



Extension of the chemical associating lattice model (CALM) to cross association

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ABSTRACT

Recently the chemical association lattice model (CALM) was introduced and applied to the calculation of excess functions and phase equilibria of binary and ternary systems with one associating component. In this paper CALM is extended to the case of cross association in binary systems. On the one hand, the model is applied to binary systems consisting of two associating components (methanol + water, ethanol + water, methanol + aniline). On the other hand binary systems consisting of a strong polar component and an associating component are studied (2-butanone + methanol, 2-butanone + ethanol, trichloromethane + methanol). Molecules as 2-butanone and trichloromethane do not form self associates but are able to form cross associates if an associating second component is present. Generally, excess Gibbs energy, excess enthalpy and vapor–liquid equilibrium are calculated and compared to experimental data. Except the excess enthalpy of the system ethanol + water there is a good agreement of the calculated data with the experimental ones.

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1. Introduction

There are two basic ways of thermodynamic treatment of associating systems, the chemical theory [1–11] and the physical theory [12–18]. In the chemical theory the association equilibrium is described by the mass action law using G^E -models [1–3] or equations of state [4–11]. In the physical theory H-bonds are treated like strong physical interactions. The statistical association fluid theory (SAFT) based on Wertheim's theory [12] and modified versions of SAFT are important examples [13–18]. G^E -models of chemical theory are restricted to moderate pressures, but they possess the advantage of simplicity. Recently, the author presented a chemical G^E -model [19,20] based on the lattice theory of Flory and Huggins and on continuous thermodynamics [21–23]. This model was applied to phase-equilibrium calculations for a wide spectrum of systems. Examples are the phase equilibrium of alkane + alcohol systems and similar systems [19,20], the flocculation of asphaltenes in crude oil systems [24] as well as the liquid–liquid equilibrium of aqueous solutions of non-ionic surfactants [25] and of ternary systems of the type water + non-ionic surfactant + alkane [26,27]. In the last mentioned system type, the aggregation of the surfactant molecules is considered in the same way as association. An improved version abbreviated by CONTAS (continuous thermodynamics of associated systems) [28] was successfully applied to the calculation of the excess functions and the phase equilibria of numerous binary associating mixtures with one associating component. Here, the composition of the

ensemble of associates is described by a continuous size-distribution function. Often, continuous thermodynamics results in essential numerical simplifications. However, in some cases the discontinuous treatment is simpler than the continuous one. Recently this was proved by the author introducing the new discontinuous model CALM (chemical association lattice model) [29]. CALM was successfully applied to the calculation of excess functions and phase equilibria of binary and ternary systems with one associating component [29]. In this paper CALM is extended to the case of cross association in binary systems. The new model is abbreviated by ECALM (extended chemical association lattice model). Firstly, the extended model is applied to the systems methanol + water, ethanol + water and methanol + aniline. Here both components of the mixture show self association. However, cross association can occur too if only one component shows self association presuming the second component is a strong polar one. In this paper the systems 2-butanone + methanol, 2-butanone + ethanol and trichloromethane + methanol are studied. For all considered systems excess Gibbs energy, excess enthalpy and vapor–liquid equilibrium (VLE) are calculated and compared to experimental data.

2. Theory

A binary liquid mixture consisting of the associating components A and B with the mole fractions x_A and x_B is considered. Such a system will show cross association. All cross associates are assumed to possess the same composition. The mole fractions within a cross associate are denoted by \bar{y}_A and \bar{y}_B . To calculate \bar{y}_A and \bar{y}_B the probabilities P_{AA} , P_{AB} and P_{BB} are considered. Here, P_{ij} is the probability

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that an arbitrarily chosen pair of neighbouring molecules of the cross associate is of the type ij ($ij = AA, AB, BB$). Generally one can note $P_{AA} = k_{AA}x_A^2$, $P_{AB} = 2k_{AB}x_Ax_B$ and $P_{BB} = k_{BB}x_B^2$ with $P_{AA} + P_{AB} + P_{BB} = 1$ and $\bar{y}_B = P_{AB}/2 + P_{BB}$. The case $k_{AA} = k_{AB} = k_{BB}$ describes the statistical cross association with $\bar{y}_B = x_B$. Usually, with $k_{AA} < k_{AB} < k_{BB}$ the mole fraction of component B within the cross associate is higher than the statistical one ($\bar{y}_B > x_B$). Thus, the model is asymmetrical. Component B is the one that dominates the cross associates. Introducing the cross-association parameters $\eta_{AA} = k_{AA}/k_{BB}$ and $\eta_{AB} = k_{AB}/k_{BB}$ with $\eta_{AA} \leq \eta_{AB} \leq 1$ and considering the condition $P_{AA} + P_{AB} + P_{BB} = 1$ the composition within the cross associate is characterized by:

$$\bar{y}_B = x_B \frac{x_A \eta_{AB} + x_B}{x_A^2 \eta_{AA} + 2x_A x_B \eta_{AB} + x_B^2}; \bar{y}_A = 1 - \bar{y}_B \quad (1)$$

