Excess Molar Volumes and Viscosities of 1-Propanol + Ethylene Glycol, + Ethylene Glycol Monomethyl, + Ethylene Glycol Dimethyl, + Diethylene Glycol Dimethyl, + Triethylene Glycol Dimethyl, + Diethylene Glycol Diethyl, and + Diethylene Glycol Dibutyl Ethers at 298.15 K

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Excess molar volumes V_m^E and viscosities η have been measured as a function of composition for binary liquid mixtures of 1-propanol, C_3H_7OH, with ethylene glycol (1,2-ethanediol), HOC_2H_4OH, ethylene glycol monomethyl ether (2-methoxyethanol), $CH_3OC_2H_4OH$, diethylene glycol dimethyl ether (bis(2-methoxyethyl) ether), $CH_3(OC_2H_4)_2OCH_3$, triethylene glycol dimethyl ether (1,2-bis(2-methoxyethoxy)ethane), $CH_3(OC_2H_4)_3OCH_3$, and diethylene glycol diethyl ether (bis(2-ethoxyethyl) ether), $C_2H_5(OC_2H_4)_2OC_2H_5$, at 298.15 K. Viscosity measurements have also been made for the mixtures 1-propanol + ethylene glycol dimethyl ether (1,2-dimethoxyethane), $CH_3OC_2H_4OCH_3$, and + diethylene glycol dibutyl ether (bis(2-butoxyethyl) ether), $C_4H_9(OC_2H_4)_2OC_4H_9$, at 298.15 K over the whole composition range. All the systems exhibit negative deviation from a mole fraction average in viscosity. The excess volumes for all mixtures are negative with the exception of 1-propanol + ethylene glycol monomethyl ether.

Introduction

This is a part of our systematic program of research concerning the experimental study of several thermodynamic and transport properties of mixtures containing oxygen (−O−) and hydroxyl (−OH) functional groups (Pal and Singh, 1995, 1996, 1997). The aim of these works is to improve our understanding of the molecular interactions of these groups. In continuation of these investigation with the mixtures of an alkoxyethanol either with an organic solvent or with water, the present paper reports the experimental excess molar volumes V_m^E and viscosity η for binary mixtures of 1-propanol (C_3H_7OH) with ethylene glycol (HOC_2H_4OH), ethylene glycol monomethyl ether ($CH_3OC_2H_4OH$), diethylene glycol dimethyl ether ($CH_3(OC_2H_4)_2OCH_3$), triethylene glycol dimethyl ether ($CH_3(OC_2H_4)_3OCH_3$), and diethylene glycol diethyl ether ($C_2H_5(OC_2H_4)_2OC_2H_5$) at 298.15 K. We have also measured the viscosities of 1-propanol (C_3H_7OH) with ethylene glycol dimethyl ether ($CH_3OC_2H_4OCH_3$) and diethylene glycol dibutyl ether ($C_4H_9(OC_2H_4)_2OC_4H_9$) at the same temperature. The aim of this work is to provide a set of values for the characterization of the influence of the size, shape, and polarity of ether or alkoxyethanol on the thermodynamic properties of mixtures when we pass from monoether to diether, triether, or tetraether. This study might be useful for the interpretation of the thermodynamic properties of liquid mixtures containing larger polyethers with 1-propanol.

Experimental Section

Materials. 1-Propanol (S.R.L., Bombay, GC 99.5%), ethylene glycol dimethyl ether (Ubichem Ltd., USA, 99%), and ethylene glycol (S.D. Fine Chemicals, Bombay, GLC 99%) were the same as those used in earlier studies (Pal and Sharma, 1997, Pal and Singh, 1995). Ethylene glycol monomethyl ether (E. Merck, Germany, GC min. 99.5%), diethylene glycol dimethyl ether (Merck-Schuchardt, FRG, GC > 99%), diethylene glycol diethyl ether (Merck-Schuchardt, FRG, GC > 98%), and diethylene glycol dibutyl ether (Merck-Schuchardt, FRG, GC > 98%) were dried over ferrous sulfate (A.R., BDH) and then fractionally distilled under reduced nitrogen gas pressure (Riddick et al., 1986; Perrin et al., 1980). Triethylene glycol dimethyl ether (Acros, USA, 99%) was used without further purification. Prior to actual measurements, all liquids were dried over 0.4 nm molecular sieves (Fluka, AG) and were partially degassed under vacuum. The purity of the solvents, as found by gas−liquid chromatographic analysis, was better than 99.5 mol %. The purities of the final samples were checked by comparing the densities and viscosities at 298.15 ± 0.01 K with their corresponding literature values (Table 1). The densities were measured with a bicapillary pycnometer that gave an accuracy of 5 parts in 10^5.

