

Partial molal volume of DMSO and Me₂CO in the mixture of water and *t*-butyl alcohol (TBA) at 278.15, 288.15 and 298.15 K ^α

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Abstract

Volume measurement can be used in the evaluation of the molecular interaction in solution. The apparent molal volumes V_a of DMSO and Me₂CO in the concentration range 0.2–1.4 mol per kg of solvent in mixed solvents of TBA and water were calculated from density data. The apparent molal volume of DMSO and Me₂CO at infinite dilution \bar{V}^0 was determined by extrapolation. The variation of \bar{V}^0 with the composition of binary mixed solvent was indicated in plots. The contribution of molecular interaction and structure to solution volumes was discussed.

INTRODUCTION

The contribution of molecular interaction to solution volumes can be divided into chemical, physical and structural effects, exhibiting expansion or shrinkage when mixed. Mixtures of *t*-butyl alcohol (TBA) and water were widely studied [1–4] by various methods and they exhibited anomalous properties in the water-rich region. Herein DMSO and Me₂CO were employed as probes to examine the molecular interaction and structural properties of binary mixtures. By measuring the densities of solutions of DMSO and Me₂CO at various concentrations in a known mixed solvent, the apparent molal volumes of DMSO and Me₂CO at infinite dilution \bar{V}^0 in that mixed solvent were determined. \bar{V}^0 is a function of the composition of binary mixtures of water and *t*-butyl alcohol. The variation should give information on the role of molecular interaction and structure in solvents and solution.

EXPERIMENTAL

t-Butyl alcohol (A.R. grade, Beijing Chemical Factory) was dried over CaO for 24 hours, refluxed over CaO for 3 hours, and finally distilled at a

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large reflux ratio. DMSO (C.P. grade, Beijing Chemical Factory) was dried over a 4A molecular sieve for 48 hours, and distilled under vacuum. Acetone (A.R. grade, Beijing Chemical Factory) was dried over CaCl_2 and distilled at a large reflux ratio. Distillates with accepted refraction index [5] were used. Water was distilled twice and its conductivity was less than $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Binary mixtures of solvents were prepared by weighing in a 250 ml volumetric flask with a tight fitting ground stopper, weighing errors being less than 5 mg. Solutions of DMSO and Me_2CO of concentration 0.2–1.4 mol per kg of solvent were also prepared by weighing in a 25 ml Erlenmeyer flask with a tight fitting ground stopper, weighing errors being less than 0.05 mg. Solution preparation was carried out as fast as possible to avoid errors due to volatility. Therefore, concentrations with four significant figures both for solvent and solute are guaranteed.

Densities of solutions and solvents were measured with a DMA 602 densimeter at 278.15, 288.15 and 298.15 K, with temperature fluctuations of less than $\pm 5 \text{ mK}$. The densimeter gives six significant figures. The effect on density because of degasification was checked and reported elsewhere [6], amounting to less than $10^{-5} \text{ g ml}^{-1}$. Therefore, the density data would then have five significant figures. The apparent molal volumes of DMSO and Me_2CO in binary solvents were calculated according to the following equation

$$V_a = [(1000 + mw)/d - 1000/d_0]/m \quad (1)$$

where V_a is apparent molar volume of DMSO and Me_2CO in solution, d and d_0 are the densities of the solution and solvent respectively, m is the concentration of DMSO and Me_2CO in mol per kg of solvent and w is the molecular weight of DMSO and Me_2CO . V_a is a linear function of m within the experimental range of solute concentration as follows

$$V_a = \bar{V}^0 + b_v m \quad (2)$$

where b_v is a constant and \bar{V}^0 is the apparent molal volume of solute at

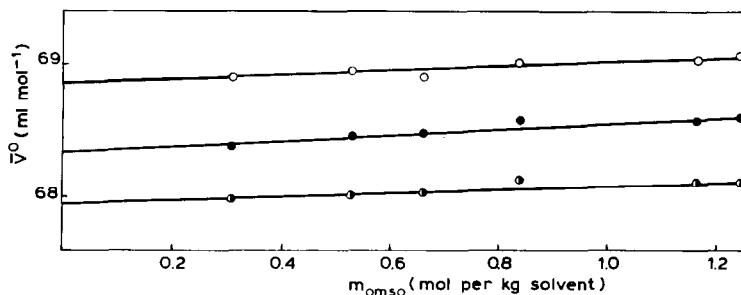


Fig. 1. An example of \bar{V}^0 from apparent molal volume by plot ($X_{\text{TBA}} = 0.4800$).

