# A New Insight to Validation of Local Composition Models in Binary Mixtures Using Molecular Dynamic Simulation

**Ali Haghtalab and Jaber Yousefi Seyf**
Dept. of Chemical Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran

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*A computational method based on molecular dynamics (MD) simulation is developed to predict the interaction parameters in local composition (LC) models such as Wilson, nonrandom two-liquid (NRTL), and universal quasichemical activity coefficient (UNIQUAC) applicable in vapor-liquid equilibrium calculations so that LC models are validated. The five binary mixtures of water-acetonitrile, water-isopropanol, methanol-chloroform, acetone-cyclohexane, and meta xylene-benzene were simulated. The MD simulations are performed using the condensed phase optimized molecular potential for atomistic simulation studies force field and all ranges of radial distribution function (RDF) are considered. In addition, the interaction parameters are determined by optimization through experimental data and are compared with the MD results. The interaction parameters are calculated through RDF where the effective radius is investigated by experimental data. The present results demonstrate that interaction parameters are composition dependent which are best fitted by a third-order polynomial relation. Based on the deviation in the activity coefficients, the results of the UNIQUAC model are more accurate than Wilson and NRTL models.* © 2015 American Institute of Chemical Engineers *AIChE J*, 62: 275–286, 2016
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## Introduction

The concept of local composition (LC) can be traced back to the quasichemical theory of Guggenheim for a lattice fluid[1] that has received much attention during the past few decades. Although the quasichemical theory is based on a lattice theory for liquid mixtures, the LC is a semiempirical expression, which is based on Boltzmann radial distribution, was postulated first time by Wilson to obtain excess Gibbs function and activity coefficient models.[2] Then Renon and Prausnitz developed the Nonrandom two-liquid (NRTL) equation which can be applied to both vapor-liquid and liquid-liquid equilibrium calculations.[3] Abrams and Prausnitz[4] introduced the so called Universal Quasichemical Activity Coefficient (UNIQUAC) model through a partition function that was further developed by Maurer and Prausnitz[5] based on a local area fraction expression.

In spite of widely extended application of the activity coefficient models based on the LC concept, there is a matter of controversy in regard to inconsistency in the Wilson LC expressions. Flemer analytically remarked that interaction parameters in LC model generally should be composition dependent[6] and McDermott proved that local mole fractions are not consistent with the bulk composition of the liquid mixture.[7] Conversely, theoretical foundation of LC has scarcely been discussed. Nakanishi and Toukubo[8] and Nakanishi et al.[9] made extensive simulations of Lennard-Jones mixtures to check validity of LC models so that they concluded the LC hypothesis presents some shortcomings, and if agreement exist, it is fortuitous, however, unfortunately, it is difficult to evaluate the accuracy of their results due to the use of the incomplete radial distribution data.[10] Moreover, they used $\varepsilon_{ij}/2$ ($\varepsilon_{ij}$ being the Lennard-Jones energy parameters) as the exponents in configurational Helmholtz free energy that was an incorrect choice as discussed by Lee et al.[11] The results of Nakanishi and coworkers[8,9] showed that the product $(x_{ji}/x_{ii}) \times (x_i/x_j)$ ($x_{ji}$ and $x_{ii}$ stand for LC, $x_i$ and $x_j$ denote bulk mole fraction) does not vary with bulk composition, but Hoheisel and Kohler presented that this LC expression for molecules of the same size is bulk composition dependent that is in a good agreement with the quasichemical model so that the LC expression such as Wilson model cannot be used at all.[11] Lee et al.[12] remarked that $\varepsilon_{ij}$ of the Lennard-Jones potential or any average of $u_{ij}(r_{ij})$ ($u_{ij}$ and $r_{ij}$ define Lennard-Jones potential and radius between particle i and j, respectively) should not be used as a interaction parameter in Wilson LC expression. Using the molecular parameters, the number of molecules of type $i$ around the central molecule $j$ ($n_{ij}$) is given as[13]

$$n_{ij}(r_{ij}) = \frac{N_i - \delta_{ij}}{V} \int_0^{r_{ij}} g_{ij}\left(r_{ij}, [\rho_k], T, [\sigma_{kl}], [\varepsilon_{kl}]\right) 4\pi r_{ij}^2 dr_{ij} \qquad (1)$$

where $g_{ij}$ is the radial distribution function (RDF) for the $i-j$ pair, $V$ is the system volume and $N_i$ is the total number of molecules of type $i$ in the mixture, and $\delta_{ij}$ is the Kronecker delta function. Normally $N_i$ is large enough in comparison to $\delta_{ij}$, so

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Correspondence concerning this article should be addressed to A. Haghtalab at haghtala@modares.ac.ir.

that $N_i - \delta_{ij} = N_i$. Thus, by approximation, the integral in Eq. 1 can be written as

$$\int_0^{r_{ij}} 4\pi r_{ij}^2 g_{ij}(r_{ij})dr_{ij} = \int_0^{r_{ij}} 4\pi r_{ij}^2 e^{-\beta W_{ij}} dr_{ij} = \int_0^{r_{ij}} 4\pi r_{ij}^2 e^{-\beta \bar{W}_{ij}} dr_{ij} = V_{ij} e^{-\beta \bar{W}_{ij}} \quad (2)$$

where instead of the RDF, an average potential mean force, $\bar{W}_{ij}$, is applied ($V_{ij}$ defines the volume at cutoff radii $r_{ij}$). Thus, the Wilson LC expression is proposed as

$$\frac{x_{ij}}{x_{ii}}\frac{x_i}{x_j} = \frac{V_{ji}}{V_{ii}} e^{-\beta(\bar{W}_{ij} - \bar{W}_{ii})} \quad (3)$$

However, $g_{ij}$ and consequently $W_{ij}$ are composition, density, and temperature dependent which confirms the work of Hoheisel and Kohler in its conclusion that the expression of $(x_{ji}/x_{ii}) \times (x_i/x_j)$ is composition dependent.[6,12]

In Eq. 1, local mole number depends on the radii $r_{ij}$ but there is an ambiguity how to decide at which distance ($r_{ij}$ as the upper limit of the integral) should be set for calculation of $n_{ij}$. In LC models, only nearest-neighbor interactions are taken into account, however, the contributions of the second and third peaks of $g_{ij}$ present considerable contribution to the energy and virial pressures of a liquid so that this long-range correction may lead to an improved accuracy by 50%.[14] Thus, taking into account only the first molecular neighborhood (first peak of RDF) will lead to large deviation in the thermodynamic properties obtained via statistical mechanics. In addition, $r_{ij}$ should be equal to $r_{ji}$ to keep consistency between $n_{ij}$ and $n_{ji}$.[10]

In addition to above discussions, presently engineers face increasingly complex and nonideal pure substances, mixtures, and operational conditions involving extremes of temperature, pressure, concentration, ionic strength, and so forth, so that carrying out such experiments to collect data are time consuming and costly. Moreover, it is cumbersome to get reliable experimental measurements at such conditions. As a possible way to address these difficulties, it seems to be valuable to use molecular simulation through statistical mechanics and related molecular simulation methodologies such as Monte Carlo[15] and Molecular Dynamics (MD)[16] that allows engineer to estimate the physical and chemical macroscopic properties of materials, inaccessible substance, and compounds at severe operating conditions. From a chemical engineering point of view, the main goal of statistical mechanics is to estimate the macroscopic properties. However, methods such as histogram reweighting[17] and Gibbs ensemble Monte Carlo simulations[18] are ideally suited for phase equilibria calculations, but to the best of our knowledge, no attempts have been performed for computation vapor liquid equilibrium and liquid-liquid equilibrium using MD.

The remarkable thing is that although in concept of LC models only nearest-neighborhood interactions are taken into account, but when experimental data are optimized to obtain the interaction parameters, effect of all molecular shells are seen in the interaction parameters. Thus, it may be concluded that the interaction parameters are a function of radius. However, we are not aware exactly what all the limitations are. In this work, we will present and discuss some preliminary results through our computer experiments (MD) for the several binary mixtures which present simple to complex behavior with reliable phase equilibria data that are validated through thermodynamic consistency tests. Accordingly, these binary mixtures are selected as water-acetonitrile (W-A), water-isopropanol (W-Iso.), methanol-chloroform (M-CH.), acetone-cyclohexane (A-Cyc.), and meta xylene-benzene (mX-B). Except meta xylene-benzene binary, all of these binary systems are associated systems with a minimum temperature azeotrope point that show a variety of polar-nonpolar systems which are difficult cases in vapor liquid equilibrium calculations. In this work, the validity of LC models, radial and composition dependence of interaction parameters in Wilson, NRTL, and UNIQUAC models are investigated. Finally, MD results in connection with these three LC models are used to computation of vapor-liquid equilibrium so that the results are compared with the experimental vapor liquid equilibrium data.

