Closed-Form Expressions for ''Chemical Theory'' of Associating Mixtures

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Various thermodynamic models have been proposed for systems containing hydrogen bonding compounds (Economou and Donohue, 1991b). The most widely used theory is based on the assumption that hydrogen bonding results in the formation of new species in the system and is referred to as chemical theory. The associated-perturbed-anisotropic-chain theory (APACT) (Ikonomou and Donohue, 1986), an equation of state that accounts for hydrogen bonding using chemical theory, was recently generalized to treat compounds that can self-associate and solvate with other compounds in the mixture (Economou et al., 1990). The resulting equations for hydrogen-bonding interactions were solved analytically for three types of binary mixtures. The first one contains an amphoteric component, which is both acidic and basic (that is, an alcohol), and a component that is only acidic (that is, chloroform) or only basic (that is, a ketone). The second type of binary mixtures contains an amphoteric component and a component that does not self-associate nor solvate (a diluent). The third type of binary mixtures contains one basic and one acidic component. However, for the general case of two or more self-associating components, the resulting expressions contained coupled infinite series so that these expressions could not be written in a closed form and were not solved analytically. Thus, approximate or numerical solutions have been proposed (Economou et al., 1990; Panayiotou, 1990; Anderko, 1991; Economou and Donohue, 1991a).

In this work, we derive expressions for the mole fraction of the monomeric species and the ratio n_T/n_0, that is a measure of the extent of the association, using an approach introduced by Nagata and Ohtsubo (1986). This approach accounts explicitly for all the different configurations of the association species of the system. We present here the closed-form equations for the general case of an associating binary mixture. These expressions are believed to be general and reduce to the analytic equations for the special cases described above. However, the need of an approximate or numerical solution for the general case of a multicomponent associating system remains.

Theory

In the ABPACT (acid-base-perturbed-anisotropic-chain theory) equation of state and in many other theories for associating systems (Economou and Donohue, 1991b), the assumption is made that hydrogen bonding results in the formation of new species. For the specific case of two bonding sites per molecule, linear chains (such as dimers and trimers) are formed. For systems where more than one associating compound is present, linear chains can contain monomer molecules from only one of the compounds or from different compounds. Specifically, for a binary mixture of components M and N where both components have one acidic (electron acceptor) site and one basic (electron donor) site, hydrogen bonding is described through the following chemical equilibria:

$$(M_i)^a + M^b \rightleftharpoons M_{i+1} \tag{1}$$

$$(N_j)^a + N^b \rightleftharpoons N_{j+1} \tag{2}$$

$$(M_i)^a + (N_j)^b \rightleftharpoons M_iN_j \tag{3}$$

$$(N_j)^a + (M_i)^b \rightleftharpoons N_jM_i \tag{4}$$

The first two equilibria account for the self-association of the two components and the remaining account for the cross-association. Throughout this work, we use the notation introduced by Economou et al. (1990). Subscripts i and j denote the number of monomers M and N in the chain molecule and can take any integer value from one to infinity. Superscript a denotes that the corresponding molecule uses its acidic site for hydrogen bonding and superscript b denotes that the molecule uses its basic site for hydrogen bonding.

Following Nagata and Ohtsubo (1986), we write the material balance for component M as:

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$$n_M = \sum_i i n_{M_i} + \sum_i \sum_j i(n_{M_iN_j} + n_{N_jM_i}) + \sum_i \sum_j \sum_k (i+k) n_{M_iN_jM_k} + \sum_i \sum_j \sum_k j n_{N_iM_jN_k} + \sum_i \sum_j \sum_k \sum_l (i+k)(n_{M_iN_jM_kN_l} + n_{N_lM_kN_jM_i}) + \ldots \quad (5)$$

Dividing the latter by n_T yields:

$$x_M \frac{n_0}{n_T} = \sum_i i z_{M_i} + \sum_i \sum_j i(z_{M_iN_j} + z_{N_jM_i}) + \sum_i \sum_j \sum_k (i+k) z_{M_iN_jM_k} + \sum_i \sum_j \sum_k j z_{N_iM_jN_k} + \sum_i \sum_j \sum_k \sum_l (i+k)(z_{M_iN_jM_kN_l} + z_{N_lM_kN_jM_i}) + \ldots \quad (6)$$

where x_M denotes the mole fraction of component M, n_0 is the number of moles in the absence of association, n_T is the number of true moles of association species, and z is the mole fraction of the association species. Similarly, the material balance for component N is given from the expression:

$$x_N \frac{n_0}{n_T} = \sum_j j z_{N_j} + \sum_i \sum_j j(z_{M_iN_j} + z_{N_jM_i}) + \sum_i \sum_j \sum_k j z_{M_iN_jM_k} + \sum_i \sum_j \sum_k (i+k) z_{N_iM_jN_k} + \sum_i \sum_j \sum_k \sum_l (j+l)(z_{M_iN_jM_kN_l} + z_{N_lM_kN_jM_i}) + \ldots \quad (7)$$

