

# GC-EoS extension to alkylphosphate imidazolium ionic liquids

Laura de Pablo Nisa<sup>1,3,5</sup>, Francisco A. Sánchez<sup>2</sup>, M.Dolores Bermejo<sup>1,5</sup>, Selva Pereda<sup>2,4</sup> \*

<sup>1</sup>High Pressure Process Group, Department of Chemical Engineering and Environmental Technology, University of Valladolid, Spain

<sup>2</sup> Planta Piloto de Ingeniería Química (PLAPIQUI), Chemical Engineering Department, Universidad Nacional del Sur (UNS) - CONICET, Camino La Carrindanga Km7, 8000B Bahía Blanca, Argentina

<sup>3</sup> Research Group TERMOCAL, Thermodynamics and Calibration, University of Valladolid, Escuela de Ingenierías Industriales, Paseo del Cauce 59, E-47011 Valladolid, Spain

<sup>4</sup> Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

<sup>5</sup> Institute of Bioeconomy (BioEcoUva), Universidad de Valladolid

\*Corresponding author. Email: spered@plapiqui.edu.ar

## Abstract

In this work, the Group Contribution Equation of State (GC-EoS) is extended to model two new ionic liquid families, namely, 1-alkyl-3-methylimidazolium dimethylphosphate ( $[-\text{MeIm}]^+[\text{Me}_2\text{PO}_4]^-$ ) and 1-alkyl-3-methylimidazolium diethylphosphate ( $[-\text{MeIm}]^+[\text{Et}_2\text{PO}_4]^-$ ). Pure group parameters for the functional groups  $[-\text{MeIm}]^+[\text{Me}_2\text{PO}_4]^-$  and  $[-\text{MeIm}]^+[\text{Et}_2\text{PO}_4]^-$  and interaction parameters between these groups and the main paraffinic and aromatic subgroups ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{ACH}$ ,  $\text{AC}$ ,  $\text{ACCH}_3$ ,  $\text{CH}_2=\text{CH}$ ) were estimated using infinite dilution activity coefficients data from literature. In order to evaluate the performance of the new parameters, the model was challenged against experimental data on phase behavior of binary mixtures, showing an average relative deviation of 4.5%.

**Keywords:** Ionic liquids, Group contribution, Equation of state, 1-alkyl-3-methylimidazolium dimethylphosphate, 1-alkyl-3-methylimidazolium diethylphosphate, GC-EoS

# 1 Introduction

In recent years, the interest in new and “green” solvents has increased, and ionic liquids are now considered to be a promising alternative to conventional solvents. By definition, Ionic Liquids are substances composed entirely of ions that are liquid at room temperature. Some of their properties make them sustainable solvents, for example, their low vapor pressure and high thermal and chemical stability, which avoids the occurrence of contamination through evaporation, and allows a high recycling ratio to be reached, respectively. Some of them are also able to dissolve biopolymers, for instance, the alkylphosphate, chloride and acetate ionic liquids all have good cellulose dissolving properties. Specifically, the ionic liquids belonging to the 1-alkyl-3-methylimidazolium dimethylphosphate  $[-\text{MeIm}]^+ [\text{Me}_2\text{PO}_4]^-$  and 1-alkyl-3-methylimidazolium diethylphosphate  $[-\text{MeIm}]^+ [\text{Et}_2\text{PO}_4]^-$  families show other favorable properties, such as low viscosity, and are also halogen free [1] cellulose processing solvents. [2] Besides, 1-ethyl-3-methylimidazolium diethylphosphate  $([\text{EtMeIm}]^+ [\text{Et}_2\text{PO}_4]^-)$  has a low melting point, which makes it very easy to handle. [2]

Phase equilibrium knowledge is required for the design and optimization of cellulose processing units. It is worth noting that there are a great deal of possible combinations of anion, cation and alkyl chain substituents that set the ionic liquid behavior, and the experimental determination of all the possible combinations is an impossible task in terms of time and costs. The Group Contribution Equation of State (GC-EoS) [3] is able to correlate the experimental data of mixtures by adjusting a set of parameters related to the functional groups present in the mixture. Using this equation, it is only necessary to correlate the data of a few ionic liquids, and it is possible to predict the behavior of the other members of a given family. It has proved to be an appropriate method to describe the phase equilibrium of several ionic liquids in mixtures with different solvents, [4–12] not only for data interpolation, but also as a reliable tool for predicting phase equilibria beyond the measured conditions. [13,14]

In this work, the GC-EoS is extended to new groups in order to describe the phase behavior of the 1-alkyl-3-methylimidazolium dimethylphosphate  $[-\text{MeIm}]^+ [\text{Me}_2\text{PO}_4]^-$  and 1-alkyl-3-methylimidazolium diethylphosphate  $[-\text{MeIm}]^+ [\text{Et}_2\text{PO}_4]^-$  families. The binary interaction parameters with  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{ACH}$ ,  $\text{AC}$ ,  $\text{ACCH}_3$  and  $\text{CH}_2=\text{CH}$  were fitted to equilibrium experimental data of binary systems found in literature, comprising infinite dilution activity coefficients of hydrocarbons in the ionic liquids under study. The extended GC-EoS is then used to predict experimental data not included in the correlation database.

