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Volumetric Properties of Dilute Aqueous Alcohol Solutions at Different Temperatures

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The densities of dilute aqueous solutions of normal alcohols (from methanol to 1-hexanol) and branched-chain alcohols (2-butanol, 2-methyl-1-propanol, and 2,2-dimethyl-1-propanol) were measured at 5, 15, 25, 35, and 45 °C by means of an oscillating-tube densimeter. The apparent molar volumes of the alcohols in aqueous solutions were determined. The temperature dependences of the limiting partial molar volume, excess partial molar volume, concentration dependence, and methylene group contribution to volume were discussed. An alternative analysis based on the use of specific units instead of molar units was also attempted. The characteristic volumetric behavior of aqueous alcohol solutions is more pronounced for shorter- or branched-chain alcohols rather than hydrophobic alcohols. There is no definitive evidence that so-called hydrophobic hydration around the alkyl groups of alcohol in water is accompanied by a prominent volume change. The unique properties, such as negative partial molar expansion, may originate from the hydrogen-bonding interactions between water and alcohol OH groups.

Much attention has been paid to the volumetric behavior of dilute aqueous alcohol solutions, where unique changes in many thermodynamic properties are observed.[1)] Since the alcohol molecule in water can be regarded as a "soluble alkane,"[2)] the interesting volumetric behavior has been usually interpreted in terms of the alkyl group–water interactions that is a so-called iceberg effect or hydrophobic hydration. On the other hand, little attention has been paid to the contributions of the hydrophilic group–water interactions to the volumetric properties.

Previously we suggested the relative importance of the hydrogen-bonding interactions between water and alcohol OH groups.[3)] For instance, the large negative excess volume observed for aqueous monohydric alcohol systems is not due to the hydrophobic effects, but mainly to geometrical factors and hydrophilic interactions. At present, however, the influence of hydrophilic groups on the water structure has not been known so clearly. Since the structure of water is very sensitive to temperature, it may be profitable to investigate the volumetric behavior at various temperatures in order to understand the solvent-structural effect more precisely.

Although there are reliable experimental data on the apparent molar volume for many aqueous alcohol solutions at 25 °C,[4)] relatively little data are available at other temperatures. In our previous papers, the volumetric properties of aqueous solutions of 2-propanol (*i*-PrOH),[5)] 2-methyl-2-propanol (*t*-BuOH),[6)] and 2-methyl-2-butanol (*t*-PenOH)[7)] have been reported over the whole miscibility range at various temperatures. By using the float method, Nakajima et al.[8)] in our laboratory have reported the apparent molar volumes of some normal alcohols at 5, 25, and 45 °C. In this paper we present the partial molar volume bahavior of nine normal and branched-chain monohydric alcohols having from one to six carbon atoms in dilute aqueous solutions at 5, 15, 25, 35, and 45 °C by using an oscillating-tube densimeter. The purpose of the present study is to clarify the factors contributing to the volumetric properties of aqueous alcohol solutions.

Experimental

The alcohols used are methanol (MeOH), ethanol (EtOH), 1-propanol (*n*-PrOH), 1-butanol (*n*-BuOH), 2-butanol (*s*-BuOH), 2-methyl-1-propanol (*i*-BuOH), 1-pentanol (*n*-PenOH), 2,2-dimethyl-1-propanol (*neo*-PenOH), and 1-hexanol (*n*-HexOH). These alcohols were purified by fractional distillation and stored over molecular sieves 3A or 4A, except for *neo*-PenOH which was purified by crystallization twice. The densities of the liquid alcohols used have been reported elsewhere.[3,5—7,9)] The water was doubly distilled by using a quartz still.

The densities of the aqueous alcohol solutions were measured relative to the density of pure water with an oscillating-tube densimeter (Anton Paar, DMA 60) operated in a phase locked loop mode using two measuring cells (DMA 601). Details of the apparatus and procedure have been described earlier.[6,10)] The densimeter was calibrated at each temperature with water[11)] and dry air. The temperature of the cells was maintained within ±0.002°C by a laboratory-made controller using a Y-cut quartz as a temperature sensor.

All solutions were prepared by successive addition of a stock solution or a pure alcohol to a known quantity of solvent water, which was degassed before using to prevent the formation of bubbles during an experiment. The addition was carried out by weight in a mixing chamber connected to the measuring cell with a Teflon® tube and a flow pump.

Results

The apparent molar volume (ϕ_{v2}) of component 2 in solution can be calculated from the measurements of solution density (ρ) by using the following equation

$$\phi_{v2} = (v - v_0)/m + vM_2 \qquad (1)$$

where v and v_0 are specific volumes ($=1/\rho$) of solution and solvent, respectively, m is molality, and M_2 is the molar mass of component 2.

