A Fluctuation Solution Theory of Activity Coefficients: Phase Equilibria in Associating Molecular Solutions

Esam Z. Hamad and G. Ali Mansoori
University of Illinois at Chicago, (M/C 063), Chicago, Illinois 60607-7052, USA

Abstract

A new analytic statistical mechanical fluctuation solution theory for activity coefficients in multicomponent mixtures is developed. This theory is based on the newly formulated exact relations among the mixture direct correlation function integrals and the closures for cross direct correlation function integrals. One major advantage of this theory is its independence from the nature of intermolecular interaction potentials in solutions which are generally unknown for complex molecules. The theory is successfully used for vapor-liquid equilibria, liquid-liquid equilibria, and phase splitting prediction and correlation of fluid mixtures consisting of polar and associating molecules.

Introduction

Definition of activity coefficients provides a convenient way of describing the nonidealties encountered in solution thermo-dynamics. However, there exists very limited theoretical understanding through which one can derive expressions for activity coefficients using the principles of statistical mechanics. As a result, most of the available analytic expressions for activity coefficients are empirical which are based on classical thermo-dynamic definition of excess properties.

Lattice theories of statistical mechanics were successful in providing us with analytic expressions for activity coefficients. There exist numerous group-contribution expressions for activity coefficients which are based on the lattice theories of statistical mechanics. The high degree of combinatorial approximations which are used in the lattice theories have made their resulting activity coefficient expressions only a limited success.

Another statistical mechanical route for the development of analytic expressions of activity coefficients is the use of Gibbs, or NPT, ensemble. Gibbs ensemble, joined with the conformal solution theory of statistical mechanics, have provided us with the formalism in systematically deriving analytic expressions of activity coefficients. The success of this technique is also limited to simple molecular fluid mixture for which the intermolecular potential energy functions are available. In the case of polar mixtures and mixtures possessing hydrogen-bonding species the route through the Gibbs ensemble will be at a loss.

The third statistical mechanical route to activity coefficients is the Kirkwood–Buff solution theory of statistical mechanics. The activity coefficient, , of component i in a mixture is defined by the following relation:

\[ \ln (x_i \gamma_i) = (\mu_i - \mu^0_i) / kT \]

where is the chemical potential of component i in the mixture, is the standard-state chemical potential of i, is the Boltzmann constant, and is the absolute temperature. By utilizing the above definition, activity coefficients in solutions are obtained from the relations between the chemical potentials, , and the fluctuation integrals, . According to the Kirkwood–Buff solution theory the expression for the chemical potential, , of component i in a binary mixture takes the following form:

\[ x_1 \left( \frac{\partial \mu_i}{\partial x_i} \right)_{\rho,T} = kT \left[ 1 + x_1 x_2 (G_{11} + G_{22} - 2G_{12}) \right] \]

where

\[ G_{ij} = \int_0^\infty \left[ \xi_{ij}(r) - 1 \right] 4\pi r^2 dr \]

is the mole fraction of component i, is the pressure, is the

\[ (3) \) Kreglewski, A. Equilibrium Properties of Fluids and Fluid Mixtures; Texas A&M University Press: College Station, TX, 1984.
\[ (5) \) Kirkwood, J. G.; Buff, F. P. J. Chem. Phys. 1951, 19, 744. \]
density, and \( g_i(r) \) is the radial distribution function of the pair of molecules \( i \) and \( j \). Expressions for \( \partial g_i / \partial x_i \) are also written in terms of direct correlation integrals\(^6\):

\[
x_i \left[ \partial g_i / \partial x_i \right]_{\rho, T} = \frac{kT}{1 - x_i \rho C_{11} - x_j \rho C_{22} + x_i x_j \rho a^2 (C_{11} C_{22} - C_{12})^2} - \frac{\sum x_k \rho C_{ik}}{1 - \sum x_k \rho C_{ik}}
\]

where

\[
C_{ij} = \int_0^\infty c_i(r)4\pi r^2 \, dr
\]

and the direct correlation function, \( c_i(r) \), is defined with respect to the radial distribution function, \( g_i(r) \), in an \( n \)-component mixture, by

\[
c_i(r_{12}) = \left[ g_i(r_{12}) - 1 \right] - \sum_{k \neq i} x_k \rho \int c_k(r_{12}) \left[ g_k(r_{22}) - 1 \right] \, dr_3
\]

