Densities, Viscosities, and Excess Properties for Binary Mixtures of Some Glycols and Polyglycols in *N*-Methylacetamide at 308.15 K

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Densities and viscosities have been measured at 308.15 K over the entire range of composition for *N*-methylacetamide with ethylene glycol, diethylene glycol, triethylene glycol, poly(ethylene glycol)-200, and poly(ethylene glycol)-300. From the experimental data, excess molar volumes (V^E) and deviations in viscosity ($\Delta\eta$) have been calculated, and the deviations are fitted to a Redlich−Kister equation to obtain the binary coefficients and estimate the standard deviations between the experimental and calculated quantities. The values of V^E are negative whereas the values of $\Delta\eta$ are positive over the entire composition range.

Introduction

As a part of our research program of measuring the physicochemical properties of binary liquid mixtures of glycols in nonaqueous solvents,[1−3] a study has been made on *N*-methylacetamide (NMA) + ethylene glycol (EG), + diethylene glycol (DEG), + triethylene glycol (TEG), + poly(ethylene glycol)-200 (PEG200), and + poly(ethylene glycol)-300 (PEG300) covering the entire range of composition.

N-Methylacetamide has been chosen as the solvent for the present study because its properties have been the subject of considerable interest due to the versatility of this compound as a solvent and its close relationship to peptides and proteins. *N*-Methylacetamide is a self-associated liquid. Due to the presence of methyl ($-CH_3$) groups on both "CO" and "NH" groups of *N*-methylacetamide, this molecule has proton accepting ability. Besides this, it is a highly polar aprotic solvent with a high dielectric constant ($\epsilon = 169$).

The glycols, on the other hand, have relatively low values of relative permittivity and dipole moments, yet they are self-associated through hydrogen bonding. Poly(ethylene glycol)s (PEGs) comprise a series of linear chain polymers of oxyethylene units with a wide variety of applications in the pharmaceutical, chemical, cosmetic, and food industries.[4] Their low toxicity and high water solubility enable their use for purification of biological materials[5] and as additives in the production of edible films for food coating.[6] Therefore, the thermodynamic properties of NMA + glycol mixtures are of interest. To determine the extent and type of interactions between NMA and glycol molecules, the densities and viscosities of these binary mixtures have been measured.

Experimental Section

N-Methylacetamide with a purity of 98% (Spectrochem, India) was used as supplied. Ethylene glycol, diethylene glycol, triethylene glycol, poly(ethylene glycol)-200, and poly(ethylene glycol)-300 (Sd. Fine, AR grade) were used after purification[7] with a purity of 98.5 to 99% for all glycols. All the samples were kept over 4 Å molecular sieves to reduce water content and were protected from atmospheric moisture and carbon dioxide.

Table 1. Comparison of Densities, ρ, and Viscosities, η, of Pure Liquids with Literature Data at 308.15 K

component	ρ/g·cm^{-3}		η/mPa·s	
	expt	lit.	expt	lit.
ethylene glycol	1.1029	1.1029[10]	10.59	10.50[12]
diethylene glycol	1.1055	1.1057[10]	17.58	17.36[11]
triethylene glycol	1.1120	1.1120[10]	23.84	22.96[11]
poly(ethylene glycol)-200	1.1124	1.1122[10]	28.06	27.93[11]
poly(ethylene glycol)-300	1.1132	1.1133[10]	41.33	41.33[13]
N-methylacetamide	0.9588	0.9584[13]	3.67	3.65[13]

Solvent mixtures were prepared by mass using a Mettler balance with a precision of ±0.01 mg. Densities of the pure liquids and their mixtures were determined by using a 15 cm^3 double-walled pycnometer as described.[8] The pycnometer with a capillary bore of about 2 mm was calibrated using conductivity water with 0.99405 g·cm^{-3} as its density at 308.15 K.[9] The pycnometer, filled with degassed liquids, was kept in a transparent-walled water bath (maintained constant to ±0.1 K) for (10 to 15) min to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a traveling microscope, which could be read to ±0.01 mm. The density values were reproducible to within 2 parts in 10^4 and are compared with available literature values in Table 1. Each experimental density value was an average of three measurements.

