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Optimization of a cubic equation of state and van der Waals mixing rules for modeling the phase behavior of complex mixtures

J.A. Lazzús
Departamento de Física, Universidad de La Serena, Casilla 554, La Serena, Chile,
e-mail: jlazzus@dfuls.cl

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A thermodynamic modeling for the vapor–liquid equilibrium of binary systems of supercritical fluids and ionic liquids is presented. The van der Waals mixing rules and a cubic equation of state are used to evaluate the fugacity coefficient on the systems. Then, a particle swarm algorithm was used to minimize the difference between calculated and experimental bubble pressure, and calculate the interaction parameters for all systems used. The results show that the bubble pressures were correlated with low deviations between experimental and calculated values. These deviations show that the proposed model is a good technique to optimize the interaction parameters of the phase equilibrium of binary systems containing supercritical fluids and ionic liquids.

Keywords: Particle swarm optimization; phase equilibrium; ionic liquids; equation of state.

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1. Introduction

In the last years, the ionic liquids (ILs) have been the object of increasing attention due to their unique physicochemical properties [1]. ILs are organic salts composed of cations and anions that are liquid at conditions around room temperature [2].

Phase equilibrium data of mixtures containing ILs are necessary for further development of some separation processes [3]. The gas solubilities data provides important information for the characterization of solutesolvent interactions and so contribute to understand the mechanisms of dissolution. From a practical point of view, gas solubility can be useful in the calculation of vapor–liquid equilibrium (VLE) [4].

On this line, VLE data for binary systems including ionic liquids, although essential for the design and operation of separation processes, are still scarce. Various models have been used to correlate experimental data of phase equilibria of these systems [3]. One of the common approaches used in the literature to correlate and predict phase equilibrium requires an equation of state (EoS) that well relates the variables temperature, pressure and volume and appropriate mixing rules to express the dependence of the equation of state parameters on the concentration [5].

2. Thermodynamic formulation

The most common and industrially important EoS are the cubic equations derived from van der Waals EoS; among these, the Peng–Robinson equation (PR) has proven to combine the simplicity and accuracy required for the prediction and correlation of volumetric and thermodynamic properties of several fluids [6].

The PR EoS was expressed as follows [7]:

$$P=\frac{RT}{V-b}+\frac{a}{V\left(V+b\right)+b\left(V-b\right)} \tag{1}$$

$$a=0.457235\frac{R^2T_c^2}{P_c}\sigma\left(T_r\right) \tag{2}$$

$$b=0.077796\frac{RT_c}{P_c} \tag{3}$$

$$\sigma(T_r)=\left[1+\kappa\left(1-\sqrt{T_r}\right)\right]^2 \tag{4}$$

$$\kappa=0.37646+1.54226\omega-0.26992\omega^2 \tag{5}$$

For mixtures, the parameters a and b are expressed as functions of the concentration of the different components in the mixture, through the so-called mixing rules. Until recent years, most of the applications of EoS to mixtures considered the use of the classical van der Waals mixing rules (vdW), with the inclusion of an interaction parameter for the force constant a and volume constant b. The PR EoS for a mixture is:

$$P=\frac{RT}{V-b_m}+\frac{a_m}{V\left(V+b_m\right)+b_m\left(V-b_m\right)} \tag{6}$$

And the classical van der Waals mixing rules are [3]:

$$a_m=\sum_i^N\sum_j^N x_ix_ja_{ij} \tag{7}$$

$$b_m=\sum_i^N\sum_j^N x_ix_jb_{ij} \tag{8}$$

the combining rules for a_{ij} and b_{ij}, with interaction parameters for the force and volume constants, are:

$$a_{ij} = \sqrt{a_i a_j}\,(1 - \alpha_{ij}) \tag{9}$$

$$b_{ij} = \frac{b_i + b_j}{2}\,(1 - \beta_{ij}) \tag{10}$$

where the parameters α_{ij} and β_{ij} in the above combining rules are calculated by regression analysis of experimental phase equilibrium data.

Then, the problem is reduced here to determine the optimal interaction parameters by minimizing the following objective function in data regression [6]:

$$f = \frac{100}{N_D}\sum_{i=1}^{N_D}\left|\frac{P^{\text{calc}} - P^{\text{exp}}}{P^{\text{exp}}}\right|_i \tag{11}$$

where N_D is the number of points in the experimental data set and P is the pressure of IL in the vapor phase, the superscript denotes the experimental (exp) data point and calculated (calc) values.

