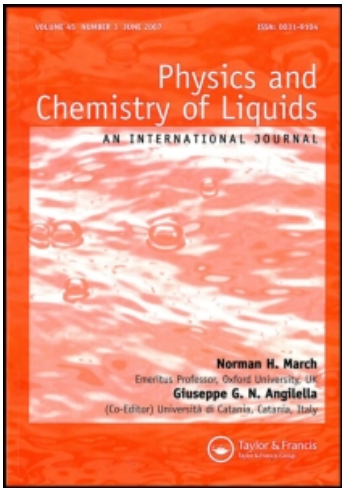

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Refractive Properties of Binary Mixtures Containing 2-Methoxyethanol and *n*-Butylamine, Isobutylamine, *sec*-Butylamine and *tert*-Butylamine

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Online publication date: 27 October 2010

To cite this Article Kinart, Cezary M. , Kinart, Wojciech J. , Chęcińska-Majak, Dorota and Ćwiklińska, Aneta(2003) 'Refractive Properties of Binary Mixtures Containing 2-Methoxyethanol and *n*-Butylamine, Isobutylamine, *sec*-Butylamine and *tert*-Butylamine', Physics and Chemistry of Liquids, 41: 4, 383 — 389
To link to this Article: DOI: 10.1080/0031910031000120603
URL: http://dx.doi.org/10.1080/0031910031000120603

Physics and Chemistry of Liquids
Vol. 41, No. 4, August 2003, pp. 383–389

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REFRACTIVE PROPERTIES OF BINARY MIXTURES CONTAINING 2-METHOXYETHANOL AND *n*-BUTYLAMINE, ISOBUTYLAMINE, *sec*-BUTYLAMINE AND *tert*-BUTYLAMINE

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(Received 17 March 2003)

Refractive index (n) and related properties such as molar refraction (R) have been investigated for 2-methoxyethanol (ME) + *n*-butylamine (*n*-BA) and 2-methoxyethanol (ME) + isobutylamine (iso-BA), 2-methoxyethanol (ME) + *sec*-butylamine (*sec*-BA) and 2-methoxyethanol (ME) + *tert*-butylamine (*tert*-BA) binary mixtures over the entire composition range, at different temperatures in the range $291.15 \leq T/\mathrm{K} \leq 313.15$. Furthermore, the excess molar refraction (R^E) and deviation from ideality refractive index (Δn) have been examined, in order to identify the presence of intermolecular complexes in these binary liquid mixtures. The results obtained have been interpreted on the basis of specific intermolecular interactions between species.

Keywords: Refractive index; 2-Methoxyethanol; *n*-Butylamine; Isobutylamine; *sec*-Butylamine; *tert*-Butylamine; Binary liquid mixtures

1. INTRODUCTION

Studies on different physicochemical properties (*macroscopic properties*) of liquid binary mixtures within wide ranges of compositions and temperatures are valuable sources of information that may be used to examine the relationship between the internal structure of the system and its physical properties. These data are very often essential for explanation of the solvent influence, one or two component, on chemical, electrochemical and biochemical processes occurring in the system. The experimental values of physical properties are often applied for calculations of other parameters characterising binary mixtures. Different theoretical, empirical and semiempirical methods have been extensively applied for this purpose. Many of them are based on

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ISSN 0031-9104 print: ISSN 1029-0451 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0031910031000120603

well-founded physical dependencies, e.g., between molecular and macroscopic parameters.

In this article, in continuation of our study on thermodynamic, transport and acoustic properties of binary mixtures containing alkoxymethanols and aprotic solvent [1–4], we report here new experimental data of the excesses molar refraction (R^E) and deviations from ideality of the refractive index of binary mixtures containing 2-methoxyethanol (ME) with *n*-butylamine (*n*-BA), isobutylamine (iso-BA), *sec*-butylamine (*sec*-BA), *tert*-butylamine (*ter*-BA) over the whole composition range, at different temperatures.

