Apparent Molar Volumes and Apparent Molar Adiabatic Compressions of Water in Some Alcohols

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The ultrasonic velocities in dilute alcoholic solutions of water have been measured in the temperature range from 5 to 45 °C. The solvent alcohols used were methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1-pentanol, and 2-methyl-2-butanol. In addition, the densities of 2-butanol and 2-methyl-1-propanol solutions of water were also measured. The apparent molar volumes and apparent molar adiabatic compressions of water in these alcohols have been evaluated. The limiting partial molar quantities are less than the molar quantities of pure water; this phenomenon is generally more pronounced for lower-chain or branched-chain alcohols. The results are discussed in connection with the hydrogen-bonding interactions, that is, the self-association of the solvent alcohols and the alcohol–water interactions.

Although the partial molar volume behavior of alcohol–water systems has been extensively investigated for several decades, most studies have concerned aqueous-rich solutions, and the partial molar volume of water in dilute alcohol solutions has hitherto received relatively little attention.[1)] In studies concerning dilute aqueous nonelectrolyte solutions, the results have often been interpreted in terms of water-structural changes caused by the introduction of hydrophobic residues, i.e., hydrophobic hydration or iceberg formation.[2)] In spite of much investigation, however, the exact nature of the iceberg has remained obscure; for instance, the net volume change accompanying iceberg formation is still open to question.[3)] Up to the present, on the other hand, little attention has been paid to the contributions of the hydrogen-bond formation between solute and solvent molecules on the volumetric properties. It appears to be fairly natural to take into account such normal hydration effects when interpreting the volumetric properties of strongly associated systems, such as alcohol–water mixtures. In order to understand more precisely the contributions of this type of hydration on the volume changes, it is desirable to study aqueous solutions in organic-rich regions, where one need not any longer take into account the ill-defined iceberg effects.

Concerning this point of view, we studied the partial molar volumes of water in various alcohols.[3—7)] Since the changes in the solution structure should be very sensitive to the temperature or pressure, the partial molar expansion or compression could be a reliable and sensitive criterion for the detection of solute–solvent interactions. Nevertheless, there have been very few studies reported concerning the partial molar compression behavior of water in organic media.[8)]

In the present paper we report on the results of sound velocity measurements for dilute solutions of water in ten monohydric alcohols having from one to five carbon atoms, and on some additional density measurements for solutions of water in two butyl alcohol isomers. The purpose of this paper is to discuss the partial molar volumes and partial molar adiabatic compressions of water in various alcohols in order to provide a better understanding concerning the factors which contribute to the volumetric behavior of strongly associated mixtures.

Experimental

The alcohols used as solvents were methanol (MeOH), ethanol (EtOH), 1-propanol (*n*-PrOH), 2-propanol (*i*-PrOH), 1-buthanol (*n*-BuOH), 2-buthanol (*s*-BuOH), 2-methyl-1-propanol (*i*-BuOH), 2-methyl-2-propanol (*t*-BuOH), 1-pentanol (*n*-PenOH), and 2-methyl-2-butanol (*t*-PenOH). These alcohols were purified by fractional distillation and stored over molecular sieves 3A or 4A. The water was doubly distilled using a quartz still.

The sound velocities (u) in the solutions were measured at a frequency of about 5 MHz by using a sing-around velocimeter constructed in our laboratory, and are given relative to the sound velocity (u_0) in pure solvent by using the relation

$$1/u = 1/u_0 + (T - T_0)/L, \qquad (1)$$

where T and T_0 are the pulse repetition periods for solution and solvent, respectively, and L is the effective path length between two piezoelectric transducers fixed to both sides of the measuring cell. The calibration of L (ca. 7 cm) was based on the sound velocities in pure water at various temperatures reported by Del Grosso and Mader.[9)] The precision of the measurements of the sound velocity difference ($u-u_0$) was estimated to be better than 1 cm s^{-1} for the dilute solution range studied.

The densities (ρ) for *i*- and *s*-BuOH solutions were measured using an oscillating-tube densimeter (Anton Paar, DMA 60/601), which was described elsewhere in detail.[3,4)]

The temperature of the measuring cell of the sound velocimeter or densimeter was maintained within ±0.002 °C by a laboratory-made controller using a Y-cut quartz as a temperature sensor.

All of the solutions were prepared by successive additions of a stock solution to a known quantity of solvent alcohols. The addition was carried out by weight in the sound velocity measuring cell or in a mixing chamber connected to the density measuring cell with a Teflon tube.

Results

The sound velocities and densities of the solvent alcohols used in this study are given in Tables 1 and 2, respectively. These tables also include some of the reference values to be compared. The agreement between our values and the values reported by other authors is generally good.

