Thermodynamic modeling based on particle swarm optimization to predict phase equilibrium of binary systems containing ionic liquids

Juan A. Lazzús *

Departamento de Física, Universidad de La Serena, Casilla 554, La Serena, Chile

ABSTRACT

Vapor–liquid equilibrium data of binary mixtures containing imidazolium ionic liquids were correlated using the UNIQUAC activity coefficient model optimized with a particle swarm algorithm. Twenty eight binary systems taken from literature were selected for this study, and the new optimization algorithm was used to determine the binary interaction parameters of each system. The results given by the model have been compared with experimental data, and show that the optimized UNIQUAC model is a good model to correlate and predict the vapor–liquid equilibrium for this type of systems.

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1. Introduction

Ionic liquids (ILs) are a new class of purely ionic, salt-like materials that are liquid at unusually low temperatures [1]. In the recent years, ILs came into focus because of their potential as alternatives for several engineering applications [2]. ILs are typically composed of a large organic cation and an inorganic polyatomic anion. There is virtually no limit in the number of possible ionic liquids since there are a large number of cations and anions that can be combined [3]. At ambient room temperature, they exist as liquids and have a wide variety of unique properties (for instance, negligible vapor pressure, favorable salvation behavior, low viscosity, and high reactivity and selectivity) [4].

The increasing utilization of ILs in chemical and industrial processes requires reliable and systematic thermophysical properties such as activity coefficients, heats of mixing, densities, solubilities, vapor–liquid equilibria (VLE), and liquid–liquid equilibria (LLE). In addition, the transport properties are also needed (viscosity, electric conductivity, mutual diffusion coefficients, etc.) [5].

Parameter optimization procedures are very important in engineering, industrial, and chemical processes for the development of mathematical models and advanced control of these processes [6]. The aim of optimization is to determine the best-suited solution to a problem under a given set of constraints. Mathematically an optimization problem involves a fitness function describing the problem, under a set of constraints representing the solution space for the problem. The optimization problem, now-a-days, is represented as an intelligent search problem, where one or more agents are employed to determine the optima on a search landscape, representing the constrained surface for the optimization problem [7].

Because of the difficulties in evaluating the first derivatives, to locate the optima for many rough and discontinuous optimization surfaces, in recent times, several derivative free optimization algorithms have emerged [8]. Particle swarm optimization (PSO) is a relatively recently devised population-based stochastic global optimization algorithm. As described by Eberhart and Kennedy, the PSO algorithm is an adaptive algorithm based on a social–psychological metaphor; a population of individuals (referred to as particles) adapt by returning stochastically toward previously successful regions [9].

For a better understanding of their thermodynamic behavior and for the development of thermodynamic models reliable experimental phase equilibrium data is required [10–12]. Nevertheless, the number of published VLE data sets is still very limited. But in particular reliable VLE data would allow to check whether g^E-models can be used for the description of the real behavior of binary systems with ionic liquids and whether binary g^E-model parameters can be applied for the prediction of the VLE behavior of higher systems containing ionic liquids [13].

In this work, isothermal vapor–liquid equilibrium data of binary mixtures containing imidazolium ionic liquids were correlated using an activity coefficient model optimized with a PSO algorithm. Twenty eight binary systems taken from literature were selected for this study. Then, the PSO algorithm was used to determine the interaction parameters for this model.

* Tel.: +56 51 204128; fax: +56 51 206658.
E-mail address: jlazzus@dfuls.cl.

2. Equation of vapor–liquid equilibrium

As known, the phase equilibrium problem to be solved consists of the calculation of some variables of the set T–P–x–y (temperature, pressure, liquid-phase concentration and vapor-phase concentration, respectively), when some of them are known. For a vapor–liquid mixture in thermodynamic equilibrium, the temperature and the pressure are the same in both phases, and the remaining variables are defined by the material balance and the "*fundamental equation of phase equilibrium*". The application of this fundamental equation requires the use of thermodynamic models which normally include binary interaction parameters [14,15].

The classical thermodynamic models commonly used in the literature to treat these mixtures at low pressure required a great amount of binary parameters to be determined from experimental data [16]. These binary parameters must be determined using experimental data for binary systems. Theoretically, once these binary parameters are known one could predict the behavior of multicomponent mixtures using standard thermodynamic relations and thermodynamic models [14].

