Towards predictive association theories

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ABSTRACT

Association equations of state like SAFT, CPA and NRHB have been previously applied to many complex mixtures. In this work we focus on two of these models, the CPA and the NRHB equations of state and the emphasis is on the analysis of their predictive capabilities for a wide range of applications. We use the term predictive in two situations: (i) with no use of binary interaction parameters, and (ii) multicomponent calculations using binary interaction parameters based solely on binary data. It is shown that the CPA equation of state can satisfactorily predict CO_2–water–glycols–alkanes VLE and water–MEG–aliphatic hydrocarbons LLE using interaction parameters obtained from the binary data alone. Moreover, it is demonstrated that the NRHB equation of state is a versatile tool which can be employed equally well to mixtures with pharmaceuticals and solvents, including mixed solvents, as well as phase equilibria in mixtures containing glycols. The importance of considering the solvation of CO_2–water (in CPA) when the model is applied to multicomponent mixtures as well as of the multiple associations in heavy glycol–water mixtures (in NRHB) is investigated.

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1. Introduction

Association models, especially in the form of equations of state which account explicitly for hydrogen bonding and related phenomena, have been proved extremely useful tools in numerous applications. These applications range from polar mixtures of relevance to the petroleum and chemical industries, up to pharmaceuticals and polymers. There is a wide range of models which fall under the heading "association models" e.g. variants of the SAFT theory, chemical theories and lattice-fluid theories. Two monographs (Kontogeorgis and Folas [1]; Prausnitz et al. [2]) and some articles (Economou [3]; Müller and Gubbins [4]; Radosz and coworkers [5]; Kontogeorgis et al. [6,7]) provide reviews. The wide applicability range is not the only factor, which contributes to the popularity and broad use of these models. Another important feature is that only few parameters (pure compound and mixture) are needed which, moreover, can have a theoretical significance or meaning, which facilitates their estimation. Nevertheless, an important question which arises is to which extent these models are predictive or how many and what type of data are required for the estimation of the involved parameters.

The investigation of the predictive capabilities of the association theories is the subject of this work. The term "predictive" requires some explanation. Both direct and indirect predictive approaches can be identified.

Under the heading direct approaches we include methods for the a priori estimation of pure compound and mixture parameters of association models such as:

(i) Use of quantum chemical, spectroscopic or group contribution methods for estimating, mostly, the pure compound parameters of SAFT-variants or lattice-based models. Group Contribution (GC)-versions of PC-SAFT, SAFT, SAFT-VR and NRHB have been proposed [8–15]. The segment number and diameter as well as the dispersion energy of SAFT-VR and PC-SAFT have been recently shown to be predicted using quantum chemical methods as well [16–20]. Recently, some of the association theories have been tested against spectroscopic data especially for the monomer fraction (von Solms et al. [21,22]; Jackson and coworkers [23]).

(ii) Using no-mixture determined interaction parameters, thus relying upon fully predictive mixing and combining rules. Alternatively, utilizing predictive schemes for estimating the interaction parameters such as the Hudson-McCoubrey method applied to PC-SAFT and SAFT-VR (Haslam et al. [24]) or the homomorph method recently used for CPA (Breil et al. [25]) for eliminating one of the two adjustable parameters required

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for solvating mixtures. The term "solvation" in this context refers to cross-associating mixtures but with one of the compounds being non self-associating e.g. water–benzene and water–acetone.

Under the heading indirect approaches, we include a variety of calculations which test the capability of models for a wide range of systems and conditions such as:

(i) Prediction of multicomponent data using binary parameters obtained solely from binary data.
(ii) Results over extensive temperature ranges using temperature independent interaction parameters.
(iii) Using the same interaction parameter for VLE, LLE, SLE, dilute conditions.
(iv) Use of the same interaction parameters for (mixture) phase behavior and other properties (enthalpies, speed of sound, etc.)

In this work we focus on one of the direct approaches (using zero value of all mixture interaction parameters) but mostly on the indirect approaches, especially on the prediction of multicomponent multiphase behavior using solely binary interaction parameters obtained from binary data.

Two models from different families of association theories have been chosen for illustrating different aspects of the predictive capabilities and limitations of the models; the CPA and the NRHB equations of state. The aim of this work is to explore the predictive abilities of such theories in fields, where the theories have been previously applied. Consequently, CPA, which is a model more oriented to industrial applications, is used in mixtures with water, glycols, acid gases and hydrocarbons, which are common chemicals in many petroleum related processes. On the other hand, the NRHB model was recently extended to pharmaceuticals and systems with complex hydrogen bonding interactions [41,42]. Consequently, in this work NRHB is applied to predict the solubility of some pharmaceuticals in pure and in mixed solvents as well as to predict the phase behavior of aqueous mixtures of glycols, in which more than one cross-hydrogen bonding interactions are observed.

