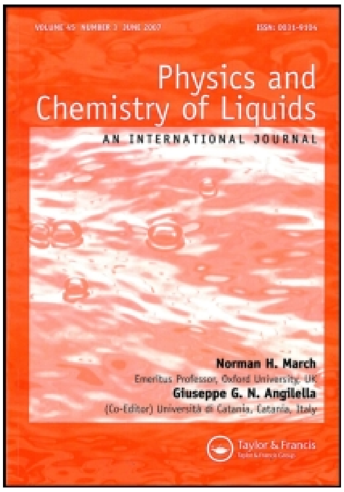

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Studies on intermolecular interactions in binary mixtures of alkoxypropanols with ethyl *tert*-butyl ether at various temperatures

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Densities and viscosities at $T = 293.15$, 298.15 and 303.15 K in the binary liquid mixtures of ethyl *tert*-butyl ether (ETBE) with propylene glycol monomethyl ether (PM), dipropylene glycol monomethyl ether (DPM) and tripropylene glycol monomethyl ether (TPM) have been measured over the entire mixture compositions. These data have been used to compute the excess molar volumes (V^{E}), the excess energies of activation for viscous flow ΔG^{*E}, the deviations in the viscosity ($\Delta\eta$) from a mole fraction average and the Grunberg–Nissan interaction parameters (d_{12}). The values of V^{E}, $\Delta\eta$, ΔG^{*E} and d_{12} are negative over the entire range of composition for all the studied binary mixtures. The changes of V^{E}, $\Delta\eta$, ΔG^{*E} and d_{12} with variations in the composition and the chain-length of the alkyl groups in the alkoxypropanol molecules are discussed in terms of the intermolecular interactions.

Keywords: Propylene glycol monomethyl ether; Dipropylene glycol monomethyl ether; Tripropylene glycol monomethyl ether; Ethyl *tert*-butyl ether; Density; Viscosity; Intermolecular interactions

1. Introduction

Alkoxyalcohols and methyl or ethyl *tert*-butyl ethers (ETBEs) are used in the chemical industry as solvents for oils and petrol and are used in gasoline formulation as octane boosters or anti-knock additives. The use of ethers has been suggested as it reduces the gasoline vapour pressure and improves its combustion. The nature and type of intermolecular interactions in the binary liquid mixtures containing alkoxyalcohols and ETBE have been studied previously [1]. In the present study, the binary liquid mixtures

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containing propylene glycol monomethyl ether (PM), dipropylene glycol monomethyl ether (DPM), tripropylene glycol monomethyl ether (TPM) and ETBE have been used. The literature review shows that the mixing properties of (ETBE + PM), (ETBE + DPM) and (ETBE + TPM) binary mixtures have not been studied before. Therefore, we have decided to carry out the measurements of density and viscosity of these mixtures. From these results the excess molar volumes, deviation of the viscosities from a mole fraction, excess energies of activation for viscous flow $\Delta G^{*\mathrm{E}}$ at $T = 293.15$, 298.15 and 303.15 K and Grunberg–Nissan interaction parameters (d_{12}) at $T = 298.15$ K have been calculated. These quantities have been fitted to the Redlich–Kister equation [2], to obtain the binary coefficients and the standard deviations. Furthermore, the experimental results have been used to describe the nature of intermolecular interactions in the studied binary liquid mixtures.

2. Experimental

2.1. *Materials*

The following materials with mole fraction purity as stated correspondingly were used: PM (Aldrich, mass fraction > 0.99), DPM (Aldrich, mass fraction > 0.98) and TPM (Aldrich, mass fraction ≥ 0.97). All alkoxypropanols were purified as previously described [1,3]. ETBE (Fluka, Switzerland, purum, mass fraction ≥ 0.97) was used. It was purified by fractional distillation using a spinning band distillation column after drying it over molecular sieves (type 4A). The purity of this solvent was confirmed by gas chromatography to be 0.999 mole fraction. The mixtures were prepared using a Sartorius balance. Conversion to molar quantities was based on the relative atomic mass table of 1985, issued by IUPAC in 1986. The maximum estimated error in the mole fractions is $\pm 10^{-4}$. The liquids were stored in a dry-box over phosphorus pentoxide and degassed by ultrasound just before the experiment. The experimental densities and the viscosities for the pure solvents, at $T = 298.15$ K, were compared with the values available in the literature and are listed in table 1.

Table 1. Densities and viscosities of pure components, at $T = 298.15$ K.

	ρ (g cm^{-3})		η (MPa s)	
Solvent	This work	Lit.	This work	Lit.
Propylene glycol monomethyl ether	0.91640	0.9165 [19] 0.9163 [20] 0.91699 [21] 0.9164 [22]	1.707	1.681 [22] 1.6714 [19] 1.7226 [21]
Dipropylene glycol monomethyl ether	0.95278	0.9527 [23] 0.9510 [24]	3.738	3.691 [24]
Tripropylene glycol monomethyl ether	0.96596	–	5.662	–
Ethyl *tert*-butyl ether	0.73559	0.73557 [25] 0.7353 [26]	0.504	–

2.2. *Measurements*

The solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of ca 90 cm^3. The maximum error in the density measurements was 2×10^{-5} g cm^{-3}. The flow times of the mixtures and the pure liquids were measured in a ViscoClock (made by Schott), equipped with an Ubbelohde capillary viscometer. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The accuracy in the viscosity measurements was ±0.001 MPa s.

