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Excess Molar Volumes and Viscosities for Binary Mixtures of 2-Propoxyethanol and of 2-Isopropoxyethanol with 2-Pyrrolidinone, *N*-Methyl-2-pyrrolidinone, *N*,*N*-Dimethylformamide, and *N*,*N*-Dimethylacetamide 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 mixtures of 2-propoxyethanol and of 2-isopropoxyethanol with 2-pyrrolidinone, *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide at 298.15 K. In all mixtures, the excess molar volumes are negative over the whole mole fraction range. From the experimental data, deviations in the viscosity $\Delta \ln \eta$ had been calculated. The excess volumes and viscosity deviations have been correlated using the Redlich−Kister polynomial equation by the method of least-squares for the estimation of the adjustable parameters and the standard errors. The viscosity data have been correlated with the equations of McAllister, Heric, and Auslaender.

Introduction

This is a part of our ongoing program of research on the thermodynamic, acoustic and transport properties of binary mixtures containing straight-chain or branched-chain alkoxyethanols as one of the components.[1−4] In continuation of our earlier investigations, we report here the new experimental data of the excess molar volumes V_m^E and viscosities η of binary solvent mixtures containing 2-propoxyethanol or 2-isopropoxyethanol with 2-pyrrolidinone, *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide over the whole composition range at 298.15 K and atmospheric pressure. The thermodynamic properties of mixtures of straight-chain or branched-chain alkoxyethanols with either alkanol[5,6] or water[7,8] have been studied. A few other studies involving the viscosities, excess molar volumes, and speeds of sound of *N*,*N*-disubstituted amides + alkanol[9−11] and + water[12] and other thermodynamic and spectroscopic properties of cyclic amide + water[12,13] and + alcohol[13] have also been performed.

We are not aware of any volumetric and viscometric data available in the literature for the present systems. The present study was undertaken with a view to studying the effect of specific interactions on the excess properties, the dependence on the position of the CH_3 group in the propoxyethanol, and the influence of *N*,*N*-disubstituted amides on cyclic amides.

Experimental Section

Materials. 2-Propoxyethanol (Acros, USA, 98 mol %) and 2-isopropoxyethanol (Merck-Schuchardt, FRG, GC > 98 mol %) were the same as those used in our earlier studies.[2,14] The *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and *N*-methyl-2-pyrrolidinone (NM2P) were SDS spectroscopy grade reagents with purity better than 99.5 mol %. The 2-pyrrolidinone (2P) was obtained from Merck-Schuchardt, FRG, with a purity higher than 99 mol %. All amide samples were purified as previously described.[15] Prior to actual measurements, all liquids were dried over 0.4 nm molecular sieves (Fluka, AG) and were partially degassed under vacuum. The densities and viscosities of these liquids were measured and compared at (298.15 ± 0.01) K and atmospheric pressure with their corresponding literature values,[7,8,12,16−21] 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.

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

	ρ/g·ccm^{-3}		η/mPa·s	
liquid	exptl	lit.	exptl	lit.
2-propoxyethanol	0.9080	0.908 223[16] 0.907 4[17]	2.351	
2-isopropoxyethanol	0.8999	0.899 6[17] 0.899 680[8] 0.899 42[7]	2.106	
N,*N*-dimethylformamide	0.9436	0.943 831 2 0.945 601 8 0.944 519	0.812	0.813 618 0.816 19
N,*N*-dimethylacetamide	0.9365	0.936 719 0.936 620	0.947	0.937 19 0.943 721
2-pyrolidinone	1.1068	1.107 20	14.222	13.320
N-methyl-2-pyrolidinone	1.0279	1.027 59[12] 1.027 920	1.687	1.666 20

