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I.-Lih Teng^a; William E. Acree Jr.^a

^a Department of Chemistry, University of North Texas, Denton, Texas, USA

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THERMODYNAMIC PROPERTIES OF TERNARY NONELECTROLYTE SOLUTIONS. TWO- AND THREE-BODY MODELS FOR PREDICTING EXCESS MOLAR VOLUMES OF CHLOROBENZENE + DIBUTYL ETHER + ALKANE MIXTURES

I-LIH TENG and WILLIAM E. ACREE, Jr.*

*Department of Chemistry, University of North Texas,
Denton, Texas 76203-5068 USA*

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Excess molar volumes have been determined for ternary chlorobenzene + dibutyl ether + cyclohexane, chlorobenzene + dibutyl ether + *n*-heptane, chlorobenzene + dibutyl ether + *n*-octane, and chlorobenzene + dibutyl ether + 2,2,4-trimethylpentane at 25°C. Results of these measurements are used to test the applications and limitations of a newly-derived predictive cubic expression for excess volumes based upon both two-body and three-body interactions. For the four ternary systems studied, the cubic expression was found to give predictions comparable to those of four previously derived equations. Differences between experimental and predicted excess molar volumes were circa $\delta V_{m,123}^E = \pm 0.030 \text{ cm}^3 \text{ mol}^{-1}$ or less at most ternary compositions.

KEY WORDS: Three-body interactions, non-electrolytes, excess molar volumes, ternary solutions

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. Development of flow calorimeters, continuous dilution dilatometers and vibrating-tube desimeters has enabled the experimental determination of excess enthalpies, heat capacities and volumes of nonelectrolyte liquid mixtures with convenience and accuracy. Continuous dilution methods, combined with chromatographic head-space sampling techniques, has reduced the experimental time needed for determination of excess Gibbs free energies and activity coefficients through conventional vapor pressure measurements. But even with today's modern instrumentation, experimental measurement of thermodynamic properties become progressively more difficult and time-consuming with each additional component beyond binary mixtures. To address this problem, researchers have turned to predictive methods to generate desired multicomponent properties.

* To whom correspondence should be addressed.

The majority of predictive expressions found in the chemical literature (see References 1–3 for a review) can be divided into one of two broadly defined categories, depending upon whether the method combines actual experimental binary data or requires curve-fitting coefficients based upon a specific mathematical reduction. The Kohler equation⁴

$$\begin{aligned} Z_{m,123}^E &= (x_1 + x_2)^2 Z_{m,12}^E [\text{at } x_1/(x_1 + x_2), x_2/(x_1 + x_2)] \\ &\quad + (x_1 + x_3)^2 Z_{m,13}^E [\text{at } x_1/(x_1 + x_3), x_3/(x_1 + x_3)] \\ &\quad + (x_2 + x_3)^2 Z_{m,23}^E [\text{at } x_2/(x_2 + x_3), x_3/(x_2 + x_3)] \end{aligned} \quad (1)$$

the Jacob–Fitzner equation,⁵

$$\begin{aligned} Z_{m,123}^E &= x_1 x_2 [x_1 + x_3/2]^{-1} [x_2 + x_3/2]^{-1} Z_{m,12}^E [\text{at } x_1 + x_3/2; x_2 + x_3/2] \\ &\quad + x_1 x_3 [x_1 + x_2/2]^{-1} [x_3 + x_2/2]^{-1} Z_{m,13}^E [\text{at } x_1 + x_2/2; x_3 + x_2/2] \\ &\quad + x_2 x_3 [x_2 + x_1/2]^{-1} [x_3 + x_1/2]^{-1} Z_{m,23}^E [\text{at } x_2 + x_1/2; x_3 + x_1/2] \end{aligned} \quad (2)$$

