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Vapor-liquid equilibrium correlations for systems containing amines using a lattice fluid equation of state with hydrogen bonding

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Abstract−The nonrandom lattice equation of state with hydrogen bonding (NLF-HB EOS) was examined for the correlation of vapor-liquid equilibria (VLE) for binary amine and hydrocarbon mixture at various temperatures. For these mixtures, the consideration of hydrogen bondings in the lattice equation of state clearly improves the prediction for VLE. The amines were divided into four groups due to the different strength of the hydrogen bonding. For all groups, different hydrogen bonding parameters were obtained and evaluated. The effects of varying hydrogen bonding energies for NLF-HB EOS are discussed. For systems containing lower amines, the NLF-HB EOS showed excellent agreement with the experimental data. For the correlation of systems containing tertiary amine molecules, binary interaction parameter had to be involved instead of hydrogen bonding parameters.

Key words: Vapor-liquid Equilibrium, Correlation, Lattice Fluid, Equation of State, Hydrogen Bonding, Amines, Hydrocarbons

INTRODUCTION

The reliable correlation and prediction of vapor-liquid equilibrium data plays an important role for many kinds of separation technologies. Collecting data on VLE is time consuming and, especially at elevated pressures, not easy to perform. Therefore, a growing number of different approaches for correlating and predicting of VLE have been suggested. One of the most common approaches is to use the equation of state to describe the excess Gibbs energy G^E [1].

Kang and coworkers [2] have compared extensive VLE calculations results of an equation of state based on lattice theory with different types of EOS and concluded that all examined EOS provide a similar degree of accuracy for most systems including polymer solution. However, the scope of this work is the reliability and the performance of lattice EOS with hydrogen bonding [3-6] for binary VLE systems containing amines.

Lattice fluid theories have a long history since Guggenheim [7]. Hydrogen bonding partition functions were first introduced by Veytzman [8] and extended for the use together with equation of states by Sanchez and coworkers [9] and Yeom et al. [5]. The lattice fluid equations of state with hydrogen bonding statistics possess the advantage of using only association-type-specific parameters for the specific group of components.

Although the introduced EOS can correlate VLE for various mixtures and conditions, the calculated values under certain circumstances are still far from experimental values without using proper binary interaction parameters. Even for group-contribution version, interaction parameter matrixes obtained from large databases are required. The aim of this study is to collect the binary interaction parameters for NLF-HB EOS for various types of mixtures at ambient condition. It is expected that modifying surface parameters of molecules can help to reduce the absolute value of binary interaction parameters because binary interaction parameters correct interchange energies of two segments and effective surface areas act as interfaces to energy exchange.

THEORY

Derivations and various aspects of NLF-HB EOS are given in the previous studies [2-6]. In this paper, we will give only the final form of the EOS. Normalization of hydrogen bonding partition function [10] was not used because it has negligible effect on the calculations. The equation of state is given as

$$\frac{\mathrm{PV}_H}{\mathrm{RT}}=\frac{\mathrm{z}}{2}\ln\left[1+\left(\frac{\mathrm{q}_M}{\mathrm{r}_M}-1\right)\rho\right]-\ln(1-\rho)+\rho\frac{l_M}{\mathrm{r}_M}-\nu_{HB}\rho-\frac{\mathrm{z}\beta}{2}\varepsilon_M\theta^2. \quad (1)$$

