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THERMODYNAMIC STUDIES OF BINARY MIXTURES CONTAINING A SELF-ASSOCIATED COMPOUND: EXCESS VOLUMES OF 1,1,3,3-TETRAMETHYLUREA–AMIDE MIXTURES

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ABSTRACT

Density measurements of 1,1,3,3-tetramethylurea–amide mixtures at 298.15 K have been performed over the whole composition range. Molar, excess and apparent molar volumes were calculated for the various systems. The trends of these functions are discussed in terms of specific interactions between the components of the solvent mixtures.

INTRODUCTION

The thermodynamic properties of binary mixtures containing a self-associated component exhibit a significant deviation from ideality, arising not only from differences in molecular size but also from the changes in the hydrogen bonding between like and unlike molecules. In this laboratory we have been interested in investigations related to the dependence of the thermodynamic property V^E of the mixture of polar and associated liquids on the nature of component molecules [1–3]. The present paper deals with the excess volumes of binary mixtures of 1,1,3,3-tetramethylurea with some amides. The amides are capable of forming strong intermolecular and intramolecular hydrogen bonding. The *N*-substituted amides are of interest for their remarkably high dielectric constants, a property which has been attributed to extensive chain-wise association through hydrogen bonding. Furthermore, the miscibility of these compounds with 1,1,3,3-tetramethylurea permits the preparation of mixed solvents covering an extremely wide range of dielectric constants.

EXPERIMENTAL

Fisher (A.C.S. Certified) formamide and dimethylformamide, IR- and GC-analysed methylformamide supplied by Aldrich, and reagent-grade methylpropionamide and butylacetamide supplied by Eastman were purified by drying over anhydrous sodium sulphate and fractionally distilling the solvent under reduced pressure immediately before use. Tetramethylurea (TMU) (Sigma Chemical Co.) was used after being refluxed with calcium hydride under a nitrogen atmosphere and distilled at 10 mm Hg. The specific conductivity of this TMU was 1.5×10^{-8} Ω^{-1} cm^{-1}. The reagents were stored in brown bottles. The densities and refractive indices of the solvents agreed closely with the accepted literature values [4,5]. All of the solutions for density measurements were prepared on a weight basis with conductivity-grade TMU. All weighings were vacuum corrected.

The density measurements were made using 10 cm^3 pycnometers were minimum graduations of 0.0005 cm^3. 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 2 h in a thermostat maintained within 0.001°C. Triplicate studies of densities of liquids and liquid mixtures agreed within 1×10^{-5} g cm^{-3}. An analysis of the experimental uncertainties led to the conclusion that the reported excess volumes of mixing were within ± 0.008 cm^3 $mole^{-1}$.

RESULTS

Mean molar volumes, V_M, of solutions and excess molar volumes were calculated by the equation

$$V_M = \frac{X_1 M_1 + X_2 M_2}{d} \tag{1}$$

and

$$V^E = V_M - X_1 V_1^0 - X_2 V_2^0 \tag{2}$$

where M_1 and M_2 are the molecular weights of amide and TMU, respectively, X_2 is mole fraction of TMU and V_1^0 and V_2^0 are the molar volumes of the pure components. Apparent molar volumes, ϕ_v, of the TMU in the mixtures were calculated from the equation

$$\phi_{v,2} = V_2^0 + \frac{V^E}{X_2} \tag{3}$$

Values of V_M, V^E and $\phi_{v,2}$ are reported in Table 1. V^E and $\phi_{v,2}$ of the amide–TMU systems are plotted as a function of TMU composition in Figs. 1 and 2, respectively.

