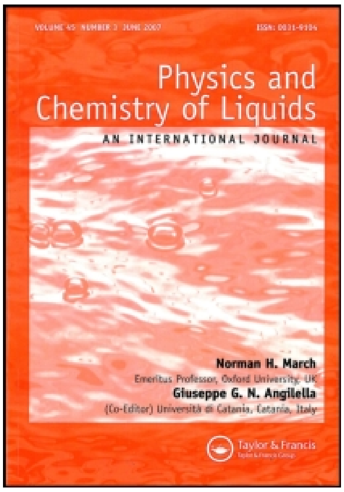

Physics and Chemistry of Liquids

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

Density, relative permittivity and refractive index for propylene glycol mono *n*-butyl ether + 2-methoxyethanol mixtures

Cezary M. Kinart[a]; Adam Bald[a]; Wojciech J. Kinart[b]; Katarzyna Nowak[a]; Zdzisław Kinart[a]
[a] Department of Chemistry, University of Łódź, Pomorska 163, Poland [b] Department of Organic Chemistry, University of Łódź, Poland

To cite this Article Kinart, Cezary M. , Bald, Adam , Kinart, Wojciech J. , Nowak, Katarzyna and Kinart, Zdzisław(2004) 'Density, relative permittivity and refractive index for propylene glycol mono *n*-butyl ether + 2-methoxyethanol mixtures', Physics and Chemistry of Liquids, 42: 1, 95 — 102

To link to this Article: DOI: 10.1080/00319100310001625044

URL: http://dx.doi.org/10.1080/00319100310001625044

Physics and Chemistry of Liquids
Vol. 42, No. 1, February 2004, pp. 95–102

Taylor & Francis
Taylor & Francis Group

DENSITY, RELATIVE PERMITTIVITY AND REFRACTIVE INDEX FOR PROPYLENE GLYCOL MONO *n*-BUTYL ETHER + 2-METHOXYETHANOL MIXTURES

CEZARY M. KINART[a,*], ADAM BALD[a], WOJCIECH J. KINART[b],
KATARZYNA NOWAK[a] and ZDZISŁAW KINART[a]

[a]*Department of Chemistry, University of Łódź, 90-236 Łódź, Pomorska 163, Poland;*
[b]*Department of Organic Chemistry, University of Łódź, 90-136 Łódź, Narutowicza 68, Poland*

(Received 3 September 2003)

Densities (ρ), relative permittivities (ε) and refractive indexes (n) at five temperatures, between 293.15 and 313.15 K, of binary mixtures of propylene glycol mono n-butyl ether (**1**) + 2-methoxyethanol (**2**), are reported. The excess molar volumes (V^E), the relative permittivity and refractive index deviations ($\Delta\varepsilon$ and Δn) were calculated from these experimental data. The results are fitted to the Redlich–Kister polynomial equation to estimate the binary coefficients and standard errors. Furthermore, the experimental results are used to disclose the nature of binary interactions in the bulk of the binary mixtures studied.

Keywords: 2-Methoxyethanol; Propylene glycol mono *n*-butyl ether; Physicochemical properties

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 [1,2].

In continuation of our program on the physicochemical and structural properties of some mixtures of alkoxyalcohols with different solvents [3–7], the present article reports density, relative permittivity and refractive index for binary mixtures containing propylene glycol mono n-butyl ether (PnB) (**1**) with 2-methoxyethanol (ME) (**2**), at various temperatures.

---

*Corresponding author. E-mail: ckinart@uni.lodz.pl

ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100310001625044

2. EXPERIMENTAL SECTION

Materials Propylene glycol mono *n*-butyl ether and 2-methoxyethanol Merck, pro-analysis, containing less than 0.05% (w/w) of water, respectively (determined by Karl–Fischer method), were used.

Propylene glycol mono *n*-butyl ether and 2-methoxyethanol, were further purified by the methods described by Pal [8] and Riddick *et al.* [9]. The purities of liquids were checked by measuring and comparing the densities at 25°C and atmospheric pressure with literature values, as shown in Table I. The mixtures were prepared by mass, with weightings accuracy to $\pm 1 \times 10^{-4}$ g. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986. The uncertainty in the mole fractions is less than 1×10^{-4}. Liquids were stored in dry-box over phosphoric pentoxide and degassed by ultrasound just before the experiment.

