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The Heat of Solution of Poly(oxyethylene) Dodecyl Ethers in Dodecane

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The heats of mixing of nonionic surfactants, poly(oxyethylene) dodecyl ethers $C_{12}H_{25}(OC_2H_4)_nOH$ ($n=0$—5) with a nonpolar liquid, dodecane were measured directly with a twin conduction microcalorimeter. A discontinuity appears on the heat of mixing *vs.* concentration curve except for $n=0$, the concentration of which decreases exponentially with n. This was regarded as the critical micelle concentration. It was deduced from the heat of solution at infinite dilution, $\Delta_s h_2^\ominus$, that the poly(oxyethylene) chain is in a cyclic state in dodecane due to intramolecular hydrogen bonding of the terminal OH group with an oxygen atom in the chain. In addition, the energy of the solute-solvent interaction, $\Delta_t u_2^\ominus$, was estimated from $\Delta_s h_2^\ominus$ and the heat of evaporation of the solute, $\Delta_e h^0$. As a consequence, the interaction energies of the OH group with nonpolar hydrocarbon are similar, regardless of whether or not the OH group is intramolecularly hydrogen bonded.

The use of nonionic surfactants in nonaqueous solutions has been developed,[1] but the dissolved states are not well understood.[2] In a previous paper,[3] the molecular state of poly(oxyethylene) dodecyl ethers, a typical series of nonionic surfactants were deduced, in the vapor phase, in which the poly(oxyethylene) chains are not extended but in cyclic states due to the intramolecular hydrogen bonding of the terminal OH group with an oxygen atom in the chain. Poly(oxyethylene) chains are also expected to be in cyclic states in a nonpolar liquid, because the vapor phase may be regarded as the most nonpolar medium. Dodecane may be the most desirable solvent in nonpolar liquids for poly(oxyethylene) dodecyl ethers, because the hydrophobic dodecyl group cannot be discerned from the solvent dodecane. In the present paper, the dissolved states of nonionic surfactant molecules in nonpolar liquids are elucidated by calorimetrically determining the heats of mixing of poly(oxyethylene) dodecyl ethers with dodecane.

Experimental

Poly(oxyethylene) dodecyl ethers, $C_{12}H_{25}(OC_2H_4)_nOH$ ($n=$ 1, 2, 3, 4, and 5), and 1-dodecanol (corresponding to $n=0$) were kindly provided by Nihon Surfactant Kogyo K. K., which have the same order of purity as those used in a previous paper.[3] The solvent was prepared by distilling G. R. grade dodecane (Wako Junyaku Co.) after drying over a sodium wire for one week.

The heats of mixing were measured with a twin conduction microcalorimeter using a mixing device for ampoules (Oyodenki Kenkyujo Co., CM-502).[4] The temperature of the cells was maintained at 29.00±0.05 °C by circulating thermostatically-controlled water around the apparatus installed in an air thermostat. A small glass ampoule containing a weighed amount of solute was immersed in 25 cm^3 of dodecane in the cell. After the establishment of thermal equilibrium, the ampoule was crushed and the liquid was stirred for 1 min. The difference in temperature between the two cells, one ampoule in either cell being empty, was recorded. This difference is due to the liberation or absorption of heat which accompanies the mixing of the solute and dodecane. The heat was estimated similarly using the method described by Murakami and Fujishiro.[5]

Results and Discussion

Critical Micelle Concentration. When n_1 mol of solvent and n_2 mol of solute are mixed, the heat of mixing, ΔH, is given by

$$\Delta H = n_1\,\Delta h_1 + n_2\,\Delta h_2, \tag{1}$$

where $\Delta h_i = h_i{}^0 - h_i$ and h_i and $h_i{}^0$ are the partial molar enthalpy in the solution and the molar enthalpy in the pure state, respectively, of component i. Then,

$$\Delta h_2 = \left(\frac{\partial \Delta H}{\partial n_2}\right)_{T,p,n_1}, \tag{2}$$

where T is the absolute temperature and p the pressure. The relations between ΔH and n_2 measured for poly(oxyethylene) dodecyl ethers with dodecane are shown in Figs. 1—6, when the amount of solvent dodecane is 25 cm^3. Since T, p, and n_1 are maintained constant under the present experimental conditions, the tangent at any point on the curves in Figs. 1—6 is equal to Δh_2 at that concentration.