In all measurements of the densities and the viscosities, a Haake model DC-30 thermostat was used at a constant digital temperature control of ±0.01 K.

3. Results and discussion

The experimental densities (ρ) obtained from the measurements of the pure solvents and for the binary mixtures at all investigated temperatures are summarized in tables 2–4. From the measured densities, the excess molar volumes V^{E} of the mixtures at the each investigated temperature were fitted to the equation:

$$V^{\mathrm{E}} = x_1 M_1\left(\rho^{-1} - \rho_1^{-1}\right) + x_2 M_2\left(\rho^{-1} - \rho_2^{-1}\right) \tag{1}$$

where M_1 and M_2 are the molar masses of the pure components and ρ_1, ρ_2 and ρ are the densities of the pure species (1 and 2) and that of the mixtures at different temperatures, respectively.

Table 2. Density (ρ) and viscosity (η) for ETBE (1) + PM (2) binary mixtures at T = 293.15, 298.15 and 303.15 K.

	ρ (g cm^{-3})			η (MPa s)		
x_1	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K
0.0000	0.92113	0.91640	0.91148	1.935	1.707	1.509
0.0506	0.90946	0.90448	0.89941	1.768	1.570	1.403
0.1011	0.89801	0.89294	0.88784	1.620	1.445	1.300
0.1502	0.88720	0.88205	0.87696	1.492	1.337	1.208
0.1999	0.87657	0.87138	0.86630	1.378	1.239	1.122
0.2521	0.86575	0.86049	0.85543	1.270	1.147	1.041
0.3003	0.85606	0.85077	0.84570	1.182	1.070	0.975
0.3489	0.84655	0.84124	0.83619	1.101	1.000	0.916
0.4001	0.83685	0.83147	0.82643	1.027	0.934	0.859
0.4489	0.82784	0.82243	0.81740	0.963	0.877	0.809
0.5000	0.81868	0.81323	0.80821	0.902	0.823	0.763
0.5501	0.80992	0.80445	0.79944	0.848	0.777	0.722
0.5996	0.80151	0.79602	0.79102	0.800	0.736	0.684
0.6508	0.79305	0.78752	0.78255	0.754	0.696	0.648
0.7004	0.78509	0.77953	0.77458	0.713	0.661	0.618
0.7500	0.77733	0.77176	0.76681	0.676	0.629	0.592
0.8000	0.76973	0.76412	0.75920	0.642	0.600	0.565
0.8507	0.76224	0.75661	0.75171	0.608	0.573	0.544
0.9006	0.75504	0.74942	0.74453	0.579	0.548	0.521
0.9500	0.74808	0.74247	0.73763	0.554	0.524	0.502
1.0000	0.74111	0.73558	0.73085	0.532	0.504	0.478

Table 3. Density (ρ) and viscosity (η) for ETBE (1) + DPM (2) binary mixtures at $T = 293.15$, 298.15 and 303.15 K.

	ρ (g cm^{-3})			η (MPa s)		
x_1	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K
0.0000	0.95721	0.95278	0.94834	4.304	3.738	3.327
0.0511	0.94851	0.94388	0.93932	3.840	3.362	3.017
0.0998	0.93984	0.93511	0.93046	3.444	3.029	2.737
0.1506	0.93050	0.92569	0.92100	3.071	2.712	2.463
0.2000	0.92121	0.91632	0.91161	2.745	2.431	2.217
0.2502	0.91158	0.90662	0.90187	2.443	2.173	1.988
0.3000	0.90185	0.89682	0.89203	2.174	1.943	1.781
0.3506	0.89180	0.88668	0.88184	1.929	1.732	1.592
0.3992	0.88196	0.87675	0.87188	1.716	1.550	1.428
0.4505	0.87138	0.86608	0.86118	1.516	1.377	1.272
0.5000	0.86094	0.85559	0.85066	1.343	1.226	1.139
0.5500	0.85019	0.84479	0.83984	1.188	1.089	1.019
0.6000	0.83923	0.83378	0.82883	1.052	0.968	0.916
0.6496	0.82814	0.82266	0.81771	0.932	0.861	0.827
0.7001	0.81662	0.81111	0.80618	0.823	0.769	0.743
0.7494	0.80513	0.79961	0.79469	0.731	0.694	0.676
0.7999	0.79309	0.78756	0.78266	0.651	0.634	0.622
0.8505	0.78070	0.77515	0.77027	0.586	0.568	0.553
0.9000	0.76818	0.76262	0.75778	0.541	0.528	0.516
0.9497	0.75509	0.74953	0.74472	0.536	0.510	0.482
1.0000	0.74111	0.73559	0.73085	0.532	0.504	0.478

Table 4. Density (ρ) and viscosity (η) for ETBE (1) + TPM (2) binary mixtures at $T = 293.15$, 298.15 and 303.15 K.