Expression for chemical potential is given as follows:

$$\begin{aligned}\mu_i/\mathrm{RT}=&(\mathrm{r}_i+l_i)\ln\left[1+\left(\frac{\mathrm{q}_M}{\mathrm{r}_M}-1\right)\rho\right]-\mathrm{r}_i\ln(1-\rho)+\ln\left(\frac{\theta_i}{\mathrm{q}_i}\right)+\left(\frac{\mathrm{z}\beta}{2}\right)\mathrm{q}_i\varepsilon_M\theta^2\\&\times\left[1-\frac{\mathrm{r}_i}{\mathrm{q}_i}-\frac{2\sum\theta_k\varepsilon_{ik}+\beta\sum\sum\sum\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+2\varepsilon_{kl}-2\varepsilon_{jk}-\varepsilon_{ik})}{\varepsilon_M\theta^2}\right]\\&-\sum_k \mathrm{d}_k^i\ln\frac{\mathrm{N}_d^k}{\mathrm{N}_{k0}}-\sum_l \mathrm{a}_l^i\ln\frac{\mathrm{N}_a^l}{\mathrm{N}_{l0}}.\end{aligned} \quad (2)$$

If associating components are present in the mixture, the following nonlinear equations have to be solved:

$$\mathrm{N}_{kl}^{HB}\mathrm{N}_r=\mathrm{N}_{k0}\mathrm{N}_{l0}\exp(-\beta \mathrm{A}_{kl}). \quad (3)$$

When there is a single type of hydrogen bonding in the mixture, this equation becomes quadratic and can be solved analytically. If there is more than one type of hydrogen bonding, a successive substitution method starting from a reasonable initial guess can be used for solving a set of nonlinear equations.

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Table 1. Pure component parameters for the NLF-HB EOS

Component name	r_i^A	ε_i^A	ε_i^B	ε_i^C	l_i	T_{Low}	T_{Up}
n-Butane	6.51	106.20	−4.61E-02	−2.38E-02	3.6	250	415
n-Hexane	8.76	116.68	−4.90E-02	−4.43E-02	5.9	280	450
n-Heptane	9.98	119.59	−5.81E-02	−5.24E-02	7.5	250	500
Methylamine	3.14	121.37	−4.26E-02	1.85E-01	0.0	263	329
Propylamine	5.56	127.74	−6.68E-02	−1.40E-01	0.0	235	350
Hexylamine	8.93	130.33	−3.90E-02	−5.88E-02	0.0	273	373
Dimethylamine	4.54	120.30	−3.76E-02	3.25E-03	0.0	202	280
Diethylamine	6.70	119.35	−2.98E-02	−4.49E-02	0.0	325	437
Trimethylamine	6.03	106.41	−3.57E-02	−1.01E-01	0.0	176	276
Triethylamine	9.00	115.11	−1.61E-02	−5.41E-02	0.0	260	400

PURE COMPONENT PARAMETERS

The components used in this study are shown in Table 1, including the NLF-HB EOS parameters. The pure component parameters for this investigation were obtained from fitting pure vapor and liquid density data sets from the Korean Thermo Physical Proper-

Table 2. Hydrogen bonding parameter

Component class	U_{kl}^{HB}	S_{kl}^{HB}	No_{Donor}	$No_{Acceptor}$
Methylamine	−1577.70	−3.50	2	1
Primary amines	−624.05	−1.29	2	1
Secondary amines	−1729.20	−4.50	1	1
Tertiary amines	0.00	0.00	0	0

Table 3. Summary of the calculation results for the NLF-HB EOS with and without binary interaction parameters

