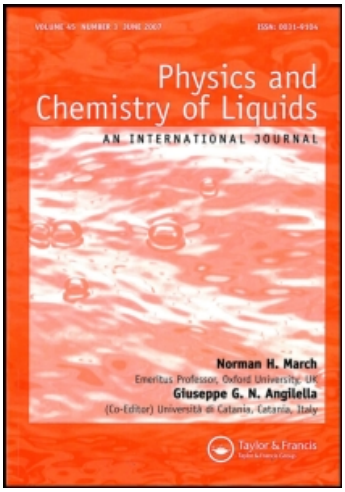

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Physical properties of the ternary mixture ethanol water 1-hexyl-3-methylimidazolium chloride at 298.15 K

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To cite this Article Gómez, E. , Calvar, N. , Domínguez, I. and Domínguez, A.(2006) 'Physical properties of the ternary mixture ethanol water 1-hexyl-3-methylimidazolium chloride at 298.15 K', Physics and Chemistry of Liquids, 44: 4, 409 — 417
To link to this Article: DOI: 10.1080/00319100600744993
URL: http://dx.doi.org/10.1080/00319100600744993

Physics and Chemistry of Liquids
Vol. 44, No. 4, August 2006, 409–417

Taylor & Francis
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Physical properties of the ternary mixture ethanol + water + 1-hexyl-3-methylimidazolium chloride at 298.15 K

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(*Received 7 March 2006; in final form 7 April 2006*)

In this work, densities and refractive indices of the ternary mixture ethanol + water + 1-hexyl-3-methylimidazolium chloride ([C_6mim][Cl]) and of the binary systems containing the ionic liquids (ILs) have been measured at 298.15 K and atmospheric pressure. Excess molar volumes and changes of refractive indices on mixing were determined from experimental data. The binary data were correlated with the Redlich–Kister equation, while the Cibulka equation was applied for the ternary system.

Keywords: 1-Hexyl-3-methylimidazolium chloride; Ternary system; Density; Refractive index; Excess molar volumes

1. Introduction

Room temperature ionic liquids (RTILs) are a class of organic molten salts that are composed entirely of anions and cations. Ionic liquids (ILs) have attracted an increasing number of scientific investigations because of their non-volatile nature, high thermal stability and favourable solvation properties. ILs have been suggested as replacements for volatile organic compounds traditionally used. These RTILs have been recently used as solvents in chemical reactions [1–3], multiphase bioprocess operations [4], liquid–liquid separations [5, 6] and batteries and fuel cells investigations [7]. Since ILs are relatively new, the lack of data for the physical properties of pure compounds and their mixtures prevent their further industrial applications. In this work, experimental data of physical properties of the binary mixtures ethanol + 1-hexyl-3-methylimidazolium chloride ([C_6mim][Cl]) and water + [C_6mim][Cl], and of the ternary mixture ethanol + water + [C_6mim][Cl] are presented.

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Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online © 2006 Taylor & Francis
DOI: 10.1080/00319100600744993

2. Experimental

Ethanol was supplied by Merck with a purity greater than 99.8%. It was degassed ultrasonically and dried over molecular sieves of type 4 Å, supplied by Aldrich and kept in an inert argon atmosphere. Water was bidistilled and deionized. IL used in this work, [C_6mim][Cl], was synthesized in our laboratory and submitted to a RMN and Positive FABMS to ensure its purity [9]. Table 1 shows a comparison between experimental and literature data of the pure components at 298.15 K.

The density of the pure liquids and mixtures were measured using a densimeter Anton Paar DSA-48, with a precision of $\pm 5 \times 10^{-5}$ g cm^{-3}. To measure the refractive indices, an automatic refractometer Abbemat-HP Dr Kernchen with a precision of $\pm 10^{-5}$ was used.

The mixtures were prepared by mass, using a balance Mettler AX-205 Delta Range with a precision of $\pm 10^{-5}$ g. Mixtures were prepared in a dry box filled with argon, since ILs in general, and particularly chlorides, are very hygroscopic. The presence of water in RTILs may affect many of their properties [10–12].

3. Results

3.1. *Binary systems*

Experimental densities, refractive indices, excess molar volumes and changes of refractive indices of binary mixtures are shown in table 2.