	ρ (g cm^{-3})			η (MPa s)		
x_1	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K
0.0000	0.97062	0.96596	0.95992	6.721	5.662	4.989
0.0499	0.96366	0.95880	0.95269	5.867	4.984	4.416
0.0998	0.95646	0.95153	0.94537	5.125	4.391	3.899
0.1500	0.94897	0.94399	0.93785	4.462	3.852	3.442
0.2000	0.94122	0.93619	0.93009	3.905	3.386	3.045
0.2563	0.93210	0.92700	0.92092	3.366	2.927	2.650
0.2997	0.92475	0.91958	0.91354	2.987	2.605	2.381
0.3479	0.91619	0.91097	0.90495	2.606	2.300	2.112
0.4014	0.90620	0.90092	0.89492	2.249	2.001	1.848
0.4523	0.89616	0.89080	0.88488	1.951	1.751	1.627
0.5004	0.88616	0.88075	0.87489	1.698	1.544	1.443
0.5445	0.87653	0.87109	0.96530	1.499	1.377	1.292
0.6003	0.86371	0.85821	0.85252	1.291	1.197	1.121
0.6419	0.85363	0.84813	0.84249	1.157	1.077	1.006
0.7000	0.83882	0.83327	0.82771	0.995	0.936	0.875
0.7539	0.82416	0.81856	0.81304	0.871	0.827	0.773
0.8001	0.81086	0.80517	0.79968	0.781	0.749	0.701
0.8554	0.79383	0.78803	0.78258	0.687	0.669	0.630
0.9009	0.77870	0.77285	0.76750	0.620	0.612	0.579
0.9482	0.76168	0.75586	0.75068	0.560	0.558	0.528
1.0000	0.74111	0.73559	0.73085	0.532	0.504	0.478

The values of V^E for all studied mixtures, at $T = 293.15$, 298.15 and 303.15 K, are summarized in tables 5–7.

Excess volumes were fitted by a Redlich–Kister type equation [2]:

$$V^E\ (\mathrm{cm^3\,mol^{-1}}) = x_1(1 - x_1)\sum_{0}^{j} k_j(2x_1 - 1)^j \tag{2}$$

The parameters k_j ($j = 0$–4) in equation (2) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation $\rho(V^E)$, are summarized in table 8.

The standard deviation values were obtained from:

$$\sigma = \left[\frac{\sum (V_{\mathrm{exptl}} - V_{\mathrm{calcd}})^2}{n - p}\right]^{1/2} \tag{3}$$

where n is the number of experimental points, p is the number of parameters, V_{exptl} and V_{calcd} are the experimental and the calculated properties, respectively.

For clarity reasons, only the variations of V^E values as a function of the mole fraction of ETBE (x_1) at one temperature ($T = 298.15$ K) for all the studied mixtures are presented in the figure 1.

Figure 1 shows that V^E is negative for all three systems with the minimum lying always near: $x_1 \approx 0.50$ for (ETBE + PM), $x_1 \approx 0.60$ for (ETBE + DPM) and $x_1 \approx 0.65$ for (ETBE + TPM) binary mixtures. The value of V^E becomes more negative as the alkyl chain length of alkoxyethanol (the number of oxypropylene groups –O–CH_2–CH_2–CH_2– in the alkoxypropanol) increases and the temperature

Table 5. Excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), excess energy of activation for viscous flow (ΔG^{*E}) and Grunberg–Nissan interaction parameter (d_{12}) for ETBE (1) + PM (2) binary mixtures.

	V^E ($\mathrm{cm^3\,mol^{-1}}$)			$\Delta\eta$ (MPa s)			ΔG^{*E} ($\mathrm{kJ\,mol^{-1}}$)			d_{12}
x_1	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K	298.15 K
0.0506	−0.099	−0.082	−0.066	−0.096	−0.076	−0.054	−1.670	−1.370	−0.810	−0.457
0.1011	−0.171	−0.152	−0.132	−0.173	−0.140	−0.105	−3.151	−2.719	−1.882	−0.476
0.1502	−0.230	−0.209	−0.191	−0.232	−0.189	−0.146	−4.411	−3.839	−2.896	−0.479
0.1999	−0.279	−0.262	−0.243	−0.277	−0.228	−0.181	−5.424	−4.819	−3.912	−0.479
0.2521	−0.323	−0.304	−0.287	−0.311	−0.257	−0.208	−6.371	−5.670	−4.821	−0.478
0.3003	−0.355	−0.339	−0.320	−0.332	−0.276	−0.224	−7.004	−6.353	−5.432	−0.479
0.3489	−0.379	−0.366	−0.348	−0.344	−0.287	−0.233	−7.555	−6.889	−5.822	−0.480
0.4001	−0.399	−0.383	−0.365	−0.347	−0.292	−0.237	−7.773	−7.260	−6.147	−0.479
0.4489	−0.407	−0.392	−0.373	−0.342	−0.290	−0.237	−7.852	−7.483	−6.388	−0.479
0.5000	−0.409	−0.393	−0.373	−0.332	−0.283	−0.231	−7.820	−7.565	−6.372	−0.478
0.5501	−0.399	−0.384	−0.364	−0.315	−0.268	−0.220	−7.615	−7.326	−6.227	−0.469
0.5996	−0.383	−0.368	−0.348	−0.294	−0.250	−0.207	−7.221	−6.922	−6.065	−0.457
0.6508	−0.358	−0.342	−0.322	−0.268	−0.228	−0.190	−6.761	−6.506	−5.788	−0.454
0.7004	−0.330	−0.311	−0.292	−0.239	−0.203	−0.169	−6.226	−5.941	−5.203	−0.449
0.7500	−0.294	−0.275	−0.254	−0.207	−0.176	−0.144	−5.513	−5.253	−4.335	−0.445
0.8000	−0.253	−0.231	−0.210	−0.171	−0.145	−0.119	−4.656	−4.376	−3.700	−0.435
0.8507	−0.206	−0.184	−0.162	−0.133	−0.111	−0.088	−3.955	−3.376	−2.438	−0.424
0.9006	−0.152	−0.131	−0.110	−0.092	−0.076	−0.059	−2.935	−2.357	−1.607	−0.420
0.9500	−0.088	−0.073	−0.056	−0.048	−0.040	−0.028	−1.626	−1.404	−0.423	−0.465

Table 6. Excess molar volume (V^{E}), deviation in viscosity ($\Delta\eta$), excess energy of activation for viscous flow (ΔG^{*E}) and Grunberg–Nissan interaction parameter (d_{12}) for ETBE (1) + DPM (2) binary mixtures.