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 de-

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

x_1	V_m^E/$cm^3 \cdot mol^{-1}$	x_1	V_m^E/$cm^3 \cdot mol^{-1}$	x_1	V_m^E/$cm^3 \cdot mol^{-1}$	x_1	V_m^E/$cm^3 \cdot mol^{-1}$	x_1	V_m^E/$cm^3 \cdot mol^{-1}$	x_1	V_m^E/$cm^3 \cdot mol^{-1}$
2-Propoxyethanol (1) + *N*,*N*-Dimethylformamide (2)											
0.0081	−0.004	0.3153	−0.137	0.6182	−0.170	0.1785	−0.092	0.4138	−0.158	0.8724	−0.094
0.0473	−0.024	0.3231	−0.138	0.6907	−0.162	0.2305	−0.111	0.4487	−0.165	0.9436	−0.051
0.0827	−0.043	0.3586	−0.148	0.7440	−0.146	0.2791	−0.124	0.4898	−0.168	0.9687	−0.029
0.1259	−0.068	0.4043	−0.160	0.8167	−0.118	0.2804	−0.127	0.5479	−0.172		
2-Propoxyethanol (1) + *N*,*N*-Dimethylacetamide (2)											
0.0013	−0.002	0.3720	−0.155	0.6015	−0.186	0.2279	−0.113	0.4898	−0.179	0.9125	−0.080
0.0036	−0.004	0.3932	−0.161	0.6406	−0.179	0.2831	−0.133	0.5006	−0.182	0.9536	−0.043
0.0362	−0.018	0.4132	−0.169	0.7339	−0.160	0.3326	−0.148	0.5332	−0.183	0.9817	−0.022
0.0912	−0.054	0.4421	−0.174	0.7983	−0.132	0.3355	−0.142	0.5506	−0.185		
0.1541	−0.087	0.4619	−0.178	0.8470	−0.116						
2-Propoxyethanol (1) + *N*-Methyl-2-pyrrolidinone (2)											
0.0028	−0.002	0.4259	−0.192	0.6162	−0.194	0.2558	−0.144	0.5318	−0.201	0.9303	−0.073
0.0167	−0.008	0.4435	−0.192	0.6744	−0.190	0.3306	−0.170	0.5370	−0.199	0.9752	−0.029
0.0634	−0.040	0.4592	−0.197	0.7422	−0.174	0.3827	−0.180	0.5807	−0.194		
0.1165	−0.076	0.4847	−0.197	0.8195	−0.145	0.3847	−0.184	0.6001	−0.190		
0.1890	−0.117	0.4941	−0.198	0.8762	−0.115						
2-Propoxyethanol (1) + 2-Pyrrolidinone (2)											
0.0038	−0.003	0.4109	−0.328	0.7097	−0.290	0.1981	−0.241	0.5314	−0.333	0.9025	−0.140
0.0214	−0.040	0.4246	−0.331	0.7437	−0.268	0.2345	−0.266	0.5642	−0.329	0.9430	−0.092
0.0549	−0.083	0.4393	−0.334	0.7746	−0.252	0.2829	−0.294	0.5859	−0.326	0.9630	−0.058
0.0724	−0.107	0.4519	−0.333	0.8204	−0.230	0.3281	−0.312	0.5936	−0.324	0.9803	−0.033
0.1204	−0.166	0.4735	−0.336	0.8538	−0.201	0.3702	−0.324	0.6463	−0.312	0.9971	−0.004
0.1610	−0.207	0.5036	−0.334	0.8794	−0.172	0.4080	−0.329	0.6773	−0.299		
2-Isopropoxyethanol (1) + *N*,*N*-Dimethylformamide (2)											
0.0022	−0.003	0.3394	−0.188	0.5570	−0.191	0.2438	−0.165	0.4434	−0.199	0.8640	−0.104
0.0317	−0.026	0.3496	−0.188	0.5998	−0.183	0.2755	−0.170	0.4915	−0.200	0.9265	−0.072
0.0769	−0.060	0.3862	−0.196	0.6724	−0.173	0.2963	−0.179	0.4996	−0.198	0.9726	−0.031
0.1318	−0.107	0.3913	−0.195	0.7220	−0.156	0.3119	−0.183	0.5300	−0.195		
0.1862	−0.138	0.4376	−0.201	0.7864	−0.136						
2-Isopropoxyethanol (1) + *N*,*N*-Dimethylacetaamide (2)											
0.0049	−0.004	0.3777	−0.171	0.5918	−0.017	0.2296	−0.130	0.4971	−0.180	0.8661	−0.089
0.0239	−0.016	0.4074	−0.177	0.6235	−0.017	0.3072	−0.158	0.5198	−0.180	0.9098	−0.065
0.0639	−0.040	0.4258	−0.177	0.7032	−0.152	0.3338	−0.163	0.5294	−0.178	0.9694	−0.028
0.1088	−0.064	0.4512	−0.179	0.7601	−0.133	0.3510	−0.170	0.5653	−0.175		
0.1612	−0.099	0.4689	−0.181	0.8106	−0.114						
2-Isopropoxyethanol (1) + *N*-Methyl-2-pyrrolidinone (2)											
0.0124	−0.018	0.4150	−0.254	0.6709	−0.246	0.2852	−0.210	0.5226	−0.262	0.9813	−0.035
0.0950	−0.087	0.4213	−0.254	0.7317	−0.226	0.3233	−0.223	0.5507	−0.264	0.9895	−0.023
0.1438	−0.130	0.4593	−0.262	0.7810	−0.204	0.3592	−0.242	0.5692	−0.262	0.9979	−0.008
0.1947	−0.160	0.4809	−0.261	0.8337	−0.176	0.3806	−0.244	0.6139	−0.257		
0.2560	−0.192	0.5057	−0.263	0.9168	−0.119						
2-Isopropoxyethanol (1) + 2-Pyrrolidinone (2)											
0.0045	−0.009	0.3380	−0.428	0.5236	−0.480	0.1708	−0.281	0.4491	−0.478	0.7772	−0.342
0.0156	−0.029	0.3527	−0.442	0.5422	−0.480	0.1972	−0.314	0.4501	−0.477	0.8211	−0.293
0.0414	−0.078	0.3554	−0.442	0.5726	−0.476	0.2209	−0.340	0.4770	−0.483	0.8704	−0.221
0.0624	−0.119	0.3775	−0.452	0.6076	−0.463	0.2580	−0.371	0.4799	−0.479	0.9280	−0.136
0.0915	−0.168	0.3847	−0.455	0.6432	−0.449	0.2936	−0.404	0.4992	−0.480	0.9839	−0.035
0.1121	−0.198	0.4100	−0.469	0.6848	−0.419	0.3226	−0.431	0.5092	−0.481		
0.1472	−0.250	0.4161	−0.470	0.7349	−0.381						

