A SIMPLE RELATION TO PREDICT OR TO CORRELATE THE EXCESS FUNCTIONS OF MULTICOMPONENT MIXTURES

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ABSTRACT

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Semi-theoretical relations for the excess functions (e.g. excess Gibbs energies G^E, excess chemical potentials) developed previously for binary mixtures have been extended to multicomponent mixtures. We postulate that contributions from two-body and three-body interactions are significant, and we propose an expression relating unlike three-body interactions to binary interactions. We have tested the relation with ternary vapor–liquid equilibria (VLE) having various chemical interactions and have found good agreement between the experimental excess functions and the predictions from the relation based solely upon binary data. Predicting fluid phase equilibria of multicomponent mixtures using existing binary data is relatively simple and, for the systems tested, appears to be considerably better than the NRTL model for VLE systems having partially or wholly negative G^E. For the systems tested having wholly positive G^E, the new model (H^3M) is superior to the NRTL model except for ethanol–water. While the model is less satisfactory for liquid–liquid equilibria (LLE) than for VLE, it is significantly better than the NRTL or UNIQUAC model for the (randomly selected) system tested. The current model is also extremely flexible for either correlating or predicting multicomponent data, and it always converges to a solution.

INTRODUCTION

Many different models exist to correlate and predict vapor–liquid equilibria (VLE): equations based upon theories (Gierycz, 1986), methods for the description of excess functions (Redlich and Kister, 1948), and equations of state (Chao and Robinson, 1986). Most models perform satisfactorily for

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binaries, but the situation becomes complicated in the case of multicomponent mixtures. Furthermore, multicomponent data that are sufficiently accurate to evaluate model parameters are rare. In this paper, we propose semi-theoretical relations for the excess functions that predict multicomponent mixture VLE behavior from binary data with good accuracy. For liquid–liquid equilibria (LLE), it is difficult to obtain an expression for the excess Gibbs energy (G^E) that is sufficiently accurate to predict multicomponent results using binary data. Prediction of ternary LLE from our relations is qualitatively correct and, for the system tested, superior to the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) relations. The model also provides a generalized relationship to correlate multicomponent data.

Some empirical forms for correlating excess functions require composition-dependent parameters (Bertrand et al., 1983). These empirical formulations have highly correlated parameters, which cause problems in their extension to multicomponent systems. We use semi-theoretical, three-parameter relations for the excess functions of binary mixtures developed by Kreglewski et al. (1985) and extend them to multicomponent mixtures using only binary data. We assume that two-body and three-body interactions are significant in our relations. To reduce the composition dependence, we have included an assumption in which we relate three-body ijk combinations to three-body binary (iij, ijj, iik, ikk, jjk, jkk) combinations. The resulting relation permits the prediction of fluid phase equilibria of multicomponent mixtures using only binary data. No further adjustable parameters are needed, and good predictions result even for systems having partially or wholly negative G^E.

We have tested the proposed relation with some ternary VLE data having complex chemical interactions using only binary, experimental excess functions. We also have correlated our relation directly to the ternary data and have obtained excellent agreement. Extension to solutions having more than three components is straightforward and prediction can use binary data, binary and ternary data or ternary data, depending upon availability and accuracy considerations. Our model can correlate irregular, binary G^E data that are partially or wholly negative over the entire composition range much better than the NRTL equation using three adjustable parameters. Our model also predicts ternary LLE better than the NRTL and UNIQUAC models in the region of the plait point; however, none of these models are quantitatively correct.

DERIVATION FOR A BINARY MIXTURE

In a mixture, molecular interactions occur between both like and unlike molecules. For example, in a binary mixture, two-body interactions occur as

1-1, 2-2, and 1-2, while three-body interactions occur as 1-1-1, 2-2-2, 1-1-2 and 1-2-2. Kreglewski et al. (1985) have assumed that the minimum of the intermolecular energy, $\bar{u}_m$, is equal to the sum of two-body and three-body interactions for binary mixtures. Goldman (1978) notes that the contributions of three-body interactions are small compared to those of two-body interactions, although Benmekki and Mansoori (1988) show that three-body interactions can be significant near a ternary critical point. Higher order interactions are generally negligible. Mathematically, this assumption is

$$\bar{u}_m = \bar{u}_m(2) + \bar{u}_m(3) \tag{1}$$

where (2) and (3) denote two-body and three-body interactions, respectively; in a random mixture approximation, we have, for a binary mixture

$$\bar{u}_m(2) = x_1^2 \bar{u}_{11} + x_2^2 \bar{u}_{22} + 2x_1 x_2 \bar{u}_{12} \tag{2}$$

and

$$\bar{u}_m(3) = x_1^3 \bar{u}_{111} + x_2^3 \bar{u}_{222} + 3x_1 x_2 (x_1 \bar{u}_{112}^* + x_2 \bar{u}_{122}^*) \tag{3}$$

Each of these individual interactions mentioned above relates to the appropriate part of the intermolecular energy; for example, $\bar{u}_{111}$ results from a three-body 1-1-1 interaction. The apparent three-body interactions, $\bar{u}_{112}^*$ and $\bar{u}_{122}^*$, are not purely cross-parameters except in the infinitely dilute limits. In a non-random mixture, some 111 and 222 clustering can occur in addition to the mixed collisions. Therefore, the apparent interactions depend upon the mole fraction; we assume empirical forms that are correct at infinite dilution, by definition correct as the component becomes pure and convenient between these limits

$$\bar{u}_{112}^* = \bar{u}_{112} (1 - c_1 x_1^n) \tag{4}$$

$$\bar{u}_{122}^* = \bar{u}_{122} (1 - c_2 x_2^n) \tag{5}$$

where $n \geq 2$ and c_1 and c_2 are constants. Empirically, we find that $n = 2$ is optimal. Equation (3) can be rewritten as

$$
\begin{aligned}
\bar{u}_m(3) &= x_1^2 \bar{u}_{111} + x_2^2 \bar{u}_{222} + x_1 x_2 [3(x_1 \bar{u}_{112}^* + x_2 \bar{u}_{122}^*) - x_1 \bar{u}_{111} - x_2 \bar{u}_{222}] \\
&= x_1^2 \bar{u}_{111} + x_2^2 \bar{u}_{222} + x_1 x_2 [x_1 (3\bar{u}_{112} - \bar{u}_{111}) + x_2 (3\bar{u}_{122} - \bar{u}_{222}) \\
&\quad - 3\bar{u}_{112} c_1 x_1^3 - 3\bar{u}_{122} c_2 x_2^3]
\end{aligned}
\tag{6}
$$

