Densities and Viscosities of Ethylene Glycol Binary Mixtures at 293.15 K

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Densities (ρ) and viscosities (η) for the binary mixtures of ethylene glycol with 2-aminoethanol, 2-chloroethanol, 2-ethoxyethanol, benzyl alcohol, pentanol-1, methanol, cyclohexanone, and acetone have been measured over the whole composition range at 293.15 K. The excess volumes and the viscosity deviations were calculated, and the results were fitted to a Redlich−Kister type polynomial relation. The corresponding parameters have been derived. The results were interpreted in terms of specific interactions between the unlike molecules.

Introduction

Ethylene glycol is an important solvent with extensive use. However, few experimental data concerning its mixtures are available in the literature (Gladden and Ghaffari, 1972; Reddy et al., 1994; Amminabhavi and Gopalakrishna, 1995; Tsierkezos and Molinou, 1998).

Ethylene glycol is self-associated because of the hydrogen bonding ability of its two hydroxylic groups; this ability is stronger in glycols than in monohydroxylic alcohols (Kundu et al., 1970). Upon mixing with polar solvents, a disruption of the associated structure occurs and specific interactions take place which give rise to interesting thermodynamic properties. The study of molecular interactions in liquid mixtures has been the subject of our work in the laboratory in recent years. Continuing this study, we report the excess volumes (V^E) and viscosity deviations ($\Delta\eta$) of the mixtures of ethylene glycol (EG) with 2-aminoethanol, 2-chloroethanol, 2-ethoxyethanol, pentanol-1, benzyl alcohol, methanol, cyclohexanone, and acetone.

The thermodynamic properties of the mixtures depend on the way in which the molecules of the pure solvents are associated during the mixing process. We use a variety of solvents which represent different types and degrees of association between unlike molecules in order to study more systematically the ethylene glycol + organic molecules interactions.

Experimental Section

Materials. The reagents, ethylene glycol (Merck, p.a. > 99.5%), methanol (Merck, p.a. > 99.8%), acetone (Merck, p.a. > 99.5%), cyclohexanone (Riedel-de Haen, p.a. > 99.8%), 2-aminoethanol (Fluka, p.a. > 99.0%), 2-chloroethanol (Fluka, p.a. > 99.0%), 2-ethoxyethanol (Fluka, p.a. > 99.5%), benzyl alcohol (Fluka, p.a. > 99.0%), and pentanol-1 (Fluka, p.a. > 99.0%) were used without purification. The purities of the liquids were assessed by comparing the densities and refractive indices with the literature values (Table 1). The agreement was very satisfactory.

The binary mixtures were prepared by mass (Mettler A210P, ±0.01 mg). The mole fractions were known to ±0.0001 in all cases.

Measurements. A digital densimeter (Anton Paar, model DMA 58) was employed for the determination of the densities of the pure components and the binary mixtures. The estimated uncertainty of the measured densities is ±0.00001 g·cm^{-3}. The DMA cell was calibrated with dry air and distilled water. The sample size was 0.7 cm^3, and the sample thermostat was controlled to ±0.01 K.

Flow times of the mixtures and the pure liquids were measured with a Schott Geräte AVS 310 unit, equipped

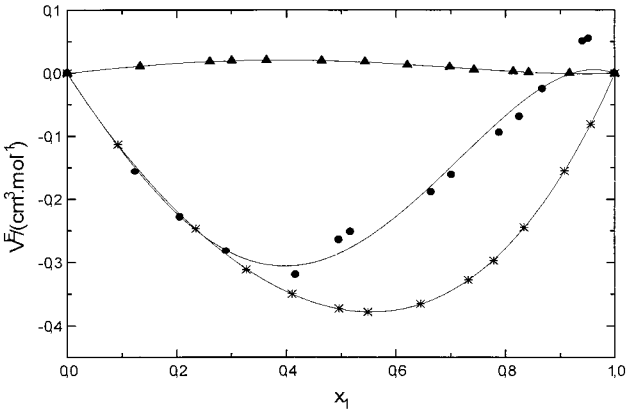

Figure 1. Excess molar volumes for ethylene glycol (1) + 2-chloroethanol (2) (▲), + 2-aminoethanol (2) (●), and + 2-ethoxyethanol (2) (∗) at 293.15 K.

