Excess Molar Volumes and Viscosities for Binary Mixtures of 2-Propoxyethanol and of 2-Isopropoxyethanol with Propylamine and Dipropylamine at (298.15, 308.15, and 318.15) K

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Excess molar volumes V_m^E and viscosities η have been measured as a function of composition for the binary mixtures of 2-propoxyethanol and of 2-isopropoxyethanol with propylamine and dipropylamine at (298.15, 308.15, and 318.15) K. From the experimental data, the deviation in the viscosity η from $\sum x_i \ln \eta_i$ has been calculated at various temperatures. The excess molar volumes are negative whereas the deviation in the viscosities is positive for all investigated systems over the whole composition range. These results suggest that the stronger hydrogen bonds between unlike molecules reduce the volume of the solution and make the solution high viscosity. A Redlich−Kister type equation was applied to fit the excess volumes and viscosity deviations, and McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities.

Introduction

The thermodynamic properties of binary mixtures of butylamine, dibutylamine, or tributylamine with a straight chain, branched-chain, or cyclic ether have been extensively studied with the aim of a better understanding about the association behavior of the amine and the ether.[1−5] A few studies involving binary amine/alcohol systems have been carried out by some other authors.[6−8]

As part of our program of research on thermodynamic, acoustic, and transport properties of binary mixtures containing branched ethers, we have recently reported excess molar volumes, viscosities, and speed of sound measurements of binary mixtures of branched ethers with water and alcohols.[9−13] In this paper, we report new experimental data of the excess molar volumes V_m^E and vicosities η of binary solvent mixtures containing 2-propoxyethanol or 2-isopropoxyethanol with propylamine and dipropylamine over the whole mole fraction range at (298.15, 308.15, and 318.15) K and atmospheric pressure. The present study was undertaken to assess whether the thermophysical properties of the 2-isopropoxyethanol + primaryamine system resemble those of the *n*-alkoxyethanols + primary amine system.[14] An attempt is also made to compare the excess molar properties of 2-propoxyethanol + propylamine or dipropylamine with those of 2-isopropoxyethanol + propylamine or dipropylamine. The effect of temperature and of specific interactions on the excess properties, the dependence on the position of the CH_3 group in the propoxyethanol, and the influence of primary to secondary amine are analyzed.

Experimental Section

Materials. 2-Isopropoxyethanol (Merck-Schuchardt, FRG, GC>98 mol %), 2-propoxyethanol (Acros, USA, 98 mol %), and propylamine (Merck-Schuchardt, FRG, GC>99 mol %) were the same as those used in our earlier studies (Pal et al., 2000; Pal and Dass, 2000). The dipropylamine was obtained from Merck-Schuchardt, FRG, with purity better than 99 mol % and was used directly. Prior to measurements, all liquids were partially degassed under vacuum and dried over 0.4 nm molecular sieves (Fluka, AG) to reduce water content. The densities and viscosities of these liquids are measured and compared at (298.15 ± 0.01) K and atmospheric pressure with their corresponding literature values,[15−18] as shown in Table 1. The densities of pure liquids 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[15]	2.106	
		0.899680[16]		
		0.8996[17]		
propylamine	0.7122	0.7121[18]	0.356	0.353[18]
dipropylamine	0.7334	0.7329[18]	0.503	

Apparatus and Procedure. Excess molar volumes, which are reproducible to ±0.003 cm^3 mol^{-1}, were measured by means of a continuous dilution dilatometer in a fashion similar to that described by Dickinson et al.[19] Details of its calibration, the experimental setup, and the operational procedures have been described previously.[20] Each run covered just over half of the mole fraction range, giving an overlap between two runs.

The kinematic viscosities of both the pure liquids and liquid mixtures were measured at (298.15, 308.15, and

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318.15) K, and atmospheric pressure was measured using an Ubbelohde suspended level viscometer. Experimental details have been given previously.[21,22] 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 was measured with an accurate stopwatch with a resolution of 0.01 s. Four or five sets of readings for the flow times were taken for the purpose of calculation of viscosity. The caps of the limbs are removed during the measurements of flow times. The measured values of kinematic viscosities (ν) were converted to dynamic viscosities (η) after multiplication by the density. The reproducibility of the viscosity estimates was found to be within ±0.003 mPa s. The mole fraction of each mixture was obtained to an accuracy of 1×10^{-4} from the measured apparent masses of the components. All measurements were corrected for buoyancy. All the measurements were carried out in a thermostat controlled well-stirred water bath, whose temperature was controlled to ±0.01 K.