For sufficiently dilute solutions, the variation of ϕ_{V2} with molality can be adequately represented by the linear relation

$$\phi_{\mathrm{V2}} = \phi_{\mathrm{V2}}{}^\circ + B_{\mathrm{V}} m \tag{2}$$

where $\phi_{\mathrm{V2}}{}^\circ$ is equal to the limiting partial molar volume ($V_2{}^\circ$) and B_{V} is an empirical constant. Figure 1 shows a typical example of the plot of ϕ_{V2} vs. m for aqueous *n*-PrOH solutions at five temperatures. Since the uncertainties of the ϕ_{V2} values are not equal but depend upon the concentrations, the values of $V_2{}^\circ$ and B_{V} were estimated by the least-squares fitting to a quadratic equation obtained by combining Eqs. 1 and 2; that is,[3]

$$(1 + mM)v - v_0 = \phi_{\mathrm{V2}}{}^\circ m + B_{\mathrm{V}} m^2. \tag{3}$$

As clearly shown in Fig. 2, where, for graphical convenience, the values of $(\phi_{\mathrm{V2}} - \phi_{\mathrm{V2}}{}^\circ)$ are plotted against molality for the normal alcohols studied at 25 °C, the linear relation of Eq. 2 holds for all solutions in the concentration range examined. The precision of the limiting partial molar volumes is believed to be better than 0.1 $\mathrm{cm^3\,mol^{-1}}$ for the most cases. In the case of *n*-HexOH, however, the error in $V_2{}^\circ$ may be somewhat larger because of its low solubility in water. Table 1 summarizes the molar volumes (V_2^*), $V_2{}^\circ$, and B_{V} for twelve alcohols studied here and reported earlier,[5—7] together with some relevant literature values of $V_2{}^\circ$. The comparison shows that, in most cases, there is a reasonable agreement between our results and literature values, especially the data reported by Nakajima et al.[8]

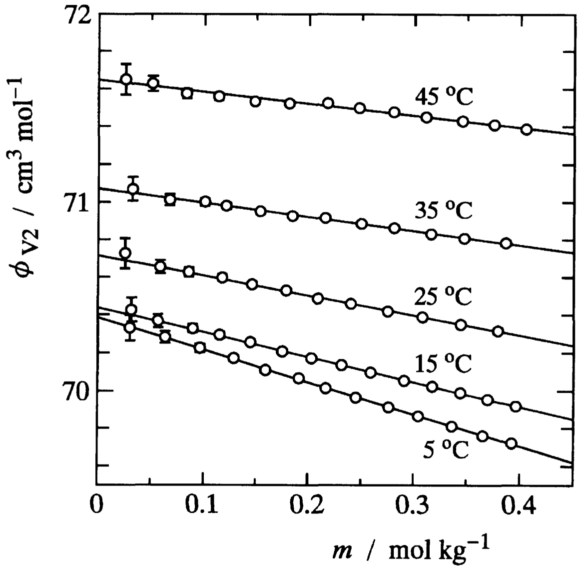

Fig. 1. Concentration dependence of the apparent molar volumes of 1-propanol in dilute aqueous solutions. The error bar indicates the uncertainty due to a density error of $\delta\rho = 2\times10^{-6}$ g cm^{-3}.

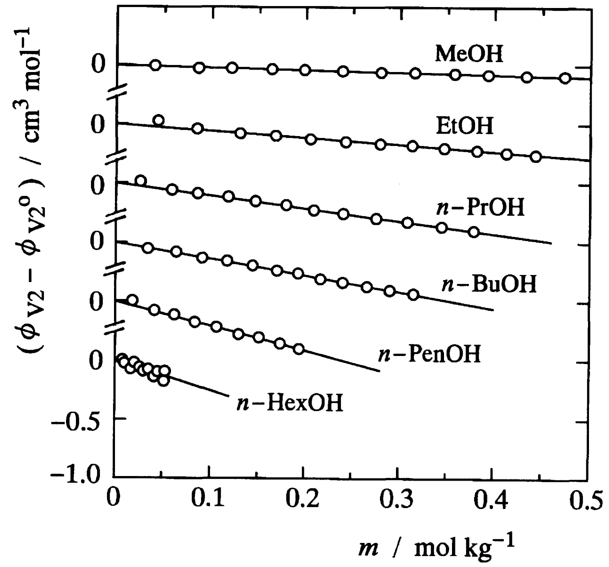

Fig. 2. Concentration dependence of the apparent molar volumes of normal alcohols in dilute aqueous solutions at 25 °C.

Discussion

Limiting Partial Molar Volumes at Various Temperatures. The volumetric behavior of dilute aqueous nonelectrolyte solutions has been discussed by many authors in connection with the structural change of solvent water. Since the hydrogen-bonded structure of water is sensitive to temperature, the temperature dependence of the partial molar volumes of solutes may serve as a reliable and sensitive criterion for the detection of the structural effects.

The limiting partial molar volumes of twelve alcohols having various alkyl chain length and chain branching are plotted in Figs. 3 and 4 as a function of temperature. With increasing chain length, the partial molar volumes of alcohols increase by 16±1 $\mathrm{cm^3\,mol^{-1}}$, caused by the contribution of each methylene group to the partial molar volume. On the other hand, the influence of chain branching seems to be complicated; i.e., the branching brings about an increase in the partial molar volumes for propyl and butyl alcohols, whereas the reverse trend is observed for pentyl alcohols.

