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Excess Molar Volumes and Viscosities for Binary Liquid Mixtures of 2-Propoxyethanol and of 2-Isopropoxyethanol with Methanol, 1-Propanol, 2-Propanol, and 1-Pentanol at 298.15 K

Amalendu Pal* and Gurcharan Dass

Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, India

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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 2-propoxyethanol and of 2-isopropoxyethanol with methanol, 1-propanol, 2-propanol, and 1-pentanol at 298.15 K and atmospheric pressure. The viscosity data have been correlated with the equations of Kendall and Monroe, Grunberg and Nissan, Tamura and Kurata, Hind, Katti and Chaudhry, and McAllister. From the experimental data, the deviation in the viscosity η from $\sum x_i \ln \eta_i$ have been calculated.

Introduction

The industrial importance of branched ethers as gasoline blending agents is increasing. The alkoxyalkanols are used extensively as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastics products. The thermodynamic properties of mixtures containing lower alcohols, alkoxyalkanols, and branched ethers thus seemed to us to be an interesting topic for study.

In continuation of our previous experimental studies on binary liquid mixtures containing branched ethers (Pal and Singh, 1997a,b; Pal et al., 1997; Pal and Sharma, 1998; Pal and Dass, 1999), we report here new experimental excess molar volumes (V_m^E) and viscosities (η) for binary mixtures of 2-propoxyethanol and of 2-isopropoxyethanol with methanol, 1-propanol, 2-propanol, and 1-pentanol over the whole mole fraction range at 298.15 K and atmospheric pressure. In a previous paper (Pal and Sharma, 1998) we have reported excess molar volumes for the 2-isopropoxyethanol + methanol, 1-propanol, or 1-pentanol systems at 298.15 K.

In this paper we were interested in ascertaining whether the thermophysical properties of the 2-propoxyethanol + primary alkanol systems resemble those of 2-isopropoxyethanol + primary alkanol systems (Pal and Sharma, 1998). We were also interested in comparing the excess molar properties of 2-propoxyethanol + 1-propanol or 2-propanol with those of 2-isopropoxyethanol + 1-propanol or 2-propanol. The effect of specific interactions on the excess properties, the dependence on the position of the OH group in the alkanol and the CH_3 group in the propoxyethanol, and the influence of the alkyl chain length of the alkanol are analyzed.

Experimental Section

Materials. Methanol (S. D. fine chemicals, Bombay, GLC min. 99.8 mol %), 1-propanol (S. R. L., Bombay, GC min. 99.5 mol %), 2-propanol (S. R. L.; Bombay, HPLC, GC min 99.8 mol %), 1-pentanol (Acros, USA, 99 mol %), and 2-isopropoxyethanol (Merck-Schuchardt, FRG, GC > 98 mol %) were the same as those used in our earlier studies (Pal and Sharma, 1998; Pal et al., 1997). The 2-propoxyethanol was obtained from Acros, USA, with purity better than 98 mol % and was used directly. Prior to measurements, all liquids were partially degassed at low pressure and dried over 0.4 nm molecular sieves (Fluka, AG). The results of the measurements of their densities and viscosities at (298.15 ± 0.01) K and atmospheric pressure are given in Table 1, together with some values taken from the literature. The densities were measured with a bicapillary pycnometer that gave an accuracy of 5 parts in 10^5. The pycnometer was calibrated at (298.15 ± 0.01) K with thrice-distilled water.

Table 1. Comparison of Experimental Densities ρ and Viscosities η of Pure Liquids with Literature Values at 298.15 K

	ρ/g cm^{-3}		η/mPa s	
liquid	exptl	lit.	exptl	lit.
2-propoxyethanol	0.9080		2.351	
2-isopropoxyethanol	0.8999	0.89942[a] 0.8996[b]	2.101	
methanol	0.7864	0.78637[c] 0.7866[d] 0.7866[e] 0.78664[f] 0.78635[g]	0.550	0.5513[c] 0.538[d] 0.550[e] 0.5531[f]
1-propanol	0.7994	0.79960[c] 0.7998[d] 0.7996[e] 0.799975[f] 0.79958[h]	1.951	1.9430[c] 1.927[d] 1.943[e] 1.9430[f]
2-propanol	0.7810	0.78126[c] 0.7809[i]	2.079	2.0436[c]
1-pentanol	0.8111	0.81080[c] 0.8110[d] 0.8107[e] 0.8115[f]	3.511	3.5128[c] 3.421[d] 3.510[e] 3.5128[f]

[a] Davis and Chacon (1991). [b] Shindo and Kusano (1979). [c] Riddick et al. (1986). [d] Aminabhavi and Patil (1998). [e] Sastry et al. (1998). [f] *TRC Thermodynamic Tables* (1998). [g] Douhéret at al. (1989). [h] Serna et al. (1997). [i] Aminabhavi and Bindu (1995).