Results and Discussion

Results of measurements of excess molar volumes and viscosities of the different binary mixtures for a number of mole fractions at (298.15, 308.15, and 318.15) K and at atmospheric pressure are given in Tables 2 and 3.

The densities of liquid mixtures were obtained from the densities of the pure liquid components and measurements on V_m^E for their binary mixtures according to the equation

$$\rho = (x_1M_1 + x_2M_2)/(V_m^E + x_1V_1^\circ + x_2V_2^\circ) \qquad (1)$$

where M_1 and M_2 represent molar masses.

The deviation of the viscosity has been calculated from the following relationship.[23, 24]

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (2)$$

where x_1 and x_2 are the mole fractions, η is the dynamic viscosity of the mixture, and η_1 and η_2 are the viscosities of components 1 and 2, respectively.

The excess molar volumes and deviations in viscosity at various temperatures for all mixtures were represented mathematically by the Redlich−Kister polynomial

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

where A_i are the polynomial coefficients 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 the standard deviations, σ. $Y(x)$ refers to V_m^E/cm^3 mol^{-1} and $\Delta\ln[\eta$/mPa s]. For all mixtures, $\sigma(V_m^E) \leq 0.003$ for the precision attainable with the dilatometer used.

Figures 1 and 2 show V_m^E and $\Delta \ln \eta$ data for the four different mixtures at 298.15 K. We have not included the experimental data at (308.15 or 318.15) K due to overcrowding on the graph. For each of the mixtures studied, V_m^E is negative over the whole mole fraction range at all three temperatures. This behavior is consistent with the H_m^E results for (a primary or a secondary amine + an alkanol):[25,26] intermolecular interactions between the NH group of the amine molecule and the OH group of the alkanol molecule lead to more negative excess enthalpies. We assume that cross complexes in ether/amine mixtures have the structure N···H−O, where interaction predominates over the hydrogen bonding between the like molecules. The value of V_m^E decreases with a rise of temperatures for all of the mixtures.

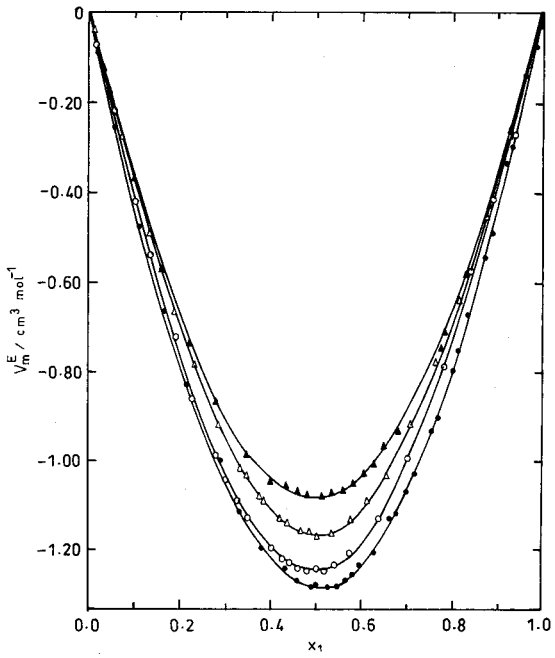

Figure 1. Comparison of the excess molar volumes V_m^E at 298.15 K for 2-propoxyethanol (1) + propylamine (2) (○), 2-propoxyethanol (1) + dipropylamine (2) (●), 2-isopropoxyethanol (1) + propylamine (2) (△), and 2-isopropoxyethanol (1) + dipropylamine (2) (▲). The solid curves have been drawn from eq 3.