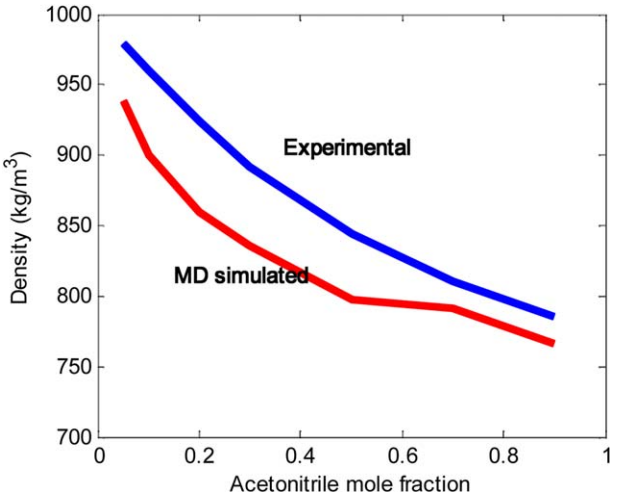


**Figure 1. MD simulated and experimental density (kg/m$^3$) at 298.15 K for the water-acetonitrile system.**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

## MD Simulations

### *Methods*

In this work, MD simulations are used to compute the RDF between the different compounds with various polarities. The simulations are performed using *ab initio* COMPASS (Condensed phase Optimized Molecular Potential for Atomistic Simulation Studies) force field.[19] In this force field, the total potential energy Epot is defined as the sum of intramolecular and intermolecular interactions and expressed as

$$\begin{aligned} E_{\text{pot}} &= (E_b + E_\theta + E_\varphi + E_\chi + E_{\text{cross}}) + (E_{\text{Cou}} + E_{\text{vdW}}) \\ &= \sum_b [k_2(b-b_\circ)^2 + k_3(b-b_\circ)^3 + k_4(b-b_\circ)^4] \\ &\quad + \sum_\theta [k_2(\theta-\theta_\circ)^2 + k_3(\theta-\theta_\circ)^3 + k_4(\theta-\theta_\circ)^4] \\ &\quad + \sum_\phi [k_1(1-\cos\phi) + k_2(1-\cos 2\phi) + k_3(1-\cos 3\phi)] \\ &\quad + \sum_\chi k_2\chi^2 + \sum_{b,b'} k(b-b_\circ)(b'-b'_\circ) + \sum_{b,\theta} k(b-b_\circ)(\theta-\theta_\circ) \end{aligned}$$

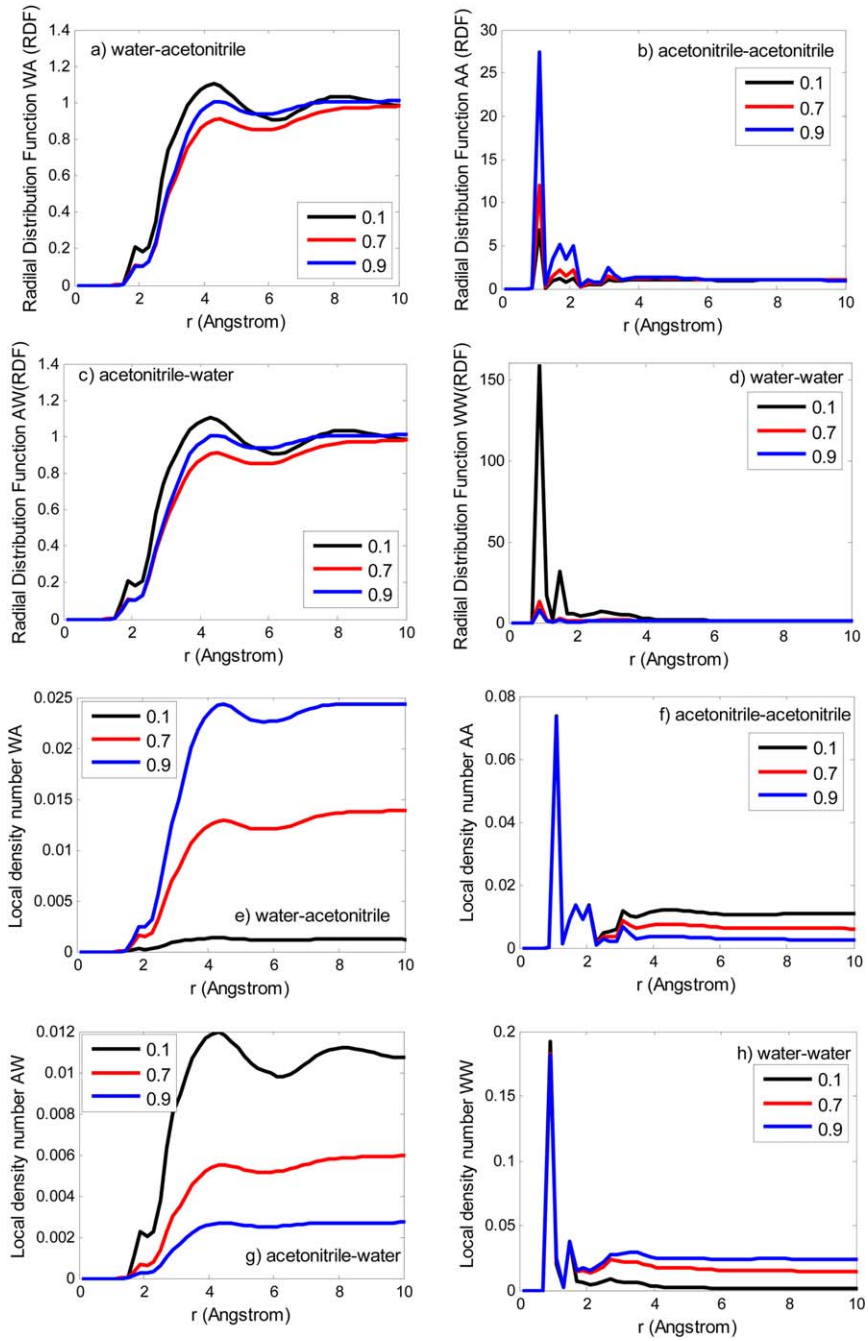


**Figure 2. RDF ($g_{ij}$) at the different water mole fraction: (a) water-acetonitrile, (b) acetonitrile- acetonitrile, (c) acetonitrile -water, and (d) water-water, and local density function (number of molecules per cubic angstrom): (e) water-acetonitrile, (f) acetonitrile-acetonitrile, (g) acetonitrile-water, and (h) water-water.**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

$$
\begin{aligned}
&+\sum_{b,\phi}(b-b_\circ)[k_1\cos\phi+k_2\cos 2\phi+k_3\cos 3\phi]\\
&+\sum_{\theta,\phi}(\theta-\theta_\circ)[k_1\cos\phi+k_2\cos 2\phi+k_3\cos 3\phi]\\
&+\sum_{\theta,\theta'}(\theta-\theta_\circ)(\theta'-\theta'_\circ)+\sum_{\theta,\theta',\phi}k(\theta-\theta_\circ)(\theta'-\theta'_\circ)\\
&+\left(\sum_{i,j}\frac{q_iq_j}{r_{ij}}+\sum_{i,j}\varepsilon_{ij}\left[\left(\frac{r^\circ_{ij}}{r_{ij}}\right)^9-\left(\frac{r^\circ_{ij}}{r_{ij}}\right)^6\right]\right)
\end{aligned}
\tag{4}
$$

where $E_b$ = bond stretching energy, $E_\theta$ = valance angle bending energy, $E_\Phi$ = dihedral torsion energy, $E_\chi$ = out-of-plane energy, $E_{cross}$ = cross-term interaction energy, $E_{Cou}$ = Coulombic interaction energy, and $E_{vdW}$ = van der Waals interaction energy. The first five terms are used for calculation of the short-range bonded interactions, whereas the last two terms represent the intermolecular and intramolecular nonbonded interactions, respectively. The electrostatic or Columbic interaction are due to the charged atoms ($i$,$j$) which can be attractive or repulsive forces whereas Lenard-Jones (LJ) potential function (LJ 9-6) defines the van der Waals interactions such as dispersion and London forces.