## 2 Thermodynamic modeling

### 2.1 The Group Contribution Equation of State

The GC-EoS was originally developed by Skjold-Jørgensen[3,15]to model gas solubility in conventional organic solvents. This model is based on the Van der Waals EoS combined with the local composition principle. It can be written as the sum of two contributions to the residual Helmholtz free energy ( $A^{res}$ ): the repulsive ( $rep$ ) (also called *free volume*) and the attractive ( $att$ ) contributions, as it is shown in Equation (1).

$$A^{res} = A^{rep} + A^{att} \quad (1)$$

The repulsive term is represented by the extended Carnahan-Starling equation developed by Mansoori and Leland[16] for hard spheres, as described in equation (2):

$$\left(\frac{A}{RT}\right)_{rep} = 3 \left(\frac{\lambda_1 \lambda_2}{\lambda_3}\right) (Y - 1) + \left(\frac{\lambda_2^3}{\lambda_3^2}\right) (-Y + Y^2 - \ln Y) + n \ln Y \quad (2)$$

where,

$$\lambda_k = \sum_i^{NC} n_i d_i^k \quad (k = 1, 2, 3) \quad (3)$$

$$Y = \left(1 - \frac{\pi \lambda_3}{6V}\right)^{-1} \quad (4)$$

in which  $n_i$  represents the number of moles of component  $i$ ,  $V$  the total volume,  $NC$  the total number of components in the mixture, and  $d_i$  the hard-sphere diameter per mole.

The hard-sphere diameter ( $d_i$ ) is considered to be temperature dependent in equation (5):

$$d_i = 1.065655 d_{ci} \left[1 - 0.12 \exp\left(-\frac{2T_{ci}}{3T}\right)\right] \quad (5)$$

where  $d_{ci}$  is the value of the hard-sphere diameter at the critical temperature  $T_{ci}$  for the pure component  $i$ .

On the other hand, the attractive contribution of the residual Helmholtz free energy is a group contribution version of the NRTL model. [17] In this contribution the interactions are assumed to take place through the group surfaces. See equation (6).

$$\left(\frac{A}{RT}\right)_{att} = -\left(\frac{z}{2}\right) \sum_{i=1}^{N_C} n_i \sum_{j=1}^{N_G} v_j^i q_j \frac{\sum_{k=1}^{N_G} \theta_k \left(\frac{g_{kj} \tilde{q} \tau_{kj}}{RTV}\right)}{\sum_{l=1}^{N_G} \theta_l \tau_{lj}} \quad (6)$$

where:

$$\tilde{q} = \sum_{i=1}^{N_C} \sum_{j=1}^{N_G} n_i v_{ij} q_j \quad (7)$$

$$\theta_j = \frac{1}{\tilde{q}} \sum_{i=1}^{N_C} n_i v_{ij} q_j \quad (8)$$

with:

$$\tau_{kj} = \exp\left(\frac{\alpha_{kj} \Delta g_{kj} \tilde{q}}{RTV}\right) \quad (9)$$

and:

$$\Delta g_{kj} = g_{kj} - g_{jj} \quad (10)$$

In equations (6) to (8),  $z$  is the coordination number set equal to 10;  $N_G$  is the number of groups,  $v_j^i$  is the number of groups  $j$  in component  $i$ ;  $q_j$  is the number of surface segments assigned to group  $j$ ;  $\theta_k$  is the surface fraction of group  $k$ ;  $q$  is the total number of surface segments;  $g_{ij}$  and  $\alpha_{ij}$  are the attractive energy and the non-randomness parameters for interactions between segments  $j$  and  $i$ , respectively.

The interactions between unlike segments are defined by equation (11):

$$g_{ji} = k_{ij} \sqrt{g_{ii} g_{jj}} \quad (11)$$

where the symmetrical parameter  $k_{ij}$  ( $k_{ij} = k_{ji}$ ) is the binary interaction parameter. Both the attractive energy ( $g_{ij}$ ) and the binary interaction parameter ( $k_{ij}$ ) are temperature dependent, as described in (12) and (13), respectively:

$$g_{ii} = g_{ii}^* \left[ 1 + g'_{ii} \left( \frac{T}{T_i^*} - 1 \right) + g''_{ii} \ln \left( \frac{T}{T_i^*} \right) \right] \quad (12)$$

$$k_{ij} = k_{ij}^* \left[ 1 + k'_{ij} \ln \left( \frac{2T}{T_i^* + T_j^*} \right) \right] \quad (13)$$

Where  $g_{ii}^*$  and  $k_{ij}^*$  are the attractive energy and binary interaction parameters at the reference temperatures  $T_i^*$  and  $(T_i^* + T_j^*)/2$ , respectively.

## 2.2 Ionic Liquid functional group

To apply the GC-EoS it is necessary to divide the ionic liquid molecule into functional groups. Breure et al. [4] showed that the anion and part of the cation, except for its alkyl chain, should be kept together in a single electroneutral group. Therefore, by adding the CH<sub>2</sub>, CH<sub>3</sub> or other functional groups to the side alkyl chain, any ionic liquid of the same family can be assembled. The characteristic groups defined in this work, [-MeIm]<sup>+</sup>[Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> and [-MeIm]<sup>+</sup>[Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>, are shown in Figure 1.

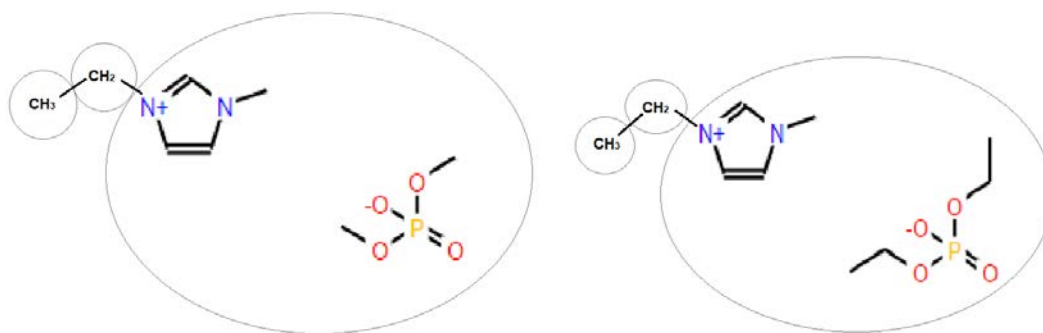


Figure 1. Group definition for [-MeIm]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> (left) and for [-MeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> (right).

