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The inclusion of organic acids dissociation in the prediction of liquid-liquid equilibrium data

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ABSTRACT

Advances in thermodynamic equilibrium have led to the recent development of binary, ternary and quaternary systems including electrolytes. However, a precise determination of phase equilibrium must consider the physical-chemical aspects of the components that will can to take place in a mixture. A solute is liable to dissociate hence the need to take this consideration into account. The chosen organic acids have attracted much attention in the research works but unfortunately, their dissociation into the aqueous phase has not been taken into the calculation of phase equilibrium. The present research work focuses on the development of the calculation of the phase equilibrium methods by including the dissociation of the chosen organic acids, for predicting the liquid-liquid equilibrium (LLE) data from the binary parameters for various ternary systems composed of {water-phosphoric acid-methylisobutylketone},{water-acetic acid-cumene},{water-propionic acid-cumene},{water-formic acid-isoamyl acetate} and {water-butyric acid-isoamyl acetate} at 298.15 K and normal atmospheric pressure, so as to be able to design electrolytes having specific properties. This requires a modeling framework that is based upon the fundamental laws and models of physics. Therefore, in our study, we used the Extended UNIQUAC model to predict the LLE data. We are newly investigating the effect of including the dissociation of the picked organic acids on prediction of phase equilibrium. The results have been compared with authors who consider no dissociation of organic acids, where they have been satisfactory.

1. Introduction

The presences of the electrolytes in aqueous solutions have a particular role in industrial processes of chemical engineering, particularly in separation processes (extraction, distillation). The peculiarity of the chosen systems can be described according to which a solute can partially dissociate, in this case, an aqueous solution contains himself the ionic species resulting from the dissociation of solute, the molecule of the undissociated solute and the molecule of solvent (water).

The prediction or correlation of liquid-liquid equilibrium data of various systems has aroused the interest of several research works. Several works have been reported in the literature, either by experimental methods or by numerical methods represented by excess Gibbs energy models (NRTL, UNIQUAC, UNIFAC.) on the liquid-liquid extraction of carboxylic acids and phosphoric acid. The common objective of these works was to see the extraction power of organic solvents used (alcohols, ethers, amines …) with respect to the extraction of these organic acids from aqueous solutions [1–12]. The authors of the works mentioned above did not consider that these organic components

dissociate in water. It is therefore reasonable to think that these organic acids dissociate in water causing ionic species in the solution. Therefore, it is necessary to include their dissociation in the calculation of the thermodynamic equilibrium. The computation of phase equilibrium of a system containing an electrolyte resulting from the dissociation of an organic acid is complex, this complexity will increase by the number of adjusted parameters, that on the one hand, and in other word in the case where the liquid-liquid equilibrium data are predicted from binary data. Indeed, the consideration of the dissociation of an organic acid can rigorously influence the equilibrium phase compositions.

The liquid-liquid equilibrium study of electrolyte solutions has a practical interest at the industrial level. In addition, experimental liquid-liquid equilibrium data of electrolyte solutions are not always available, hence the need to model and predict the thermodynamic properties through precise models that account for all interactions between molecular and ionic species.

The objective of this work is to consider the dissociation of carboxylic acids (i.e. acetic, formic, propionic and butyric acids) and phosphoric acid by comparing the influence of this consideration on the

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equilibrium phase compositions with respect to authors [6,7,12] who did not include, it on the one side, and the other to study the capacity of the Extended UNIQUAC model to predict the liquid-liquid equilibrium data of chosen systems from binary data. They are all type I systems, where two binaries are completely miscible and the third binary is partially miscible. Two types of data sources are distinguished, the interaction parameters for the completely miscible binaries are adjusted using the vapor–liquid equilibrium data if they exist and the liquid-liquid equilibrium (mutual solubility) data are used in order to determine the interaction parameters for the partially miscible binary. The Extended UNIQUAC model has been applied for five systems: water-phosphoric acid-methylisobutylketone-(H^+,$H_2PO_4^-$), water-acetic acid-cumene-(H^+,CH_3COO^-), water-propionic acid-cumene-(H^+,$CH_3CH_2COO^-$), water-formic acid-isoamyl acetate-(H^+,$HCOO^-$) and water-butyric acid-isoamyl acetate-(H^+,$CH_3CH_2CH_2COO^-$) at T = 298.15 K.

2. Thermodynamic modeling

2.1. The basis of the calculation of the liquid-liquid equilibrium

The activity coefficient and the mole fraction are the grandeurs necessary to describe the liquid-liquid equilibrium, where they are expressed by the following equation:

$$\begin{cases} x_i^{aq}\gamma_i^{aq} = x_i^{org}\gamma_i^{org} \\ \sum_{i=1}^{N} x_i^{aq} = 1 \qquad i = 1, N \\ \sum_{i=1}^{N} x_i^{org} = 1 \end{cases} \tag{1}$$

Where N is the number of the Components, x_i^{aq} and x_i^{org} are respectively the mole fractions in the aqueous phase and in the organic phase of component (i). γ_i^{aq} and γ_i^{org} are respectively the activity coefficients in the aqueous phase and in the organic phase of component (i).

