# Partial Molar Volumes in Aqueous Mixtures of Nonelectrolytes. I. *t*-Butyl Alcohol

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The densities of mixtures of *t*-butyl alcohol (TBA) with water (W) have been measured at various temperatures over a wide range of concentrations. From these data the apparent ($V_{\phi,2}$) and partial ($V_2$) molar volumes as well as partial molar expansibilities ($E_2$) have been evaluated for both components. The limiting partial molar volumes, $V^{\infty}_{TBA}$ and $V^{\infty}_{W}$, were smaller than the molar volume of TBA and water, respectively, at all temperatures studied. The values of $E^{\infty}_{TBA}$ was negative at temperatures below 15 °C and the value of $E_W$ was also negative at all temperatures. Characteristic extrema were observed for the $V_{TBA}(X_{TBA})$ and $E_{TBA}(X_{TBA})$ curves in the water-rich region and for the $V_W(X_W)$ curve in the TBA-rich region. The unusual volumetric behavior found for the TBA–water mixtures at both ends of the composition may be attributed to the formation of strong hydrogen bonding between water and TBA molecules and to the unique properties of pure water, itself (i.e., the very small size of water molecules and the existence of a cluster structure).

There have been a number of studies on the volumetric behavior of mixtures of water with nonelectrolytes. Most of them have concerned water-rich solutions and have discussed structural changes of the solvent water caused by the introduction of nonpolar groups (i.e., so-called hydrophobic hydration or iceberg formation).

In 1959 Kauzmann turned his attention to data concerning negative volume changes during the transfer of hydrocarbons from nonpolar solvents to water and pointed out that iceberg formation results in a large decrease in volume.[1] He regarded this fact as a clear indication that the structures present in an iceberg are quite different from those in ordinary ice; in other words, an iceberg has a more dense structure than that of ordinary ice. On the other hand, Némethy and Scheraga,[2] Franks,[3] and Desnoyers and Arel[4] have postulated that an iceberg has a bulky structure like ordinary ice but that the increase in the volume due to iceberg formation can be largely overcome by the loss of free space due to the filling of solutes in the cavities of the iceberg. At present the latter interpretation appears to be generally accepted by many authors.

In any event, however, they have assumed *a priori* that the volume change accompanying iceberg formation can be estimated directly from measurements of the volume change during the transfer of nonpolar solutes from a nonpolar medium to water. This is apparently an oversimplified assumption. A volume change upon mixing two liquids can arise from a variety of origins. In their review article Handa and Benson[5] pointed out the following factors: (1) Differences in the sizes and shapes of the component molecules, (2) differences in the intermolecular interaction energy, (3) structural changes, and (4) the formation of new chemical species. In my opinion, many authors have overestimated factor (3) in order to interpret the unusual volumetric behavior of aqueous mixtures. It should be noted, furthermore, that the exact nature of icebergs has remained obscure; consequently, the volume change accompanying iceberg formation is still open to question. As has been claimed by Hvidt[6] and Nakajima et al.,[7] there is no explicit evidence as to whether iceberg formation results in an increase or decrease in volume.

It is well known that many unusual thermodynamic and spectroscopic properties have been observed for dilute aqueous solutions of *t*-butyl alcohol (TBA).[3,8,9] These have, in general, been interpreted in terms of an iceberg formed around the *t*-butyl group in water. Thus, TBA has been regarded as a typical hydrophobic structure-maker, although TBA is completely miscible with water in any proportion at room temperature (i.e., very hydrophilic in nature).

While many authors have reported the partial molar volumes of TBA in aqueous solutions,[10—18] precise studies of water dissolved in TBA (i.e., the partial molar volume of water in the TBA-rich region) are scare. It would be interesting to investigate the behavior of water in the absence of the characteristic structure of liquid water in order to clarify the interactions between water and TBA. The purpose of this study is to present precise density data regarding TBA–water mixtures at various temperatures over the whole concentration range, whenever possible, and to discuss the partial molar volume behavior at both ends of the concentration range.

## Experimental

The solution densities, $\rho$, were measured using an oscillating-tube densimeter (DMA 60) that was described earlier.[19] In this study, two measuring cells (DMA 601) were used under the operation of a phase locked loop (PLL) mode in order to minimize the drift of period measurements. In most case the solutions were prepared by successive additions of a concentrated solution or a pure solute to a known quantity of solvent. The addition was carried out by

weight in a mixing chamber connected to the measuring cell with a teflon tube and a flow pump.

For very dilute solutions of water in TBA, the measurements were carried out as before.[20] The water concentration was determined with an automatic Karl-Fischer titration apparatus (Hiramuma, AQ 3) immediately after density measurements for each solution.

