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THERMOPHYSICAL PROPERTIES OF 1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE SOLUTION FROM 293.15 TO 323.15 K

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Abstract - Aqueous systems composed of ionic liquid make up a new alternative for use in processes involving the separation of biomolecules. The objective of this experiment was to obtain the thermo-physical properties of density, refractive index, electrical conductivity, molar volume, thermal expansion coefficient and apparent specific volume of the ionic liquid 1-ethyl-3-methylimidazolium chloride. The thermo-physical properties of aqueous solutions of this ionic liquid were measured as a function of the mass fraction w = (0.05, 0.125, 0.2, 0.275 and 0.35), temperature T = (293.15, 303.15, 313.15 and 323.15) K and pH = (7.5, 8.0 and 8.5). Models representing the combined effects between variables were fit since they are required for industrial applications where the physical parameters must be accurately calculated. Models representing the combined effects of the variables temperature, mass fraction and pH values of ionic liquid were adjusted and presented good fit.
Keywords: Thermodynamic properties; Binary mixtures; Ionic liquid; Models.

INTRODUCTION

Ionic liquids (ILs) are organic salts which have a low melting point. They have unique physical-chemical properties, with negligible vapor pressure, non-flammable, non-explosive, electrochemically and thermally stable, and can be easily recycled. These salts present extremely low vapor pressures, and this feature has attracted attention given their potential as solvents to replace volatile organic solvents for a large variety of chemical reactions, separation processes and other applications. Such compounds have many favorable properties which make them attractive for many applications (Ficke et al. 2010; França et al. 2009; Muhammad et al. 2012).

Due to these characteristics, the ILs have been extensively studied in two-phase aqueous systems (ATPS). These systems consist of two aqueous phases rich in two structurally different compounds which are immiscible, where they separate into two phases above certain concentration values. The ATPS may be formed from polymer, surfactant and salt, which may be strategically combined to achieve high selectivity and efficiency for the extraction and purification of biomolecules (Vicente et al., 2014). However, most polymers used to form the phases have high viscosity and form turbid solutions, interfering in determination of the analytes. In recent years it has been demonstrated that ionic liquids are a viable alternative for ATPS composed of common polymers since they present unique advantages, such as low viscosity, formation of emulsion, absence of volatile organic solvents, rapid phase separation and high extraction efficiency (Yan et al., 2014).

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The ATPS formed by ionic liquid have been successfully applied to separate, concentrate, isolate and purify biocompounds. Several studies with ILs have been published in recent years, including their application in complete removal of dyes, recovery of antibiotics, ethanol and butanol from fermentation broth, acetone, removal of organic contaminants from aqueous waste streams and protein partitioning (Ferreira et al., 2014; Huddleston et al., 1998; Fadeev and Meagher, 2001; Du et al., 2007; Dreyer et al., 2009). For these reasons, predicting the basic thermophysical properties of the phase forming systems at various concentrations and temperatures is also an indispensable requirement for the design and scale up of a wide range of separation process.

Given the above, the present study sought to evaluate the thermophysical properties of density, thermal expansion coefficient, molar volume, specific volume, refractive index and electrical conductivity of binary mixtures of water + 1-ethyl-3-methylimidazolium chloride in various conditions of pH, temperature and mass fraction.

EXPERIMENTAL SECTION

Materials

The 1-ethyl-3-methylimidazolium chloride (CAS: 65039-09-0) was purchased from Sigma Aldrich. Potassium hydroxide (CAS: 1310-58-3) and hydrochloric acid (CAS: 7647-01-0) were purchased from Vetec Fine Chemicals (Brazil) and Synth, respectively. All reagents were of analytical grade and used without further purification. The entire experiment was conducted at the Process Engineering Laboratory of the State University of Southwest Bahia (UESB), Itapetinga campus – Bahia, Brazil.

Methods

Preparation of solutions

Aqueous solutions of 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl) were prepared using an analytical balance M254A (Bel Engineering) with an accuracy of ± 0.0001 g. Stock solutions of 1-ethyl-3-methylimidazolium chloride ($w = 0.50$) were prepared for each pH value (7.5, 8.0 and 8.5) by addition of hydrochloric acid or potassium hydroxide when required. These pH values were chosen because they are commonly used in ATPS for separation of biomolecules (Sampaio et al., 2017). Appropriate quantities of the stock solution were diluted in tubes and shaken manually to obtain the desired mass fraction w = (0.05, 0.125, 0.2, 0.275 and 0.35). The analyses were performed at temperatures of T = (293.15, 303.15, 313.15 and 323.15) K, in all prepared solutions. Distilled water was used in all the experiments.

Density

The densities of the solutions were determined using a Bench Digital densimeter DMA 5000M (Anton Paar) with accuracy of ±5 x 10^{-6} g·cm^{-3} and repeatability of ±1 x 10^{-6} g·cm^{-3} in the operating range of 0 to 3 g·cm^{-3}. The temperature range of the equipment is 273.15 K to 363.15 K with an accuracy of ±0.01 K and repeatability of ±0.001 K.

Refractive Index

For the refractive index, the digital refractometer Q767BD (Quimis) was used with accuracy of ±0.0002 and wavelength of 589 nanometers, as is conventionally done. This device was connected to a thermostatic bath (Tecnal, Te-184), allowing for temperature control with an accuracy of 0.1 K. The equipment was calibrated with distilled water at the studied temperature, and the sample was then placed in the prism of the refractometer for direct reading.

Electrical conductivity

Electrical conductivity was determined using a bench digital conductivity meter Q795m (Quimis) with a precision of 0.5 %. The equipment was calibrated with a standard 0.01 M KCl solution. The temperature of the samples was controlled in a thermostatic bath (Tecnal, Te-184), allowing for temperature control to within 0.1 K.

