

CONCEPTUAL PROGRESS IN SURFACTANT SOLUTIONS

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Abstract - Concepts on Surfactant solutions developed based on the pertinent facts will be explained. Solubility of an ionic surfactant in water enormously increases above the melting point of the hydrated solid surfactant, because (ordinary) ionic surfactant in a liquid state disperses in water forming micelles. So that the micellar solution is (transparent) one phase and the system is treated by the pseudo-phase dispersion model. Based on such understanding, ionic surfactants which will not "salt out" in hard water were obtained, i.e., depressing the melting points of hydrated bi-valent salts of ionic surfactants by various devices. Important concepts are obtained from the studies of such ionic surfactants; (1) series of ionic surfactants whose hydrophile lipophile balance (HLB) change continuously are obtainable by changing the types, valencies and concentration of counterions, and (2) a well balanced surfactant exhibits large solubilizing power and very small interfacial tension at the oil-water interface. HLB of ionic surfactants which possess two hydrocarbon chains, are usually well balanced. Ionic surfactants as well as nonionics whose hydrophile lipophile property is well balanced are promising for various applications, such as microemulsion, multi-layer adsorption, flotation, tertiary oil recovery etc..

THE USE OF MODELS OR CONCEPTS IN PHYSICAL SCIENCE

It is my great honor and privilege to participate the 3rd International Conference on Surface and Colloid Science in Stockholm 1979 by presenting the Plenary Lecture on the Conceptual Progress in Surfactant Solutions.

The treatment of solutions has traditionally long been dominated by theories designed primarily for molecularly mixed solutions. Such solutions are comparatively rare among so many practically important systems. The most striking feature of these relatively unexplored solutions may be the dissolution due to the orientation, arrangement and structure formation of molecules, which are otherwise practically insoluble by random mixing only. Among these, surfactant solution is the most typical.

I would like to talk on the concepts developed while I apply solution thermodynamics to surfactant solutions in order to clarify their various peculiar and unique solution properties.

Concepts or models, to be valid, have to be consistent with all pertinent facts. A theory, to be widely applicable, should be simple and should not use many parameters. I have long admired the style of Peter Debye for research.

He knew that physical phenomena must have simple explanations. If a theory was not yet simple then it was not yet right—it was unfinished and imperfect. To achieve simplicity one must identify the essentials and isolate the irrelevancies. To recognize the essentials, to express them clearly and pictorially, and then to pursue their consequences with superb experimental facts was Debye's style.

PSEUDO-PHASE DISPERSION MODEL OF MICELLAR SOLUTION

Surfactant dissolves in water in singly dispersed state up to the saturation concentration above which hydrated solid surfactant phase separates below the melting point (Krafft point) of hydrated surfactant and micelles are formed above the melting point as shown in Fig. 1. The aggregation number of surfactant per micelle is not infinite but finite thus we designate it as pseudo-phase. Thermodynamic functions, such as the partial molal free energy, enthalpy, entropy etc. stay nearly constant with concentration above the critical micelle concentration (cmc). The solution is transparent one phase because the size of micelles is usually so small compared with the wave length of light. This means practically infinite solubility. Actually, the solubility of an ionic surfactant in water suddenly and enormously increases several degrees above the Krafft point (1), i.e., the melting point of hydrated

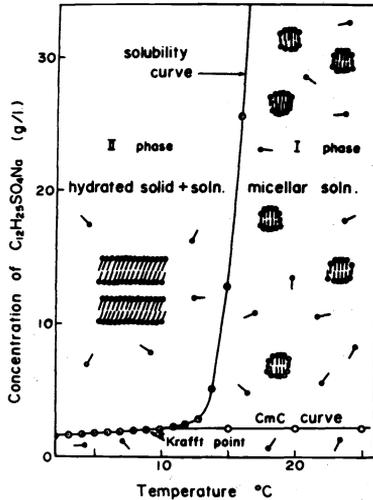


Fig. 1. Phase diagram of $C_{12}H_{25}SO_4Na-H_2O$ system close to the Krafft point. The region of micellar solution (one phase) corresponds to two phase solution (aqueous solution + excess liquid solute) in ordinary system.

solid surfactant (2). Since the solute-solid and liquid(micelle)-solid equilibrium curves constitute the solubility curve, the physical meaning of the solubility curve is different from that of ordinary compounds. Otherwise surfactant which possesses long hydrocarbon chain will be practically insoluble by random (molecular) mixing only. Since the melting point of hydrated nonionic surfactant is low, hydrophilic nonionic surfactant disperses similarly forming micelles. The solution is treated by the pseudo-phase separation model (2) and thermodynamics of small systems (3).