## 2.3 Parametrization of the repulsive term

The repulsive term comprises one unique characteristic parameter, which is the hard-sphere diameter at critical temperature ( $d_{ci}$ ). Usually this parameter is derived from the pure component critical properties, or by fitting a vapor pressure data point. [3] However, none of this data is available for the ionic liquids. In this work,  $d_{ci}$  was calculated using the correlation developed by Espinosa et al. [18] for high molecular weight natural compounds,

and applied later to ionic liquids by Breure et al. [4] and Bermejo et al. [5] As shown in Equation (14), this correlation estimates  $d_{ci}$  based on the normalized Van der Waals molecular volume of the compound ( $r_{vdW}$ ), which is easy information to calculate in the case of normal organic compounds, but it is not available for the ionic liquids, which require a number of assumptions to be made in order to attain a representative value. Later, Pereda et al. [9] showed that the  $r_{vdW}$  can be estimated by a simple linear relation with respect to the molar volume of the ionic liquid at 298K ( $v_{298K}$ ).

$$\log(d_{ci}) = 0.4152 + 0.4128 \log(r_{vdW}) \quad (14)$$

$$r_{vdW} = 0.039 \cdot v_{298K} (\text{cm}^3 \text{mol}^{-1}) \quad (15)$$

Table 1 summarizes the van der Waals volume and critical diameters for the ionic liquids studied in this work.

Table 1. Molecular weight ( $M_w$ ), molar volume ( $v$ ) at 298 K, van der Waals volume ( $r_{vdW}$ ), and critical diameter ( $d_c$ ) for the ionic liquids.

Ionic Liquid	$M_w / \text{g} \cdot \text{mol}^{-1}$	$v / \text{cm}^3 \cdot \text{mol}^{-1}$	Source	$r_{vdW}$	$d_c / \text{cm} \cdot \text{mol}^{-1/3}$
[EtMeIm] <sup>+</sup> [Et <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	264.26	230.57	[19]	8.992	6.4432
[EtMeIm] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	194.17	194.10	[20]	7.570	6.0000
[BuMeIm] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	264.26	227.43	[21]	8.870	6.4033
[Me <sub>2</sub> Im] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	222.18	176.57	[22]	6.886	5.7671

## 2.4 Parametrization of the attractive term

The pure group parameters for the CH<sub>3</sub>, CH<sub>2</sub>, ACH, AC, ACCH<sub>3</sub> and CH<sub>2</sub>=CH groups, and their respective binary interaction parameters, can be found elsewhere. [23]

The surface area  $q_i$  for the new groups, [-MeIm]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> and [-MeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>, were calculated by subtracting the surface area parameter of the alkyl chain substituents ( $q_{\text{CH}_3}$  and  $q_{\text{CH}_2}$ ) from the total van der Waals area of the ionic liquid molecules ( $Q_i$ ), which can be derived from their van der Waals volume ( $r_{vdW}$ ) using equation (16). [9]

$$Q_i = \frac{z-2}{z} r_{vdW,i} + \frac{z}{2} \quad (16)$$

where  $z$  is the coordination number. The pure group parameters of  $[-\text{MeIm}]^+ [\text{Me}_2\text{PO}_4]^-$  and  $[-\text{MeIm}]^+ [\text{Et}_2\text{PO}_4]^-$  and the binary interaction parameter involving the aforementioned groups were fitted by correlating the infinite dilution activity coefficient.

Table 2 summarizes the experimental database of the binary systems used for correlating the model parameters, and to challenge its predictive capacity. The tables also report the range of temperature covered by the data (in all cases at atmospheric pressure), and the source of the experimental data. In the case of activity coefficient data, authors report a typical uncertainty value of 5% in all cases.

Table 2. Infinite dilution activity coefficient database. Data uncertainty reported in all cases is 5%.