Molar Volume

The molar volume (V_m) is the volume occupied by one mole of a substance at a fixed temperature and pressure. The V_m of the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride was calculated using the following equation:

$$V_m = \frac{M}{\rho} \tag{1}$$

where: M is the molecular mass in g·mol^{-1}, ρ is the density in g·cm^{-3} and V_m is the molar volume cm^3·mol^{-1}.

Thermal Expansion Coefficient

The density calculated for the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride was used to calculate the thermal expansion coefficient (α_p), using the following equation:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{2}$$

where: ρ is the density obtained in g·cm^{-3}.

Apparent specific volume

The apparent specific volume ($v_{2\emptyset}$) was calculated from the density data using equation 3:

$$v_{2\varnothing} = \frac{1}{\rho}\left[1 + \frac{\rho_0 - \rho}{w\rho_0}\right] \quad (3)$$

where: ρ (g·cm^{-3}) and ρ_0 (g·cm^{-3}) are the densities of the ionic solution and pure water, respectively.

Statistical analysis

All statistical analyses were performed using SAEG v.9.1 (Ribeiro Júnior, 2001). The experiment was conducted in a completely randomized design (CRD) with two replications and in triplicate. The experimental data obtained was fitted to polynomial models, where the correlation coefficient was calculated for the treatment means. Correlation coefficients between the predicted and real values were calculated for all models. The standard deviation for each property was also calculated. All analyses were performed considering a 5% significance level. The expanded uncertainties in density, refractive index, electrical conductivity, molar volume, apparent specific volume and thermal expansion coefficient were calculated as combined uncertainties multiplied by 2. The coverage factor of 2 yields a 95% confidence interval.

RESULTS AND DISCUSSION

Density, refractive index and electrical conductivity of the binary mixtures

The density, refractive index and electrical conductivity of ionic liquid solutions were measured at different temperatures T = (293.15, 303.15, 313.15 and 323.15) K, pH values (7.5, 8.0 and 8.5) and mass fraction w = (0.05, 0.12, 0.2, 0.275 and 0.35). Table 1 shows the mean and standard deviation of these properties in all conditions studied.

Figures 1, 2 and 3 shows the mean of these properties in all conditions studied. The density, refractive index and electrical conductivity of the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride increased with increasing mass fraction of the ionic liquid and decreased with the increase in temperature at each pH condition studied. Muray et al. (2013) observed similar behavior, studying thermo-physical properties of ionic liquid imidazolium base. Similar behavior for density was found by Rafie et al. (2016) studying the volumetric properties of ionic liquids in sucrose aqueous solution at different temperatures and ambient pressure.

The decrease in density with increasing temperature can be due to the increased mobility of liquid molecules from the increase in thermal energy, making the interactions within the system weaker and causing the volume expansion and reducing the density (Siongco et al., 2013). Figure 4 shows the comparison of measured densities for the (1-ethyl-3-methylimidazolium chloride + water) binary system in this work at different pH values and the literature at T= 303.15 K. This discrepancy in slopes may come from differences in values of pH and also small differences in the densities due to pressure.

Similar behavior can be observed for the index of refraction for all mass fractions of 1-ethyl-3-

Table 1. Density (ρ), refractive index (n_D) and conductivity (κ) of the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride at the different mass fraction (0.05, 0.12, 0.2, 0.275 and 0.35), temperatures T = (293.15, 303.15, 313.15 and 323.15) K and pH (7.5, 8.0 and 8.5)[a].

T /K	w	ρ/g·cm^{-3}	n_D	κ/10^{-3}mS·cm^{-1}
		pH 7.5		
293.15	0.050	1.0039±0.0001	1.3416±0.0001	17.5446±0.7642
	0.125	1.0130±0.0001	1.3537±0.0001	40.6085±0.3863
	0.200	1.0242±0.0001	1.3678±0.0001	65.0967±1.5680
	0.275	1.0355±0.0001	1.3826±0.0009	87.4540±1.8243
	0.350	1.0476±0.0004	1.3962±0.0005	107.8054±3.0910
303.15	0.050	1.0000±0.0001	1.3406±0.0003	17.6565±0.5265
	0.125	1.0099±0.0001	1.3527±0.0003	40.5151±0.5184
	0.200	1.0205±0.0001	1.3664±0.0001	64.8170±1.4372
	0.275	1.0313±0.0001	1.3812±0.0005	87.2676±2.3521
	0.350	1.0430±0.0004	1.3948±0.0002	107.3345±3.4826
313.15	0.050	0.9966±0.0001	1.3391±0.0001	17.4303±1.2536
	0.125	1.0057±0.0001	1.3518±0.0001	38.1956±0.1174
	0.200	1.0162±0.0001	1.3648±0.0003	61.6610±1.2508
	0.275	1.0266±0.0002	1.3797±0.0011	83.1728±2.1267
	0.350	1.0380±0.0004	1.3927±0.0005	102.9411±3.4685
323.15	0.050	0.9926±0.0001	1.3374±0.0004	17.9765±0.9637
	0.125	1.0002±0.0001	1.3504±0.0001	39.6268±1.1170
	0.200	1.0111±0.0005	1.3630±0.0005	63.7163±1.3768
	0.275	1.0214±0.0002	1.3778±0.0008	85.8561±2.6360
	0.350	1.0326±0.0004	1.3908±0.0005	105.9541±3.6763

