

Thermodynamic Study of Solvents Type Ionic Liquids: Application in the Substitution of Polluted Solvents

Hind Bouafia¹⁺ and Mourad Korichi²

^{1,2}Kasdi Merbah University, Laboratory of Dynamic, Interactions and Reactivity of Systems (DIRE)

Abstract. Ionic Liquids have been classed as alternatives solvents that offer possibilities to switch ordinary chemical processes into clean and green technologies grace to their favorable physicochemical properties, such as their non volatility in the atmosphere. Thermodynamic modeling of the liquid-liquid equilibria is very important for the design, optimization and control of transformations and separations operations. The optimization of the separation process is one of the most important branches in process design. The objective of this work is to use the experimental liquid-liquid equilibria data of ternary systems involving ionic liquids as solvents for the estimation of new interaction parameters of the thermodynamic model UNIFAC. The optimal values of these parameters have been obtained by a calculation program of FORTRAN 90 based on Nelder-Mead's Simplex optimization method. The examination of the results permitted to conclude that the UNIFAC model give better predictions for the 41 studied systems, with root mean square error between experimental and calculated compositions about 2.17 %.

Keywords: Ionic liquids, liquid-liquid equilibria, optimization, interaction parameters, UNIFAC, FORTRAN 90, Nelder-Mead's Simplex method

1. Introduction

Ionic liquids (ILs) have recently been revealed as interesting clean alternatives to classical organic solvents in a wide range of chemical, biochemical, separation and electrochemical applications. Ionic liquids (ILs) are organic salts that are liquid in a temperature range around or below room temperature. They normally consist of an organic cation, the most commonly used being dialkylimidazolium, N-alkylpyridinium and tetraalkylammomium salts, and a polyatomic inorganic anion such as [BF₄], [PF₆], and [NTf₂]. The most important advantage of ILs is their nondetectable vapor pressure, which makes them environmentally benign solvents compared with volatile organic solvents (VOSs). They also show good chemical and thermal stability and can be used at high temperatures. Additionally, the physical-chemical properties of ionic liquids, such as their hydrophobicity, density, viscosity, melting point, polarity, and solvent properties, can be tailored by varying the substitutive group on the cation or the combined anion. Indeed, this feature is a key factor for realizing successful extraction processes because appropriate combinations of the cationic and anionic parts of the solvent can be made [1].

The study of the liquid-liquid equilibrium for systems involving ionic liquids have been made by different works [2-18]. However, just a few studies using group contribution methods like UNIFAC, for the thermodynamic modeling of ternary systems containing ionic liquids as solvents [19, 20].

The aim of this study was to use the experimental liquid-liquid equilibria data of ternary systems with ionic liquids selected from the literature to estimate new interaction parameters of the thermodynamic model UNIFAC between the different functional groups, so we richen the literature by these parameters. The best values of these parameters are exploited to calculate the liquid-liquid equilibrium data for forty-one ternary

⁺ Corresponding author. Tel.: + 21359494683 fax: +21329701043.
E-mail address: bouafia.hind@yahoo.fr

systems within rage temperature of 283.15 K to 348.2 K, summarized in 403 tie-lines. The results are very acceptable, with root mean square error between experimental and calculated compositions about 2.17 %.

2. UNIFAC Method

The UNIFAC equation for the activity coefficient of (molecular) component i is [3]:

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{Combinatorial}} + \underbrace{\ln \gamma_i^R}_{\text{Residual}} \quad (1)$$

In this method, the molecular activity is separated into two parts: combinatorial part provides the contribution due to differences in molecular size and shape, and the residual part provides the contribution due to molecular interactions [3]. For the choice of UNIFAC functional groups, the ionic liquids were divided in two groups, cation and anion; the approach is different from that of Lei et al. and Alevizou et al., who used the imidazolium ring as a functional group [19]. The structural parameters for volume and surface area, R_k and Q_k , for the groups used in this work are shown in Table 1.

