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EXCESS VOLUMES AND VISCOSITY OF WATER—SULFOLANE MIXTURES AT 30, 40 AND 50°C

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ABSTRACT

Densities and viscosities of water—sulfolane mixtures have been measured at 30, 40 and 50°C over the whole mole fraction range. From density data apparent molar volumes of both components and deviations from ideal volumes of mixing have been evaluated at the three temperatures. From viscosity data activation parameters of viscous flow have been computed. Data obtained seem to confirm that sulfolane acts as a structure-breaker to water even at low concentrations.

INTRODUCTION

We are interested in the physical and thermodynamic properties of binary solutions where one of the components is sulfolane (TMS). Previously we have measured the properties of dioxane—TMS [1], benzene—TMS [2] and carbon tetrachloride—TMS [3] mixtures. In this paper the densimetric and viscosimetric properties of water—TMS mixtures at 30, 40 and 50°C over the whole composition range are reported. Previous conductometric measurements [4] of several electrolytes in water—TMS mixtures were explained by assuming that TMS breaks down the water structure even at low concentrations. To gain further information about water—TMS interactions, we thought it might be interesting to study these mixtures both densimetrically and viscosimetrically since these techniques are useful in showing structural changes of solvent mixtures.

EXPERIMENTAL

Densities

Density measurements were carried out with an Anton Paar DMA O2C densimeter [5]. The constancy of the thermostats, used for densimetric and viscosimetric measurements, was always better than 0.01°C at all temperatures. Calibration of the densimeter at the three temperatures was carried out with water [6] and aqueous solutions of NaCl [7]. The estimated error in the density measurements was $\pm 5 \times 10^{-6}$ g cm^{-3}.

Viscosities

Viscosity measurements were made with suitable Ubbelohde suspended-level viscometers. Two photocells were attached to the viscometers above and below the measurement bulb. The viscometers and lamp photocell assemblies were coupled to a Hewlett-Packard auto-viscometer, which provided automatic influxing in preparation for the efflux measurements and digital display of efflux time in milliseconds. The accuracy of the viscometric measurements was estimated to be better than 0.1%.

Materials

TMS and water were purified as described in the literature [8].

RESULTS

Densities

Density values of the mixtures as a function of the mole fraction of TMS, X_{TMS}, at 30, 40 and 50°C are reported in Table 1, which also shows values of excess volumes, V^{E}, at the three temperatures calculated on the basis of eqn. (1)

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

where X_1 and X_2 are the molar 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 TMS at the three temperatures. The experimental values of V^{E} were compared with the calculated values by fitting the data to an equation of the type

$$V^{\mathrm{E}} = X_1 X_2[A + B(X_2 - X_1) + C(X_2 - X_1)^2 + D(X_2 - X_1)^3 + \ldots] \qquad (2)$$

The parameters of eqn. (2) were selected by the least squares method. These parameters are reported in Table 2 together with the standard deviations

$$\sigma = [\Sigma(V_{\mathrm{obs}}^{\mathrm{E}} - V_{\mathrm{calc}}^{\mathrm{E}})^2/(n - m)]^{1/2}$$

with n data points and m parameters.

Furthermore, values of apparent molar volume, ϕ_{V}, of both components are calculated by the equation

$$\phi_{\mathrm{V},1} = \frac{M_1}{d} - \frac{(d - d_2^0) \times 10^3}{m_1 d d_2^0} \qquad (3)$$

where m_1 is the molality of component 1 and the other symbols are defined above. The following density values of water, 0.995647, 0.992216 and 0.988036 g cm^{-3}, have been used at 30, 40 and 50°C, respectively [6].

