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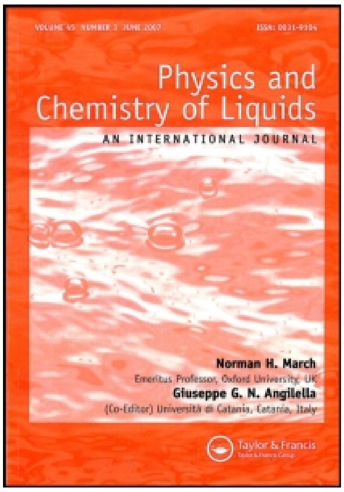

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A NEW PREDICTIVE RELATION FOR TERNARY EXCESS VOLUMES

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Excess volume data, reported in the literature, have been analyzed in light of a new predictive expression which estimates the ternary properties from measured binary data. The analysis showed that the new equation gives an accurate estimate of the excess property for mixtures possessing only dispersion forces. The predictions are also comparable to those computed from relations derived previously.

KEY WORDS: Thermodynamic properties, predictive methods, excess volumes, ternary mixtures.

INTRODUCTION

For years chemical engineers have recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow and heat transfer. The published literature contains thermodynamic data for a large number of binary mixtures, data for ternary systems are relatively scarce, and data for higher-order multicomponent systems are virtually nonexistent. Even with today's modern instrumentation, experimental measurements of thermodynamic properties become progressively more difficult and time-consuming with each additional component beyond binary mixtures. To address this problem, researchers[1–7] tried to develop empirical and semi-empirical equations which permit both reduction/correlation of measured thermodynamic properties and prediction of multicomponent data from binary results. Most attempts were based upon the assumption that multicomponent mixtures include mainly pair-wise interactions. However, Hwang *et al.*[8] recently derived a semi-empirical relationship that includes contributions from both two-body and three-body interactions. The derived expression was found to correlate exactly binary excess free energy data and also to predict fairly accurately ternary free energies of several aqueous-organic systems.

Extension of the basic model to other thermodynamic properties such as enthalpies, heat capacities, volumes, and compressibilities merits consideration. Hence we propose to test the applications and limitations of the newly-derived model using experimental excess volumes of six ternary mixtures together with the results for the constituent binaries. The ternary mixtures include interactions ranging from simple nonspecific physical interactions to much stronger specific interactions. To familiarize readers with the procedure used to derive the new relations, we will first briefly review the derivation as given by Hwang *et al.*[8]

DEVELOPMENT OF BINARY MIXING MODEL AND CORRELATION EXPRESSIONS

Binary mixtures contain two-body interactions (e.g., 1-1, 2-2 and 1-2), and three-body interactions (e.g., 1-1-1, 2-2-2, 1-1-2 and 1-2-2) to a much lesser extent. Higher-order interactions are generally negligible. Random mixing requires that internal energy contributions from all two-body interactions be

$$u_m(2) = x_1^2 u_{11} + x_2^2 u_{22} + 2x_1 x_2 u_{12} \tag{1}$$

and from all three-body interactions be

$$u_m(3) = x_1^3 u_{111} + x_2^3 u_{222} + 3x_1 x_2 (x_1 u^*_{112} + x_2 u^*_{122}) \tag{2}$$

given as a simple summation over all possible interactions, and that the number of each type of interaction must be proportional to a weighted mole fraction product. Molecular interactions between molecules 1 and 2 are counted twice as either 1-2 or 2-1, whereas ternary interactions are triply degenerate. For simplicity the present model is restricted to molecules of comparable size so that Raoult's law will represent a good approximation of the entropic contribution to the overall free energy of mixing.

The apparent three-body interactional parameters u^*_{112} and u^*_{122} are not purely cross-parameters except in infinitely dilute solutions. In a non-random mixture, some 111 and 222 clustering may occur along with mixed collisions. Hence the apparent interactions are concentration dependent. The empirical forms for the apparent interactions at infinite dilution are assumed to be

$$u^*_{112} = u_{112}(1 - c_1 x_1^2) \tag{3}$$

$$u^*_{122} = u_{122}(1 - c_2 x_2^2) \tag{4}$$

where c_1 and c_2 denote constants. Through suitable mathematical manipulation, Eqs. (2)–(4) can be combined as follows

$$\begin{aligned} u_m(3) &= x_1^2 u_{111} + x_2^2 u_{222} + x_1 x_2 [3(x_1 u^*_{112} + x_2 u^*_{122}) - x_1 u_{111} - x_2 u_{222}] \\ &= x_1^2 u_{111} + x_2^2 u_{222} + x_1 x_2 [x_1(3u_{112} - u_{111}) + x_2(3u_{122} - u_{222}) \\ &\quad - 3u_{112} c_1 x_1^3 - 3u_{122} c_2 x_2^3] \end{aligned} \tag{5}$$