The data for V^E were fitted to the smoothing equation

$$\frac{V^E}{X_1(1 - X_1)} = A + B(2X_1 - 1) + C(2X_1 - 1)^2 + D(2X_1 - 1)^3$$

TABLE 1

Densities, d (g cm^{-3}), molar volumes, V_m (cm^3 mole^{-1}), excess volumes, V^E (cm^3 mole^{-1}) and apparent molar volumes ϕ_v (cm^3 mole^{-1}) of TMU–amide mixtures at 298.15 K as a function of the mole fraction of TMU, X_{TMU}

X_{TMU}	d	V_M	V^E_{TMU}	$\phi_{v,TMU}$
Formamide–TMU mixtures at 298.15 K				
0	1.1340	39.7178		
0.0135	1.1231	40.9587	0.0804	128.8006
0.0352	1.1142	42.6717	0.1010	123.6367
0.0759	1.0989	45.9014	0.0307	121.1877
0.1235	1.0844	49.6388	−0.0899	120.0491
0.1797	1.0682	54.1354	−0.1492	119.9493
0.2473	1.0517	59.5587	−0.2880	119.9478
0.3301	1.0334	66.3150	−0.4100	120.2910
0.4340	1.0210	74.3618	−0.5478	119.5428
0.5679	1.003	85.1962	−0.6102	119.7994
0.7474	0.9850	99.7208	−0.6013	120.0001
0.8874	0.9720	111.3039	−0.3682	120.3872
1	0.9619	120.8026		
Methylformamide–TMU mixtures at 298.15 K				
0	1.0110	58.4273		
0.0198	0.9978	60.2012	0.6724	154.7562
0.0510	0.9957	62.2513	0.6920	131.6010
0.1079	0.9912	65.8135	0.6585	126.8316
0.1717	0.9878	69.7299	0.5973	124.2352
0.2439	0.9844	74.1609	0.5180	122.9415
0.3259	0.9817	79.1369	0.4204	121.9661
0.4204	0.9779	84.9652	0.3165	121.5261
0.5303	0.9749	91.6669	0.2050	120.8917
0.6594	0.9709	99.6411	0.0873	120.9288
0.8146	0.9674	108.1332	−0.0701	120.7158
0.9207	0.9653	115.6838	−0.1766	120.6151
1	0.9619	120.8026		
Dimethylformamide–TMU mixtures at 298.15 K				
0	0.9480	77.0992		
0.02597	0.9448	78.5430	0.3081	131.2102
0.06623	0.9460	80.2826	0.2833	125.4687
0.1376	0.9482	83.3389	0.2209	122.4461
0.2148	0.9503	86.6569	0.1678	121.5951
0.2985	0.9521	90.2828	0.1353	121.2657
0.3895	0.9543	94.1856	0.06331	120.9668
0.4891	0.9563	98.4786	0.003144	120.8110
0.5983	0.9584	103.1748	−0.07345	120.6830
0.7186	0.9602	104.0688	−0.1274	120.6329
0.8365	0.9630	113.3453	−0.2308	120.4976
0.9388	0.9636	117.8514	−0.2729	120.5081
1	0.9619	120.8026		

TABLE 1 (continued)

X_{TMU}	d	V_M	V^E_{TMU}	$\phi_{v,TMU}$
N-*methylpropionamide – TMU mixtures at 198.15 K*				
0	0.9325	93.3948		
0.0313	0.9351	94.1192	−0.0402	117.4628
0.0953	0.9374	95.8750	−0.1322	119.2200
0.1620	0.9397	97.7059	−0.1940	119.9304
0.2310	0.9433	99.4616	−0.2669	119.9802
0.3402	0.9469	102.4394	−0.3502	120.0010
0.4164	0.9502	104.4173	−0.3922	120.1008
0.5370	0.9536	107.7351	−0.4300	120.3010
0.6652	0.9574	111.1942	−0.4319	120.3801
0.7557	0.9594	113.7074	−0.4103	120.4001
0.8501	0.9614	111.8378	−0.3710	120.4304
0.9489	0.9632	114.7130	−0.1802	120.5003
1	0.9619	120.8026		
N-*Butylacetamide – TMU mixtures at 298.15 K*				
0	0.8953	128.5603		
0.0426	0.8989	128.0975	−0.0504	117.6984
0.1266	0.9044	127.4206	−0.1535	119.5585
0.2102	0.9101	126.7237	−0.1994	119.8231
0.2926	0.9161	125.9926	−0.2757	119.8851
0.4150	0.9245	124.9935	−0.3399	119.9658
0.4955	0.9298	124.3763	−0.3370	120.1163
0.6149	0.9377	123.4685	−0.3500	120.2796
0.7325	0.9457	122.5609	−0.3169	120.3699
0.8098	0.9518	121.8646	−0.2580	120.4000
0.8866	0.9560	121.4176	−0.1804	120.5040
0.9622	0.9617	120.7845	−0.0724	120.6010
1	0.9619	120.8026		

