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

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Density measurements have been carried out on a series of dilute aqueous solutions of *n*-alkanols and *α,ω*-alkane diols. The apparent molal volumes, ϕ_V, have been derived, and the ϕ°_V values (V°_2) at an infinite dilution have been estimated. The $\bar{V}^\circ_2$, the $\partial^2\bar{V}^\circ_2/\partial T$, and the $\partial^2\bar{V}^\circ_2/\partial T^2$ of the CH_2, the CH_3, and the CH_2OH groups were obtained from the dependence of the $\bar{V}^\circ_2$ and its temperature behavior upon the alkyl-chain length. It was found that the $\partial^2\bar{V}^\circ_2/\partial T^2$ value well reflects the structural effect.

Much attention has been devoted to the effect of the structural change in water caused by a solute on the thermodynamic properties.[1–4] On the basis of the data of the partial specific volumes, φ_v, of 15 nonelectrolytes in dilute aqueous solutions, Neal and Goring found that the $\partial^2\varphi_v^\circ/\partial T^2$ value of the hydrophobic compounds is positive, while that of the hydrophilic compounds is negative.[5] A similar discussion has been made by Hepler in relation to the pressure dependence of the partial molal heat capacity.[6] Further, Neal and Goring found that the specific expansibility, $\partial\varphi_v^\circ/\partial T$, and the concentration dependence of φ_v is closely related to the hydrophobic-hydrophilic balance in a solute.[5] This difference in the volumetric behavior between the hydrophobic and the hydrophilic compounds is considered to be related to the structural change in water caused by a solute. The purpose of the present paper is to obtain further information about the structural effect on the basis of the effect of the successive addition of the CH_2 group in the series of *n*-alkanols and *α,ω*-alkane diols on the partial molal volume and its temperature and concentration behavior.

Experimental

Materials. The *n*-alkanols from methanol to pentanol and the *α,ω*-alkane diols from 1,2-ethanediol to 1,6-hexanediol were used for the experiments. The best grade available from commercial sources (mostly guaranteed reagents) was dried over calcium sulfate and then fractionally distilled. The 1,6-hexanediol was distilled without such pretreatment. The water used was obtained by the distillation of deionized water by a quartz still and was degassed immediately before use.

Density Measurements. The densities were obtained by a float method analogous to that used by Desnoyers and Arel.[7] The float was suspended to the pan of the balance (Mettler: H20T) by a nylon thread 110 micron in diameter and was immersed in the solution in a thermostated cell. The water circulating in the cell was taken from a well-insulated bath kept at a constant temperature (±0.002 °C). The difference between the density of the solution, d, and that of the water, d_0, is obtained from weights, W and W_0, of the float in the solution and in water by means of this relation: $d-d_0=(W-W_0)/V$, where V is the volume of the float. The volume of the float is about 200 ml. The accuracy of the density measurement is within $\pm 10^{-6}$ g/ml. The density of pure water was taken from Kell's data.[8]

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

The apparent molal volume, ϕ_v, was obtained from the relation:

$$\phi_v = \frac{1000(d_0-d)}{mdd_0} + \frac{M}{d} \tag{1}$$

where m is the molality and M, the molecular weight of the solute.

Results

Some typical examples of the plot of ϕ_v *vs.* concentration (m) are shown in Fig. 1. The ϕ_v (m) is linearly related to m in the concentration range studied (0.01—0.2 mol/kg). The limiting partial molal volume, $\bar{V}^\circ_2$ ($=\phi^\circ_v$), is obtained from the linear extrapolation of the ϕ_v (m) to an infinite dilution. The experimental error estimated in the $\bar{V}^\circ_2$ is within 0.1 ml/mol. The values of V°_2 of *n*-butanol at 5 and 25 °C are in agreement with the values reported by Franks and Smith[9] within 0.03 ml/mol. The values of $\bar{V}^\circ_2$ and the slope of ϕ_v (m) are summarized in Table 1.

