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VOLUMETRIC PROPERTIES OF BINARY MIXTURES OF ALCOXYETHANOLS WITH *tert*-BUTYL ETHYL ETHER AT VARIOUS TEMPERATURES

C. M. Kinart[1*], *Aneta Ćwiklińska*[1] *and W. J. Kinart*[2]

[1]Department of Chemistry, University of Łódź, Pomorska 163, 90 236 Łódź, Poland
[2]Department of Organic Chemistry, University of Łódź, Narutowicza 68, 90 136 Łódź, Poland

Densities at 293.15, 298.15, 303.15, 308.15 and 313.15 K of the binary liquid mixtures made of *tert*-butyl ethyl ether with either 2-ethoxyethanol, or 2-(2-ethoxy)ethoxyethanol, or 2-[2-(2-ethoxy)ethoxy]ethoxyethanol have been measured over the whole mixture compositions. These data have been used to compute the excess molar volumes (V^E). The excess molar volumes always are negative over the entire range of composition for all the binary mixtures investigated. The changes of V^E with variations of the composition and the chain-length of the alkyl groups in the alkoxyethanol molecules are discussed in terms of possible intermolecular interactions.

Keywords: *density, 2-ethoxyethanol, 2-(2-ethoxy)ethoxyethanol, 2-[2-(2-ethoxy)ethoxy]ethoxyethanol, intermolecular interactions, tert-butyl ethyl ether*

Introduction

Alkoxyalkohols and methyl- or *tert*-butyl ethyl ether are used in chemical industry as the solvents for oils and petrol, and are used on gasoline modification as octane boosters or anti-knock additives. The use such of ethers has been suggested to reduce the gasoline vapour pressure or for improving its combustion.

The nature and types of intermolecular interactions in binary liquid mixtures containing alkoxyethanols or *tert*-butyl ethyl ether have previously been studied [1–7]. In the present studies, the 2-ethoxyethanol (EE), 2-(2-ethoxy)ethoxyethanol (DEE), 2-[2-(2-ethoxy) ethoxy]ethoxyethanol (TEE) and *tert*-butyl ethyl ether (TBEE) have been used. The literature review shows that the physico-chemical properties of (EE+TBEE), (DEE+TBEE) and (TEE+TBEE) binary mixtures have not been studied up to now. Therefore, we have decided to carry out the measurements of the densities in these mixtures. From these results, the excess molar volumes at 293.15, 298.15, 303.15, 308.15 and 313.15 K have been calculated. These data have been fitted to the Redlich–Kister equation [8], to obtain the binary coefficients and standard deviations. Furthermore, the experimental results have been used to elucidate the nature of intermolecular interactions displayed in the bulk of binary mixtures studies herein.

Experimental

Materials

The following materials with mole fraction purity as stated were used: 2-ethoxyethanol (Merck – Schuchardt FRG, GC>99.0 mass%), 2-(2-ethoxy)ethoxyethanol (Merck – Schuchardt FRG, GC>98.0 mass%) and 2-[2-(2-ethoxy)ethoxy]ethoxyethanol (Fluka, Switzerland, purum, GC≥97.0 mass%). All three alkoxyethanols were further purified by the methods described by Pal *et al*. [9]. *tert*-Butyl ethyl ether (Fluka, Switzerland, purum, GC≥97.0 mass%) was used. It was purified by fractional distillation using a spinning band distillation column, after its drying over molecular sieves (type 4A). The purity of this solvent was confirmed by a gas chromatography to be 99.9 mass%. The mixtures were prepared just before us by mass on a Sartorius balance of the type ING1, operating in a dry box to avoid atmospheric moisture. Conversion to molar quantities was based on the relative atomic mass table published in 1985, next issued by IUPAC in 1986. The error in the mole fraction *tert*-butyl ethyl ether is estimated to be less than $\pm 1 \cdot 10^{-4}$. Liquids were stored in a dry-box over P_2O_5, and were degassed by ultrasound just prior the experiment. Experimental densities for the pure solvents, at 298.15 K, are compared with values available in the literature and listed in Table 1. The differences between the measured and the literature values can be ascribed both to different measurement methods used, and to the different purification procedures employed by other authors [10].