Pertinent facts to support this model are 1) the solubility of ionic surfactant suddenly increases above the melting point of hydrated surfactant (4), 2) the surface tension stays nearly constant with the concentration above the cmc (5) which means the activity or chemical potential of surfactant stays nearly constant above the cmc (6), 3) an intense light scattering of the swollen micellar solution (7), etc. etc.

Professor McBain concluded that the surface excess of surfactant is nearly zero, if the surface tension stays nearly constant with concentration. He had studied the surface excess by the microtome method (8). However, it is not at all a peculiar phenomenon, but a important and pertinent fact predictable from the pseudo-phase separation(dispersion) model.

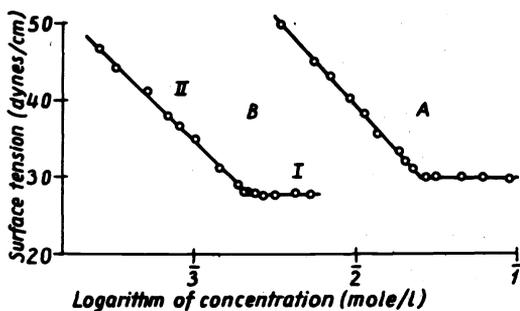


Fig. 2. The surface tension in aqueous solutions of pure nonionic surfactants, (A) octyl and (B) decyl glucosides, stays nearly constant with the concentration above the cmc. Applying the Gibbs adsorption isotherm to region I, we can conclude that the activity of surfactant above the cmc stays nearly constant with the concentration. In the case of ionic surfactants, the concentration of counterions has to be kept constant in order to know the change of activity of surfactant with concentration (5c).

CRITICAL MICELLIZATION CONCENTRATION RANGE

The surface tension of surfactant solutions depresses from that of pure water to about 30 - 38 dynes/cm at the cmc, and then stays nearly constant. Namely, the surface activity of surfactant molecules is inversely proportional to the cmc (9,10). Solubilization of third substances occurs above the cmc. So that it is desirable to depress the cmc and increase the solubilizing power as much as possible.

The cmc is derived either 1) statistical thermodynamically equating the electro-chemical potential of surfactant ions in the micellar state and that in the singly dispersed ions(11), or 2) thermodynamically by evaluating the electrical and non-electrical free energy change at micellization (12).

$$\ln \text{cmc} = -\frac{m\omega}{kT} + \frac{i}{Z} K_g \left[\ln \frac{2000i\sigma^2}{DNkT} - \ln C_g \right] + \ln \frac{1000}{N_U} - 1 \tag{1}$$

$$\ln x_{\text{cmc}} = -\frac{m\omega}{kT} - \frac{i}{Z} K_g \ln x_g + \text{const.} \tag{2}$$

Where m is the number of carbon atoms in hydrocarbon chain, ω the free energy required to transfer a methylene group from micellar interior to aqueous solution, i the number of ionic groups in surfactant molecule, K_g the experimental constant, Z the number of valency of counterions, σ the surface charge density on micelle surface, N the Avogadro number, C_g and x_g the concentration of counterions in moles/l. and mole fraction unit respectively, U the free volume per micelle forming species. If no salt is added, $C_g = \text{cmc}$ and we obtain,

$$\ln \text{cmc} = -\frac{m\omega}{kT} - \frac{i}{Z} K_g \ln \text{cmc} + \text{const.} \tag{3}$$

or

$$\ln \text{cmc} = -\frac{m\omega}{(1+iK_g/Z)kT} + \text{const.} \tag{4}$$

The correlations between the cmc values and the number of carbon atoms in hydrocarbon chain for various series of surfactants are shown in Fig. 3.