Excess molar volumes, changes of refractive indices on mixing for binary and ternary systems were calculated through the equations (1) and (2) respectively:

$$V^{\mathrm{E}} = \sum_{i=1}^{N} x_i \cdot M_i \cdot \left(\rho^{-1} - \rho_i^{-1}\right) \tag{1}$$

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{2}$$

where x_i is the mole fraction, ρ and n_D are the density and refractive index on mixture and ρ_i and n_{Di} are the density and refractive index of pure components.

The values of the binary systems were fitted to a Redlich–Kister [13] type equation:

$$\Delta Q = x_i x_j \sum_{p=0}^{m} B_p \left(x_i - x_j\right)^p \tag{3}$$

Table 1. Comparison of measured pure component properties data with literature values at $T = 298.15$ K.

	ρ (g cm^{-3})		$10^{-3\eta}$ (Pa s)	
Component	Expt.	Lit.	Expt.	Lit.
Ethanol	0.78545	0.78546[a]	1.082	1.082[a]
Water	0.99710	0.99705[a]	0.890	0.890[a]

[a] [8].

Table 2. Densities, ρ, refractive indices, n_D, excess molar volumes, V^E, and changes of refractive indices, Δn_D for binary mixtures at $T = 298.15$ K.

x_1	ρ (g cm^{-3})	n_D	V^E (cm^3 mol^{-1})	Δn_D
Ethanol + [C$_6$mim][Cl]				
0.0000	1.0404	1.52182	0.000	0.0000
0.0980	1.0328	1.52022	−0.084	0.0143
0.1960	1.0240	1.51336	−0.170	0.0234
0.2898	1.0140	1.50603	−0.229	0.0313
0.4075	0.9997	1.49228	−0.424	0.0367
0.5680	0.9727	1.47741	−0.557	0.0480
0.7044	0.9405	1.45530	−0.696	0.0480
0.7955	0.9097	1.43465	−0.651	0.0422
0.9047	0.8570	1.40175	−0.460	0.0271
0.9445	0.8315	1.38605	−0.355	0.0178
1.0000	0.7854	1.35920	0.000	0.0000
Water + [C$_6$mim][Cl]				
0.0000	1.0404	1.52182	0.000	0.0000
0.1032	1.0411	1.51718	−0.196	0.0149
0.2001	1.0420	1.51563	−0.395	0.0317
0.3013	1.0422	1.51066	−0.470	0.0459
0.3890	1.0423	1.50890	−0.521	0.0608
0.5125	1.0422	1.49981	−0.564	0.0751
0.5926	1.0412	1.49319	−0.514	0.0836
0.6972	1.0387	1.48167	−0.407	0.0919
0.8007	1.0342	1.46350	−0.285	0.0933
0.9088	1.0236	1.42700	−0.132	0.0773
1.0000	0.9972	1.33240	0.000	0.0000

where ΔQ is V^E (cm^3 mol^{-1}) or Δn_D, x_i is the mole fraction, B_p are the fitting parameters and m is the degree of the polynomic expansion.

Figure 1 shows the excess molar volumes and the changes of refractive indices on mixing for both the binary mixtures containing ionic liquid, plotted against the mole fraction. As is shown in figure 1(a), the excess molar volumes are negative over the whole composition range for both the systems.

The excess molar volume of the binary system ethanol + [C$_6$mim][Cl] presents a minimum in a composition of $x_1 \approx 0.7$. The negative values of the molar excess volume in the binary system ethanol + [C$_6$mim][Cl] indicate that relatively few ethanol molecules fit into the free volume between the relatively large ions of [C$_6$mim][Cl] upon mixing. Thus, the negative values of the molar excess volume show that this effect is due to the ion–dipole interactions between ethanol and [C$_6$mim][Cl]. A similar behaviour is observed for methanol + [C$_4$mim][PF$_6$] and acetonitrile + [C$_4$mim][PF$_6$], as reported by Zafarani-Moatter [14], and methanol + 4MBPBF$_4$, as reported by Heintz [15].

The binary system water + [C$_6$mim][Cl] presents a minimum at a mole fraction of 0.5 approximately. This behaviour can be attributed to hydrogen bonds between the water molecules and ILs. This result agrees with the work of Miki *et al.* [16].

