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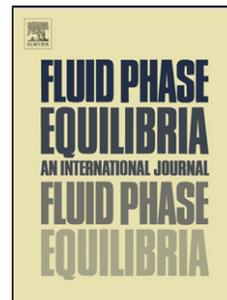
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Present Status of the Modified UNIFAC Model for the Prediction of Phase Equilibria and Excess Enthalpies for Systems with Ionic Liquids

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Abstract

The modified UNIFAC (Dortmund) parameter matrix for ionic liquids has been extended. Two new main groups for the anions alkylsulfate $[RSO_4]^-$ and hexafluorophosphate $[PF_6]^-$ were introduced. Additionally new interaction parameters for pyrrolidinium $[RMPYR]^+$ and pyridinium $[RPY]^+$ cations as well as 1for trifluoromethanesulfonate $[OTF]^-$ and tetrafluoroborate $[BF_4]^-$ anions have been fitted to the available experimental data. In addition existing parameters have been revised. This article will give an overview about the current status of the modified UNIFAC (Dortmund) parameter matrix for ionic liquids. Typical results are presented for various systems. For the further development vapor-liquid equilibria and excess enthalpies were measured.

Keywords: Ionic liquids; Vapor-liquid equilibria; Excess enthalpies; Activity coefficients at infinte dilution; Modified UNIFAC (Dortmund)

1. Introduction

Because of their interesting thermophysical properties, like negligible vapor pressure, high solubility of organic and inorganic compounds, thermal stability, etc., there exist a wide range of possible applications for ionic liquids. In addition ionic liquids are often discussed as solvents for

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green chemistry, due to their low flammability and non-toxicity. Therefore ionic liquids have gained increasing attention over the last years. Some practical applications for ionic liquids are the replacement of conventional solvents e.g. in separation processes, such as extraction, extractive distillation, absorption, etc.. Since there is a wide range of possible anions, cations and substituents, ionic liquids can be applied for a given separation problem. Therefore ionic liquids are often denoted as designer solvents. To select the best suited ionic liquid, this means to choose the most appropriate combination of ions and substituents, a reliable knowledge about the phase equilibrium behavior is required. As already shown in a previous paper [1] the modified UNIFAC (Dortmund) group contribution model [2] allows a reliable prediction of the phase equilibrium behavior for systems containing ionic liquids.

The application of modified UNIFAC (Dortmund) was extended to ionic liquids by Kato and Gmehling [3] and Nebig and Gmehling [4]. But in these references mainly results for imidazolium cations [RMIM]$^+$ and bis(trifluoromethylsulfonyl)imide [BTI]$^-$ anions were shown. Recently an extension to piperidinium cations was presented by Paduszyński and Domańska [5]. In this present work new sets of interaction parameters for [RPY]$^+$, [RMPYR]$^+$, [OTF]$^-$, [BF$_4$]$^-$, [RSO$_4$]$^-$ and [PF$_6$]$^-$ are introduced to the modified UNIFAC (Dortmund) parameter matrix. At the same time existing parameters were revised. Typical prediction results for various systems are given.

2. Experimental Section

Excess enthalpies for the system water - [EMIM]$^+$[EtSO$_4$]$^-$ at 363.15 K and vapor-liquid equilibria for the systems benzene - [BMIM]$^+$[PF$_6$]$^-$, 1-butanol - [HPY]$^+$[BTI]$^-$, methanol - [OMPYR]$^+$[BTI]$^-$, ethanol - [OMPYR]$^+$[BTI]$^-$ and 1-propanol - [OMPYR]$^+$[BTI]$^-$ have been measured.

2.1. Materials and Purities

The investigated ionic liquids [EMIM]$^+$[EtSO$_4$]$^-$ and [BMIM]$^+$[PF$_6$]$^-$ were obtained from IOLITEC, [HPY]$^+$[BTI]$^-$ and [OMPYR]$^+$[BTI]$^-$ from Merck. The chemicals used were further

purified before use as described in [1]. Table 1 gives an overview about all used components, their suppliers and purities.

2.2 Excess Enthalpies

Excess enthalpies for the system water (1) – $[EMIM]^+[EtSO_4]^-$ (2) at 363.15 K were measured with an isothermal flow calorimeter from Hart Scientific (model 7501) as described in [1] and [6]. To verify that no reaction takes place during the measurements the resulting mixture was checked for ethanol by gas-chromatography, as a product of a possible reaction between water and $[EMIM]^+[EtSO_4]^-$. But no ethanol was detected. In Table 2 the experimental h^E-data are listed.

2.3 Vapor-Liquid Equilibria

Binary vapor-liquid equilibria were measured under isothermal conditions with a computer-driven static apparatus, as described in [7]. The degassed components were injected to the equilibrium cell stepwise via a piston pump. To reach equilibrium the mixture was stirred. A pressure sensor (Druck type PDCR 4010 max. Pressure 350 kPa) was used to measure the pressure inside the cell. After pressure constancy was observed the composition of the mixture was changed by injecting a well-known volume of one of the components. The experimental data for the system benzene (1) – $[BMIM]^+[PF_6]^-$ at 343.15 K are given in Table 3. Table 4 lists the experimental data points for the system 1-butanol (1) – $[HPY]^+[BTI]^-$ (2) at 353.15 K. The experimental data for the systems methanol - $[OMPYR]^+[BTI]^-$, ethanol - $[OMPYR]^+[BTI]^-$ 1-propanol - $[OMPYR]^+[BTI]^-$ at 353.15 K can be found in Table 5.

3. Modified UNIFAC

Figure 1 shows the anions and cations for which now modified UNIFAC (Dortmund) parameters are available. The required group interaction parameters were fitted simultaneously to activity coefficients at infinite dilution (γ^∞), binary vapor-liquid equilibria (VLE) and excess

enthalpies (h^E) using the Simplex-Nelder-Mead method [8]. The experimental data were either taken from own measurements or the Dortmund Data Bank [9]. In total 2758 VLE data points, 742 h^E data points and 2604 γ^∞ data points were used for fitting the group interaction parameters for systems with ionic liquids.

A revision of existing parameters was necessary, because before the [RMIM]$^+$ and [BTI]$^-$ parameters were fitted simultaneously to experimental data [4]. The fitted group interaction parameters complicated the fitting process for the parameters of the new main groups, leading to poor results. By fitting the parameters of the groups independently, the quality of the prediction results for the new interaction parameters could be greatly improved. Furthermore the number of required group interaction parameters could be reduced to the a and b parameters, whereby the quality of the prediction results was not affected in the limited temperature range covered by the experimental data. The present status of the modified UNIFAC (Dortmund) parameter matrix for ionic liquids is shown in Figure 2. The group interaction parameters are listed in Table 6. The additionally required values for the van der Waals volumes R_k and surface areas Q_k are given in Table 7.

4. Results and Discussion

Prediction results for vapor liquid-equilibria, excess enthalpies and activity coefficients at infinite dilution are presented below together with the experimental data. Figure 3 shows experimental VLE data of systems consisting of n-hexane and ionic liquids of the type [RMIM]$^+$[BTI]$^-$ at 353.15 K [10], [11] together with prediction results using modified UNIFAC (Dortmund) parameters from this work as well as from [4]. Both parameter sets describe the experimental data with a similar accuracy. Experimental excess enthalpies for systems of acetone respectively 2-butanone with [BMIM]$^+$[BTI]$^-$ at 353.15 K [11] together with the predicted results using modified UNIFAC (Dortmund) using the old and the new parameters are shown in Figure 4. The system shows exothermal behavior. Both predictions are in qualitative agreement with the experimental data. In Figure 5 activity coefficients at infinite dilution of benzene and toluene in [HMIM]$^+$[BTI]$^-$ [3], [12], [13], [14] and the prediction using both matrices are shown. As can be seen the experimental data from the different references are scattering. While the parameters from [4] describe the experimental activity coefficients of benzene from [13] better, the parameters from this work are in better agreement with experimental data from [3] and [12].

The activity coefficients of toluene are described with similar quality with both sets of parameters.

As an example for the prediction results using the new interaction parameters, Figure 6 shows experimental and predicted excess enthalpies for the systems of benzene respectively *m*-xylene with [BMIM]$^+$[OTF]$^-$ [15]. Both systems are well described by modified UNIFAC (Dortmund), even though again the predicted minimum value of the exothermic excess enthalpies is a little stronger negative than the experimental one. In Figure 7 the vapor-liquid equilibrium of the system cyclohexane and [HMIM]$^+$[OTF]$^-$ [15] together with the prediction result of modified UNIFAC (Dortmund) is shown. The model gives a very precise prediction for this system with only small deviations from the experimental data. The activity coefficients at infinite dilution for a few alcohols in [BMIM]$^+$[OTF]$^-$ [15], [16], [17] are shown in Figure 8 together with the predicted results using modified UNIFAC (Dortmund). The experimental data points from the different data sources are scattering, but the prediction seems to be ok.