The composition dependence becomes simpler if we assume

$$3\bar{u}_{112} - \bar{u}_{111} = 3\bar{u}_{122} - \bar{u}_{222} \equiv \delta \bar{u}_{(3,12)} \tag{7}$$

where $\delta \bar{u}_{(3,ij)}$ denotes removing the effect of pure three-body interactions

from mixed interactions. Substitution of eqns. (2), (6) and (7) into eqn. (1) produces

$$
\begin{aligned}
\bar{u}_m &= x_1^2(\bar{u}_{11} + \bar{u}_{111}) + x_2^2(\bar{u}_{22} + \bar{u}_{222}) \\
&\quad + x_1 x_2\big[(2\bar{u}_{12} + \delta\bar{u}_{(3,12)}) - 3\bar{u}_{112}c_1 x_1^3 - 3\bar{u}_{122}c_2 x_2^3\big] \\
&= x_1(\bar{u}_{11} + \bar{u}_{111}) + x_2(\bar{u}_{22} + \bar{u}_{222}) + x_1 x_2\big[(2\bar{u}_{12} + \delta\bar{u}_{(3,12)}) - (\bar{u}_{11} + \bar{u}_{111}) \\
&\quad - (\bar{u}_{22} + \bar{u}_{222}) - 3\bar{u}_{112}c_1 x_1^3 - 3\bar{u}_{122}c_2 x_2^3\big] \\
&= x_1\epsilon_{11} + x_2\epsilon_{22} + x_1 x_2\big(\epsilon_{12} - \epsilon_{11} - \epsilon_{22} - 3\bar{u}_{112}c_1 x_1^3 - 3\bar{u}_{122}c_2 x_2^3\big)
\end{aligned}
\tag{8}
$$

where

$$
\epsilon_{11} \equiv \bar{u}_{11} + \bar{u}_{111} \tag{9}
$$

$$
\epsilon_{22} \equiv \bar{u}_{22} + \bar{u}_{222} \tag{10}
$$

$$
\epsilon_{12} \equiv 2\bar{u}_{12} + \delta\bar{u}_{(3,12)} \tag{11}
$$

To convert $\bar{u}_m$ into a thermodynamic energy function, we have used the lattice model value for the excess Helmholtz energy, A^E/RT, at a given temperature, volume and composition, which results from subtracting $\bar{u}_m$ from $(x_1\epsilon_{11} + x_2\epsilon_{22})$ followed by multiplication by $z/2kT$, where z is the coordination number and k is the Boltzmann constant

$$
A^E/RT = x_1 x_2\big(a_0 + a_1 x_1^3 + a_2 x_2^3\big) \tag{12}
$$

where

$$
a_0 = (\epsilon_{11} + \epsilon_{22} - \epsilon_{12})z/2kT \tag{13}
$$

$$
a_1 = 3\bar{u}_{112}c_1 z/2kT \tag{14}
$$

$$
a_2 = 3\bar{u}_{122}c_2 z/2kT \tag{15}
$$

For this model, the relationship between the excess Helmholtz function and the excess Gibbs function is

$$
G^E/RT = A^E/RT - O\big[(\Delta V)^2/2\beta V\,RT\big] \tag{16}
$$

where ΔV is the volume change on mixing, β is the compressibility, and G^E is the excess Gibbs energy. Assuming that $(\Delta V)^2/2\beta V\,RT$ is negligible

$$
G^E/RT = x_1 x_2\big(a_0 + a_1 x_1^3 + a_2 x_2^3\big) \tag{17}
$$

which has a form similar to a Margules equation, but this specific form has traceable bases in theory and cannot be represented exactly by a Margules equation. The molar excess chemical potential, μ_1^E/RT, resulting from eqn. (17) is

$$
\mu_1^E/RT = x_2(1 - x_1)\big[a_0 + 4a_1 x_1^3\big] + a_2 x_2^4\big[1 - 4x_1\big] \tag{18}
$$

Liquid-phase non-idealities for the binary mixtures thus can be described by the general relations

$$G^{E(ij)}/RT = x_i x_j \left(a_0^{(ij)} + a_i^{(ij)} x_i^3 + a_j^{(ij)} x_j^3 \right) \tag{19}$$

$$\mu_i^{E(ij)}/RT = x_j (1 - x_i)\left[a_0^{(ij)} + 4a_i^{(ij)} x_i^3 \right] + a_j^{(ij)} x_j^4 \left[1 - 4x_i \right] \tag{20}$$

$$\mu_j^{E(ij)}/RT = x_i (1 - x_j)\left[a_0^{(ij)} + 4a_j^{(ij)} x_j^3 \right] + a_i^{(ij)} x_i^4 \left[1 - 4x_j \right] \tag{21}$$

where superscript (ij) denotes any binary mixture. Note that eqn. (21) can be obtained by interchanging subscript i with subscript j in eqn. (20), and each binary mixture has three adjustable parameters.