On the other hand, in figure 1(b), we can see that the change of refractive index presents a maximum of $x_1 \approx 0.6$ in the binary system ethanol + [C$_6$mim][Cl] and a maximum of $x_1 \approx 0.8$ in water + [C$_6$mim][Cl].

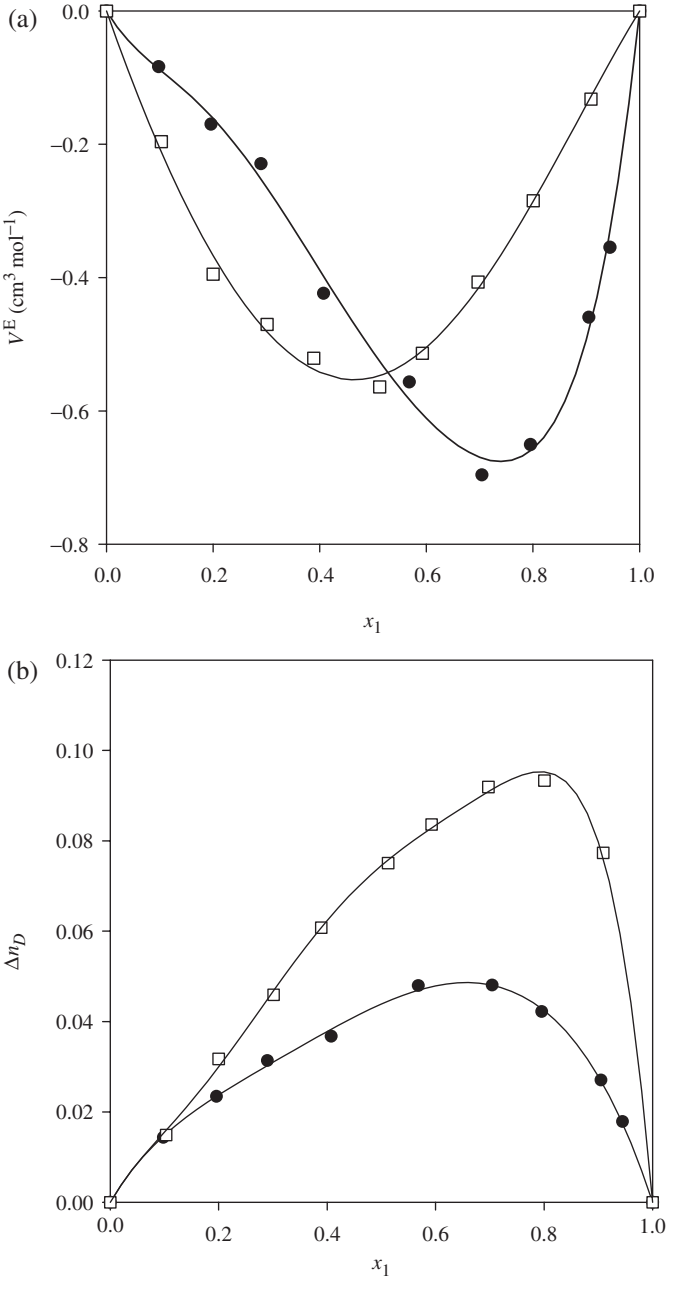

Figure 1. Variation of excess molar volumes (a) and changes in refractive indices (b) for the binary mixtures (●) ethanol + [C_6mim][Cl] and (□) water + [C_6mim][Cl] at 298.15 K plotted against mole fraction.

3.2. *Ternary system*

Experimental results of the ternary system are reported in table 3. The binary and ternary values of density and refractive index have been fitted to a polynomial expansion:

$$Q = \sum_{i=1}^{3} \sum_{j=1}^{m} A_{ij} w_i^j \tag{4}$$

Table 3. Densities, ρ, refractive indices, n_D, excess molar volumes, V^E, and changes of refractive indices, Δn_D for ternary system, ethanol + water + [C$_6$mim][Cl], at $T = 298.15$ K.