* Author for correspondence: ckinart@uni.lodz.pl

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Table 1 Densities of pure components, at T=298.15 K

Solvent	ρ/g cm^{-3}	
	this work	literature
tert-butyl ethyl ether	0.73559	0.73557 [23] 0.7353 [24]
2-ethoxyethanol	0.92515	0.92572 [25] 0.9258 [26]
2-(2-ethoxy)ethoxyethanol	0.98433	0.9839 [27] 0.98468 [28]
2[2-(2-ethoxy)ethoxy]ethoxyethanol	1.01647	1.0161 [29] 1.01703 [30]

Measurements

The densities were determined by means of a bicapillary type Lipkin pycnometer, with a capacity of ca. 90 cm^3. Double distilled, deionized and degassed water with a specific conductance of $1\cdot10^{-7}$ Ω^{-1} cm^{-1} was used for the calibration. The maximum error in the density measurements was $\pm1\cdot10^{-5}$ g cm^{-3}. In all the volumetric measurements, a Haake model DC-30 thermostat was used at a constant digital temperature control of ±0.01 K.

Results and discussion

The experimental densities (ρ) obtained from the measurements of the pure neat solvents and for the binary mixtures at all investigated temperatures are summarized in Tables 2–4. Many investigations of the density behaviour of liquids have been reported in the literature, and the best representation of the results as a function of temperature is given by the following equation:

Table 2 Densities (ρ) and excess molar volumes (V^E) for *tert*-butyl ethyl ether (1)+2-ethoxyethanol (2) binary mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K

	TBEE (1)+EE (2)									
	Temperature/K									
x_1	ρ/g cm^{-3}					V^E/cm^3 mol^{-1}				
	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
0.0000	0.92908	0.92515	0.92050	0.91609	0.91138	–	–	–	–	–
0.0500	0.91737	0.91300	0.90807	0.90333	0.89830	–0.149	–0.119	–0.091	–0.062	–0.033
0.1001	0.90633	0.90181	0.89665	0.89179	0.88658	–0.325	–0.294	–0.244	–0.207	–0.166
0.1489	0.89604	0.89125	0.88609	0.88110	0.87577	–0.506	–0.459	–0.411	–0.364	–0.316
0.2002	0.88555	0.88067	0.87534	0.87029	0.86486	–0.689	–0.647	–0.581	–0.531	–0.477
0.2511	0.87544	0.87031	0.86503	0.85986	0.85435	–0.862	–0.803	–0.744	–0.685	–0.626
0.2999	0.86591	0.86048	0.85525	0.84994	0.84433	–1.005	–0.921	–0.869	–0.796	–0.728
0.3486	0.85635	0.85085	0.84548	0.84012	0.83442	–1.101	–1.019	–0.949	–0.871	–0.795
0.4000	0.84629	0.84072	0.83533	0.82995	0.82421	–1.161	–1.079	–1.005	–0.926	–0.848
0.4511	0.83642	0.83074	0.82532	0.81989	0.81410	–1.189	–1.101	–1.021	–0.936	–0.852
0.5000	0.82694	0.82129	0.81589	0.81051	0.80475	–1.165	–1.088	–1.009	–0.931	–0.853
0.5502	0.81738	0.81172	0.80637	0.80103	0.79531	–1.116	–1.045	–0.971	–0.899	–0.827
0.5999	0.80806	0.80244	0.79713	0.79185	0.78617	–1.041	–0.982	–0.911	–0.848	–0.783
0.6520	0.79860	0.79298	0.78777	0.78255	0.77694	–0.956	–0.905	–0.846	–0.792	–0.737
0.6999	0.79009	0.78453	0.77938	0.77424	0.76869	–0.862	–0.826	–0.773	–0.731	–0.687
0.7499	0.78158	0.77601	0.77093	0.76582	0.76030	–0.775	–0.743	–0.699	–0.663	–0.625
0.8000	0.77335	0.76774	0.76268	0.75758	0.75207	–0.692	–0.659	–0.616	–0.580	–0.542
0.8505	0.76529	0.75962	0.75458	0.74947	0.74394	–0.602	–0.564	–0.521	–0.481	–0.441
0.9000	0.75751	0.75179	0.74672	0.74159	0.73604	–0.489	–0.448	–0.396	–0.351	–0.305
0.9499	0.74951	0.74382	0.73887	0.73382	0.72834	–0.303	–0.271	–0.236	–0.203	–0.170
1.0000	0.74111	0.73559	0.73085	0.72598	0.72069	–	–	–	–	–