MULTICOMPONENT MIXTURES

In the case of a ternary mixture

$$\bar{u}_m(2) = x_1^2 \bar{u}_{11} + x_2^2 \bar{u}_{22} + x_3^2 \bar{u}_{33} + 2x_1 x_2 \bar{u}_{12} + 2x_1 x_3 \bar{u}_{13} + 2x_2 x_3 \bar{u}_{23} \tag{22}$$

and

$$\begin{aligned}
\bar{u}_m(3) = {}& x_1^3 \bar{u}_{111} + x_2^3 \bar{u}_{222} + x_3^3 \bar{u}_{333} + 3x_1 x_2 (x_1 \bar{u}_{112}^* + x_2 \bar{u}_{122}^*) \\
&+ 3x_1 x_3 (x_1 \bar{u}_{113}^* + x_3 \bar{u}_{133}^*) + 3x_2 x_3 (x_2 \bar{u}_{223}^* + x_3 \bar{u}_{233}^*) \\
&+ 6x_1 x_2 x_3 \bar{u}_{123}^*
\end{aligned} \tag{23}$$

We use derivations similar to those in the binary mixture but in the ternary mixture $x_1 = 1 - x_2 - x_3$, and eqn. (23) becomes

$$\begin{aligned}
\bar{u}_m(3) = {}& x_1^2 \bar{u}_{111} + x_2^2 \bar{u}_{222} + x_3^2 \bar{u}_{333} \\
&+ x_1 x_2 \left[(x_1 + x_2)\delta \bar{u}_{(3,12)} - 3\bar{u}_{112} c_1^{(12)} x_1^3 - 3\bar{u}_{122} c_2^{(12)} x_2^3 \right] \\
&+ x_1 x_3 \left[(x_1 + x_3)\delta \bar{u}_{(3,13)} - 3\bar{u}_{113} c_1^{(13)} x_1^3 - 3\bar{u}_{133} c_3^{(13)} x_3^3 \right] \\
&+ x_2 x_3 \left[(x_2 + x_3)\delta \bar{u}_{(3,23)} - 3\bar{u}_{223} c_2^{(23)} x_2^3 - 3\bar{u}_{233} c_3^{(23)} x_3^3 \right] \\
&+ 6x_1 x_2 x_3 \bar{u}_{123}^*
\end{aligned} \tag{24}$$

Again, we desire to reduce the composition dependence of the terms in parentheses in this equation. We adopt an approximation similar to that used by McGregor et al. (1987) for third virial coefficients and assume

$$3\bar{u}_{ijk}^* = \bar{u}_{iii} + \bar{u}_{jjj} + \bar{u}_{kkk} + \tfrac{1}{2}\left(\delta \bar{u}_{ij} + \delta \bar{u}_{ik} + \delta \bar{u}_{jk} \right) \tag{25}$$

and, expanding upon eqn. (7)

$$\begin{aligned}
\delta \bar{u}_{ij} &= \left(3\bar{u}_{iij} - \bar{u}_{iii} \right) - \bar{u}_{iii} - \bar{u}_{jjj} \\
&= \left(3\bar{u}_{ijj} - \bar{u}_{jjj} \right) - \bar{u}_{iii} - \bar{u}_{jjj} \\
&= \delta \bar{u}_{(3,ij)} - \bar{u}_{iii} - \bar{u}_{jjj}
\end{aligned} \tag{26}$$

Substituting eqn. (26) into eqn. (25) provides

$$\bar{u}_{ijk}^* = \tfrac{1}{6}\big[\big(3\bar{u}_{iij} - \bar{u}_{iii}\big) + \big(3\bar{u}_{ikk} - \bar{u}_{kkk}\big) + \big(3\bar{u}_{jjk} - \bar{u}_{jjj}\big)\big]$$

$$= \tfrac{1}{6}\big[\delta\bar{u}_{(3,ij)} + \delta\bar{u}_{(3,ik)} + \delta\bar{u}_{(3,jk)}\big] \qquad (27)$$

Note that the three-body ijk combination is related to three-body binary combinations that occur in the manner prescribed by eqn. (27). Hamad et al. (1988) demonstrated that $\delta\bar{u}_{ij}$, given by eqn. (26), is insensitive to temperature variations. Equation (27) should be a reasonable approximation for small, unlike, three-body interactions. Substitution of eqns. (22), (24) and (27) into eqn. (1) produces

$$\bar{u}_m = x_1(\bar{u}_{11} + \bar{u}_{111}) + x_2(\bar{u}_{22} + \bar{u}_{222}) + x_3(\bar{u}_{33} + \bar{u}_{333})$$

$$+ x_1 x_2\big[(2\bar{u}_{12} + \delta\bar{u}_{(3,12)}) - (\bar{u}_{11} + \bar{u}_{111}) - (\bar{u}_{22} + \bar{u}_{222}) - 3\bar{u}_{112}c_1^{(12)}x_1^3$$

$$- 3\bar{u}_{122}c_2^{(12)}x_2^3\big] + x_1 x_3\big[(2\bar{u}_{13} + \delta\bar{u}_{(3,13)}) - (\bar{u}_{11} + \bar{u}_{111}) - (\bar{u}_{33} + \bar{u}_{333})$$

$$- 3\bar{u}_{113}c_1^{(13)}x_1^3 - 3\bar{u}_{133}c_3^{(13)}x_3^3\big] + x_2 x_3\big[(2\bar{u}_{23} + \delta\bar{u}_{(3,23)})$$

$$- (\bar{u}_{22} + \bar{u}_{222}) - (\bar{u}_{33} + \bar{u}_{333}) - 3\bar{u}_{223}c_2^{(23)}x_2^3 - 3\bar{u}_{233}c_3^{(23)}x_3^3\big] \qquad (28)$$

which reduces to

$$\bar{u}_m = x_1\epsilon_{11} + x_2\epsilon_{22} + x_3\epsilon_{33}$$

$$+ x_1 x_2\big(\epsilon_{12} - \epsilon_{11} - \epsilon_{22} - 3\bar{u}_{112}c_1^{(12)}x_1^3 - 3\bar{u}_{122}c_2^{(12)}x_2^3\big)$$

