Thermochimica Acta, 169 (1990) 185–191
Elsevier Science Publishers B.V., Amsterdam

PARTIAL MOLAL VOLUME OF ACETONITRILE IN MIXTURES OF WATER AND *t*-BUTYL ALCOHOL AT 278.15, 288.15 AND 298.15 K *

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(Received 25 August 1989; in final form 28 September 1989)

ABSTRACT

Volume measurement can be used in the evaluation of the molecular interaction in solution. The apparent molal volumes, V_a of acetonitrile in the concentration range 0.2–1.4 mol (kg solvent)$^{-1}$ in known mixed solvents of TBA and water have been calculated from density data. $\bar{V}^0$, the apparent molal volume of acetonitrile in the solvent at infinite dilution, has been determined by extrapolation. A plot indicates the variation of $\bar{V}^0$ with the composition of binary mixed solvent. The contribution of molecular interaction and structural effects on the solution volume is discussed.

INTRODUCTION

The contribution of the molecular interaction to solution volume can be divided into chemical, physical and structural effects, and results in increasing or decreasing the volume of solution on mixing. Mixtures of *t*-butyl alcohol (TBA) and water were widely studied [1–6] by various methods, and exhibited anomalous properties in the water-rich region. Acetonitrile was employed as a probe to examine the molecular interaction and structural effects on binary mixtures. By measuring the densities of solutions of acetonitrile at several concentrations in known mixed solvents, the apparent molal volume of acetonitrile at infinite dilution, $\bar{V}^0$, in that mixed solvent was determined. $\bar{V}^0$ is a function of the composition of the binary mixture of water and *t*-butyl alcohol. The variation should give some information about the role of molecular interactions and structural aspects in solutions and solvents.

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* Presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, P.R. China, 25–28 August 1989.

EXPERIMENTAL

t-Butyl alcohol, A.R. grade reagent from the Beijing Chemical Factory, was dried over CaO for 24 h, refluxed over CaO for 3 h, and finally distilled with a large reflux ratio. The distillate of correct refractive index [7] was used. Acetonitrile was C.P. grade reagent from the Guangzhou Chemical Factory and was dried over P_2O_5. The distillate of correct refractive index was used. Water was distilled twice and its conductivity was less than 1×10^{-6} ohm^{-1} cm^{-1}.

Binary mixtures were prepared by weighing in a 250 ml volumetric flask fitted with a ground stopper. The weighing error was less than 5 mg. Solutions of acetonitrile of concentration 0.2–1.2 mol (kg solvent)$^{-1}$ were also prepared by weighing in a 25 ml Erlenmeyer flask fitted with a ground stopper. The weighing error was ± 0.05 mg. The procedure for the solution preparation was completed as quickly as possible in order to avoid volatilization errors. Concentrations to four significant figures for both solvent and solute can therefore be relied on.

The 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 5 mK. The densimeter gives results to six significant figures. The influence of degasification on density has been checked and reported elsewhere [8], and proved to be less than 1×10^{-5} g ml^{-1}. The density data should therefore have five significant figures. The apparent molal volume of acetonitrile in certain binary solvents was calculated according to the equation

$$V_a = \left[\frac{(1000 + mw)}{d} - \frac{1000}{d_0} \right] \Big/ m \qquad (1)$$

where V_a is the apparent molal volume of acetonitrile in solution, d and d_0 are the densities of the solution and solvent, respectively, m is the concentration of acetonitrile in mol (kg solvent)$^{-1}$ and w is the molecular weight of acetonitrile.