Table 1. Properties of Pure Liquids at 298.15 K

liquid	ρ/g·cm^3 exptl	ρ/g·cm^3 lit.	η/mPa·s exptl	η/mPa·s lit.
1-propanol	0.7994	0.79960[a]	1.951	1.943[a]
ethylene glycol	1.1098	1.1100[a]	17.877	
ethylene glycol monomethyl ether	0.9602	0.96024[a]	1.532	1.5414[b]
ethylene glycol dimethyl ether	0.8626	0.86262[c]	0.420	0.424[d]
diethylene glycol dimethyl ether	0.9389	0.93873[e]	0.985	0.989[a]
triethylene glycol dimethyl ether	0.9807	0.98067[e]	1.950	1.96[f]
diethylene glycol diethyl ether	0.9035	0.9033[g]	1.241	
diethylene glycol dibutyl ether	0.8781	0.87830[h]	2.122	

[a] Riddick et al. (1986) [b] Muhuri and Hazra (1995). [c] Douhéret et al. (1993). [d] Das et al. (1994). [e] Tovar et al. (1997). [f] Wallace et al. (1968). [g] Roux et al. (1978). [h] Serna et al. (1997).

Apparatus and Procedure. Excess molar volumes were measured by a continuous-dilution dilatometer in

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Table 2. Excess Molar Volume V_m^E for the Binary Mixtures at 298.15 K

x_2	V_m^E/ cm^3·mol^{-1}	x_2	V_m^E/ cm^3·mol^{-1}	x_2	V_m^E/ cm^3·mol^{-1}	x_2	V_m^E/ cm^3·mol^{-1}	x_2	V_m^E/ cm^3·mol^{-1}	x_2	V_m^E/ cm^3·mol^{-1}
1-Propanol (1) + Ethylene Glycol (2)											
0.0020	−0.002	0.1127	−0.091	0.2752	−0.193	0.4571	−0.256	0.6336	−0.275	0.8614	−0.174
0.0136	−0.013	0.1391	−0.111	0.3088	−0.203	0.4775	−0.259	0.6804	−0.266	0.8990	−0.142
0.0323	−0.030	0.1757	−0.139	0.3421	−0.221	0.5093	−0.269	0.7262	−0.251	0.9330	−0.099
0.0552	−0.046	0.2052	−0.154	0.3800	−0.231	0.5438	−0.273	0.7671	−0.236	0.9685	−0.052
0.0875	−0.074	0.2396	−0.173	0.4289	−0.250	0.5861	−0.276	0.8334	−0.199	0.9964	−0.009
1-Propanol (1) + Ethylene Glycol Monomethyl Ether (2)											
0.0093	0.002	0.1127	0.022	0.3199	0.045	0.4928	0.053	0.6702	0.046	0.8740	0.021
0.0224	0.005	0.1515	0.028	0.3656	0.048	0.5333	0.052	0.7145	0.043	0.9270	0.011
0.0373	0.009	0.1809	0.032	0.4149	0.051	0.5808	0.050	0.7737	0.038	0.9572	0.008
0.0527	0.012	0.2299	0.037	0.4466	0.052	0.6286	0.048	0.8252	0.030	0.9821	0.003
0.0721	0.015	0.2629	0.041								
1-Propanol (1) + Diethylene Glycol Dimethyl Ether (2)											
0.0060	−0.003	0.0873	−0.035	0.2880	−0.071	0.4513	−0.072	0.6682	−0.048	0.8683	−0.019
0.0180	−0.009	0.1037	−0.040	0.3274	−0.073	0.5017	−0.069	0.7011	−0.044	0.9007	−0.014
0.0347	−0.014	0.1404	−0.049	0.3519	−0.074	0.5614	−0.063	0.7708	−0.034	0.9496	−0.008
0.0504	−0.022	0.1720	−0.057	0.3913	−0.073	0.6192	−0.056	0.8164	−0.027	0.9807	−0.003
0.0653	−0.028	0.2420	-0.067								
1-Propanol (1) + Triethylene Glycol Dimethyl Ether (2)											
0.0096	−0.010	0.1201	−0.096	0.3462	−0.152	0.4992	−0.148	0.6918	−0.121	0.8976	−0.059
0.0242	−0.025	0.1415	−0.108	0.3864	−0.154	0.5441	−0.143	0.7564	−0.108	0.9518	−0.031
0.0410	−0.043	0.1763	−0.123	0.4062	−0.156	0.6022	−0.136	0.7933	−0.098	0.9751	−0.016
0.0643	−0.063	0.2114	−0.134	0.4527	−0.152	0.6401	−0.130	0.8269	−0.087	0.9934	−0.006
0.0977	−0.086	0.2770	−0.145								
1-Propanol (1) + Diethylene Glycol Diethyl Ether (2)											
0.0080	−0.016	0.1143	−0.168	0.3274	−0.304	0.5128	−0.304	0.6747	−0.246	0.8664	−0.124
0.0240	−0.040	0.1483	−0.202	0.3631	−0.309	0.5597	−0.292	0.7382	−0.210	0.9181	−0.084
0.0340	−0.059	0.1929	−0.240	0.4116	−0.313	0.5992	−0.280	0.7730	−0.188	0.9619	−0.038
0.0542	−0.087	0.2518	−0.275	0.4507	−0.310	0.6384	−0.265	0.8215	−0.160	0.9867	−0.013
0.0802	−0.123	0.2836	−0.285								

