Correlation of liquid–liquid equilibria of non-ideal binary systems using the non-random, two-liquid model

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Abstract: The non-random, two-liquid (NRTL) model with three different forms of temperature dependant parameters was used to correlate the liquid––liquid equilibrium data for systems of alcohols with alkanes, and alcohols with two ionic liquids: 1–butyl-2,3-dimethylimidazolium tetrafluoroborate ([bmmim][BF4]) and 1-butyl-3-ethylimidazolium tetrafluoroborate ([beim][BF4]). Different temperature dependences of the NRTL parameters were tested on thirteen literature experimental liquid–liquid equilibrium data for binary systems.

Keywords: liquid – liquid equilibria, NRTL model, optimization, ionic liquids, modeling.

INTRODUCTION

The liquid–liquid equilibria (LLE) established in non-ideal mixtures with strong positive deviations from the Raoult Law is essential for the design and development of separation processes. Liquid–liquid solubility data are valuable in studies of the applicability of activity coefficient models. For accurate process and equipment modeling, development and design, it is important to have a reliable thermodynamic model for a good system description. Ionic liquids (ILs) have become popular in recent years as possible "green" replacements for conventional organic, volatile and toxic solvents. Their unique thermophysical properties, mainly a very low vapor pressure, assign them in the group of "green" solvents. Ionic liquids are liquid salts based on large organic cations and small anions that determine their physicochemical properties. Potential applications that

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have been reported in the literature,[1] which include using ILs as reaction media, heat transfer fluids, and potential solvents for liquid extraction processes, *etc*.

Activity coefficient models, such as UNIQUAC,[2] UNIFAC[3] and NRTL[4] models, have already been successfully used for the correlation and prediction of the vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE) and other thermodynamic properties of very complex systems.[5–7]

In this paper, the applicability of the NRTL model on selected mixtures of alcohols with alkanes,[8] and two ionic liquids, *i.e.*, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bmmim][BF4][9] and 1-butyl-3-ethylimidazolium tetrafluoroborate [beim][BF4],[10] were examined. NRTL (non-random two-liquid model) is an activity coefficient model that correlates the activity coefficients γ_i of a component *i* with its mole fractions x_i in the liquid phase. It is applicable to soluble and partially soluble liquids, multicomponent vapor–liquid, liquid–liquid, and vapor–liquid–liquid equilibria.

MODELING OF LIQUID–LIQUID EQUILIBRIA

Thermodynamic criteria for liquid–liquid equilibria could be given as:

$$\gamma_i^{I} x_i^{I} = \gamma_i^{II} x_i^{II} \quad , \quad i = 1, 2, \cdots, m \tag{1}$$

where γ_i^{I} is the activity coefficient of component *i* in phase I, γ_i^{II} is the activity coefficient of component *i* in phase II, x_i^{I} is a mole fraction of component *i* in phase I, x_i^{II} is the mole fraction of component *i* in phase II and *m* is the number of components in a mixture.

Since the NRTL model[4] has already been tested mainly on non-ideal mixtures with alkanes,[11] in this paper, the applicability of this model was extended to alcohol + ionic liquids binary systems. The NRTL model is defined as follow:

$$\frac{G^{E}}{RT} = x_1 x_2 \left(\frac{\tau_{12} G_{12}}{x_2 + G_{12} x_1} + \frac{\tau_{21} G_{21}}{x_1 + G_{21} x_2} \right) \tag{2}$$

The activity coefficients *γ* for binary systems are expressed with following equations:

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{12} G_{12}}{\left(x_2 + G_{12} x_1 \right)^2} + \tau_{21} \left(\frac{G_{21}}{x_1 + G_{21} x_2} \right)^2 \right] \tag{3}$$

$$\ln \gamma_2 = x_1^2 \left[\frac{\tau_{21} G_{21}}{\left(x_1 + G_{21} x_2 \right)^2} + \tau_{12} \left(\frac{G_{12}}{x_2 + G_{12} x_1} \right)^2 \right] \tag{4}$$