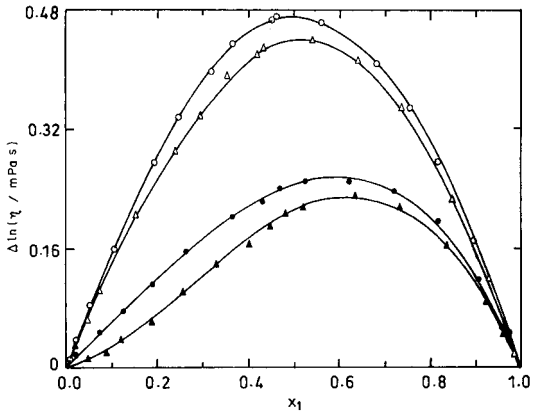

Figure 2. Viscosity deviations $\Delta \ln \eta$ at 298.15 K for 2-propoxyethanol (1) + propylamine (2) (○), 2-propoxyethanol (1) + dipropylamine (2) (●), 2-isopropoxyethanol (1) + propylamine (2) (△), and 2-isopropoxyethanol (1) + dipropylamine (2) (▲). The solid curves have been drawn from eq 3.

There are striking differences in the variation of V_m^E at equimolar concentrations for 2-propoxyethanol + propylamine or dipropylamine and 2-isopropoxyethanol + propylamine or dipropylamine mixtures, as is evident in Figure 1. The excess molar volumes of the former systems are more negative than those of the later ones. That is, branching of the alkyl chain at the carbon, as in 2-isopropoxyethanol, results in an increase in V_m^E with propylamine or dipropylamine. This is probably due to the inductive effect of the alkyl group in the branched-chain ethers, which increases the electron density in the oxygen atom, resulting in an energetically favored[27] cross-bonding N···H−O compared to N−H···O. However, this is very important with (2-propoxyethanol + propylamine), which results in high negative values of V_m^E compared to those

Table 2. Excess Molar Volumes V_m^E for the Binary Mixtures at Various Temperatures