x_1	x_2	ρ (g cm^{-3})	n_D	V^E (cm^3 mol^{-1})	Δn_D
0.0549	0.7567	1.0216	1.45831	−0.418	0.0906
0.1054	0.7163	1.0098	1.45364	−0.525	0.0861
0.1932	0.6460	0.9892	1.44553	−0.668	0.0779
0.0520	0.8615	1.0084	1.42339	−0.336	0.0718
0.1008	0.8173	0.9943	1.41988	−0.505	0.0676
0.1461	0.7761	0.9814	1.41663	−0.636	0.0637
0.1118	0.4552	1.0255	1.49314	−0.575	0.0745
0.0575	0.5585	1.0319	1.48868	−0.542	0.0821
0.1637	0.4956	1.0150	1.47932	−0.598	0.0791
0.0542	0.6594	1.0287	1.47701	−0.487	0.0889
0.1077	0.6221	1.0183	1.47228	−0.550	0.0863
0.1502	0.5925	1.0101	1.46777	−0.593	0.0839
0.7887	0.0847	0.8849	1.41520	−0.685	0.0372
0.8212	0.0594	0.8779	1.41213	−0.639	0.0346
0.8572	0.0519	0.8611	1.40220	−0.569	0.0285
0.6070	0.2006	0.9292	1.43738	−0.778	0.0529
0.6051	0.0999	0.9504	1.45576	−0.716	0.0529
0.6528	0.0296	0.9488	1.45733	−0.680	0.0497
0.6557	0.0517	0.9441	1.45352	−0.701	0.0503
0.0467	0.5540	1.0337	1.49097	−0.541	0.0814
0.4178	0.2450	0.9791	1.46858	−0.675	0.0620
0.5638	0.1836	0.9480	1.45208	−0.746	0.0565
0.6365	0.1529	0.9302	1.44037	−0.762	0.0518
0.7320	0.1128	0.9027	1.42465	−0.738	0.0433
0.3855	0.3435	0.9749	1.46070	−0.699	0.0676
0.5031	0.2778	0.9499	1.44715	−0.758	0.0602
0.6273	0.2083	0.9191	1.43047	−0.791	0.0500
0.7205	0.1562	0.8929	1.41624	−0.762	0.0406
0.2691	0.5313	0.9818	1.45207	−0.703	0.0750
0.4188	0.4225	0.9485	1.43647	−0.791	0.0620
0.5023	0.3618	0.9284	1.42682	−0.825	0.0543
0.6146	0.2801	0.9008	1.41394	−0.839	0.0436
0.6105	0.2931	0.8972	1.41089	−0.849	0.0422
0.6546	0.1484	0.9242	1.43663	−0.764	0.0503
0.0408	0.9476	0.9890	1.35378	−0.237	0.0194
0.9030	0.0000	0.8575	1.40198	−0.485	0.0273
0.0504	0.9440	0.9833	1.34716	−0.284	0.0137
0.0502	0.9468	0.9817	1.34374	−0.282	0.0107
0.2244	0.3265	1.0119	1.48997	−0.586	0.0644
0.3065	0.2919	0.9992	1.48176	−0.619	0.0638
0.3032	0.3581	0.9943	1.47485	−0.644	0.0697
0.3996	0.3085	0.9761	1.46417	−0.692	0.0659
0.1104	0.5270	1.0239	1.48387	−0.571	0.0809
0.3436	0.1977	0.9992	1.48705	0.592	0.0545

where Q is ρ ($g\,cm^{-3}$) or n_D, and W_i is the weight fraction of the component i. Due to the difference of mass between the ionic liquid and the other components ($M_{W(EtOH)} = 46.069\,g\,mol^{-1}$, $M_{W(H_2O)} = 18.015\,g\,mol^{-1}$, $M_{W([C_6mim][Cl])} = 202.73\,g\,mol^{-1}$), weight fraction is used instead of molar fraction. For the binary mixture ethanol + water, not determined experimentally in this work, literature data had been used [17].

Figure 2 shows the lines of constant densities and refractive indices of the ternary mixture plotted against weight fraction. For the sake of clarity in figures, weight fraction is used for the reason explained above.

The results of the ternary system ethanol + water + [C_6mim][Cl] were correlated using the Cibulka [18] equation for the excess properties:

$$\Delta Q_{123} = \Delta Q_{bin} + x_1 x_2 (1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \quad (5)$$

where,

$$\Delta Q_{bin} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23}. \quad (6)$$

The experimental results of the ternary mixture are show in table 3. To our knowledge, no results concerning this mixture have been published earlier.