Measurements Solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of *ca.* 90 cm^3. Double distilled, deionized and degassed water with a specific conductance of $1 \times 10^{-7}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ was used for the calibration. The maximum error in the density measurements was $4 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$.

The relative permittivity measurements were carried out at 3 MHz, using a bridge of the type OH-301 (made in Radelcis, Hungary). The thermostatic stainless steel measuring cell was of C3 ($1 < \varepsilon < 25$) type. The cell was calibrated with standard pure liquids, such as acetone, butan-1-ol and dichloromethane. All these solvent were of spectrograde quality or higher. The relative permittivity for the standards were taken from the literature [1,10]. The accuracy in the relative permittivity measurements was ± 0.02.

The refractive indexes (Na-D line, at $\lambda = 589$ nm) were measured by an automatic refractometer DR 5000 Krüss. The accuracy in the refractive index measurements was $\pm 3 \times 10^{-5}$.

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

3. RESULTS AND DISCUSSION

The experimental data of density (ρ), relative permittivity (ε) and refractive index (n) obtained from the measurements of the pure solvents and for the analyzed binary mixtures at all investigated temperatures are summarized in Tables I and II.

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

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

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.

The deviation of the relative permittivity from a mole fraction average was calculated by:

$$\Delta\varepsilon = \varepsilon - (x_1 \cdot \varepsilon_1 + x_2 \cdot \varepsilon_2) \tag{2}$$

TABLE I Experimental density (ρ) and relative permittivity (ε) for the PnB (**1**) + ME (**2**) binary system, at various temperatures

x_1	$\rho\,(\mathrm{g\,cm^{-3}})$					ε				
T (K)	*293.15*	*298.15*	*303.15*	*308.15*	*313.15*	*291.15*	*293.15*	*298.15*	*303.15*	*308.15*
0.0000	0.96535	0.96076	0.95549	0.95066	0.94680	17.41	16.96	16.59	16.16	15.78
0.0250	0.96101	0.95645	0.95132	0.94654	0.94268	16.84	16.41	16.05	15.64	15.28
0.0500	0.95691	0.95238	0.94731	0.94259	0.93872	16.29	15.86	15.53	15.13	14.81
0.0750	0.95301	0.94849	0.94352	0.93881	0.93493	15.76	15.34	15.02	14.64	14.33
0.1000	0.94928	0.94480	0.93989	0.93522	0.93132	15.25	14.85	14.53	14.17	13.87
0.1250	0.94576	0.94127	0.93644	0.93177	0.92788	14.75	14.34	14.06	13.71	13.43
0.2000	0.93607	0.93162	0.92696	0.92234	0.91841	13.37	12.99	12.71	12.41	12.16
0.3000	0.92502	0.92057	0.91608	0.91150	0.90750	11.70	11.37	11.11	10.89	10.60
0.3489	0.92024	0.91579	0.91138	0.90679	0.90276	10.96	10.65	10.40	10.20	9.93
0.4000	0.91564	0.91116	0.90681	0.90223	0.89816	10.26	9.92	9.72	9.55	9.27
0.5000	0.90756	0.90306	0.89881	0.89420	0.89007	9.03	8.72	8.53	8.34	8.15
0.6000	0.90053	0.89598	0.89181	0.88719	0.88298	7.99	7.73	7.55	7.30	7.19
0.7000	0.89434	0.88973	0.88562	0.88097	0.87669	7.12	6.88	6.78	6.60	6.40
0.8001	0.88880	0.88414	0.88008	0.87540	0.87106	6.29	6.15	6.05	5.88	5.73
0.8973	0.88395	0.87921	0.87521	0.87050	0.86610	5.81	5.61	5.54	5.38	5.19
0.9500	0.88149	0.87672	0.87274	0.86802	0.86359	5.59	5.39	5.31	5.12	4.93
1.0000	0.87926	0.87447	0.87050	0.86577	0.86131	5.44	5.22	5.13	4.93	4.72

