The Effect of Poly(oxyethylene) Alkyl Ethers, Alkanediols, and Alkanols on the Critical Micelle Concentration of Sodium Dodecyl Sulfate

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The effect of the addition of the homologues of poly(oxyethylene) alkyl ethers ($C_mH_{2m+1}(OCH_2CH_2)_nOH$: $m=3$—6, $n=1$—4), α,ω-alkanediols ($m=4$—6, 8), and 1-alkanols ($m=2$—7) on the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) was examined. The homologous additives are appropriate for studying the effect of polar groups as well as an alkyl group. The CMC decreases with an increase in the concentration of additive. The rate of CMC-decrease estimated at the infinite dilution of the additive increases with the length of alkyl chain in each homologue. The dependence of the rate on the alkyl chain length is the same for all the homologues with longer chain ($m\geq 4$ for ethers and alkanols, and $m>6$ for alkanediols). This is ascribed to the complete transfer of the long alkyl chain into the interior of micelles. The dependence of rate on the number of polar groups (OH, OCH_2CH_2) is as follows. The rate for alkanediol is lower than that for alkanol with a given alkyl chain. The rate for ethers increases asymptotically with the length of oxyethylene chain. The result for alkanediol is ascribed to the pronounced hydrophilic nature, and that for ethers to the reduction of electrostatic repulsive force between ionic head groups of the surfactant in micelles.

Successive addition of a small amount of normal 1-alkanols and their isomers to a surfactant solution depresses critical micelle concentration (CMC) of several, ionic[1—3] and nonionic[4] surfactants. The rate of CMC-decrease, defined as the decrement of CMC caused by unit increase of additive concentration, increases with an increase in the number of carbon atoms of the alkyl chain. Systematic studies on the effect of additives have so far been restricted to alkanols, because of the authors' interest[1—4] in the hydrophobic behavior of the alkyl chain in the additives dissolved in the surfactant solutions. No systematic study seems to have been made on the effect of additives having various hydrophilic polar groups on the CMC of surfactant solutions. The study is necessary for finding the factor governing the micelle formation and solubilization of surfactants.

This paper deals with the effect of homologous additives, poly(oxyethylene) alkyl ethers, α,ω-alkanediols, and 1-alkanols, on the CMC of sodium dodecyl sulfate. The homologues are appropriate for studying the effect of their polar groups as well as a methylene group in their alkyl chain, since the hydrophilic property of the additives can be altered successively by the number of oxyethylene and hydroxyl groups. The present study gives information on the mixed micelle, consisting of an ionic surfactant and a poly(oxyethylene)-type nonionic one.[5—10]

Experimental

Materials. Sodium dodecyl sulfate (SDS), water, normal 1-alkanols (C_2—C_7), and poly(oxyethylene) alkyl ethers ($C_mH_{2m+1}(OCH_2CH_2)_nOH$: $m=3$, $n=1$; $m=4$, 5, $n=1$—4) were the same as given in the previous studies.[11,12] The ethers ($m=6$, $n=1$, 2, Tokyo Kasei Kogyo Co., Ltd. G. R. grade) were used without further purification. α,ω-Alkanediols (C_4—C_6, C_8) were used after distillation through a 1 m column under reduced pressure.

Determination of CMC. The conductivity of aqueous SDS solution prepared with a solvent containing a small amount of the additives was measured on a Yanagimoto Model MY-7 conductivity meter. Measurements were carried out in a water-thermostat controlled within 25± 0.01 °C. The critical micelle concentration (CMC) of SDS in an aqueous additive solution was taken as the SDS concentration at the break point in the plot of specific conductance *vs.* SDS concentration.[13] The CMC of SDS in water was determined to be 8.30 mmol/kg.

Results and Discussion

For all the additives, the CMC of SDS decreases linearly with an increase in the concentration of the additives within their low concentration regions, deviating gradually upwards from linearity at higher concentrations as shown in Fig. 1 for 1-pentanol and its derivatives. This is in line with the systems of alkanols and surfactants.[1—4] The rate of CMC-decrease, *k*, is determined by the limiting slope of the straight line where at least four points fall on each straight line. The values of *k* are given in Table 1.

The logarithm of $-k$ is plotted in Fig. 2 against the number of carbon atoms, *m*, in alkyl chain in each homologue. The lines are of similar form, a monotonic

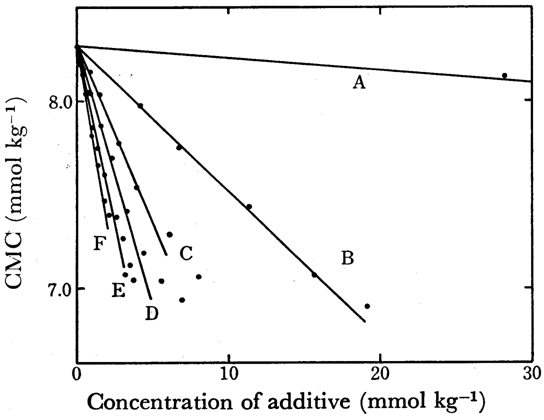

Fig. 1. The relation between CMC of SDS and concentration of additives (1-pentanol derivatives). A: Alkanediol, B: alkanol, C: ether, $n=1$, D; $n=2$, E: $n=3$, F; $n=4$.

