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Thermodynamic and physicochemical properties of binary solvent mixtures of hexamethylphosphoric triamide with aliphatic alcohols. A viscometric study

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Abstract

Viscosities measured for binary solvent mixtures of hexamethylphosphoric triamide (HMPTA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-2-propanol at 303.15 K were used to calculate the excess viscosities and excess Gibbs energies of activation of flow. Both excess quantities were positive for all mixtures except the excess viscosities for the HMPTA–2-propanol and HMPTA–1-butanol mixtures, which were negative. The hydrogen bonding interactions in the mixtures are discussed through comparison of the results with the excess volumes of the same mixtures.

INTRODUCTION

This investigation forms part of the author's studies on the thermodynamic and physicochemical properties of binary solvent mixtures of different amides. In earlier studies our main interest has been in the properties of mixtures of aliphatic carboxamides with aliphatic alcohols [1–3] and in the role of intermolecular interactions, especially hydrogen bonding interactions, in determining the properties of the mixtures. The carboxamides are relatively good proton acceptors [4,5]. The results for their mixtures have been compared with those for the mixtures of methanesulfonamides [6], which possess considerably less proton accepting ability than the corresponding carboxamides [4,7–9]. HMPTA, on the other hand, is a considerably better proton acceptor than the corresponding carboxamides [4,10,11]. For example, the equilibrium constants for the formation of 1:1 hydrogen bonded complexes between phenol and hexamethylphosphoric triamide (HMPTA), *N*,*N*-dimethylacetamide and *N*,*N*-dimethylmethanesulfonamide are 1830, 134 and 13.7 $dm^3\ mol^{-1}$, respectively, at 298 K [4,8,11]. With these results in mind it was of interest to examine the

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properties of the HMPTA–aliphatic alcohol mixtures as well. In an earlier communication [12] we have reported the excess volumes of binary mixtures of HMPTA with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-2-propanol. Here we report viscosities, excess viscosities and excess Gibbs energies of activation of flow for the same mixtures at the same temperature (303.15 K) as in the earlier studies.

EXPERIMENTAL

The alcohols were the same as those used earlier [1]. HMPTA, the same as earlier [12], a zur Synthese product (E. Merck AG), was purified by distillations under reduced pressure. For comparison, samples were also made of a Uvasol product for spectroscopy (E. Merck AG), which was distilled before use.

Viscosities were measured as before [1,2,6] with Cannon–Ubbelohde viscometers [13] (Cannon Instrument Co) equipped with an optoelectronic device for measuring the efflux time. The reproducibility in the viscosity measurements was 0.005 mPa s or better. Densities were available from the previous study [12].

RESULTS AND DISCUSSION

The measured viscosities of the pure components and the mixtures are collected in Table 1. The viscosities of the pure compounds are in good agreement with the literature values. The values for the alcohols were compared with literature values in an earlier communication [1]. The value of HMPTA is 2.928 mPa s at 303.15 K (literature 2.934 mPa s, an interpolated value from ref. 14).

To describe deviations of the viscosity of the mixtures from rectilinear dependence on mole fraction, we calculated the excess viscosity η^E with the equation [15]

$$\eta^E = \eta - [(1-x)\eta_1 + x\eta_2] \tag{1}$$

where η, η_1 and η_2 are viscosities of the mixture, alcohol and HMPTA, respectively, and x is the mole fraction of HMPTA.

Using Eyring's absolute rate theory as applied to the viscosity of mixtures, with the assumption of a linear dependence of $\Delta G^{\neq}$ on composition for ideal systems, we have [16,17]

$$\eta = (hN/V)\exp\left[\left(\Sigma x_i \Delta G_i^{\neq} + \Delta G^{\neq E}\right)/RT\right] \tag{2}$$

where $\Delta G_i^{\neq}$ is the Gibbs energy of activation of viscous flow for pure species i equal to $RT[\ln(V_i\eta_i/hN)]$; $\Delta G^{\neq E}$ is the excess Gibbs energy of activation of viscous flow of the mixture and has been regarded as a measure of the deviation of the solution viscosity from ideal solution behavior [17].