Apparatus and Procedure. Excess molar volumes reproducible to ±0.003 cm^3 mol^{-1} were measured directly with a continuous dilution dilatometer, as described by

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* To whom correspondence should be addressed.

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Dickinson et al. (1975). Details of the calibration, the experimental set up, and the measuring procedure have been given elsewhere (Pal and Singh, 1994). The mole fraction of each mixture was obtained to an accuracy of 1 × 10^{-4} from the measured apparent mass of one of the components. All apparent masses were corrected for buoyancy. Each run covered just over half of the mole fraction range, giving an overlap between two runs.

The kinematic viscosities ν ($=\eta/\rho$) of pure liquids and liquid mixtures were measured at 298.15 K and at atmospheric pressure using an Ubbelohde suspended level viscometer (Concalves et al., 1991). The viscometer was calibrated so as to determine the two constants A and B in the equation $\eta/\rho = At - B/t$, obtained by measuring the flow time t with thrice-distilled water and twice-distilled benzene and cyclohexane (Riddick et al., 1986). The details of the apparatus and procedure have been described previously (Pal and Singh, 1996; Pal and Singh, 1997). The viscometer is filled with liquid or liquid mixtures, and its limbs are closed with Teflon caps, taking due precautions to minimize the evaporation losses. The flow-time measurements were made using an electronic stopwatch with a precision of ±0.01 s. An average of four or five sets of flow times for each liquid or liquid mixture was taken for the purpose of calculation of viscosity. The caps of the limbs are removed during the measurements of flow time. The measured values of the kinematic viscosities were converted to dynamic viscosities after multiplication by the density. The reproducibility of the viscosity estimates was found to be within ±0.003 mPa s. A thermostatically controlled, well-stirred water bath where temperature was controlled to ±0.01 K was used for all the measurements.

Results

Results of measurements of excess molar volumes for 2-propoxyethanol + methanol, + 1-propanol, + 2-propanol, and + 1-pentanol and for 2-isopropoxyethanol + 2-propanol at 298.15 K are listed in Table 2 and graphically represented in Figure 1.

The V_m^E values are used to compute the densities ρ of the mixtures from

$$\rho = (x_1M_1 + x_2M_2)/(V_m^E + x_1V_1 + x_2V_2) \tag{1}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molar masses, and V_1 and V_2 are the molar volumes of ethers and alcohols, respectively.

The deviations of the viscosities were calculated from the following relationship (Aucejo et al., 1996; Heric, 1966)

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{2}$$

where η is the dynamic viscosity of the mixtures and η_1 and η_2 are the viscosities of components 1 and 2, respectively.

Data on derived densities and viscosities at 298.15 K are given in Table 3. The results of V_m^E and $\Delta \ln \eta$ for each mixture are fitted to the Redlich−Kister (1948) polynomial equation of the form

$$Y(x) = x_1x_2\sum_{i=1}^{n}A_i(x_1 - x_2)^i \tag{3}$$

where A_i is the polynomial coefficient and n is the polynomial degree. The values of the coefficients, A_i, obtained by the least-squares method, with all points weighted equally, are presented in Table 4 together with their standard