Compound		$T$ (K)	$P$ (bar)	No exp. points	ARD% ( $\gamma$ )	Source
Ionic liquid	Solute					
$[\text{EtMeIm}]^+ [\text{Et}_2\text{PO}_4]^-$	Pentane*	303.15 - 343.15	1.01	5	12	[24]
	Hexane	303.15 - 343.15	1.01	5	5.0	[24]
	Heptane*	303.15 - 343.15	1.01	5	12	[24]
	Octane	303.15 - 343.15	1.01	5	8.2	[24]
	Nonane*	303.15 - 343.15	1.01	5	3.0	[24]
	Decane*	303.15 - 343.15	1.01	5	7.9	[24]
	Styrene*	303.15 - 343.15	1.01	5	0.22	[24]
	Benzene*	303.15 - 343.15	1.01	5	0.23	[24]
	Toluene	303.15 - 343.15	1.01	5	7.5	[24]
	o-Xilene*	303.15 - 343.15	1.01	5	7.5	[24]
	m-Xilene*	303.15 - 343.15	1.01	5	2.8	[24]
	p-Xilene*	303.15 - 343.15	1.01	5	7.9	[24]
$[\text{Me}_2\text{Im}]^+ [\text{Me}_2\text{PO}_4]^-$	Pentane*	313.15 - 363.15	1.01	6	3.1	[25]
	Hexane	313.15 - 363.15	1.01	6	1.1	[25]
	Heptane	313.15 - 363.15	1.01	6	3.1	[25]
	Octane	313.15 - 363.15	1.01	6	5.0	[25]
	Nonane	313.15 - 363.15	1.01	6	3.4	[25]
	Decane*	313.15 - 363.15	1.01	6	5.2	[25]
	Styrene*	313.15 - 363.15	1.01	6	0.72	[25]
	Benzene*	313.15 - 363.15	1.01	6	3.3	[25]
	Toluene	313.15 - 363.15	1.01	6	7.0	[25]
	o-Xilene*	313.15 - 363.15	1.01	6	1.2	[25]
	m-Xilene*	313.15 - 363.15	1.01	6	2.9	[25]
	p-Xilene*	313.15 - 363.15	1.01	6	5.2	[25]
$[\text{EtMeIm}]^+ [\text{Me}_2\text{PO}_4]^-$	Benzene*	313.15 - 363.15	1.01	6	3.5	[25]
	Toluene	313.15 - 363.15	1.01	6	2.2	[25]
	Styrene*	313.15 - 363.15	1.01	6	2.0	[25]

	o-Xilene*	313.15 - 363.15	1.01	6	0.80	[25]
	m-Xilene*	313.15 - 363.15	1.01	6	4.2	[25]
	p-Xilene*	313.15 - 363.15	1.01	6	4.0	[25]
[BuMeIm] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	Octane*	313.15 - 363.15	1.01	6	8.8	[26]
	Nonane	313.15 - 363.15	1.01	6	4.4	[26]
	Decane*	313.15 - 363.15	1.01	6	8.9	[26]
	Ethylbenzene*	313.15 - 363.15	1.01	6	2.7	[26]

\* Data used for the correlation, ARD%: average relative deviation between GCA-EoS and experimental data

### 3 Results and discussion

The first parameters fitted were those required to describe the ionic liquids properties, i.e. the pure group energy parameters ( $g_{ii}^*$ ,  $g'_{ii}$ ,  $g''_{ii}$ ) of the ionic core and the interaction parameters with groups forming the alkyl chain (CH<sub>2</sub> and CH<sub>3</sub>), and therefore, only binary data with *n*-alkanes was initially considered. In particular, the correlation of these parameters is based on the experimental infinite dilution activity coefficients of *n*-alkanes in the ionic liquids studied here. On the other hand, the parameter *q* was not fitted, since it was estimated from molar volume in literature using the method described in section 2.4. The data sets used in the correlation were selected in order to fit the widest temperature range possible. The rest of the data sets were used in order to challenge the predictive capacity of the GC-EoS with the new parameters.

Table 3 reports the parameters of the new GC-EoS ionic liquid groups, together with the alkyl and aromatic groups. As can be seen in Table 3, only the pure group parameters of the ionic liquids are fitted in this work, while the parameters of all other groups were taken from literature.[23] In addition, table 4 reports all the binary interaction parameters used in this work, likewise the pure group parameters, in the case of binary parameters only those involving the new ionic liquid groups were fitted. This new set of parameters is able to correlate and predict all the assessed experimental data with the accuracy indicated in Table 2. Table 5 shows the critical temperature and pressure of the ionic liquids used for the correlation.



Table 3. GC-EoS pure group parameters.  $T_i^*$  is the reference temperature,  $q_i$  is the surface area of  $i$  and  $g^*$ ,  $g'$ , and  $g''$  are the pure group energy parameters and their temperature dependence (see equation 12).

Group	$T^* / \text{K}$	$q$	$g^* / \text{atm}\cdot\text{cm}^6\cdot\text{mol}^{-2}$	$g'$	$g''$	Source
-MeImMe <sub>2</sub> PO <sub>4</sub>	600	4.8513	1154081	-0.2941	0	This work
-MeImEt <sub>2</sub> PO <sub>4</sub>	600	6.0116	1170489	-0.1153	0	This work
CH <sub>3</sub>	600	0.848	316910	-0.9274	0	[23]
CH <sub>2</sub>	600	0.540	356080	-0.8755	0	[23]
ACH	600	0.400	723210	-0.606	0	[23]
AC	600	0.285	723210	-0.606	0	[23]
ACCH <sub>3</sub>	600	0.968	506290	-0.8013	0	[23]
CH <sub>2</sub> =CH	600	1.176	337980	-0.6764	0	[23]

Table 4. GC-EoS binary interaction parameters correlated in this work.

Group $i$	Group $j$	$k_{ij}^*$	$k_{ij}'$	$\alpha_{ij}$	$\alpha_{ji}$	Source
-MeImMe <sub>2</sub> PO <sub>4</sub>	CH <sub>3</sub>	1.0169	-0.0477	-1.868	-3.1969	This work
	CH <sub>2</sub>	1.0169	-0.0477	-2.3677	-1.1145	This work
	ACH	0.9144	0.0939	0	0	This work
	AC	0.9822	-0.0761	4.0314	-12.0482	This work
	ACCH <sub>3</sub>	0.8826	0.0618	12.8818	-0.767	This work
	CH <sub>2</sub> =CH-	1.0076	0.0894	-2.0427	-1.6513	This work
-MeImEt <sub>2</sub> PO <sub>4</sub>	CH <sub>3</sub>	0.999	-0.0084	8.7504	-1.8958	This work
	CH <sub>2</sub>	0.999	-0.0084	1.3137	-1.0597	This work
	ACH	0.9677	0.0614	0	0	This work
	ACCH <sub>3</sub>	0.9822	0.0563	1.5544	-0.8988	This work
CH <sub>3</sub>	CH <sub>2</sub>	1	0	0	0	[23]
	ACH	1.041	0.094	0.391	0.391	[23]
	AC	1.041	0.094	0.391	0.391	[23]
	ACCH <sub>3</sub>	0.975	0	0	0	[23]
	CH <sub>2</sub> =CH-	1	0	0	0	[23]
CH <sub>2</sub>	ACH	1.041	0.094	0.391	0.391	[23]
	AC	1.041	0.094	0.391	0.391	[23]
	ACCH <sub>3</sub>	0.975	0	0	0	[23]
	CH <sub>2</sub> =CH-	1	0	0	0	[23]
ACH	AC	1	0	0	0	[23]

