

The role of monomer fraction data in association theories—Can we improve the performance for phase equilibrium calculations?



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ABSTRACT

Monomer fraction (fraction of non-hydrogen bonded molecules) data obtained from spectroscopy are available for a few associating compounds. Such data can be used for testing the performance of association models like CPA and SAFT or alternatively be employed in the model development. But how accurate and how useful are such data today and how successful is their use in the context of association models? In this work we attempt to answer these questions in the case of the CPA model and for ethanol. CPA has been already successfully used to describe thermodynamic properties of many ethanol containing mixtures, using an ethanol parameter set that was adjusted to experimental vapor pressure and liquid density data. We present in this work a new parameter set for ethanol which is estimated using experimental vapor pressure, liquid density data as well as the experimental monomer fractions for liquid ethanol. Using both the existing (“old”) and the new parameter sets, we perform an extensive comparison of CPA results for a wide range of ethanol-containing systems, with water and alkanes as well as multicomponent water–ethanol–hydrocarbon liquid–liquid equilibria and hydrate curves with different ethanol content as inhibitor. There are some differences in the performance of CPA with the two sets but on average the results are similar. This may indicate that monomer fraction data are not very useful in this case or that ethanol monomer fraction data are not accurate and both possibilities are discussed.

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1. Introduction

The hydrogen bonding behavior of associating fluids, such as alcohols, water and carboxylic acids is a dominant factor defining their thermodynamic properties. Consequently, it has to be successfully accounted for in the modeling of such fluids using equation of state models. The degree of hydrogen bonding is frequently measured/presented as the fraction of monomers, or in other words the fraction of unbonded molecules (molecules that do not participate in hydrogen bonds).

Experimental monomer fraction data have been used in several recent works for the parameterization and development of equation of state models [1–7]. However, as reported by Kontogeorgis et al. [7], what remains to be seen is whether including monomer fraction data in the estimation of the characteristic pure fluid parameters, which each model requires, renders parameters

that result in improved calculations for thermodynamic properties (and especially for the phase behavior) of mixtures.

Experimental monomer fraction data for alcohols have been presented by Luck [8], Lien [9], and Fletcher and Heller [10]. In this work, we use such data as they were transformed and used by von Solms et al. [1] in their work of validating association theories against spectroscopic data. Furthermore, various association models are mentioned in this work, especially the CPA, PC-SAFT and NRHB equations of state. However, it should be mentioned that all the CPA, PC-SAFT or NRHB calculations presented in this article for estimating the monomer fractions, using the 2B, 3B or 4C association schemes [1], were performed using the same approach with von Solms et al. [1].

They will not be described further here and the reader is referred to the original publications or recent books [11–14]. The available experimental data for alcohols, as well as the CPA predictions using the ethanol pure fluid parameters from Folas [15] (see also Folas et al. [16]) are shown in Fig. 1. These ethanol CPA parameters (and others, as it is mentioned next in this section) are presented in Table 1. First of all, it can be seen that Folas et al. [16] CPA parameters fail to describe the monomer fraction data (fraction of unbonded molecules) for pure liquid ethanol. At a second level, it can be seen that the experimental data for ethanol almost coincide with the experimental data for methanol. This was not expected,

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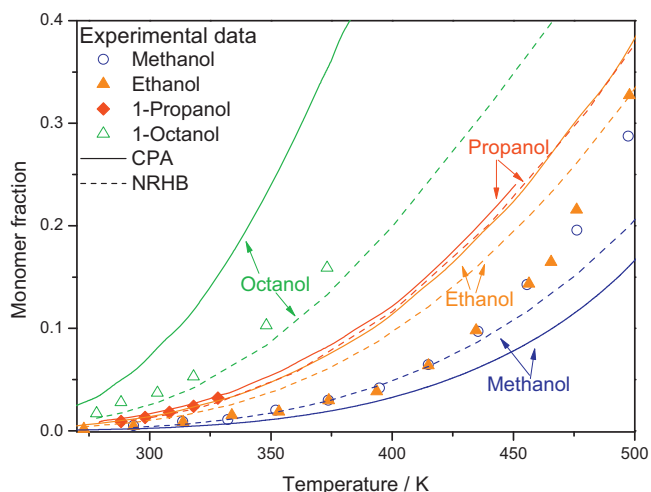


Fig. 1. Experimental monomer fraction data for alcohols, CPA and NRHB predictions. Experimental data are from Luck [8], Lien [9], and Fletcher and Heller [10]. CPA and NRHB pure fluid parameters were adopted from literature [6,16].

since methanol and ethanol have quite different properties, e.g. their dielectric constants are 32.6 and 24.3, respectively. However, it is unclear whether it is the ethanol or the methanol data (or none of them) that should be questioned, since these are the only experimental data that can be found in the literature. From Fig. 1, it is also observed that, as expected, the monomer fractions increase with alcohols' molecular weight, if data up to 1-octanol are accounted for. The same reasonable trend is observed also for various other association models such as the NRHB theory [6,14] as it is also shown in Fig. 1.

