



Modeling of single- and multi-stage extraction in the system of water, acetone, butanol, ethanol and ionic liquid



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ABSTRACT

This paper investigates liquid-liquid equilibrium (LLE) in the mixture of acetone, butanol, ethanol (ABE) and water in combination with three hydrophobic ionic liquids:

1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf₂N],
1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF₆];
and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide [bmp][Tf₂N].

To model the LLE, the non-random two-liquid (NRTL) equation was used. The experimental data were taken from the cited work of Kamiński et al. (2014), where the unknown equation parameters had been determined with the help of Matlab programming. In this work, however, Aspen Plus™ software was employed as it readily facilitates further simulations of the extraction step. Different yet similarly accurate sets of the NRTL parameters were obtained. After the model formulation, single-stage and multi-stage extraction processes were simulated and examined in terms of ABE recovery effects.

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1. Introduction

n-Butanol is a very important intermediate for many chemical processes [1–3] and a promising gasoline alternative [4–7]. Currently, butanol is synthesized mostly via petrochemical routes [8,9]; however, the oldest production method, reaching back to the beginning of the 20th century, is based on the biological conversion of organic substrate. This traditional process, termed Acetone-Butanol-Ethanol (ABE) fermentation, was relinquished in the 1950s and early 1960s [10–12] but nowadays there are worldwide tendencies to bring it back to operation [13–17] and liquid-liquid extraction is considered to be one of the most favorable methods of butanol recovery from dilute fermentation broths [18–23].

To design the extraction unit, one needs an experimentally validated model of the thermodynamic equilibrium between the phases containing all components of the feed solution and the extracting agent. Several semi-empirical mathematical models can be used for data correlation; nevertheless, the so-called local composition models, i.e. NRTL and UNIQUAC, are the most popular.

Often, the NRTL model shows a little higher degree of accuracy [24–29]. There are many examples of successful application of the NRTL equation in characterizing liquid-liquid systems containing water as well as uncommon organic substances such as ionic liquids [26,27,29–37]; nonetheless, usually ternary systems are studied.

This article discusses modeling liquid-liquid extraction of acetone, *n*-butanol and ethanol from quaternary aqueous solutions (imitating the fermentation broth) with selected ionic liquids, i.e.

1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [bmim][Tf₂N],
1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF₆]
and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide [bmp][Tf₂N],

which was accomplished by means of the NRTL equation, chosen because of its confirmed accuracy and availability of parameters identifying binary interactions between the common constituents of the above-mentioned systems, i.e. acetone, butanol, ethanol and water.

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The related experimental equilibrium data can be found in our previous work [38] where a different optimization and calculation procedure was proposed (based on Matlab programming) and the main focus put on verifying the idea of utilizing the NRTL equation to accurately predict single-stage equilibria in the investigated quinary systems.

This work, however, concentrates mainly on the performance of the respective ionic liquids and the possibility of simulating the extraction process, which is of considerable practical importance. For the purpose of simulation, the Aspen Plus™ software was employed. The unknown NRTL parameters, defining the interactions between the ionic liquids and the rest of the mixture components (i.e. acetone, butanol, ethanol and water), were determined using the experimental data taken from Ref. [38] and further used to analyze practical aspects of single- and multi-stage extraction.

2. Results and discussion

2.1. Calculation of NRTL parameters

The following form of the NRTL equation, defining the activity coefficient γ_i of component i in an n -component liquid phase, was used while performing calculations with Aspen Plus:

$$\ln \gamma_i = \frac{\sum_{j=1}^n x_j \tau_{ji} G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^n x_m \tau_{mj} G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right) \quad (1)$$

In Eq. (1), x stands for mole fractions of the respective components in the liquid phase concerned while parameters G and τ may be calculated as:

$$G_{ij} = \exp(-c_{ij} \tau_{ij}) \quad (2)$$

$$\tau_{ij} = a_{ij} + b_{ij}/T = \frac{\Delta g_{ij}}{RT} \quad (3)$$

$$a_{ii}, b_{ii}, c_{ii} = 0 \quad \tau_{ii} = 0 \quad G_{ii} = 1 \quad (4)$$

The value of τ involves the temperature dependence of binary interactions between species i and j , where Δg_{ij} defines the energies of interaction between molecule pairs, R is the universal gas constant and T is the absolute temperature.