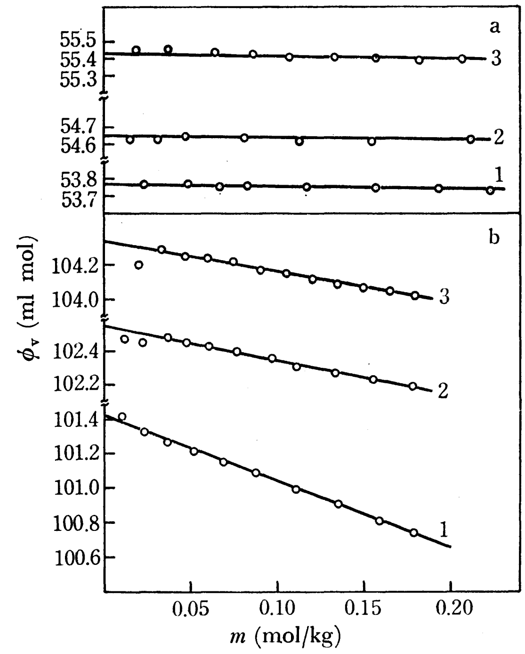

Fig. 1. Apparent molal volumes of 1,2-ethanediol (a) and *n*-pentanol (b) in water at 5 (1), 25 (2), and 45 °C (3).

TABLE 1. VALUES OF $\bar{V}_2^\circ(=\phi_v^\circ)$ AND $\partial\phi_v/\partial m$ AT 5, 25, AND 45 °C

n	$\bar{V}_2$ (mol/ml)			$-\partial\phi_v/\partial m$ (ml kg/mol^2)		
	5 °C	25 °C	45 °C	5 °C	25 °C	45 °C
		$H(CH_2)_nOH$				
1	38.10	38.17	38.52	0.3	0.2	0.1
2	55.12	55.08	55.52	0.9	0.6	0.3
3	70.48	70.74	71.56	1.8	1.1	0.6
4	86.00	86.63	87.94	3.0	1.5	0.8
5	101.43	102.55	104.34	3.8	2.1	1.8
		$(CH_2)_n(OH)_2$				
2	53.77	54.65	55.43	0.1	0.1	0.1
3	71.40	71.89	72.55	0.6	0.4	0.3
4	87.81	88.36	89.18	1.2	0.8	0.4
5	103.54	104.43	105.63	1.6	1.2	0.4
6	119.16	120.39	122.05	2.8	1.5	0.7

Discussion

Partial Molal Volumes of CH_2 and CH_3 Groups. The limiting partial molal volume is expressed by the following expression:

$$\bar{V}_2^\circ = \bar{V}_{2,0}^\circ + \Delta\bar{V}_i^\circ + \Delta\bar{V}_h^\circ \qquad (2)$$

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

The $\bar{V}^\circ_2$ increment per CH_2 group is illustrated in Fig. 2 as a function of the chain length. The increments in the two homologs are different in their dependence upon the chain length, but they approach a common value as the chain length increases. The increment seems to become constant at $n=3$—4 in *n*-alkanol and at $n=5$—6 in α,ω-alkane diol. The deviation in the $\bar{V}^\circ_2$ increment per CH_2 group in a homologous series is frequently discussed in connection with the range of influence of the polar group on the structure of water.[7,10] This deviation in the V°_2 increment, however, is also observed in the case of the homologous series of *n*-alkanol in several nonaqueous solvents without the hydrogen-bonded structure, and the dependence of the $\bar{V}^\circ_2$ increment on the chain length partly resembles that in water.[11] In view of this fact, it is difficult to interpret this deviation only in terms of the effect of the polar group on the water structure.

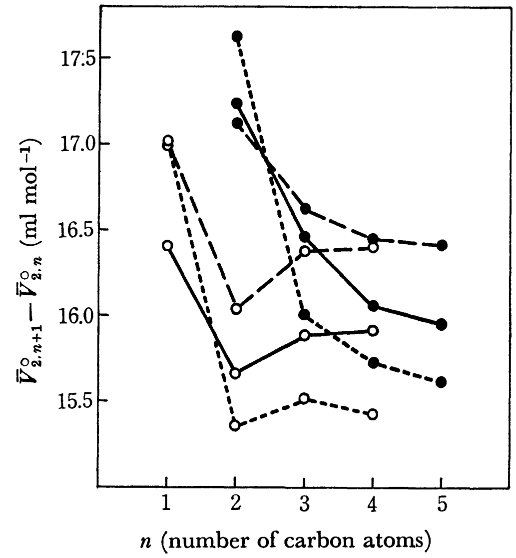

Fig. 2. The $\bar{V}^\circ_2$ increments per CH_2 group as a function of a chain length at 5 (-----), 25 (——), and 45 °C (– – –). ○: $H(CH_2)_n$-OH, ●: $(CH_2)_n$-$(OH)_2$.