and the BAB equation^{6,7}

$$\begin{aligned} Z_{m,123}^E &= (x_1 + x_2)(f_1 + f_2) Z_{m,12}^E [\text{at } x_1/(x_1 + x_2), x_2/(x_1 + x_2)] \\ &\quad + (x_1 + x_3)(f_1 + f_3) Z_{m,13}^E [\text{at } x_1/(x_1 + x_3), x_3/(x_1 + x_3)] \\ &\quad + (x_2 + x_3)(f_2 + f_3) Z_{m,23}^E [\text{at } x_2/(x_2 + x_3), x_3/(x_2 + x_3)] \end{aligned} \quad (3)$$

where $f_1 = x_1 \Gamma_1 / (x_1 \Gamma_1 + x_2 \Gamma_2 + x_3 \Gamma_3)$, etc., would fall into the first category. The various symbols are defined in the Appendix at the end of the manuscript. Each equation requires a prior knowledge of the ternary composition and the thermodynamic excess properties of the three contributing sub-binary systems at specific mole fractions, $Z_{m,ij}^E$ [at x_i^0, x_j^0]. The binary data could be available in the literature in tabular or graphical form, or as coefficients of some arbitrarily determined least squares equation. Predictive methods that fall into the second broad category would include predictive forms of the Redlich–Kister equation⁸

$$\begin{aligned} Z_{m,123}^E &= x_1 x_2 [A_{12} + B_{12}(x_1 - x_2)^2 + C_{12}(x_1 - x_2)^3 + \dots] \\ &\quad + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3)^2 + C_{13}(x_1 - x_3)^3 + \dots] \\ &\quad + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3)^2 + C_{23}(x_2 - x_3)^3 + \dots] \end{aligned} \quad (4)$$

and Wilson equation⁹

$$\begin{aligned} G_{m,123}^E &= RT [x_1 \ln(x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}) + x_2 \ln(x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}) \\ &\quad + x_3 \ln(x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3)] \end{aligned} \quad (5)$$

just to list a couple. The various A_{ij} , B_{ij} , C_{ij} , Λ_{ij} , etc. coefficients are obtained by parameterizing experimental binary data in accordance with the appropriate binary reduction of Eqs. 4 and 5.

The afore-mentioned Kohler, Jacob–Fitzner, BAB and Wilson models, along with many others found in the chemical literature,^{1–4,10–16} assume that multi-component mixtures include mainly pair-wise binary interactions. Higher-order molecular interactions were neglected in order to arrive at a tractable predictive expression. However, Hwang *et al.*¹⁷ 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 isothermal compressibilities merits consideration. To pursue this idea further, we report experimentally determined excess molar volumes for ternary chlorobenzene + dibutyl ether + cyclohexane, chlorobenzene + dibutyl ether + *n*-heptane, chlorobenzene + dibutyl ether + *n*-octane, and chlorobenzene + dibutyl ether + 2,2,4-trimethylpentane mixtures at 25.0°C. Volumetric properties of the remaining nine sub-binaries are published elsewhere.^{18,19} Results of these measurements are compared to predicted values based upon the Kohler, Redlich–Kister, BAB and Hwang *et al.* equations.

EXPERIMENTAL METHOD

Chlorobenzene (Aldrich HPLC, 99.9 + %), *n*-heptane (Aldrich HPLC, 99 + %), cyclohexane (Aldrich HPLC, 99.9 + %), *n*-octane (Aldrich, 99 + % anhydrous), 2,2,4-trimethylpentane (Aldrich HPLC, 99.7 + %), and dibutyl ether (Aldrich, 99 + % anhydrous) were stored over molecular sieves to remove trace amounts of water. Gas chromatographic analysis showed solvent purities to be 99.8% (or better), which is well within the manufacturer's stated claims. Ternary solvent mixtures were prepared by weight so that concentrations could be calculated to 0.0001 mole fraction.

Densities were measured with an Anton PAAR DMA 55 calculating precision density meter thermostated with a Neslab closed-loop refrigerating constant temperature bath. The reproducibility of the programmable circulating thermostat was better than 0.005 K while fluctuations in the bath temperature were within 0.003 K during the actual time required for each series of measurements. Samples were pre-equilibrated in the temperature bath for over 30 minutes and then introduced into the vibrating densimeter tube via a glass syringe. One of the pure solvents was periodically run after several binary/ternary mixtures, and the measured density for the pure liquid was used in V_m^E computations. Picker *et al.*²⁰ describe the mechanical design and precision of vibrating-tube densimeters, as well as the calculational methods, in greater detail.

