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Partition Coefficients of Alkanols and Polyoxyethylene Alkyl Ethers in the Dodecane–Water System at 25 °C

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The partition coefficients of normal alkanols (R_mOH, $m=2$ to 6) and a number of polyoxyethylene normal alkyl ethers (R_mE_nOH, $n=1,2$ $m=2$ to 5; $n=3,4$ $m=4,5$) in the dodecane–water system have been determined at a high dilution at 25 °C. From the finding that the standard free energies of the transfer of the solutes from water to the dodecane phase show a linear relation with the number of methylene and oxyethylene groups, the contribution of the groups to the free energy was obtained as -0.858 for alkanols and -0.808 kcal/mol methylene group for ethers, and 0.655 kcal/mol oxyethylene group respectively. Extrapolation to zero oxyethylene in the linear relationship for the normal alkylethers gave standard free energies of transfer less than those for normal alkanols with the same alkyl chain length. Thus, the alkanol is more hydrophilic than the hypothetical "ether" with no oxyethylene group. The difference in the free energies is discussed from the viewpoint of intramolecular hydrogen-bond formation in the polyoxyethylene chain in the dodecane phase.

In spite of the importance and usefulness of the data of the partition coefficient for amphiphiles between water and the nonpolar phase for the study of colloid chemistry, only a few systematic investigations[1,2] have ever been made. The process of the transfer of amphiphiles from an aqueous to a nonpolar phase seems of much interest in many respects. Davies[3] proposed a relation of the hydrophile-lipophile balance (HLB) with the partition coefficenet, and further estimated the "group number". The solubilization and micelle formation are regarded as a partition process, especially in the treatment by the phase-separation model for micell formation.[4] The solubilities of alkanols[5] and hydrocarbons[6] in water are also a measure of a similar process of transfer.

The standard free energy of transfer obtained from the partition coefficients can be applied to such transfer processes in colloid chemistry, and the comparison of the free energies for different processes yields useful information about the environment around a solute molecule. It is well known that the physicochemical properties of the alkyl[7] or polyoxyethylene derivatives[8] show a linear dependence on the number of methylene or oxyethylene groups. In the present investigation, the contribution of each group contained in the solute molecules to the standard free-energy changes of transfer was tentatively estimated. Dodecane is chosen as the nonpolar phase because of its low mutual solubility with water as well as because of the possibility of disregarding a specific interaction with solute molecules. Normal alkanols and polyoxyethylene alkyl ethers are chosen for the solutes; the former are simple amphiphilic compounds, and the later, model compounds for nonionic surfactants.

Experimental

Materials. The normal alkanols (R_mOH, $m=2$ to 6) and some ($m=2$ to 4, $n=1,2$) of the polyoxyethylene normal alkyl ethers (R_mE_nOH) used as solutes were commercially available (Tolyo Kasei, G.R. and E.P. grade). They were dehydrated and distilled prior to use. The other ethers ($m=4$, $n=3$, 4; $m=5$, $n=1$ to 4) were prepared by the Williamson reaction of the corresponding glycol and alkyl bromide.[9] Their purification was carried out by the following procedure. After the addition of a large amount of water to the reaction mixture, the ether was repeatedly extracted with a small amount of hexane. Each hexane fraction was analyzed by g-l chromatography, whereupon diether was found to be rich in the earlier fractions, and glycol, in the later ones. The middle fractions, being rich in monoether, were collected and evaporated. The extract was distilled to obtain monoether under reduced pressure. The purities of the compounds were confirmed to be above 98% by g-l chromatography. The dodecane (Tokyo Kasei, G. R. grade) was first distilled and used once as a nonpolar phase for the measurement of the partition coefficient; it was then repeatedly washed with an amount of water sufficiently large to remove a solute, and used in the next run.

