

Prediction and correlation of the phase behaviour of non-ideal binary systems by combining an equation of state with the COSMO-RS model

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Introduction

The application of equations of state to model the phase behaviour of mixtures is advantageous since one model is used for all phases. Equations of state can be used over a wide range of temperatures and pressures. They handle the properties of gases as well as of liquids and polymers and can be applied to the gaseous, liquid and supercritical state. Although recent research has created a number of powerful molecular based equations of state - see [1] and the references within - in industrial process design, cubic equations play still an important role. The success of the cubic equations of state is due to their relatively simple mathematical structure, which particularly makes the calculation of the volume and the derivation of the fugacity coefficient less complex. Its simple extension to mixtures led to the success of the cubic equations of state but also to a nearly unmanageable number of mixing rules [1,2]. One approach among these mixing rules is the combination of the equation of state with an excess Gibbs energy model. Particularly for mixtures with strong interacting components the cubic equations of state provides a poor description of the non-ideal mixing behaviour. To overcome these problems Huron and Vidal proposed an alternative approach [3]. They equated the excess Gibbs energy from an activity coefficient model with that of the equation of state at infinite pressure and described successfully a number of non-ideal systems. However, the Huron-Vidal mixing rule does not satisfy the quadratic composition dependence of the second virial coefficient. Since Huron and Vidal equated the excess Gibbs energies at infinite pressure, parameter tables for G^{ex} -models could not be used because they are fitted to low pressure data. Based on the approach of Huron and Vidal a number of authors have proposed mixing rules which satisfy the quadratic composition dependence of the second virial coefficient and allow the use of G^{ex} -parameter tables [4-15]. In this work it is proposed to use the Peng-Robinson equation of state together with the Wong-Sandler (WS) mixing rule and predict the excess Gibbs energy of the mixture using the a priori model COSMO-RS. The WS mixing rule has been chosen since they satisfy the quadratic

concentration dependence of the second virial coefficient and is correct at high- and low-pressure limit.

Theory

As example the Peng-Robinson equation of state is used:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (1)$$

where P is the pressure, T the temperature, v the molar volume, R the ideal gas constant, a and b the parameters representing the attractive interactions and repulsive interactions. For the mostly non-ideal components considered here the modification of Stryjek and Vera [16]. Pure component parameters a and b are obtained from:

$$a(T) = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (2),$$

$$\alpha(T) = \left[1 + \kappa (1 - T_r^{0.5}) \right]^2 \quad (3),$$

$$\kappa = \kappa_0 + \kappa_1 (1 + T_r^{0.5}) (0.7 - T_r) \quad (4),$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (5),$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (6).$$

T_c is the critical temperature, P_c the critical pressure, ω the acentric factor, κ_1 a component specific constant, and T_r the reduced temperature.

When the WS-mixing rule is applied, the mixing parameters are calculated in the following way:

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (7)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right)}{2} (1 - k_{ij}) \quad (8)$$

$$\frac{G_\gamma^E}{CRT} = \frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT} \quad (9)$$

In Eq. 9 C is an equation of state specific constant which is $C = \ln(\sqrt{2} - 1) / \sqrt{2}$, k_{ij} is the binary interaction parameter. G^{ex} is the excess Gibbs energy calculated here with the

COSMO-RS [17] model. Orbey and Sandler [18] reformulated equation (8) – the combination rule - in the following way:

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}(b_i + b_j) - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}). \quad (10)$$

Further they introduced a modified version of the NRTL equation for calculating the Gibbs excess energy. The only difference from the classical NRTL model is the definition of the local composition, which leads to the introduction of the volume parameter b_j in the calculation of G_{ij} :

$$\frac{G_\gamma^E}{RT} = \sum_i x_i \left(\frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \right) \quad (11)$$

and

$$G_{ji} = b_j \exp(-\alpha \tau_{ji})$$

b_j is the volume parameter of the equation of state for component j. This model can be used for binary mixtures as a four parameter mixing rule. Orbey and Sandler found that by setting the α parameter to a constant value, the binary interaction parameter k_{ij} to zero and using

$$\tau_{21} = \ln \tau_{12}^\infty - \tau_{12} \frac{b_1}{b_2} \exp(-\alpha \tau_{12}) \quad (12)$$

to determine τ_{ij} , it is possible to predict the phase behavior of several nonideal mixtures of organic components by only knowing the activity coefficients at infinite dilution. In this work we used the COSMO-RS model for predicting the activity coefficient at infinite dilution.

