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THERMODYNAMIC PROPERTIES OF TERNARY NON-ELECTROLYTE SOLUTIONS: PREDICTION OF EXCESS VOLUMES FROM MEASURED BINARY DATA

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ABSTRACT

Limitations and applications of four popular expressions for predicting multicomponent thermodynamic properties from measured binary data are re-examined using volumetric data for 37 ternary systems. All four methods provide very reasonable estimates of the ternary excess volumes. For computerized calculations and mathematical representation of experimental data, the BAB, Kohler and Jacob–Fitzner equations are preferred over the Redlich–Kister equation. The mathematical forms of the BAB, Kohler and Jacob–Fitzner equation are both symmetrical and independent of the manner in which the properties of the three contributing binary systems are reported.

INTRODUCTION

For many years the chemical industry has 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 densimeters has enabled the experimental determination of excess enthalpies, heat capacities and volumes of non-electrolyte liquid mixtures with convenience and accuracy. Utilization of continuous dilution methods, combined with chromatographic head-space sampling techniques, has reduced the experimental time needed for the determination of excess Gibbs free energies and activity coefficients through conventional vapor pressure measurements. But 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.

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In the chemical literature, properties for binary mixtures are relatively abundant, properties for ternary systems are scarce and properties for higher-order multicomponent systems are virtually non-existent. To address this problem, researchers have turned to predictive methods as a way to generate desired quantities. Several years ago, Bertrand, Acree and Burchfield [1,2] developed a general equation for the mathematical representation and estimation of the thermodynamic and extra-thermodynamic properties of multicomponent systems based only on the properties of the contributing binary systems, independent of the manner in which these data are represented. This equation, referred to as the BAB equation, takes the general predictive form

$$\Delta\bar{Z}^{\mathrm{ex}}_{1,2,\ldots,N} = \sum_{i=1}^{N} \sum_{j>i} (X_i + X_j)(f_i + f_j)\left(\Delta\bar{Z}^{\mathrm{ex}}_{ij}\right)^{\star} \quad (1)$$

in which Z represents any extensive thermodynamic or extra-thermodynamic property and $(\Delta\bar{Z}^{\mathrm{ex}}_{ij})^{\star}$ is the excess property of the ij binary system at a mole fraction composition $(X_i^{\star},\ X_j^{\star})$ such that

$$X_i^{\star} = 1 - X_j^{\star} = X_i/(X_i + X_j) \quad (2)$$

and the molar ratio is the same as in the multicomponent system. Weighted mole fraction compositions, f_i, are calculated for a ternary system as

$$f_i = X_i\Gamma_i/(X_1\Gamma_1 + X_2\Gamma_2 + X_3\Gamma_3) \quad (3)$$

The weighting factors Γ_i provde a rough measure of the skew of the binary excess mixing property from a symmetric curve with an extremum at the equimolar composition.

Like many of the numerous predictive expressions suggested in the past, the predictive accuracy of the BAB equation was tested using available experimental data. At the time the BAB equation first appeared in 1981 [3], published multicomponent data were scarce. The BAB predictions were compared to excess enthalpies of 33 ternary and 2 quaternary systems, excess volumes of 16 ternary systems, and the excess Gibbs free energies of 8 ternary systems at several temperatures. During the past seven years, data for a large number of ternary systems have been measured and reported in the chemical literature. As additional experimental data becomes available, the limitations and applications of the different predictive methods should be re-examined. Recently Pando et al. [4] discussed the limitations of various methods for predicting excess enthalpies of 42 ternary systems. To add to this comparison, we here re-examine the predictive abilities of the BAB [1,2], Redlich–Kister [5], Kohler [6] and Jacob–Fitzner [7] equations using volumetric data for 37 ternary systems.

CALCULATIONAL METHODS AND PREDICTIVE EXPRESSIONS

A summarized comparison between predicted and experimental excess volumes is presented in Table 1. The number of individual data points for a given system ranges from a minimum of 8 $\Delta\bar{V}^{ex}$'s for the methyl ethyl ketone + alcohol + hydrocarbon mixtures to a maximum of 42 $\Delta\bar{V}^{ex}$'s for the ternary *n*-heptane + *n*-octane + cyclohexane system. The binary properties needed for the predictions were either determined as part of the ternary studies or referenced the author's earlier papers. Computations were performed on an IBM personal computer. Input parameters included ternary mole fraction compositions and coefficients for generating binary $\Delta\bar{V}^{ex}$'s. Generally, binary volumetric data were parametrized in the chemical literature in terms of the Redlich–Kister equation