Table 3 Densities (ρ) and excess molar volumes (V^E) for *tert*-butyl ethyl ether (1)+2-(2-ethoxy)ethoxyethanol (2) binary mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K

	TBEE (1)+DEE (2)									
	Temperature/K									
x_1	ρ/g cm^{-3}					V^E/cm^3 mol^{-1}				
	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
0.0000	0.98842	0.98433	0.97965	0.97534	0.97097	–	–	–	–	–
0.0500	0.97776	0.97344	0.96851	0.96405	0.95953	–0.262	–0.249	–0.218	–0.207	–0.199
0.1000	0.96672	0.96217	0.95717	0.95264	0.94801	–0.475	–0.446	–0.410	–0.397	–0.387
0.1501	0.95541	0.95063	0.94562	0.94104	0.93631	–0.655	–0.609	–0.577	–0.565	–0.553
0.2000	0.94396	0.93897	0.93396	0.92931	0.92447	–0.811	–0.750	–0.720	–0.707	–0.691
0.2498	0.93238	0.92720	0.92215	0.91742	0.91248	–0.944	–0.870	–0.838	–0.820	–0.799
0.2999	0.92056	0.91523	0.91011	0.90528	0.90023	–1.054	–0.972	–0.932	–0.906	–0.878
0.3497	0.90863	0.90320	0.89799	0.89306	0.88790	–1.137	–1.051	–1.000	–0.965	–0.930
0.3999	0.89641	0.89091	0.88562	0.88060	0.87535	–1.191	–1.107	–1.044	–1.001	–0.958
0.4502	0.88398	0.87848	0.87309	0.86801	0.86267	–1.215	–1.142	–1.064	–1.015	–0.967
0.5002	0.87145	0.86590	0.86053	0.85540	0.85000	–1.208	–1.139	–1.062	–1.010	–0.959
0.5500	0.85883	0.85329	0.84792	0.84278	0.83734	–1.176	–1.118	–1.041	–0.990	–0.939
0.5997	0.84613	0.84060	0.83528	0.83014	0.82468	–1.124	–1.077	–1.006	–0.958	–0.908
0.6504	0.83311	0.82760	0.82234	0.81722	0.81174	–1.055	–1.019	–0.956	–0.914	–0.867
0.7003	0.82027	0.81476	0.80957	0.80447	0.79900	–0.978	–0.951	–0.896	–0.859	–0.817
0.7503	0.80741	0.80189	0.79675	0.79166	0.78619	–0.896	–0.874	–0.825	–0.791	–0.753
0.7998	0.79468	0.78913	0.78401	0.77893	0.77347	–0.807	–0.787	–0.740	–0.707	–0.673
0.8498	0.78176	0.77617	0.77107	0.76599	0.76053	–0.702	–0.681	–0.632	–0.600	–0.568
0.9000	0.76861	0.76299	0.75793	0.75287	0.74741	–0.558	–0.536	–0.488	–0.460	–0.428
0.9500	0.75517	0.74955	0.74459	0.73962	0.73417	–0.343	–0.324	–0.289	–0.273	–0.244
1.0000	0.74111	0.73559	0.73085	0.72598	0.72069	–	–	–	–	–

$$\rho(t) = \sum_{0}^{i} a_i t^i \quad (1)$$

a_i (i=0–3) are empirical constants and t is the Celsius temperature. The a_i coefficients of this fitting procedure are listed in Tables 5–7, along with the standard deviations σ(ρ) for each binary mixture.

