Thermochimica Acta, 81 (1984) 15–21
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EXCESS VOLUMES AND VISCOSITY OF SULFOLANE–TETRAMETHYLUREA MIXTURES AT 25, 35 AND 45°C

DOW M. MAHARAJH

Department of Chemistry, The University of the West Indies, St. Augustine, Trinidad (West Indies)

(Received 11 May 1984)

ABSTRACT

Densities and viscosities of sulfolane–tetramethylurea mixtures have been measured at 25, 35 and 45 °C over the whole mole fraction range. Excess and apparent molar volumes were calculated for the system at each temperature. From viscosity data, activation parameters of viscous flow have been computed. The trends of these functions are discussed in terms of specific interactions between the components of the solvent mixtures.

INTRODUCTION

The physical and thermodynamic properties of binary mixtures where one of the components is tetramethylurea (TMU) are the topic of interest. Previously, the properties of water–TMU [1], alcohols–TMU [2] and amides–TMU [3] mixtures were measured. In this paper the densimetric and viscosimetric properties of sulfolane–TMU mixtures at 25, 35 and 45 °C over the entire composition range are reported. It was thought to be interesting to study these mixtures by these techniques since they are useful in showing structural changes of solvent mixtures.

EXPERIMENTAL

TMU (Sigma Chemical Co.) was purified as described in the literature [4]. Sulfolane (TMS) was purified as described in the literature [5]. The densities and refractive indices of the solvent agreed closely with the accepted literature values [4,5].

Density measurements

The densities of solutions were measured using Lipkin bicapillary pycnometers with graduated arms, and having capacities of approximately

10 cm^3. One limb was bent over near the top to allow filling by capillary action. The pycnometers were calibrated using various quantities of degassed conductivity water, which reached a series of heights in the capillaries. When the liquid had reached thermal equilibrium in the thermostatted bath, heights were measured relative to graduated markings using a cathetometer. A calibration curve was then constructed for each pycnometer. The precision achieved in density measurements was $\pm 0.001\%$.

Viscosity measurements

Viscosity measurements were made using Ostwald-type viscometers. The present work was concerned solely with relative viscosities, η/η_0, and it was found sufficiently precise to take

$$\eta/\eta_0 = t\rho/t_0\rho_0$$

where η, t and ρ refer to the solution; and η_0, t_0 and ρ_0 refer to the TMU. t_0 for each viscometer and ρ_0 were redetermined for every batch of TMU used.

Temperature regulation for the above measurements at 25, 35 and 45 °C ± 0.01 °C was obtained in a thermostatically-controlled water bath with the absolute temperature determined by a calibrated Beckman thermometer.

RESULTS

Densities

Excess volumes of the mixtures as a function of TMU, X_{TMU}, at 25, 35 and 45 °C are reported in Table 1, which shows values of excess volumes,

TABLE 1

Excess volumes of mixing, V^{E} (cm^3 mol^{-1}), for the binary mixtures at 298.15, 308.15 and 318.15 K

X_{TMU}	$V^{\mathrm{E}}_{298.15}$	$V^{\mathrm{E}}_{308.15}$	$V^{\mathrm{E}}_{318.15}$
0.03165	−0.04047	−0.08270	−0.06224
0.09663	−0.20915	−0.23482	−0.18014
0.1639	−0.35860	−0.40545	−0.29741
0.2337	−0.53750	−0.53930	−0.40523
0.3433	−0.72634	−0.62230	−0.52540
0.4199	−0.83296	−0.80352	−0.60021
0.5406	−1.0090	−0.87914	−0.62810
0.6691	−1.1202	−0.83402	−0.60014
0.7583	−1.1082	−0.78203	−0.58750
0.8519	−1.01837	−0.63093	−0.48235
0.9496	−0.70020	−0.32270	−0.23145

V^E, at the three temperatures calculated on the basis of eqn. (1)

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

where X_1 and X_2 are the mole fractions of the components, M_1 and M_2 are the relative molar masses, and 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 volumes plotted against the mole fraction of TMU at the three temperatures.