For the tetrafluoroborate anion in [4] only interaction parameters with alkanes were available. In this paper the parameters for tetrafluoroborate with additional main groups were fitted. In Figure 9 the experimental vapor-liquid equilibria of 1-butene respectively 1-hexene with [BMIM]$^+$[BF$_4$]$^-$ at 363.15 K [15] are shown together with the prediction results. Both systems are well predicted using modified UNIFAC (Dortmund). A comparison of the experimental excess enthalpies for the systems ethanol with [BMIM]$^+$[BF$_4$]$^-$ respectively [HMIM]$^+$[BF$_4$]$^-$ at 303.15 K [18], [19] and the predicted results using modified UNIFAC (Dortmund) is shown in Figure 10. For both systems the predicted results are in good agreement with experimental data. In Figure 11 the activity coefficients of various alcohols in [MBPY]$^+$[BF$_4$]$^-$ [20], [21] are shown together with predicted results. Also for these systems satisfying results are obtained using modified UNIFAC (Dortmund).

In our previous paper [1] the application of modified UNIFAC (Dortmund) for a few systems containing alcohols and ionic liquids with sulfate-based anions was presented. Further results for systems with sulfate-based anions are shown in Figure 12, where the predicted vapor-liquid equilibria of benzene respectively toluene with [EMIM]$^+$[EtSO$_4$]$^-$ [22] are shown together with the experimental data. Both systems are very well described by modified UNIFAC. The excess enthalpies for the system of water and [EMIM]$^+$[EtSO$_4$]$^-$ at 303.15 K [23] and 363.15 K are

shown in Figure 13. As can be seen from Figure 13 the prediction using modified UNIFAC (Dortmund) is in qualitative agreement with the experimental values. The mean relative deviation of the predicted result from the experimental data for both temperatures is approx. 13.4 %. The activity coefficients of different aromatics in [EMIM]$^+$[EtSO$_4$]$^-$ [22], [24], [25] are shown in Figure 14 together with prediction using modified UNIFAC (Dortmund). As can be seen the prediction is in good agreement with the experimental data.

As new main group for modified UNIFAC (Dortmund) the [PF$_6$]$^-$ anion was introduced. In Figure 15 the predicted vapor-liquid equilibria for the system of benzene- [BMIM]$^+$[PF$_6$]$^-$ at 343.15 K are compared with the experimental data. As can be seen there is good agreement between the experimental data and the prediction using modified UNIFAC (Dortmund) with only small deviations close to the miscibility gap. Figure 16 shows the experimental excess enthalpies for the systems of ethanol respectively 2-propanol with [BMIM]$^+$[PF$_6$]$^-$ at 288.15 K [26] together with the predicted results. As can be seen also here a good agreement between the experimental data and prediction results for both systems is obtained.

Also for the pyridinium cation group interaction parameters for a few new group pairs have been fitted. In Figure 17 the excess enthalpies for the systems methanol respectively 1-propanol with [MBPY]$^+$[BF$_4$]$^-$ at 298.15 K [27] are shown together with prediction results using modified UNIFAC (Dortmund). The model describes both systems with only small deviations. The vapor-liquid equilibrium for the system 1-butanol - [HPY]$^+$[BTI]$^-$ at 353.15 K and the predicted results are shown in Figure 18. The prediction is in good agreement with the experimental data. In Figure 19 the vapor-liquid equilibria for the systems of benzene respectively toluene with [EPY]$^+$[BTI]$^-$ at 353.15 K [15] are shown together with the prediction using modified UNIFAC (Dortmund). The prediction for the system containing benzene is in good agreement with the experimental values, while the predicted system pressures for the system containing toluene are lower than the experimental data. The vapor-liquid equilibrium for the system cyclohexane with [EPY]$^+$[BTI]$^-$ at 353.15 K [15] together with the prediction result are presented in Figure 20. For this system only small deviations between experimental data and predicted values are observed. In Figure 21 the activity coefficients at infinite dilution of a few alkanes in [MBPY]$^+$[BTI]$^-$ [28] and their prediction are shown. The prediction is in the range of the experimental data, but shows a slightly different temperature dependence of the activity coefficients. Unfortunately no excess enthalpies are available to decide about the correct temperature dependence.

As for the pyridinium cation also new interaction parameters were fitted for the pyrrolidinium cation. In Figure 22 vapor-liquid equilibria for methanol, ethanol and 1-propanol with the ionic liquid [OMPYR]$^+$[BTI]$^-$ at 353.15 K are shown together with the predicted results. For all three systems the prediction results are in good agreement with the experimental data. The excess enthalpies for the system of cyclohexane and [BMPYR]$^+$[BTI]$^-$ at 303.15 K [15] and the predicted values are shown at Figure 23. The prediction agrees with the experimental data at high concentrations for the ionic liquid and the cycloalkane. The predicted minimum value deviates from the experimental one and shows a stronger negative value. In Figure 24 the activity coefficients at infinite dilution of various alcohols in [BMPYR]$^+$[OTF]$^-$ [14], [29] are shown together with prediction using modified UNIFAC (Dortmund). As can be seen the experimental data are well described using modified UNIFAC (Dortmund).

5. Conclusion

The main focus of this work was the extension and revision of the modified UNIFAC (Dortmund) parameter matrix for ionic liquids. Two new main groups [RSO$_4$]$^-$ and [PF$_6$]$^-$ were introduced. Also new interaction parameters for the already existing main groups [RPY]$^+$, [RMPYR]$^+$, [OTF]$^-$ and [BF$_4$]$^-$ have been fitted to experimental data to close the "gaps" in the parameter matrix. In addition the group interaction parameters for [RMIM]$^+$ and [BTI]$^-$ and the have been revised. In total today group interaction parameters for 81 group combinations are available for ionic liquids.

The quality of the predictions has been demonstrated for vapor-liquid equilibria, excess enthalpies and activity coefficients at infinite dilution for various systems. For a few systems experimental data were measured, e.g. excess enthalpies for the system water - [EMIM]$^+$[EtSO$_4$]$^-$ at 363.15 K and vapor-liquid equilibria for the systems of benzene - [BMIM]$^+$[PF$_6$]$^-$, 1-butanol - [HPY]$^+$[BTI]$^-$ and different alcohols with [OMPYR]$^+$[BTI]$^-$.

As was demonstrated modified UNIFAC (Dortmund) provides reliable results for various systems and therewith extends the applicability of software packages for process development with ionic liquids.

Because of the still limited experimental data base of binary systems with ionic liquids, there is a demand for new experimental data. This would allow the extension of the present parameter matrix by adding new main groups (ions) and the revision of poor group interaction parameters.

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Figure Captions

Figure 1

Cations and anions used in modified UNIFAC.

Figure 2

Current status of the modified UNIFAC parameter matrix for ionic liquids.

Figure 3

Experimental and predicted vapor-liquid equilibria for n-hexane (1) – [EMIM]$^+$[BTI]$^-$ (2) (◆), [HMIM]$^+$[BTI]$^-$ (2) (▲), [OMIM]$^+$[BTI]$^-$ (2) (■) at 353.15 K, Experimental Data [EMIM]$^+$[BTI]$^-$ [10], [HMIM]$^+$[BTI]$^-$, [OMIM]$^+$[BTI]$^-$ [11], modified UNIFAC (this work) (—), modified UNIFAC [4] (- -).

Figure 4

Experimental and predicted excess enthalpies for acetone (1) (◆) and 2-butanone (1) (△) – [BMIM]$^+$[BTI]$^-$ (2) at 353.15 K. Experimental Data [11], modified UNIFAC (this work) acetone (—), 2-butanone (══); modified UNIFAC [4] acetone (- -), 2-butanone (= =)

Figure 5

Experimental and predicted activity coefficients of benzene (◆, ◇, ◈) and toluene (▲,△,▲) in [HMIM]$^+$[BTI]$^-$, Experimental Data (◆,▲) [3], (◇,△) [12], (◈) [13], (▲) [14] modified UNIFAC (this work) (—), modified UNIFAC [4] (- -).

Figure 6

Experimental and predicted excess enthalpies for benzene (1) at 363.15 K (◆) and *m*-xylene (1) at 353.15 K (▲) – [BMIM]$^+$[OTF]$^-$ (2). Experimental data [15], modified UNIFAC (—).

Figure 7

Experimental and predicted vapor-liquid equilibria for cyclohexane (1) - [HMIM]$^+$[OTF]$^-$ (2) at 363.15 K. Experimental data (◆) [15], modified UNIFAC (—).