2. EXPERIMENTAL

Materials

2-methoxyethanol, *n*-butylamine, isobutylamine, *sec*-butylamine, *tert*-butylamine Merck, pro-analysis, containing less than 0.05% (w/w) of water, respectively (determined by Karl–Fischer method), were used. ME and aliphatic amines were further purified by the methods reported by Riddick *et al.* [5]. The mixtures were prepared by weighing with an accuracy $\pm 1 \times 10^{-4}$ g. The conversions to molar quantities were based on the relative atomic mass table (1985), issued by IUPAC in 1986. The uncertainty in the mole fractions is less than 1×10^{-4}. All liquids were stored in a dry-box over P_2O_5, and were degassed by ultrasounds just before the experiments.

Measurements

The refractive indexes n_D (Na-*D* line, at $\lambda = 589$ nm) were measured by an automatic refractometer DR 5000 Krüss, with a resolution 1×10^{-5} and an accuracy of 3×10^{-5}. Each experimental temperature was maintained with an accuracy of ± 0.01 K.

3. RESULTS AND DISCUSSION

The experimental data of refractive index (n) obtained from the measurements of the neat solvents and for the analysed binary mixtures at all investigated temperatures are summarised in Tables I and II.

From the measured refractive indexes (see Tables I and II) the deviations values of refractive indexes (Δn) of all the mixtures, at the each investigated temperature, were fitted to the equation:

$$\Delta n = n - (\phi_1 \cdot n_1 + \phi_1 \cdot n_2) \tag{1}$$

where: n_1, n_2, and n are the refractive indexes of the pure species [1(ME) and 2(amine)] and that of the mixtures at different temperatures, respectively; ϕ_1 and ϕ_2 are the volume fractions.

The values of Δn of the all studied binary mixtures, at 298.15 K, are shown graphically in Fig. 1.

TABLE I Experimental refractive index (n) for the ME(1) + n-BA(2) and ME(1) + *iso*-BA(2) binary system, at various temperatures

ϕ_1	x_1	*293.15* [K]	*298.15* [K]	*303.15* [K]	*308.15* [K]	*313.15* [K]
ME + n-butylamine						
0.0000	0.0000	1.40106	1.39925	1.39744	1.39563	1.39382
0.0402	0.0501	1.40237	1.40047	1.39850	1.39667	1.39481
0.0811	0.1000	1.40349	1.40158	1.39957	1.39765	1.39578
0.1230	0.1502	1.40454	1.40258	1.40053	1.39857	1.39669
0.1658	0.2001	1.40543	1.40349	1.40140	1.39941	1.39753
0.2094	0.2506	1.40625	1.40427	1.40218	1.40017	1.39827
0.2541	0.3000	1.40689	1.40492	1.40284	1.40081	1.39890
0.2997	0.3499	1.40746	1.40545	1.40339	1.40138	1.39945
0.3463	0.4001	1.40787	1.40585	1.40382	1.40180	1.39989
0.3940	0.4503	1.40808	1.40611	1.40411	1.40208	1.40018
0.4428	0.5001	1.40824	1.40625	1.40424	1.40222	1.40034
0.4927	0.5502	1.40822	1.40625	1.40424	1.40222	1.40037
0.5426	0.5998	1.40810	1.40612	1.40412	1.40209	1.40026
0.5961	0.6499	1.40784	1.40585	1.40384	1.40182	1.40001
0.6497	0.6499	1.40744	1.40544	1.40341	1.40139	1.39962
0.7045	0.7496	1.40689	1.40488	1.40285	1.40083	1.39912
0.7607	0.7999	1.40619	1.40417	1.40216	1.40014	1.39848
0.8183	0.8508	1.40537	1.40335	1.40135	1.39935	1.39772
0.8773	0.8993	1.40444	1.40243	1.40047	1.39850	1.39692
0.9379	0.9500	1.40335	1.40139	1.39942	1.39748	1.39597
1.0000	1.0000	1.40211	1.40021	1.39831	1.39642	1.39499
ME + isobutylamine						
0.0000	0.0000	1.39724	1.39454	1.39175	1.38889	1.38593
0.0399	0.0500	1.39864	1.39595	1.39316	1.39028	1.38735
0.0807	0.1001	1.39998	1.39728	1.39450	1.39161	1.38872
0.1224	0.1511	1.40123	1.39855	1.39577	1.39288	1.39003
0.1650	0.2000	1.40232	1.39965	1.39689	1.39401	1.39121
0.2086	0.2513	1.40334	1.40070	1.39795	1.39509	1.39234
0.2531	0.2996	1.40419	1.40157	1.39885	1.39601	1.39332
0.2986	0.3519	1.40497	1.40238	1.39970	1.39689	1.39426
0.3451	0.4002	1.40557	1.40301	1.40036	1.39759	1.39502
0.3928	0.4491	1.40605	1.40352	1.40090	1.39818	1.39568
0.4415	0.4989	1.40640	1.40391	1.40133	1.39866	1.39623
0.4914	0.5501	1.40661	1.40415	1.40163	1.39902	1.39667
0.5425	0.6000	1.40668	1.40426	1.40179	1.39923	1.39697
0.5948	0.6521	1.40659	1.40422	1.40181	1.39932	1.39715
0.6485	0.6999	1.40638	1.40406	1.40170	1.39927	1.39719
0.7034	0.7502	1.40601	1.40375	1.40145	1.39911	1.39711
0.7597	0.8000	1.40550	1.40330	1.40107	1.39880	1.39691
0.8175	0.8512	1.40484	1.40270	1.40055	1.39837	1.39658
0.8768	0.9000	1.40407	1.40200	1.39993	1.39783	1.39616
0.9376	0.9492	1.40317	1.40118	1.39920	1.39719	1.39563
1.0000	1.0000	1.40211	1.40020	1.39832	1.39641	1.39499