DEVELOPMENT OF BINARY MIXING MODEL AND CORRELATION EXPRESSIONS

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.*¹⁷ 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

$$u_m(2) = x_1^2 u_{11} + x_2^2 u_{22} + 2x_1 x_2 u_{12} \quad (6)$$

and from all three-body interactions be

$$u_m(3) = x_1^3 u_{111} + x_2^3 u_{222} + 3x_1 x_2 (x_1 u_{112}^* + x_2 u_{122}^*) \quad (7)$$

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

$$u_{112}^* = u_{112}(1 - c_1 x_1^2) \quad (8)$$

$$u_{122}^* = u_{122}(1 - c_2 x_2^2) \quad (9)$$

where c_1 and c_2 denote constants. Through suitable mathematical manipulation, Eqs. (7)–(9) can be combined as follows

$$\begin{aligned} u_m(3) &= x_1^2 u_{111} + x_2^2 u_{222} + x_1 x_2 [3(x_1 u_{112}^* + x_2 u_{122}^*) - x_1 u_{111} - x_2 u_{222}] \\ &= x_1^2 u_{111} + x_2^2 u_{222} + x_1 x_2 [x_1(3u_{112} - u_{111}) + x_2(3u_{122} - u_{222}) \\ &\quad - 3u_{112}c_1 x_1^3 - 3u_{122}c_2 x_2^3] \end{aligned} \quad (10)$$

The compositional dependence can be further simplified by assuming that

$$3u_{112} - u_{111} = 3u_{122} - u_{222} = \delta u_{(3,12)} \quad (11)$$

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

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

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

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

$$A^E = x_1x_2(a_0 + a_1x_1^3 + a_2x_2^3) \quad (13)$$

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.¹⁷ Similarly, the model yields the following relation between excess Helmholtz and Gibbs functions

$$G^E = A^E - (\Delta V)^2/2\beta V + \dots \quad (14)$$

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 case for pressures not too far removed from 1.0 atm., then the Gibbs and Helmholtz free energies are identical

$$A^E = G^E = x_1x_2(a_0 + a_1x_1^3 + a_2x_2^3) \quad (15)$$

Differentiation of Eq. (15) with respect to pressure and temperature gives the following expressions

$$V^E = x_1x_2(v_0 + v_1x_1^3 + v_2x_2^3) \quad (16)$$

$$H^E = x_1x_2(h_0 + h_1x_1^3 + h_2x_2^3) \quad (17)$$

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. (15)–(17) to adequately describe the behavior of every binary system that might be encountered which contains only nonspecific physical interactions 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

$$u_m(2) = x_1^2 + x_2^2 u_{22} + x_3^2 u_{33} + 2x_1 x_2 u_{12} + 2x_1 x_3 u_{13} + 2x_2 x_3 u_{23} \quad (18)$$

and ten ternary interactions

$$u_m(3) = x_1^3 u_{111} + x_2^3 u_{222} + x_3^3 u_{333} + 3x_1 x_2 (x_1 u_{112}^* + x_2 u_{122}^*) + 3x_1 x_3 (x_1 u_{113}^* + x_3 u_{133}^*) + 3x_2 x_3 (x_2 u_{223}^* + x_3 u_{233}^*) + 6x_1 x_2 x_3 u_{123}^* \quad (19)$$

which result from molecular interactions between similar (u_{ii}) and dissimilar (u_{ij} 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. (19) as follows

$$u_m(3) = x_1^2 u_{111} + x_2^2 u_{222} + x_3^2 u_{333} + x_1 x_2 [(x_1 + x_2) \delta u_{(3,12)} - 3u_{112} c_1^{(12)} x_1^3 - 3u_{122} c_2^{(12)} x_2^3] + x_1 x_3 [(x_1 + x_3) \delta u_{(3,13)} - 3u_{113} c_1^{(13)} x_1^3 - 3u_{133} c_3^{(13)} x_3^3] + x_2 x_3 [(x_2 + x_3) \delta u_{(3,23)} - 3u_{223} c_2^{(23)} x_2^3 - 3u_{233} c_3^{(23)} x_3^3] + 6x_1 x_2 x_3 u_{123}^* \quad (20)$$

