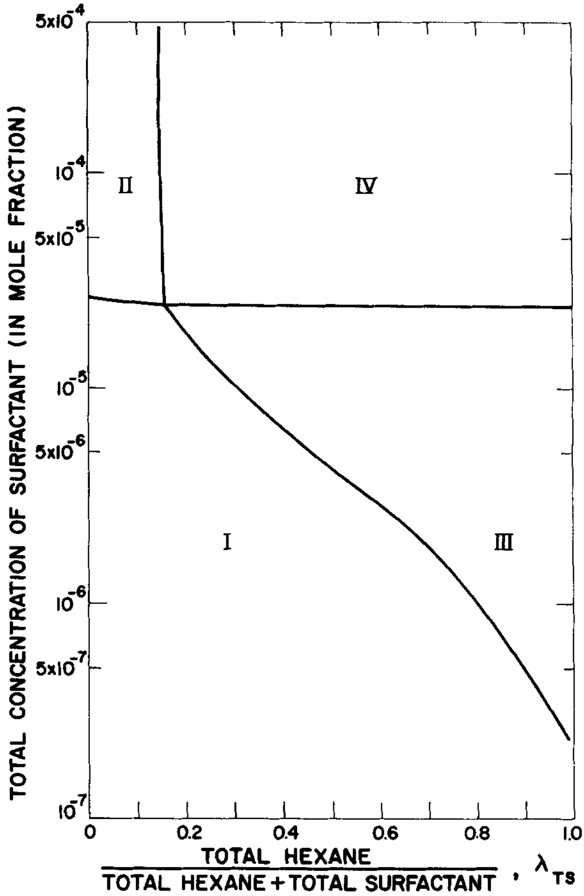

FIGURE 6. Phase diagram for the solubilization of hexane in cetyl pyridinium chloride micelles.

between regions II and IV. Figures 8 to 10 include also the weight average aggregation numbers of the micelles formed in the absence of any solubilizate.

For all three surfactant solutions, the average size of the micelles in the presence of solubilizate is larger than that in its absence. The increase in the micellar size is particularly large for octyl glucoside (Figure 8).

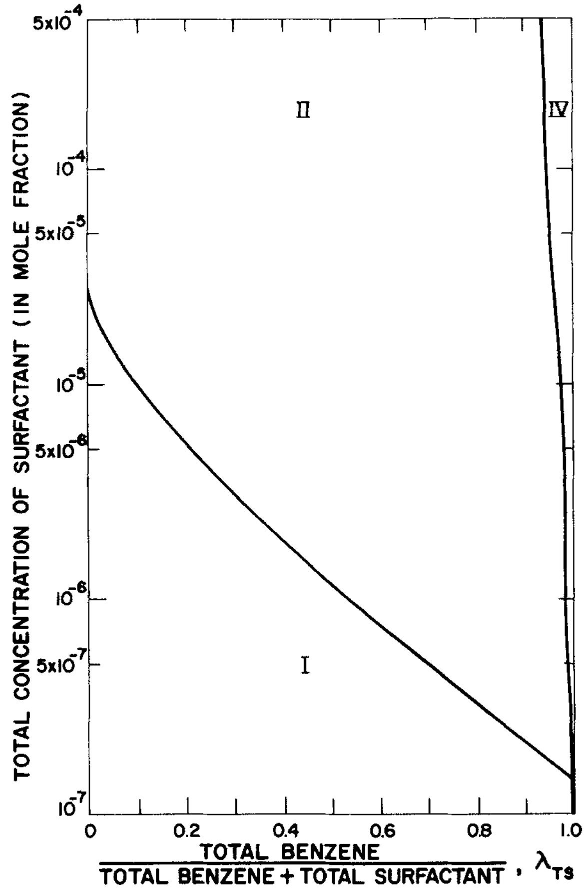

FIGURE 7. Phase diagram for the solubilization of benzene in cetyl pyridinium chloride micelles.