	ACCH <sub>3</sub>	1.007	0	0	0	[23]
	CH <sub>2</sub> =CH-	0.984	0	0	0	[23]
AC	ACCH <sub>3</sub>	1.007	0	0	0	[23]
	CH <sub>2</sub> =CH-	0.984	0	0	0	[23]
ACCH <sub>3</sub>	CH <sub>2</sub> =CH-	1.034	0	0	0	[23]

Table 5. GC-EoS pure compounds parameters.  $T_c$  and  $P_c$  are the critical temperature and pressure, respectively.

Compound	$T_c$ / K	$P_c$ / bar	Source
[EtMeIm] <sup>+</sup> [Et <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	789.0	27.8	[27]
[Me <sub>2</sub> Im] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	869.4	20.3	[27]
[EtMeIm] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	748.6	34.7	[27]
[BuMeIm] <sup>+</sup> [Me <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	951.5	10.1	[27]

Normal hydrocarbons from pentane to decane were correlated first, since alkyl groups (CH<sub>3</sub> and CH<sub>2</sub>) are also part of the pure ionic liquid molecule. Figures 2 and 3 show GC-EoS correlation (dashed lines) and predictions (solid lines) of n-alkanes in [EtMeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> and [BuMeIm]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>, respectively. As can be seen, in both cases, a good accuracy is attained between the experimental data and GC-EoS.

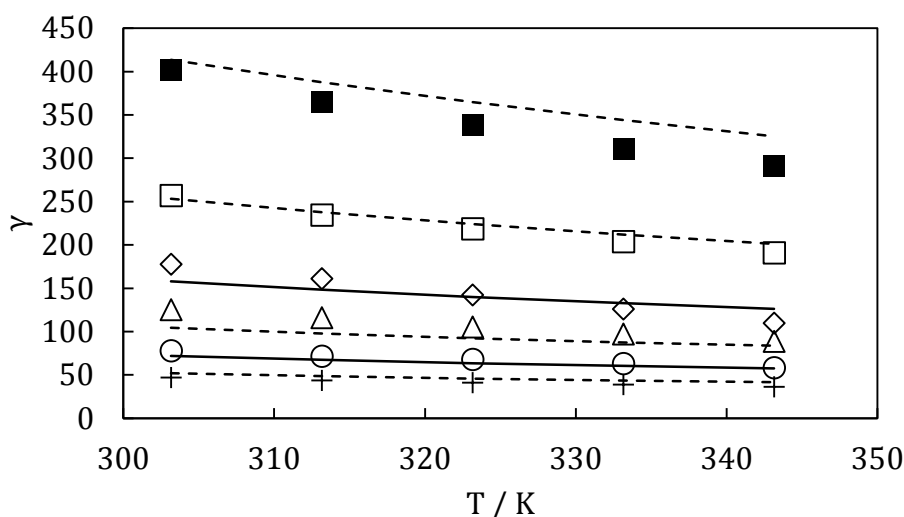


Figure 2. Activity coefficients at infinite dilution ( $\gamma$ ) in [EtMeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> as a function of the temperature ( $T$ ) of different hydrocarbons: Decane (■); Nonane (□); Octane (◇); Heptane (△); Hexane (○) and Pentane (+). Dashed lines represent the correlation and solid lines represent the prediction using GC-EoS.

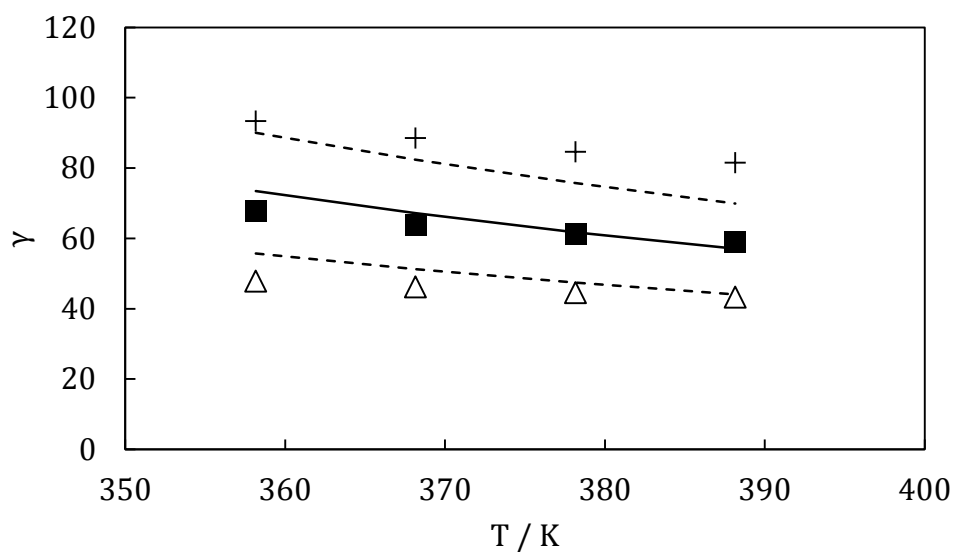


Figure 3. Activity coefficients at infinite dilution ( $\gamma$ ) in  $[\text{BuMeIm}]^+ [\text{Me}_2\text{PO}_4]^-$  as a function of the temperature ( $T$ ) of different hydrocarbons: Decane (+); Nonane (■), and Octane ( $\Delta$ ). Dashed lines represent the correlation and solid lines represent the prediction using GC-EoS.