	V^{E} ($cm^3\,mol^{-1}$)			$\Delta\eta$ (MPa s)			ΔG^{*E} ($kJ\,mol^{-1}$)			d_{12}
x_1	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K	298.15 K
0.0511	−0.194	−0.175	−0.161	−0.271	−0.211	−0.170	−0.632	−0.312	−0.093	−0.127
0.0998	−0.333	−0.312	−0.291	−0.484	−0.386	−0.306	−1.225	−0.827	−0.195	−0.115
0.1506	−0.451	−0.430	−0.407	−0.665	−0.539	−0.435	−1.914	−1.478	−0.693	−0.159
0.2000	−0.550	−0.528	−0.507	−0.805	−0.660	−0.540	−2.635	−2.238	−1.351	−0.184
0.2502	−0.639	−0.618	−0.596	−0.917	−0.756	−0.626	−3.551	−3.082	−2.157	−0.152
0.3000	−0.720	−0.697	−0.672	−0.998	−0.825	−0.691	−4.534	−3.957	−3.074	−0.256
0.3506	−0.792	−0.768	−0.740	−1.053	−0.872	−0.736	−5.609	−4.933	−4.034	−0.318
0.3992	−0.852	−0.825	−0.794	−1.082	−0.897	−0.762	−6.798	−5.911	−5.019	−0.316
0.4505	−0.905	−0.872	−0.840	−1.089	−0.904	−0.772	−8.082	−7.022	−6.118	−0.337
0.5000	−0.938	−0.906	−0.872	−1.075	−0.895	−0.764	−9.433	−8.226	−7.095	−0.449
0.5500	−0.960	−0.927	−0.893	−1.041	−0.870	−0.741	−10.811	−9.521	−8.065	−0.574
0.6000	−0.966	−0.935	−0.902	−0.989	−0.830	−0.702	−12.107	−10.763	−8.712	−0.618
0.6496	−0.957	−0.929	−0.899	−0.922	−0.776	−0.649	−13.424	−12.011	−9.117	−0.792
0.7001	−0.931	−0.907	−0.880	−0.840	−0.705	−0.579	−14.837	−12.837	−9.728	−0.850
0.7494	−0.887	−0.868	−0.845	−0.746	−0.620	−0.516	−15.998	−13.099	−9.899	−0.934
0.7999	−0.818	−0.803	−0.783	−0.636	−0.517	−0.426	−16.768	−13.111	−9.999	−1.070
0.8505	−0.712	−0.701	−0.683	−0.510	−0.419	−0.351	−16.714	−12.892	−9.912	−1.376
0.9000	−0.564	−0.553	−0.541	−0.368	−0.299	−0.247	−14.940	−11.006	−8.071	−1.703
0.9497	−0.340	−0.332	−0.324	−0.186	−0.157	−0.139	−7.880	−6.372	−6.099	−1.872

Table 7. Excess molar volume (V^{E}), deviation in viscosity ($\Delta\eta$), excess energy of activation for viscous flow (ΔG^{*E}) and Grunberg–Nissan interaction parameter (d_{12}) for ETBE (1) + TPM (2) binary mixtures.

	V^{E} ($cm^3\,mol^{-1}$)			$\Delta\eta$ (MPa s)			ΔG^{*E} ($kJ\,mol^{-1}$)			d_{12}
x_1	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K	293.15 K	298.15 K	303.15 K	298.15 K
0.0499	−0.130	−0.099	−0.075	−0.545	−0.421	−0.348	−0.443	−0.241	−0.098	−0.144
0.0998	−0.266	−0.230	−0.189	−0.978	−0.756	−0.640	−0.864	−0.456	−0.398	−0.143
0.1500	−0.408	−0.374	−0.329	−1.331	−1.036	−0.870	−1.499	−0.948	−0.691	−0.175
0.2000	−0.552	−0.519	−0.476	−1.578	−1.244	−1.042	−1.819	−1.359	−0.903	−0.190
0.2563	−0.708	−0.677	−0.628	−1.769	−1.413	−1.183	−2.094	−1.886	−1.231	−0.209
0.2997	−0.822	−0.787	−0.739	−1.879	−1.511	−1.256	−2.692	−2.609	−1.499	−0.245
0.3479	−0.932	−0.897	−0.845	−1.962	−1.568	−1.308	−3.655	−3.090	−1.883	−0.261
0.4014	−1.038	−1.003	−0.945	−1.988	−1.591	−1.330	−4.448	−3.723	−2.365	−0.288
0.4523	−1.117	−1.078	−1.025	−1.971	−1.578	−1.322	−5.374	−4.416	−2.870	−0.321
0.5004	−1.173	−1.134	−1.084	−1.926	−1.537	−1.289	−6.608	−5.073	−3.347	−0.356
0.5445	−1.207	−1.172	−1.124	−1.852	−1.476	−1.241	−7.562	−5.636	−3.838	−0.390
0.6003	−1.233	−1.198	−1.157	−1.715	−1.369	−1.160	−8.191	−6.043	−4.629	−0.425
0.6419	−1.236	−1.208	−1.166	−1.591	−1.274	−1.087	−8.552	−6.455	−5.400	−0.465
0.7000	−1.224	−1.196	−1.154	−1.394	−1.115	−0.956	−8.932	−6.556	−5.728	−0.508
0.7539	−1.180	−1.151	−1.101	−1.184	−0.946	−0.815	−8.815	−6.235	−5.691	−0.539
0.8001	−1.119	−1.080	−1.020	−0.988	−0.786	−0.679	−8.374	−5.487	−5.113	−0.546
0.8554	−0.989	−0.935	−0.864	−0.740	−0.581	−0.500	−7.697	−4.214	−3.752	−0.538
0.9009	−0.806	−0.745	−0.674	−0.525	−0.403	−0.346	−6.928	−2.899	−2.411	−0.510
0.9482	−0.510	−0.458	−0.399	−0.293	−0.213	−0.184	−5.754	−1.509	−1.311	−0.479

