EXCESS VOLUMES OF BINARY LIQUID MIXTURES OF 1,1,3,3-TETRAMETHYLUREA WITH ALCOHOLS

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ABSTRACT

The densities of solutions of 1,1,3,3-tetramethylurea (TMU) and alcohols were measured at 298.15 K. Excess volumes were calculated for TMU with methanol, ethanol, n-butanol and t-butanol from the experimental density measurements at 298.15 K over the entire composition range. The V^E data follow the order: methanol > t-butanol > n-butanol > ethanol. The results have been explained in terms of self-association and the hydrogen-bond donating abilities of alcohols.

INTRODUCTION

The non-ideal behaviour of binary mixtures containing a self-associated component is primarily due to specific interactions arising from the hydrogen bond between the polar groups of the component molecules. Several previous papers [1,2] from our laboratory have been concerned with the effect of water on tetramethylurea. As a continuation of these investigations, the present paper reports excess volumes and apparent molal volumes for binary mixtures of tetramethylurea with methanol, ethanol, n-butanol and t-butanol.

EXPERIMENTAL

Fisher A.C.S. certified grade methanol, ethanol, n-butanol and t-butanol were purified according to standard established procedures [3]. Tetramethylurea (Sigma Chemical Co.) was used after being refluxed with calcium hydride under a nitrogen atmosphere and distilled at 10 mm.Hg. The reagents were stored in brown bottles and fractionally distilled immediately before use. The densities and refractive indices of the solvents agreed closely with the accepted literature values [4,5]. All the solutions for density mea-

surement were prepared on a weight basis with conductivity grade TMU. All weighings were vacuum corrected.

The density measurements were made using 10 cm³ pycnometers with minimum graduations of 0.0005 cm³. The insides of the capillaries were coated with dimethyldichlorosilane to prevent adhesion of liquid droplets. The pycnometers were calibrated four times with conductivity water at 298.15 K. The pycnometers were completely immersed for at least two hours in a thermostat maintained within 0.001°C. The reproducibility in weighing the pycnometers and reading the menisci was within 2 ppm. The imprecision in the determination of V^E (cm³ mole^{-1}) is estimated to be less than (0.0004 ± 0.001 cm³ mole^{-1}).

RESULTS AND DISCUSSION

Density values of the mixtures as a function of the mole fraction of TMU at 298.15 K are reported in Table 1. Excess volumes, V^E, were calculated on

TABLE 1

Excess volumes of mixing, V^E, for the binary mixtures at 198.15 K

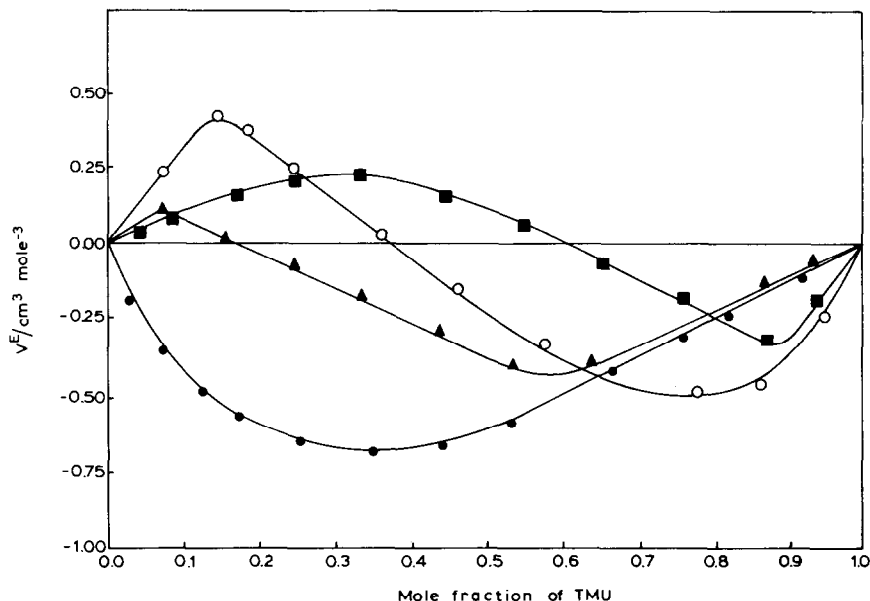| X_2	V^E (cm³ mole^{-1})	X_2	V^E (cm³ mole^{-1})
CH_3OH (1) + TMU (2)		C_2H_5OH (1) + TMU (2)	
0.0773	0.2440	0.0198	−0.1840
0.1827	0.3742	0.0509	−0.3566
0.2510	0.4388	0.1077	−0.4827
0.4388	−0.1205	0.1714	−0.5741
0.5023	−0.2252	0.2435	−0.6510
0.5727	−0.3066	0.3255	−0.6800
0.6801	−0.4751	0.4199	−0.6750
0.7510	−0.5013	0.5296	−0.5821
0.8400	−0.4898	0.6588	−0.4250
0.9566	−0.2480	0.8129	−0.2501
n-C_4H_9OH (1) + TMU (2)		t-C_4H_9OH (1) + TMU (2)	
0.0777	0.0995	0.0316	0.0285
0.1593	0.0704	0.0798	0.0802
0.2452	−0.0675	0.1633	0.1522
0.3356	−0.1753	0.2507	0.1880
0.4310	−0.2934	0.3424	0.2306
0.5319	−0.2934	0.4383	0.1705
0.6387	−0.4841	0.5393	0.0760
0.7518	−0.4024	0.6455	−0.5092
0.8722	−0.2827	0.7575	−0.1808
	−0.0325	0.8754	−0.3331