The binary interaction parameters are defined as follows:

$$G_{12} = \exp\left(-\alpha_{12} \tau_{12}\right) ; \ \tau_{12} = \frac{\Delta g_{12}}{RT} \tag{5}$$

$$G_{21} = \exp\left(-\alpha_{21} \tau_{21}\right) ; \ \tau_{21} = \frac{\Delta g_{21}}{RT} \tag{6}$$

$$G_{12} \neq G_{21}, \ \alpha_{12} = \alpha_{21}$$

where α is the NRTL excess free energy non-randomness parameter, T is the temperature and R is the gas constant. Parameters Δg_{12} and Δg_{21} are NRTL excess free energy model binary interaction temperature dependent parameters.

Since, as shown previously,[12-14] temperature has strong influence on excess properties or equilibria calculations, thus several different forms of temperature dependence for the parameters Δg_{12} and Δg_{21} were introduced:

Form I

$$\Delta g_{12} = A_{12} + B_{12}T$$
$$\Delta g_{21} = A_{21} + B_{21}T \tag{7}$$

Form II

$$\Delta g_{12} = A_{12} + B_{12}T + C_{12}T^2$$
$$\Delta g_{21} = A_{21} + B_{21}T + C_{21}T^2 \tag{8}$$

Form III

$$\Delta g_{12} = A_{12} + B_{12}T + C_{12}/T^2$$
$$\Delta g_{21} = A_{21} + B_{21}T + C_{21}/T^2 \tag{9}$$

The corresponding sets of binary interaction parameters (A_{ij}, B_{ij} and C_{ij} in Eq. (7)–(9)) were determined by minimizing the objective function (Eq. (10)) using the Monte Carlo method with a linear congruent generator of pseudorandom numbers:[15]

$$F_{obj} = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\gamma_{j,i}^{I} x_{j,i}^{I} - \gamma_{j,i}^{II} x_{j,i}^{II} \right)^2 \to \min \tag{10}$$

where n is the number of experimental data.

With the obtained optimized parameters, using Eq. (1), the mole fractions $x_{1,\text{cal}}^{'}$ and $x_{1,\text{cal}}^{"}$ were calculated by the Wegstein method[16] over the entire range of investigated temperatures T.

RESULTS AND DISCUSSION

Experimental data at different temperatures were taken from the literature.[8–10] According to the results of preliminary investigations, the non-randomness parameter α_{12} was set as the constant value of 0.3 for all the selected binary systems.

A deviation of the calculated liquid composition in both liquid phases from the experimental values, $x_{1,i,\text{exp}}^{I}$ and $x_{1,i,\text{exp}}^{II}$, is expressed as an absolute average deviations $\Delta(x)$, and an absolute average percent deviation $PD(x)$, for each binary system:

$$\Delta(x) = \left(\frac{100}{2n} \right) \sum \left[\left| \left(x_{1,i,\text{exp}}^{I} - x_{1,i,\text{cal}}^{I} \right) \right| + \left| \left(x_{1,i,\text{exp}}^{II} - x_{1,i,\text{cal}}^{II} \right) \right| \right] \tag{11}$$

$$PD(x), \% = \left(\frac{100}{2n} \right) \sum_{i=1}^{n} \left\{ \left| \left(x_{1,i,\text{exp}}^{I} - x_{1,i,\text{cal}}^{I} \right) / x_{1,i,\text{exp}}^{I} \right| + \right.$$
$$\left. + \left| \left(x_{1,i,\text{exp}}^{II} - x_{1,i,\text{cal}}^{II} \right) / x_{1,i,\text{exp}}^{II} \right| \right\} \tag{12}$$

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TABLE I. Results of LLE correlation of selected binary systems