An Ubbelohde viscometer was used for determining the viscosities of the pure liquids and the binary liquid mixtures. The apparatus was submerged in a thermostatic bath at 308.15 K. The viscometer was calibrated using the chemicals supplied by Aldrich Chemical Co., USA, with the following purities: benzene, 99.5 atom %; toluene, 99%; carbon tetrachloride, 99%. The flow time measurements were made with a stopwatch having a precision of ±0.1 s, and each value was an average of 10 measurements. Viscosities are reproducible to ±0.5% and compared with the available literature values in Table 1.

A pycnometer of the Parker and Parker type with minor modifications was employed to determine the densities of liquids and liquid mixtures. The double-stem pycnometer

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Table 2. Mole Fraction, *x*, of *N*-Methylacetamide, Density, ρ, Viscosity, η, Deviations in Viscosity, $\Delta\eta$, and Excess Molar Volume, V^E, for Binary Mixtures of *N*-Methylacetamide with Ethylene Glycol, Diethylene Glycol, Triethylene Glycol, Poly(ethylene glycol)-200 and Poly(ethylene glycol)-300 at 308.15 K

x	ρ / g·cm^{-3}	η / mPa·s	$\Delta\eta$ / mPa·s	V^E / cm^3·mol^{-1}
		NMA + EG		
0.0000	1.1031	10.59	0.00	0.00
0.0847	1.0895	10.09	0.08	−0.13
0.2120	1.0683	9.27	0.14	−0.21
0.3298	1.0494	8.48	0.18	−0.24
0.4247	1.0349	7.86	0.21	−0.25
0.5255	1.0205	7.17	0.22	−0.26
0.6275	1.0063	6.43	0.18	−0.24
0.7471	0.9905	5.56	0.14	−0.20
0.8412	0.9786	4.86	0.09	−0.16
0.9347	0.9673	4.16	0.04	−0.10
1.0000	0.9589	3.67	0.00	0.00
		NMA + DEG		
0.0000	1.1056	17.59	0.00	0.00
0.1121	1.0944	16.13	0.10	−0.19
0.2394	1.0799	14.47	0.22	−0.31
0.3419	1.0674	13.11	0.28	−0.39
0.4564	1.0522	11.57	0.34	−0.44
0.5574	1.0378	10.17	0.34	−0.46
0.6538	1.0232	8.80	0.31	−0.46
0.7649	1.0053	7.20	0.25	−0.44
0.8343	0.9930	6.16	0.18	−0.38
0.9252	0.9752	4.80	0.08	−0.22
1.0000	0.9589	3.67	0.00	0.00
		NMA + TEG		
0.0000	1.1121	23.84	0.00	0.00
0.1142	1.1037	21.93	0.39	−0.23
0.2059	1.0957	20.39	0.70	−0.36
0.3069	1.0856	18.59	0.94	−0.44
0.4265	1.0718	16.35	1.12	−0.51
0.5415	1.0563	14.01	1.09	−0.53
0.6392	1.0410	11.91	0.96	−0.52
0.7266	1.0253	9.98	0.80	−0.47
0.8278	1.0045	7.74	0.60	−0.37
0.9307	0.9795	5.30	0.24	−0.22
1.0000	0.9589	3.67	0.00	0.00
		NMA + PEG200		
0.0000	1.1124	28.07	0.00	0.00
0.1004	1.1065	26.58	0.96	−0.15
0.2076	1.0990	24.81	1.80	−0.27
0.3145	1.0902	22.78	2.38	−0.38
0.4289	1.0793	20.32	2.71	−0.50
0.5478	1.0654	17.59	2.88	−0.59
0.6112	1.0565	15.79	2.63	−0.61
0.7022	1.0411	12.94	2.00	−0.56
0.8462	1.0090	8.53	1.10	−0.37
0.9348	0.9827	5.66	0.40	−0.18
1.0000	0.9589	3.67	0.00	0.00
		NMA + PEG300		
0.0000	1.1133	41.34	0.00	0.00
0.1089	1.1094	40.25	3.01	−0.28
0.2248	1.1039	37.52	4.65	−0.47
0.3458	1.0969	33.84	5.53	−0.68
0.4691	1.0875	28.47	4.80	−0.84
0.5748	1.0770	23.49	3.80	−0.94
0.7021	1.0593	17.59	2.70	−0.99
0.8413	1.0285	11.05	1.40	−0.81
0.9148	1.0032	7.68	0.80	−0.56
0.9695	0.9773	5.12	0.30	−0.25
1.0000	0.9589	3.67	0.00	0.00