TABLE 1

Densities, d (g cm^{-3}) and excess volumes, V^E (cm^3 mole^{-1}) of water—TMS mixtures at 30, 40 and 50°C as a function of the mole fraction of TMS, X_{TMS}

X_{TMS}	30°C		40°C		50°C	
	d	V^E	d	V^E	d	V^E
0	0.995647	0	0.992216	0	0.988036	0
0.0174	1.020171	−0.034	1.015868	−0.025	1.010961	−0.018
0.0206	1.024249	−0.039	1.019792	−0.028	1.014742	−0.019
0.0359	1.042542	−0.064	1.037590	−0.049	1.032058	−0.036
0.0636	1.070071	−0.091	1.064219	−0.066	1.057950	−0.044
0.0738	1.078768	−0.096	1.072591	−0.067	1.066368	−0.049
0.0902	1.091872	−0.110	1.085302	−0.077	1.078641	−0.053
0.1145	1.108349	−0.115	1.101435	−0.079	1.094544	−0.055
0.1570	1.132310	−0.125	1.124719	−0.080	1.117390	−0.052
0.1883	1.146610	−0.125	1.138814	−0.079	1.131135	−0.047
0.2397	1.165856	−0.120	1.157828	−0.076	1.149825	−0.041
0.2881	1.180360	−0.111	1.171971	−0.061	1.163679	−0.023
0.3372	1.192462	−0.099	1.183847	−0.046	1.175472	−0.010
0.3694	1.199302	−0.090	1.190846	−0.046	1.182307	−0.007
0.4265	1.209639	−0.067	1.201121	−0.028	1.192476	0.011
0.4508	1.213440	−0.055	1.204808	−0.013	1.196242	0.020
0.4740	1.216966	−0.049	1.208318	−0.008	1.199689	0.025
0.5003	1.220681	−0.042	1.211896	0.002	1.203284	0.033
0.5683	1.229019	−0.017	1.220308	0.017	1.211556	0.049
0.6066	1.233227	−0.009	1.224366	0.030	1.215587	0.060
0.6598	1.238366	0.009	1.229546	0.041	1.220741	0.068
0.6780	1.240011	0.014	1.231150	0.046	1.222372	0.070
0.7525	1.246180	0.028	1.237247	0.058	1.228592	0.069
0.7747	1.247867	0.031	1.239008	0.055	1.230362	0.063
0.7788	1.248110	0.035	1.239320	0.054	1.230531	0.071
0.8003	1.249627	0.040	1.240945	0.050	1.232159	0.065
0.8531	1.253359	0.035	1.244589	0.045	1.235783	0.057
0.9038	1.256618	0.030	1.247847	0.035	1.239060	0.042
0.9247	1.257959	0.022	1.249191	0.025	1.240396	0.030
0.9574	1.259945	0.011	1.251146	0.013	1.242360	0.015
0.9741	1.260890	0.007	1.252079	0.009	1.243278	0.011
0.9876	1.261630	0.005	1.252818	0.005	1.244015	0.006
1	1.262331	0	1.253512	0	1.244701	0

TABLE 2

Values of the least squares parameters in eqn. (2) and standard deviations

Temp. (°C)	A	B	C	D	σ
30	−0.1526	0.8227	−0.3947		0.009
40	0.0119	0.6202	−0.3448	0.2356	0.006
50	0.1400	0.5632	−0.2943	0.1596	0.005

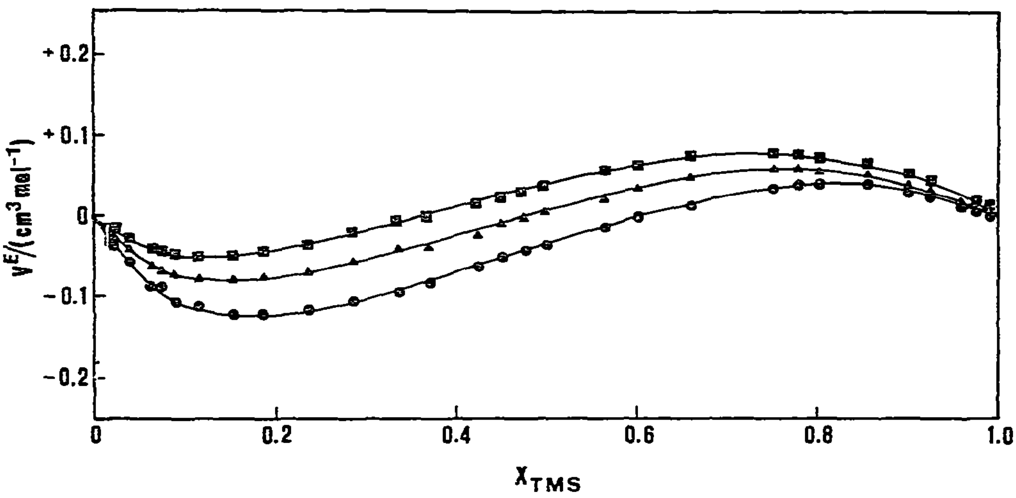

Fig. 1. Excess volumes of water—TMS mixtures at 30(●), 40(▲), and 50°C (■).