For a ternary system the three equations of equilibrium are [3]:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (i = 1,2,3) \quad (2)$$

Here we have equation (2) with four unknowns: x_1^I , x_2^I , x_1^{II} and x_2^{II} . Mole fractions x_3^I and x_3^{II} are not independent because they are constrained by material balances [3]:

$$x_1^I + x_2^I + x_3^I = 1 \quad (3)$$

$$x_1^{II} + x_2^{II} + x_3^{II} = 1 \quad (4)$$

To calculate liquid-liquid equilibria in a ternary system, we need to perform an isothermal flash calculation where we introduce two additional equations and one additional unknown α [3]:

$$z_i = x_i^I \alpha + x_i^{II} (1 - \alpha) \quad (i = 1,2) \quad (5)$$

where z_i is the mole fraction of component i in the feed; α is the mole fraction of the feed that becomes liquid I in equilibrium with liquid II. We do not apply equation (5) to the third component because in addition to the material balance, we also have the overall constraint [3]:

$$z_1 + z_2 + z_3 = 1 \quad (6)$$

At a known temperature and z_1 , z_2 given set, three equations (2) and two equations (5) can be solved simultaneously for five unknowns: x_1^I , x_2^I , x_1^{II} , x_2^{II} and α [3].

Table 1: UNIFAC volume and surface area structural parameters for the groups used.

Fonctionnel groupe k	R_k	Q_k
[CH ₃] [3]	0.9011	0.848
[CH ₂] [3]	0.6744	0.540
[C] [3]	0.2195	0.000
[CH ₂ =CH] [3]	1.3454	1.176
[ACH] [3]	0.5313	0.400
[ACCH ₃] [3]	1.2663	0.968
[ACCH] [3]	0.8121	0.348
[OH] [3]	1.0000	1.200
[CH ₂ O] [3]	0.9183	0.780
[C ₄ H ₄ S] [3]	2.8569	2.140
[BMIM] [19]	6.0334	4.791
[DMIM] ou [MMIM]	4.0102	3.171

[Emim] [19]	4.7280	3.664
[E-2,3dmim]	5.6291	4.512
[PMIM]	5.3807	4.2275
[HMIM] [20]	7.4045	5.782
[EMpy]	5.2993	3.955
[BMpyr]	6.624	6.0904
[3-Mebupy] [19]	6.6481	5.035
[BF ₄] [19]	1.7856	1.494
[DCA]	2.2234	1.844
[EtSO ₄]	3.6647	2.962
[MeSO ₄]	2.8798	2.4
[MP]	2.2151	1.87
[NTf ₂]	5.166	5.262
[TfO] [19]	2.8913	2.411

3. Parameter Estimation

The estimation of UNIFAC interaction parameters are obtained by the minimization of the objective function F , using an isothermal flash calculation executed in the FORTRAN 90. The program based on Nelder-Mead's Simplex method.

$$F = \sum_j^M \sum_i^{N-1} \left\{ (x_{ij}^{I,exp} - x_{ij}^{I,calc})^2 + (x_{ij}^{II,exp} - x_{ij}^{II,calc})^2 \right\} \quad (7)$$

Where M is the number of the tie-lines and N is the number of components. The superscripts

I and II refer to the two liquid phases in equilibrium, while the superscripts 'exp' and 'calc' refer to the experimental and calculated values of the liquid phase composition.

For the evaluation of the accordance between the experimental and calculated compositions in each system, the root mean square error (RMSE), defined in the equation (8) was calculated:

$$RMSE = 100 \sqrt{\frac{\sum_j^M \sum_i^N (x_{ij}^{I,exp} - x_{ij}^{I,calc})^2 + (x_{ij}^{II,exp} - x_{ij}^{II,calc})^2}{2MN}} \quad (8)$$

4. Results and Discussion

Table 2 shows the best values of the UNIFAC interaction parameters estimated by the method mentioned aforetime. Table 3 shows the results of the correlation for the forty-one ternary systems, expressed as deviations between experimental and calculated compositions, according to equation (2). In Table 3 we remark that some values of RMSE are rather elevated (6.22 %, 5.06 %, 5.78 %,.....) comparing with the others. The small values of RMSE are mainly due to the poor predictions of the low mole fractions for the ionic liquid in the alkane rich phase and the aliphatic mole fraction in the ionic liquid rich phase, and the inverse is correct. The Fig. 1-Fig. 3 show the results for two selected systems.