The average ratio of solubilizate to surfactant molecules remains almost constant being nearly independent of the size of the micelle and the concentration of the surfactant. This ratio is larger for benzene than for hexane, indicating preferential solubilization of benzene in all three surfactant solutions. The average ratios of solubilizate to surfactant molecule in micelles are: 1.00 for benzene, 0.19 for hexane in octyl glucoside solu-

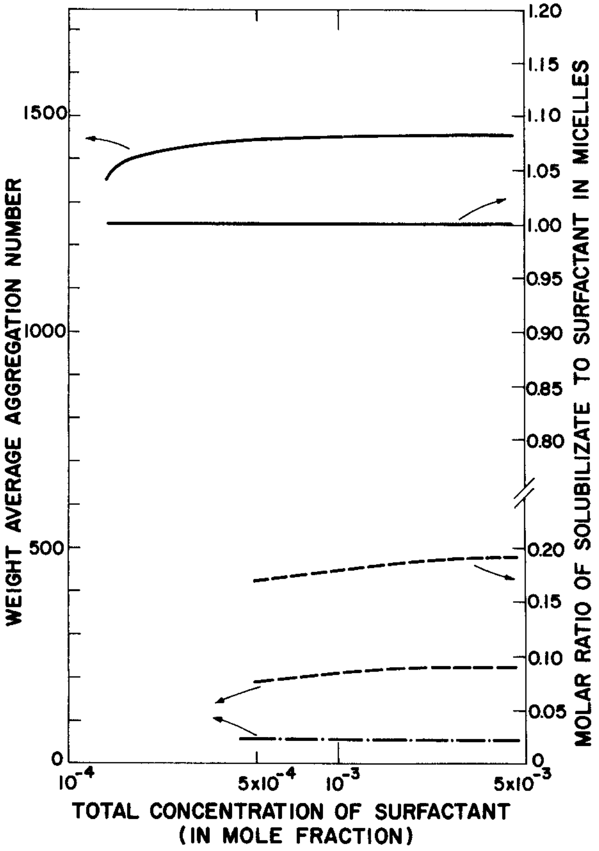

FIGURE 8. Dependence of the average aggregation number and the average ratio of solubilizate to surfactant in micelles on the total concentration of octyl glucoside. Solubilizate: —— benzene, ---- hexane, —·—·— none, pure micelles.

tions; 3.75 for benzene, 0.12 for hexane in sodium dodecyl sulfate solutions; and 13.2 for benzene, 0.16 for hexane in cetyl pyridinium chloride solutions. These results suggest that an increase of the hydrocarbon chain length of the surfactant tail increases the solubilizate to surfactant ratio in the micelles. The above numbers indicate that the amounts solubilized and the