It has been well-known that the most remarkable feature of the partial molar volume of alcohols in water is its low temperature dependence, i.e., a low (even negative in some cases) partial molar thermal expansion $(\partial V_2/\partial T)$. Furthermore, it is characterized by a large positive $\partial^2 V_2/\partial T^2$ derivative.[8]

Examination of Table 1 and Fig. 3 clearly indicates that the negative partial molar expansion can be found for EtOH, *i*-PrOH, and *t*-BuOH at lower temperatures than about 15 °C. Similar results have been reported in some references.[8,14,24] By diffferentiating Eq. 1 with respect to temperature and setting $\partial v/\partial T = 0$ at the

Table 1. Molar Volumes, Limiting Partial Molar Volumes, and B_v Parameters for Alcohols in Water$^{\mathrm{a)}}$

t/°C	V_2^*	V_2°	B_v	V_2° in references
MeOH				
5	39.79	38.09	−0.30	38.10$^{\mathrm{b)}}$
15	40.26	38.05	−0.21	38.13$^{\mathrm{c)}}$
25	40.74	38.18	−0.19	38.17$^{\mathrm{b)}}$ 38.68$^{\mathrm{c)}}$ 38.25$^{\mathrm{d)}}$ 38.13$^{\mathrm{e)}}$ 38.10$^{\mathrm{f)}}$
35	41.24	38.33	−0.14	
45	41.75	38.57	−0.13	38.52$^{\mathrm{b)}}$
EtOH				
5	57.44	55.12	−0.92	55.12$^{\mathrm{b)}}$ 55.1$^{\mathrm{g)}}$
15	58.06	55.02	−0.70	54.98$^{\mathrm{c)}}$
25	58.69	55.10	−0.58	55.08$^{\mathrm{b)}}$ 55.08$^{\mathrm{c)}}$ 55.12$^{\mathrm{d)}}$ 55.08$^{\mathrm{e)}}$ 55.08$^{\mathrm{f)}}$ 55.0$^{\mathrm{g)}}$
35	59.34	55.31	−0.48	
45	60.02	55.65	−0.43	55.52$^{\mathrm{b)}}$
n-PrOH				
5	73.71	70.38	−1.70	70.48$^{\mathrm{b)}}$ 70.4$^{\mathrm{g)}}$ 70.48$^{\mathrm{h)}}$
15	74.43	70.44	−1.30	70.58$^{\mathrm{c)}}$
25	75.17	70.71	−1.05	70.74$^{\mathrm{b)}}$ 70.68$^{\mathrm{c)}}$ 70.63$^{\mathrm{d)}}$ 70.68$^{\mathrm{f)}}$ 70.8$^{\mathrm{g)}}$ 70.75$^{\mathrm{i)}}$
35	75.94	71.07	−0.76	71.08$^{\mathrm{i)}}$
45	76.74	71.65	−0.63	71.56$^{\mathrm{b)}}$
i-PrOH				
5	75.38	71.80	−1.97	71.62$^{\mathrm{h)}}$
15	76.16	71.72	−1.58	71.83$^{\mathrm{j)}}$
25	76.97	71.82	−1.23	71.93$^{\mathrm{i)}}$ 71.89$^{\mathrm{j)}}$ 71.60$^{\mathrm{k)}}$ 71.79$^{\mathrm{l)}}$
35	77.82	72.11	−1.06	72.10$^{\mathrm{i)}}$
45	78.73	72.52	−0.84	
n-BuOH				
5	90.30	85.88	−2.51	86.00$^{\mathrm{b)}}$ 86.5$^{\mathrm{g)}}$ 86.00$^{\mathrm{h)}}$ 86.02$^{\mathrm{m)}}$
15	91.14	86.21	−1.98	
25	92.00	86.63	−1.39	86.63$^{\mathrm{b)}}$ 86.48$^{\mathrm{d)}}$ 86.64$^{\mathrm{f)}}$ 86.5$^{\mathrm{g)}}$ 86.62$^{\mathrm{i)}}$ 86.65$^{\mathrm{m)}}$
35	92.89	87.29	−1.06	87.27$^{\mathrm{i)}}$
45	93.81	88.07	−0.77	87.94$^{\mathrm{b)}}$
i-BuOH				
5	91.17	85.80	−2.48	85.81$^{\mathrm{m)}}$
15	92.02	86.07	−1.93	
25	92.90	86.46	−1.40	86.75$^{\mathrm{d)}}$ 86.73$^{\mathrm{m)}}$
35	93.82	87.04	−1.09	
45	94.79	87.79	−0.79	
s-BuOH				
5	90.57	86.18	−2.85	86.00$^{\mathrm{h)}}$ 86.27$^{\mathrm{m)}}$
15	91.45	86.29	−2.27	
25	92.38	86.55	−1.76	86.53$^{\mathrm{d)}}$ 86.66$^{\mathrm{e)}}$ 86.64$^{\mathrm{i)}}$ 86.55$^{\mathrm{m)}}$ 86.66$^{\mathrm{n)}}$
35	93.37	87.08	−1.40	87.04$^{\mathrm{i)}}$
45	94.42	87.73	−1.01	
t-BuOH				
0.5	—	87.89	−3.48	87.95$^{\mathrm{m)}}$
5	—	87.75	−3.25	87.92$^{\mathrm{m)}}$
10	—	86.73	−2.83	87.88$^{\mathrm{o)}}$
15	—	87.27	−2.50	
25	—	87.81	−2.00	87.73$^{\mathrm{d)}}$ 87.86$^{\mathrm{f)}}$ 87.80$^{\mathrm{m)}}$ 87.76$^{\mathrm{o)}}$
26	95.10	87.79	−1.90	
35	96.25	88.19	−1.62	88.55$^{\mathrm{p)}}$
45	97.61	88.74	−1.21	88.87$^{\mathrm{p)}}$
n-PenOH				
5	106.80	101.27	−3.25	101.43$^{\mathrm{b)}}$ 101.1$^{\mathrm{g)}}$ 101.43$^{\mathrm{h)}}$
15	107.74	101.84	−2.33	
25	108.71	102.62	−2.08	102.55$^{\mathrm{b)}}$ 102.88$^{\mathrm{d)}}$ 102.3$^{\mathrm{g)}}$ 102.62$^{\mathrm{i)}}$
35	109.71	103.51	−1.59	103.46$^{\mathrm{i)}}$
45	110.75	104.53	−0.93	104.34$^{\mathrm{b)}}$
neo-PenOH				
5	—	101.09	−3.51	
15	—	101.63	−2.88	
25	—	102.29	−2.28	101.87$^{\mathrm{d)}}$ 102.32$^{\mathrm{l)}}$
35	—	103.05	−1.76	
45	—	104.04	−1.23	
t-PenOH				
5	107.19	100.81	−4.29	
15	108.39	100.94	−3.11	
25	109.62	101.37	−2.76	101.15$^{\mathrm{l)}}$
35	110.91	102.11	−2.54	
45	112.27	102.94	−2.21	
n-HexOH				
5	123.22	116.65	−4.09	117.10$^{\mathrm{h)}}$
15	124.27	117.48	−2.30	
25	125.36	118.47	−2.52	118.65$^{\mathrm{i)}}$
35	126.48	119.67	−2.11	119.64$^{\mathrm{i)}}$
45	127.63	120.96	−1.28	