One can easily show that $\bar{y}_B \geq x_B$ if $\eta_{AA} \leq \eta_{AB} \leq 1$. Thus, all B-monomers are incorporated in cross associates but, except the case of statistical cross association, not all A-molecules. The remaining A-molecules are assumed to form self associates. Then there are two ensembles, the ensemble of the cross associates (ca) containing all B-molecules together with a part of the A-molecules, and the ensemble of the self associates (A) containing only A-molecules. If component A has a very low tendency to form self associates the ensemble (A) will be mainly consisting of monomers. In the case of statistical cross association ($\eta_{AA} = \eta_{AB} = 1$) all A-molecules and all B-molecules are involved in the ensemble of the cross associates. In this very special case ensemble (A) does not exist. The associates of both ensembles show a discontinuous size distribution that will be calculated as previously published [29]. To derive the excess Gibbs energy of the system the same approach as outlined for the case of systems with only one associating component may be applied [29]. The final result for the molar excess Gibbs energy reads:

$$\begin{aligned} \frac{G_m^E}{RT} = & x_A \ln \left(\frac{\psi_A}{x_A} \right) + x_B \ln \left(\frac{\psi_B}{x_B} \right) + r_B x_B \psi_A \chi(T) \\ & - x_A (1-L) \left[1 + \frac{1}{\tilde{K}_A \psi_A (1-L)} \right] \ln \left[1 + \tilde{K}_A \psi_A (1-L) \right] \\ & - \frac{x_B}{y_B} \left[1 + \frac{1}{\tilde{K}^{(ca)} (\psi_B + \psi_A L)} \right] \ln \left[1 + \tilde{K}^{(ca)} (\psi_B + \psi_A L) \right] \\ & + x_A [(1-L) \ln(1-L) + L \ln L] + x_A C_A + x_B C_B. \end{aligned} \quad (2)$$

The first two terms of Eq. (2) present the well-known Flory–Huggins contribution for the ideal-athermal solution. Here, R is the universal gas constant and T the temperature. x_A, x_B are the usual mole fractions of the components A and B. The segment fractions ψ_A, ψ_B of the components A and B given by:

$$\psi_A = \frac{r_A x_A}{r_A x_A + r_B x_B}; \quad \psi_B = \frac{r_B x_B}{r_A x_A + r_B x_B}. \quad (3)$$

The quantities r_A and r_B are the segment numbers of the molecules A and B. The third term is the contribution of the physical interactions characterized by the χ -parameter of the Flory–Huggins theory. Here, the temperature dependence of the χ -parameter is restricted to:

$$\chi(T) = A_0 + \frac{A_1}{T} + \frac{A_2}{T^2}. \quad (4)$$

The remaining terms in Eq. (2) are association contributions. In this the quantity L is given by:

$$L = \frac{x_B \bar{y}_A}{x_A \bar{y}_B}. \quad (5)$$

The quantities C_A and C_B being independent of concentration read:

$$\begin{aligned} C_A = & (1 - \eta_{AA} / \eta_{AB}) \left\{ \left[1 + \frac{1}{\tilde{K}_A (1 - \eta_{AA} / \eta_{AB})} \right] \ln \left[1 + \tilde{K}_A (1 - \eta_{AA} / \eta_{AB}) \right] \right. \\ & \left. - \ln(1 - \eta_{AA} / \eta_{AB}) \right\} \\ & + (\eta_{AA} / \eta_{AB}) \left\{ \left[1 + \frac{1}{\tilde{K}_A (\eta_{AA} / \eta_{AB})} \right] \ln \left[1 + \tilde{K}_A (\eta_{AA} / \eta_{AB}) \right] \right. \\ & \left. - \ln(\eta_{AA} / \eta_{AB}) \right\}, \end{aligned} \quad (6a)$$

$$C_B = \left(1 + \frac{1}{\tilde{K}_B} \right) \ln(1 + \tilde{K}_B). \quad (6b)$$

The quantities \tilde{K}_A, \tilde{K}_B and $\tilde{K}^{(ca)}$ are defined by:

$$\tilde{K}_A = K_A \exp(1); \tilde{K}_B = K_B \exp(1); \tilde{K}^{(ca)} = K^{(ca)} \exp(1). \quad (7)$$

Here K_A and K_B are the association constants of the pure components A and B and $K^{(ca)}$ is the association constant of the cross associates given by

$$\ln K^{(ca)} = \bar{y}_A \ln K_A + \bar{y}_B \ln K_B. \quad (8)$$

A detailed derivation of Eq. (2) is outlined in the Appendix. It has to be noted that the Gibbs excess energy may be calculated in a straight forward way. There are no equations to have to be solved by iterative procedures.

Let us discuss two special cases. One of them cases is the statistical cross association ($\eta_{AA} = \eta_{AB} = 1$). In this special case there are only cross associates. Furthermore, there is $\bar{y}_A = x_A$ and $\bar{y}_B = x_B$. Then, Eq. (2) changes into the essentially simpler form:

$$\begin{aligned} \frac{G_m^E}{RT} = & x_A \ln \left(\frac{\psi_A}{x_A} \right) + x_B \ln \left(\frac{\psi_B}{x_B} \right) + r_B x_B \psi_A \chi(T) \\ & - \left(1 + \frac{1}{\tilde{K}^{ca}} \right) \ln(1 + \tilde{K}^{ca}) + x_A \left(1 + \frac{1}{\tilde{K}_A} \right) \ln(1 + \tilde{K}_A) \\ & + x_B \left(1 + \frac{1}{\tilde{K}_B} \right) \ln(1 + \tilde{K}_B). \end{aligned} \quad (9)$$

If additionally $\tilde{K}_A = \tilde{K}_B$ the contribution of the association vanishes completely. If the molecules A and B are of the same type and possess a similar size all terms of Eq. (9) are small. Therefore, systems as methanol + ethanol show small absolute values for the excess Gibbs energy (and for the excess enthalpy too).

Another special case is $\eta_{AA} = \eta_{AB} = 0$ in the limit $\tilde{K}_A \rightarrow 0$. There is only the self association of the B-molecules and thus, Eq. (2) turns into the usual result of the CALM (see Eq. (8) in [29]).

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