For 1-dodecanol ($n=0$), ΔH is proportional to n_2 and, therefore, Δh_2 is constant over the measurement range, as shown in Fig. 1. This means that such concentrations

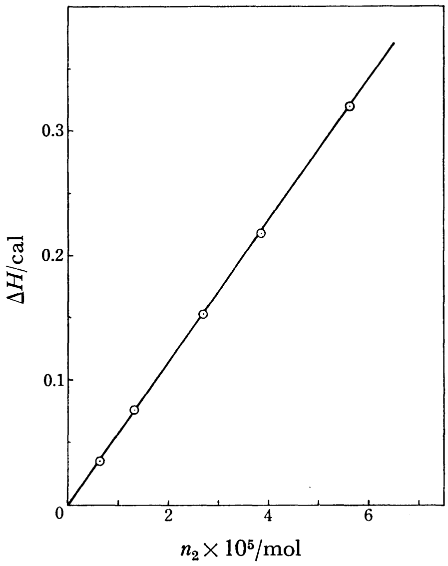

Fig. 1. Heat of mixing ΔH of n_2 mol of 1-dodecanol with 25 cm^3 of dodecane at 29 °C.

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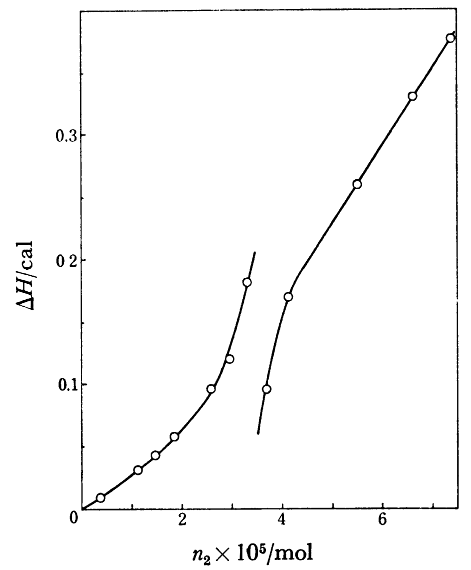

Fig. 2. Heat of mixing ΔH of n_2 mol of $C_{12}H_{25}OC_2H_4OH$ with 25 cm^3 of dodecane at 29 °C.

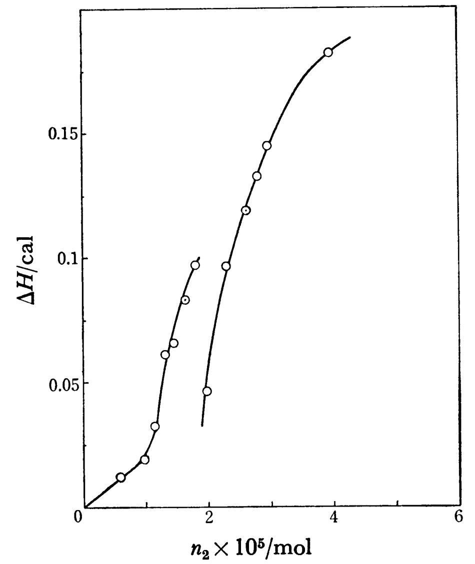

Fig. 3. Heat of mixing ΔH of n_2 mol of $C_{12}H_{25}(OC_2H_4)_2$-OH with 25 cm^3 of dodecane at 29 °C.