We return now to Folas et al. [16] CPA parameters for ethanol. They have been estimated using primarily vapor pressure and liquid density data, although the percentage error in vapor pressure is around 2.3%. Clearly, such parameters were selected after consideration also of mixture data, possibly LLE for ethanol–hydrocarbon mixtures, as this approach has been previously used in the CPA work for other associating compounds such as water, methanol and glycol [11]. In this direction, Folas [15] concludes that LLE data for the binary mixture of an associating component with alkanes can be used as a “guide” for selecting the best pure component parameters for the associating fluid, among various successful sets for vapor pressures and liquid densities. According to this approach, the LLE data is not directly included in the parameter estimation, but is used for screening among the successful pure compound parameter sets. Typically, by following this procedure a single set of optimum pure component parameters is obtained. Furthermore, Folas [15] and Folas et al. [16] have presented CPA results for the description of the low pressure and high pressure LLE of binary mixtures of ethanol with *n*-dodecane, *n*-tetradecane and *n*-hexadecane. The results, especially the low pressure ones, are in good agreement with experimental data. In all cases, calculations

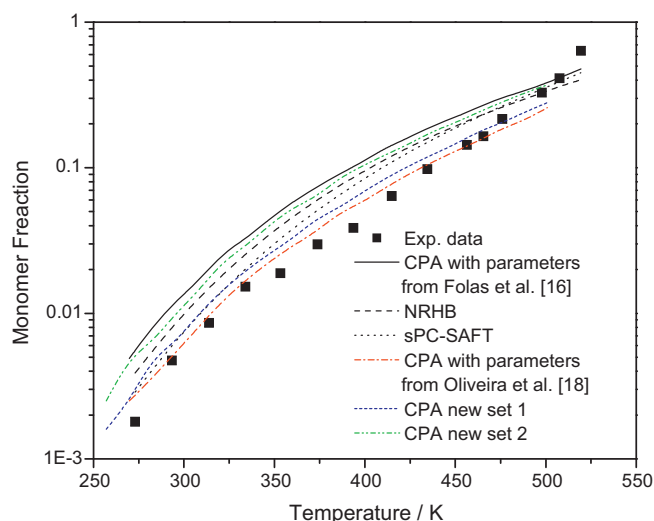


Fig. 2. Monomer fraction for ethanol with three association theories. Experimental data (points) [8], NRHB, CPA and sPC-SAFT predictions (lines). CPA pure fluid parameters were taken from Refs. [16,18], while the sPC-SAFT and the NRHB parameters are from Ref. [17].

are shown using the 2B and the 3B association schemes for ethanol. From the findings of the study and considering the very satisfactory performance of the model for the aforementioned systems, the 2B association scheme was selected for further modeling of alcohol systems. Satisfactory predictions have been presented for a few water–alcohol–hydrocarbon systems.

CPA pure fluid parameters for ethanol were also published from Oliveira et al. [18]. They are also shown in Table 1. Such parameters were not extensively tested in describing the LLE of ethanol systems. However, as shown in Fig. 2, they accurately describe the experimental monomer fraction data for ethanol. We have also estimated in this work two new parameter sets of ethanol, which are shown in Table 1. Especially set 1 results in low deviations for vapor pressures and liquid densities, and simultaneously gives rather accurate predictions for the monomer fractions of pure ethanol. This set for CPA is similar with the one proposed by Kontogeorgis et al. [7] in their work of using simultaneously vapor pressures, densities and monomer fraction data in the parameter estimation. Fig. 2 shows the ethanol monomer fraction predictions with CPA, using all the aforementioned parameter sets, as well as with other association models (PC-SAFT and NRHB). It can be observed that the predictions using the CPA parameters estimated by Oliveira et al. [18] are in very good agreement with the experimental data. The predictions using the parameter set of Folas et al. [16] show the highest deviations from experimental data. The new parameter set 1, which shows the lowest deviations in vapor pressures and liquid densities, presents good agreement with the monomer fraction experimental data. Parameter set 2, results in similar monomer fraction predictions as the NRHB and sPC-SAFT models.

Table 1

CPA parameters for ethanol and percentage average deviations for vapor pressure and molar volume (the 2B association scheme is used for ethanol).

T_c (K)	b (L/mol)	a_0 (L ² bar/mol ²)	c_1	ε (bar L/mol)	β (-)	%AAD ^a in P^{sat}	%AAD ^a in V^{liq}	Temp. range (T_r)
Folas et al. [16]								
513.92	0.04908	8.67160	0.7369	215.32	0.0080	2.33	0.58	0.5–0.97
Oliveira et al. [18]								
514.7	0.04751	6.84150	0.9392	213.36	0.0192	0.24	1.17	0.5–0.97
New set 1								
513.92	0.04769	7.30598	0.8264	220.00	0.0132	0.57	0.62	0.5–0.97
New set 2								
513.92	0.04881	8.41094	0.7247	220.00	0.0080	1.89	0.48	0.5–0.97

^a %AAD = $(100/n) \sum |x_{exp} - x_{calc}|/x_{exp}$, where n is the number of experimental points and x stands for P^{sat} or V^{liq} (or mole fractions in Tables 3–5,7,8).

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