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

$$3u_{123}^* = u_{111} + u_{222} + u_{333} + 1/2(\delta u_{12} + \delta u_{13} + \delta u_{23}) \quad (21)$$

and then uses the resulting approximation to expand Eq. (11) to

$$\begin{aligned} \delta u_{ij} &= (3u_{ijj} - u_{iii}) - u_{iii} - u_{jjj} \\ &= (3u_{ijj} - u_{jjj}) - u_{iii} - u_{jjj} \\ &= \delta u_{3,ij} - u_{iii} - u_{jjj} \end{aligned} \quad (22)$$

ternary systems. Direct substitution of Eq. (22) into Eq. (21) yields

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

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. (18)–(23), the internal energy and excess molar Gibbs free energy of the ternary mixture can be expressed by the equations

$$\begin{aligned} u_m &= x_1 \varepsilon_{11} + x_2 \varepsilon_{22} + x_3 \varepsilon_{33} \\ &+ x_1 x_2 (\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} - 3u_{112} c_1^{(12)} x_1^3 - 3u_{122} c_2^{(12)} x_2^3) \\ &+ x_1 x_3 (\varepsilon_{13} - \varepsilon_{11} - \varepsilon_{33} - 3u_{113} c_1^{(13)} x_1^3 - 3u_{133} c_3^{(13)} x_3^3) \\ &+ x_2 x_3 (\varepsilon_{23} - \varepsilon_{22} - \varepsilon_{33} - 3u_{223} c_2^{(23)} x_2^3 - 3u_{233} c_3^{(23)} x_3^3) \end{aligned} \quad (24)$$

$$\begin{aligned} G^{E(123)} &= x_1 x_2 (a_0^{(12)} + a_1^{(12)} x_1^3 + a_2^{(12)} x_2^3) \\ &+ x_1 x_3 (a_0^{(13)} + a_1^{(13)} x_1^3 + a_2^{(13)} x_3^3) \\ &+ x_2 x_3 (a_0^{(23)} + a_1^{(23)} x_2^3 + a_2^{(23)} x_3^3) \end{aligned} \quad (25)$$

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

$$\begin{aligned} V^{E(123)} &= x_1 x_2 (v_0^{(12)} + v_1^{(12)} x_1^3 + v_2^{(12)} x_2^3) + x_1 x_3 (v_0^{(13)} + v_1^{(13)} x_1^3 + v_3^{(13)} x_3^3) \\ &+ x_2 x_3 (v_0^{(23)} + v_1^{(23)} x_2^3 + v_2^{(23)} x_3^3) \end{aligned} \quad (26)$$

and

$$\begin{aligned} H^{E(123)} &= x_1 x_2 (h_0^{(12)} + h_1^{(12)} x_1^3 + h_2^{(12)} x_2^3) + x_1 x_3 (h_0^{(13)} + h_1^{(13)} x_1^3 + h_2^{(13)} x_3^3) \\ &+ x_2 x_3 (h_0^{(23)} + h_1^{(23)} x_2^3 + h_2^{(23)} x_3^3) \end{aligned} \quad (27)$$

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.