The compositional dependence can be further simplified by assuming that

$$3u_{112} - u_{111} = 3u_{122} - u_{222} = \delta u_{(3,12)} \tag{6}$$

where $\delta u_{(3,ij)}$ eliminates the effect of pure three-body interactions, u_{111} and u_{222}, from mixed interactions. The minimum in the molar internal energy, u_m, is the sum of

$$\begin{aligned}
u_m &= u_m(2) + u_m(3) \\
&= x_1^2(u_{11} + u_{111}) + x_2^2(u_{22} + u_{222}) + x_1x_2[2u_{12} + \delta u_{(3,12)} - 3u_{112}c_1x_1^3 \\
&\quad -3u_{122}c_2x_2^3] \\
&= x_1(u_{11} + u_{111}) + x_2(u_{22} + u_{222}) + x_1x_2[2u_{12} + \delta u_{(3,12)} - (u_{11} + u_{111}) \\
&\quad - (u_{22} + u_{222}) - 3u_{112}c_1x_1^3 - 3u_{122}c_2x_2^3] \\
&= x_1\varepsilon_{11} + x_2\varepsilon_{22} + x_1x_2(\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} - 3u_{112}c_1x_1^3 - 3u_{122}c_2x_2^3)
\end{aligned} \tag{7}$$

where $\varepsilon_{11} \equiv u_{11} + u_{111}$, $\varepsilon_{22} \equiv u_{22} + u_{222}$, and $\varepsilon_{12} \equiv 2u_{12} + \delta u_{(3,12)}$.

Recalling that the model assumes that the entropic contribution is described by Raoult's law, u_m is converted to the excess Helmholtz energy,

$$A^E = x_1x_2(a_0 + a_1x_1^3 + a_2x_2^3) \tag{8}$$

by subtracting $(x_1\varepsilon_{11} + x_2\varepsilon_{22})$ from u_m; with $a_0 = -(\varepsilon_{11} + \varepsilon_{22} - \varepsilon_{12})$, $a_1 = -3u_{112}c_1$, and $a_2 = -3u_{122}c_2$. A more rigorous treatment involving chemical lattice theory and coordination numbers is presented elsewhere.[8] Similarly, the model yields the following relation between excess Helmholtz and Gibbs functions

$$G^E = A^E - (\Delta V)^2/2\beta V + \cdots \tag{9}$$

where ΔV denotes volume change on mixing, β is the compressibility and G^E is excess Gibbs free energy. If $(\Delta V)^2/2\beta V$ and higher-order terms are negligible, as will often be the case for pressures not too far removed from 1.0 atm., then the Gibbs and Helmholtz free energies are identical

$$A^E = G^E = x_1x_2(a_0 + a_1x_1^3 + a_2x_2^3) \tag{10}$$

Differentiation of Eq. (10) with respect to pressure and temperature gives the following expressions

$$V^E = x_1x_2(v_0 + v_1x_1^3 + v_2x_2^3) \tag{11}$$

$$H^E = x_1x_2(h_0 + h_1x_1^3 + h_2x_2^3) \tag{12}$$

for the excess volumes and excess enthalpies, respectively. As an informational note, the volumetric and enthalpic coefficients are defined by $v = (\partial a/\partial P)_{T,x}$ and

$h = [\partial(a/T)/\partial T^{-1}]_{P,x}$. Careful examination of the G^E, V^E and H^E-expressions reveals that each one is just a three-parameter mathematical form. Unlike many of the strictly empirical curve-fitting equations suggested in the past, this particular solution model contains no provisions for additional parameters. Based upon our past experience in parameterizing both enthalpic and volumetric data, we fully expect that Eqs. (10)–(12) to adequately describe the behavior of every binary system that might be encountered which contains only nonspecific physical ineractions and/or moderately strong specific interactions of the dipole–dipole type.

