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SAFT-VR-Mie with an incorporated polar term for accurate holistic prediction of the thermodynamic properties of polar components

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ABSTRACT

The SAFT-VR Mie equation of state is extended to polar components and their mixtures by incorporating an explicit polar term into the residual Helmholtz energy expansion. The transferability of the Jog & Chapman (JC) and Gross & Vrabec (GV) polar terms to this framework is demonstrated, yielding the SAFT-VR Mie-JC and SAFT-VR Mie-GV models. Numerical challenges common to the parameterization of both SAFT-VR Mie and polar SAFT are found to characterize the regression of parameter sets in these new models, most notably for the JC term. These challenges hampered the performance of SAFT-VR Mie-JC, which was consistently outperformed by its GV counterpart as a result. Excellent predictions of mixture behaviour for ketones, esters and ethers are in evidence if the *mixture data* (MD) and *fixed polar parameter* (FPP) regression approaches are employed to yield unique parameter sets. The performance of the latter is particularly significant, as accurate predictions for both phase equilibrium and speed of sound are in evidence from parameter sets regressed using pure component properties alone, without the need for experimental mixture data. Based on the functional groups and systems under investigation, the SAFT-VR Mie-GV model with *FPP* parameter sets represents a holistic, predictive approach for the thermodynamic description of polar components and their mixtures.

1. Introduction

To date, the accurate description of phase equilibria has been the driving force in the development of fundamental, state-of-the-art thermodynamic models. This singular focus has meant that description of other thermodynamic properties has taken a backseat in thermodynamic model development, which has led to largely correlative results for these properties. As the predictability of phase equilibria plateaus however, a more holistic approach to model development is beginning to emerge. This approach takes into account the very nature of thermodynamic properties and their interconnectivity through the Helmholtz free energy.

The Statistical Associating Fluid Theory (SAFT) [1–4] framework is arguably the most successful example of this approach to thermodynamic model development. SAFT has been successfully implemented in a number of variants and their subsequent modifications, including the perturbed chain (PC)-SAFT [5], SAFT for potentials of variable range (SAFT-VR) [6,7] and group contribution SAFT (GC-SAFT) [8] variants. The capacity of these models to predict, or at least correlate, phase equilibria has been demonstrated extensively in recent years, with no clear superiority of any one variant. The *holistic* predictive strength of these models is still largely unaddressed however, and is gaining more attention in the literature [9–15].

In particular, recent studies have investigated model performance applied to speed of sound, among other derivative properties, for pure components and mixtures [9–15]. These studies tend to share a common finding; namely that a single parameter set cannot be used to generate accurate predictions of *both* phase equilibria and other thermodynamic derivative properties. The parameter regression method may be modified to yield better predictions for either equilibrium or derivative properties, but this comes at the expense of accuracy in the other. Even when one resorts to fitting binary interaction parameters (BIPs) for a better correlative fit, one finds that a single BIP does not consolidate the quality of the fit for both sets of properties simultaneously. These findings thus suggest that the problem is an inherent flaw in the common theory of these SAFT variants that has remained unaddressed due to the priority given to phase equilibria predictions.

SAFT-VR Mie [9,10] not only considers the prediction of

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thermodynamic derivative properties, but explicitly incorporates their consideration into the model's development. Indeed, the model has recently been modified [12] to consider a third order perturbation, compared to the standard second order treatment of its contemporaries. The resulting model holds the promise of holistic strength, exhibiting accurate predictions for phase equilibria, derivative properties and even critical properties.

To date, application of this refined equation of state (EoS) to real components has largely been limited to n-alkanes as well as smaller chain alcohols, perfluoroalkanes, carbon dioxide and water [12,16,17]. Application to mixture data has been even more restricted, with a focus on industrially relevant reservoir fluid and carbon capture mixtures, yielding accurate results in both cases [18]. This selected application raises questions about the broader applicability of the model when considering different homologous groups and chemical families. Dipolar molecules are one such consideration, where the components' thermodynamic properties are strongly influenced by their permanent dipole moment (μ). Accounting for dipolar behaviour requires explicit treatment in other SAFT variants [19], but SAFT-VR Mie's capacity to accurately account for these interactions has yet to be tested.

The aim of this work is thus to extend the applicability of this promising EoS to other components of practical interest. Our interest is the application of SAFT-VR Mie to dipolar components and their mixtures given that such components have yet to be considered in the new framework. In particular, our goal is to identify a predictive approach that allows for an accurate, holistic description of these components and their mixtures. The results presented will be analysed using equivalent predictions of polar sPC-SAFT as reference, given our experience with this model [20–22] and its success in predicting phase equilibria of polar components. In order to focus on the exclusive treatment of these dipolar interactions, the scope of the work presented here is limited to dipolar non-self-associating components and their mixtures; specifically ketones, ester and ethers.