Finally, the activity coefficient, \( \gamma_i \), of component \( i \) is obtained by integrating eqs 2 or 4 with respect to the mole fraction. Equation 1 then becomes

\[
\ln \gamma_i = \int x_i \left[ 1 - x_i \rho C_{11} + G_{22} - 2G_{12} \right] \times \left[ 1 + x_i x_j \rho (G_{11} + G_{22} - 2G_{12}) \right]^{-1} \, dx_i
\]

This equation, in principle, could be used to calculate the activity coefficients provided information about \( G_{ij} \) integrals are available. One major advantage of this formalism is the fact that there is no need for direct information about the intermolecular potential energy functions of species of the mixture. However, the lack of sufficient knowledge about \( G_{ij} \) (or \( C_{ij} \)) integrals and their relationships has limited the utility of this theory. For mixtures of species with model intermolecular potential energy functions it has been possible to calculate \( G_{ij} \) (or \( C_{ij} \)) integrals and as a result the activity coefficients from statistical mechanics. Equation 7 has some utility for complex solutions (mixtures consisting of highly asymmetric, polar, and hydrogen-bonding species) only at infinite dilution.

The theory reported here provides us with a strong tool for developing analytic expressions for activity coefficients of multicomponent mixtures by using eq. 7 and a number of newly discovered characteristics of direct correlation function integrals in mixtures. This theory is shown to be applicable to complex multicomponent mixtures at finite concentrations as well as solutions at infinite dilutions.

**Theory of Multicomponent Activity Coefficients**

Let us consider a single-phase multicomponent solution consisting of \( n \) components. The chemical potential, \( \mu_i \), of every species in this mixture is a function of \( n + 1 \) independent variables

\[
\mu_i = \mu_i(T, p, x_1, x_2, ..., x_n)
\]

Using this expression one can write the following equations between the mixed second derivatives of the chemical potential:

\[
\frac{\partial^2 \mu_i / \partial x_i \partial x_j}{\partial P} = \frac{\partial^2 \mu_i / \partial P \partial x_j}{\partial x_i \partial x_j} = \left[ \frac{\partial^2 \mu_i / \partial x_j \partial x_k}{\partial x_i \partial x_j} \right]_{\rho, T} \quad i, j = 1, ..., n
\]

\[
\frac{\partial^2 \mu_i / \partial x_i \partial x_k}{\partial x_j} = \frac{\partial^2 \mu_i / \partial x_k \partial x_j}{\partial x_i} \quad i, j, k = 1, ..., n \quad i \neq k
\]

In the above equations \( \partial^2 \mu_i / \partial x_i \partial x_j \) and partial molar volume, \( \bar{v}_i \), are related to the direct correlation function integrals by\(^6\):

\[
N_i(\partial^2 \mu_i / \partial x_i \partial x_j) = kT[\bar{v}_j - x_i \bar{v}_1 + \rho C_{1j} - \rho \sum_{k \neq i} x_k C_{ik} + C_{jk}] + \rho^2 \sum_{k \neq i} x_k x_i C_{ik} (C_{ij} - C_{ji}) / [1 - \rho \sum_{k \neq i} x_k x_i C_{ik}] + \rho^2 \sum_{k \neq i} x_k x_i C_{ik} (C_{ij} - C_{ji}) / [1 - \rho \sum_{k \neq i} x_k x_i C_{ik}] + \rho^2 \sum_{k \neq i} x_k x_i C_{ik} (C_{ij} - C_{ji}) / [1 - \rho \sum_{k \neq i} x_k x_i C_{ik}]
\]

By replacing eqs 10 and 11 in eqs 8 and 9 we will derive a number of expressions between \( C_{ij} \)'s of the mixture. In an \( n \)-component mixture there exist \( n(n + 1)/2 \) direct correlation function integrals which are considered as unknowns in eqs 8 and 9. Note that there are \( n(n - 1) \) relations of the type in eq 8 and \( n(n - 1)(n - 2)/2 \) relations of the type in eq 9. Of all these equations only \( n(n + 1)/2 - 1 \) of them are independent. Since there are \( n(n + 1)/2 \) unknowns, one additional relation will be needed to determine all the unknowns regardless of the number of components involved.

The resulting equations for direct correlation function integrals consist of a set of nonlinear partial differential equations. A general analytic solution of this set of equations for multicomponent mixtures does not seem feasible at the present time. Numerical solutions of these equations are generally involved and lengthy and could require the use of multivariable finite difference techniques. In what follows we report the analytic solution of these equations for mixtures at low to moderate pressures.