Figure 8

Experimental and predicted activity coefficients of methanol ($\lozenge$, $\diamond$, $\blacklozenge$), ethanol ($\triangle$, $\triangle$, $\blacktriangle$), 1-propanol ($\bigcirc$, $\circ$, $\bullet$) and 1-butanol ($\square$, $\blacksquare$) in [BMIM]$^+$[OTF]$^-$, Experimental Data ($\lozenge$, $\triangle$, $\bigcirc$) [15], ($\diamond$, $\triangle$, $\circ$, $\square$) [16], ($\blacklozenge$, $\blacktriangle$, $\bullet$, $\blacksquare$) [17], modified UNIFAC (—).

Figure 9

Experimental and predicted vapor-liquid equilibria for 1-butene (1) ($\blacklozenge$) and 1-hexene (1) ($\blacktriangle$) – [BMIM]$^+$[BF$_4$]$^-$ (2) at 363.15 K. Experimental data [15], modified UNIFAC (—).

Figure 10

Experimental and predicted excess enthalpies for ethanol (1) – [BMIM]$^+$[BF$_4$]$^-$ (2) ($\blacktriangle$) and [HMIM]$^+$[BF$_4$]$^-$ (2) ($\blacklozenge$) at 303.15 K. Experimental data ethanol - [BMIM]$^+$[BF$_4$]$^-$ [18], ethanol - [BMIM]$^+$[BF$_4$]$^-$ [19], modified UNIFAC (—).

Figure 11

Experimental and predicted activity coefficients of methanol ($\blacklozenge$, $\diamond$), ethanol ($\blacktriangle$, $\triangle$), 1-propanol ($\bullet$) and 1-butanol ($\blacksquare$) in [MBPY]$^+$[BF$_4$]$^-$. Experimental Data ($\blacklozenge$, $\blacktriangle$, $\bullet$, $\blacksquare$) [20], ($\diamond$, $\triangle$) [21], modified UNIFAC (—).

Figure 12

Experimental and predicted vapor-liquid equilibria for benzene (1) ($\blacklozenge$) and toluene (1) ($\blacktriangle$) – [EMIM]$^+$[EtSO$_4$]$^-$ (2) at 353.15 K. Experimental data [22], modified UNIFAC (—).

Figure 13

Experimental and predicted excess enthalpies for water (1) - [EMIM]$^+$[EtSO4]$^-$ (2) at 303.15 K ($\blacktriangle$) and 363.15 K ($\blacklozenge$). Experimental data 303.15 K [23], modified UNIFAC (—).

Figure 14

Experimental and predicted activity coefficients of benzene ($\blacklozenge$, $\diamond$, $\lozenge$), toluene ($\blacktriangle$, $\triangle$, $\triangle$), p-xylene ($\bullet$) and mesitylene ($\blacksquare$) in [EMIM]$^+$[EtSO$_4$]$^-$. Experimental Data ($\blacklozenge$, $\blacktriangle$, $\bullet$, $\blacksquare$) [22], ($\diamond$, $\triangle$) [24], ($\lozenge$, $\triangle$) [25], modified UNIFAC (—).

Figure 15

Experimental and predicted vapor-liquid equilibria for benzene (1) – [BMIM]$^+$[PF$_6$]$^-$ (2) at 343.15 K. Experimental data (◆), modified UNIFAC (—).

Figure 16

Experimental and predicted excess enthalpies for ethanol (1) (▲) and 2-propanol (1) (◆) – [BMIM]$^+$[PF$_6$]$^-$ (2) at 288.15 K. Experimental data [26], modified UNIFAC (—).

Figure 17

Experimental and predicted excess enthalpies for methanol (1) (◆) and 1-propanol (1) (▲) – [MBPY]$^+$[BF$_4$]$^-$ (2) at 298.15 K. Experimental data [27], modified UNIFAC (—).

Figure 18

Experimental and predicted vapor-liquid equilibria for 1-butanol (1) – [HPY]$^+$[BTI]$^-$ (2) at 353.15 K. Experimental data (◆), modified UNIFAC (—).

Figure 19

Experimental and predicted vapor-liquid equilibria for benzene (1) (▲) and toluene (1) (◆) – [EPY]$^+$[BTI]$^-$ (2) at 363.15 K. Experimental data [15], modified UNIFAC (—).

Figure 20

Experimental and predicted vapor-liquid equilibria for cyclohexane (1) – [EPY]$^+$[BTI]$^-$ (2) at 353.15 K. Experimental data (◆) [15], modified UNIFAC (—).

Figure 21

Experimental and predicted activity coefficients of heptane (◆), octane (▲), nonane (●) and decane (■) in [MBPY]$^+$[BTI]$^-$. Experimental Data [28], modified UNIFAC (—).

Figure 22

Experimental and predicted vapor-liquid equilibria for methanol (1) (■), ethanol (1) (▲) and 1-propanol (1) (◆) – [OMPYR]⁺[BTI]⁻ (2) at 353.15 K. modified UNIFAC (—).

Figure 23

Experimental and predicted excess enthalpies for 2-butanone (1) – [BMPYR]⁺[BTI]⁻ (2) at 303.15 K. Experimental data (◆) [15], modified UNIFAC (—).

Figure 24

Experimental and predicted activity coefficients of methanol (◆), ethanol (▲, △), 1-propanol (●) and 1-butanol (■) in [BMPYR]⁺[OTF]⁻. Experimental Data (△) [14] (◆, ▲, ●, ■) [29], modified UNIFAC (—).

Table 1. Supplier and purity of the chemicals used.

Component	Supplier	Purity (% Mass)
benzene	Roth	99.9
methanol	VWR	99.5
ethanol	VWR	99.9
1-propanol	VWR	99.9
2-propanol	VWR	99.8
[EMIM]$^+$[EtSO$_4$]$^-$	IOLITEC	99
[EMIM]$^+$[MeSO$_4$]$^-$	IOLITEC	99
[EMIM]$^+$[HSO$_4$]$^-$	IOLITEC	99
[BMIM]$^+$[PF$_6$]$^-$	IOLITEC	99
[HPY]$^+$[BTI]$^-$	Merck	99
[OMPYR]$^+$[BTI]$^-$	Merck	99

Table 2. Excess enthalpies for water (1)-[EMIM]$^+$[EtSO$_4$]$^-$ (2) at 363.15 K

x_1	H^E [J·mol^{-1}]	x_1	H^E [J·mol^{-1}]
0.0568	-142.9	0.5544	-800.0
0.1109	-270.4	0.6095	-814.4
0.1648	-372.4	0.6653	-814.2
0.2223	-463.7	0.7208	-798.7
0.2771	-549.6	0.7767	-758.1
0.3324	-618.7	0.8326	-671.0
0.3868	-684.4	0.8883	-531.0
0.4430	-735.5	0.9441	-292.3
0.4986	-774.2		

Standard uncertainties are u(x) = +/- 0.0005, u(T) = +/- 0.01 K
and u(H^E) = +/- 0.5 J/mol

Table 3. Vapor-liquid equilibria for benzene (1) – [BMIM]$^+$[PF$_6$]$^-$ at 343.15 K.

x_1	P [kPa]	x_1	P [kPa]
0.00619	0.8374	0.79357	73.23
0.01788	2.401	0.83768	73.24
0.03048	4.041	0.87598	73.24
0.05246	6.848	0.90808	73.26
0.07816	10.08	0.93425	73.28
0.11265	14.41	0.95438	73.31
0.15735	20.06	0.96866	73.34
0.21363	26.89	0.97881	73.37
0.28263	35.14	0.98570	73.39
0.35931	44.04	0.99038	73.41
0.43797	52.81	0.99393	73.43
0.51513	60.88	0.99639	73.44
0.58742	67.73	0.99841	73.46
0.65235	72.69	1.00000	73.47
0.71098	73.18		

Standard uncertainties are u(x) = +/- 0.0005, u(T) = +/- 0.01 K

and u(P) = +/- 0.005 kPa

Table 4. Vapor-liquid equilibria for 1-butanol (1) – [HPY]$^+$[BTI]$^-$ at 353.15 K.

x_1	P [kPa]	x_1	P [kPa]
0.01503	0.4838	0.85053	20.68
0.03606	1.162	0.88349	20.96
0.05372	1.734	0.91133	21.16
0.08515	2.743	0.93424	21.33
0.12293	3.934	0.95266	21.44
0.17025	5.393	0.96674	21.54
0.22970	7.229	0.97679	21.60
0.30093	9.347	0.98407	21.66
0.38301	11.69	0.98919	21.71
0.46749	13.89	0.99279	21.74
0.54829	15.79	0.99568	21.77
0.62244	17.30	0.99745	21.79
0.68770	18.46	0.99906	21.81
0.74317	19.29	1.00000	21.82
0.81275	20.22		

Standard uncertainties are u(x) = +/- 0.0005, u(T) = +/- 0.01 K
and u(P) = +/- 0.005 kPa

Table 5. Vapor-liquid equilibria for different alcohols and [OMPYR]$^+$[BTI]$^-$ at 353.15 K.

