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Fluid Phase Equilibria 254 (2007) 174–187
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Continuous thermodynamics of binary associating systems

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Received 14 December 2006; received in revised form 20 February 2007; accepted 22 February 2007
Available online 28 February 2007

Abstract

A new chemical model is presented that permits the calculation of the excess functions and of the phase equilibrium for binary systems with one associating component. The chemical equilibrium between the associated species is described on the base of continuous thermodynamics. Therefore, the model is abbreviated by CONTAS (continuous thermodynamics of associating systems). Mostly, only three parameters for each binary system have to be fitted to experimental data. Two further parameters describing the temperature dependence of the association constant are specific for the associating component. The model is applied to 15 systems of the type non-polar component A + associating component B where, the associating components are methanol, ethanol, aniline and water. Based on the same set of parameters the excess Gibbs energy, the excess enthalpy, the vapor–liquid equilibrium and the liquid–liquid equilibrium (if there is one) are calculated. In all cases the results are reasonably well.
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Keywords: Method of calculation; Continuous thermodynamics; Associating systems; Excess Gibbs energy; Excess enthalpy; Liquid–liquid equilibrium; Vapor–liquid equilibrium

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1. Introduction

Two basic ways of thermodynamic treatment of associating systems are known from literature, the chemical theory [1–14] and the physical theory [15–20]. In the chemical theory mass action law is applied to the association equilibrium. These models may be divided into G^E-models [1–5] and equations of state [6–14]. In the physical theory H-bonds are treated like strong physical interactions. Recently, statistical association fluid theory (SAFT) [16,17] and several modified versions (for instance PC-SAFT) are often applied [18–20]. On the one side, the SAFT equation of state and its modifications are highly accurate and cover a large pressure range. On the other side the most SAFT versions require a relatively high numerical expense. G^E-models of chemical theory are much simpler and could be sufficient in the range of moderate pressures. However, older models of this type cannot describe the vapor–liquid equilibrium (VLE) and the liquid–liquid equilibrium (LLE) simultaneously. In associating systems there are many associates being similar to each other but differing in size. So, recently, the author presented a chemical G^E-model [21,22] based on continuous thermodynamics [23–25] and Flory–Huggins theory. Originally, this model was introduced to calculate the phase equilibrium of alkane + alcohol systems and similar systems. However, the model has been proven to be useful for a wider spectrum of mixtures. So, the flocculation of asphaltenes in crude oil systems could be successfully described [26]. Furthermore, the model is able to calculate the liquid–liquid equilibrium of aqueous solutions of non-ionic surfactants [27]. In this, the micellization of the surfactant molecules is considered in the same way as association. Continuous thermodynamics is a powerful tool in calculating the phase equilibrium of systems consisting of very many similar components (e.g. polydisperse polymer systems). Flory–Huggins theory well known from polymer thermodynamics is suitable if the molecules are very different in size. The model previously introduced [21,22] has been proven to be able to describe VLE and LLE simultaneously. This is an important advantage compared to older chemical theories. Nevertheless, there are some shortages. Firstly, for VLE calculation the vapor pressure as function of temperature of the hypothetical pure associates is needed. Secondly, the theoretical treatment does not include explicit expressions for the excess functions.

This paper introduces an improved treatment called continuous thermodynamics of associated systems (CONTAS). Here,

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Abbreviations: CONTAS, continuous thermodynamics of associating systems; LLE, liquid–liquid equilibrium; VLE, vapor–liquid equilibrium; VLLE, vapor–liquid–liquid equilibrium

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doi:10.1016/j.fluid.2007.02.031

explicit equations for the excess functions and the activity coefficients are derived. The phase equilibrium calculation, now is based on the expressions of the activity coefficients. So, the VLE calculation is essentially simplified and improved compared to the previous model [21,22]. The equations for the binodal curve are the same as presented previously [21,22]. However, additionally, equations for the spinodal curve and for the critical point of the LLE are derived. The fundamentals of the CONTAS model are treated in the next section. In Section 3, the excess functions and the phase equilibria of 15 systems of the type non-polar component + associating component (methanol, ethanol, aniline and water) are calculated and compared with the experimental data.

2. Theory

2.1. Association equilibrium and distribution function

A binary liquid mixture consisting of a non-polar component A and an associating component B is considered. The B molecules form associates assumed to fulfil the following equilibrium:

$$B_{r-r'} + B_{r'} \rightleftarrows B_r. \tag{1}$$

Here, $B_{r-r'}$, $B_{r'}$, B_r are associates with the association degrees $r-r'$, r', r giving the number of monomers within an associate. The association degree can take values between 1 and ∞. In the framework of continuous thermodynamics the association degree is not restricted to whole numbers. Continuous thermodynamics [23,24] is applied to the association equilibrium (1). In this, the activity coefficients are described by Flory–Huggins theory. Furthermore, the chemical potential of the hypothetical pure associates is assumed to depend linearly on the association degree. In this way (for details see Appendix A) the segment-molar distribution of the associates reads:

$$W_{\mathrm{s}}(r) = -\lambda \exp[\lambda(r-1)]. \tag{2}$$

The quantity λ describes the width of the size distribution of the associates. λ can take only negative values and originates from the solution of the equation:

$$\exp(\lambda - 1) + \lambda K \psi_{\mathrm{B}} = 0, \tag{3}$$

where K is the association constant only depending on temperature T and, ψ_{B} is the segment-mole fraction of the associating component B given by

$$\psi_{\mathrm{B}} = \frac{x_{\mathrm{B}}}{x_{\mathrm{A}} r_{\mathrm{A}} + x_{\mathrm{B}}}. \tag{4}$$