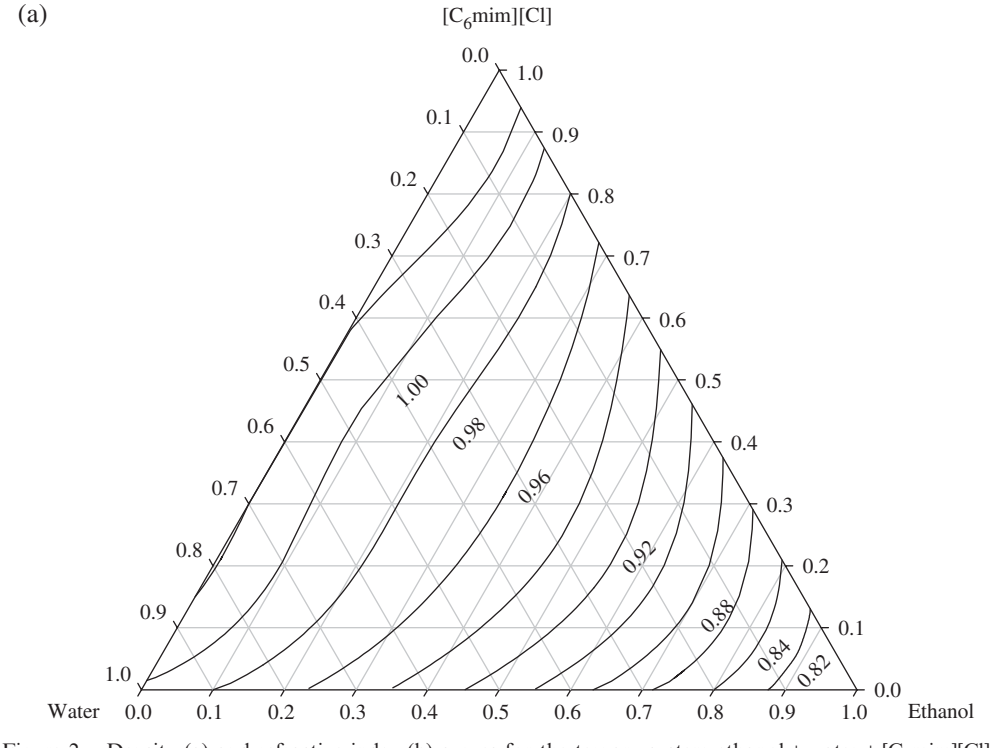

Figure 2. Density (a) and refractive index (b) curves for the ternary system ethanol + water + [C_6mim][Cl] at 298.15 K plotted against weight fraction.