The increment in the case of a longer chain length corresponds to the partial molal volume of the CH_2 group free from the influence of the OH groups. The values are shown in Table 2. The value of $\bar{V}^\circ_2(CH_2)$ is in good agreement with the corresponding value obtained from the homologous organic salts.[7,10]

Since, as may be seen from Fig. 2, the range of influence of the OH group is at most up to the γ-CH_2 group, the $\bar{V}^\circ_2$ values of the $(CH_2)_3OH$ group in *n*-butanol and in 1,6-hexanediol should be similar. Therefore, the difference between the $\bar{V}^\circ_2$ of *n*-butanol and a half of that of 1,6-hexanediol corresponds to the $V^\circ_2(CH_3)$ value outside the region of influence of the OH group. The $\bar{V}^\circ_2$ of the CH_2OH group in the long-chain alcohols was estimated by assuming that the $\bar{V}^\circ_2$ values of both the β- and the γ-CH_2 groups are similar to the $\bar{V}^\circ_2(CH_2)$ value free from the influence of the OH groups. The results are shown in Table 2. The $\bar{V}^\circ_2(CH_3)$ value calculated from the data[10] of $CH_3(CH_2)_3COONa$ and $(CH_2)_6(COONa)_2$ at 25 °C is 26.3 ml/mol, in good agreement with our result.

The $\bar{V}^\circ_2$ values of CH_3CH_3 and $CH_3CH_2CH_3$ calculated from the $\bar{V}^\circ_2$ values of the CH_2 and the CH_3 groups are in agreement with the experimental values of 53.3[12] and 51.2[13] for ethane and of 67.0[13] for propane at 25 °C.

Temperature Dependence of the $\bar{V}^\circ_2$. Figure 3 shows the limiting partialmolal expansibilities, $\partial\bar{V}^\circ_2/\partial T(\approx\Delta\bar{V}^\circ_2$

TABLE 2. VALUES OF $\bar{V}^\circ_2$, $\partial\bar{V}^\circ_2/\partial T$, AND $\partial^2\bar{V}^\circ_2/\partial T^2$ OF CH_3, CH_2, AND CH_2OH GROUPS

	V°_2 (ml/mol)			$\partial\bar{V}^\circ_2/\partial T\times10^2$ (ml/mol deg)		$\partial^2\bar{V}^\circ_2/T^2\times10^4$ (ml/mol deg^2)
	5 °C	25 °C	45 °C	15 °C	35 °C	25 °C
CH_3	26.3	26.4	26.9	0.0_7	2.3_5	10.2
CH_2	15.5	15.9	16.4	2.1	2.4	2.2
CH_2OH[a)]	$28._7$	$28._4$	$28._3$	$-1._3$	$-0._7$	1.0
$1/2(CH_2OH)_2$[b)]	26.89	27.33	27.72	2.2	2.0	−1.3

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

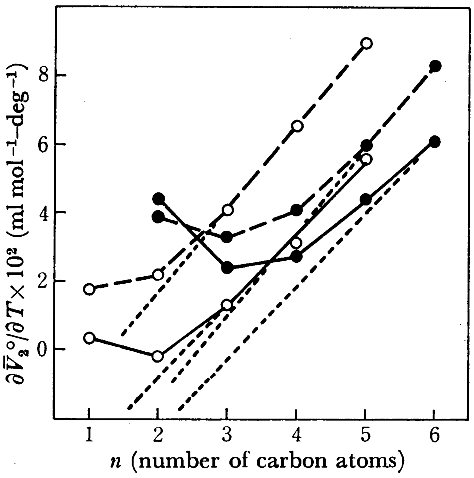

Fig. 3. Plot of the $\partial\bar{V}^\circ_2/\partial T$ against a chain length at 15 (——) and 35 °C (----), symbols as for Fig. 2.

$/\Delta T$) at 15 and 35 °C as a function of the chain length. The $\partial\bar{V}^\circ_2/\partial T$ values seem to fall on straight lines, with a similar slope, as the chain length increases. The $\partial\bar{V}^\circ_2/\partial T$ values seem to fall on straight lines when the chain length, n, is 3 for n-alkanol and 5—6 for α,ω-alkane diol. The region of the influence of the OH group on the $\partial\bar{V}^\circ_2/\partial T$ increment per CH_2 group seems to be up to the β- or the γ-CH_2 groups. This finding is similar to that observed in the $\bar{V}^\circ_2$ increment. The $\partial V^\circ_2/\partial T$ value of the CH_2 group free from the influence of the OH group is obtained from the slope of the straight line. By the same procedure as was used in the preceding section, the $\partial\bar{V}^\circ_2/\partial T$ values of the CH_3 and the CH_2OH groups were estimated. The values are shown in Table 2.

