THERMODYNAMIC MODELING OF AZEOTROPIC MIXTURES WITH [EMIM][TfO] WITH CUBIC-PLUS-ASSOCIATION AND CUBIC EOSs

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Abstract - Ionic liquids (ILs) are organic salts that are liquids at room temperature and have low vapor pressure. These characteristics render ILs potential substitutes of organic solvents and inorganic salts in separation of azeotropic mixtures. This work presents vapor-liquid equilibrium modeling of the azeotropic mixture acetone + methanol + 1-ethyl-3-methylimidazolium-trifluoromethanesulfonate and ethanol + water + 1-ethyl-3-methylimidazolium-trifluoromethanesulfonate with the Cubic-Plus-Association Equation of State (CPA EoS). The azeotropic ternary mixture phase behavior was properly predicted using binary interaction parameters that were adjusted from binary mixture phase equilibrium data. Results show that the CPA EoS provides a better description of experimental data as compared to the Peng-Robinson-Wong-Sandler Equation of State (PRWS EoS).

Keywords: Cubic-Plus-Association Equation of State, ionic liquids, azeotropic mixtures.

INTRODUCTION

Azeotrope formation occurs in a variety of chemical and industrial processes, as in ethanol and methyl acetate production. The most common process to remove components in an azeotrope point is extractive distillation. This consists of the addition of a relatively non-volatile component (entrainer) to increase relative volatility. Although widely used, extractive distillation requires a high energetic burden. Ethanol separation from water is a typical example, since it demands distillation columns in series. Moreover, most of the entrainers are often organic solvents and inorganic salts that cause corrosion and accumulation in the distillation column, hindering recycle. Recently, ionic liquids (ILs) have been used as an alternative to traditional entrainers because they are chemically stable organic salts that remain liquid over a broad temperature range and have a very low vapor pressure. They can also be recycled easily and mixed with the reflux stream without accumulating in the less-volatile components at the top of the distillation column (Orchillés *et al.*, 2007). Phase behavior prediction of ILs in azeotropic mixtures is of great utility to verify if these are able to break the azeotrope point due to all the advantages which come with the use of ILs. A common strategy to describe ILs phase equilibrium is the use of either Gibbs free energy models such as the Non-Random-Two-Liquid (NRTL) (Renon and Prausnitz, 1968) and Universal Quasi Chemical

(UNIQUAC) models (Anderson and Prausnitz, 1978) or Gibbs free energy models associated with the Peng-Robinson-Wong-Sandler Equation of State (PRWS EoS) (Peng and Robinson, 1976; Wong *et al*., 1992). In these models, the strong interactions present in systems such as hydrogen bonding result in deviations from ideal mixture behavior and are taken into account implicitly in the energy parameters. An alternative methodology to describe ILs phase behavior is the use of the Cubic-Plus-Association Equation of State (CPA EoS) (Kontogeorgis *et al*., 2006). This is a hybrid equation of state that combines the Soave-Redlich-Kwong (SRK EoS) (Soave, 1972) to take into account physical interactions and the association term from the Statistical-Associating-Fluid-Theory (SAFT EoS) (Chapman *et al*., 1990; Huang and Radosz, 1990) in order to describe hydrogen-bond formation. The CPA EoS has already provided satisfactory results in mixtures with ionic liquids (Maia *et. al.*, 2012).

In this work, we study the vapor-liquid equilibrium of the azeotropic mixtures acetone + methanol and ethanol-water with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][TfO]), Figure 1, as entrainer with CPA. Moreover, we define the best association strategy which is able to account for the [emim][TfO] effect on the acetone + methanol and ethanol + water azeotropic mixtures. We decided to study the IL with those components due to the fact that the mixture methanol-acetone is essential for the production of synthetic hydrocarbons via the Fischer-Tropsch process (Wilsak *et al*., 1986). Moreover, the development of new separation processes for the ethanol-water mixture is important for the energy industry such as in the production of biodiesel and anhydrous alcohol used in automotive engines (Gil *et al*, 2008).
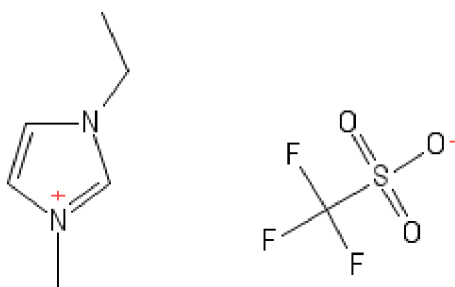
Figure 1: 2D structure of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