$m = 0$, the partial molal volume of solute, obtained by the least-squares method. Fig. 1 is an example for \bar{V}^0 from apparent molal volume by plot.

RESULTS AND DISCUSSION

\bar{V}^0 and relative molal volume V_d ($V_d = \bar{V}^0 - V_0$) for DMSO and Me_2CO in mixed binary solvents with various ratios of *t*-butanol and water at 278.15, 288.15 and 298.15 K are listed in Tables 1 and 2, where V_0 is molar volume of pure DMSO and Me_2CO at the respective temperatures (V_0 for

TABLE 1

Volume properties of DMSO in the mixed solvent of H_2O -TBA

A_{TBA}	\bar{V}^0			V_d		
	278.15	288.15	298.15	278.15	288.15	298.15
0.0000	67.78	68.27	68.72	-2.26	-2.39	-2.58
0.0079	66.61	67.42	68.25	-3.43	-3.24	-3.05
0.0110	66.27	67.20	68.01	-3.77	-3.46	-3.29
0.0169	65.72	66.73	67.60	-4.32	-3.93	-3.70
0.0189	65.62	66.74	67.54	-4.42	-3.92	-3.76
0.0277	65.12	66.48	67.46	-4.92	-4.18	-3.84
0.0305	65.10	66.50	67.50	-4.94	-4.16	-3.80
0.0473	65.27	66.53	67.57	-4.77	-4.13	-3.73
0.0658	66.30	67.09	67.91	-3.74	-3.57	-3.39
0.1117	67.33	67.57	67.88	-2.71	-3.09	-3.42
0.1970	67.48	67.85	68.27	-2.56	-2.81	-3.03
0.4800	67.95	68.34	68.86	-2.09	-2.32	-2.44

TABLE 2

Volume properties of Me_2CO in the mixed solvent of H_2O -TBA

X_{TBA}	\bar{V}^0			V_d		
	278.15	288.15	298.15	278.15	288.15	298.15
0.0000	65.42	66.19	66.90	-6.42	-6.66	-7.14
0.0079	64.23	65.39	66.06	-7.61	-7.46	-8.03
0.0110	63.79	64.95	65.97	-8.05	-7.90	-8.07
0.0169	63.36	64.50	65.62	-8.48	-8.35	-8.42
0.0189	63.23	64.58	65.81	-8.61	-8.27	-8.23
0.0296	62.64	64.40	65.68	-9.20	-8.45	-8.36
0.0473	63.75	65.61	67.13	-8.09	-7.24	-6.91
0.0658	66.28	67.23	68.59	-5.56	-5.62	-5.45
0.1117	67.59	68.35	69.09	-4.25	-4.50	-4.95
0.1970	68.57	69.23	70.20	-3.27	-3.62	-3.84
0.4800	70.81	71.73	72.64	-1.03	-1.12	-1.40

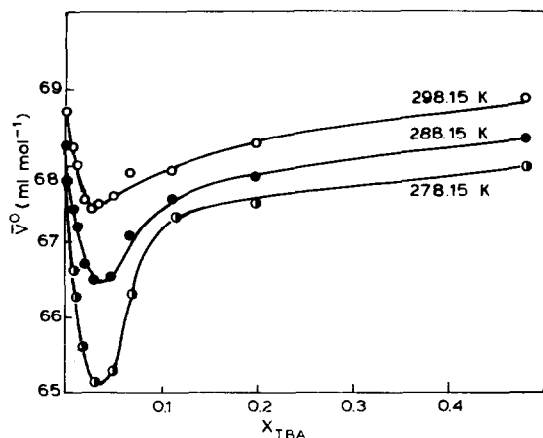


Fig. 2. Plots of \bar{V}^0 for DMSO vs. X_{TBA} for mixed solvents.