Continues on the next page

Continued from Table 1

T /K	w	ρ/g·cm^{-3}	n_D	κ/10^{-3}mS·cm^{-1}
		pH 8.0		
293.15	0.050	1.0043±0.0001	1.3414±0.0001	16.6523±0.4220
	0.125	1.0137±0.0001	1.3535±0.0001	39.7316±0.6737
	0.200	1.0239±0.0001	1.3676±0.0001	62.7498±0.2775
	0.275	1.0350±0.0001	1.3812±0.0001	83.5054±4.5756
	0.350	1.0469±0.0001	1.3954±0.0001	103.3806±1.7279
303.15	0.050	1.0015±0.0001	1.3404±0.0001	16.6523±0.4485
	0.125	1.0104±0.0001	1.3522±0.0001	39.8251±0.2771
	0.200	1.0202±0.0001	1.3663±0.0001	63.2166±0.3827
	0.275	1.0308±0.0001	1.3797±0.0001	83.6921±4.3116
	0.350	1.0423±0.0001	1.3938±0.0001	102.9166±2.6478
313.15	0.050	0.9979±0.0001	1.3388±0.0002	16.0550±0.5440
	0.125	1.0065±0.0001	1.3513±0.0001	38.4293±0.6457
	0.200	1.0159±0.0001	1.3647±0.0001	60.4849±0.0129
	0.275	1.0262±0.0001	1.3780±0.0003	79.3894±3.7525
	0.350	1.0373±0.0001	1.3919±0.0005	98.6143±2.0328
323.15	0.050	0.9934±0.0001	1.3375±0.0004	16.7187±0.3161
	0.125	1.0020±0.0001	1.3498±0.0001	39.8625±0.6461
	0.200	1.0111±0.0001	1.3631±0.0004	62.4534±0.5195
	0.275	1.0210±0.0002	1.3761±0.0006	82.2503±3.7510
	0.350	1.0320±0.0001	1.3893±0.0001	101.9130±1.9156
		pH 8.5		
293.15	0.050	1.0048±0.0002	1.3414±0.0001	16.6693±0.1053
	0.125	1.0143±0.0001	1.3542±0.0001	40.3545±0.4767
	0.200	1.0252±0.0001	1.3688±0.0001	59.9509±0.7293
	0.275	1.0367±0.0002	1.3830±0.0001	81.6592±0.0442
	0.350	1.0494±0.0001	1.3981±0.0001	102.4296±0.0442
303.15	0.050	1.0019±0.0002	1.3404±0.0001	16.6959±1.6150
	0.125	1.0110±0.0001	1.3529±0.0001	40.5327±0.0427
	0.200	1.0215±0.0001	1.3675±0.0001	60.4862±0.4783
	0.275	1.0325±0.0002	1.3813±0.0001	81.8447±0.7336
	0.350	1.0447±0.0001	1.3963±0.0001	102.2526±0.2182
313.15	0.050	0.9983±0.0002	1.3391±0.0002	17.1746±1.8654
	0.125	1.0070±0.0001	1.3520±0.0003	41.2442±0.3189
	0.200	1.0171±0.0001	1.3658±0.0001	61.2896±0.2325
	0.275	1.0278±0.0002	1.3800±0.0001	82.9370±0.8661
	0.350	1.0397±0.0001	1.3950±0.0002	103.7576±0.5100
323.15	0.050	0.9939±0.0002	1.3379±0.0002	18.0786±1.7400
	0.125	1.0025±0.0001	1.3507±0.0002	42.6684±0.5454
	0.200	1.0122±0.0002	1.3644±0.0001	63.3420±1.0086
	0.275	1.0228±0.0002	1.3783±0.0001	86.0201±0.6099
	0.350	1.0343±0.0001	1.3930±0.0001	107.4759±1.7396

[a]For densities the standard uncertainty for temperature is *u*(T) = 0.001 K, for refractive index and electrical conductivity the standard uncertainty for temperature is *u*(*T*) = 0.11 K. For densities, refractive index and electrical conductivity the standard uncertainty for mass fraction is *u*(*w*) = 0.0001. Expanded uncertainties are: for density: *Uc*(*ρ*) = 0.0004 g·cm^{-3}, for refractive index: *Uc* (n_D) = 0.0011 and electrical conductivity: *Uc*(κ) = 1.72 mS·cm^{-1} (0.95 level of confidence).

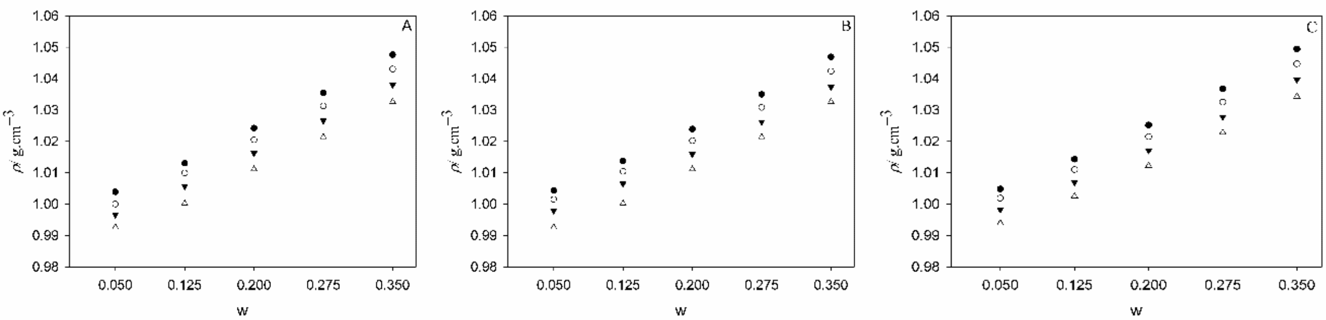

Figure 1. Density ρ of binary mixtures of water + chloride, 1-ethyl-3-methyl imidazolium as a function of the mass fraction at different temperatures, T/K: ●, 293.15; ○, 303.15; ▼, 313.15; Δ, 323,15 at each value pH: (A) 7.5, (B) 8.0 and (C) 8.5.