COMPARISON OF EXPERIMENTAL AND PREDICTED VALUES

Experimental data for the four ternary systems, at 22 different mole fraction compositions, are given in Table 1. Uncertainties in the reported $V_{m,123}^E$ are believed to be on the order of *circa* $\pm 0.01 \text{ cm}^3 \text{ mol}^{-1}$ based upon replicate density determinations and error propagations. Chemical impurities could conceivably result in a systematic error which would not be detected in the replicate measurements. As argued by Lepori *et al.*²¹ in an investigation on sources of errors in V_m^E , purity of substances is not a crucial factor if the contaminant is non-reactive. In the case of a mixture of compounds 1 and 2, obeying a one-parameter equation of the $V_{m,12}^E = x_1 x_2 v_{12}$ type, the effect of a single impurity (component 4) contaminating solvent 1 can be evaluated through

$$\delta V_{m,12}^E / V_{m,12}^E = (1 - P_1)(v_{24} - v_{14}P_1 - v_{12})/v_{12} \quad (28)$$

where P_1 is the degree of purity (in mole fraction) of component 1 and v_{ij} is the parameter for mathematically describing $V_{m,ij}^E$. Generally, an impurity is chemically very similar to the contaminated solvent, i.e., $v_{12} \approx v_{24}$ and $v_{14} < v_{12}$, so that the systematic error in $V_{m,12}^E$ is less than $(1 - P_1)$, or less than $\pm 1\%$ in the present study. The above argument can be readily extended to ternary systems, where trace non-reactive impurities could be present in either one, two or all three of the presumably "pure" solvents.

Inspection of Table 2 reveals that Eq. (26) provides very reasonable estimates of the excess molar volumes of ternary chlorobenzene + dibutyl ether + alkane mixtures. Differences between measured and calculated $V_{m,123}^E$ values were *circa* $\pm 0.030 \text{ cm}^3 \text{ mol}^{-1}$ (or less) at most of the ternary compositions studied, which is only slightly larger than the estimated experimental uncertainty. The various $v_0^{(ij)}$, $v_1^{(ij)}$ and $v_2^{(ij)}$ coefficients used in the $V_{m,123}^E$ predictions were computed from the smoothed experimental binary data^{18,19} at mole fractions of $x_i = 0.20, 0.50$ and 0.80 . The actual numerical values of the v -coefficients depend upon the compositions used. Our three mole fractions were judiciously selected in order to minimize root mean squared deviations between experimental and back-calculated values. Small errors/uncertainties in the v -coefficients do not significantly affect $V_{m,ij}^E$ 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 $x_i x_j = 0.25$. As shown in Table 3 the binary reduction of the cubic model, Eq. (16), gives an excellent mathematical representation of the excess molar volume data of all nine subbinaries.

Also included in Table 2 are the corresponding predictions based upon the Redlich-Kister, Kohler, Jacob-Fitzner and BAB equations discussed in the Introduction section. The BAB weighting factors were evaluated in a relative sense (Γ_i/Γ_j) from the measured binary data. To insure that these ratios obey

$$\Gamma_1/\Gamma_3 = (\Gamma_1/\Gamma_2)(\Gamma_2/\Gamma_3) \quad (29)$$

Table 1 Excess molar volumes ($\text{cm}^3 \text{mol}^{-1}$) of ternary chlorobenzene + dibutyl ether + alkane mixtures at 25.0°C.

