J. of Supercritical Fluids 55 (2010) 724–734

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Interfacial properties of mixtures containing supercritical gases

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ARTICLE INFO

Article history:
Received 13 June 2010
Received in revised form
27 September 2010
Accepted 28 September 2010

Keywords:
Liquid-vapor equilibrium
Surface tension
PCP-SAFT-EOS
Density gradient theory
Supercritical fluids

ABSTRACT

The paper aims to the prediction of interfacial properties of binary mixtures using only pure component interfacial properties and bulk-properties of the mixture, like phase equilibria. This approach follows strictly the basic idea from Van der Waals. In principle, this goal can be reached by the application of the density gradient theory in combination with an equation of state. This paper focuses on the thermodynamic description of the phase and the surface properties for binary systems, if a supercritical component, like nitrogen or carbon dioxide (CO_2), is present in the mixture. Whereas nitrogen can be treated as non-polar component, carbon dioxide has a strong quadrupole moment. Using PCP-SAFT-EOS in combination with the density gradient theory the prediction of the surface tensions of mixtures close to experimental data is possible.

1. Introduction

Van der Waals remarks in his famous Nobel Lecture, held on 12. of December, 1910:

> "The first incentive to this my life's work came to me when, after my studies at university, I learned of the treatise by Clausius (1857) on the nature of the motion which we call heat. . . .Clausius' treatise was a revelation for me although it occurred to me at the same time that if a gas in the extremely dilute state, where the volume is so large that the molecules can be regarded as points, consists of small moving particles, this is obviously still so when the volume is reduced; indeed, such must still be the case down to the maximum compression and also in liquids, which can only be regarded as compressed gases at low temperatures. Thus I conceived the idea that there is no essential difference between the gaseous and the liquid state of matter – that the factors which, apart from motion of the molecules, act to determine the pressure must be regarded as quantitatively different when the density changes and perhaps also when the temperature changes, but that they must be very factors which exercise their influence throughout, And so the ides of continuity occurred to me."

This basic idea opened the way to the thermodynamic description of phase – and interfacial properties [i.e. [1–6]].

The paper aims to the calculation of interfacial properties (interfacial tension, interfacial profile's, interfacial thickness and relative enrichment in the interface) of pure components and binary mixtures using an equation of state. We focus on the following binary mixtures:

$$N_2 + \text{n-alkane}\,(\text{n-hexane},\ \text{n-heptane},\ \text{n-octane and n-decane})$$

$$CO_2 + \text{n-alkane}\,(\text{n-heptane},\ \text{n-decane},\ \text{n-octane and tetradecane})$$

$$CO_2 + \text{cyclohexane}$$

Some of these systems were already studied in the literature [i.e. [1–5]] using different equations of state and/or different approaches for the interface. The most important exigency of the model applied here is: using experimental data of the pure components and the phase equilibria of the binary mixture (bulk-properties) in combination with the model should allow the prediction of the interfacial tensions of the mixture without any additional parameter of the interface properties. The model should be able to describe the surface tension related to the liquid-vapor equilibrium (VLE).

The experimental information entering the theoretical framework are the following: the surface tension of the pure substances at one temperature and the bulk-phase behavior of the binary mixture. If a supercritical component is present in the binary mixture, the challenge of this theoretical treatment consists in the extrapolation of the so-called influence parameter of a wide temperature range, because the surface tension of this component can

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doi:10.1016/j.supflu.2010.09.040

only be measured at very low temperatures. However, the phase equilibrium in the mixture is established at normal or at high temperatures.

The theoretical predictions were verified using experimental data taken from the literature. However, if no experimental data were available in the literature, the surface tensions were measured using the pendant drop method.

2. Theory

In order to meet the above requirements the density gradient theory (DGT) developed by van der Waals [7] and Cahn–Hilliard [8] for pure components and extended by Poser and Sanchez [9] to binary mixtures is used. This procedure allows the calculation of the interfacial properties based on bulk-properties of the binary mixture and the surface tension of the pure component. The model can be applied for VLE and LLE [10–15].

The DGT [7–9] of inhomogeneous systems provides a means for relating an equation of state to surface properties. The density gradient theory leads to a general expression for the Helmholtz free energy density of an inhomogeneous system. A method was developed for calculating the surface tension and density profiles of a pure liquid and mixtures in equilibrium with its vapor using this expression in combination with an equation of state.

Using this approach, the surface tension of mixtures consisting of non-polar component [16] and mixtures consisting of non-polar molecules and molecules carry a dipole or quadrupole moment [17] can be predicted within the experimental error. One of the last extensions of the well-known Perturbed-Chain-Statistical Association Fluid theory [18–20] (PC-SAFT) is the application to molecules having a dipole [21] or a quadrupole [22] moment. This new equation of state is called PCP-SAFT and allows to taking into account the dipole or the quadrupole moment without any additional adjustable parameter. The main focus of this contribution is the calculation of the interfacial properties if a supercritical component, which can be non-polar (nitrogen) or having a quadrupole moment (CO_2), is involved.