COSMO-RS uses the COSMO approach developed by Klamt and Schüürmann [19] to predict an activity coefficient of a component in mixture. It is based on the calculation of the electrostatic interaction of a solute with the surrounding solvent. The solvent is treated as a continuous media of dielectric constant ϵ . The solute is embedded inside an arbitrary shaped cavity in the continuum. Klamt and Schüürmann [19] developed an efficient approach which replaces the dielectric medium of permeability ϵ with the scaled screening charges of a conductor. A COSMO calculation provides the screening charges on the surface of the cavity and is usually carried out at an adequate quantum level which is provided by the density functional theory. A COSMO calculation gives the energy, the geometry, and the screening charge density σ on the surface of a solute after quantum chemical self-consistency and

geometry optimization loops. The transfer from the state of the molecule embedded in a virtual conductor to the real solvent is done by applying the COSMO-RS concept [20]. For further details see the publications of Klamt and co-workers [20,21]. As a result a COSMO-RS calculation provides the chemical potential of a component i in the mixture. The activity coefficient γ of a component i can be written as:

$$\gamma_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \quad (13)$$

where μ_i is the chemical potential of i in the mixture and μ_i^0 is the chemical potential of the pure component, the reference state.

$$G_{COSMO-RS}^E = RT \sum_i x_i \ln \gamma_i \quad (14)$$

The combining Eq. 9 and 14 enables one to predict the mixing parameters a_m and b_m .

Results:

The ability of COSMO-RS to predict the excess Gibbs energy was tested at the system acetone-water at 298.15K. Figure 1 shows the results in comparison with the NRTL model. It can be seen that COSMO-RS predicts the excess Gibbs energy in almost the same ways NRTL does.

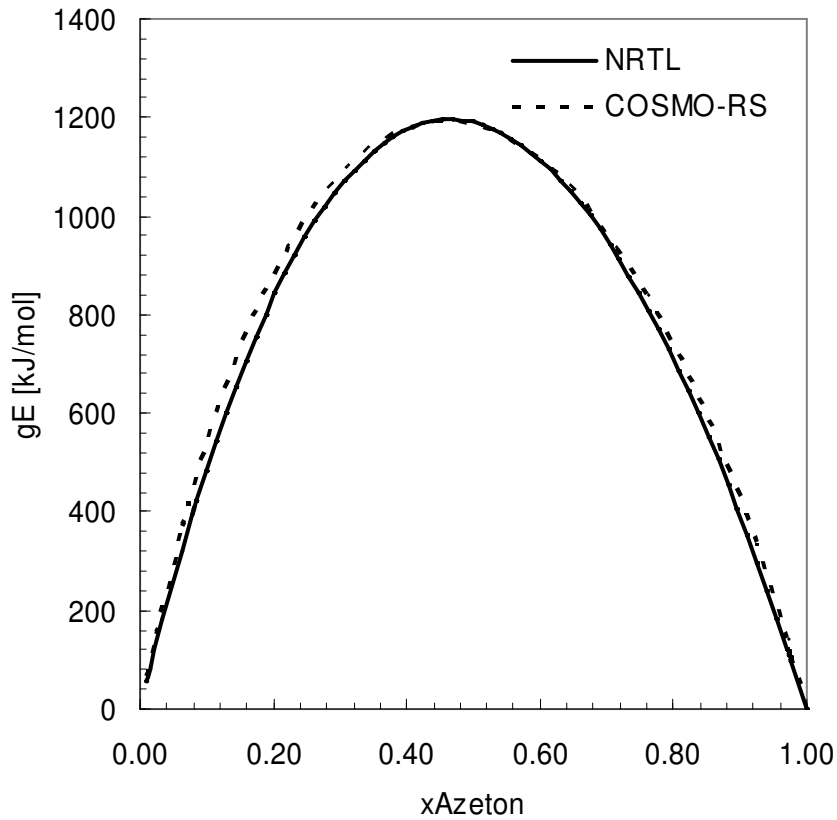


Figure 1 excess Gibbs energy in the system acetone-water at 298.15K

The performance of the mixing rule in combination with the COSMO-RS model will be shown at different binary mixtures.

As an example here the binary mixture of acetone-water are presented at temperatures between 323K and 523K.