**Analytic Solutions for Low to Moderate Pressures.** For liquids at low to moderate pressures it can be assumed that the activity coefficient is not dependent on pressure. In mathematical form using eq 1 this means

\[
[\partial \ln \gamma_i / \partial P]_{\rho, T} = [\partial \mu_i / \partial P]_{\rho, T} / kT = 0
\]

As a result of this approximation eq 8 reduces to the following expression \( [\partial \mu_i / \partial x_i]_{\rho, T} = 0 \) or \( \bar{v}_i = \bar{v}_j \), where \( \bar{v}_i \) is the molar volume of pure component \( i \). As a result of this approximation eq 11 can be written in the following form:

\[
\rho \sum_{j=1}^{n} x_j \mu_j = [1 - \rho \sum_{j=1}^{n} x_j \mu_j] \quad i = 1, ..., n
\]

By considering that

\[
\rho (1 - \sum_{j=1}^{n} x_j \mu_j) = (kT \gamma)^{-1}
\]

Equation 12 then becomes

\[
\sum_{j=1}^{n} x_j \rho C_{ij} = 1 - \bar{v}_i / (kT \gamma) \quad i = 1, ..., n
\]

where the mixture isothermal compressibility is now given by

\[
\kappa_T = -\sum_j x_j (\partial \ln \gamma_j / \partial P) / \sum_i x_i \bar{v}_i
\]

The set of relations in eq 9 do not simplify upon making the assumption of low pressure. To overcome this difficulty and to provide the one additional relation needed, the following closure relation is assume to be valid for all cross direct correlation function integrals \( C_{ij} \) \( i \neq j \):

\[
C_{ij} = \alpha_j C_{ii} + \alpha_i C_{ij} \quad i, j = 1, ..., n \quad i \neq j
\]

where \( \alpha_i \) and \( \alpha_j \) are binary interaction parameters. In an earlier publication\(^7\) we have shown this form of the closure expression is quite satisfactory in representing the cross direct correlation function integrals of a variety of nonpolar, polar, and hydrogen-bonding binary mixtures. Substituting eq 16 in eq 14 gives the following set of linear equations

\[
(\sum x_i \bar{v}_j) \rho C_{11} + x_2 \alpha_2 \rho C_{22} + ... + x_n \alpha_n \rho C_{nn} = 1 - \bar{v}_1 / (kT \gamma)
\]

\[
x_1 \alpha_2 \rho C_{12} + (\sum x_i \bar{v}_j) \rho C_{22} + ... + x_n \alpha_n \rho C_{nn} = 1 - \bar{v}_2 / (kT \gamma)
\]

\[
... + x_n \alpha_n \rho C_{1n} + x_2 \alpha_2 \rho C_{22} + ... + (\sum x_i \bar{v}_j) \rho C_{nn} = 1 - \bar{v}_n / (kT \gamma)
\]

where summations run from \( j = 1 \rightarrow n \) and \( \alpha_i = 1 \). The above

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relations represent a set of \( n \) linear equations in the unknowns \( \rho C_{ij} \). To solve for \( \rho C_{ij} \) it is more convenient to use matrix notations

\[
A - C = b
\]

where \( A \) is a matrix with elements \( A_{ij} = \sum x_i a_{ij} \), \( A_j = x_i a_{ij} \), and \( b \) and \( C \) are vectors with elements \( b_i = 1 - v_i/kT_x \) and \( C_i = \rho C_{ii} \) respectively. The solution of eq 18 is

\[
\rho C_{kk} = \sum_{i=1}^{n} |A|_{ik} b_i / |A| \quad \text{ (19)}
\]

where \( |A|_{ik} \) is the cofactor of the element \( A_{ik} \) in the matrix \( A \), and \( |A| \) is the determinant of \( A \). By using the direct correlation function integrals calculated above in the following equation one can derive the expression for the activity coefficients of a species in a multicomponent mixture in the following form

\[
N(\ln \gamma_k / \partial N_k) = 1 - \rho C_{kk} + v_k [kT \sum (\partial x_i / \partial p)]^{-1} \quad \text{ (20)}
\]

As an example of application of this theory it will be used for vapor–liquid and liquid–liquid equilibria calculation of binary mixtures.

