Apparent Molal Volumes and Adiabatic Compressibilities of *n*-Alkanols and α,ω-Alkane Diols in Dilute Aqueous Solutions at 5, 25, and 45°C. II. Apparent Molal Adiabatic Compressibilities

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Ultrasonic velocity measurements have been made on a series of dilute aqueous solutions of *n*-alkanols and α,ω-alkane diols by means of the sing-around method. The apparent molal adiabatic compressibilities, ϕ_K, have been derived, and the ϕ°_K at an infinite dilution has been estimated. The ϕ°_K values per CH_2 and CH_3 groups were estimated from the additivity of the ϕ°_K value for each group. The values are negative at low temperatures and markedly decrease with a decrease in the temperature. This fact suggests that the iceberg formation makes a negative contribution to the ϕ°_K.

Shigehara,[1] Conway and Verrall,[2] and Laliberte and Conway[3] have discussed the effect of the iceberg formation[4] (the hydrophobic hydration) around CH_2 groups on the adiabatic compressibility in terms of its dependence on the alkyl chain length of organic salts. In view of the fact that the structural effect is sensitive to the temperature, the study of the temperature dependence of the compressibility is of use in order to obtain further information concerning the structural effect. In the present paper we wish to report our findings regarding the apparent molal adiabatic compressibilities, ϕ_K, of a series of *n*-alkanols and α,ω-alkane diols in dilute aqueous solutions and their temperature dependence. The ϕ°_K data will be discussed in relation to the ϕ°_V data presented in the previous paper (Part I).[5]

Experimental

Materials. The same samples as were used in Part I, $H(CH_2)_nOH$ (n=1—5) and $(CH_2)_n(OH)_2$ (n=2—6), were used for the experiments.

Ultrasonic Velocity Measurements. The ultrasonic velocity measurements in solutions were made with the sing-around velocimeter developed by Greenspan and Tschieg.[6] Two quartz transducers were mounted at the ends of a glass tube. A pulse from the first transducer travels through the liquid in the time L/u, where u is the sound velocity and L is the effective path length. The pulse received by the second transducer is used to retrigger the first transducer to send another pulse, thus repeating the process. The pulse repetition frequency, f, is determined by the pulse transit time in the liquid, L/u, and the total electronic delay time, t_e, as follows:

$$\frac{1}{f} = \frac{L}{u} + t_e \tag{1}$$

The f value was measured by using a 6-figure digital electronic counter. The constants, L and t_e, were determined from the best fittings on the sound vilocity of water[7] at various temperatures from 5 to 45 °C. The accuracy of the ultrasonic velocity measurements was within ± 1 cm/s.

The solutions were prepared by adding weighed amounts of a sample into a cell containing a known amount of pure water.

The coefficient of the adiabatic compressibility, κ, was calculated from the $\kappa = 1/du^2$ relation, where d is the density and is obtained from the data in Part I. The apparent molal adiabatic compressibility of the solute, ϕ_K, is defined by the $\phi_K = -(\partial\phi_V/\partial T)_s$ relation;[8] it is calculated by means of the following formula:

$$\phi_K = \frac{1000(\kappa - \kappa_0)}{md_0} + \phi_V\kappa \tag{2}$$

where ϕ_V is the apparent molal volume and is obtained from the data in Part I.

Results

Figure 1 shows the experimental $\phi_K(m)$ results for *n*-butanol and 1,2-ethanediol at 5, 25, and 45 °C. The $\phi_K(m)$ is linearly related to the concentration, as was observed in the case of $\phi_V(m)$ in Part I. The limiting partial molal compressibility, $\bar{K}^\circ_2(=\phi^\circ_K)$, was obtained from the linear extrapolation of the $\phi_K(m)$ to an infinite dilution. The $\bar{K}^\circ_2$ values and slopes of the $\phi_K(m)$ are summarized in Table 1.

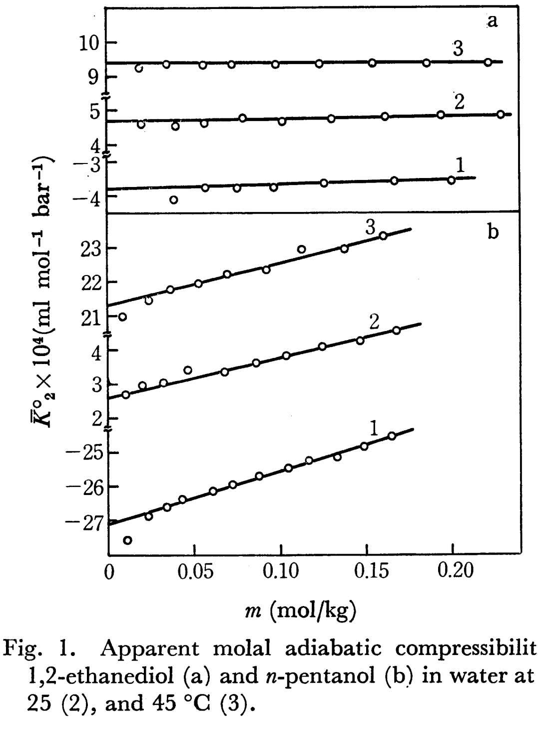

Fig. 1. Apparent molal adiabatic compressibilities of 1,2-ethanediol (a) and *n*-pentanol (b) in water at 5 (1) 25 (2), and 45 °C (3).

