Densities and Viscosities of Mixtures of Some Glycols and Polyglycols in Dimethyl Sulfoxide 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 binary liquid mixtures of dimethyl sulfoxide with ethylene glycol, diethylene glycol, triethylene glycol, poly(ethylene glycol)-200, poly(ethylene glycol)-300, propylene glycol, and polypropylene glycol-1025. From these results excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), and Grunberg and Nissan interaction parameters (d) have been calculated, and the excess parameters are fitted to a Redlich−Kister equation. 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,[1,2] an attempt has been made to study the behavior of dimethyl sulfoxide (DMSO) + ethylene glycol (EG), + diethylene glycol (DEG), + triethylene glycol (TEG), + poly(ethylene glycol)-200 (PEG200), + poly(ethylene glycol)-300 (PEG300), + propylene glycol (PG), and + polypropylene glycol-1025 (PPG1025) binary mixtures covering the entire range of composition.

DMSO was chosen because of its wide range of applicability as a solvent in chemical and biological processes involving both plants and animals. It is a highly polar aprotic solvent because of its S=O group and has a large dipole moment and relative permittivity (μ = 3.9 D and ϵ = 46.6 at 298.15 K).

The glycols, on the other hand, have relatively low values of relative permittivity and dipole moment, 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.[3] Their low toxicity and high water solubility enable their use for purification of biological materials[4] and as additives in the production of edible films for food coating.[5] Therefore, thermodynamic properties of DMSO + glycols mixtures are of interest because DMSO provides an >S=O group and glycols provide an OH group for interactions. To determine the extent and type of interactions between DMSO and glycol molecules, the densities and transport properties of these binary mixtures have been measured.

Experimental Section

Dimethyl sulfoxide (Sd. Fine, AR grade) was used as supplied. Ethylene glycol, diethylene glycol, triethylene glycol, poly(ethylene glycol)-200, poly(ethylene glycol)-300 (Sd. Fine, AR grade), propylene glycol, and polypropylene glycol-1025 (Spectochem, India) were used after purification.[6] All the samples were kept over 4 Å molecular sieves to reduce the 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} expt	ρ/g·cm^{-3} lit.	η/mPa·s expt	η/mPa·s lit.
ethylene glycol	1.102 94	1.102 94[8]	10.591	10.505[11]
diethylene glycol	1.105 57	1.105 78[8]	17.588	17.364[10]
triethylene glycol	1.112 09	1.112 09[8]	23.841	22.961[10]
poly(ethylene glycol)-200	1.112 43	1.112 28[8]	28.066	27.938[10]
poly(ethylene glycol)-300	1.113 28	1.113 39[8]	41.336	41.336[12]
propylene glycol	1.026 17		25.336	
polypropylene glycol-1025	0.993 89			82.328
dimethyl sulfoxide	1.085 48	1.085 60[9]	1.614	1.645[9]

Solvent mixtures were prepared by mass using a Mettler balance with a precision of ±0.01 mg. Densities of pure liquids and their mixtures were determined by using a 15 cm^3 double-walled pycnometer as described.[7] The pycnometer was calibrated using conductivity water with 0.994 05 g·cm^{-3} as its density at 308.15 K. The pycnometer filled with air bubble free 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 in10^4 and are compared with the available literature values and are given in Table 1. Each experimental density value was an average of three measurements.

An Ubbelohde viscometer was used for determining the viscosities of pure liquids and the binary liquid mixtures. The apparatus was submerged in a thermostatic bath at 308. 15 K. The viscometer was calibrated using high-purity benzene, toluene, and carbon tetrachloride at the working temperature. 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 ±0.005 mPa·s and compared with the available literature values and are included in Table 1.

Results

The excess functions V^E and $\Delta\eta$ and the interaction parameter, d, were calculated from the experimentally

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10.1021/je0101395 CCC: $22.00
Published on Web 03/08/2002