Equation (1) reproduces the experimental density values with an average uncertainty, evaluated by means of the relation:

$$\overline{\Delta\rho} = \frac{\sum \left| \rho_{cal} - \rho_{exp} \right|}{N} \quad (2)$$

where N is the number of experimental points.

The values of $\overline{\Delta\rho}$=±2.3·10^{-5} g cm^{-3} for (TBEE+EE), $\overline{\Delta\rho}$=±2.9·10^{-5} g cm^{-3} for (TBEE+DEE) and $\overline{\Delta\rho}$=±3.2·10^{-5} g cm^{-3} for (TBEE+TEE) binary liquid mixtures.

The variation of the density with binary composition was studied by using the following equation:

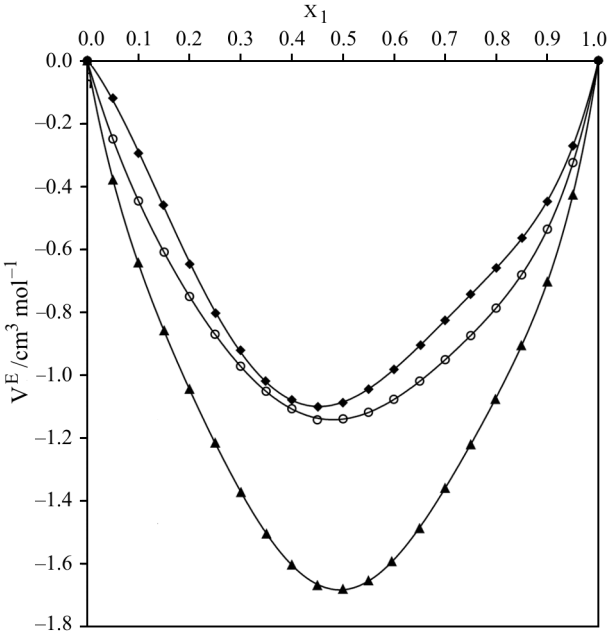

Fig. 1 Plots of excess molar volume (V^E) *vs*. mole fraction TBEE for ■ – TBEE (1)+EE (2), ○ – TBEE (1)+DEE (2) and ▲ – TBEE (1)+TEE (2) binary liquid mixtures, at 298.15 K

Table 4 Densities (ρ) and excess molar volumes (V^E) for *tert*-butyl ethyl ether (1)+2-[2-(2-ethoxy)ethoxy]ethoxyethanol (2) binary mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K

