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Temperature Dependence of Association of Methanol, Ethanol, and 1-Propanol

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Arnold and Packard[1] reported that the signal from the hydroxylic proton in the NMR spectra of methanol and ethanol moves towards high fields with temperature rise, but not those of CH_2 and CH_3 groups. The effect of temperature on the shifts of OH signals has been accounted for by the rupture of the hydrogen bonds. In the present paper, the variation of the relative concentrations of the monomer and the n-mer (linear or cyclic) with temperature calculated from the chemical shifts of OH protons are discussed.

Results and Discussion

In order to determine the state of association of alcohols, the method of Saunders and Hyne[2] was applied. The following equilibrium is assumed between monomer and a single species of n-mer:

$$n(\text{R-OH}) \rightleftharpoons (\text{R-OH})_n$$

$$K_n = M_n/(nM_1{}^n). \tag{1}$$

The equilibrium constant K_n is given by means of Eq. (1) where M_1 and M_n are the molar concentrations of monomer and n-mer, respectively, in terms of monomer unit. The observed resonance frequency is given by

$$\delta_{\text{obsd}} = (\delta_1 M_1 + \delta_n M_n)/C \tag{2}$$

where δ_1 and δ_n represent characteristic shifts of a proton in monomer and n-mer, respectively. C is the total concentration of alcohol in mol/l. In order to determine δ_1, the variation of the shift of OH protons in dilute solution in cyclohexane characterized by a small effect on the shift of OH protons, was measured at relatively high temperatures near the boiling point of either alcohol or cyclohexane at concentrations 10^{-2}—10^{-4} (mol/l), where the shifts varied little with concentration. The value of δ_1 was obtained by extrapolation to infinite dilution. Since it was reported by Luck and Ditter[3] that there are few monomers in pure methanol and ethanol below about −80 °C, the shift of OH proton in pure alcohols just above the melting point was taken to be δ_n. The values of δ_1 and δ_n are given in Table 1 together with temperatures of measurements. The values of M_1 and M_n at various temperatures were calculated by substituting the shifts δ_1 and δ_n into Eq. (2). The logarithms of M_1 and M_n thus obtained from Eq. (2) were plotted against the reciprocal of the absolute temperature in Figs. 1 and 2.

Table 1. Chemical shift of monomer and n-mer

Alcohol	$\dfrac{\delta_1{}^{a)}}{\text{Hz}}$	$\dfrac{\delta_n}{\text{Hz}}$
Methanol	205 (+30 °C)	592 (−90 °C)
Ethanol	185 (+60 °C)	639 (−100 °C)
1-Propanol	199 (+70 °C)	640 (−90 °C)

a) Solvent: cyclohexane

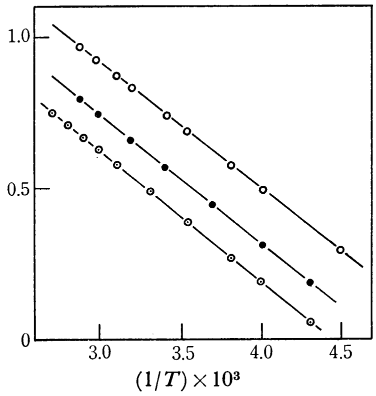

Fig. 1. Plot of logarithm of M_1 against reciprocal of absolute temperature.
○: methanol, ●: ethanol, ⊙: 1-propanol

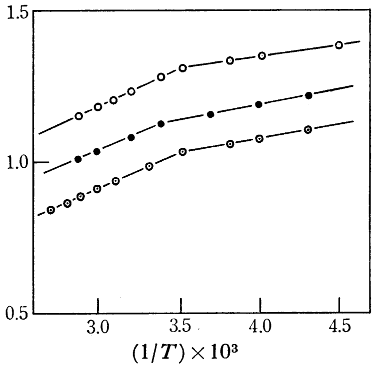

Fig. 2. Plot of logarithm of M_n against reciprocal of absolute temperature.
○: methanol, ●: ethanol, ⊙: 1-propanol

The plot of $\log(M_1)$ against $1/T$ gives a straight line for the three different alcohols, an inflection point appearing at about +30 °C for the plot of $\log(M_n)$ against $1/T$. According to the integrated van't Hoff equation

$$\ln(K_n) = -\Delta H/RT + D \tag{3}$$

where D is constant, it is expected that the plot of $\log(K_n)$ against $1/T$ will give a line which has an inflection point around +30 °C. By conbining Eq. (1) with Eq. (3), we have

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[1] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1609 (1951).

[2] M. Saunders and J. B. Hyne, *ibid.*, **29**, 253, 1319 (1958), *ibid.*, **31**, 270 (1959).