Table 8. Coefficients k_j and standard deviations $\sigma(V^E)$ of equation (2) for (ETBE + PM), (ETBE + DPM) and (ETBE + TPM) binary mixtures at $T = 293.15$, 298.15 and 303.15 K.

T (K)	k_0	k_1	k_2	k_3	k_4	$\sigma(V^E)$ (cm^3 mol^{-1})
ETBE + PM						
293.15	−1.6325	0.1605	0.1340	−0.0641	−0.6189	0.0010
298.15	−1.5717	0.1752	0.2021	−0.0756	−0.3107	0.0010
303.15	−1.4913	0.1883	0.1829	−0.0738	0.0840	0.0010
ETBE + DPM						
293.15	−3.7560	−1.1431	−0.8028	−0.7048	−1.7482	0.0010
298.15	−3.6240	−1.1055	−1.0268	−0.8930	−1.2773	0.0010
303.15	−3.4881	−1.0711	−1.1549	−1.0243	−0.9573	0.0010
ETBE + TPM						
293.15	−4.6896	−1.9198	−0.7881	−2.8981	−1.9293	0.0014
298.15	−4.5340	−2.0156	−1.1173	−2.5014	−0.4725	0.0015
303.15	−4.3310	−2.1578	−1.1767	−1.9049	0.6401	0.0015

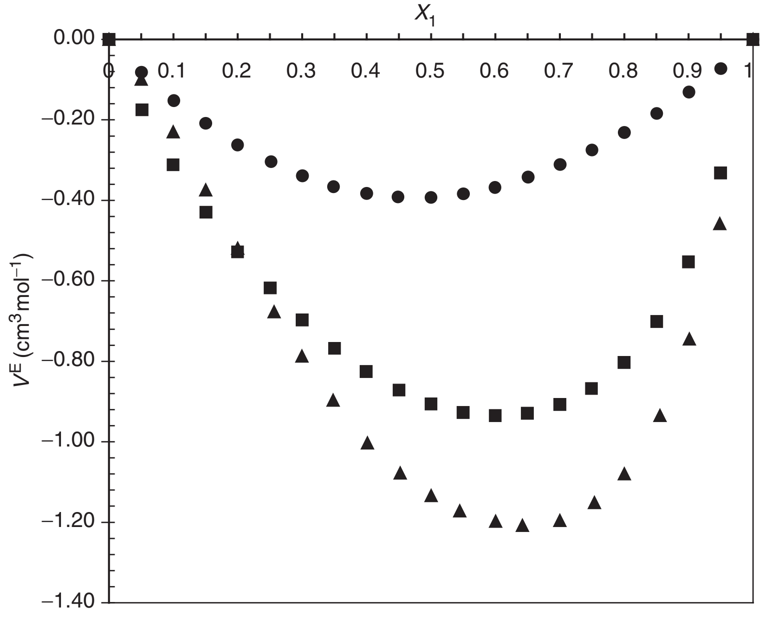

Figure 1. Plot of excess molar volume (V^E) against mole fraction ETBE for (●) ETBE (1) + PM (2), (■) ETBE (1) + DPM (2) and (▲) ETBE (1) + TPM (2) binary liquid mixtures, at $T = 298.15$ K.

decreases (see tables 5–7):

$$V^E_{\min}(\text{ETBE} + \text{TPM}) > V^E_{\min}(\text{ETBE} + \text{DPM}) > V^E_{\min}(\text{ETBE} + \text{PM})$$

The $V^E_{\min}$ values are represented in figure 2 with the number of oxypropylene groups –O–CH$_2$–CH$_2$–CH$_2$– in the studied alkoxypropanols, at each studied temperature. This dependence is not linear and it shows a slight curvature. The negative values of V^E are the result of contributions of several factors [4–6].