Water and TBA were purified as before,[20] the latter being further purified by fractional crystallization. No trace of impurities in the TBA was detected using gas chromatography.

## Results and Discussion

In a mixture of components 1 and 2, the apparent molar volume of the component 2, $V_{\phi,2}$, is given by

$$V_{\phi,2} = X_1M_1(\rho_1^* - \rho)/X_2\rho_1^*\rho + M_2/\rho, \quad (1)$$

where $X$ and $M$ are the mole fraction and the molar mass of the component 1 or 2 and $\rho_1^*$ is the density of component 1. The density of water, $\rho_w^*$, was taken from Kell.[21] The density of pure TBA, $\rho_{TBA}^*$, was determined by extrapolating the $\rho$ values to infinite dilution. The estimated values of $\rho_{TBA}^*$ are 0.77940, 0.77529, 0.77008, 0.76476, and 0.75937 g cm$^{-3}$ at 26, 30, 35, 40, and 45 °C, respectively.

In Fig. 1 the apparent molar volumes of TBA, $V_{\phi,TBA}$, at 25 °C are compared with various values from the literature and generally show good agreement. In particular, the values in extremely dilute solutions given by Franks and Smith[12] are in excellent agreement with the present data within the experi-

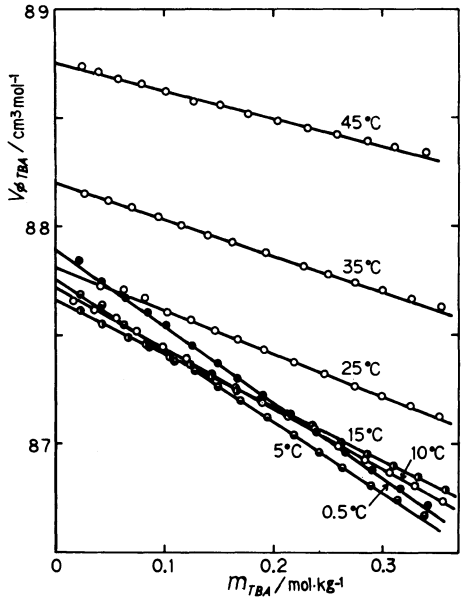


Fig. 2. Apparent molar volumes of TBA in very dilute aqueous solutions at various temperatures.