x_1	V_m^E / cm^3 mol^{-1}	x_1	V_m^E / cm^3 mol^{-1}	x_1	V_m^E / cm^3 mol^{-1}	x_1	V_m^E / cm^3 mol^{-1}	x_1	V_m^E / cm^3 mol^{-1}	x_1	V_m^E / cm^3 mol^{-1}
2-Propoxyethanol (1) + Propylamine (2)											
298.15 K											
0.0174	−0.076	0.3461	−1.124	0.5425	−1.232	0.2298	−0.857	0.4608	−1.243	0.8427	−0.573
0.0511	−0.217	0.3829	−1.184	0.5713	−1.208	0.2782	−0.989	0.4827	−1.245	0.8876	−0.414
0.1010	−0.420	0.3997	−1.196	0.6381	−1.125	0.3030	−1.043	0.5007	−1.242	0.9382	−0.230
0.1339	−0.540	0.4297	−1.223	0.7015	−0.996	0.3235	−1.085	0.5212	−1.245		
0.1835	−0.720	0.4372	−1.227	0.7768	−0.787						
308.15 K											
0.0256	−0.124	0.3685	−1.270	0.5350	−1.366	0.2764	−1.078	0.4413	−1.362	0.8401	−0.675
0.0533	−0.250	0.3704	−1.282	0.5580	−1.351	0.2935	−1.123	0.4705	−1.376	0.9113	−0.394
0.1006	−0.456	0.3918	−1.321	0.6231	−1.280	0.3203	−1.180	0.4807	−1.372	0.9645	−0.161
0.1612	−0.707	0.3970	−1.316	0.6794	−1.170	0.3362	−1.221	0.5099	−1.374		
0.2246	−0.922	0.4325	−1.355	0.7604	−0.947						
318.15 K											
0.0167	−0.097	0.4207	−1.397	0.6416	−1.304	0.2359	−1.051	0.5148	−1.425	0.7802	−0.968
0.0463	−0.264	0.4429	−1.408	0.6455	−1.297	0.2756	−1.165	0.5427	−1.409	0.8617	−0.668
0.0898	−0.491	0.4775	−1.424	0.6844	−1.225	0.3292	−1.280	0.5563	−1.403	0.9040	−0.484
0.1395	−0.705	0.4948	−1.430	0.6870	−1.217	0.3883	−1.364	0.5713	−1.394	0.9623	−0.203
0.1858	−0.891	0.5136	−1.425	0.7272	−1.115	0.3920	−1.370	0.6390	−1.311	0.9663	−0.182
2-Propoxyethanol (1) + Dipropylamine (2)											
298.15 K											
0.0221	−0.089	0.5251	−1.279	0.7643	−0.898	0.3338	−1.111	0.6254	−1.205	0.9232	−0.330
0.0614	−0.251	0.5452	−1.277	0.7982	−0.793	0.3786	−1.181	0.6510	−1.163	0.9324	−0.296
0.1154	−0.467	0.5674	−1.260	0.8148	−0.746	0.4303	−1.242	0.6754	−1.120	0.9626	−0.166
0.1693	−0.661	0.5760	−1.260	0.8357	−0.668	0.4584	−1.264	0.6998	−1.064	0.9837	−0.075
0.2215	−0.825	0.5828	−1.250	0.8702	−0.543	0.4922	−1.277	0.7182	−1.026	0.9929	−0.029
0.3083	−1.057	0.5931	−1.235	0.8842	−0.488	0.5008	−1.277	0.7557	−0.927		
308.15 K											
0.0234	−0.110	0.4378	−1.285	0.6716	−1.140	0.3466	−1.176	0.5413	−1.297	0.8716	−0.554
0.0846	−0.384	0.4847	−1.312	0.6954	−1.093	0.3483	−1.179	0.5960	−1.260	0.9249	−0.335
0.1816	−0.750	0.4871	−1.309	0.7189	−1.034	0.3885	−1.244	0.6269	−1.218	0.9850	−0.071
0.2582	−0.987	0.5376	−1.306	0.7889	−0.838	0.4287	−1.281	0.6658	−1.150		
318.15 K											
0.0116	−0.054	0.4343	−1.331	0.6321	−1.265	0.2804	−1.074	0.5445	−1.347	0.8267	−0.765
0.0550	−0.263	0.4513	−1.342	0.6658	−1.207	0.3116	−1.145	0.5783	−1.320	0.9039	−0.455