similar fashion to that described by Dickinson et al. (1975). Details of calibration, experimental setup, and operational procedure have been described previously (Pal and Singh, 1994). The mercury meniscus, as well as the reference mark, was measured with the help of a cathetometer that could read corect to ±0.001 cm. The results for excess molar volumes are reproducible to ±0.003 cm^3·mol^{-1}. The composition of each mixture was obtained with an accuracy of 1×10^{-4} from the measured apparent masses of the components. Corrections were made for buoyancy.

Kinematic viscosities of the pure liquids and the mixtures were measured at 298.15 K with a calibrated Ubbelohde suspended level viscometer, and the detailed procedure was described in our earlier paper (Pal and Singh, 1997). The kinematic viscosity (ν) and dynamic viscosity (η) were computed from the relation

$$\nu = At - B/t \quad (1)$$

$$\eta = \nu\rho \quad (2)$$

where A and B are the characteristic constants of the viscometer, ρ is the density, and t is the efflux time. The flow-time measurements were made using an accurate stopwatch with a precision of ±0.01 s. The average of four or five sets of flow times for each fluid was taken for the purpose of the calculation of viscosity. Viscosities are reproducible to ±0.003 mPa·s. A thermostatically controlled, well-stirred water bath whose temperature was controlled to ±0.01 K was used for all the measurements.

The densities ρ of the mixtures at the appropriate mole fractions used in the kinematic viscosity measurements were obtained from molar volume of pure components and excess molar volumes from the cubic spline interpolation procedure. In the case of the mixtures 1-propanol + ethylene glycol dimethyl ether and + diethylene glycol dibutyl ether, densities at the particular composition were computed from the excess molar volumes reported earlier (Pal and Sharma, 1998).