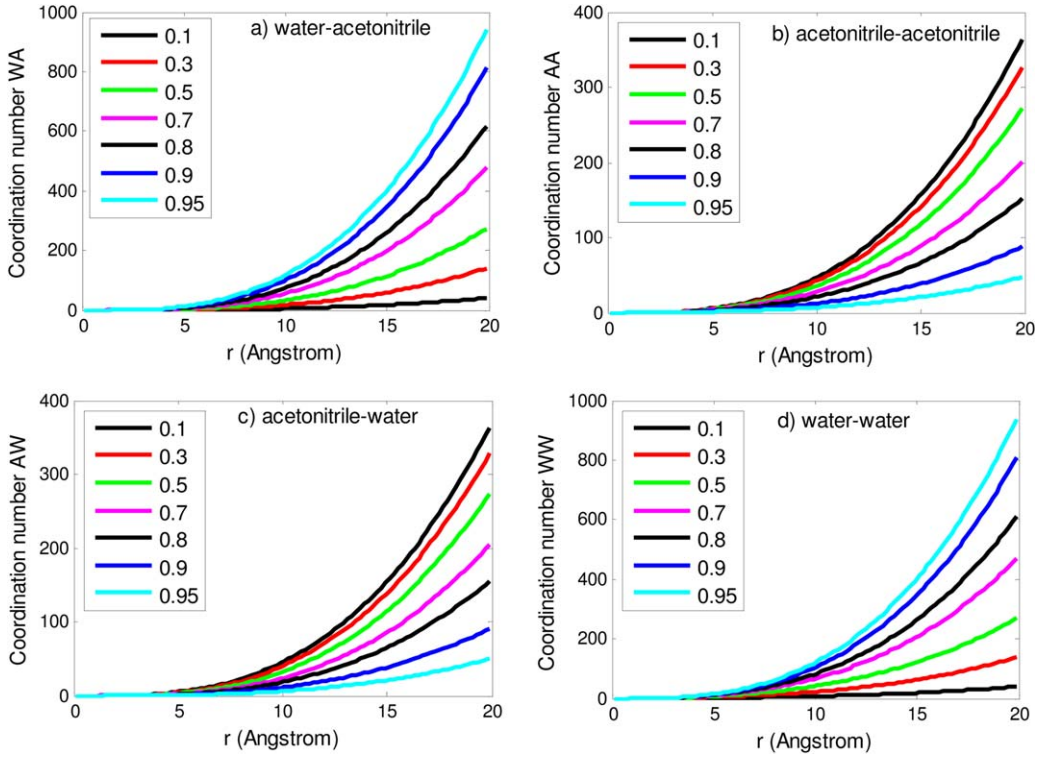


**Figure 3. Coordination number *n*: (a) water-acetonitrile, (b) acetonitrile-acetonitrile, (c) acetonitrile-water, and (d) water-water as a function of radius at the different water mole fraction.**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

### *MD procedure for the water + acetonitrile mixture*

The molecular structure of water and acetonitrile were obtained from the Cambridge Structural Database. The *ab initio* COPMASS force field was used for MD simulations so that first, the stable molecular configuration of water and acetonitrile are specified by minimization of energy although conjugate gradient method. The binary of water + acetonitrile with different mole fraction (0.1–0.9, 0.3–0.7, 0.5–0.5,

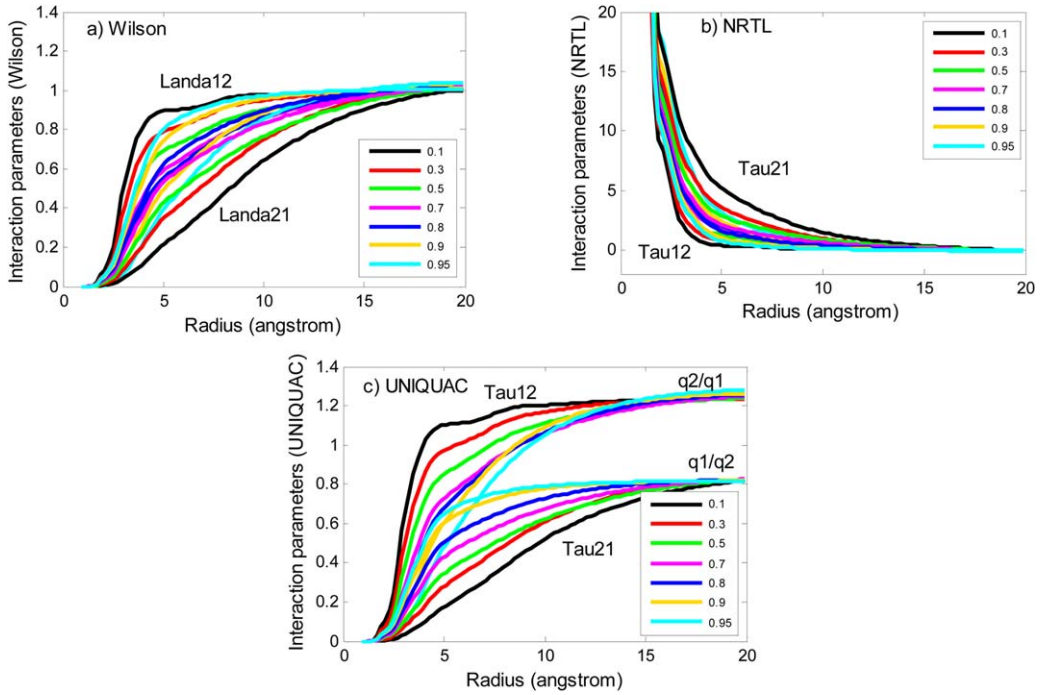


**Figure 4. The interaction parameters in terms of radius at the different composition for the water-acetonitrile system (a) Wilson, (b) NRTL, and (c) UNIQUAC.**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

**Table 1. MD Simulation and Experimental Data Optimization Results Using Effective Radius, Interaction Parameters, and Deviation in Activity Coefficients**

| Wilson (MD Results) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Water-Acetonitrile[26] | | | | | Water-Isopropanol[27] | | | | |
| Water Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation | Water Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| 0.100 | 3.400 | 0.613 | 0.061 | 0.660 | 0.100 | 19.000 | 0.801 | 0.096 | 0.138 |
| 0.300 | 3.400 | 0.485 | 0.121 | 0.877 | 0.300 | 20.000 | 0.633 | 0.143 | 0.021 |
| 0.500 | 3.400 | 0.380 | 0.166 | 1.275 | 0.500 | 20.000 | 0.508 | 0.194 | 0.033 |
| 0.700 | 3.600 | 0.344 | 0.266 | 1.812 | 0.700 | 23.000 | 0.411 | 0.268 | 0.132 |
| 0.800 | 3.800 | 0.342 | 0.371 | 2.218 | 0.900 | 25.000 | 0.274 | 0.429 | 0.428 |
| 0.900 | 3.800 | 0.255 | 0.462 | 2.737 | | | | | |
| 0.950 | 4.200 | 0.243 | 0.637 | 3.110 | | | | | |
| Wilson (Experimental Data Optimization) | | | | | | | | | |
| 0.020–0.976 | – | 0.566 | 0.057 | 0.627 | 0.090–0.976 | – | 2.390 | 0.200 | 0.050 |
| NRTL* (MD Results) | | | | | | | | | |
| Water-Acetonitrile | | | | | Water-Isopropanol | | | | |
| Methanol Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation | Acetone Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| 0.100 | 9.800 | 0.080 | 1.593 | 3.237 | 0.100 | 9.800 | 0.068 | 1.766 | 0.905 |
| 0.300 | 8.600 | 0.263 | 1.476 | 2.983 | 0.300 | 11.800 | 0.221 | 1.590 | 0.755 |
| 0.500 | 8.400 | 0.519 | 1.336 | 2.663 | 0.500 | 11.600 | 0.421 | 1.363 | 0.588 |
| 0.700 | 7.800 | 0.899 | 1.100 | 2.162 | 0.700 | 12.000 | 0.688 | 1.102 | 0.407 |
| 0.800 | 7.000 | 1.200 | 0.920 | 1.746 | 0.900 | 11.400 | 1.265 | 0.650 | 0.136 |
| 0.900 | 6.000 | 1.767 | 0.690 | 1.054 | | | | | |
| 0.950 | 6.000 | 2.321 | 0.488 | 0.568 | | | | | |
| NRTL (Experimental Data Optimization) | | | | | | | | | |
| 0.020–0.976 | – | 2.720 | 0.205 | 0.367 | 0.090–0.976 | – | 1.177 | −1.158 | 0.044 |
| UNIQUAC (MD Results) | | | | | | | | | |
| Water-Acetonitrile | | | | | Water-Isopropanol | | | | |
| Methanol Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation | Acetone Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| 0.100 | 6.600 | 1.122 | 0.271 | 1.322 | 0.100 | 7.000 | 1.677 | 0.194 | 0.217 |
| 0.300 | 5.600 | 0.995 | 0.317 | 1.047 | 0.300 | 8.600 | 1.556 | 0.234 | 0.130 |
| 0.500 | 5.400 | 0.870 | 0.367 | 0.787 | 0.500 | 9.000 | 1.439 | 0.284 | 0.068 |
| 0.700 | 5.200 | 0.736 | 0.438 | 0.530 | 0.700 | 10.000 | 1.309 | 0.341 | 0.025 |
| 0.800 | 5.000 | 0.667 | 0.493 | 0.412 | 0.900 | 10.600 | 1.136 | 0.439 | 0.007 |
| 0.900 | 4.800 | 0.555 | 0.569 | 0.292 | | | | | |
| 0.950 | 5.200 | 0.493 | 0.658 | 0.231 | | | | | |
| UNIQUAC (Experimental Data Optimization) | | | | | | | | | |
| 0.020–0.976 | – | 0.562 | 0.636 | 0.214 | 0.090–0.976 | – | 1.134 | 0.466 | 0.006 |