$$+ x_1 x_3\big(\epsilon_{13} - \epsilon_{11} - \epsilon_{33} - 3\bar{u}_{113}c_1^{(13)}x_1^3 - 3\bar{u}_{133}c_3^{(13)}x_3^3\big)$$

$$+ x_2 x_3\big(\epsilon_{23} - \epsilon_{22} - \epsilon_{33} - 3\bar{u}_{223}c_2^{(23)}x_2^3 - 3\bar{u}_{233}c_3^{(23)}x_3^3\big) \qquad (29)$$

where ϵ_{ii} and ϵ_{ij} are defined as in eqns. (9)–(11). The molar excess Gibbs energy for the ternary mixture (again invoking the lattice model) is

$$G^{E(123)}/RT = x_1 x_2\big(a_0^{(12)} + a_1^{(12)}x_1^3 + a_2^{(12)}x_2^3\big)$$

$$+ x_1 x_3\big(a_0^{(13)} + a_1^{(13)}x_1^3 + a_3^{(13)}x_3^3\big)$$

$$+ x_2 x_3\big(a_0^{(23)} + a_2^{(23)}x_2^3 + a_3^{(23)}x_3^3\big)$$

or

$$G^{E(123)}/RT = \sum_{i=1}^{2}\sum_{j=i+1}^{3} x_i x_j\big(a_0^{(ij)} + a_i^{(ij)}x_i^3 + a_j^{(ij)}x_j^3\big)$$

$$= \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} G^{E(ij)}/RT \quad (m = 3) \qquad (30)$$

where m denotes the total number of components, superscript (123) denotes a ternary mixture and $a_0^{(ij)}$, $a_i^{(ij)}$ and $a_j^{(ij)}$ are the parameters determined

from the three constituent binaries. If these binary parameters are established, we have a relation that predicts multicomponent mixture behavior using only binary data. These parameters can be considered adjustable, and eqn. (30) becomes a correlation model for multicomponent data.

The molar excess chemical potential for the ternary mixture, $\mu_1^{E(123)}/RT$, is

$$
\begin{aligned}
\mu_1^{E(123)}/RT &= x_2(1 - x_1)\left[a_0^{(12)} + 4a_1^{(12)}x_1^3\right] + a_2^{(12)}x_2^4\left[1 - 4x_1\right] \\
&\quad + x_3(1 - x_1)\left[a_0^{(13)} + 4a_1^{(13)}x_1^3\right] + a_3^{(13)}x_3^4\left[1 - 4x_1\right] \\
&\quad - x_2x_3\left[a_0^{(23)} + 4a_2^{(23)}x_2^3 + 4a_3^{(23)}x_3^3\right] \\
&= \mu_1^{E(12)}/RT + \mu_1^{E(13)}/RT + \mu_1^{E(23)}/RT
\end{aligned}
\tag{31}
$$

or, in general

$$
\begin{aligned}
\mu_l^{E(123)}/RT &= \mu_l^{E(12)}/RT + \mu_l^{E(13)}/RT + \mu_l^{E(23)}/RT \\
&= \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} \mu_l^{E(ij)}/RT \quad (m = 3)
\end{aligned}
\tag{32}
$$

where $l \in \{1, 2, 3\}$. If $l = i$, $\mu_i^{E(ij)}/RT$ is obtained from eqn. (20). Secondly, if $l = j$, $\mu_j^{E(ij)}/RT$ is obtained from eqn. (21). Finally, if $l \neq i \neq j$

$$
\mu_l^{E(ij)}/RT = -x_ix_j\left[a_0^{(ij)} + 4a_i^{(ij)}x_i^3 + 4a_j^{(ij)}x_j^3\right]
\tag{33}
$$

Note that we have included only the fundamental assumptions (eqns. (7), (27) and the lattice model) throughout our derivation; this extension to ternary and higher mixtures is not by superposition. The generalized correlation form for multicomponent mixtures has a sound theoretical basis.

The derivation can be extended to higher order multicomponent mixtures in a manner similar to that used for ternaries. The resulting expression for G^E of a general multicomponent mixture is

$$
G^{E(I_1 \cdots I_m)}/RT = \sum_{i<} \sum_{j} G^{E(ij)}/RT
\tag{34}
$$

and for μ^E is

$$
\mu_l^{E(I_1 \cdots I_m)}/RT = \sum_{i<} \sum_{j} \mu_l^{E(ij)}/RT
\tag{35}
$$

where $i \in \{I_1, I_2, \ldots, I_{m-1}\}$, $j \in \{I_2, I_3, \ldots, I_m\}$, $l \in \{I_1, I_2, \ldots, I_m\}$, with $I_1 < I_2 < \ldots < I_m$ being indices of constituent components. Again, $G^{E(ij)}/RT$ is obtained from eqn. (19) and $\mu_l^{E(ij)}/RT$ can be determined from eqn. (20), (21) or (33), depending upon l. Only binary data are needed to predict multicomponent mixture behavior.