where X_1 is the mole fraction of the amides. The values of the constants A, B, C and D, evaluated by the method of least squares and the standard deviation for excess volumes, $\sigma(V^E)$, are given in Table 2.

TABLE 2

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

	A	B	C	D	$\sigma(V^E)$ (cm^3 $mole^{-1}$)
Formamide + TMU	−2.3160	−0.9108	0.4641	0.007	
Methylformamide + TMU	1.3673	−1.5602	4.4049	−5.6071	0.009
Dimethylformamide + TMU	−0.2553	−0.2259	0.1047	−6.0590	0.008
N-Methylpropionamide + TMU	2.4486	−1.2561	−1.4468	−2.2724	0.004
N-Butylacetamide + TMU	−1.2701	−0.1270	−1.8235	−2.1830	0.008

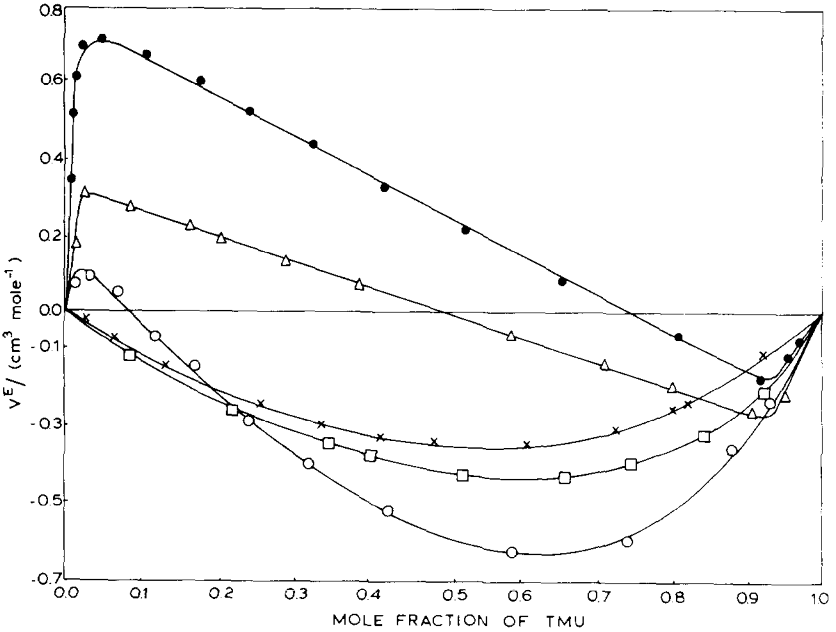

Fig. 1. Molar excess volumes, V^E, of amides and tetramethylurea mixtures at 298.15 K. ○, Formamide; ●, methylformamide; ▲, dimethylformamide; ■, *N*-methylpropionamide; ×, *N*-butylacetamide.