Furthermore, values of apparent molar volumes, ϕ_v, of TMU are calculated by the equation

$$\phi_{v,2} = \frac{M_2}{d} - \frac{(d - d_1^0) \times 10^3}{m_2 d d_2^0} \tag{2}$$

where m_2 is the molality of TMU.

ϕ_v values of TMU are shown in Table 2. Figure 2 shows the trends of $\phi_{v,\text{TMU}}$ as a function of X_{TMU} at the three temperatures.

Viscosities

Table 3 reports values of experimental viscosities in mPa s at 25, 35 and 45 °C. Experimental data were treated on the basis of Eyring et al.'s absolute rate theory [6] to the process of viscous flow according to the equation

$$\eta = \frac{hN}{V} \exp\left(\frac{-\Delta S^{\neq}}{R} \right) \exp\left(\frac{\Delta H^{\neq}}{RT} \right) \tag{3}$$

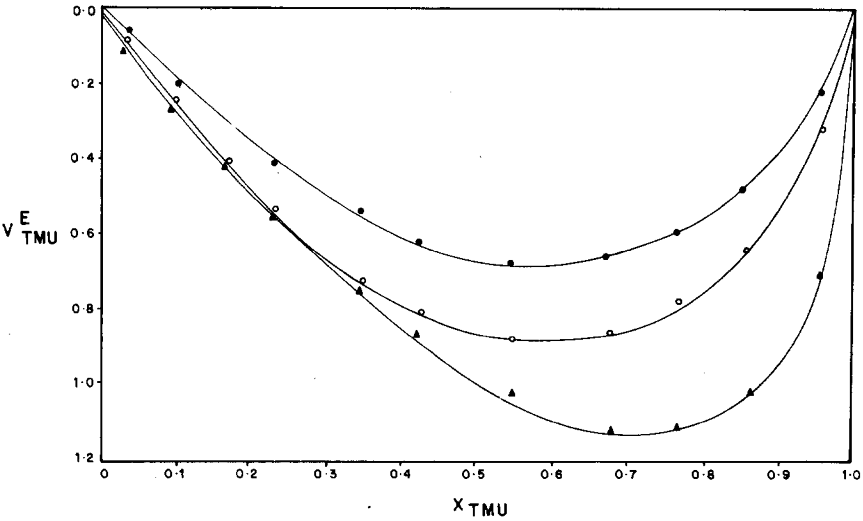

Fig. 1. Excess volumes, V^E, of TMS–TMU mixtures at 25 (▲), 35 (○) and 45 °C (●).

TABLE 2

Apparent molar volumes for the binary mixtures at 298.15, 308.15 and 318.15 K

X_{TMU}	$\phi^{298.15}_{\mathrm{v,TMU}}$	$\phi^{308.15}_{\mathrm{v,TMU}}$	$\phi^{315.15}_{\mathrm{v,TMU}}$
0.03165	119.72	120.41	122.03
0.09663	118.97	119.80	121.63
0.1639	118.66	119.43	121.34
0.2337	118.56	119.16	121.07
0.3433	118.64	119.45	120.90
0.4199	118.83	119.63	120.94
0.5406	119.15	115.95	121.13
0.6691	119.52	120.25	121.43
0.7583	119.78	120.48	121.65
0.8519	120.06	120.72	121.88
0.9496	120.35	120.90	122.16

where h, N and R are Plank's, Avogadro's and the molar gas constants, respectively; V is the molar volume; and $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the activation entropy and activation enthalpy of viscous flow, respectively.