scribed elsewhere.[22] Details of its calibration and operational procedures have been described previously.[23] 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 the mass measurements were performed on an electrical balance (Dhona 200D, India) accurate to four decimal places. All apparent masses were corrected for buoyancy. Each run covered just over half of the range of x_1, so as to give an overlap between two runs.

The kinematic viscosities of both the pure liquids and liquid mixtures were measured at 298.15 K and atmospheric pressure with a Ubbelohde suspended level viscometer,[24] having a capillary bore with an internal diameter of about 1 mm and a capillary length of 65 mm. The viscometers were calibrated, and two constants A and B, of the viscometer in the equation $\eta = \rho(At - B/t)$ were obtained by measuring the flow time t with high purity (benzene, toluene, and water)[20] at the working temperature. 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. The arithmetic mean 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 flow time for water at 298.15 K was about 348 s. The other experimental details have been given in our earlier papers.[25,26] The measured values of the kinematic viscosities (ν) were converted to dynamic viscosities (η) after multiplication by the density. The reproducibility of viscosity results was found to be within ±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.

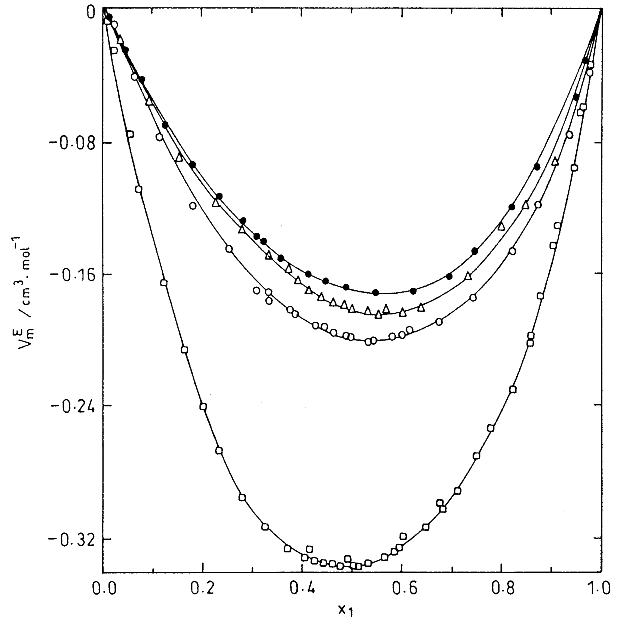

Figure 1. Comparison of the excess molar volumes V_m^E at 298.15 K for 2-propoxyethanol (1) + *N*,*N*-dimethylformamide (2), ●; + *N*,*N*-dimethylacetamide (2), △; + 2-pyrrolidinone (2), □; + *N*-2-methyl-2-pyrrolidinone (2), ○. The solid curves have been drawn from eq 4.

Results and Discussion

The experimental excess molar volumes of the different binary mixtures versus mole fraction at 298.15 K are given in Table 2 and are graphically represented in Figures 1 and 2. The viscosities were fitted to a polynomial

$$\eta/\text{mPa·s} = \sum A_i x_1^{\,i} \qquad (1)$$

by the method of least-squares with equal weights assigned to each point. The values of the coefficients A_i and standard deviations σ are listed in Table 4a.

The V_m^E values are used to compute the densities ρ of liquid mixtures according to the equation

$$\rho = (x_1M_1 + x_2M_2)/(V_m^E + x_1V_1^* + x_2V_2^*) \qquad (2)$$

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 alkoxyethanol (1) and amide (2), respectively.

The deviation in viscosities has been calculated from the following relationship[27,28]

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (3)$$

where η, η_1, and η_2 are the viscosities of the mixture and components 1 and 2, respectively. Data on derived densities and viscosities for the different binary mixtures at 298.15 K are shown in Table 3.

The values of V_m^E and $\Delta \ln \eta$ for each mixture were represented mathematically by the Redlich−Kister polynomial:

$$Y(x) = x_1x_2\sum_{i=0} A_i(x_1 - x_2)^i \qquad (4)$$

Values of the coefficients A_i and standard deviation σ are summarized in Table 4b.