0.0891	−0.414	0.4802	−1.353	0.6740	−1.190	0.3689	−1.254	0.5899	−1.318	0.9304	−0.337
0.1504	−0.663	0.5058	−1.359	0.7338	−1.051	0.4019	−1.303	0.6271	−1.266	0.9745	−0.127
0.2354	−0.953	0.5282	−1.354	0.7804	−0.920						
2-Isopropoxyethanol (1) + Propylamine (2)											
298.15 K											
0.0114	−0.042	0.3785	−1.083	0.6157	−1.088	0.2324	−0.782	0.4845	−1.155	0.8713	−0.449
0.0308	−0.118	0.3823	−1.084	0.6550	−1.026	0.2850	−0.910	0.4993	−1.164	0.9245	−0.266
0.0735	−0.274	0.4221	−1.129	0.7077	−0.915	0.3340	−1.010	0.5325	−1.160	0.9684	−0.113
0.1355	−0.486	0.4319	−1.135	0.7629	−0.775	0.3449	−1.029	0.5732	−1.128		
0.1877	−0.658	0.4658	−1.155	0.8122	−0.636						
308.15 K											
0.0164	−0.055	0.3602	−1.110	0.5919	−1.186	0.2165	−0.738	0.4648	−1.227	0.8892	−0.392
0.0512	−0.170	0.3927	−1.165	0.6689	−1.057	0.2631	−0.881	0.4965	−1.235	0.9334	−0.232
0.0962	−0.329	0.4098	−1.183	0.7564	−0.837	0.3076	−1.001	0.5069	−1.239		
0.1610	−0.552	0.4408	−1.221	0.8169	−0.648	0.3550	−1.100	0.5490	−1.230		
318.15 K											
0.0148	−0.074	0.3810	−1.235	0.6091	−1.227	0.2364	−0.932	0.5092	−1.299	0.8476	−0.621
0.0357	−0.169	0.4064	−1.263	0.6459	−1.163	0.2910	−1.075	0.5570	−1.283	0.9014	−0.416
0.0607	−0.282	0.4446	−1.294	0.6853	−1.089	0.3533	−1.191	0.5597	−1.280	0.9734	−0.118
0.0975	−0.438	0.4624	−1.300	0.7341	−0.978	0.3665	−1.216	0.5909	−1.244		
0.1903	−0.786	0.5086	−1.299	0.7769	−0.855						
2-Isopropoxyethanol (1) + Dipropylamine (2)											
298.15 K											
0.0436	−0.170	0.4572	−1.068	0.6458	−0.975	0.2718	−0.862	0.5601	−1.063	0.8268	−0.588
0.0977	−0.366	0.4775	−1.073	0.6773	−0.927	0.3496	−0.977	0.5828	−1.048	0.8797	−0.423
0.1606	−0.569	0.5111	−1.075	0.7707	−0.741	0.3997	−1.038	0.6054	−1.026	0.9280	−0.260
0.2218	−0.735	0.5366	−1.072	0.7812	−0.707	0.4361	−1.063	0.6262	−1.002	0.9633	−0.135
308.15 K											
0.0208	−0.083	0.4615	−1.112	0.6562	−0.934	0.2809	−0.899	0.5646	−1.093	0.9212	−0.292
0.0662	−0.262	0.4837	−1.118	0.7316	−0.839	0.3305	−0.989	0.6017	−1.061	0.9701	−0.117
0.1110	−0.426	0.5140	−1.120	0.7677	−0.755	0.3834	−1.057	0.6047	−1.059		
0.1686	−0.610	0.5241	−1.110	0.8221	−0.610	0.4333	−1.097	0.6532	−0.996		
0.2288	−0.778	0.5608	−1.102	0.8668	−0.475						
318.15 K											
0.0199	−0.090	0.4341	−1.163	0.6484	−1.076	0.2476	−0.881	0.5363	−1.183	0.8864	−0.466
0.0707	−0.303	0.4644	−1.185	0.6955	−0.999	0.2824	−0.951	0.5713	−1.163	0.9230	−0.326
0.1125	−0.467	0.4776	−1.190	0.7482	−0.885	0.3314	−1.048	0.5945	−1.143	0.9727	−0.120
0.1682	−0.652	0.5067	−1.192	0.7989	−0.746	0.3827	−1.117	0.6003	−1.137		
0.2070	−0.775	0.5355	−1.185	0.8442	−0.605	0.4281	−1.160	0.6291	−1.102		