*Nonrandomness factor in NRTL model were set as 0.3.

0.7–0.3, 0.8–0.2, 0.9–0.1, and 0.95–0.05) were simulated. The MD studies showed that a number 200 molecules is sufficient to simulate a binary mixture, however, 400 molecules are fixed in the present MD simulations. Thus, an amorphous cell with 400 molecules of water + acetonitrile with the different mole fractions were generated at 298.15 K so that the dimension of the cell varies against mole fraction. The energies of the amorphous cell were minimized by the steepest decent and Fletcher–Reeves conjugate gradient procedure to remove unfavorable overlaps to attain the lowest energy state. The energy minimized cell was utilized as an initial state for the equilibrium stage in which at this stage NVT (200 ps) to NPT (2000 ps) ensembles are followed so that this procedure was used to avoid entrapment of the simulated system in a metastable state of local high energy minima. In this work, the MD package of Material Studio V.6 is used. In both NVT and NPT ensembles, time step and the cutoff values were set at 1 fs (femtosecond) and 18.5 angstrom, respectively. The decay constant of thermostat and time constant of barostat ensembles were set at 0.1 and 1 ps (picosecond), respectively. Ewald and atom-based summation methods used for computation of electrostatic and van der Waals forces, respectively. Moreover, the Berendsen and Anderson algorithm were used to achieve the temperature and pressure of the system, respectively. It should be noted that long-range correction to the energy or pressure was not considered during the MD calculations. In this simulation, the density and total energy was used as criteria to check the stability and equilibrium of the unit cell.

**Table 2. MD Simulation and Experimental Data Optimization Results for Effective Radius, Interaction Parameters, and Deviation in Activity Coefficients**

| Wilson (MD Results) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Methanol-Chloroform[28] | | | | | Acetone-Cyclohexane[29] | | | |
| Methanol Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation | Acetone Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| 0.100 | 43.000 | 0.874 | 0.282 | 2.407 | 0.100 | 4.600 | 0.603 | 0.1113 | 2.286 |
| 0.300 | 36.000 | 0.698 | 0.338 | 1.989 | 0.300 | 4.000 | 0.378 | 0.1706 | 0.876 |
| 0.500 | 30.000 | 0.614 | 0.407 | 1.720 | 0.500 | 4.000 | 0.304 | 0.2527 | 0.294 |
| 0.700 | 26.000 | 0.488 | 0.452 | 1.376 | 0.700 | 4.000 | 0.226 | 0.3434 | 0.294 |
| 0.900 | 25.000 | 0.319 | 0.594 | 0.767 | 0.900 | 4.600 | 0.162 | 0.557 | 0.405 |
| Wilson (Experimental Data Optimization) | | | | | | | | |
| 0.008–0.964 | – | 0.131 | 0.894 | 0.169 | 0.016–0.963 | – | 0.215 | 0.3434 | 0.020 |
| NRTL* (MD Results) | | | | | | | | |
| Methanol-Chloroform | | | | | Acetone-Cyclohexane | | | |
| Methanol Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation | Acetone Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| 0.100 | 64.000 | 0.126 | 1.658 | 0.430 | 0.100 | 9.400 | 0.217 | 1.992 | 0.4267 |
| 0.300 | 61.000 | 0.328 | 1.286 | 0.733 | 0.300 | 7.000 | 0.555 | 1.679 | 0.089 |
| 0.500 | 52.000 | 0.503 | 0.990 | 1.014 | 0.500 | 6.800 | 0.898 | 1.332 | 0.069 |
| 0.700 | 49.000 | 0.700 | 0.660 | 1.355 | 0.700 | 6.400 | 1.365 | 1.008 | 0.464 |
| 0.900 | 45.000 | 1.020 | 0.300 | 1.803 | 0.900 | 7.600 | 1.821 | 0.373 | 1.731 |
| NRTL (Experimental Data Optimization) | | | | | | | | |
| 0.008–0.964 | – | −0.266 | 2.327 | 0.120 | 0.016–0.963 | – | 0.771 | 1.4929 | 0.031 |
| UNIQUAC (MD Results) | | | | | | | | |
| Methanol-Chloroform | | | | | Acetone-Cyclohexane | | | |
| Methanol Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation | Acetone Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| 0.100 | 8.400 | 1.455 | 0.159 | 0.218 | 0.100 | 8.400 | 1.267 | 0.3389 | 0.030 |
| 0.300 | 8.000 | 1.258 | 0.233 | 0.640 | 0.300 | 6.600 | 1.146 | 0.4035 | 0.115 |
| 0.500 | 7.200 | 1.145 | 0.307 | 1.041 | 0.500 | 6.600 | 1.041 | 0.4688 | 0.304 |
| 0.700 | 7.000 | 1.039 | 0.386 | 1.422 | 0.700 | 6.400 | 0.950 | 0.5471 | 0.605 |
| 0.900 | 7.000 | 0.919 | 0.495 | 1.859 | 0.900 | 7.600 | 0.803 | 0.6445 | 1.064 |
| UNIQUAC (Experimental Data Optimization) | | | | | | | | |
| 0.008–0.964 | – | 1.562 | 0.125 | 0.132 | 0.016–0.963 | – | 1.126 | 0.358 | 0.037 |

*Nonrandomness factor in NRTL model were set as 0.3.

### *Radial distribution and local density functions*

As presented in Figure 1, the simulated density values are in good agreement with the experimental data given in literature.[20,21] In the MD production stage, the unit cell was subjected to the NVT ensemble for 2000 ps to generate data for calculation of the RDF. The Nosé–Hoover dynamics was applied to control the temperature because it produces true canonical ensembles in both coordinate and momentum spaces.[22,23] The center-of-mass of the molecules was determined for the water and acetonitrile so that the RDF was defined by center to center (center-of-mass) as[24]

$$g(r_{ij}) = \rho^{-2}\left\langle \sum_i \sum_{j\neq i} \delta(r_i)\delta(r_j - r) \right\rangle = \frac{V}{N^2}\sum_i \sum_{j\neq i} \delta(r - r_{ij}) = \frac{\rho(r_{ij})}{\rho_{\text{bulk}}} \tag{5}$$

where $g(r_{ij})$ gives the probability that a molecule of type $i$ will be found surrounding a molecule of type $j$ at a radial distance $r_{ij}$, so that the local location of a molecule can be determined by RDF. As noted previously, in Eq. 1, the coordination number is written in terms of $g(r_{ij})$. For mixture of water (W) and acetonitrile (A), the coordination numbers are defined as

$$n_{\text{WA}} = \frac{n_{\text{W}}}{V}\int_0^r 4\pi r^2 g_{\text{WA}}(r)dr; \quad n_{\text{AA}} = \frac{n_{\text{A}}}{V}\int_0^r 4\pi r^2 g_{\text{AA}}(r)dr \tag{6}$$

$$n_{\text{AW}} = \frac{n_{\text{A}}}{V}\int_0^r 4\pi r^2 g_{\text{AW}}(r)dr; \quad n_{\text{WW}} = \frac{n_{\text{A}}}{V}\int_0^r 4\pi r^2 g_{\text{WW}}(r)dr \tag{7}$$

