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Heat of Evaporation of Polyoxyethylene Dodecyl Ethers

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Synopsis. The heat of evaporation has been measured by the vapor pressure method for polyoxyethylene dodecyl ethers, $C_{12}H_{25}(OC_2H_4)_nOH$ ($n=0$, 1, 2, 3, and 4). It has been deduced that the polyoxyethylene chain is in a cyclic state in the vapor phase due to the intramolecular hydrogen bonding of the terminal OH group with an oxygen atom in the chain.

Measurements of heat of solution have been carried out for the study of the dissolved state of surfactant in solution.[1—4] In order to deduce the dissolved state energetically from the heat of solution, we should know the intermolecular cohesive energy of the solute in a pure liquid or solid state. The measurement of heat of evaporation is useful for obtaining the cohesive energy of a pure liquid, since cohesion in the vapor phase is negligible below the normal pressure. We have tried to obtain the relation between the heat of evaporation and degree of polymerization of the polyoxyethylene chain in polyoxyethylene dodecyl ethers, typical nonionic surfactants.

Polyoxyethylene dodecyl ethers, $C_{12}H_{25}(OC_2H_4)_nOH$ ($n=0$, 1, 2, 3, and 4), were obtained from Nippon Surfactant Industry Co., dodecanol corresponding to $n=0$. Each sample has a purity above 99% and no distribution of polymerization in the hydrophilic part as verified by gas chromatography.

The heat of evaporation was obtained by the vapor pressure method. The apparatus used was a glass semimicrodistiller (Shibata Glass Co.) with a large gas tank inserted in the vacuum line between the distiller and the pump to eliminate the fluctuation of pressure in the apparatus. The pressure was kept constant, the liquid in the bottle was heated gently with an electric heater, and the temperature was recorded in both vapor and liquid phases. The temperature of liquid phase had slowly risen, several hours after which that of vapor phase rose steeply and remained at a certain temperature. The constant temperature of vapor phase was regarded to be the boiling point corresponding to the pressure.

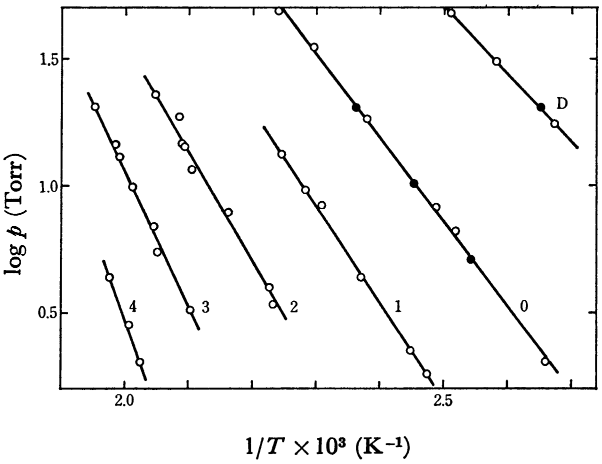

Fig. 1. The variation of vapor pressure with temperature for $C_{12}H_{25}(OC_2H_4)_nOH$ ($n=0$—4) and dodecane (D).

Table 1. Molar heats of evaporation ($\Delta_e h$) of $C_{12}H_{25}(OC_2H_4)_nOH$ ($n=0$—4) and dodecane (D)

n	$\Delta_e h$ (kcal/mol)
0	15.1
1	17.7
2	19.7
3	25.3
4	31.0
D	12.7

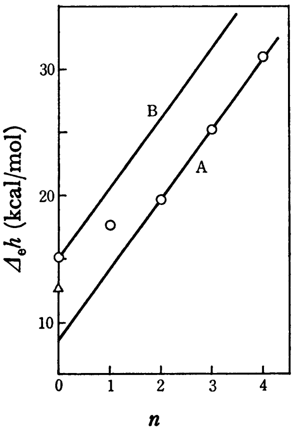

Fig. 2. The relationship between molar heat of evaporation ($\Delta_e h$) and degree of polymerization of $C_{12}H_{25}(OC_2H_4)_nOH$.
△: the value of dodecane

The results obtained in the pressure range 2—30 Torr are shown in Fig. 1 for polyoxyethylene dodecyl ethers of the degree of polymerization n up to 4 and dodecane. For dodecanol ($n=0$) and dodecane, the observed values (open circle) agree well with the values in the literature (filled circle).[5] If the molar volume of the liquid phase is neglected in comparison with that of the vapor, and if the vapor phase is assumed to behave as a perfect gas and the molar heat of evaporation $\Delta_e h$ is independent of temperature, then the equation of Clausius-Clapeyron can be written as[6]

$$\ln p = -\frac{\Delta_e h}{RT} + C \tag{1}$$

where p is the vapor pressure at the absolute temperature T, R the gas constant, and C a constant independent of temperature. The fact that the plots of $\log p$ *vs.* $1/T$ (Fig. 1) lie in a straight line for every sample indicates that the molar heat of evaporation is independent of temperature in the range of measurements.

The molar heats of evaporation obtained from the inclinations of the straight lines are listed in Table 1. The relationship between the molar heat of evaporation $\Delta_e h$ and the degree of polymerization n of the polyoxyethylene chain is shown in Fig. 2. $\Delta_e h$ increases linearly with n in the range 2—4, as shown by the straight line A. Its inclination gives 5.6 kcal/mol of an oxyethylene unit, which corresponds roughly to the molar heat of evaporation of dimethyl ether, 5.1 kcal/mol.[7] This means that the situation does not differ among the molecules in the range, except in the number of oxyethylene units. The extrapolated value of line A to $n=0$, however, is less than the molar heat of evaporation of the dodecanol, which corresponds to $n=0$, by *ca.* 6.6 kcal/mol. This means that the terminal OH groups of polyoxyethylene chain is not in the same state as in the alcoholic OH group. The terminal OH group may be considered to be intramolecular hydrogen bonded with an oxygen atom in the polyoxyethylene chain in the vapor phase, because the exothermic 6.6 kcal/mol corresponds to the energy of a hydrogen bond.[8] It may be reasonable to consider that the polyoxyethylene chain in the liquid state is in a linearly extended state, because it is more probable for the terminal OH group to interact with the neighboring molecule, and the extrapolated value is less than the molar heat of evaporation of dodecane (triangle in Fig. 2).

The molar heat of evaporation of $n=1$ is higher than line A by *ca.* 3.5 kcal/mol, which can be interpreted by the loss of energy of the intramolecular hydrogen bond since the molecule can form a 5-membered ring only. The fact also confirms the concept that the polyoxyethylene chain is cyclic in the vapor phase owing to the intramolecular hydrogen bonding.

If a molecule were to be linearly extended with no intramolecular hydrogen bond as in the liquid phase, the value of $\Delta_e h$ would fall on a straight line B parallel to line A and pass through the value of dodecanol. Thus, the molar cohesive energies of these liquids are equal to the values corresponding to line B minus RT, which is the work of volume expansion at the evaporation of 1 mol of liquid.

References

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