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

	V_m^E		V_m^E		V_m^E
x_1	$cm^3\ mol^{-1}$	x_1	$cm^3\ mol^{-1}$	x_1	$cm^3\ mol^{-1}$
2-Propoxyethanol (1) + Methanol (2)					
0.0060	−0.013	0.2313	−0.323	0.5655	−0.349
0.0129	−0.032	0.2462	−0.331	0.6068	−0.329
0.0339	−0.073	0.2747	−0.346	0.6531	−0.303
0.0462	−0.096	0.2852	−0.353	0.7217	−0.261
0.0626	−0.126	0.3002	−0.360	0.7629	−0.230
0.0954	−0.176	0.3444	−0.371	0.8175	−0.186
0.1230	−0.214	0.3807	−0.376	0.8482	−0.159
0.1570	−0.259	0.4313	−0.377	0.8822	−0.127
0.1895	−0.290	0.4884	−0.369	0.9123	−0.098
0.2134	−0.302	0.5250	−0.360	0.9721	−0.037
2-Propoxyethanol (1) + 1-Propanol (2)					
0.0100	−0.003	0.2636	−0.083	0.4813	−0.095
0.0454	−0.015	0.3019	−0.088	0.5549	−0.094
0.0781	−0.027	0.3248	−0.091	0.6329	−0.087
0.1143	−0.040	0.3540	−0.094	0.7555	−0.069
0.1499	−0.050	0.3629	−0.095	0.8496	−0.042
0.1923	−0.062	0.3824	−0.095	0.9834	−0.004
0.2258	−0.069	0.4112	−0.096		
0.2518	−0.081	0.4161	−0.096		
2-Propoxyethanol (1) + 2-Propanol (2)					
0.0301	−0.004	0.3337	−0.041	0.6023	−0.033
0.0756	−0.010	0.3773	−0.042	0.6643	−0.028
0.1335	−0.021	0.3908	−0.043	0.7170	−0.024
0.1712	−0.024	0.4096	−0.044	0.7708	−0.018
0.2212	−0.030	0.4344	−0.043	0.8609	−0.010
0.2506	−0.035	0.4605	−0.042	0.9336	−0.005
0.2914	−0.037	0.4633	−0.042	0.9678	−0.002
0.3094	−0.038	0.5356	−0.041		
2-Propoxyethanol (1) + 1-Pentanol (2)					
0.0172	0.004	0.3442	0.053	0.5579	0.055
0.0321	0.009	0.3629	0.054	0.6008	0.052
0.0649	0.015	0.3854	0.055	0.6666	0.048
0.0906	0.021	0.4002	0.055	0.7122	0.044
0.1133	0.025	0.4351	0.056	0.7769	0.035
0.1611	0.034	0.4515	0.056	0.8212	0.030
0.2021	0.040	0.4721	0.056	0.8785	0.021
0.2531	0.045	0.4951	0.057	0.9214	0.014
0.3058	0.050	0.5148	0.057	0.9796	0.004
2-Isopropoxyethanol (1) + 2-Propanol (2)					
0.0023	−0.002	0.3787	−0.010	0.6498	−0.012
0.0355	−0.004	0.3839	−0.010	0.7092	−0.011
0.0753	−0.006	0.4100	−0.011	0.7731	−0.010
0.1232	−0.007	0.4357	−0.011	0.8759	−0.008
0.1655	−0.008	0.4742	−0.012	0.9384	−0.006
0.2370	−0.008	0.5014	−0.013	0.9863	−0.003
0.2829	−0.009	0.5377	−0.015		
0.3330	−0.010	0.5707	−0.013		

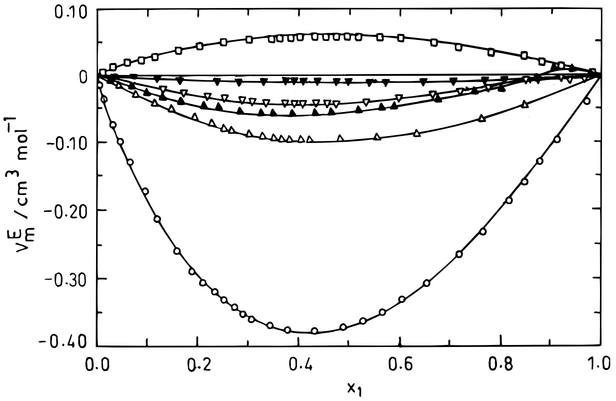

Figure 1. Excess molar volume V_m^E for 2-propoxyethanol (1) + methanol (2) (○), + 1-propanol (2) (△), + 2-propanol (2) (▽), and + 1-pentanol (2) (□) and for 2-isopropoxyethanol (1) + 1-propanol (2) (▲) (Pal and Sharma, 1998) and + 2-propanol (2) (▼) at 298.15 K. The solid curves have been drawn from eq 3.