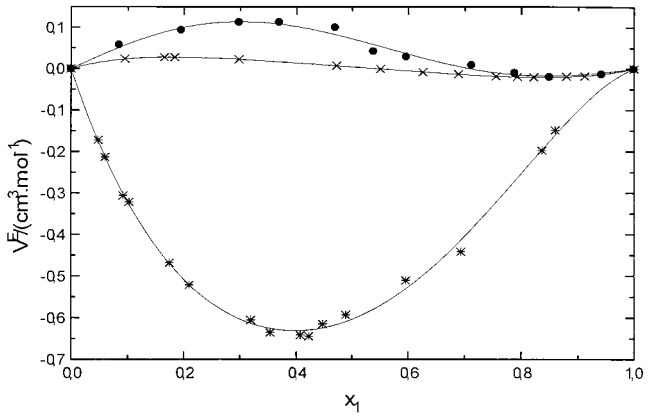

Figure 2. Excess molar volumes for ethylene glycol (1) + pentanol-1 (2) (●), + benzyl alcohol (2) (×), and + methanol (2) (∗) at 293.15 K.

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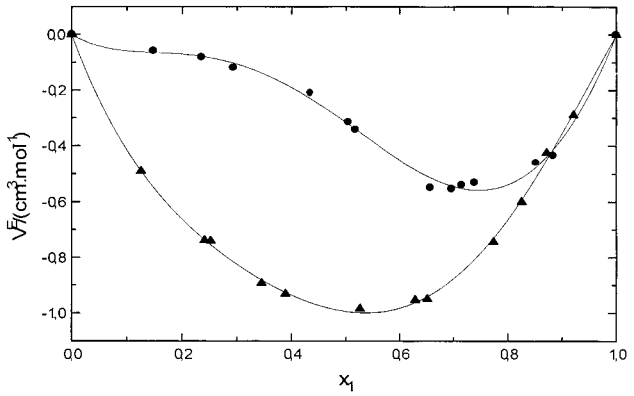

Figure 3. Excess molar volumes for ethylene glycol (1) + cyclohexanone (2) (●) and + acetone (2) (▲) at 293.15 K.

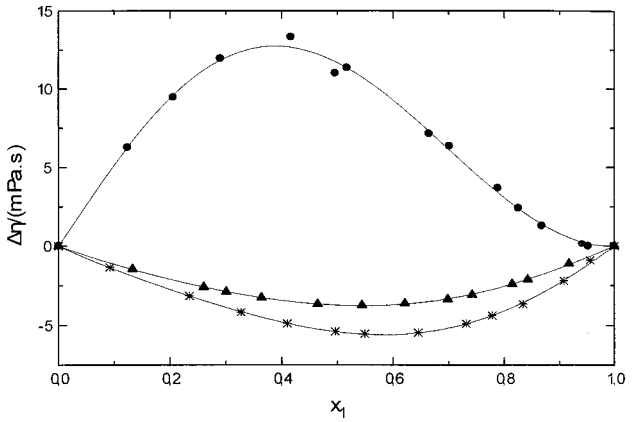

Figure 4. Viscosity deviations of ethylene glycol (1) + 2-aminoethanol (2) (●), 2-chloroethanol (2) (▲), and + 2-ethoxyethanol (2) (∗) at 293.15 K.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with Literature Values at 293.15 K

	ρ(exp)/(g·cm^{-3})	ρ(ref)/(g·cm^{-3})	n_D(exp)	n_D (ref)
ethylene glycol	1.113 23	1.113 50[a]	1.4319	1.4318[a]
		1.112 020[c]		
2-aminoethanol	1.016 37	1.018 00[b]	1.4548	1.4541[b]
2-chloroethanol	1.202 71	1.200 30[b]	1.4424	1.4419[b]
2-ethoxyethanol	0.931 38	0.931 00[b]	1.4086	1.4075[b]
benzyl alcohol	1.045 52	1.045 35[b]	1.5406	1.5396[b]
pentanol-1	0.814 68	0.814 80[a]	1.4108	1.4100[a]
methanol	0.791 45	0.791 29[a]	1.3294	1.3284[a]
		0.790 004[c]		
cyclohexanone	0.949 30	0.947 80[b]	1.4516	1.4507[b]
acetone	0.790 15	0.791 17[a]	1.3520	1.3587[a]

[a] TRC Databases for Chemistry and Engineering 1991−8. [b] *CRC Handbook of Chemistry and Physics* 1993−4. [c] Lee and Hong, 1990.

with an Ubbelohde capillary viscometer. The viscometer was calibrated with conductivity water. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The viscometer was placed in a thermostat (model Schott CT 050/2) electronically controlling the set temperature. The temperature was maintained constant within ±0.03 K. The viscosities were averaged from four readings. The accuracy in the viscosity measurements was ±0.001 mPa·s.

