

## Apparent molal volumes of alcohols in aqueous solutions at different temperatures

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Apparent molal volumes, ( $\phi_v$ ) of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl and *tert*-butyl alcohols in aqueous solutions are reported at 2°, 4°, 6°, 8°, and 10°C for the first time. The trends of  $\phi_v$  against molality (*m*) curves have been interpreted in terms of effect of dissolved solute (alcohol) on structure of water. It has been concluded that lower alcohols even at lower temperatures get dissolved in the natural cavities available in the water structure whereas higher alcohols have difficulty in finding suitable cavities in water structure and hence tend to indicate phase separation. The results have also been interpreted in terms of predominance of solute-solute interactions at lower temperatures.

Volumetric properties of aqueous solutions of alcohols have been extensively studied<sup>1-4</sup>. It is generally observed that there is a loss in volume of alcohols on dissolution in water i.e. the limiting partial molal volume ( $\phi_v^0$ ) is smaller than the volume of the pure liquid solute at the same temperature. Eley<sup>5</sup> explained such results by expressing the view that water contains ice like cavities ready for small nonpolar solute molecules to enter. This approach is supported by compressibility studies by Kaulgud and Rao at different temperatures<sup>6</sup> (5°, 25° and 45°C). However very little information is available regarding the thermodynamic properties of alcohols between 0° and 10°C. It has always been interesting to study the behaviour of dissolved solute in aqueous solution around the temperature of maximum density of water (TMD, 4°C) as changes in the extent of hydrogen bonding between water molecules caused by the dissolved solute molecules are bound to be more predominant at TMD. With this view we have undertaken the measurement of densities of aqueous solutions of alcohols, namely, MeOH, EtOH, *n*-PrOH, *i*-PrOH, *n*-BuOH, *i*-BuOH, *s*-BuOH and *t*-BuOH below TMD i.e., at 2°, 4° and above TMD, 6°, 8° and 10°, to obtain apparent molal volumes ( $\phi_v$ ) as a function of concentration and other derived parameters.

### Materials and Methods

The alcohols i.e. methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *s*-butyl *iso*-butyl, and *t*-butyl (all A.R. grade) were further purified by standard method<sup>7</sup>. The densities agreed well with literature to better than  $\pm 0.0001$  g/ml for all the alcohols<sup>8</sup>.

The density measurements for aqueous solution of alcohols were carried out by using the single float method<sup>9</sup> and Sartorius model 2474 single pan/semi-microbalance having facility to weigh below the pan. Doubly distilled water was used throughout the experimental work. In this method a weighed quantity ( $\sim 170$  g) of doubly distilled water was taken in the stainless steel cylinder (capacity 500 ml). The glass float (plunger) weighted with mercury (volume  $\sim 32$  ml) was suspended from the pan of the balance by a thin nylon thread into the distilled water taken in the cylinder. The cylinder was kept in a constant temperature bath. The temperature of bath was kept constant to  $\pm 0.001^\circ\text{C}$  by circulating the coolant liquid from MK-70 cryostat (accuracy  $\pm 0.02^\circ\text{C}$ ).

To begin with, the required amount of alcohol was added in the water in the stainless steel cylinder. The solution was stirred with the glass stirrer, and allowed to attain constant temperature. The constant weight of the plunger was noted in this solution. In this way by adding the solute successively to water, 8-10 readings were taken. The density measurements of each alcohol in aqueous solution were made in 2-3 different runs. Considering the accuracy of temperature ( $\pm 0.001^\circ\text{C}$ ), weight ( $\pm 0.01$  mg) and the volume of the float ( $\sim$

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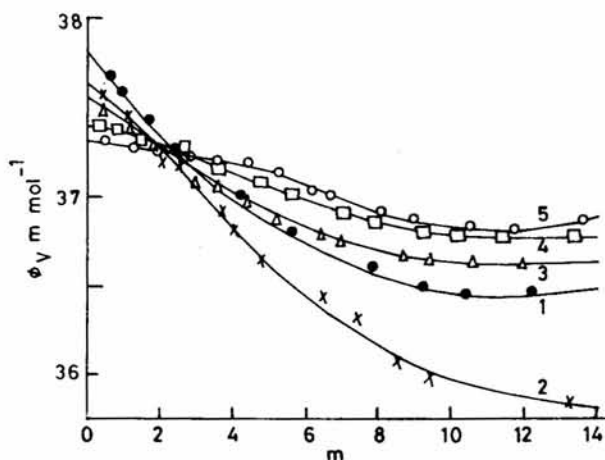