x_1	x_2	$V_{m,123}^E$	x_1	x_2	$V_{m,123}^E$
Chlorobenzene (1) + dibutyl ether (2) + cyclohexane (3)					
0.1145	0.0667	0.259	0.7633	0.1317	-0.166
0.5369	0.0635	0.203	0.2860	0.1732	0.228
0.7399	0.0617	0.028	0.3212	0.3860	-0.042
0.1323	0.3897	0.255	0.5674	0.1666	-0.023
0.1282	0.6132	0.086	0.3980	0.2351	0.063
0.8391	0.0609	-0.059	0.4834	0.2904	-0.138
0.6857	0.2007	-0.245	0.2406	0.2908	0.169
0.5015	0.3784	-0.329	0.4472	0.1308	0.154
0.2806	0.5885	-0.226	0.2207	0.1317	0.271
0.1529	0.7066	-0.078	0.6684	0.1317	-0.063
0.6001	0.2891	-0.312	0.2685	0.4753	-0.061
Chlorobenzene (1) + dibutyl ether (2) + <i>n</i> -heptane (3)					
0.1370	0.0847	-0.088	0.7820	0.1300	-0.334
0.6041	0.0722	-0.321	0.3370	0.1951	-0.280
0.7786	0.0648	-0.280	0.3386	0.4243	-0.374
0.1358	0.4512	-0.130	0.6079	0.1811	-0.396
0.1495	0.6441	-0.202	0.4356	0.2617	-0.385
0.8595	0.0609	-0.236	0.5120	0.3089	-0.471
0.7091	0.2080	-0.432	0.2824	0.3302	-0.284
0.5194	0.3927	-0.503	0.4936	0.1524	-0.371
0.2939	0.6074	-0.413	0.2668	0.1595	-0.207
0.1513	0.7455	-0.247	0.7070	0.1379	-0.372
0.6163	0.2910	-0.483	0.2771	0.5114	-0.344
Chlorobenzene (1) + dibutyl ether (2) + <i>n</i> -octane (3)					
0.1504	0.0813	0.021	0.7908	0.1375	-0.293
0.6187	0.0763	-0.165	0.3463	0.2077	-0.120
0.7876	0.0670	-0.194	0.3567	0.4165	-0.290
0.1579	0.4637	-0.074	0.6199	0.1864	-0.287
0.1494	0.6579	-0.155	0.4528	0.2688	-0.263
0.8655	0.0615	-0.168	0.5116	0.3092	-0.344
0.7031	0.2175	-0.383	0.2808	0.3533	-0.138
0.5276	0.3907	-0.476	0.5149	0.1585	-0.201
0.2947	0.6080	-0.373	0.2823	0.1644	-0.065
0.1522	0.7466	-0.244	0.7060	0.1417	-0.269
0.6276	0.2971	-0.446	0.2865	0.5248	-0.255
Chlorobenzene (1) + dibutyl ether (2) + 2,2,4-trimethylpentane					
0.1492	0.0941	-0.170	0.7946	0.1367	-0.367
0.6302	0.0723	-0.404	0.3558	0.2175	-0.424
0.7889	0.0668	-0.327	0.3594	0.4257	-0.486
0.1527	0.4788	-0.297	0.6218	0.1871	-0.481
0.1544	0.6568	-0.296	0.4576	0.2724	-0.491
0.8665	0.0603	-0.251	0.5284	0.3161	-0.537
0.7067	0.2172	-0.468	0.2880	0.3505	-0.431
0.5263	0.3926	-0.554	0.5241	0.1545	-0.456
0.2982	0.6122	-0.458	0.2835	0.1743	-0.338
0.1614	0.7398	-0.301	0.7149	0.1410	-0.435
0.6271	0.2970	-0.519	0.2973	0.5247	-0.448

Table 2 Summarized comparison between experimental excess molar volumes of ternary chlorobenzene + dibutyl ether + alkane mixtures and predicted values based upon the Hwang *et al.*, Redlich-Kister, Kohler, Jacob-Fitzner and BAB models.

<i>Ternary system</i>	<i>Dev.</i> ^a
Chlorobenzene (1) + dibutyl ether (2) + cyclohexane (3)	
Hwang <i>et al.</i> cubic model (Eq. 26)	0.027
Redlich-Kister model (Eq. 4)	0.031
Kohler model (Eq. 1)	0.035
Jacob-Fitzner model (Eq. 2)	0.031
BAB model (Eq. 3)	0.041
Chlorobenzene (1) + dibutyl ether (2) + <i>n</i> -heptane (3)	
Hwang <i>et al.</i> cubic model (Eq. 26)	0.009
Redlich-Kister model (Eq. 4)	0.009
Kohler model (Eq. 1)	0.012
Jacob-Fitzner model (Eq. 2)	0.009
BAB model (Eq. 3)	0.037
Chlorobenzene (1) + dibutyl ether (2) + <i>n</i> -octane (3)	
Hwang <i>et al.</i> cubic model (Eq. 26)	0.016
Redlich-Kister model (Eq. 4)	0.019
Kohler model (Eq. 1)	0.023
Jacob-Fitzner model (Eq. 2)	0.019
BAB model (Eq. 3)	0.014 ^b
Chlorobenzene (1) + dibutyl ether (2) + 2,2,4-trimethylpentane (3)	
Hwang <i>et al.</i> cubic model (Eq. 26)	0.013
Redlich-Kister model (Eq. 4)	0.010
Kohler model (Eq. 1)	0.015
Jacob-Fitzner model (Eq. 2)	0.010
BAB model (Eq. 3)	0.030

^a Dev. = $\{\sum [(V_m^E)^{\text{exp}} - (V_m^E)^{\text{calc}}]^2 / (n-1)\}^{1/2}$, units are cm³ mol⁻¹.