The quantity r_{A} is the segment number of the non-polar A-molecules or, respectively, the number of lattice sites that are occupied by a molecule of type A if a B-monomer is presumed to occupy one site. x_{A}, x_{B} are the usual mole fractions of the components A and B. $\psi_{\mathrm{B}} W_{\mathrm{s}}(r)\,\mathrm{d}r$ gives the segment-mole fraction of all associates with values of r within the interval [r, $r+\mathrm{d}r$). According to Eqs. (2)–(4) the distribution function is influenced by temperature and concentration. Furthermore, it is very important to know the number average of B-monomers (segments) forming an associate. This mean association degree can be calculated by (Appendix A):

$$\frac{1}{\bar{r}_{\mathrm{B}}} = \lambda \exp(-\lambda) \left\{ 0.57721567 + \ln|\lambda| + \sum_{i=1}^{\infty} \frac{\lambda^i}{i \cdot i!} \right\}. \tag{5}$$

In most cases (except if $\bar{r}_{\mathrm{B}} \approx 1$) only the first 10 terms of the series expansion are important.

2.2. Excess functions and activity coefficients

Based on the distribution function (2) the molar excess Gibbs energy may be derived (for details see Appendix B) as follows:

$$\frac{G_{\mathrm{m}}^{\mathrm{E}}}{RT} = x_{\mathrm{A}} \ln\left(\frac{\psi_{\mathrm{A}}}{x_{\mathrm{A}}}\right) + x_{\mathrm{B}} \ln\left(\frac{\psi_{\mathrm{B}}}{x_{\mathrm{B}}}\right) + (x_{\mathrm{A}} r_{\mathrm{A}} + x_{\mathrm{B}}) \psi_{\mathrm{A}} \psi_{\mathrm{B}} \chi + x_{\mathrm{B}} \left(\lambda - \lambda_* - \ln \psi_{\mathrm{B}} + \frac{1}{\bar{r}_{*\mathrm{B}}} - \frac{1}{\bar{r}_{\mathrm{B}}}\right). \tag{6}$$

The first two terms represent the ideal-athermic contribution originating from Flory–Huggins theory. The third term describes the effect of intermolecular interactions based on the Flory–Huggins χ-parameter as simple as possible. If necessary, this term could be improved by multiplying with a suitable function $g(\psi_{\mathrm{B}})$. The last term of Eq. (6) describes the associating effects. The quantity λ has to be calculated by solving Eq. (3). λ_* is the value of λ for $x_{\mathrm{B}} = 1$. $\bar{r}_{\mathrm{B}}$ and $\bar{r}_{*\mathrm{B}}$ are determined using Eq. (5) where $\lambda = \lambda_*$ in the case of $\bar{r}_{*\mathrm{B}}$.

The activity coefficients are derived in the usual way from the molar excess Gibbs energy (see Appendix B). The result reads:

$$\ln \gamma_{\mathrm{A}} = \ln\left(\frac{\psi_{\mathrm{A}}}{x_{\mathrm{A}}}\right) + 1 - \frac{\psi_{\mathrm{A}}}{x_{\mathrm{A}}} \left(x_{\mathrm{A}} + \frac{x_{\mathrm{B}}}{\bar{r}_{\mathrm{B}}}\right) + r_{\mathrm{A}} (\psi_{\mathrm{B}})^2 \chi, \tag{7a}$$

$$\ln \gamma_{\mathrm{B}} = \ln\left(\frac{\psi_{\mathrm{B}}}{x_{\mathrm{B}}}\right) + \left(\psi_{\mathrm{B}} + \frac{\psi_{\mathrm{A}}}{\bar{r}_{\mathrm{B}}}\right) - \frac{\psi_{\mathrm{B}}}{x_{\mathrm{B}}} + (\psi_{\mathrm{A}})^2 \chi + \lambda - \lambda_* - \ln \psi_{\mathrm{B}} + \frac{1}{\bar{r}_{*\mathrm{B}}} - \frac{1}{\bar{r}_{\mathrm{B}}}. \tag{7b}$$

Knowing the molar excess Gibbs energy it is easy to find an expression for the molar excess enthalpy (see Appendix B). This expression reads:

$$H_{\mathrm{m}}^{\mathrm{E}} = -x_{\mathrm{B}} \psi_{\mathrm{A}} R T^2 \frac{\mathrm{d}\chi}{\mathrm{d}T} - x_{\mathrm{B}} R T^2 \left(\frac{1}{\bar{r}_{\mathrm{B}}} - \frac{1}{\bar{r}_{*\mathrm{B}}}\right) \frac{\mathrm{d}\ln K}{\mathrm{d}T}. \tag{8}$$

The first term describes the intermolecular interactions and the second one the association effects. In this paper for all non-aqueous systems the χ-parameter is assumed to depend on the temperature by the expression:

$$\chi(T) = A_0 + \frac{A_1}{T}. \tag{9}$$

Here, A_0, A_1 are parameters that have to be fitted to experimental data. Furthermore, the temperature dependence of the association constant is to be the following:

$$K(T) = K_0 \exp\left(-\frac{\Delta H_{\mathrm{as}}}{RT}\right). \tag{10}$$

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