Fig. 1—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous methyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

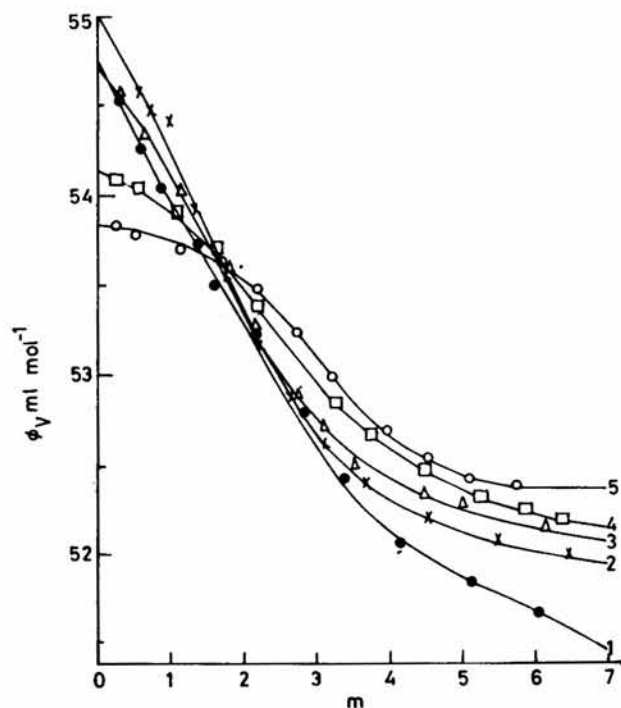


Fig. 2—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous ethyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

32 ml) the accuracy in the density measurements was of the order of  $\pm 10$  ppm. The volume of the plunger was determined at different temperatures first by weighing it in air and then in doubly distilled water. It was calibrated by measuring the densities of aqueous solutions of sodium chloride at 25°C. It was observed that our density values are in good agreement with the literature.

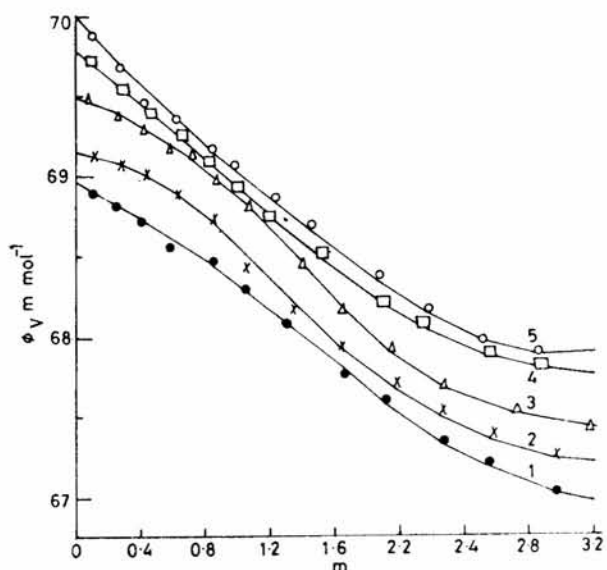


Fig. 3—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous *n*-propyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

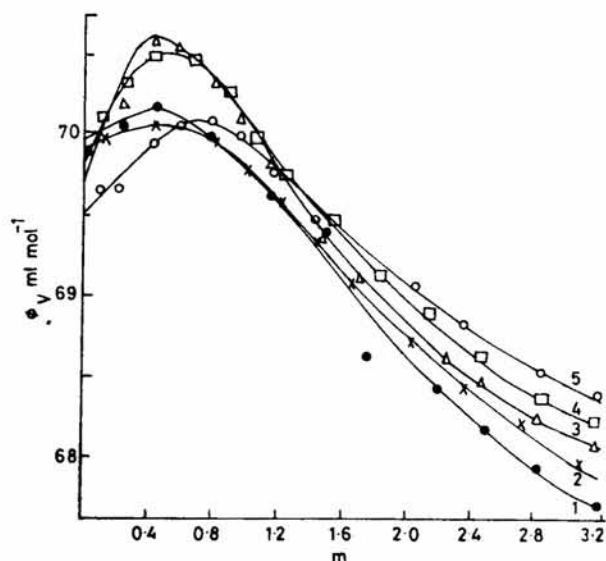


Fig. 4—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous isopropyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

#### Calculations of derived parameters

The apparent molal volume ( $\phi_v$ ) of the solutes have been calculated using the following equation.

$$\phi_v = \frac{1000(d_0 - d)}{m d d_0} + \frac{M_2}{d} \quad \dots (1)$$

where  $M_2$  is the molecular weight of the solute and  $m$  is its molality.  $d_0$  and  $d$  are the densities of solvent and solution respectively.