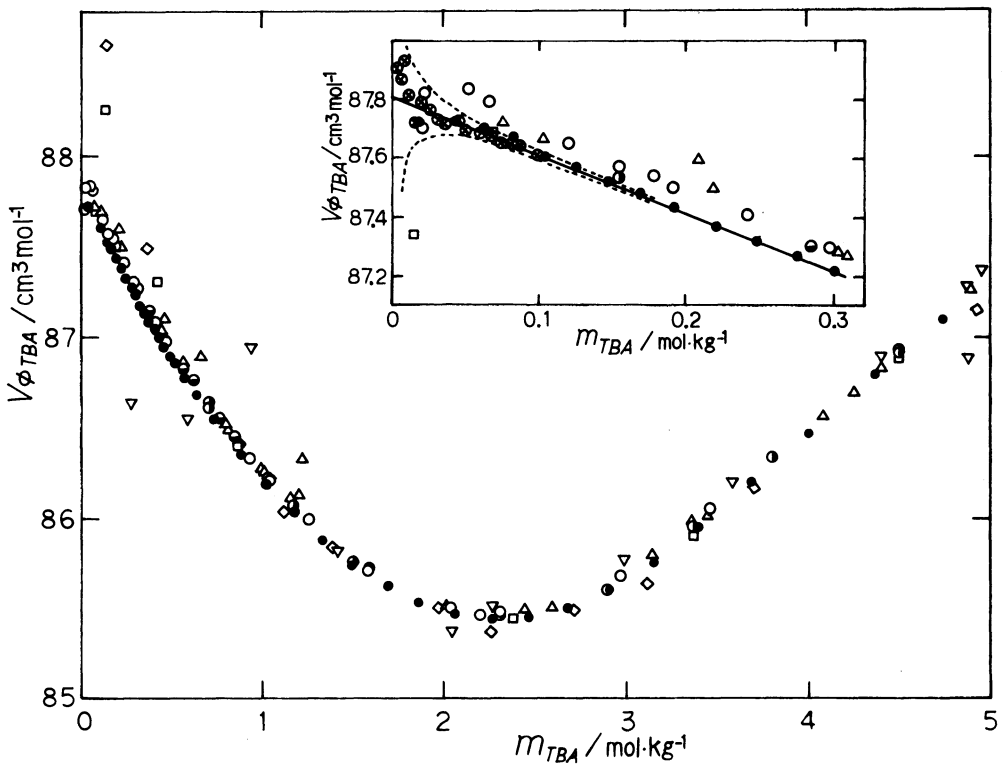


Fig. 1. Apparent molar volumes of TBA in the water-rich region at 25 °C as a function of molality. The dotted lines represent the uncertainties in $V_{\phi,TBA}$ corresponding to $\delta\rho = \pm 2 \times 10^{-6}$ g cm$^{-3}$.
●: This work, ○: Ref. 15, ◑: Ref. 13, ◒: Ref. 14, ⊗: Ref. 12, ◇: Ref. 11, □: Ref. 16, △: Ref. 17, ▽: Ref. 18.

mental uncertainty of the density measurement: $\delta\rho=\pm 2\times 10^{-6}$ g cm$^{-3}$.

**Limiting Partial Molar Volume.** For very dilute solutions, the apparent molar volume of solute 2 can be represented by a linear form:

$$V_{\phi,2} = V_2^\infty + A_2 m, \quad (2)$$

where $V_2^\infty$ is the limiting partial molar volume of component 2, $A_2$ an empirical constant, and $m$ the molality. The results for TBA in water and for water in TBA are plotted in Figs. 2 and 3, respectively, and the parameters of Eq. 2 are summarized in Table 1. The value of $V_{TBA}^\infty$ at 25 °C is in good agreement with that from the literature: 87.82,[12] 87.90,[13] 87.73,[14] and 87.76 cm$^3$ mol$^{-1}$.[15] No precise $V_W^\infty$ data were available with which the presented results could be compared.

The temperature dependence of $V_{TBA}^\infty$ is shown in Fig. 4, including the results for *n*-butyl alcohol (NBA) solutions obtained by Nakajima et al.[7] The values of $V_{BA}^\infty$ are smaller than the molar volumes of neat butyl alcohols, $V_{BA}^*$, at all temperatures. Figure 5 shows the temperature dependence of the excess limiting partial molar volume defined by

$$V_{BA}^E = V_{BA}^\infty - V_{BA}^*. \quad (3)$$

The values of $V_{TBA}^*$ below 25 °C were evaluated from the temperature dependence of the densities of neat TBA. As described in the Introduction, a negative $V_2^E$ has, in general, been regarded as a characteristic of iceberg formation.[1-4,8,9] If this is relevant the negative $V_2^E$ would have to be reduced as the temperature is raised, since water structural effects become progressively reduced with increasing temperature. Thus, Kauzmann[1] has explained the larger negative values of $V_2^E$ at lower temperatures for aliphatic hydrocarbon in water reported by

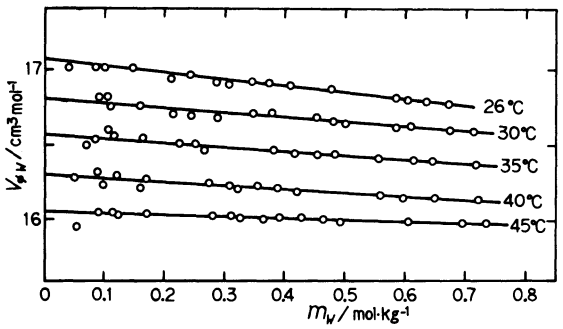


Fig. 3. Apparent molar volumes of water in dilute TBA solutions at various temperatures.

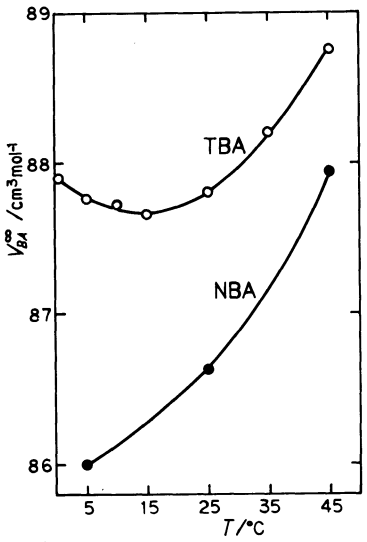


Fig. 4. Limiting partial molar volumes of TBA and NBA[7] in water as a function of temperature.

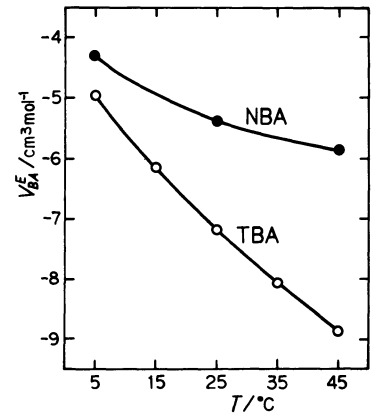


Fig. 5. Excess limiting partial molar volumes of TBA and NBA[7] in water as a function of temperature.