**Binary Mixture Calculations.** For binary liquid mixtures at low to moderate pressures the following expressions for the direct correlation function integrals were derived

\[
\rho C_{ij} = \frac{W(1 - a_i v_i x_i + (a_{ij} x_j + a_{ji} x_i) x_i x_j + a_{ij} x_i)^2}{L_1}\]

where \( a_{ij} \) is a ternary parameter, \( \rho C_{ij} \) is the activity coefficient of species \( i \) in a multicomponent mixture in the following form

\[
\gamma_1 = -\int_0^x (\rho C_{12} / W - 1) \, dx / x_1 \quad \text{ (24)}
\]

Substituting for \( \rho C_{ij} \) from eq 22 and performing the integration results in the analytical expression for activity coefficient

\[
\ln \gamma_1 = -L_1 \tau \ln \left[ x_1 + \frac{L_2}{L_1} x_2 \right] + \left( 1 / 2 \right) L_1 \tau - 1 + \left[ (a_{12} x_2 + (a_{12} - 1) x_2 + (a_{12} / (a_{12} - 1) x_2) \right] / \left( 2 \alpha_{12} L_2 - L_1 \right) \ln \left[ 1 + \alpha_1 x_2 / \tau \right] \quad \text{ (25)}
\]

where

\[
L_1 = kT \kappa_1 / v_2, \quad L_2 = kT \kappa_2 / v_2, \quad a = \alpha_1 + \alpha_2 - 1, \quad q = 1 - 4(1 / 2) \alpha_{12}^{1 / 2}
\]

\[
\tau = \left( 1 / 2 \right) \left( 1 - 2 \alpha_{12} \pm \sqrt{a} \right) / a
\]

The expression for \( \ln \gamma_2 \) is obtained by interchanging subscripts 1 and 2 in eq 25 and in the expression for \( \tau a \). The quantities \( a \), \( q \), and \( \tau \) remain unchanged under this operation. To test the activity coefficient expressions, they are used for vapor–liquid and liquid–liquid equilibria calculations of a number of binary systems.

**Applications and Results**

**Applications of Vapor–Liquid Phase Equilibria.** To test vapor–liquid–vapor (VLE) prediction by the new activity coefficient expressions a number of systems are chosen. The vapor phase is assumed to be an ideal gas and the vapor pressure of the pure components, \( p_i^0 \), is represented by the Antoine equation. Two pure liquid properties are needed in the activity coefficient equation: Specific volume and isothermal compressibility. The VLE data are fitted to the activity coefficient expressions by minimizing the following objective function

\[
S = \sum (p - p_{exp})^2 / S_p + \sum (y - y_{exp})^2 / S_y \quad \text{ (27)}
\]

where \( S_p \) and \( S_y \) are the sum of squares resulting from minimizing \( \sum (p - p_{exp})^2 \) and \( \sum (y - y_{exp})^2 \) individually.

The results of calculations are shown in Table I. Comparison is made with the Wilson correlation which is selected because

\[
(10) \text{ Handbook of Chemistry and Physics: CRC Press: Boca Raton, FL, 1979.}
\]

\[
\]
**TABLE I: Parameters of the Present Activity Coefficient Model and Comparisons with Wilson Correlation**

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ [°C]</th>
<th>$a_{21}$</th>
<th>$a_{12}$</th>
<th>$S_p$</th>
<th>$S_y$</th>
<th>$S_p$</th>
<th>$S_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol + water</td>
<td>60</td>
<td>0.3869</td>
<td>0.3561</td>
<td>2.0</td>
<td>0.10</td>
<td>1.0</td>
<td>0.07</td>
</tr>
<tr>
<td>ethanol + water</td>
<td>40</td>
<td>0.2900</td>
<td>0.3799</td>
<td>1.4</td>
<td>0.09</td>
<td>1.1</td>
<td>0.13</td>
</tr>
<tr>
<td>ethanol + water</td>
<td>55</td>
<td>0.2920</td>
<td>0.4048</td>
<td>0.7</td>
<td>0.14</td>
<td>0.4</td>
<td>0.13</td>
</tr>
<tr>
<td>ethanol + water</td>
<td>70</td>
<td>0.2942</td>
<td>0.4255</td>
<td>1.6</td>
<td>0.11</td>
<td>0.6</td>
<td>0.13</td>
</tr>
<tr>
<td>1-propanol + water</td>
<td>30</td>
<td>0.2392</td>
<td>0.2722</td>
<td>0.07</td>
<td>0.46</td>
<td>0.09</td>
<td>0.64</td>
</tr>
<tr>
<td>ethyl acetate + ethanol</td>
<td>40</td>
<td>0.5105</td>
<td>0.2989</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>ethanol + benzene</td>
<td>25</td>
<td>0.1028</td>
<td>0.6393</td>
<td>0.009</td>
<td>0.008</td>
<td>0.004</td>
<td>0.01</td>
</tr>
<tr>
<td>ethanol + benzene</td>
<td>40</td>
<td>0.09741</td>
<td>0.6458</td>
<td>0.2</td>
<td>0.07</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>ethanol + benzene</td>
<td>55</td>
<td>0.09688</td>
<td>0.6498</td>
<td>0.9</td>
<td>0.13</td>
<td>0.5</td>
<td>0.13</td>
</tr>
<tr>
<td>acetone + chloroform</td>
<td>25</td>
<td>0.2907</td>
<td>0.6404</td>
<td>0.04</td>
<td>0.24</td>
<td>0.04</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*In this table $S_p = 10^{-2} \sum (p - p_{exp})^2$ and $S_y = 10^{-2} \sum (y - y_{exp})^2$.