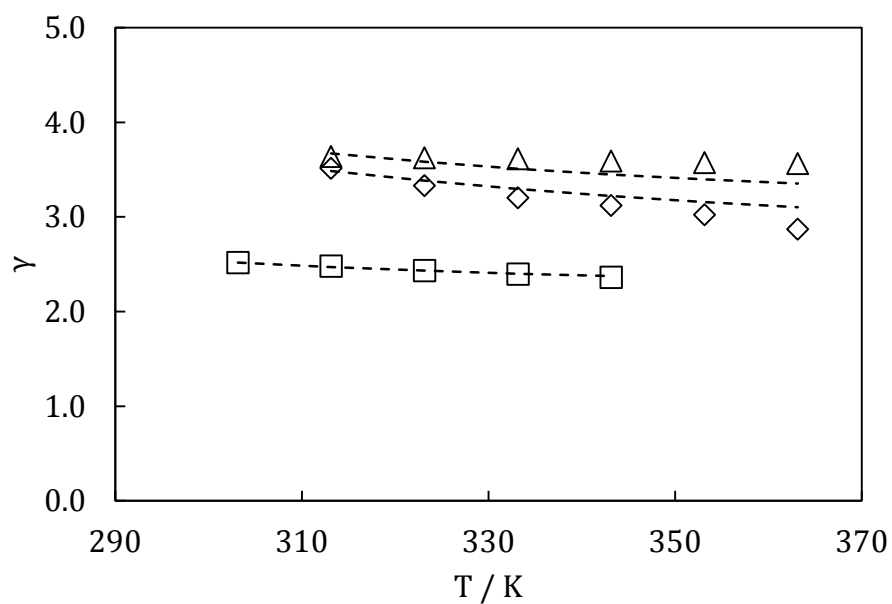


Figure 4. Infinite dilution activity coefficients ( $\gamma$ ) of benzene in:  $[\text{EtMeIm}]^+ [\text{Et}_2\text{PO}_4]^-$  ( $\square$ );  $[\text{Me}_2\text{Im}]^+ [\text{Me}_2\text{PO}_4]^-$  ( $\Delta$ ); and  $[\text{EtMeIm}]^+ [\text{MePO}_4]^-$  ( $\diamond$ ). Dashed lines: GC-EoS correlation.

In a second stage, aromatic compounds were considered. Therefore, the binary interaction parameters of the ACH groups were fitted with experimental data available for the infinite dilution activity coefficients of benzene in ionic liquid, and the results are shown in Figure 4. Moreover, data on xylene derivatives allows the parameters for the ACCH<sub>3</sub> group to be also correlated. The GC-EoS correlation of experimental data is represented in Figure 5 and Figure 6.

In the case of benzene (Figure 4), according to our knowledge, there is no more data available to check the predictive capacity of the model. The model correlates the binary data of benzene in [EtMeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> with high precision, however it is less accurate in the case of benzene in [Me<sub>2</sub>Im]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> and [EtMeIm]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>. In these cases, it is worth noting that the ionic liquids share the same group, -MeImMe<sub>2</sub>PO<sub>4</sub>. In consequence, the result is a compromise between both data sets. Regarding the behavior of xylenes in imidazolium phosphate ionic liquids, Figure 5 and 6 show experimental data and GCA-EoS correlation of the three isomers (m- p- and o-xylene) with [Me<sub>2</sub>Im]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> and [EtMeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>, respectively. In both cases, the GCA-EoS reproduces the temperature dependence of the experimental data correctly, showing almost the same activity coefficients for m- and p-xylenes, while slightly lower values for o-xylene. Since the three hydrocarbons are defined by the same groups, the pure component normal boiling points control the outcome of the model. It should be noted that, p- and m-xylene depict almost the same normal boiling point (411 K and 412 K, respectively), while that of o-xylene is 417 K. Those values of normal boiling points make that GCA-EoS activity coefficients are higher for p-xylene and lower for o-xylene. In contrast, the experimental data show higher values for m-xylene in both ionic liquids.