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We demonstrate next how to use eqns. (34) and (35) for a (1234) quaternary mixture because it demonstrates additional flexibility. For a $(1 \ldots m)$ m-component mixture, eqns. (34) and (35) reduce to

$$G^{E(1 \ldots m)}/RT = \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} G^{E(ij)}/RT \tag{36}$$

$$\mu_l^{E(1 \ldots m)}/RT = \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} \mu_l^{E(ij)}/RT \tag{37}$$

where $I_1 = 1$, $I_2 = 2, \ldots,$ and $I_m = m$. For an (ijk) ternary mixture with $i < j < k$, eqn. (34) becomes

$$G^{E(ijk)}/RT = G^{E(ij)}/RT + G^{E(ik)}/RT + G^{E(jk)}/RT \tag{38}$$

where $I_1 = i$, $I_2 = j$ and $I_3 = k$. This equation suggests that one ternary mixture can be used to replace three constituent binaries for predicting multicomponent mixture behavior. Similarly, an m-component mixture can be used to replace a total number of $\frac{1}{2}m(m-1)$ constituent binaries. The flexibility of our relations enhances their usefulness. From eqn. (36)

$$G^{E(1234)}/RT = G^{E(12)}/RT + G^{E(13)}/RT + G^{E(14)}/RT$$
$$+ G^{E(23)}/RT + G^{E(24)}/RT + G^{E(34)}/RT \tag{39}$$

and from eqn. (38)

$$G^{E(134)}/RT = G^{E(13)}/RT + G^{E(14)}/RT + G^{E(34)}/RT \tag{40}$$

Substituting eqn. (40) into eqn. (39) produces

$$G^{E(1234)}/RT = G^{E(12)}/RT + G^{E(23)}/RT + G^{E(24)}/RT + G^{E(134)}/RT \tag{41}$$

In this example, we can use vapor–liquid equilibrium measurements either for six constituent binaries using eqn. (39) or three binaries together with one ternary using eqn. (41) to determine the required binary parameters for predicting quaternary mixture behavior. This flexibility can be important if, for example, (13) information is not available but (134) information is available. From eqn. (37) and if $l = 1$

$$\mu_1^{E(1234)}/RT = \mu_1^{E(12)}/RT + \mu_1^{E(13)}/RT + \mu_1^{E(14)}/RT$$
$$+ \mu_1^{E(23)}/RT + \mu_1^{E(24)}/RT + \mu_1^{E(34)}/RT$$
$$= \mu_1^{E(12)}/RT + \mu_1^{E(23)}/RT + \mu_1^{E(24)}/RT + \mu_1^{E(134)}/RT \tag{42}$$

If we allow all the fixed binary parameters to be adjustable, then eqn. (34) becomes a correlation model for multicomponent data, and the total number of parameters required for m-component mixtures is $\frac{3}{2}m(m-1)$.

RESULTS AND DISCUSSION

The paucity of accurate multicomponent data causes problems in model-ing multicomponent behavior. Empirical models for describing excess func-tions of complex binary mixtures achieve only limited success when ex-tended to multicomponent systems. The thermodynamic relation

$$G^{E} = RT\sum_{i} x_{i} \ln \gamma_{i} \tag{43}$$

relates G^{E} to γ_{i}, the individual activity coefficient; while

$$RT \ln \gamma_{i} = \left(\frac{\partial nG^{E}}{\partial n_{i}}\right)_{T,P,n_{j\neq i}} = \mu_{i}^{E} \tag{44}$$

provides γ_{i} from G^{E} by differentiation. Therefore, the key problem in calculating multicomponent vapor–liquid equilibria is to find an expression for G^{E} that provides a good approximation for the properties of the mixture. We have developed simple semi-theoretical relations for G^{E} and its deriva-tive μ_{i}^{E} of a multicomponent mixture that overcome the above-mentioned difficulties.

The Kreglewski et al. (1985) model for binaries with three parameters has been verified in this work. We have compared this relation with the three-parameter NRTL (non-random two-liquid) equation and have listed the results in Table 1. As mentioned above, more than three parameters are normally required when using Margules equations. The excess Gibbs en-ergies of these binaries have irregular forms, e.g. G^{E} of the hexafluoroben-zene–benzene and nitromethane–acetonitrile systems pass through zero when plotted against mole fraction and for chloroform–acetone and nitromethane–acetone systems the G^{E} are all negative versus mole fraction. In these cases, our relation performs much better than the NRTL equation. In addition, our model is superior to the NRTL model for chloroform–methanol or ethanol. G^{E} for these systems is uniformly positive.

We have selected several ternary systems with complex chemical interac-tions to demonstrate the accuracy of the relations. The references for reported G^{E} data for the ternary systems and their constituent binaries, obtained from vapor–liquid equilibrium measurements, appear in Table 2. Different forms of Margules or modified Margules equations (3–6 parame-ters) are reported to correlate these constituent binaries. The ternary data are correlated with different Wohl expressions, and the correlation results sometimes yield composition-dependent parameters. The varieties of em-pirical forms complicate the calculation of excess chemical potentials or activity coefficients. In addition, an extension to multicomponent mixture behavior is intractable in such circumstances.

TABLE 1

Parameters in eqn. (19) determined from binary G^E data and a comparison of eqn. (19) and the NRTL equation for binary systems

Components (1)–(2)	T (K)	$a_0^{(12)}$	$a_1^{(12)}$	$a_2^{(12)}$	R.m.s. dev. [a] eqn. (19)	R.m.s. dev. NRTL
Hexafluorobenzene– benzene	303.15	−0.11709	−0.15668	0.33645	2.3	26.0
Hexafluorobenzene– benzene	313.15	−0.08891	−0.13803	0.31047	2.3	26.5
Nitromethane– acetonitrile	298.15	−0.00095	0.07321	−0.00550	0.3	0.5
Chloroform– acetone	323.15	−0.77618	0.23410	−0.08863	1.6	6.3
Nitromethane– acetone	298.15	−0.11164	0.10203	−0.04395	0.7	4.0
Chloroform– ethanol	323.15	1.00107	0.62108	−0.54762	1.1	14.7
Chloroform– methanol	323.15	1.27510	0.68559	−0.47099	2.4	5.6

[a] $\{[\sum_{i=1}^{M}(G_i^E - G_{i,\text{calc}}^E)^2][M - n]^{-1}\}^{1/2}$, where M denotes the total number of data points and n is the number of fitted parameters; G^E in J mol^{-1}.

