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The Distribution of Higher Alcohols in Aqueous Micellar Solutions

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The distribution coefficients, K, for 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol between the sodium dodecyl sulfate (SDS) micellar and aqueous phases were measured directly, with the gas chromatographic technique was used to measure the vapor pressure of the alcohols. The standard free energy change of penetration, ΔG_p°, of the alcohol from the aqueous to the micellar phase was obtained using the equation: $\Delta G_p^\circ = -RT\ln K$. There is a linear relation between ΔG_p° and the carbon number of the alcohol.

The change in the standard free energy of an alcohol for a transition from the aqueous to the micellar phase, ΔG_p°, is indispensable to the study of solubilization of additives in surfactant solutions. In spite of the necessity of evaluating ΔG_p°, no values of ΔG_p° have yet been reported for an aqueous alcohol solution. Though Kaufman[1)] and Dalen, Gerritsma, and Wijkstra[2)] have reported the solubilization of organic additives in organic solvents, they were unable to calculate the distribution coefficient because of a lack of an accurate knowledge of the critical micelle concentration (CMC) in the organic solvent.

Concerning the effect of alcohol on decreasing the CMC, Ward[3)] and Herzfed, Corrin, and Harkins[4)] have pointed out the importance of evaluating ΔG_p°. Shirahama and Kashiwabara[5)] have discussed thermodynamically the relation between ΔG_p° and the CMC decrease of systems containing alcohol. However, since the ΔG_p° were not measured but were estimated values deduced from the physical constants of the alcohols, the theoretical equation does not correspond to their experimental results. Thus, an experimental determination of the ΔG_p° values would be useful in their thermodynamical discussion.

In this paper, experimental work on the distribution coefficients is reported. These experiments are thought to be very important for the discussion of the interaction of surfactants and additives. The distribution coefficients were evaluated by measuring the vapor pressure of the alcohol in an aqueous alcohol solutions both in the presence and absence of sodium dodecyl sulfate (SDS) employing a gas chromatograph. This technique, to the best of the authors' knowledge, has not yet been applied to this kind of problem.

Experimental

Method. 5 ml vapor samples equilibrated with alcohol solutions were introduced from a gas loop by means of a six-way sampling valve into a Shimadzu GC-3BF gas chromatograph equipped with a flame ion detector. Helium was used as the carrier gas at flow rates of 50, 80, and 100 ml/min through a 3 mm × 2 m column. The column packing was 5 or 10% polyethylene glycol 6000 on a 30—60 mesh Flusin T support, and 5% Versamid 900 on a 60—80 mesh Uniport KS support. The operating temperature was 120—160 °C.

The experimental arrangement for the gas chromatographic measurements is shown in Fig. 1. The measuring process was similar to the reported by Kaufman.[1)] To prevent foam from overflowing to the outer part of the bottle, the helium was passed for four minutes in order to saturate the vapor, which was then introduced into the gas chromatograph. The helium flow was stopped for twelve minutes in order to reduce the quantity of foam. The sampling procedure was standardized to allow a uniform 1.5 min period for the valve in the sampling position.

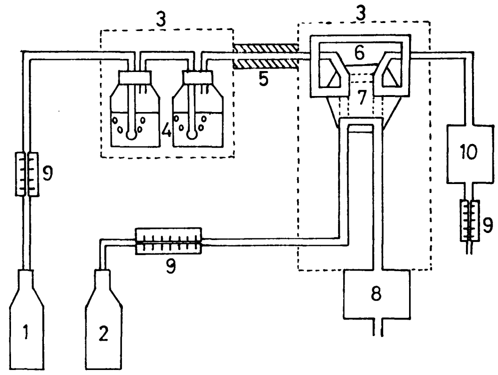

Fig. 1. Experimental arrangement for measuring vapor pressure by gas chromatograph.
(1): Helium cylinder for saturator, (2): helium cylinder for gas chromatograph, (3): thermostat, (4): saturator, (5): ribbon heater, (6): sampling loop, (7): sampling valve, (8): gas chromatograph, (9): flow meters, (10): ballast.
(Solid lines in the sampling valve denote a standby position; dotted lines denote a sampling position.)

The 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol peaks were well-resolved, symmetrical and only slightly tailed.

The measurement of the electric conductivity of the SDS solution was made using a Towa Denpa Co., Ltd. Model CG-201PL universal bridge. An electric conductivity cell of the dip type was bright-platinized and immersed in a 100-ml polyethylene beaker which was maintained at 25 °C in a thermostat.

The SDS concentration was varied by adding portions of a concentrated SDS solution containing an alcohol.