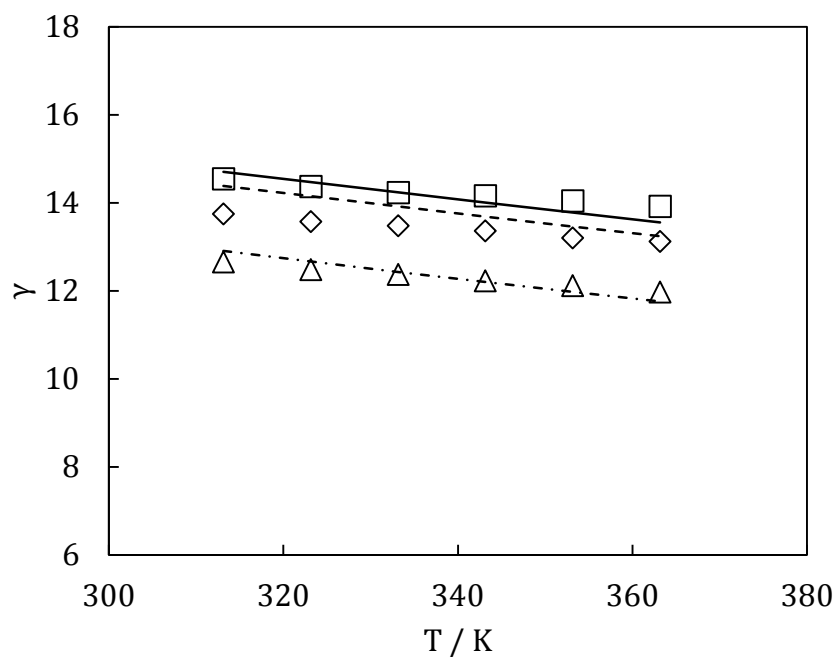


Figure 5. Activity coefficients at infinite dilution ( $\gamma$ ) in  $[\text{Me}_2\text{Im}]^+ [\text{Me}_2\text{PO}_4]^-$  of: o-Xylene ( $\Delta$  and dotted-dashed line); m-Xylene ( $\square$  and dashed line); and p-Xylene ( $\diamond$ , and solid line). Lines: GC-EoS correlation.

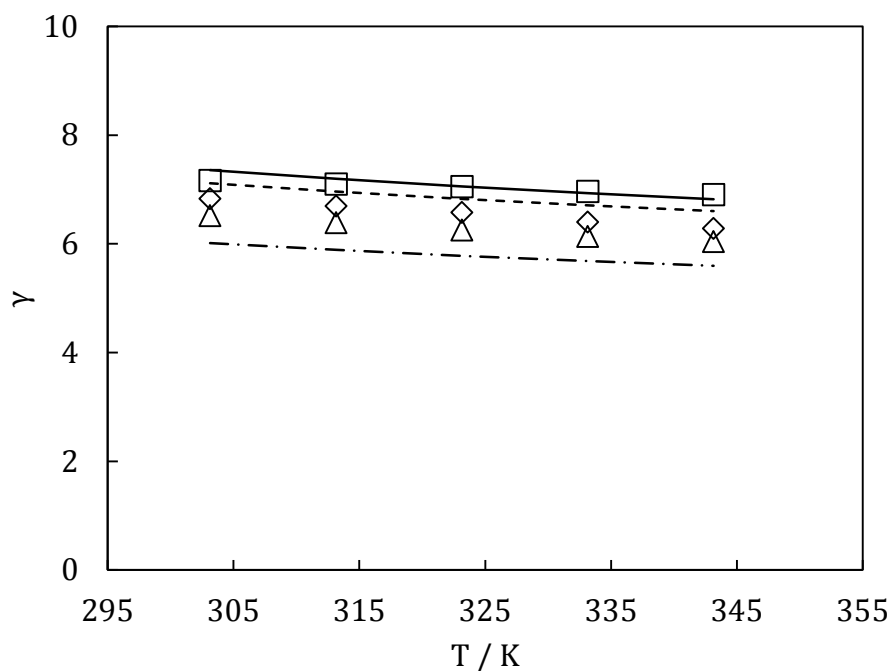


Figure 6. Activity coefficients at infinite dilution ( $\gamma$ ) in  $[\text{EtMeIm}]^+ [\text{Et}_2\text{PO}_4]^-$  of: o-Xylene ( $\Delta$  and dotted-dashed line); m-Xylene ( $\square$  and dashed line); and p-Xylene ( $\diamond$  and solid line). Lines: GC-EoS correlation.

The GC-EoS predictive capacity with the new parameters were also checked against experimental data on infinite dilution activity coefficients of toluene in ionic liquids, as shown in Figure 7. The agreement between the model and the experimental data is also good in this case. In this work, styrene behavior with phosphate derived ionic liquids was also modeled (see Figure 8), which allows the binary parameters of the olefinic group to be fitted with the new ionic liquid groups.

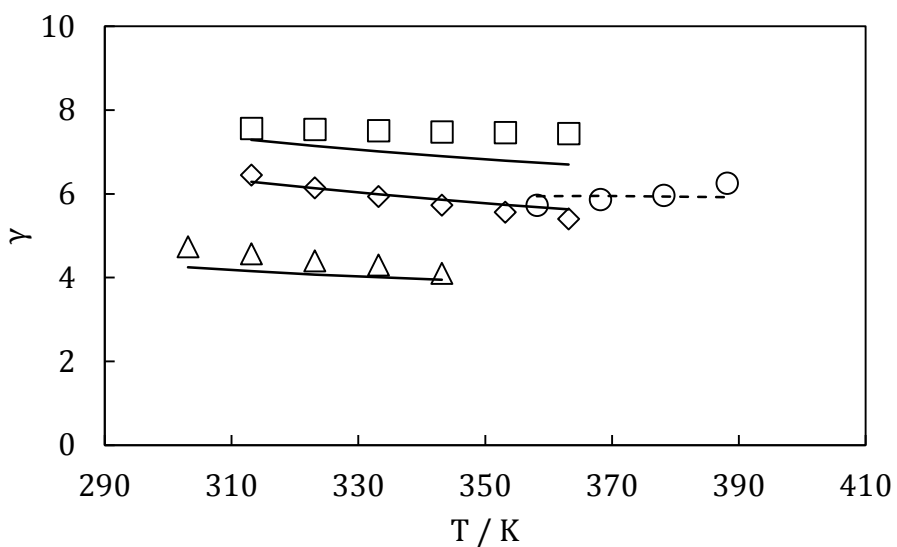


Figure 7. Activity coefficients at infinite dilution ( $\gamma$ ) of toluene in: (□) [Me<sub>2</sub>Im]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>; (◇) [EtMeIm]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>; (△) [EtMeIm]<sup>+</sup> [Et<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>; (○) Ethylbenzene in [BuMeIm]<sup>+</sup> [Me<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>. Solid lines: GC-EoS predictions. Dashed lines: GCA-EoS correlation.