a) Units: cm^3 mol^{-1} for V_2^* and $V_2{}^\circ$; cm^3 kg mol^{-2} for B_v. b) Ref. 8. c) Ref. 12. d) Ref. 13. e) Ref. 14. f) Ref. 15. g) Ref. 16. h) Ref. 17. i) Ref. 18. j) Ref. 19. k) Ref. 20. l) Ref. 21. m) Ref. 22. n) Ref. 23. o) Ref. 24. p) Ref. 25.

temperature of the maximum density (TMD), one can obtain the following expression for the apparent molar thermal expansion ($\partial\phi_{\mathrm{v}2}/\partial T$) of solute in aqueous solution at TMD.

$$\partial\phi_{\mathrm{v}2}/\partial T = -v_0\alpha_0/m \tag{4}$$

where α_0 is thermal expansion coefficient of pure water. From this equation we can expect that TMD for dilute aqueous solutions of these alcohols is higher than that of pure water, 3.98 °C. In fact, this expectation has been well confirmed by the TMD measurements by Wada and Umeda.[26]

It has been, in general, considered that the positive shift of TMD or the negative partial molar thermal expansion is caused by the hydrophobic hydration around nonpolar solutes.[1] However, this idea does not necessarily coincide with our results described in Figs. 3 and 4. Namely, the negative partial molar expansion was observed, not for more hydrophobic alcohols such as

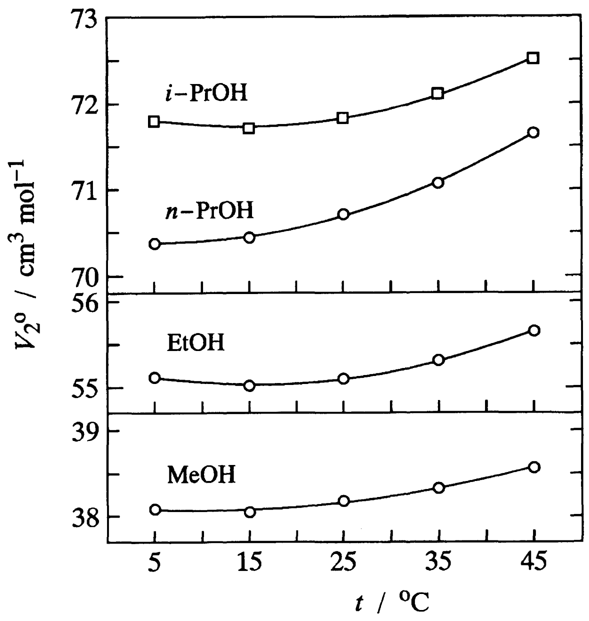

Fig. 3. Limiting partial molar volumes of methanol, ethanol, 1-propanol, and 2-propanol in water.

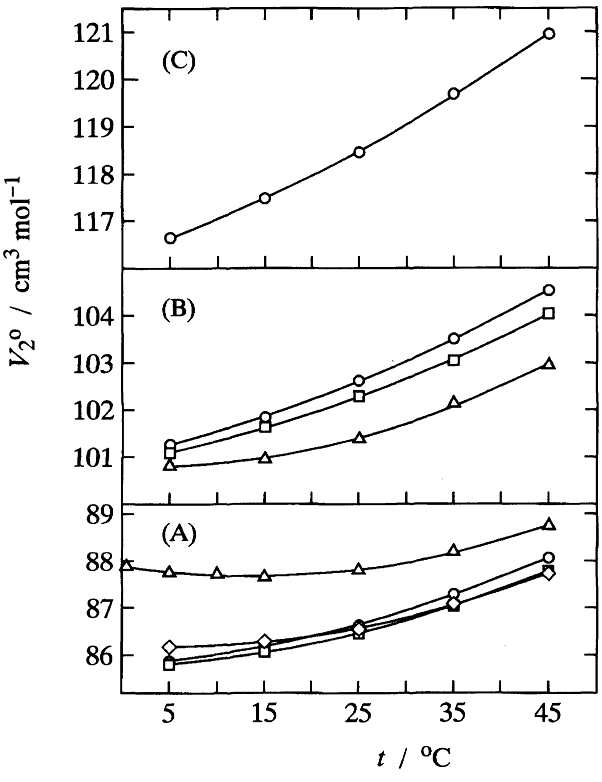

Fig. 4. Limiting partial molar volumes of alcohols in water. A: *n*-BuOH (○); *i*-BuOH (□); *s*-BuOH (◇); *t*-BuOH (△), B: *n*-PenOH (○); *neo*-PenOH (□); *t*-PenOH (△), C: *n*-HexOH (○).

pentyl or hexyl alcohols, but for rather shorter-chain alcohols such as EtOH, *i*-PrOH, or *t*-BuOH.