From the obtained deviations between experimental and calculated compositions, we can conclude the reliability of UNIFAC interaction parameters estimated by the Simplex minimization, and the capacity of the UNIFAC method to correlate the liquid-liquid equilibrium data, with global root mean square error about 2.17 % for all 403 tie-lines. These results are considered extremely satisfactory.

Table 2: UNIFAC energy interaction parameters.

m	n	a_{mn} (K)	a_{nm} (K)
[BMIM]	[DCA]	-380.46	-1951.3

[BMIM]	[MeSO ₄]	650.98	-3950.9
[BMIM]	[NTf ₂]	25.909	-1654
[BMIM]	[ACH]	3619.9	-796.19
[BMIM]	[ACCH ₃]	-207.03	1869.4
[BMIM]	[C ₄ H ₄ S]	6250.9	-1052.3
[EMIM]	[EtSO ₄]	-895.94	-614.42
[EMIM]	[NTf ₂]	85.148	-1282.8
[EMIM]	[ACH]	-412.13	-203.75
[EMIM]	[ACCH ₃]	566.73	361.93
[DMIM]	[MP]	1481.7	384.03
[DMIM]	[CH ₃]	480.72	639.35
[DMIM]	[CH ₂]	480.72	639.35
[DMIM]	[ACH]	26.375	1318.6
[DMIM]	[OH]	-94.883	-171.89
[DMIM]	[C ₄ H ₄ S]	-143.99	1504.9
[HMIM]	[NTf ₂]	-776.90	-1363.9
[HMIM]	[TfO]	186.82	-2010.9
[HMIM]	[DCA]	-1133.8	-2054.6
[HMIM]	[ACCH ₃]	-322.91	3925.8
[PMIM]	[NTf ₂]	-535.13	-219.54
[PMIM]	[CH ₃]	5.1848	108.56
[PMIM]	[CH ₂]	5.1848	108.56
[PMIM]	[OH]	-128.41	547.11
[EMpy]	[EtSO ₄]	-5564.3	250.53
[EMpy]	[NTf ₂]	-125.43	80.753
[EMpy]	[CH ₃]	2416.8	2912.4
[EMpy]	[CH ₂]	2416.8	2912.4
[EMpy]	[ACH]	410.11	-314.85
[EMpy]	[ACCH ₃]	248.69	695.34
[E-2,3dmim]	[EtSO ₄]	-1014.0	7503.6
[E-2,3dmim]	[CH ₃]	-134.49	1628.5
[E-2,3dmim]	[CH ₂]	-134.49	1628.5
[E-2,3dmim]	[CH ₂ =CH]	528.68	-179.12
[E-2,3dmim]	[OH]	-275.64	1536.0
[BMpyr]	[NTf ₂]	609.27	-776.45
[BMpyr]	[TfO]	-606.74	-327.75
[BMpyr]	[CH ₃]	214.96	-6.4017
[BMpyr]	[CH ₂]	214.96	-6.4017
[BMpyr]	[ACH]	-104.60	-60.392
[BMpyr]	[ACCH ₃]	-69.932	1758.5
[BMpyr]	[OH]	82.450	-138.50
[3-Mebupy]	[DCA]	-637.71	-3555.6

[DCA]	[CH ₃]	-105.47	-410.50
[DCA]	[CH ₂]	-105.47	-410.50
[DCA]	[ACH]	-577.99	-367.40
[DCA]	[ACCH ₃]	-337.45	-384.85
[DCA]	[ACCH]	-337.45	-384.85
[DCA]	[OH]	-135.31	-2099.7
[NTf ₂]	[CH ₃]	53.834	72.763
[NTf ₂]	[CH ₂]	53.834	72.763
[NTf ₂]	[ACH]	21.535	42.249
[NTf ₂]	[ACCH ₃]	79.335	6821.8
[NTf ₂]	[OH]	209.28	51.420
[EtSO ₄]	[CH ₃]	99.536	205.69
[EtSO ₄]	[CH ₂]	99.536	205.69
[EtSO ₄]	[C]	99.536	205.69
[EtSO ₄]	[CH ₂ O]	-745.57	4637.9
[EtSO ₄]	[ACH]	1909.6	3903.3
[EtSO ₄]	[ACCH ₃]	197.94	2118.8
[EtSO ₄]	[CH ₂ =CH]	533.02	239.27
[EtSO ₄]	[OH]	-4.8721	-1174.8
[MeSO ₄]	[CH ₃]	-449.52	1820.1
[MeSO ₄]	[CH ₂]	-449.52	1820.1
[MeSO ₄]	[ACH]	-503.58	3336.1
[MeSO ₄]	[ACCH ₃]	-9.1882	3744.1
[MeSO ₄]	[OH]	1566.7	16.301
[MP]	[CH ₃]	118.68	300.03
[MP]	[CH ₂]	118.68	300.03
[MP]	[ACH]	-93.537	6464.1
[MP]	[OH]	79.320	161.26
[MP]	[C ₄ H ₄ S]	149.90	2419.2
[TfO]	[ACH]	-289.95	21153.4
[TfO]	[ACCH ₃]	298.89	1714.3