Materials. Wako Pure Chemical Industries, Ltd. SDS for biochemical use was carefully dried in a vacuum for twenty hours. The 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol of high purity (higher than 99%) were used. The water used was passed through a Nihon Millipore Co., Ltd. Milli-Q2 Systems until its specific conductivity fell below 10^{-7} Ω^{-1} cm^{-1}.

Results and Discussion

Figure 2 displays two curves obtained directly from the gas chromatographic measurements. In Fig. 2, 1-heptanol is shown as an example. The upper or calibration curve represents the data taken from a series

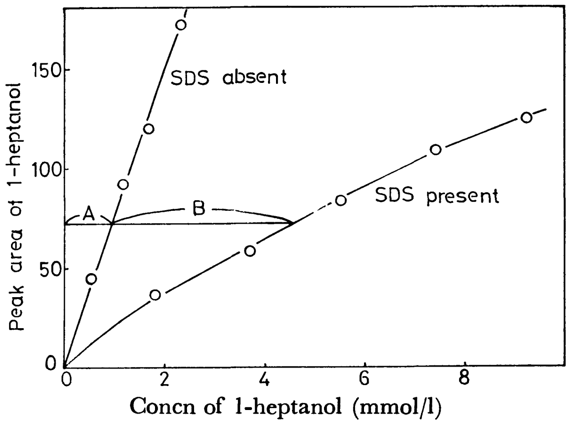

Fig. 2. Calibration curve for the aqueous 1-heptanol solution and typical results for the same solution in the presence of SDS (at 25 °C).
(A): 1-Heptanol fraction remaining in the aqueous phase, (B): 1-heptanol fraction existing in the micellar phase.

of solutions without SDS, while the lower curve shows the data for a similar solution to which a specific amount of SDS was added.

For the purposes of this study, it is unnecessary to know the absolute concentration of the alcohol in the vapor phase, provided that a relationship between the peak area and the compositions of the solutions has once been established. Owing to the self association of the alcohol in the solution, the slopes of the curves decrease as the concentration of the alcohol increases.

The horizontal separation between the two curves at any ordinate represents A and B. B corresponds to the alcohol fraction existing in the micellar phase and A to the alcohol fraction remaining in the aqueous phase. From these curves, the distribution coefficient was calculated from the following equations:

$$Y_a = (18\times A)/1000, \tag{1}$$

$$X_a = B/(S-\mathrm{CMC}(C_a)+B), \tag{2}$$

and

$$K = X_a/Y_a, \tag{3}$$

where Y_a is the molar fraction of the alcohol in the aqueous phase, X_a the molar fraction of the alcohol in the micellar phase, S the total concentration of SDS added, C_a the concentration of the alcohol in the solution, CMC (C_a) the CMC of SDS in the presence of the alcohol, and K the distribution coefficient of the alcohol (the ratio of the concentration in the micellar phase to that in the aqueous phase).

In Fig. 3, the molar fractions of the alcohol (1-heptanol, for example) in the micellar phase are plotted against the mole fractions of the alcohol in the aqueous phase. The amount of SDS was 40 mmol/l. From these results, we evaluated the distribution coefficients using the least-squares method.

The values of K and $\Delta G_p{}^\circ$ calculated from

$$\Delta G_p{}^\circ = -RT\ln K \tag{4}$$

are shown in Table 1.

Some work[1,2] has been reported on the solubilization of organic additives by surfactant micelles in organic solvents. Kaufman[1] has given the solubilization ratios computed for the sodium, cesium, barium, magnesium, and zinc salts of 1,8- dinonyl-4-naphthalene sulfonic acid as a function of methanol, propylamine, and acetic acid in toluene. However, because an accurate value of the CMC was inaccessible for organic solvents containing organic additives, no concentration of micellized surfactant was reported. Therefore, an accurate distribution coefficient could not be obtained, because the total surfactant concentration was employed instead of the micellized surfactant concentration.

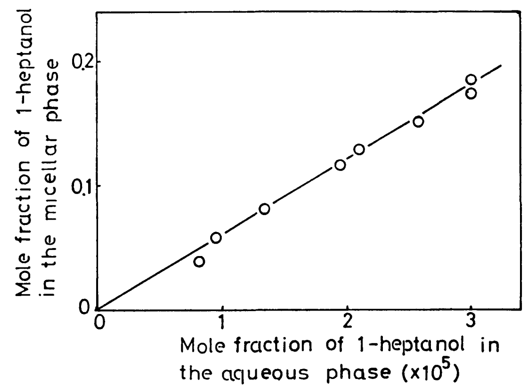

Fig. 3. Distribution of 1-heptanol between the aqueous and the micellar phases (at 25 °C).