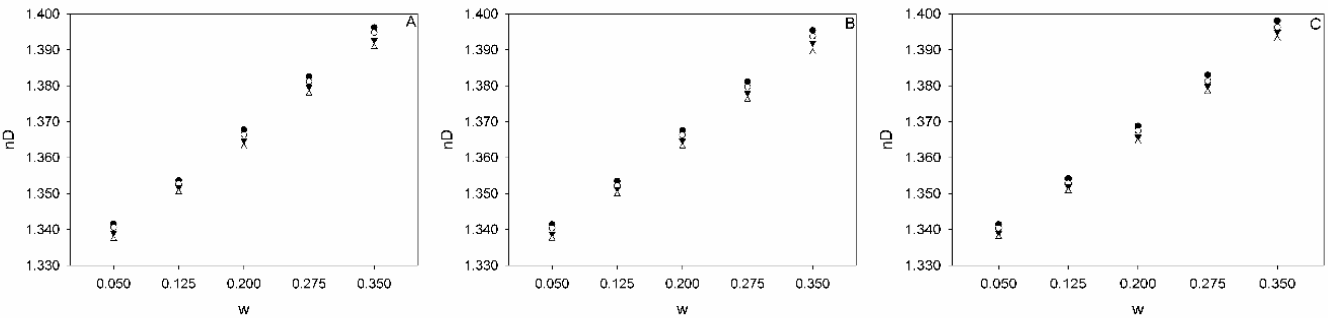

Figure 2. Refractive index n_D of binary mixtures of water + chloride, 1-ethyl-3-methyl imidazolium as a function of the mass fraction at different temperatures, T/K: ●, 293.15; ○, 303.15; ▼, 313.15; Δ, 323,15 at each value pH: (A) 7.5, (B) 8.0 and (C) 8.5.

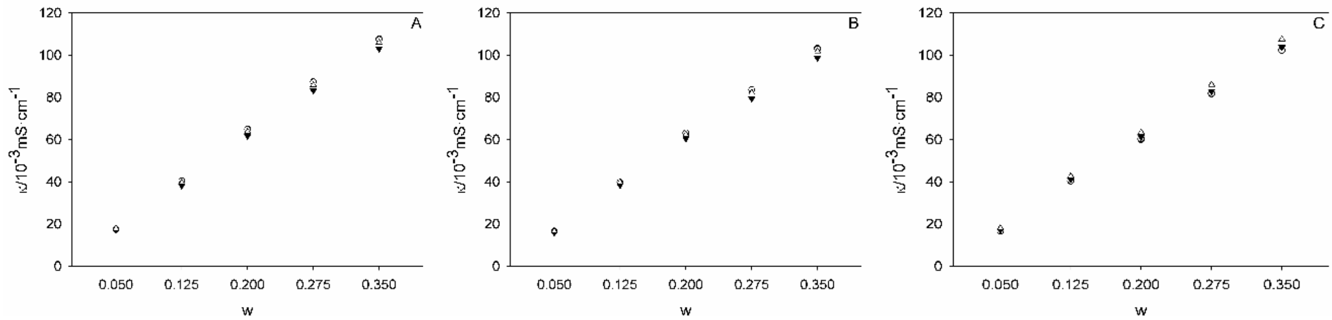

Figure 3. Electrical conductivity κ of binary mixtures of water + chloride, 1-ethyl-3-methyl imidazolium as a function of the mass fraction at different temperatures, T/K: ●, 293.15; ○, 303.15; ▼, 313.15; Δ, 323.15 at each value pH: (A) 7.5, (B) 8.0 and (C) 8.5.binary mixtures of water + chloride, 1-ethyl-3-methyl imidazolium.

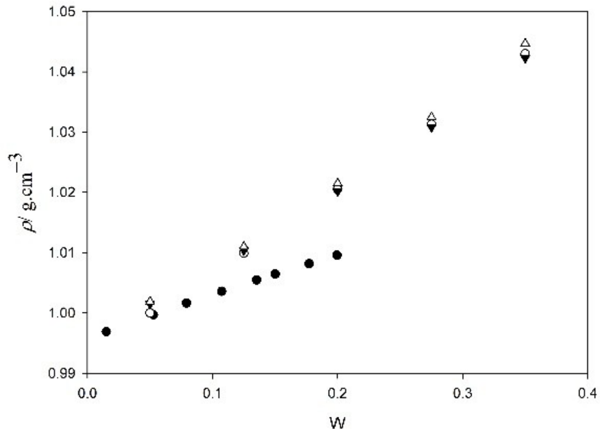

Figure 4. Comparison of measured densities for (water + 1-ethyl-3-methyl imidazolium chloride) binary system with the literature at T=303.15 K: ● (Rafie et al. (2015); Rafie et al. (2016)); this work ○, pH 7.5; ▼, pH 8.0; Δ, pH 8.5.

methylimidazolium chloride, temperature and pH values. Regarding the temperature, at constant mass fraction of 1-ethyl-3-methylimidazolium chloride, an increase in temperature causes an expansion of the liquid volume, reducing the concentration and decreasing in the refractive index of the aqueous solutions. It was also noted that the refractive index increased with increasing mass fraction of 1-ethyl-3-methylimidazolium chloride. Similar behavior was observed by Tang et al. (2014), who observed that the index of refraction increased with the mass fraction of the ionic liquid.

It can be seen that the electrical conductivity increased with increasing mass fraction of 1-ethyl-3-methylimidazolium chloride due to the increase in the amount of ions present in the aqueous solution (Xu et al., 2015).