TABLE II Experimental refractive index (n) for the PnB (**1**) + ME (**2**) binary system, at various temperatures

x_1	n				
T(K)	*293.15*	*298.15*	*303.15*	*308.15*	*313.15*
0.0000	1.40211	1.40021	1.39831	1.39642	1.39499
0.0250	1.40256	1.40070	1.39883	1.39697	1.39554
0.0500	1.40301	1.40116	1.39932	1.39745	1.39602
0.0750	1.40348	1.40162	1.39979	1.39791	1.39647
0.1000	1.40395	1.40211	1.40027	1.39837	1.39690
0.1250	1.40445	1.40259	1.40072	1.39880	1.39731
0.2000	1.40593	1.40404	1.40213	1.40013	1.39857
0.3000	1.40486	1.40590	1.40396	1.40189	1.40024
0.3489	1.40867	1.40669	1.40474	1.40263	1.40095
0.4000	1.40965	1.40765	1.40568	1.40356	1.40184
0.5000	1.41128	1.40924	1.40724	1.40507	1.40331
0.6000	1.41272	1.41065	1.40862	1.40642	1.40459
0.7000	1.41401	1.41190	1.40983	1.40759	1.40570
0.8001	1.41517	1.41304	1.41092	1.40862	1.40668
0.8973	1.41604	1.41387	1.41171	1.40937	1.40739
0.9500	1.41676	1.41454	1.41235	1.40999	1.40796
1.0000	1.41728	1.41502	1.41280	1.41040	1.40835

where ε_1, ε_2 and ε are the relative permittivities of the pure species (**1** and **2**), and that of the mixtures at different temperatures, respectively.

The deviation of the refractive index from a mole fraction average was calculated by:

$$\Delta n = n - (\phi_1 \cdot n_1 + \phi_2 \cdot n_2) \tag{3}$$

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

Excess volume, deviations of relative permittivity and refractive index were fitted by a Redlich–Kister type equations [10]:

$$V^E/\mathrm{cm^3\,mol^{-1}} \quad \text{or} \quad \Delta\varepsilon = x_1\cdot(1-x_1)\sum_{j=0}^{k} a_j\cdot(2x_1-1)^j \tag{4}$$

and

$$\Delta n = \phi_1\cdot(1-\phi_1)\sum_{j=0}^{k} a_j\cdot(2\phi_2-1)^j \tag{5}$$

The parameters a_j of Eqs. (4) and (5) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation $\sigma(V^E)$, $\sigma(\Delta\varepsilon)$ and $\sigma(\Delta n)$ are summarized in Table III.

The variations of V^E, $\Delta\varepsilon$ with the mole fraction and Δn with the volume fraction of ME at 298.15 K are presented in Figs. 1, 2 and 3, respectively. Figure 1 shows that the excess molar volumes are positive for all these investigated systems, with the maximum lying always near $x_1 \approx 0.35$ for PnB + ME binary mixtures.

For these binaries, there are different effects that may contribute to V_m^E, and these will be taken into account in order to rationalize a non-ideal behaviour of this solvent system [8,11].

TABLE III Parameters a_j of Eqs. (4) and (5), and standard deviations $\sigma(V^E)$, $\sigma(\Delta)$ and $\sigma(n)$ for the PnB + ME binary system, at various temperatures

PnB + ME					
	a_0	a_1	a_2	a_3	σ
T (K)			293.15		
V^E ($\mathrm{cm^3\,mol^{-1}}$)	0.6622	−0.4197	0.0200	−0.0151	5.6×10^{-4}
$\Delta\varepsilon$	−9.5552	1.1524	−0.8291	−0.6484	2.2×10^{-2}
Δn	−0.0041	0.0024	−0.0008	−0.0015	6.1×10^{-6}
T (K)			298.15		
V^E ($\mathrm{cm^3\,mol^{-1}}$)	0.5462	−0.4048	0.0176	0.0006	4.8×10^{-4}
$\Delta\varepsilon$	−9.3893	1.2592	−0.3608	−0.3036	1.5×10^{-2}
Δn	−0.0037	0.0022	−0.0001	−0.0012	5.0×10^{-6}
T (K)			303.15		
V^E ($\mathrm{cm^3\,mol^{-1}}$)	0.4773	−0.3713	−0.0125	0.0250	5.5×10^{-4}
$\Delta\varepsilon$	−9.2481	1.4100	0.1015	−0.4060	1.5×10^{-2}
Δn	−0.0033	0.0023	0.0006	−0.0018	3.3×10^{-6}
T (K)			308.15		
V^E ($\mathrm{cm^3\,mol^{-1}}$)	0.3956	−0.3272	−0.0289	0.0312	9.6×10^{-4}
$\Delta\varepsilon$	−8.7748	0.7552	0.2429	0.8484	2.7×10^{-2}
Δn	−0.0031	0.0024	0.0013	−0.0024	3.1×10^{-6}
T (K)			313.15		
V^E ($\mathrm{cm^3\,mol^{-1}}$)	0.3286	−0.3009	−0.0357	0.0407	10.7×10^{-3}
$\Delta\varepsilon$	−8.4210	1.3579	0.6026	−0.5012	0.7×10^{-2}
Δn	−0.0029	0.0024	0.0017	−0.0026	3.6×10^{-6}