Table 3: UNIFAC correlation results for LLE.

Systems	Tie-lines	T (°C)	Reference	RMSE (%)
Benzene + n-heptane + [BMIM][BF ₄]	8	25	[2]	5.06
Benzene + n-heptane + [DMIM][MP]	8	25	[2]	0.86
Thiophene + n-heptane + [BMIM][BF ₄]	9	25	[2]	2.32
Thiophene + n-heptane + [DMIM][MP]	9	25	[2]	1.20
1-propanol + n-heptane + [DMIM][MP]	8	25	[2]	0.39
1-pentanol + n-heptane + [DMIM][MP]	5	25	[2]	3.58
Ethanol + Hexene + [E-2,3dmim] [EtSO ₄]	8	40	[4]	0.53
Ethanol + Heptene + [E-2,3dmim] [EtSO ₄]	8	40	[4]	5.78

Ethanol + TAEE + [Emim][EtSO ₄]	12	25	[5]	0.31
Ethanol + Heptane + [Bmim][MeSO ₄]	16	25	[6]	4.54
Toluene + Heptane + [Emim][EtSO ₄]	20	40.05	[7]	0.99
Toluene + Heptane + [Emim][EtSO ₄]	20	75.05	[7]	1.70
Benzene + Heptane + [BMpyr][NTf ₂]	17	25	[8]	0.71
Toluene + Heptane + [3-Mebupy][DCA]	7	30	[9]	1.55
Toluene + Heptane + [3-Mebupy][DCA]	7	55	[9]	4.51
Toluene + Heptane + [BMIM][DCA]	7	30	[9]	0.52
Toluene + Heptane + [BMIM][DCA]	7	55	[9]	2.21
Benzene + Hexane + [3-Mebupy][DCA]	11	30	[9]	1.12
Benzene + Hexane + [3-Mebupy][DCA]	10	55	[9]	2.14
p-xylene + Hexane + [3-Mebupy][DCA]	11	30	[9]	0.50
p-xylene + Hexane + [3-Mebupy][DCA]	11	55	[9]	1.86
Cumene + Nonane + [3-Mebupy][DCA]	11	30	[9]	3.22
Cumene + Nonane + [3-Mebupy][DCA]	11	55	[9]	4.53
Benzene + Octane + [EMpy][EtSO ₄]	9	10	[10]	0.50
Benzene + Octane + [EMpy][EtSO ₄]	8	25	[10]	1.09
Benzene + Nonane + [EMpy][EtSO ₄]	9	10	[10]	1.15
Benzene + Nonane + [EMpy][EtSO ₄]	9	25	[10]	0.30
Toluene + Cyclohexane + [BMim][MeSO ₄]	9	25	[11]	6.22
Toluene + Heptane + [BMpyr][TfO]	10	25	[12]	1.44
Toluene + Cyclohexane + [BMpyr][TfO]	10	25	[12]	1.55
Toluene + Heptane + [HMim][NTf ₂]	10	25	[13]	3.52
Ethanol + Heptane + [EMim][NTf ₂]	8	25	[14]	3.16
Ethanol + Heptane + [PMim][NTf ₂]	8	25	[14]	0.32
Ethanol + Heptane + [BMim][NTf ₂]	9	25	[14]	3.42
Ethanol + Heptane + [HMim][NTf ₂]	8	25	[14]	0.64
Ethanol + Hexane + [BMpyr][NTf ₂]	8	25	[15]	3.69
Ethanol + Hexane + [BMpyr][TfO]	8	25	[15]	1.43
Toluene + Heptane + [EMim][NTf ₂]	10	25	[16]	1.06
Toluene + Heptane + [EMpy][NTf ₂]	10	25	[16]	3.50
Ethanol + Hexane + [HMim][TfO]	9	25	[17]	5.61
Ethanol + Hexane + [HMim][DCA]	10	25	[17]	0.61
Global (403 tie-lines)				