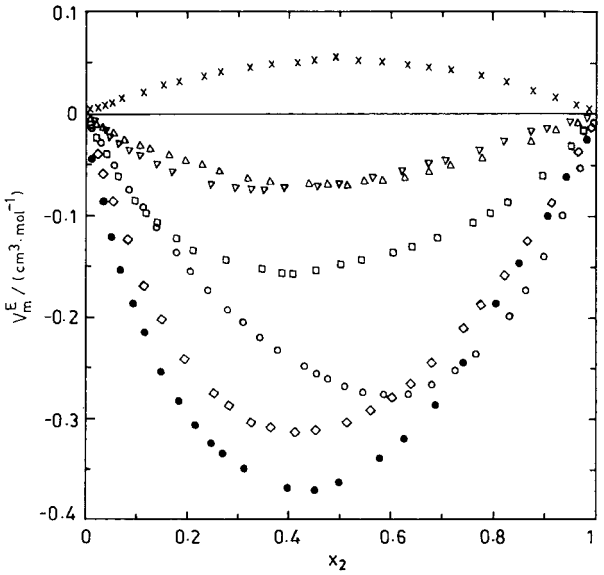

Figure 1. Excess molar volume (V_m^E) for 1-propanol (1) + ethylene glycol (2), (○); + ethylene glycol monomethyl ether (2), (×); + ethylene glycol dimethyl ether (2), (△) (Pal and Sharma, 1997); + diethylene glycol dimethyl ether (2), (▽); + triethylene glycol dimethyl ether (2), (□); + diethylene glycol diethyl ether (2), (◇); + diethylene glycol dibutyl ether (2), (●) (Pal and Sharma, 1997) at 298.15 K.

Results and Discussion

Tables 2 and 3 give the experimental results of the excess molar volumes and viscosities at 298.15 K at various mole