$$\Delta\bar{V}_{ij}^{ex} = X_i X_j \sum_{w=0}^{r} (A_w)_{ij}(X_i - X_j)^w \tag{4}$$

and the various $(A_w)_{ij}$ parameters were inputted. Subroutines could be easily added to accommodate binary coefficients for Legendre polynomials [8], the Wilson equation [9], the UNIQUAC model [10], the NRTL equation [11] and/or other expressions which might be used to mathematically represent excess enthalpies and Gibbs free energies. As noted previously, the BAB equation (as well as the other three predictive expressions) predicts multicomponent thermodynamic and extra-thermodynamic properties.

BAB weighting factors were evaluated in a relative sense (Γ_i/Γ_j) from the measured binary data. To insure that these ratios obey

$$\Gamma_1/\Gamma_3 = (\Gamma_1/\Gamma_2)(\Gamma_2/\Gamma_3) \tag{5}$$

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

$$\frac{\Gamma_i^{raw}}{\Gamma_j^{raw}} = \frac{2\left(\Delta\bar{V}_{ij}^{ex}\right)_{1/3}^{\star} - \left(\Delta\bar{V}_{ij}^{ex}\right)_{2/3}^{\star}}{2\left(\Delta\bar{V}_{ij}^{ex}\right)_{2/3}^{\star} - \left(\Delta\bar{V}_{ij}^{ex}\right)_{1/3}^{\star}} \tag{6}$$

as recommended by Bertrand, Acree and Burchfield [1]. In eqn. (6) the binary properties $(\Delta\bar{V}_{ij}^{ex})_{1/3}^{\star}$ and $(\Delta\bar{V}_{ij}^{ex})_{2/3}^{\star}$ refer to compositions $X_i = 0.3333$ and $X_i = 0.6666$, respectively. The three raw weighting factor ratios are then combined and normalized to an average of approximately 100 by

$$\Gamma_1 = 300/[(\Gamma_1^{raw}/\Gamma_1^{raw}) + (\Gamma_2^{raw}/\Gamma_1^{raw}) + (\Gamma_3^{raw}/\Gamma_1^{raw})] \tag{7}$$

$$\Gamma_2 = 300/[(\Gamma_1^{raw}/\Gamma_2^{raw}) + (\Gamma_2^{raw}/\Gamma_2^{raw}) + (\Gamma_3^{raw}/\Gamma_2^{raw})] \tag{8}$$

and

$$\Gamma_3 = 300/[(\Gamma_1^{raw}/\Gamma_3^{raw}) + (\Gamma_2^{raw}/\Gamma_3^{raw}) + (\Gamma_3^{raw}/\Gamma_3^{raw})] \tag{9}$$

TABLE 1

Comparison between experimental excess volumes and values predicted from the Redlich–Kister, Kohler, Jacob–Fitzner and BAB equations [a]