CPA EOS

The functional form of the CPA EoS can be expressed for mixtures in terms of pressure:

$$P^{CPA} = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}(\bar{V} + b)} - $$
$$\frac{1}{2}\left(\frac{RT}{\bar{V}}\right)\left(1 + \frac{1}{\bar{V}}\frac{\partial \ln g}{\partial(1/\bar{V})}\right)\sum_i x_i \sum_{A_i}\left(1 - X_{A_i}\right) \quad (1)$$

The pressure due to the associative contribution in Equation (1) is the CPA simplified version (Michelsen, 2006). This associative pressure takes into account site-site interactions due to hydrogen bonding between molecules of the same type (self-association) and different molecular types (cross association). The mole fraction X_{A_i} of non-bonded molecules at site A is defined by:

$$X_{A_i} = \frac{1}{1 + (1/\bar{V})\sum_j x_j \sum_{B_j} X_{B_j}\Delta^{A_i B_j}} \quad (2)$$

The summation is done over all association sites, the association strength $\Delta^{A_i B_j}$ between the site A in molecule i and site B in molecule j is given by:

$$\Delta^{A_i B_j} = g_{ij}\left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1\right]b_{ij}\beta^{A_i B_j} \quad (3)$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and volume, respectively. In Equation (3), the radial distribution is $g_{ij} = 1/(1 - 1.9\eta)$, with $\eta = b/4\bar{V}$, where $b_{ij} = (b_i + b_j)/2$.

The energy parameter in Equation (1) has the Soave temperature dependency form, whereas the parameter b is temperature independent:

$$a(T) = a_0\left(1 + c_1\left(1 - \sqrt{T_r}\right)\right)^2 \quad (4)$$

where T_r is the reduced temperature, a_0 and c_1 are non-associative parameters to be estimated for pure substances.

Therefore, for pure components, there are three parameters (a_{0i}, c_{1i} and b_i) for non-associating components and five (a_{0i}, c_{1i}, b, $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$) for associating components. When the CPA EoS is applied to mixtures, the a and b parameters are calculated from the van der Waals mixing rules.

These mixing association parameters are calculated from mixtures of pure components through combination rules. The energy association parameter is calculated with the arithmetic rule and the volume parameter with the geometric rule (Derawi *et al.*, 2003; Wolbach and Sandler, 1998). Different types of association schemes are described elsewhere (Huang and Radosz, 1990).

PARAMETER ESTIMATION

The critical parameters for the ionic liquid [emin][TfO] are available in the literature (Valderrama and Roja, 2009). The parameter of the pure component UNIQUAC model for the ILs and the solvents are available elsewhere (Santiago *et al.*, 2009; Banerjee *et al.*, 2005; Anderson and Prausnitz, 1978). CPA EOS parameters for pure solvents (methanol and acetone) are obtained by minimizing Equation (5) based on deviations between experimental (DIADEM, 2000) and calculated vapor-pressure and saturated-liquid-density data. CPA EOS parameters for [emim][TfO] were adjusted with Equation (6) from liquid density data at 1 bar (Garcia-Miaja *et al.*, 2009; Vercher *et al.*, 2007). The estimation of the vapor pressure has not been made due the lack of data for [emin][TfO] and the really low vapor pressure for ionic liquids in general. In order to analyze the prediction of the CPA EOS, the vapor pressure of this ionic liquid was calculated for a temperature range of 298-600 K and the values were within a range of 0.01-4 bar .

$$FO_1 = \sum_{i=1}^{N} \left[\frac{\left| P_{sat\ i}^{cal} - P_{sat\ i}^{exp} \right|}{P_{sat\ i}^{exp}} \right]^2 + \sum_{i=1}^{N} \left[\frac{\left| \rho_{sat\ i}^{cal} - \rho_{sat\ i}^{exp} \right|}{\rho_{sat\ i}^{exp}} \right]^2 \qquad (5)$$

$$FO_2 = \sum_{i=1}^{N} \left[\frac{\left| \rho_{L\ i}^{cal} - \rho_{L\ i}^{exp} \right|}{\rho_{L\ i}^{exp}} \right]^2 \qquad (6)$$

The binary interaction parameters for CPA and PRWS EoS were estimated from the vapor-liquid equilibrium (VLE) data with the following equation:

$$FO_3 = \sum_{i=1}^{N} \left[\frac{\left| T_{\ i}^{cal} - T_{\ i}^{exp} \right|}{P_{\ i}^{exp}} \right]^2 + \sum_{i=1}^{N} \left| y_{\ i}^{cal} - y_{\ i}^{exp} \right|^2 \qquad (7)$$

The Particle Swarm Optimization (PSO) (Schwaab *et al.,* 2008) combined with the Simplex algorithms (Nelder and Mead, 1965) were employed to minimize the objective functions.