2. Theory

2.1. Parameterization

In addition to the traditional SAFT segment diameter (σ), segment number (m) and dispersion energy (ε/k), SAFT-VR Mie introduces two further parameters to describe a pure, non-associating component [12]. The attractive and repulsive range parameters (λ_a and λ_r respectively) characterize both the shape and width of the Mie intermolecular potential function. This variable treatment is supported by physical arguments, as a universal potential function has long since been considered a simplified approximation [12]. In order to reduce the number of parameters that require fitting however, the value of the attractive exponent can be set equal to 6 - the value corresponding to the range of London dispersion forces common to all components [12,16,17]. Thus only the *repulsive* exponent is introduced as an additional fitted parameter when comparing SAFT-VR Mie to the likes of sPC-SAFT. This approach is credited for allowing SAFT-VR Mie to overcome the limitations of the fixed square-well or Lennard-Jones potentials used by other SAFT variants, and yields better predictions of derivative properties [10].

2.2. Accounting for polarity

The effects of polar interactions were approximated in the original SAFT framework by incorporating them into the dispersion term of the residual Helmholtz energy expansion. Dipolar interactions are fundamentally different however, exhibiting strong, anisotropic forces that occur over longer ranges than typical dispersion forces. The result of this approach was artificially large dispersion energy parameters (ε/k) for pure components, and excessively large BIPs necessary to fit mixture data [23]. A cursory analysis of the parameterization of SAFT-VR Mie would lead one to believe that application of the EoS to dipolar components in its current form would produce similar results. More generally, the additional *repulsive* range parameter cannot reasonably be expected to provide the greater predictive capacity necessary to capture the *attractive* effects of dipolar interactions. This is evident from the SAFT-VR Mie prediction for VLE in the acetone/n-hexane system using parameters regressed for acetone in Fig. 1 (more extensive examples are given in Ref. [24]). It is clear that some improvement is made over the equivalent prediction of nonpolar sPC-SAFT, even qualitatively predicting an azeotrope where its counterpart could not, but the shared shortcomings between the models are still plainly apparent.

A physically sound alternative may be to allow the dipolar interactions to be accounted for through a variable attractive range parameter, λ_a. A similar approach was tested by Dufal et al. [18] who assessed different parameter sets considering λ_a as either adjustable or fixed for nonpolar components. Leaving λ_a adjustable often yielded better correlation of component properties, but the resulting values of λ_a were frequently at odds with the physical understanding of the quantity. As a result, those parameter sets based on the London dispersion attractive range (viz. $\lambda_a = 6$) were favoured to maintain physical relevance of the model parameters. Following these conclusions, it appears a more explicit approach to modelling polar components may be necessary.

Given the EoS's relative youth, a specific polar theory has not been developed for SAFT-VR Mie, although attempts have been made at such development for its predecessors. SAFT-VR + D [26,27] took an implicit approach to accounting for polarity by accounting for the effect of dipolar interactions at the monomer and chain level rather than adding an explicit polar term. While the SAFT-VR + D EoS showed good results when compared to molecular simulation data of dipolar associating and non-associating fluids, application to the properties of real fluids and their mixtures was limited to the vapour pressure and saturated liquid density of water [27]. To our knowledge, no further results have

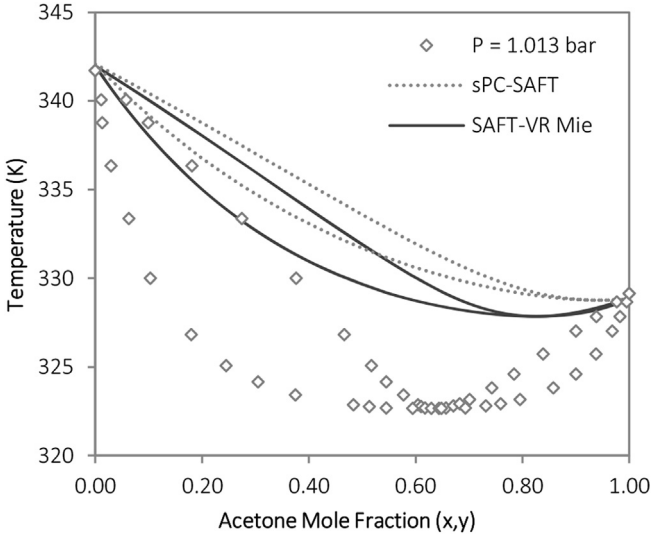

Fig. 1. Comparison of nonpolar sPC-SAFT and SAFT-VR Mie predictions for the acetone/n-hexane system [25] at 1.013 bar. Neither model accurately captures behaviour in the absence of a polar term.