x_1	P [kPa]	x_1	P [kPa]	x_1	P [kPa]
methanol (1)-[OMPYR]$^+$[BTI]$^-$ (2)		ethanol (1)-[OMPYR]$^+$[BTI]$^-$ (2)		1-propanol (1)-[OMPYR]$^+$[BTI]$^-$ (2)	
0.02745	4.687	0.03062	3.586	0.01373	0.8016
0.07554	13.17	0.05736	6.660	0.04012	2.331
0.12136	21.53	0.08646	10.11	0.06659	3.907
0.18245	32.89	0.15021	17.85	0.10901	6.462
0.24879	45.23	0.21579	25.90	0.15714	9.437
0.32601	59.76	0.29044	35.11	0.21695	13.25
0.41039	76.00	0.36637	44.66	0.28965	17.86
0.49778	92.68	0.44946	54.82	0.37209	23.01
0.58379	108.9	0.53704	65.25	0.46203	28.44
0.66123	123.3	0.61932	74.49	0.54850	33.38
0.72745	135.3	0.69064	82.02	0.62706	37.51
0.78243	144.9	0.75080	87.90	0.69560	40.75
0.82685	152.4	0.80018	92.40	0.75336	43.19
0.86204	157.9	0.83976	95.77	0.80065	44.97
0.89059	162.5	0.85677	97.23	0.82443	45.95
0.91829	166.5	0.87229	98.36	0.84009	46.30
0.93678	169.2	0.88687	99.52	0.86024	47.06
0.95213	171.5	0.91181	101.3	0.89034	47.91
0.96456	173.3	0.93282	102.7	0.91598	48.56
0.97439	174.9	0.95003	103.9	0.93721	49.06
0.98771	177.1	0.96378	104.8	0.95431	49.45
0.99162	177.8	0.97458	105.6	0.96781	49.75
0.99434	178.3	0.98262	106.1	0.97792	49.99
0.99626	178.6	0.98819	106.6	0.98496	50.15
0.99756	178.9	0.99210	106.9	0.98991	50.29
0.99856	179.1	0.99472	107.1	0.99323	50.39
0.99918	179.2	0.99648	107.3	0.99546	50.48
0.99969	179.4	0.99780	107.4	0.99713	50.54
1.00000	179.4	0.99870	107.5	0.99831	50.60
		0.99944	107.6	0.99927	50.65
		1.00000	107.6	1.00000	50.69

Standard uncertainties are u(x) = +/- 0.0005, u(T) = +/- 0.01 K

and u(P) = +/- 0.005 kPa

Table 6. Group interaction parameters for modified UNIFAC (Dortmund).

Main groups		Group interaction parameters		
1	2	a_{12} (K)	b_{12}	c_{12} (K^{-1})
		a_{21} (K)	b_{21}	c_{21} (K^{-1})
CH_2	Imidazolium	70.38 77.78	0.24511 0.83298	-
CH_2	Pyridinium	656.53 -307.86	-4.2237 3.6100	0.0074475 -0.0081757
CH_2	Pyrrolidinium	283.82 907.38	-3.9547 0.46568	0.010375 -0.0055872
CH_2	BTI	1260.0 996.53	-4.5544 -5.4846	0.0067607 0.0095873
CH_2	OTF	1094.3 243.46	-1.1189 -1.0356	-
CH_2	BF_4	360.80 454.56	2.0530 -1.4738	-0.016699 0.0010454
CH_2	SO_4	1859.4 1131.3	4.0631 -0.93175	-
CH_2	PF_6	4041.5 3504.3	-3.9070 2.6629	-0.025448 -0.033020
C=C	Imidazolium	-44.341 1753.13	-0.65212 -3.1121	-
C=C	Pyridinium	1625.9 159.81	-2.4011 1.8532	-
C=C	Pyrrolidinium	-92.730 -1151.3	-0.25088 4.7125	-
C=C	BTI	566.29 -1213.9	-0.14057 5.1401	-
C=C	OTF	2980.0 724.91	4.8237 -4.7941	-0.027251 0.0056279
C=C	BF_4	1230.8 4896.2	0.17033 -1.8607	0.014150 -0.025489
C=C	SO_4	2487.6 1804.0	-3.2818 -5.1811	-
C=C	PF_6	-2399.7 658.20	-0.27451 0.57714	0.032952 -0.0078001
ACH	Imidazolium	277.44 -223.75	-0.18430 0.27810	-
ACH	Pyridinium	161.77 785.45	-0.56713 -3.0911	-
ACH	Pyrrolidinium	-1304.1 26.389	3.8744 0.38631	0.0039496 -0.0027586
ACH	BTI	825.92 20.272	-4.3554 -0.33187	0.0085572 0.0025793
ACH	OTF	1690.1 -15.356	-3.3881 -0.15571	0.0202432 -0.0001404
ACH	BF_4	626.96 2116.4	-4.3061 -2.1106	-
ACH	SO_4	1014.7 877.60	-1.7309 -1.9658	-
ACH	PF_6	4899.8 -969.623	-3.5343 3.8131	-0.035831 0.0028389
$ACCH_2$	Imidazolium	930.71 365.40	-4.3040 -1.2039	0.0078410 -0.0007792
$ACCH_2$	Pyridinium	453.46 3997.2	-2.0385 -2.9940	-

ACCH$_2$	Pyrrolidinium	-935.39	1.2639	0.0041351
		4101.4	-1.1982	-0.018601
ACCH$_2$	BTI	-313.94	2.0613	-
		-134.67	1.3846	
ACCH$_2$	OTF	1077.5	-2.4388	-
		-998.07	4.4879	
ACCH$_2$	BF$_4$	524.31	-4.2686	-
		1259.5	-1.9179	
ACCH$_2$	SO$_4$	1113.43	-0.42831	-
		-281.47	1.0074	
ACCH$_2$	PF$_6$	335.11	2.2665	0.023928
		3792.1	-2.5541	-0.021729
OH	Imidazolium	292.65	-1.5915	-
		147.07	2.0843	
OH	Pyridinium	1178.0	5.3377	-
		1044.9	-3.7127	
OH	Pyrrolidinium	-348.76	1.9247	-
		1003.5	-2.4842	
OH	BTI	1026.3	-3.1778	-
		-792.99	3.8768	
OH	OTF	-159.86	2.4180	-
		662.13	-3.2813	
OH	BF$_4$	-2448.2	-2.1400	0.033283
		-234.39	4.0195	-0.013471
OH	SO$_4$	225.02	-4.3271	0.0030855
		448.38	-1.6166	0.0005180
OH	PF$_6$	-352.18	-1.5836	0.0090199
		1751.4	-1.1000	-0.014892
CH$_3$OH	Imidazolium	-704.23	-1.2624	0.014963
		152.72	2.1786	-0.0098745
CH$_3$OH	Pyridinium	53.778	-0.97910	-
		94.629	0.30192	
CH$_3$OH	Pyrrolidinium	-1230.5	3.9100	-
		1142.9	-2.9243	
CH$_3$OH	BTI	-348.95	1.4146	-
		2127.9	-4.1474	
CH$_3$OH	OTF	1741.1	-4.7372	-
		-558.68	1.1140	
CH$_3$OH	BF$_4$	-671.26	1.5864	-0.0048637
		985.44	-2.4215	-0.0062036
CH$_3$OH	SO$_4$	1037.6	-5.4610	-
		1421.6	0.3414	
H$_2$O	Imidazolium	659.21	-0.59252	0.045160
		151.31	-3.0090	0.0019814
H$_2$O	Pyridinium	-1616.2	5.3231	-
		275.75	-1.9706	
H$_2$O	BTI	2770.9	-2.0094	-
		1996.7	-5.4745	
H$_2$O	OTF	318.21	-1.4238	-
		385.01	-2.4900	
H$_2$O	BF$_4$	2707.2	-2.5112	-0.0022558
		-399.19	0.16195	-0.0067585
H$_2$O	SO$_4$	206.26	-2.5726	0.0032526
		-371.20	0.99046	-0.0008070
CH$_2$CO	Imidazolium	173.44	-5.5270	0.016098
		958.37	-4.7301	0.0047161
CH$_2$CO	Pyridinium	331.15	-1.1142	-
		-30.955	-0.71244	
CH$_2$CO	Pyrrolidinium	99.550	0.45575	-
		-1504.2	4.6306	