Fig. 1. Excess volume of mixing, V^E, as a function of the composition for binary mixtures of tetramethylurea with various alcohols at 298.15 K. $\bigcirc$, Methanol; $\bullet$, ethanol; $\blacktriangle$, n-butanol; $\blacksquare$, t-butanol.

the basis of the equation

$$V^E = X_1 M_1 \left(\frac{1}{d} - \frac{1}{d_1^0} \right) + X_2 M_2 \left(\frac{1}{d} - \frac{1}{d_2^0} \right) \tag{1}$$

where X_1 and X_2 are the mole fractions of the components, M_1 and M_2 are the molecular weights, d_1^0 and d_2^0 are the densities of the pure components and d is the density of the mixture. Figure 1 shows values of excess volume plotted against the mole fraction of TMU. The experimental values of V^E were compared with the calculated values by fitting the data to an equation of the type

$$V^E = X_1 X_2 \left[A + B(X_2 - X_1) + C(X_2 - X_1)^2 + D(X_2 - X_1)^3 + \dots \right] \tag{2}$$

TABLE 2

Parameters of eqn. (1) at 298.15 K and standard deviations, $\sigma(V^E)$, of experimental values

System	A	B	C	D	$\sigma(V^E)$ (cm^3 mole^{-1})
CH$_3$OH + TMU	-0.8087	-3.3950	0.5535	-2.6210	0.004
C$_2$H$_5$OH + TMU	-2.3936	1.1974	-1.1408	2.3494	0.005
n-C$_4$H$_9$OH + TMU	-1.6710	-1.6641	3.3628	1.6613	0.004
t-C$_4$H$_9$OH + TMU	0.5436	-1.8038	-2.4248	-1.4183	0.003

TABLE 3

Apparent molar volumes for the binary mixtures at 298.15 K

| X_2	$\phi_{v,TMU}$	X_2	$\phi_{v,TMU}$
CH_3OH (1) + TMU (2)		C_2H_5OH (1) + TMU (2)	
0.0773	123.9636	0.0198	107.3863
0.1827	122.8612	0.0509	113.7269
0.2510	121.1812	0.1077	116.3000
0.4388	120.5276	0.1714	117.4005
0.5613	120.3012	0.2435	118.1956
0.5727	120.2666	0.3255	118.7670
0.6801	119.8421	0.4199	119.2111
0.7510	120.1313	0.5296	119.6559
0.8400	120.2205	0.6588	120.1718
0.9566	120.6428	1.8129	120.5292
n-C_4H_9OH (1) + TMU (2)		t-C_4H_9OH (1) + TMU (2)	
0.0777	122.1499	0.0316	121.7691
0.1593	121.0000	0.0798	121.8254
0.2452	120.3485	0.1633	121.7246
0.3356	120.2971	0.2507	121.5690
0.4310	120.1337	0.3424	121.5178
0.5319	119.9025	0.4383	121.1805
0.6387	120.1775	0.5393	120.9299
0.7518	120.4354	0.6455	120.7485
0.8722	120.7605	0.7575	120.5885
		0.8754	120.4035
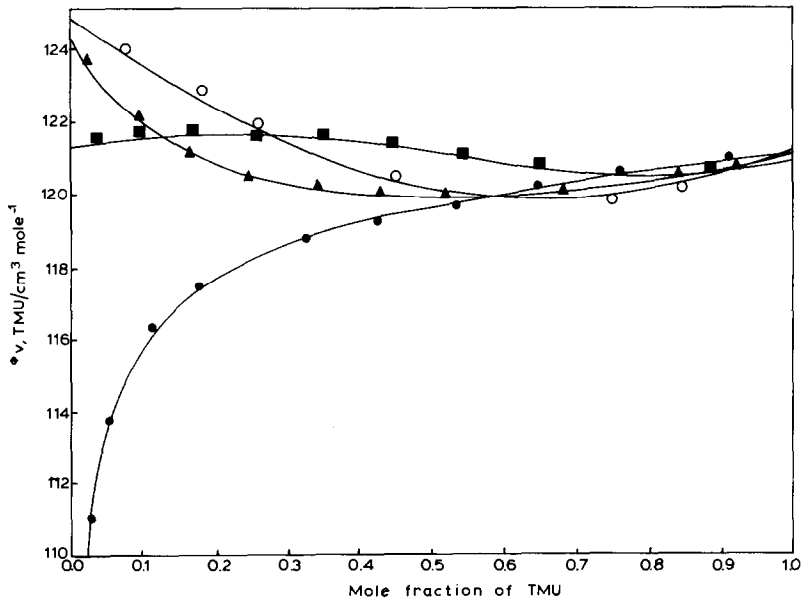
Fig. 2. Apparent molar volumes of tetramethylurea in alcohol–tetramethylurea mixtures at 298.15 K. ○, Methanol; ●, ethanol; ▲, n-butanol; ■, t-butanol.