Next, the parameters in the relation for the constituent binary mixtures of a ternary, obtained by non-linear least-squares fitting of G^E data, and the root-mean-square (r.m.s.) deviations of G^E in J mol^{-1}, which are within

TABLE 2

References of the reported G^E data for the ternary systems and their constituent binaries

Components	Reference
1,4-Dioxane (1)–ethanol (2)–water (3)	Balcázar-Ortiz et al. (1979)
1,4-Dioxane (1)–ethanol (2)	Balcázar-Ortiz et al. (1979)
1,4-Dioxane (1)–water (3)	Balcázar-Ortiz et al. (1979)
Ethanol (2)–water (3)	Balcázar-Ortiz et al. (1979)
Acetonitrile (1)–ethanol (2)–water (3)	Wilson et al. (1979)
Acetonitrile (1)–ethanol (2)	Wilson et al. (1979)
Acetonitrile (1)–water (3)	Wilson et al. (1979)
Ethanol (2)–water (3)	Wilson et al. (1979)
Acetone (1)–ethanol (2)–water(3)	Chaudhry et al. (1980)
Acetone (1)–ethanol (2)	Chaudhry et al. (1980)
Acetone (1)–water (3)	Chaudhry et al. (1980)
Ethanol (2)–water (3)	Chaudhry et al. (1980)

TABLE 3

Parameters in eqn. (19) determined from binary G^E data at 323.15 K and a comparison of eqn. (19) and the NRTL equation

Components (i)–(j)	$a_0^{(ij)}$	$a_i^{(ij)}$	$a_j^{(ij)}$	R.m.s. dev. [a] of G^E in J mol^{-1}	R.m.s. dev. by NRTL
Balcázar-Ortiz et al. (1979)					
1,4-Dioxane (1)–ethanol (2)	0.91217	−0.00577	0.16044	0.8	0.3
1,4-Dioxane (1)–water (3)	1.77017	0.14667	0.22200	0.4	0.3
Ethanol (2)–water (3)	1.20200	−0.31520	0.57920	4.4	1.0
Wilson et al. (1979)					
Acetonitrile (1)–ethanol (2)	1.15317	0.02067	0.20000	3.7	3.2
Acetonitrile (1)–water (3)	1.96986	0.05572	0.60662	1.7	2.6
Ethanol (2)–water (3)	1.20867	−0.35483	0.56349	4.5	2.3
Chaudhry et al. (1980)					
Acetone (1)–ethanol (2)	0.69480	−0.01624	0.08654	0.0	0.4
Acetone (1)–water (3)	1.72526	−0.00120	0.52191	1.0	1.6
Ethanol (2)–water (3)	1.21048	−0.33801	0.49041	3.3	2.5

[a] $\{[\sum_{i=1}^{M}(G_i^E - G_{i,calc}^E)^2][M - n]^{-1}\}^{1/2}$, where M denotes the total number of data points and n is the number of fitted parameters.

experimental errors, are listed in Table 3. The inconsistencies found from different G^E data in the common ethanol–water binary sometimes exceed 10 J mol^{-1}. We have compared the results with those calculated from the NRTL equation and find similar r.m.s. deviations, which are also given in Table 3, for these binaries. The NRTL equation provides a significantly better representation of G^E data than H^{3}M only for the ethanol–water mixture.

The predictions based upon fixed (or determined) binary parameters are in reasonably good agreement with G^E data and excess chemical potentials. The percentage deviations between the predictions and the reported excess functions, including the available ternary data, are shown in Table 4. The overall, averaged percentage deviation of the predicted excess chemical potentials, μ_1^E, from our relations is ~ 5–6%.

We have also predicted ternary excess functions based upon binary parameters of the NRTL equation, which are listed in Table 4. Slightly better results are obtained from the NRTL equation. For the three ternary systems that we investigated here, their constituent binaries all have positive G^E values against mole fraction. A more accurate representation of the ethanol–water mixture might produce a better prediction for these ternary systems. Similar results are obtained for all three excess chemical potentials of the 1,4-dioxane–ethanol–water system, which are given in Table 5.

TABLE 4

Averaged percentage deviations between the predictions of the H^3M and NRTL models and the reported G^E and μ_1^E

Components	M [a]	Av. dev. of G^E [b] (%)	Av. dev. of μ_1^E [c] (%)
H^3M			
1,4-Dioxane (1)–ethanol (2)–water (3)	26	5.77	7.48
Acetonitrile (1)–ethanol (2)–water (3)	48	1.87	3.06
Acetone (1)–ethanol (2)–water (3)	57	5.22	6.35
NRTL			
1,4-Dioxane (1)–ethanol (2)–water (3)	26	5.69	6.02
Acetonitrile (1)–ethanol (2)–water (3)	48	0.59	1.89
Acetone (1)–ethanol (2)–water (3)	57	2.11	3.16

[a] M denotes the total number of experimental ternary data points.

[b] $\sum_{i=1}^{M}\left|\left[G_i^E - G_{i,calc}^E\right]\left[G_i^E\right]^{-1}\right| \times 100/M$.

[c] $\sum_{i=1}^{M}\left|\left[\mu_{1,i}^E - \mu_{1,i,calc}^E\right]\left[\mu_{1,i}^E\right]^{-1}\right| \times 100/M$.

TABLE 5

Averaged percentage deviations between the predictions of the H^3M and NRTL models and the reported excess chemical potentials for 1,4-dioxane–ethanol–water

Model	μ_1^E [a] (%)	μ_2^E (%)	μ_3^E (%)
H^3M	7.48	19.98	5.31
NRTL	6.02	18.36	4.10

[a] $\sum_{i=1}^{M}\left|\left[\mu_{1,i}^E - \mu_{1,i,calc}^E\right]\left[\mu_{1,i}^E\right]^{-1}\right| \times 100/M$, where M denotes total number of ternary data points.