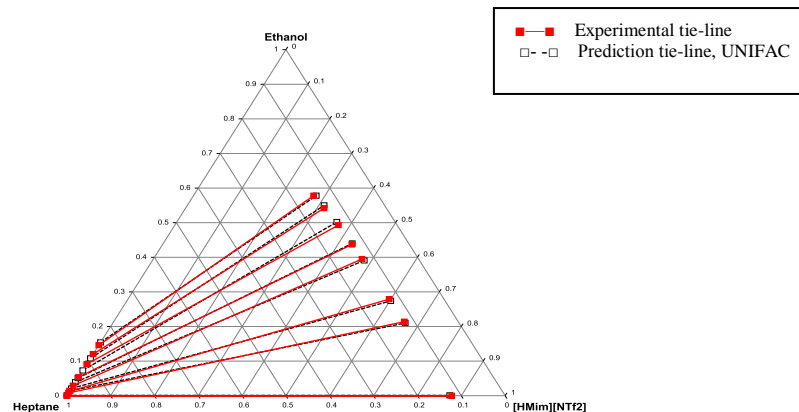


Fig. 1: Liquid-liquid equilibria for the Ethanol + Heptane + [HMIM][NTf₂] system at 298.15 K.

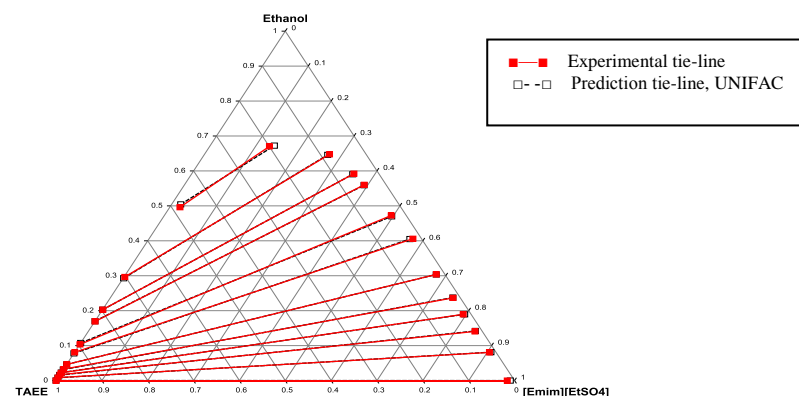


Fig. 2: Liquid-liquid equilibria for the Ethanol + TAEE + [Emim][EtSO₄] system at 298.15 K.

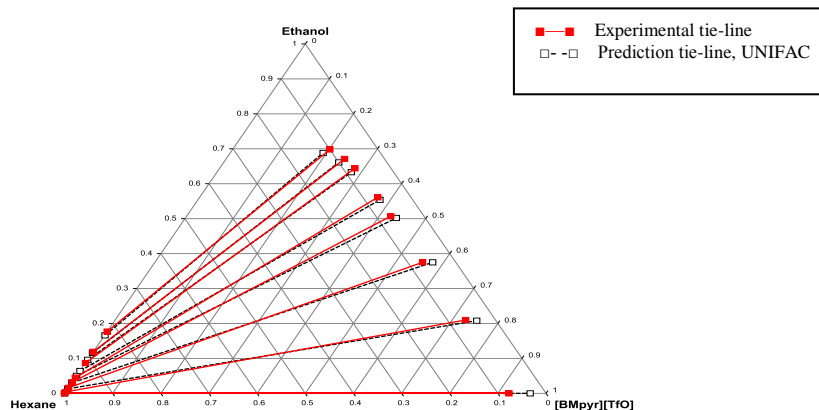


Fig. 3: Liquid-liquid equilibria for the Ethanol + Hexane + [BMpyr][TfO] system at 298.15 K