The excess of the molar refraction (R^E) from a mole fraction (x) average was calculated from the following equation:

$$R^E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{d} - \left(\frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{M_1}{d_1} + \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \frac{M_2}{d_2} \right) \tag{2}$$

where: M_1 and M_2 are the molar masses of the pure components and d_1, d_2 and d are the densities of the pure species [1(ME) and 2(amine)] and that of the mixtures at different temperatures, respectively. The values of R^E of the binary mixtures are shown graphically in Fig. 2.

TABLE II Experimental refractive index (n) for the ME(1) + *sec*-BA(2) and ME(1) + *tert*-BA(2) binary system, at various temperatures

ϕ_1	x_1	*293.15* [K]	*298.15* [K]	*303.15* [K]	*308.15* [K]	*313.15* [K]
ME+sec-butylamine						
0.0000	0.0000	1.39344	1.39065	1.38788	1.38513	1.38240
0.0394	0.0505	1.39568	1.39280	1.39000	1.38719	1.38443
0.0797	0.1005	1.39774	1.39485	1.39203	1.38915	1.38641
0.1210	0.1496	1.39960	1.39673	1.39389	1.39101	1.38829
0.1632	0.2008	1.40138	1.39853	1.39571	1.39286	1.39018
0.2063	0.2492	1.40288	1.40007	1.39728	1.39446	1.39181
0.2505	0.3002	1.40427	1.40150	1.39874	1.39597	1.39337
0.2958	0.3495	1.40542	1.40270	1.40000	1.39729	1.39474
0.3421	0.4009	1.40641	1.40374	1.40106	1.39842	1.39595
0.3895	0.4491	1.40712	1.40450	1.40186	1.39927	1.39686
0.4382	0.5001	1.40768	1.40510	1.40251	1.39996	1.39762
0.4880	0.5489	1.40799	1.40545	1.40292	1.40042	1.39813
0.5392	0.6001	1.40812	1.40560	1.40311	1.40066	1.39844
0.5916	0.6489	1.40803	1.40553	1.40310	1.40069	1.39855
0.6454	0.7009	1.40771	1.40524	1.40287	1.40049	1.39842
0.7006	0.7456	1.40726	1.40483	1.40252	1.40017	1.39819
0.7573	0.8006	1.40651	1.40414	1.40190	1.39961	1.39772
0.8155	0.8496	1.40566	1.40336	1.40118	1.39894	1.39715
0.8753	0.9005	1.40460	1.40241	1.40031	1.39816	1.39648
0.9368	0.9489	1.40347	1.40140	1.39938	1.39733	1.39577
1.0000	1.0000	1.40211	1.40021	1.39831	1.39642	1.39499
ME + tert-butylamine						
0.0000	0.0000	1.37879	1.37762	1.37467	1.37173	
0.0379	0.0503	1.38144	1.38015	1.37712	1.37413	
0.0768	0.1002	1.38416	1.38288	1.37983	1.37682	
0.1167	0.1502	1.38697	1.38567	1.38265	1.37962	
0.1576	0.2008	1.38983	1.38846	1.38546	1.38245	
0.1996	0.2503	1.39258	1.39104	1.38808	1.38509	
0.2428	0.3004	1.39522	1.39349	1.39055	1.38761	
0.2872	0.3502	1.39763	1.39570	1.39280	1.38988	
0.3328	0.4002	1.39974	1.39768	1.39425	1.39191	
0.3798	0.4502	1.40152	1.39938	1.39653	1.39368	
0.4280	0.5009	1.40293	1.40084	1.39802	1.39519	
0.4777	0.5510	1.40395	1.40199	1.39921	1.39640	
0.5289	0.6009	1.40462	1.40287	1.40013	1.39735	
0.5816	0.6491	1.40497	1.40345	1.40076	1.39802	
0.6359	0.7004	1.40508	1.40381	1.40117	1.39850	
0.6918	0.7495	1.40500	1.40391	1.40134	1.39874	
0.7496	0.8003	1.40477	1.40380	1.40130	1.39882	
0.8092	0.8500	1.40445	1.40351	1.40110	1.39876	
0.8707	0.9007	1.40404	1.40309	1.40080	1.39861	
0.9343	0.9498	1.40353	1.40262	1.40048	1.39843	
1.0000	1.0000	1.40281	1.40211	1.40021	1.39831	

