

# A Lattice Model for Intramolecular and Intermolecular Association in Alkane + Nonionic Surfactant Systems

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## 알칸과 비이온계면활성 계를 위한 분자 내외부 회합을 위한 격자모델

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### Abstract

Intramolecular association is an important contribution to the overall hydrogen bonding in supercritical fluid systems, especially in systems of colloidal and biological interest. Amphiphile systems, especially micelle and microemulsion systems, showed highly non-ideal behavior due to the intermolecular association and intramolecular association.

The objective of this research is to present a lattice fluid equation of state that combines the quasi-chemical nonrandom lattice fluid model with modified Veytsman statistics for intra + inter molecular association to calculate phase behavior for mixture containing surfactant systems. The present EOS could correlate the literature data well for mixtures containing nonionic surfactant systems

### 1. Introduction

Surfactant system shows highly non-ideal phase behavior because of the intermolecular association and intramolecular association. Many equations of state such as PR model [1] and SAFT model [2] were successfully capable of describing thermodynamic properties for non-associating systems and inter-molecular associating systems. Phase behavior for mixtures containing surfactant systems has been needed in these industrial applications [3-5].  $C_iE_j$ , an abbreviation of homologous series of nonionic amphiphiles  $CH_3(CH_2)_{i-1}-(OCH_2CH_2)_j-OH$ , is a particularly interesting class of substances due to the presence of oxygen(O) and hydroxyl(OH) group in a same molecule. This OHO research is the so-called TOM project [6-8]. Inter- and intra-hydrogen bonds of this ethoxylated alcohol amphiphiles lead the phase behavior of the systems with these substances highly non-ideal.

Intra-molecular association has been investigated in lattice fluids [9,10] and its application to equation of state (EOS) frameworks have been researched by many groups. The non-random hydrogen-bonding (NRHB) EOS with intra-molecular association [11,12] and the non-random lattice fluid hydrogen-bonding EOS with intra- and inter-molecular association (NLFHBi) [13] as an application of Guggenheim's lattice fluid theory obtained a satisfactory agreement between experimental and calculated phase equilibria properties. However, A close look reveals that the precedent lattice fluid models with intra-molecular associating term have a combinatorial mismatching problem during the arrangement of donors and acceptors which lead the combination into not a H-bond but an original molecule itself.

In this study, we presented a modified Veytsman statistics for inter- and intra- molecular association, combined it with the quasi-chemical

non-random lattice fluid (QLF) [14,15] as a physical description of fluids, and finally tested the present model with the literature data for mixtures containing surfactant systems.

## 2. Thermodynamic Model

The configurational lattice-fluid partition function for systems with associating interactions can be approximated as a product of the physical and chemical contributions. The chemical contribution comes from the associating interaction. The associating part of the partition function is

$$\Omega_A = \left( \frac{\tilde{\rho}}{rN} \right)^{N_{11}+N_{12}} c^{N_{1B}} \Omega \exp \left( - \frac{\sum_{ij} A_{ij}}{kT} \right) \quad (1)$$

where  $c$  is the flexibility parameter [10] that represents the probability that the intra-molecular bonding site is adjacent to each other. And in the above expression, the first term means the coordination factor,  $\Omega$  is the number of arrangements, and the last term indicates the free energy marginal sum of association.  $\Omega$  is derived from combinatorial calculation by adopting the argument of Veytsman, so that the partition function due to the hydrogen bonding was derived to count the number of arrangements of hydrogen bonding interaction.