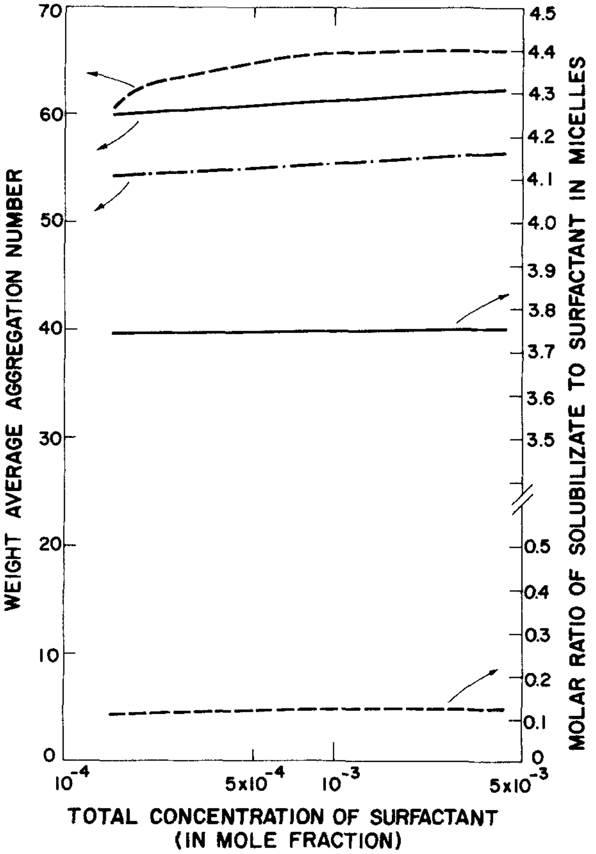

FIGURE 9. Dependence of the average aggregation number and the average ratio of solubilizate to surfactant in micelles on the total concentration of sodium dodecyl sulfate. Solubilizate: —— benzene, ---- hexane, —·—·— none, pure micelles.

selectivity can be large. Of course, in conditions under which Type II solubilization (microemulsions) will occur, the solubilizate to surfactant ratio can be even larger. The selectivity will probably be unsatisfactory for reasons discussed later in the paper.

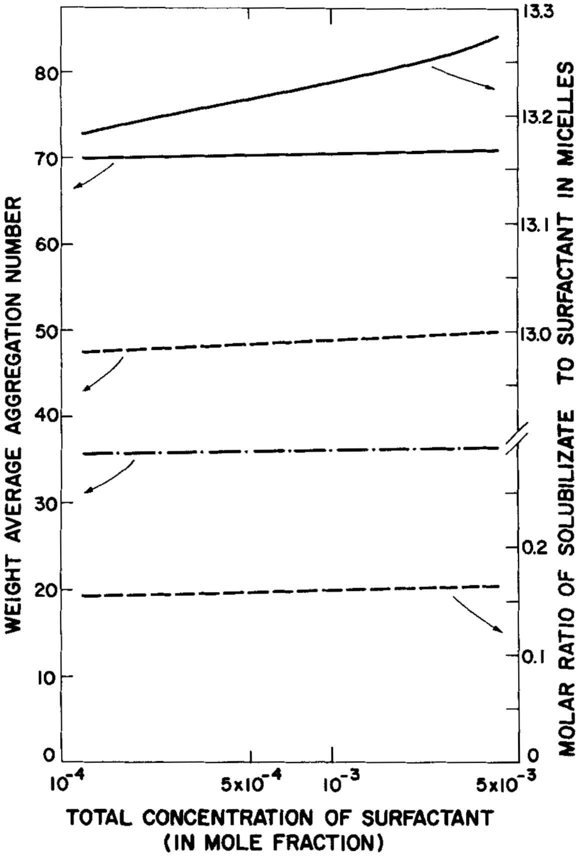

FIGURE 10. Dependence of the average aggregation number and the average ratio of solubilizate to surfactant in micelles on the total concentration of cetyl pyridinium chloride. Solubilizate: —— benzene, ---- hexane, —·—·— none, pure micelles.

The average aggregation numbers increase only slightly as the total surfactant concentration increases. This is the behavior observed in monodispersed micellar solutions and is in contrast to that observed in polydispersed micellar solutions [17]. The approximately monodisperse nature of the micelles containing solubilizate is also indicated by the value of near unity estimated for the ratio between the weight average aggregation number and the number average aggregation number.

C. Origin of the Preferential Solubilization of Benzene

The preferential solubilization of benzene can be examined in terms of various factors, which determine the solubilization behavior of surfactants. Equation (5) for the size distribution of micelles shows that an increasing concentration of the singly dispersed solubilizate favors solubilization and benzene has a much higher solubility limit (4.6×10^{-4}) compared to that of hexane (4.24×10^{-6}). However, the free energy gain associated with the transfer of benzene molecules from an aqueous medium to a hydrocarbon phase is smaller than that for hexane. (This is, in fact, reflected by the higher solubility of benzene in water.) This constitutes a significant factor in the favor of hexane. The above two effects approximately cancel each other in this case and thus cannot explain the preferential solubilization of benzene.