TABLE 6

Binary parameters of the H^3M and NRTL models for ternary LLE prediction

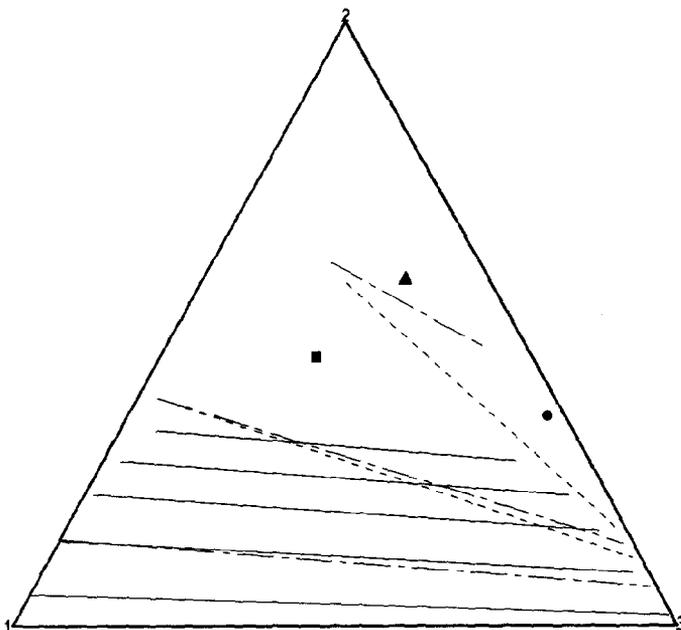| Components (i)–(j)	T (K)			
H^3M		$a_0^{(ij)}$	$a_i^{(ij)}$	$a_j^{(ij)}$
Water (1)–ethanol (2)	323.15	1.21048	0.49041	−0.33801
Water (1)–benzene (3)	318.15	5.0	2.70625	0.23419
Ethanol (2)–benzene (3)	318.15	1.60728	−0.06030	0.76300
NRTL		α_{ij}	$\tau_{ij}T$	$\tau_{ij}T$
Water (1)–ethanol (2)	313.15	0.2946	505.45	−6.8514
Water (1)–benzene (3)	318.15	0.2	1903.0	1095.1
Ethanol (2)–benzene (3)	318.15	0.2899	99.636	638.74

Fig. 1. The system water (1)–ethanol (2)–benzene (3) at 45°C. (- - -, ●) Predicted tie lines and plait point using the NRTL and UNIQUAC models. (— · —, ▲) Predicted tie lines and plait point using H^3M. (——, ■) Experimental tie lines and correlated plait point using ternary data and the UNIQUAC model.

For LLE prediction, we have selected a commonly encountered system, water–ethanol–benzene. For miscible pairs of components, the binary parameters come from binary VLE data (water–ethanol, Chaudhry et al., 1980; ethanol–benzene, Brown and Smith, 1954). We have used binary mutual solubility data to determine two of the binary parameters for the immiscible water–benzene mixture (Sørensen and Arlt, 1979) and kept a_0 constant. The binary parameters together with those for NRTL determined from Sørensen and Arlt are listed in Table 6. The results appear in Fig. 1. Our prediction is considerably better than both the NRTL and UNIQUAC predictions when approaching the plait point, but is still of limited accuracy in the region of the plait point.

Several advantages exist for our new relation. It appears able to correlate any binary G^E data with a single, simple form, which is important for predicting multicomponent properties. Determination of the parameters in our relation is more stable numerically than that of the NRTL relation. It has great flexibility; note that any combination of the binary, ternary, etc. systems can be used to predict the multicomponent system. For example, one ternary mixture can replace three constituent binaries in a multicompo-

TABLE 7

Parameters in eqn. (30) determined from ternary G^E data at 323.15 K

| | System [a] | | |
	A	B	C
$a_0^{(12)}$	0.68901	0.92047	0.53325
$a_1^{(12)}$	9.15258	0.70021	0.42165
$a_2^{(12)}$	−7.30541	0.90411	0.45745
$a_0^{(13)}$	1.75800	2.04623	1.73114
$a_1^{(13)}$	−8.41188	−0.23927	−0.09799
$a_3^{(13)}$	7.39127	0.44075	0.49913
$a_0^{(23)}$	1.12902	1.23085	1.11035
$a_2^{(23)}$	7.11506	−0.58504	−0.32198
$a_3^{(23)}$	−6.10795	0.68418	0.83900

[a] System A: 1,4-dioxane (1)–ethanol (2)–water (3); system B: acetonitrile (1)–ethanol (2)–water (3); system C: acetone (1)–ethanol (2)–water (3).

nent prediction, thus taking advantage of all existing data (not limited to binary data). Also, the chemical potentials can be calculated easily by eqn. (35) without lengthy and tedious differentiation from other composition-dependent empirical G^E models.

Our relation can correlate m-component mixtures. If we allow all the parameters in eqn. (30) to be adjustable, the r.m.s. deviations of the ternary excess Gibbs energy for the systems of Table 1 are correlated within experimental errors. The parameters appear in Table 7 and the r.m.s. deviations of G^E, together with the average percentage deviations between the correlated results and the reported G^E, appear in Table 8. Very small averaged percentage deviations ($\sim 0.2\%$) result for these ternary systems. In short, the simplicity, flexibility, predicting and correlating capability are the

TABLE 8

Root-mean-square and averaged percentage deviations of G^E using our relation as a correlation model

Components	M [a]	R.m.s. dev. [b] (J mol^{-1})	Av. dev. [c] (%)
1,4-Dioxane (1)–ethanol (2)–water (3)	26	0.3	0.02
Acetonitrile (1)–ethanol (2)–water (3)	48	5.6	0.39
Acetone (1)–ethanol (2)–water (3)	57	3.2	0.27

[a] M denotes the total number of experimental ternary data points.