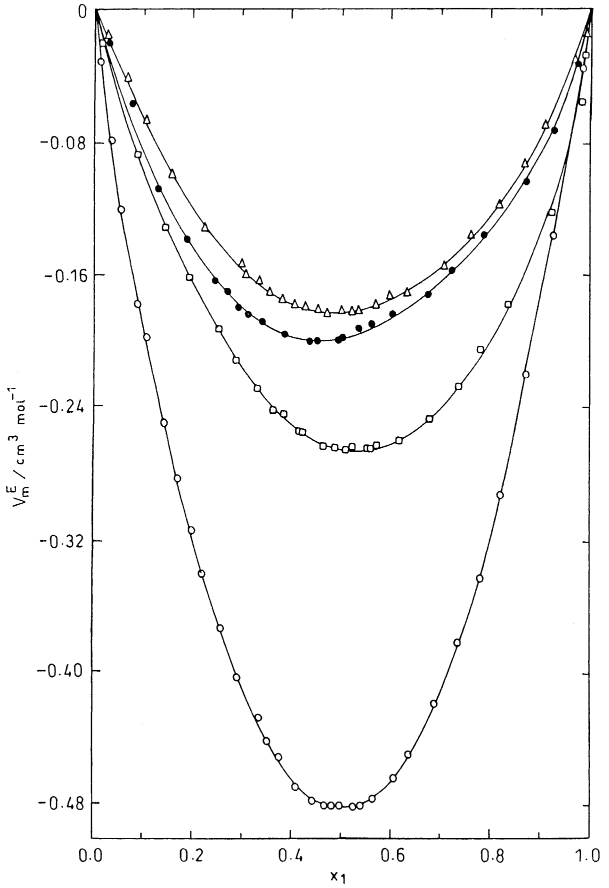

Figure 2. Comparison of the excess molar volumes V_m^E at 298.15 K for 2-isopropoxyethanol (1) + *N*,*N*-dimethylformamide (2), ●; + *N*,*N*-dimethylacetamide (2), △; + 2-pyrrolidinone (2), □; + *N*-2-methyl-2-pyrrolidinone (2), ○. The solid curves have been drawn from eq 4.

Figures 1 and 2 show V_m^E data for the four different mixtures at 298.15 K. For each of the mixtures studied, V_m^E is negative over the whole mole fraction range. In all mixtures, the minimum occurs around $x_1 = 0.5$. The minimum of the tertiary amide is roughly half that of the secondary amide. These large negative values of V_m^E arise because of increased interactions between alkoxyethanol and amide or very large differences in the molar volumes of the pure components. The behavior is consistent with that of the V_m^E for 2-pyrrolidinone + polyethers[29] and + 1-alkanols[30] and for straight-chain or branched-chain alkoxyethanols + lower alcohols[5,14] and + water.[7,31] This behavior may be compared with the positive H_m^E results for mixtures of *N*,*N*-dimethylformamide with butan-1-ol,[10] which are due to the break up of the dipolar interaction present in *N*,*N*-dimethylformamide. The observed V_m^E values may be explained qualitatively by postulating two opposing sets of contributions: (a) contraction due to hydrogen bonding between amides and alkoxyethanols or breakdown of the self-association of the components, and (b) specific interaction between the alkoxyethanol and the amide molecules. This interaction may be considered as the reaction between alkoxyethanol as Lewis acid and DMF and DMA as Lewis base. The excess molar volumes of the (2-isopropoxyethanol + amide) mixtures are more negative than those of the (2-propoxyethanol + amide) mixtures, as is evident in Figures 1 and 2. The most striking features in Figures 1 and 2 are the strong similarity between the composition dependence curves of the two propoxyethanols + *N*,*N*-dimethylacetamide, which is in sharp contrast to the differences between the curves for the two propoxyethanols + *N*,*N*-dimethylformamide. A considerable part

Table 3. Densities 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) + *N*,*N*-Dimethylformamide (2)											
0.0076	0.9433	0.821	0.3521	0.9294	1.305	0.1416	0.9378	0.998	0.6982	0.9172	1.895
0.0172	0.9429	0.834	0.4414	0.9261	1.458	0.1927	0.9357	1.070	0.7555	0.9154	1.989
0.0290	0.9424	0.846	0.5181	0.9233	1.582	0.2640	0.9329	1.180	0.8533	0.9123	2.164
0.0502	0.9415	0.874	0.5987	0.9205	1.726	0.2944	0.9317	1.223	0.9398	0.9098	2.308
0.1029	0.9393	0.948	0.6457	0.9190	1.809	0.3428	0.9294	1.289	0.9729	0.9088	2.345
2-Propoxyethanol (1) + *N*,*N*-Dimethylacetamide (2)											
0.0049	0.9364	0.951	0.3842	0.9258	1.536	0.1253	0.9332	1.125	0.7250	0.9158	2.094
0.0086	0.9363	0.956	0.4022	0.9252	1.578	0.1780	0.9317	1.202	0.8523	0.9122	2.260
0.0134	0.9362	0.961	0.4678	0.9233	1.679	0.2555	0.9295	1.322	0.9508	0.9094	2.339
0.0272	0.9358	0.982	0.5258	0.9216	1.786	0.3191	0.9277	1.426	0.9790	0.9086	2.345
0.0419	0.9354	1.010	0.5917	0.9197	1.897	0.3487	0.9268	1.478			
0.0739	0.9346	1.049	0.6504	0.9180	1.987						
2-Propoxyethanol (1) + 2-Pyrrolidinone (2)											
0.0058	1.1052	13.966	0.4698	0.9971	5.028	0.2214	1.0507	8.048	0.8327	0.9334	2.977
0.0150	1.1028	13.552	0.5219	0.9871	4.651	0.2526	1.0434	7.522	0.8764	0.9266	2.801
0.0350	1.0974	12.829	0.5519	0.9814	4.440	0.3008	1.0325	6.831	0.9045	0.9223	2.695
0.0681	1.0887	11.702	0.6236	0.9684	3.983	0.3725	1.0170	5.947	0.9327	0.9180	2.592
0.1013	1.0802	10.721	0.6987	0.9554	3.576	0.3786	1.0157	5.895	0.9694	0.9125	2.473
0.1517	1.0675	9.453	0.7597	0.9452	3.317	0.4257	1.0060	5.419	0.9865	0.9100	2.409
2-Propoxyethanol (1) + *N*-Methyl-2-pyrrolidinone (2)											
0.0057	1.0271	1.693	0.3852	0.9786	2.132	0.1786	1.0046	1.891	0.7673	0.9336	2.355
0.0142	1.0260	1.702	0.4436	0.9714	2.186	0.2186	0.9995	1.940	0.8387	0.9257	2.365
0.0273	1.0243	1.719	0.5011	0.9644	2.244	0.2578	0.9945	1.996	0.8702	0.9222	2.362
0.0609	1.0199	1.756	0.5422	0.9595	2.280	0.2966	0.9896	2.038	0.9445	0.9141	2.359
0.1004	1.0147	1.803	0.6093	0.9516	2.311	0.3343	0.9849	2.078	0.9760	0.9106	2.354
0.1386	1.0097	1.847	0.6638	0.9453	2.343						
2-Isopropoxyethanol (1) + *N*,*N*-Dimethylformamide (2)											
0.0025	0.9435	0.815	0.4723	0.9205	1.420	0.1908	0.9337	1.066	0.7959	0.9075	1.874
0.0124	0.9430	0.827	0.5200	0.9185	1.491	0.2558	0.9304	1.142	0.8833	0.9042	2.005
0.0296	0.9421	0.854	0.5620	0.9167	1.543	0.3145	0.9276	1.213	0.9392	0.9021	2.069
0.0480	0.9411	0.885	0.6131	0.9147	1.617	0.3440	0.9262	1.247	0.9642	0.9012	2.093
0.0898	0.9389	0.932	0.6641	0.9126	1.697	0.3645	0.9252	1.274	0.9942	0.9001	2.104
0.1476	0.9359	1.006	0.7547	0.9091	1.818	0.4159	0.9229	1.340			
2-Isopropoxyethanol (1) + *N*,*N*-Dimethylacetamide (2)											
0.0063	0.9363	0.956	0.4419	0.9199	1.555	0.1712	0.9301	1.167	0.8097	0.9066	2.044
0.0140	0.9360	0.970	0.4958	0.9180	1.630	0.2095	0.9286	1.225	0.8670	0.9046	2.083
0.0243	0.9356	0.983	0.5445	0.9162	1.704	0.2923	0.9255	1.336	0.9066	0.9032	2.098
0.0518	0.9346	1.016	0.6028	0.9141	1.782	0.3534	0.9232	1.422	0.9627	0.9012	2.102
0.0792	0.9336	1.049	0.6671	0.9118	1.871	0.3673	0.9227	1.443	0.9854	0.9004	2.105
0.1131	0.9323	1.092	0.7594	0.9084	1.973	0.3996	0.9215	1.494	0.9940	0.9001	2.106
2-Isopropoxyethanol (1) + 2-Pyrrolidinone (2)											
0.0071	1.1048	13.903	0.5125	0.9849	4.439	0.2699	1.0374	7.051	0.8880	0.9175	2.528
0.0159	1.1023	13.591	0.5675	0.9741	4.067	0.3267	1.0244	6.264	0.9155	0.9131	2.412
0.0316	1.0980	12.930	0.6092	0.9662	3.792	0.3725	1.0142	5.709	0.9430	0.9088	2.304
0.0611	1.0899	11.920	0.6833	0.9525	3.388	0.4121	1.0056	5.308	0.9583	0.9064	2.252
0.1046	1.0784	10.572	0.7418	0.9421	3.111	0.4371	1.0004	5.073	0.9786	0.9033	2.193
0.1603	1.0640	9.092	0.7986	0.9323	2.871	0.4623	0.9951	4.846			
0.2294	1.0470	7.709	0.8498	0.9238	2.672						
2-Isopropoxyethanol (1) + *N*-Methyl-2-pyrrolidinone (2)											
0.0040	1.0274	1.691	0.4055	0.9727	1.989	0.1577	1.0062	1.814	0.7639	0.9277	2.134
0.0105	1.0265	1.702	0.4494	0.9670	2.011	0.2017	1.0001	1.843	0.8354	0.9191	2.127
0.0362	1.0230	1.729	0.5127	0.9589	2.045	0.2462	0.9940	1.882	0.9185	0.9094	2.120
0.0624	1.0194	1.753	0.5735	0.9511	2.073	0.3116	0.9851	1.929	0.9736	0.9030	2.109
0.0880	1.0159	1.764	0.6423	0.9425	2.096	0.3451	0.9807	1.955	0.9914	0.9009	2.107
0.1136	1.0123	1.779	0.7229	0.9326	2.118	0.3748	0.9767	1.969			