System	Form	A_{12}	B_{12} / K	C_{12} / K²	A_{21}	B_{21} / K	C_{21} / K²	Δx	$PD(x)$ / %
methanol(1)+ heptane(2)	I	5087.152	-0.4564683	–	19068.33	-51.82681	–	1.1	2.1
	II	5373.153	-11.85111	3.44×10^{-2}	17946.13	-37.81441	-3.41×10^{-2}	1.0	1.9
	III	6582.356	-5.347746	8.63×10^{-5}	17504.41	-46.74835	-5.84×10^{-2}	1.4	2.5
methanol(1)+ decane(2)	I	9741.815	-8.631523	–	17998.42	-45.65529	–	0.9	1.7
	II	10398.24	-12.24016	4.71×10^{-3}	17612.17	-43.87271	-1.80×10^{-3}	1.0	1.9
	III	10653.80	-11.54547	3.06×10^{-4}	17418.83	-43.77454	-9.46×10^{-2}	1.0	1.9
methanol(1)+ nonane(2)	I	9819.706	-10.32724	–	17513.98	-45.01369	–	0.8	1.8
	II	10649.05	-15.72755	8.61×10^{-3}	17674.68	-44.15396	-4.23×10^{-3}	1.1	2.1
	III	9869.354	-10.53669	4.10×10^{-2}	17492.56	-44.91943	-7.95×10^{-2}	1.2	2.3
methanol(1)+ octane(2)	I	6089.4	-1.358492	–	19274.21	-51.37226	–	0.4	0.7
	II	7095.347	-6.992282	7.21×10^{-3}	16934.27	-38.08940	-1.80×10^{-2}	0.9	1.7
	III	6647.037	-3.251477	2.42×10^{-4}	17732.54	-46.33763	7.07×10^{-5}	1.2	2.3
1-propanol(1)+ bmimBF4(2)	I	30157.50	-59.87851	–	27303.17	-92.20162	–	1.5	1.8
	II	32523.29	-74.07758	2.04×10^{-2}	27863.01	-95.27888	4.48×10^{-3}	1.4	1.7
	III	31043.13	-62.86951	4.77×10^{-1}	26275.95	-88.77695	5.25×10^{-2}	1.7	2.1
2-propanol(1)+ bmimBF4(2)	I	32575.63	-62.92048	–	32172.99	-109.8133	–	1.5	1.8
	II	34798.18	-73.84294	1.17×10^{-2}	31146.13	-106.5383	4.03×10^{-4}	1.7	1.9
	III	33149.74	-64.75449	-7.39×10^{-2}	31826.74	-108.7165	3.63×10^{-1}	1.6	1.8
1-butanol(1)+ bmimBF4(2)	I	34239.07	-69.87634	–	37660.18	-117.7754	–	1.8	2.3
	II	35268.58	-73.24624	7.59×10^{-4}	36517.72	-114.4179	1.45×10^{-4}	1.6	2.0
	III	35934.61	-75.05195	3.81×10^{-4}	35839.66	-112.2911	-7.64×10^{-2}	1.7	2.1
1-pentanol(1)+ bmimBF4(2)	I	53557.86	-126.0032	–	26890.21	-78.81150	–	1.5	2.2
	II	51991.45	-121.2727	6.38×10^{-4}	37356.00	-140.2646	8.97×10^{-2}	1.6	2.2
	III	53454.68	-125.7185	5.62×10^{-5}	26914.41	-78.82802	3.22×10^{-4}	1.6	2.3