Equation (3) predicts linear plots for ln (ηV) against T^{-1} for all the mixtures. From these plots mean values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated

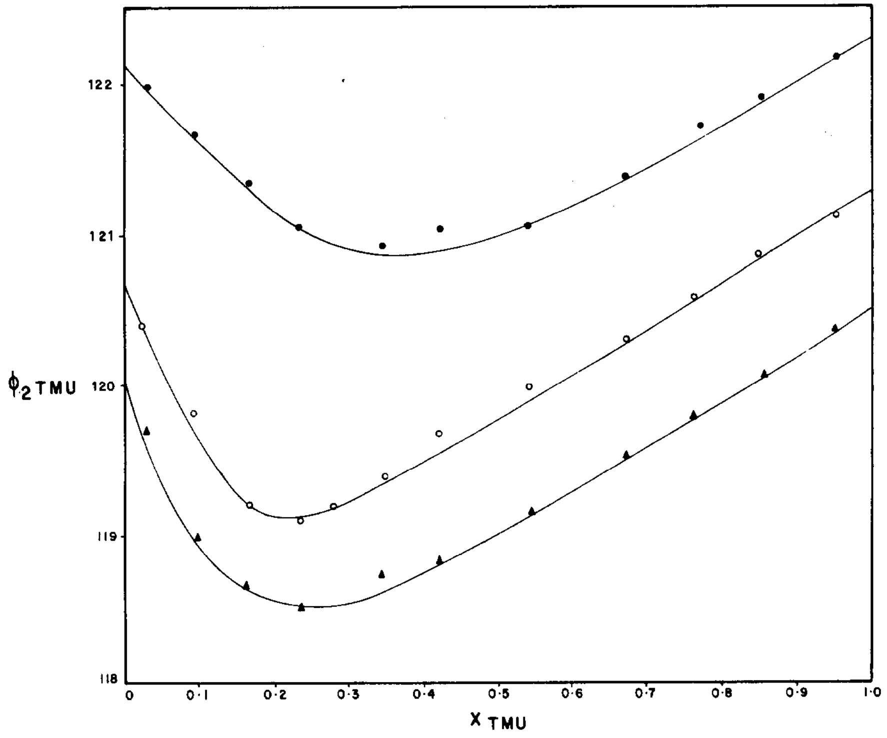

Fig. 2. Apparent molar volumes, ϕ_v, of TMS–TMU mixtures at 25 (▲), 35 (○) and 45 °C (●).

TABLE 3

Viscosities, η(mPa s), of TMU–TMS mixtures at 298.15, 308.15 and 318.15 K

X_{TMU}	η		
	298.15 K	308.15 K	318.15 K
0	10.2750	8.2585	6.2555
0.03165	10.0260	7.3775	5.4966
0.09663	8.8650	6.3632	4.9312
0.1639	7.5291	5.5482	4.4071
0.2337	6.0051	4.6791	3.6870
0.3433	4.7271	3.6982	3.0075
0.4199	4.0500	3.1428	2.6108
0.5406	3.1680	2.5301	2.0995
0.6691	2.5380	2.0383	1.7621
0.7583	2.1861	1.7747	1.4881
0.8519	1.8940	1.5552	1.3561
0.9496	1.5683	1.3281	1.1406
1	1.3950	1.2257	1.0621

for the measured temperature interval, and hence $\Delta G^{\neq}$ values were obtained at 25 °C (Table 4).

Values of excess function, $Y^{\neq E}$, can be obtained assuming that thermodynamic parameters of activation, $Y^{\neq}$, for an ideal solution are given by the equation

$$Y^{\neq} = X_1 Y_1^{\neq} + X_2 Y_2^{\neq} \qquad (4)$$

where X_1 and X_2 are the mole fractions of the two components and $Y_1^{\neq}$ and

TABLE 4

Activation parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ of viscous flow for TMU–TMS mixtures