Figure 2 presents a plot of the RDF, $g_{ij}(r)$, and local density function, $\rho_{ij}(r)$, for water-acetonitrile, acetonitrile- acetonitrile, and water-water at the different water mole fractions. At high value of radius, RDF and local density functions approach to unity and bulk density, respectively, as shown in Figure 2 and supporting information. As it can be seen by this Figure, the RDF is changing against the mole fraction and radius so that

**Table 3. MD Simulation and Experimental Data Optimization Results for Effective Radius, Interaction Parameters, and Deviation in Activity Coefficients**

| Wilson (MD Results) | | | | |
|---|---|---|---|---|
| Meta Xylene Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| Meta Xylene-Benzene[30] | | | | |
| 0.100 | 26.800 | 1.004 | 1.027 | 0.068 |
| 0.300 | 28.600 | 1.004 | 1.007 | 0.073 |
| 0.500 | 28.400 | 1.006 | 1.005 | 0.073 |
| 0.700 | 29.800 | 1.009 | 1.003 | 0.073 |
| 0.900 | 31.000 | 1.031 | 1.003 | 0.068 |
| Wilson (Experimental Data Optimization) | | | | |
| 0.071–0.956 | – | 2.390 | 0.200 | 0.050 |
| NRTL* (MD Results) | | | | |
| Meta Xylene Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| Meta Xylene-Benzene | | | | |
| 0.100 | 20.800 | −0.006 | −0.039 | 0.066 |
| 0.300 | 28.600 | −0.014 | −0.024 | 0.067 |
| 0.500 | 28.600 | −0.021 | −0.016 | 0.067 |
| 0.700 | 29.600 | −0.031 | −0.010 | 0.067 |
| 0.900 | 24.800 | −0.043 | −0.004 | 0.066 |
| NRTL (Experimental Data Optimization) | | | | |
| 0.071–0.956 | – | 1.177 | −1.158 | 0.044 |
| UNIQUAC (MD Results) | | | | |
| Water Mole Fraction | Effective Radius ($r^*$) | $\tau_{ij}$ | $\tau_{ji}$ | Deviation |
| Meta Xylene-Benzene | | | | |
| 0.100 | 14.800 | 0.672 | 1.386 | 0.056 |
| 0.300 | 11.400 | 0.659 | 1.403 | 0.055 |
| 0.500 | 12.200 | 0.647 | 1.423 | 0.055 |
| 0.700 | 12.000 | 0.632 | 1.440 | 0.054 |
| 0.900 | 14.600 | 0.620 | 1.462 | 0.052 |
| UNIQUAC (Experimental Data Optimization) | | | | |
| 0.071–0.956 | – | 0.382 | 1.212 | 0.037 |

the high peak value of RDF or local density function represents the amount of local mole fraction deviation from bulk mole fraction. By increasing mole fraction of water, the contributions of the second and third peaks decrease so that only the first peak is dominated. The coordination number in terms of radius and water mole fraction is presented in Figure 3. As it is observed with increasing water mole fraction, the water molecules surrounding water and acetonitrile molecules enhance. Conversely, the LC in terms of the RDF are written as

$$\frac{n_{ij}}{n_{jj}} = \frac{n_i}{n_j} \frac{\int_0^{rij} 4r_{ij}^2 g_{ij}(r_{ij}) dr_{ij}}{\int_0^{rjj} 4r_{jj}^2 g_{jj}(r_{jj}) dr_{jj}} \tag{8}$$

so that Eq. 8 is approximated by Wilson as[2]

$$\frac{x_{ij}}{x_{jj}} \equiv \frac{x_i}{x_j} \Omega_{ij}; \quad \Omega_{ij} = \frac{\int_0^{rij} 4r_{ij}^2 g_{ij}(r_{ij}) dr_{ij}}{\int_0^{rjj} 4r_{ij}^2 g_{jj}(r_{jj}) dr_{jj}} \tag{9}$$

Equation 9 is used as a LC expression with the different forms of the interaction energies for the three known LC activity coefficients models of Wilson, NRTL, and UNIQUAC. It has been shown that all these LC models can be more rigorously derived from the two-fluid theory. If we compare Eq. 9 with Wilson, NRTL, and UNIQUAC LC models, the interaction parameters can be written in terms of RDF as[25]

$$(\tau_{ij})_{\text{Wilson}} = \Omega_{ij}; \quad (\tau_{ij})_{\text{NRTL}} = -\frac{1}{\alpha_{ij}} \ln \Omega_{ij}; \quad (\tau_{ij})_{\text{UNIQUAC}} = \left(\frac{q_j}{q_i}\right) \Omega_{ij} \tag{10}$$

where $\alpha$ is the nonrandomness in NRTL LC model and "$q$" presents the volume structural parameter of a given molecule. Thus, using Eq. 10, the interaction energy parameters of Wilson, NRTL, and UNIQUAC models can be calculated through RDF which is obtained by MD simulation. To obtain the interaction parameters of a LC model, it is common to calculate

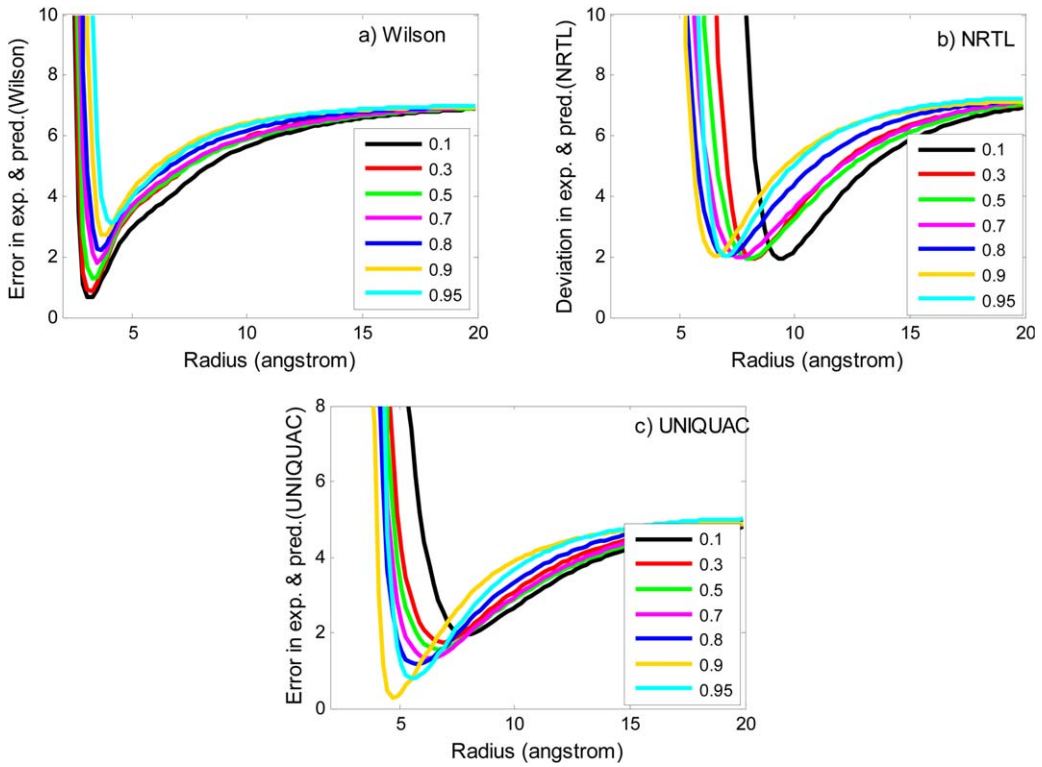


**Figure 5. Deviation in predicted and experimental activity coefficient against radius at the different composition for the water-acetonitrile system: (a) Wilson, (b) NRTL, and (c) UNIQUAC.**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

these parameters through optimization of experimental data so that all discrepancy of the model parameters is related to the quality of the experimental data; however, using MD simulation data, one incorporates the long distance interaction effects through RDF. For this reason, the interaction parameters are calculated beyond the nearest-neighborhood interactions so that this issue is a matter of controversy.[12] In the other words, the LC interaction parameters are dependent on the concentration, temperature, and radius through RDF.