[b] $\{[\sum_{i=1}^{M}(G_i^E - G_{i,\text{calc}}^E)^2][M - n]^{-1}\}^{1/2}$, where n is the number of fitted parameters.

[c] $\sum_{i=1}^{M}\left|\left[G_i^E - G_{i,calc}^E\right]\left[G_i^E\right]^{-1}\right| \times 100/M$.

useful features of our relations; these factors are important in engineering applications.

CONCLUSION

We have developed relations for the excess Gibbs energy and activity coefficients for multicomponent systems using only binary parameters. In our derivation, two-body and three-body intermolecular interactions have been included, and unlike three-body ijk combinations, have been related to three-body binary combinations. These result in a sound theoretical basis for our relations and for their extension to multicomponent systems. Unlike other models, such as van Laar or Margules, which require additional ternary parameters (Wohl expressions) for a satisfactory correlation, our relations can describe multicomponent behavior without any additional adjustable parameters. Our model can correlate any forms of binary G^E data and the results are better than those from the NRTL model with the same number of parameters for irregular G^E binaries. The model also predicts LLE with reasonable accuracy (superior to the NRTL and UNIQUAC models for water–ethanol–benzene).

In addition, a generalized correlation model has been provided for mixtures with complex chemical interactions and/or any number of components. The success of the relations in either predicting or correlating the available ternary data with complex chemical reactions reinforces their usefulness and validity. The correlation capability is within experimental precision and the average percentage deviation of the excess Gibbs energies predicted from binary data is accurate to better than 5%.

LIST OF SYMBOLS

a_i parameters (eqns. (13), (14), (15))
A molar Helmholtz energy
c_i constants (eqns. (4), (5))
G molar Gibbs free energy
k Boltzmann constant
R gas constant (8.314471 J K^{-1} mol^{-1})
T temperature
$\bar{u}$ intermolecular energy
$\delta\bar{u}_{(3,ij)}$ $3\bar{u}_{iij} - \bar{u}_{iii} = 3\bar{u}_{ijj} - \bar{u}_{jjj}$ (eqn. (7))
$\delta\bar{u}_{ij}$ $3\bar{u}_{iij} - 2\bar{u}_{iii} - \bar{u}_{jjj} = 3\bar{u}_{ijj} - \bar{u}_{iii} - 2\bar{u}_{jjj}$ (eqn. (26))
x_i mole fraction of component i
z coordination number

(2)   contribution from two-body interactions

(3)   contribution from three-body interactions

Greek letters

γ_i activity coefficient of component i

ϵ sum of two- and three-body energy terms (eqn. (8))

μ molar chemical potential

Superscripts

E   excess function

(ij) binary mixture

(ijk) ternary mixture

*   apparent

Subscripts

ij individual two-body interaction terms

ijk individual three-body interaction terms

m   mixture

REFERENCES

Abrams, D.S. and Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J., 21: 116–128.

Balcázar-Ortiz, A.M., Patel, R.B., Abbott, M.M. and Van Ness, H.C., 1979. Excess thermodynamic functions for ternary systems. 5. Total-pressure data and G^E for 1,4-dioxane-ethanol–water at 50°C. J. Chem. Eng. Data, 24: 133–136.

Benmekki, E.-H. and Mansoori, G.A., 1988. The role of mixing rules and three-body forces in the phase behavior of mixtures: simultaneous VLE and VLLE calculations. Fluid Phase Equilibria, 41: 43–57.

Bertrand, G.L., Acree, W.E. and Burchfield, T.E., 1983. Thermochemical excess properties of multicomponent systems: representation and estimation from binary mixing data. J. Solution Chem., 12: 327–346.

Brown, I. and Smith, F., 1954. Liquid–vapour equilibria. IV. The system ethanol + benzene at 45°C. Austr. J. Chem., 7: 264–268.

Chao, K.C. and Robinson, R.L., 1986. Equations of state—Theories and Applications. ACS Sym. Ser. 300, American Chemical Society, Washington DC.

Chaudhry, M.M., Van Ness, H.C. and Abbott, M.M., 1980. Excess thermodynamic functions for ternary systems. 6. Total-pressure data and G^E for acetone–ethanol–water at 50°C. J. Chem. Eng. Data, 25; 254–257.

Gierycz, P., 1986. Thermodynamics of mixtures of n-methylpyrrolidone with hydrocarbons and their hydroxyl derivatives. Thermochim. Acta, 108: 229–238.

Goldman, S., 1978. The effect of three-body dispersion forces in liquids on solubilities and related functions. J. Chem. Phys., 69: 3775–3781.

Hamad, E.Z., Mansoori, G.A. and Hall, K.R., 1988. Statistical mechanical test of MHEMHS model of the interaction third virial coefficients. Fluid Phase Equilibria, 43: 205–212.

Kreglewski, A., Marsh, K.N. and Hall, K.R., 1985. A simple relation for the excess functions of nonrandom mixtures. Fluid Phase Equilibria, 21: 25–37.

McGregor, D.R., Holste, J.C., Eubank, P.T., Marsh, K.N., Hall, K.R. and Schouten, J., 1987. An interaction model for third virial coefficients which provides simplified equations for mixtures. Fluid Phase Equilibria, 35: 153–164.

Redlich, O. and Kister, A., 1948. Algebraic representation of thermodynamic properties and the classification of solutions. Ind. Eng. Chem., 40: 345–348.

Renon, H. and Prausnitz, J.M., 1968. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J., 14: 135–144.

Sørensen, J.M. and Arlt, W., 1979. Liquid–liquid equilibrium data collection, Vol. 5, Part 1: p. 341, DECHEMA, Frankfurt/Main.

Wilson, S.R., Patel, R.B., Abbott, M.M. and Van Ness, H.C., 1979. Excess thermodynamic functions for ternary systems. 4. Total-pressure data and G^E for acetonitrile–ethanol–water at 50°C. J. Chem. Eng. Data, 24: 130–132.