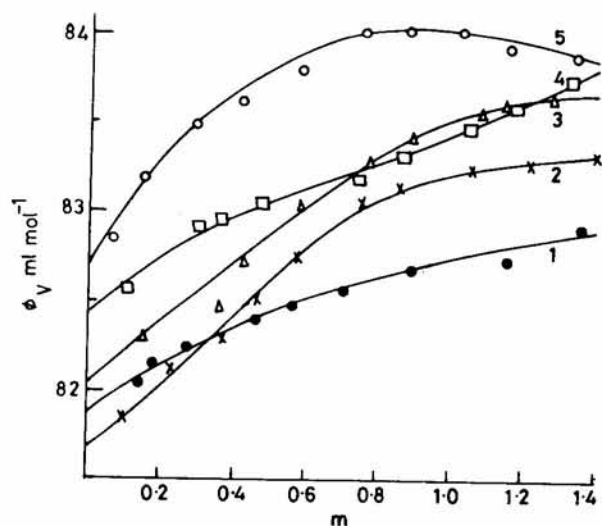


Fig. 5—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous *n*-butyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

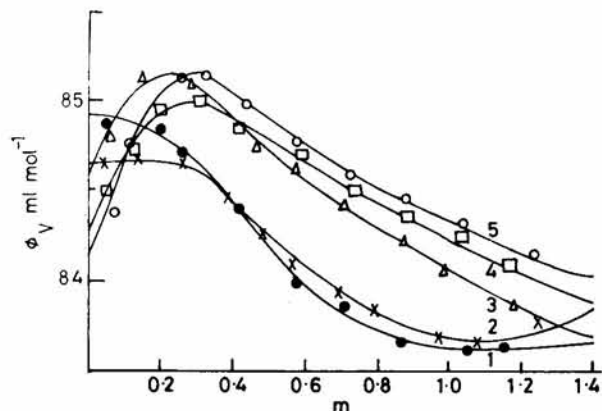


Fig. 6—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous isobutyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

For nonelectrolytes if  $\phi_v$  against  $m$  is plotted, one gets the limiting apparent molal volumes ( $\phi_v^0$ ). Although we plotted  $\phi_v$  against  $m$ , we do not intend to determine  $\phi_v^0$  as the  $\phi_v$ s has been extrapolated from higher concentration.  $\phi_v^0$  obtained thus are not considered to be reliable and hence are at interpreted in this work.

### Results and Discussion

Figure (1-8) show the variation of  $\phi_v$  as a function of concentration ( $m$ ) of all the alcohols at all temperatures studied in this work. It is observed that:

(i) The apparent molal volume ( $\phi_v$ ) goes through a minimum in the case of MeOH, EtOH, *n*-PrOH and *t*-BuOH.

(ii)  $\phi_v$  goes initially through a maximum in the case of *i*-PrOH, *n*-BuOH, *i*-BuOH and *s*-BuOH

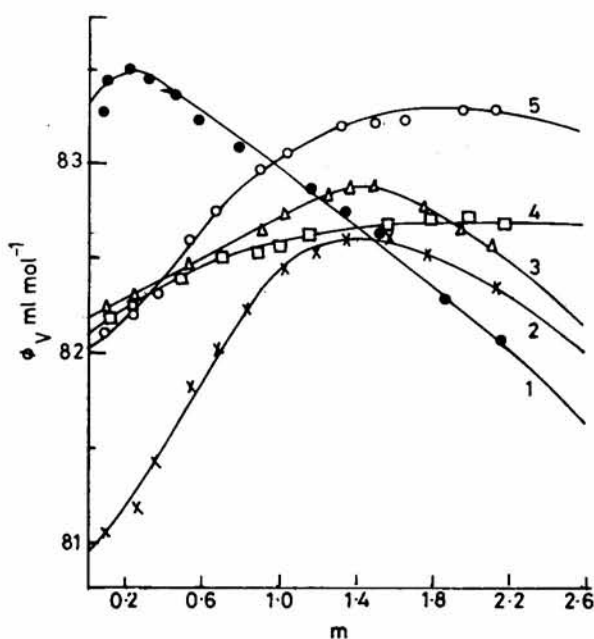


Fig. 7—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous *sec*-butyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