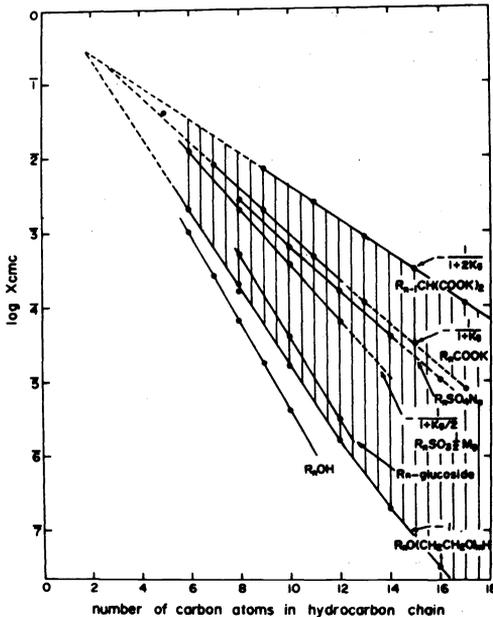


Fig. 3. Correlations between the cmc values and the number of carbon atoms in hydrocarbon chain for various series of surfactants. Solubility of alcohols, R_nOH, is also shown for comparison.

Conclusions drawn from Fig. 3. are as follows:

1. The log x_{cmc} values decrease almost linearly to the number of carbon atoms. The longer the hydrocarbon chain of surfactants the larger the energy required to transfer surfactant molecules from a micelle to the bulk of solution, and the cmc values are depressed geometrically. (Cf. equation (2))

2. The slopes of the log cmc vs. the hydrocarbon chain length changes from $-\omega/kT$ for nonionics, $-\omega/(1+K_g/2)kT$ for bi-valent salts of ionics, $-\omega/(1+K_g)kT$ for 1:1 type ionics to $-\omega/(1+2K_g)kT$ for surfactants which possess two ionic groups. These relations are excellent agreement with equation (4).

3. The log cmc value of a nonionic surfactant and $(1+K_g)\log$ cmc of 1:1 type ionic surfactant of the same chain length are close.

4. The cmc values mostly fall on the shadowed domain in Fig. 3. We can estimate the cmc value of a given surfactant from the hydrocarbon chain length and the types of surfactants.

How to depress the CMC

Since it is important to depress the cmc, several ways of depressing the cmc are enumerated.

- (1) Use longer chain surfactant.
The cmc decreases to 1/3 per CH_2 in nonionics and to 1/2 per CH_2 in ionics (without added salts).
- (2) Use nonionics.
The cmc of nonionics is much smaller than the corresponding ionics.
- (3) Add salts.
The cmc values of ionics decrease inversely proportional to the K_g (~ 0.6)th power of the concentration of uni-valent counterions.
- (4) Add multi-valent counterions.
The cmc values of ionics are efficiently depressed, but the ionics often precipitate by the addition of multi-valent counterions (salt-out).
- (5) Add surface active counterions.
- (6) Add nonionic surface active materials.
- (7) Add higher homologs.

The longer the hydrocarbon chain of surfactant, the lower the cmc. However, the Krafft point becomes higher with the hydrocarbon chain length and the concentration of counterions. Since the physical meaning of the Krafft point is given (2), it is easy to conceive various devices to depress the Krafft point and increase the solubility of surfactant enormously.

DEVICES OF IONIC SURFACTANT APPLICABLE IN HARD WATER

Ordinary ionic surfactants are salted out and cannot be used in hard water, because they are not soluble in the presence of multivalent cations. The surface tension of the aqueous surfactant solution is not depressed well, because a hydrated solid (multi-valent salt of) surfactant precipitate before the solution reaches the cmc. Micelles are not formed, nor does solubilization of oily substances occur in the solution.

The melting point of hydrated solid soap is instantly raised more than 100°C in the presence of a very small amount of calcium ions and calcium soap precipitate. It is not raised so much if the ionic group is sulfate, sulfonate, etc.. The Krafft point of $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ is 9°C and that of $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{1/2Ca}$ is 50°C . Hence, the Krafft point could be depressed below the room temperature by various devices. Thus we could get ionic surfactants tolerable in hard water. As an example the Krafft points and cmc values of $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n\text{SO}_4(1/z)\text{Me}$ type surfactants are listed in Table 1 (13,14).

TABLE 1. Krafft points and cmc values of $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n\text{SO}_4(1/z)\text{Me}$.