Let us consider this with  $N_1$   $C_jE_j$  molecules and  $N_2$  alkanemolecules.  $N_1$   $C_jE_j$  surfactants have a hydroxyl group containing type 1 proton donor and type 1 acceptor and  $x$  ether groups containing type 2 acceptor. Three types of associating interactions are possible, that is, inter-molecular  $\text{OH}\cdots\text{OH}$ , inter-molecular  $\text{OH}\cdots\text{O}^-$ , and intra-molecular  $\text{OH}\cdots\text{O}^-$ . Let there be  $N_{11}$  inter-molecular hydrogen bonds of  $\text{OH}\cdots\text{OH}$ ,  $N_{12}$  inter-molecular hydrogen bonds of  $\text{OH}\cdots\text{O}^-$ , and  $N_{1B}$  intra-molecular hydrogen bonds of  $\text{OH}\cdots\text{O}^-$ . The total number of proton donor is  $N_1$  and the non-interacting proton donor  $N_{10}$  is

$$N_{10} = N_1 - N_{11} - N_{12} - N_{1B} \quad (2)$$

The number of arrangements available is counted by 3 steps.

- (i) Selecting proton donor and acceptor
- (ii) Counting the arrangements between the interacting species
- (iii) Eliminating over-count

Step (i), (ii) are the same as Missopolinou and Panayiotou's Veytsman statistics [10], but step (iii) has mathematical difference which is originated from the overcount problem during the combinatorial calculation. Classical Veytsman statistics assumed that the combinatorial arrangement doesn't have any mismatch such as molecule itself, not hydrogen bonding. But during the arrangement, the proton donor and acceptor from the same molecule doesn't form the hydrogen bonding. It forms the original molecule itself. This can happen in the middle of arrangement with a certain possibility. So this overcount from the combinatorial should be removed. Let the equivalent term that indicates the possibility of overcount is  $\Omega_{\text{iii}}$ , then the term is expressed by the subtraction of the possibility from 1. The summation of the possibility from the overcount that has to be subtracted can be simplified as following.

$$1 - \left(1 - \frac{1}{N_1}\right)^{N_{11}} \quad (3)$$

This term can be replaced by an exponential term because the number of donor and acceptor is Avogadro's scale, that is limiting case of the definition of  $e$ . The resulting expression from iii is

$$\Omega_{\text{iii}} = \exp\left(-\frac{N_{11}}{N_1}\right) \exp\left(-\frac{xN_{12}}{xN_1 - N_{1B}}\right) \quad (4)$$

The resulting equation  $\Omega$  is

$$\Omega = \frac{x^{N_{1B}} (N_1!)^2 (xN_1 - N_{1B})! \exp\left(-\frac{N_{11}}{N_1}\right) \exp\left(-\frac{xN_{12}}{xN_1 - N_{1B}}\right)}{N_{1B}! N_{11}! N_{12}! N_{10}! (N_1 - N_{11})! (xN_1 - N_{1B} - N_{12})!} \quad (5)$$

The exponential terms which are obtained by simple calculation of its probability are representing the elimination of the over-counting mentioned above.

Combining equation (1) and (5) provides the resulting expression of associating partition function.

$$\Omega_A = \frac{x^{N_{1B}}(N_1!)^2(xN_1 - N_{1B})!\exp(-\frac{N_{11}}{N_1})\exp(-\frac{xN_{12}}{xN_1 - N_{1B}})}{N_{1B}!N_{11}!N_{12}!N_{10}!(N_1 - N_{11})!(xN_1 - N_{1B} - N_{12})!} \cdot c^{N_{1B}} \left(\frac{\tilde{P}}{rN}\right)^{N_{11}+N_{12}} \exp\left(-\frac{\sum N_{ij}A_{ij}}{kT}\right) \quad (6)$$

The associating contribution of Helmholtz free energy,  $A_A^c$  is written as followings.

$$A_A^c = -kT \ln \Omega_A \quad (7)$$

where  $\Omega_A$  is expressed in eqn (6). And the Helmholtz free energy consists of physical and chemical part. Omitting details in the derivation, the resulting expression for the configurational Helmholtz free energy is written as

$$A^c = A_P^c + A_A^c \quad (8)$$

The physical contribution,  $A_P^c$  was given by Shin et al. [14,15].