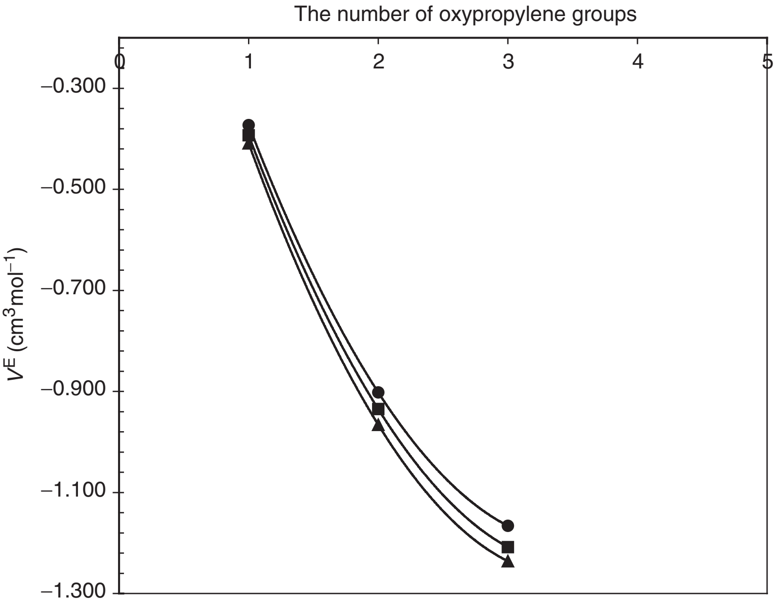

Figure 2. Plot of the function V^E_{min} against the numbers of oxypropylene groups in the studied alkoxypropanols for (●) ETBE + PM, (■) ETBE + DPM and (▲) ETBE + TPM binary liquid mixtures, at $T = 293.15$, 298.15 and 303.15 K.

Aliphatic ethers can be classified as homomorphic products obtained by replacing a –CH$_2$– group in alkanes by oxygen atom. Intermolecular interactions between the polar components and ether are proposed to occur via intermolecular complex formation and/or n–π interactions [7]. Alkoxypropanols are a very interesting class of the solvents, due to the simultaneous presence of the alkoxy and hydroxyl groups in the same molecule, which allow their self-association *via* intra- and/or intermolecular hydrogen bonds. The formation of the intermolecular hydrogen bonds is more favourable when the molecules are in the gauche conformations [8–10]. The addition of pure ETBE to alkoxypropanols would disrupt their self-associated structure (hence ETBE acts likewise as an inert solvent). Then, the alkoxypropanol molecules may interact by dipole–dipole forces and/or intermolecular hydrogen bonds with ETBE molecules.

Another effect that gives rise to a negative contribution to the excess volumes is the difference in the molecular sizes between the two components in the binary mixtures (contraction due to free volume difference of unlike molecules). The PM, DPM, TPM and ETBE molecules have different molar volumes at $T = 298.15$ K as pure species: $V(\mathrm{PM}) = 98.344\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$; $V(\mathrm{DPM}) = 155.550\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$; $V(\mathrm{TPM}) = 213.554\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ and $V(\mathrm{ETBE}) = 138.908\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. It can be seen that this effect should be significant and of great importance for (TPM + ETBE) binary mixtures. Probably, it is the main cause for the shift of the minimum value V^E_{min}, with the increase of the number of –O–CH$_2$–CH$_2$–CH$_2$– groups in alkoxypropanols, towards the richer in ETBE region of the studied binary mixtures.

From the measured viscosities the deviation in the viscosity from a mole fraction average, at the each investigated temperature, were calculated from the following equation:

$$\Delta\eta = \eta - (x_1\eta_2 + x_2\eta_2) \tag{4}$$

where η_1, η_2 and η are the viscosities of the ETBE, alkoxypropanols, and the mixtures, respectively.

The excess energies of activation for the viscous flow were obtained from the equation:

$$\Delta G^{*\mathrm{E}} = RT\{(\ln \eta V) - [x_1(\ln \eta_1 V_1) + x_2(\ln \eta_2 V_2)]\} \tag{5}$$

where V_1, V_2 and V are the molar volumes of the ETBE, alkoxypropanols, and the mixtures, respectively.

Each set of values have been fitted to the Redlich–Kister type equation [2]:

$$\begin{aligned} \Delta\eta\ (\mathrm{MPa\,s}) &= x_1 \cdot (1 - x_1) \sum_{j=0}^{k} \alpha_j \cdot (2x_2 - 1)^j \\ \Delta G^{*\mathrm{E}}\ (\mathrm{kJ\,mol^{-1}}) &= x_1 \cdot (1 - x_1) \sum_{j=0}^{k} \beta_j \cdot (2x_2 - 1)^j \end{aligned} \tag{6}$$

The parameters α_j and β_j ($j = 0$–4) in equation (6) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation σ, are summarized in tables 9 and 10. The standard deviation values were obtained from equation (3).

For clarity reasons, only the variations of $\Delta\eta$ and $\Delta G^{*\mathrm{E}}$ values as a function of the mole fraction of ETBE (x_1) at one temperature $T = 298.15$ K for all the studied mixtures are presented in the figures 3 and 5.

Figure 3 and tables 5–7 show that the $\Delta\eta$ deviations, for all investigated systems and temperatures, are negative with the minimum lying always near $x_1 \approx 0.40$ for (ETBE + PM), (ETBE + DPM) and (ETBE + TPM) binary mixtures. The negative values of $\Delta\eta$ over the entire mole fraction range may also occur, where dispersion forces are dominated, particularly for the systems having different molecular sizes [7,11–13].

Table 9. Coefficients α_j and standard deviations $\sigma(\Delta\eta)$ of equation (6) for (ETBE + PM), (ETBE + DPM) and (ETBE + TPM) binary mixtures at $T = 293.15$, 298.15 and 303.15 K.