Neal and Goring found that the temperature dependence of the limiting partial specific volume, $\partial\bar{v}^\circ_2/\partial T$-$(=\partial\bar{V}^\circ_2/\partial T/M)$, of hydrophobic compounds is lower than that of hydrophilic compounds at low temperatures, and proposed that the $\partial\bar{v}^\circ_2/\partial T$ value is a useful measure of the effect of a nonelectrolyte on the water structure.[5] Figure 4 shows the plot of the $\partial\bar{v}^\circ_2/\partial T$ value against the chain length. It is evident from the figure that, contrary to the proposal by Neal and Goring, the $\partial\bar{v}^\circ_2/\partial T$ value obviously increases with the increase in the hydrophobic part of a solute. As may be seen from Column 5 in Table 2, the expansibility of the CH_2 group is markedly larger than those of the CH_3 and the CH_2OH groups. The increase in the $\partial\bar{v}^\circ_2/\partial T$ value with the increase in the chain length results from the large expansibility of the CH_2 group.

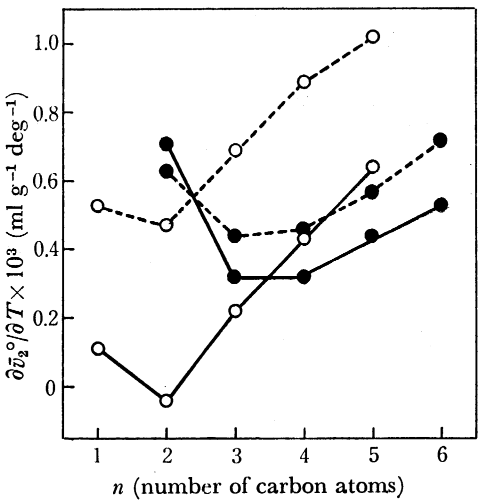

Fig. 4. Plot of the limiting specific expansibility, $\partial\bar{v}_2{}^\circ/\partial T^2$ against a chain length at 15 (——) and 35 °C (----), symbols as for Fig. 2.

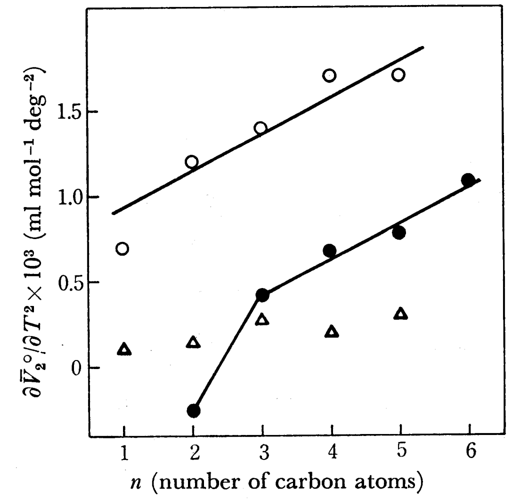

Fig. 5. Plot of the $\partial^2\bar{V}^\circ_2/\partial T^2$ against a chain length at 25 °C, symbols as for Fig. 2. △ corresponds to the $\partial^2\bar{V}_2/\partial T^2$ of pure alcohols calculated from the data in Ref. 14.

Figure 5 shows the plot of the $\partial^2\bar{V}^\circ_2/\partial T^2$ in solution and the $\partial^2\bar{V}^\circ_2/\partial T^2$ of pure alcohols at 25 °C against the chain length. It is noteworthy that the $\partial^2\bar{V}^\circ_2/\partial T^2$ of n-alkanol is remarkably high when compared with $\partial^2\bar{V}_2/\partial T^2$. From Eq. (2), $\partial^2\bar{V}^\circ_2/\partial T^2$ is given as:

$$\partial^2\bar{V}^\circ_2/\partial T^2 = \partial^2\bar{V}^\circ_{2,0}/\partial T^2 + \partial^2\Delta\bar{V}^\circ_i/\partial T^2 + \partial^2\Delta\bar{V}^\circ_h/\partial T^2 \quad (3)$$