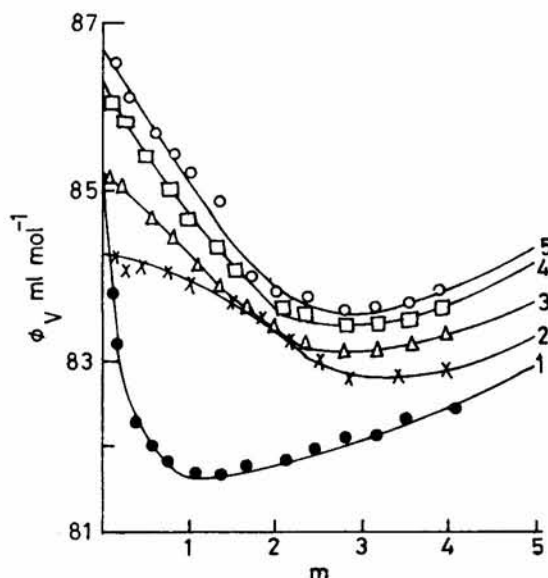


Fig. 8—Plots of apparent molal volume ( $\phi_v$ ) against molality ( $m$ ) of aqueous *tert*-butyl alcohol. 1, 2°C; 2, 4°C; 3, 6°C; 4, 8°C and 5, 10°C

and show distinct trends of minimum at higher concentrations.

The case of *n*-PrOH is interesting in that trends of positive  $d\phi_v/dm$  at low temperature (4°C) are discernible but not pronounced.

It is known that all the above alcohols exhibit negative limiting slopes  $(d\phi_v/dm)_{m \rightarrow 0}$  at 25°C. In view of this the findings of the present work for slopes between 0-10°C must be termed as remark-

Table 1—The values of  $(dk/dT)_{4^\circ\text{C}}$  and  $b$  for all the alcohols

Compound	$(dk/dT)_{4^\circ\text{C}}$	$b \times 10^{-3}$ (Eq. 3)	$b \times 10^{-3}$ (Lit.)
MeOH	0.6	-2.13	-1.5 <sup>a</sup> , -0.985 <sup>b</sup>
EtOH	1.8	-6.4	-4.1 <sup>a</sup> , -2.95 <sup>b</sup>
<i>n</i> -PrOH	0.9	-3.19	-6.4 <sup>a</sup> , -6.91 <sup>b</sup>
<i>i</i> -PrOH	-2.3	+9.3	No data
<i>n</i> -BuOH	18	-63.9	-13.4 <sup>a</sup> , -14.8 <sup>b</sup>
<i>i</i> -BuOH	87	-309	-14.0 <sup>a</sup> , -7.0 <sup>b</sup>
<i>s</i> -BuOH	4	-14.2	-14.0 <sup>a</sup> , +5.6 <sup>b</sup>
<i>t</i> -BuOH	4.6	-16.3	-26.2 <sup>a</sup> , +32 <sup>b</sup>

a—Wada &amp; Umeda, ref. 6

b—Kaulgud ref. 7

able. The above behaviour of alcohols at lower temperature around temperature of maximum density (TMD) can be rationalized as follows.

The lower alcohols like, MeOH, EtOH, and *n*-PrOH are accommodated in the cavities of water molecules ultimately showing loss of volume on dissolution even at low temperatures; *t*-BuOH being a symmetrical molecule also shows loss in volume. But branch chained alcohols like *i*-PrOH, *n*-BuOH and *s*-BuOH show positive  $d\phi_v/dm$ . This indicates the difficulty of these molecules in getting accommodated in the cavities presumably on account of non-availability of cavities of suitable size at low temperatures. Thus at low temperature these molecules of higher alcohols prefer to stay together indicating stronger solute-solute interactions. However, in concentrated region voids are made in the water structure due to gradual destruction of water structure wherein alcohol molecules are accommodated showing negative  $d\phi_v/dm$ . The above interpretation is supported by true limiting compressibility ( $\phi_v^0$ ) values reported<sup>6</sup> at 5°C. It has been observed that lower alcohols show either positive or small negative values, whereas higher alcohols show large negative values. However, *t*-BuOH though large being symmetrical shows a small negative value. Franks and Smith<sup>11</sup> have shown that all butanols have negative for  $\phi_v$  with molality  $< 0.1$  at 0.5°C and 5°C. The present positive slopes of  $\phi_v$  curves for higher alcohols suggest a possible minimum below our lowest concentration (0.1 *m*) in  $\phi_v$  curves. Overall  $\phi_v$  against *m* curves then thus resemble miscelle forming systems.