Table 1. Values of $\bar{K}^\circ_2$ $(=\phi^\circ_K)$ and $\partial\phi_K/\partial m$ at 5, 25, and 45 °C

n	$\bar{K}^\circ_2\times10^4$ (ml/mol bar) 5 °C	25 °C	45 °C	$\partial\phi_K/\partial m$ (ml kg/mol^2 bar) 5 °C	25 °C	45 °C
			$H(CH_2)_nOH$			
1	7.3	12.6	15.9	−1.1	−0.3	−0.1
2	−0.8	10.0	16.5	−1.7	−1.0	−0.4
3	−10.8	6.3	16.9	0.3	0.7	1.0
4	−19.0	4.6	19.0	6.4	1.6	4.1
5	−27.1	2.6	21.3	15.5	11.8	12.6
			$(CH_2)_n(OH)_2$			
2	−3.8	4.7	9.4	1.1	0.7	0.0
3	−0.7	9.5	15.2	1.5	0.3	2.6
4	−5.3	9.4	17.7	1.3	0.0	−0.4
5	−12.2	8.1	19.9	7.5	2.8	1.6
6	−18.9	6.6	21.6	12.1	6.7	3.8

Discussion

Partial Molal Adiabatic Compressibilities of CH_2 and CH_3 Groups. The limiting partial molal adiabatic compressibility is expressed as follows:

$$\bar{K}^\circ_2 = \bar{K}^\circ_{2,0} + \Delta\bar{K}^\circ_i + \Delta\bar{K}^\circ_h \tag{3}$$

where $\Delta\bar{K}^\circ_i$ and $\Delta\bar{K}^\circ_h$ are the compressibility change resulting from the iceberg formation around the hydrophobic group and the hydration by the hydrophilic group respectively, and where $\bar{K}^\circ_{2,0}$ is the partial molal compressibility under the conditions when the iceberg formation and the hydration would not occur.

The $\bar{K}^\circ_2$ increment per CH_2 group is illustrated in Fig. 2 as a function of the chain length. The pattern of the behavior of the $\bar{K}^\circ_2$ increment resembles that of the $\bar{V}^\circ_2$ increment (*cf.* Fig. 2 in Part I). The $\bar{K}^\circ_2$ increments in the two series approach a similar value with the increase in the chain length. This value corresponds to the $\bar{K}^\circ_2$ value of the CH_2 group free from the influence of the OH groups. The $\bar{K}^\circ_2$ values of the CH_3 and CH_2OH groups in long-chain alcohols were estimated by the same procedure as was described in Part I. These results are shown in Table 2. The $\bar{K}^\circ_2(CH_2)$ calculated from the $\bar{K}^\circ_2$ data[2] of n-Pr_4N^+ and n-Bu_4N^+ is -2.6×10^{-4} ml/mol bar at 25 °C. This value is somewhat smaller than our result. The $\bar{K}^\circ_2(CH_2)$ obtained from the compressibility data[1] for a series of surface-active substances is -0.6×10^{-4} ml/mol bar at 30 °C. This value is in agreement with the value estimated from our results at 25 and 45 °C.

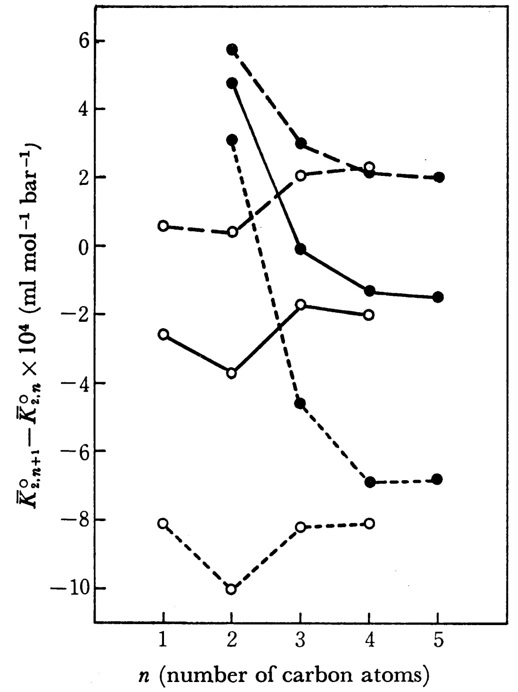

Fig. 2. The $\bar{K}^\circ_2$ increments per CH_2 group as a function of a chain length at 5 (------), 25 (——), and 45 °C (– – – –).
○: $H(CH_2)_nOH$, ●: $(CH_2)_n(OH)_2$.