Table 3. Densities ρ and Viscosities η for the Binary Mixtures at Various Temperatures

	298.15 K		308.15 K		318.15 K	
X	ρ/g cm^{-3}	η/mPa s	ρ/g cm^{-3}	η/mPa s	ρ/g cm^{-3}	η/mPa s
2-Propoxyethanol (1) + Propylamine (2)						
0.0000	0.7122	0.356	0.7012	0.328	0.6904	0.291
0.0069	0.7143	0.365	0.7033	0.336	0.6926	0.296
0.0201	0.7182	0.383	0.7074	0.346	0.6967	0.307
0.0540	0.7282	0.429	0.7176	0.385	0.7071	0.335
0.1049	0.7428	0.509	0.7325	0.446	0.7221	0.382
0.1955	0.7675	0.678	0.7575	0.574	0.7472	0.481
0.2496	0.7813	0.797	0.7715	0.668	0.7611	0.550
0.3215	0.7986	0.969	0.7891	0.800	0.7786	0.655
0.3686	0.8093	1.103	0.7999	0.895	0.7893	0.722
0.4528	0.8271	1.338	0.8178	1.075	0.8073	0.853
0.4581	0.8282	1.355	0.8189	1.088	0.8083	0.862
0.5595	0.8473	1.629	0.8382	1.289	0.8278	1.015
0.6789	0.8670	1.925	0.8581	1.510	0.8480	1.175
0.7520	0.8777	2.082	0.8689	1.628	0.8590	1.265
0.8162	0.8864	2.191	0.8776	1.715	0.8678	1.320
0.8943	0.8961	2.282	0.8873	1.803	0.8776	1.385
0.9697	0.9047	2.333	0.8959	1.867	0.8859	1.435
1.0000	0.9080	2.351	0.8992	1.895	0.8890	1.448
2-Propoxyethanol (1) + Dipropylamine (2)						
0.0000	0.7334	0.503	0.7248	0.444	0.7154	0.386
0.0247	0.7376	0.530	0.7290	0.463	0.7196	0.401
0.0750	0.7462	0.592	0.7376	0.511	0.7282	0.435
0.1250	0.7549	0.657	0.7462	0.564	0.7368	0.473
0.1902	0.7663	0.753	0.7576	0.636	0.7482	0.529
0.2692	0.7802	0.889	0.7715	0.737	0.7620	0.602
0.3692	0.7979	1.090	0.7891	0.883	0.7795	0.709
0.4334	0.8093	1.228	0.8005	0.985	0.7908	0.782
0.4760	0.8168	1.329	0.8080	1.058	0.7983	0.833
0.5289	0.8261	1.463	0.8173	1.153	0.8075	0.903
0.6230	0.8425	1.686	0.8338	1.318	0.8240	1.021
0.7230	0.8599	1.940	0.8513	1.507	0.8413	1.157
0.8063	0.8752	2.136	0.8666	1.656	0.8566	1.269
0.8114	0.8916	2.293	0.8830	1.780	0.8729	1.362
0.9598	0.9009	2.322	0.8923	1.846	0.8821	1.413
0.9731	0.9033	2.333	0.8945	1.863	0.8844	1.428
1.0000	0.9080	2.351	0.8992	1.895	0.8890	1.448
2-Isopropoxyethanol (1) + Propylamine (2)						
0.0000	0.7122	0.356	0.7012	0.328	0.6904	0.291
0.0207	0.7182	0.381	0.7072	0.347	0.6966	0.305
0.0475	0.7258	0.413	0.7149	0.372	0.7044	0.328
0.0745	0.7334	0.451	0.7225	0.398	0.7122	0.350
0.1534	0.7546	0.575	0.7439	0.493	0.7339	0.425
0.2413	0.7766	0.732	0.7662	0.615	0.7563	0.517
0.2917	0.7885	0.841	0.7783	0.702	0.7684	0.578
0.3559	0.8027	0.992	0.7928	0.808	0.7829	0.662
0.4223	0.8164	1.147	0.8067	0.935	0.7969	0.746
0.4366	0.8193	1.183	0.8096	0.966	0.7998	0.767
0.5416	0.8386	1.445	0.8292	1.145	0.8197	0.905
0.6413	0.8548	1.681	0.8455	1.319	0.8365	1.032
0.7365	0.8686	1.875	0.8592	1.464	0.8507	1.142
0.8564	0.8839	2.047	0.8746	1.577	0.8664	1.252
0.9246	0.8917	2.077	0.8826	1.617	0.8744	1.283
0.9899	0.8988	2.099	0.8901	1.645	0.8815	1.309
1.0000	0.8999	2.106	0.8912	1.649	0.8825	1.315
2-Isopropoxyethanol (1) + Dipropylamine (2)						
0.0000	0.7334	0.503	0.7248	0.444	0.7154	0.386
0.0484	0.7412	0.544	0.7326	0.476	0.7233	0.410
0.0855	0.7472	0.581	0.7386	0.505	0.7294	0.435
0.1225	0.7533	0.625	0.7446	0.534	0.7355	0.458
0.1899	0.7644	0.704	0.7557	0.599	0.7466	0.502
0.2514	0.7746	0.798	0.7659	0.671	0.7569	0.555
0.3234	0.7866	0.918	0.7780	0.760	0.7690	0.617
0.3933	0.7984	1.046	0.7897	0.855	0.7807	0.685
0.4465	0.8073	1.154	0.7987	0.941	0.7897	0.747
0.4820	0.8133	1.237	0.8046	1.001	0.7957	0.785
0.5205	0.8197	1.313	0.8111	1.058	0.8022	0.830
0.6318	0.8384	1.571	0.8298	1.242	0.8209	0.959
0.7300	0.8549	1.776	0.8462	1.381	0.8374	1.076
0.8358	0.8725	1.959	0.8639	1.516	0.8552	1.187
0.9190	0.8864	2.057	0.8777	1.595	0.8690	1.268
0.9596	0.8932	2.087	0.8845	1.618	0.8758	1.292
1.0000	0.8999	2.106	0.8912	1.649	0.8825	1.315