Since $\partial^2\bar{V}^\circ_{2,0}/\partial T^2$ in Eq. (3) is free from the structural effect caused by a solute, $\bar{V}^\circ_{2,0}$ may be expected to be almost linearly related to the temperature; that is, $\partial^2\bar{V}^\circ_{2,0}/\partial T^2$ may be expected to be negligible. If this is accepted, the observed $\partial^2\bar{V}^\circ_2/\partial T^2$ values of hydrophobic compounds and those of hydrophilic compounds should correspond to the positive $\partial^2\Delta\bar{V}^\circ_2/\partial T^2$ and the

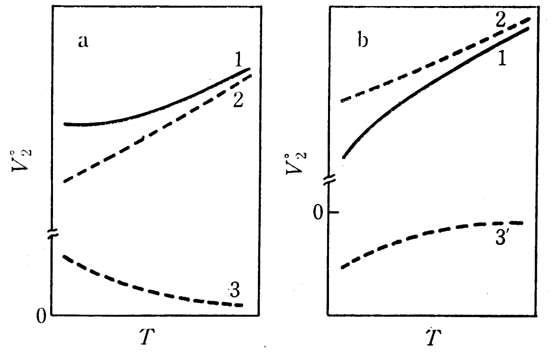

Fig. 6. Schematical figures of the temperature dependence of $\bar{V}_2{}^\circ$, $\bar{V}^\circ_{2,0}$, and $\Delta\bar{V}_i{}^\circ$ for hydrophobic compounds (a) and $\bar{V}_2{}^c$, $\bar{V}^\circ_{2,0}$, and $\Delta\bar{V}_h{}^\circ$ for hydrophilic compounds (b). (1): $\bar{V}_2{}^\circ$, (2): $\bar{V}^\circ_{2,0}$ (3): $\bar{V}_i{}^\circ$, and (3′): $\bar{V}_h{}^\circ$.

negative $\partial^2 \Delta \bar{V}^\circ{}_h / \partial T^2$ respectively.[5] By assuming the linear change of $\bar{V}^\circ{}_{2,0}$ with the temperature and the monotonous decrease in the structural effect with an increase in the temperature, the temperature dependences of $\bar{V}^\circ{}_2$, $\bar{V}^\circ{}_{2,0}$, and $\Delta \bar{V}^\circ{}_i$ for hydrophobic compounds and of $\bar{V}^\circ{}_2$, $\bar{V}^\circ{}_{2,0}$, and $\Delta \bar{V}^\circ{}_h$ for hydrophilic compounds are schematically shown in Figs. 6a and 6b respectively. It may be seen from the figure that $\Delta \bar{V}^\circ{}_i$ is positive and that $\Delta \bar{V}^\circ{}_h$ is negative.

The $\partial^2 \bar{V}^\circ{}_2 / \partial T^2$ values lie on straight lines with the same slope except for 1,2-ethanediol. We note that the distance to the OH group does not significantly affect the $\partial^2 \bar{V}^\circ{}_2 / \partial T^2$ increment per CH_2 group. The present results, therefore, seem to indicate that the water structure[15] around the CH_2 group is only slightly affected by the OH group. A similar result is obtained from the linear dependence of the limiting partial molal heat capacity on the chain length for the different solute series.[16]

The $\partial^2 V^\circ{}_2 / \partial T^2$ value of the CH_2 group is obtained from the slope of the straight lines in Fig. 5. On the basis of the additivity of the $\partial^2 V^\circ{}_2 / \partial T^2$ value for each group, the $\partial^2 V^\circ{}_2 / \partial T^2$ values of the CH_3 and the CH_2OH groups except for 1,2-ethanediol were estimated. These values are given in Column 7 of Table 2. The positive $\partial^2 \bar{V}^\circ{}_2 / \partial T^2$ values of the CH_2 and CH_3 groups reflect the effect of the iceberg formation around these groups.

As is shown in Fig. 5, only the $\partial^2 \bar{V}^\circ{}_2 / \partial T^2$ value of 1,2-ethanediol deviates from the straight line and is negative. Further, Table 2 shows that the $\bar{V}^\circ{}_2$ and the $\partial \bar{V}^\circ{}_2 / \partial T$ values of the CH_2OH group in 1,2-ethanediol apparently differ from those of the CH_2OH group in long-chain alcohols. These findings 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 from those in monovalent alcohols. The negative $\partial^2 \bar{V}^\circ{}_2 / \partial T^2$ values observed in glycerol,[5] glucose,[5] and sucrose[17] may also be attributed to the effect of the adjacent OH groups.