Results and Discussion

The experimental values of density and viscosity for all mixtures at different compositions and at 293.15 K are listed in Table 2.

Table 2. Experimental Densities (ρ) and Viscosities (η) of Ethylene Glycol Binary Mixtures at 293.15 K

x_1	ρ/(g·cm^{-3})	η/(mPa·s)	x_1	ρ/(g·cm^{-3})	η/(mPa·s)
Ethylene Glycol (1) + 2-Aminoethanol (2)					
0.0000	1.016 37	24.099	0.7010	1.085 79	28.138
0.1246	1.030 38	29.944	0.7890	1.093 38	25.166
0.2055	1.039 15	32.898	0.8248	1.096 52	23.798
0.2907	1.048 09	35.071	0.8691	1.100 18	22.483
0.4172	1.060 83	36.008	0.9427	1.106 30	21.115
0.4960	1.067 49	33.468	0.9527	1.107 22	20.924
0.5176	1.069 34	33.729	1.0000	1.113 23	20.806
0.6654	1.082 76	29.062			
Ethylene Glycol (1) + 2-Chloroethanol (2)					
0.0000	1.202 71	3.588	0.6211	1.150 81	10.660
0.1328	1.192 39	4.422	0.6983	1.143 60	12.255
0.2605	1.182 07	5.484	0.7424	1.139 44	13.295
0.3003	1.178 77	5.879	0.8141	1.132 42	15.205
0.3636	1.173 47	6.593	0.8422	1.129 63	15.976
0.4644	1.164 81	7.922	0.9168	1.122 02	18.256
0.5437	1.157 79	9.223	1.0000	1.113 23	20.806
Ethylene Glycol (1) + 2-Ethoxyethanol (2)					
0.0000	0.931 38	2.138	0.6451	1.029 77	8.722
0.0923	0.942 59	2.519	0.7319	1.047 71	10.905
0.2349	0.961 44	3.380	0.7782	1.057 91	12.290
0.3267	0.974 76	4.070	0.8336	1.070 63	14.039
0.4103	0.987 75	4.910	0.9075	1.088 74	16.877
0.4957	1.002 02	6.008	0.9556	1.101 21	19.077
0.5486	1.011 44	6.840	1.0000	1.113 23	20.806
Ethylene Glycol (1) + Benzyl Alcohol (2)					
0.0000	1.045 52	6.536	0.6888	1.082 56	14.692
0.0946	1.048 88	7.031	0.7556	1.088 13	16.050
0.1648	1.051 73	7.627	0.7929	1.091 46	16.823
0.1834	1.052 53	7.781	0.8219	1.094 17	17.416
0.2979	1.057 86	8.824	0.8789	1.099 78	18.747
0.4721	1.067 45	10.982	0.9113	1.103 21	19.362
0.5503	1.072 45	12.180	1.0000	1.113 23	20.806
0.6255	1.077 72	13.482			
Ethylene Glycol (1) + Pentanol-1 (2)					
0.0000	0.814 68	4.030	0.5964	0.943 39	9.655
0.0857	0.827 99	4.274	0.7130	0.982 21	12.321
0.1963	0.847 24	4.916	0.7884	1.011 16	14.033
0.2991	0.867 45	5.660	0.8506	1.037 67	15.902
0.3697	0.882 87	6.324	0.9407	1.080 96	18.941
0.4694	0.907 08	7.484	1.0000	1.113 23	20.806
0.5395	0.926 59	8.676			
Ethylene Glycol (1) + Methanol (2)					
0.0000	0.791 45	0.587	0.4072	0.961 09	2.906
0.0476	0.815 58	0.724	0.4225	0.966 22	3.085
0.0598	0.821 60	0.766	0.4474	0.973 76	3.338
0.0918	0.836 89	0.914	0.4889	0.986 58	3.824
0.1023	0.841 54	0.918	0.5955	1.017 42	5.485
0.1742	0.873 37	1.243	0.6932	1.043 99	7.481
0.2098	0.888 21	1.409	0.8360	1.077 11	11.431
0.3191	0.930 09	2.142	0.8590	1.081 96	12.301
0.3538	0.942 84	2.413	1.0000	1.113 23	20.806
Ethylene Glycol (1) + Cyclohexanone (2)					
0.0000	0.949 30	2.315	0.6565	1.040 44	9.855
0.1495	0.964 07	2.735	0.6965	1.048 23	11.022
0.2349	0.973 43	3.114	0.7152	1.051 79	11.200
0.2930	0.980 55	3.566	0.7398	1.056 74	12.401
0.4345	0.999 86	4.882	0.8522	1.081 26	17.589
0.5042	1.011 37	5.922	0.8845	1.088 99	18.735
0.5172	1.013 75	6.179	1.0000	1.113 23	20.806
Ethylene Glycol (1) + Acetone (2)					
0.0000	0.790 15	0.337	0.6291	0.987 04	3.034
0.1258	0.827 65	0.439	0.6515	0.994 88	3.393
0.2405	0.861 92	0.625	0.7734	1.036 11	6.123
0.2517	0.865 11	0.651	0.8254	1.053 53	7.897
0.3451	0.894 27	0.912	0.8715	1.068 48	9.970
0.3891	0.908 10	1.086	0.9210	1.085 92	13.185
0.5257	0.952 34	1.910	1.0000	1.113 23	20.806