In order to evaluate the model performance, we define the relative deviation averages as:

$$\Delta P(\%) = \left(1/N\right) \sum_{i=1}^{N} \left| \frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right| x100 \qquad (8)$$

$$\Delta \rho(\%) = \left(1/N\right) \sum_{i=1}^{N} \left| \frac{\rho_i^{exp} - \rho_i^{cal}}{\rho_i^{exp}} \right| x100 \qquad (9)$$

$$\Delta T(\%) = \left(1/N\right) \sum_{i=1}^{N} \left| \frac{T_i^{exp} - T_i^{cal}}{T_i^{exp}} \right| x100 \qquad (10)$$

$$\Delta y = \left(1/N\right) \sum_{i=1}^{N} \left| y_i^{exp} - y_i^{cal} \right| \qquad (11)$$

ASSOCIATION SCHEMES

The CPA EoS parameter estimation requires a strategy to define how the components associate. Among the schemes tested the ones that presented better results are illustrated in Figure 2.
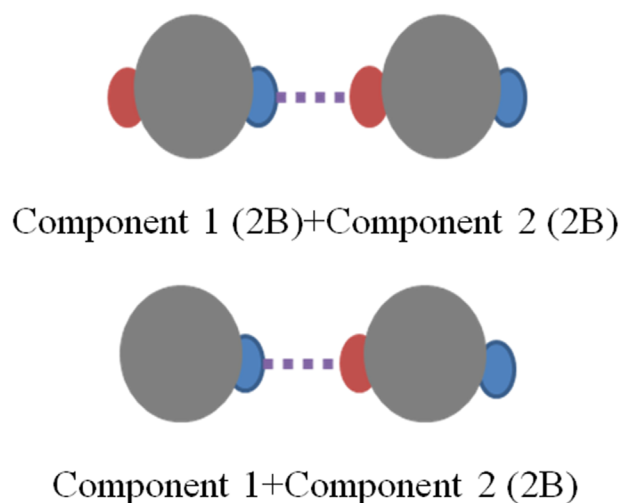

Figure 2: Association scheme modified from Chapman *et al.* (1990).

The nomenclature 2B indicates the association scheme. The 2B scheme is used for components that have a receptor site and a donor electron pair per molecule, such as alcohols. In the second approach, the components with no nomenclature next to them have no self-association but are capable of forming hydrogen bonds with another component that has self-association, for example acetone. This ability to form hydrogen bonds only within the mixture is represented by the association volume of the mixture (β_{ij}) and by the association energy of the mixture (Kleiner and Sadowski, 2007). The association volume of the mixture is estimated from VLE data and the association energy of mixture is equal to half the association energy of the component that has self–association.

## RESULTS AND DISCUSSION

Pure Components

Table 1 shows the CPA EoS pure-component parameters estimated for this study. We observe that the CPA EOS provides excellent correlation for pure components, showing low vapor-pressure and saturated--liquid-density deviations for solvents, and low liquid--density deviations at 1 bar for ILs.

Figure 3 summarizes the results for pure density of [emin][TfO] with the strategies explained above.

Acetone + Methanol + [emim][TfO]

Tables 2 and 3 present binary parameters and relative deviations obtained for the binary mixtures Acetone + Methanol, [emim][TfO] + Acetone and [emim][TfO] + Methanol with the PRWS-NRTL and PRWS-UNIQUAC models, respectively.

The PRWS-NRTL EoS requires four binary parameters in order to describe all binary mixtures and
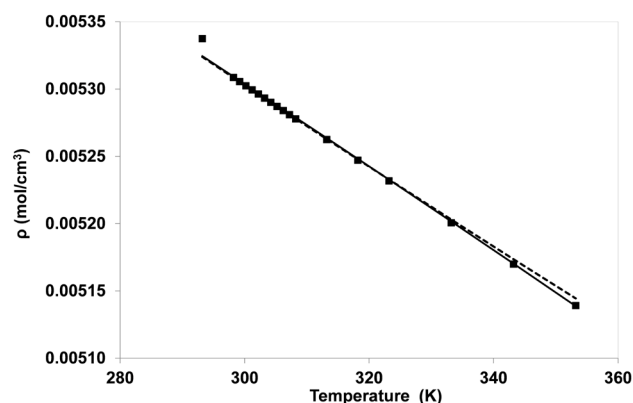
Figure 3: Different association strategies for the density: [emim][TfO] (solid line) and [emim][TfO] (2B) (dashed line). Experimental data (■) (Garcia-Miaja *et. al.*, 2009; Vercher *et al.*, 2007).

give satisfactory results. The small temperature deviations suggest that the PRWS-NRTL EoS is able to describe those binary mixtures. For the same binary mixtures, the PRWS-UNIQUAC EoS requires three binary parameters. The PRWS-UNIQUAC EoS results

Table 1: CPA parameters for pure components.