RESULTS AND DISCUSSION

V_a is a linear function of m and is shown in Fig. 1 for *t*-butyl alcohol at $X_{TBA} = 0.01569$ as an example. Data for V_a in certain mixed solvents was fitted to the equation

$$V_a = \overline{V}^0 + b_v m \qquad (2)$$

by the least squares method in the range of m of about 0.2–1.2 mol (kg solvent)$^{-1}$. $\overline{V}^0$ is the apparent molal volume of solute at infinite dilution in a known mixed binary solvent and can be regarded as the partial molal

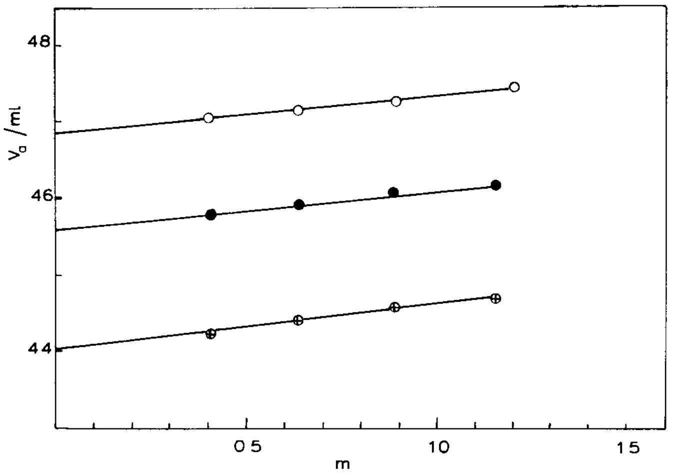

Fig. 1. Plots of V_a vs. *m* of acetonitrile in mixed solvent at: ○, 298.15 K; ●, 288.15 K; ⊕, 278.15 K.

volume, $\bar{V}^0$, of acetonitrile in that solvent. $\bar{V}^0$ varies with the composition of binary solvent at a fixed temperature. Let V_0 be the mole volume of acetonitrile in the pure state and $V_d = \bar{V}^0 - V_0$. The mole fraction of *t*-butyl alcohol, X_{TBA}, together with $\bar{V}^0$ and V_d at three temperatures, are given in Table 1. The plots of $\bar{V}^\circ$ for the solute vs. X_{TBA} are shown in Fig. 2 for 298.15, 288.15 and 278.15 K. $\bar{V}^\circ$ goes through a characteristic minimum in the water-rich region at $X_{TBA} \approx 0.03$. This minimum becomes more pronounced as the temperature is lowered. Beyond the minimum, the increase in $\bar{V}^\circ$ is sharp. It approaches a constant value when the mole fraction of *t*-butyl alcohol is greater than 0.1. This means that, initially, acetonitrile

TABLE 1

X_{TBA}, $\bar{V}^0$, and V_d

X_{TBA}	$\bar{V}^0$/ml			V_d/ml		
	298.15	288.15	278.15	298.15	288.15	278.15
0	47.20	46.50	45.55	5.66	5.62	5.87
0.0159	46.90	45.60	44.05	5.96	6.52	7.37
0.0245	46.84	45.56	43.80	6.02	6.56	7.62
0.0359	47.87	46.31	44.38	4.99	5.81	7.04
0.0417	48.51	46.96	44.73	4.35	5.16	6.69
0.0526	49.59	48.58	46.70	3.27	3.54	4.72
0.1222	50.84	50.50	50.13	2.02	1.62	1.29
0.1869	50.98	50.78	50.29	1.88	1.34	1.13
0.2818	51.36	50.87	50.34	1.50	1.25	1.08
0.4159	51.84	51.26	50.76	1.02	0.86	0.66
0.7022	52.55	51.83	51.16	0.31	0.29	0.26