From the experimental data, polynomial models were adjusted to the thermophysical properties as a function of temperature, mass fraction and pH of the ionic liquid by fitting the experimental data to the general model (Eq. 4), and thereby obtaining the combined effect of these properties with regards to the three variables. Non-significant parameters were eliminated based on the Student's t-test and p-value less than 0.05.

$$\begin{aligned}\psi &= \beta_1 + \beta_2 w + \beta_3 T + \beta_4 p + \beta_5 w^2 + \\ &+ \beta_6 T^2 + \beta_7 p^2 + \beta_8 w^3 + \beta_9 T^3 + \beta_{10} w^4 + \\ &+ \beta_{11} wT + \beta_{12} wp + \beta_{13} Tp + \beta_{14} wTp\end{aligned} \quad (4)$$

where: ψ is the thermodynamic property and β_1, β_2, β_3, β_4, β_5, β_6, β_7, β_8, β_9, β_{10}, β_{11}, β_{12}, β_{13} and β_{14} are constants determined from the experimental data.

Table 2 shows the coefficients obtained from the polynomial regression (Eq. 4) for density (ρ),

Table 2. Fixed parameters for the models (Eq. 4) for density (ρ), refractive index (n_D) and electrical conductivity (κ) for binary mixtures of water + 1-ethyl-3-methylimidazolium chloride.

Parameters	Properties		
	ρ/g.cm^{-3}	n_D	κ/10^{-3} mS.cm^{-1}
β_1	1.0866	1.3739	1300.4804
β_2	0.2746	0.0011	4.0230
β_3	-0.0003	-0.0001	-4.5354
β_4	0.0014	ns	-151.3819
β_5	ns	0.00001	-0.0086
β_6	ns	ns	0.0052
β_7	ns	ns	6.2508
β_{11}	-0.0004	ns	Ns
β_{12}	ns	ns	-0.0980
β_{13}	ns	ns	0.1690
R^2	0.9966	0.9449	0.9984
Correlation coefficient	0.9987	0.9996	0.9995

ns: not significant. The parameters β_8, β_9, β_{10} and β_{14} are not in the table because they were not significant for any property.

refractive index (n_D) and electrical conductivity (κ). The fit between experimental and predicted data by the model was satisfactory, with R^2 values and correlation coefficients greater than 0.94.

Table 2 points to an inverse relationship for the temperature behavior for the density and refractive index. This indicates that the increase in temperature causes a decrease in these thermodynamic properties in question. The decrease of these properties with temperature is due to the increased mobility of the molecules of binary mixtures, causing a volume expansion and the decrease of intermolecular interactions (Siongco et al. 2013).

Moreover, binary mixtures had positive coefficients for the mass fraction of 1-ethyl-3-methylimidazolium chloride, confirming that the presence of the ionic liquid contributed to increasing the density and refractive index.

It can also be seen in Table 2 that the electrical conductivity was more affected by the mass fraction of 1-ethyl-3-methylimidazolium chloride than by temperature, confirming that the increase in the mass fraction of 1-ethyl-3-methylimidazolium chloride increases the electrical conductivity.

Figures 5, 6 and 7 show the data predicted by the model with regards to density, refractive index and electrical conductivity as a function of temperature and mass fraction obtained from Eq. 4 when the pH values were fixed. It was observed that for all thermodynamic properties the term related to temperature was negative, indicating that the three previously mentioned properties were negatively affected by the increase in this variable. In contrast, the parameter related to mass fraction was positive, indicating that there is an increase in these properties with the increase of this variable.

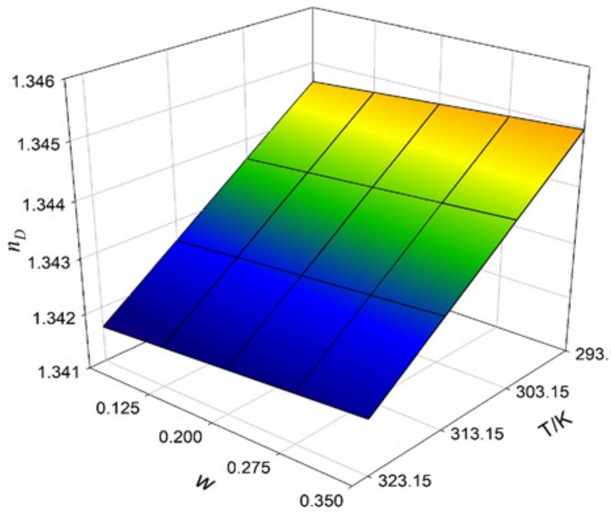

Figure 6. Refractive index n_D of binary mixtures of water + 1-ethyl-3-methyl imidazolium chloride predicted by the model.

Apparent specific volume, molar volume and thermal expansion coefficient of the binary mixtures

From the experimental data obtained for density and from equations 1 to 3, the properties of molar volume, thermal expansion coefficient and apparent specific volume were calculated for the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride at different temperatures T = (293.15, 303.15, 313.15 and 323.15) K, pH values (7.5, 8.0 and 8.5) and mass fraction w = (0.05, 0.12, 0.2, 0.275 and 0.35). The results are shown in Table 3.