DMSO at 278.15 K was obtained from extrapolation of values at higher temperatures). It is considered to be significant to discuss the variation of V_d with compositions of solvents by using extrapolated values of V_0 , \bar{V}^0 and V_d as functions of X_{TBA} are shown in Figs. 2–5. As in the case of acetonitrile, in water-rich regions partial molal volumes \bar{V}^0 of DMSO and Me_2CO decrease dramatically with the addition of TBA, and have minima around $X_{\text{TBA}} = 0.03$, then increase sharply until $X_{\text{TBA}} = 0.1$, and become rather flat afterwards. The plots for DMSO are almost parallel with the horizontal ordinate here; however, the plots for Me_2CO are still up. As the temperature is lowered, the minima of \bar{V}^0 become more pronounced, the lowest being at 278.15 K. V_d is the difference in volume between that occupied by a mole solute in solution and that in a pure state. The values should correspond to those of \bar{V}^0 . However, plots of V_d vs. X_{TBA} at the three temperatures studied intersect when X_{TBA} is around 0.06. This phenomenon occurs for all three solutes, namely CH_3CN , DMSO and Me_2CO . Therefore it is important to consider the variation of this property with composition.

Baumgartner et al. [2] suggested a clathrate structure in the TBA– H_2O mixture with TBA : $\text{H}_2\text{O} = 1 : 17$ obtained from ultrasonic velocity studies. Fang et al. [3] studied the transfer free energies of NaCl and KCl from water to mixtures of water and TBA with emf measurements, and obtained maxima for the transfer entropies of salts at X_{TBA} around 0.06–0.07. This means that solutions of TBA– H_2O possess maximum order at this composition. Iwasaki et al. [4] suggested a formation of an $[\text{H}_2\text{O}]_{150}(\text{TBA})_5$ hydrate-like structure by light scattering. Desnoyer et al [7] measured the partial molal volume of TBA in water as a function of X_{TBA} and found minima in water-rich regions, with deeper dips at lower temperatures. Results and suggestions from other researchers on water–TBA mixtures and the character of volume variation of the third components in binary mixtures as investigated in the present work agree. Some explanations follow.

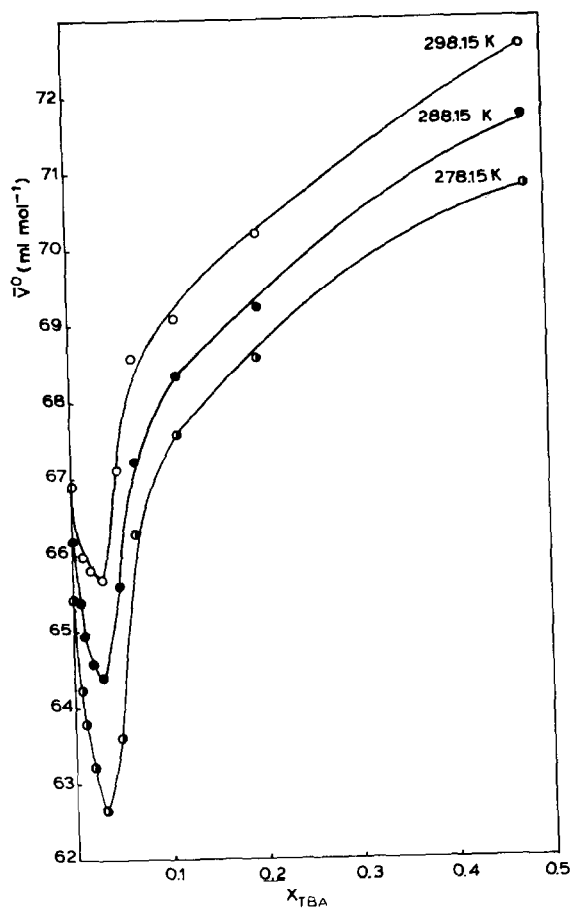


Fig. 3. Plots of \bar{V}^0 for Me₂CO vs. X_{TBA} for mixed solvents.

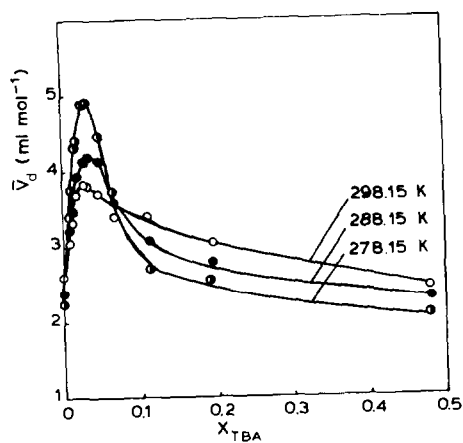


Fig. 4. Plots of V_d for DMSO vs. X_{TBA} relative molal volume V_d ($V_d = \bar{V}^0 - V_0$). V_0 is mole volume of pure DMSO.