Finally, the overall material balance is:

$$1 = \sum_i z_{M_i} + \sum_j z_{N_j} + \sum_i \sum_j (z_{M_iN_j} + z_{N_jM_i}) + \sum_i \sum_j \sum_k z_{M_iN_jM_k} + \sum_i \sum_j \sum_k z_{N_iM_jN_k} + \sum_i \sum_j \sum_k \sum_l (z_{M_iN_jM_kN_l} + z_{N_lM_kN_jM_i}) + \ldots \quad (8)$$

The chemical equilibria (Eqs. 1–4) are described by the following equations:

$$K_1 = \frac{\phi_{M_{i+1}}}{\phi_{M_i^a} \phi_{M_1^b} P} \frac{z_{M_{i+1}}}{z_{M_i} z_{M_1}} \quad (9)$$

$$K_2 = \frac{\phi_{N_{j+1}}}{\phi_{N_j^a} \phi_{N_1^b} P} \frac{z_{N_{j+1}}}{z_{N_j} z_{N_1}} \quad (10)$$

$$K_{12} = \frac{\phi_{M_iN_j}}{\phi_{M_i^a} \phi_{N_j^b} P} \frac{z_{M_iN_j}}{z_{M_i} z_{N_j}} \quad (11)$$

$$K_{21} = \frac{\phi_{N_jM_i}}{\phi_{N_j^a} \phi_{M_i^b} P} \frac{z_{N_jM_i}}{z_{N_j} z_{M_i}} \quad (12)$$

where ϕ is the fugacity coefficient and the superscripts a and b in the fugacity coefficients of the associating species denote that the species form a hydrogen bond using an acidic site or a basic site, respectively. To evaluate the ratio of fugacity coefficients, an equation of state is needed. One equation that is convenient to use is PACT, but other equations could be used. Finally, the mole fraction of the association species can be expressed in terms of the mole fraction of the monomers. Details of the derivation are given by Economou et al., (1990). For the self-association species, it is:

$$z_{M_i} = \left(K_1 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{i-1} z_{M_1}^i \quad (13)$$

$$z_{N_j} = \left(K_2 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{j-1} z_{N_1}^j \quad (14)$$

For the cross-association species, the resulting expressions are slightly more complicated. For example for the species M_iN_j, it is:

$$z_{M_iN_j} = K_{12} \left(\frac{n_T}{n_0} \frac{RT}{v_0}\right) \left(K_1 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{i-1} z_{M_1}^i \times \left(K_2 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{j-1} z_{N_1}^j \quad (15)$$

and for species N_jM_i:

$$z_{N_jM_i} = K_{21} \left(\frac{n_T}{n_0} \frac{RT}{v_0}\right) \left(K_1 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{i-1} z_{M_1}^i \times \left(K_2 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{j-1} z_{N_1}^j \quad (16)$$

whereas for the species $M_iN_jM_k$:

$$z_{M_iN_jM_k} = K_{12} K_{21} \left(\frac{n_T}{n_0} \frac{RT}{v_0}\right)^2 \left(K_1 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{i+k-2} z_{M_1}^{i+k} \times \left(K_2 \frac{n_T}{n_0} \frac{RT}{v_0}\right)^{j-1} z_{N_1}^j \quad (17)$$

and so on. Eqs. 13–17 are substituted back to the material balances (Eqs. 6–8). For any real number α, where $0 \le \alpha \le 1$, the finite series in the resulting equations converge as follows:

$$\sum_{i=1}^{\infty} \alpha^i = \frac{\alpha}{1-\alpha} \quad (18)$$

$$\sum_{i=1}^{\infty} i \alpha^i = \frac{\alpha}{(1-\alpha)^2} \quad (19)$$

Finally, the following closed-form equations are obtained:

$$x_M = W_1 \frac{[1 + W_2(a_{12} - a_2)][1 + W_2(a_{21} - a_2)]}{[1 - a_1 W_1 - a_2 W_2 + (a_1 a_2 - a_{12} a_{21}) W_1 W_2]^2} \tag{20}$$