The existing methods to solve phase equilibrium systems obtain only local solutions. It has been demonstrated that for cases of systems containing supercritical fluids, the optimum values of the interaction parameters depend on the searching interval and on the initial value of used interaction parameters [8].

Parameter estimation procedures are very important in engineering, industrial, and chemical process for development of mathematical models, since design, optimization and advanced control of bioprocesses depend on model parameter values obtained from experimental data [2]. The use of heuristic optimization methods, such particle swarm optimization (PSO), for the parameter estimation is very promising [6]. This biologically-deriver method represents an excellent alternative to find a global optimum for phase equilibrium calculations [3].

3. Particle swarm optimization

The PSO algorithm is initialized with a population of random particles and the algorithm searches for optima by updating generations [9]. In a PSO system, each particle is "flown" through the multidimensional search space, adjusting its position in search space according to its own experience and that of neighboring particles. The particle therefore makes use of the best position encountered by itself and that of its neighbors to position itself toward an optimal solution [10]. The performance of each particle is evaluated using a predefined fitness function, which encapsulates the characteristics of the optimization problem [11].

Let s and v denote a particle position and its corresponding velocity in a search space, respectively. Therefore, the $k-th$ particle is represented in the n-dimensional search space as:

$$s_k = \left(s_k^1, s_k^2, ..., s_k^n\right) \tag{12}$$

And the current velocity of the $k-th$ particle is represented as:

$$v_k = \left(v_k^1, v_k^2, ..., v_k^n\right) \tag{13}$$

Let the current personal best position of particle k and $f(s)$ be the target function which will be minimized.

$$p_k = \left(p_k^1, p_k^2, ..., p_k^n\right) \tag{14}$$

Then the best position p_k is determined by:

$$p_k(t{+}1) = \begin{cases} p_k(t), & \text{if } f(s_k(t{+}1)) \geq f(p_k(t)) \\ s_k(t{+}1), & \text{if } f(s_k(t{+}1)) < f(p_k(t)) \end{cases} \tag{15}$$

In each iteration, every particle calculates its velocity according to the following formula:

$$v_k(t+1) = wv_k(t) + c_1 r_1(p_k(t) - s_k(t)) + c_2 r_2(p_g(t) - s_k(t)) \tag{16}$$

where t is the current step number, w is the inertia weight, c_1 and c_2 are the acceleration constants, and r_1, r_2 are element from two randon sequences in the range (0,1). The current position of the particle is determined by $s_k(t)$; p_k is the best one of the solutions this particle has reached, p_g is the best one of the solutions all the particles have reached [10].

The variable w is responsible for dynamically adjusting the velocity of the particles, so it is responsible for balancing between local and global search, hence requiring fewer iterations for the algorithm to converge [6]. A low value of inertia weight implies a local search, while a high value leads to a global search. Applying a large inertia weight at the start of the algorithm and making it decay to a small value through the PSO execution makes the algorithm search globally at the beginning of the search, and search locally at the end of the execution [2]. The following weight function w is used in Eq. (16):

$$w = w_{\text{max}} - \frac{w_{\text{max}} - w_{\text{min}}}{t_{\text{max}}}t \tag{17}$$

Generally, the value of each component in v can be clamped to the range $[-v_{\text{max}}, v_{\text{max}}]$ control excessive roaming of particles outside the search space [10]. After calculating the velocity, the new position of every particle is:

$$s_i\,(t+1) = s_i\,(t) + v_i\,(t+1) \tag{18}$$

The PSO performs repeated applications of the update equations above until a specified number of iteration has been exceeded, or until the velocity updates are close to zero [9]. The scheme of the PSO algorithm is presented in detail in Table I.

4. Results and discussion

PSO algorithm was used for minimize the difference between calculated and experimental bubble pressure in Eq. (11). Table II shows the selected parameters for the PSO algorithm.

TABLE I. Scheme of the PSO algorithm development in this study.