Secondly, benzene has a smaller molecular volume. For a given molecular ratio of solubilizate to surfactant in a micelle, the increase of the hydrocarbonaceous surface area exposed to water caused by benzene is smaller than that due to hexane. In addition, the interfacial tension of benzene-water is lower than that of hexane-water. Both the lower interfacial tension and the smaller increase in interfacial area imply a smaller increase in the positive free energy of the micelle-water interface. This is a significant factor which favors benzene. The decrease in the steric repulsions between the head groups is larger when hexane molecules are solubilized because of the surface area change mentioned above. Even though this factor favors hexane, its magnitude is not large enough.

D. Comparison Between Type I and Type II Solubilization

As already mentioned, only solubilization between the surfactant tails (Type I solubilization) is predicted by our computations, for the surfactants and conditions considered in this paper. Solubilization as microemulsions (Type II solubilization) does not occur because, in contrast to Type I, the entropy of mixing between the surfactant tails and solubilizate molecules is absent, and, in addition, the entropy of the entire system is smaller, since a small number of large particles of Type II replaces a much larger number of small particles of Type I. There is, however, another factor, which favors Type II over Type I; namely, the hydrocarbon-water interface per surfactant molecule which is smaller for Type II. This factor is not large enough for the present surfactants and conditions.

The selectivity of Type II solubilization is expected to be much lower than for Type I, because the interfacial free energy effect discussed in the previous section no longer exists.

E. Solubilization of Binary Solubilizate Mixture

Figure (11) provides the extent of solubilization of benzene and hexane from a solubilizate mixture in the three surfactant solutions as a function of the total concentration of the surfactant in the aqueous solution. The calculations have been carried out for aqueous solutions in equilibrium with an equimolar mixture of benzene and hexane. In all three surfactant solutions the molar (selectivity) ratio of benzene to hexane solubilized is of the order of 10. The number of benzene molecules solubilized per surfactant molecule in a micelle increases from 0.54 for octyl glucoside, to 1.32 for sodium dodecyl sulfate and 2.65 for cetyl pyridinium chloride. Figure (12) shows the variation of the selectivity ratio of benzene to hexane solubilized in the three surfactant solutions as a function of the composition of the organic phase in equilibrium with the aqueous phase. As one would expect, the selectivity ratio is very large when the organic phase is benzene rich and progressively decreases as the organic phase becomes hexane rich. However, the selectivity ratio remains greater than 2 even when the organic phase has a molar composition of 90 percent hexane. This suggests that effective removal

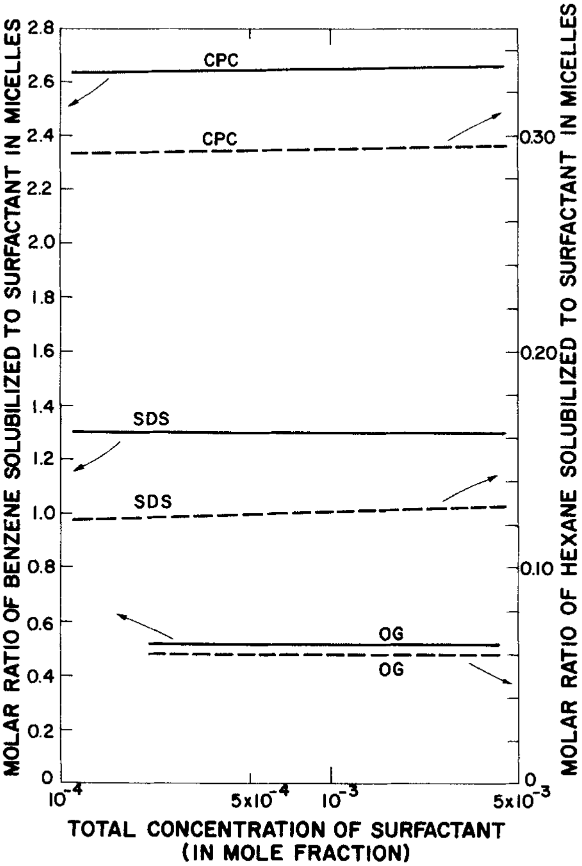

FIGURE 11. Dependence of the average ratio of benzene solubilized to surfactant and of hexane solubilized to surfactant in micelles on the total concentration of surfactant (when the aqueous phase is in equilibrium with an equimolar solubilizate mixture of benzene and hexane). —— benzene, ---- hexane. CPC is for cetyl pyridinium chloride, SDS is for sodium dodecyl sulfate and OG is for octyl glucoside.