V^E and $\Delta\eta$ were calculated from the experimental data according to the following equations:

$$V^E = V_m - \sum_{i=1}^{2} V_i x_i \quad (1)$$

$$\Delta\eta = \eta_m - \sum_{i=1}^{2} \eta_i x_i \quad (2)$$

where x_i, V_i, and η_i represent the mole fraction, molar volume, and viscosity of the ith pure component of the mixture. V_m and η_m are the molar volume and viscosity of the mixture, respectively. The molar volume, V_m, of the mixture was calculated from the following equation:

$$V_m = \sum_{i=1}^{2} x_i M_i / \rho_m \quad (3)$$

where ρ_m is the mixture density and M_i represents the molecular weight of the component i in the mixture.

The experimental values of V^E and $\Delta\eta$ are fitted to the Redlich−Kister equation:

$$Y = x_1 x_2 \sum_{k=0}^{n} A_k (2x_1 - 1)^k \quad (4)$$

where Y represents the excess volume or the viscosity deviations and A_k the parameters.

The number of parameters A_k used was obtained from the calculated and experimental values according to the equation

$$\sigma = \left[\frac{\sum (Y_{expt} - Y_{calcd})^2}{n - p}\right]^{1/2} \quad (5)$$

where n and p are the number of experimental points and parameters, respectively, and σ is the standard deviation. The values of A_k and σ, are presented in Table 3.

In Figure 1 the excess molar volumes of ethylene glycol with 2-aminoethanol and 2-ethoxyethanol show negative deviations. This effect can be attributed to the heteroassociation, which exceeds the positive contribution to V^E, arising from the breaking up of the self-associated-like molecules, of ethylene glycol.

The 2-aminoethanol and 2-ethoxyethanol molecules exhibit a strong ability for hydrogen bond formation, as the molecules possess hydrogen bond donors on the OH− group and acceptors on the oxygen or nitrogen atom.

In the ethylene glycol + 2-chloroethanol mixture the slight positive V^E values (0.01 $cm^3 mol^{-1}$) suggest that the interaction between unlike molecules and the disruption of the hydrogen bonding in ethylene glycol or 2-chloroethanol molecules are balanced. The mixture shows an almost ideal behavior.

In Figure 2, the V^E values of ethylene glycol + methanol mixture show strong negative deviations. According to reports (Dewan et al., 1991, 1992), methanol exists in the pure state, as a cyclic dimer and can be dissociated by the addition of a polar solvent in monomers and open dimers forming complex configurations.

The mixtures of ethylene glycol with benzyl alcohol and pentanol-1 show positive deviations. Pentanol aggregates consist, in the pure form, of monomers and cyclic dimers in a 1:1 equilibrium (Dewan et al., 1991, 1992). The breaking up of the self-associated aggregates leads to positive contributions, but the heteroassociation in this case is small, as the hydrogen bond formation ability is reduced, compared to that with lower alcohols (Aminabhavi et al., 1993). In the ethylene glycol + benzyl alcohol mixture, the V^E values are close to zero. This effect can be attributed to

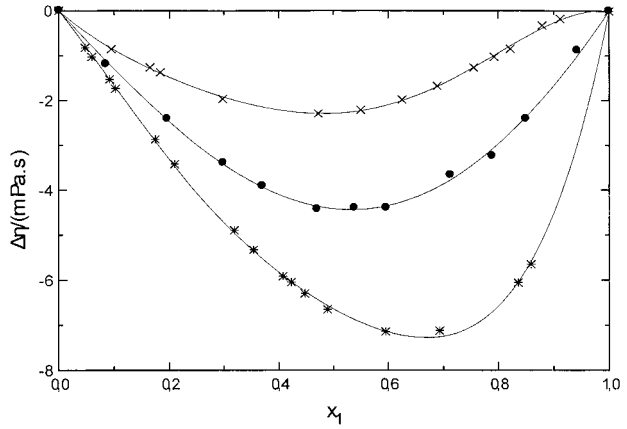

Figure 5. Viscosity deviations of ethylene glycol (1) + benzyl alcohol (2) (×), + pentanol-1 (2) (●), and + methanol (2) (∗) at 293.15 K.