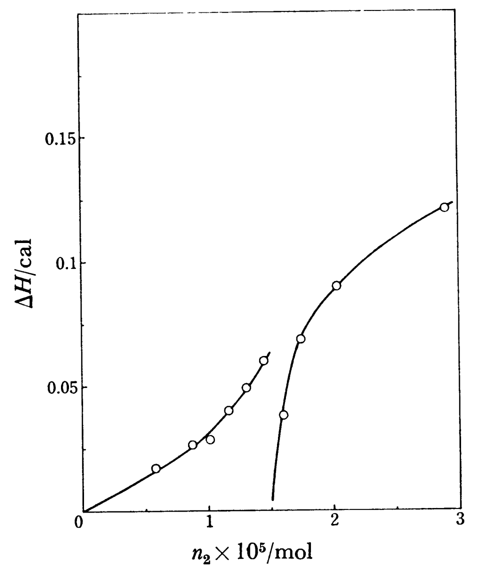

Fig. 4. Heat of mixing ΔH of n_2 mol of $C_{12}H_{25}(OC_2H_4)_3$-OH with 25 cm^3 of dodecane at 29 °C.

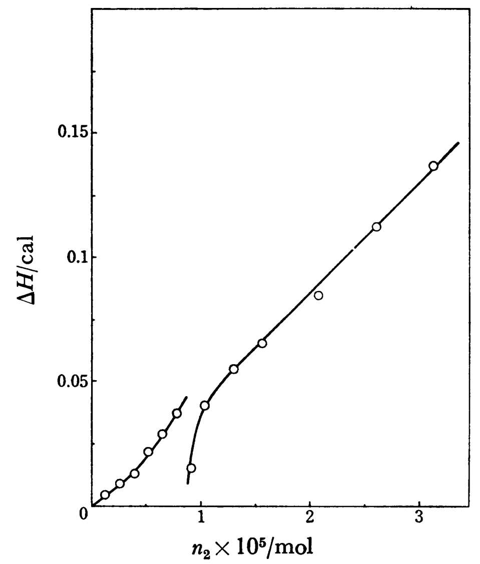

Fig. 5. Heat of mixing ΔH of n_2 mol of $C_{12}H_{25}(OC_2H_4)_4$-OH with 25 cm^3 of dodecane at 29 °C.

are dilute enough so that the solutions can be regarded as ideal dilute solutions. Thus, the value of Δh_2 estimated from the inclination is equal to the heat of solution at infinite dilution, $\Delta_s h_2^{\ominus}$.

For $n=1$—5, ΔH is not proportional to n_2 and Δh_2 is not constant even in the same concentration region where the solution of 1-dodecanol is ideally dilute, as shown in Figs. 2—6. In such a concentration region, the solution not only deviates from the condition of an ideal dilute solution, but also there appears a discontinuous point on the curve of ΔH *vs.* n_2, where ΔH decreases abruptly with increasing concentration, regardless of n. Such discontinuous phenomena have been found by Hutchinson *et al.*[6] for aqueous sodium alkyl sulfates solutions. They have shown that the discontinuity concentration, DC, is in good agreement with the critical micelle concentration, CMC. Then, the observed DC is also assumed to correspond to the CMC of poly(oxyethylene) dodecyl ethers in dodecane, the values of which are listed in Table 1.

The plot of log DC was found to decrease linearly with n, the number of oxyethylene units in a poly(oxyethylene) chain, as shown in Fig. 7. Such a relationship resembles those between CMC for aqueous solutions and the number of methylene groups in a hydrophobic alkyl chain of a homologous series of surfactants.[7] According to the theory of micellization,[8] the linear relation means that each methylene group of the homologs makes an equal energy contribution, when an alkyl group is transferred from the aqueous solution into a micelle. The linear relation between log DC and n, therefore, confirms the assumption that the DC corre-