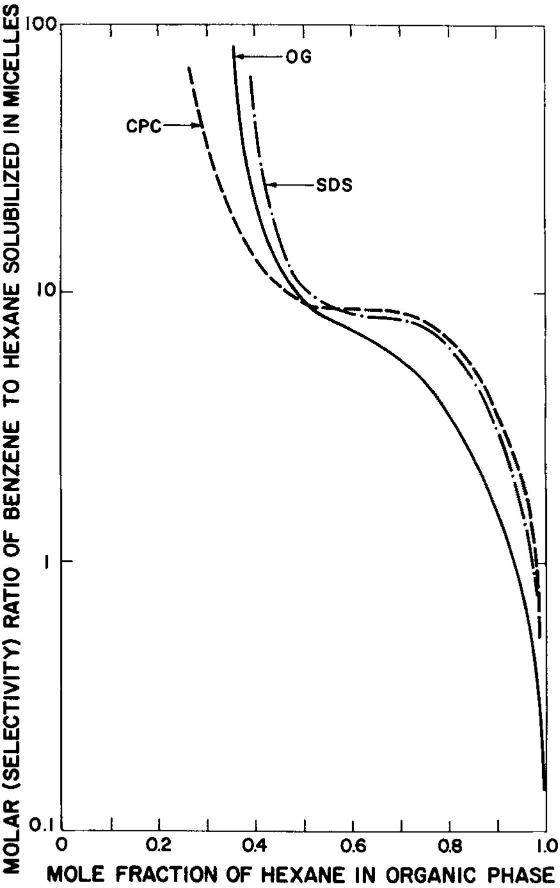

FIGURE 12. Dependence of the molar (selectivity) ratio of benzene solubilized to hexane solubilized in micelles on the composition of the solubilizate phase in equilibrium with the aqueous surfactant solution. Surfactant: ---- CPC is for cetyl pyridinium chloride, —·—·— SDS is for sodium dodecyl sulfate, —— OG is for octyl glucoside. The total concentration of the surfactant in the aqueous solution is 10^{-3} (in mole fraction units).

of benzene from a binary mixture is possible as long as the concentration of benzene in the binary mixture is larger than 10 percent.

F. Experimental Studies on Selective Solubilization

An experimental program to measure the selective solubilization of benzene from an equimolar binary mixture of benzene + hexane is currently in progress. Preliminary experiments have been conducted with 0.1 M cetyl pyridinium chloride as the surfactant system. The surfactant solution is contacted with a binary mixture of benzene + hexane of known initial composition. The final composition of the hydrocarbon mixture is determined following solubilization. After correcting for the concentrations of singly dispersed benzene and hexane in water, the amount of solubilized benzene and hexane have been determined. The results indicate that the ratio of moles of benzene solubilized to that of hexane is over 7. Further, about one molecule of benzene is solubilized for every surfactant molecule present in the micelles. Additional surfactants are being explored to identify conditions of concentration, ionic strength and temperature under which the amounts solubilized are large and the selectivity remains appreciable.

CONCLUSIONS

A thermodynamic approach to solubilization in aqueous micellar solutions has been developed on the basis of which phase diagrams for solubilization of hexane and benzene in three surfactant solutions have been constructed. In general, the critical micelle concentration at which the micelles begin to appear is lower than the CMC in the absence of solubilizate. The average aggregation numbers of the micelles are larger than in the absence of solubilizates. In all the cases, the micelles are almost monodispersed and contain an equal number of solubilizate molecules.