It should be noted that the $\bar{K}^\circ_2(CH_2)$ and the $\bar{K}^\circ_2(CH_3)$ values are negative at low temperatures and markedly decrease with a decrease in the temperature. As it is clear that the $\bar{K}^\circ_{2,0}$ value is always positive, the negative value of $\bar{K}^\circ_2$ can be attributed to the negative $\Delta\bar{K}^\circ_i$ value. This suggests that the iceberg is less compressible than bulk water.[2]

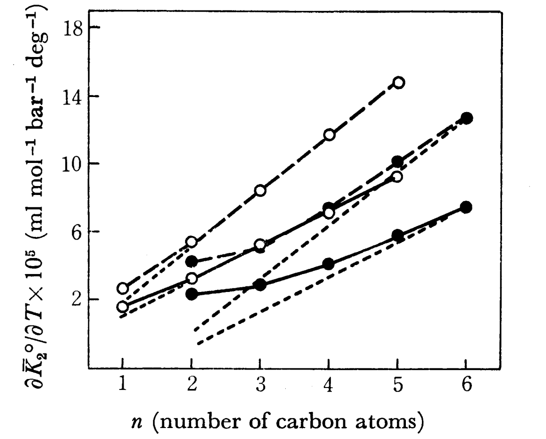

Fig. 3. Plot of the $\partial\bar{K}^\circ_2/\partial T$ against a chain length at 15 (– – – –) and 35 °C (——), symbols as for Fig. 2.

Temperature Dependence of the $\bar{K}^\circ_2$. Figure 3 shows the plot of the $\partial\bar{K}^\circ_2/\partial T(\approx\Delta\bar{K}^\circ_2/\Delta T)$ values at 15 and 35 °C against a chain length. The $\partial\bar{K}^\circ_2/\partial T$ values in both series approach straight lines with the same slope with an increase in the chain length. The pattern of the deviation from the straight lines resembles that of

Table 2. Values of $\bar{K}^\circ_2$, $\partial\bar{K}^\circ_2/\partial T$, and $\partial^2\bar{K}^\circ_2/\partial T^2$ of CH_3, CH_2, and CH_2OH groups

	$\bar{K}^\circ_2\times10_4$ (ml/mol bar) 5 °C	25 °C	45 °C	$\partial\bar{K}^\circ_2/\partial T\times10^5$ (ml/mol bar deg) 15 °C	35 °C	$\partial^2\bar{K}^\circ_2/\partial T^2\times10^7$ (ml/mol bar deg^2) 25 °C
CH_3	-9.5_5	1.3	8.0_5	5.5	3.0	−8.0
CH_2	−8.0	1.8	2.1	3.2	2.1	−5.4
CH_2OH[a)]	$6._5$	$6._8$	$6._7$	$-0._2$	$-0._7$	−2.4
$1/2(CH_2OH)_2$[b)]	−1.9	2.4	4.7	2.13	1.16	−4.6

a) CH_2OH group in long chain alcohols. b) CH_2OH group in 1,2-ethanediol.

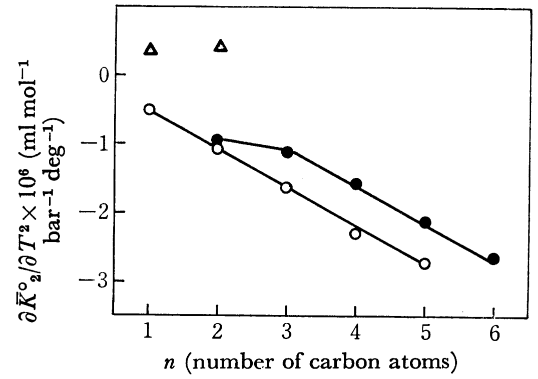

Fig. 4. Plot of the $\partial^2\bar{K}^\circ_2/\partial T^2$ against a chain length at 25 °C, symbols as for Fig. 2. △ corresponds to the $\partial^2 K_2/\partial T^2$ of pure alcohols calculated from the data in Ref. 9, where K_2 is $-(\partial V_2/\partial P)_s$.

$\partial\bar{V}^\circ_2/\partial T$ in Part I. The slope of the straight lines corresponds to the $\partial\bar{K}^\circ_2/\partial T$ value of the CH_2 group outside the region of influence of the OH group. The $\partial\bar{K}^\circ_2/\partial T$ values of the CH_3 and CH_2OH groups in long-chain alcohols were estimated as before. These results are given in Table 2.