Procedure. Aqueous solutions of a desired solute were prepared at concentration of *ca.* 10^{-3} to 10^{-2} mol/kg. A sample prepared from a known weight of the aqueous solution and of dodecane was maintained for a day at room temperature; then the sample was stirred in a thermostat and kept at 25±0.05 °C for about seven hours. This operation was performed for at least six aqueous solutions with different concentrations of a given solute. Then the sample was allowed to stand and a quantity of the aqueous phase was pipetted out. The solute concentration of the aqueous phase in equilibrium was determined at 25±0.005 °C by using a Ostwald-type viscometer the flow time of which was *ca.* 9 min. The solute concentration in the dodecane phase was obtained from the material balance relation.

Results and Discussion

Figure 1 shows the logarithmic relations between the solute concentrations in the dodecane and water phases for R_mE_nOH ($m=5$, $n=2$ to 4) as illustrative examples. All the plots dropped on a straight line, with a unity slope for each solute; therefore, we can conclude that the solute is dissolved in the monomeric state in each phase, as may be seen from the spectroscopic data for alkanols,[1] and the partition coefficient does not depend on the concentration within the region studied.

The partition coefficient is expressed as:

$$K_x = x_o/x_w \qquad (1)$$

where x_o and x_w are the mole fractions of solute in

TABLE 1. PARTITION COEFFICIENTS IN *n* DODECANE-WATER SYSTEM AT 25 °C

Compound	K_x	Compound	K_x	Compound	K_x
R_2OH	$8.67(\pm0.09)\times10^{-2}$	R_2E_1OH	$9.95(\pm0.58)\times10^{-2}$	R_2E_2OH	$3.30(\pm0.04)\times10^{-2}$
R_3OH	$3.74(\pm0.10)\times10^{-1}$	R_3E_1OH	$5.94(\pm0.48)\times10^{-1}$	R_3E_2OH	$1.88(\pm0.08)\times10^{-1}$
R_4OH	$1.70(\pm0.07$	R_4E_1OH	$2.37(\pm0.10)$	R_4E_2OH	$8.56(\pm0.32)\times10^{-1}$
R_5OH	$7.24(\pm0.11)$	R_5E_1OH	$9.38(\pm0.23)$	R_5E_2OH	$3.16(\pm0.01)$
R_6OH	$2.74(\pm0.16)\times10$				
		R_4E_3OH	$2.84(\pm0.06)\times10^{-1}$	R_4E_4OH	$9.40(\pm0.11)\times10^{-2}$
		R_5E_3OH	$1.06(\pm0.006)$	R_5E_4OH	$3.61(\pm0.08)\times10^{-1}$

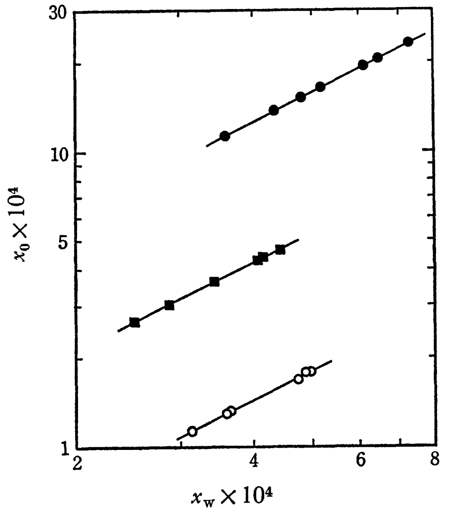

Fig. 1. The relation between the solute concentrations in *n*-dodecane and water phase.
●: R_5E_2OH, ■: R_5E_3OH, ○: R_5E_4OH.

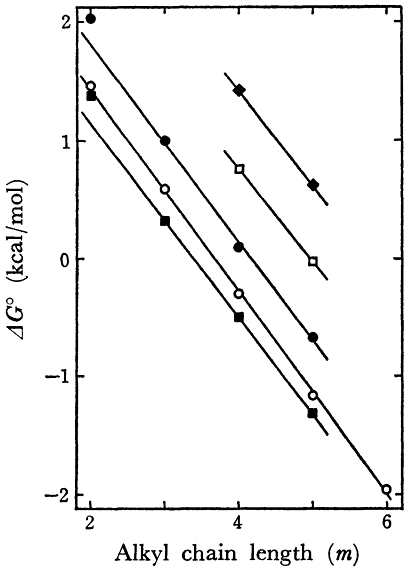

Fig. 2. The dependence of ΔG° on the alkyl chain length (*m*).
○: R_mOH, ■: R_mE_1OH, ●: R_mE_2OH,
□: R_mE_3OH, ◆: R_mE_4OH.

