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Modeling of phase equilibria with CPA using the homomorph approach

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ABSTRACT

For association models, like CPA and SAFT, a classical approach is often used for estimating pure-compound and mixture parameters. According to this approach, the pure-compound parameters are estimated from vapor pressure and liquid density data. Then, the binary interaction parameters, k_{ij}, are estimated from binary systems; one binary interaction parameter per system. No additional mixing rules are needed for cross-associating systems, but combining rules are required, e.g. the Elliott rule or the so-called CR-1 rule. There is a very large class of mixtures, e.g. water or glycols with aromatic hydrocarbons, chloroform–acetone, esters–water, CO_2–water, etc., which are classified as “solvating” or “induced associating”. The classical approach cannot be used and the cross-association interactions are difficult to be estimated a priori since usually no appropriate experimental data exist, while the aforementioned combining rules cannot capture the physical meaning of such interactions (as at least one of the compounds is non-self-associating). Consequently, very often one or more of the interaction parameters are optimized to experimental mixture data. For example, in the case of the CPA EoS, two interaction parameters are often used for solvating systems; one for the physical part (k_{ij}) and one for the association part (β^{cross}). This limits the predictive capabilities and possibilities of generalization of the model. In this work we present an approach to reduce the number of adjustable parameters in CPA for solvating systems. The so-called homomorph approach will be used, according to which the k_{ij} parameter can be obtained from a corresponding system (homomorph) which has similar physical interactions as the solvating system studied. This leaves only one adjustable parameter for solvating mixtures, the cross-association volume (β^{cross}). It is shown that the homomorph approach can be used with success for mixtures of water and glycols with aromatic hydrocarbons as well as for mixtures of acid gases (CO_2, H_2S) with alcohols and water. The homomorph approach is less satisfactory for mixtures with fluorocarbons as well as for aqueous mixtures with ethers and esters. In these cases, CPA can correlate liquid–liquid equilibria for solvating systems using two adjustable parameters. The capabilities and limitations of the homomorph approach are discussed.

1. Introduction

Cross-association is a frequent phenomenon in hydrogen bonding mixtures, e.g. those containing two self-associating compounds such as water–alcohols and amine-acids. Description of such mixtures with association theories can be done with explicit combining rules, see Eqs. (7) and (8) next. There are, however, many more cross-associating mixtures in which one (or none!) of the compounds are self-associating.

We will use the term “solvation” or “induced association” for these mixtures. Still, the strong cross-interactions, due to hydrogen bonding or Lewis acid-Lewis base interactions in general, have marked influence in phase behavior. For example, the solubilities in water–aromatic hydrocarbons are much higher than those in water–aliphatic hydrocarbons due to acid–base interactions (because of the π-electrons of the aromatic rings). The same is true for the solubilities of glycols in aromatic hydrocarbons compared to glycols with the corresponding alkanes. Equivalently, the hydrogen bonds explain the strong interactions in chloroform–acetone mixtures, which result to complex solid formation at low temperatures. The typically used combining rules in association theories cannot be directly applied to solvating mixtures.

For example, in the case of the CPA equation of state [1–3], the equation expressed for mixtures in terms of pressure P, is:

$$P = \frac{RT}{V_m - b} - \frac{\alpha}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \tag{1}$$

where X_{A_i} is the mole fraction of the molecule i not bonded at site A, x_i is the mole fraction of component i, g is the radial distribution function, ρ is the molar density (=$1/V_m$), while, the co-volume

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parameter, b, and the cross-energy parameter, α, are obtained using the van der Waals one fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad b = \sum_i x_i b_i \tag{2}$$

X_{A_i} can be calculated based on the association strength $\Delta^{A_iB_j}$ between two sites belonging to two different molecules (site A on molecule i and site B on molecule j):

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_iB_j}} \tag{3}$$

where the association strength is calculated as

$$\Delta^{A_iB_j} = g(\rho) \left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_iB_j} \tag{4}$$

with the radial distribution function $g(\rho) = 1/(1 - 1.9n)$, $n = (1/4)b\rho$ and $b_{ij} = (b_i + b_j)/2$.

For pure fluids, the energy parameter of the EoS is given by a Soave-type temperature dependency, while b_i is temperature independent:

$$\alpha_i = a_{0,i} \left[1 + c_{1,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \tag{5}$$

Thus, b_i, $\alpha_{0,i}$, $c_{1,\mathrm{i}}$ are fluid specific parameters. In Eq. (4), the parameters $\varepsilon^{A_iB_i}$ and $\beta^{A_iB_i}$ are called the association energy and the association volume, respectively, and usually are also treated as fluid specific parameters. Consequently, in total, five pure-compound parameters are needed for hydrogen bonding compounds (b_i, $\alpha_{\mathrm{o},i}$, $c_{1,i}$, $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$).

CPA has been extensively used since 1996 and for the details of the model, the reader is referred to the various publications, e.g. Refs. [1–3]. In this work we focus solely on the combining rules and the interaction parameters, with emphasis on the cross-associating and solvating mixtures.