	TBEE (1)+TEE (2)									
	Temperature/K									
x_1	ρ/g cm^{-3}					V^E/cm^3 mol^{-1}				
	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
0.0000	1.02104	1.01647	1.01205	1.00755	1.00301	–	–	–	–	–
0.0501	1.01238	1.00741	1.00266	0.99782	0.99293	–0.432	–0.379	–0.333	–0.283	–0.234
0.0996	1.00282	0.99757	0.99256	0.98751	0.98236	–0.728	–0.643	–0.563	–0.480	–0.398
0.1502	0.99238	0.98696	0.98179	0.97655	0.97122	–0.960	–0.859	–0.754	–0.653	–0.550
0.1999	0.98170	0.97613	0.97083	0.96549	0.96001	–1.158	–1.045	–0.926	–0.813	–0.697
0.2502	0.97050	0.96480	0.95945	0.95400	0.94841	–1.337	–1.216	–1.095	–0.971	–0.847
0.3005	0.95889	0.95311	0.94767	0.94218	0.93653	–1.495	–1.373	–1.244	–1.120	–0.995
0.3506	0.94690	0.94104	0.93556	0.93003	0.92430	–1.630	–1.505	–1.375	–1.252	–1.123
0.4000	0.93457	0.92866	0.92319	0.91760	0.91187	–1.726	–1.604	–1.481	–1.353	–1.233
0.4502	0.92152	0.91557	0.91003	0.90450	0.89867	–1.788	–1.669	–1.539	–1.425	–1.298
0.5000	0.90797	0.90196	0.89649	0.89091	0.88507	–1.800	–1.681	–1.565	–1.449	–1.327
0.5500	0.89379	0.88775	0.88228	0.87669	0.87087	–1.771	–1.654	–1.541	–1.425	–1.315
0.5955	0.88038	0.87431	0.86885	0.86327	0.85744	–1.707	–1.593	–1.483	–1.370	–1.262
0.6498	0.86380	0.85772	0.85225	0.84669	0.84083	–1.598	–1.488	–1.377	–1.270	–1.160
0.7000	0.84795	0.84184	0.83640	0.83083	0.82497	–1.470	–1.360	–1.255	–1.145	–1.041
0.7502	0.83162	0.82552	0.82008	0.81454	0.80868	–1.325	–1.221	–1.115	–1.009	–0.906
0.7982	0.81560	0.80950	0.80410	0.79857	0.79272	–1.178	–1.077	–0.975	–0.871	–0.770
0.8491	0.79812	0.79202	0.78669	0.78121	0.77539	–1.005	–0.906	–0.813	–0.716	–0.621
0.9000	0.77996	0.77396	0.76871	0.76334	0.75758	–0.786	–0.703	–0.622	–0.541	–0.457
0.9500	0.76122	0.75538	0.75030	0.74510	0.73949	–0.481	–0.427	–0.371	–0.315	–0.259
1.0000	0.74111	0.73559	0.73085	0.72598	0.72069	–	–	–	–	–

$$\rho(x_1) = \sum_0^j b_j x_1^j \text{ where } j=0\text{–}6 \quad (3)$$

which could be fitted to the experimental data at each temperature using a least-squares method. The values of b_j coefficients and the standard deviations σ(ρ) are reported in Table 8. The goodness-of-fit of this procedure is ascertained by a mean deviation $\overline{\Delta\rho}=\pm 1.8\cdot 10^{-5}$ g cm^{-3} for (TBEE+EE), $\overline{\Delta\rho}=\pm 0.9\cdot 10^{-5}$ g cm^{-3} for (TBEE+DEE) and $\overline{\Delta\rho}=\pm 0.9\cdot 10^{-5}$ g cm^{-3} for (TBEE+TEE) binary liquid mixtures.

From the measured densities the excess molar volumes V^E of the mixtures, at the each investigated temperature, were calculated from the equation:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \quad (4)$$

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 each temperatures, respectively.

Excess volumes were fitted by a Redlich–Kister type equation [8]:

$$V^E\,[\text{cm}^3\,\text{mol}^{-1}] = x_1(1-x_1)\sum_0^j k_j(2x_1-1)^j \quad (5)$$

The parameters k_j (j=0–4) in Eq. (5) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation σ(V^E), are summarized in Table 9.

Standard deviation values were obtained from:

$$\sigma = \left[\frac{\sum (V_{exp} - V_{calcd})^2}{n-p}\right]^{1/2} \quad (6)$$

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

For clarity reasons, only the variations of V^E values as a function of the mole fraction of *tert*-butyl ethyl ether (x_1) at one temperature (T=298.15 K) for all the studied mixtures are presented in Fig. 1.

Figure 1 shows V^E is always negative for all three systems with the minimum positioned near by: x_1≈0.45 for (TBEE+EE), x_1≈0.45 for (TBEE+DEE)

Table 5 Coefficients a_i and standard deviations σ(ρ) of Eq. (1) for (TBEE+EE) binary mixtures