CH_2CO	BTI	824.12 670.00	-2.8837 -5.0523	0.0041569 0.0074865
CH_2CO	OTF	571.66 -1449.6	-4.4398 4.4455	-
CH_2CO	BF_4	147.25 177.82	-2.7445 -2.2500	-
CH_2CO	SO_4	519.49 3306.4	-5.4673 0.15196	0.0068391 -0.0082641
cycl-CH_2	Imidazolium	-883.93 360.08	4.0287 -1.3721	-
cycl-CH_2	Pyridinium	-1078.5 1039.8	3.6515 -3.5154	-
cycl-CH_2	Pyrrolidinium	-501.67 -935.61	1.6261 4.6740	-
cycl-CH_2	BTI	493.77 986.96	-4.1078 -2.8500	0.011921 0.0018563
cycl-CH_2	OTF	1654.6 -171.23	-4.2484 0.6214	-
cycl-CH_2	BF_4	-381.96 2358.5	-3.0058 -1.3092	0.0076136 0.013784
cycl-CH_2	SO_4	449.51 4258.3	2.1727 0.3403	0.036050 -0.029654
cycl-CH_2O	Imidazolium	-617.04 -323.68	2.4018 -0.1306	-
cycl-CH_2O	Pyridinium	277.99 122.99	0.25973 -1.9646	-
cycl-CH_2O	BTI	826.09 -450.77	-0.93908 0.94786	-
cycl-CH_2O	OTF	-312.45 186.74	1.1260 -0.97860	-
cycl-CH_2O	BF_4	580.10 4927.3	-2.2443 -0.6351	-0.0080098 -0.035174
Imidazolium	BTI	-103.05 283.17	-1.4285 -5.1459	0.0094424 0.020800
Imidazolium	OTF	133.40 -591.04	-2.6481 0.45605	-0.0025991 -0.0035024
Imidazolium	BF_4	-107.37 1094.9	-3.9086 -4.1098	0.0005537 0.0000263
Imidazolium	SO_4	-113.01 -35.932	-1.4838 -1.5214	-
Imidazolium	PF_6	4542.1 -4116.3	0.85207 -1.7140	-0.051820 -0.0073933
Pyridinium	BTI	-254.70 855.71	-0.46519 -1.1402	-
Pyridinium	BF_4	4209.5 -1680.0	-0.75036 4.4084	-0.035667 -0.0092342
Pyrrolidinium	BTI	-516.84 -1403.3	-3.5941 -4.0258	0.016096 0.038246
Pyrrolidinium	OTF	-1138.0 1824.8	0.70013 -4.2695	-

Table 7. Modified UNIFAC (Dortmund) relativ van der Waals volumes R_k and surface areas Q_k for the used groups.

Main Group	Subgroup	R_K	Q_K
CH_2 [30]	CH_3	0.6325	1.0608
	CH_2	0.6325	0.7081
	CH	0.6325	0.3554
	C	0.6325	0.0000
C=C [30]	CH_2=CH	1.2832	1.6016
	CH=CH	1.2832	1.2489
	CH_2=C	1.2832	1.2489
	CH=C	1.2832	0.8962
	C=C	1.2832	0.4582
ACH [30]	ACH	0.3763	0.4321
	AC	0.3763	0.2113
$ACCH_2$ [30]	$ACCH_3$	0.9100	0.9490
	$ACCH_2$	0.9100	0.7962
	ACCH	0.9100	0.3769
OH [30]	OH (P)	1.2302	0.8927
	OH (S)	1.0630	0.8663
	OH (T)	0.6895	0.8345
CH_3OH [30]	CH_3OH	0.8585	0.9938
H_2O [30]	H_2O	1.7334	2.4561
CH_2CO [30]	CH_3CO	1.7048	1.6700
	CH_2CO	1.7048	1.5542
cycl-CH_2 [30]	Cycl-CH_2	0.7136	0.8635
	Cycl-CH	0.3479	0.1071
	Cycl-C	0.3470	0.0000
cycl-CH_2O [30]	THF	1.7023	1.8784
	Cycl-CH_2O	1.4046	1.4000
	Trioxane	1.0413	1.0116
Imidazolium	$C_3H_3N_2$	1.8430	1.6997
	$C_3H_2N_2$	1.3662	0.6797
Pyridinium	C_5H_5N	2.1094	2.5106
	C_5H_4N	2.4873	2.4457
Pyrrolidinium	C_4H_8N	2.7867	2.7723
BTI	BTI	5.6210	5.9463
OTF	OTF	3.3710	2.0001
BF_4	BF_4	3.9628	0.6214
SO_4	SO_4	0.9903	3.5249
	HSO_4	1.5654	3.8076
PF_6	PF_6	3.8183	3.6018

cations

1-alkyl-3-methyl-
imidazolium

N-alkyl-
pyridinium

N-alkyl-N-methyl-
pyrrolidinium

anions

trifluoromethane-
sulfonate

tetrafluoro-
borate

alkylsulfate

bis(trifluoromethylsulfonyl)imide

hexafluoro-
phosphate
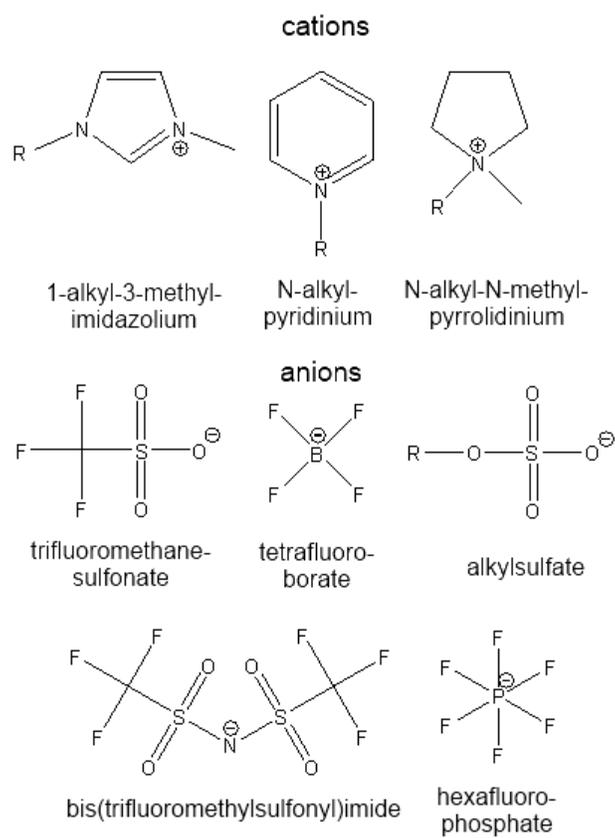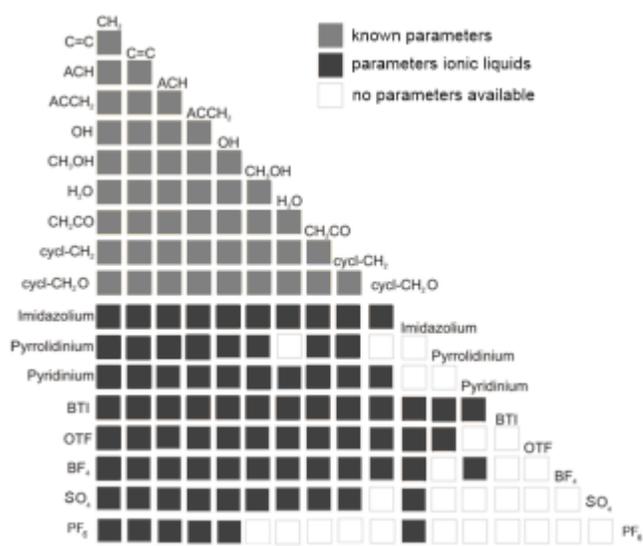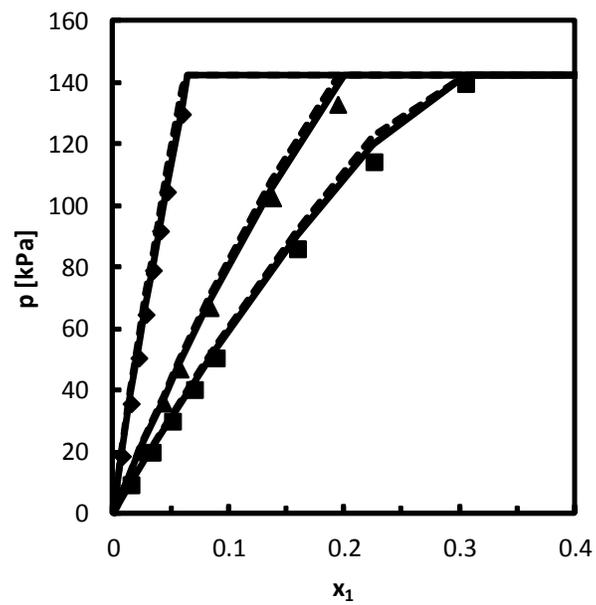
Figure 1