## Results and Discussion

Following the simulation of the water-acetonitrile system at the different water mole fraction and 298.15, the RDFs are extracted and the interaction parameters in terms of water mole fraction and radius for the three LC models are obtained. It is suitable to calculate the interaction parameters with the first and second shells of RDF, however, this does not give good results because the limits of the integral in the numerator

**Table 4. The Coefficients of the Interaction Parameters in Third-Order Polynomial Relation for Wilson, NRTL, and UNIQUAC**

| | $\tau_{ij}$* | | | | $\tau_{ji}$* | | | |
|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | A | B | C | D |
| System | | | | Wilson | | | | |
| W(1)-A(2) | −1.089 | 1.923 | −1.324 | 0.735 | 1.947 | −2.167 | 0.959 | −0.018 |
| W(1)-Iso. (2) | −0.864 | 1.457 | −1.330 | 0.921 | 0.859 | −0.836 | 0.471 | 0.056 |
| M(1)-CH. (2) | −1.416 | 2.076 | −1.480 | 1.001 | 0.884 | −1.064 | 0.650 | 0.224 |
| A(1)-Cyc. (2) | −1.410 | 2.680 | −1.948 | 0.770 | 1.043 | −0.998 | 0.606 | 0.058 |
| mX(1)-B(2) | 0.170 | −0.179 | 0.078 | 0.999 | −0.169 | 0.323 | −0.200 | 1.044 |
| System | | | | NRTL | | | | |
| W(1)-A(2) | 7.671 | −8.428 | 3.687 | −0.231 | −2.222 | 2.011 | −1.154 | 1.693 |
| W(1)-Iso. (2) | 2.751 | −2.495 | 1.488 | −0.062 | −1.501 | −1.202 | −1.230 | 1.881 |
| M(1)-CH. (2) | 1.559 | −1.877 | 1.576 | −0.016 | −1.113 | 1.653 | −2.337 | 1.874 |
| A(1)-Cyc. (2) | −0.090 | 0.784 | 1.304 | 0.082 | −2.878 | 3.210 | −2.615 | 2.230 |
| mX(1)-B(2) | −0.035 | 0.036 | −0.051 | −0.001 | 0.087 | −0.166 | 0.132 | −0.051 |
| System | | | | UNIQUAC | | | | |
| W(1)-A(2) | −0.747 | 0.897 | −0.928 | 1.207 | 1.052 | −1.164 | 0.605 | 0.219 |
| W(1)-Iso. (2) | −0.487 | 0.519 | −0.752 | 1.747 | 0.319 | −0.256 | 0.273 | 0.169 |
| M(1)-CH. (2) | −1.006 | 1.799 | −1.551 | 1.592 | 0.314 | −0.336 | 0.470 | 0.115 |
| A(1)-Cyc. (2) | −0.752 | 1.060 | −0.956 | 1.354 | 0.192 | −0.147 | 0.355 | 0.305 |
| mX(1)-B(2) | 0.026 | −0.040 | −0.048 | 0.677 | 0.032 | −0.035 | 0.101 | 1.376 |

$\tau_{ji}^* = A \times x^3 + B \times x^2 + C \times x^1 + D$, $x$ = mole fraction of component 1 in a binary system.

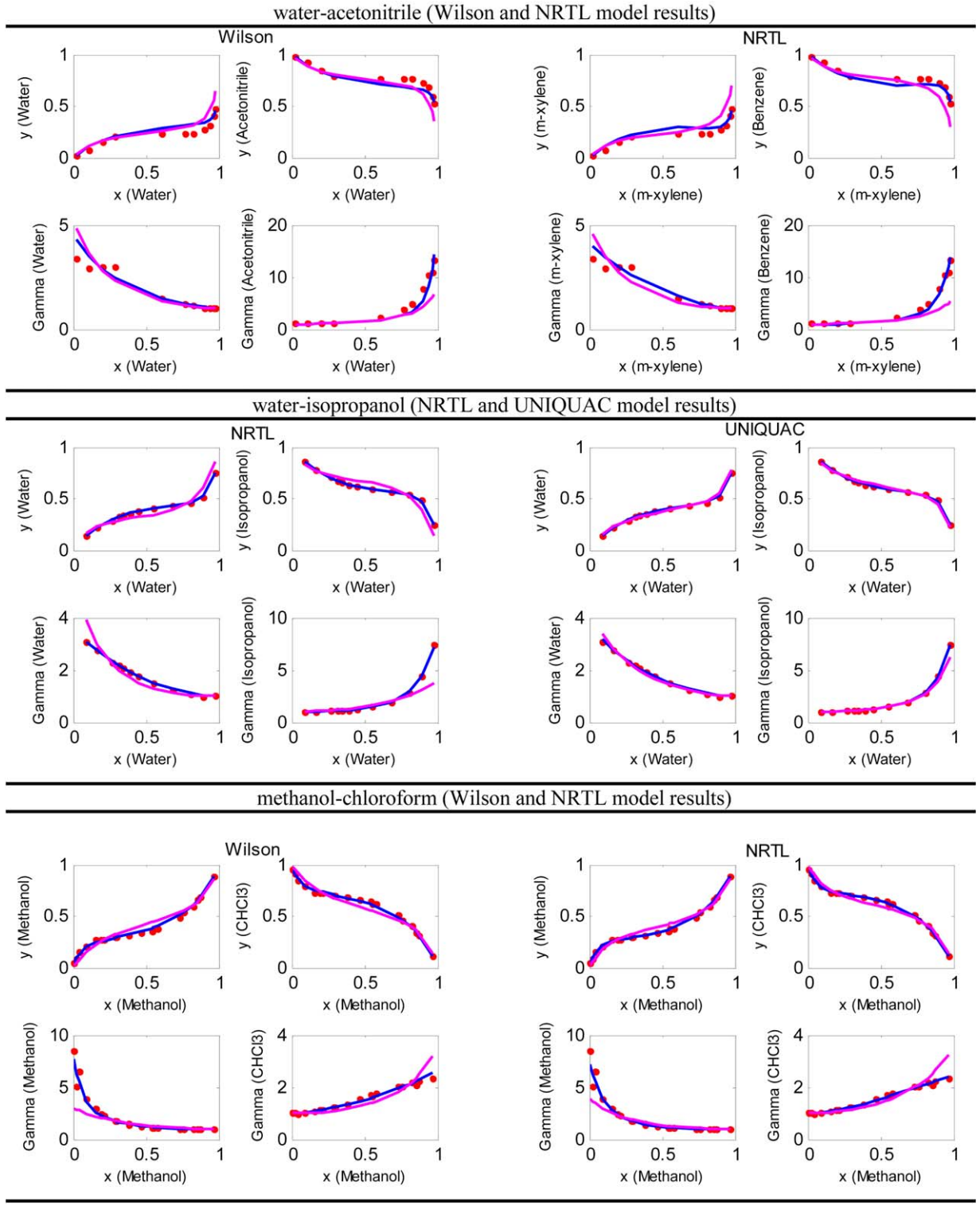


**Figure 6. The vapor liquid equilibrium diagrams of the vapor mole fraction and activity coefficient vs. liquid mole fraction for the methanol-chloroform, water-isopropanol, water-acetonitrile systems; • (experiment), −− (optimization), −− (MD simulation).**

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and denominator of the Ω function are different. Moreover, $r_{ij}$ were set equal to $r_{ji}$ to keep consistency between the $n_{ji}$.[10] Thus, one can conclude that there exists an effective radius which gives the optimized results. Based on the RDF of the water-acetonitrile system, the interaction parameters for the three LC models are presented in Figure 4. The MD simulation shows that in the higher radius, the Wilson interaction parameters should approach one so that this result can be inference from Eq. 9, because at higher radius, $g_{ij}$ and $g_{jj}$ approach one so that the parameters of $\tau_{ij}$ and $\tau_{ji}$ become one. At higher radius for NRTL model, these parameters approach zero value and in the case of UNIQUAC model, upper limit of $\tau_{ij}$ and $\tau_{ji}$