Excess Partial Molal Volume. The excess partial molal volume in an infinite dilution, $\bar{V}_2^{\circ E}$, is defined as:

$$\bar{V}_2^\circ = V_2 + \bar{V}_2^{\circ E} \tag{4}$$

where V_2 is the molal volume of a pure solute. It is known that the $V_2^{\circ E}$ value of the hydrophobic compounds is negative and that the absolute value of $V^\circ{}_2$ increases as the hydrophobicity increases (*cf.* Fig. 7).[14,18] These facts can be interpreted by the idea that the structural change of water caused by the hydrophobic group results in a volume contraction.[14,18] However, there appear to be some questions in considering the $V_2^{\circ E}$ as a measure of the structural effect, as will be described below.[19] From the view point that the negative $V_E^{\circ 2}$ value is attributable to the iceberg formation, Franks and Smith proposed that the increase in $|V_2^{\circ E}|$ with an increase in the temperature proves the structure promotion by the hydrophobic group.[9] However, this proposal seems to be questionable in view of the conventional concept that the structural effect decreases as the temperature increases. From Eqs. (2) and (4), the $V_2^{\circ E}$ value is given by:

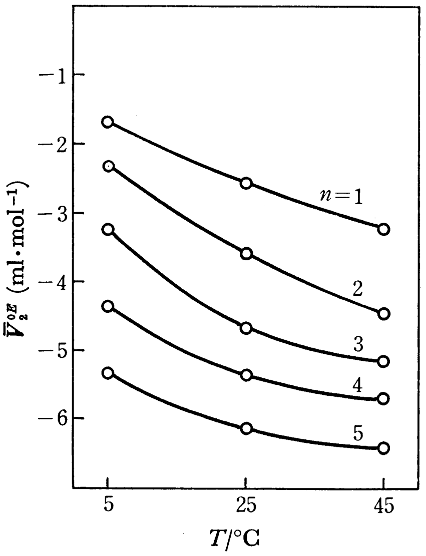

Fig. 7. Plot of the $\bar{V}_2^{\circ E} (= \bar{V}_2 - V_2)$ of *n*-alkanols, $H(CH_2)_n$-OH, against temperature. The V_2 values were obtained from the data in Ref. 14 and 21.

$$\bar{V}_2^{\circ E} = (\bar{V}_{2,0}^\circ - V_2) + \Delta V_i^\circ + \bar{V}_h^\circ \tag{5}$$

The $\bar{V}_2^{\circ E}$ does not directly reflect the structural effect unless the $(\bar{V}^\circ{}_{2,0} - V_2)$ value is negligible. In the previous section we concluded that the $\Delta V^\circ{}_i$ is positive (*cf.* Fig. 6a). Therefore, the $(V^\circ{}_{2,0} - V_2)$ must be negative in order for $V_2^{\circ E}$ to be negative. Judging from the fact that the $V^\circ{}_2$ decreases as the cohesive energy densities of solvents increase,[13,20] the $\bar{V}^\circ{}_{2,0}$ value can be expected to be small in water, a highly cohesive liquid; therefore, the $(\bar{V}^\circ{}_{2,0} - V_2)$ is negative. If the negative $(\bar{V}^\circ{}_{2,0} - V_2)$ value is accepted, the increase in $|V_2^{\circ E}|$ with an increase in the temperature (Fig. 7) can be interpreted in terms of the monotonous decrease in the positive $\Delta \bar{V}^\circ{}_i$.

Concentration Dependence of the ϕ_V. The slopes of $\phi_V(m)$, $\partial \phi_V / \partial m$, are shown in Table 1. The $\partial \phi_V / \partial m$ value is negative and increases numerically with an increase in the chain length and with a decrease in the temperature. Although the factor determining the slope is of a complicated nature, the above finding appears to indicate that the slope is mainly related to the effect of the hydrophobic groups on the water structure. This tendency of the slope can be interpreted in terms of the overlapping of the icebergs.[22] The contribution of the icebergs to the ϕ_V value, ΔV_i, is positive, as has been shown in the previous section. The decrease in the contribution of the $\Delta \bar{V}_i$ with the increase in the concentration due to the overlapping of the icebergs results in the decrease in the ϕ_V value.

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