Table 3. Densities ρ and Viscosities η for the Binary Mixtures at 298.15 K

x_2	ρ/g·cm^{-3}	η/mPa·s	x_2	ρ/g·cm^{-3}	η/mPa·s	x_2	ρ/g·cm^{-3}	η/mPa·s	x_2	ρ/g·cm^{-3}	η/mPa·s
1-Propanol (1) + Ethylene Glycol (2)											
0.0111	0.8021	2.005	0.1912	0.8475	3.012	0.5096	0.9386	6.052	0.7998	1.0355	11.676
0.0207	0.8044	2.055	0.2372	0.8598	3.320	0.5452	0.9497	6.565	0.8400	1.0500	12.753
0.0321	0.8072	2.115	0.2938	0.8753	3.751	0.5843	0.9622	7.175	0.8875	1.0674	14.134
0.0482	0.8111	2.198	0.3450	0.8896	4.192	0.6533	0.9848	8.397	0.9180	1.0787	15.079
0.0722	0.8171	2.331	0.3886	0.9022	4.617	0.6993	1.0004	9.322	0.9609	1.0949	16.496
0.0979	0.8235	2.467	0.4295	0.9142	5.053	0.7522	1.0186	10.503	0.9812	1.1026	17.204
0.1442	0.8353	2.723	0.4681	0.9258	5.512						
1-Propanol (1) + Ethylene Glycol Monomethyl Ether (2)											
0.0072	0.8006	1.938	0.1162	0.8187	1.767	0.4575	0.8745	1.532	0.7779	0.9255	1.494
0.0141	0.8018	1.926	0.1639	0.8266	1.713	0.4938	0.8803	1.521	0.8231	0.9326	1.497
0.0297	0.8044	1.898	0.2144	0.8349	1.666	0.5359	0.8871	1.510	0.8729	0.9404	1.502
0.0471	0.8073	1.867	0.2667	0.8435	1.624	0.5856	0.8950	1.503	0.9153	0.9470	1.507
0.0620	0.8097	1.844	0.3227	0.8526	1.589	0.6298	0.9021	1.497	0.9597	0.9539	1.520
0.0767	0.8122	1.821	0.3699	0.8603	1.567	0.6793	0.9099	1.494	0.9808	0.9572	1.525
0.0973	0.8156	1.792	0.4118	0.8671	1.548	0.7347	0.9187	1.493			
1-Propanol (1) + Ethylene Glycol Dimethyl Ether (2)											
0.0095	0.8003	1.881	0.1741	0.8142	1.109	0.4764	0.8353	0.636	0.8198	0.8543	0.459
0.0215	0.8013	1.798	0.2034	0.8164	1.024	0.5241	0.8382	0.600	0.8625	0.8563	0.447
0.0405	0.8030	1.678	0.2436	0.8195	0.942	0.5700	0.8410	0.572	0.9004	0.8581	0.439
0.0628	0.8050	1.552	0.2926	0.8231	0.842	0.6239	0.8440	0.536	0.9269	0.8593	0.435
0.0941	0.8077	1.397	0.3474	0.8269	0.764	0.6795	0.8470	0.509	0.9590	0.8608	0.427
0.1096	0.8090	1.329	0.3848	0.8294	0.722	0.7142	0.8490	0.495	0.9842	0.8619	0.424
0.1355	0.8111	1.228	0.4255	0.8321	0.678	0.7632	0.8515	0.476			
1-Propanol (1) + Diethylene Glycol Dimethyl Ether (2)											
0.0064	0.8011	1.913	0.1632	0.8377	1.333	0.4652	0.8869	1.038	0.7757	0.9207	0.975
0.0122	0.8027	1.881	0.2064	0.8461	1.251	0.5109	0.8927	1.024	0.8190	0.9250	0.976
0.0238	0.8057	1.816	0.2619	0.8562	1.177	0.5509	0.8975	1.009	0.8649	0.9284	0.977
0.0358	0.8088	1.756	0.2976	0.8623	1.140	0.5982	0.9029	0.994	0.9094	0.9320	0.984
0.0546	0.8134	1.671	0.3254	0.8668	1.119	0.6569	0.9092	0.984	0.9425	0.9346	0.989
0.0803	0.8196	1.567	0.3716	0.8739	1.086	0.7110	0.9143	0.976	0.9722	0.9369	0.988
0.1176	0.8280	1.443	0.4168	0.8804	1.065						
1-Propanol (1) + Triethylene Glycol Dimethyl Ether (2)											
0.0081	0.8030	1.918	0.1327	0.8493	1.614	0.4606	0.9227	1.598	0.8162	0.9658	1.812
0.0165	0.8066	1.884	0.1747	0.8619	1.573	0.5153	0.9310	1.625	0.8625	0.9699	1.848
0.0245	0.8100	1.856	0.2259	0.8756	1.549	0.5714	0.9387	1.653	0.9112	0.9740	1.888
0.0336	0.8138	1.824	0.2757	0.8875	1.544	0.6283	0.9459	1.684	0.9347	0.9758	1.904
0.0480	0.8196	1.781	0.3226	0.8977	1.548	0.6732	0.9512	1.713	0.9568	0.9775	1.919
0.0692	0.8277	1.725	0.3691	0.9068	1.563	0.7227	0.9565	1.743	0.9775	0.9791	1.935
0.0946	0.8368	1.670	0.4157	0.9152	1.578	0.7726	0.9617	1.778			
1-Propanol (1) + Diethylene Glycol Diethyl Ether (2)											
0.0070	0.8013	1.918	0.1283	0.8282	1.541	0.4592	0.8713	1.259	0.7662	0.8928	1.222
0.0129	0.8028	1.894	0.1736	0.8362	1.458	0.5239	0.8768	1.243	0.8311	0.8962	1.226
0.0249	0.8058	1.844	0.2229	0.8439	1.396	0.5856	0.8815	1.231	0.8815	0.8986	1.231
0.0395	0.8085	1.788	0.2672	0.8502	1.354	0.6363	0.8850	1.227	0.9142	0.9000	1.235
0.0516	0.8122	1.747	0.3115	0.8558	1.320	0.6742	0.8875	1.225	0.9468	0.9014	1.239
0.0695	0.8163	1.687	0.3638	0.8619	1.291	0.7119	0.8898	1.224	0.9756	0.9025	1.240
0.0970	0.8221	1.611	0.4026	0.8659	1.280						
1-Propanol (1) + Diethylene Glycol Dibutyl Ether (2)											
0.0034	0.8004	1.944	0.1509	0.8306	1.832	0.4376	0.8582	1.884	0.7531	0.8720	2.016
0.0097	0.8021	1.937	0.1955	0.8367	1.824	0.4827	0.8608	1.901	0.8095	0.8736	2.039
0.0158	0.8038	1.930	0.2419	0.8421	1.827	0.5400	0.8638	1.925	0.8656	0.8751	2.061
0.0252	0.8062	1.917	0.2937	0.8473	1.837	0.5983	0.8664	1.949	0.9083	0.8761	2.079
0.0426	0.8105	1.895	0.3481	0.8519	1.851	0.6416	0.8682	1.968	0.9447	0.8769	2.096
0.0734	0.8172	1.866	0.3959	0.8554	1.868	0.6954	0.8701	1.990	0.9742	0.8776	2.111
0.0979	0.8219	1.849									

fractions. The plots of excess molar volume (V_m^E) against the mole fraction of the glycol ether are given in Figure 1.