Figure 2

Figure 3
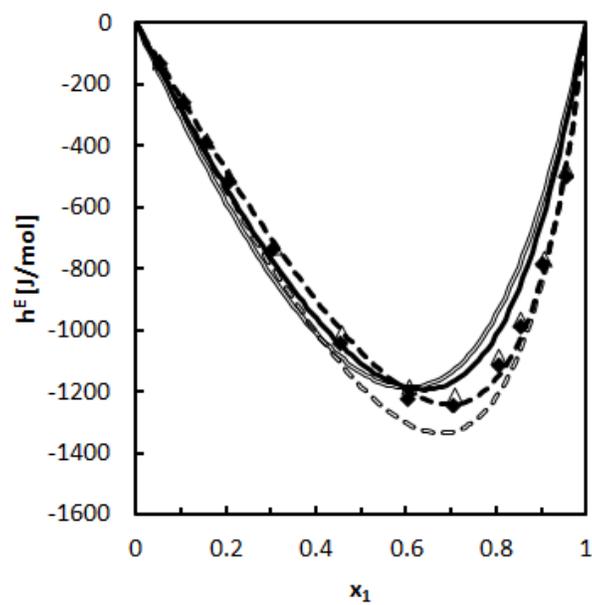
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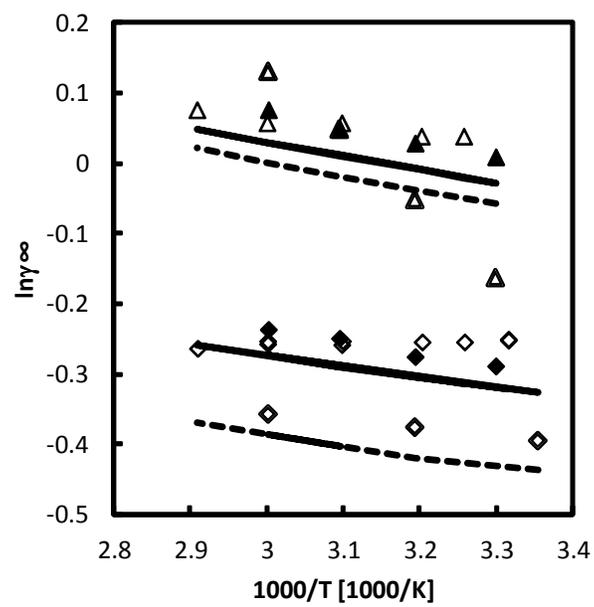
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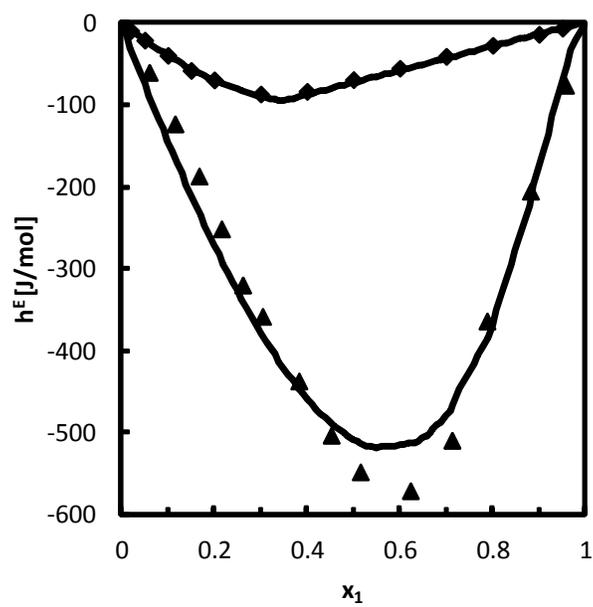
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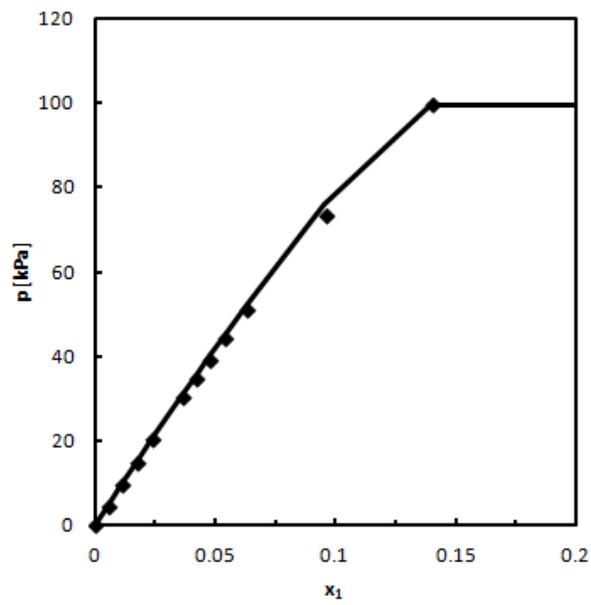
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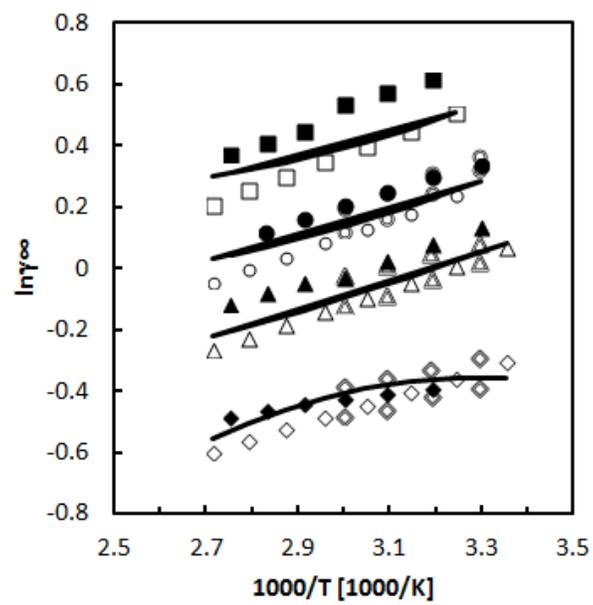
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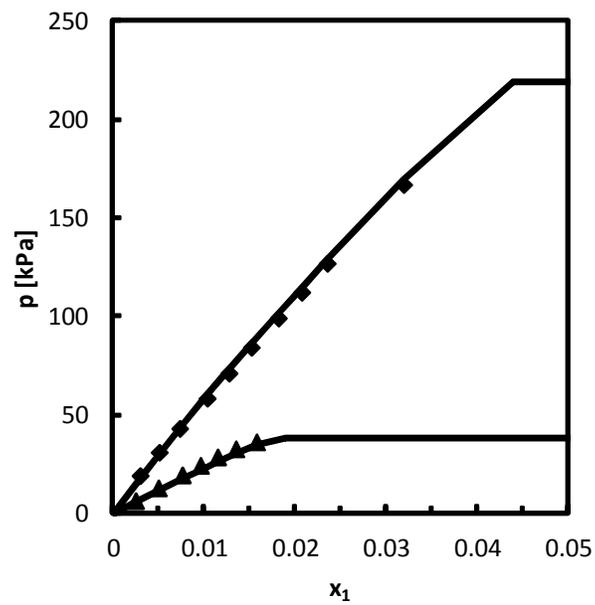
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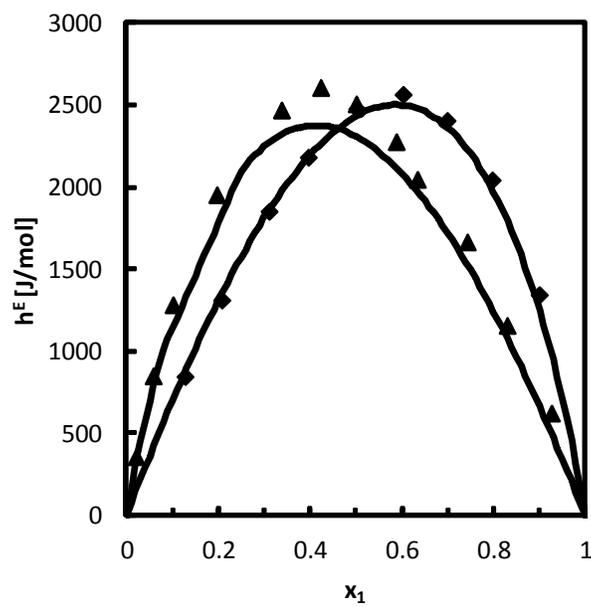
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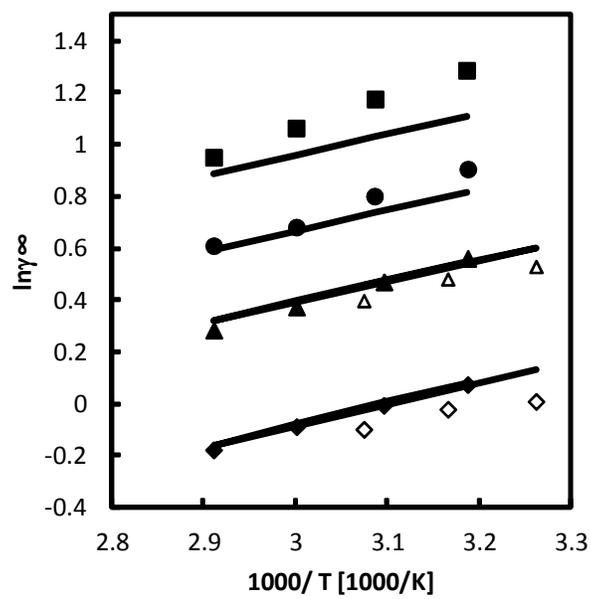
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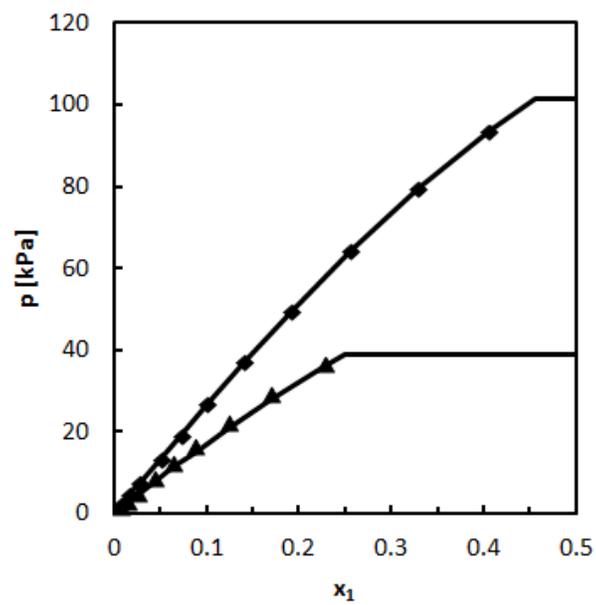
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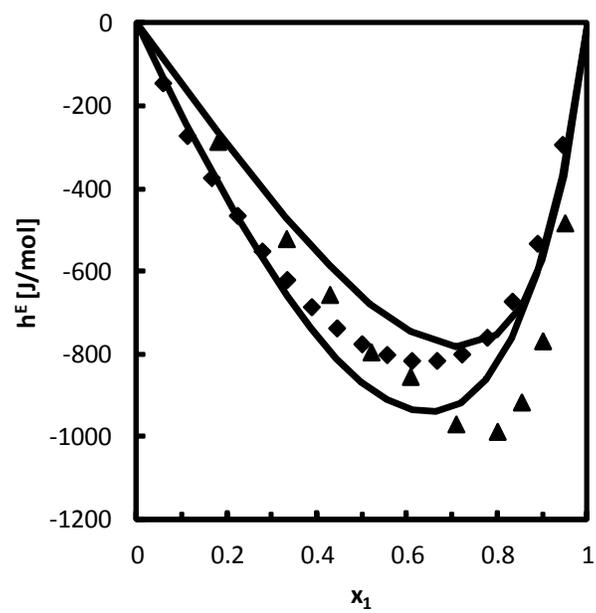
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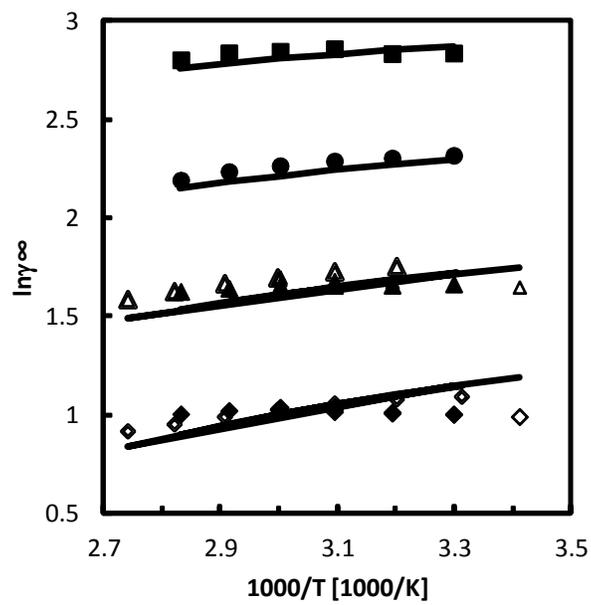