Components	a_0 (bar.L^2.mol^{-2})	b (L/mol)	c_1	ε^{AB} (bar. L.mol^{-1})	$\beta^{AB} \cdot 10^3$	$\Delta\rho$ (%)	ΔP (%)
Acetone (2B)	7.79	0.059	1.00	111.7	296.79	0.40	0.1
Acetone	13.93	0.062	0.81	-	-	0.92	0.8
Methanol (2B)	3.77	0.031	0.83	213.4	42.22	1.00	0.7
Ethanol (2B)	7.49	0.048	0.72	231.2	9.42	0.62	0.3
Water (4C)	1.06	0.014	0.55	173.3	68.56	0.3	0.7
[emim][TfO]	64.15	0.163	0.06	-	-	0.03	-
[emim][TfO](2B)	34.45	0.155	0.01	755.6	0.15	0.03	-

Table 2: Binary interaction parameters for PRWS-NRTL EoS for binary mixtures.

	NRTL					
	k_{12}	α_{12}	τ_{12}	τ_{21}	ΔT(%)	Δy
Acetone + methanol	0.35	0.30	2.42	-1.38	0.014	0.05
Acetone+[emim][TfO]	0.52	0.09	-11.11	17.30	0.032	-
Methanol+[emim][TfO]	0.46	0.18	-1.83	2.17	0.014	-
Acetone+methanol+[emim][TfO]					0.205	-

**Table 3:** Binary interaction parameters for PRWS-UNIQUAC EoS for binary mixtures.

	UNIQUAC				
	k_{12}	u_{12} (K)	u_{21} (K)	ΔT (%)	Δy
Acetone + methanol	-0.311	617.0	40.18	0.012	0.06
Acetone+[emim][TfO]	0.671	-412.4	702.86	0.031	-
Methanol+[emim][TfO]	0.723	-452.1	920.09	0.061	-
Acetone+methanol+[emim][TfO]				0.756	-

for binary mixtures are also in excellent agreement with the experimental data. Table 4 shows that the CPA EoS offers a good prediction of experimental data with two or only one binary interaction parameters.

Table 4: Binary interaction parameters for CPA EoS for binary mixtures.

	k_{ij}	β_{ij}	ΔT (%)	Δy
Acetone(2B)+Methanol(2B)	0.07	-	0.11	0.01
Acetone+Methanol(2B)	0.11	1.2	0.06	0.40
Ethanol(2B)+Water(4C)	-0.01	-	0.13	0.93
[emim][TfO]+Acetone	-0.02	-	0.17	-
[emim][TfO] (2B)+Acetone(2B)	0.01	-	0.12	-
[emim][TfO]+Methanol(2B)	-0.06	1.3	0.05	-
[emim][TfO] (2B)+Methanol(2B)	-0.15	-	0.17	-
[emim][TfO] (2B)+Ethanol(2B)	-0.03	-	0.04	-
[emim][TfO] (2B)+Water(4C)	-0.77	-	0.29	-
[emim][TfO]+Ethanol(2B)	-0.09	-	0.13	-
[emim][TfO]+Water(4C)	-0.93	-	1.02	-

For the EOS CPA, we tested different association schemes as observed in Table 4 in order to describe the behavior of binary mixtures. We verified that there is no significant difference between the strategies (See Figures 4 and 5).
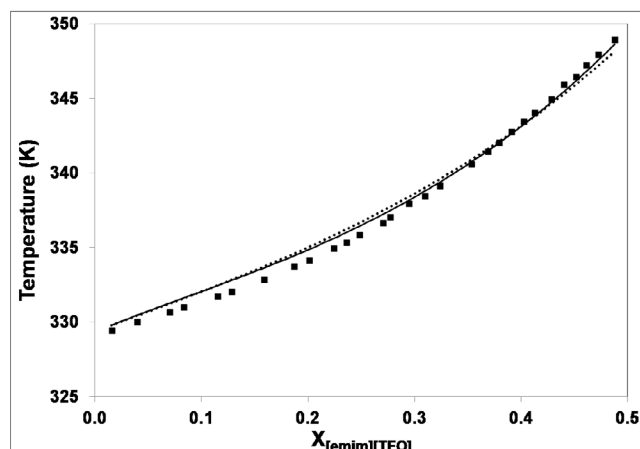