Ionic surfactants	Cmc(equiv/l.) at 25°C	Krafft point $^\circ\text{C}$
$\text{C}_{12}\text{H}_{25}\text{SO}_4\text{0.5Ca}$	0.0024 (at 55°C)	50
$\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{0.5Ca}$	0.00092	15
$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_2\text{SO}_4\text{0.5Ca}$	0.00071	<0
$\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{0.5Mg}$	0.00096	<0
$\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	0.0081	9
$\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{Na}$	0.0042	5
$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_2\text{SO}_4\text{Na}$	0.0030	<0
$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_6\text{SO}_4\text{Na}$	0.0016	<0
$\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{K}$	0.0036	24
$\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{NH}_4$	0.0036	<0

The Krafft points of almost all $C_{12}H_{25}(OCH_2CH_2)_nSO_4(1/z)Me$ type surfactants studied were lower than $15^\circ C$. For example, $C_{12}H_{25}OCH_2CH_2SO_4 \cdot 0.5Ca$ dissolves well in the presence of 1 equiv./l. of $CaCl_2$ at $25^\circ C$ (13). An interpretation of the physical meaning of the Krafft point resulted in ionic surfactants applicable in hard water (2).

Series of ionic surfactants whose HLB change continuously

The other important outcome from the device of ionic surfactant applicable in hard water is the finding that the hydrophile-lipophile-balance (HLB) of an ionic surfactant can be changed fairly widely by changing 1) the types of counterions, 2) the number of the valency of counterions and 3) the concentration of counterions (13). If the hydrophile-lipophile property of surfactant changes from hydrophilic to more balanced state by changing the types of counterions, the solubilizing power increases and the surface tension decreases. The effect of the types of counterions on the solubilizing power of $C_{12}H_{25}OCH_2CH_2SO_4(1/z)Me$ toward cyclohexane is shown in Fig. 4.

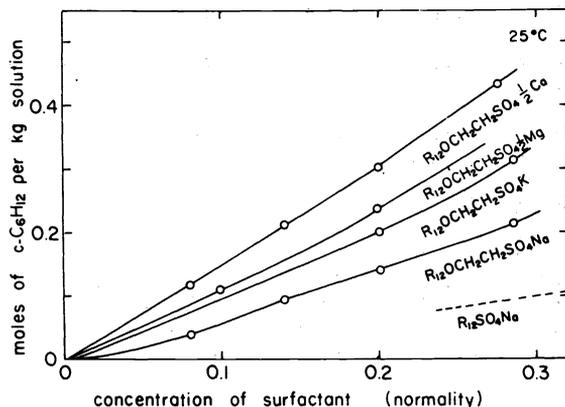


Fig. 4. The effect of the types of counterions on the solubilizing power of $C_{12}H_{25}OCH_2CH_2SO_4(1/z)Me$ toward cyclohexane at $25^\circ C$ (13).

Solubilizing powers of Ca, Mg, K and Na salts were 4.7, 3.8, 3.3 and 2.3 times larger than that of $C_{12}H_{25}SO_4Na$. The surface tension above the cmc of respective surfactants stay nearly constant. These values also change with the types of gegenions. The relation between the solubilization of cyclohexane per mole of micellar surfactant and the lowest surface tension for a series of $C_{12}H_{25}OCH_2CH_2SO_4(1/z)Me$ are plotted in Fig. 5.

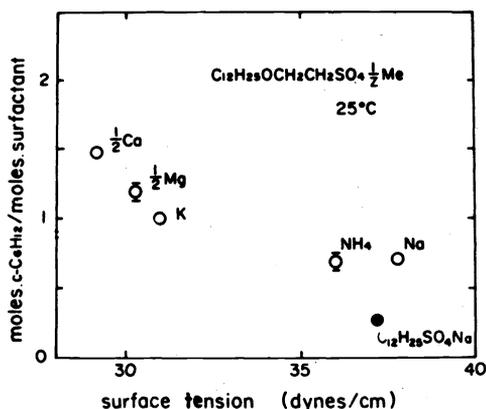


Fig. 5. The correlation among the types of counterions, the solubilizing power and surface tension in aqueous solutions above the respective cmcs of $C_{12}H_{25}OCH_2CH_2SO_4(1/z)Me$ at $25^\circ C$ (13).

It is evident that the lower the surface tension, the larger the solubilizing power of this type of surfactant. The solubilization is larger when the hydrophile-lipophile property of surfactant are well balanced. We well know that the HLB changes continuously with ethylene-oxide chain length in a series of nonionic surfactants. Now, we have a series of ionic surfactants whose HLB changes continuously. This finding as well as excellent properties of the hydrophile lipophile balanced ionic surfactant lead me to new research.