TABLE 3

Apparent molar volumes, ϕ_V ($cm^3\ mole^{-1}$) of water—TMS mixtures at 30, 40 and 50°C

x_{TMS}	30°C		40°C		50°C	
	$\phi_{V,TMS}$	ϕ_{V,H_2O}	$\phi_{V,TMS}$	ϕ_{V,H_2O}	$\phi_{V,TMS}$	ϕ_{V,H_2O}
0	93.06[a]	18.09	94.25[a]	18.16	95.41[a]	18.23
0.0174	93.24	18.06	94.42	18.13	95.52	18.22
0.0206	93.31	18.05	94.47	18.13	95.59	18.21
0.0359	93.42	18.03	94.50	18.11	95.55	18.20
0.0636	93.78	18.00	94.84	18.09	95.85	18.19
0.0738	93.90	17.99	94.95	18.08	95.89	18.18
0.0902	93.98	17.97	95.02	18.07	95.96	18.18
0.1145	94.20	17.96	95.18	18.07	96.07	18.17
0.1570	94.40	17.95	95.36	18.06	96.17	18.17
0.1883	94.54	17.94	95.45	18.06	96.30	18.18
0.2397	94.70	17.94	95.56	18.06	96.38	18.18
0.2881	94.81	17.94	95.66	18.07	96.47	18.20
0.3372	94.91	17.95	95.73	18.09	96.52	18.22
0.3694	94.96	17.95	95.75	18.08	96.53	18.22
0.4265	95.04	17.98	95.80	18.11	96.57	18.25
0.4508	95.08	18.00	95.84	18.13	96.59	18.27
0.4740	95.10	18.00	95.85	18.14	96.60	18.28
0.5003	95.12	18.01	95.87	18.16	96.61	18.30
0.5683	95.17	18.06	95.90	18.20	96.63	18.35
0.6066	95.19	18.07	95.92	18.23	96.65	18.39
0.6598	95.21	18.12	95.93	18.28	96.65	18.43
0.6780	95.23	18.14	95.95	18.30	96.66	18.45
0.7525	95.24	18.21	95.95	18.39	96.64	18.51
0.7747	95.24	18.23	95.94	18.40	96.63	18.51
0.7788	95.24	18.23	95.94	18.40	96.64	18.56
0.8003	95.25	18.31	95.95	18.48	96.63	18.56
0.8531	95.24	18.33	95.92	18.47	96.60	18.62
0.9038	95.23	18.40	95.91	18.50	96.59	18.67
0.9247	95.22	18.38	95.90	18.49	96.58	18.64
0.9574	95.21	18.35	95.88	18.47	96.56	18.59
0.9741	95.21	18.38	95.88	18.51	96.56	18.64
0.9876	95.20	18.46	95.88	18.56	96.55	18.70
1	95.20	18.48[a]	95.87	18.58[a]	96.55	18.71[a]

[a] Extrapolated values.

Experimental values of TMS density at the same temperatures were 1.262331, 1.253512 and 1.244701 g cm^{-3}.

ϕ_V values of TMS and water are shown in Table 3. Figure 2 shows the trends of $\phi_{V,TMS}$ as a function of X_{TMS} at the three temperatures.

Viscosities

Table 4 reports values of experimental viscosities in mPa s at 30, 40 and 50°C. Experimental data were treated on the basis of Eyring et al.'s theory [9] according to the equation

$$\eta = \frac{hN}{V} \exp(-\Delta S^{\neq}/R) \exp(\Delta H^{\neq}/RT) \tag{4}$$

where h, N and R are Planck'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 (4) predicts linear plots for $\ln(\eta V)$ against T^{-1} for all the mixtures. From these plots mean values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated for the measurement temperature interval and hence $\Delta G^{\neq}$ values were obtained at 30°C (Table 5).

