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Critical Micelle Concentration Reduction of Aqueous Sodium Dodecyl Sulfate Solutions upon the Addition of Alcohols

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Synopsis. Linear relations were found between the critical micelle concentration (CMC) reduction and the carbon number of the alcohols added both at 313.15 K and 328.15 K. The slopes of the CMC reduction against the carbon number of the alcohols are almost the same at 298.15, 313.15, and 328.15 K.

It is well known that upon the addition of alcohols to surfactant micellar solutions, the critical micelle concentration (CMC) decreases.[1–5] Flockhart[4] has reported the effect of temperature on the CMC of sodium dodecyl sulfate (SDS) in water and in aqueous ethanol solutions. Shirahama and Kashiwabara[5] have already discussed the CMC reduction effects due to alcohols (C_2—C_4) on aqueous SDS solutions at 298.15 K.

The present authors have already reported the CMC reduction of SDS upon the addition of 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol, and the distribution coefficients of the alcohols between the aqueous and micellar phases.[6] The relation between the CMC reduction, the distribution coefficients and the standard free energy changes of penetration of the alcohols has been discussed thermodynamically.[7] An important factor which governs the CMC reduction effects is the molar fraction of the alcohol in the micellar phase, because the molar fraction of the alcohol in the micellar phase has a great influence on the chemical potential of the mixed micelle.[7]

Since these results were obtained only at 298.15 K, further work is required at various other temperatures. In this paper, experimental work on the CMC reduction due to the addition of alcohols to the aqueous SDS solutions at 313.15 and 328.15 K is reported.

Experimental

Method. The CMC was determined using the electric conductivity method at 313.15 and 328.15 K. Details of the procedures have been described in a previous paper.[6]

Materials. SDS for biochemical use (Wako Pure Chemical Industries, Ltd.) was recrystallized twice from ethanol, and was carefully dried in vacuo for 50 h. 1-Butanol, 1-pentanol, 1-hexanol, and 1-heptanol of high purity (higher than 99%) were used. The water used was passed through Milli-Q2 Systems (Nihon Millipore Co.) until its specific conductivity fell below $10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Results and Discussion

Table 1. CMC values for SDS to which a small amount of alcohol was added

	313.15 K		328.15 K	
	Alcohol concn (mmol/dm^3)	CMC (mmol/dm^3)	Alcohol concn (mmol/dm^3)	CMC (mmol/dm^3)
Pure water		8.47		9.57
1-Butanol	43.01	7.18	41.16	8.62
	78.24	6.53	77.70	7.24
	122.94	5.45	116.57	6.46
1-Pentanol	12.71	7.30	14.55	8.29
	26.08	6.47	25.77	7.43
	38.24	5.49	40.01	6.45
1-Hexanol	3.731	7.60	5.121	8.13
	7.375	6.59	9.683	6.93
	11.267	6.01	14.095	6.12
1-Heptanol	1.041	7.92	1.559	8.49
	2.117	6.89	2.303	7.87
	3.126	6.30	3.068	7.45

Table 2. CMC decrease upon the addition of alcohol

$\ln(-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}Y_a)$

	298.15 K[6]	313.15 K	328.15 K
1-Butanol	5.36	5.24	5.12
1-Pentanol	6.45	6.33	6.30
1-Hexanol	7.57	7.56	7.55
1-Heptanol	8.54	8.51	8.38

The CMC of aqueous SDS solutions containing 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol at 313.15 and 328.15 K are shown in Table 1. The more hydrophobic and the more concentrated the alcohols added, the more marked becomes the reduction in the CMC. These results follow the same trend as the results for 298.15 K.[6] Also at 313.15 and 328.15 K, the penetration of the alcohols into the micelle from the aqueous phase decreases the chemical potentials of the micelles and, therefore, decreases the CMC. To discuss the standard free energy changes of penetration of the alcohols from the aqueous to micellar phases at 313.15 and 328.15 K, these CMC data will be useful.

The limiting values of $\ln(-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}Y_a)$ at $Y_a=0$ (Y_a is the molar fraction of alcohol in the aqueous phase) were computed using the second-degree least-square method and are shown in Table 2. There are linear relations between $\ln(-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}Y_a)$ and the temperature for each alcohol, as illustrated in Fig. 1. Their slopes are -8.0×10^{-3}, -5.1×10^{-3}, -8.2×10^{-4}, and $-5.4\times10^{-3}\ \mathrm{K}^{-1}$ for 1-butanol, 1-pentanol, 1-

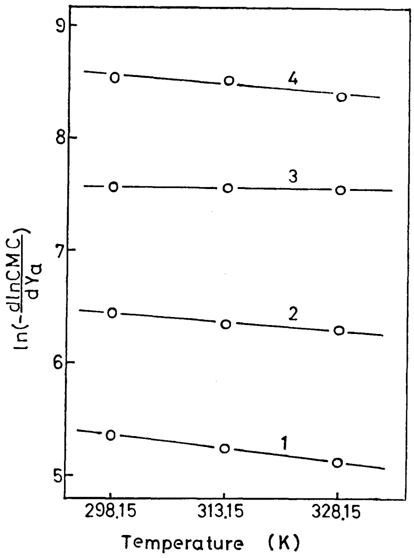

Fig. 1. $\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a)$ as a function of temperature.
(1) 1-Butanol, (2) 1-pentanol,
(3) 1-hexanol, (4) 1-heptanol.

hexanol, and 1-heptanol, respectively. For 1-butanol, 1-pentanol, and 1-hexanol, the slopes decreases with increasing carbon number of the alcohols, but for 1-heptanol the slope is higher than expected. The reason for this is still not clear.

Linear relations between the $\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a)$ and the carbon number of the alcohols are found again at 298.15, 313.15, and 328.15 K. The following equations were obtained using the first-degree least-squares method, thus

$$\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a) = 1.07n + 1.11 \quad \text{at } 298.15\,\mathrm{K}, \tag{1}$$[7]

$$\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a) = 1.10n + 0.84 \quad \text{at } 313.15\,\mathrm{K}, \tag{2}$$

and $$\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a) = 1.10n + 0.77 \quad \text{at } 328.15\,\mathrm{K}, \tag{3}$$

where n is the carbon number of the alcohol.

In the papers of Shirahama and Kashiwabara[5] and of Hayase and Hayano,[7] the relation between $\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a)$ and n were discussed combining the distribution coefficients of the alcohols between the aqueous and micellar phases. Accordingly, it was shown the relation is between $\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a)$, instead of $\ln(-\mathrm{dCMC}/\mathrm{d}Y_a)$, and n, although a linear relation does exist between $\ln(-\mathrm{dCMC}/\mathrm{d}Y_a)$ and n.

In Eqs. 1, 2, and 3 the slopes are almost same (1.1) for the three temperatures. Namely, the CMC reduction effect of the methylene group is the same for the temperature range studied. But, the higher the temperature, the less the CMC reduction effect of each alcohol. Equations 1, 2, and 3 can be rewritten in the following equation,

$$\ln(-\mathrm{dlnCMC}/\mathrm{d}Y_a) = An + B, \tag{4}$$

where A is independent of the temperature, and B is dependent on the temperature.

Accordingly, the CMC reduction effect can be divided into an alcohol carbon number dependent part (the first term) and a temperature dependent part (the second term). Though the physical meaning of Eq. 4 is not clear at present, it is of interest to measure the validity of the equation for other surfactants and additives.

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