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Solid–liquid equilibrium using the SAFT-VR equation of state: Solubility of naphthalene and acetic acid in binary mixtures and calculation of phase diagrams

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ABSTRACT

A solid–liquid equilibrium (SLE) thermodynamic model based on the SAFT-VR equation of state (EOS) is presented. The model allows for the calculation of solid–liquid phase equilibria in binary mixtures at atmospheric pressure. The fluid (liquid) phase is treated with the SAFT-VR approach, where molecules are modelled as associating chains of tangentially bonded spherical segments interacting via square-well potentials of variable range. The equilibrium between the liquid and solid phase is treated following a standard thermodynamic method that requires the experimental temperature and enthalpy of fusion of the solute. The model is used to calculate the solubilities of naphthalene and acetic acid in common associating and non-associating organic solvents and to determine the solid–liquid phase behaviour of binary mixtures with simple eutectics. The SAFT-VR pure component model parameters are determined by comparison to experimental vapour pressure and saturated liquid density data with the choice of association models according to the nature of the molecule; in addition, an unlike adjustable parameter (k_{ij}) is used to model the solutions. The solubility data of naphthalene and acetic acid in both associating and non-associating solvents are reproduced essentially within the accuracy of the experimental measurements. The phase boundaries and the position of the eutectic points in the binary mixtures considered are, in most cases, reproduced with the accuracy commensurate with the industrial applications. Overall, the results presented show that the SAFT-VR EOS can be used with confidence for the prediction of the SLE of binary systems at atmospheric pressure.

1. Introduction

Solid–liquid equilibrium (SLE) thermodynamic models are useful in designing processes that either promote solid precipitation, such as crystallization, or prevent it, such as fouling in pipelines and plant equipment, and in solid–liquid extraction processes, such as leach mining operations and extraction of natural products.

The solubility of a solid compound 1 in a liquid phase L can be obtained using [1]

$$\ln x_1^L = -\frac{\Delta_{\text{fus}} h}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{fus}}}\right) - \ln \gamma_1(T, P, x_1^L) \tag{1}$$

where T and P are the temperature and pressure, R is the ideal gas constant and $\Delta_{\text{fus}}h$ and T_{fus} refer to the molar enthalpy and temperature of fusion of the pure solid, respectively; these are usually taken from experimental data, and γ_1 is the activity coefficient of the compound in the liquid phase. The expression given by Eq. (1) is obtained following a straight forward derivation from the isofugacity (equacondition of phase equilibrium), with a number of approximations [1], and leads to reliable estimates of solubility if the activity coefficient can be obtained accurately. As a result, most existing SLE thermodynamic models are based on activity coefficient approaches, such as the Wilson [2], NRTL [3], UNIQUAC [4] and especially the predictive UNIFAC [5] and modified UNIFAC (Do) [6] approaches. Gmehling et al. [7] have shown that UNIFAC is suitable for modelling the SLE of binary mixtures by calculating the solubilities of naphthalene + solvent, anthracene + solvent and phenanthrene + solvent systems and the eutectic points of mixtures containing acetone, benzene, phenol and acetic acid as solutes. Jakob et al. [8] have obtained good results with UNIFAC and modified UNIFAC (Do) by calculating the SLE of systems of technical interest which contain indane, xylene and tetrachloromethane.

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Lohmann et al. [9] successfully applied the modified UNIFAC (Do) to predict the SLE of binary mixtures containing benzaldehyde, dodecane, benzene and other organic compounds. However, they obtained quite poor results for the system cyclohexane + phenol, which have been overcome by refitting the group contribution parameters between the main groups of these compounds. In addition, the solid–liquid equilibrium of multicomponent alkane mixtures, which are of interest in the context of wax deposition prediction has been studied in a number of works by Coutinho et al. [10–12], Peng et al. [13], and Mahmoud et al. [14]. The latter have considered a number of systems containing pyrene and *n*-alkanes using the UNIFAC equation to model the systems; however they found that a readjustment of the UNIFAC parameters was needed to obtain good agreement with the experimental data. Domanska and co-workers have studied in a series of papers the SLE of ionic liquids [15–18] and fragrance molecules [19,20] in a number of solvents, including water, *n*-hexane, aromatic hydrocarbons and a number of *n*-alkanols, presenting new experimental data and correlations using the Wilson, UNIQUAC and NRTL equations at ambient and high pressures [21,22]. Eutectics with and without immiscibility in the liquid phase are observed experimentally in some of the mixtures, and the three correlating methods above are found to provide equivalent results when comparing to the experimental data.

