



# Equation of state based on the hole-lattice theory and surface-charge density (COSMO): Part B – Vapor–liquid equilibrium for mixtures



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## ABSTRACT

In our previous study [1], an equation of state based on hole-lattice theory augmented with the surface charge-densities, i.e.,  $\sigma$ -profiles, was developed and applied for pure components. Here, we extend this equation of state to mixtures in order to describe vapor–liquid equilibrium (VLE) data at low and high pressures. VLE data properties of 98 binary mixtures in (40 isobaric and 58 isothermal) at low pressures were predicted using only the pure components parameters obtained in previous work and  $\sigma$ -profiles calculations. This systems were divided in nonpolar–nonpolar, nonpolar–polar, polar–polar, practically immiscible and carboxylic acid systems. The performance of the proposed EoS were compared with those calculations from COSMO-SAC. For isobaric systems, the equation of state and COSMO-SAC showed, respectively, 0.6% and 0.5% average relative deviation for temperature, and 0.02 for vapor-phase mole fraction. For isothermic systems, the equation of state and COSMO-SAC presented an average relative deviation of 9.9% and 7.5% for pressure and absolute average deviation of 0.03 for vapor-phase mole fraction were reported. The equation of state was also tested for high pressure phase equilibria calculations. Satisfactory results were obtained for isothermal binary mixtures studied. This new equation of state can be used to predict VLE at low and high pressures.

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## 1. Introduction

Several predictive models have been developed to describe thermodynamic properties of mixtures. An important and useful example is UNIFAC [2], an activity coefficient model based on the local composition theory and the group contribution method, that has been applied since 1975. Many versions of UNIFAC were reported, as Skjold-Jorgensen et al. [3], Gmehling et al. [4], Macedo et al. [5], Tiegs et al. [6], Hansen et al. [7], Wittig et al. [8].

Another very successful activity coefficient model recently developed is COSMO-RS [9], actually presented in a series of versions such as COSMO-RS models [10,11], as well as COSMO-SAC [12–15], COSMO-OI [16], COSMO-SAC-vap [17], F-SAC [18–20] and COSMO-SAC-dsp [21]. Most of those models use, even partially, the  $\sigma$ -profiles obtained from COSMO quantum chemical calculations, i.e., a discrete probability distributions of segments

presenting different values of charge density. These distributions are generated from surface charge-densities calculated by density-functional theory.

Activity coefficient models are developed for incompressible phases, and then do not account for pressure effects. Therefore, they are not adequate to describe low density phases and high pressure systems. On the other hand, equations of state can describe both incompressible and compressible phases. Additionally, an equation of state can also provide other pure properties such as the saturation pressure, enthalpy of vaporization and second virial coefficient, for example.

An example of predictive equation of state, we can cite the Mattedi–Tavares–Castier (MTC) [22], which is based on the generalized van der Waals theory [23] in conjunction with n-fluid theory [24] and uses the group contribution method for predictive purposes, in a similar way as UNIFAC models. In MTC equation, the groups are divided depending on their polarity levels using a large number of parameters.

In our previous work [1], a new equation of state was developed from the hole-lattice theory and that is mathematically similar to the Mattedi et al. [22] equation of state. However, it uses the

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surface-charge densities from Mullins et al. [13] databank and the energy term from Lin and Sandler [12], resulting in three parameters per component, which were estimated from pure substance data. This equation was tested to predict pure component properties such as vapor pressure, enthalpy of vaporization and second virial coefficient. Here, we extend the equation of state (called here  $\sigma$ -MTC) and tested the EoS performance to predict the vapor–liquid equilibria, for binary mixtures at low pressure and near to critical region, using only the parameters estimated in Costa et al. [1] for pure compounds.

## 2. Equation of State

The partition function obtained from the generalized van der Waals theory for a mixture is [24]:

$$Q(\underline{N}, V, T) = Q^{at}(\underline{N}, V, T)Q^{res}(\underline{N}, V, T) \quad (1)$$

where:

$$Q^{at}(\underline{N}, V, T) = \left[ \prod_{i=1}^{n_c} \frac{\zeta_i(T)}{N_i!} \left( \frac{V}{\Lambda_i^3} \right)^{N_i} \right] \left[ \frac{V_f}{V} \right]^N \quad (2)$$

$$Q^{res}(\underline{N}, V, T) = \exp \left[ -\frac{1}{K_b} \int_0^{1/T} E_0(\underline{N}, V, \xi) d(\xi) \right] \quad (3)$$

where  $Q^{at}$  is the athermal contribution to the partition function, which includes the intramolecular contribution and the repulsive forces,  $Q^{res}$  is the residual contributions to the partition function, that represents attractive forces contributions,  $\zeta_i(T)$  is a function for intermolecular degree of freedom,  $N$  is the total number of molecules, given by  $N = \sum_{i=1}^{n_c} N_i$ ,  $n_c$  is the number of components,  $\Lambda_i$  is the de Broglie wavelength,  $V_f$  is the free volume,  $K_b$  is the Boltzmann constant and  $E_0$  is the configurational internal energy.