Systems and references	T [K]	NLF-HB EOS with k_{ij}			NLF-HB EOS	
		k_{ij}	ΔP^a	Δx^b	ΔP^a	Δx^b
Methylamine+n-Hexane [12]	253.15	−2.98E-04	1.213	0.000	1.245	0.000
	273.15	4.20E-04	0.550	0.000	0.594	0.000
	293.15	−4.44E-04	0.766	0.000	0.807	0.000
Methylamine+n-Butane [13]	233.15	−1.34E-03	1.787	0.000	1.909	0.000
	253.15	5.99E-03	0.657	0.000	2.298	0.000
	273.15	8.41E-03	0.299	0.000	2.379	0.000
Methylamine+n-Nonane [13]	253.15	−3.49E-03	1.838	0.000	3.887	0.000
	273.15	−2.62E-03	1.835	0.000	2.777	0.000
	293.15	−4.92E-03	2.299	0.000	3.378	0.000
Propylamine+n-Hexane [14]	293.15	−6.49E-04	0.779	0.000	0.843	0.000
	303.15	6.80E-05	0.616	0.000	0.616	0.000
	313.25	3.27E-04	0.808	0.000	0.841	0.000
Hexylamine+n-Hexane [15,16]	313.25	−6.69E-03	0.626	0.456	3.698	0.621
	323.15	−7.60E-03	0.358	0.679	4.337	0.992
	333.15	−1.09E-02	0.495	0.994	6.882	2.129
Dimethylamine+n-Hexane [17]	253.15	1.21E-03	1.930	0.000	2.346	0.000
	273.15	2.06E-03	1.636	0.000	2.051	0.000
	293.15	6.01E-04	1.412	0.000	1.460	0.000
Diethylamine+n-Hexane [18]	323.15	−2.05E-02	0.220	0.000	7.077	0.000
	333.15	−2.21E-02	0.288	0.000	7.285	0.000
	343.15	−2.33E-02	0.334	0.000	7.477	0.000
Diethylamine+n-Heptane [19]	308.15	−2.49E-02	0.611	1.032	13.645	4.793
	328.15	−2.76E-02	0.421	0.714	11.183	4.342
Trimethylamine+n-Hexane [20]	233.15	−6.80E-03	1.571	0.000	6.118	0.000
	253.15	−1.04E-02	1.076	0.000	7.802	0.000
	273.15	−1.54E-02	0.657	0.000	9.632	0.000
Triethylamine+n-Heptane [19]	333.15	−2.94E-02	0.297	0.416	12.922	4.263
	353.15	−3.23E-02	0.251	0.301	13.333	4.167
Triethylamine+n-Hexane [16,21]	298.15	−8.82E-03	1.330	0.000	3.257	0.000
	333.15	−2.13E-02	0.251	0.161	7.119	2.984

$^a\Delta P=\frac{100}{N_{Data}}\sum_i\left|\frac{P_i^{exp}-P_i^{cal}}{P_i^{exp}}\right|$. $^b\Delta x=\frac{100}{N_{Data}}\sum_i\left|x_i^{exp}-x_i^{cal}\right|$

ties Data Bank (KDB) [11]. The energy parameters required for each component were assumed to be temperature dependent of the following form:

$$\varepsilon_{ii}/k = (\varepsilon_i^A/k) + (\varepsilon_{ii}^B/k)(T - T_0) + (\varepsilon_{ii}^C/k)(T\ln T_0/T + T - T_0), \qquad (4)$$

where T_0=298.15 K. The size parameters were defined to be constant over the temperature as shown below:

$$r_i = r_i^A. \qquad (5)$$

The temperatue dependence was removed from the size parameter because the lattice hard sphere volume was considered to be temperature dependent in the following form:

$$V_{HS} = A + Be^{-C/T}. \qquad (6)$$

The bulkiness factor for each componet was incoorporated in the following matter:

$$zq_i = rz_i - 2r_i + 2 - 2l_i. \qquad (7)$$

A nonzero bulkiness factor l_i reflects the molecules are branched, interconnected or has more or less surface area than predicted value from segment chain length. The bulkiness factors used in this study are also given in Table 1. For associating components, hydrogen-bonding parameters are required, where

$$A_{kl}^{HB} = U_{kl}^{HB} - TS_{kl}^{HB}. \qquad (8)$$

The hydrogen bonidng parameters for amines were optimized to match 30 experimental VLE isotherms and shown in Table 2.

RESULT AND DISCUSSION

In this work, all examined systems were correlated by using the nonrandom lattice fluid equation of state with hydrogen bonding. Bulkiness factors were used to reduce the numbers of needed binary interaction coefficients for each mixture. Thus, in this study only one binary coefficient was used to successfully correlate vapor-liquid phase equilibria in a satisfying manner.