with a bulb of 15 cm^3 capacity on one of the stems was used. The stems are made of a Pyrex glass tube of a bore of about 2 mm and are bent to the sides, making an obtuse angle at the bend. The vertical part of the stem containing the bulb is about 5 cm in length and carries a mark in the middle to read the liquid level. A mark is also made on the second stem at the same level to read the difference between the liquid levels in the two stems. The inclined part of each of the stems is 4 cm. The enlargement of the stems serves as an "overflow cup" when liquids are raised to temperatures above room temperature. The open ends of the stems are closed by suitable Teflon caps in order to prevent the loss of liquids due to evaporation.

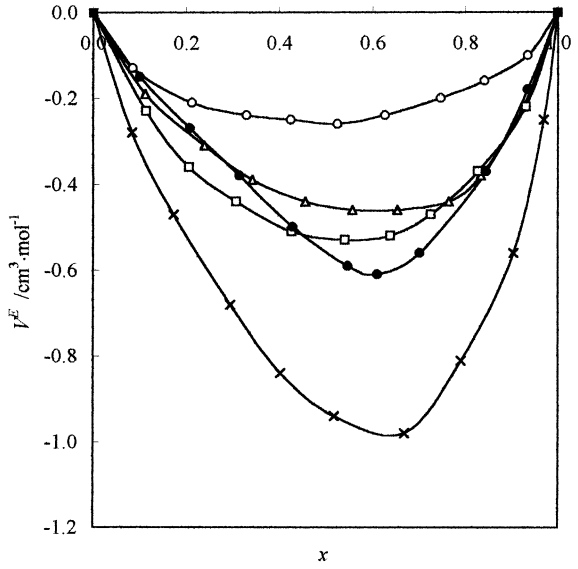

Figure 1. Mole fraction of *N*-methylacetamide versus excess molar volumes for *N*-methylacetamide + (○) ethylene glycol; + (△) diethylene glycol; + (□×ff) triethylene glycol; + (●) poly-(ethylene glycol)-200; and + (×) poly(ethylene glycol)-300 at 308.15 K.

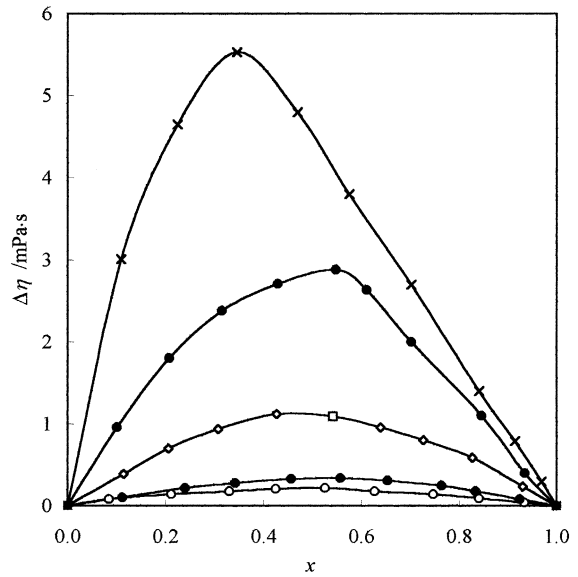

Figure 2. Mole fraction of *N*-methylacetamide versus deviations in viscosities for *N*-methylacetamide + (○) ethylene glycol; + (△) diethylene glycol; + (□×ff) triethylene glycol; + (●) poly(ethylene glycol)-200; and + (×) poly(ethylene glycol)-300 at 308.15 K.