TABLE I. Continued

System	Form	A_{12}	B_{12} / K	C_{12} / K^2	A_{21}	B_{21} / K	C_{21} / K^2	Δx	$PD(x)$ / %
1-hexanol(1)+	I	49936.84	-107.3189	–	28338.00	-78.08791	–	7.0	9.1
bmmimBF4(2)	II	51858.6	-112.6044	7.46×10^{-5}	29127.44	-80.50168	1.37×10^{-4}	7.7	9.8
	III	51096.18	-110.7159	1.16×10^{-2}	29527.43	-81.41587	8.71×10^{-2}	7.8	10.0
1-propanol(1)+	I	59010.53	-159.9736	–	131588.5	-45.58663	–	9.3	12.7
[beim][BF4](2)	II	44997.4	-115.0678	9.47×10^{-5}	76522.65	24.14385	1.92×10^{-4}	9.8	13.2
	III	55920.75	-149.9795	8.98×10^{-4}	60180.19	61.61889	2.86×10^{-4}	9.6	13.0
1-butanol(1)+	I	48474.45	-119.7651	–	69304.97	-32.84957	–	6.8	9.3
[beim][BF4](2)	II	48229.33	-119..1960	8.00×10^{-4}	69885.73	-31.36758	3.02×10^{-4}	6.9	9.5
	III	49631.26	-123.4535	5.36×10^{-4}	69835.64	-43.50067	8.09×10^{-4}	6.4	8.9
1-pentanol(1)+	I	63974.78	-159.6538	–	99311.70	-39.39230	–	4.5	6.4
[beim][BF4](2)	II	77238.06	-199.6191	1.20×10^{-3}	116575.8	-32.10275	6.07×10^{-3}	5.5	7.8
	III	77454.04	-199.9958	3.77×10^{-3}	12815.49	-31.30017	7.97×10^{-3}	5.6	7.9
1-hexanol(1)+	I	45819.51	-101.8396	–	28302.13	-80.91595	–	2.1	2.8
[beim][BF4](2)	II	44934.4	-103.5405	1.20×10^{-2}	34551.99	-108.6523	2.78×10^{-2}	1.4	1.9
	III	41762.36	-89.93496	6.12×10^{-2}	31163.7	-89.36466	2.70×10^{-2}	1.5	2.1

The results for the applied models are presented in Table I. The obtained results are given as the absolute average deviations $\Delta(x)$ and the absolute average percent deviations $PD(x)$. The results are in good agreement with the selected experimental data. Graphical representations of the experimental data and the calculated results for all the suggested temperature forms of parameters Δg_{12} and
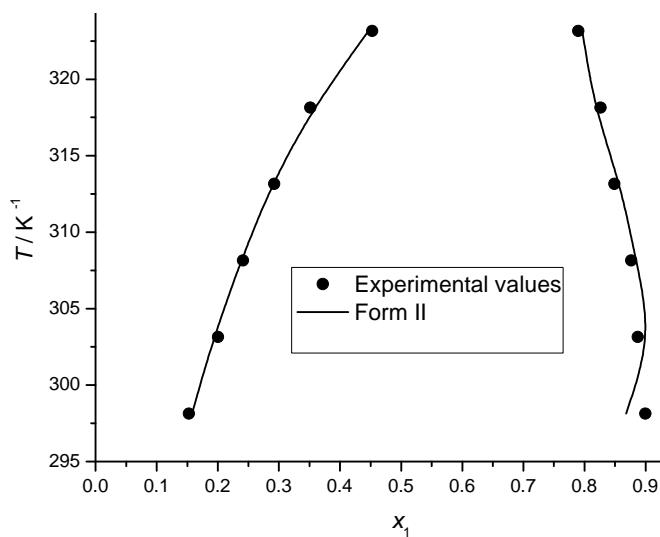

Fig. 1. Phase diagram – Experimental and calculated values of the LLE binary system methanol (1) + heptane (2).
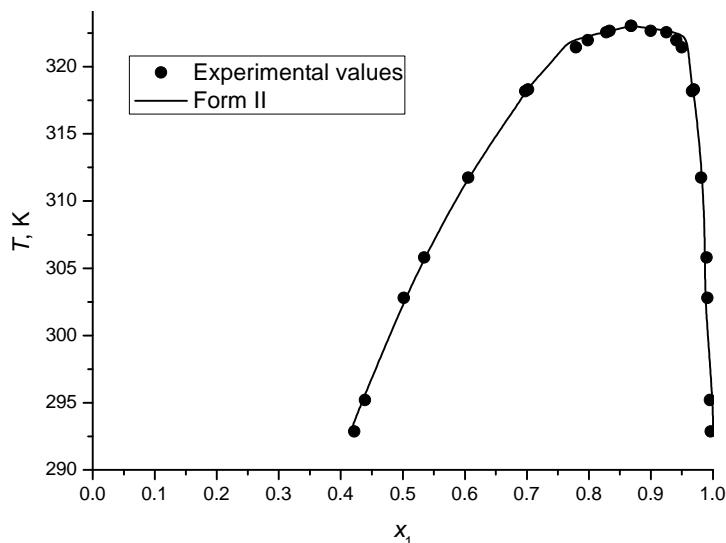
Fig. 2. Phase diagram – Experimental and calculated values of the LLE binary system 1-propanol (1) + bmmim[BF4] (2).