of the negative contributions in the mixtures of 2-propoxyethanol or 2-isopropoxyethanol + 2-pyrrolidinone as compared to 2-propoxyethanol or 2-isopropoxyethanol + *N*-methyl-2-pyrrolidinone is very likely due to formation of hydrogen bonds between the CO groups of the 2-pyrrolidinone and the H atom of alkoxyethanol. The more negative excess volumes for the mixtures of 2-pyrrolidinone indicate that substitution of a proton for the methyl group of *N*-methyl-2-pyrrolidinone results in less negative contribution to the excess volumes. Again, dissociation of self-associated species of 2-pyrrolidinone by 2-isopropoxyethanol and simultaneous interaction, mainly due to hydrogen bonding in addition to the interstitial accommodation, lead to more negative V_m^E values for 2-isopropoxyethanol + 2-pyrrolidinone compared with those for 2-propoxyethanol + 2-pyrrolidinone mixtures. This contrasts with the behavior of the V_m^E values for 2-propoxyethanol or 2-isopropoxyethanol + 1-propanol or 2-propanol,[2] where the V_m^E values are more negative with 2-propoxyethanol. It may be concluded that branching of the alkyl chain at the α-carbon, as in 2-isopropoxyethanol, results in a decrease in V_m^E with all the amide molecules studied here. Also, this behavior may be compared with the V_m^E results for the mixtures 2-propoxyethanol and 2-isopropoxyethanol with water[7,31] or

Table 4. Values of the Parameters and Standard Deviation σ for the Various Mixtures

		A_0	A_1	A_2	A_3	A_4	σ
		(a) of Eq 1 for η/mPa·s					
2-propoxyethanol (1) +							
N,*N*-dimethylformamide (2)		0.814	1.169	0.845	−0.431		0.005
N,*N*-dimethylacetamide (2)		0.946	1.359	0.429	0.470	−0.849	0.004
2-pyrrolidinone (2)		14.133	−39.290	64.807	−56.793	19.553	0.029
N-methyl-2-pyrrolidinone (2)		1.690	0.955	1.556	−3.198	1.347	0.005
2-isopropoxyethanol (1) +							
N,*N*-dimethylformamide (2)		0.811	1.495	−1.396	2.734	−1.526	0.006
N,*N*-dimethylacetamide (2)		0.949	1.300	−0.235	1.460	−1.373	0.005
2-pyrrolidinone (2)		14.178	−40.713	67.013	−58.156	19.853	0.030
N-methyl-2-pyrrolidinone (2)		1.695	0.784	0.002	−0.379		0.005
		(b) for Eq 4					
2-propoxyethanol (1) +							
N,*N*-dimethylformamide (2)	V_m^E/cm^3·mol^{-1}	−0.680	−0.155	−0.078			0.002
	Δln(η/mPa·s)	0.460	0.033	0.148	0.150		0.004
N,*N*-dimethylacetamide (2)	V_m^E/cm^3·mol^{-1}	−0.720	−0.189	−0.089			0.003
	Δln(η/mPa·s)	0.610	0.159	0.049			0.003
2-pyrrolidinone (2)	V_m^E/cm^3·mol^{-1}	−1.339	0.071	−0.440	−0.158		0.003
	Δln(η/mPa·s)	−0.743	0.443	−0.011			0.003
N-methyl-2-pyrrolidinone (2)	V_m^E/cm^3·mol^{-1}	−0.793	−0.108	−0.175	−0.190		0.002
	Δln(η/mPa·s)	0.473	0.045	−0.139			0.002
2-isopropoxyethanol (1) +							
N,*N*-dimethylformamide (2)	V_m^E/cm^3·mol^{-1}	−0.786	0.144	−0.216	−0.274		0.003
	Δln(η/mPa·s)	0.436	−0.022	0.129	−0.022	0.316	0.003
N,*N*-dimethylacetamide (2)	V_m^E/cm^3·mol^{-1}	−0.721	0.057	−0.037	−0.197		0.002
	Δln(η/mPa·s)	0.590	0.184	0.148			0.003
2-pyrrolidinone (2)	V_m^E/cm^3·mol^{-1}	−1.929	−0.002	−0.123	0.033		0.003
	Δln(η/mPa·s)	−0.753	0.442	−0.073			0.003
N-methyl-2-pyrrolidinone (2)	V_m^E/cm^3·mol^{-1}	−1.057	−0.069	−0.010	−0.305	−0.498	0.003
	Δ ln(η/mPa·s)	0.316	0.067	0.011	−0.080		0.003