LARGE SOLUBILIZING POWER AND VERY SMALL OIL-WATER INTERFACIAL TENSION BY BALANCED SURFACTANT

Ionic surfactant whose hydrophile-lipophile property is balanced

Since more balanced ionic surfactants exhibited better properties, various ways to obtain hydrophile-lipophile balanced surfactant were examined;

- (1) by partially replacing the ionic surfactant with lipophilic cosurfactants.
- (2) by replacing uni-valent counterions with multi-valent counterions.
- (3) by increasing the concentration of counterions.
- (4) by decreasing the charge density of surfactants, i.e., by using surfactants which possess two (or more) hydrocarbon chains.

Fig. 6. illustrates the solubilization of C_6H_{12} in 5wt% aqueous solution of $C_{12}H_{25}OCH_2CH_2SO_4 0.5Ca + C_8H_{17}O(CH_2CH_2O)_2H$ as a function of the composition of surfactants (14). The interfacial tension between excess oil and aqueous micellar solution are also indicated on the solubilization curve. W_m means oil solubilized aqueous micellar solution phase.

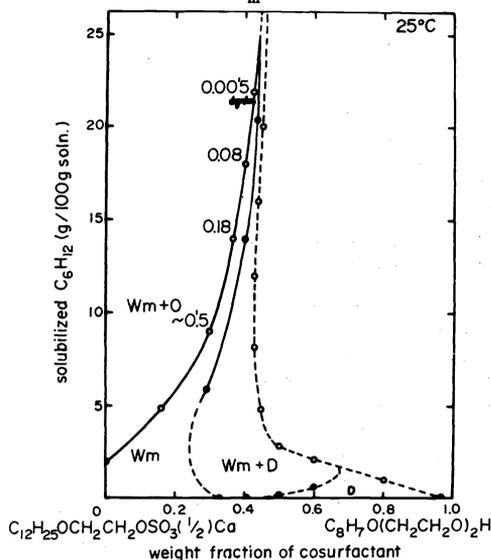


Fig. 6. Solubilization of C_6H_{12} in 5wt% aqueous solution of $C_{12}H_{25}OCH_2CH_2SO_4 0.5Ca + C_8H_{17}O(CH_2CH_2O)_2H$ as a function of composition. Numbers are interfacial tension between excess oil and aqueous solution at 25°C (14).

The relation between the solubilizing power and the HLB of ionic surfactants, $C_{12}H_{25}OCH_2CH_2SO_4(1/z)Me$, with the types of counterions is shown in Fig. 7. (14).

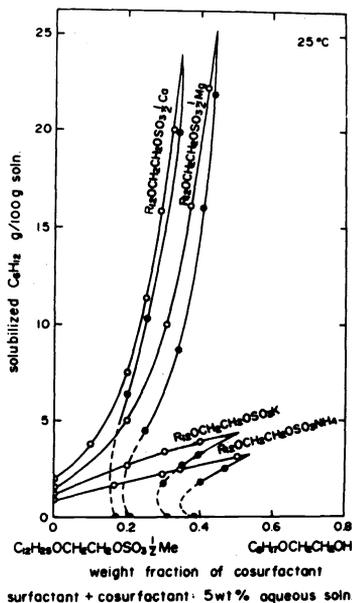


Fig. 7. The effect of the types of counterions on the solubilization of C_6H_{12} and the HLB of ionic surfactants, $C_{12}H_{25}OCH_2CH_2SO_4(1/z)Me$ at 25°C.

A large solubilizing power and a very small oil-water interfacial tension in solutions of hydrophile-lipophile balanced surfactants are observed either in aqueous or in non-aqueous solutions of nonionic surfactants as well as ionic surfactants (16,17). Fig. 10 illustrates a large solubilizing power of oil (or water) in aqueous (or non-aqueous) solution containing 5 wt%/system of $C_9H_{19}C_6H_4O(CH_2CH_2O)_{8.6}H$ close to the phase inversion temperature in emulsion (PIT;HLB-temperaturē) (18).

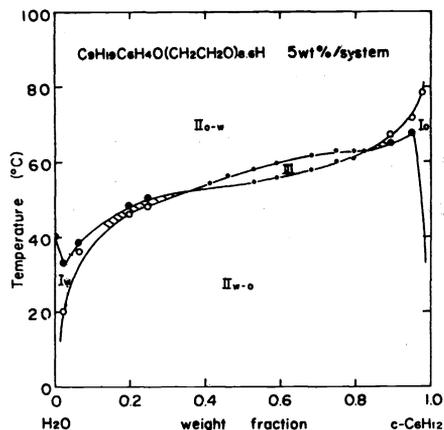


Fig. 10. The effect of temperature on the phase diagram of water + cyclohexane containing 5 wt%/system of $C_9H_{19}C_6H_4O(CH_2CH_2O)_{8.6}H$ (18).