dodecan and in the water phase, respectively. The partition coefficients for each solute were determined for at least six samples with different concentrations of the solute; the mean values for a given solute are listed in Table 1, along with their standard deviations. The expression of the partition coefficient in the mole fraction is convenient not only for the thermodynamic discussion of the transfer phenomena between different phases, but also for indicating the independence of the kind of nonpolar-phase substances (normal hydrocarbons containing different chain lengths), although the partition coefficient in molarity depends on the kind of nonpolar-phase substance, as may be supposed from the results for alkanols reported by Aveyard and Mitchell.[1]

The standard free energy of the transfer of a solute from the water to the dodecane phase can be calculated from the K_x value assuming ideality, because it is a value at a high dilution;

$$\Delta G^\circ = -RT\ln K_x \qquad (2)$$

The ΔG° value is plotted against the chain length in the alkyl group in Fig. 2, and the plot for a homologous series shows a linear relation except for R_mE_nOH with $m=2$. We can now assume that ΔG° is divisible into independent additive contributions from each group constituting the solute molecule:

$$\Delta G^\circ = \Delta G^\circ_{CH_2}(m-1) + \Delta G^\circ_{CH_3} + \Delta G^\circ_g \qquad (3)$$

where $\Delta G^\circ_{CH_2}$, $\Delta G^\circ_{CH_3}$, and ΔG°_g are the contributions from the methylene, terminal methyl, and polar groups respectively. A least-squares treatment gives the $\Delta G^\circ_{CH_2}$ and $(\Delta G^\circ_{CH_3}+\Delta G^\circ_g)$, as may be seen for $\Delta G^\circ_{CH_2}$ in Table 2. The $\Delta G^\circ_{CH_2}$ values are −0.858 and −0.808 kcal/mol for R_mOH and R_mE_nOH respectively in the table; they are numerically comparable with the corresponding values for alkyl derivatives in the related processes.[5–7] The standard free energy of the transfer of one mole of the methylene group from water to micelle or to an air-water interface is about −0.65 kcal/mol, a little less negative than the present value.

The estimation of ΔG°_g in Eq. (3) requires $\Delta G^\circ_{CH_3}$;

TABLE 2. STANDARD FREE ENERGY CONTRIBUTIONS FROM METHYLENE AND POLAR GROUPS

Compound	m[a)]	$-\Delta G^\circ_{CH_2}$ (kcal/mol)	ΔG°_g (kcal/mol)
R_mOH	2—6	0.858	4.39
R_mE_1OH	3—5	0.818	4.05
R_mE_2OH	3—5	0.837	4.75
R_mE_3OH	4—5	0.781	5.19
R_mE_4OH	4—5	0.799	5.89
		0.808[b)]	

a) Range of alkyl chain length for least-squres treatment. b) Mean value of $\Delta G^\circ_{CH_2}$ for ethers alone.

therefore, the value is estimated as −2.10 kcal/mol from the available data for the solubility[6] of liquid alkanes (m=5 to 8) in water at 25 °C, from the assumption of an additive contribution[11] such as:

$$\Delta G^\circ = \Delta G^\circ_{\rm CH_2}(m-2) + 2\Delta G^\circ_{\rm CH_3} \tag{4}$$

