Liquid–liquid interfacial tensions of binary water-hydrocarbons mixtures via gradient theory and CPA equation of state

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A B S T R A C T

The combination of the gradient theory of inhomogeneous interfaces (GTII) with cubic plus association equation of state (CPA EoS) was applied for the correlation of liquid–liquid interfacial tensions of water-hydrocarbons mixtures (alkanes and aromatics) as a function of temperature and pressure. In order to give predictive capability to the proposed method, all binary parameters of the CPA EoS were set to zero, except for aromatics in which one solvation and one binary parameter are required for appropriate description of phase equilibria. GTII was employed in the Helmholtz energy framework, assuming no volume change upon mixing. For binary mixtures, this approximation avoids the time consuming density profile computation and it makes the calculations similar when using excess Gibbs energy models. Only one adjustable constant was necessary to correlate interfacial tensions with less than 1% deviation, in the range of temperatures of the available experimental data. This constant corrects the geometrical mean rule in the estimation of cross influence parameters. The overall average deviation from measured interfacial tensions at 0.1 MPa (0.14 mN/m) is similar to the reported experimental errors (from 0.04 to 0.4 mN/m). Using the parameters determined at 0.1 MPa, the effect of pressure over the interfacial tensions were determined. The proposed model, in general, over-predicts interfacial tensions, especially at very high pressures.

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1. Introduction

The interfacial properties of mixtures are of fundamental importance in the design of processes where two liquid phases are in equilibrium. Among these processes, we can mention the liquid–liquid extraction and the emulsification/desemulsification of partially miscible liquids. The latter process is particularly important in tertiary oil recovery, where surfactants are introduced to reservoirs in order to modify the oil–water–rock wettability and to promote ease removal of oil that cannot be recovered by gas injection. Interfacial tension (σ) is also a parameter for many correlations for mass transport properties through fluid interfaces.

For modeling and estimation of σ, several approaches have been developed. By way of illustration, we mention some of these methods: Parachor [1], the principle of corresponding states [2], thermodynamic correlations [3–5], the gradient theory of inhomogeneous interfaces (GTII) [6–8], density functional theory (DFT) [9–12] and molecular simulations [13–15]. The GTII and DFT approaches combine a theory of inhomogeneous fluid with an equation of state or a model of solution. For engineering purposes, Perry's handbook [16] presents some empirical correlations for σs from binary and ternary water–oil mutual solubilities. Despite having no theoretical basis, these correlations suggest that a model for estimating mutual solubilities may also do so for σ.

Recently, great effort has been made in the use of the GTII to determine interfacial properties, e.g., the surface tension and the concentration profiles at interfaces. van der Waals [17] first introduced this theory. In 1958 Cahn and Hilliard [6] reformulated van der Waals' theory, deriving an excess energy term due to the concentration gradient in the interface. Bongiorno et al. [7] and Poser and Sanchez [8] generalized the Cahn–Hilliard model for multicomponent systems, which made the modeling of density

Nomenclature

List of symbols
A Helmholtz energy
A, B, C Constants in Eq. (28)
a Mixture dispersive parameter
a_{0i}, c_{1i} Parameters for calculating a
a_0 Helmholtz energy density of the homogeneous phase
b Co-volume
c_{ij} Influence parameters
g Simplified distribution function
I Interfacial area
k_{12} Binary interaction parameter for van der Waals mixing rule
l_{12} Binary parameter for cross influence parameter calculation
n_c Number of carbon atoms in the n-alkanes chain
p Pressure
R Gas constant
T, T_r Temperature and reduced temperature
V Volume
x_i Mole fraction of component i
X_{A_i} Mole fraction of component i not bound at site A
z Compressibility or distance at interface