Table 5. Values of the Parameters and Standard Percentage Deviation for the (Alkoxyethanol + Amide) Systems Respresented by Eqs 5−7

	eq 5				eq 6				eq 7			
	Z_{1112}	Z_{1122}	Z_{2221}	σ	A	B	C	σ	B_{12}	B_{21}	A_{21}	σ
2-propoxyethanol (1) +												
N,*N*-dimethylformamide (2)	0.86	0.26	0.46	0.38	0.53	0.08	0.14	0.38	2.47	0.22	3.15	0.40
N,*N*-dimethylacetamide (2)	2.52	2.12	1.45	0.26	0.62	0.16	0.05	0.25	1.72	0.15	1.90	0.27
2-pyrrolidinone (2)	3.61	5.06	6.47	0.24	−0.68	0.43	−0.01	0.24	−1.08	−0.95	−0.31	1.14
N-methyl-2-pyrrolidinone (2)	2.54	2.41	1.98	0.15	0.48	0.04	−0.14	0.15	0.60	0.25	0.49	0.21
2-isopropoxyethanol (1) +												
N,*N*-dimethylformamide (2)	0.81	0.23	0.48	0.33	0.50	−0.04	0.31	0.33	−0.93	−1.03	−0.89	0.36
N,*N*-dimethylacetamide (2)	2.40	1.94	1.43	0.30	0.60	0.19	0.15	0.29	2.78	−0.02	2.76	0.36
2-pyrrolidinone (2)	3.39	4.70	6.40	0.26	−0.69	0.44	0.07	0.24	−0.72	−1.40	−0.21	1.18
N-methyl-2-pyrrolidinone (2)	2.35	2.06	1.93	0.25	0.32	0.04	0.02	0.24	0.86	0.25	0.64	0.38

1-propanol and 2-propanol with water:[32] branching of the alkyl chain at the α-carbon leads to more negative excess molar volumes. Further, because of the steric hindrance of the two methyl groups of DMF, the strength of interactions due to the formation of O—H···O as compared to O—H···N bonds is expected to decrease with straight-chain rather than with branched-chain alkoxyethanols. In other words, the inductive effect of the alkyl group in the branched-chain alkoxyethanol increases the electron density in the oxygen atom, enhancing the formation of O—H···O bonding. The existence of a strong O—H···O bond has also been confirmed through our IR studies.

We have determined the η and calculated the Δ ln η at 298.15 K. Figure 3 reveals that η decreases with 2-pyrrolidinone and increase for all other mixtures with an increase in the mole fraction x_1 of alkoxethanol. Figure 4 shows that Δ ln η is positive over the entire composition range for all the mixtures except alkoxyethanol + 2-pyrrolidinone mixtures. These results support the fact that mixing of 2-pyrrolidinone with alkoxyethanols tends to break the associations present in 2-pyrrolidinone and/or prevent the subsequent formation of a hydrogen bond in addition to the interstitial accommodation due to the difference in shape and size of the component molecules, resulting in an overall increase in the viscosities of the mixtures. This behavior also finds support from the negative values of V_m^E. According to some other authors,[33,34] the predominance of specific interactions is excepted to result in positive Δ ln η values. This reveals that the strength of the intermolecular hydrogen bonding is not the only factor influencing the Δ ln η values of liquid mixtures, but the molecular sizes and shapes of the components are also equally important.

Assuming a four-body model, McAllister[35] proposed the following relation for the viscosities of mixtures

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln Z_{1112} + 6x_1^2x_2^2 \ln Z_{1122} + 4x_1x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 2x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (5)$$