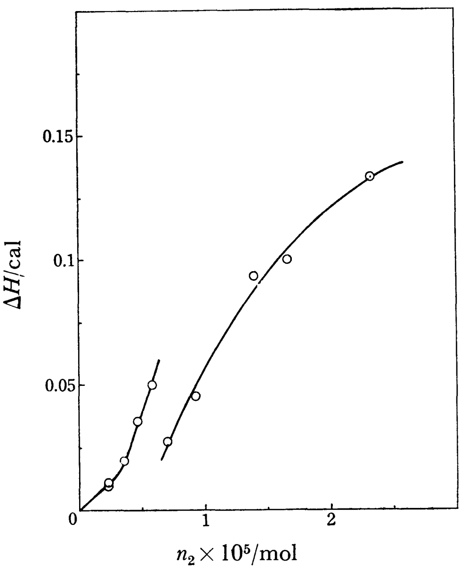

Fig. 6. Heat of mixing ΔH of n_2 mol of $C_{12}H_{25}(OC_2H_4)_5$-OH with 25 cm^3 of dodecane at 29 °C.

TABLE 1. CRITICAL MICELLE CONCENTRATIONS CMC, HEATS OF MICELLIZATION $\Delta_m h_2$, HEATS OF SOLUTION AT INFINITE DILUTION $\Delta_s h_2^{\ominus}$, AND INTERACTION ENERGIES WITH SOLVENT $\Delta_i u_2^{\ominus}$ OF $C_{12}H_{25}(OC_2H_4)_nOH$ IN DODECANE AT 29 °C

n	CMC mol m^{-3}	$\Delta_m h_2$ kcal mol^{-1}	$\Delta_s h_2^{\ominus}$ kcal mol^{-1}	$\Delta_i u_2^{\ominus}$ kcal mol^{-1}
0			5.6	−8.9
1	1.40	5.0	2.3	−14.8
2	0.75	4.0	1.5	−17.6
3	0.60	3.2	2.6	−22.2
4	0.35	4.0	3.2	−27.2
5	0.26	6.0	4.1	−31.9

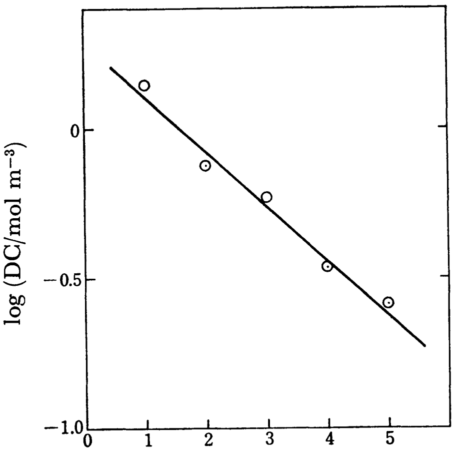

Fig. 7. The relationship between discontinuity concentration DC and degree of polymerization n of $C_{12}H_{25}$-$(OC_2H_4)_nOH$ in dodecane at 29 °C.

sponds to the CMC. In addition, the state of an oxyethylene unit in the lipophobic chain would not be different depending whether it exists in micelle or in dodecane.

Hutchinson *et al.* have also shown that the discontinuous change in the heat of mixing per mol of solute at the CMC corresponds to the heat of micellization.[6] The values of the heat of micellization, which are listed in Table 1, were estimated by dividing the abrupt changes in ΔH at the DC by n_2. They exhibit no tendency to increase linearly with n, which is expected from the linear relation between log CMC and n. These may not always reflect equilibrium properties, because of the complexity of the dissolving process of the surfactant, especially around the CMC, involving the alternate formation and destruction of micelles. Actually, both endothermic and exothermic parts were often found in a chart at such concentrations. Even if the heat of micellization cannot always be obtained correctly, the measurement of the heat of mixting is recommended as the preferred method for determining the CMC, especially for organic solutions.