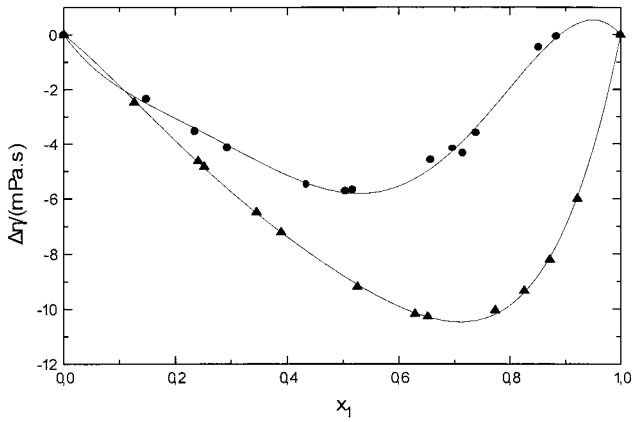

Figure 6. Viscosity deviations of ethylene glycol (1) + cyclohexanone (2) (●) and + acetone (2) (▲) at 293.15 K.

Table 3. Parameters and Standard Deviations of Excess Functions of Ethylene Glycol Binary Mixtures

function	A_0	A_1	A_2	A_3	σ
Ethylene Glycol (1) + 2-Aminoethanol (2)					
V^E/(cm^3·mol^{-1})	−1.1375	0.8101	0.6411		0.0170
$\Delta\eta$/(mPa·s)	46.6969	−36.3881	−21.5118	9.6142	0.3983
Ethylene Glycol (1) + 2-Chloroethanol (2)					
V^E/(cm^3·mol^{-1})	0.0764	−0.0633	−0.0462		0.3787
$\Delta\eta$/(mPa·s)	−14.9156	−3.0694	1.2420	2.0749	0.0308
Ethylene Glycol (1) + 2-Ethoxyethanol (2)					
V^E/(cm^3·mol^{-1})	−1.4958	−0.3052	−0.1589		0.0008
$\Delta\eta$/(mPa·s)	−21.6672	−8.4218	0.9555	3.8805	0.0438
Ethylene Glycol (1) + Benzyl Alcohol (2)					
V^E/(cm^3·mol^{-1})	0.0153	−0.1909	0.0207	−0.1571	0.0004
$\Delta\eta$/(mPa·s)	−9.1503	0.9987	4.3894	5.0257	0.0382
Ethylene Glycol (1) + Pentanol-1 (2)					
V^E/(cm^3·mol^{-1})	0.2884	−0.7131	−0.0653	0.3067	0.0102
$\Delta\eta$/(mPa·s)	−17.6615	−2.5954	1.8285		0.0924
Ethylene Glycol (1) + Methanol (2)					
V^E/(cm^3·mol^{-1})	−2.4143	1.0681	0.1041	0.7313	0.0096
$\Delta\eta$/(mPa·s)	−26.5487	−13.4128	−12.1882	−9.9956	0.0515
Ethylene Glycol (1) + Cyclohexanone (2)					
V^E/(cm^3·mol^{-1})	−1.2658	−2.7536	−1.7740	0.8817	0.0223
$\Delta\eta$/(mPa·s)	−23.1085	−5.3580	20.7300	31.0070	0.2669
Ethylene Glycol (1) + Acetone (2)					
V^E/(cm^3·mol^{-1})	−3.9792	−0.5504	−0.4604	1.5088	0.0151
$\Delta\eta$/(mPa·s)	−35.1284	−25.5424	−21.7798	−15.4347	0.0872

a balance between the physical interactions leading to the breaking up of the self-associated molecules and the specific interactions between the polar groups of the unlike molecules.

In Figure 3, both acetone and cyclohexanone exhibit negative deviations, which can be attributed to attractive interactions between the carbonyl of the ketones and the hydroxylic groups of the ethylene glycol molecules.

In Figures 4−6 the $\Delta\eta$ values are negative with the exception of the mixture ethylene glycol + 2-aminoethanol, which exhibits strong positive deviation.

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