TBEE (1)+EE (2)					
x_1	$a_0 \cdot 10$	$a_1 \cdot 10^3$	$a_2 \cdot 10^5$	$a_3 \cdot 10^7$	$\sigma(\rho) \cdot 10^5$/g cm^{-3}
0.0000	9.3706	0.0693	–2.8972	2.8000	12.7
0.0500	9.2956	–0.2918	–1.9428	1.8000	10.4
0.1001	9.1899	–0.2997	–2.0486	1.9333	13.4
0.1489	9.1377	–0.8055	–0.4400	0.2000	8.9
0.2002	9.0327	–0.7726	–0.6543	0.4667	11.8
0.2511	8.9809	–1.2724	0.9542	–1.2666	6.0
0.2999	8.9448	–1.8702	2.8743	–3.3333	0.5
0.3486	8.8491	–1.8443	2.7086	–3.1333	1.9
0.4000	8.7626	–1.9834	3.1457	–3.6000	1.7
0.4511	8.6814	–2.1512	3.6543	–4.1333	0.7
0.5000	8.5876	–2.1672	3.7229	–4.2000	1.4
0.5502	8.5024	–2.2806	4.1086	–4.6000	0.8
0.5999	8.4111	–2.3097	4.2343	–4.7333	1.3
0.6520	8.3308	–2.4714	4.8029	–5.3333	0.3
0.6999	8.2468	–2.4965	4.9286	–5.4667	0.2
0.7499	8.1742	–2.6360	5.4200	–6.0000	1.2
0.8000	8.1035	–2.7554	5.8057	–6.4000	1.9
0.8505	8.0392	–2.9235	6.3600	–7.0000	3.0
0.9000	7.9674	–2.9762	6.5000	–7.1333	3.0
0.9499	7.9012	–3.1414	7.1114	–7.8000	4.3
1.0000	7.8148	–3.1576	7.2943	–8.0000	5.2

and $x_1 \approx 0.50$ for (TBEE+TEE) binary mixtures. The value of V^E_{min} becomes more negative as the alkyl chain length of alkoxyethanol (the number of oxyethylene groups –O–CH_2–CH_2– in the alkoxyethanol) increases, while the temperature decreases (Tables 2–4):

$$V^E_{min}(\text{TBEE} + \text{TEM}) >$$
$$V^E_{min}(\text{TBEE} + \text{DEM}) > V^E_{min}(\text{TBEE} + \text{ME})$$

In all the studied mixtures, the large negative values of V^E are the result of contributions of several factors [11–16].

The negative values of V^E over the entire mole fraction range may be attributed mainly to the association through intermolecular hydrogen bonds between oxygen of the –O– groups of the *tert*-butyl ethyl ether and hydrogen atom of the H–O– group of alkoxyethanol molecules. The negative values of V^E suggest that the interactions between alkoxyethanol and TBEE would probably predominate.

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 (e.g. alcohol or alkoxyalcohol) and ether are proposed to occur via intermolecular complex formation and/or *n*–π interactions [17]. Alkoxyethanols are a very interesting class of the solvents, due to the simultaneous presence of the oxy and hydroxyl groups in the same molecule, which allow their self-association via intra- and/or intermolecular hydrogen bonds. The formation of intermolecular hydrogen bonds is more favourable when the molecules are in the gauche conformations [18–22]. For these molecules 5- and 6-membered rings, of quite different strengths, are possibly formed [18]. The addition of pure *tert*-butyl ethyl ether to alkoxyethanols would disrupt their self-associated structure (hence TBEE acts likewise as an inert solvent). Then, the alkoxyethanol molecules may interact by dipole–dipole forces and/or intermolecular hydrogen bonds with TBEE molecules.

Another effect that gives rise to a negative contribution to excess volumes is the difference in molecular sizes between the two components of the respective binary mixtures. The EE, DEE, TEE and TBEE molecules have different molar volumes at T=298.15 K as pure species: V(EE)=97.416 cm^3 mol^{-1}; V(DEE)=136.314 cm^3 mol^{-1}; V(TEE)=175.342 cm^3 mol^{-1} and V(TBEE)=138.908 cm^3 mol^{-1}. It can be seen that this

Table 6 Coefficients a_i and standard deviations σ(ρ) of Eq. (1) for (TBEE+DEE) binary mixtures