^b Weighting factors approximated with molar volumes.

Table 3 Curve-fitting coefficients of the Hwang *et al.* cubic equation obtained from binary excess molar volume data.

<i>Component (i) + component (j)</i>	$v_0^{(ij)}$	$v_1^{(ij)}$	$v_2^{(ij)}$	<i>Dev.</i> ^a
Chlorobenzene + dibutyl ether	-2.26959	-0.38946	0.12990	0.004
Chlorobenzene + cyclohexane	1.25425	-0.69933	0.87893	0.004
Chlorobenzene + <i>n</i> -heptane	-1.07399	-0.41993	0.87922	0.005
Chlorobenzene + <i>n</i> -octane	-0.16336	-0.67891	0.37567	0.002
Chlorobenzene + 2,2,4-trimethylpentane	-1.23858	-0.95431	0.35464	0.009
Dibutyl ether + cyclohexane	1.44733	-0.29679	1.14674	0.004
Dibutyl ether + <i>n</i> -heptane	0.31267	-0.07106	0.00402	0.002
Dibutyl ether + <i>n</i> -octane	0.51293	-0.09447	0.30482	0.005
Dibutyl ether + 2,2,4-trimethylpentane	-0.38515	-0.01563	0.09073	0.003

^a Dev. = $\{\sum [(V_m^E)^{\text{exp}} - (V_m^E)^{\text{calc}}]^2 / (n-1)\}^{1/2}$, units are cm³ mol⁻¹.

we first computed a raw weighting factor ratio ($\Gamma_i^{\text{raw}}/\Gamma_j^{\text{raw}}$) from binary excess molar volumes at mole fractions $x_i = 0.3333$ and $x_i = 0.6666$

$$\frac{\Gamma_i^{\text{raw}}}{\Gamma_j^{\text{raw}}} = \frac{2V_{m,ij}^E[\text{at } x_i = 0.3333] - V_{m,ij}^E[\text{at } x_i = 0.6666]}{2V_{m,ij}^E[\text{at } x_i = 0.6666] - V_{m,ij}^E[\text{at } x_i = 0.3333]} \quad (30)$$

as recommended by Bertrand, Acree, and Burchfield.⁶ The three raw weighting factor ratios were then combined and normalized to an average value of approximately 100 by

$$\Gamma_1 = 300/[(\Gamma_1^{\text{raw}}/\Gamma_1^{\text{raw}}) + (\Gamma_2^{\text{raw}}/\Gamma_1^{\text{raw}}) + (\Gamma_3^{\text{raw}}/\Gamma_1^{\text{raw}})] \quad (31)$$

$$\Gamma_2 = 300/[(\Gamma_1^{\text{raw}}/\Gamma_2^{\text{raw}}) + (\Gamma_2^{\text{raw}}/\Gamma_2^{\text{raw}}) + (\Gamma_3^{\text{raw}}/\Gamma_2^{\text{raw}})] \quad (32)$$

and

$$\Gamma_3 = 300/[(\Gamma_1^{\text{raw}}/\Gamma_3^{\text{raw}}) + (\Gamma_2^{\text{raw}}/\Gamma_3^{\text{raw}}) + (\Gamma_3^{\text{raw}}/\Gamma_3^{\text{raw}})] \quad (33)$$

These computations become meaningless if a ratio of raw weighting factors calculated from Eq. (30) has a negative value (or an abnormally high or low value) as can happen if the binary mixing property shows a point of inflection when plotted versus mole fraction. This is uncommon, however, and if the ratios of raw weighting factors were less than 1/10 greater than 10 times the ratio of molar volumes, we have simply used pure component molar volumes for weighting factors of all components. Only for chlorobenzene + dibutyl ether + *n*-octane was it necessary to approximate weighting factors with molar volumes. Summarized comparison given in Table 2 further documents that the predictions based upon the Hwang *et al.* cubic expression are either comparable to (Redlich–Kister, Jacob–Fitzner, Kohler) or slightly superior than (BAB) those of the other four models considered here.