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

x_1	ρ/g cm^{-3}	η/mPa s	x_1	ρ/g cm^{-3}	η/mPa s	x_1	ρ/g cm^{-3}	η/mPa s	x_1	ρ/g cm^{-3}	η/mPa s
2-Propoxyethanol (1) + Methanol (2)											
0.0024	0.7873	0.553	0.1590	0.8327	0.865	0.3895	0.8692	1.394	0.7153	0.8955	2.014
0.0177	0.7930	0.581	0.1826	0.8377	0.914	0.4426	0.8749	1.499	0.7701	0.8984	2.115
0.0410	0.8010	0.620	0.2208	0.8450	0.989	0.4816	0.8786	1.577	0.8053	0.9002	2.160
0.0504	0.8040	0.644	0.2613	0.8519	1.084	0.5329	0.8831	1.680	0.8437	0.9019	2.194
0.0697	0.8100	0.673	0.2874	0.8559	1.149	0.5596	0.8852	1.737	0.8812	0.9035	2.248
0.0903	0.8159	0.729	0.3049	0.8585	1.199	0.6366	0.8907	1.878	0.9415	0.9059	2.323
0.1252	0.8249	0.801	0.3410	0.8634	1.284	0.6677	0.8927	1.927	0.9884	0.9076	2.347
2-Propoxyethaol (1) + 1-Propanol (2)											
0.0085	0.8008	1.950	0.1295	0.8200	1.944	0.4185	0.8572	2.031	0.7324	0.8876	2.186
0.0212	0.8030	1.945	0.1570	0.8240	1.948	0.4527	0.8609	2.046	0.7821	0.8917	2.219
0.0386	0.8058	1.944	0.2095	0.8313	1.961	0.5174	0.8677	2.072	0.8530	0.8973	2.257
0.0573	0.8088	1.944	0.2715	0.8396	1.976	0.5743	0.8733	2.103	0.9063	0.9013	2.294
0.0817	0.8127	1.943	0.3230	0.8460	1.994	0.6243	0.8781	2.125	0.9599	0.9052	2.326
0.0917	0.8142	1.942	0.3675	0.8513	2.010	0.6804	0.8831	2.151			
2-Propoxyethanol (1) + 2-Propanol (2)											
0.0175	0.7843	2.056	0.2052	0.8166	1.967	0.4072	0.8456	1.997	0.7297	0.8829	2.159
0.0326	0.7871	2.039	0.2490	0.8233	1.967	0.4661	0.8532	2.019	0.7751	0.8875	2.192
0.0724	0.7943	2.009	0.2950	0.8301	1.970	0.5167	0.8594	2.041	0.8315	0.8929	2.230
0.0909	0.7976	1.994	0.3499	0.8379	1.977	0.5560	0.8640	2.061	0.8979	0.8990	2.275
0.1266	0.8038	1.980	0.3980	0.8444	1.993	0.6058	0.8697	2.084	0.9565	0.9043	2.318
0.1696	0.8109	1.971				0.6612	0.8758	2.119			
2-Propoxyethanol (1) + 1-Pentanol (2)											
0.0215	0.8133	3.463	0.2194	0.8330	2.928	0.5387	0.8642	2.574	0.8114	0.8903	2.404
0.0339	0.8145	3.418	0.2669	0.8376	2.847	0.5721	0.8674	2.548	0.8483	0.8938	2.389
0.0569	0.8168	3.355	0.3270	0.8436	2.776	0.6100	0.8710	2.524	0.8888	0.8976	2.374
0.0878	0.8199	3.254	0.3773	0.8485	2.720	0.6569	0.8755	2.493	0.9244	0.9009	2.363
0.1148	0.8226	3.179	0.4289	0.8535	2.667	0.7066	0.8803	2.458	0.9630	0.9045	2.353
0.1461	0.8257	3.103	0.4842	0.8589	2.610	0.7368	0.8832	2.441	0.9898	0.9070	2.350