TBEE (1)+DEE (2)					
x_1	$a_0 \cdot 10$	$a_1 \cdot 10^3$	$a_2 \cdot 10^5$	$a_3 \cdot 10^7$	$\sigma(\rho) \cdot 10^5$/g cm^{-3}
0.0000	9.9698	0.0787	–3.2343	3.5334	11.8
0.0500	9.8737	0.0298	–3.2800	3.6667	13.6
0.1000	9.8056	–0.3820	–2.0114	2.3333	12.6
0.1501	9.7446	–0.9072	–0.3286	0.5333	10.5
0.2000	9.6769	–1.3823	1.2086	–1.1333	7.9
0.2498	9.5956	–1.7215	2.2686	–2.2667	6.1
0.2999	9.4972	–1.9076	2.8229	–2.8667	5.0
0.3497	9.3844	–1.9571	2.9343	–3.0000	4.8
0.3999	9.2628	–1.9477	2.8600	–2.9334	4.7
0.4502	9.1266	–1.8148	2.4000	–2.4667	6.5
0.5002	9.0134	–1.9451	2.8543	3.0000	4.8
0.5500	8.8883	–1.9629	2.9429	3.1333	5.0
0.5997	8.7680	–2.0460	3.2714	3.5334	4.0
0.6504	8.6470	–2.1601	3.7171	–4.0667	3.3
0.7003	8.5297	–2.2887	4.1886	–4.6000	1.9
0.7503	8.4113	–2.4041	4.6029	–5.0667	0.9
0.7998	8.2935	–2.5022	4.9229	–5.4000	0.3
0.8498	8.1755	–2.6175	5.3000	–5.8000	0.6
0.9000	8.0590	–2.7789	5.8515	–6.4000	1.4
0.9500	7.9516	–3.0826	6.9343	–7.6000	1.7
1.0000	7.8148	–3.1576	7.2943	–8.0000	5.2

Table 7 Coefficients a_i and standard deviations σ(ρ) of Eq. (1) for (TBEE+TEE) binary mixtures

TBEE (1)+TEE (2)					
x_1	$a_0 \cdot 10$	$a_1 \cdot 10^3$	$a_2 \cdot 10^5$	$a_3 \cdot 10^7$	$\sigma(\rho) \cdot 10^5$/g cm^{-3}
0.0000	10.4206	–1.2274	1.1343	–1.2667	2.3
0.0501	10.3631	–1.4525	1.6400	–1.8000	3.0
0.0996	10.2908	–1.6398	2.0857	–2.2667	1.9
0.1502	10.1923	–1.6662	2.0714	–2.2667	2.5
0.1999	10.1027	–1.8192	2.5000	–2.7333	1.8
0.2502	10.0070	–1.9744	2.9743	–3.2667	3.5
0.3005	9.8973	–2.0207	3.0600	–3.3333	2.4
0.3506	9.7926	–2.1713	3.5400	–3.8667	2.4
0.4000	9.6709	–2.1815	3.5486	–3.8667	4.6
0.4502	9.5630	–2.4160	4.3314	–4.7333	7.6
0.5000	9.4419	–2.5711	4.8657	–5.3333	4.2
0.5500	9.3023	–2.5875	4.8915	–5.3333	4.9
0.5955	9.1789	–2.6994	5.2629	–5.7333	5.1
0.6498	9.0212	–2.7858	5.5600	–6.0667	4.1
0.7000	8.8713	–2.8764	5.8657	–6.4000	5.4
0.7502	8.7110	–2.9108	5.9886	–6.5333	4.6
0.7982	8.5564	–2.9754	6.2257	–6.8000	5.4
0.8491	8.3954	–3.1308	6.7772	–7.4000	6.2
0.9000	8.2139	–3.1567	6.9429	–7.6000	5.1
0.9500	8.0244	–3.1728	7.1171	–7.8000	5.0
1.0000	7.8148	–3.1576	7.2943	–8.0000	5.2

Table 8 Coefficients b_j and standard deviations $\sigma(\rho)$ of Eq. (3) for (TBEE+EE), (TBEE+DEE) and (TBEE+TEE) binary mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K