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References

1. W. E. Acree, Jr., *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, Inc., Orlando, FL (1984), Chapter 4.
2. 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.
3. C. Pando, J. A. R. Renuncio, J. A. G. Calzon, J. J. Christensen and R. M. Izatt, *J. Solution Chem.*, **16**, 503 (1987).
4. F. Kohler, *Monatsh. Chem.*, **91**, 738 (1960).
5. K. T. Jacob and K. Fitzner, *Thermochim. Acta*, **18**, 197 (1977).
6. G. L. Bertrand, W. E. Acree, Jr. and T. E. Burchfield, *J. Solution Chem.*, **12**, 327 (1983).
7. W. E. Acree, Jr. and G. L. Bertrand, *J. Solution Chem.*, **12**, 755 (1983).
8. O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 135 (1948).

9. G. M. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964).
10. C. C. Tsao and J. M. Smith, Applied Thermodynamics, *Chem. Eng. Prog. Symp.*, Series No. 7, 107 (1953).
11. A. R. Mathieson and J. C. J. Thynne, *J. Chem. Soc.*, 3713 (1956).
12. P. P. Singh, S. Maken, and M. Bhatia, *Indian J. Chem.*, **29A**, 108 (1990).
13. W. E. Acree, Jr., *Indian J. Chem.*, **30A**, 733 (1991).
14. R. P. Rastogi, J. Nath, and S. S. Das, *J. Chem. Eng. Data*, **22**, 249 (1977).
15. G. W. Toop, *Trans. TMS-AIME*, **233**, 850 (1965).
16. A. A. Sayar, *Chem. Eng. Comm.*, **80**, 127 (1989).
17. C.-A. Hwang, J. C. Holste, K. R. Hall and G. A. Mansoori, *Fluid Phase Equilib.*, **62**, 173 (1991).
18. I.-L. Teng and W. E. Acree, Jr., *Phys. Chem. Liq.*, **24**, 249 (1992).
19. I.-L. Teng and W. E. Acree, Jr., *Phys. Chem. Liq.*, in press.
20. P. Picker, E. Tremblay, and C. Jolicoeur, *J. Solution Chem.*, **3**, 377 (1974).
21. L. Lepori, M. Mengheri, and V. Mollica, *J. Phys. Chem.*, **87**, 3520 (1983).

APPENDIX: GLOSSARY OF SYMBOLS

f_i	Weighted mole fraction composition of component i
$h_i^{(JK)}$	Adjustable "curve-fit" parameter in the two/three-body interaction mixing model for describing excess molar enthalpies of the JK binary system
u_{ij}	Two-body interactional energy involving molecules i and j
u_{ijj}	Three-body interactional energy involving molecules i , i and j
$v_i^{(JK)}$	Adjustable "curve-fit" parameter in the two/three-body interaction mixing model for describing excess molar volumes of the JK binary system
$V_{m,ij}^E$	Excess molar volume of the ij binary system
$V_{m,123}^E$	Excess molar volume of the ternary system
x_i	Mole fraction composition of component i
x_i^0, x_j^0	Mole fraction composition of components in the ij sub-binary system
Z_m^E	Generalized intensive thermodynamic excess property
Γ_i	Weighting factor of component i used in the BAB equation Weighting factors provide a rough measure of the skew of the binary excess property from a symmetrical curve centered at 0.50 mole fraction
Λ_{ij}	Adjustable "curve-fit" parameter used in the Wilson equation for describing the excess Gibbs free energies of the ij binary system.