$$x_N = W_2 \frac{[1 + W_1(a_{12} - a_1)][1 + W_1(a_{21} - a_1)]}{[1 - a_1 W_1 - a_2 W_2 + (a_1 a_2 - a_{12} a_{21}) W_1 W_2]^2} \tag{21}$$

$$\frac{n_T}{n_0} = \frac{W_1 + W_2 + (a_{12} + a_{21} - a_1 - a_2) W_1 W_2}{1 - a_1 W_1 - a_2 W_2 + (a_1 a_2 - a_{12} a_{21}) W_1 W_2} \tag{22}$$

where $W_1 = n_{M_1}/n_0$, $W_2 = n_{N_1}/n_0$, $a_1 = K_1 RT/v_0$, $a_2 = K_2 RT/v_0$, $a_{12} = K_{12} RT/v_0$, $a_{21} = K_{21} RT/v_0$. Equations 20 and 21 are solved numerically for W_1 and W_2, and the result is substituted to Eq. 22.

By setting $x_N = 0$, Eqs. 20 and 22 reduce to the equations for the pure self-associating component derived by Ikonomou and Donohue (1986). In addition, if one makes all the equilibrium constants in Eqs. 20-22 equal, then the associating components become indistinguishable and one will obtain the results for a pure self-associating component.

The acid-base-perturbed-anisotropic-chain theory is given by:

$$Z = 1 + Z^{\text{assoc}} + Z^{\text{rep}} + Z^{\text{attr}} \tag{23}$$

where

$$Z^{\text{assoc}} = \frac{n_T}{n_0} - 1 \tag{24}$$

and Z^{rep} and Z^{attr} are given by Vimalchand and Donohue (1985).

For the case of a binary mixture where component M has one acidic and one basic site and component N has one basic site only, the chemical equilibria are described by Eqs. 1 and 3. In that case, $K_2 = K_{21} = 0$ and so Eqs. 20-22 reduce to the expressions:

$$x_M = W_1 \frac{1 + W_2 a_{12}}{(1 - a_1 W_1)^2} \tag{25}$$

$$x_N = W_2 \frac{1 + W_1(a_{12} - a_1)}{1 - a_1 W_1} \tag{26}$$

$$\frac{n_T}{n_0} = \frac{W_1 + W_2 + (a_{12} - a_1) W_1 W_2}{1 - a_1 W_1} \tag{27}$$

Equations 25-27 can be solved analytically and are the same as the equations derived by Economou et al. (1990).

For the case of a binary mixture where component M has one acidic site and component N has one basic site, only cross-association occurs resulting in the formation of dimers. In that case, only K_{12} has a nonzero value and Eqs. 20-22 reduce to the expressions:

$$x_M = W_1(1 + W_2 a_{12}) \tag{28}$$

$$x_N = W_2(1 + W_1 a_{12}) \tag{29}$$

$$\frac{n_T}{n_0} = W_1 + W_2 + a_{12} W_1 W_2 \tag{30}$$

Equations 28-30 are derived also by Economou et al. (1990) and solved analytically.

The equations presented here are general and can be applied to any type of mixture that contains species that hydrogen-bond. In addition, these equations reduce to all those derived previously by Ikonomou and Donohue (1988) and Economou et al. (1990) for specific cases including a binary mixture of an amphoteric and an acidic component, a binary mixture of an amphoteric and a basic component, a binary mixture of an acidic and a basic component, and a binary mixture of an amphoteric and a diluent component. Further, calculations obtained from the equations presented here give exactly the same results as the equations derived by Economou et al. (1990). In a previous article by Economou et al. (1990), extensive comparisons of the model predictions with experimental data were presented. Therefore, comparison of the equations derived in this work with experimental data are not presented.

Conclusions

In this work, chemical theory expressions for binary mixtures of associating fluids were derived. The resulting equations are closed-form and appear to be general. Though no general analytic solution to the equations has yet been found, they do readily reduce to all previously derived analytic solutions for special cases. This approach can be generalized for multicomponent associating systems resulting in closed-form expressions that eliminate the infinite series presented by Economou et al. (1990). However, these closed-form equations still must be solved numerically.

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Notation

a = KRT/v_0
i, j, k, l = number of monomer molecules in the chain molecule
K = equilibrium constant
M = component M
N = component N
n_0 = number of moles in the absence of association
n_T = number of true moles
P = pressure
R = gas constant
T = temperature
v_0 = molar volume
W = mole fraction of monomers
x = mole fraction in the absence of association
Z = compressibility factor
z = true mole fraction

Greek letters

ϕ = fugacity coefficient

Superscripts

a = acidic
assoc = association
attr = attractive

b = basic
rep = repulsive

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