In this regard we shall call attention to the facts that the shift of TMD for aqueous benzene solution is apparently the same as that expected for an ideal solution.[26] This is in agreement with the results that the partial molar expansions of benzene derivatives in water are practically the same as the molar expansions of neat solutes near 5 °C.[27,28] This is also the case for the other hydrophobic solutes such as dichloromethane[12] or alkyl acetates.[29]

On the basis of the thermodynamic relation

$$(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P \qquad (5)$$

Hepler[30] has postulated a criterion for discriminating between solutes in water as being "structure makers" or "structure breakers." It has been known that a positive $\partial^2 V_2{}^\circ/\partial T^2$ value is observed for many monofunctional nonelectrolytes such as alcohols or tetraalkylammonium halides, and negative value for very polar nonelectrolytes such as urea or various inorganic electrolytes.

Figure 5 represents the chain length dependence of the $\partial^2 V_2{}^\circ/\partial T^2$ values at 25 °C estimated by the least squares fitting of the limiting partial molar volumes as a function of temperature. The figure also includes the values of $\partial^2 V_2{}^*/\partial T^2$ estimated from the molar volumes of neat alcohols. It can be seen that the latter values are very small compared with the former, because the molar volumes of many alcohols increase rather linearly with temperature in the temperature range studied. In contrast, $\partial^2 V_2{}^\circ/\partial T^2$ values for normal alcohols are large and positive, and increase with the chain length up to propanol. It is apparent that the value converges toward a common value for longer-chain alcohols. A very similar variation of the $\partial^2 V_2{}^\circ/\partial T^2$ with chain length has been reported for some organic electrolyte solutions.[31]

On the other hand, the chain-branching appears to bring about a pronounced increase in $\partial^2 V_2{}^\circ/\partial T^2$. It is, however, to be noted that the effect is obvious only in the substitution of a hydrogen atom on α-carbon by a methyl group, as indicated by a broken line, whereas the branching effect are scarcely visible for *i*-BuOH and *neo*-PenOH, that is, the substitution on β-carbon. An

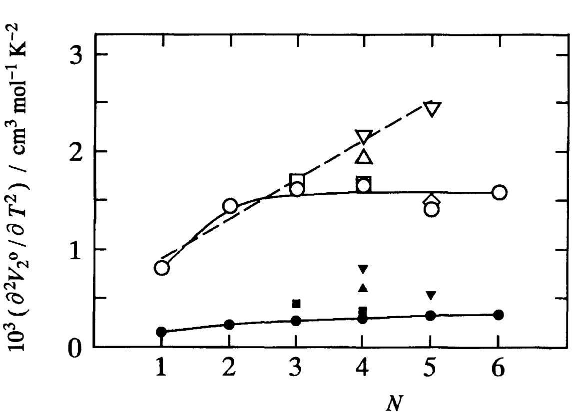

Fig. 5. Plot of $\partial^2 V_2{}^\circ/\partial T^2$ against chain length of alcohols at 25 °C. Normal alcohols (○); *i*-PrOH and *i*-BuOH (□); *s*-BuOH (△); *t*-BuOH and *t*-PenOH (▽); *neo*-PenOH (◇). The filled symbols refer to $\partial^2 V_2^*/\partial T^2$ for neat alcohols.

analogous feature has been reported in the studies of the partial molar volumes,[32)] the shifts of the temperature of maximum density of water,[33)] and the enthalpies of transfer from DMF to water.[34)] These results suggest that the interactions between water and methyl group adjacent to a polar group might be distinguishable from the interactions between water and the hydrocarbon moieties apart from the polar group. We suppose that the large $\partial^2 V_2{}^\circ/\partial T^2$ is closely associated with the hydrophilic hydration of polar group.

Pratial Molar Volume of a Methylene Group. The contribution of a methylene group to the limiting partial molar volume can be estimated by the following subtraction process:

$$V^\circ(\mathrm{CH_2}) = V^\circ(N+1) - V^\circ(N) \qquad (6)$$

where $V^\circ(N)$ represents the partial molar volume of a normal alcohol containing N carbon atoms. The $V^\circ(\mathrm{CH_2})$ values estimated at various temperatures are illustrated as a function of N in Fig. 6, in which analogous methylene contributions, $V^*(\mathrm{CH_2})$, calculated from the molar volumes of neat alcohols[3)] are also described by closed symbols for comparison.