The viscosity deviations from a linear dependence on mole fraction average were obtained from the following relationship

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where η, η_1, and η_2 are the viscosities of the mixture and components 1 and 2, respectively. The variations of $\Delta\eta$ with mole fraction at 298.15 K are shown in Figures 2 and 3, respectively.

The composition dependence of the excess molar volume and viscosity deviation are correlated by the Redlich−Kister polynomial

$$F(x) = x_1x_2\sum_{i=0}^{n}A_i(x_2 - x_1)^i \tag{4}$$

In each case, the optimum number of coefficients A_i was ascertained from an examination of the variation of the standard deviation with n

$$\sigma(F(x)) = [\sum\{(F(x)_{exptl} - (F(x)_{calcd}\}^2/(p - n)]^{1/2} \tag{5}$$

where p is the total number of experimental points and n is the number of parameters. The values adopted for the

Table 4. Smoothing Coefficients A_i and Standard Deviations $\sigma(F(x))$ of Eq 4 for Binary Mixtures at 288.15 K

system	$F(x)$	A_0	A_1	A_2	A_3	$\sigma(F(x))$
1-propanol (1) +						
ethylene glycol (2)	V_m^E/cm^3·mol^{-1}	−1.0628	−0.3641	−0.2632		0.002
	$\Delta\eta$/mPa·s	−15.9678	−4.9968	−0.3042	0.1895	0.003
ethylene glycol monomethyl ether (2)	V_m^E/cm^3·mol^{-1}	0.2085	−0.0061	0.0054		0.001
	$\Delta\eta$/mPa·s	−0.8844	0.3360	−0.2404	0.0460	0.001
ethylene glycol dimethyl ether (2)	$\Delta\eta$/mPa·s	−2.2667	1.5420	−1.2970	0.7670	0.003
diethylene glycol dimethyl ether (2)	V_m^E/cm^3·mol^{-1}	−0.2726	0.1663	−0.0339		0.001
	$\Delta\eta$/mPa·s	−1.7648	1.1796	−1.1751	0.9439	0.001
triethylene glycol dimethyl ether (2)	V_m^E/cm^3·mol^{-1}	−0.5908	0.1846	−0.3278		0.001
	$\Delta\eta$/mPa·s	−1.3284	0.9521	−1.0449	0.8619	0.002
diethylene glycol diethyl ether (2)	V_m^E/cm^3·mol^{-1}	−1.2218	0.3650	−0.2260		0.002
	$\Delta\eta$/mPa·s	−1.3841	0.9638	−0.8998	0.6307	0.002
diethylene glycol dibutyl ether (2)	$\Delta\eta$/mPa·s	−0.5052	0.4772	−0.4647	0.2269	0.001

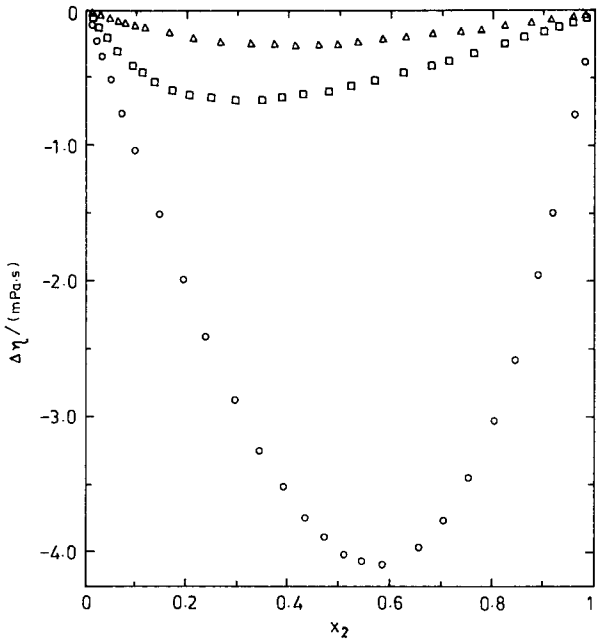

Figure 2. Viscosity deviations ($\Delta\eta$) for 1-propanol (1) + ethylene glycol (2), (○); + ethylene glycol monomethyl ether (2), (△); + ethylene glycol dimethyl ether (2), (□) at 298.15 K.