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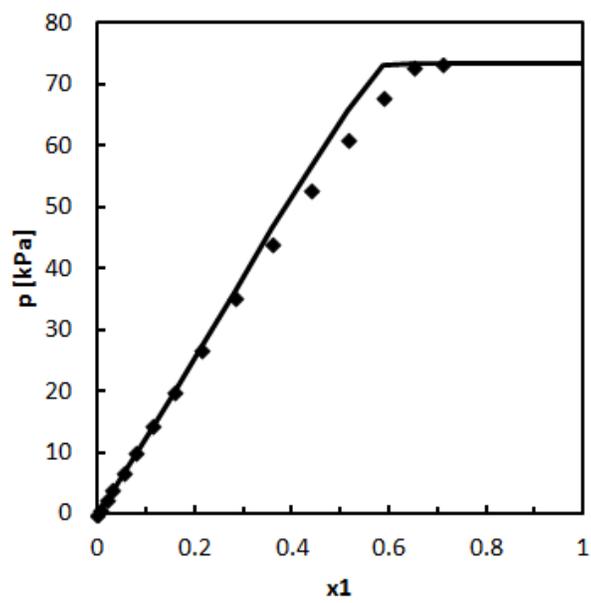
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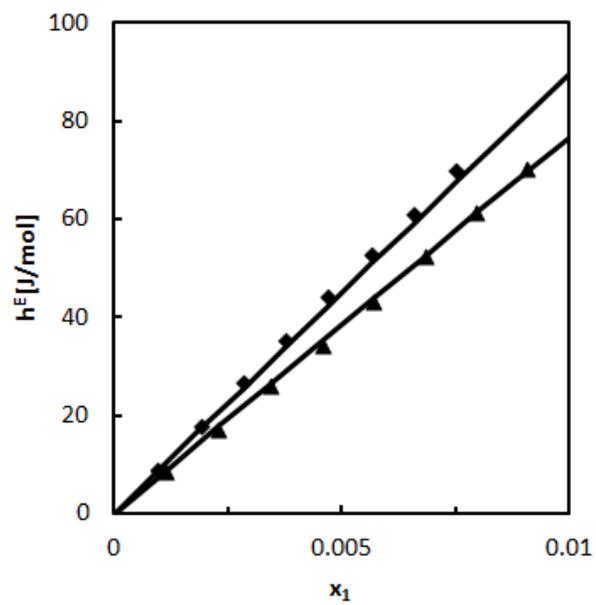
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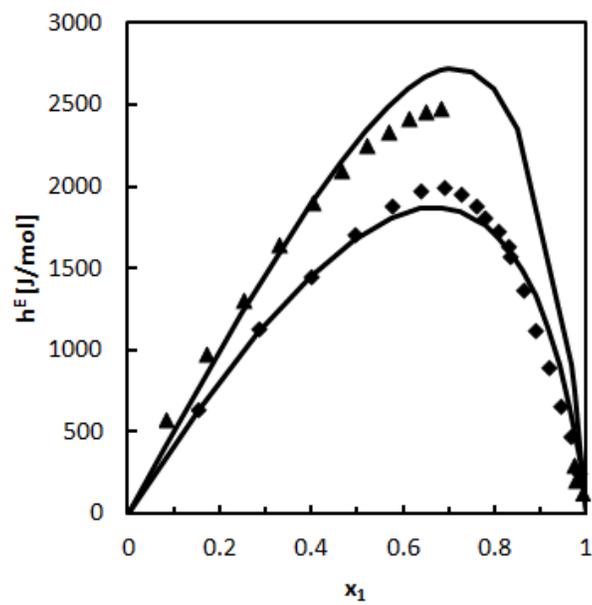
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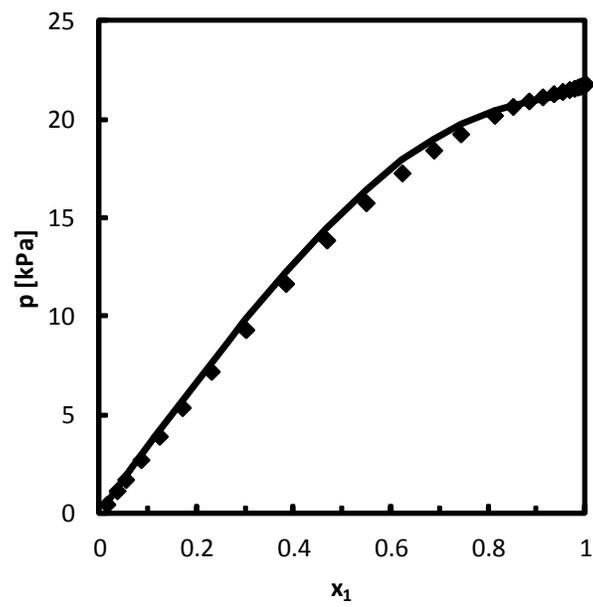
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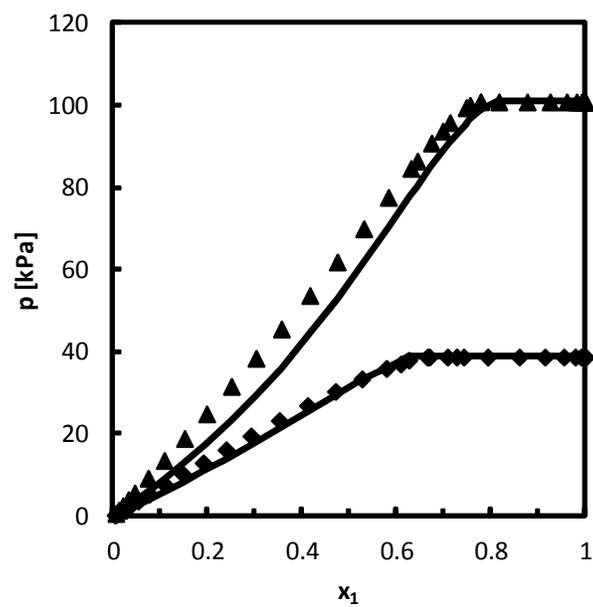
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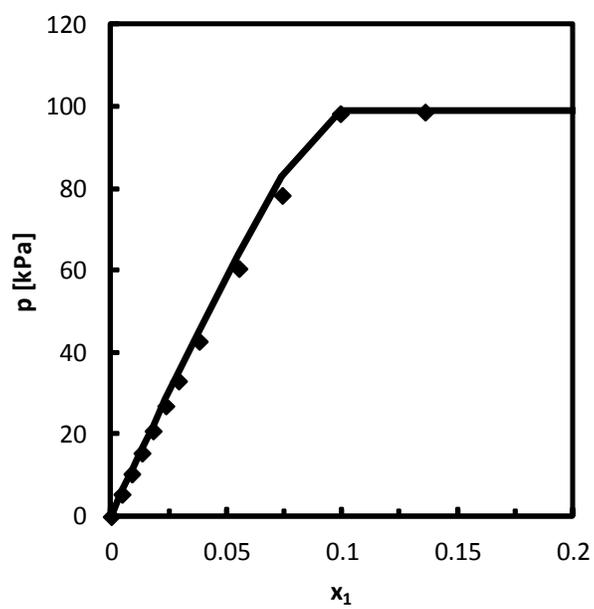
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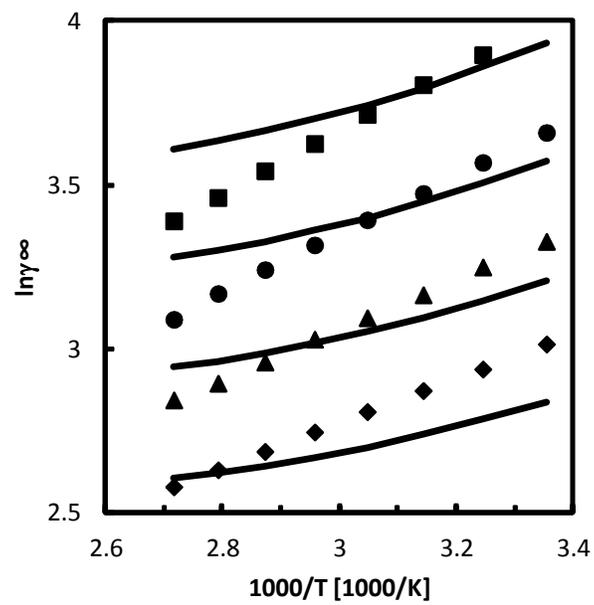
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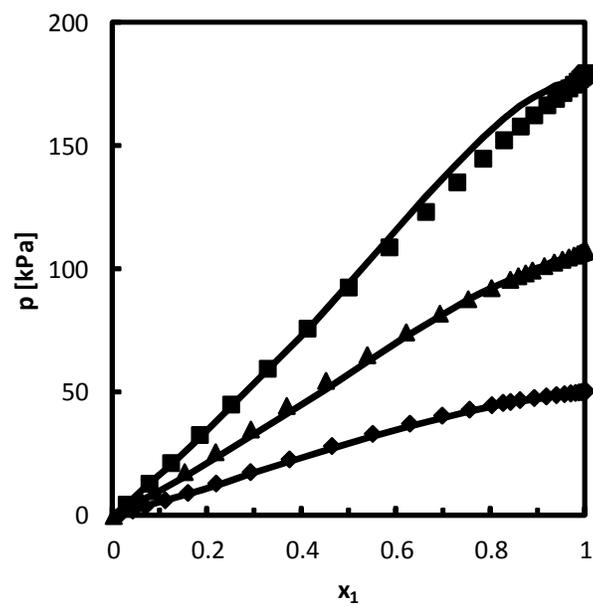
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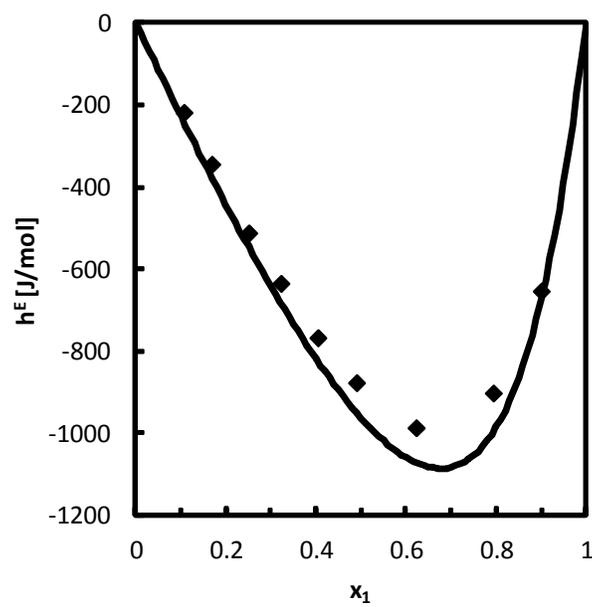
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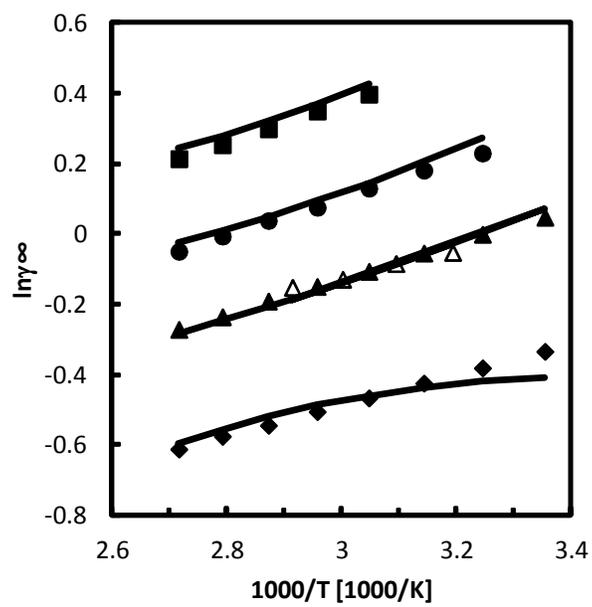
Figure 24