Table 1. Limiting Partial Molar Volumes and Deviation Constants for TBA-Water Mixtures

| $T$ / °C | $V_{TBA}^\infty$ / cm$^3$ mol$^{-1}$ | $A_{TBA}$ / cm$^3$ kg mol$^{-2}$ | $T$ / °C | $V_W^\infty$ / cm$^3$ mol$^{-1}$ | $A_W$ / cm$^3$ kg mol$^{-2}$ |
|---|---|---|---|---|---|
| 0.5 | 87.89 | −3.52 | 26 | 17.07 | −0.44 |
| 5 | 87.76 | −3.29 | 30 | 16.80 | −0.30 |
| 10 | 87.72 | −2.82 | 35 | 16.56 | −0.26 |
| 15 | 87.66 | −2.47 | 40 | 16.30 | −0.23 |
| 25 | 87.81 | −2.01 | 45 | 16.05 | −0.10 |
| 35 | 88.20 | −1.68 | | | |
| 45 | 88.75 | −1.26 | | | |

Masterton;[22] he had explained his results in terms of a break down of the water structure around hydrocarbons. On the contrary, Fig. 5 shows that the value of $V_{BA}^{E}$, as well as for many other alcohols, becomes very strongly negative as the temperature is increised. This is more significant for $V_{TBA}^{E}$ than $V_{NBA}^{E}$.

Evidently, a complicated situation can take place through an assumption that the observed volume change in the transfer of nonpolar solutes from nonpolar medium to water is taken just as the volume change accompanying iceberg formation. Volume changes must arise from a number of factors, not only from iceberg formation even in aqueous systems.

The large negative $V_2^E$ observed for aqueous systems can be well explained in terms of the unique properties of solvent water itself, not the water-structural change caused by the introduction of solutes. Recently, Lee[23] investigated the partial molar volume based on a hard-sphere mixture model and clearly showed that the negative volume change is due to the small size of water molecules. This is the same conclusion that was postulated earlier by Assarsson and Eirich.[24] On the basis of the scaled particle theory, French and Criss[25] wrote: "The small $V_2$ values of nonelectrolytes in water are understandable in light of the low compressibility of water. Structural considerations are not neccessary." In addition, the linear correlation between the partial molar volumes of solutes and the compressibility coefficients of solvents has been illustrated by Hamilton and Stokes[26] and Dack.[27] That is to say, the volume of liquids is primarily given by the repulsive forces of hard spheres. Therefore, the greatest part of the negative $V_2^E$ observed for aqueous systems can be ascribed to the fact that the free volume in water or in dilute aqueous mixtures is considerably smaller than that in most organic systems, while the solute-solvent hydrogen bonding probably plays a role in the volume change for polar mixtures. Thus, the negative temperature dependence of $V_{BA}^{E}$ (Fig. 5) can be interpreted in terms of the difference in the expansibilities of neat butyl alcohols and aqueous butyl alcohol solutions. The pronounced effect for TBA, compared to NBA, can also be explained by the fact that the expansivity of neat TBA ($\alpha$=1.294 kk$^{-1}$ at 25 °C) is much larger than that of neat NBA ($\alpha$=0.948 kK$^{-1}$ at 25 °C).

On the basis of the thermodynamic relation

$$(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_p, \quad (4)$$

Hepler[28] has postulated a criterion for discriminating between solutes in water as being "structure maker" or "structure breaker." It is well known that the limiting partial molar expansibility, $E_2^\infty(=\partial V_2^\infty/\partial T)$, of various alcohols in water greatly decreases with decreasing temperature (that is $\partial^2 V_2^\infty/\partial T^2>0$; therefore, alcohols have been regarded as structure makers), and it is in some cases negative at low temperatures.[7,15,29] In fact, Fig. 4 shows that the $V_{TBA}^\infty(T)$ curve passes through a minimum at about 15 °C. The results coincide with a prediction from the fact that the temperature of maximum density (TMD) of dilute TBA solutions is higher than that of pure water (3.98 °C).[30,31] The TMD of $D_2O$ (11.23 °C) is higher than that of $H_2O$; this is one piece of evidence for supporting the idea that $D_2O$ is more structured than $H_2O$ at ordinary temperatures.[32] In analogy with this consideration, it is possible to consider that the introduction of TBA brings about a solvent water with more structure. Such a consideration leads us to the idea that iceberg formation is accompanied by a positive volume change;[6,7,33] this is in conflict with the generally accepted view.