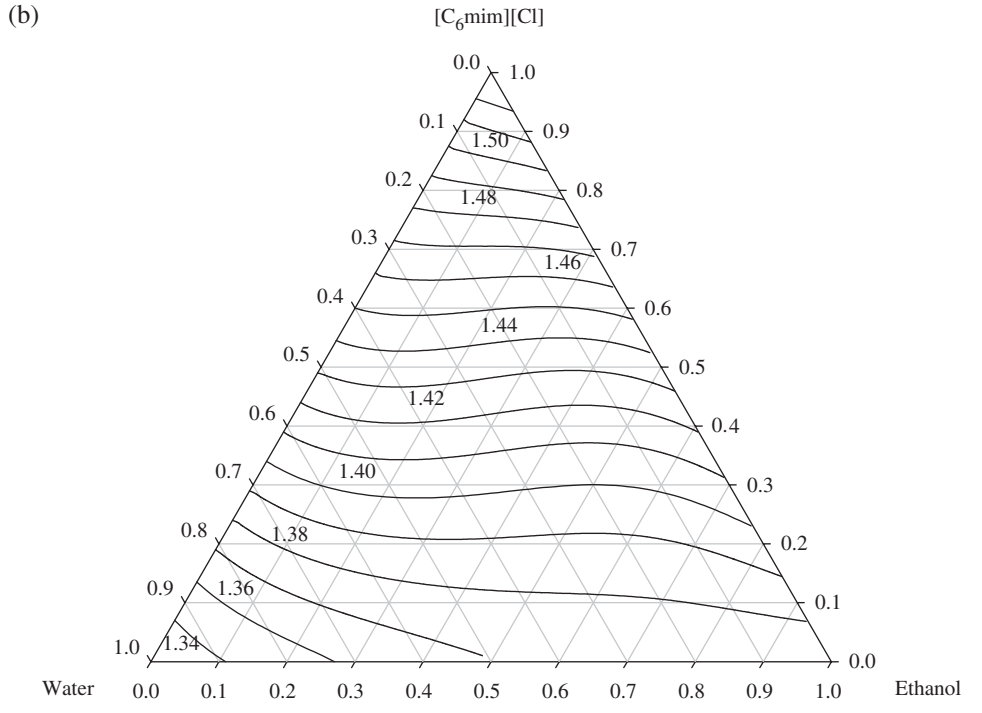

Figure 2. Continued.

Table 4. Parameters A_{ij}, B_p, and C_i of equations (3)–(5) and root-mean-square deviations.

			Ethanol + [C6mim][Cl]			
V^E	$B_0 = -2.0460$	$B_1 = -2.2797$	$B_2 = -0.8556$	$B_3 = -0.8414$	$B_4 = -1.5591$	$\sigma = 0.018$
Δn_D	$B_0 = 0.1754$	$B_1 = 0.1061$	$B_2 = 0.0749$	$B_3 = -0.0246$	$B_4 = 0.0340$	$\sigma = 7.0 \times 10^{-4}$
			Water + [C6mim][Cl]			
V^E	$B_0 = -2.1994$	$B_1 = 0.3825$	$B_2 = 0.4638$	$B_3 = 0.1059$	$B_4 = -0.0690$	$\sigma = 0.013$
Δn_D	$B_0 = 0.29801$	$B_1 = 0.2041$	$B_2 = 0.1281$	$B_3 = 0.3776$	$B_4 = 0.3640$	$\sigma = 0.001$
			Ethanol + water + [C6mim][Cl]			
ρ	$A_{11} = 0.7617$	$A_{21} = 0.1339$	$A_{31} = -0.2191$	$A_{41} = 0.1093$		
	$A_{12} = 1.0176$	$A_{22} = -0.0862$	$A_{32} = 0.2151$	$A_{42} = -0.1057$		
	$A_{13} = 1.0938$	$A_{23} = -0.2095$	$A_{33} = 0.2311$	$A_{43} = -0.1184$		$\sigma = 7.1 \times 10^{-3}$
n_D	$A_{11} = 1.4682$	$A_{21} = -0.1625$	$A_{31} = 0.2297$	$A_{41} = -0.1160$		
	$A_{12} = 1.4358$	$A_{22} = 0.1965$	$A_{32} = 0.2380$	$A_{42} = 0.1282$		
	$A_{13} = 1.3354$	$A_{23} = 0.1280$	$A_{33} = -0.2671$	$A_{43} = 0.1360$		$\sigma = 9.9 \times 10^{-4}$
V^E	$C_1 = -0.5742$	$C_2 = 9.1900$	$C_3 = 16.107$			$\sigma = 0.0297$
Δn_D	$C_1 = -0.5009$	$C_2 = 1.0012$	$C_3 = 1.2067$			$\sigma = 9.3 \times 10^{-4}$

Parameters of the fitting equations (equations (3)–(5)) and the corresponding root-mean-square deviations are listed in table 4.

Figure 3(a) and (b) show the calculated isolines against mole fraction corresponding to ternary excess molar volumes, and changes of refractive indices, respectively. Excess molar volumes are negative over the whole composition range. These negative values suggest that the molecular packing is the prevailing factor in this property.