The peculiar behaviour of these alcohols at low temperatures might be due to the effect of dissolved solutes on the structure of water around its TMD also. It has been shown by Wada and Ume-

da that the structural effects of dissolved solute on the TMD of water can be quantitatively studied<sup>12</sup>.

The observed change in TMD ( $\Delta\theta$ ) can be written as sum of two terms  $\Delta\theta_{\text{id}}$  and  $\Delta\theta_{\text{str}}$ .  $\Delta\theta_{\text{id}}$  represents the decrease in TMD when the solution behaves ideally i.e.  $\Delta V_x M = 0$  and  $\Delta\theta_{\text{str}}$  is the contribution to change in TMD when  $\Delta V_x M \neq 0$ . By knowing the molar volume ( $V_2^0$ ) and coefficient of expansion ( $\alpha_2$ ) of pure liquids it is possible to evaluate  $\Delta\theta_{\text{str}}$ . It has been shown by Wada and Umeda that  $\Delta\theta_{\text{str}}$  can be expressed in the form of a quadratic equation with respect to solute mole fraction ( $x_2$ ) as:

$$\Delta\theta_{\text{str}} = ax_2 + bx_2^2 \quad \dots (2)$$

where  $a$  and  $b$  are constants. Kaulgud<sup>13</sup> further proved that the values of  $a$  and  $b$  can also be calculated from volumetric measurements at different temperatures. Thus

$$a = \frac{d/dT(\bar{V}_2^0 E)_4^0}{2(1-x_2)\alpha_1 V_1^0} \quad \text{and} \quad b = \frac{-dk/dT}{2(1-x_2)\alpha_1 V_1^0} \quad \dots (3)$$

where  $\bar{V}_2^0 E$  is the limiting excess volume at 4°C and  $dk/dT$  is the temperature coefficient of slopes of  $\phi_v$  against mole fraction  $(d\phi_v/dx_2)_4^0$  in dilute solutions.  $V_1^0$  and  $\alpha_1$  are the molar volume and coefficient of expansion of pure water at 3.98°C.

Positive and negative  $a$  values show respectively the structure strengthening and structure breaking ability of the dissolved solute. Kaulgud showed that positive values of  $b$  reflect solute-solute interactions predominant at higher temperature and negative  $b$  values reflect solute-solute interactions predominant at lower temperature. In Table 1 are collected the  $(dk/dT)_{4^\circ\text{C}}$  and  $b$  values computed from our volumetric data at different temperature around 4°C. It is observed that our values are in good agreement with literature, except for *i*-BuOH. In the case of *i*-BuOH the sign is the same but the magnitude of our value is quite high. The concentration range studied by us and reported in the literature overlaps in all the cases. Thus from the above  $b$  values it is concluded that in the case of MeOH, EtOH, *n*-PrOH, *n*-BuOH, *i*-BuOH, *s*-BuOH and *t*-BuOH, solute-solute interactions are more predominant at lower temperature. However, the magnitude seems to be higher in the case of higher alcohols. *i*-PrOH must be having solute-solute interactions more predominant at higher temperature. Higher negative  $b$  values for higher alcohols also indicate phase separation at lower temperature which is supported by positive limiting  $d\phi_v/dm$ .

Kozac *et al.*<sup>14</sup> computed B coefficients from Eq. (4).

$$\ln \gamma_1 = B x_2^2 + C x_2^3 \dots (4)$$

where  $\gamma_1$  is the solvent activity coefficient, B and C are the pairwise and triplet coefficients and  $x_2$  is the mole fraction of the solute. It has been observed that B-coefficient goes on increasing as chain length increases. However, for MeOH and *t*-BuOH it is negative suggesting again loss in volume on dissolution in water. The increase in the B-coefficient values as chain length increases also suggest the increase in extent of hydrophobic hydration. It has been suggested that in the higher concentration range higher alcohols form alcohol miscelles.

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