Table 1. Sound Velocities in Pure Alcohols a)

	5 °C	15 °C	25 °C	35 °C	45 °C
MeOH	1169.63	1135.31	1102.40	1069.27	1036.79
		1148.7 c)	1116.7 c)	1084.7 c)	1052.7 c)
		1143.7 d)	1097.70 e)		
			1097.57 f)		
			1101.80 g)		
			1103.0 h)		
			1097.48 i)		
EtOH	1212.42	1177.02	1142.39	1108.26	1074.63
	1267.3 c)	1233.4 c)	1199.6 c)	1165.7 c)	1131.8 c)
		1177.8 j)	1136.65 e)	1112 k)	
			1141.20 f)	1107.9 j)	
			1142.29 g)		
			1143.5 h)		
			1143.1 j)		
			1160 k)		
			1142.4 l)		
n-PrOH	1275.85	1240.23	1205.22	1170.89	1136.93
	1273.8 c)	1240.1 c)	1206.3 c)	1172.6 c)	1138.9 c)
			1205.42 f)		
			1205.17 g)		
			1205.9 h)		
			1205.3 l)		
i-PrOH	1209.08	1173.44	1138.09	1102.84	1067.25
	1211.3 c)	1176.0 c)	1140.6 c)	1105.3 c)	1070.0 c)
		1156.3 m)	1134.26 e)	1182 k)	
			1213 k)		
			1131.8 m)		
			1138.09 n)		
n-BuOH	1308.76	1273.76	1239.34	1205.59	1172.13
	1310.7 c)	1276.7 c)	1242.7 c)	1208.8 c)	1174.8 c)
			1239.39 g)		
			1240.0 h)		
i-BuOH	1256.29	1221.50	1187.58	1153.83	1120.53
	1256.9 c)	1223.2 c)	1189.6 c)	1155.9 c)	1122.2 c)
			1200 o)	1164 o)	
s-BuOH	1283.31	1247.21	1210.96	1174.43	1137.45
	1284.9 c)	1248.2 c)	1211.5 c)	1174.8 c)	1138.1 c)
t-BuOH b)	1115.81	1098.04	1076.15	1054.31	1032.95
	1217.5 c)	1200.7 c)	1179.6 c)	1158.6 c)	1137.6 c)
n-PenOH	1343.79	1308.75	1274.42	1240.44	1206.94
	1344.0 c)	1310.6 c)	1277.2 c)	1243.8 c)	1210.4 c)
			1275.18 g)		
t-PenOH	1252.81	1214.96	1178.44	1142.29	1106.07
	1263.6 c)	1225.8 c)	1188.0 c)	1150.3 c)	1112.5 c)

a) Unit: $\mathrm{m\,s^{-1}}$. b) At 26, 30, 35, 40, and 45 °C. c) Calculated from the Table in Ref. 10. d) Ref. 11. e) Ref. 12. f) Ref. 13. g) Ref. 14. h) Ref. 15. i) Ref. 16. j) Ref. 17. k) Ref. 18. l) Ref. 19. m) Ref. 20. n) Ref. 21. o) Ref. 22.

Table 2. Densities of Pure Alcohols a)

	5 °C	15 °C	25 °C	35 °C	45 °C
i-BuOH	0.81305	0.80551	0.79793	0.79001	0.78197
			0.79987 b)	0.79213 b)	
			0.79779 c)		
			0.797083 d)		
s-BuOH	0.81838	0.81054	0.80240	0.79389	0.78503
			0.80241 e)	0.79378 e)	
			0.80251 c)		
			0.801660 d)		
			0.80247 f)		

a) Unit: $\mathrm{g\,cm^{-3}}$. b) Ref. 22. c) Ref. 23. d) Ref. 24. e) Ref. 25. f) Ref. 26.

The apparent molar quantities (ϕ_{Q}) of the solute in solution can be calculated from the corresponding specific quantities of solution (q) and of solvent (q_0) by the relation

$$\phi_{\mathrm{Q}} = (q - q_0)/m + qM, \tag{2}$$

where m is the molality and M the molar mass of the solute. In the present study, ϕ_{Q} refers to the apparent molar volume (ϕ_{V}) or the apparent molar adiabatic compression (ϕ_{K}) and q refers to the specific volume ($v=1/\rho$) or specific adiabatic compression ($k=-(\partial v/\partial P)_{\mathrm{s}}=(v/u)^2$).