Table 4. Smoothing Coefficients A_i and Standard Deviations $\sigma\{Y(x)\}$ of Eq 3 for the Binary Mixtures at Various Temperatures

$Y(x)$	A_1	A_2	A_3	A_4	A_5	$\sigma\{Y(x)\}$
2-Propoxyethanol (1) + Propylamine (2)						
298.15 K						
V_m^E/cm^3 mol^{-1}	−4.989	0.213	0.965	0.166		0.003
Δ ln{η/mPa s}	1.890	0.070	−0.248	−0.014		0.004
308.15 K						
V_m^E/cm^3 mol^{-1}	−5.510	0.115	0.848			0.003
Δ ln{η/mPa s}	1.580	0.050	−0.367	0.049		0.003
318.15 K						
V_m^E/cm^3 mol^{-1}	−5.707	0.163	−0.111	0.096		0.003
Δ ln{η/mPa s}	1.425	0.109	−0.415	0.052	0.146	0.002
2-Propoxyethanol (1) + Dipropylamine (2)						
298.15 K						
V_m^E/cm^3 mol^{-1}	−5.124	−0.205	0.768	0.112		0.003
Δ ln{η/mPa s}	0.973	0.422	0.054	0.024		0.003
308.15 K						
V_m^E/cm^3 mol^{-1}	−5.242	0.035	0.513			0.003
Δ ln{η/mPa s}	0.722	0.304	0.093	−0.079	−0.245	0.003
318.15 K						
V_m^E/cm^3 mol^{-1}	−5.432	−0.081	0.377			0.002
Δ ln{η/mPa s}	0.578	0.275	0.070	0.001	−0.187	0.002
2-Isopropoxyethanol (1) + Propylamine (2)						
298.15 K						
V_m^E/cm^3 mol^{-1}	−4.645	0.033	1.046	0.146		0.003
Δ ln{η/mPa s}	1.757	0.194	−0.181	0.007		0.003
308.15 K						
V_m^E/cm^3 mol^{-1}	−4.962	−0.040	1.727	−0.086		0.003
Δ ln{η/mPa s}	1.515	0.223	−0.321	0.033		0.003
318.15 K						
V_m^E/cm^3 mol^{-1}	−5.215	0.214	0.574	−0.046		0.003
Δ ln{η/mPa s}	1.275	0.135	−0.112	0.037		0.003
2-Isoropoxyethanol (1) + Dipropylamine (2)						
298.15 K						
V_m^E/cm^3 mol^{-1}	−4.317	0.049	0.372	0.120		0.003
Δ ln{η/mPa s}	0.847	0.596	−0.109	−0.030		0.003
308.15 K						
V_m^E/cm^3 mol^{-1}	−4.474	0.136	0.487	0.028		0.003
Δ ln{η/mPa s}	0.728	0.537	−0.246	−0.114	0.038	0.003
318.15 K						
V_m^E/cm^3 mol^{-1}	−4.753	0.006	0.216	0.059		0.003
Δ ln{η/mPa s}	0.487	0.402	−0.039	−0.003		0.003

for (2-isopropoxyethanol + propylamine). On the other hand, the V_m^E values obtained for the mixture (2-propoxyethanol + dipropylamine) are more negative than those obtained with (2-propoxyethanol + propylamine) at 298.15 K. This is due to strong association between the nitrogen atom acting as proton acceptor and the OH group of the ether molecule. However, results in Table 2 show that V_m^E values for (2-propoxyethanol + propylamine) are much more negative than those for (2-propoxyethanol + dipropylamine) at 308.15 K and 318.15 K, indicating that the association between the propylamine and the ether is much greater than that between the dipropylamine and the ether at higher temperatures. A similar effect on H_m^E was seen with (butylamine or dibutylamine + straight chain ethers):[1,3] with secondary amine H_m^E is much more positive, indicating less association than that between the butylamine and the ether. Further, the strength of interaction is expected to decrease with straight chain and branched ethers at 308.15 K and 318.15 K with the increasing number of C_3H_7 groups attached to the nitrogen or the amine hydrogen in dipropylamine. In general, the longer the alkyl group of the straight chain ether,[14] the stronger is the association with propylamine. Again, one can generate a comparison