DEVELOPMENT OF TERNARY MIXING MODEL AND PREDICTIVE EXPRESSIONS

The basic model presented in the preceding section can be easily extended to ternary and higher-order multicomponent systems. In the case of ternary mixtures, the internal energy is described in terms of six binary interactions

$$u_m(2) = x_1^2 u_{11} + x_2^2 u_{22} + x_3^2 u_{33} + 2x_1x_2u_{12} + 2x_1x_3u_{13} + 2x_2x_3u_{23} \tag{13}$$

and ten ternary interactions

$$\begin{aligned} u_m(3) = {} & x_1^3 u_{111} + x_2^3 u_{222} + x_3^3 u_{333} + 3x_1x_2(x_1u_{112}^* + x_2u_{122}^*) \\ & + 3x_1x_3(x_1u_{113}^* + x_3u_{133}^*) + 3x_2x_3(x_2u_{223}^* + x_3u_{233}^*) + 6x_1x_2x_3u_{123}^* \end{aligned} \tag{14}$$

which result from molecular interactions between similar (u_{ii}) and dissimilar (u_{iij} and u_{ijk}) mixture components. Using steps analogous to those employed in the case of binary mixtures, and remembering that in the ternary mixture the mole fraction compositions are inter-related via $x_1 = 1 - x_2 - x_3$, we rewrite Eq. (14) as follows

$$\begin{aligned} u_m(3) = {} & x_1^2 u_{111} + x_2^2 u_{222} + x_3^2 u_{333} + x_1x_2[(x_1 + x_2)\delta u_{(3,12)} - 3u_{112}c_1^{(12)}x_1^3 \\ & - 3u_{122}c_2^{(12)}x_2^3] + x_1x_3[(x_1 + x_3)\delta u_{(3,13)} - 3u_{113}c_1^{(13)}x_1^3 - 3u_{133}c_3^{(13)}x_3^3] \\ & + x_2x_3[(x_2 + x_3)\delta u_{(3,23)} - 3u_{223}c_2^{(23)}x_2^3 - 3u_{233}c_3^{(23)}x_3^3] + 6x_1x_2x_3u_{123}^* \end{aligned} \tag{15}$$

In order to reduce the compositional dependence of the terms in the parentheses, one first assumes that

$$3u_{123}^* = u_{111} + u_{222} + u_{333} + 1/2(\delta u_{12} + \delta u_{13} + \delta u_{23}) \tag{16}$$

and then uses the resulting approximation to expand Eq. (6) to

$$\begin{aligned} \delta u_{ij} &= (3u_{iij} - u_{iii}) - u_{iii} - u_{jjj} = (3u_{ijj} - u_{jjj}) - u_{iii} - u_{jjj} \\ &= \delta u_{3,ij} - u_{iii} - u_{jjj} \end{aligned} \tag{17}$$

ternary systems. Direct substitution of Eq. (17) into Eq. (16) yields

$$\begin{aligned} u_{123} &= 1/6[(3u_{112} - u_{111}) + (3u_{133} - u_{333}) + (3u_{223} - u_{222})] \\ &= 1/6[\delta u_{(3,12)} + \delta u_{(3,13)} + \delta u_{(3,23)}] \end{aligned} \tag{18}$$

a mathematical relationship between the three-body 123 interactional term and the various binary combinations, which should be applicable in the case of small, dissimilar three-body interactions.

After suitable algebraic manipulation of Eqs. (13)–(18), the internal energy and excess molar Gibbs free energy of the ternary mixture can be expressed by the equations

$$\begin{aligned} u_m &= x_1\varepsilon_{11} + x_2\varepsilon_{22} + x_3\varepsilon_{33} \\ &\quad + x_1x_2(\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} - 3u_{112}c_1^{(12)}x_1^3 - 3u_{122}c_2^{(12)}x_2^3) \\ &\quad + x_1x_3(\varepsilon_{13} - \varepsilon_{11} - \varepsilon_{33} - 3u_{113}c_1^{(13)}x_1^3 - 3u_{133}c_3^{(13)}x_3^3) \\ &\quad + x_2x_3(\varepsilon_{23} - \varepsilon_{22} - \varepsilon_{33} - 3u_{223}c_2^{(23)}x_2^3 - 3u_{233}c_3^{(23)}x_3^3) \end{aligned} \tag{19}$$

$$\begin{aligned} G^{E(123)} &= x_1x_2(a_0^{(12)} + a_1^{(12)}x_1^3 + a_2^{(12)}x_2^3) + x_1x_3(a_0^{(13)} + a_1^{(13)}x_1^3 + a_2^{(13)}x_3^3) \\ &\quad + x_2x_3(a_0^{(23)} + a_1^{(23)}x_2^3 + a_2^{(23)}x_3^3) \end{aligned} \tag{20}$$

Again the entropic contribution to the configurational entropy has been described in terms of Raoult's law, and the various ε_{ii} and ε_{ij} are defined in accordance with the binary reduction.