Table 2. Mole Fraction, *x*, of Dimethyl Sulfoxide, Density, *ρ*, Viscosity, *η*, Deviation in Viscosity, Δ*η*, Excess Molar Volume, V^E, and Grunberg and Nissan Interaction Parameter, *d*, for Binary Mixtures of Dimethyl Sulfoxide (DMSO) with EG, DEG, TEG, PEG200, PEG300, PG, and PPG1025 at 308.15 K

x	ρ/g·cm^{-3}	η/mPa·s	$\Delta\eta$/mPa·s	V^E/cm^3·mol^{-1}	d
		DMSO + EG			
0.0000	1.103 07	10.591	0.000	0.0000	
0.0799	1.102 11	10.204	0.330	−0.0417	1.539
0.2060	1.101 01	9.506	0.764	−0.1255	1.709
0.3426	1.100 01	8.715	1.200	−0.2228	1.997
0.4387	1.098 75	8.143	1.490	−0.2572	2.285
0.5397	1.096 95	7.399	1.653	−0.2617	2.644
0.6459	1.094 58	6.235	1.442	−0.2320	2.997
0.7517	1.091 67	4.953	1.110	−0.1609	3.505
0.8456	1.089 02	3.731	0.731	−0.0858	4.194
0.9271	1.086 89	2.599	0.331	−0.0255	5.021
1.0000	1.085 48	1.614	0.000	0.0000	
		DMSO + DEG			
0.0000	1.105 57	17.588	0.000	0.0000	
0.0978	1.105 33	16.692	0.667	−0.1077	2.056
0.1794	1.105 02	15.847	1.125	−0.1891	2.203
0.2569	1.104 60	14.942	1.458	−0.2574	2.361
0.3945	1.102 95	13.487	2.201	−0.3117	2.834
0.4797	1.101 75	12.357	2.432	−0.3367	3.177
0.5804	1.100 04	10.834	2.517	−0.3505	3.703
0.6748	1.097 62	8.995	2.186	−0.3111	4.290
0.7945	1.093 87	6.227	1.330	−0.2276	5.264
0.9146	1.089 08	3.442	0.464	−0.0935	7.086
1.0000	1.085 48	1.614	0.000	0.0000	
		DMSO + TEG			
0.0000	1.112 09	23.841	0.000	0.0000	
0.1087	1.111 71	22.191	0.766	−0.1435	2.281
0.2067	1.111 06	20.681	1.434	−0.2432	2.528
0.3232	1.109 77	18.831	2.174	−0.3181	2.901
0.4502	1.107 79	16.765	2.931	−0.3644	3.476
0.5602	1.105 57	14.597	3.208	−0.3825	4.132
0.6564	1.102 96	12.331	3.080	−0.3647	4.914
0.7413	1.099 93	9.801	2.437	−0.3148	5.774
0.8542	1.094 49	6.237	1.382	−0.1895	7.703
0.9450	1.089 19	3.367	0.531	−0.0755	11.300
1.0000	1.085 48	1.614	0.000		
		DMSO + PEG-200			
0.0000	1.112 43	28.066	0.000	0.0000	
0.0958	1.112 29	26.611	1.080	−0.1458	2.545
0.1888	1.111 98	25.097	2.025	−0.2648	2.791
0.2928	1.111 17	23.262	2.941	−0.3431	3.132
0.3887	1.110 10	21.615	3.831	−0.3898	3.573
0.5495	1.107 43	18.141	4.610	−0.4183	4.577
0.6291	1.105 62	15.622	4.197	−0.4141	5.190
0.7178	1.102 88	12.237	3.158	−0.3758	6.023
0.7924	1.099 80	9.229	2.124	−0.3140	6.997
0.9105	1.093 05	4.837	0.856	−0.1686	10.334
1.0000	1.085 48	1.614	0.000	0.0000	
		DMSO + PEG-300			
0.0000	1.11328	41.336	0.000	0.0000	
0.1178	1.11315	38.328	1.671	−0.1823	2.950
0.2376	1.11309	34.798	2.900	−0.3891	3.304
0.3421	1.11245	31.555	3.808	−0.4647	3.730
0.4207	1.11181	29.165	4.540	−0.5111	4.168
0.5182	1.11074	26.084	5.332	−0.5516	4.888
0.6204	1.10911	22.312	5.620	−0.5668	5.926
0.7171	1.10662	17.582	4.731	−0.5272	7.251
0.8512	1.10054	10.131	2.606	−0.3742	10.695
0.9385	1.09415	5.127	1.070	−0.2455	16.573
1.0000	1.08548	1.614	0.000	0.0000	
		DMSO + PG			
0.0000	1.026 17	25.461	0.000	0.0000	
0.0978	1.032 94	23.788	0.659	−0.0805	2.2876
0.1962	1.039 91	21.911	1.129	−0.1688	2.4800
0.2951	1.046 97	19.945	1.521	−0.2573	2.7399
0.3943	1.053 80	17.978	1.920	−0.3245	3.0976
0.4941	1.060 37	15.819	2.141	−0.3679	3.5492
0.5943	1.066 19	13.233	1.944	−0.3554	4.0856
0.6950	1.071 45	10.578	1.691	−0.3008	4.9012
0.7962	1.076 23	7.618	1.144	−0.2104	6.0999
0.9166	1.081 98	4.109	0.506	−0.1056	9.2163
1.0000	1.085 48	1.614	0.000	0.0000	
		DMSO + PPG-1025			
0.0000	0.993 89	82.328	0.000	0.0000	
0.1248	0.997 35	79.685	7.430	−2.3380	4.195
0.2317	1.000 92	76.319	12.690	−4.1560	4.693
0.3311	1.004 6	74.259	18.660	−5.4360	5.414
0.4389	1.008 78	71.329	24.430	−6.1390	6.427
0.5472	1.014 31	66.648	28.490	−6.6380	7.832
0.6581	1.021 95	58.845	29.630	−6.7360	10.010
0.7514	1.027 68	49.484	27.800	−5.3880	13.094
0.8649	1.038 48	31.556	19.040	−3.1650	20.901
0.9347	1.049 69	11.347	4.460	−1.2860	27.751
1.0000	1.085 48	1.614	0.000	0.0000	