Step	Description
01	Initialize algorithm. Set constants: t_{max}, v_{max}, w, c_1, c_2
02	Randomly initialize the swarm positions $s_0^i \in \mathrm{R}^n$ for i= 1, . . . , p
03	Randomly initialize particle velocities v_0^i for i = 1, . . . , p
04	Set $t = 1$ Evaluate function value f_k^i using design space coordinates s_k^i:
05	If $f_k^i \leq f_{\text{best}}^i$ then $f_{\text{best}}^i = f_k^i$, $p_k^i = s_k^i$ If $f_k^i \leq f_{\text{best}}^g$ then $f_{\text{best}}^g = f_k^i$, $p_k^g = s_k^i$
06	If stopping condition is satisfied then stop algorithm
07	Update all particle velocities v_k^i for i = 1, . . . , p
08	Update all particle positions s_k^i for i = 1, . . . , p
09	Otherwise set $t = t + 1$ goes to step 5

TABLE II. Parameters used in the PSO algorithm.

PSO Parameters	Value
Number of particles in swarm	100
Number of generations	1000
Cognitive component (c_1)	1.49
Social component (c_2)	1.49
Maximum velocity (v_{max})	12
Minimum inertia weight (w_{min})	0.4
Maximum inertia weight (w_{max})	0.41

TABLE III. Thermodynamic properties of the substances involved in this study.

Substance	T_c(K)	P_c(MPa)	ω
[C_2mim] [PF_6]	663.5	1.95	0.6708
[C_2mim][PF_4]	585.3	2.36	0.7685
[C_6mim][PF_6]	754.3	1.55	0.8352
[C_8mim][BF_4]	726.1	1.60	0.9954
CO_2	304.2	7.38	0.2236
CHF_3	299.0	4.82	0.2642

TABLE IV. Details on the phase equilibrium data of the five systems used in this study.

No.	System	Ref.	N_D	ΔT (K)	ΔP (MPa)	Δx
1	CHF_3+[C_2mim][PF_6]	[12]	100	308-363	1-52	0.1-0.9
2	CO_2+[C_2mim][PF_6]	[13]	74	313-358	1-97	0.1-0.6
3	CO_2+[C_6mim][PF_6]	[14]	98	308-359	1-95	0.1-0.7
4	CO_2+[C_2mim][BF_4]	[15]	40	303-323	2-13	0.1-0.6
5	CO_2+[C_8mim][BF_4]	[16]	99	308-363	1-85	0.1-0.8

TABLE V. Interaction parameters calculated with the PSO algorithm.

System	α_{ij}	β_{ij}	$\|\%\Delta P\|$
1	-0.01302	-0.06598	9.8
2	-0.11921	-0.09741	8.6
3	0.04798	-0.01030	6.4
4	0.12064	-0.05809	6.8
5	0.48241	-0.01463	9.5

TABLE VI. Mean values of the variables of interest for PSO, GA and LMA.

Parameter	PSO	GA	LMA
Iteration best solution (t_{max})	700	350	950
CPU time (s)	550	345	2189
Unique solutions in the final population (%)	90	75	–
Accuracy of solutions (%)	95.02	85.1	80.03
Minimun deviation (%)	0.31	1.52	6.03
Maximun deviation (%)	12.34	22.18	34.29
Average deviation (%)	8.22	12.78	18.11

Five binary vapor-liquid phase systems containing supercritical fluid with ionic liquids were considered in this study. Table III shows the thermodynamic properties of the substances used. In this Table, T_c is the critical temperature, P_c is the critical pressure, and ω is the acentric factor (taken from [6]). The details of the experimental vapor-liquid equilibrium data taken from Refs. 12 to 16 are presented in Table IV.

Table V shows the calculated parameters α_{ij} and β_{ij} using the PR–vdW + PSO in Eq. (11). Figure 1 shows the interaction parameters determined with the PSO algorithm. The results show that the pressures of the ILs in the vapor phase were correlated with low deviations between experimental and calculated values (average deviations of $|\%\Delta P|$ were below 10%). Figure 2 shows an example of the accuracy of the proposed thermodynamic model to describe the

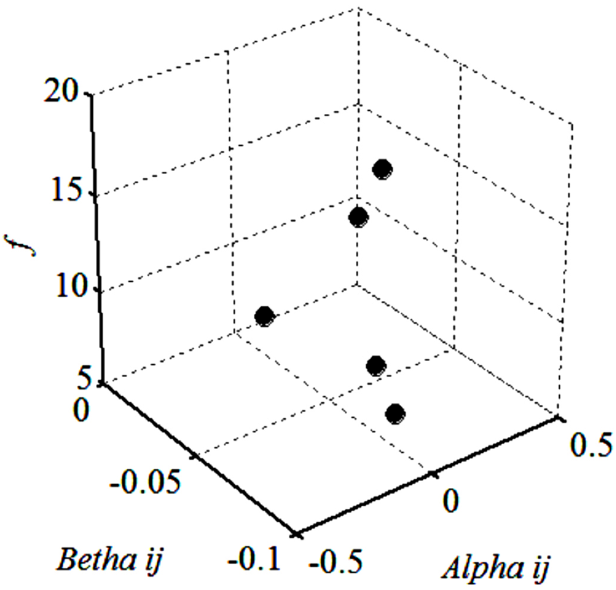

FIGURE 1. Deviation obtained for the interaction parameters by minimizing the objective function.