Excess molar refraction and deviations of refractive index were fitted by a Redlich–Kister type equation [6]:

$$\Delta n = \phi_1 \cdot (1 - \phi_1) \sum_{j=0}^{k} a_j \cdot (2\phi_2 - 1)^j \tag{3}$$

$$R^E/\mathrm{cm}^3\,\mathrm{mol}^{-1} = x_1 \cdot (1 - x_1) \sum_{j=0}^{k} a_j \cdot (2x_2 - 1)^j \tag{4}$$

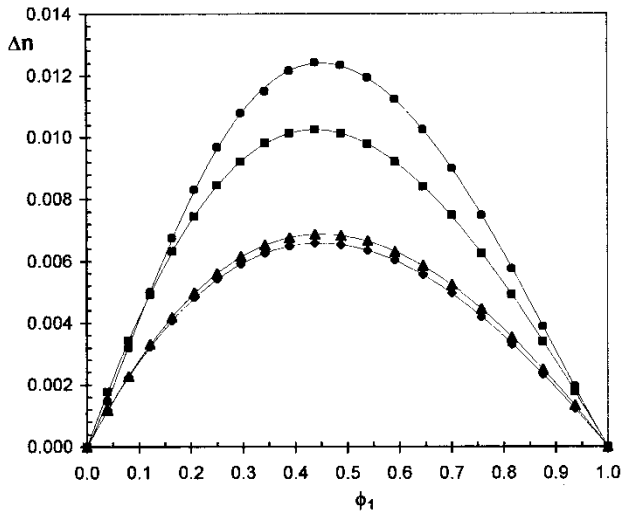

FIGURE 1 Plot of Δn as a function of composition for ME + *n*-BA (◆), ME + *iso*-BA (▲), ME + *sec*-BA (■), and ME + *tert*-BA (●), at 298.15 K.

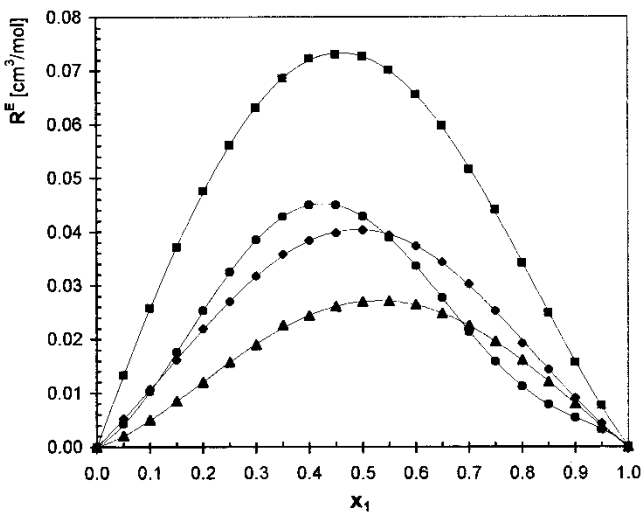

FIGURE 2 Plot of R^E as a function of composition for ME + *n*-BA (◆), ME + *iso*-BA (▲), ME + *sec*-BA (■), and ME + *tert*-BA (●), at 298.15 K.

The parameters a_j of Eqs. (3) and (4) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation $\sigma(V^E)$, are summarised in Tables III and IV.

Standard deviation values were obtained from

$$\sigma = \left[\frac{\sum (X_{\text{exptl}} - X_{\text{calcd}})^2}{n - p}\right]^{1/2} \tag{5}$$

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

TABLE III Parameters a_j of Eqs. (3) and (4), and standard deviations $\sigma(\Delta n)$ and $\sigma(R^E)$ for 2-methoxyethanol + *n*-butylamine and 2-methoxyethanol + isobutylamine

	a_0	a_1	a_2	a_3	a_4	σ
2-Methoxyethanol + n-butylamine						
T/K			293.15			
Δn	0.0266	−0.0056	0.0005	0.0001	0.0002	1.9×10^{-5}
R^E/cm^3 mol^{-1}	0.1694	−0.0113	−0.0669	−0.0053	0.0136	3.6×10^{-4}
T/K			298.15			
Δn	0.0261	−0.0056	−0.0005	0.0001	0.0001	1.3×10^{-5}
R^E/cm^3 mol^{-1}	0.1614	−0.0094	−0.0929	−0.0030	0.0188	2.7×10^{-4}
T/K			303.15			
Δn	0.0255	−0.0053	−0.0021	0.0015	0.0001	1.3×10^{-5}
R^E/cm^3 mol^{-1}	0.1533	−0.0074	−0.1190	−0.0008	0.0241	2.2×10^{-4}
T/K			308.15			
Δn	0.0248	−0.0050	−0.0033	0.0014	0.0008	1.1×10^{-5}
R^E/cm^3 mol^{-1}	0.1450	−0.0055	−0.1430	0.0015	0.0267	2.5×10^{-4}
T/K			313.15			
Δn	0.0238	−0.0048	−0.0028	0.0012	−0.0002	1.2×10^{-5}
R^E/cm^3 mol^{-1}	0.1373	−0.0036	−0.1711	0.0037	0.0347	3.2×10^{-4}
2-Methoxyethanol + isobutylamine						
T/K			293.15			
Δn	0.0278	−0.0054	−0.0004	0.0005	−0.0001	1.1×10^{-5}
R^E/cm^3 mol^{-1}	0.1100	0.0211	−0.0510	0.0006	−0.0009	0.3×10^{-4}
T/K			298.15			
Δn	0.0272	−0.0054	−0.0003	0.0007	−0.0005	1.3×10^{-5}
R^E/cm^3 mol^{-1}	0.1082	0.0202	−0.0559	0.0017	−0.0009	1.3×10^{-4}
T/K			303.15			
Δn	0.0265	−0.0052	−0.0006	0.0006	−0.0001	1.3×10^{-5}
R^E/cm^3 mol^{-1}	0.1061	0.0202	−0.0609	0.0020	0.0005	1.2×10^{-4}
T/K			308.15			
Δn	0.0256	−0.0048	−0.0008	0.0007	−0.0002	1.1×10^{-5}
R^E/cm^3 mol^{-1}	0.1038	0.0214	−0.0654	−0.0003	0.0019	0.3×10^{-4}
T/K			313.15			
Δn	0.0251	−0.0047	−0.0009	0.0005	−0.0003	1.2×10^{-5}
R^E/cm^3 mol^{-1}	0.1016	0.0216	−0.0696	−0.0011	0.0010	0.3×10^{-4}

The Δn values for all the studied binary liquid mixtures are generally positive in all experimental conditions. It is known that graphs analogous to that shown in Fig. 1 can be applied to confirm the presence of stable intermolecular complexes in binary liquid mixtures, which stoichiometric composition can be fixed on the abscissa in reference to the largest deviations [7–10]. In the present binary mixtures, the refractive index deviations are positive for each binary systems with a maximum lying always nearly at $\phi_1 \approx 0.45$ (which corresponds to the same values of mole fraction $x_1 \approx 0.5$ for analysed mixtures). As evidenced from the calculations, the refractive index deviations decrease with an increase of the temperature (see Tables III and IV).

Figure 2 shows that the excesses of the molar refraction are also positive for each binary system, with a maximum lying always nearly $x_1 \approx 0.5$ for ME with *n*-butylamine, isobutylamine, and *sec*-butylamine and nearly $x_1 \approx 0.4$ for ME + *tert*-butylamine binary mixtures. As suggested by other authors [8–11], the study of this extra thermodynamic parameter for binary liquid systems represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometry and their relative thermostability. The position of the relative

TABLE IV Parameters a_j of Eqs. (3) and (4), and standard deviations $\sigma(\Delta n)$ and $\sigma(R^E)$ for 2-methoxyethanol+*sec*-butylamine and 2-methoxyethanol+*tert*-butylamine

	a_0	a_1	a_2	a_3	a_4	σ
2-Methoxyethanol + sec-butylamine						
T/K			293.15			
Δn	0.0411	−0.0106	−0.0012	0.0007	0.0006	2.4×10^{-5}
R^E/cm^3 mol^{-1}	0.2987	−0.0695	−0.0780	−0.0045	0.0111	1.7×10^{-4}
T/K			298.15			
Δn	0.0403	−0.0113	−0.0028	0.0020	0.0002	1.9×10^{-5}
R^E/cm^3 mol^{-1}	0.2907	−0.0674	−0.1054	−0.0021	0.0181	1.6×10^{-4}
T/K			303.15			
Δn	0.0396	−0.0109	−0.0033	0.0022	−0.0001	1.9×10^{-5}
R^E/cm^3 mol^{-1}	0.2831	−0.0661	−0.1307	0.0032	0.0245	2.4×10^{-4}
T/K			308.15			
Δn	0.0389	−0.0010	−0.0052	0.0031	−0.0003	2.3×10^{-5}
R^E/cm^3 mol^{-1}	0.2766	−0.0637	−0.1568	0.0043	0.0383	3.1×10^{-4}
T/K			313.15			
Δn	0.0382	−0.0109	−0.0058	0.0037	−0.0004	2.3×10^{-5}
R^E/cm^3 mol^{-1}	0.2714	−0.0586	−0.1761	0.0041	0.0494	5.2×10^{-4}
2-Methoxyethanol + tert-butylamine						
T/K			291.15			
Δn	0.0540	−0.0203	−0.0164	0.0189	0.0029	3.1×10^{-5}
R^E/cm^3 mol^{-1}	0.1895	−0.1242	−0.1762	0.1397	0.0960	0.9×10^{-4}
T/K			293.15			
Δn	0.0501	−0.0145	−0.0074	0.0091	−0.0069	2.8×10^{-5}
R^E/cm^3 mol^{-1}	0.1834	−0.1234	−0.1837	0.1339	0.1010	0.8×10^{-4}
T/K			298.15			
Δn	0.0486	−0.0140	−0.0083	0.0074	−0.0072	1.4×10^{-5}
R^E/cm^3 mol^{-1}	0.1716	−0.1233	−0.1968	0.1399	0.1016	0.6×10^{-4}
T/K			303.15			
Δn	0.0472	−0.0159	−0.0076	0.0117	−0.0094	2.8×10^{-5}
R^E/cm^3 mol^{-1}	0.1557	−0.1233	−0.2008	0.1472	0.0943	0.7×10^{-4}

minima in the plots of R^E *versus* x_1, could be taken as the true composition of these intermolecular complexes.

The results obtained in this work seem to indicate that the respective stable intermolecular complexes of the ME · *n*-BA, ME · *iso*-BA, ME · *sec*-BA or 2ME · 3*tert*-BA types would be formed in the studied binary mixtures.

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