However, structural considerations based on the sign of $\partial^2 V_2/\partial T^2$ or the shift in TMD also lead to the conclusion that benzene has little influence on the structure of water and that aliphatic hydrocarbon is a structure breaker.[28,30] This conclusion may be essentially in conflict with the definition of an iceberg. Furthermore, it should be noted that an anomalous negative expansibility has been observed even for the organic solvent systems described below.

The limiting partial molar volumes of water, $V_W^\infty$, in TBA are plotted as a function of temperature in Fig. 6, together with $V_W^\infty$ in the other three isomeric butyl alcohols.[20,34] The values of $V_W^\infty$ are always smaller than the molar volume of water, $V_W^*$. This is probably due to a large $V_W^*$ resulting from the water cluster, in addition to the factors operating in $V_2^E$ for aqueous solutions as pointed out before. It is of interest that for four butyl alcohol solvents the $V_W^\infty$ in TBA alone decreases monotonously as the temperature is increased. Such a negative $E_2^\infty$ behavior in organic solvents has been also observed for urea in methanol[26]

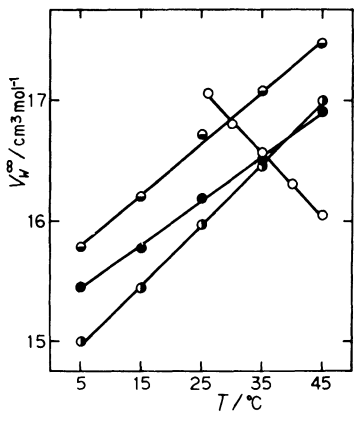


Fig. 6. Limiting partial molar volumes of water in four isomeric butanols.
○: TBA, ●: NBA,[20] ◑: isobutyl alcohol,[34] ◒: *s*-butyl alcohol.[34]

and water in methanol,[20] but is highly pronounced for the present system. Needless to say, in the absence of the water structure in the TBA-rich region, the volumetric behavior is not explicable by the structural change of water. Both the negative $E^{\infty}_{TBA}$ and $E^{\infty}_{W}$ may arise from a more effective packing due to a difference in the size and the strong hydrogen bonding between water and TBA molecules.

**Concentration Dependence of Apparent and Partial Molar Volumes.** The empirical constant $A_2$ of Eq. 2 is associated with solute-solute interactions. The values of $A_{TBA}$ and $A_W$ estimated from Figs. 2 and 3, respectively, are plotted in Fig. 7; this includes, for comparison, the values for NBA-water mixtures.[7,20] For dilute aqueous alcohol solutions the $A_2$ value is negative and becomes more negative with increasing the size of the hydrocarbon group and decreasing the temperature.[7,14] Therefore, such a negative $A_2$ value has, in general, been ascribed to iceberg formation.[4] As can be seen from Fig. 7, the $A_{BA}$ values for aqueous TBA and NBA solutions are comparable with each other at all temperatures, while it has often been considered that the structural effect of TBA is much larger than that of NBA.[9] The absolute values of $A_W$ are very small compared to those of $A_{BA}$. As will be described below, the variation of $A_2$ values with the size of solutes may mostly depend on the molar scale employed in Eq. 2. This problem is closely associated with the difference in the molality range in which Eq. 2 holds for an aqueous TBA solution (Fig. 2) and for a solution of water in TBA (Fig. 3).

From the $V_{\phi,2}$ values, the partial molar volume of component 2 at finite concentrations is given by

$$V_2 = V_{\phi,2} + X_1X_2(\partial V_{\phi,2}/\partial X_2)_{T,P} \quad (5)$$

The values of $(\partial V_{\phi,2}/\partial X_2)_{T,P}$ were evaluated by a local fitting procedure[35] in which five consecutive values of $V_{\phi,2}$ were represented by a quadratic equation in a certain mole fraction range.

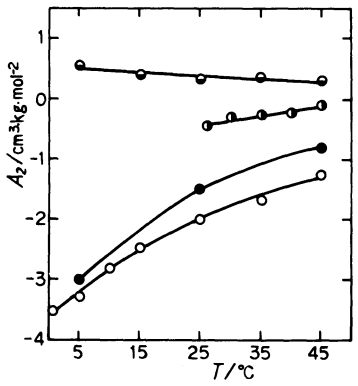


Fig. 7. Coefficient $A_2$ of Eq. 2 as a function of temperature.
○: TBA in water, ●: NBA in water,[7] ◑: water in TBA, ◒: water in NBA.[20]

Figure 8 shows the concentration dependences of the apparent and partial molar volumes of TBA and water over the whole mole fraction range at 35 °C. As is well known, the $V_{TBA}(X_{TBA})$ curve has a sharp minimum at a very low mole fraction. It is worth noting that the $V_W(X_W)$ curve also has a minimum, though not so outstanding compared to that for $V_{TBA}$. This obscure minimum in the $V_W(X_W)$ curve is apparently due to a comparison based on the molar scale. When the molar masses of the two components in binary mixtures differ significantly ($M_{TBA}$ is about 4 times $M_W$), it may be better to compare the extent of the volume change based on the unit-mass scale rather than the molar scale. Figure 9 illustrates the apparent and partial specific volumes of TBA and water as a function of the weight fraction of TBA. The depth and the position of the two minima are comparable with each other. Thus, the volumetric behavior of the TBA-water mixture is unusual at both ends of the

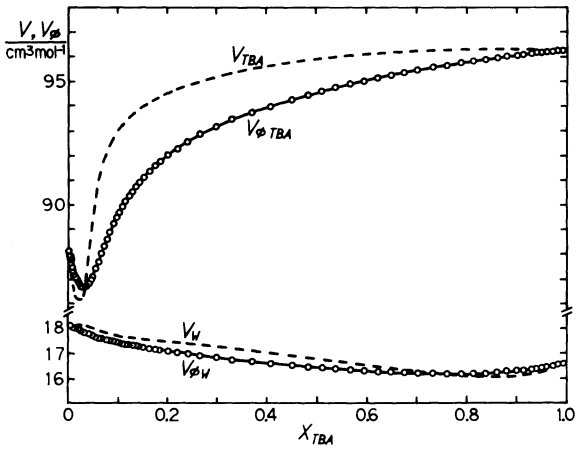


Fig. 8. Apparent and partial molar volumes of TBA and water in their mixtures as a function of mole fraction of TBA.

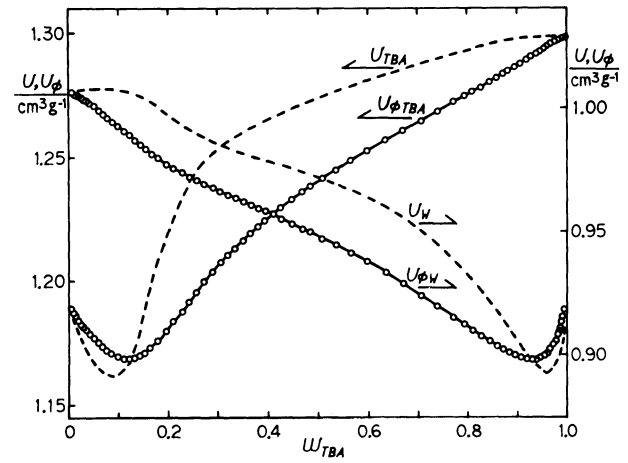


Fig. 9. Apparent and partial specific volumes of TBA and water in their mixtures as a function of weight fraction of TBA.

concentration range.

In Fig. 10 are shown the concentration dependences of $V_{TBA}$ in the water-rich region at various temperatures. The appearance of the characteristic minimum in dilute aqueous solutions has also been associated with iceberg formation on the basis of the fact that it becomes more pronounced and shifts to a lower concentration as the alkyl group increases in size.[3,8] As can be seen from Fig. 10, the minimum is similarly more pronounced but occurs at a higher concentration as the temperature is lowered. On the other hand, Nakagawa et al.[36] have reported that the increase in the pressure also causes a more pronounced minimum and shifts it to a higher concentration. That is to say, such a minimum behavior is affected in a similar manner by a decrease in the temperature and by an increase in the pressure, both of which bring about a decrease in the volume in the usual way. The explanation of the minimum by using iceberg formation is, therefore, not consistent since iceberg formation may be less significant with both the increases in the temperature and the pressure.

It is worth noting that a similar behavior is found for the $V_W(X_W)$ curves in Fig. 11, where the minimum is also very pronounced and shifts to a higher concentration with decreasing temperature. A minimum in the $V_W(X_W)$ curve has been observed in tetrahydrofuran,[37] but not in *n*-alcohols.[20]

The appearance of a minimum in the $V_2(X_2)$ curve at a certain concentration means that the packing of the component molecules takes place more effectively up to this concentration. The exact nature of such a packing effect is not clear since the concentration dependence is a very complex phenomenon and is attributable to various types of solute-solvent and solute-solute interactions, which may include the destruction of self-associations in water and in TBA and the formation of hydrogen-bonded associations between water and TBA molecules.