We can obtain the minimization of Helmholtz energy from these three partial differentiations of equation (6). Let there be  $\beta = 1/kT$  hereafter.

$$\frac{\partial \beta A_A^c}{\partial N_{11}} = 0 \quad (9)$$

$$\frac{\partial \beta A_A^c}{\partial N_{12}} = 0 \quad (10)$$

$$\frac{\partial \beta A_A^c}{\partial N_{1B}} = 0 \quad (11)$$

By using the Stirling's approximation, the maximum term condition is obtained. Rearranging and solving the equations gives the number of  $N_{11}$ ,  $N_{12}$ ,  $N_{1B}$

The EOS and the chemical potential expression due to the associating interaction is derived from the configurational partition function.

$$P_A = P_A^c = -\left(\frac{\partial A_A^c}{\partial V}\right)_{T, N_i} = -\frac{1}{v^*} \left(\frac{\partial A_A^c}{\partial N_0}\right)_{T, N_i} \quad (12)$$

To obtain the pressure term from association, the Helmholtz free energy should be differentiated with regard to  $N_0$ .

The resulting expression is as following.

$$P_A = -\frac{1}{\beta v^*} (v_{11} + v_{12}) \tilde{P} \quad (13)$$

where  $v_{11}$ ,  $v_{12}$  is defined by

$$v_{11} = N_{11}/rN, \quad v_{12} = N_{12}/rN \quad (14)$$

The EOS is rearranged into the reduced variable type, and the resulting equation is as following.

$$\left(\frac{\tilde{P}}{\tilde{T}}\right)_A = -(v_{11} + v_{12}) \tilde{P} \quad (15)$$

The chemical potential was obtained by differentiation of the free energy with regard to the number of i-th component's mole fraction. In this case, the contribution from associating interaction is derived from  $A_A^c$ .

$$\mu_{A,i} = \left(\frac{\partial A_A^c}{\partial n_i}\right)_{T, V, n_j} = N_a \left(\frac{\partial A_A^c}{\partial N_i}\right)_{T, V, N_j} \quad (16)$$

Where  $N_a$  is Avogadro's number. After some mathematical steps, the resulting chemical potential is expressed as following.

$$\frac{\mu_{A,1}}{RT} = \ln \frac{(N_1 - N_{1B} - N_{11} - N_{12})(N_1 - N_{11})}{N_1^2} + x \ln \frac{xN_1 - N_{1B} - N_{12}}{xN_1 - N_{1B}} - \frac{N_{11}}{N_1^2} - \frac{x^2 N_{12}}{(xN_1 - N_{1B})^2} \quad (17)$$

After normalization of the partition function due to association [16], we can obtain the exact expression of associating contribution for EOS and chemical potential without physical part.

$$\left(\frac{\tilde{P}}{\tilde{T}}\right)_A = -(v_{11} + v_{12} - v_{11}^o - v_{12}^o) \tilde{P} \quad (18)$$

$$\frac{\mu_{A,1}}{RT} = \ln \frac{(N_1 - N_{1B} - N_{11} - N_{12})(N_1 - N_{11})}{(N_1 - N_{1B}^o - N_{11}^o - N_{12}^o)(N_1 - N_{11}^o)} + x \ln \frac{(xN_1 - N_{1B} - N_{12})(xN_1 - N_{1B}^o)}{(xN_1 - N_{1B}^o - N_{12}^o)(xN_1 - N_{1B}^o)} - \frac{N_{11}}{N_1^2} + \frac{N_{11}^o}{N_1^2} - \frac{x^2 N_{12}}{(xN_1 - N_{1B})^2} + \frac{x^2 N_{12}^o}{(xN_1 - N_{1B}^o)^2} \quad (19)$$

Finally the quasi-chemical nonrandom (intra+inter) molecular associating lattice fluid [QIALF] EOS and the chemical potential are combined by physical and chemical contribution.