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

	A_0	A_1	A_2	A_3	A_4	A_5	σ
			DMSO + EG				
V^E/cm^3·mol^{-1}	−1.0667	−0.0147	0.8420	−0.1239	−0.0272	0.3968	0.0131
$\Delta\eta$/mPa·s	6.3301	1.6765	−4.2729	−1.7935	2.8704	−0.2539	0.1961
			DMSO + DEG				
V^E/cm^3·mol^{-1}	−1.3663	−0.2624	−0.1693	0.7817	0.6117	−0.5927	0.0327
$\Delta\eta$/mPa·s	10.0128	3.5301	−7.6912	−10.9849	4.3395	6.3764	0.1730
			DMSO + TEG				
V^E/cm^3·mol^{-1}	−1.5102	−0.4067−0.2624	1.2972	0.4915	−1.0600	0.0165	
$\Delta\eta$/mPa·s	12.4986	6.5148	−6.9907	−14.3370	2.6855	10.5377	0.1526
			DMSO + PEG-200				
V^E/cm^3·mol^{-1}	−1.6642	−0.3147	−0.5861	0.7662	0.4157	−0.9746	0.0109
$\Delta\eta$/mPa·s	18.1484	6.1609	−19.9623	−27.7460	14.8935	25.0784	0.1035
			DMSO + PEG-300				
V^E/cm^3·mol^{-1}	−2.1947	−0.9997	−0.8389	3.8837	0.5006	−6.6408	0.0396
$\Delta\eta$/mPa·s	20.9321	14.1447	−5.6207	−34.0372	0.5404	23.5129	0.2608
			DMSO + PG				
V^E/cm^3·mol^{-1}	−1.4697	−0.2915	1.0837	0.6514	−0.8584	−0.9543	0.0126
$\Delta\eta$/mPa·s	8.3907	0.7490	−5.6411	−2.2746	5.5205	0.4344	0.2254
			DMSO + PPG-1025				
V^E/cm^3·mol^{-1}	−26.1493	−8.6438	−7.2865	0.8076	20.5798	−1.7762	0.8087
$\Delta\eta$/mPa·s	105.1476	30.8088	60.2251	369.3635	−94.4931	−584.7037	8.8121