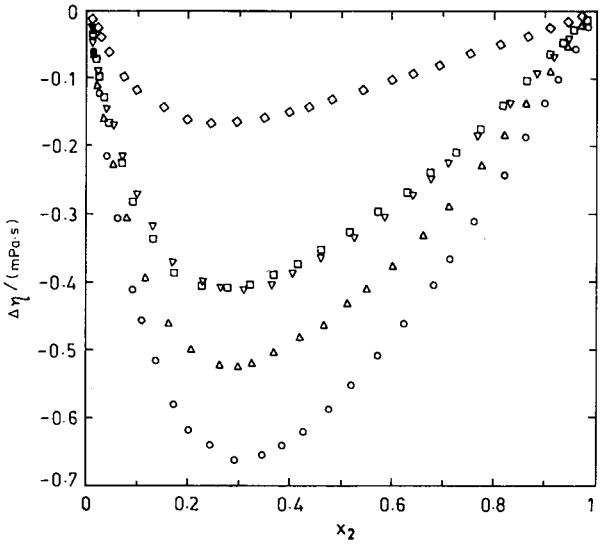

Figure 3. Viscosity deviations ($\Delta\eta$) for 1-propanol (1) + ethylene glycol dimethyl ether (2), (○); + diethylene glycol dimethyl ether (2), (△); + triethylene glycol dimethyl ether (2), (□); + diethylene glycol diethyl ether (2), (▽); + diethylene glycol dibutyl ether (2), (◇) at 298.15 K.

coefficients A_i and standard deviation $\sigma(F(x))$ associated with the use of eq 5 are recorded in Table 4. $F(x)$ represents V_m^E or $\Delta\eta$.

The excess molar volumes at 298.15 K for 1-propanol + diethylene glycol dimethyl ether or diethylene glycol diethyl ether obtained in this laboratory and those reported by Serna et al. (1997) from density values obtained using the Anton−Paar vibrating-tube densimeter are very similar over the whole mole fraction range.

For each of the mixtures studied, the V_m^E values are negative over the whole mole fraction range with the exception of 1-propanol with ethylene glycol monomethyl ether, symmetrical for mixtures with monoethers and slightly skewed toward the region of high mole fraction of 1-propanol for mixtures with polyethers. These results, and those from Serna et al. (1997) (not shown in Figure 1) and Pal and Sharma (1997), show that, for each polyether, the V_m^E decreases as the *n*-alkyl chain end length of the diethers or the triethers increases. When the *n*-alkyl chain end of the polyether is fixed, the V_m^E for both ethylene glycol dimethyl ether (Pal and Sharma, 1997) and diethylene glycol dimethyl ether are very close, whereas the V_m^E is more negative for triethylene glycol dimethyl ether. This behavior may be compared with the V_m^E results for mixtures of *n*-alkoxyethanols with 1-butanol (Cobos et al. 1988): V_m^E decreases as the *n*-alkyl chain end length as well as the polar head group of the alkoxyethanol increases. Again, there is a very obvious increase in the magnitudes of the excess molar volumes with each substitution of a methyl group for a hydroxyl hydrogen, as in case of ethylene glycol monomethyl ether and ethylene glycol dimethyl ether. Interestingly, for the ethylene glycol (symmetrical diol), the V_m^E is more negative than of the immediately asymmetrical monoether, that is, ethylene glycol monomethyl ether. This contrasts with the behavior of V_m^E in (polyether + water) (Douhéret et al., 1993), which varies regularly with each substitution of hydroxy by methoxy groups in the molecule of ethylene glycol.

Figures 2 and 3 show that the deviation in viscosity is negative for all systems over the entire range of composition. The negative values of $\Delta\eta$ may be attributed to (i) the existence of dispersion and dipolar forces between unlike molecules and (ii) the difference in size and shape of unlike molecules. The absolute values of $\Delta\eta$ for the mixtures fall in the following order.