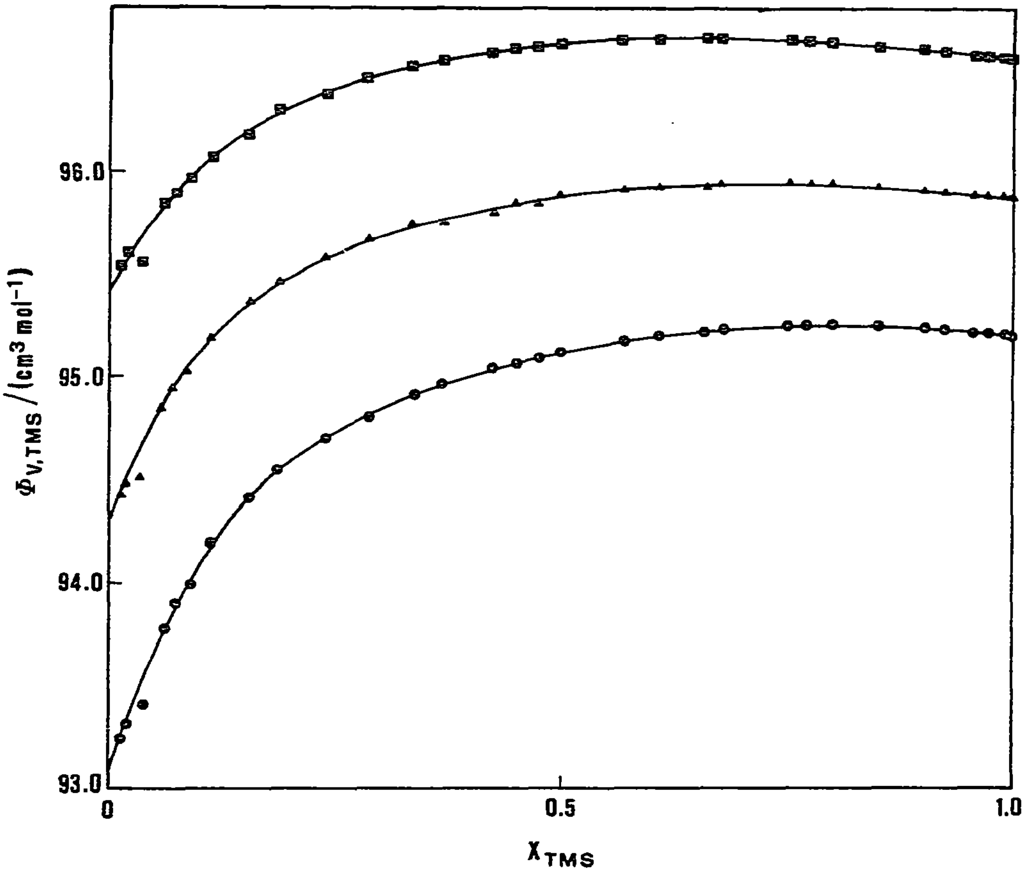

Fig. 2. Apparent molar volumes of water—TMS mixtures at 30(●), 40(▲), and 50°C (▣).

TABLE 4

Viscosities, η (mPa s) of water—TMS mixtures at 30, 40 and 50°C

x_{TMS}	η		
	30°C	40°C	50°C
0	0.7976	0.6531	0.5472
0.0147	0.8884	0.7245	0.6051
0.0208	0.9245	0.7530	0.6290
0.0701	1.255	1.014	0.8410
0.0744	1.273	1.029	0.8536
0.0958	1.429	1.152	0.9537
0.1435	1.761	1.414	1.165
0.1586	1.852	1.484	1.221
0.1924	2.101	1.681	1.379
0.2900		2.219	1.814
0.3022	2.856	2.267	1.850
0.4496	3.865	3.059	2.486
0.6077	4.963	3.923	3.184
0.6106	5.004	3.962	3.217
0.7490	6.085	4.807	3.896
0.7813	6.555	5.182	4.197
1	10.29	7.947	6.306