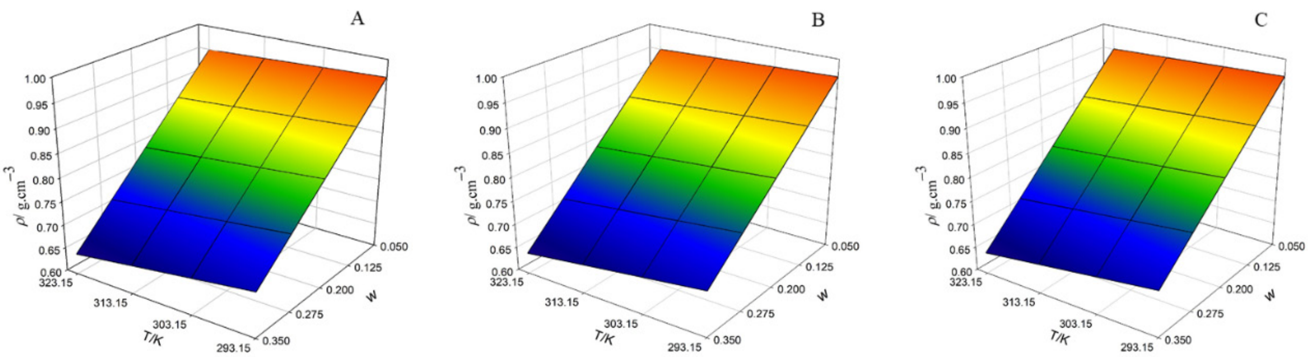

Figure 5. Density ρ of binary mixtures of water + 1-ethyl-3-methyl imidazolium chloride predicted by the model at different values of pH (A) 7.5 (B) 8.0 and (C) 8.5.

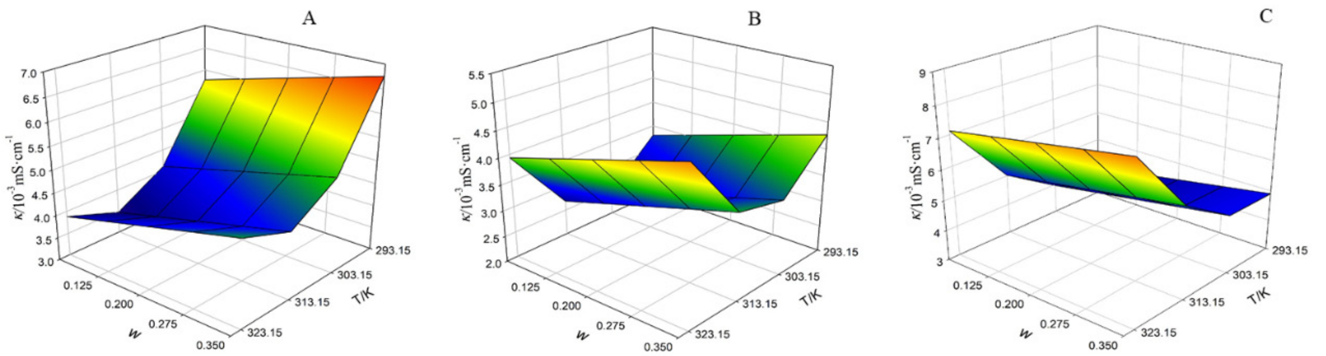

Figure 7. Electrical conductivity κ binary mixtures of water + 1-ethyl-3-methyl imidazolium chloride predicted by the model at different values of pH (A) 7.5 (B) 8.0 and (C) 8.5.

Table 3. Apparent specific volume ($v_{2Ø}$), molar volume (V_m) and thermal expansion coefficient (α_p) of the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride at different mass fractions (0.05, 0.12, 0.2, 0.275 and 0.35), temperatures T = (293.15, 303.15, 313.15 and 323.15) K and pH (7.5, 8.0 and 8.5).

T/K	w	$v_{2\phi}$/g·cm^{-3}	V_m/cm^3·mol^{-1}	α_p/K^{-1}
		pH 7.5		
293.15	0.050	0.8871±0.0009	146.0508±0.0061	0.3444±0.0001
	0.125	0.8722±0.0007	144.7430±0.0116	0.3416±0.0001
	0.200	0.8503±0.0003	143.1545±0.0079	0.3382±0.0001
	0.275	0.8354±0.0006	141.5942±0.0194	0.3348±0.0001
	0.350	0.8203±0.0014	139.9591±0.0525	0.3313±0.0001
303.15	0.050	0.9163±0.0003	146.6156±0.0021	0.3457±0.0001
	0.125	0.8785±0.0003	145.1814±0.0051	0.3427±0.0001
	0.200	0.8587±0.0003	143.6738±0.0083	0.3394±0.0001
	0.275	0.8441±0.0006	142.1659±0.0185	0.3362±0.0001
	0.350	0.8292±0.0013	140.5791±0.0508	0.3327±0.0001
313.15	0.050	0.9199±0.0025	147.1254±0.0177	0.3469±0.0001
	0.125	0.8878±0.0009	145.7863±0.0149	0.3441±0.0001
	0.200	0.8661±0.0004	144.2804±0.0102	0.3409±0.0001
	0.275	0.8521±0.0007	142.8196±0.0228	0.3377±0.0001
	0.350	0.8371±0.0013	141.2564±0.0479	0.3343±0.0001
323.15	0.050	0.9189±0.0003	147.7131±0.0023	0.3483±0.0001
	0.125	0.9035±0.0007	146.5963±0.0117	0.3460±0.0001
	0.200	0.8744±0.0027	145.0039±0.0656	0.3425±0.0001
	0.275	0.8596±0.0010	143.5481±0.0321	0.3394±0.0001
	0.350	0.8444±0.0009	141.9960±0.0335	0.3361±0.0001
		pH 8.0		
293.15	0.050	0.8784±0.0006	145.9903±0.0040	0.3442±0.0001
	0.125	0.8661±0.0001	144.6432±0.0019	0.3414±0.0001
	0.200	0.8522±0.0003	143.1995±0.0079	0.3383±0.0001
	0.275	0.8376±0.0002	141.6642±0.0074	0.3350±0.0001
	0.350	0.8228±0.0004	140.0552±0.0153	0.3315±0.0001
303.15	0.050	0.8857±0.0005	146.4019±0.0033	0.3452±0.0001
	0.125	0.8739±0.0001	145.1070±0.0023	0.3425±0.0001
	0.200	0.8605±0.0004	143.7187±0.0099	0.3395±0.0001
	0.275	0.8463±0.0004	142.2377±0.0118	0.3363±0.0001
	0.350	0.8317±0.0004	140.6726±0.0149	0.3330±0.0001
313.15	0.050	0.8926±0.0008	146.9351±0.0054	0.3465±0.0001
	0.125	0.8809±0.0002	145.6737±0.0027	0.3438±0.0001
	0.200	0.8679±0.0004	144.3225±0.0093	0.3410±0.0001
	0.275	0.8540±0.0005	142.8804±0.0156	0.3379±0.0001
	0.350	0.8395±0.0004	141.3466±0.0140	0.3346±0.0001
323.15	0.050	0.9020±0.0020	147.5952±0.0142	0.3480±0.0001
	0.125	0.8873±0.0002	146.3333±0.0025	0.3454±0.0001
	0.200	0.8746±0.0003	145.0083±0.0080	0.3426±0.0001
	0.275	0.8613±0.0110	143.6009±0.0343	0.3396±0.0001
	0.350	0.8465±0.0003	142.0755±0.0126	0.3363±0.0001