Figure 4: Different association schemes: [emim][TfO] (2B) + Acetone(2B) (solid line) and [emim][TfO] + Acetone CPA EoS (dashed line). Experimental data (■) (Orchillés *et al.*, 2007).
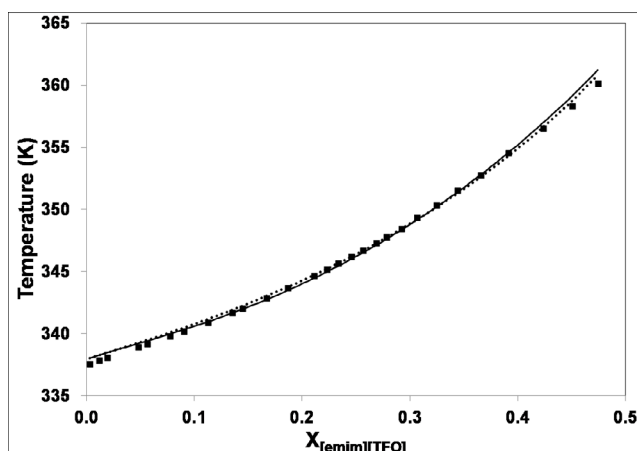
Figure 5: Different association schemes: [emim][TfO] (2B) + Methanol (2B) (solid line) and [emim][TfO] + Methanol(2B) CPA EoS (dashed line). Experimental data (■) (Orchillés *et al.*, 2007).

Using the estimated binary parameters, the behavior of the ternary mixture [emim][TfO] + acetone + methanol was predicted varying the mole fraction of the IL. The results in Figures 6 and 7 and Table 5 show an inaccurate description of this mixture's vapor fraction with the PRWS-NRTL and PRWS-UNIQUAC EOSs, especially for larger mole fractions of [emim][TfO]. At low compositions, the PRWS-NRTL EoS provides a better prediction compared with the PRWS-UNIQUAC EoS. However, the PRWS-NRTL EoS poorly describes the ternary mixture with IL mole fractions equal to 0.250 and 0.360. We observe clearly the formation of a double azeotrope, which is not in agreement with experimental data. There is no prediction of a double azeotrope with the PRWS-UNIQUAC EoS, but the overall description of experimental data is very poor.
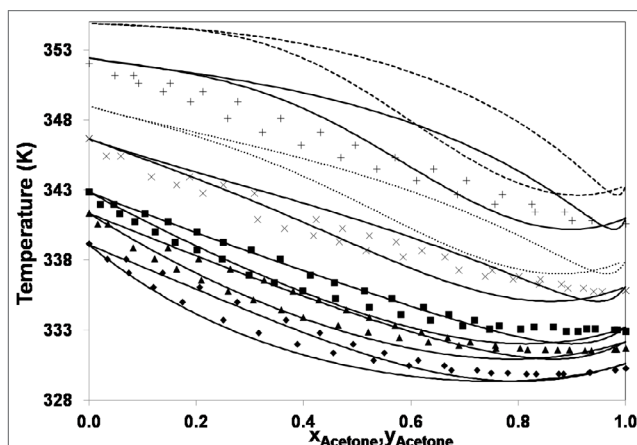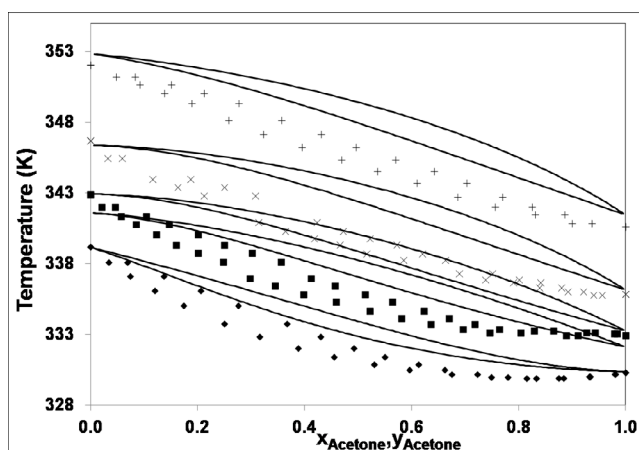

Figure 6: VLE for Acetone + Methanol + [emim][TfO]. Experimental data (Orchillés *et al.*, 2007) for $X_{[emim][TfO]}$: (♦) 0.055; (▲) 0.125; (■) 0.165; (x) 0.250 and (+) 0.360. PRWS-NRTL EoS for $X_{[emim][TfO]}$: 0.30 (dotted line); 0.40 (dashed line); all the other compositions (solid line).