In the case of a mixture including an electrolyte, the liquid-liquid equilibrium of an electrolyte (j) is described by the Eq. (2):

$$\begin{cases} x_{ca\pm j}^{aq}\gamma_{ca\pm j}^{aq} = x_{ca\pm j}^{org}\gamma_{ca\pm j}^{org} \end{cases} \tag{2}$$

$\gamma_{ca\pm j}^{aq}$ and $\gamma_{ca\pm j}^{org}$ are the mean ionic activity coefficients of an electrolyte (j) in the aqueous phase and in the organic phase, respectively. The mean ionic activity coefficient of an electrolyte (j) is defined as follow:

$$\gamma_{ca\pm j} = \left(\gamma_{c+}^{\upsilon_{c+}} \times \gamma_{a-}^{\upsilon_{a-}}\right)^{\left[\frac{1}{\upsilon_{c+}+\upsilon_{a-}}\right]} \tag{3}$$

Where υ_{c+} and υ_{a-} are respectively the stoichiometric coefficients for the cation and for the anion. $x_{ca\pm j}^{aq}$ and $x_{ca\pm j}^{org}$ are respectively the mean ionic mole fractions of an electrolyte (j) in the aqueous phase and in the organic phase. These quantities are calculated in the same manner as shown in Eq. (3).

2.2. The thermodynamic model

In this work, we use the model proposed by Nicolaisen et al. [13], extended version to the electrolytes solutions. The model is based on the concept of local compositions proposed by Abrams and Prausnitz [14], Maurer and Prausnitz [15], this original version of the UNIQUAC model is extended by the addition of the Debye-Hückel term [16,17]. The excess Gibbs energy (G^E) is composed of three terms: an electrostatic term, a combinatorial term (entropic) and a residual term (enthalpic):

$$\frac{G^E}{RT} = \frac{G_{D-H}^E}{RT} + \frac{G_{Com}^E}{RT} + \frac{G_{Res}^E}{RT} \tag{4}$$

The expression of the excess Gibbs energy of combinatorial and

residual terms that take into account the short range forces are identicals to those used in original UNIQUAC model. The combinatorial term is given as follows:

$$\frac{G_{Com}^E}{RT} = \sum_i x_i ln\left(\frac{\varphi_i}{x_i}\right) - \frac{Z}{2}\sum_i x_i q_i ln\left(\frac{\varphi_i}{\theta_i}\right) \tag{5}$$

Z = 10 is the co-ordination number, x_i is the mole fraction, φ_i and θ_i are respectively volume and surface area fractions of component (i).

$$\varphi_i = \frac{r_i x_i}{\sum_k r_k x_k} \qquad \theta_i = \frac{q_i x_i}{\sum_k q_k x_k} \tag{6}$$

r_i and q_i are respectively volume and surface area parameters of component (i). The residual term is given as follows:

$$\frac{G_{Res}^E}{RT} = -\sum_i x_i q_i ln\left(\sum_j \theta_j \psi_{ji}\right) \tag{7}$$

The interaction parameter ψ_{ji} is given by:

$$\psi_{ji} = exp\left(-\frac{\Delta u_{ji}}{RT}\right) \tag{8}$$

T is the absolute temperature and R is the ideal gas constant. Δu_{ji} is the binary interaction parameters.

The Debye-Hückel [18] term which represents the interactions between ions, long range forces, is given as follows:

$$\frac{G_{D-H}^E}{RT} = -x_w M_w \frac{4A}{b^3}\left[ln(1 + b\sqrt{I}) - b\sqrt{I} + \frac{b^2 I}{2}\right] \tag{9}$$

$$A = [1.131 - 1.335*10^{-3}*(T - 273.15) + 1.164*10^{-5} \\ *(T - 273.15)^2] \ kg^{1/2} \ mol^{-1/2} \tag{10}$$

Where, x_w is the mole fraction of water, M_w is the molecular weight of water, $b = 1.5 (Kg \ mol^{-1})^{1/2}$ is a constant. A is the Debye-Hückel parameter defined in Eq. (10) and I is the ionic strength is given by:

$$I = \frac{1}{2}\sum_j z_j^2 m_j \tag{11}$$

m_j is the molality and z_j is the charge of ion (j).

The activity coefficient of the Debye-Hückel term is obtained by partial molal differentiation of the Eq. (9). The activity coefficient of an ionic species (j) is:

$$ln\gamma_j^{D-H} = -z_j^2 \frac{A\sqrt{I}}{1 + b\sqrt{I}} \tag{12}$$

The activity coefficient of water is:

$$ln\gamma_w^{D-H} = M_w \frac{2A}{b^3}\left[1 + b\sqrt{I} - \frac{1}{1 + b\sqrt{I}} - 2ln(1 + b\sqrt{I})\right] \tag{13}$$

The activity coefficients of the combinatorial and residual terms are obtained by partial molal differentiation of the Eqs. (5, 7).

The symmetrical activity coefficient of combinatorial term of component (i) is:

$$ln\gamma_i^{Com} = ln\left(\frac{\varphi_i}{x_i}\right) - \frac{\varphi_i}{x_i} + 1 - \frac{Z}{2}q_i\left[ln\left(\frac{\varphi_i}{\theta_i}\right) - \frac{\varphi_i}{\theta_i} + 1\right] \tag{14}$$

The symmetrical activity coefficient of residual term of component (i) is

$$ln\gamma_i^{Res} = q_i\left[1 - ln\left(\sum_j \theta_j \psi_{ji}\right) - \sum_j \frac{\theta_j \psi_{ij}}{\sum_l \theta_l \psi_{lj}}\right] \tag{15}$$

Eqs. (14) and (15) must be normalized at infinite dilution by setting $x_w = 1$

The unsymmetrical activity coefficient of combinatorial term of component (i) is: