

Volume Properties of Aqueous Solutions of *tert*-Butyl Alcohol at Temperatures between 5 and 25 °C

AASE HVIDT, RENÉ MOSS and GERDA NIELSEN

Chemistry Laboratory III, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Measurements are reported for the density of aqueous solutions of *tert*-butyl alcohol at 5, 10, 20 and 25 °C. The concentration and the temperature dependence of the volume of the solutions are discussed. The experimental results support the assumption that nonpolar groups promote "icelike" structures in liquid water. The data indicate that the formation and the break-down of the "icelike" structures (the hydrophobic solvation) occur in equilibria which are very sensitive to changes in the concentration and/or temperature. Volume changes following shifts in these solvation equilibria may explain the volumetric behaviour typical of dilute aqueous solutions of nonpolar solutes.

The thermodynamic properties of aqueous solutions of nonpolar substances are intensively examined, and the nonideal behaviour of the solutions is discussed on the basis of the McMillan-Mayer theory,¹ the scaled-particle theory,² or the cosphere-solvation concept of Gurney.^{3,4} The discussion of experimental data generally supports the suggestion originally made by Frank and Evans,⁵ that nonpolar solutes promote "icelike" structures* in liquid water, but recent review articles on water and aqueous solutions stress the fact that there does not exist an adequate theory by which the concentration dependence of the thermodynamic quantities of dilute aqueous solutions of nonpolar solutes can be established.⁶⁻⁸

The aim of the present investigation of volume properties of aqueous solutions of *tert*-

* The term "icelike" is used throughout this paper as a brief notation for water structures characterized by a lower energy, a lower entropy and a larger volume than the average energy, entropy and volume of pure water.

butyl alcohol is to discuss to what extent volumetric investigations of aqueous solutions may contribute to the elucidation of the nature of interactions between nonpolar groups and water, the so-called hydrophobic interactions or hydrophobic solvation.

EXPERIMENTAL

Densities were measured with digital densimeters, models DMA 02 and DMA 21, available from Anton Paar, Austria. Water from a constant temperature bath was circulated through the metal block of the densimeter at a flow rate of 6 dm³ min⁻¹ and the thermal stability of the bath was better than 5 × 10⁻³ °C. The densimeters were calibrated with pure water and with toluene; the calibration with water was repeated immediately before and after each measurement of the density of a mixture. The reproducibility of the measurements was better than 5 × 10⁻⁴ g cm⁻³ for dilute aqueous solutions, but for organic liquids variations up to 10⁻⁴ g cm⁻³ have been observed. This difference in reproducibility is most likely related to differences between the coefficients of the thermal expansion of water and organic liquids.

The *tert*-butyl alcohol used was from Fluka (*purum*, > 99 %), m.p. 23–25 °C. The water was distilled from alkaline permanganate. All solutions were prepared by weighing the components.

RESULTS

Measurements of the density, *d*, of aqueous solutions of *tert*-butyl alcohol at 5, 10, 20, and 25 °C are summarized in Table 1. The reproducibility of the measurements is better than 5 on the last digit shown.

Table 1. Density, g cm⁻³, of *tert*-butyl alcohol–water mixtures; *w* is the weight fraction of the alcohol.

<i>w</i>	5 °C	10 °C	20 °C	25 °C
0	0.999965 ^a	0.999700 ^a	0.998203 ^a	0.997044 ^a
0.00109	0.999769	0.999502	0.998012	0.996854
0.00502	0.999053	0.998785	0.997299	0.996146
0.0100	0.998162	0.997907	0.996339	0.995181
0.0300	0.994949	0.994659	0.993039	0.991852
0.0600	0.990882	0.990456	0.988746	0.987436
0.100	0.986499	0.985799	0.983517	0.981933
0.150	0.982181	0.980808	0.977410	0.97520
0.200	0.977576	0.97511	0.97036	0.96697
0.250	0.97007	0.96665	0.96060	0.95670
0.300	0.96002	0.95630	0.94994	0.9452
0.400	0.93747	0.93370	0.9266	0.9218
0.500	0.91443	0.9106	0.9031	
0.740	0.85940	0.8550	0.8474	0.8424

^a From Ref. (9).