Ternary system [b]	Eqn. (10)		Eqn. (11)		Eqn. (12)		Eqn. (1)	
	σ	$\|d_{max}\|$	σ	$\|d_{max}\|$	σ	$\|d_{max}\|$	σ	$\|d_{max}\|$
$C_7H_{16}+C_8H_{18}+C_6H_{12}$	0.020	0.040	0.026	0.048	0.020	0.040	0.004	0.010
$C_7H_{16}+C_9H_{20}+C_6H_{12}$	0.023	0.037	0.030	0.053	0.023	0.037	0.007	0.014
$CH_2Br_2+CH_3C_6H_5+p-(CH_3)_2C_6H_4$	0.010	0.023	0.012	0.022	0.010	0.023	0.013	0.027
$CH_2Br_2+C_6H_6+o\text{-}(CH_3)_2C_6H_4$	0.017	0.028	0.020	0.029	0.017	0.028	0.021	0.030
$CH_2Br_2+C_6H_6+CH_3C_6H_5$	0.004	0.010	0.007	0.015	0.004	0.010	0.009	0.017
$C_6H_6+CH_3C_6H_5+C_2H_4Cl_2$	0.011	0.039	0.012	0.042	0.011	0.039	0.013	0.043
$C_6H_{12}+CH_2Cl_2+CH_3C_6H_5$	0.090	0.103	0.093	0.113	0.090	0.103	0.041	0.054
$C_6H_{12}+CHCl_3+p\text{-}(CH_3)_2C_6H_4$	0.031	0.043	0.025	0.035	0.031	0.043	0.018	0.028
$C_6H_{12}+CH_2Cl_2+p\text{-}(CH_3)_2C_6H_4$	0.097	0.109	0.099	0.114	0.097	0.109	0.047	0.054
$C_2H_5COCH_3+C_3H_7OH+C_9H_{20}$	0.073	0.084	0.074	0.087	0.073	0.084	0.079	0.094
$C_2H_5COCH_3+C_5H_{11}OH+C_7H_{16}$	0.045	0.078	0.048	0.078	0.045	0.078	0.050	0.079 [c]
$C_6H_{12}+CHCl_3+CH_3C_6H_5$	0.044	0.052	0.041	0.049	0.044	0.052	0.029	0.037
$C_6H_{12}+CCl_4+CH_3C_6H_5$	0.009	0.011	0.010	0.014	0.009	0.011	0.009	0.011
$CH_2Br_2+C_6H_6+p\text{-}(CH_3)_2C_6H_4$	0.017	0.027	0.020	0.031	0.017	0.027	0.021	0.028
$C_6H_6+o\text{-}(CH_3)_2C_6H_4+C_2H_4Cl_2$	0.004	0.010	0.006	0.010	0.004	0.010	0.005	0.009
$C_2H_5COCH_3+C_4H_9OH+C_9H_{20}$	0.016	0.025	0.017	0.024	0.016	0.025	0.054	0.063
$C_2H_5COCH_3+C_6H_{13}OH+C_9H_{20}$	0.043	0.059	0.043	0.057	0.043	0.059	0.031	0.042
$C_7H_{16}+C_{10}H_{22}+C_6H_{12}$	0.023	0.037	0.029	0.046	0.023	0.037	0.005	0.009

$CH_2Br_2 + CH_3C_6H_5 + o\text{-}(CH_3)_2C_6H_4$	0.007	0.016	0.008	0.016	0.007	0.016	0.009	0.019
$C_6H_6 + p\text{-}(CH_3)_2C_6H_4 + C_2H_4Cl_2$	0.004	0.012	0.005	0.010	0.004	0.012	0.006	0.017
$C_6H_{12} + CCl_4 + p\text{-}(CH_3)_2C_6H_4$	0.019	0.025	0.017	0.028	0.019	0.025	0.024	0.033
$C_2H_5COCH_3 + C_6H_{13}OH + C_7H_{16}$	0.028	0.044	0.024	0.038	0.028	0.044	0.025	0.041[c]
$C_2H_5COCH_3 + C_3H_7OH + C_8H_{18}$	0.034	0.064	0.037	0.069	0.034	0.064	0.028	0.062
$CCl_4 + C_6H_6 + p\text{-}(CH_3)_2C_6H_4$	0.008	0.011	0.008	0.010	0.008	0.011	0.009	0.012
$C_2H_5COCH_3 + C_3H_7OH + C_7H_{16}$	0.109	0.132	0.114	0.132	0.109	0.132	0.120	0.139
$C_2H_5COCH_3 + C_5H_{11}OH + C_9H_{20}$	0.007	0.011	0.009	0.017	0.007	0.011	0.060	0.075
$C_2H_5COCH_3 + C_4H_9OH + C_8H_{18}$	0.037	0.049	0.040	0.049	0.037	0.049	0.041	0.052
$C_2H_5COCH_3 + C_4H_9OH + C_7H_{16}$	0.049	0.079	0.047	0.078	0.049	0.079	0.060	0.102
$C_2H_5COCH_3 + C_6H_{13}OH + C_8H_{18}$	0.079	0.100	0.083	0.104	0.079	0.100	0.078	0.100[c]
$C_6H_{12} + C_3H_7COCH_3 + C_6H_6$	0.048	0.073	0.042	0.067	0.048	0.073	0.046	0.076
$C_2H_5COCH_3 + C_5H_{11}OH + C_8H_{18}$	0.058	0.093	0.060	0.091	0.058	0.093	0.088	0.123
$CH_2Br_2 + C_5H_5N + C_6H_7N$	0.036	0.124	0.035	0.123	0.036	0.124	0.031	0.116
$C_5H_5N + C_6H_7N + C_6H_{12}$	0.031	0.058	0.042	0.081	0.031	0.058	0.020	0.037
$C_6H_6 + p\text{-}(CH_3)_2C_6H_4 + CH_3C_6H_4Cl$	0.025	0.080	0.027	0.086	0.025	0.080	0.031	0.092
$C_7H_8 + o\text{-}(CH_3)_2C_6H_4 + CH_3C_6H_4Cl$	0.010	0.019	0.010	0.018	0.010	0.019	0.009	0.015
$C_6H_6 + C_7H_8 + CH_3C_6H_4Cl$	0.018	0.049	0.019	0.050	0.018	0.049	0.020	0.051
$C_6H_6 + o\text{-}(CH_3)_2C_6H_4 + CH_3C_6H_4Cl$	0.025	0.073	0.027	0.085	0.025	0.073	0.025	0.073