SLE models based on cubic equations of state (EOS), such as Soave–Redlich–Kwong (SRK) [23] and Peng and Robinson (PR) [24], are not as common, but some interesting applications can also be found in the literature. Domanska and co-workers [25,26] have successfully applied the SRK EOS to correlate the high-pressure SLE of *n*-alkane binary mixtures and Derevich and Pershukov [27] have obtained good results modelling the formation/deposition of solid paraffinic wax compounds in reservoir fluids with the PR EOS. A new latticed-based equation of state method especially designed for hydrogen-bonding systems has been applied to model the phase behaviour of pharmaceuticals [28,29], including the SLE. This approach incorporates a compressible lattice, which means that pressure effects can be taken into account. Within equation of state approaches, the statistical associating fluid theory (SAFT) [30,31] (see also Refs. [32–34] for recent reviews of the field), provides a state-of-the-art route to the activity coefficient calculation of complex fluids. The key advantage is its ability to describe the phase equilibrium of complex fluids with different molecular structures (from small molecules to polymers) including the effect of associating interactions (e.g., hydrogen bonding), which are not explicitly taken into account in traditional approaches. The Huang and Radosz version of SAFT for Lennard–Jones associating chains [35,36], a copolymer method [37] and the perturbed chain SAFT (PC-SAFT) equation [38,39] approach have already been successfully applied to model the SLE of associating, polar and polymer systems. Ghosh and Chapman [40] have been able to relate the onset of polymer agglomeration in slurry processes with the solubility of polyethylene in various liquid (carrier) phases by using an SLE thermodynamic model paired with the original SAFT equation. In a similar work, the co-polymer version of SAFT has also been used to study the SLE of naphthalene, *n*-alkanes and polyethylene in hydrocarbon solutions [41]. SLE models are particularly useful in the prediction of the solubility of organics of pharmaceutical and biological interest (e.g., aminoacids). The PC-SAFT approach has been successfully used to calculate the activity coefficient of such solutes in a number of works [42–46]. In addition, the SLE of mixtures that present complex-solid formation (such as hydrates or solvates) has also been modelled combining a chemical approach with a solubility model [47].

In this contribution, we use the SAFT-VR approach [48,49] to study the solubility of naphthalene and acetic acid in organic solvents at ambient pressure and calculate the solid–liquid phase diagrams of three binary mixtures with simple eutectic (propanoic acid + acetic acid, pyrene + *n*-octacosane and benzene + diethoxymethane). Describing the SLE of these systems is of great technical interest because of its applicability. For instance, solubility data of naphthalene are very important in understanding the dissolution of this compound in organic solvent/water mixtures, which is fundamental in chemical engineering, pharmacology, toxicology and environmental science [50]. Also, solubility data of acetic acid, an important chemical commodity used primarily as a raw material for vinyl acetate monomer [51], is very useful to fully understand its thermodynamic behaviour. SLE data of the mixture pyrene + *n*-octacosane is important to describe the phase transformations of systems of heavy hydrocarbons and heavy petroleum fractions [14]. Analyzing the solubility of the mixture benzene + diethoxymethane is fundamental in the design of synthesis and separation of diethoxymethane, an acetal mainly used as a raw material for perfumes, agricultural chemicals, pharmaceuticals and fragrances [52]. Finally, SLE data of propanoic acid + acetic acid, a key mixture in biological metabolism and in the quality of foodstuffs [53], is important to describe the properties of these fatty acids. All the selected mixtures are used to validate the proposed approach and establish a well-grounded procedure that may allow further improvements for more complex systems.

2. Solid–liquid equilibrium with SAFT-VR

In this work, we use the SAFT version for potentials of variable range (SAFT-VR) to determine the thermodynamic properties required for solving the SLE of binary mixtures (i.e., the activity coefficient of the solid compound in the liquid phase, cf. Eq. (1)). Specifically, we use the SAFT-VR EoS based on the square-well potential, which is described in detail elsewhere [48,49].

2.1. The SAFT-VR equation of state

In the SAFT-VR approach, the total Helmholtz free energy A of a mixture of associating chain molecules is written as [48,49],

$$\frac{A}{nRT} = \frac{A^{\mathrm{IDEAL}}}{nRT} + \frac{A^{\mathrm{MONO}}}{nRT} + \frac{A^{\mathrm{CHAIN}}}{nRT} + \frac{A^{\mathrm{ASSOC}}}{nRT} \qquad (2)$$

where n is the total number of moles in the mixture, T is the absolute temperature and R is the ideal gas constant. The term A^{IDEAL} corresponds to the ideal free energy of the mixture, A^{MONO}, A^{CHAIN} and A^{ASSOC} are the residual contributions to the free energy due to monomer–monomer repulsive and attractive (dispersion) interactions, to the formation of molecular chains, and to intermolecular association (hydrogen bonding), respectively. The expressions required for all the terms in Eq. (2) can be found in Refs. [48,49] and the reader is referred to them for more details.

2.2. Solid–liquid phase equilibrium

In this work, we consider the case of SLE where the liquid phase is a mixture of dissolved solute and solvent, and the solid phase does not contain any solvent. The following equation describes the SLE in this case [1],

$$\ln x_1^l \gamma_1(T, P, x_1^L) = \frac{\Delta_{\mathrm{fus}} h}{RT_{\mathrm{tr}}}\left(\frac{T_{\mathrm{tr}}}{T} - 1\right) - \frac{\Delta c_p}{R}\left(\frac{T_{\mathrm{tr}}}{T} - 1\right) + \left(\frac{\Delta c_p}{R}\right)\ln\frac{T_{\mathrm{tr}}}{T} \qquad (3)$$

where T_{tr} is the triple point temperature and $\Delta c_p = c_p$ (liquid) − c_p (solid) is the change in the heat capacity of the solute. Since the triple point temperature and the temperature of fusion (i.e. at atmospheric pressure) are similar, T_{tr} can be replaced by the temperature