Figure 12 shows the partial molar expansibilities, $E_2(=\partial V_2/\partial T)$, of TBA and water at 40 °C over the whole mole fraction range. The $E_{TBA}(X_{TBA})$ curve is characterized by a remarkable maximum and an

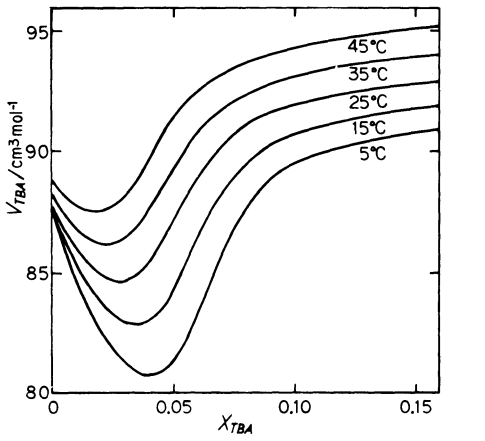


Fig. 10. Partial molar volumes of TBA in the water-rich region at various temperatures.

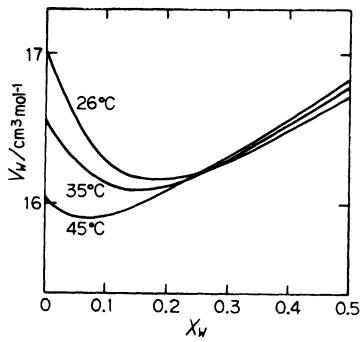


Fig. 11. Partial molar volumes of water in the TBA-rich region at various temperatures.

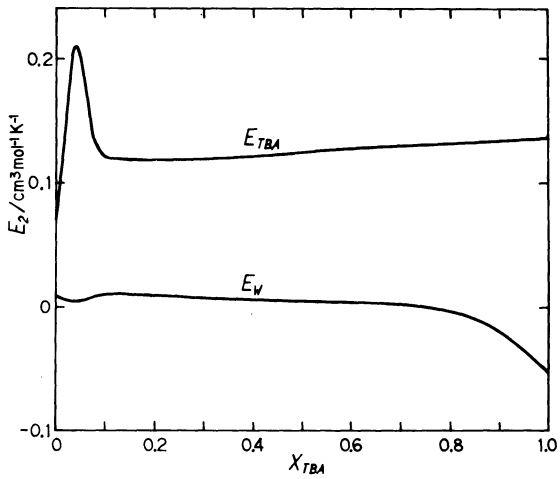


Fig. 12. Partial molar expansibilities of TBA and water as a function of mole fraction of TBA at 40 °C.

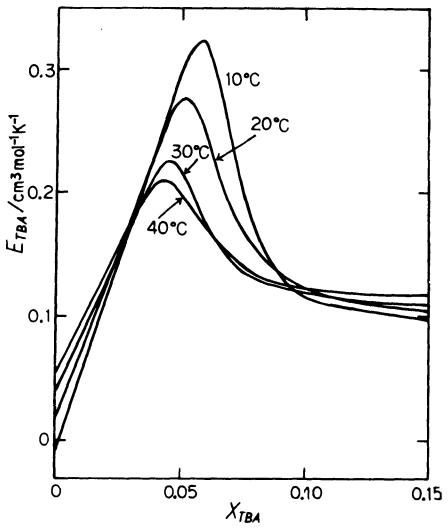


Fig. 13. Partial molar expansibilities of TBA in the water-rich region at various temperatures.

indistinct minimum at low $X_{TBA}$. The variation of the maximum with temperature is shown in Fig. 13. The maximum is more pronounced and occurs at higher concentration as the temperature is decreased. These are analogous to the minimum behavior in $V_{TBA}$ (Fig. 10). However, it is noteworthy that the concentration of the maximum in $E_{TBA}$ is higher than that for the minimum in $V_{TBA}$; i.e., the position of the $E_{TBA}$ maximum coincides with that where $V_{TBA}$ increases abruptly beyond the minimum with increasing concentration.

On the other hand, no extremum is found for the $E_W(X_W)$ curve in the TBA-rich regions. Consequently, the appearance of the $E_{TBA}$ maximum may be associated with the destruction of the water structure. The expansibility of dilute aqueous TBA solutions is unusually small through the existence of the cluster structure of water initially present in solvent water. As the concentration is increased, the water cluster is progressively disrupted and the expansibility of the solution increases most steeply at the concentration referring to the $E_{TBA}$ maximum. A further addition of TBA may extinguish most of the bulky water structure, and the volumetric behavior of the solution approximates more and more closely to that of neat TBA. In fact, Fig. 8 and 12 show that the values of $V_{TBA}$ and $E_{TBA}$ slightly depend on the mole fraction for $X_{TBA}>0.1$ and are comparable to those for neat TBA.