The calculations indicate preferential solubilization of (aromatic) benzene compared to that of (aliphatic) n-hexane. The selectivity for benzene over hexane from an equimolar binary mixture is about 10 for the octyl glucoside, sodium dodecyl sulfate and cetyl pyridinium chloride systems. The molar ratio of solubilizate to surfactant molecules increases as the hydrocarbon chain length of the surfactant tail increases. The preferential solubilization of benzene is caused by its smaller molecular volume and lower interfacial tension against water. These results suggest the possibility of removing aromatics by solubilization from a mixture of aromatic and aliphatic hydrocarbons.

ACKNOWLEDGEMENTS

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APPENDIX

A. Notations and Definitions

a_p = cross-sectional area of the polar head group of surfactant

a_o = area per surfactant molecule shielded from contact with water = 21 Å^2 (if $a_p > 21\ \text{Å}^2$); = a_p (if $a_p < 21\ \text{Å}^2$)

C_1 = molar concentration of singly dispersed surfactant molecules, moles/litre

C_{add} = molar concentration of added salt, moles/litre

g = number of surfactant molecules in a micelle

h = Planck's constant, = 6.625×10^{-27} ergs sec

$\bar{I}_1$ = average moment of inertia of a singly dispersed surfactant molecule, = $(2/5)m\ (3v/4\pi)^{2/3}$

j' = number of solubilizate molecules of kind S' in a micelle

j'' = number of solubilizate molecules of kind S" in a micelle

k = Boltzmann constant, = 1.38×10^{-16} erg/°K

K = equilibrium constant for counterion binding

ℓ_o = length of hydrocarbon tail of surfactant, = $(1.5 + 1.269\ n_c)$ Å

n_c = number of CH_2 and CH_3 groups per hydrocarbon chain

T = absolute temperature, = 298°K, in the present calculations

v_W = volume of water molecule, = 30Å^3

β = degree of dissociation of the ionic head groups, = $\beta^*/[\{K(C_1 + C_{add})\} + 1]$

β^* = the value of β at zero ionic strength

γ = surface tension of the hydrocarbon tail of the surfactant molecule

γ_s = surface tension of the solubilizate molecule

δ = distance of separation between the hydrophobic surface and the location of charge on the polar head group of surfactant

ε = electronic charge, = 4.8 x 10^{-10} esu

κ = reciprocal Debye length, = $(C_1 + C_{add})^{1/2}/(3.08 \times 10^{-8})\ \mathrm{cm}^{-1}$ at 25°C

ξ = empirical constant appearing in the equation for interfacial tension of hydrocarbons against water

σ = interfacial tension of hydrocarbon against water

Total Surfactant Concentration = $(N_1 + \sum\sum_{gj'}\sum_{j''} gN_{gj'j''})/F$

Total Concentration of Solubilizate S' = $(N_{1S'} + \sum\sum_{gj'}\sum_{j''} j'N_{gj'j''})/F$

Total Concentration of Solubilizate S" = $(N_{1S''} + \sum\sum_{gj'}\sum_{j''} j''N_{gj'j''})/F$.

Fraction of Singly Dispersed Solubilizate S' = $\lambda_{1S'}$ = $N_{1S'}/(N_1 + N_{1S'} + N_{1S''})$

Fraction of Total Solubilizate S' = $\lambda_{TS'}$ = $(N_{1S'} + \sum\sum_{gj'}\sum_{j''} j'N_{gj'j''})/(N_1 + N_{1S'} + N_{1S''} + \sum\sum_{gj'}\sum_{j''}[g+j'+j'']N_{gj'j''})$

Fraction of Total Solubilizate S" = $\lambda_{TS''}$ = $(N_{1S''} + \sum\sum_{gj'}\sum_{j''} j''N_{gj'j''})/(N_1 + N_{1S'} + N_{1S''} + \sum\sum_{gj'}\sum_{j''}[g+j'+j'']N_{gj'j''})$