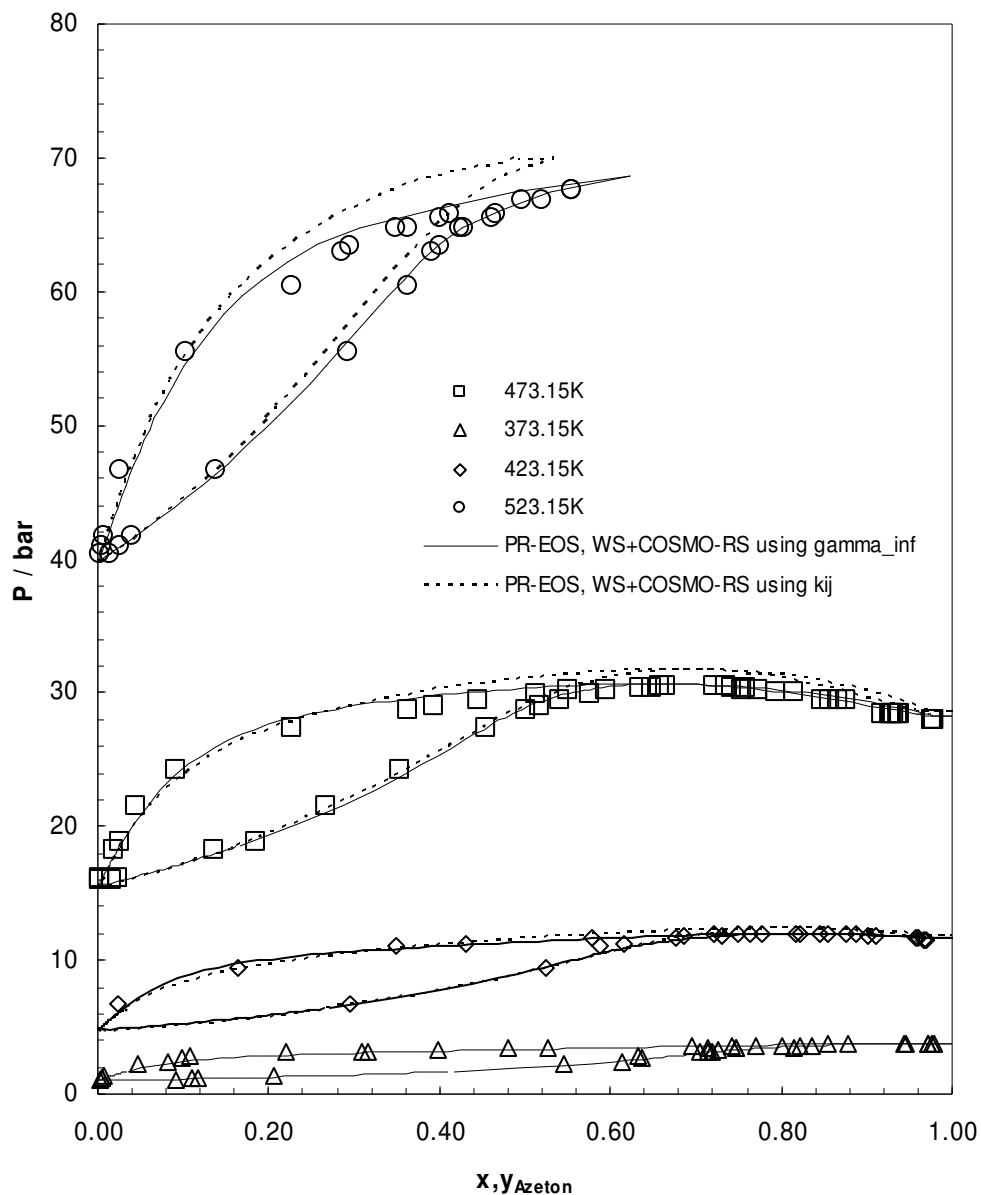


Figure 2 Predictions (dashed lines) and correlations (solid lines) of the vapour-liquid equilibrium for the acetone-water system. With the original and the reformulated Wong-Sandler mixing rule and the modified Peng-Robinson equation of state. Experimental data: Griswold, J.; Wong, S. Y., Chem. Eng. Progr. Symp. Ser., 48, 1952

The solid lines in figure 2 are correlations where one binary interaction parameter has been fitted to low temperature data. This parameter was held constant in all calculations. The dashed lines are pure predictions using the reformulated mixing rule and predicting the activity coefficients at infinite dilution with the COSMO-RS model. As can be seen, the predictions are in good agreement with the experimental data except for the data at 523K.

Conclusions

The combination of the Wong-Sandler mixing rules with the COSMO-RS model is able to predict and correlate the phase behaviour of nonideal binary mixtures. By fitting a binary

interaction parameter to experimental at a low temperature it is possible to extrapolate the phase behaviour up to the supercritical region of the low boiler.

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