## Conclusion

The characteristic volumetric behavior observed for dilute aqueous TBA solutions has been generally interpreted in terms of iceberg formation around the *t*-butyl group. The present study clearly shows that some anomalies can be found for the TBA–water mixture at both ends of the concentration. This fact confirms my suspicion that the volumetric behavior of aqueous TBA solutions may be irrelevant to iceberg formation. The peculiarity of the TBA–water mixture may be mainly attributed to the very small radius of water molecules, strong hydrogen-bonding between water and TBA molecules, and the cluster structure of pure water; not to iceberg formation by the introduction of TBA molecules.

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### References

1) W. Kauzmann, *Adv. Protein Chem.*, **14**, 1 (1959).
2) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).
3) F. Franks, *Ann. New York Acad. Sci.*, **125**, 277 (1965).
4) J. E. Desnoyers and M. Arel, *Can. J. Chem.*, **45**, 359 (1967).
5) Y. P. Handa and G. C. Benson, *Fluid Phase Equil.*, **3**, 185 (1979).
6) A. Hvidt, *Ann. Rev. Biophys. Bioeng.*, **12**, 1 (1983); *J. Chem. Thermodyn.*, **3**, 663 (1971).
7) T. Nakajima, T. Komatsu, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **48**, 783 (1975).
8) F. Franks and D. J. G. Ives, *Quart. Rev.*, **20**, 1 (1966).
9) F. Franks and D. S. Reid, "Water, a Comprehensive Treatise," ed by F. Franks, Plenum Press, New York (1973), Vol. 2, p. 323.
10) K. Nakanishi, *Bull. Chem. Soc. Jpn.*, **33**, 793 (1960).
11) K. Nakanishi, N. Kato, and M. Maruyama, *J. Phys. Chem.*, **71**, 814 (1967).
12) F. Franks and H. T. Smith, *Trans. Faraday Soc.*, **64**, 2962 (1968); *J. Chem. Eng. Data*, **13**, 538 (1968).
13) L. Avédikian, G. Perron, and J. E. Desnoyers, *J. Solution Chem.*, **4**, 331 (1975).
14) C. Jolicoeur and G. Lacroix, *Can. J. Chem.*, **54**, 624 (1976).
15) C. de Visser, G. Perron, and J. E. Desnoyers, *Can. J. Chem.*, **55**, 856 (1977).
16) A. Hvidt, R. Moss, and G. Nielsen, *Acta Chem. Scand.* **B32**, 274 (1978).
17) G. Perron and J. E. Desnoyers, *J. Chem. Thermodyn.*, **13**, 1105 (1981).
18) J. F. Alary, M. A. Simard, J. Dumont, and C. Jolicoeur, *J. Solution Chem.*, **11**, 755 (1982).
19) M. Sakurai and T. Nakagawa, *J. Chem. Thermodyn.*, **14**, 269 (1982).
20) M. Sakurai and T. Nakagawa, *J. Chem. Thermodyn.*, **16**, 171 (1984).
21) G. S. Kell, *J. Chem. Eng. Data*, **20**, 97 (1975).
22) W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954).
23) B. Lee, *J. Phys. Chem.*, **87**, 112 (1983).
24) P. Assarsson and F. R. Eirich, *J. Phys. Chem.*, **72**, 2710 (1968).
25) R. N. French and C. M. Criss, *J. Solution Chem.*, **10**, 713 (1981).
26) D. Hamilton and R. H. Stokes, *J. Solution Chem.*, **1**, 213 (1972).
27) M. R. J. Dack, *Aust. J. Chem.*, **29**, 779 (1976).
28) L. G. Hepler, *Can. J. Chem.*, **47**, 4613 (1969).
29) S. Cabani, G. Conti, and E. Matteoli, *J. Solution Chem.*, **5**, 751 (1976).
30) G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn.*, **35**, 646 (1962).
31) M. Sakurai, T. Komatsu, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **45**, 1038 (1972).
32) E. M. Arnett and D. R. McKelvey, "Solute-Solvent Interactions," ed by J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York (1969), p. 343.
33) D. M. Alexander and D. J. T. Hill, *Aust. J. Chem.*, **18**, 605 (1965).
34) M. Sakurai, unpublished results.
35) H. C. Zegers and G. Somsen, *J. Chem. Thermodyn.*, **16**, 225 (1984).
36) M. Nakagawa, H. Inubushi, and T. Moriyoshi, *J. Chem. Thermodyn.*, **13**, 171 (1981).
37) M. Sakurai and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **55**, 1641 (1982).