Fig. 1a presents the specific volume v ($=d^{-1}$) of the solutions as a function of the weight fraction, w , of the alcohol. The curves in this figure are obtained by a cubic spline smoothing of the experimental data;¹⁰ the spline smoothing minimizes the curvature of the fitted curve as well as the sum of the square of the deviations of the data points, weighted according to the experimental error.

The apparent molar volume of the alcohol, $V_{app,1}$, presented in Fig. 1b as a function of the mol fraction, x , is calculated from the spline-fitted data as

$$V_{app,1} = M_1 \frac{v - (1-w)v_o^o}{w} \quad (1)$$

In this formula, and in the following, the subscripts 1 and o refer to the alcohol and to water, respectively, and the superscript o denotes the pure state. M_1 is the molar mass of the alcohol, $M_1 = 74.12$ g mol⁻¹.

$V_{app,1}$ may be expressed in terms of molar quantities as

$$V_{app,1} = \frac{V - (1-x)V_o^o}{x} = V_1^o + \frac{V_{excess}}{x} \quad (2)$$

where $V_{excess} = V - (xV_1^o + (1-x)V_o^o)$ is the molar excess volume of the solutions. It is seen from the expression (2) that the variation of $V_{app,1}$ with concentration is the variation of the excess volume of the solutions *per mol of the*

alcohol. The advantages of presentations of volumetric data on aqueous solutions in terms of the apparent molar volume of the solute are discussed in Ref. (11).

The estimated value of $V_{app,1}$ at zero concentration (that is the partial molar volume of the alcohol at infinite dilution) is 88.3 cm³ mol⁻¹, practically independent of the temperature between 5 and 25 °C.

The thermal expansion of the solutions in the temperature ranges 5–10 °C and 20–25 °C is illustrated in Fig. 1c by plots of $\Delta v/\Delta T = [v(T + \Delta T) - v(T)]/\Delta T$ vs. w , and in Fig. 1d by plots of $\Delta V_{app,1}/\Delta T = [V_{app,1}(T + \Delta T) - V_{app,1}(T)]/\Delta T$ vs. x . Values obtained from the data in Table 1 for $w < 0.03$ are ignored in Fig. 1c and 1d because the experimental error is too large to permit an estimate of the small thermal expansion characteristic of the solutions in this concentration range.

DISCUSSION

The partial molar volume of tert-butyl alcohol at infinite dilution. The volumetric measurements presented in this paper are in satisfactory agreement with corresponding measurements reported in the literature,^{11–13} but the value estimated of the partial molar volume of *tert*-butyl alcohol at infinite dilution (88.3 cm³ mol⁻¹) is slightly larger than the