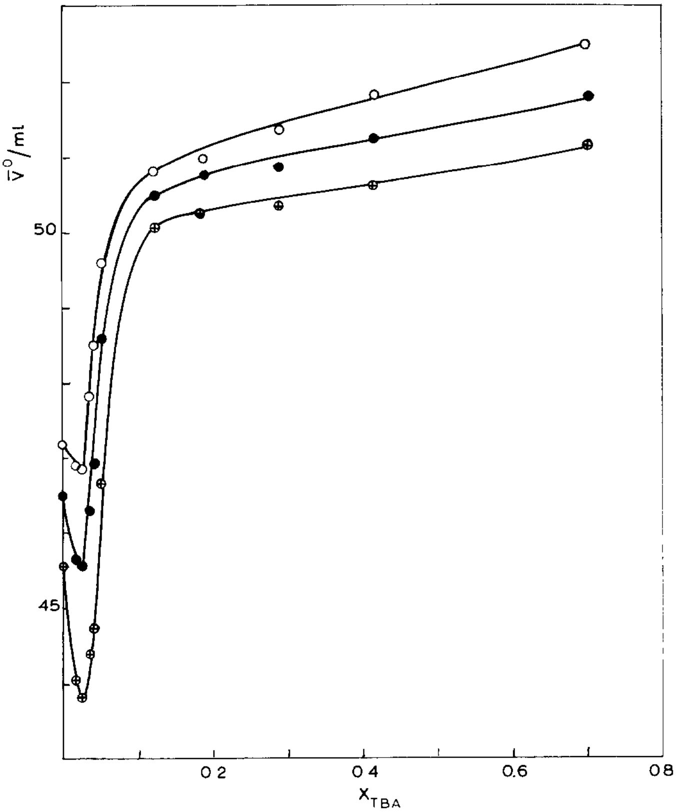

Fig. 2. Plots of $\bar{V}^0$ of acetonitrile vs. X_{TBA} of mixed H_2O–TBA solvent at: ○, 298.15 K; ●, 288.15 K; ⊕, 278.15 K.

becomes more compact as the *t*-butyl alcohol content increases. This occurs until the minimum, after which point it decreases sharply. The volume variation of acetonitrile with increasing TBA content approaches a constant value when X_{TBA} is larger than 0.15. V_d represents the difference in volume occupied by one mole of acetonitrile in a known solvent and that occupied in the pure state. The plots of $-V_d$ vs. X_{TBA} are shown in Fig. 3. The plots pass through maxima which become larger as the temperature is lowered. However, the curves intersect at $X_{TBA} = 0.05$–0.06, after which $-V_d$ is smaller at lower temperatures, decreasing with increasing X_{TBA}, and the curves approach each other.

t-Butyl alcohol forms solid clathrates with water in the presence of a help gas such as H_2S as $2H_2S \cdot TBA \cdot 17H_2O$ [2,5] and Glew et al. [5] explained the anomalous properties of aqueous solutions of TBA with 3–8% solute in terms of a clathrate cage model, i.e. the dilute aqueous solutions consist of solute molecules stabilizing adjacent water molecules into ordered, hydrogen-bonded shells, similar to clathrate cages. Iwasaki and Fujiyama [2] studied binary mixtures of TBA and water by light scattering. From the

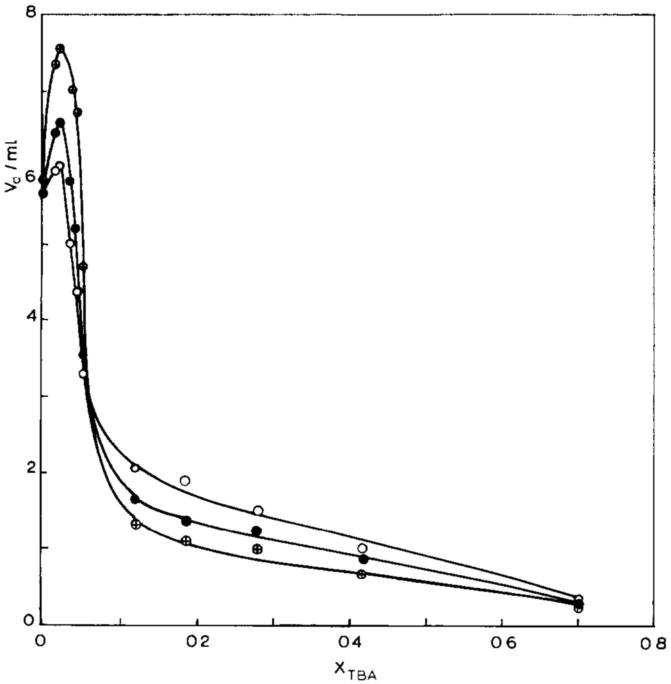

Fig. 3. Plots of V_d vs. X_{TBA} at: ○, 298.15 K; ●, 288.15 IK; ⊕, 278.15 K.