Heat of Solution at Infinite Dilution. From Eq. 2, the heat of solution at infinite dilution, $\Delta_s h_2^{\ominus}$, is expressed by

$$\Delta_s h_2^{\ominus} = \lim_{n_1 \to 0} \Delta h_2 = \lim_{n_1 \to 0} \left(\frac{\partial \Delta H}{\partial n_2} \right)_{T,p,n_1} . \quad (3)$$

Then, $\Delta_s h_2^{\ominus}$ can be obtained from the initial slope of the straight lines passing through the origin in Figs. 1—6. The values thus estimated are listed in Table 1. It was found that $\Delta_s h_2^{\ominus}$ increases linearly with n in the range 2—5, as shown in Fig. 8. This means that all oxyethylene units in a poly(oxyethylene) chain of $n=$ 2—5 are in equal states in dodecane, as has been described previously for the heats of evaporation of these compounds.[3] From the slope of the line, it requires *ca.* 0.8 kcal mol^{-1} for the oxyethylene unit to transfer a poly(oxyethylene) dodecyl ether from the pure liquid state to the dodecane solution for $n=2$—5.

The straight line in Fig. 8 passes through the origin, which is *ca.* 5.6 kcal mol^{-1} less than the value for 1-dodecanol ($n=0$). These phenomena suggest that the terminal OH group of the poly(oxyethylene) chain is

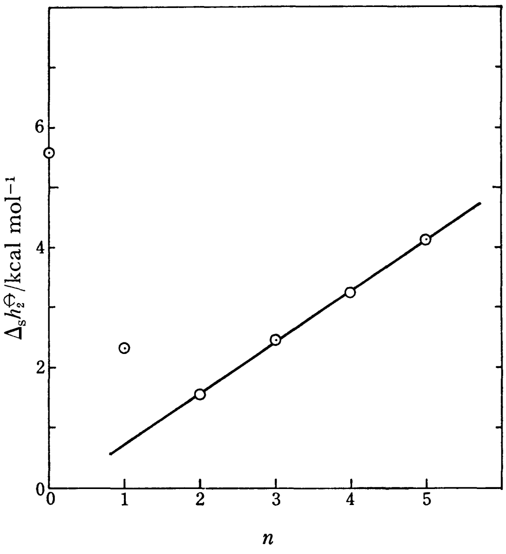

Fig. 8. Heat of solution at infinite dilution $\Delta_s h_2^{\ominus}$ *vs.* n plot for $C_{12}H_{25}(OC_2H_4)_nOH$ in dodecane at 29 °C.

not in the same state as the alcoholic OH group dissolved in dodecane, because both the alcoholic and terminal OH groups in their pure states are considered not to be so different energetically but to interact with one of the neighboring molecules due to intermolecular hydrogen bonding. As already deduced for the vapor phase,[3] for the nonpolar dodecane solution the terminal OH group of the poly(oxyethylene) chain is believed to interact with an oxygen atom in the chain and thus the chain is in a cyclic state due to intramolecular hydrogen bonding. A signal due to intramolecular hydrogen bonding has been observed by means of infrared spectroscopy for similar substances, the monomer and dimer of ethylene glycol and their monomethyl ethers, in nonpolar carbon tetrachloride.[9,10] Because an energy of 5.6 kcal mol^{-1}, the difference between $\Delta_s h_2^{\ominus}$ for 1-dodecanol and the straight line for $n=2$—5, corresponds exactly to that of 1 mol of a hydrogen bond[11] (although this is slightly less than the corresponding value for evaporation, 6.2 kcal mol^{-1}), almost all the molecules would be in cyclic states due to intramolecular hydrogen bonding.

The value of $\Delta_s h_2^{\ominus}$ for $n=1$ is *ca.* 1.5 kcal mol^{-1} higher than that expected from the linear relation for $n=2$—5. This increase in energy can be interpreted from the fact that the molecule of $n=1$ can only form a 5-membered ring, for intramolecular hydrogen bonding. The 5-membered ring is expected to have a higher energy for hydrogen bonding than 8-membered or larger rings,[12] because it has been found that the infrared absorption-band shift of the OH group due to the 8-membered ring is appreciably larger than that due to the 5-membered ring.[10]