Adjustable parameters a , b and c , known for the common constituents of the mixture, i.e. water, acetone, butanol and ethanol, are available in the Aspen Plus database and presented in the work of Kamiński et al. [38]. The unknown parameters related to the ionic liquids (Tables 1–3) were estimated using the Aspen Plus built-in *Britt-Luecke* optimization algorithm. Following the recommendations of Renon & Prausnitz [39] and Simoni et al. [40], the symmetrical parameter c was calculated within 0.2 and 0.3 limits. The

Table 1
NRTL parameters estimated for [bmim][Tf₂N].

Component i	[bmim][Tf ₂ N]	[bmim][Tf ₂ N]	[bmim][Tf ₂ N]	[bmim][Tf ₂ N]
Component j	Acetone	Butanol	Ethanol	Water
a_{ij}	4.8058	7.3943	-0.5244	-1.9696
a_{ji}	-11.0308	-1.6831	-11.0784	6.9062
b_{ij}	-2072.296	-2624.412	-109.335	517.123
b_{ji}	3680.375	661.821	4322.628	347.293
c_{ij}	0.300	0.300	0.300	0.200

Table 2
NRTL parameters estimated for [hmim][PF₆].

Component i	[hmim][PF ₆]	[hmim][PF ₆]	[hmim][PF ₆]	[hmim][PF ₆]
Component j	Acetone	Butanol	Ethanol	Water
a_{ij}	-0.8900	7.6118	-4.9364	-3.2688
a_{ji}	-1.7091	-3.1650	-1.0910	5.7463
b_{ij}	-262.550	-2472.853	1390.291	935.437
b_{ji}	843.386	1080.740	1394.274	581.816
c_{ij}	0.300	0.300	0.300	0.200

Table 3
NRTL parameters estimated for [bmp][Tf₂N].

Component i	[bmp][Tf ₂ N]	[bmp][Tf ₂ N]	[bmp][Tf ₂ N]	[bmp][Tf ₂ N]
Component j	Acetone	Butanol	Ethanol	Water
a_{ij}	-0.4630	5.9298	-1.5873	-2.4432
a_{ji}	-1.0350	-0.7116	-4.6865	7.7811
b_{ij}	-422.834	-2124.385	291.952	764.513
b_{ji}	636.225	385.920	2324.060	11.760
c_{ij}	0.300	0.300	0.300	0.214

explanation for such an approach is given in Ref. [38].

The resulting values of parameter c are consistent with the assumptions of Simoni et al. [40], i.e. they are equal to 0.3 for apparently miscible binaries (ionic liquid + ABE) and 0.2 for binaries manifesting a miscibility gap (ionic liquid + water). A moderate exception has been observed in relation to the interactions involving [bmp][Tf₂N] and water (Table 3). Still, the value of c is close to 0.2; therefore, it proves the principle rather than contradicts it.

It should be noted that the NRTL parameters estimated with the help of Aspen Plus are different from those calculated using Matlab software and given in Ref. [38]; nevertheless, they provide similar results when predicting the single-stage equilibrium compositions in the analyzed systems. It suggests that there exist equivalent sets of the adjustable NRTL parameters, depending on the accepted optimization method and the optimized objective function, which in the systems under consideration is a function of 20 variables. The error values presented in section 3.2 are comparable to the values calculated with Matlab [38]; however, Aspen Plus enables subsequent simulations of the extraction process.

2.2. Model validation

The proposed procedure was first tested on the equilibrium data used to estimate the NRTL equation parameters and then validated in a way similar to that described in Ref. [38]. For this purpose, two additional sets of experimental data (also available in Ref. [38]) were used (81 extraction experiments performed with [hmim][PF₆] and 45 experiments performed with [bmim][Tf₂N]). To imitate the experimental setup, a mixer-settler unit equivalent to one theoretical stage was simulated with Aspen Plus. The single-stage equilibrium compositions of the raffinate and extract were predicted using the experimental feed and extractant amounts, feed compositions and temperature as the input quantities.

The level of agreement between the experimental and predicted (approximated) compositions of both phases at equilibrium was assessed by calculating the root-mean-square errors, given by Eqs. (5) and (6), and relative percentage errors, given by Eqs. (7) and (8):

$$RMSE_{Ke} = \sqrt{\frac{\sum_{i=1}^p (w_{Kei}^{exp} - w_{Kei}^{app})^2}{p}} \quad (5)$$

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