dependence on concentration they suggested that, in the concentration range $0 < X_{TBA} < 1/22$, water molecules form polyhedra surrounding each TBA molecule and the polyhedra are dispersed in water. In the concentration range $1/22 < X_{TBA} < 0.16$, hydrate-like structures of the form $(H_2O)_{105}(TBA)_5$ is dispersed in TBA, and when $X_{TBA} > 0.16$, the associated complex $5[(H_2O)_{21} \cdot TBA]$ breaks down gradually with increasing X_{TBA}. Desnoyers and co-workers [1] measured the partial molal volume of TBA in water as a function of X_{TBA}. Their plot of $\overline{V}^0$ vs. X_{TBA} is similar to ours, but with the minimum located at a higher X_{TBA} value of about 0.06. Baumgartner and Atkinson [3] studied TBA–H_2O mixtures using ultrasonic velocities and their findings supported a clathrate structure of 1 : 17. They also studied the ternary mixtures TBA–PO–H_2O and TBA–THF–H_2O, and observed that the maxima correspond quite well to linear superpositions of the maxima corresponding to individual solutes measured separately at the same total concentration. This is in accordance with the fact that the X_{TBA} values corresponding to the minima in Fig. 2 are smaller than the values of Desnoyers and his co-workers. Fang and Liu [6] in this laboratory studied the transfer free energies of NaCl and KCl from water to mixtures of water and TBA, and their temperature coefficients, by EMF measurements on a double cell. They calculated the transfer entropies with maxima at $X_{TBA} \approx$ 0.06–0.07, which supported a clathrate model of TBA : H_2O = 1 : 17.

The variation in $\bar{V}^\circ$ and V_d of acetonitrile with the mole fraction, X_{TBA}, of binary solvents may be explained as follows.

(1) In the water-rich region with X_{TBA} less than that for the H_2O–TBA clathrate structure, acetonitrile molecules are surrounded by water. Addition of TBA molecules causes the environment of the acetonitrile molecules to be more ordered, the compact effect increasing with increasing TBA. The variation of $\bar{V}^\circ$ of acetonitrile with X_{TBA} goes through a minimum. The plots of the $\bar{V}^\circ$ values of acetonitrile in binary mixed solvents vs. x_{TBA} are similar to that of the partial molal volume of TBA in aqueous solution [11]. The structural factor may dominate the volume character.

(2) Thermal motion of molecules disturbs the clathrate structure thus weakening the compact effect on the solute as the temperature rises, resulting in a smaller dip at higher temperatures (see Fig. 2). It seems reasonable that the particular interaction favouring the "17 hydrate" structure in the solid clathrate should persist in the liquid state, albeit in a dynamic form.

(3) The interaction of polar acetonitrile molecules with water and TBA promotes order in solution. Therefore, the minima of $\bar{V}^\circ$ of acetonitrile in mixed solvents shift to lower values of X_{TBA} compared with the partial molal volume of TBA in aqueous solution.

(4) The plots of V_d vs. X_{TBA} for various temperatures in Fig. 3 intersect at an X_{TBA} value of about 0.06. This may be explained as follows. At X_{TBA} values less than the clathrate composition of about 1:17, the structural effect contributes the predominantly to the volume aspect, which becomes more pronounced at lower temperatures. X_{TBA} values larger than this, acetonitrile is dispersed in the TBA, and the contribution to volume is mainly due to the change in the free volume because of molecular motion, which decreases as the temperature decreases. Therefore, the relative positions of the three temperature curves are in reverse order before and after the intersection.

(5) It seems that in TBA–H_2O solvents, acetonitrile is surrounded only by water molecules at $X_{TBA} < 0.03$, by both water and TBA at $0.03 < X_{TBA} < \sim 0.15$, and by mainly TBA at $X_{TBA} > \sim 0.15$.

ACKNOWLEDGMENT

Support from the National Foundation of Natural Science of China is gratefully acknowledged.

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