TABLE 1. THE VALUE OF k FOR HOMOLOGOUS ADDITIVES

m	$-k$ (mol kg^{-1}/mol kg^{-1})					
	n of ether[a)]				Alkanol	Alkanediol
	1	2	3	4		
2					0.0013	
3	0.021				0.0087	
4	0.072	0.11	0.14	0.18	0.028	0.0012
5	0.19	0.28	0.38	0.47	0.078	0.0066
6	0.48	0.78			0.21	0.022
7					0.53	
8						0.18

a) Poly(oxyethylene) alkyl ether.

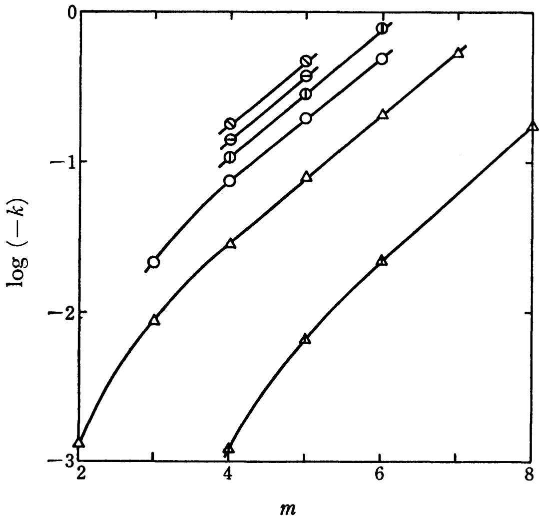

Fig. 2. The relation between log($-k$) and alkyl chain length (m). Homologue of alkanediol (△), alkanol (△), ethers of $n=1$ (○), $n=2$ (⦶), $n=3$ (⊖), $n=4$ (⊘).

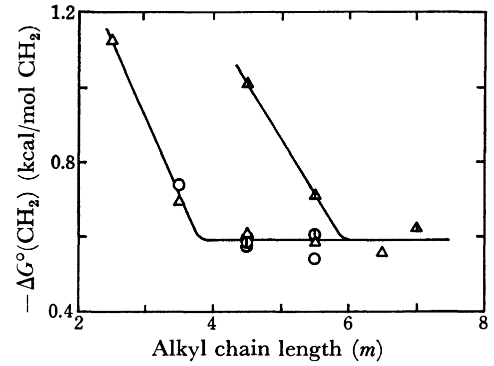

Fig. 3 The relation between $\Delta G^\circ(\mathrm{CH_2})$ and alkyl chain length (m). The mark of each homologue is the same as that in the legend in Fig. 2.

increase in log ($-k$) as a function of m being found to be linear above a certain number of m. For each homologous series, a standard free energy change of transfer per methylene group, $\Delta G^\circ(\mathrm{CH_2})$, from aqueous environment to micelles can be calculated by [2,3]

$$\Delta G^\circ(\mathrm{CH_2}) = -RT\,\mathrm{d}\ln(-k)/\mathrm{d}m \qquad (1)$$

or by its approximation

$$\Delta G^\circ(\mathrm{CH_2}) = -RT\{\ln(-k_{m+1}) - \ln(-k_m)\} \qquad (2)$$

as a function of m. The $\Delta G^\circ(\mathrm{CH_2})$ value, calculated from each pair of neighboring k values taken from the appropriate column in Table 1, is plotted against m in Fig. 3. The plots of alkanol and its poly(oxyethylene) ethers can be regarded as giving a single curve. For all the homologues, the absolute value of $\Delta G^\circ(\mathrm{CH_2})$ decreases initially with the increasing m, and then takes a constant value (-590 cal/mol $\mathrm{CH_2}$)* from about $m=4$ for alkanols and ethers, and from about 6 for alkanediols. The value is comparable with the corresponding free energy value in the process of hydrophobic bond formation (*ca.* -600 cal/mol $\mathrm{CH_2}$).[14,15] Thus, for each series of homologues including alkanediols which bears polar groups at both end positions of the alkyl chain, the methylene groups remote from the polar group by more than about three carbon atoms can be transferred from aqueous environment to the non-polar interior of micelles. This is in line with the view that, in the process of micelle formation of surfactant alone, the hydration of the four methylene groups adjacent to its head group is retained.[16] In other words, the shorter alkyl-chain compounds are probably transferred incompletely (at most, up to the surface region of micelles) or not at all (changing only the property of aqueous medium) owing to their remarkable miscibility with water. The results are supported by the previous findings[11] that the partial molar volumes of 1-butanol and longer-chain 1-alkanols are higher in the micellar solution of SDS than in water, no difference being observed for 1-propanol and lower ones; the lower alkanols are not solubilized to a great extent.