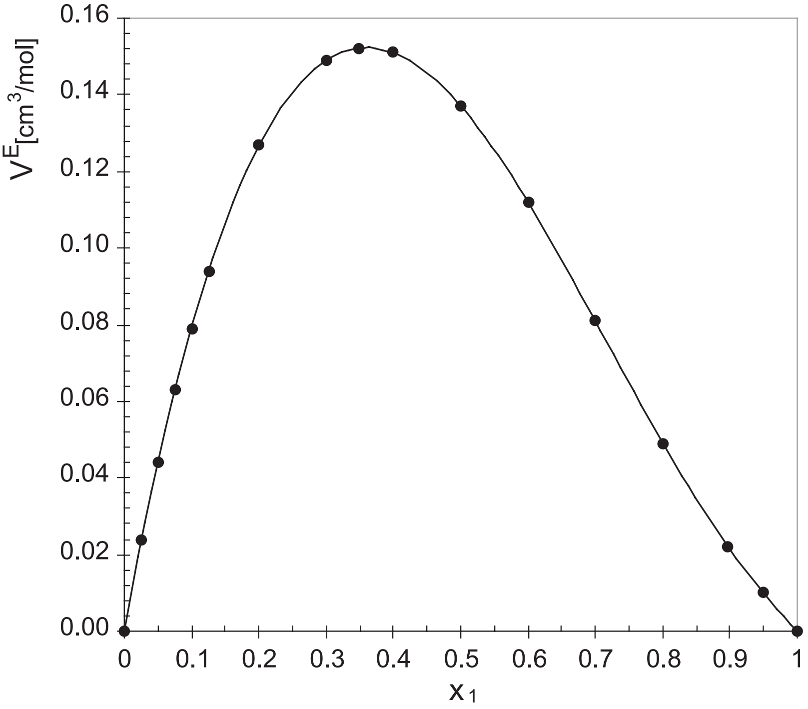

FIGURE 1 Plot of V^E as a function of composition for PnB + ME mixtures, at 298.15 K.

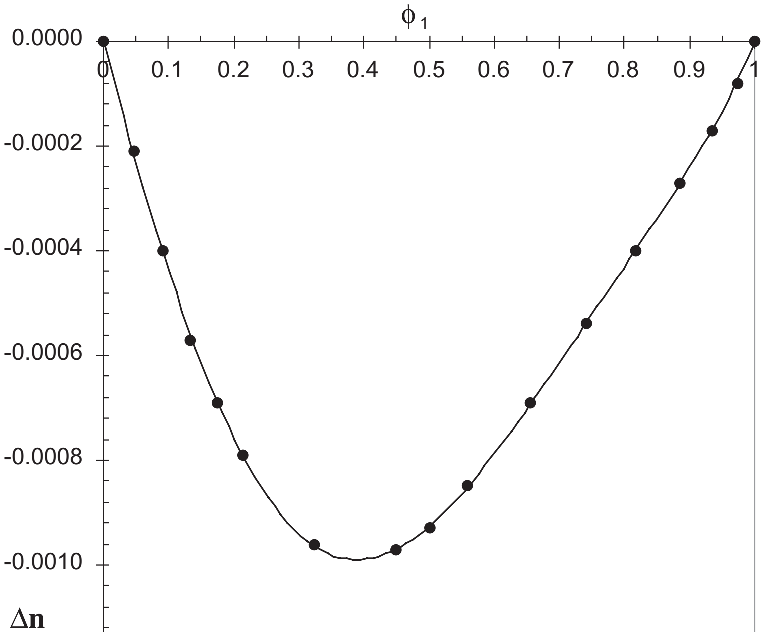

FIGURE 2 Plot of Δn as a function of composition for PnB + ME mixtures, at 298.15 K.