Solute-solvent Interaction. The heat of condensation of 1 mol of solute from the vapor phase to solution at infinite dilution, $\Delta_i h_2^{\ominus}$, may be expressed in terms of the heat of evapration, $\Delta_e h_2^0$, and the heat of solution at infinite dilution, $\Delta_s h_2^{\ominus}$, as

$$\Delta_i h_2^{\ominus} = \Delta_s h_2^{\ominus} - \Delta_e h_2^0, \tag{4}$$

according to the Born-Harber cycle:

$$\begin{tikzcd}
 & \text{solute vapor} \arrow[dl, "\Delta_i h_2^{\ominus}"'] & \\
\text{solution} & & \text{solute liquid.} \arrow[ll, "\Delta_s h_2^{\ominus}"] \arrow[ul, "\Delta_e h_2^0"']
\end{tikzcd}$$

When the interaction between solute molecules is neglected in the vapor phase, the interaction energy of the solute with the surrounding solvent molecules in the solution, $\Delta_i u_2^{\ominus}$, can be expressed as

$$\Delta_i u_2^{\ominus} = \Delta_i h_2^{\ominus} + RT, \tag{5}$$

where R is the gas constant. $\Delta_i u_2^{\ominus}$ is considered to be the most suitable measure of the affinity for a given solute and solvent combination. The values of $\Delta_i u_2^{\ominus}$ for poly(oxyethylene) dodecyl ethers in dodecane listed in Table 1 were calculated from the data for $\Delta_s h_2^{\ominus}$ in the present paper and those for $\Delta_e h_2^0$ from a previous paper.[3] The relationship between $\Delta_i u_2^{\ominus}$ and n is shown in Fig. 9. A linear relation holds not only for $n=2$—5, as in Fig. 8, but also for $n=0$ for which the value of $\Delta_i u_2^{\ominus}$ falls near the straight line. This reveals that the interaction of an alcoholic OH group with dodecane is indistinguishable from that of the terminal OH group of the poly(oxyethylene) chain for $n=2$—5. Thus, it is concluded that the energy of interaction of the OH group with dodecane does not depend on whether it is free or intramolecularly bonded to an ether oxygen atom. If this is true, the upward deviation of $n=1$ from the straight line can be ascribed to changes in the energy of the intramolecular hydrogen bond in the 5-membered ring and/or in the rate for the 5-membered ring to free an OH group, when the molecules are transferred from the vapor phase to the dodecane solution. The slope of the straight line gives an energy of *ca.* −4.7 kcal mol^{-1}, which is the interaction energy of an oxyethylene unit with dodecane. Since the cohesive energy of a hydrocarbon is estimated to be *ca.* −0.8 kcal mol^{-1} of the methylene group,[13] the interaction energy of an ether oxygen atom with dodecane results in an energy of *ca.* −3.1 kcal mol^{-1}, provided that the additivity holds for the interaction energy in oxyethylene unit.

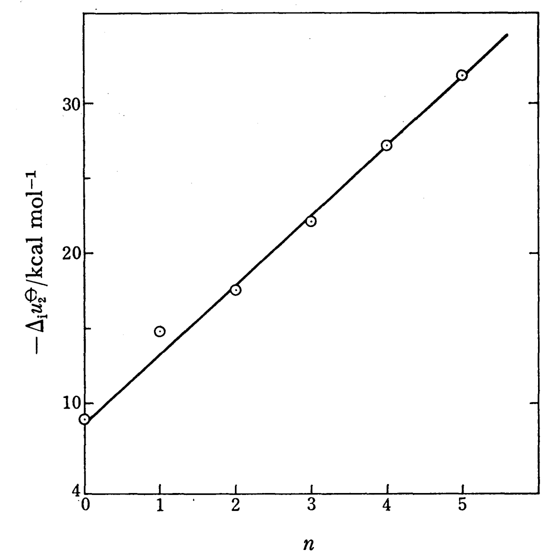

Fig. 9. Intraction energy with dodecane $\Delta_i u_2^{\ominus}$ *vs.* n plot for $C_{12}H_{25}(OC_2H_4)_nOH$ at 29 °C.

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