The left-hand side of the figure corresponds to an aqueous surfactant solution containing a small amount of cyclohexane. Nonionic surfactant dissolves in water at relatively low temperature and solubilizes oil. Realm I_w is the oil swollen micellar solution. Solubilization of oil in an aqueous surfactant solution increases markedly close to the cloud point. Shaded area means that the solution of this area scatters a large amount of light and called microemulsion. Above the cloud point a water phase separates from the swollen micellar solution and it changes into surfactant phase. A large amount of water and oil dissolves in the surfactant phase. If the fraction of oil in the system above the cloud point is increased an oil phase, the 3rd phase appears. The central realm indicated by III means a three phase region composed of water, oil and surfactant phases. Since a large amount of oil and water dissolves in surfactant phase, the volume fraction of the surfactant phase is large and the water or oil phase disappears owing to a small change of composition or temperature. Thus the three phase realm is narrow and small. It becomes larger in more dilute solution. The right hand side of Fig. 10 corresponds to a non-aqueous solution of surfactant at higher temperature. Realm I_o is a water swollen micellar solution of C_6H_{12} , one phase. Solubilization of water increases with the temperature decrease particularly close to the cloud point in non-aqueous solution, but an oil phase separates from the solution and the solution changes from C_6H_{12} phase to surfactant phase below the cloud point. In two phase regions II_{o-w} and II_{w-o} , the system forms W/O and O/W type emulsions, respectively, and there is a phase inversion temperature in emulsion between them. The change of the volume fraction of respective phases and the interfacial tension between these phases as a function of temperature is shown in Fig. 11.

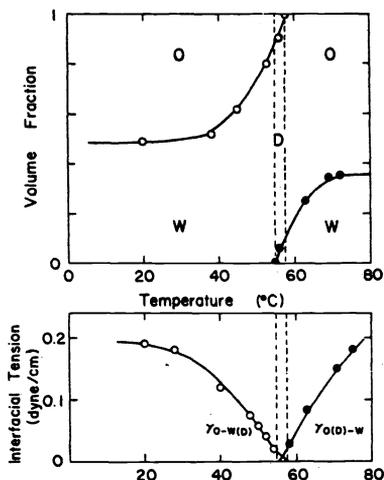


Fig. 11. The oil-water interfacial tension. The system is composed of 5wt% of $C_9H_{19}C_6H_4O(CH_2CH_2O)_{8.6}H$, 47.5wt% of water and 47.5wt% of cyclohexane.

From the composition of the optimum mixing ratio of ionic surfactant and cosurfactant for solubilization and/or the composition at which lamellar liquid crystal of surfactant + cosurfactant + water separate we can estimate the HLB of ionic surfactant. Solubilized amount of oil is about 5 times large compared with the total weight of surfactant in solution. Well solubilized solution scatters a large amount of light and such system is called microemulsion regardless the system is water continuous or oil continuous. It is evident in Fig. 7. that less cosurfactant is necessary to reach the maximum solubilization of hydrocarbon for Ca or Mg salts compared with K, NH_4 or Na salts. The solubilization is much larger in the case of better balanced surfactant. Fig. 8. illustrates the change of HLB of ionic surfactant, $\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{Na}$, with the increasing concentration of added NaCl (14).

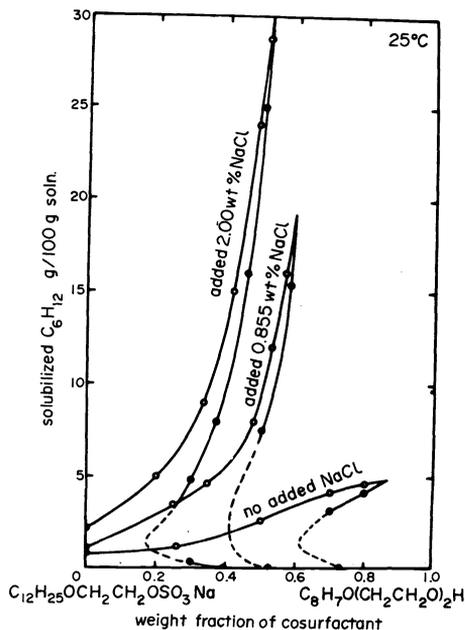


Fig. 8. The effect of the concentration of NaCl on the solubilization of C_6H_{12} in 5wt% aqueous solution of $\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{SO}_4\text{Na} + \text{C}_8\text{H}_{17}\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$ at 25°C.