For sufficiently dilute solutions, the variation of ϕ_{Q} with the concentration can be adequately represented by

$$\phi_{\mathrm{Q}} = \phi_{\mathrm{Q}}{}^{\circ} + B_{\mathrm{Q}}m. \tag{3}$$

The infinite dilution value ($\phi_{\mathrm{Q}}{}^{\circ}$), which is equal to the limiting partial molar quantity (Q°), and an experimental parameter (B_{Q}) can be evaluated by the linear regression of this equation. In practice, however, this linear regression can not always give an accurate estimate of the parameters, because the uncertainties of the calculated ϕ_{Q} values are not constant throughout. As a typical example, the apparent molar volumes of water in *i*-BuOH and the apparent molar adiabatic compressions of water in EtOH at various temperatures are plotted as a function of concentration in Figs. 1 and 2, respectively. It is clear that the error in ϕ_{Q} due to a given uncertainty in q rapidly increases as the concentration is reduced. For example, in the case of the volume, for a uncertainty of $\delta\rho=\pm2\times10^{-6}$ $\mathrm{g\,cm^{-3}}$ the error in ϕ_{V} is only ±0.006 $\mathrm{cm^3\,mol^{-1}}$ at $m=0.5$ $\mathrm{mol\,kg^{-1}}$, while the same density error leads to $\delta\phi_{\mathrm{V}}=\pm0.06$ $\mathrm{cm^3\,mol^{-1}}$ at $m=0.05$ $\mathrm{mol\,kg^{-1}}$. For adiabatic compression, in a similar manner as the volume, the uncertainty $\delta u=\pm1$ $\mathrm{cm\,s^{-1}}$ results in a ϕ_{K} error of about ±0.4 and ±0.04 $\mathrm{cm^3\,GPa^{-1}\,mol^{-1}}$ at $m=0.05$ and 0.5 $\mathrm{mol\,kg^{-1}}$, respec-

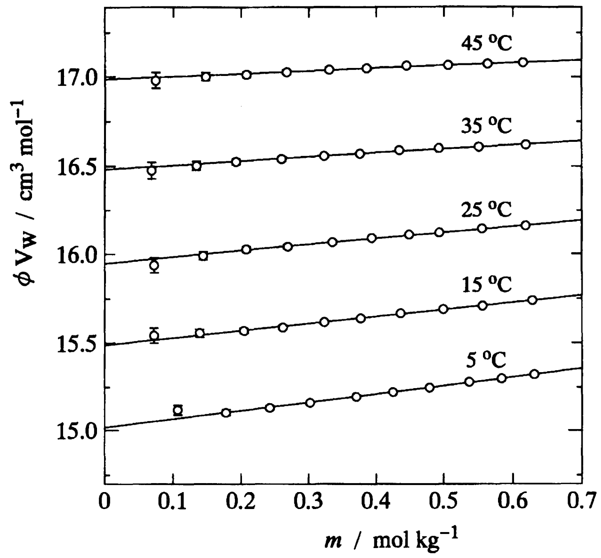

Fig. 1. Concentration dependence of the apparent molar volumes of water in 2-methyl-1-propanol. The bars indicate the uncertainties due to a density error of $\delta\rho=2\times10^{-6}$ g cm^{-3}.

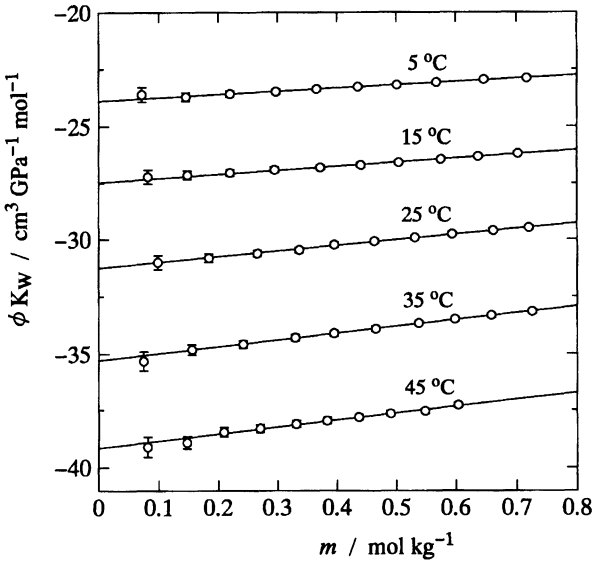

Fig. 2. Concentration dependence of the apparent molar adiabatic compressions of water in ethanol. The bars indicate the uncertainties due to sound velocity and density errors of $\delta u=1$ cm s^{-1} and $\delta\rho=2\times10^{-6}$ g cm^{-3}, respectively.

tively. Instead of the linear regression of Eq. 3, therefore, we evaluated the parameters $\phi_Q{}^\circ$ and B_Q by the least-squares fitting to a quadratic equation obtained by combining Eqs. 2 and 3; that is,

$$(1+mM)q-q_0=\phi_Q{}^\circ m+B_Q m^2. \qquad (4)$$

The limiting partial molar volumes of water ($V_W{}^\circ$) in various alcohols studied here and reported earlier[3,5—7] are summarized in Table 3, in which the data for *n*-alcohol solutions were recalculated by using Eq. 4 from our original data.[5] Table 3 also includes some of the literature values, though there have been only a few reliable volumetric data for alcohol–water mixtures in highly organic-rich regions with which the results presented here can be directly compared. It can be seen that there is, in general, good agreement with the exception of *i*-PrOH.