T (K)	α_0	α_1	α_2	α_3	α_4	$\sigma(\Delta\eta)$ (MPa s)
ETBE + PM						
293.15	−1.3267	0.5524	−0.2012	−0.0046	−0.0254	0.0003
298.15	−1.1265	0.4340	−0.0931	−0.0088	−0.0237	0.0007
303.15	−0.9218	0.3302	−0.1222	−0.0241	0.2410	0.0009
ETBE + DPM						
293.15	−4.2948	0.9620	−0.5092	−0.1881	−0.2016	0.0037
298.15	−3.5843	0.7512	−0.3266	−0.1683	0.0053	0.0036
303.15	−3.0582	0.7056	0.2398	−0.4435	−0.4862	0.0038
ETBE + TPM						
293.15	−7.6971	2.8470	−0.5113	0.4910	−0.9688	0.0065
298.15	−6.1494	2.2950	−0.5889	0.2529	0.0953	0.0024
303.15	−5.1600	1.7297	−0.7348	0.4406	0.3251	0.0023

Table 10. Coefficients α_j and standard deviations $\sigma(\Delta G^{*E})$ of equation (6) for (ETBE + PM), (ETBE + DPM) and (ETBE + TPM) binary mixtures at $T = 293.15$, 298.15 and 303.15 K.

T (K)	β_0	β_1	β_2	β_3	β_4	$\sigma(\Delta G^{*E})$ (kJ mol^{-1})
ETBE + PM						
293.15	−31.3017	6.1710	0.2750	−7.3240	−5.7901	0.050
298.15	−29.9570	2.9868	5.1238	−2.0342	−4.1466	0.060
303.15	−25.4800	0.8794	−1.4723	2.5479	19.5612	0.089
ETBE + DPM						
293.15 K	−37.1661	−52.9266	−54.6020	−57.5469	−31.4065	0.464
298.15 K	−33.1514	−47.2815	−38.6476	−32.0609	−14.3894	0.022
303.15 K	−28.4868	−33.4994	−3.3487	−36.1059	−44.6009	0.235
ETBE + TPM						
293.15	−26.5381	−33.4202	4.2441	−12.7133	−52.9692	0.444
298.15	−20.2245	−26.2613	−10.4464	14.0877	18.6492	0.081
303.15	−13.5332	−27.7954	−28.5680	18.9526	37.8030	0.139

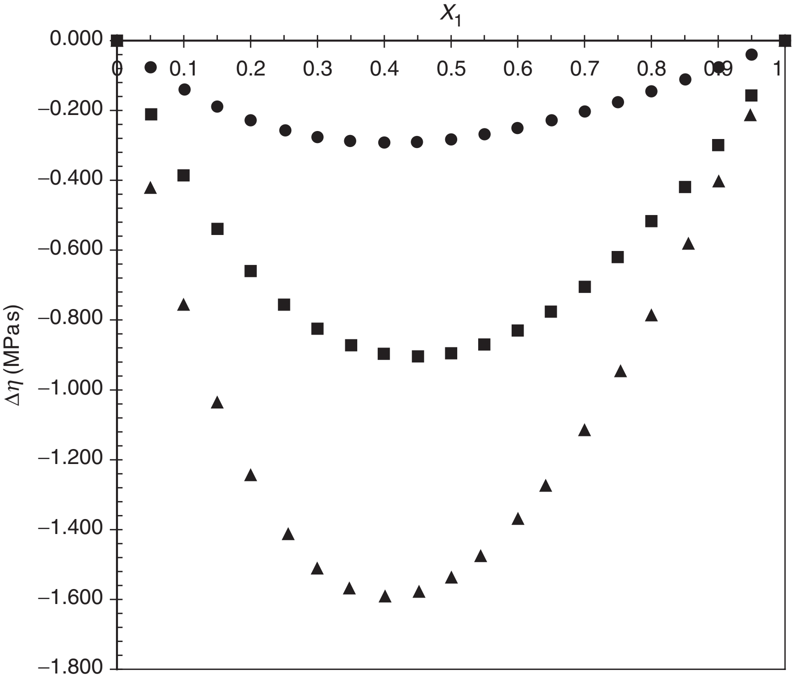

Figure 3. Plot of deviations in the viscosity ($\Delta\eta$) against mole fraction of ETBE for (●) ETBE (1) + PM (2), (■) ETBE (1) + DPM (2) and (▲) ETBE (1) + TPM (2) binary liquid mixtures, at $T = 298.15$ K.

The following dependence is observed in the studied mixtures:

$$\Delta\eta_{\min}(\text{ETBE} + \text{TPM}) > \Delta\eta_{\min}(\text{ETBE} + \text{DPM}) > \Delta\eta_{\min}(\text{ETBE} + \text{PM})$$

This effect is also supported by the negative values of V^{E} and suggests that the strength of the intermolecular interaction is not the only factor influencing the $\Delta\eta_{\min}$ of the studied liquid mixtures, but the molecular size of the components is also equally important.