Graphical Abstract
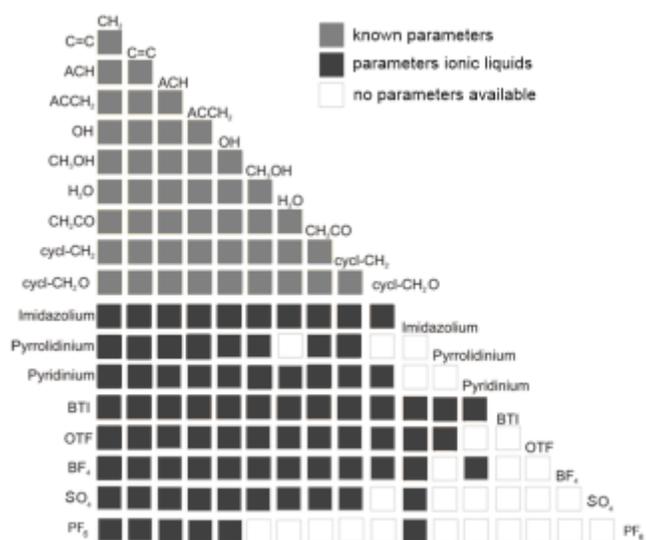
Current status of the modified UNIFAC parameter matrix for ionic liquids.

Highlights

New experimental vapor-liquid equilibria for systems with ionic liquids were measured

New excess enthalpies for systems with ionic liquids were measured

The extended and revised modified UNIFAC parameters for ionic liquids are presented

Typical results for VLE, Excess enthalpies and activity coefficients for various system with ionic liquids are shown