Differentiation of G^E with respect to pressure and temperature gives the following expressions for the excess volume

$$\begin{aligned} V^{E(123)} &= x_1x_2(v_0^{(12)} + v_1^{(12)}x_1^3 + v_2^{(12)}x_2^3) + x_1x_3(v_0^{(13)} + v_1^{(13)}x_1^3 + v_2^{(13)}x_3^3) \\ &\quad + x_2x_3(v_0^{(23)} + v_1^{(23)}x_2^3 + v_2^{(23)}x_3^3) \end{aligned} \tag{21}$$

and

$$\begin{aligned} H^{E(123)} &= x_1x_2(h_0^{(12)} + h_1^{(12)}x_1^3 + h_2^{(12)}x_2^3) + x_1x_3(h_0^{(13)} + h_1^{(13)}x_1^3 + h_2^{(13)}x_3^3) \\ &\quad + x_2x_3(h_0^{(23)} + h_1^{(23)}x_2^3 + h_2^{(23)}x_3^3) \end{aligned} \tag{22}$$

The nine v- and h-coefficients can be obtained by either curve-fitting binary volumetric and enthalpic data or by parameterizing experimental ternary data. From an operational standpoint, the former method is preferred in that experimental ternary data are relatively scarce, and it is far less time-consuming to compute three sets of three parameters each than one large set of nine parameters.

RESULTS AND DISCUSSION

Excess volumes of six select ternary mixtures and the corresponding constituent binaries were retrieved from the published literature.[9–14] The ternary mixtures are listed in Table 1, along with the various binary parameters, which were computed from the smoothed experimental data at mole fraction compositions of $x_i = 0.2$, 0.5 and 0.8. The actual numerical values of the v-coefficients are determined by the compositions used. Our three mole fractions were selected in order to try to minimize root mean squared deviations between experimental and back calculated values. Small errors/uncertainties in the v-coefficients do not significantly affect V^E-computations near the two pure components because one is always multiplying by a decreasing $x_i x_j$ term. Uncertainties become more important; however, near the equimolar composition where $x_i x_j$ reaches its maximum value of $x_i x_j = 0.25$. Results of our present calculations indicated that Eq. (11) correlated excess volume data for the 18 binary systems to within the estimated experimental uncertainties.

Next the ternary excess volumes were predicted using Equation (21) and the binary parameters. The averaged percentage deviations between predicted and reported excess volumes are given in Table 2 along with the number of data points for each mixture. The deviations are close to experimental error in the first three mixtures which include mainly dispersion forces. Hence the new equation gives an accurate

Table 1 The ternary and binary mixtures and the parameters determined from binary V^E data

Ternary/binary mixtures	$v_0^{(ij)}$	$v_1^{(ij)}$	$v_2^{(ij)}$
n-Heptane (1) + *n*-nonane (2) + cyclohexane (3)			
n-Heptane (1) + *n*-nonane (2)	−0.2352	−0.0174	0.0652
n-Heptane (1) + cyclohexane (3)	1.0999	−0.2339	0.8851
n-Nonane (2) + cyclohexane (3)	1.7080	−0.3609	1.2324
Carbon tetrachloride (1) + benzene (2) + *p*-xylene (3)			
Carbon tetrachloride (1) + benzene (2)	0.0430	0.0000	0.0000
Carbon tetrachloride (1) + *p*-xylene (3)	−0.0311	0.0033	−0.0120
Benzene (2) + *p*-xylene (3)	0.8313	0.0954	−0.1965
Methylene bromide (1) + benzene (2) + toluene (3)			
Methylene bromide (1) + benzene (2)	0.9850	−0.2619	−0.7381
Methylene bromide (1) + toluene (3)	0.7608	0.0059	−0.1726
Benzene (2) + toluene (3)	0.4173	−0.1768	−0.2816
Methylene bromide (1) + pyridine (2) + *β*-picoline (3)			
Methylene bromide (1) pyridine (2)	1.2073	0.1578	−0.0565
Methylene bromide (1) + *β*-picoline (3)	1.4280	0.2342	−0.6182
Pyridine (2) + *β*-picoline (3)	0.1893	−0.1190	−0.1476
1,1,1-Trichloroethane (1) + 1-propanol (2) + *n*-heptane (3)			
1,1,1-Trichloroethane (1) + 1-propanol (2)	−0.0396	1.6610	−0.3439
1,1,1-Trichloroethane (1) + *n*-heptane	1.9917	0.2118	−0.9691
1-Propanol (2) + *n*-heptane (3)	1.3986	−0.7258	0.3150
Methyl ethyl ketone (1) + 1-propanol (2) + *n*-octane (3)			
Methyl ethyl ketone (1) + 1-propanol (2)	−0.1748	0.0303	0.0012
Methyl ethyl ketone (1) + *n*-octane (3)	3.5344	−0.8120	0.2330
1-Propanol (2) + *n*-octane (3)	1.7726	0.4561	−0.6867