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Continued from Table 3

T/K	w	$v_{2\phi}$/g·cm^{-3}	V_m/cm^3·mol^{-1}	α_p/K^{-1}
		pH 8.5		
293.15	0.050	0.8688±0.0040	145.9903±0.0040	0.3442±0.0001
	0.125	0.8604±0.0008	144.6432±0.0019	0.3414±0.0001
	0.200	0.8446±0.0001	143.1995±0.0079	0.3383±0.0001
	0.275	0.8300±0.0008	141.6642±0.0074	0.3350±0.0001
	0.350	0.8140±0.0001	140.0552±0.0153	0.3315±0.0001
303.15	0.050	0.8765±0.0039	146.4019±0.0033	0.3452±0.0001
	0.125	0.8686±0.0005	145.1070±0.0023	0.3425±0.0001
	0.200	0.8532±0.0001	143.7187±0.0099	0.3395±0.0001
	0.275	0.8389±0.0008	142.2377±0.0118	0.3363±0.0001
	0.350	0.8231±0.0001	140.6726±0.0149	0.3330±0.0001
313.15	0.050	0.8836±0.0045	146.9352±0.0054	0.3465±0.0001
	0.125	0.8760±0.0001	145.6737±0.0027	0.3438±0.0001
	0.200	0.8609±0.0002	144.3225±0.0093	0.3410±0.0001
	0.275	0.8468±0.0009	142.8804±0.0156	0.3379±0.0001
	0.350	0.8311±0.0001	141.3466±0.0140	0.3346±0.0001
323.15	0.050	0.8904±0.0048	147.5952±0.0142	0.3480±0.0001
	0.125	0.8824±0.0004	146.3333±0.0025	0.3454±0.0001
	0.200	0.8684±0.0009	145.0083±0.0080	0.3426±0.0001
	0.275	0.8536±0.0007	143.6009±0.0343	0.3396±0.0001
	0.350	0.8382±0.0001	142.0755±0.0126	0.3363±0.0001

[a]For apparent specific volume, molar volume and thermal expansion coefficient the standard uncertainty for temperature is u(T) = 0.001 K and for mass fraction is $u(w)$ = 0.0001. Expanded uncertainties are for apparent specific volume: $Uc(v_{2Ø})$ = 0.002 g·cm^{-3}, for molar volume: $Uc(V_m)$ = 0.6508 cm^3·mol^{-1} and for thermal expansion coefficient: $Uc(\alpha_p)$ 0.0020 = K^{-1} (0.95 level of confidence).

The molar volume, thermal expansion coefficient and apparent specific volume of the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride decreased with an increase in mass fraction and increased with an increase in temperature.

Similar behavior for the apparent molar volume was found by Rafie et al. (2015) studying the ionic liquid, 1-ethyl-3-methyl imidazolium chloride in aqueous lithium nitrate, lithium bromide, and lithium chloride solutions at temperatures 298.15 to 318.15 K.

Using the same procedures as above, polynomial models were fit to the properties of molar volume, thermal expansion coefficient and apparent specific volume of the binary mixtures as a function of temperature, mass fraction and pH of the ionic liquids, by fitting the experimental data to the general model (Eq. (4)). Table 4 shows the coefficients obtained from the polynomial regression (Eq. 4) for the properties of apparent specific volume ($v_{2Ø}$), molar volume (V_m) and thermal expansion coefficient (α_p).

Figures 8, 9 and 10 show the data predicted by the model with respect to specific volume, molar volume and thermal expansion coefficient as a function of

Table 4. Fixed parameters of the models (eq. 4) for apparent specific volume ($v_{2Ø}$), molar volume (V_m) and thermal expansion coefficient (α_p) for the binary mixtures of water + 1-ethyl-3-methylimidazolium chloride.

Constants	Properties		
	$v_{2Ø}$/g.cm^{-3}	V_m/cm^3.mol^{-1}	α_p/K^{-1}
β_1	0.8764	131.8090	0.3040
β_2	-0.0082	-0.3314	-0.0004
β_3	0.0008	0.0520	0.0001
β_4	-0.0276	ns	ns
β_{11}	ns	0.0005	ns
β_{12}	0.0008	ns	ns
R^2	0.9751	0.9978	0.9950
Correlation coefficient	0.9907	0.9993	0.9991

ns: not significant. The parameters β_5, β_6, β_7, β_8, β_9, β_{10}, β_{13} and β_{14} are not in the table because they were not significant for any property.