Table 5: Deviation for the ternary mixture Acetone +Methanol + [emim][TfO] for different IL mole fractions.

$X_{[emim][TfO]}$	0.055		0.125		0.165		0.250		0.360	
	ΔT (%)	Δy	ΔT (%)	Δy	ΔT (%)	Δy	ΔT (%)	Δy	ΔT (%)	Δy
UNIQUAC	0.38	0.03	0.88	0.03	0.81	0.03	0.73	0.02	0.70	0.02
NRTL	0.14	0.01	0.12	0.03	0.14	0.03	0.24	0.04	0.42	0.06
CPA (2B)	0.17	0.01	0.17	0.01	0.22	0.01	0.29	0.01	0.30	0.01
CPA (no self association)	0.10	0.01	0.11	0.02	0.09	0.01	0.11	0.01	0.09	0.01

Figure 7: VLE Acetone + Methanol + [emim][TfO]. Experimental data (Orchillés *et al.*, 2007) for $X_{[emim][TfO]}$: (♦) 0.055; (▲) 0.125; (■) 0.165; (x) 0.250 and (+) 0.360. PRWS-UNIQUAC EoS (solid line).
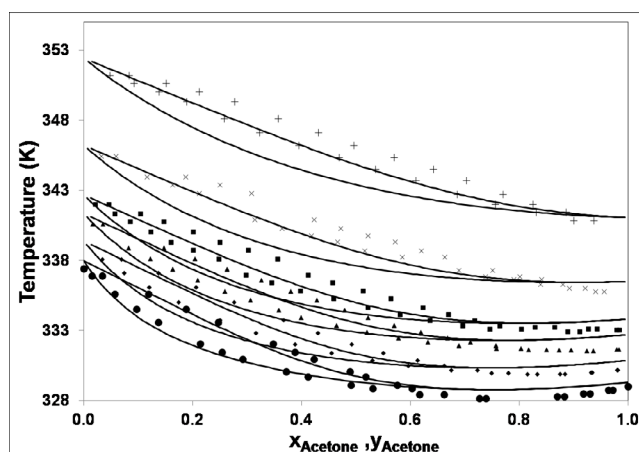
Figure 8: Acetone (2B) + Methanol(2B) + [emim][TfO](2B). VLE Experimental data (Orchillés *et al.*, 2007) for $X_{[emim][TfO]}$: (●) 0.0; (♦) 0.055; (■) 0.165; (x) 0.250 and (+) 0.360. CPA EoS (solid line).
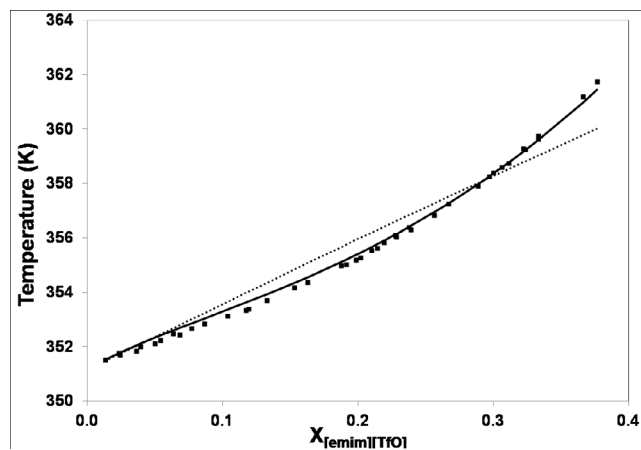
When the ternary mixture is predicted with the CPA EoS, we observe that there is a significant improvement compared with the other EOSs (see Table 5). In the prediction of the ternary mixture containing [emim][TfO], we consider acetone and methanol with the 2B association scheme and the CPA EoS qualitatively predicts the ternary phase behavior, as one can observe in Figure 8. However, this association scheme is not accurate for the data correlation of the mixture, especially for higher mole fractions of [emim][TfO].