The parameters are reported in Table 2 together with the standard deviations

$$\sigma = \left[\frac{\epsilon \left(V_{obs}^{E} - V_{calcd}^{E} \right)^{2}}{n - m} \right]^{1/2}$$

with n data points and m parameters.

Furthermore, the apparent molal volumes, ϕ_{v}, were calculated from the measured densities, d, by the equation

$$\phi_{v} = \frac{(1000 + nM)/d - 1000/d_{0}^{1}}{m}$$

where m is the molality of the component and the other symbols are as defined before. The ϕ_{v} values of TMU are shown in Table 3. Figure 2 shows the trends of ϕ_{TMU} as a function of X_{TMU} at 298.15 K.

DISCUSSION

The densities of pure methanol, ethanol, n-butanol and t-butanol at 298.15 K can be favourably compared with the values previously reported in the literature [5]. Molar excess volumes calculated from density measurements of methanol–TMU, ethanol–TMU, n-butanol–TMU and t-butanol–TMU at 298.15 K are shown in fig. 1. V^{E} values for methanol–TMU and t-butanol–TMU are negative in TMU-rich mixtures and positive in TMU-poor mixtures. The ethanol–TMU system shows V^{E} negative over the whole composition range, with a maximum at $X_{TMU} \simeq 0.35$. V^{E} trends in Fig. 1 show that interaction between TMU and ethanol are much stronger than those between TMU and methanol, n-butanol or t-butanol. The curves for methanol–TMU, n-butanol–TMU, and t-butanol–TMU are all negative but skewed toward high TMU mole fractions. The relative order of the molar excess volumes for the mixtures of TMU with alcohols is $CH_{3}OH > t$-butanol $> n$-butanol $>$ ethanol.

The molar excess volumes for ethanol–TMU are negative, in agreement with the formation of the AB complex. The greater volume contraction for mixtures of two systems cannot, however, be attributed exclusively to stronger molecular interactions since differences in the shape and size of the two components have contributions which overlap the previous ones.

For the systems, methanol–TMU and t-butanol–TMU, initial increases in excess volumes show an increase in hydrogen bonding formation, then a shift towards less bonding formation takes place, with an increase in the volume of the solution compared to the theoretical value. On adding more and more TMU, interactions between TMU and methanol and t-butanol molecules grow less and less important and thus a decrease in volume of the solution compared to the theoretical value is obtained, as seen in Fig. 1.

It was observed by Armitage et al. [6] and De Visser et al. [7] that the

trends of the apparent molar volumes of the co-solvent against mole fractions are highly characteristic in showing what types of interactions take place between the molecules of the system. In fact, a minimum in the ϕ_v curves appear on adding methanol and n-butanol to TMU, Fig. 2, as in the case of $H_2O + N,N$-dimethylacetamide [7], H_2O + dimethylsulfoxide [7], $H_2O + N,N$-dimethylformamide [7], and H_2O + t-butyl alcohol [7] systems. On this basis, the $\phi_{v,TMU}$ trend suggests that TMU increases the long-range order of bonding. However, in the case of ethanol and t-butanol no minimum is observed in the ϕ_v curves, but the curve is smoothed, as happens for the H_2O + formamide and H_2O + acetonitrite mixtures [7]. On this basis, the $\phi_{v,TMU}$ trend suggests that TMU reduces the long-range order of bonding.

A comparative study of the extent of the hydrogen bonding in TMU + alcohol mixtures from the analysis of the excess thermodynamic functions (H^E, G^E, S^E, C_p^E, V^E) must take into account the contribution to the excess thermodynamic functions of molecular interactions which take place in pure liquids. In fact, the thermodynamic excess functions of the mixtures are the results of a series of structural and energetic factors characteristic of the solution and of pure liquids. These thermodynamic excess functions are presently being investigated in this laboratory.

REFERENCES

1 D.M. Maharajh and C.W. Okpala, J. Chem. Eng. Data, 26 (1981) 378.
2 D.M. Maharajh, Thermochim. Acta, 52 (1982) 83.
3 J.A. Riddick and W.B. Bunger (Eds.), Techniques of Organic Chemistry, Vol. II, Wiley-Interscience, New York, 1970.
4 J. Timmermans, Physico-Chemical Constants, Vol. II, Elsevier, Amsterdam, 1965.
5 D.M. Maharajh, A. Guiseppi-Elie and C. Okpala, J. Chem. Eng. Data, 25 (1980) 384.
6 D.A. Armitage, M.J. Blandamer, M.J. Foster, N.J. Hiffen, K.W. Morcom, M.C.R. Symons and M.J. Wooten, Trans. Faraday Soc., 64 (1968) 1193.
7 C.D. Visser, W.J.M. Henvelsland, L.A. Dunn and G. Somsen, J. Chem. Soc., Faraday Trans. 1, 74 (1978) 1159.