(i) the addition of an OC_2H_4 group at the middle of the ether molecule: ethylene glycol dimethyl ether > diethylene glycol dimethyl ether > triethylene glycol dimethyl-ether

(ii) increasing the *n*-alkyl chain length of the ether molecule: diethylene glycol dimethyl ether > diethylene glycol diethyl ether > diethylene glycol dibutyl ether

(iii) replacing the hydroxyl hydrogen by methyl group: ethylene glycol > ethylene glycol dimethyl ether > ethylene glycol monomethyl ether (Figure 2).

Literature Cited

Cobos, J. C.; García, I.; Casanova, C.; Roux Desgranges, G.; Grolier, J.-P. E. Excess properties of mixtures of some *n*-alkoxyethanols with organic solvents. III. V_m^E and C_p^E with Butan-1-ol at 298.15 K. *Thermochim. Acta* **1988**, *131*, 73−78.

Das, B.; Roy, M. N.; Hazra, D. K. Densities and viscosities of the binary aqueous mixtures of tetrahydrofuran and 1,2-dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* **1994**, *1*, 93−97.

Dickinson, E.; Hunt, D. C.; McLure, I. A. Excess volume of mixing of nearly spherical molecules 2. Mixtures containing cyclic dimethylsiloxanes. *J. Chem. Thermodyn.* **1975**, *7*, 731−740.

Douhéret, G.; Davis, M. I.; Hernandez, M. E.; Flores, H. Excess Molar Volumes of Some Polyethers + Water Systems. *J. Indian Chem. Soc.* **1993**, *70*, 395−401.

Muhuri, P. K.; Hazra, D. K. Densities & Viscosities of Propylene Carbonate + 2-Methoxyethanol at 298.15, 308.15 and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 582−585.

Pal, A.; Singh, Y. P. Excess molar volumes and apparent molar volumes of $[xH(CH_2)_4O(CH_2)_2O(CH_2)_2OH + (1 - x)H_2O]$ at the temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 1063−1070.

Pal, A.; Singh, W. Excess molar volumes of binay mixed solvents containing 2-ethoxyethanol and ethylene glycol, propylene glycol, glycerol and cyclohexane at 298.15 K. *Indian J. Chem.* **1995**, *34A*, 389−392.

Pal, A.; Singh, W. Excess Molar Volumes of 2-[2-(2-Alkoxyethoxy)-ethoxy]ethanols with Trichloroethylene and Tetrachloroethylene at 298.15 and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*, 181−184.

Pal, A.; Singh, W. Speeds of Sound and Viscosities in Aqueous Poly(ethylene glycol) Solutions at 303.15 and 308.15 K. *J. Chem. Eng. Data* **1997**, *42*, 234−237.

Pal, A.; Sharma, S. Excess molar volumes of an (1-alcohol + 2,5-dioxahexane or 5,8,11-trioxapentadecane or 2-isopropoxyethanol) at 298.15 K. *Fluid Phase Equilib.* **1997**, in press.

Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1980.

Riddick, J. A.; Bunger, W. S.; Sakano, T. *Organic Solvents. Techniques of Chemistry*, 4th ed.; John Wiley and Sons: New York, 1986; Vol. II.

Roux, G.; Perron, G.; Desnoyers, J. E. The heat capacities and volumes of some low molecular weight amides, ketones, esters, and ethers in water over the whole solubiity range. *Can J. Chem.* **1978**, *56*, 2808−2814.

Serna, A.; García de la Fuente, I.; Gonzalez, J. A.; Cobos, J. C. In *Proceedings of the Second International Workshop on Vapour−Liquid Equilibria and Related Properties in Binary and Ternary Mixtures of Ethers, Alkanes and Alkanols*, held under the auspices of (IUPAC), Valladolid, Spain, July 3−6, 1996). *Fluid Phase Equilib.*, **1997** in press.

Tovar, C. A.; Carballo, E.; Cerdeiriña, C. A.; Romaní, L. Excess Molar volumes and Excess Molar Heat Capacities of Mixtures Containing (Mono and Poly) Ethers + Ethyl Acetate. *J. Chem. Eng. Data* **1997**, *42*, 1085−1089.

Wallace, W. J.; Shepard, C. S.; Underwood, C. Densities, Refractive Indices, Molar Refractions, Viscosities, and Dielectric constants of Triethylene Glycol Dimethyl Ether−Water Solutions at 25 °C. *J. Chem. Eng. Data* **1968**, *13*, 11−13.

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