Δg_{21} for the methanol + heptane, 1-propanol + [bmmim][BF4] and 1-pentanol + + [bmmim][BF4] binary systems are shown in Figs. 1–3, respectively. For the binary systems of alcohols with alkanes, all the applied forms of temperature dependent parameters gave very good results, with deviations of about 2 %, as is given in Table I. For the binary systems of alcohols with the ionic liquid 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bmmim][BF4], as could be seen from Table I, the deviations in the composition calculations are very good, up to 2 %, except for the system with 1-hexanol for which the deviation is higher, up to 10 %, for all forms. The presented deviations rise for all suggested temperature forms with increasing number of carbon atoms. The best result obtained for the alcohol and ionic liquids mixtures was $\Delta(x) = 1.4$ for system 1-propanol + + bmimm[BF4]. For binary systems of alcohols with ionic liquid 1-butyl-3-ethyl-imidazolium tetrafluoroborate [beim][BF4], the deviations were higher, up to 13 % and decrease for all the investigated temperature relationships with increasing number of carbon atoms.
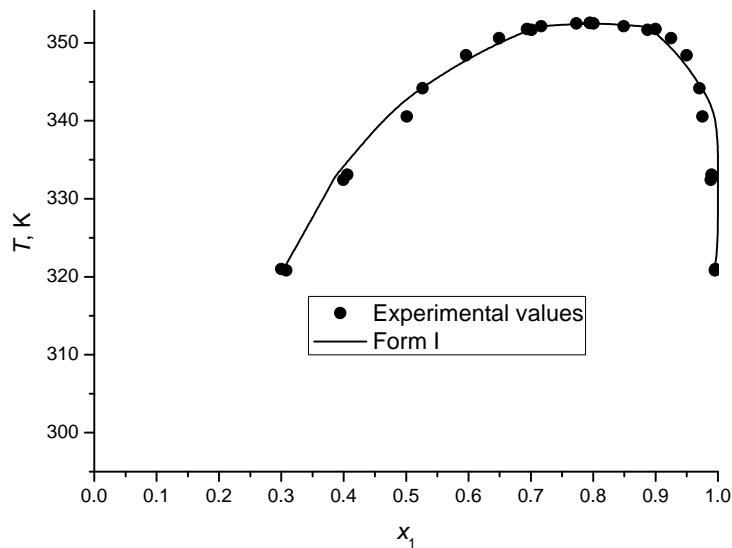

Fig. 3. Phase diagram – Experimental and calculated values of the LLE binary system 1-pentanol (1) + bmmim[BF4] (2).

CONCLUSIONS

Liquid–liquid equilibrium data for thirteen binary systems including alcohols, alkanes, and two ionic liquids at different temperatures were correlated by the NRTL model with three different temperature dependences of the parameters Δg_{12} and Δg_{21}. All three forms of temperature dependent parameters could reproduce most accurately the experimental mutual solubility for all mixtures, with similar results and overall deviations less than 3 %.

ИЗВОД

КОРЕЛИСАЊЕ РАВНОТЕЖЕ ТЕЧНО–ТЕЧНО НЕИДЕАЛНИХ БИНАРНИХ СИСТЕМА ПОМОЋУ NRTL МОДЕЛА

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NRTL модел са три различита температурно зависна параметра коришћен је за коре-лисање равнотеже течно–течно за бинарне системе алкохола са алканима, као и алко-хола са две јонске течности: 1–butyl-2,3-dimethylimidazolium tetrafluoroborate ([bmmim] [BF4]) и 1-butyl-3-ethylimidazolium tetrafluoroborate ([beim][BF4]). У раду су тестиране три различите форме температурне зависности параметара NRTL модела. Равнотежа течност–течност је моделована на тринаест бинарних система. Код свих система су добијени веома задовољавајући резултати са средњим грешкама око 3 %, коришћењем све три форме температурне зависности.

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