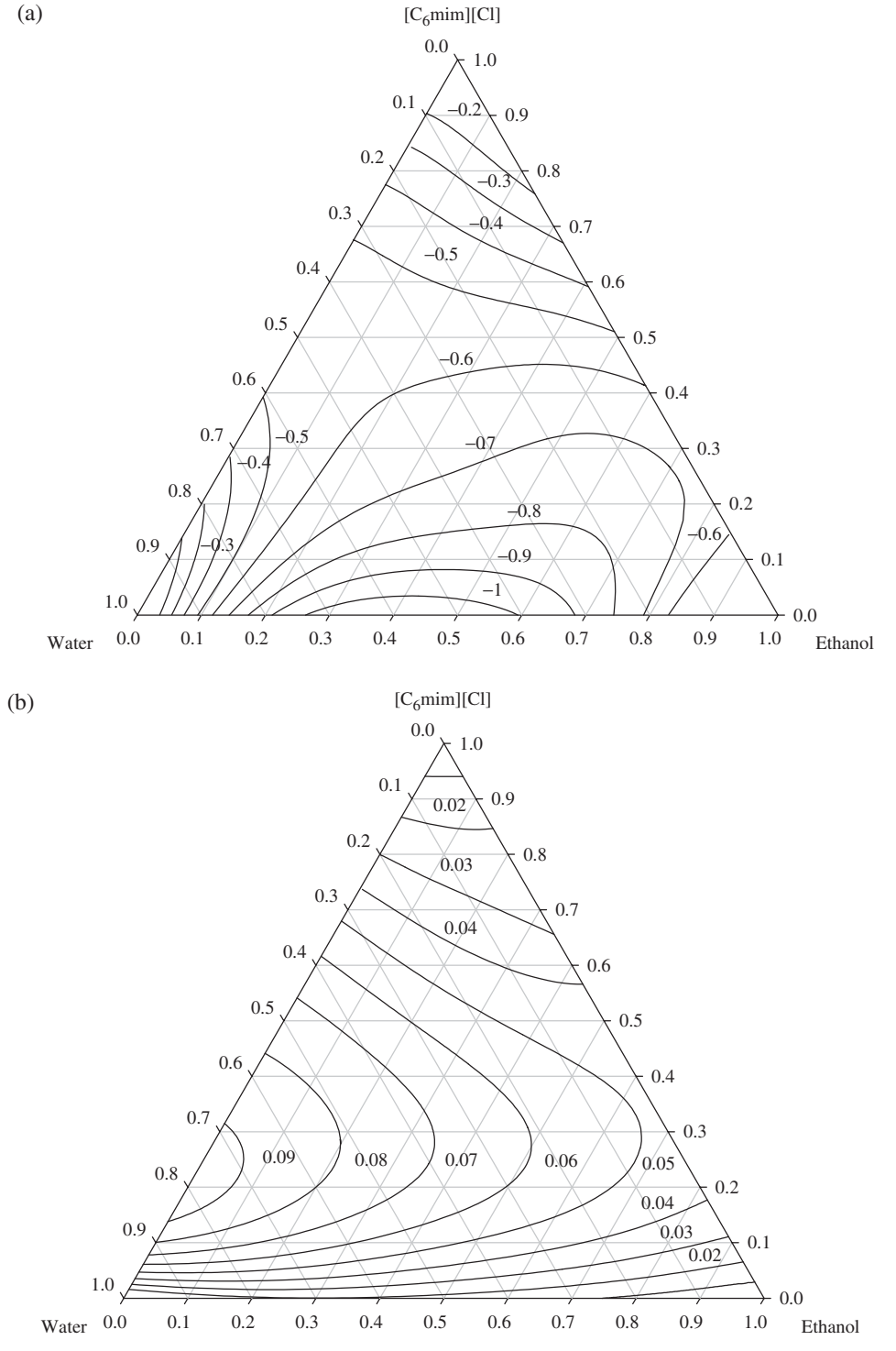

Figure 3. Variation of (a) excess molar volumes and (b) changes in refractive indices curves for the ternary system ethanol + water + [C$_6$mim][Cl] at 298.15 K plotted against mole fraction.

The measured ternary changes of refractive indices show positive deviations from ideal behaviour over the whole composition range.

4. Conclusions

In this work, the densities and refractive indices were experimentally determined for the binary systems ethanol + [C$_6$mim][Cl], water + [C$_6$mim][Cl] and for the ternary mixture ethanol + water + [C$_6$mim][Cl]. With these experimental data, excess properties such as the excess molar volumes and changes in refractive indices were calculated for the binary and ternary systems. The binary excess molar volumes and changes in refractive indices were correlated reliably with the Redlich–Kister equation while the Cibulka equation was applied successfully for the ternary mixtures. The excess molar volumes are negative over the whole composition range while changes of refractive indices are positive.

Acknowledgement

The authors would like to sincerely thank Professor José Tojo Suarez, Chairperson of Advanced Separation Process Group, who has recently passed away, for his continuous dedication and for valuable discussions.

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