The group additivity scheme has been proposed by many authors, and Cabani et al.[4)] have discussed in detail about the group contribution to the partial molar volumes and heat capacities of organic nonelectrolytes in water. It is well-known that the partial molar heat capacities of a homologous series in water vary in proportion to the molar mass of the solutes and are scarcely affected by terminal groups.[35)] For the case of the partial molar volume, on the other hand, such a proportionality is only approximate; that is, the methylene contribution is usually dependent on the nature of the terminal functional group.[8,20,31,36)] Figure 6 clearly shows that the partial molar volume of a methylene group varies in zigzag depending on the chain lengths, especially for shorter-chain alcohols. Nakajima et al.[8)] and Sakurai et al.[31,32)] have suggested that such a variation in $V^\circ(\mathrm{CH_2})$ results from the influence of the polar group upon the hydrophobic hydration around alkyl chains of the solutes.

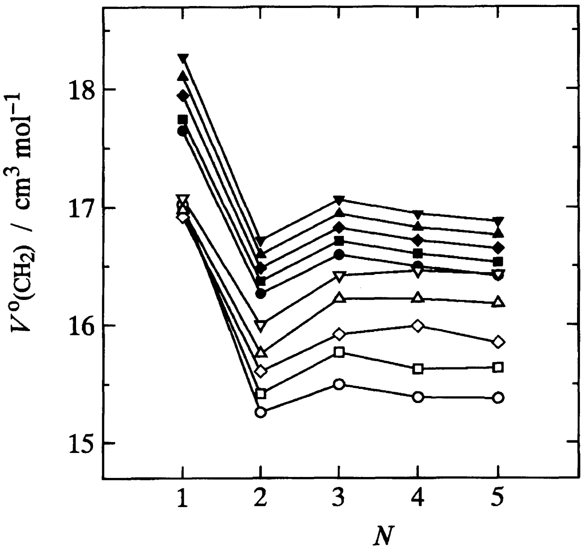

Fig. 6. Contribution of a methylene group to the limiting partial molar volumes of alcohols. 5 °C (○); 15 °C (□); 25 °C (◇); 35 °C (△); 45 °C (▽). The filled symbols refer to the contribution to the molar volumes of neat alcohols.

It should be noted, however, that the $V^*(\mathrm{CH_2})$ values also varies with chain length in a manner very similar to the $V^\circ(\mathrm{CH_2})$ values, as is illustrated in Fig. 6. A similar chain-length dependence of $V^\circ(\mathrm{CH_2})$ can be obtained from the data for normal alcohols in some organic solvents such as ethanol, benzene, or cyclohexane.[37)] These facts suggest that the inconsistent contribution of a methylene group to the partial molar volume may not originate from the solute–solvent interactions but may be a reflection of the volumetric properties of solute itself. For instance, the molar volume of methanol is rather small, due to more effective packing of molecules compared with other normal alcohols,[3)] and, therefore, the $V^*(\mathrm{CH_2})$ value evaluated from the molar volumes of methanol and ethanol becomes fairly large.

Nevertheless, the temperature dependence of $V^\circ(\mathrm{CH_2})$ could be a manifestation of the structural change of water induced by the introduction of a methylene group. Figure 6 shows that the $V^\circ(\mathrm{CH_2})$ at $N=1$, which is the volume increment accompanying the substitution of a hydrogen atom on α-carbon by a methyl group, has a negative temperature dependence at lower temperatures. This is distinct from the $V^\circ(\mathrm{CH_2})$ estimated from longer-chain homologues or $V^*(\mathrm{CH_2})$. Such a negative expansion behavior for the methylene group may be associated with the negative partial molar thermal expansion observed for some shorter-chain or branched-chain alcohols at low temperatures, as was described in the previous section.[32)] On the other hand, the partial molar volume of the methylene group apart from the OH group has a larger temperature dependence than $V^*(\mathrm{CH_2})$. The same tendency has been observed in the results for a series of some alkyl acetates,[29)] which are more hydrophobic than alcohols. The large partial molar expansion of a methylene group may be principally due to the repulsive interactions between hydrophobic group and water.

Excess Partial Molar Volume. It is well-known that the excess limiting partial molar volume ($V_2^\mathrm{E} = V_2^\circ - V_2^*$) is extremely negative for alcohols in water. The longer or more branched the alkyl group is, the more negative is the V_2^E value. Therefore, the negative V_2^E value has often been regarded as the criterion of the hydrophobic hydration.[1,2,38)] If this is relevant, the negative V_2^E would have to be reduced in magnitude as the temperature is raised, because water-structural influences become progressively reduced with increasing temperature. As is shown in Fig. 7, however, the

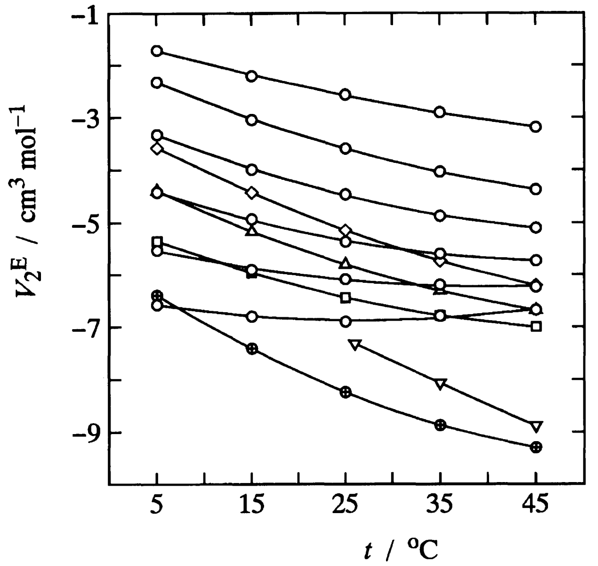

Fig. 7. Excess partial molar volumes of alcohols in water. Normal alcohols having from one (top) to six carbon atoms (bottom) (○); *i*-PrOH (◇); *i*-BuOH (□); *s*-BuOH (△); *t*-BuOH (▽); *t*-PenOH (⊕).