2.1. Pure components

The Cahn–Hilliard Theory [8] describes the thermodynamic properties of a system where an interface exists between two equilibrium phases. In the interface between liquid and gas phase of pure substance in thermodynamic equilibrium only the density, ρ, varies continuously from the bulk liquid density, ρ^L, to the vapor density, ρ^V. Assuming that the density gradient is small compared with the reciprocal of the intermolecular distance allows the density ρ and its derivatives to handle as independent variables. This means that the Helmholtz free energy F for a system with an interface can be obtained by expanding the Helmholtz free energy F in a Taylor series about the equilibrium bulk state. Following Cahn and Hilliard [8], one finds for the surface tension, σ, for a planar surface:

$$\sigma = 2\int_{\rho^L}^{\rho^V} \sqrt{\kappa \Delta\omega(\rho)}\, d\rho \tag{1}$$

The tension can be calculated directly from the influence parameter, κ, and the Helmholtz free energy density, $\Delta\omega(\rho)$, of homogeneous fluid. This quantity is also called grand thermodynamic potential. Geometrically, $\Delta\omega(\rho)$ can be represented as the vertical distance between the curve of $F(\rho)$ versus ρ and a common tangent touching $F(\rho)$ at the vapor and liquid densities, ρ^L and ρ^V (Fig. 1).

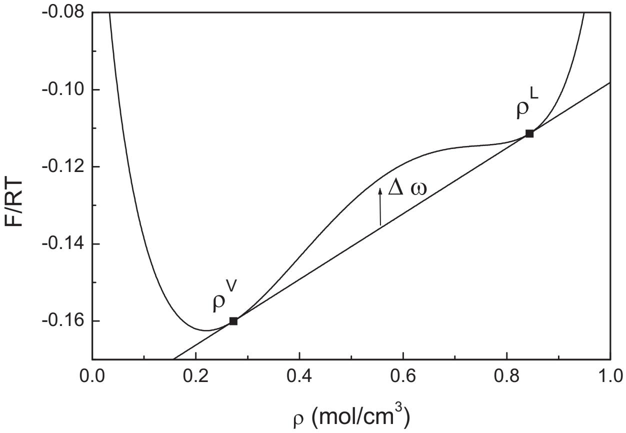

Fig. 1. Explanation of the grand thermodynamic potential $\Delta\omega(\rho)$ for pure components.

The density profile, $\rho(z)$ in the direction perpendicular to the surface, can be determined as

$$z = z_0 + \int_{\rho^0}^{\rho} \sqrt{\frac{\kappa}{\Delta\omega(\rho)}}\, d\rho \tag{2}$$

where z^0 and ρ^0 represent an arbitrarily chosen origin and composition. The z-origin can be arbitrarily located at a density of $\rho^0 = (\rho^L + \rho^V)/2$. A distance z may be determined for any ρ lying between the bulk densities by numerical evaluation of the integral in Eq. (2).

Before any interfacial properties can be computed, it is necessary to find the thermodynamic equilibrium densities between which the interface is formed. The densities of the vapor and the liquid phase can be calculated at a given temperature. Such calculations are carried out using the Maxwell criterion. Subsequently, the expressions Eqs. (1) and (2) can be used to calculate both surface tensions and density profiles if κ and $\Delta\omega$ are known. The influence parameter, κ, has a molecular theoretical definition [8] but is not usually calculable. Thus, it is treated as a parameter of the fluid in the same spirit as the parameter of semi empirical models. Equations of state (PCP-SAFT) will be used to evaluate the grand thermodynamic potential, $\Delta\omega$. This equation is briefly described next.

2.1.1. PCP-SAFT-EOS

The PCP-SAFT-EOS [21,22] is a further development of the PC-SAFT-EOS [18–20]. The PC-SAFT-EOS is based on the SAFT-EOS originally developed by Chapman et al. [23,24]. In the PC-SAFT-EOS, the chain-length dependence of the attractive (dispersive) interactions is also taken into account. A hard-chain fluid serves as a reference for the perturbation theory, rather than spherical molecules as in the original SAFT version. In the model, molecules are conceived to be chains composed of tangent spherical segments. The pair potential for the segment of a chain is given by a modified square-well potential. The attractive interactions are treated as a perturbation to the reference system. The equation of state is given as an ideal gas contribution (id), a hard-chain contribution (hc), and a perturbation contribution, which accounts for the attractive interactions (disp), a contribution arising from the self-association of polar molecules (assoc) and additionally a contribution taking dipolar or quadrupole interaction (polar) into account:

$$F = F^{\text{id}} + F^{\text{hc}} + F^{\text{disp}} + F^{\text{assoc}} + F^{\text{polar}} \tag{3}$$

More details can be found in the papers of Gross and Sadowski [18–20]. The heart of the PCP-SAFT-EOS is the new additional term