The binary data sets were taken from the electronic version of the Dortmund Data Bank (DDB). For each system, different datasets at various temperatures were correlated. The original references are shown together with the correlation results in Table 3.

For amines, the consideration of bulkiness factors as introduced in the chapter did lead to an improvement in the calculation results; thus, the bulkiness factors for amines were set to zero.

The amines were divided into four different groups to represent the different strength of the hydrogen binding. Due to the small size of the Methylamine molecule, separate hydrogen bonding parameters have been fitted. For the other amines, the hydrogen binding parameters were fitted considering different groups for primary, secondary and tertiary amines. For tertiary amines, only one proton acceptor exists and no proton donor is present in the molecules. For this reason, the hydrogen bonding parameters for tertiary amines were set to zero. The obtained parameters are summarized in Table 2.

For lower amines, the correlation results with and without binary interaction parameter show a similar degree of accuracy. In Fig. 1,

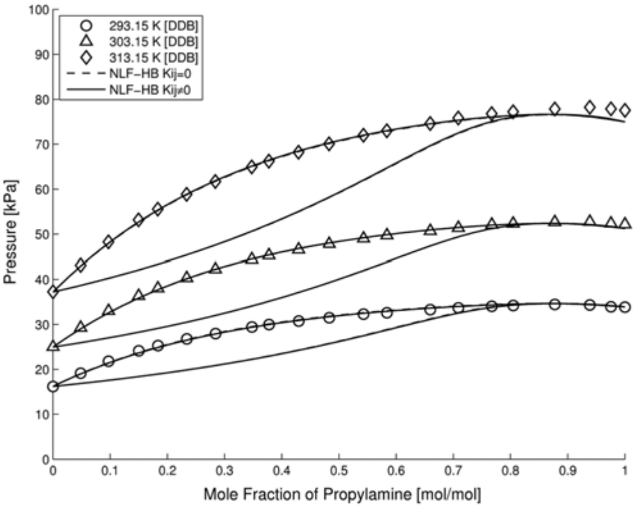

Fig. 2. Correlation results for the propylamine+n-hexane system at different temperatures.

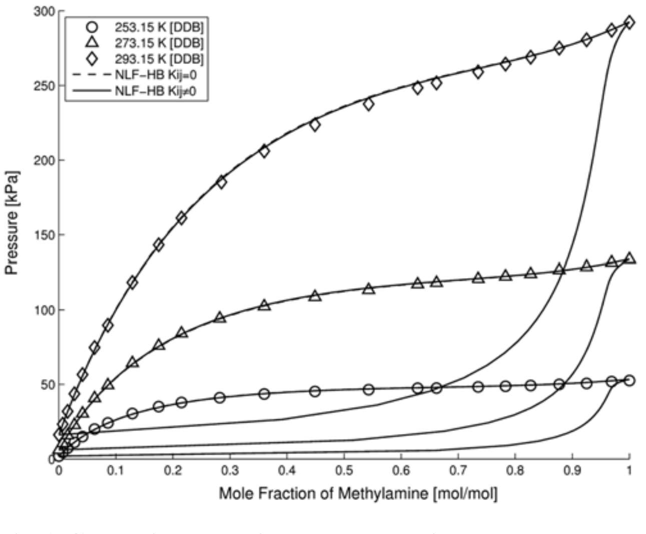

Fig. 1. Correlation result for the methylamine+n-hexane system at different temperatures.