Values of the 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

$$Y^{\neq} = X_1 Y_1^{\neq} + X_2 Y_2^{\neq} \tag{5}$$

TABLE 5

Activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ of viscous flow for water—TMS mixtures

x_{TMS}	$\Delta H^{\ddagger}$ (cal mole^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mole^{-1})	$\Delta G^{\ddagger}$ (30°C) (cal mole^{-1})
0	3586	4.70	2161
0.0147	3636	4.54	2260
0.0208	3659	4.49	2298
0.0701	3781	3.93	2590
0.0744	3780	3.88	2604
0.0958	3822	3.65	2716
0.1435	3903	3.23	2924
0.1586	3928	3.14	2976
0.1924	3976	2.88	3103
0.3022	4095	2.21	3425
0.4496	4166	1.35	3757
0.6077	4183	0.50	4031
0.6106	4186	0.43	4056
0.7490	4205	−0.14	4247
0.7813	4206	−0.17	4257
1	4637	−0.21	4701

TABLE 6

Excess free energy $G^{\ddagger E}$ (cal mole^{-1}) of viscous flow for water—TMS mixtures

X_{TMS}	$G^{\ddagger E}$		
	30°C	40°C	50°C
0	0	0	0
0.0147	62	62	63
0.0208	86	87	88
0.0701	249	253	258
0.0744	256	260	265
0.0958	312	317	323
0.1435	397	405	413
0.1586	412	420	428
0.1924	453	461	471
0.2900		509	521
0.3022	496	506	517
0.4496	450	461	473
0.6077	324	337	350
0.6106	323	336	349
0.7490	180	192	204
0.7813	162	175	187
1	0	0	0

where X_1 and X_2 are the mole fractions of two components and $Y_1^{\neq}$ and $Y_2^{\neq}$ are the activation parameters of pure components. Thus we calculated $G^{\neq E}$ values for water—TMS mixtures reported in Table 6.

DISCUSSION

Let us now discuss the density data. It was observed by Armitage et al. [10] and De Visser [11] that, in the case of water—organic solvent mixtures, the trends of the apparent molar volumes of the co-solvent against mole fraction are highly characteristic in showing what types of interactions take place between water molecules and those of the co-solvent. In fact, a minimum in the ϕ_V curves appears on adding hydrophobic solvent to water, as in the case of H_2O + *N,N*-dimethylacetamide [11], H_2O + dimethyl sulfoxide [11], H_2O + *N,N*-dimethylformamide [11], and H_2O + *tert*-butyl alcohol [11] systems. However, in the case of a hydrophilic co-solvent no minimum is observed in the ϕ_V curves, but the curve is smoothed, as happens for the H_2O + formamide and H_2O + acetonitrile mixtures [11]. On this basis, the $\phi_{V,TMS}$ trend suggests that TMS reduces the long-range order of water. The formation of hydrogen bonds between water and TMS molecules and the effect of dilution could explain this behavior.

The same conclusion can be reached by observing the trend of excess volumes of the water—TMS system reported in Fig. 1. Initial decreases in excess volumes show that the collapse of the water structure and thus a shift toward dense water takes place, with a consequent decrease in the volume of the solution compared to the theoretical value. On adding more and more TMS, interactions between water and TMS molecules grow more and more important and thus an increase in volume of the solution compared to the theoretical value is obtained, as can be seen in Fig. 1. The dependence of V^E on the temperature can also be explained by considering that the increase of temperature decreases the water structure. Therefore the initial minimum of V^E decreases with increase in temperature, while the maximum at greater TMS percentage increases.

Analogous conclusions may be drawn from the viscosity data of the water—TMS mixtures. In fact, following the conclusions of Reed and Taylor [12] and Meyer et al. [13], the $G^{\neq E}$ parameter may be considered a reliable criterion to detect or to exclude the presence of interaction 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 can be seen from Table 6, this is what happens in the water—TMS system.

The structure-breaking properties of TMS found by us through density and viscosity measurements are in agreement with the results obtained by McDonald et al. [14] who have studied the influence of a small addition of TMS on the temperature of maximum density of water, and also with the measurements of the heat of mixing and vapor pressure of water—TMS systems reported by Benoit and Choux [15].

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