The density values of the solutions used for sound velocity measurements were calculated from the $V_W{}^\circ$ and B_V values by using Eq. 4. Table 4 summarizes the limiting partial molar adiabatic compressions of water ($K_W{}^\circ$) and the B_K values in various alcohols at five temperatures. As far as we know, no comparable data can be found in the literature, except for MeOH, EtOH, and *n*-PrOH at 25 °C, reported by Kiyohara and Benson.[13] Since they measured the sound velocities and excess volumes[29] over the entire composition range, only a few data points are available in the alcohol-rich region in which we are interested. Nevertheless, the $K_W{}^\circ$ values estimated from the apparent molar adiabatic compressions of water at concentrations of less than 2 mol kg^{-1} are in excellent agreement with our results.

Discussion

A volume change upon mixing two liquids can arise from a variety of origins.[32] At first, one should consider a geometrical factor; that is, the difference in size of the component molecules provides a significant contribution toward the volumetric behavior of aqueous mixtures, since the molecular size of water differs significantly from another component in most organic nonelectrolyte-water systems. This contribution is normally accompanied by a negative volume change as well as a negative compression change. In fact, the excess volume data for a number of binary aqueous mixtures[32,33] clearly show that the mixing water with organic substances results in more or less a contraction in volume. A few exceptional results are the positive volume change observed for very dilute water solutions in nonpolar solvents, such as benzene[34] or carbon tetrachloride,[35] where repulsive interactions may be predominant.

In mixtures of water with alcohols, in addition to the geometrical contribution, it is inevitable to consider various interactions between components; that is, attractive interactions due to the hydrogen-bond formation between alcohol–alcohol, alcohol–water, and water–water molecules and repulsive interactions between water and alkyl group of alcohols. As a general rule, the attractive interactions bring about a reduction in both the volume and compression, and repulsive interactions are accompanied by opposite changes. It appears that this general rule is by no means clear when aqueous solutions at water-rich regions are considered, since the well-known tetrahedral structure of water (water–water hydrogen bonding) results in an increase in the volume or compression; furthermore, less definitive effects of

Table 3. Limiting Partial Molar Volumes of Water in Alcohols[a]

	5 °C	15 °C	25 °C	35 °C	45 °C
MeOH	14.73(−0.04)	14.67(−0.06)	14.48(−0.03)	14.29(0.06)	14.19(0.08)
	14.55[c]	14.44[c]	14.41[c]	14.34[c]	14.23[c]
	14.42[d]	14.44[d]	14.43[d]		
		14.7[e]	14.5[e]		
		14.4[f]	14.3[f]	14.1[f]	
	14.71[g]		14.49[g]		14.20[g]
EtOH	13.68(0.23)	13.80(0.18)	13.81(0.23)	13.99(0.13)	14.12(0.15)
		13.8[f]	13.9[f]	14.0[f]	
n-PrOH	14.62(0.31)	14.88(0.29)	15.09(0.30)	15.49(0.25)	15.83(0.19)
		14.8[f]	15.1[f]	15.6[f]	
i-PrOH	13.69(0.42)	14.08(0.38)	14.51(0.32)	14.97(0.24)	15.45(0.15)
	14.27[g]		15.03[g]		15.78[g]
n-BuOH	15.44(0.48)	15.77(0.36)	16.18(0.27)	16.49(0.30)	16.90(0.26)
i-BuOH	15.02(0.49)	15.49(0.40)	15.95(0.35)	16.48(0.23)	16.99(0.16)
s-BuOH	15.76(0.20)	16.33(0.04)	16.81(−0.04)	17.19(−0.08)	17.53(−0.15)
t-BuOH[b]	17.07(−0.44)	16.80(−0.30)	16.56(−0.26)	16.30(−0.23)	16.05(−0.10)
		16.694[h]	16.523[h]	16.326[h]	16.193[h]
n-PenOH	16.18(0.37)	16.53(0.28)	16.89(0.22)	17.33(0.04)	17.71(0.08)
t-PenOH	15.24(0.07)	14.68(0.44)	14.56(0.53)	14.61(0.57)	14.70(0.55)

a) Unit: cm^3 mol^{-1}. The B_V values of Eq. 3 are in parentheses. b) The temperatures are 26, 30, 35, 40, and 45 °C in turn from left to right. c) Ref. 4. d) Ref. 27. e) Ref. 28. f) Ref. 29. g) Ref. 30. h) Ref. 31.