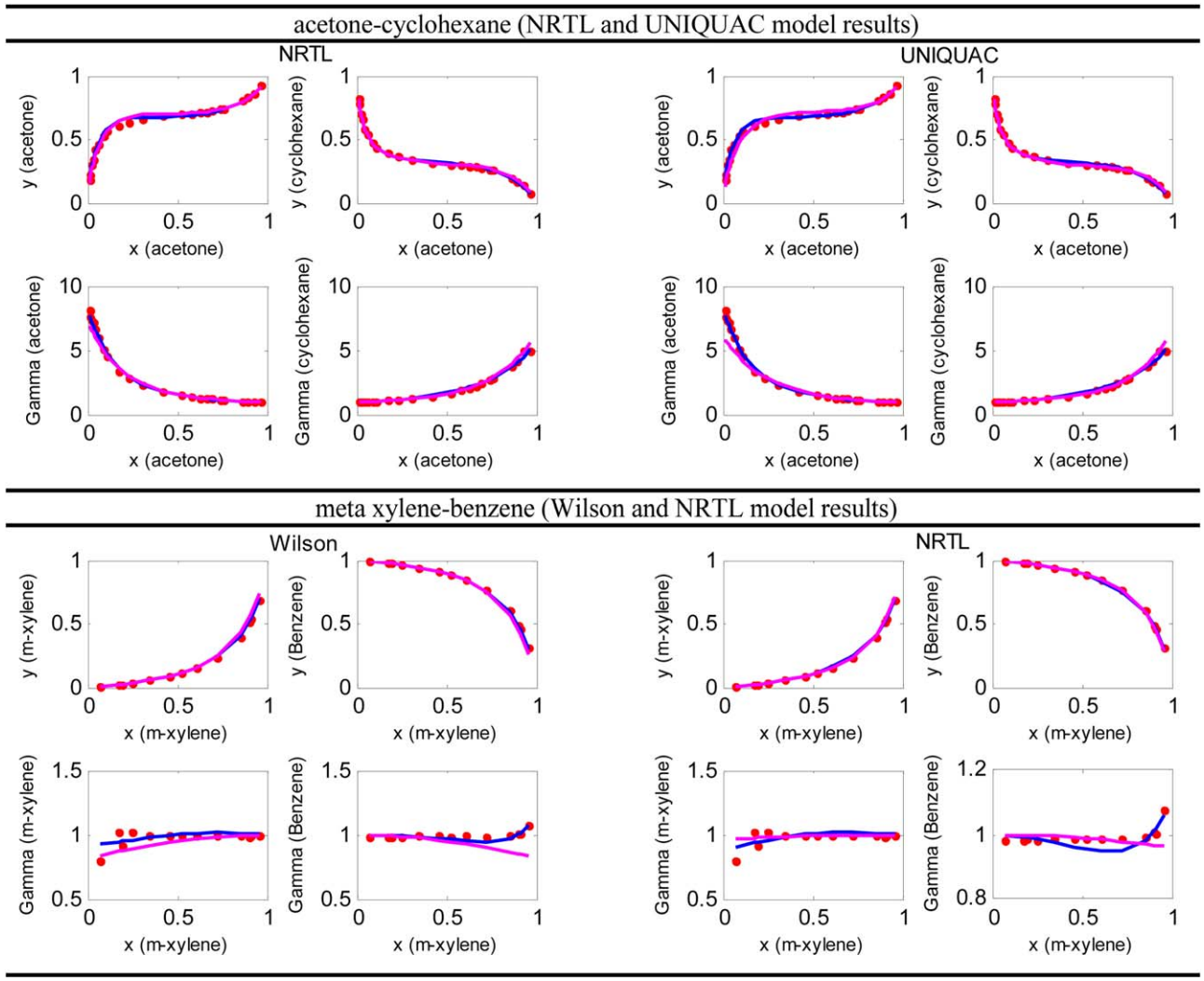


**Figure 7. The vapor liquid equilibrium diagrams of the vapor mole fraction and activity coefficient vs. liquid mole fraction for the acetone-cyclohexane and meta xylene-benzene systems; • (experiment), −− (optimization), −− (MD simulation).**

**[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

approach to $q_j/q_i$ and $q_i/q_j$, respectively. Thus, at each radius, a value for an interaction parameter can be calculated so that a lot of specific interaction parameters are obtained that can be a drawback. To solve this shortcoming, by an inspection, an optimum radius should be specified to reduce the deviation between the calculated and experiment. Finally, the results of MD simulation are compared through the following deviation relation for the activity coefficients of the water-acetonitrile system.

$$\text{Deviation}(r)=\sum_{i=1}^{2}\left(\frac{\gamma_{\text{calc}(i).}(r)-\gamma_{\text{exp}(i).}}{\gamma_{\text{exp}(i).}}\right)^2 \qquad (11)$$

where the subscripts "calc" and "exp" stand for the calculated and experiment, respectively. The experimental data for this system[26] is checked by Herington and Van Ness test which is used as vapor liquid equilibrium consistency criteria. At the effective radius ($r^*$), the effective interaction parameters are calculated at each mole fraction. The simulation results show that the interaction parameters should be composition dependent, while in LC concept is considered independent of composition. Thus, the present results are remarkable so that the composition dependency of the interaction parameters had been previously discussed by Flemr and McDermott.[6,7] For the three LC models, the effective radius, deviation in activity coefficient, and the effective interaction parameters against mole fraction are presented for the water-acetonitrile, water-isopropanol, methanol-chloroform, acetone-cyclohexane, and meta xylene-benzene systems as shown in Tables 1–3. Also, the interaction parameters are calculated by optimization of the experimental data as presented in these tables. As one can see the interaction parameters from MD simulations are in good agreement with those are obtained from optimization of the experimental data. For example, in Wilson model using MD, for water-acetonitrile system $\tau_{12}$ and $\tau_{21}$ are 0.613 and 0.061, respectively, that are nearly close to the values of 0.566 and 0.057 obtained by experimental data optimization in water mole fraction of 0.1. Moreover, using MD, the interaction parameters of UNIQUAC model are 0.493 and 0.658 for water-acetonitrile at water mole fraction 0.95 that these values are 0.562 and 0.636 using the experimental data. However,

**Table 5. Average Interaction Parameters of Wilson, NRTL, and UNIQUAC and Deviation in Activity Coefficient from MD Simulation**

| | Wilson | | | NRTL | | | UNIQUAC | | |
|---|---|---|---|---|---|---|---|---|---|
| Mixture | $\tau_{12}$ | $\tau_{21}$ | Deviation | $\tau_{12}$ | $\tau_{21}$ | Deviation | $\tau_{12}$ | $\tau_{21}$ | Deviation |
| W-A | 0.419 | 0.223 | 0.404 | 0.703 | 1.239 | 1.844 | 0.856 | 0.394 | 0.761 |
| W-Iso. | 0.546 | 0.205 | 0.049 | 0.457 | 1.357 | 0.544 | 1.450 | 0.285 | 0.074 |
| M-CH. | 0.588 | 0.420 | 1.646 | 0.551 | 0.954 | 1.101 | 1.152 | 0.322 | 1.106 |
| A-Cyc. | 0.324 | 0.293 | 0.471 | 0.994 | 1.235 | 0.108 | 1.033 | 0.485 | 0.400 |
| mX-B | 1.010 | 1.203 | 0.184 | −0.022 | −0.019 | 0.067 | 0.647 | 1.421 | 0.055 |

$\Lambda_{ij} \equiv \exp(-(\varepsilon_{ij} - \varepsilon_{jj})/\mathrm{RT})$, $(\tau_{ij})_{\mathrm{NRTL}} \equiv (-(g_{ij} - g_{jj})/\mathrm{RT})$, $(\tau ij)_{\mathrm{UNIQUAC}} \equiv (-(u_{ij} - u_{jj})/\mathrm{RT})$.

there is a deviation between the values of the NRTL model parameters using MD simulation and the experimental data for the water-acetonitrile system as shown in Table 1. Commonly, the binary interaction parameters are obtained using optimization of the experimental data so that this optimization often gives multiple solutions through the different initializations that finally the results are close to the experimental data,[31] however, physically, only one set of the interaction parameters values presents the correct answer that is obtained by statistical mechanics. As one can see using MD, the calculated interaction parameters for the Wilson and UNIQUAC LC models are more consistent with those obtained from experimental data. However, for NRTL model in the case of water-isopropanol, $\tau_{21}$ is −1.158 from experimental data optimization. Whereas the MD results for this parameter gives positive values of 1.766, 1.590, 1.363, 1.102, and 0.650 in all mole fraction. In the case of methanol-chloroform, $\tau_{12}$ is −0.266 while MD for this parameter gives the values of 0.126, 0.328, 0.503, 0.700, and 1.020 in all mole fractions. Moreover, for the meta xylene-benzene system, both the calculated $\tau_{12}$ and $\tau_{21}$ using MD results are negative at all mole fractions, while the value of $\tau_{12}$ using optimization of experimental data is positive for NRTL model as shown in Table 3. Figure 5 shows the deviation in predicted and experimental activity coefficient against radius at the different composition for the water-acetonitrile system using the three activity coefficient models. In overall, the UNIQUAC results are better than NRTL model and NRTL model is better than the Wilson model.The interaction parameters for the five binary mixtures were best fitted to a third-order polynomial relation as shown in Table 4.