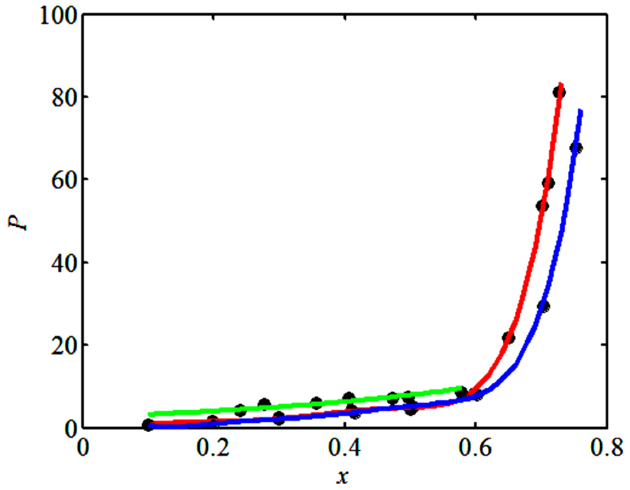

FIGURE 2. Calculated (solid line) and experimental (circles) vapor-liquid equilibrium at 313 K for the systems: 3 (red), 4 (green), and 5 (blue).

VLE of binary systems containing ILs with supercritical fluids. The figure shows experimental and correlated values of VLE for three systems used in this study.

A comparison was made between of the results obtained with the PSO algorithm and the results obtained with another two algorithms: genetic algorithm (GA) [17], and Levenberg–Marquart algorithm (LMA) [18]. Note that, GA and LMA are commonly used in these problems. Table VI shows the mean values of the above variables of interest for these three algorithms. In this table, the best variables were calculated as an average of the best solution found by the three algorithms for all systems, and to evaluate the quality of the entire set of solutions that each algorithm provides. In general PSO performs better than GA and LMA, with accuracy of 95% and average deviation below than 10%. Figure 3 shows a comparison between the PSO algorithm development in this work, with GA and LMA. This figure shows the average pressure deviations found with the three algorithms for all the ionic liquids considered in this work. These results represent a tremendous increase in accuracy to predict the phase equilibrium of these complex mixtures and, shows that the use of the proposed thermodynamic model (PR-vdW + PSO) was crucial.

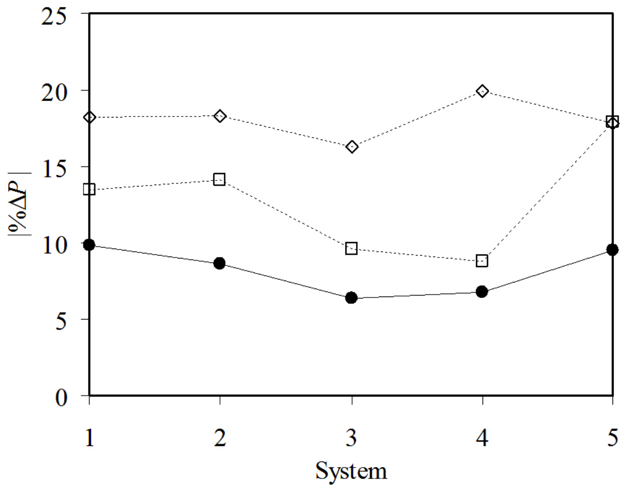

FIGURE 3. Comparison between PSO (◯), GA (□), and LMA (Δ) optimizations used on all systems of this study. In this figure, the systems are listed as in Table V.

5. Conclusions

Based on the results and discussion presented in this study, the following main conclusions are obtained: (i) the PR–vdW model is appropriate to modeling the high–pressure phase equilibrium of binary systems containing supercritical fluids with ionic liquids; (ii) the PSO algorithm is a good tools for the calculation of the optimum values for the interaction parameters used in the proposed model. The results show that the pressures of the ILs in the vapor phase were correlated with low deviations between experimental and calculated values.

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