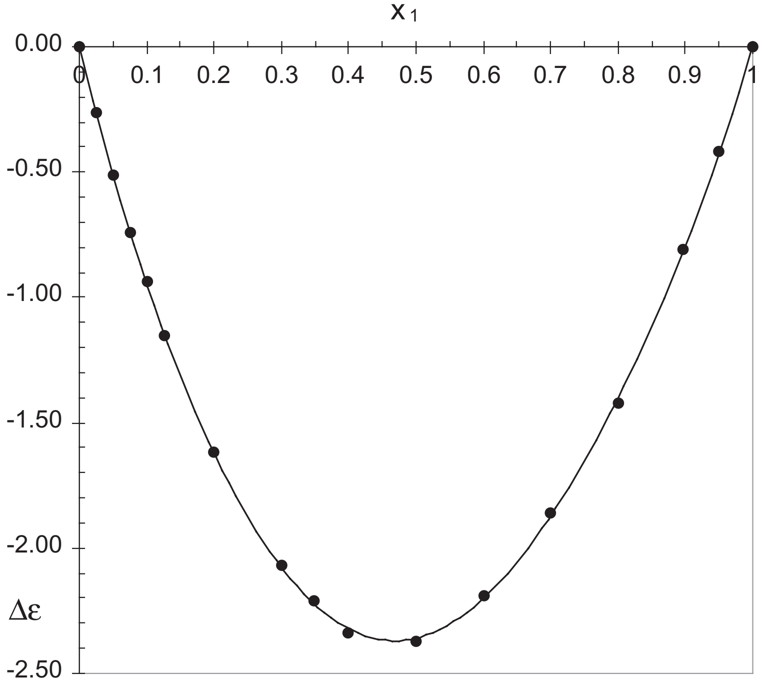

FIGURE 3 Plot of $\Delta\varepsilon$ as a function of composition for PnB + ME mixtures, at 298.15 K.

One of the effects that may contribute to V_m^E is due to homocooperative interactions of ME and PnB molecules on mixing the two neat liquids. This would correspond to a volumetric expansion, and a positive contribution to V_m^E should be expected. The another effects that may have positive contributions to V_m^E are the interactions between the hydrophobic and apolar groups (groups in the alkyl chains) in one species and the polar groups in another, thus producing a valuable microheterogeneity at molecular level.

After these considerations, we may assume that in the ME + PnB liquid mixtures all the effects, discussed above, should be taken into account as they may contribute to the V_m^E values. In our opinion, the appropriate positive contributions might be due to the formation of a weak PnB · 2ME adduct in this binary solvent system.

Similar conclusions can be drawn from the analysis of the refractive index deviations. Figure 2 shows that the refractive index deviations are negative for analyzed binary system, with a minimum lying always nearly $\phi_1 \approx 0.50$ (which corresponds to the same values of mole fraction $x_1 \approx 0.35$ for analyzed mixtures). As evidenced from the calculations, the refractive index deviations decrease with an increase in the temperature (see Tables II and III).

Figure 3 shows that the relative permittivity deviations are also negative for PnB + ME binary system, with a minimum lying always nearly $x_1 \approx 0.50$. As evidenced from the calculations, the relative permittivity deviations decrease with an increase in the temperature (see Tables I and III).

As suggested by other authors [1,12], 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. In the case of our research in this article, the shifts ε_{12} from the linear behaviour of non-interacting ideal system (see Fig. 3) should correspond to the stabilization energy for PnB + ME binary mixtures and the formation of the stable PnB · ME complexes.

From the experimental values of relative permittivities (ε_{12}) (see Table I), the temperature coefficients of the relative permittivity, denoted α_{12}, viz.:

$$\alpha_{12} = \frac{1}{\varepsilon} \cdot \left[\frac{d\varepsilon}{d(1/T)} \right] \tag{6}$$

at 298.15 K, were calculated (see Fig. 4).

The composition range of liquid binary mixtures within which α_{12} or its excess attain their highest values should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic considerations [13]) as a region characterized by maximal intermolecular interactions between two different components of the given binary liquid mixture.

For PnB + ME studied mixtures, the α_{12} *vs* x_1 curves are W-shaped, being negative at the ends and positive at x_1 from about 0.20 to 0.80. In the case of all studied mixtures, we observed the tendency to achieve the maximum by the function α_{12} at *ca.* $x_1 \approx 0.50$. This effect can be accounted for by maximal intermolecular interactions between ME and PnB, which lead to the formation of stable PnB · ME intermolecular complexes [2,13].