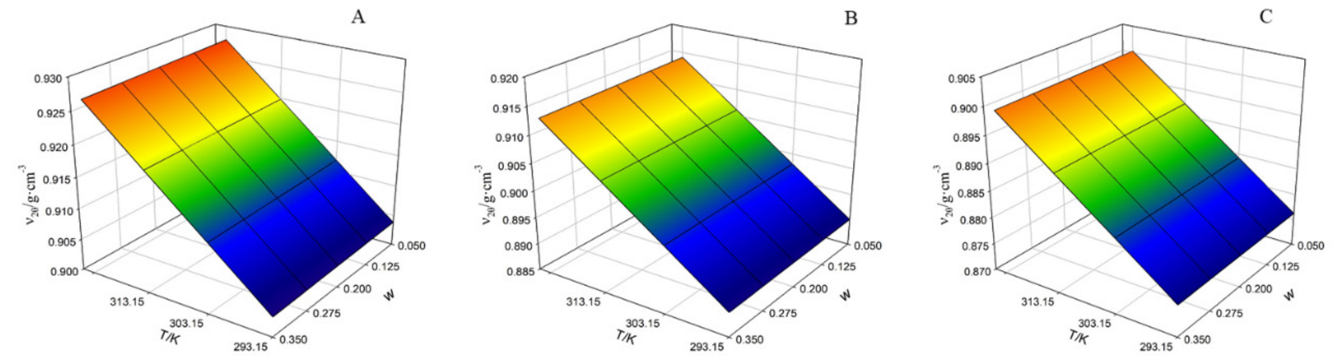

Figure 8. Specific volume $v_{2Ø}$ of binary mixtures of water + 1-ethyl-3-methyl imidazolium chloride predicted by the model at different values of pH (A) 7.5 (B) 8.0 and (C) 8.5.

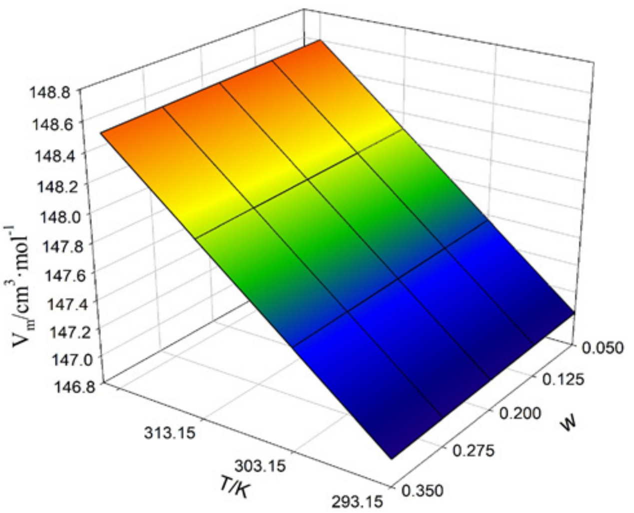

Figure 9. Molar volume V_m of binary mixtures of water + 1-ethyl-3-methyl imidazolium chloride predicted by the model.

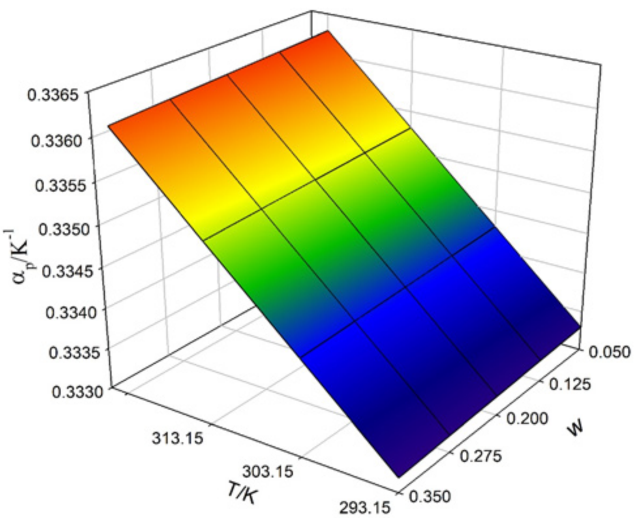

Figure 10. Coefficient of thermal expansion α_p of binary mixtures of water + 1-ethyl-3-methyl imidazolium chloride predicted by the model.

the temperature and mass fraction obtained from eq. 4, in which the pH was fixed for each value. It can be observed in the figures that the values of these 3 properties decreased as the mass fraction increased and increased with increases in temperature.

CONCLUSION

It was possible to obtain experimental data for the properties density (ρ), electrical conductivity (κ) and refractive index (n_D), under various conditions of temperature, mass fraction and pH of aqueous solutions of the ionic liquid. From the experimental data for the density it was possible calculate the apparent specific volume ($v_{2\emptyset}$), the coefficient of thermal expansion (α_p) and molar volume (V_m). Polynomial models for the properties presented satisfactory fits to the experimental data. The results were satisfactory and can be used for the design and scale up of separation process under such experimental conditions.

NOMENCLATURE

W	mass fraction
T	temperature, K
ILs	ionic liquids
ATPS	two-phase aqueous systems
([C_2mim]Cl)	1-ethyl-3-methylimidazolium chloride
P	density, g·cm^{-3}
V_m	molar volume, cm^3·mol^{-1}
α_p	thermal expansion coefficient, K^{-1}
$v_{2\emptyset}$	apparent specific volume, cm^3·g^{-1}
n_D	refractive index
K	electrical conductivity, mS·cm^{-1}
CRD	completely randomized design
ψ	thermophysical property
β	adjusted parameter
R^2	correlation coefficient

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