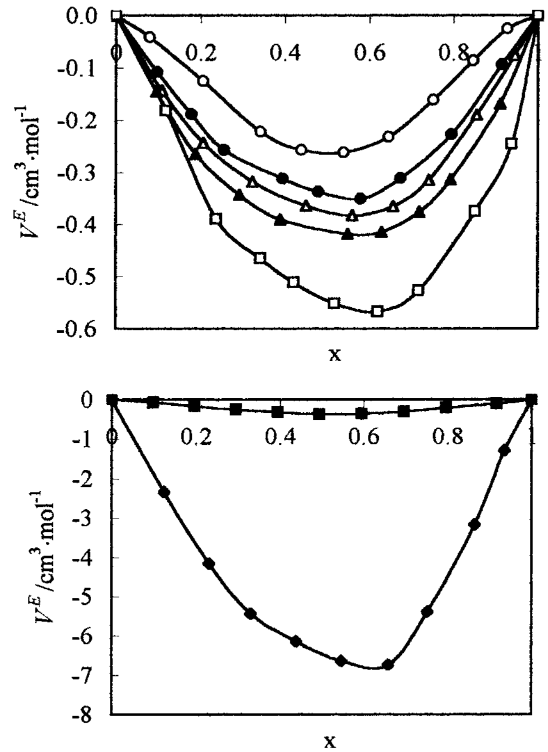

Figure 1. Mole fraction of dimethyl sulfoxide versus excess molar volumes for dimethylsulfoxide + (○) ethylene glycol, (●) diethylene glycol, (△) triethylene glycol, (▲) poly(ethylene glycol)-200, (□) poly-(ethylene glycol)-300, (■) propylene glycol, and (◆) polypropylene glycol-1025 at 308.15 K.

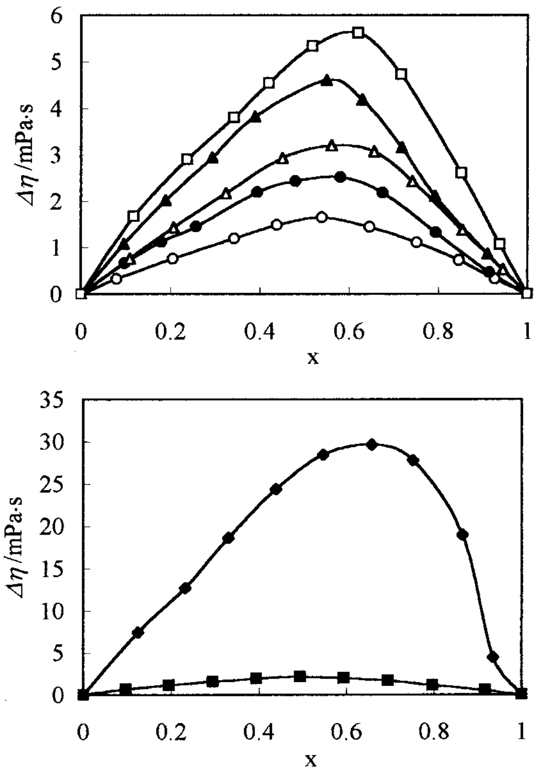

Figure 2. Mole fraction of dimethyl sulfoxide versus deviations in viscosities for dimethyl sulfoxide + (○) ethylene glycol, (●) diethylene glycol, (△) triethylene glycol, (▲) poly(ethylene glycol)-200, (□) poly(ethylene glycol)-300, (■) propylene glycol, and (◆) polypropylene glycol-1025 at 308.15 K.

determined ρ and η using eqs 1−3, and the values are presented in Table 2 along with the values of ρ, η, and mole fraction of DMSO (x).

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

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

$$\ln \eta = x \ln \eta_1 + (1 - x) \ln \eta_2 + x(1 - x)d \quad (3)$$

The variations of V^E and $\Delta\eta$ with mole fraction of DMSO are shown graphically in Figures 1 and 2, respectively. The excess functions were fitted to the Redlich−Kister equation of the form

$$Y^E = x(1 - x)\sum A_i(2x - 1)^{i-1} \quad (4)$$

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 the least-squares procedure.

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

$$\sigma(Y^E) = [\sum(Y^E{}_{obs} - Y^E{}_{cal})^2/(m - n)]^{1/2} \quad (5)$$

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

The excess molar volumes, V^E (Figure 1), are negative over the entire mole fraction range. Mixing of DMSO with glycols tends to break the associates present in glycol molecules with a subsequent increase in V^E. However, because of simultaneous interaction, mainly due to the hydrogen bonding between DMSO and glycol molecules in addition to the interstitial accommodation due to the difference in shape and size of the component molecules, resulting in an overall decrease in V^E with mole fraction of DMSO, the values of V^E become more negative as the chain length of the glycol molecules increases and are in the following order.

DMSO + EG < + DEG < + PG < + TEG < + PEG-200 < + PEG-300 < + PPG-1025

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 >S═O group of the DMSO molecules.

A correlation between the signs of $\Delta\eta$ and V^E has been observed for a number of binary solvent systems;[2,7] that is, if $\Delta\eta$ is positive, V^E is negative and vice versa. In the present study this holds true (Figure 2).

The interaction parameter, d, is another useful parameter for the study of intermolecular interactions between binary liquid mixtures. The positive d values for the present systems under study confirm complex formation between the component molecules[2,7] as a result of strong molecular interactions.

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

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Received for review April 27, 2001. Accepted November 20, 2001.

JE0101395