### 3. Results and Discussion

In this study the QIALF model was tested for mixtures containing surfactant systems and was compared with the quasi-chemical nonrandom molecular associating lattice fluid (QALF) model [17], PR EOS and SAFT EOS. The QALF EOS has 3 molecular parameters for pure fluids:  $v_i^*$ ,  $r_i$ ,  $\varepsilon_{ii}$ , and the QIALF EOS has 4 molecular

parameters:  $v_i^*$ ,  $r_i$ ,  $\varepsilon_{ii}$ ,  $c$

Pure parameters are fitted to liquid density and vapor pressure data from the Korea thermophysical properties Data bank(KDB) [18].

Pure parameters QALF and QiALF EOS are listed in Table 1. We use the inter-molecular associating energy parameters for alkoxyethanol,  $U_{11}^A = -25.1$  kJ/mol of Renon and Prausnitz [19],  $S_{11}^A = -26.5$  J/(molK) as given by Panayiotou [20] and  $U_{12}^A = -22.0$  kJ/mol,  $S_{12}^A = -52.0$  J/(mol K) of Nagata and Tamura [21]. We set the intra-molecular associating energy parameters  $U_{int ra}^A = -10.47$  kJ/mol,  $S_{int ra}^A = -16.0$  J/(molK) as given by Missopolinou et al. [11].

The binary interaction parameter,  $k_{ij}$ , is determined in this calculation such that the deviation of calculated values from experimental data is minimal.

The Marquardt algorithm was used to minimize the following objective function, the Root Mean Square Deviations (RMSD) for pressure:

$$RMSD = \left\{ \frac{1}{N_{exp}} \sum_i \left[ \frac{P_{exp} - P_{cal}}{P_{exp}} \right]^2 \right\}^{1/2} \quad (20)$$

where  $N_{exp}$  is the number of experimental data points and  $P_{exp}$  and  $P_{cal}$  are the experimental and the calculated pressures, respectively.

The published data [22–24] for alkoxyethanol + alkane systems were correlated with the MALF, MiALF. Binary parameters and the RMSD for alkoxyethanol + alkane systems are shown in Table 2. In Figures 1 and 2, the calculated P–x equilibria of the QALF, QiALF EOF for the  $C_1E_1$  + cyclohexane, the  $C_2E_1$  + n-heptane systems were compared with the literature data. The present QiALF EOS, which considered a contribution from intra-molecular associations, represented better calculated results than the QALF EOS in alkoxyethanol + alkane systems. The PR EOS showed less calculated results than the QiALF and QALF model, because it had no associating contribution.

## 4. Conclusion

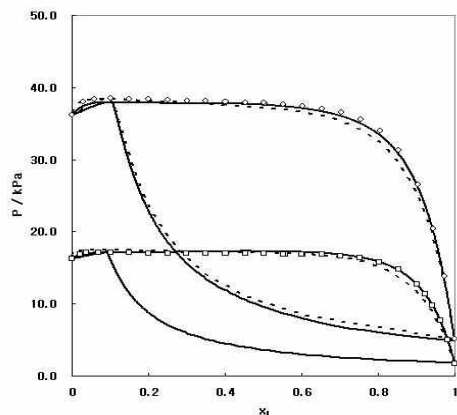
In this study, we presented a modified Veytsman statistics for inter- and intra- molecular association and combined it with the quasi-chemical nonrandom lattice fluid model. The over-counting in the course of the combinatorial calculation was removed from the lattice model including the associating interaction term. The present EOS could correlate the literature data well for mixtures containing nonionic surfactant systems.

[Table 1] Molecular parameters of pure fluids for the QALF and QiALF EOS.