Greek letters
β, β_{12} Volume of association and cross volume of association
Δ Association strength
ε Energy of association
η Reduced density
κ_{ij} Influence parameters
μ_ι Chemical potential of substance i
ρ Molar density
σ Interfacial tension
ω Grand potential density

and composition change across the interface possible. These reformulations allow estimation of σ from chemical potential models, whether from equations of states or from liquid solutions theories. Several combinations of the GTII with equations of state have been published. Examples of EoS used for these calculations are Peng- Robinson EoS [18–22], SAFT family [22–26], cubic plus association (CPA) EoS [27–29] among others. On the other hand, from solution models, Enders and Quitzsch [30] calculated liquid–liquid σ for water-surfactant (ethylene glycol isobutyl ether and diethylene glycol diethyl ether) mixtures. Grunnert et al. [31,32], using Koningsveld–Kleintjens excess Gibbs energy model, calculated interfacial tensions of ternary mixtures from binary data. Cahn and Hilliard [6] also used this approach through the theory of regular solutions. Assuming null volume of mixing, Zeiner et al. [33] combined the lattice-cluster theory, a modified Wertheim association term and GTII for modeling interfacial tension of hyperbranched polymers over associating compounds (water and 1-propanol).

For engineering purposes, the prediction of water–oil interfacial tensions are usually performed through semi-empirical methods resembling those presented by Freitas et al. [34] and Apostoluk and Drzymała [35]. More theoretically founded models have also been used for modeling this type of mixtures. For methane–water mixtures, linear gradient theory (LGT) [36] was successfully employed to correlate/predict water–methane

vapor–liquid σ with PR [20,36], SRK [20] and CPA [29] EoSs at low and high pressures. The LGT method assumes that local densities profiles across interface are linear and σs can be estimated with no need to determine local densities relationships in the interface. This approach, however, cannot predict interface local densities higher than the ones in the equilibrium bulk phases and cannot be used to study the effect of surface active compounds over the properties of water–oil interfaces. On the other hand, Cornelisse et al. [37,38] made use of the GTII combination with APACT and PR EoSs for hexane–water and for benzene–water liquid–liquid tensions. They found good agreement for temperature dependence of the measured data with both EoSs, adjusting only one parameter. However, the pressure dependence was not very well described with the same constant. Llovell et al. [39], using DFT coupled to SAFT-VR EoS, estimated σ as a function of temperature and pressure for hexane–water mixtures. Their results are in reasonable quantitative agreement with measured data, considering they did not use any adjustable parameter. Difficulties arise, however, when an attempt to predict σ versus p curves is made. They found negative slopes whereas experimental slopes are positive.

In this work, the GTII–CPA combination was used in the correlation of measured liquid–liquid σ for binary mixtures water-hydrocarbons. Unlike the usual GTII-EoS combination, we used the Amagat's rule approximation (volume of mixing equal zero) in the determination of local densities profiles in the interface. This makes σ determination similar to the approach employing models of solution. For binary mixtures, only one independent variable is sufficient to describe the densities' profiles.

This paper is organized as follows. Section 2 describes the theoretical background of the proposed method. Its three central elements are: (i) CPA EoS and its combining and mixing rules; (ii) the GTII main equations and (iii) the simplifications in the GTII equations when using the Amagat' rule (AR) approximation. Section 3 presents the estimation of influence parameters for some pure compounds, the determination of the binary parameters that correct the geometrical mean rule for cross influence parameters and the correlation/predictions of σ as a function of temperature and pressure for hydrocarbon-water liquid–liquid interfaces. The last section summarizes the results of this work and presents perspectives of use of the developed method for the description the σ behavior of multicomponent water-hydrocarbons-surfactants systems.

2. Theoretical background

2.1. CPA equation of state

The CPA EoS [40] is a result of the Helmholtz partition in two contributions, namely physical and association:

$$A = A_{\text{phys}} + A_{\text{as}} \tag{1}$$

where A is the Helmholtz energy and the subscripts phys and as refer to physical and association contributions, respectively. Soave-Redlich-Kwong (SRK) [41] EoS describes the physical contribution whereas Wertheim term employed in SAFT equations [42] describes the association contribution. The resulting EoS, written in terms of compressibility and density, is given by the following expression:

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