We can see the improvement in the prediction of the behavior of the ternary mixture considering both acetone and the IL without self-association, as shown in Figure 9. Despite the satisfactory results, it is necessary to point out that the difference between association strategies may be related to the anomalous behavior of acetone, and the absence of terms in the CPA EoS that explicitly account for possible ion formation due to the presence of ILs.
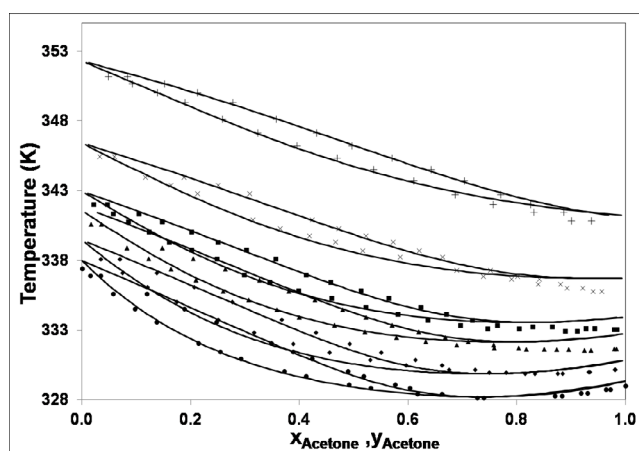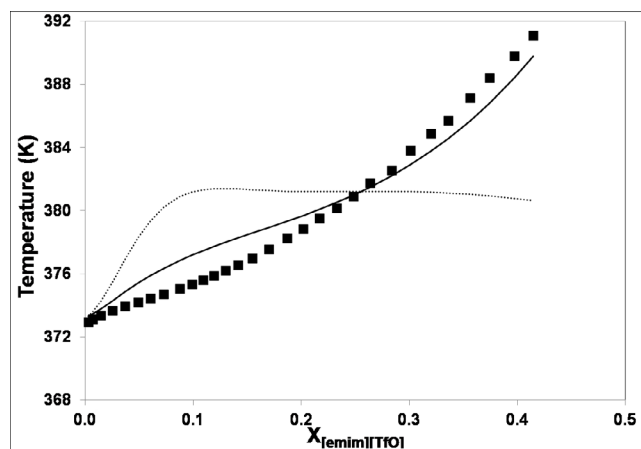

Figure 9: Acetone + Methanol (2B) + [emim][TfO]. VLE Experimental data (Orchillés *et al.*, 2007) for $X_{[emim][TfO]}$: (●) 0.0; (♦) 0.055; (■) 0.165; (x) 0.250 and (+) 0.360. CPA EoS (solid line).

Water + Ethanol+ [emim][TfO]

Table 4 shows that the CPA EoS gives a good prediction of VLE of binary mixtures when the ionic liquid is considered to be an associative component. When the ionic liquid is considered to be a non-associative component, the deviation is higher compared to experimental data. This behavior can be seen clearly in Figures 10 and 11.

Using the estimated binary parameters, the behavior of the ternary mixture [emim][TfO] + ethanol + water was predicted varying the mole fraction of the IL. The results in Figures 12 and 13 and in Table 6 show that the best association scheme for this mixture is the one that considers [emin][TfO] to be a 2B component, as expected due to the results from the binary mixture.
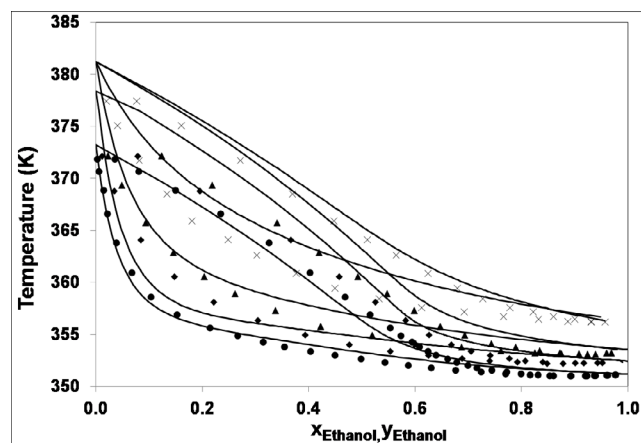

Figure 10: Different association strategies: [emim][TfO] (2B)+Ethanol(2B) (solid line) and [emim][TfO] + Ethanol. CPA EoS (dashed line). Experimental data (■) (Orchillés *et al.*, 2010).