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[a] Units of the standard deviation and maximum deviation are $cm^3\ mol^{-1}$.

[b] Excess volumes are from refs. 12–21.

[c] Ratio of weighting factors for one binary system was negative, and molar volumes were used for weighting factors.

These computations become meaningless if a ratio of raw weighting factors calculated from eqn. (6) 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 or 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 methyl ethyl ketone + 1-hexanol + *n*-heptane, methyl ethyl ketone + 1-hexanol + *n*-octane and methyl ethyl ketone + 1-pentanol + *n*-heptane systems was it necessary to approximate weighting factors with molar volumes.

Also included in the summarized comparison are calculated values based on three other very popular predictive expressions. The Redlich–Kister equation [5] predicts ternary excess volumes using

$$\Delta\bar{V}^{\text{ex}} = X_1X_2\sum_{w=0}^{r}(A_w)_{12}(X_1-X_2)^w + X_1X_3\sum_{w=0}^{s}(A_w)_{13}(X_1-X_3)^w + X_2X_3\sum_{w=0}^{t}(A_w)_{23}(X_2-X_3)^w \tag{10}$$

The $(A_w)_{ij}$ parameters were determined through a least-squares analysis of binary data according to the appropriate binary reduction of eqn. (10). The Redlich–Kister method requires that the binary excess volumes be mathematically represented in terms of eqn. (4) as the $(A_w)_{ij}$ values are used as coefficients in the predictive ternary expression.

The Kohler equation [6] predicts the ternary excess volumes from

$$\Delta\bar{V}^{\text{ex}} = (X_1+X_2)^2(\Delta\bar{V}_{12}^{\text{ex}})^\star + (X_1+X_3)^2(\Delta\bar{V}_{13}^{\text{ex}})^\star + (X_2+X_3)^2(\Delta\bar{V}_{23}^{\text{ex}})^\star \tag{11}$$

The measured binary properties $(\Delta\bar{V}_{ij}^{\text{ex}})^\star$ at binary compositions $(X_i^\star, X_j^\star)$ are such that $X_i^\star = 1 - X_j^\star = X_i/(X_i+X_j)$. Inspection of the BAB and Kohler equations reveals that the two predictive methods are identical when the BAB weighting factors of the three components are equal.

The Jacob–Fitzner equation [7] also estimates ternary properties using

$$\Delta\bar{V}^{\text{ex}} = \frac{X_1X_2(\Delta\bar{V}_{12}^{\text{ex}})^\star}{(X_1+X_3/2)(X_2+X_3/2)} + \frac{X_1X_3(\Delta\bar{V}_{13}^{\text{ex}})^\star}{(X_1+X_2/2)(X_3+X_2/2)} + \frac{X_2X_3(\Delta\bar{V}_{23}^{\text{ex}})^\star}{(X_2+X_1/2)(X_3+X_1/2)} \tag{12}$$

and the actual numerical volumetric data $(\Delta\bar{V}_{ij}^{\text{ex}})^\star$. The binary compositions $(X_i^\star, X_j^\star)$ are defined such that $X_i^\star - X_j^\star = X_i - X_j$. Equations (11) and (12) are symmetrical and independent of the manner in which the binary properties are reported. Users of the Kohler and Jacob–Fitzner equations need not specify a particular component, and do not have to reparameterize binary data in accordance with a specific mathematical form as might be the case using the Redlich–Kister equation.

RESULTS AND DISCUSSION

A summarized comparison of the predictive abilities of the BAB, Redlich–Kister, Kohler and Jacob–Fitzner equations is presented in Table 1. Results of our many calculations are given as the standard deviation between predicted and observed values, σ, and the absolute value of the maximum deviation for a single data point, $|d_{\max}|$. Careful examination of Table 1 reveals that there is no a priori way of guessing which predictive method will provide the "best" predictions for a given ternary system.