The relation between log ($-k$) and the number of hydroxyl groups and oxyethylene groups (n) is shown in

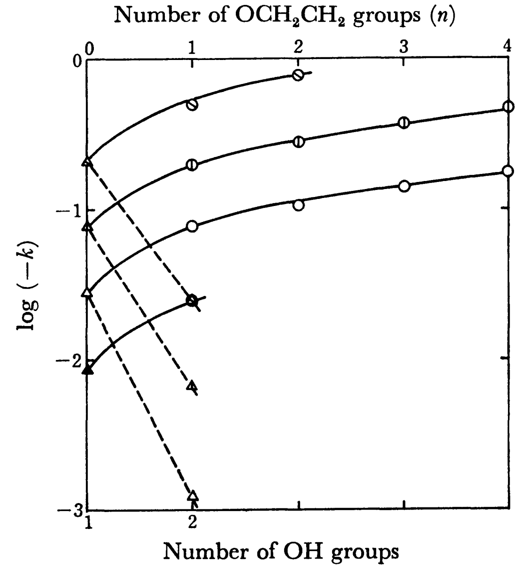

Fig. 4. The relation between log($-k$) and the number of oxyethylene (n) and of hydroxyl groups. Solid line refers to ether: $m=3$ (●), $m=4$ (○), $m=5$ (⦶), $m=6$ (⊘), and broken line to hydroxyl derivatives: $m=3$ (▲), $m=4$ (△), $m=5$ (△), $m=6$ (△).

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* 1 cal=4.18$_4$ J.

Fig. 4. With alkanediols, log $(-k)$ is lower than that for alkanol with the same alkyl chain. However, for ethers, log $(-k)$ increases asymptotically with an increase in n, where alkanol is regarded as an ether with $n=0$. The tendencies are also seen in Fig. 1.

When a small amount of a nonionic amphiphilic substance is added to an ionic surfactant solution to form mixed micelles, the following main factors controlling the CMC-decrease can be considered: (i) thermodynamic factor by which the free energy of mixing decreases, and (ii) electrostatic factor by which the repulsive force decreases among ionic head groups in the surface region of micelles. Both hydroxyl and oxyethylene groups are hydrophilic.[12,13] From the view that an additive dissolves undergoing partition between a polar aqueous phase and a non-polar micellar one, the decreasing tendency of log $(-k)$ with the number of hydroxyl groups (Fig. 4) might be caused for the reason that alkanediol is more difficult to be transferred to the micellar phase than alkanol because of the higher hydrophilicity of the former. Thus, (i) would be the predominant factor.

The tendency of ethers to increase (Fig. 4) is explained as follows. The oxyethylene chain, which wedges off among the ionic head groups, occupies a large space in the ionic surface region of micelles to reduce ionic repulsive force. In addition, the hydrophilic nature of an oxyethylene group is less remarkable than that of a hydroxyl group.[18] The increase in the number of oxyethylene groups may not prevent effectively the solubilization of an additive in contrast with that in the number of hydroxyl groups. Thus, factor (ii) is likely to be more effective than factor (i). The present results are reasonably compared with those of the mixed micelles consisting of an ionic surfactant and a poly(oxyethylene)-type nonionic one, since the present ethers are similar to the nonionic surfactant in molecular structure. This explanation is in line with the results of potentiometric study on a mixed surfactant system: the degree of dissociation of the mixed micelles increases with an increase in the proportion of nonionic component.[8,10] It is also supported by the results obtained in the determination of CMC, in which the break in the curve of specific conductance *vs.* concentration of SDS in water becomes less sharp[5,10] with increase in the content of additive. The tendency becomes remarkable as the oxyethylene chain in ethers is lengthened. The asymptotical curve for ethers (Fig. 4) suggests that an oxyethylene group more remote from the alkyl chain has fewer occasions to approach the surface of micelle near enough to interact appreciably with ionic head groups scattering on it. Another suggestion is as follows. The longer the oxyethylene chain, the more powerful the hydrophilic nature of the ether molecule, and the more difficult the transfer of the ether molecule into micelles, as in the case of alkanediol. As a result, factor (i), the decrease of ether-concentration in micelles, may be added gradually to factor (ii).

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