5. Conclusions

Ionic liquids present a new generation of solvents, less toxic, non inflammable and less pollute. The experimental liquid-liquid equilibrium data for forty-one systems involving different ionic liquids were exploited to estimate the UNIFAC energy interaction parameters using Nelder-Mead's Simplex method where we developed a program implemented in FORTRAN 90. With these parameters, the experimental data were correlated and the results show that the calculated compositions are in good according with the experimental compositions. This work assured the capacity of UNIFAC method to correlate liquid-liquid equilibrium of systems using the estimated energy interaction parameters between the functional groups. The results are extremely satisfactory, with deviations in phase compositions of 2.17%.

6. Acknowledgements

We thank the University of Kasdi Merbah in Ouargla, Algeria; we also thank the reviewers for their helpful suggestions.

7. References

- [1] F. J. Hernandez-Fernandez, A. P. de los Rios, D. Gomez, M. Rubio, G. Villora. *AICHE J.* 2010, **56**: 1213-1217.
- [2] A. L. Revelli. *Etude thermodynamique des liquides ioniques: Applications à la protection de l'Environnement*. Inst. Nat. Polytech, Lorraine, 2010.
- [3] B. E. Poling, J. M. Prausnitz, J. P. O'connell. *Properties of gases and liquids*. Fifth edition, The McGraw-Hill Companies, Inc. USA, 2001.
- [4] T. Banerjee, K. K. Verma, A. Khanna. *AICHE J.* 2008, **54**: 1874-1885.
- [5] A. Arce, O. Rodriguez, A. Soto. *Chem.Eng. Sci.* 2006, **61**: 6929 – 6935.
- [6] A. B. Pereiro, A. Rodriguez. *Separation and Purification Technology J.* 2008, **62**: 733–738.
- [7] G. W. Meindersma. *Extraction of Aromatics from Naphtha with Ionic Liquids*; University of Twente, The Netherlands, 2005.
- [8] A. B. Pereiro, A. Rodriguez. *AICHE J.* 2009, **56**: 381-386.
- [9] A. R. Hansmeier. *Ionic Liquids as Alternative Solvents for Aromatics Extraction*, Technische Universiteit Eindhoven, 2010.
- [10] E. J. Gonzalez, N. Calvar, E. Gomez, A. Dominguez. *J. Chem. Thermodynamics.* 2010, **42**: 104–109.
- [11] I. Dominguez, N. Calvar, E. Gomez, A. Dominguez. *J. Chem. Thermodynamics.* 2011, **43**: 705–710.
- [12] R. G. Seoane, E. Gomez, E. J. Gonzalez, A. Dominguez. *J. Chem. Thermodynamics .* 2012, **47**: 402–407.
- [13] S. Corderi, E. J. Gonzalez, N. Calvar, A. Dominguez. *J. Chem. Thermodynamics.* 2012, **53**: 60–66.
- [14] R. G. Seoane, E. J. Gonzalez, B. Gonzalez. *J. Chem. Thermodynamics.* 2012, **53**: 152–157.
- [15] S. Corderi, B. Gonzalez. *J. Chem. Thermodynamics.* 2012, **55**: 138–143.
- [16] S. Corderia, N. Calvarb, E. Gomeza, A. Domingueza. *Fluid Phase Equilibria.* 2012, **315**: 46–52.
- [17] S. Corderia, B. Gonzaleza, N. Calvarb, E. Gomeza. *Fluid Phase Equilibria.* 2013, **337**: 11– 17.
- [18] K. H. Sumon. *extraction of aromatics using green solvents based on ionic liquids*, King fahd university of petroleum and minerals, Dhahran, Saudi Arabia, 2005.
- [19] R. S. Santiago, G. R. Santos, M. Aznar. *Fluid Phase Equilibrium.* 2010, **295**: 93-97.
- [20] R. S. Santiago, M. Aznar. *Fluid Phase Equilibrium.* 2011, 303: 111-114.