



Modification of Peng Robinson EOS for modelling (vapour + liquid) equilibria with electrolyte solutions

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ABSTRACT

A modification of the extended Peng–Robinson equation of state (PR-EOS) is presented to describe the (vapour + liquid) equilibria of systems containing water and salts. The modification employs three additional terms including a Born term, a Margules term and two terms separately used for estimation of the long-range electrostatic interactions (the Debye–Huckel (DH) or the mean spherical approximation (MSA) terms). Effects of two mixing rules, first, the Panagiotopoulos and Reid mixing rule (PR) and, second, the Kwak and Mansoori mixing rule (KM), on the final values of VLE calculations are also investigated. The results show that the KM mixing rule is more appropriate than the PR mixing rule. The proposed equation of state is used to calculate the (vapour + liquid) equilibrium (VLE) of the systems containing (water + sodium sulphate + carbon dioxide) and (water + sodium chloride + carbon dioxide) at high pressure. The comparison of calculated results with the experimental data shows that a combination of KM mixing rule with the DH term results a more accurate VLE values.

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1. Introduction

Salt containing and more specifically aqueous electrolyte solutions play an important role in a variety of processes such as solution crystallization, ion exchange, waste water treatment, protein precipitation, fertilizer production, reverse osmoses of aqueous solutions, and reactive distillation in electrolyte media [1,2]. Although simulation of these processes can be used for creating of the best flow sheet, design of the equipment and selection of the optimum operation conditions, the accuracy of results depends on the quality of thermodynamic models to provide the correct description of dependence on temperature, pressure, and composition in multi-component systems. In this line of research, the theoretical and experimental studies of phase equilibrium for different systems have been presented in the literature. In order to prevent expensive and time-consuming in experimental studies, searching for the reliable models to describe the behaviour of electrolyte solutions is required. Different models have been emerged in the literature to describe the behaviour of electrolyte solutions. The development of a thermodynamic model for aqueous electrolytes has been followed in two approaches, either to an activity coefficient model for ambient pressure condition or to an equation of state especially for high pressure. The reviews of different approaches can be found in Sieder and Maurer [3] and in Myers *et al.* [4]. For solutions at conditions far below the critical point

of components, several activity coefficient models have been developed to represent the (vapour + liquid) equilibrium (VLE) in electrolyte systems. Examples for electrolyte g^E -models are the electrolyte NRTL model, the Pitzer model and the other presented works in the literature [4–11]. For systems at high pressure conditions, however, excess Gibbs free energy models are ineffective. An alternate description of high-pressure phase equilibria is provided by a single equation of state to calculate the fugacity of each species in each of the equilibrium phases. For high-pressure phase equilibrium calculations, widely used cubic equations of state without any additional terms to involve the effects of salts and ions on the phase equilibrium are not suitable. In order to include the strong forces between ions and polar molecules and to reduce the deviation between the experimental data and calculation results, several researches have proposed various equations of state. There are various kinds of pathway to describe the electrolytes with equation of state such as a well-known theory called SAFT, statistical association fluid theory [12,13], the extension of cubic equation of state by summing separate contributions to the Helmholtz energy [3,14–19] and the group contribution equation of state (GC-EOS) [20].

On the other hand, an effective mixing rule is required to apply an EOS for VLE calculations of complex mixtures. Since the classical quadratic mixing rules are not sufficiently flexible to correlate the phase behaviour of mixtures containing strongly polar and associating components, several authors introduced empirical modifications to enhance the flexibility. Many researchers have proposed different mixing rules by combining the excess Gibbs free energy

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models and equations of state, such as Wong–Sandler or Orbey–Sandler mixing rules [21]. Other researchers have presented mixing rules by making relevance between the parameters of EOS and the parameters (energy and volume) of the potential function such as Kwak and Mansoori (KM) mixing rule [22], in which the constants used for the mixing rule are temperature independent. Another modification of mixing rule occurs by replacing the composition-independent combining rule with the composition-dependent expressions such as the Panagiotopolus and Reid mixing rule [23].

In our recent work [24], based on the model proposed by Sieder and Maurer [3], an extension of the PR-EOS was used for calculation of phase equilibrium in the systems containing supercritical CO₂, water and salt. In this EOS, three additional terms were added to PR-EOS to estimate the effect of salts on the (vapour + liquid) equilibrium of the system. In our previous work [25], the additional term of Born was added to the model proposed by Sieder and Maurer [3] to involve the Helmholtz energy change due to charging neutral particles against its own electrostatic field.

In this work, a new extension of Peng–Robinson equation of state (EPR-EOS) has been presented for prediction of phase equilibrium in systems of (water + carbon dioxide), (water + sodium sulphate + carbon dioxide), and (water + sodium chloride + carbon dioxide). The proposed equation of state is used as a single model to calculate the fugacity of each species in both liquid and vapour phases over a wide range of temperature and pressure. The new EOS is based upon non-electrolyte and electrolyte contributions to the Helmholtz energy change. Effects of ionic species are included in the model by adding a Born term to involve the effect of Born energy contribution, a Margules term for the short-range electrostatic interactions between ions and solvents and two terms separately used for estimation of the long-range electrostatic interactions (Debye–Huckel (DH) or mean spherical approximation (MSA) terms). In this work the Kwak and Mansoori [22] and the Panagiotopoulos and Reid [23] mixing rules are used to extend the proposed EOS to mixture.