Solution behavior of Aerosol OT [Sodium 1,2-bis(2-ethylhexyloxycarbonyl)-1-ethanesulfonate] in water + cyclohexane as a function of temperature shown in Fig. 9 tells us that an ionic surfactant which possesses two hydrocarbon chains is a balanced surfactant. Aerosol OT

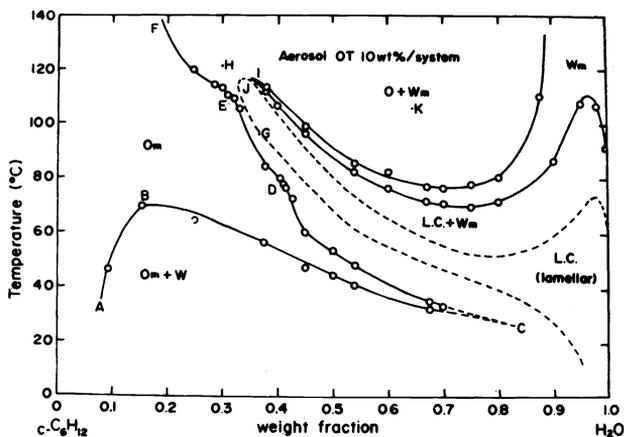


Fig. 9. The phase diagram of water-cyclohexane system containing 10wt% of purified commercial Aerosol OT as a function of temperature. (Estimated amount of Na_2SO_4 as impurity is about 0.6 wt% against Aerosol OT.) (15).

dissolves in C_6H_{12} and solubilizes a large amount of water at relatively low temperature, but it dissolves in water and solubilizes a large amount of C_6H_{12} at relatively high temperature (15). O_m is a cyclohexane solution of Aerosol OT in which water is solubilized, W_m is an aqueous solution of Aerosol OT in which C_6H_{12} is solubilized and L.C. is liquid crystal.

Phase inversion temperature (PIT, HLB-temperature) of nonionic surfactants, such as polyoxyethylene alkylaryl ethers, in emulsion changes with the oxyethylene chain length. Thus an optimum nonionic surfactant whose PIT is close to a given temperature, exhibits a large solubilizing power. For a definite nonionic surfactant, the PIT (HLB-temperature) is fixed, and that is the optimum temperature for solubilization. If a temperature of the system is raised the interaction between water and the hydrophilic moiety of surfactant decreases. Hence, the temperature increase of a system and the decrease in the oxyethylene chain length of a surfactant molecule may have the similar effect on the solubility behavior of surfactant. Actually the phase diagram of nonionic surfactant mixtures in $H_2O + C_6H_{12}$ as a function of the ethyleneoxide chain length of surfactant is similar to the temperature change as shown in Fig. 12 (18).

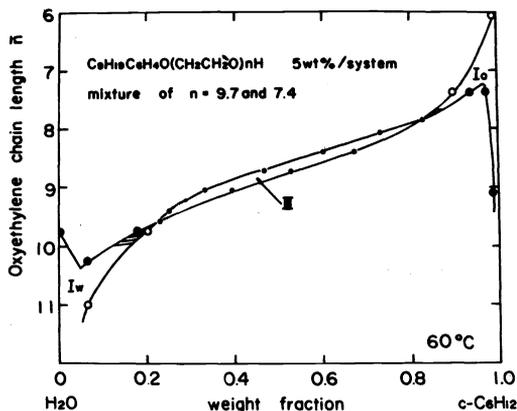


Fig. 12. The effect of the average oxyethylene chain length of nonionic surfactant mixtures on the phase diagram of water + C_6H_{12} containing 5wt%/system of $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$ at 60°C (18).

Instead of hydrophilic and lipophilic nonionic surfactant mixtures, hydrophilic ionic and lipophilic nonionic surfactant or hydrophilic nonionic and lipophilic ionic surfactant mixtures may similarly behave. Fig. 13 illustrates the phase diagram observed in solution of ionic surfactant + cosurfactant + water + oil system (19). Octyl ammonium chloride and octylamine were chosen as surfactant and cosurfactant, respectively. Because, the phase diagram of this four component system is well studied by Friberg (20) and this system is promising to get a phase diagram similar to Figs. 10 and 12.