0.1776	0.8288	3.025	0.4911	0.8596	2.608	0.7698	0.8863	2.426			
2-Isopropoxyethanol (1) + Methanol (2)											
0.0120	0.7906	0.569	0.1871	0.8354	0.897	0.4120	0.8668	1.324	0.7775	0.8916	1.832
0.0276	0.7958	0.602	0.2119	0.8399	0.946	0.4685	0.8722	1.415	0.8335	0.8939	1.912
0.0500	0.8027	0.637	0.2575	0.8474	1.036	0.5152	0.8760	1.485	0.8955	0.8963	1.975
0.0732	0.8093	0.684	0.2683	0.8491	1.056	0.5447	0.8783	1.529	0.9189	0.8972	2.003
0.1063	0.8179	0.749	0.3161	0.8558	1.145	0.6149	0.8830	1.624	0.9415	0.8980	2.032
0.1319	0.8239	0.795	0.3643	0.8617	1.235	0.6869	0.8872	1.719	0.9701	0.8989	2.064
0.1558	0.8291	0.842				0.7416	0.8899	1.789			
2-Isopropoxyethanol (1) + 1-Propanol (2)											
0.0192	0.8024	1.947	0.1486	0.8211	1.927	0.4251	0.8534	1.929	0.7000	0.8783	1.996
0.0257	0.8034	1.944	0.1863	0.8260	1.923	0.4749	0.8584	1.938	0.7606	0.8830	2.015
0.0450	0.8064	1.941	0.2438	0.8332	1.919	0.5261	0.8633	1.949	0.8023	0.8861	2.025
0.0645	0.8093	1.938	0.2942	0.8392	1.914	0.5659	0.8669	1.958	0.8623	0.8905	2.042
0.0810	0.8117	1.933	0.3545	0.8460	1.916	0.6184	0.8715	1.971	0.8845	0.8920	2.052
0.1072	0.8154	1.930	0.3782	0.8485	1.921	0.6608	0.8751	1.983	0.9485	0.8964	2.014
2-Isopropoxyethanol (1) + 2-Propanol (2)											
0.0272	0.7858	2.051	0.2006	0.8137	1.929	0.4259	0.8438	1.903	0.7300	0.8765	1.991
0.0618	0.7918	2.009	0.2467	0.8203	1.914	0.4507	0.8468	1.908	0.7886	0.8820	2.014
0.0768	0.7943	1.995	0.2976	0.8274	1.900	0.5015	0.8527	1.918	0.8718	0.8894	2.049
0.0920	0.7968	1.986	0.3502	0.8343	1.899	0.5529	0.8584	1.930	0.9241	0.8938	2.064
0.1373	0.8040	1.959	0.3949	0.8400	1.902	0.6181	0.8654	1.948	0.9782	0.8982	2.083
0.1766	0.8101	1.941				0.6764	0.8713	1.971			
2-Isopropoxyethanol (1) + 1-Pentanol (2)											
0.0159	0.8126	3.466	0.1931	0.8287	2.952	0.4848	0.8548	2.473	0.8198	0.8842	2.191
0.0312	0.8139	3.405	0.2267	0.8317	2.881	0.4956	0.8558	2.461	0.8573	0.8875	2.167
0.0461	0.8153	3.354	0.2585	0.8346	2.819	0.5246	0.8583	2.432	0.8964	0.8909	2.142
0.0653	0.8171	3.292	0.2966	0.8380	2.748	0.5561	0.8611	2.397	0.9259	0.8935	2.133
0.0867	0.8190	3.234	0.3417	0.8421	2.677	0.6012	0.8651	2.357	0.9558	0.8961	2.116
0.1097	0.8211	3.160	0.3843	0.8459	2.610	0.6643	0.8706	2.297	0.9775	0.8979	2.110
0.1370	0.8236	3.099	0.4446	0.8512	2.526	0.7168	0.8752	2.261			
0.1627	0.8259	3.029				0.7741	0.8802	2.218			