Results

The excess functions V^E and $\Delta\eta$ were calculated from the experimentally determined ρ and η using eqs 1 and 2, and the values are presented in Table 2 along with the values of ρ, η, and mole fraction of NMA (x).

$$V^E = V - \{xV_1 + (1 - x)V_2\} \quad (1)$$

$$\Delta\eta = \eta - \{x\eta_1 + (1 - x)\eta_2\} \quad (2)$$

The variations of V^E and $\Delta\eta$ with mole fraction of NMA are shown graphically in Figures 1 and 2, respectively. The

Table 3. Values of the Parameters of Eq 4 and Standard Deviations, σ (Eq 5), for NMA + Glycol Mixtures at 308.15 K

property	A_0	A_1	A_2	A_3	A_4	A_5	σ
			NMA + EG				
V^E/cm^3·mol^{-1}	−1.0313	−0.0065	−0.0922	0.7192	−1.0467	−0.8178	0.0109
$\Delta\eta$/mPa·s	0.8562	−0.0842	−0.5181	0.0475	0.7283	−0.3682	0.0313
			NMA + DEG				
V^E/cm^3·mol^{-1}	−1.8046	−0.3695	−0.8096	−1.6061	−0.4728	1.7143	0.0125
$\Delta\eta$/mPa·s	1.3396	0.2399	−0.0533	−0.3468	−0.5244	0.3140	0.0240
			NMA + TEG				
V^E/cm^3·mol^{-1}	−2.1169	−0.4596	−0.4072	1.4385	−0.7152	−2.3602	0.0220
$\Delta\eta$/mPa·s	4.4295	- 1.0118	−0.7333	3.8235	−0.2027	−3.3968	0.0958
			NMA + PEG-200				
V^E/cm^3·mol^{-1}	−2.2512	−1.4391	0.2749	1.6314	−0.4921	−0.9109	0.0222
$\Delta\eta$/mPa·s	11.3209	−0.8287	−4.7384	−2.1965	1.6567	0.2609	0.4890
			NMA + PEG-300				
V^E/cm^3·mol^{-1}	−3.5251	−2.2089	−1.0354	−0.2172	−1.8204	−0.4452	0.0572
$\Delta\eta$/mPa·s	18.5304	−17.7618	0.5453	13.9936	4.8111	−10.4682	0.6663

excess functions were fitted to the Redlich−Kister equation of the form

$$Y^E = x(1-x)\sum A_i(2x-1)^{i-1} \quad (3)$$

where Y^E is V^E or $\Delta\eta$ and A_i are the coefficients of the fitting equation. In each case the coefficients were determined by a least squares procedure.

The parameters are presented in Table 3 together with standard deviations, σ, defined by

$$\sigma(Y^E) = [\sum(Y^E_{obs} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (4)$$

where m is the total number of experimental points and n is the number of A_i coefficients considered.

The excess molar volume, V^E (Figure 1), versus composition plots show that V^E is negative for all the mixtures over the entire composition range at 308.15 K. These large negative values of V^E arise due to increased interactions between *N*-methylacetamide and glycols or a very large difference in the molar volumes of the pure components. One can quote the two opposing sets of contributions: (a) expansion due to dipole−dipole interactions of the glycol with the *N*-methylacetamide or of the *N*-methylacetamide with the glycol and size differences; (b) contraction due to the hydrogen-bonded complexes between *N*-methylacetamide and glycol. The actual value of V^E would depend on the relative strengths of the two opposing effects. The experimental values of V^E suggest that the latter effect is more prominent than the former. The magnitude of the minima increases from EG to PEG-300 (Figure 1); at the same time, it is shifted toward the NMA-rich region. The values of V^E become more negative as the chain length of the glycol molecules increases and are in the following order.

NMA + EG < + DEG < + TEG < + PEG-200 < + PEG-300

This order may reflect the strong hydrogen bonding between unlike molecules. This is due to the etheric oxygen, which enhances the ability of the −OH group of the glycol to form hydrogen bonds with the C═O groups of *N*-methylacetamide molecules.

A correlation between the signs of $\Delta\eta$ and V^E has been observed for a number of binary solvent systems;[3,8] that is, if $\Delta\eta$ is positive, V^E is negative and vice versa. In the present study this holds true (Figure 2).

From the above studies it is concluded that the presence of strong interactions between unlike molecules is characterized by negative V^E and positive $\Delta\eta$.

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