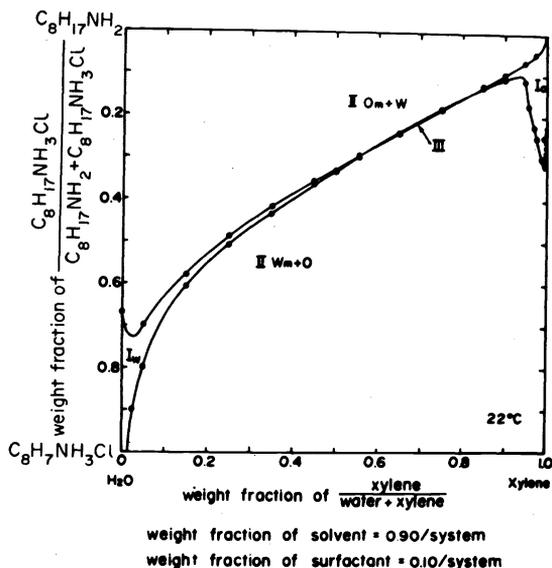


Fig. 13. Phase equilibria of $C_8H_{17}NH_3Cl$, $C_8H_{17}NH_2$, H_2O and $p-(CH_3)_2C_6H_4$ at 22°C. The total concentration of $C_8H_{17}NH_3Cl + C_8H_{17}NH_2$ is 10wt%/system and that of water + p-xylene is 90wt%/system (19).

Phase equilibria of the same system which contain a total of 20wt% of octyl ammonium chloride and octylamine are shown in Fig. 14 (21).

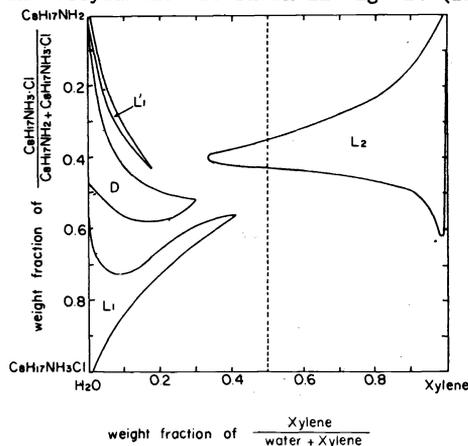


Fig. 14. Phase equilibria of octylamine, octyl ammonium chloride, water and p-xylene at 22°C. Octylamine + octyl ammonium chloride, and p-xylene + water were kept 20wt% and 80wt% of the system, respectively.

Three liquid phases, L_1 , L_1' , L_2 , and one liquid crystalline phase, D, existed. The region L_2' , a swollen micellar solution of p-xylene, was much larger than in Fig. 13. The interfacial tension between p-xylene and water as a function of the weight fraction of surfactant and cosurfactant along the dotted line in Fig. 14 are shown in Fig. 15 (21).

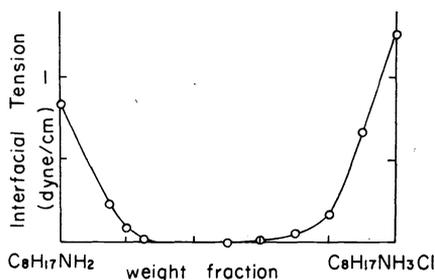


Fig. 15. The change in interfacial tension between p-xylene(40wt%) and water(40wt%) in the presence of the different compositions of octylamine and octyl ammonium chloride(total 20wt%) at 22°C (21).

The interfacial tension is very small close to the swollen micellar solution in which the weight fraction of octyl ammonium chloride is about 0.34 - 0.44 against octylamine. All these results indicate that the solubilization is large and the interfacial tension between oil-water is very small when the HLB of adsorbed mixed surfactant layer at the interface is just balanced regardless ionic or nonionic surfactants and aqueous or nonaqueous solutions. A surfactant which is well balanced in brine and which does not need cosurfactant to attain a very low interfacial tension between petroleum and brine at a given temperature is the most suitable surfactant for tertiary oil recovery.

Acknowledgement - The financial support from the Japan Society for the Promotion of Science for the Japan-U.S. Cooperative Science Program is gratefully acknowledged.

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