deviations, σ. $Y(x)$ represents V_m^E and $\Delta \ln \eta$. For all mixtures $\sigma(V_m^E) < 0.003$ for the precision attainable with the dilatometer used.

Correlating Equations

Several relations have been proposed to evaluate the dynamic viscosity η of liquid mixtures, and these are classified according to the numbers of adjustable parameters used to account for the deviation from some average (Irving, 1977). We will consider here some of the more commonly used semiempirical models for analyzing the viscosity of liquid mixtures based on zero, one, and two parameters. An attempt has been made to check the suitability of the equation for experimental data fits by taking into account the number of empirical adjustment-coefficients.

Table 4. Smoothing Coefficients A_i and Standard Deviations $\sigma[Y(x)]$ of Eq 3 for the Binary Mixtures at 298.15 K

$Y(x)$	A_1	A_2	A_3	$\sigma[Y(x)]$
2-Propoxyethanol (1) + Methanol (2)				
V_m^E/cm³ mol⁻¹	−1.4667	0.5000	−0.2598	0.002
Δ ln[η/mPa s]	1.4141	−0.3252	0.0616	0.007
2-Propoxyethanol (1) + 1-Propanol (2)				
V_m^E/cm³ mol⁻¹	−0.3940	0.0529	0.0481	0.002
Δ ln[η/mPa s]	−0.1456	0.0873	−0.0465	0.001
2-Propoxyethanol (1) + 2-Propanol (2)				
V_m^E/cm³ mol⁻¹	−0.1652	0.0704	0.0788	0.001
Δ ln[η/mPa s]	−0.3320	0.2204	−0.1236	0.002
2-Propoxyethanol (1) + 1-Pentanol (2)				
V_m^E/cm³ mol⁻¹	0.2250	−0.0326	−0.0003	0.001
Δ ln[η/mPa s]	−0.4016	0.1448	−0.0697	0.004
2-Isopropoxyethanol (1) + Methanol (2)				
Δ ln[η/mPa s]	1.2271	−0.5510	0.0660	0.003
2-Isopropoxyethanol (1) + 1-Propanol (2)				
Δ ln[η/mPa s]	−0.1664	0.0478	0.0025	0.002
2-Isopropoxyethanol (1) + 2-Propanol (2)				
V_m^E/cm³ mol⁻¹	−0.0473	−0.0121	−0.0361	0.001
Δ ln[η/mPa s]	−0.3450	0.2047	−0.0554	0.002
2-Isopropoxyethanol (1) + 1-Pentanol (2)				
Δ ln[η/mPa s]	−0.3984	0.0946	−0.0250	0.001

The equation of Kendall and Monroe (1917), which has no adjustable parameter, is expressed as

$$\eta = (x_1\eta_1^{1/3} + x_2\eta_2^{1/3})^3 \tag{4}$$

The equations of Grunberg-Nissan (1949), Tamura and Kurata (1952), Hind (1960), and Katti and Chaudhry (1964) have one adjustable parameter. Grunberg and Nissan (1949) provided the following empirical equation containing one adjustable parameter. The expression is

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2G_{12} \tag{5}$$

where G_{12} is a parameter proportional to the interchange energy. Tamura and Kurata (1952) developed the following expression for the viscosity of binary liquid mixtures

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12} \tag{6}$$

where ϕ_1 and ϕ_2 are the volume fractions and T_{12} is the interaction parameter. Hind et al. (1960) suggested the following equation

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \tag{7}$$

where H_{12} is attributed to unlike pair interactions.

Katti and Chaudhry (1964) derived the following equation

$$\ln \eta V = x_1 \ln V_1\eta_1 + x_2 \ln V_2\eta_2 + x_1x_2W_{\text{vis}}/RT \tag{8}$$

where W is an adjustable parameter and V_i is the molar volume of pure component i.

McAllister's (1960) two-parameter equation, based on Eyring's theory of absolute reaction rates, takes into account interactions of both like and unlike molecules by a two-dimensional three-body model. The equation is

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln Z_{12} + 3x_1x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + 3x_1^2x_2 \ln(2/3 + M_2/3M_1) + 3x_1^2x_2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1) \tag{9}$$

where Z_{12} and Z_{21} are interaction parameters and ν_i is the kinematic viscosity of pure component i.

To perform a numerical comparison of the correlating capability of eqs 4−9, we calculated the standard percentage deviation (σ/%) using the relation

$$\sigma\,(\%) = [(1/(p - k))\sum(100(\eta_{\text{exp}} - \eta_{\text{cal}})/\eta_{\text{exp}})^2]^{1/2} \tag{10}$$

where p represents the number of experimental data and k the number of numerical coefficients in the respective equations.