Assuming that, in the present solutes, the terminal methyl group in the alkyl group makes the same contribution to ΔG° as that in the normal alkanes, the $\Delta G^\circ_{\rm g}$ values can be calculated by means of Eq. (3); they are tabulated in Table 2. Those are not an intrinsic value for the polar group itself, but an apparent value (extrapolated value) of the standard free energy of the transfer of the polar group from water to dodecane, for the property of the methylene group proximal to the polar group may differ from that of the separate one, as may be seen from Fig. 2. The value is, however, useful, considering the hydrophilic properties of whole of the solute molecule, which consists of a long alkyl chain and a polar group. The $\Delta G^\circ_{\rm g}$ value for $\rm R_{\it m}OH$, *i.e.*, for the OH group (denoted by $\Delta G^\circ_{\rm OH}$), is 4.39 kcal/mol; this value is comparable to the standard free energy of transfer, about 4 kcal/mol, of water from liquid water into hydrocarbons obtained from the data for solubility of water in hydrocarbons.[12] This implies that the most important factor govering $\Delta G^\circ_{\rm OH}$ is the dehydration of the group.

The relation between ΔG° for $\rm R_{\it m}E_{\it n}OH$ and the number of the oxyethylene group in the ethers is shown in Fig. 3, together with $\Delta G_{\rm g}^\circ$; the ΔG° value for $\rm R_{\it m}OH$ is also plotted at n=0 for comparison. It is evident from the linear relation for each ether containing the same alkyl-chain length that the contribution of an oxyethylene group to ΔG°, denoted by $\Delta G^\circ_{\rm E}$, is additive. A similar relation is also seen for $\Delta G_{\rm g}^\circ$ in Fig. 3. Therefore, Eq. (3) may be rewritten as follows for $\rm R_{\it m}E_{\it n}OH$:

$$\Delta G^\circ = \Delta G^\circ_{\rm CH_2}(m-1) + \Delta G^\circ_{\rm CH_3} + \Delta G^\circ_{\rm E}n + \Delta G^\circ_{\langle\rm OH\rangle} \tag{5}$$

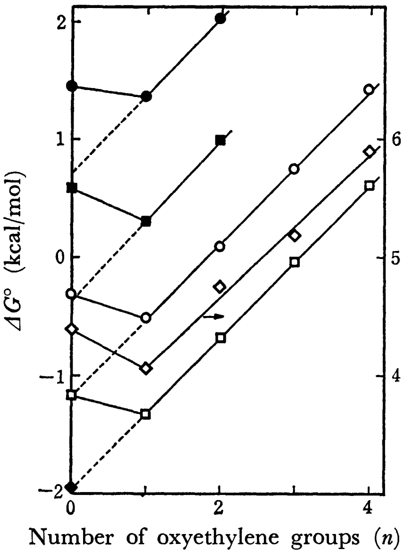

Fig. 3. The dependence of ΔG° and $\Delta G_{\rm g}^\circ$ on the number of oxyethylene groups (n), ΔG° for $\rm R_{\it m}OH$ is plotted at n=0.
●: $\rm R_2E_{\it n}OH$, ■: $\rm R_3E_{\it n}OH$, ○: $\rm R_4E_{\it n}OH$,
□: $\rm R_5E_{\it n}OH$, ◇: $\Delta G_{\rm g}^\circ$, ◆: $\rm R_6OH$.
For dotted line, see in text.

TABLE 3. VALUES OF $\Delta G^\circ_{\rm E}$, $\Delta G^\circ_{\langle\rm ROH\rangle}$, AND $\Delta G^\circ_{\rm HB}$

Compound	n[a]	$\Delta G^\circ_{\rm E}$ (kcal/mol)	$\Delta G^\circ_{\langle\rm ROH\rangle}$ (kcal/mol)	$-\Delta G^\circ_{\rm HB}$ (kcal/mol)
$\rm R_2E_{\it n}OH$	1—2	0.654	0.714	0.736
$\rm R_3E_{\it n}OH$	1—2	0.682	−0.373	0.956
$\rm R_4E_{\it n}OH$	1—4	0.639	−1.17	0.852
$\rm R_5E_{\it n}OH$	1—4	0.644	−1.97	0.797
mean value		0.655		0.835
polar group[b]	1—4	0.596	3.48	0.91

a) Range the number of oxyethylene groups for least-squares treatment. b) Obtained from $\Delta G^\circ_{\rm g}$.