The fundamental equation of vapor–liquid equilibrium can be expressed as the equality of fugacities of each component in the mixture in both phases [16]:

$$\overline{F}_i^L = \overline{F}_i^V. \tag{1}$$

The fugacity of a component in the vapor phase is usually expressed through the fugacity coefficient $\overline{\phi}_i^V$:

$$\overline{F}_i^V = y_i \overline{\phi}_i^V P. \tag{2}$$

The fugacity of a component in the liquid phase is expressed through either the fugacity coefficient $\overline{\phi}_i^L$ or the activity coefficient γ_i:

$$\overline{F}_i^L = x_i \overline{\phi}_i^L P \tag{3}$$

$$\overline{F}_i^L = x_i \gamma_i f_i^0. \tag{4}$$

In these equations, y_i is the mole fraction of component in the vapor phase, x_i is the mole fraction of component in the liquid phase, P is the pressure, and f_i^0 is the fugacity at a reference state of the pure component. The fugacity is related to the temperature, the pressure, the volume and the concentration through a standard thermodynamic relation [17].

If the fugacity coefficient is used in both phases, the method of solution of the phase equilibrium problem is known as "*the equation of state method*". Then, equation of state (EoS) and a set of mixing rules are needed, to express the fugacity coefficient as a function of the temperature, the pressure and the concentration [15]. Modern equation of state methods includes an excess Gibbs free energy model (g^E) in the mixing rules of the equation of state, giving origin to the so-called "*equation of state + g^E model*" [18]. This means that an activity coefficient model (γ) is used to describe the complex liquid phase, and the fugacity coefficient (ϕ) is calculated using a simple equation of state. If the fugacity coefficient is used for the vapor phase and the activity coefficient is used for the liquid phase the equilibrium problem is known as "*the gamma–phi method*". This method has given acceptable results for some systems [15,16].

Most models available in literature for the activity coefficient are of the correlating type (van Laar, Margules, Redlich–Kister, Wilson, NRTL and UNIQUAC), meaning that experimental data are needed to calculate certain empirical parameters; although some predictive models are also available (UNIFAC, ASOG). These predictive models have been used in several applications, and recently including mixtures with some ILs [10–13]. But to the best of the author's knowledge, there are no systematic studies on binary mixtures, such as the one presented here, where the author has included several compounds and ILs.

3. Equation of state method

From the relation between the fugacity, the Gibbs free energy, and an EoS, the fugacity coefficient can be calculated as [16]:

$$\ln \overline{\phi}_i = \frac{1}{RT} \int_{\infty}^{V} \left[\frac{RT}{V} - \left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_{j \neq i}} \right] dV - \ln Z \tag{5}$$

where V is the total volume, N_i is the number moles of specie i, and Z is the compressibility factor. Thus, the experimental vapor–liquid phase data can be correlated with the Peng–Robinson (PR) EoS [19], and the Wong and Sandler (WS) mixing rule [14].

The PR EoS can be expressed as follows [19]:

$$P = \frac{RT}{V - b} + \frac{a}{V(V + b) + b(V - b)} \tag{6}$$

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T_r) \tag{7}$$

$$b = 0.077796 \frac{RT_c}{P_c} \tag{8}$$

$$\alpha(T_r) = \left[1 + \kappa \left(1 - \sqrt{T_r} \right) \right]^2 \tag{9}$$

$$\kappa = 0.37646 + 1.54226\omega - 0.26992\omega^2 \tag{10}$$

For mixtures the Eq. (6) can be extended as:

$$P = \frac{RT}{V - b_m} + \frac{a_m}{V(V + b_m) + b_m(V - b_m)}. \tag{11}$$

And the WS mixing rules used in this EoS can be summarized as follows [15]:

$$b = \frac{\sum_i^N \sum_j^N x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_i^N \frac{x_i a_i}{b_i RT} - \frac{A_\infty^E(x)}{\Omega RT}} \tag{12}$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left(b_i + b_j \right) - \frac{\sqrt{a_i a_j}}{RT} \left(1 - I_{ij} \right) \tag{13}$$

$$a_m = b_m \left(\sum_i^N \frac{x_i a_i}{b_i} + \frac{A_\infty^E(x)}{\Omega} \right) \tag{14}$$

In these equations a_m and b_m are the EoS constants, I_{ij} as the adjustable parameter with $\Omega = 0.34657$, and $A_\infty^E(x)$, the excess Helmholtz free energy at the limit of infinite pressure is calculated using an activity coefficient model and assuming that $A_\infty^E \approx A_0^E \approx g_0^E$ [18].

4. Activity coefficient model

To calculate the excess Gibbs free energy at the limit of zero pressure (g_0^E), the UNIQUAC activity coefficient model was used.

The universal-quasi-chemical theory [20], from which the UNIQUAC model is derived, can be expressed in terms of the g^E as:

$$g_i^E = g_{i,C}^E + g_{i,R}^E \tag{15}$$