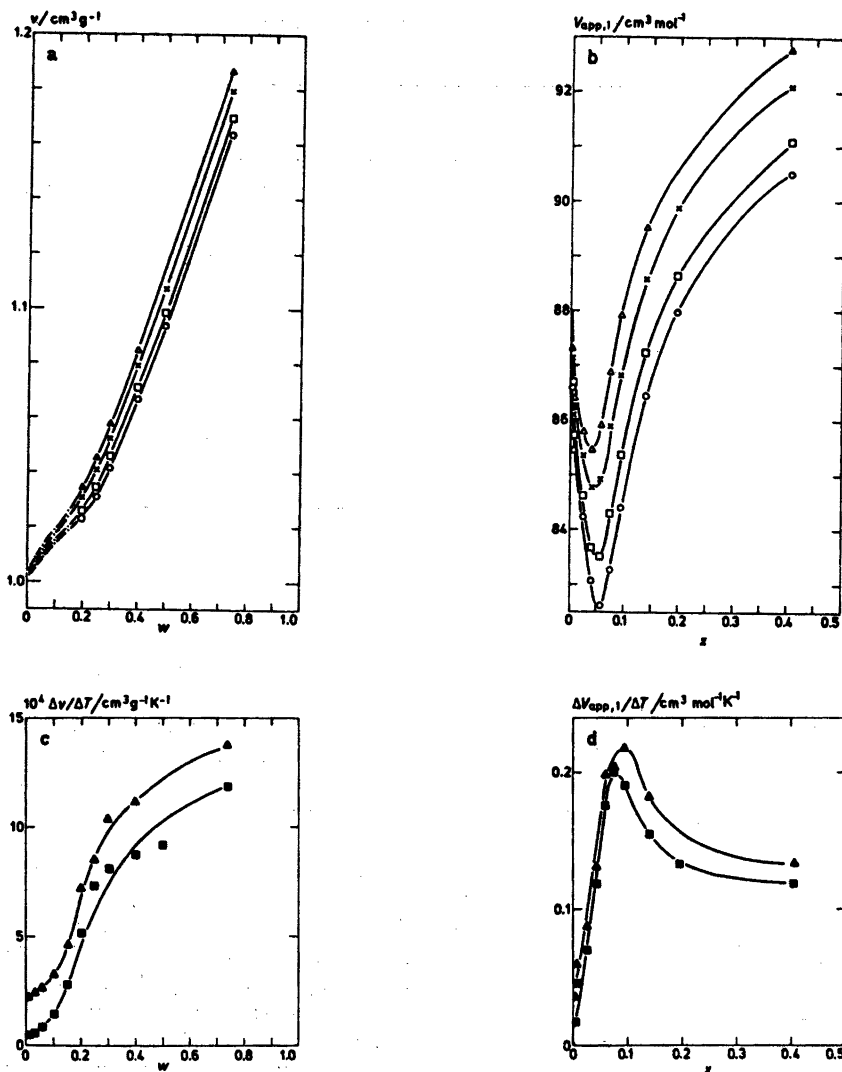


Fig. 1. Volumetric properties of aqueous solutions of *tert*-butyl alcohol. a, The specific volume of the solutions. b, The apparent molar volume of the alcohol. c, The change with temperature of the specific volume. d, The change with temperature of the apparent molar volume of the alcohol. w is the weight fraction, and x is the mol fraction of the alcohol. Δ , 25 °C; \times , 20 °C; \square , 10 °C; \circ , 5 °C; \blacktriangle , 20–25 °C; \blacksquare , 5–10 °C.

values 87.76,¹¹ 87.90¹² and 87.95 cm³ mol⁻¹¹³ available in the literature. The discrepancy between the estimates may be ascribed to well-known problems involved in the extrapolation of the experimental data to zero concentration. The strong concentration dependence, and the scattering of values of $V_{app,1}$ [calculated according to eqn. (1)] for w approaching zero com-

PLICATE the extrapolation; the value obtained for $w = 0$ depends to some extent on the extrapolation procedure applied, and on the lower limit of the concentration range in which the measurements are made.

The concentration dependence of the volume of aqueous solutions of tert-butyl alcohol. The concentration dependence of the volume of aqueous

solutions of *tert*-butyl alcohol illustrated in Fig. 1a and 1b is typical of aqueous solutions of substances which contain both polar and nonpolar groups. The specific volume of the solutions as a function of the weight fraction is concave ($d^2v/dw^2 < 0$) at low alcohol concentrations, and convex ($d^2v/dw^2 > 0$) at higher concentrations, so that the apparent molar volume of the alcohol as a function of the concentration exhibits a minimum. Differently expressed, in a series expansion in the concentration, c , of the apparent molar volume of the alcohol

$$V_{\text{app},1} = V_1^\infty + a_1c + a_2c^2 + \dots \quad (3)$$

a_1 is negative, but some of the higher coefficients are positive.

A similar concentration dependence of the volume has been observed for aqueous solutions of other alcohols,¹⁴⁻¹⁶ ketones,¹⁵ esters,¹⁷ alkylamides,¹⁸ or alkyl substituted ammonium salts,¹⁹ whereas the specific volume of aqueous solutions of urea or formamide (*i.e.* of solutions in which alkyl groups are absent) is a convex function of the weight fraction at all concentrations, so that the apparent molar volume of the solute is a monotonic, increasing function of the concentration.¹⁵ Negative values of a_1 in eqn. (3) are therefore considered to be a typical feature of aqueous solutions of nonpolar substances.

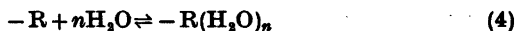
The initial slope of the curve in Fig. 1b for *tert*-butyl alcohol at 25 °C is $(dV_{\text{app},1}/dx)_{x=0} = -180 \text{ cm}^3 \text{ mol}^{-1}$, corresponding to $(dV_{\text{app},1}/dc)_{c=0} = -3.2 \text{ cm}^3 \text{ mol}^{-1} \text{ molar}^{-1}$ where c is the molar concentration of the alcohol. Values of a_1 in eqn. (3) available in the literature are $-1.89 \text{ cm}^3 \text{ mol}^{-1} \text{ molar}^{-1}$ ¹¹ and $-2.3 \text{ cm}^3 \text{ mol}^{-1} \text{ molar}^{-1}$.¹⁰ The estimate of the initial slope of the experimental curves is very sensitive to the procedure applied in the extrapolation of the experimental data to zero concentration; in the following, the average of the three available values, $-2.5 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1} \text{ molar}^{-1}$, is taken as the best estimate.

Negative values of a_1 in eqn. (3), apparently typical of aqueous solutions of substances which contain alkyl groups, have been discussed along the lines of the McMillan-Mayer theory,²⁰ and in accordance with this theory they have been taken as experimental evidence that pairwise interactions between nonpolar solute particles

in aqueous solution are followed by negative volume changes.

The solute-solute interaction has been described by Friedman and coworkers^{3,4} in terms of the cosphere-solvation concept of Gurney.²¹ At infinite dilution a nonpolar solute particle is assumed to be surrounded by a cosphere of bulky water, and the decrease of the apparent molar volume of the solute observed with increasing concentration is ascribed to an overlapping of cospheres of different molecules. In dilute solutions at the molar concentration c the overlapping volume is approximately $\frac{1}{2}V_{\text{cosphere}}^2 c 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$. If the specific volume of the cospheres is, say, 10 % larger than the specific volume of bulk water, the volume of the cospheres would have to be about $225 \text{ cm}^3 \text{ mol}^{-1}$ in order that the overlapping effect may account for the above-mentioned value of $a_1 = -2.5 \text{ cm}^3 \text{ mol}^{-1} \text{ molar}^{-1}$. This large value calculated of the cosphere volume – or the corresponding contribution $22.5 \text{ cm}^3 \text{ mol}^{-1}$ to the molar volume of the alcohol at infinite dilution – cannot be entirely excluded, but it indicates that an overlapping of hydrophobic cospheres may not be the main reason of the steepness of the curves in Fig. 1b for x approaching zero.

In an alternative approach to an interpretation of the concentration dependence of the volume of dilute aqueous solutions it is suggested that the decrease of the apparent molar volume of nonpolar solutes with increasing concentration is due to a shift in mobile equilibria between different structures in the water near the nonpolar groups.^{10,22} As originally suggested by Frank and Evans⁵ the formation of “icelike” water structures around nonpolar groups – R may be considered as solvation equilibria



for which $\Delta H^\ominus < 0$, $\Delta S^\ominus < 0$, and $\Delta V^\ominus > 0$.

The formation of the “icelike” water structures does occur as a series of stepwise reactions, $-R(\text{H}_2\text{O})_i + \text{H}_2\text{O} \rightleftharpoons -R(\text{H}_2\text{O})_{i+1}$. The formulation (4) is an oversimplification of the solvation process; it emphasizes, but exaggerates the cooperativity of the component reactions.

The equilibrium constant of the equilibrium (4) may be expressed as

$$\frac{p}{(1-p)c_{\text{H}_2\text{O}}^n} = K \quad (5)$$

where p is the probability that an $-R$ group is solvated according to the reaction (4)

$$p = Kc_{\text{H}_2\text{O}}^n / (1 + Kc_{\text{H}_2\text{O}}^n) \quad (6)$$

and

$$\frac{dp}{dc_{\text{H}_2\text{O}}} = \frac{1}{c_{\text{H}_2\text{O}}} np(1-p) \quad (7)$$

The contribution to the apparent molar volume of the solute, due to the equilibrium (4), is $p\Delta V^\ominus$, and the dependence of this contribution on the alcohol concentration is

$$\frac{dp\Delta V^\ominus}{dc} = -\frac{V_1}{V_0} \frac{dp}{dc_{\text{H}_2\text{O}}} \Delta V^\ominus = -\frac{V_1}{V_0} n \frac{dp}{dc_{\text{H}_2\text{O}}} \Delta V^\ominus \quad (8)$$

where ΔV^\ominus is the standard volume change of the reaction (4) *per mol of water*.

On the assumption that the concentration dependence of the apparent molar volume of *tert*-butyl alcohol in dilute aqueous solutions is due mainly to shifts in equilibria like (4), a combination of the formulae (7) and (8) leads to the following expression of the initial slope of the experimental curves

$$\left(\frac{dV_{\text{app},1}}{dc}\right)_{c=0} \cong -88 \times 10^{-3} n^2 p_{c=0} (1-p_{c=0}) \Delta V^\ominus \quad (9)$$

The values of the three parameters n , $p_{c=0}$, and ΔV^\ominus entering eqn. (9) cannot be determined from an experimental estimate of $(dV_{\text{app},1}/dc)_{c=0}$ and a numerical fitting to the experimental data on $V_{\text{app},1}$ over a larger concentration range is hampered by the overlapping of different volume effects, predominating at higher alcohol concentrations.²² The expression (9), compared with the initial slope of the experimental curves in Fig. 1b may, however, serve to illustrate that the existence in the alcohol solutions of equilibria like (4) may explain the steepness of the curves in Fig. 1b in the most water-rich concentration range. (For example the values $n=11$, $p_{c=0}=0.5$, and $\Delta V^\ominus=1 \text{ cm}^3 \text{ mol}^{-1}$ introduced into eqn. (9) lead to $(dV_{\text{app},1}/dc)_{c=0} = -2.6 \text{ cm}^3 \text{ mol}^{-1} \text{ molar}^{-1}$, in agreement with the experimental estimate at 25°C.) The essential points are that the formation and the break-

down of "icelike" water structures around a nonpolar group, as described in eqn. (4), are highly cooperative reactions ($n \gg 1$) and that these solvation equilibria are far from completely displaced to the right, even at infinite dilution. The lack of any experimental evidence of an inflection point on the curves in Fig. 1b at low alcohol concentrations indicates that the probability of solvation of the nonpolar groups $p \leq 0.5$ at all alcohol concentrations studied.

The temperature dependence of the volume of aqueous solutions of tert-butyl alcohol. Figs. 1c and 1d illustrate that the thermal expansion of dilute aqueous solutions of *tert*-butyl alcohol is small, and that the apparent molar expansion of the alcohol decreases strongly when the concentration approaches zero. This temperature dependence of the volume and large values of the heat capacity,¹¹ are typical features of dilute aqueous solutions of nonpolar solutes,²³ and they are in accordance with the existence in the solutions of mobile equilibria like (4).