[3] W. A. P. Luck and W. Ditter, *Ber. Bunsenges. Phys. Chem.*, **72**, 365 (1968).

$$\ln(\mathrm{M}_n) = -\Delta H/RT + D + \ln(n) + n\ln(M_1) \qquad (4)$$

On the other hand, Fig. 1 gives the following empirical formula for the variation of the monomer concentration with temperature:

$$\ln(M_1) = A/T + B \qquad (5)$$

where A and B are the constants characteristic of each alcohol. By substituting Eq. (4) into Eq. (5), we obtain

$$\ln(M_n) = (-\Delta H/R + nA)/T + nB + D + \ln(n) \qquad (6)$$

The slope of the line for the plot of $\log(M_n)$ against $1/T$ in Fig. 2 corresponds to $(-\Delta H/R+nA)$ in Eq. (6). This indicates that the inflection at about +30 °C results from the change in $-\Delta H$ or/and n. For several values of n, we have calculated the values of $-\Delta H$ in high and low temperature ranges for each alcohol. The results are given in Table 2. Dividing the values of $-\Delta H$ by n (for cyclic form) and $n-1$ (for linear form), we obtained $-\Delta H$ per hydrogen bond for both cyclic and linear forms (Table 3). It is expected that $-\Delta H$ per hydrogen bond does not vary much with the form of aggregate. For the change of $-\Delta H$ at +30 °C, two possibilities can be considered from the results of Table 3; the increase of the size (n) of aggregates in linear state, and the change of the form from linear to a cyclic one with smaller value of n with increasing temperature. Thermodynamically the increase in the degree of association with temperature rise can not be considered. It could be concluded that the linear form is converted into the cyclic form of lower degree of association with a rise in temperature.

TABLE 2. $-nA$ AND $-\Delta H$ FOR VARIOUS VALUES OF n

Sample	n	$-nA\times10^{-3}$	$-\Delta H$ kcal mol^{-1} Below 30 °C	$-\Delta H$ kcal mol^{-1} Above 30 °C
Methanol	2	1.98	4.2	5.1
	3	2.97	6.3	7.1
	4	3.96	8.2	9.1
	5	4.95	10.2	11.0
	6	5.94	12.2	13.0
Ethanol	2	2.00	4.4	5.0
	3	3.00	6.4	7.0
	4	4.01	8.4	9.0
	5	5.01	10.4	11.0
	6	6.01	12.4	13.0
1-Propanol	2	2.06	4.5	5.2
	3	3.09	6.5	7.2
	4	4.12	8.6	9.3
	5	5.15	10.6	11.3
	6	6.18	12.6	13.4

TABLE 3. VALUE OF $-\Delta H$ PER HYDROGEN BOND

Sample	n	$-\Delta H$ kcal mol^{-1} Below 30 °C		Above 30 °C	
		Linear	Cyclic	Linear	Cyclic
Methanol	2	4.17	2.09	5.13	2.56
	3	3.13	2.09	3.55	2.36
	4	2.75	2.06	3.02	2.28
	5	2.54	2.04	2.76	2.21
	6	2.43	2.03	2.60	2.16
Ethanol	2	4.43	2.22	4.97	2.48
	3	3.21	2.14	3.48	2.32
	4	2.81	2.11	2.79	2.24
	5	2.60	2.08	2.74	2.19
	6	2.48	2.07	2.59	2.16
1-Propanol	2	4.46	2.23	5.19	2.60
	3	3.25	2.17	3.62	2.41
	4	3.85	2.14	3.10	2.32
	5	2.65	2.12	2.83	2.27
	6	2.54	2.11	2.68	2.23

Experimental

Methanol and ethanol of reagent grade were refluxed for 24 hr over calcium oxide and then fractionally distilled. It was then dried over calcium, and fractionally redistilled twice under nitrogen atmosphere. Similar procedures were applied to the purification of 1-propanol, except that sodium was used instead of calcium. Cyclohexane of reagent grade was dried over sodium and then fractionally distilled twice. From the results of the specific conductivity measurements of the alcohols and cyclohexane at +25 °C (methanol, 1.0×10^{-8} ohm$^{-1}\cdot$cm^{-1}, ethanol, 1.5×10^{-9} ohm$^{-1}\cdot$cm^{-1}, 1-propanol, 2.0×10^{-10} ohm$^{-1}\cdot$cm^{-1}, cyclohexane, 1.0×10^{-14} ohm$^{-1}\cdot$cm^{-1}), it was confirmed that the reagents were highly dried. For NMR measurements, the purified alcohols were sealed in NMR sample tubes. NMR measurements were carried out in a temperature range of from just above melting point to near boiling point of each alcohol, on an JNM-4H-100 NMR spectrometer (Japan Electron Optics Co.) operating at a frequency of 100 MHz. Tetramethylsilane was employed as an internal standard. No temperature dependence of the CH_2 and CH_3 proton signals was observed. Experimental errors were within ±0.5 Hz and ±0.5 °C.