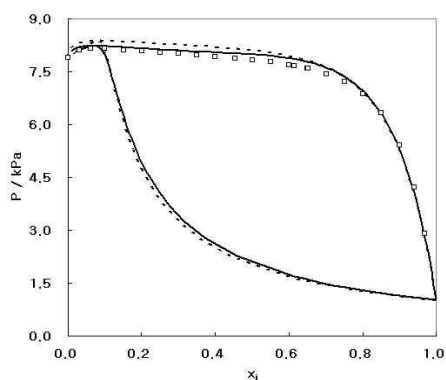
| QALF EOS | $v_i^*$<br>cm <sup>3</sup> /mol | $r_i$ | $\varepsilon_{ii}/k$ ,<br>K |       |
|----------|---------------------------------|-------|-----------------------------|-------|
| $C_1E_1$ | 20.665                          | 3.753 | 149.95                      |       |
| $C_2E_1$ | 19.831                          | 4.749 | 141.44                      |       |
| $C_3E_1$ | 20.197                          | 6.393 | 141.42                      |       |
| QALF EOS | $v_i^*$<br>cm <sup>3</sup> /mol | $r_i$ | $\varepsilon_{ii}/k$ ,<br>K | $c$   |
| $C_1E_1$ | 16.126                          | 4.776 | 147.54                      | 0.046 |
| $C_2E_1$ | 16.208                          | 5.764 | 140.41                      | 0.063 |
| $C_3E_1$ | 18.095                          | 7.075 | 137.01                      | 0.076 |

[Table 2] Binary Parameters and RMSD of the QALF and QiALF EOS for  $C_iE_j$  + alkane systems

|                              | T / K  | QALF EOS |       | QiALF EOS |       |
|------------------------------|--------|----------|-------|-----------|-------|
|                              |        | $k_{ij}$ | RMSD  | $k_{ij}$  | RMSD  |
| $C_1E_1$<br>+ n-hexane       | 313.15 | 0.009    | 0.066 | 0.042     | 0.056 |
|                              | 323.15 | 0.009    | 0.045 | 0.043     | 0.041 |
| $C_1E_1$<br>+<br>cyclohexane | 303.15 | 0.020    | 0.033 | 0.048     | 0.016 |
|                              | 323.15 | 0.020    | 0.039 | 0.049     | 0.017 |
| $C_2E_1$<br>+ n-hexane       | 303.15 | 0.012    | 0.032 | 0.030     | 0.015 |
|                              | 323.15 | 0.013    | 0.020 | 0.032     | 0.007 |
| $C_2E_1$<br>+<br>cyclohexane | 303.15 | 0.015    | 0.027 | 0.029     | 0.030 |
|                              | 323.15 | 0.014    | 0.024 | 0.029     | 0.016 |
| $C_2E_1$<br>+<br>n-heptane   | 303.15 | 0.013    | 0.022 | 0.031     | 0.019 |
|                              | 323.15 | 0.015    | 0.009 | 0.032     | 0.011 |
| $C_3E_1$<br>+ n-hexane       | 303.15 | 0.001    | 0.020 | 0.018     | 0.017 |
|                              | 313.15 | -0.001   | 0.018 | 0.018     | 0.012 |
|                              | 323.15 | -0.003   | 0.024 | 0.019     | 0.010 |
| $C_3E_1$<br>+<br>n-heptane   | 303.15 | 0.003    | 0.026 | 0.021     | 0.011 |
|                              | 313.15 | 0.003    | 0.030 | 0.021     | 0.012 |
|                              | 323.15 | 0.001    | 0.017 | 0.022     | 0.012 |



[Figure 1] Vapor-liquid equilibria of the  $C_1E_1$  (1) + cyclohexane (2) system: Experimental data at ( $\square$ ) 303.15 K; ( $\circ$ ) 323.15 K; dotted lines: QALF EOS, solid lines: QiALF EOS.



[Fig. 2] Vapor-liquid equilibria of the  $C_2E_1$  (1) + n-heptane (2) system: Experimental data at ( $\square$ ) 303.15 K; dotted lines: QALF EOS, solid lines: QiALF EOS.

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