Table 4. Limiting Partial Molar Adiabatic Compressions of Water in Alcohols[a]

	5 °C	15 °C	25 °C	35 °C	45 °C
MeOH	−20.9(−0.2)	−25.3(−0.1)	−30.4(0.8)	−37.0(1.7)	−44.1(2.5)
			−30.0[c]		
EtOH	−23.9(1.4)	−27.4(1.8)	−31.2(2.4)	−35.3(2.9)	−39.1(3.0)
			−31.2[c]		
n-PrOH	−14.3(2.3)	−15.9(2.7)	−17.4(2.9)	−18.3(2.9)	−19.2(3.0)
			−17.0[c]		
i-PrOH	−27.2(5.1)	−27.8(4.7)	−28.4(4.5)	−29.1(4.2)	−29.7(3.3)
n-BuOH	−8.6(3.2)	−8.8(2.9)	−9.0(3.0)	−8.9(2.8)	−8.6(2.6)
i-BuOH	−15.6(5.0)	−15.7(4.9)	−15.3(4.4)	−14.5(3.8)	−13.6(3.2)
s-BuOH	−10.0(3.4)	−8.5(2.2)	−7.3(1.5)	−6.5(0.6)	−6.7(0.2)
t-BuOH[b]	−10.6(−2.8)	−15.6(−1.7)	−22.0(−0.4)	−29.1(0.8)	−36.2(2.5)
n-PenOH	−3.5(3.1)	−3.2(2.9)	−2.7(2.5)	−1.8(1.8)	−1.0(1.5)
t-PenOH	−27.5(4.7)	−32.6(6.5)	−35.6(7.4)	−37.6(7.4)	−39.6(7.2)

a) Unit: cm^3 GPa^{-1} mol^{-1}. The B_K values of Eq. 3 are in parentheses. b) The temperatures are 26, 30, 35, 40, and 45 °C in turn from left to right. c) Estimated from the sound velocity[13] and density[29] data at lower concentration range less than 2 mol kg^{-1}.

the hydrophobic hydration (alkyl group–water interactions) may further complicate the situation regarding the volumetric behavior.[3]

For alcohol-rich solutions, on the other hand, one need not take into account the effects of any structural change of water caused by the introduction of hydrophobic groups. Therefore, we would expect that the volume and compression properties studied here can be interpreted more simply in terms of the geometrical contributions and general attractive and repulsive interactions described above. The temperature dependence of the hydrogen-bonding interactions can be considered to be significantly large, whereas, the geometrical factors may be less dependent on the temperature. In order to elucidate the volumetric behavior, therefore, it is useful to investigate the partial molar volume or compression at various temperatures. Although there have been partial molar volume data available for several polar and nonpolar solvents at 25 °C,[36] little reliable data are available at other temperatures.

The limiting partial molar volumes ($V_W{}^\circ$) and adiabatic compressions ($K_W{}^\circ$) of water are plotted as a function of temperature in Figs. 3 and 4, respectively. The figures also include the molar volume ($V_W{}^*$) and molar compression ($K_W{}^*$) of pure water for a comparison. The values of $V_W{}^\circ$ or $K_W{}^\circ$ in the alcohols studied

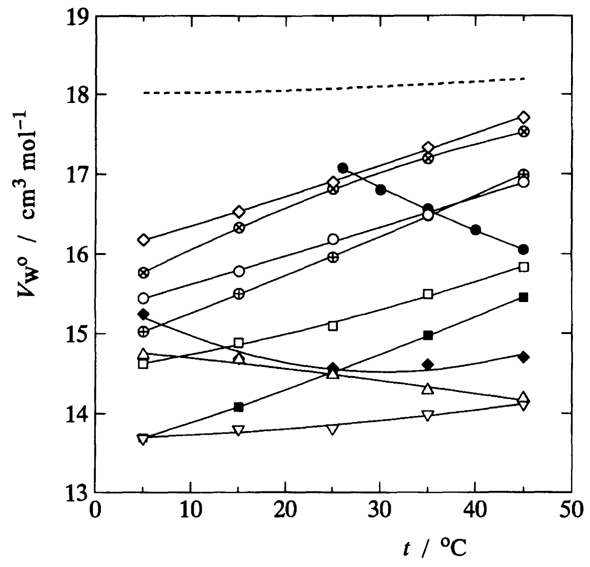

Fig. 3. Temperature dependence of the limiting partial molar volumes of water in various alcohols. MeOH (△); EtOH (▽); *n*-PrOH (□); *i*-PrOH (■); *n*-BuOH (○); *i*-BuOH (⊕); *s*-BuOH (⊗); *t*-BuOH (●); *n*-PenOH (◇); *t*-PenOH (◆). The broken line refers to the molar volume of pure water.