2. Modeling the phase equilibria for multicomponent mixtures with CO_2 using the CPA EoS

CO_2-containing mixtures are very important in various applications in the oil and gas industry, supercritical fluid extraction, catalytic reactions in supercritical media as well as in processes related to CO_2 capture, transport and storage. In many of these applications, CO_2 is in mixtures containing water, hydrocarbons and polar chemicals and it is of paramount importance not only to describe the phase behavior of the constituent binaries but also to predict the multicomponent multiphase equilibria of CO_2-containing mixtures. This is especially the case as such multicomponent data are rather scarce.

While the capability of the CPA EoS for other types of multicomponent systems e.g. water–alcohol–hydrocarbons has been illustrated [6,7,26], only very recently multicomponent mixtures with acid gases (H_2S) have been considered (Tsivintzelis et al. [27]). We evaluate here the performance of the model for multicomponent mixtures with CO_2. It has been previously [7,49] illustrated that explicitly accounting for the solvation is important in CO_2–water and CO_2–small alcohol mixtures. In the study of the phase behavior of multicomponent mixtures containing CO_2 and water, it is important to investigate how accounting for solvation of CO_2 in water affects the predictions of the CPA model. Solvation is accounted for using the modified CR-1 rule, i.e. the cross-association energy is half the value of the hydrogen

Table 1
CPA binary parameters used for CO_2–water–TEG ternary system.

	k_{ij}	ε_{cross} (bar L/mol)	β_{cross}
Case A (CO₂ inert)			
Water–TEG	−0.2010	CR1: 154.96	CR1: 0.0361
CO₂–water	−0.0232	–	–
CO₂–TEG	0.0390	–	–
Case B1 (solvation of CO₂ in water and TEG using mCR-1)			
Water–TEG	−0.2010	CR1: 154.96	CR1: 0.0361
CO₂–water	0.1380	mCR1: 83.28	0.0911
CO₂–TEG	0.0394	mCR1: 71.69	0.0003
Case B2 (solvation of CO₂ in water and TEG using the experimental value for the CO₂–water cross association energy, ε_{cross})			
Water–TEG	−0.2010	CR1: 154.96	CR1: 0.0361
CO₂–water	0.1141	Exp.: 142.0	0.0162
CO₂–TEG	0.0397	mCR1: 71.69	0.0006

bonding compound, while the cross-association volume is fitted, together with the k_{ij} interaction parameter. Thus, correlation of phase behavior of solvating mixtures typically involves adjusting two interaction parameters to experimental data. This raises the question whether the improvement seen for such (binary) mixtures attributed to appropriate accounting of an existing solvation effect or is it in reality a result of the use of a second adjustable interaction parameter?

The performance of the model with emphasis on the role of solvation will be here illustrated for two ternary mixtures: CO_2–water–TEG and CO_2–water–methane as well as for the quaternary system water–TEG–CO_2–methane.

Calculations were performed using three approaches. Firstly, CO_2 was considered as inert compound (case A). In a second step solvation of CO_2 in water and glycols was assumed. Firstly, the modified CR-1 rule (mCR-1) was used in order to obtain parameters for CO_2–water or CO_2–glycols cross-interactions (case B1). CO_2 was modeled assuming two proton acceptor sites. In a different approach, parameters for the CO_2–water cross-interactions were adopted from experimental studies (case B2). No experimental cross-interaction data are available for CO_2–glycols, thus mCR-1 rule is used in all cases for this system. The CR-1 rule is used for water–TEG. CO_2 was modeled assuming one site. Pure fluid parameters were adopted from previous studies [27,36], unless otherwise indicated in the text. All binary interaction parameters were adopted from the corresponding binary systems (using VLE and/or LLE data) and they are presented, for the three systems, in Tables 1–3.

Takahashi et al. [28] report the solubility of CO_2 in aqueous TEG solutions at various temperatures as a function of pressure. Experimental data and CPA predictions are presented in Fig. 1.

Table 2
CPA binary parameters used for CO_2–water–methane ternary system.

	k_{ij}	ε_{cross} (bar L/mol)	β_{cross}
Case A (CO₂ inert)			
H₂O–CO₂	−0.0232	–	–
Methane–H₂O	0.0098	–	–
Methane–CO₂	0.0882	–	–
Case B1 (solvation of CO₂ in water using mCR-1)			
H₂O–CO₂	0.1380	mCR1: 83.275	0.0911
Methane–H₂O	0.0098	–	–
Methane–CO₂	0.0882	–	–
Case B2 (solvation of CO₂ in water using the experimental value for the cross association energy, ε_{cross})			
H₂O–CO₂	0.1141	Exp.: 142.0	0.0162
Methane–H₂O	0.0098	–	–
Methane–CO₂	0.0882	–	–