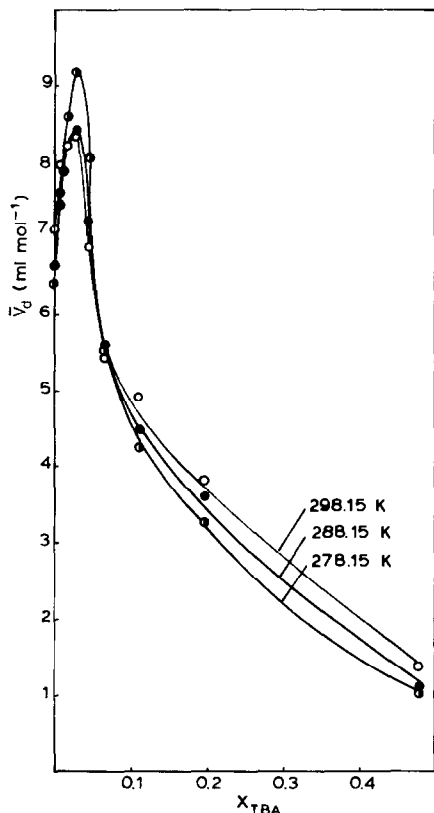


Fig. 5. Plots of \bar{V}_d of Me_2CO vs. X_{TBA} .

(1) At $X_{\text{TBA}} = 0.03$, solvents consist of a mixture of clathrate and bulk water. Interactions of the solute, DMSO or Me_2CO , with both solvent structures cause shrinkage of the volume of solution and exhibit minima of \bar{V}^0 for solutes with this solvent composition.

(2) Increase in molecular thermal motion reduces the interaction of the solute with both solvent structures and causes a decrease in shrinkage. Therefore, the trend of a decrease in volume \bar{V}^0 gets smaller as the temperature rises.

(3) A possible explanation for the intersection of plots for \bar{V}_d vs. X_{TBA} at different temperatures in Figs. 4 and 5 may be put forth. When X_{TBA} of the solvent is smaller than that for clathrate, volume shrinkage of the solute results from the two factors mentioned above. They become more significant as the temperature decreases. Thus the decrease in the volume of solute from the pure state to the state in mixed solvent appears more pronounced at lower temperatures. When X_{TBA} is larger than that for clathrate, the solute disperses into TBA gradually. The thermal motion of the molecules increases the difference between the volume of solute in the pure state and in solution. It makes the decrease in volume more pronounced at higher temperatures,

thus resulting in an intersection. The concentration of mixed solvent at the intersecting point may then be the composition for the clathrate compound.

(4) When X_{TBA} is larger than 0.1, solute disperses into TBA principally. There is no dramatical change in interaction between solute-solvent molecules as X_{TBA} increases. Thus the variation of \bar{V}^0 becomes flat, especially when \bar{V}^0 of DMSO approaches a constant value, possibly due to the formation of a complex of DMSO-TBA with a fixed composition.

These preliminary discussions on the above-mentioned phenomena, solvent composition at the minima of \bar{V}^0 and the intersection for plots of V_d vs. X_{TBA} at different temperatures, are herewith presented, and they will open up new vistas for further study.

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REFERENCES

- 1 R. Battino, *Chem. Rev.*, 71 (1971) 5.
- 2 E.K. Baumgartner and G. Atkinson, *J. Phys. Chem.*, 75 (1971) 2336.
- 3 L.Q. Fang, and R.L. Liu, *Acta Chim. Sinica*, 43 (1985) 415.
- 4 K. Iwasaki and T. Fujiyama, *J. Phys. Chem.*, 80 (1977) 1908.
- 5 J.A. Riddick, and W.B. Bunger, *Organic Solvent*, Wiley-Interscience, New York, 1970.
- 6 R.L. Liu and Z.F. Li, Abstract of International Conference on Chemical Thermodynamics and Calorimetry, Beijing, A20, 1989.
- 7 J.E. Desnoyer, G. Perron and C. Devisser, *Can. J. Chem.*, 55 (1977) 856.