Figure 12: Ethanol (2B) +Water (4C) + [emim][TfO]. VLE Experimental data (Orchillés *et al.*, 2010) for $X_{[emim][TfO]}$: (●) 0.0; (♦) 0.055; (■) 0.1 and (x) 0.215. CPA EoS (solid line).
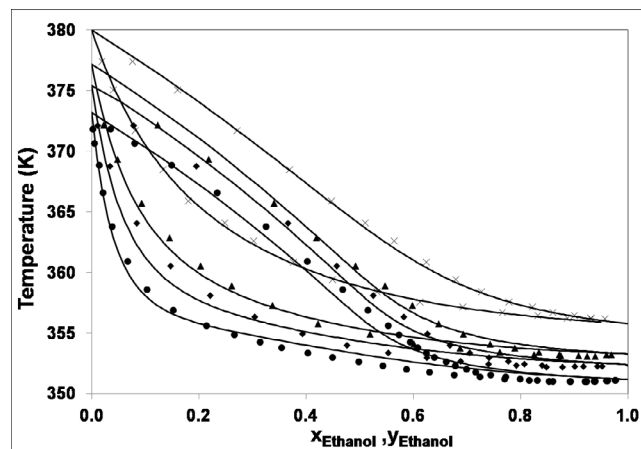

Figure 11: Different association schemes: [emim][TfO] (2B) + Water (4C) (solid line) and [emim][TfO] + Water(4C) CPA EoS (dashed line). Experimental data (■) (Orchillés *et al.*, 2010).

Figure 13: Ethanol (2B) +Water (4C) + [emim][TfO] (2B). VLE Experimental data (Orchillés *et al.*, 2010) for $X_{[emim][TfO]}$: (●) 0.0; (♦) 0.055; (■) 0.1 and (x) 0.215. CPA EoS (solid line).

Table 6: Deviation for the ternary mixture Ethanol + Water + [emim][TfO] for different IL mole fractions.

$x_{[emim][TfO]}$	0.055		0.1		0.215	
	ΔT	Δy	ΔT	Δy	ΔT	Δy
CPA (2B)	0.26	0.03	0.13	0.02	0.05	0.01
CPA (no self association)	0.31	0.04	0.31	0.04	0.63	0.06

When the ternary mixture is predicted considering [emin][TfO] as 2B, a significant improvement in the prediction is observed mainly for higher concentrations of the ionic liquid.

These results show an anomalous behavior of the ionic liquid [emim][TfO], as its association scheme varies according to the other components in the mixture.

CONCLUSIONS

This work shows that the CPA, PRWS-NRTL and PRWS-UNIQUAC EoSs are able to describe binary mixtures [emim][TfO] + Acetone, and [emim][TfO] + Methanol. However, the CPA EoS describes the mixture [emim][TfO] + Acetone better than the PRWS EoS. We observe better predictions of the ternary mixture phase behavior with the CPA EoS, especially for the association scheme in which acetone and [emim][TfO] are non-associative, and can form cross association with methanol. We also observe that results for the ternary mixture [emim][TfO] + Acetone + Methanol are sensitive to the association scheme. This can be attributed to the absence of terms in the CPA EoS that take into account electrostatic interactions, in addition to the anomalous behavior of acetone. The study of the mixture [emim][TfO] + Ethanol + Water with the EOS CPA for two association schemes for the ionic liquid showed that for this specific case the ionic liquid has a 2B association scheme. These results show that the better association scheme for [emim][TfO] depend on the nature of the components of the mixture.

ACKNOWLEDGEMENT

NOMENCLATURE

a_0	=	parameter in the energy term (a) (bar. $L^2.mol^{-2}$)
b	=	co-volume parameter (L/mol)
c_1	=	parameter in the energy term
k_{12}	=	binary interaction parameter
g	=	radial distribution function
N	=	number of components
P	=	pressure (bar)
R	=	gas constant (bar.L.mol^{-1}.K^{-1})
T	=	temperature (K)
T_r	=	reduced temperature
u_{12}	=	UNIQUAC energy interaction parameter (K)
$\overline{V}$	=	Molar volume (L/mol)
x	=	mole fraction in the liquid phase
X_{Ai}	=	mole fraction of the component not bonded at site A
y	=	mole fraction in the vapor phase

Greek Letters

α_{12}	=	NRTL dimensionless parameter
β^{AB}	=	association volume of the mixture (L)
Δ^{AB}	=	strength of interaction between sites A and B (L.mol^{-1})
ε^{AB}	=	energy of association (bar.L.mol^{-1})
ρ	=	molar density (mol/cm^3)
τ_{12}	=	NRTL energy interaction parameter

Superscripted/Subscripts

cal	=	calculated value
exp	=	experimental values
i, j	=	components
L	=	liquid
sat	=	saturated

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