Table 1. The distribution coefficients (K) of alcohol between the aqueous and micellar phases and the standard free energy changes of penetration of the alcohols ($\Delta G_p{}^\circ$) (at 25 °C)

	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol
K	3.00×10^2	7.22×10^2	2.25×10^3	6.02×10^3
$\Delta G_p{}^\circ$ (kcal/mol)	−3.38	−3.90	−4.57	−5.16

Table 2. CMC values for SDS in water to which a small amount of alcohol was added (at 25 °C)

Alcohol concn (mmol/l)		CMC (mmol/l)
Pure water		8.01
1-Butanol	43.74	6.96
	116.9	5.32
	204.4	4.18
1-Pentanol	15.41	6.86
	31.15	5.70
	64.45	4.17
1-Hexanol	2.683	7.32
	5.584	6.61
	9.227	5.89
1-Heptanol	0.7354	7.54
	1.918	6.89
	3.178	6.45

Since, in this experiment, accurate values of the CMC using the conductivity method were obtained, as given in Table 2, it is now possible to evaluate the distribution coefficients. Our results for the CMC values both in pure water and in the presence of 1-butanol agree approximately with those of Shirahama and Kashiwabara.[5)]

As shown in Table 1, $\Delta G_p°$ is a linear function of the carbon number of the alcohol. As the carbon number of the alcohol increases, the $\Delta G_p°$ decreases. Similarly, the standard free energy change of micellization, $\Delta G_m°$, decreases as the carbon number of the surfactant increases.[6)] This can be understood since an increase in the carbon number of the alcohol is expected to result in an increased hydrophobic interaction with the surfactant micelles. In other words, penetration of the alcohol into the micellar phase becomes more favorable for an increase in the carbon number of the alcohol. Thus, it is reasonable that this tendency of the $\Delta G_p°$ to decrease parallels the tendency of solubility of the alcohol in water to decrease.

$\Delta G_p°$ is linearly related to the carbon number of the alcohol as follows:

$$\Delta G_p° = -0.60n - 0.95, \tag{5}$$

where n is the carbon number of the alcohol.

The increment of $\Delta G_p°$ per methylene group is -0.60 kcal/mol. Kresheck and Hargraves[6)] have investigated the $\Delta G_m°$ of the sodium octyl-, decyl-, and dodecyl sulfate series and found that the increment of the $\Delta G_m°$ per methylene group was approximately from -0.55 to -0.32 kcal/mol. The absolute value of the increment of the $\Delta G_p°$ per methylene group is a little larger than that of the $\Delta G_m°$ per methylene group.

Mankowich[7)] has reported on the solubilization of Orange OT in aqueous sodium dodecyl benzene sulphonate solutions. In his paper, the standard free energy changes of the solubilization of Orange OT from the non-micellar phase to the micellar phase were reported to be from -5.4 to -5.8 kcal/mol in the range 25—50 °C. In his method, the solubilities of Orange OT both above the CMC and at the CMC were measured. The concentration (mol/l) of Orange OT in the micellar phase was calculated from the solubility of Orange OT above the CMC, and the concentration (mol/l) of Orange OT in the non-micellar phase was calculated from the solubility of Orange OT at the CMC. Then, the standard free energy change was computed from these two concentrations. However, his method is inconvenient for evaluating $\Delta G_p°$, because the solubilities of 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol are much higher than that of Orange OT, and the CMC values are altered in the presence of the alcohols.

Aveyard and Lawrence[8)] and Larsen and Magid[9)] reported the standard enthalpy change of penetration, $\Delta H_p°$, of the alcohol from the aqueous phase to the micellar phase obtained using the calorimetric method. If the $\Delta H_p°$ of their results (1-butanol: 0.5 kcal/mol, 1-pentanol: 0.4 kcal/mol, 1-hexanol: 0.4 kcal/mol) are employed, it is possible to estimate the standard entropy change of penetration, $\Delta S_p°$, of the alcohol using the following equation:

$$\Delta G_p° = \Delta H_p° - T\Delta S_p°. \tag{6}$$

The results are 13.0, 14.4, and 18.7 cal/mol K for 1-butanol, 1-pentanol, and 1-hexanol, respectively. From these results, it may be considered that penetration of the alcohol from the aqueous to the micellar phases exhibits entropy dependence rather than enthalpy dependence. This is similar to the case of micellization of surfactants, namely, penetration of the alcohol from the aqueous to the micellar phases may be attributed to the release of the compact iceberg structure of water molecules around the hydrophobic parts of the alcohol.

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