Using the n-fluid theory and lattice models [24], a fluid with a total volume  $V$  is described by a lattice with a coordination number equal to  $Z$ , containing  $M$  cells, each one with a fixed volume  $V^*$ . The lattice is filled with  $n_c$  different compounds, each one occupying  $r_i$  sites and having  $Zq_i$  external contacts. A total of  $M - \sum r_i N_i$  void cells present and, therefore, the total volume  $V$  is given by  $V^* M$ .

Considering additivity for  $r_i$  and  $Zq_i$ , the average values for  $r$  and  $Zq$  are [22]:

$$r = \sum_{i=1}^{n_c} x_i r_i \quad (4)$$

$$Zq = \sum_{i=1}^{n_c} x_i Zq_i \quad (5)$$

Defining the reduced volume as [22]:

$$\tilde{v} = \frac{V^* M}{V^* r N} = \frac{M}{r N} = \frac{V}{V_p} \quad (6)$$

where  $V_p$  is the packing volume ( $NrV^*$ ).

The athermal contribution, obtained using the Staverman–Guggenheim model to compute size and geometry effects, is obtained by Ref. [25]:

$$\begin{aligned} \ln Q^{at}(\underline{N}, V, T) &= \sum_{i=1}^{n_c} N_i \ln [\zeta_i(T)] + \left( 1 - \frac{Z}{2} \right) \ln [M!] - \sum_{i=1}^{n_c} \ln [N_i!] \\ &\quad - \ln [(M - rN)!] + \frac{Z}{2} \ln [(M - rN + qN)!] \\ &\quad + \ln M \sum_{i=1}^{n_c} \varrho_i N_i \end{aligned} \quad (7)$$

where the bulkiness factor,  $\varrho_i$ , is given by:

$$\varrho_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \quad (8)$$

In this work, we assume  $\varrho_i$  equal to zero for all molecules, i.e., the molecules are treated as linear equivalent. With this assumption, the number of estimated parameters is reduced, without losing important information. It is important to emphasize that this simplification was used previously, in which the parameters were estimated using pure component data with a negligible loss of accuracy.

For the residual contribution, assuming the interaction energy between a void site and any other segment equal to zero, pairwise additivity is valid and considering only the interaction between first neighbor, the expression for the configurational internal energy can be deduce as [22]:

$$E_0 = \psi r N (q/r)^2 \sum_{i=1}^{n_c} \sum_{a=1}^{n_s} \sum_{j=1}^{n_c} \sum_{b=1}^{n_s} \frac{S_{i,a} S_{j,b} u_{i,a,j,b} \gamma_{i,a,j,b}}{\tilde{v} - 1 + (q/r) \Gamma_{i,a}} \quad (9)$$

where [22]:

$$\Gamma_{i,a} = \sum_{j=1}^{n_c} \sum_{b=1}^{n_s} \nu_{j,b} \frac{x_j q_j}{q} \gamma_{i,a,j,b} \quad (10)$$

$$\gamma_{i,a,j,b} = \exp \left[ \frac{-u_{i,a,j,b}}{RT} \right] \quad (11)$$

$$S_{j,b} = \nu_{j,b} \frac{x_j q_j}{\sum_{k=1}^{n_c} x_k q_k} \quad (12)$$

and  $\Psi$  is a structural parameter which was considered equal to one,  $Q_{i,a}$  is the area parameter of a segment  $a$  in a molecule  $i$ , which is the same for all segments in one molecule,  $u_{i,a,j,b}$  is the interaction energy between nearest neighbor segments in the lattice,  $\nu_{i,a}$  is the fraction of segments of type  $a$  in the molecule  $i$  and  $n_s$  is the number of segments in a molecule  $i$  [22].

The  $Q^{res}$  term resulting expression is given by Ref. [22]:

$$\ln Q^{res}(\underline{N}, V, T) = -\Psi \sum_{i=1}^{n_c} \sum_{a=1}^{n_s} N_i \nu_{i,a} Q_{i,a} \ln \left[ \frac{\tilde{v} - 1 + q/r}{\tilde{v} - 1 + (q/r) \Gamma_{i,a}} \right] \quad (13)$$

From the partition function, all the properties, including the equation of state and the chemical potential, can be derived. The compressibility factor ( $z$ ) is given by the following expression:

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