### *Vapor liquid equilibrium calculation*

For vapor liquid equilibrium calculations, we can use composition dependent correlations for the interaction parameters, but for practical use, the average values of the interaction parameters are calculated as

$$\bar{\tau}_{ij} = \frac{\int_{x(1)}^{x(N)} \tau_{ij}(x)dx}{\int_{x(1)}^{x(N)} dx} \tag{12}$$

Thus, these average values of interaction parameters of the Wilson, NRTL, and UNIQUAC LC models are used to calculate the activity coefficient for these five systems so that their values and deviation with experiment are presented in Table 5. Also the phase equilibrium diagrams for these five binary mixtures are shown in Figures 6 and 7. In vapor liquid equilibrium calculations, the gamma-phi approach is used so that the fugacity of liquid phase is calculated through an activity coefficient model and the vapor fugacity is computed using an equation of sate. However, for the case studies in this work, the vapor phase is assumed to be ideal gas and the fugacity coefficient is set to unity. The activity coefficients are calculated through the three activity coefficient models using the interaction parameters obtained by MD as explained above. The total pressure and the vapor compositions are obtained using the bubble pressure calculation algorithm. Finally, from the present results, one may conclude that the MD simulation approach is a strong tool for phase equilibrium calculation in the applied thermodynamics.

## Conclusions

By means of full atomistic MD simulations, we have simulated successfully the five binary mixtures (water-acetonitrile, water-isopropanol, methanol-chloroform, acetone-cyclohexane, and meta xylene-benzene). This study illustrates that MD simulation method can be used as an effective tool to examine validity of the LC models so that the interaction parameters of the LC models can be obtained by RDF. Although the concept of LC considers only nearest-neighborhood molecules, but the results showed that the second and third peaks of RDF present a considerable contribution in the interaction parameters.

This study demonstrated that the interaction parameter should be composition dependent that have been already shown by Flemr[6] so that for all the five binary mixtures, composition dependent of interaction parameters were best fitted to a third-order polynomial equation. Through the optimization of experimental data, the multiple solutions were obtained for the interaction parameters, however, one solution is existed physically, which can be validated by statistical mechanics through computer experiment using MD. The present MD results were more consistence with Wilson and UNIQUAC models. In NRTL model, their interaction parameters were obtained using the experimental data optimization so that the MD simulation were not consistence for the methanol-chloroform, meta xylene-benzene, and water-isopropanol systems while the vapor liquid equilibrium calculation results in both cases were in good agreement with the experiment. Moreover, using MD, the proposed method presented potential application in vapor liquid equilibrium calculations that were verified for the five binary mixtures. Finally, application of this method for computation of liquid-liquid and solid-liquid equilibriums is promising results in the future.

## Literature Cited


1. Guggenheim EA. *Mixtures: The Theory of the Equilibrium Properties of Some Simple Classes of Mixtures, Solutions and Alloys.* Oxford: Clarendon Press, 1979.
2. Wilson GM. Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J Am Chem Soc.* 1964;86(2):127–130.
3. Renon H, Prausnitz JM. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* 1968;14(1):135–144.

4. Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J*. 1975;21(1):116–128.
5. Maurer G, Prausnitz JM. On the derivation and extension of the UNIQUAC equation. *Fluid Phase Equilib*. 1978;2:91–99.
6. Flemr V. A note on excess Gibbs energy equations based on local composition concept. *Collect Czechoslovak Chem Commun*. 1976;41: 3347–3349.
7. McDermott C, Ashton N. Note on the definition of local composition. *Fluid Phase Equilib*. 1977;1(1):33–35.
8. Nakanishi K, Toukubo K. Molecular dynamics studies of Lennard-Jones liquid mixtures. V. Local composition in several kinds of equimolar mixtures with different combining rule. *J Chem Phys*. 1979; 70(12):5848–5850.
9. Nakanishi K, Okazaki S, Ikari K, Higuchi T, Tanaka H. Free energy of mixing, phase stability, and local composition in Lennard-Jones liquid mixtures. *J Chem Phys*. 1982;76(1):629–636.
10. Renon H. NRTL: an empirical equation or an inspiring model for fluids mixtures properties? *Fluid Phase Equilib*. 1985;24(1–2):87–114.
11. Hoheisel C, Kohler F. Local composition in liquid mixtures. *Fluid Phase Equilib*. 1984;16(1):13–24.
12. Lee LL, Chung TH, Starling KE. A molecular theory for the thermodynamic behavior of polar mixtures. I. The statistical-mechanical local-composition model. *Fluid Phase Equilib*. 1983;12(1–2):105–124.
13. Hill TL. *Statistical Mechanics: Principles and Selected Applications*. New York: Dover Publications, 1987.
14. Verlet L. Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Phys Rev*. 1967; 159(1):98–103.
15. Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E. Equation of state calculations by fast computing machines. *J Chem Phys*. 1953;21(6):1087–1092.
16. Alder BJ, Wainwright TE. Studies in molecular dynamics. I. General method. *J Chem Phys*. 1959;31(2):459–466.
17. Ferrenberg AM, Swendsen RH. New Monte Carlo technique for studying phase transitions. *Phys Rev Lett*. 1988;61(23):2635–2638.
18. Panagiotopoulos AZ. Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble. *Mol Phys*. 1987;61(4):813–826.
19. Sun H. COMPASS: an ab initio force-field optimized for condensed-phase applications overview with details on alkane and benzene compounds. *J Phys Chem B*. 1998;102(38):7338–7364.
20. Moreau C, Douhéret G. Thermodynamic behavior of water-acetonitrile mixtures excess volumes and viscosities. *Thermochim Acta*. 1975;13(4):385–392.
21. Van Meurs N, Somsen G. Excess and apparent molar volumes of mixtures of water and acetonitrile between 0 and 25°C. *J Solution Chem*. 1993;22(5):427–436.
22. Nosé S. A molecular dynamics method for simulations in the canonical ensemble. *Mol Phys*. 1984;52(2):255–268.
23. Hoover WG. Canonical dynamics: equilibrium phase-space distributions. *Phys Rev A*. 1985;31(3):1695–1697.
24. Allen MP, Tildesley DJ. *Computer Simulation of Liquids*. Oxford [u.a.]: Clarendon Press [u.a.], 1997.
25. Elliott JR, Lira CT. *Introductory Chemical Engineering Thermodynamics*, 2nd ed. Upper Saddle River, NJ: Prentice Hall PTR, 2012.
26. Treiner C, Tzias P, Chemla M, Poltoratskii GM. Solvation of tetrabutylammonium bromide in water+acetonitrile mixtures at 298.15 K from vapour pressure measurements of dilute solutions. *J Chem Soc Faraday Trans 1*. 1976;72:2007–2015.
27. Sazonov VP. Liquid-liquid-vapor isothermal equilibrium in a nitromethane-isopropyl alcohol-water system. *Zhurnal Prikl Khimii*. 1986;59:1451–1460.
28. Kireev VA, Sitnikov IP. Determination of pressure and vapor composition and the heat of evaporation of mixtures of methyl alcohol with chloroform and the change of free energy and entropy during their formation. *Zhurnal Organicheskoi Khimii*. 1941;15:492.
29. Tasić A, Djordjević B, Grozdanić D, Afgan N, Malić D. Vapour-liquid equilibria of the systems acetone-benzene, benzene-cyclohexane and acetone-cyclohexane at 25°C. *Chem Eng Sci*. 1978;33(2):189–197.
30. Boublík T, Benson GC. Molar excess Gibbs free energies of benzene-m-xylene mixtures. *Can J Chem*. 1969;47(4):539–542.
31. Jacq J, Asselineau L. Binary liquid-liquid equilibria, multiple solutions for the NRTL equation. *Fluid Phase Equilib*. 1983;14:185–192.

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