V_2^E values become more negative with the increase in temperature for the most alcohols studied, except for *n*-HexOH at higher temperatures.

The negative excess volume observed for various aqueous systems should be interpreted in principle in terms of the volume change on mixing of different molecular sizes of the components[39] and/or the difference in cohesive energy density of the components.[40] The larger negative V_2^E values found for longer-chain alchohols may be a matter of course, since V_2^E is taken as a molar unit. That is to say, the solutes with larger molar mass bring about necessarily the larger variation in the molar properties. The considerations in terms of specific quantities will be discussed in the next section in more detail.

The more negative V_2^E for branched-chain alcohols compared with normal chain homologues may originate from the larger molar volumes of the neat alcohols because of less closed packing of molecules due to steric hindrance.[3] The negative temperature dependence of V_2^E arises from the lower partial molar expansion of alcohols in water compared with the molar expansions of neat alcohols. The former behavior may be associated with hydrophilic hydration, as was described above. It is apparent that the negative V_2^E can not be an immediate consequence of the hydrophobic hydration.

Partial Specific Volumes. When physical properties of binary mixtures composed of very different molecular sizes are concerned, it is more appropriate to describe them in the form of specific quantities instead of molar quantities.[6,41,42] As to the solute–solvent interactions operated in aqueous solutions, the ratio of the hydrophilic to hydrophobic hydrations is reflected in the partial specific quantities, while the partial molar quantities are the reflection of the net changes in both the hydrations.

The limiting partial specific volumes ($v_2^\circ = V_2^\circ/M_2$) and excess limiting partial specific volumes ($v_2^E = V_2^E/M_2$) of normal alcohols are shown as a function of temperature in Figs. 8 and 9, respectively. The values of v_2° decrease with the number of carbon atoms in the alcohols, except for methanol. This variation in v_2° with chain length is roughly the same as that in the specific volume of the neat alcohols. The excess partial specific volumes, therefore, do not give so large variations in magnitude with the difference in the chain length of the alcohols (see Fig. 9). Furthermore, a marked temperature dependence of the excess partial specific volume is apparent for the shorter-chain alcohols. Thus, we can

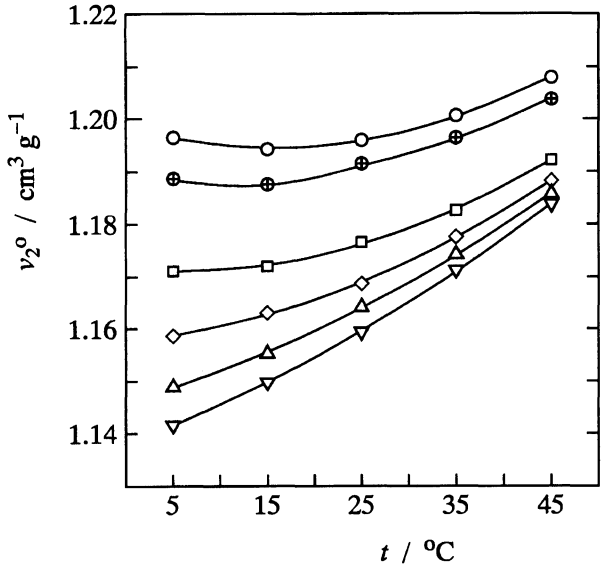

Fig. 8. Limiting partial specific volumes of normal alcohols in water. MeOH (⊕); EtOH (○); *n*-PrOH (□); *n*-BuOH (◇); *n*-PenOH (△); *n*-HexOH (▽).

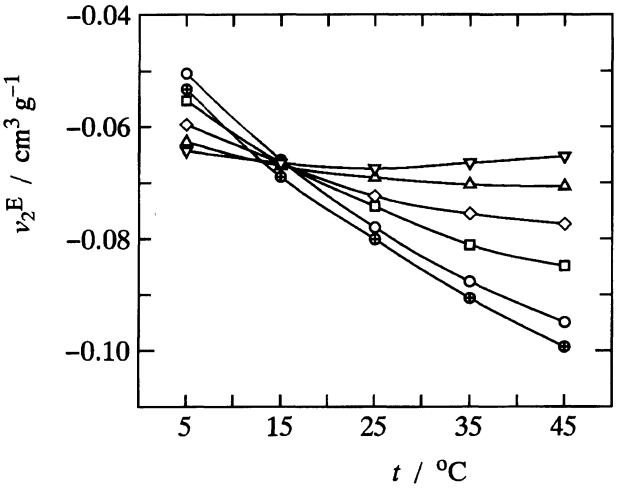

Fig. 9. Excess partial specific volumes of normal alcohols in water. MeOH (⊕); EtOH (○); *n*-PrOH (□); *n*-BuOH (◇); *n*-PenOH (△); *n*-HexOH (▽).

not recognize any indication of the increase in the hydrophobic effects with increasing chain length, since the hydrophobic hydration is considered to be very sensitive to temperature.