2. Theory

For a multi-component system of {polar solvent (such as water) + non-polar solvent (such as carbon dioxide) + ionic solute (such as sodium sulphate)}, the extended Peng Robinson equation of state EPR-EOS for calculation of Helmholtz energy can be presented as follows:

$$A = A^0 + \Delta A^{IG} + \delta A_{nonionic} + \delta A_{ionic}, \quad (1)$$

where A^0 is the Helmholtz energy of pure components in the ideal gas state at (T, P^0) ; ΔA^{IG} is the Helmholtz energy change for mixing of ideal gases. $\delta A_{nonionic}$ and δA_{ionic} are the Helmholtz energy changes due to interactions between non-ionic and ionic species, respectively. The $\delta A_{nonionic}$ is constructed by summation of the repulsive and attractive terms based on the Melhem [26] modification of PR-EOS:

$$\Delta A^{rep}(T, V, \vec{n}) = RT \sum_{i=1}^{N_c} n_i \ln \frac{V}{V - bn_T}, \quad (2)$$

$$\Delta A^{att}(T, V, \vec{n}) = \frac{a(T)n_T}{2\sqrt{2}b} \ln \frac{V + bn_T(1 - \sqrt{2})}{V + bn_T(1 + \sqrt{2})}. \quad (3)$$

For mixtures, two different mixing rules are used.

(i) The mixing rule suggested by Kwak and Mansoori [22]:

$$a_{mix} = C_{mix} + d_{mix}RT - 2\sqrt{C_{mix}d_{mix}RT} \quad (4)$$

$$C_{mix} = \sum_i^n \sum_j^n x_i x_j (1 - k_{ij})(C_i C_j)^{1/2}, \quad (5)$$

$$b_{mix} = \sum_i^n \sum_j^n x_i x_j (1 - l_{ij})[(b_i^{1/3} + b_j^{1/3})/2]^3, \quad (6)$$

$$d_{mix} = \sum_i^n \sum_j^n x_i x_j (1 - m_{ij})[(d_i^{1/3} + d_j^{1/3})/2]^3, \quad (7)$$

(ii) The Panagiotopoulos and Reid mixing rule [23]:

$$b_{mix} = \sum x_i b_i, \quad (8)$$

$$a_{mix} = \sum \sum (1 - K_{ij}) x_i x_j \sqrt{a_i a_j}, \quad (9)$$

$$K_{ii} = 0, \quad K_{ij} = k_{ij} - (k_{ji} - k_{ij})x_i \quad \text{and} \quad k_{ij} \neq k_{ji}, \quad (10)$$

where both binary interaction parameters (k_{ji} and k_{ij}) may depend on temperature. The Helmholtz energy change due to interactions between ionic species may be considered by three separate terms including the Born energy ΔA^{Born} that is required to charge uncharged ions in a medium of dielectric constant D_m , the short-range electrostatic interaction ΔA^{ia} and the long-range electrostatic interaction. The long-range electrostatic interaction is obtained by the Debye–Huckel (DH) term, ΔA^{DH} , or the mean spherical approximation (MSA) term, ΔA^{MSA}

$$\delta A_{ionic} = \Delta A^{Born} + \Delta A^{ia} + (\Delta A^{DH} \text{ or } \Delta A^{MSA}). \quad (11)$$

The effect of the Born energy on the Helmholtz energy change of the system ΔA^{Born} is given by [16]:

$$\Delta A^{Born} = RT \sum_{i=1}^{N_i} \frac{(z_i e)^2 N_A n_i}{4\pi \epsilon_0 D_m \sigma_i}, \quad (12)$$

where N_i is the number of ionic species, D_m is the dielectric constant of electrolyte solution and σ_i is the diameter of i ion. Based on the Margules equation, the short-range electrostatic interaction, ΔA^{ia} is obtained by following equation [3]:

$$\Delta A^{ia}(T, \vec{n}) = \frac{RT}{n_T} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} n_i n_j B_{ij} + \frac{RT}{n_T^2} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \sum_{k=1}^{N_c} n_i n_j n_k C_{ijk}. \quad (13)$$

It has been assumed that the binary and ternary interaction parameters are symmetric and the values of these parameters for ionic–ionic interactions are zero ($B_{ii} = C_{iii} = 0$). Therefore only the interaction parameters between ionic and non-ionic species

TABLE 1
Critical properties and EOS substance-specific parameters [3].

Component	T_c/K	P_c/MPa	M	n	ω
CO ₂	304.2	7.38	0.6877	0.3813	0.224
H ₂ O	647.3	22.05	0.8795	0.0565	0.345

T_c : critical temperature, P_c : critical pressure, ω : acentric factor, m and n : substance-specific parameters.

TABLE 2
Mean ionic diameter d .

Ion	$10^{10} \cdot d/m$	Reference
SO ₄ ²⁻	3.87	[16]
Na ⁺	3.14	[17]
Cl ⁻	3.62	[17]

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