Discussion

For each of the mixtures studied, V_m^E is negative over the whole mole fraction range, with the exception of 1-pentanol with 2-propoxyethanol. There are striking differences between the curves of the excess molar volumes for 2-propoxyethanol + 1-propanol or 2-propanol and 2-isopropoxyethanol + 1-propanol and 2-propanol mixtures, as is evident in Figure 1. The excess molar volumes of the former systems are more negative than those of the latter ones. That is, branching of the alkyl chain at the carbon, as in 2-isopropoxyethanol, results in an increase in V_m^E with 1-propanol and 2-propanol. Further, because of the steric hindrance of the alkyl groups in 2-propanol, the strength of interaction is expected to decrease with straight chain and branched ethers. Figure 1 also shows the excess molar volumes of 2-isopropoxyethanol + 1-propanol mixtures (Pal and Sharma, 1998). The excess molar volumes for this system are negative at high mole fraction of 1-propanol. Again, one can generate a comparison of 2-propoxyethanol and 2-isopropoxyethanol either with 1-propanol or 2-propanol systems. The most striking feature of Figure 1 is the strong similarity between the composition dependence curves of the two propoxyethanol + 2-propanol systems, which is in sharp contrast to the differences between the two propoxyethanol + 1-propanol curves. The excess molar volumes become progressively less negative with the branching of the alkyl chain at the α carbon, with the exception of methanol system. This behavior may be compared with the V_m^E results for the mixtures 2-propoxyethanol and 2-isopropoxyethanol with water (Roux, 1982; Davis and Chacon, 1991) or 1-propanol and 2-propanol with water (Davis and Ham, 1991): branching of the alkyl chain at the α carbon leads to more negative excess molar volumes. These results, and those from Pal and Sharma (1998), show that, for mixtures of *n*-alkanols with 2-propoxyethanol or 2-isopropoxyethanol, the V_m^E increases with the increasing of the chain length of the *n*-alkanol. That is, with increasing the chain length of the *n*-alkanol, the strength of the specific interaction between unlike molecules is expected to decrease or become less important: V_m^E increases and becomes positive for the larger *n*-alkanols.

We have determined the viscosities (η) and calculated the deviations in viscosity (Δ ln η) for the different binary mixtures over the whole mole fraction range. Figures 2 and 3 illustrate that the viscosity deviations are negative for all mixtures except in 2-propoxyethanol or 2-isopropoxyethanol + methanol systems. For each ether, the magnitude of the negative deviations increases as the alkyl chain

Table 5. Values of the Parameters and Standard Percentage Deviations for the Binary Mixtures Represented by Eqs 5−9 and 4−9

	eq 4	eq 5		eq 6		eq 7		eq 8		eq 9		
	σ/%	G_{12}	σ/%	T_{12}	σ/%	H_{12}	σ/%	W_{vis}/RT	σ/%	Z_{12}	Z_{21}	σ/%
2-propoxyethanol (1) +												
methanol (2)	16.59	1.27	3.86	1.34	4.29	1.69	3.14	1.97	3.59	2.46	2.00	2.26
1-propanol (2)	2.82	−0.16	0.64	1.97	0.31	1.97	0.55	−0.07	0.56	2.47	2.29	0.20
2-propanol (2)	6.97	−0.37	1.64	1.84	0.99	1.82	1.50	−0.29	1.57	2.49	2.16	0.43
1-pentanol (2)	8.00	−0.41	1.10	2.28	1.59	2.26	1.68	−0.41	1.09	2.81	3.02	0.45
2-isopropoxyethanol (1) +												
methanol (2)	15.01	1.27	3.86	1.29	2.19	1.56	1.06	1.78	5.03	1.93	2.02	0.51
1-propanol (2)	3.09	−0.17	0.73	1.88	0.70	1.86	0.73	−0.08	0.71	2.26	2.24	0.71
2-propanol (2)	6.95	−0.37	1.45	1.76	0.94	1.72	1.46	−0.28	1.37	2.31	2.10	0.24
1-pentanol (2)	8.06	−0.41	0.66	2.13	1.34	2.10	1.45	−0.40	0.66	2.59	2.98	0.15

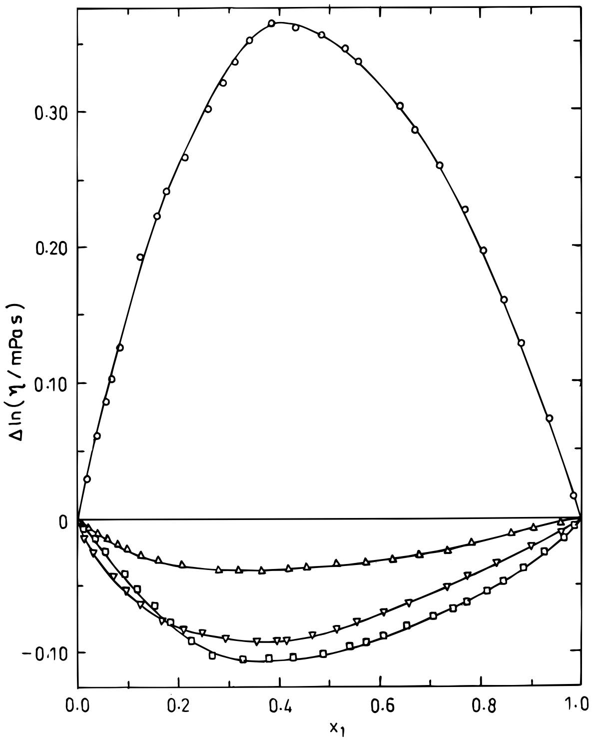

Figure 2. Viscosity deviations $\Delta \ln \eta$ for 2-propoxyethanol (1) + methanol (2) (○), + 1-propanol (2) (△), + 2-propanol (2) (▽), and + 1-pentanol (2) (□) at 298.15 K. The solid curves have been drawn from eq 3.