The shift in the equilibrium (4) with a change in temperature may be expressed as

$$\frac{dp}{dT} = \frac{dp}{d \ln K} \frac{d \ln K}{dT} = p(1-p) \frac{\Delta H^\ominus}{RT^2} \quad (10)$$

where $dp/d \ln K = p(1-p)$ is obtained by differentiating eqn. (6).

The contribution to the apparent molar thermal expansion and to the apparent molar heat capacity of the solute due to a displacement of the equilibrium (4) is $dp\Delta V^\ominus/dT$ and $dp\Delta H^\ominus/dT$, respectively. Assuming that ΔV^\ominus and ΔH^\ominus are practically independent of the temperature it follows from (10) that

$$\frac{dp}{dT} \Delta V^\ominus = n^2 p(1-p) \frac{\Delta V^\ominus \Delta H^\ominus}{RT^2} < 0 \quad (11)$$

and

$$\frac{dp}{dT} \Delta H^\ominus = n^2 p(1-p) \frac{\Delta H^\ominus{}^2}{RT^2} > 0 \quad (12)$$

In eqns. (11) and (12) $\Delta V^\ominus > 0$, and $\Delta H^\ominus < 0$ are the changes in the standard thermodynamic functions of the equilibrium (4) per mol of water.

The apparent molar heat capacity of *tert*-butyl alcohol at infinite dilution in aqueous solution at 25°C is $463.6 \text{ J K}^{-1} \text{ mol}^{-1}$, and the

heat capacity of the pure alcohol is $210 \text{ J K}^{-1} \text{ mol}^{-1}$.¹¹ The expression (12) shows that this large difference between the heat capacity of the alcohol in aqueous solutions and in the pure state may be due to solvation effects of the type here discussed for quite small values of ΔH^{\ominus} (e.g. for $n=11$, $\Delta H^{\ominus} \sim 250 \text{ J per mol of water}$).

The concentration dependence of the expression (11) is

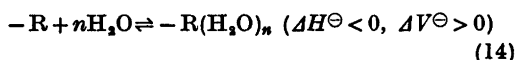
$$\frac{d^2p}{dTdc} \Delta V^{\ominus} = n^2(1-2p) \frac{\Delta V^{\ominus} \Delta H^{\ominus}}{RT^2} \frac{dp}{dc} \quad (13)$$

where $\Delta V^{\ominus} > 0$, $\Delta H^{\ominus} < 0$, and $dp/dc < 0$. The positive slope of the curves in Fig. 1d compared with eqn. (13) thus supports the assumption that $p < \frac{1}{2}$ (i.e. $(1-2p) > 0$) even at the lowest alcohol concentration considered ($x \cong 0.01$).

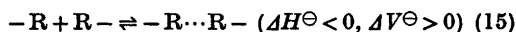
CONCLUSIONS

Considerations of the volumetric behaviour of aqueous solutions of *tert*-butyl alcohol and of other nonelectrolytes lead to the following conceptions about the conditions in aqueous solutions of nonpolar solutes:

Two types of equilibria are important for the thermodynamic properties of *dilute* aqueous solutions of substances which contain nonpolar groups - R. They are solvation equilibria



and solute-solute associations



At infinite dilution the equilibrium (15) is completely displaced towards the left, but experimental data indicate that equilibrium (14) is close to the state where half of the nonpolar groups are solvated.

With increasing solute concentration the equilibria (14) and (15) are displaced in opposite directions, (14) to the left, and (15) to the right. In *dilute* solutions the negative volume changes following the displacement of eqn. (14) with increasing solute concentration appear to be numerically larger than the positive volume changes following the displacement of eqn. (15). Shifts in hydrophobic solvation equilibria like (14) with concentration or temperature may

explain the unique volume and heat capacity properties of dilute aqueous solutions of nonpolar solutes.

At higher concentrations of solutes which contain both polar and nonpolar groups, effects due to hydrophobic solvation become negligible. Solvation of the polar groups and associations of the solute molecules predominate the concentration and the temperature dependence of the thermodynamic properties of concentrated solutions.

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