For the present binary mixtures $\Delta G^{\neq E}$ was calculated from [16]

$$\Delta G^{\neq E} = RT\{\ln \eta V - [(1-x)\ln \eta_1 V_1 + x \ln \eta_2 V_2]\} \tag{3}$$

where V, V_1 and V_2 are the molar volumes (available from ref. 12) of the mixture, alcohol and HMPTA, respectively. The excess quantities are presented in Table 1. To aid comparison of the excess viscosities and the excess Gibbs energies of flow with the excess volumes, the excess volumes of the mixtures are included in the table.

As shown in Table 1, both excess quantities are positive for all the mixtures studied, except the excess viscosities for the mixtures of HMPTA with 2-propanol and 1-butanol, which are negative. For the primary alcohols, the values decrease as the length of the alkyl chain of the alcohol increases. The values for the secondary alcohol 2-propanol are smaller, but the values for the tertiary alcohol 2-methyl-2-propanol are considerably greater than those for the primary analogues.

The excess quantities may be used as a measure of changes that occur in intermolecular interactions and geometrical effects when the components are mixed. As mentioned above, the molecules of HMPTA are good proton acceptors. They also possess a large dipole moment of 5.37 D and are capable of association by dipole–dipole interactions [18,19]. The O–H group of the alcohols is a proton donor of moderate capability, and the molecules of pure alcohols are extensively self-associated by hydrogen bonding [4,5,20]. The dipole moment of the lowest aliphatic alcohols is about 1.6–1.8 D [21]. In addition, the molecules of the components differ considerably from each other in size and shape, so it is evident that no solution theory is available to allow quantitative interpretation of the viscosity and volume behavior of their mixtures.

A qualitative interpretation of the results can be made on the basis of the observation that mixtures where strong specific interactions between like components are predominant are characterized by large positive values of η^E and $\Delta G^{\neq E}$ [14,15,22,23]. For example, strong interactions between HMPTA and water result in the values for η^E (max) of about 7 mPa s and for $\Delta G^{\neq E}$ (max) of about 6 kJ mol^{-1} for the HMPTA–water system at 298 K [14]. Since HMPTA is a good proton acceptor, hydrogen bonding interactions evidently make significant contributions in its mixtures with proton donors.

The excess viscosities and excess Gibbs energies of activation of flow for the mixtures of HMPTA with the lowest aliphatic alcohols are positive but much smaller in value than those for the HMPTA–water system. This indicates that in the HMPTA–alcohol mixtures considerable contributions are due to hetero-association equilibria, but these are smaller than in the HMPTA–water mixtures and to a greater degree balanced by opposite

TABLE 1

Viscosities η, excess viscosities η^E, excess Gibbs energies of activation of flow $\Delta G^{\neq E}$ and excess volumes V^E of the binary mixtures at 303.15 K