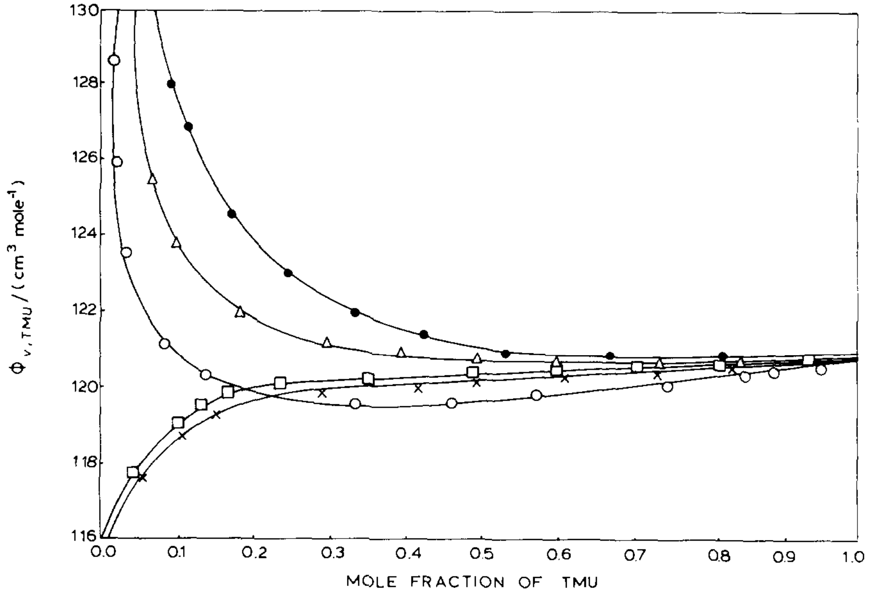

Fig. 2. Apparent molar volumes of tetramethylurea in amide–tetramethylurea mixtures at 298.15 K. ○, Formamide; ●, methylformamide; ▲, dimethylformamide; ■, *N*-methylpropionamide; ×, *N*-butylacetamide.

DISCUSSION

The binary mixtures of *N*-methylpropionamide and *N*-butylacetamide studied exhibit contraction on mixing over the entire composition ranges, see Fig. 1. A large negative excess volume, though slightly skewed in the water-rich region, is seen in Fig. 1 for the binary mixtures containing formamide. In the case of the TMU–formamide mixtures, this can indicate that the hydrogen bonding between formamide and TMU is slightly stronger than that in the pure formamide. Increasing the alkyl chain length tends to decrease the volumetric effects. This is due to the decrease in acidic character of the amide resulting in relatively weaker hydrogen bonding with TMU. The difference between V^E at equimolar concentrations for methylformamide solutions and for *N*-methylpropionamide solutions, suggests that the number of carbon atoms in the parent acid influences the amide–TMU interactions.

It is evident that the TMU molecules strongly interact with the amide group of the formamide. The volumetric effects arising from this interaction supersedes the positive contribution to V^E due to the structure-breaking of the aggregates of formamide. In the case of methylformamide and dimethylformamide, both V^E are skewed. For dimethylformamide, V^E is symmetrically skewed at $X_{TMU} \simeq 0.5$, whilst for methylformamide, it is skewed at $X_{TMU} \simeq 0.75$. The self-associated aggregates of higher amides are relatively easier to break, thus the V^E values are higher than V^E for formamide. However, the hydrogen bond energy between the amides and TMU, and, consequently, the volumetric effects arising therefrom normally decrease with the increase in substitution of the amidic hydrogen with an alkyl group. This is due to the decrease in acidic character of the amide and also the steric hindrance caused by the alkyl group, resulting in a relatively weaker hydrogen bonding with TMU. Experimentally determined V^E values for binary mixtures of amides does not follow the expected trend, viz. formamide < dimethylformamide < methylformamide. The large V^E for methylformamide mixtures compared with those containing dimethylformamide reflects the ease of breaking of the intermolecular structures of dimethylformamide and its relatively weaker hydrogen bonding interactions with TMU.

It was observed by Armitage et al. [6] and Visser et al. [7] that the trends of the apparent molar volumes of the co-solvent vs. mole fractions are highly characteristic in showing what types of intereactions take place between the molecules of the system. In fact, a minimum in the curves for formamide, methylformamide and dimethylformamide appears on adding these solvents to TMU, suggesting that these amides increase the long-range order of bonding with TMU. On the other hand, the regular trend of $\phi_{v,TMU}$, i.e. no minimum is observed, but the curve is smoothed for *N*-methylpropionamide and *N*-butylacetamide, indicates that these amides gradually break down the hydrogen bonding between the amides and TMU.

Further work on these systems are presently being done in our laboratories to obtain other thermodynamic properties

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