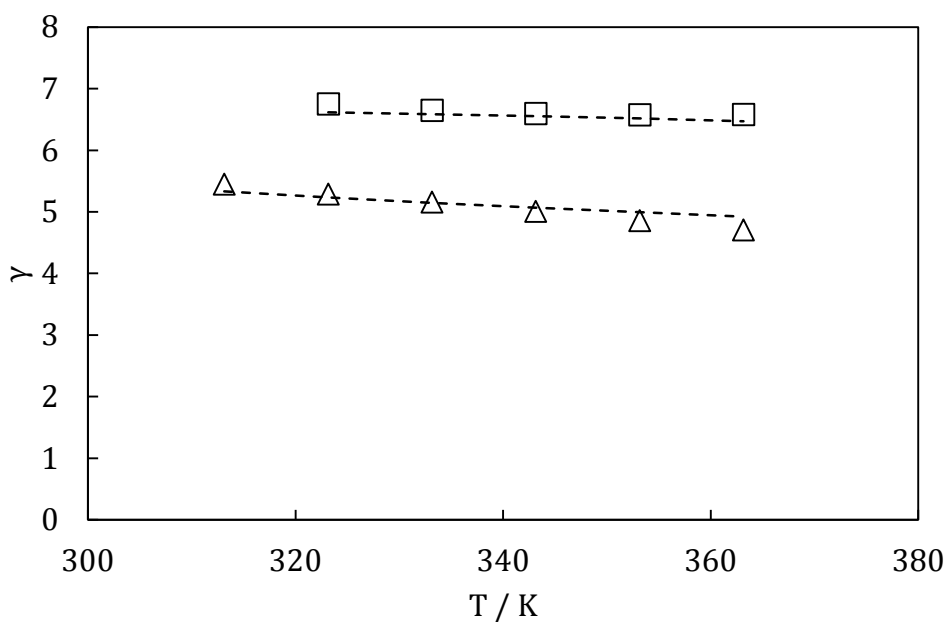


Figure 8. Activity coefficients at infinite dilution ( $\gamma$ ) of: (□), Styrene in  $[\text{Me}_2\text{Im}]^+ [\text{Me}_2\text{PO}_4]^-$ ; (△), Styrene in  $[\text{EtMeIm}]^+ [\text{Me}_2\text{PO}_4]^-$ . Dashed lines: GCA-EoS correlation.

## 4 Conclusions

In this work, the GC-EoS table of parameters was extended to model two families of ionic liquids, namely, 1-alkyl-3-methylimidazolium dimethylphosphate and 1-alkyl-3-methylimidazolium diethylphosphate. This required the definition of two new groups, (-MeImMe<sub>2</sub>PO<sub>4</sub>) and (-MeImEt<sub>2</sub>PO<sub>4</sub>), and to fit their pure energy and binary interaction parameters with other functional groups: CH<sub>3</sub>, CH<sub>2</sub>, ACH, AC, ACCH<sub>3</sub> and CH<sub>2</sub>=CH. Most of the parameters were correlated to the experimental infinite dilution activity coefficients of a variety of paraffins and aromatic compounds. The results show good correlation with the experimental data available, as well as good predictive capacity of those data sets not considered in the parameterization procedure; it is possible to describe infinite dilution activity coefficient with an average relative deviation of 4.5%.

## List of symbols

$A$	Helmholtz free energy
%ARD	Average relative deviation
%Max	Maximum deviation

$d_{ci}$	value of the hard-sphere diameter at the critical temperature $T_c$ for the pure component $i$ . =  $\text{cm}\cdot\text{mol}^{1/3}$
$g^*, g', g''$	attractive energy parameter for interactions between segments $j$ and $i$ , and its dependence with temperature  =  $\text{atm}\cdot\text{cm}^6\cdot\text{mol}^{-2}$
$k$	coverage factor
$k^*_{ij}, k'_{ij}$	binary interaction parameter, and its dependence on temperature.
$M_w$	molar weight  =  $\text{g}\cdot\text{mol}^{-1}$
$n$	number of experimental data
$P$	pressure  =  bar
$P_c$	critical pressure  =  bar
$Q_i$	reduced Van der Waals surface of component $i$
$q_j$	reduced Van der Waals surface of group $j$
$r_{vdW}$	normalized Van der Waals molecular volume
$T$	temperature  =  K
$T_c$	critical temperature  =  K
$T^*$	reference temperature  =  K
$v$	molar volume  =  $\text{cm}^3\cdot\text{mol}^{-1}$
$v_{298K}$	molar volume of the ionic liquid at 298 K  =  $\text{cm}^3\cdot\text{mol}^{-1}$
$u(z)$	uncertainty of the measurement $z$
$x_i$	molar fraction of the component $i$  =  $\text{mol}\cdot\text{mol}^{-1}$
Greek symbols	
$\alpha_{ij}, \alpha_{ji}$	NRTL non-randomness parameter between groups $i$ and $j$
$\gamma_i$	activity coefficient of the substance $i$

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