Table 2 Average percentage deviations between predicted and experimental excess volumes

Ternary mixtures	*M*[a]	*Deviations*[b]
n-Heptane (1) + *n*-nonane (2) + cyclohexane (3)	37	4.48
Carbon tetrachloride (1) + benzene (2) + *p*-xylene (3)	11	5.30
Methylene bromide (1) + benzene (2) + toluene (3)	13	6.45
Methylene bromide (1) + pyridine (2) + *β*-picoline (3)	18	12.19
1,1,1-Trichloroethane (1) + 1-propanol (2) + *n*-heptane (3)	10	13.23
Methyl ethyl ketone (1) + 1-propanol (2) + *n*-octane (3)	9	9.91

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

[b] Deviations (%) $= (100/M) \sum_{i=1}^{M} |[V_i^E - V_{i,\text{calc}}^E]/[V_i^E]|$.

estimate of ternary excess volume from those of the constituent binaries. However, deviations for ternary mixtures: methylene bromide + pyridine + *β*-picoline; 1,1,1-trichloroethane + 1-propanol + *n*-heptane; and methyl ethyl ketone + 1-propanol + *n*-octane, far exceed experimental uncertainty. This may be ascribed to presence of dipolar and strong specific interactions, viz., hydrogen bonding between like and unlike molecules. Finally the predictions of the new equation are comparable to those of the Redlich–Kister,[1] BAB,[2–4] Kohler,[6] Jacob-Fitzner[7] and other empirical expressions[15–17] which have been derived previously. More detailed comparisons of the predictive abilities of Eqs. (21) and (22) will be presented in subsequent papers.

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References

1. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 135 (1948).
2. G. L. Bertrand, W. E. Acree, Jr. and T. E. Burchfield, *J. Solution Chem.*, **12**, 327 (1983).
3. W. E. Acree, Jr. and G. L. Bertrand, *J. Solution Chem.*, **12**, 755 (1983).
4. J. W. McCargar and W. E. Acree, Jr., *Thermochim. Acta*, **149**, 363 (1989).
5. C. C. Tsao and J. M. Smith, Applied Thermodynamics, *Chem. Eng. Prog. Symp., Series No. 7*, 107 (1953).
6. F. Kohler, *Monatsh. Chem.*, **91**, 738 (1960).
7. K. T. Jacob and K. Fitzner, *Thermochim. Acta*, **18**, 197 (1977).
8. C.-A. Hwang, J. C. Holste, K. R. Hall and G. A. Mansoori, *Fluid Phase Equilibr.*, **62**, 173 (1991).
9. J. A. Somoza, M. Garcia, C. Rey, J. R. Rodriguez and V. P. Villar, *J. Chem. Thermodyn.*, **16**, 1053 (1984).
10. R. P. Rastogi, J. Nath and S. S. Das, *J. Chem. Eng. Data*, **22**, 249 (1977).
11. P. P. Singh and V. K. Sharma, *Can. J. Chem.*, **61**, 2321 (1983).
12. P. P. Singh, R. K. Nigam, S. P. Sharma and S. Aggarwal, *Fluid Phase Equilibr.*, **18**, 333 (1986).
13. U. Srinivasulu and P. R. Naidu, *Ind. J. Technol.*, **27**, 577 (1989).
14. G. R. Naidu and P. R. Naidu, *J. Chem. Eng. Data*, **27**, 57 (1982).
15. W. E. Acree, Jr., *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, Inc., Orlando, FL (1984), Chapter 4.
16. J. M. Prausnitz, R. N. Lichtenthaler and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd edition, Prentice-Hall, Englewood Cliffs, NJ (1986), Chapters 6 and 7.
17. C. Pando, J. A. R. Renuncio, J. A. G. Calzon, J. J. Christensen and R. M. Izatt, *J. Solution Chem.*, **16**, 503 (1987).