X_{TMU}	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (kJ K^{-1} mol^{-1})	$\Delta G^{\neq}$ (25 °C) (kJ mol^{-1})
0	8.9316	−0.1766	61.5849
0.03165	23.6866	−0.1593	71.1819
0.09663	21.7993	−0.1633	70.4872
0.1639	19.3966	−0.1650	68.5913
0.2337	17.8751	−0.1682	68.0239
0.3433	17.1684	−0.1700	67.8539
0.4199	16.6696	−0.1716	67.8321
0.5406	15.3809	−0.1746	67.4379
0.6691	13.8594	−0.1765	66.4829
0.7583	13.3689	−0.1783	66.5290
0.8519	12.8867	−0.1811	66.8817
0.9496	11.6122	−0.1891	67.9924
1.0000	9.6076	−0.1899	66.2263

TABLE 5

Excess free energy, $G^{\neq E}$ (kJ mol^{-1}), of viscous flow for TMU–TMS mixtures

X_{TMU}	$G^{\neq E}$		
	25 °C	35 °C	45 °C
0	0	0	0
0.03165	9.4501	9.2729	9.0956
0.09663	8.4399	8.2937	8.1473
0.1639	6.2457	6.1079	5.9701
0.2337	5.3546	5.2392	5.1241
0.3433	4.6756	4.7160	4.4523
0.4199	4.2983	4.1924	4.0866
0.5406	3.3439	3.2520	3.1601
0.6691	1.7252	1.7025	1.6124
0.7583	1.4240	1.3407	1.2568
0.8519	1.3428	1.2745	1.2062
0.9406	0.3768	0.3228	0.1824
1.0	0	0	0

$Y_2^{\neq}$ are the activation parameters of pure components. Thus, $G^{\neq E}$ values for TMS–TMU mixtures are reported in Table 5.

DISCUSSION

As shown in Fig. 1, molar excess volumes, V^E, for the mixtures of TMU + TMS are all negative over the entire composition range at all three temperatures. The volumetric data show that in the system TMU + TMS studied here, there are strong interactions between unlike chemical species with the formation of hydrogen bonding. A decrease in excess volumes shows that the collapse of the TMS structure and thus a shift towards a more TMU structure takes place, with a consequent decrease in the volume of solution compared to the theoretical value. On adding more and more TMU, interactions between TMS and TMU molecules grow more and more important and thus an increase in volume of the solution compared to the theoretical value is obtained. The dependence of V^E on temperature can also be explained by considering that the increase in temperature decreases the TMS structure. Therefore, the minimum of V^E decreases with increasing temperature.

As shown in Fig. 2, a minimum in the ϕ_v curves appear at all three temperatures. This minimum appears on adding the hydrophilic solvent TMU to TMS. On this basis, the $\phi_{v,TMU}$ trend suggests that TMU increases the long-range order of TMS.

Analogous conclusions may be drawn from the viscosity data of TMU–TMS mixtures. In fact, following the conclusions of Reed and Taylor

[7] and Meyer et al. [8], the $G^{\neq E}$ parameter may be considered a reliable criterion to detect or to exclude the presence of interactions between unlike molecules. According to these authors, positive values of $G^{\neq E}$ can be seen in binary systems where specific interactions between unlike molecules take place. As seen in Table 5, this is what happens in the TMU–TMS system at all three temperatures.

REFERENCES

1 D.M. Maharajh, A. Guiseppi-Elie and C.W. Okpala, J. Chem. Eng. Data, 25 (1980) 384.
2 D.M. Maharajh, Thermochim. Acta, 67 (1983) 67.
3 D.M. Maharajh, Thermochim. Acta, 68 (1983) 43.
4 D.M. Maharajh and C.W. Okpala, J. Chem. Eng. Data, 26 (1981) 378.
5 M. Castagnolo, L. Janelli, G. Petrella and A. Sacco, Z. Naturforsch., Teil A, 26 (1971) 755.
6 H.E. Eyring, R.E. Powell and N.E. Roseveare, Ind. Eng. Chem., 33 (1941) 430.
7 T.M. Reed and T.E. Taylor, J. Phys. Chem., 63 (1959) 58.
8 R. Meyer, M. Meyer, J. Metzger and A. Peneloux, J. Chim. Phys., 68 (1971) 406.