In conclusion, the pesent results suggest that the partial molar (specific) volumes of alcohols do not reflect so-called hydrophobic hydration, even if such a special hydration is actually present in aqueous solutions. In this connection, we note a recent theoretical study by Soda,[43] who suggests that the hydrated water around a nonpolar solute is energetically similar to bulk water. Anomalously low partial molar expansion characteristic of some aqueous alcohol solutions may be attributed to hydrophilic hydrations, although the molecular reason for the hydration is by no means clear at the present time.[3]

Concentration Dependence of Apparent Molar and Specific Volumes. The concentration dependence of the apparent molar volume in dilute solution is given by the B_v parameter in Eq. 2. The values obtained for normal alcohols are illustrated in Fig. 10 as a function of temperature. It is evident that the values are negative and increase in magnitude with increasing chain length or decreasing temperature. From these fact the negative B_v has often been considered as a measure of the hydrophobic hydration.[1] However, it is not such an easy matter to give a satisfactory explanation for the concentration dependence of the apparent or partial molar volume.[6]

The somewhat obscure nature of the B_v parameter can also be seen in this study. For instance, we shall call attention to the variation in the B_v values obtained for four isomeric butyl alcohols at various temperatures (see Fig. 11). The B_v values for *t*-BuOH, which has often been regarded as a solute exhibiting a typical hydrophobic hydration,[1] are in fact slightly more negative than those for the other isomers. However, we note that the temperature dependence of B_v is about the same among butyl alcohol isomers. Namely, the slopes in Fig. 11 are almost identical. The values of V_2°, on the other hand, show different temperature dependences, as is shown in Fig. 4A. This is also the case for the three isomers of pentyl alcohols.

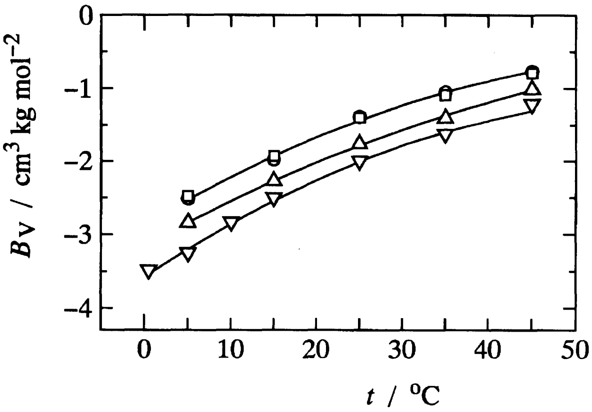

Fig. 11. The B_V parameter in Eq. 2 for four isomeric butyl alcohols. *n*-BuOH (○); *i*-BuOH(□); *s*-BuOH (△); *t*-BuOH (▽).

An alternative representation of the concentration dependence can be made by plotting the apparent specific volume ($\phi_{vs}=\phi_{v2}/M_2$) against weight fraction (w). For dilute solutions the linear relation corresponding to Eq. 2 is given by

$$\phi_{vs} = \phi_{vs}{}^\circ + b_v w \tag{7}$$

The values of b_v for normal alcohols are shown in Fig. 12. It should be noted that there appears to be no significant difference in the b_v values and in their temperature dependences for these alcohols, except for methanol. Hence, we conclude that the parameter B_v or b_v does not reflect the interactions due to the structural change of solvent water.

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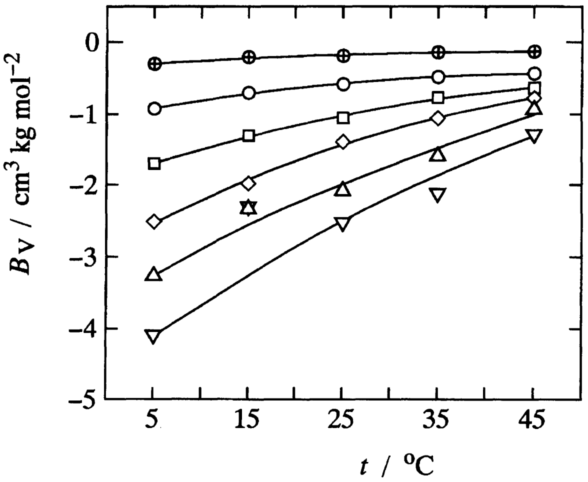

Fig. 10. The B_v parameter in Eq. 2 for normal alcohols. MeOH (⊕); EtOH (○); *n*-PrOH (□); *n*-BuOH (◇); *n*-PenOH (△); *n*-HexOH (▽).

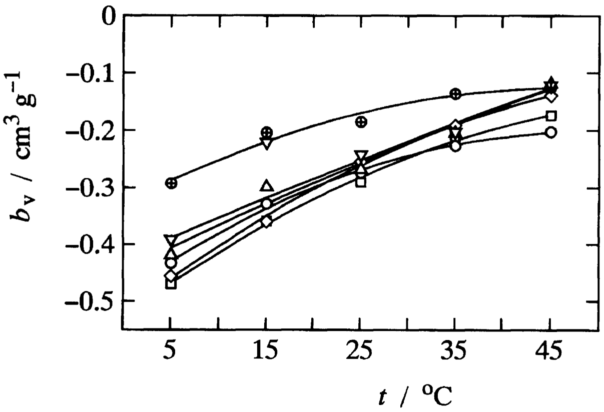

Fig. 12. The b_v parameter in Eq. 7 for normal alcohols. MeOH (⊕); EtOH (○); *n*-PrOH (□); *n*-BuOH (◇); *n*-PenOH (△); *n*-HexOH (▽).

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