x [a]	η (mPa s)	η^E (mPa s)	$\Delta G^{\neq E}$ (J mol^{-1})	V^{Eb} (cm^3 mol^{-1})
Methanol + HMPTA				
0.0	0.513			
0.0993	0.829	0.076	1105	−0.395
0.2036	1.145	0.140	1656	−0.592
0.2984	1.401	0.167	1834	−0.648
0.3941	1.630	0.165	1818	−0.648
0.4882	1.846	0.154	1695	−0.597
0.5898	2.070	0.133	1472	−0.501
0.6978	2.308	0.110	1166	−0.382
0.7780	2.476	0.084	893	−0.281
0.8966	2.722	0.044	440	−0.143
Ethanol + HMPTA				
0.0	0.994			
0.1007	1.255	0.066	489	−0.193
0.2043	1.461	0.072	702	−0.263
0.2959	1.627	0.061	780	−0.250
0.3983	1.807	0.043	788	−0.245
0.5079	2.005	0.029	740	−0.175
0.5998	2.180	0.026	668	−0.136
0.6980	2.362	0.018	547	−0.117
0.8012	2.557	0.014	390	−0.070
0.9052	2.750	0.005	197	−0.042
1-Propanol + HMPTA				
0.0	1.728			
0.0989	1.896	0.049	200	−0.139
0.1996	1.991	0.024	257	−0.150
0.3022	2.102	0.012	298	−0.114
0.4027	2.217	0.006	315	−0.076
0.4525	2.272	0.001	311	−0.057
0.5980	2.444	0.001	279	−0.026
0.6994	2.569	0.002	237	−0.008
0.7809	2.666	0.001	185	0.014
0.8672	2.766	0.002	118	0.023
2-Propanol + HMPTA				
0.0	1.779			
0.0867	1.855	−0.024	80	−0.053
0.1008	1.870	−0.025	94	−0.051
0.1839	1.937	−0.053	113	0.006
0.2608	1.991	−0.088	142	0.087
0.3481	2.075	−0.104	160	0.164
0.4017	2.136	−0.105	171	0.183
0.5056	2.279	−0.081	201	0.194
0.6052	2.407	−0.067	194	0.174
0.7050	2.547	−0.042	178	0.135
0.7928	2.668	−0.022	146	0.107
0.8899	2.791	−0.010	86	0.037

TABLE 1 (continued)

x [a]	η (mPa s)	η^E (mPa s)	$\Delta G^{\neq E}$ (J mol^{-1})	V^{Eb} (cm^3 mol^{-1})
1-Butanol + HMPTA				
0.0	2.271			
0.0872	2.283	−0.045	5	−0.087
0.1988	2.312	−0.090	11	−0.078
0.2977	2.351	−0.122	14	−0.041
0.3888	2.404	−0.122	23	0.000
0.4941	2.487	−0.109	43	0.039
0.5894	2.567	−0.091	53	0.048
0.6891	2.655	−0.069	56	0.041
0.7954	2.745	−0.049	44	0.039
0.8991	2.834	−0.028	23	0.020
2-Methyl-2-propanol + HMPTA				
0.0	3.378			
0.0784	3.704	0.361	298	−0.143
0.1030	3.722	0.390	328	−0.199
0.1988	3.624	0.335	331	−0.097
0.2201	3.547	0.268	292	−0.042
0.3076	3.400	0.160	237	0.096
0.4051	3.263	0.067	180	0.255
0.4476	3.230	0.053	171	0.294
0.5093	3.185	0.036	157	0.317
0,6062	3.118	0.013	128	0.298
0.7077	3.068	0.008	106	0.245
0.8008	3.020	0.002	75	0.159
0.9029	2.973	0.001	40	0.080
1.0	2.928			

[a] Mole fraction of HMPTA. [b] Ref. 12.

contributions due to the rupture of the self-associated structures of the pure components. The decrease in the relative effect of the positive contributions in the order methanol > ethanol > 1-propanol > 2-propanol > 1-butanol is in agreement with the results of Kuopio et al. [24]. They studied by a near-IR technique the formation of 1 : 1 hydrogen bonded complexes between HMPTA and alcohols in carbon tetrachloride solution, and found that both the extent and strength of the association decrease in the order methanol > ethanol > 2-propanol > 2-methyl-2-propanol.

The viscosity behavior of the mixtures of all alcohols except 2-methyl-2-propanol corresponds to the volume behavior of the mixtures [12]. However, the values of η^E and $\Delta G^{\neq E}$ for the HMPTA–2-methyl-2-propanol system are considerably greater than would be expected on the basis of the near-IR results for the hydrogen bonding and on the basis of the excess volumes. This suggests to us that the geometrical effects of the globular molecules of 2-methyl-2-propanol affect the viscosities in a different way from that in which they affect the excess volumes.

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