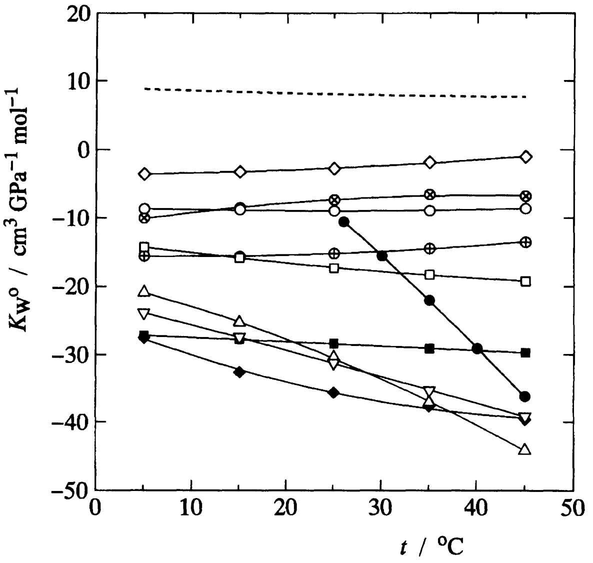

Fig. 4. Temperature dependence of the limiting partial molar adiabatic compressions of water in various alcohols. MeOH (△); EtOH (▽); *n*-PrOH (□); *i*-PrOH (■); *n*-BuOH (○); *i*-BuOH (⊕); *s*-BuOH (⊗); *t*-BuOH (●); *n*-PenOH (◇); *t*-PenOH (◆). The broken line refers to the molar adiabatic compression of pure water.

here are smaller than the corresponding molar values of the pure water; that is, the excess limiting partial molar quantities of water ($Q_\mathrm{W}{}^\mathrm{E}=Q_\mathrm{W}{}^\circ-Q_\mathrm{W}{}^*$) are negative. It is well known that the water in the pure liquid state retains significantly a bulky open structure similar to that of ice. This structure may contribute to an increase in the volume and compression, particularly at lower temperatures; one can thus observe a well-known minimum in the specific volume at 4 °C and in the adiabatic compressibility coefficient at about 64 °C. It is apparent that the loss of such an open structure of water in alcohol-rich regions induces a negative part of the $V_\mathrm{W}{}^\mathrm{E}$ and $K_\mathrm{W}{}^\mathrm{E}$ values. This contribution of course results in a more negative excess volume or compression at lower temperatures. The temperature-insensitive geometrical contributions mentioned above, on the other hand, may bring about more negative excess quantities for solvents with larger molecular size. On the basis of these considerations, de Visser et al.[37] have accounted for their results of the partial molar volumes of water in some polar solvents at 25 °C.

However, this is not the case for the present systems. As displayed in Figs. 3 and 4, both $V_\mathrm{W}{}^\mathrm{E}$ and $K_\mathrm{W}{}^\mathrm{E}$ are less negative with increasing chain length of the *n*-alcohols, except for MeOH. As clearly shown in the results of the benzene derivatives[34] and halogenated hydrocarbon solutions,[35] the partial molar volume of water increases in hydrophobic solvents, and is much larger than the molar volume of water (18 cm^3 mol^{-1}). Thus, in general, the more hydrophobic is the alkyl group of the solvents, the larger is the $V_\mathrm{W}{}^\circ$ value caused by repulsive interactions between water and nonpolar residues.

Figure 5 shows plots of the limiting partial molar compressions against the limiting partial molar volumes of water in the various alcohols at 25 °C. Roughly speaking, the smaller is the $V_\mathrm{W}{}^\circ$ value the more negative is the $K_\mathrm{W}{}^\circ$ value. It seems that a linear correlation exists between $V_\mathrm{W}{}^\circ$ and $K_\mathrm{W}{}^\circ$ for *n*-chain alcohols with the exception of methanol. For branched-chain alco-