As already mentioned, the van der Waals one fluid mixing rules are used in the SRK part of the model. For the cross-energy parameter, α (see Eq. (2)), the geometric mean rule is used for the energy parameter a_{ij}, and one interaction parameter k_{ij} is often employed:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{6}$$

For cross-associating mixtures, two successful rules which have been used for CPA are the so-called CR-1 rule [4]:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \quad \text{and} \quad \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} = \beta^{\mathrm{cross}} \tag{7}$$

and the Elliott rule [5]:

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \tag{8}$$

Eq. (8) and the first relation of Eq. (7) stem from the following equation:

$$K_{\mathrm{cross}} = \sqrt{K_{ii}K_{jj}} \tag{9}$$

where K_{cross} and K_{ii} (K_{jj}) is the equilibrium constant for the cross- and self-association, respectively, while Eq. (9) stems from the following relation:

$$\Delta H_{\mathrm{cross}} = \frac{\Delta H_{ii} + \Delta H_{jj}}{2} \tag{10}$$

where $\Delta H_{\mathrm{cross}}$ and ΔH_{ii} (ΔH_{jj}) is the association enthalpy for the cross- and self-association, respectively, According to Prausnitz et al. [6] the latter relation is generally satisfactory for the cross-association enthalpy in chemical theories. Usually, CPA is applied using the combining rules of Eqs. (6)–(8). However, several other combining rules have been suggested for molecular equations of state [7–9]. Eqs. (7) and (8) can be used for mixtures of water with alcohols or glycols and other cross-associating systems, where both compounds are hydrogen bonding.

In the case of solvating systems, Folas et al. [4] have proposed the so-called modified CR-1 rule:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon_{\mathrm{associating}}}{2} \text{ and } \beta^{A_iB_j} = \beta^{\mathrm{cross}} \text{ (fitted)} \tag{11}$$

The first relation of Eq. (11) stems from the first relation of Eq. (7) considering that the association energy for the non-self-associating fluid is equal to zero. However, due to the limited physical basis of this relation, the cross-association volume, $\beta^{A_iB_j}$, must be optimized from the experimental data, typically together with k_{ij} (of Eq. (6)) for solvating mixtures. Here, it should be noted that, for such systems, there is no combining rule with strong physical basis.

Having two interaction parameters to fit is possible when extensive data is available but is not always convenient. Trends of the interaction parameters may be obscured, it may be difficult to generalize them and use them for mixtures for which few data are available. It may not, moreover, be clear in some cases whether successful correlation results for solvating systems are due to the explicit account of the solvation or the additional interaction parameter used.

For all these reasons, it is useful to develop a method for describing solvating systems using a single adjustable parameter. One such method which makes use of the physical meaning of the interaction parameters is offered by the so-called homomorph approach. Homomorph, a greek word meaning "same shape", is not a novel concept in thermodynamics. It has been used, e.g. from Anderko [10,11] in connection to his chemical theory. Anderko presents also suitable choices for the homomorphs of alcohols and water.

In our work, the homomorph approach is used as a way to reduce the number of parameters needed to be estimated in the case of a solvating system. The concept is that the k_{ij} interaction parameter, which describes corrections from the geometric mean rule of the cross-energy parameter in the physical term of the model, can be taken from the corresponding "homomorph system" leaving only one interaction parameter, $\beta^{A_iB_j}$, to be fitted to data for the solvating mixture. In this direction, a successful homomorph should be a non-associating compound, which has similar molecular weight and, as much as possible, similar structure to the solvating compound. In the majority of the studied systems normal alkanes were considered as homomorphs of the particular solvating substances. Consequently, normal alkanes with similar molecular weight were selected as homomorphs of aromatic hydrocarbons, glycols, alkanols, ethers and esters. In the same direction, normal perfluoroalkanes were selected as the homomorphs of aromatic fluorocarbons. In some cases, other hydrocarbons could have been chosen as the homomorphs of the aforementioned compounds (i.e. cyclic alkanes as the homomorphs of aromatic hydrocarbons). However, it was not always possible to find experimental data for the phase equilibrium of the corresponding binary systems in order to estimate the binary parameters and test the homomorph approach.

The idea works two-ways. One way is to substitute the solvating substance by its aliphatic counterpart (e.g. n-hexane in the case of benzene), and determine the binary interaction coefficient (k_{ij}) of the substituted system (e.g. water–n-hexane). Using the binary interaction coefficient of the aliphatic system, it is only the binary association coefficient β^{cross} that needs to be determined from the original system (e.g. water–benzene). The second way is to substitute the solvent by a non-solvating alternative (e.g. methanol/ethane), determine the k_{ij} of the substituted system (e.g. ethane–H_2S), re-introduce this k_{ij} to the original binary (e.g. methanol–H_2S) and finally determine the β^{cross}. Both approaches will be used in this work.