Number Average Aggregation Number $\bar{g}_n$ = $(\sum\sum_{gj'}\sum_{j''} g\, N_{gj'j''})/(\sum\sum_{gj'}\sum_{j''} N_{gj'j''})$

Weight Average Aggregation Number $\bar{g}_w$ = $(\sum\sum_{gj'}\sum_{j''} g^2 N_{gj'j''})/(\sum\sum_{gj'}\sum_{j''} gN_{gj'j''})$

Average Fraction of Solubilizate S' in Micelles = $\langle j'/g \rangle$ = $\sum\sum_{gj'}\sum_{j''}(j'/g)N_{gj'j''}/\sum\sum_{gj'}\sum_{j''}N_{gj'j''}$

Average Fraction of Solubilizate S" in Micelles $= \langle j''/g \rangle =$

$$\sum_g \sum_{j'} \sum_{j''} (j''/g) N_{gj'j''} / \sum_g \sum_{j'} \sum_{j''} N_{gj'j''}$$

B. Definition of Transfer Free Energies

For the transfer of molecules from water to bulk hydrocarbon phase:

$$\psi = \Phi_{HH} - \Phi_{HW} + kT\, \ell n\, (Q_{W*}/Q_W)^{a}$$

$$\psi_S = \Phi_{HH,S} - \Phi_{HW,S} + kT\, \ell n\, (Q_{W*}/Q_W)^{a_S}$$

For the transfer of molecules from water to the hydrocarbon like interior of micelles:

$$\psi^* = \Phi^*_{HH} - \Phi_{HW} + kT\, \ell n\, (Q_{W*}/Q_W)^{a}$$

$$\psi^*_S = \Phi^*_{HH,S} - \Phi_{HW,S} + kT\, \ell n\, (Q_{W*}/Q_W)^{a_S}$$

[The subscript S indicates always the solubilizate.]

C. Estimation of Hydrocarbon Mixture-Water Interfacial Tension

Surface tension of hydrocarbon mixture $= \gamma_{mix} = (g\gamma + j'\gamma_{S'} + j''\gamma_{S''})/(g+j'+j'')$

Interfacial tension of hydrocarbon mixture against water $= \sigma_{mix} = 73 + \gamma_{mix} - \xi_{mix}\,[73 \times \gamma_{mix}]^{1/2}$

Empirical coefficient in the expression for interfacial tension $= \xi_{mix} = (g\xi + j'\xi_{S'} + j''\xi_{S''})/(g+j'+j'')$

D. Geometrical Properties of Micelles (Type I and II)

For Spherical Micelles (Type I solubilization):

$$r_{gj'j''} = [3(gv_H+j'v_{S'}+j''v_{S''})/4\pi]^{1/3} < \ell_o$$

$$A_{gj'j''} = 4\pi r^2_{gj'j''}$$

$$\bar{I}_{gj'j''} = (2/5)(mg + m_{S'}j'+m_{S''}j'')r^2_{gj'j''}$$

For Cylindrical Micelles (Type I solubilization):

$$r_{gj'j''} = \ell_o$$

$$L = [(gv_H+j'v_{S'}+j''v_{S''}) - (4/3)\pi\ell_o^3]/\pi\ell_o^2$$

$$A_{gj'j''} = 4\pi\ell_o^2+2\pi L\ell_o$$

$$\bar{I}_{gj'j''} = (mg+m_{S'}j'+m_{S''}j'')[(\ell_o^2/2)\{(\ell_o^2/4) + ((L+\ell_o)^2/12)\}^2]^{1/3}$$

For Spherical Micelles (Type II solubilization):

$$r_{gj'j''} = [3(gv_H+j'v_{S'}+j''v_{S''})/4\pi]^{1/3}$$

$$A_{gj'j''} = 4\pi r^2_{gj'j''}$$

$$\bar{I}_{gj'j''} = (2/5)(mg+m_{S'}j'+m_{S''}j'')\ r^2_{gj'j''}$$

[In all the above relations, for single solubilizate systems
$j'' = 0,\ j' = j$]