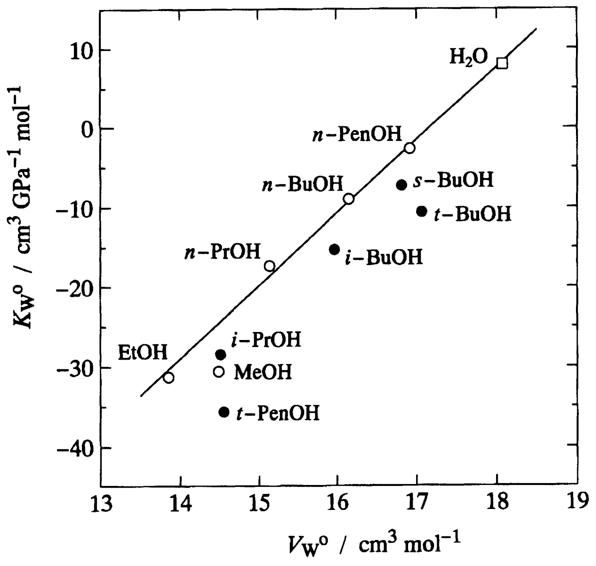

Fig. 5. Relation between the limiting partial molar volumes and the limiting partial molar adiabatic compressions of water in various alcohols at 25 °C.

hols and methanol, the reduction in compression is more pronounced. It is interesting to note that the point for the pure water falls on a straight line for the *n*-alcohol series. This finding is in agreement with the conclusion by DeGrandpré et al.[38] that the state of water molecules in higher alcohols is comparable to that existing in pure liquid water, even though nothing can be said concerning the structural aspects of the hydrogen-bonded complexes.

The alteration of solvent association by the introduction of solutes may be one of the decisive factors in determining the partial molar quantities of water in polar solvent systems. The specific volumes (v^*) and adiabatic compressibility coefficients ($\beta^* = -(\partial v^*/\partial P)_S/v^*$) of neat alcohols at 25 °C are plotted as a function of the number (N) of carbon atoms in the alcohols in Figs. 6 and 7, respectively. It is known that for the *n*-alcohol series the molar volumes or molar compressions increase almost linearly with the chain length, except for methanol.[39] The smooth curves in Figs. 6 and 7 are drawn on the basis of an assumption concerning the methylene group additivity using the data of the *n*-alcohols from ethanol to 1-hexanol; i.e., $V^*(\mathrm{CH_2}) = 16.69\ \mathrm{cm^3\,mol^{-1}}$ and $K^*(\mathrm{CH_2}) = 8.43\ \mathrm{cm^3\,GPa^{-1}\,mol^{-1}}$. It is evident from these figures that the volume and compressibility of methanol are much lower than those expected from the regular variation in the *n*-alcohol series. Thus, the packing of the methanol molecules in the pure liquid state may be considered to be more effective than that of the other *n*-alcohols. The addition of water to methanol is, therefore, accompanied by a less significant reduction in the volume or compression and, hence, the partial molar volume or compression of water in methanol is fairly larger than that expected for the *n*-alcohol series.

For branched-chain alcohols, on the other hand, the specific volumes and compressibility coefficients are larger than the corresponding *n*-chain isomers. This may be accounted for by a decrease in the fraction of hydrogen bonding due to the branching of the alkyl chains. The spectroscopic evidence suggests that the content of hydrogen bonds in alcohols decreases in the order *n*- > *sec*- > *tert*-alcohols because of a steric hindrance.[40—42] Thus, the comparatively lower values of $V_W{}^\circ$ or $K_W{}^\circ$ in branched-chain alcohols can be qualitatively explained from the point of view of the low packing densities of the solvents. This is just a reverse situation of the methanol solution of high packing density explained above.

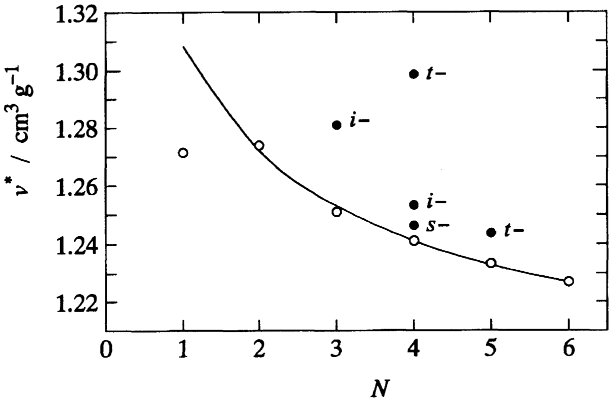

Fig. 6. Specific volumes of neat alcohols at 25 °C as a function of the number (N) of carbon atoms in the alcohols. The open circles refer to the *n*-alcohols and the filled circles to the branched-chain alcohols. The curve drawn is that predicted from the group-additivity principle (see text).