where ν refers to the kinematic viscosity of the mixture

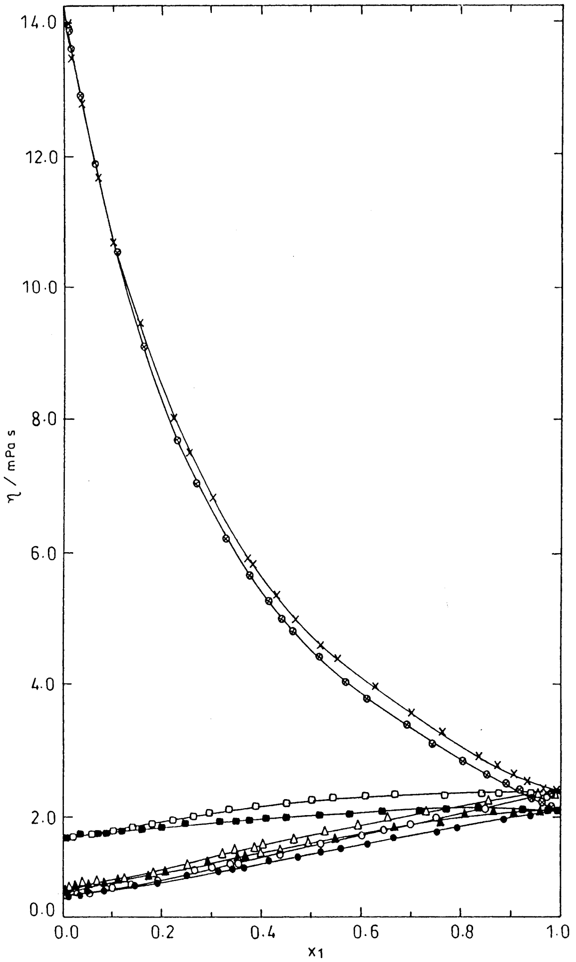

Figure 3. Viscosity η at 298.15 K for 2-propoxyethanol (1) + *N*,*N*-dimethylformamide (2), ○; + *N*,*N*-dimethylacetamide (2), △; + 2-pyrrolidinone (2), ×; + *N*-2-methyl-2-pyrrolidinone (2), □; and 2-isopropoxyethanol (1) + *N*,*N*-dimethylformamide (2), ●; + *N*,*N*-dimethylacetamide (2), ▲; + 2-pyrrolidinone (2), ⊗; + *N*-2-methyl-2-pyrrolidinone (2), ■. The solid curves have been drawn from eq 1.

and where ν_1 and ν_2 are the kinematic viscosities of pure components 1 and 2, respectively; Z_{1112}, Z_{1122}, and Z_{2221} are adjustable parameters which are characteristic of the system.

Heric[36] suggested the following relation for correlating the kinematic viscosities of the binary liquid mixtures

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1M_1 + x_2M_2) + x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2] \quad (6)$$

where *a*, *b*, and *c* are adjustable parameters.

Auslaender[37] developed the following expression for kinematic viscosities of binary mixtures

$$x_1(x_1 + B_{12}x_2)(\nu - \nu_1) + A_{21}x_2(B_{21}x_2 + x_2)(\nu - \nu_2) = 0 \quad (7)$$

where B_{12}, A_{21}, and B_{21} are the parameters representing binary 12 interactions. The correlating ability of eqs 5−7 was tested by calculating the standard percentage deviation σ (%) between the experimental and the calculated viscosities as

$$\sigma\,(\%) = [1/(n - k)\sum(100(\nu_{\text{exp}} - \nu_{\text{cal}})/\nu_{\text{exp}})^2]^{1/2} \quad (8)$$

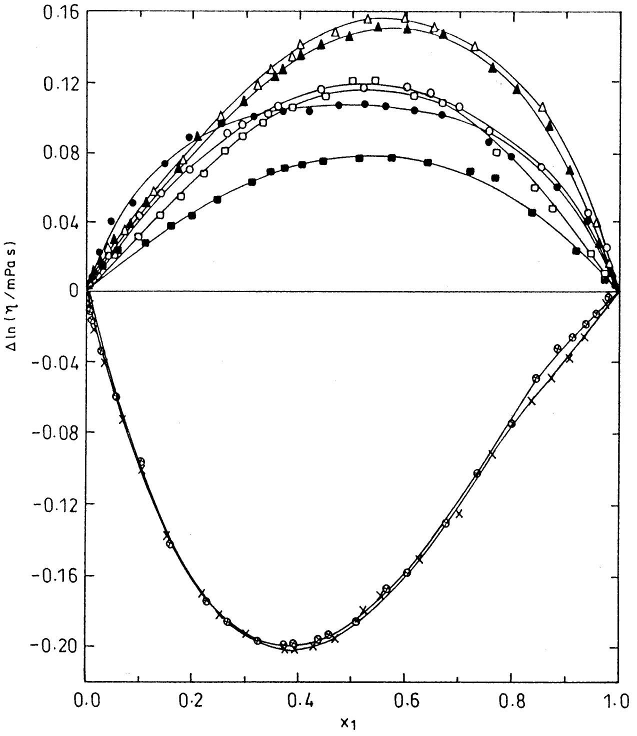

Figure 4. Viscosity deviations $\Delta \ln \eta$ at 298.15 K for 2-propoxyethanol (1) + *N*,*N*-dimethylformamide (2), ○; + *N*,*N*-dimethylacetamide (2), △; + 2-pyrrolidinone (2), ×; + *N*-2-methyl-2-pyrrolidinone (2), □; and 2-isopropoxyethanol (1) + *N*,*N*-dimethylformamide (2), ●; + *N*,*N*-dimethylacetamide (2), ▲; + 2-pyrrolidinone (2), ⊗; + *N*-2-methyl-2-pyrrolidinone (2), ■. The solid curves have been drawn from eq 4.

where *n* represents the number of experimental points and *k* the number of numerical coefficients in the respective equations.

The values of the different parameters and the percentage standard deviations are given in Table 5. It is observed that the McAllister and the Heric relations fit the experimental results better as compared to the Auslaender equation, as the σ/% values for the latter equation are larger than the others in all the systems.

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