![Figure 3](image3.png)

**Figure 3.** Vapor-liquid composition ($x$-$y$) diagram for ethanol (1) + benzene (2) at 55 °C. The squares are the experimental data, the solid curve is the present theory, and the dashed curve is Wilson correlation. It gave the best overall fit to the large number of mixtures studied in VLE calculations. Table I also includes parameters $a_{21}$ and $a_{12}$, and optimized values of $S_p$ and $S_y$.

![Figure 4](image4.png)

**Figure 4.** Composition versus temperature ($x$-$T$) diagram for liquid-liquid equilibrium of methanol (1) + heptane (2). The squares are the experimental data and the solid curve is the present theory.

![Figure 5](image5.png)

**Figure 5.** Composition versus temperature ($x$-$T$) diagram for liquid-liquid equilibrium of formic acid (1) + benzene (2). The squares are the experimental data and the solid curve is the present theory.
### TABLE II: LLE Parameters* of the Present Activity Coefficient Model for Different Binary Mixtures

<table>
<thead>
<tr>
<th>system</th>
<th>$\alpha_{210}$</th>
<th>$\alpha_{120}$</th>
<th>$S \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol + heptane</td>
<td>-1070.9</td>
<td>1.0243</td>
<td>0.12</td>
</tr>
<tr>
<td>methanol + cyclohexane</td>
<td>-980.29</td>
<td>1.0191</td>
<td>0.12</td>
</tr>
<tr>
<td>formic acid + benzene</td>
<td>-748.15</td>
<td>0.97983</td>
<td>1.7</td>
</tr>
<tr>
<td>phenol + octane</td>
<td>-1077.0</td>
<td>1.0031</td>
<td>7.3</td>
</tr>
<tr>
<td>methanol + carbon disulfide</td>
<td>-797.20</td>
<td>1.0186</td>
<td>0.45</td>
</tr>
<tr>
<td>nitrobenzene + hexane</td>
<td>-975.97</td>
<td>1.0027</td>
<td>2.0</td>
</tr>
<tr>
<td>1,3-dihydroxybenzene + benzene</td>
<td>-937.02</td>
<td>1.0032</td>
<td>5.5</td>
</tr>
</tbody>
</table>

*In this table $S = L/1 - x/Ilr_{1}/[x_{1}/2l_{2}] + x_{2}/2l_{2}l_{2}$.

LLE, because it always satisfies inequality.29

The present activity coefficient theory is tested versus experimental LLE data.12 For the variation of the isothermal compressibilities with temperature, which is needed in this calculation, a three-parameter equation13 is used.

The temperature and pure component volume dependence of parameters $\alpha_{21}$ and $\alpha_{12}$ for a number of organic binary systems exhibiting LLE are represented by the following expressions.

$$\alpha_{21} = \frac{c_{2}}{c_{1}} \exp(\alpha_{210}/kT)$$

$$\alpha_{12} = \alpha_{120}(c_{1}/c_{2})$$

where superscripts (1) and (2) are for phases 1 and 2, respectively.

Table II shows values of parameters $\alpha_{210}$ and $\alpha_{120}$ and optimum $S$ for a number of binary systems. The variation of the compositions of two LLE systems (methanol + heptane and formic acid + benzene) with temperature is shown in Figures 4 and 5.

According to these figures the agreement with the data is satisfactory. The largest deviation of theory from experimental data occurs near the upper critical solution temperature. Overall the present technique is capable of formulating analytic expressions for activity coefficients in mixtures. For this purpose it is necessary to define closure expressions for the cross direct correlation function integrals. Application of the activity coefficient expression resulting from this technique for vapor–liquid and liquid–liquid equilibria calculations has been as successful as the other activity coefficient expressions available.

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