Figure 4 shows the $\partial^2\bar{K}^\circ_2/\partial T^2$ value and the $\partial^2 K_2/\partial T^2$ value at 25 °C, where K_2 is $-(\partial V_2/\partial P)_s$, as a function of the chain length. It is noteworthy that the $\partial^2\bar{K}^\circ_2/\partial T^2$ has a large negative value in contrast with the slightly positive value of the $\partial^2\bar{K}_2/\partial T^2$ of pure alcohols From Eq. (3), $\partial^2\bar{K}^\circ_2/\partial T^2$ is given as:

$$\partial^2\bar{K}^\circ_2/\partial T^2 = \partial\bar{K}^\circ_{2,0}/\partial T^2 + \partial^2\Delta K^\circ_i/\partial T^2 + \partial^2\Delta\bar{K}^\circ_h/\partial T^2 \quad (4)$$

Since $\partial^2\bar{K}^\circ_{2,0}/\partial T^2$ in Eq. (4) is free from the structural effect, it can be expected that the $\bar{K}^\circ_{2,0}$ almost linearly relates with the temperature; that is, $\partial^2\bar{K}^\circ_{2,0}/\partial T^2$ is negligible. Therefore, the negative values of $\partial^2\bar{K}^\circ_2/\partial T^2$ shown in Fig. 4 result from the negative values of $\partial^2\Delta\bar{K}^\circ_i/\partial T^2$ and $\partial^2\Delta\bar{K}^\circ_h/\partial T^2$. By assuming a monotonous decrease in the structural effect with an increase in the temperature, the temperature dependences of ΔK°_i and ΔK°_h are schematically shown in Fig. 5. As may be seen from the figure, the negative values of the K°_2 at low temperatures are related to the large negative values of $\partial^2\Delta\bar{K}^\circ_i/\partial T^2$ and $\partial^2\Delta\bar{K}^\circ_h/\partial T^2$.

The $\partial^2\bar{K}^\circ_2/\partial T^2$ values in both series lie on the straight lines with the same slope except for 1,2-ethanediol (Fig. 4). The $\partial^2\bar{K}^\circ_2/\partial T^2$ of the CH_2 group is evaluated from the slope of the straight lines. The $\partial^2\bar{K}^\circ_2/\partial T^2$ values of the CH_3 and the CH_2OH groups except for 1,2-ethanediol are estimated on the basis of the additivity of the $\partial^2\bar{K}^\circ_2/\partial T^2$ value for each group. The values are given in Table 2.

Only 1,2-ethanediol deviates from the straight line, as is shown in Fig. 4; the $\bar{K}^\circ_2$ and the $\partial\bar{K}^\circ_2/\partial T$ of the CH_2OH group in 1,2-ethanediol apparently differ from those of the CH_2OH group in long-chain alcohols, as has been shown in the cases of the $\bar{V}^\circ_2$ and the $\partial\bar{V}^\circ_2/\partial T$ (*cf.* Table 2 in Part I). These results suggest that the effect of the adjacent OH groups in 1,2-ethanediol on the water structure differs from that of the OH groups existing relatively apart in higher diols and those in monovalent alcohols.

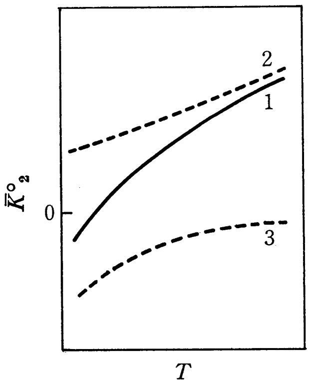

Fig. 5. Schematical figure of the relation between the temperature dependence of K°_2 and $\Delta\bar{K}^\circ_i$(or $\Delta\bar{K}^\circ_h$).
(1): $\bar{K}^\circ_2$, (2): $\bar{K}^\circ_{2,0}$, (3): $\Delta\bar{K}^\circ_i$ or $\Delta\bar{K}^\circ_h$.

Concentration Dependence of the ϕ_K. The slopes of $\phi_K(m)$, $\partial\phi_K/\partial m$, are shown in Table 1. The dependences of the slope upon the temperature and the chain length are not as clear as those for $\phi_V(m)$ presented in Part I, but it appears that the slopes are positive and increase with an increase in the chain length and with a decrease in the temperature, in contrast to the case of the slope of the $\phi_V(m)$. This tendency, as in the explanation of the slope of the $\phi_V(m)$ proposed in Part I, can be interpreted in terms of the overlapping of the icebergs.[10] The value of ΔK°_i resulting from the iceberg formation is negative, as was shown in the previous section. The contribution of the $\Delta\bar{K}^\circ_i$ to the ϕ_K becomes less negative with an increase in the concentration due to the overlapping of the icebergs; this results in the increase in the ϕ_K value.

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