Also indicated in Table 1 is the fact that the Redlich–Kister predictions are numerically identical to those of the Jacob–Fitzner equation. This will be the case anytime that binary data for all three sub-binaries are mathematically represented via the Redlich–Kister equation. To prove this, one recalls that $(\Delta\bar{V}_{ij}^{\mathrm{ex}})^{\star}$ values used in the Jacob–Fitzner equation are calculated at binary mole fractions such that $X_i^{\star} - X_j^{\star} = X_i - X_j$. For the binary mixture containing components 1 and 2, the ternary and sub-binary mole fractions are related as follows

$$X_1^{\star} = X_1 + X_3/2 \quad \text{and} \quad X_2^{\star} = X_2 + X_3/2 \tag{13}$$

and the corresponding binary $(\Delta\bar{V}_{12}^{\mathrm{ex}})^{\star}$ is given by

$$(\Delta\bar{V}_{12}^{\mathrm{ex}})^{\star} = (X_1 + X_3/2)(X_2 + X_3/2) \sum_{w=0}^{r} (A_w)_{12}(X_1 - X_2)^w \tag{14}$$

Similar Redlich–Kister expressions exist

$$(\Delta\bar{V}_{13}^{\mathrm{ex}})^{\star} = (X_1 + X_2/2)(X_3 + X_2/2) \sum_{w=0}^{s} (A_w)_{13}(X_1 - X_3)^w \tag{15}$$

$$(\Delta\bar{V}_{23}^{\mathrm{ex}})^{\star} = (X_2 + X_1/2)(X_3 + X_1/2) \sum_{w=0}^{t} (A_w)_{23}(X_2 - X_3)^w \tag{16}$$

for the remaining two sub-binary systems. By combining eqns. (12) and (14)–(16) it is fairly easy to show that the Redlich–Kister and Jacob–Fitzner predictions are mathematically identical under this set of conditions.

During the course of these predictions, we did explore the possibility of using each equation as the point-of-departure in the mathematical representation of multi-component properties. The difference between predicted and experimentally observed excess volumes were expressed as

$$(\Delta\bar{V}^{\mathrm{ex}})^{\mathrm{exp}} - (\Delta\bar{V}^{\mathrm{ex}})^{\mathrm{pred}} = \sum_{i,j,k} X_i X_j X_k Q_{ijk} \tag{17}$$

with Q-functions of varying complexity. We have found that ternary systems with no strongly polar components can be adequately described with a single constant, $Q_{123} = A_{123}$. In mixtures of non-polar and strongly polar substances, i.e. hydrocarbons and alcohols, two parameters are often required to represent the ternary data

$$Q_{123} = A_{123} + B_{123} X_1 \tag{18}$$

in which component 1 represents the "odd" component, either the polar component mixed with two non-polar components or the non-polar component mixed with two polar components. The general expression for parameterization might take the form

$$\begin{aligned} Q_{123} = A_{123} &+ B_{123}(X_1 - X_2) + B_{132}(X_1 - X_3) + B_{231}(X_2 - X_3) \\ &+ C_{123}(X_1 - X_2)^2 + C_{132}(X_1 - X_3)^2 + C_{231}(X_2 - X_3)^2 + \ldots \end{aligned} \tag{19}$$

with the number of parameters needed determined by the complexity of the ternary system and the experimental uncertainty of the measured data. Although any of the three predictive equations can serve as the point-of-departure for this mathematical representation, we did find it easier to parameterize the deviations from the BAB equation. Also the BAB equation (as well as the Kohler and Jacob–Fitzner equations) gave greater freedom in describing the binary data as its predictive form is independent of the manner in which the properties of the three sub-binaries are reported.

Readers are reminded that prediction of multicomponent properties and mathematical representation of experimental data will become increasingly more important with computerized design calculations and data base storage. The BAB, Kohler and Jacob-Fitzner equations are ideally suited for today's computerized calculations. General applicability to thermodynamic excess properties for many systems of varying complexity makes all three equations very useful for a broad range of design problems. The ability to utilize any description of the properties of the contributing binary systems is an important feature for computerized calculations as subroutines can be added to the main program to handle each new binary equation which might be developed in future years.

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