Temperature/K	b_0	b_1	b_2	b_3	b_4	b_5	b_6	$\sigma(\rho)\cdot10^5$/g cm^{-3}
				TBEE (1)+EE (2)				
293.15	0.92909	–0.24299	0.18289	–0.30120	0.11429	0.20631	–0.14730	2.6
298.15	0.92513	–0.25112	0.21651	–0.44399	0.43447	–0.11562	–0.29792	2.9
303.15	0.92050	–0.26080	0.28342	–0.68774	0.88396	–0.51017	0.10168	2.2
308.15	0.91607	–0.26809	0.32539	–0.85453	1.22644	–0.83554	0.21624	2.6
313.15	0.91136	–0.27642	0.37439	–1.04249	1.59905	–1.18134	3.36146	3.3
				TBEE (1)+DEE (2)				
293.15	0.98843	–0.20909	–0.10440	0.29672	–0.64520	0.67035	–0.25571	1.1
298.15	0.98434	–0.21335	–0.11059	0.32447	–0.65729	0.64578	–0.23779	1.6
303.15	0.97965	–0.22018	–0.05265	–0.08856	–0.20978	0.25358	–0.10832	3.8
308.15	0.97534	–0.22444	–0.01939	–0.06652	–0.11174	–0.04426	–0.00647	1.0
313.15	0.97097	–0.22833	–0.00001	–0.1546	0.29612	–0.21618	–0.05272	0.3
				TBEE (1)+TEE (2)				
293.15	1.02105	–0.16034	–0.29974	–0.87358	–1.72553	1.57161	–0.53952	1.0
298.15	1.01648	–0.16997	–0.26185	–0.77130	–1.55983	1.42957	–0.49011	1.1
303.15	1.01206	–0.17809	–0.23314	–0.70394	–1.45315	1.33386	–0.45463	1.5
308.15	1.00756	–0.18586	–0.20655	–0.64360	–1.36042	1.25156	–0.42391	1.4
313.15	1.00302	–0.19443	–0.17541	–0.56254	–1.22499	1.12956	–0.37961	1.9

Table 9 Coefficients k_j and standard deviations $\sigma(V^E)$ of Eq. (5) for (TBEE+EE), (TBEE+DEE) and (TBEE+TEE) binary mixtures at 293.15, 298.15, 303.15, 308.15 and 313.15 K

Temperature/K	k_0	k_1	k_2	k_3	$\sigma(V^E)$/cm^3 mol^{-1}
			TBEE (1)+EE (2)		
293.15	–4.5940	1.4519	0.4973	–4.0349	0.020
298.15	–4.3040	1.1635	0.5395	–3.5178	0.011
303.15	–4.0271	1.0784	0.7500	–3.4064	0.003
308.15	–3.7415	0.8591	0.8473	–3.0225	0.009
313.15	–3.4585	0.6730	0.9737	–2.7174	0.019
			TBEE (1)+DEE (2)		
293.15	–4.7475	0.7931	–1.1414	–2.1455	0.023
298.15	–4.4808	0.3774	–1.1456	–1.5745	0.021
303.15	–4.2167	0.4660	–1.0600	–1.5816	0.008
308.15	–4.0332	0.5279	–1.1048	–1.5093	0.003
313.15	–3.8470	0.5821	–1.1151	–1.3572	0.003
			TBEE (1)+TEE (2)		
293.15	–7.0282	0.3284	–1.3222	–1.1222	0.048
298.15	–6.5683	0.2181	–0.6665	–0.9660	0.044
303.15	–6.1018	0.0371	–0.0321	–0.6757	0.042
308.15	–5.6445	–0.0933	0.6321	–0.4668	0.039
313.15	–5.1844	–0.2727	1.2827	–0.1737	0.035

effect is significant and of a great importance for (EE+TBEE) binary mixtures.

The results obtained in this work seem to indicate that the molecules of the studied binary mixtures may be interconnected, by a network of various interactions such as dipolar and/or hydrogen bonds, to form quite stable intermolecular complexes [1–7, 31–33].

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