Table 5. Correlated Results of McAllister's Models

		three-body model			four-body model			
system	T/K	Z_{12}	Z_{21}	AAD%	Z_{1112}	Z_{1122}	Z_{2221}	AAD%
2-propoxyethanol + propylamine	298.15	2.7435	1.5158	0.59	2.5637	2.8404	1.0852	0.21
	308.15	2.0970	1.2101	0.84	1.9381	2.3299	0.8764	0.22
	318.15	1.6476	0.9635	0.79	1.5241	1.8250	0.7240	0.17
2-propoxyethanol + dipropylamine	298.15	2.6358	1.2753	0.23	2.6600	1.8173	1.1062	0.20
	308.15	1.9038	1.0916	0.58	1.9539	1.4785	0.9196	0.21
	318.15	1.4850	0.8559	0.18	1.5091	1.1583	0.7571	0.18
2-isopropoxyethanol + propylamine	298.15	2.5298	1.3714	0.66	2.4364	2.4929	1.0226	0.21
	308.15	1.9939	1.0938	0.59	1.8305	2.1058	0.8212	0.28
	318.15	1.5157	0.8952	0.32	1.4690	1.5434	0.7212	0.20
2-isopropoxyethanol + dipropylamine	298.15	2.4721	1.1154	0.32	2.3850	1.7550	0.9652	0.19
	308.15	1.8960	0.9392	0.58	1.7922	1.4689	0.8076	0.19
	318.15	1.4146	0.7731	0.24	1.4227	1.0735	0.7021	0.23

of 2-propoxyethanol or 2-isopropoxyethanol with propylamine or dipropylamine systems. The excess molar volumes become progressively less with the branching of the alkyl chain at the α carbon. This behavior may be compared with the V_m^E results for the mixtures 2-propoxyethanol and 2-isopropoxyethanol with water[15,28] or 1-propanol and 2-propanol with water:[29] branching of the alkyl chain at the α-carbon leads to more negative V_m^E.

Figure 2 shows that the deviation in viscosity $\Delta \ln \eta$ is positive over the entire composition range for all systems at all temperatures. (The viscosities of all binary mixtures decrease with the increase of temperature.) For each ether, the η results of the mixtures at all three temperatures follow the sequence propylamine > dipropylamine. A further comparison of data at different temperatures shows that the temperature coefficient $(\delta\eta/\partial T)_P$ is decreasing for all mixtures with increasing temperature. Furthermore, the magnitude of positive deviations decreases with each ether as the viscosity from primary amine to secondary amine increased. As evidenced from the calculations, the viscosity deviations decrease with an increase of temperature.

McAllister's multibody interaction model[30] (1960) was widely used to correlate kinematic viscosity (ν) data. The two-parameter McAllister 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 three-body model was defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \quad (4)$$

and the four-body model was given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln Z_{1112} + 6x_1^2 x_2^2 \ln Z_{1122} + 4x_1 x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 2x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (5)$$

where Z_{12}, Z_{21}, Z_{1112}, Z_{1122}, and Z_{2221} are model parameters. The values of the McAllister's adjustable parameters are reported in Table 5 together with the average deviations (AAD%) between the calculated and experimental values. The values of the AAD(%) are in the range from 0.2 to 0.8% for eq 4 with two parameters and from 0.2 to 0.3% for eq 5 for three parameters. Use of the three-parameters equation reduces the AAD(%) values significantly below that of the two-parameters equation. That is, the correlating ability significantly improves for those nonideal systems as the number of adjustable parameters is increased.

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