where $\Delta G^\circ_{\langle\rm OH\rangle}$ is the apparent contribution of the OH group in the ether molecule to the ΔG°, distinct from the contribution of that in $\rm R_{\it m}OH$. The $\Delta G^\circ_{\rm E}$ listed in Table 3 can be obtained by the least-squares treatment of $\rm R_{\it m}E_{\it n}OH$. The mean value for all of the ethers studied is 0.655 kcal/mol, which is comparable with the value of 0.60 kcal/mol obtained from the partition coefficients of homogeneous octylphenoxypolyethoxyethanols in the *iso*-octane–water system investigated by Crook *et al.*[2] The positive value of $\Delta G^\circ_{\rm E}$ may result from a positive change in the enthalpy of dehydration exceeding a positive change in entropy; this shows that the oxyethylene group behaves as a hydrophilic group, as is usual for nonionic surfactants, *e.g.*, the CMC of a surfactant, polyoxyethylene alkyl ether, increases with the increase in the number of the groups.[8]

The infercept of the line for $\rm R_{\it m}E_{\it n}OH$ in Fig. 3 is more negative than the ΔG° for $\rm R_{\it m}OH$ with the same alkyl-chain length. This means that the OH group situated in the terminal portion of the polyoxyethylene chain is not in the same state as that in $\rm R_{\it m}OH$; *i.e.*, the former is less hydrophilic than the latter. Yamaguchi *et al.*[13] deduced, from their calorimetric study, that, for polyoxyethylene dodecylethers in dodecane, intramolecular hydrogen-bond formation occurs between the terminal OH group and an oxygen atom in the polyoxyethylene chain; this is unlike the results for normal dodecanol. The ΔG° at n=0 in Eq. (5) is expressed as $\Delta G^\circ_{\langle\rm ROH\rangle}$, which is distinct from the value for $\rm R_{\it m}OH$ (denoted by $\Delta G^\circ_{\rm ROH}$). If the OH group in $\rm R_{\it m}E_{\it n}OH$ in the monomeric and nonhydrogen bonding state behaves thermodynamically in the same way as that in $\rm R_{\it m}OH$ in dodecane, it may be considered that the difference between $\Delta G^\circ_{\langle\rm ROH\rangle}$ and $\Delta G^\circ_{\rm ROH}$ is a standard free energy change ($\Delta G^\circ_{\rm HB}$) for hydrogen-bond formation in the dodecane phase, *i.e.*:

$$\Delta G^\circ_{\rm HB} = \Delta G^\circ_{\langle\rm ROH\rangle} - \Delta G^\circ_{\rm ROH} \tag{6}$$

The calculated $\Delta G^\circ_{\rm HB}$ values for the present ethers containing different alkyl-chain lengths are in good agreement with each other; their mean value is −0.835 kcal/mol, as is shown in Table 3. A similar value corresponding to $\Delta G^\circ_{\rm HB}$ can be obtained as the difference between $\Delta G^\circ_{\langle\rm OH\rangle}$ and $\Delta G^\circ_{\rm OH}$, −0.91 kcal/mol, but this value is less reliable because of the scattering of the $\Delta G^\circ_{\rm g}$ values, as may be seen from Fig. 3. It happens that this value is numerically coincident with

$\Delta G^\circ_{CH_2}$; ΔG° for R_mE_nOH becomes equal to that for $R_{m+1}OH$, as may be seen from Fig. 3. From the ΔG°_{HB} obtained here and the enthalpy of hydrogen-bond formation, −5.19 kcal/mol, for alkanol in alkanes, as was established in the calorimetric study by Aveyard and Mitchell,[1] we can evaluate the corresponding entropy, −14.5 eu., by assuming that the enthalpy for the intermolecular hydrogen-bond formation of alkanol is the same as for the intramolecular one in the polyoxyethylene chain. These thermodynamic parameters for hydrogen-bond formation seem reasonable compared with the published values.[14,15]

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