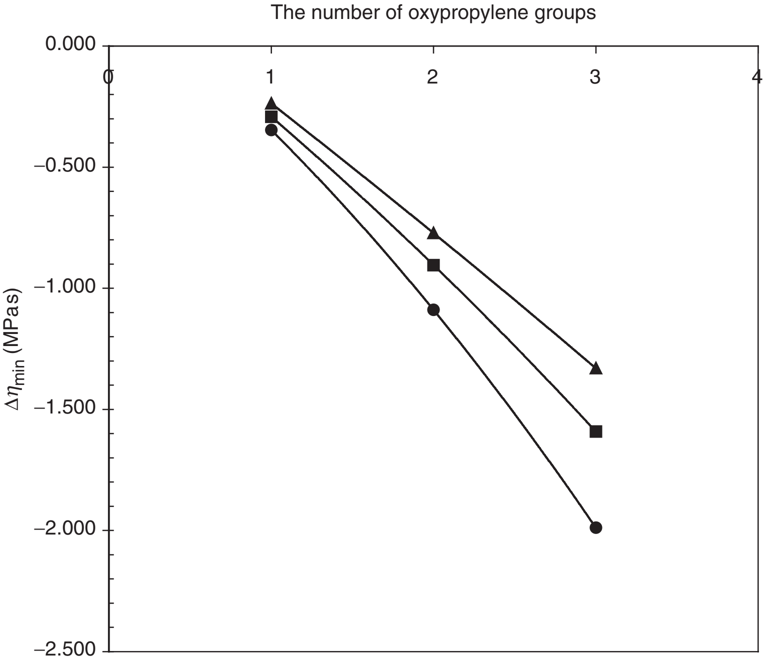

Figure 4. Plot of the function $\Delta\eta_{\min}$ against the number of oxypropylene groups in the studied alkoxypropanols for (●) ETBE + PM, (■) ETBE + DPM and (▲) ETBE + TPM binary liquid mixtures, at $T = 293.15$, 298.15 and 303.15 K.

The values $\Delta\eta_{\min}$ are represented in figure 4 with the number of oxypropylene groups –O–CH_2–CH_2–CH_2– in the studied alkoxypropanols, at each studied temperature. This dependence (similarly as $V^{E}_{\min}$) is not linear and it shows a slight curvature.

The sign of the values of the excess Gibbs energies of activation for viscous flow ΔG^{*E} can be considered as a reliable criterion for detecting or excluding the presence of interactions between unlike molecules [14–16]. Figure 5 and table 10 shows that the excess ΔG^{*E}, for all investigated systems and temperatures, are negative with the minimum lying always near: $x_1 \approx 0.50$ for (ETBE + PM), $x_1 \approx 0.80$ for (ETBE + DPM) and $x_1 \approx 0.70$ for (ETBE + TPM) binary mixtures. Like $\Delta\eta$, the negative ΔG^{*E} values are also indicative for the presence of the dispersion forces in the studied mixtures [14–16].

Similar conclusions could be drawn from the analysis of the values of the Grunberg–Nissan interaction parameter (d_{12}). As suggested by other authors [15–18], this parameter is regarded as a measure of the strength of interactions between the dissimilar molecules. The negative value of the d_{12} parameter gives an indication of the dispersion force interactions between unlike molecules in the mixed solvent [16].

From the measured viscosities the Grunberg–Nissan interaction parameter, was calculated (at $T = 298.15$) using the equation:

$$d_{12} = \frac{(\ln\eta - x_1 \ln\eta_1 - x_2 \ln\eta_2)}{x_1 x_2} \qquad (7)$$

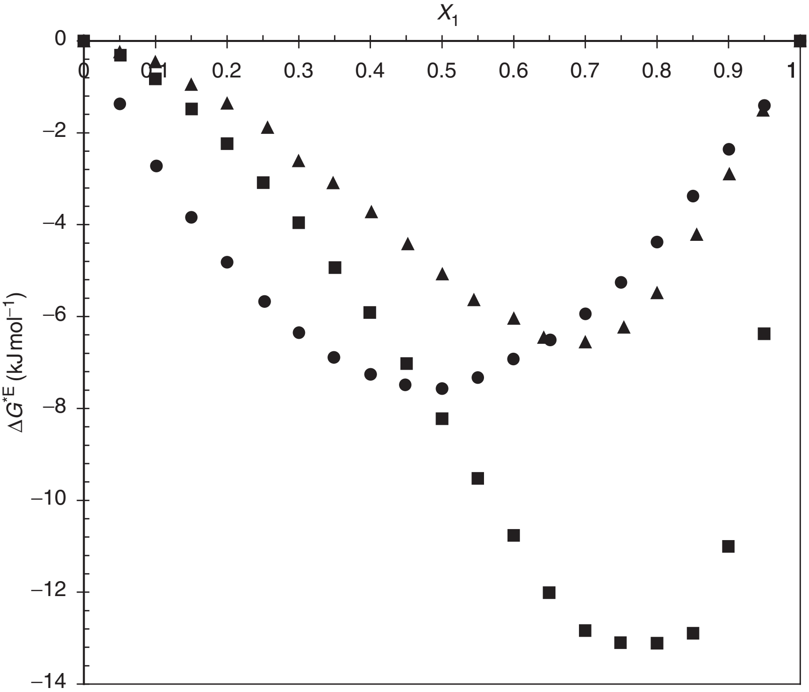

Figure 5. Plot of excess Gibbs energy of activation for viscous flow (ΔG^{*E}) against mole fraction of ETBE for (●) ETBE (1) + PM (2), (■) ETBE (1) + DPM (2) and (▲) ETBE (1) + TPM (2) binary liquid mixtures, at $T = 298.15$ K.

The values of d_{12}, for (ETBE + PM), (ETBE + DPM) and (ETBE + TPM) binary mixtures, are summarized in tables 5–7. For all studied mixtures, the values of d_{12} are negative. Like $\Delta\eta$ and ΔG^{*E}, the negative values of the Grunberg–Nissan interaction parameter suggest the dominance of the dispersion interaction between ETBE and the studied alkoxypropanols.

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