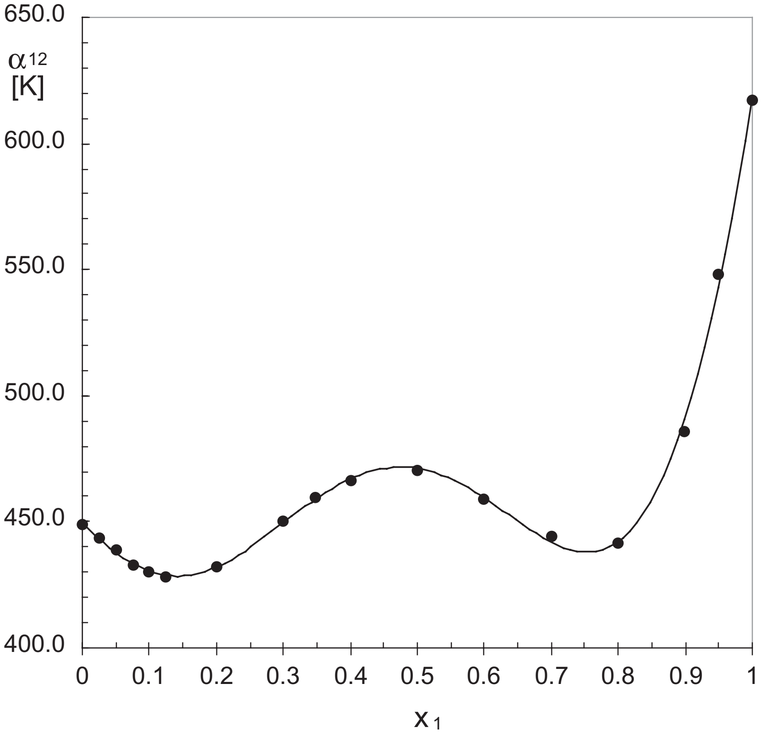

FIGURE 4 Plot of α_{12} as a function of composition for PnB + ME mixtures, at 298.15 K.

The results obtained in this work seem to indicate that the respective stable intermolecular complexes of the PnB · 2ME or PnB · ME types would be formed in the studied binary mixtures of PnB + ME.

References

[1] M. Cocchi, P. de Benedetti, R. Seeber, L. Tassi and A. Ulrici (1999). *J. Chem. Inf. Comput. Sci.*, **39**, 1190.
[2] C.M. Kinart and W. Kinart (2000). *J. Phys. Chem. Liq.*, **38**, 155.
[3] C.M. Kinart, W.J. Kinart and A. Ćwiklińska (2001). *Phys. Chem. Liq.*, **39**, 589.
[4] C.M. Kinart, W.J. Kinart and A. Ćwiklińska (2002). *J. Chem. Eng. Data*, **47**, 23.
[5] C.M. Kinart, W.J. Kinart and A. Ćwiklińska (2002). *J. Therm. Anal. Cal.*, **68**, 307.
[6] C.M. Kinart, W.J. Kinart and D. Chęcińska-Majak (2002). *J. Chem. Eng. Data*, **47**, 1537.
[7] C.M. Kinart, W.J. Kinart, D. Chęcińska-Majak and A. Ćwiklińska (2003). *Phys. Chem. Liq.*, **41**, 383.
[8] A. Pal and A. Kumar (1999). *J. of Solution Chem.*, **28**, 153.
[9] J.B. Riddick, W.B. Bunger and T.K. Sakano (1986). In: *Organic Solvents. Physical Properties and Methods of Purification*. J. Wiley Publ., New York.
[10] O. Redlich and A.T. Kister (1948). *Ing. Eng. Chem.*, **40**, 345.
[11] F. Corradini, A. Marchetti, M. Tagliazucchi and L. Tassi (1995). *Bull. Chem. Soc. Jpn.*, **68**, 3373.
[12] G. Goldoni, L. Marcheselli, G. Pistoni and L. Tassi (1992). *J. Chem. Soc., Faraday Trans.*, **88**, 2003.
[13] M.T. Räetzsch, H. Kahlen and H. Resner (1974). *Z. Physik. Chem. Leipzig*, **255**, 115.