length or viscosity of the *n*-alkanol increased. Similar behavior exists for $\Delta \ln \eta$ of 2-propoxyethanol + 2-propanol and 2-isopropoxyethanol + 2-propanol. The positive $\Delta \ln \eta$ suggests the specific interactions present in the mixtures (Fort and Moore, 1966). The strong positive deviations in the viscosity for 2-propoxyethanol or 2-isopropoxyethanol−methanol binary mixtures would imply that (i) the mixture is more viscous than the corresponding ideal mixture and (ii) the specific interactions results in a negative V_m^E, as shown in Figure 1. In fact, the $\Delta \ln \eta$ values are more positive in 2-propoxyethanol + methanol mixtures than in 2-isopropoxyethanol + methanol. This reveals that the strength of the specific interactions is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular sizes and shapes of the components are equally important factors.

The results of the correlating equations (eqs 4−9) are complied in Table 5. The values of the different adjustable parameters are reported in Table 5 together with the percentage standard deviations (σ/%) between the calculated and experimental values. The values of σ are in the range from 3.1 to 16.6% for eq 4 without any adjustable parameter; from 0.3 to 5.0% for the single-parameter equations (eqs 5−8); and from 0.2 to 2.3% for the two-parameter equation (eq 9). On analysis of the results of eqs 5−8 in Table 5, the two equations (eqs 5 and 8) of Grunberg-Nissan and Katti and Chaudhry give nearly identical results except for 2-isopropoxyethanol−methanol. Both Tamura and Kurata (1952) (eq 6) and Hind et al. (1960) (eq 7) represent the behavior of binary mixtures with lower alcohols satisfactorily as compared to Grunberg and Nissan (1948) (eq 5) and Katti and Chaudhry (1964) (eq 8). But with the 2-propanol system, the equations of Tamura and Kurata (1952) (eq 6) and Katti and Chaudhry (1964) (eq 8) are more suitable when the values of σ (%) are lower than that of the one-parameter equations (eqs 5 and 7). Use of the two-parameter equation (eq 9) reduces the σ (%) values significantly below that of the single-parameter equations. From this study, it can be concluded that the correlating ability significantly improves for those nonideal systems as the number of adjustable parameters is increased.

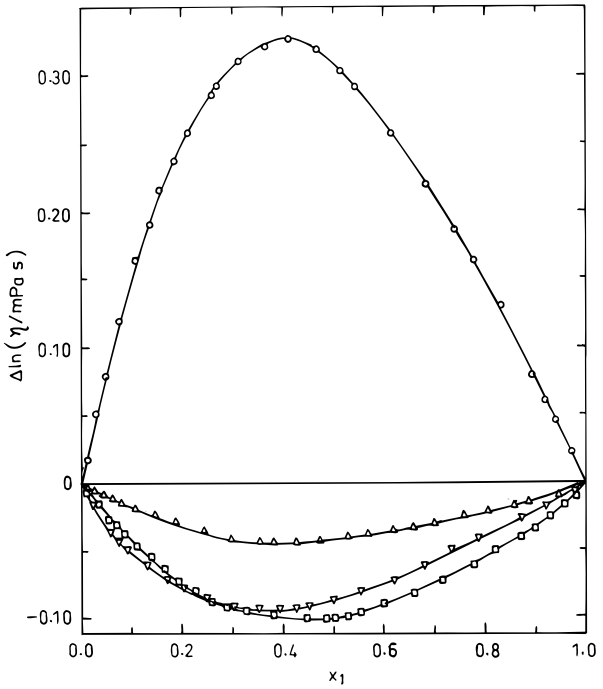

Figure 3. Viscosity deviations $\Delta \ln \eta$ for 2-isopropoxyethanol (1) + methanol (2) (○), + 1-propanol (2) (△), + 2-propanol (2) (△), and + 1-pentanol (2) (□) at 298.15 K. The solid curves have been drawn from eq 3.

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