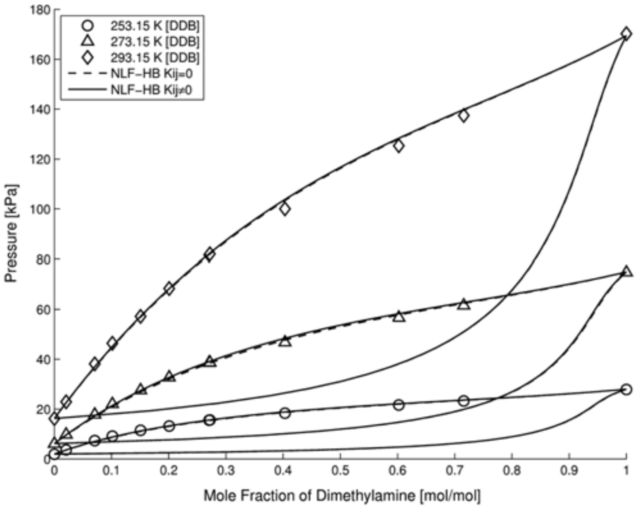

Fig. 3. Correlation results for the dimethylamine+n-hexane system at different temperatures.

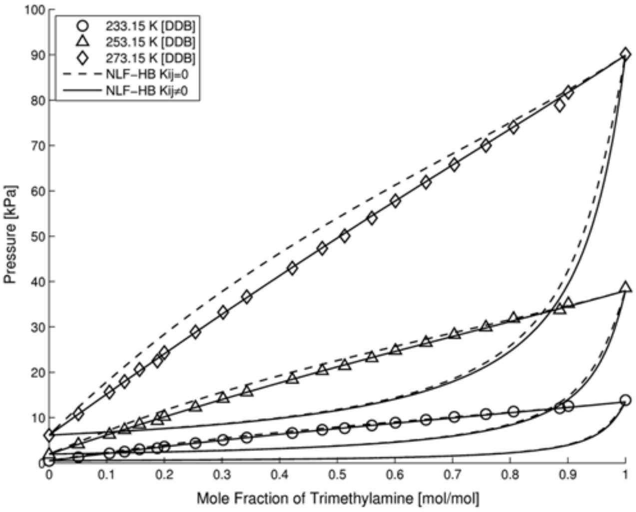

Fig. 4. Correlation results for the trimethylamine+n-hexane system at different temperatures.

the correlation for the methylamine+n-hexane is shown. As mentioned before, the graph shows a similar behavior with and without interaction coefficient. Figs. 2 and 3 show the same good agreement for the propylamine+n-hexane and dimethylamine+n-hexane systems.

The calculation results for the trimethylamine+n-hexane system are presented in Fig. 4. In this case, the system contains a tertiary amine, and the use of a binary interaction coefficient clearly improves the correlation performance for that kind of system. Table 3 shows the summary of all examined systems.

CONCLUSION

A principal goal for applied equations of states is the capability of reliable correlation with the least amount of necessary parameters. In this study, the capability of the NLF-HB EOS for the correlation of binary amine+hydrocarbon systems could be shown. By the consideration of hydrogen bonding parameters, the correlation results were satisfying for systems containing lower amines. For systems containing bigger amines - especially, tertiary amines - the use of one binary interaction parameter clearly improves the calculation.

NOMENCLATURE

a : number of acceptor groups
A : temperature dependent free energy
d : number of donor groups
G : Gibbs energy
k : interaction coefficient
l : bulkiness factor
N : number of lattice sites
P : pressure
q : surface area parameter
r : segment number parameter
R : gas constant=8.314 J/(mol K)
S : hydrogen bonding entropy
T : temperature in K
U : hydrogen bonding enthalpy
v : molar volume
V_H : molar lattice cell volume
V_{HS} : lattice hard sphere volume
z : lattice coordination number=10

Greek Letters

β : 1/kT
ε : interaction energy parameter
μ : chemical potential
Θ : surface area fraction
ρ : reduced density

Superscripts

A, B, C : parameter identifier
E : excess
HB : hydrogen bonding
k, *l* : acceptor or donor

Subscripts

0 : reference point
i, j, k, *l* : component index, donor group or acceptor group
M : mixture

Abbreviation

EOS : equation of state
HB : hydrogen bonding
KDB : Korean thermo physical properties Data Bank
DDB : Dortmund data bank
NLF : nonrandom lattice fluid
VLE : vapor-liquid equilibrium

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