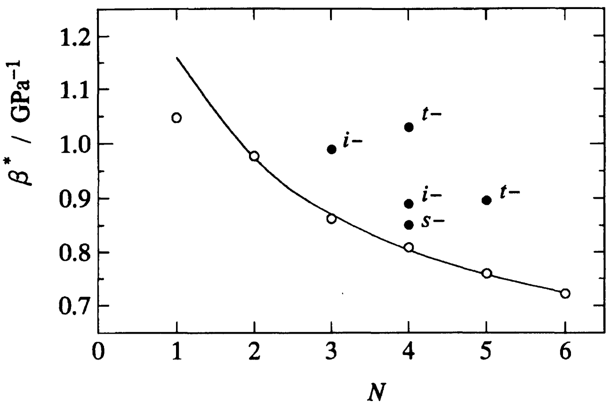

Fig. 7. Adiabatic compressibility coefficients of neat alcohols at 25 °C as a function of the number (N) of carbon atoms in the alcohols. The open circles refer to the *n*-alcohols and the filled circles to the branched-chain alcohols. The curve drawn is that predicted from the group-additivity principle (see text).

The temperature dependence of $V_W{}^\circ$ and $K_W{}^\circ$ is particularly interesting in order to elucidate the solute–solvent and solvent–solvent interactions. We previously reported that the partial molar volume of water increases significantly with increasing temperature in benzene derivatives[4,34] or in more hydrophobic alcohols, such as 1-octanol.[5] It seems likely that this volumetric behavior can be ascribed primarily to the dissolved monomeric water molecules in hydrophobic solvents without any associations. On the contrary, Fig. 3 shows that, with the exception of higher alcohols, the temperature dependence of $V_W{}^\circ$ is rather small and becomes negative for MeOH, *t*-BuOH, and *t*-PenOH. A similar trend can be observed for the compression behavior in Fig. 4, in which the negative temperature dependence can be seen for many systems. These findings suggest that the volumetric properties of these solutions may be attributed more predominantly to an alteration of the hydrogen-bonding interactions rather than a simple geometrical contributions, since the latter would bring about a more negative excess volume or compression at lower temperatures, as mentioned above. Since water–alcohol hydrogen bond is generally stronger than the alcohol–alcohol bond,[40] the introduction of water to pure alcohols may break down self-associations in the alcohols, and new hydrogen bond will be formed between the alcohols and water molecules. With increasing temperature, the self-association of the alcohols may be weakened and the contributions from the water–alcohol bonding may, consequently, become more pronounced to the solution properties. Considering the negative contribution of the hydrogen-bonding to the volumetric properties, therefore, the partial molar volume and compression of water in alcohols has a smaller temperature dependence compared with those in nonpolr solvents, and even has a negative temperature dependence in some cases.

It should be noted that in *t*-BuOH and perhaps in *t*-PenOH at lower temperatures, the partial molar volume of water is peculiar in its rather high value and in having an extraordinarily negative temperature dependence. In this regard we call attention to the fact that the melting temperatures of *t*-BuOH and *t*-PenOH are 25.8 and −8.8 °C, respectively, whereas those of the other alcohols studied are much lower (from −78 °C for *n*-PenOH to −126 °C for *n*-PrOH). For such two highly branched-chain alcohol systems, therefore, the temperature range covered in this study is just above their melting point, and hence the self-association of the solvent might be appreciably retained. The addition of water to these solvents at near to the melting temperature could not form a very strong water–alcohol hydrogen bond, and brought about a less volume reduction compared to the other alcohol systems. With increasing temperature, such an effect can be steadily diminished and, hence, the partial molar volume of water is rapidly decreased.

The concentration dependence of the apparent molar volume of water (B_V) is also worthy of note, since it is negative in *t*-BuOH solution at all of the temperatures studied and in *s*-BuOH solution at higher temperatures, as can be seen in Table 3. Since the $V_W{}^\circ$ values in these alcohols are less than the molar volume of pure water, the negative B_V value means that the partial molar volume of water vs. mole fraction curve passes through a minimum at a certain concentration, as described earlier.[3)] An analogous concentration dependence can be seen in the apparent molar adiabatic compressions of water in these alcohols (Table 4). In this connection it is relevant to note that a similar minimum in V_W has been observed for some polar organic solvents, such as tetrahydrofuran,[43,44)] acetonitrile,[45,46)] and 1,4-dioxane.[47)] In general, the concentration dependence of the apparent molar quantities has been correlated with the solute–solute interactions (in the present case, water–water or perhaps water–alcohol–water interactions). In spite of much investigation, however, the discussion from the molecular viewpoint for the concentration dependence of the apparent or partial molar volumes remains poorly understood.[3)] At present, we have no clear explanation for the existence of the minimum in the concentration dependence of $\phi_{V,W}$ or $\phi_{K,W}$. Further studies concerning the other solvent systems must be desirable in order to obtain a clearer description of the concentration dependence of the apparent molar volume or compression of water.

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