

Comments on "Topological investigation of molecular interactions in ternary mixtures of non-electrolytes: Excess Gibbs free energy of mixing"

The paper "Topological investigation of molecular interactions in ternary mixtures of non-electrolytes: Excess Gibbs free energy of mixing" by Singh, Maken and Bhatia¹ presents an interesting approach for predicting ternary \bar{G}_{ijk}^E values from measured binary data. While the advantage of topological approaches over the more conventional thermodynamic solution models is certainly debatable, this comment deals primarily with the thermodynamic validity of several equations contained in the paper under reference.

First, the authors assume that i-j and i-k interactions in the ternary solution make independent contributions to the activity coefficient of component, *i*

$$\ln \gamma_i = (\ln \gamma_i)_{i-j} + (\ln \gamma_i)_{i-k}$$

$$RT \ln \gamma_i = \frac{x_j V_j A_{ij} f_{ij} + x_k V_k A_{ik} f_{ik}}{x_i V_i + (x_j + x_k)(V_j + V_k)} \quad \dots (1)$$

where x_i and V_i refer to the mole fraction and molar volume respectively of component *i*, A_{ij} denotes the interaction energy per mole of i-j contact and f_{ij} measures the effectiveness of the i-j contact. Similarly, activity coefficients of *j* and *k* in the ternary mixture are given by,

$$RT \ln \gamma_j = \frac{x_i V_i A_{ji} f_{ji} + x_k V_k A_{jk} f_{jk}}{x_j V_j + (x_i + x_k)(V_i + V_k)} \quad \dots (2)$$

$$RT \ln \gamma_k = \frac{x_i V_i A_{ki} f_{ki} + x_j V_j A_{kj} f_{kj}}{x_k V_k + (x_i + x_j)(V_i + V_j)} \quad \dots (3)$$

The ternary excess molar Gibbs free energy of mixing, \bar{G}_{ijk}^E , was obtained by combining the three activity coefficient expressions, under the additional constraints that $f_{ij} = f_{ji}$, $f_{ik} = f_{ki}$ and $f_{jk} = f_{kj}$.

$$\begin{aligned} \bar{G}_{ijk}^E = & [x_i V_i + (x_j + x_k)(V_j + V_k)]^{-1} \\ & [x_i x_j A_{ij} f_{ij} (V_i + V_j) + x_i x_k A_{ik} f_{ik} (V_i + V_k) \\ & + x_j x_k A_{jk} f_{jk} (V_j + V_k)] \quad \dots (4) \end{aligned}$$

A careful examination of Eq. 4 reveals that it fails to reduce to an appropriate binary description when $x_k = 0$,

$$(\bar{G}_{ijk}^E)_{x_k=0} = [x_i V_i + x_j (V_j + V_k)]^{-1} [x_i x_j A_{ij} (V_i + V_k) f_{ij}] \quad \dots (5)$$

containing both the molar volume of the absent third component and a "ternary" f_{ij} parameter. This particular mathematical reduction cannot properly describe the three sub-binary systems, and it is highly doubtful if the model will be applicable near infinite dilution of any component.

Second, inclusion of ternary f_{ij} and f_{ik} parameters creates ambiguities/problems when Eq. 1 is used to describe the activity coefficient of solute *i* at infinite dilution ($x_i \approx 0$) in both a binary solvent mixture,

$$RT \ln \gamma_i^\infty = \frac{x_j^0 V_j A_{ij} f_{ij}}{V_j + V_k} + \frac{x_k^0 V_k A_{ik} f_{ik}}{V_j + V_k} \quad \dots (6)$$

$$x_j^0 = 1 - x_k^0 = x_j / (x_j + x_k)$$

and the two pure solvents,

$$RT \ln (\gamma_i^\infty)_j = V_j A_{ij} f_{ij} / (V_j + V_k) \quad \dots (7)$$

$$RT \ln (\gamma_i^\infty)_k = V_k A_{ik} f_{ik} / (V_j + V_k) \quad \dots (8)$$

where x_j^0 and x_k^0 refer to binary solvent compositions calculated as if the solutes were not present. The ternary parameters remain in the pure solvent reductions and readers are left to decide how the f_{ij} and f_{ik} values are obtained. Assuming for the moment that the binary and ternary f_{ij} values (and also f_{ik} values) are equal, then combination of Eqs 6-8 yields,

$$\ln \gamma_i^\infty = x_j^0 \ln (\gamma_i^\infty)_j + x_k^0 \ln (\gamma_i^\infty)_k \quad \dots (\text{Eq. 9})$$

a linear relationship between $\ln \gamma_i^\infty$ and solvent mole fraction composition. Such an expression is incapable of describing an extremum in the $\ln \gamma_i^\infty$ versus x_j^0 curve, and hence cannot be applied to systems in which a sparingly soluble solute exhibits either a maximum or minimum mole fraction solubility. While perhaps not all that common, maximum mole fraction solubilities have been reported for benzoic acid dissolved in cyclohexane + *n*-hexane and cyclohexane + *n*-heptane mixtures², and for anthracene in benzene + iodobenzene, benzene + iodoethane, cyclohexane + iodoethane and cyclohexane + iodoethane mixtures³.

Third, through basic thermodynamic relationships the activity coefficient of component *i* can be obtained by differentiating the ternary excess Gibbs free energy with respect to n_i . Performing this differentiation one finds that $RT \ln \gamma_i$ contains an additional term representing j-k interactions, and is by no means identical to Eq. 1.

$$RT \ln \gamma_i = [\partial(n_i + n_j + n_k) \bar{G}_{ijk}^E / \partial n_i]_{T,P,n_j,n_k}$$

$$= (1/\rho)^2 [(n_j + n_k)(V_j + V_k)n_j A_{ij} f_{ij} (V_i + V_j)$$

$$+ (n_j + n_k)n_k (V_j + V_k)A_{ik} f_{ik} (V_i + V_k)$$

$$- V_i n_j n_k A_{jk} f_{jk} (V_j + V_k)] \dots (10)$$

where $\rho = n_i V_i + (n_j + n_k)(V_j + V_k)$

The basic assumption of j-k interactions used in Eqs 2 and 3 to define $\ln \gamma_j$ and $\ln \gamma_k$ requires that these interactions now be included in the $\ln \gamma_i$ description. Similarly, it can be shown that Eqs. 2 and 3 are also not the derivatives of \bar{G}_{ijk}^E as required by the thermodynamic definition of partial molar quantities and activity coefficients.

Finally, Eqs 1-3 fail to satisfy the Gibbs-Duhem equation,

$$\left[n_i \left(\frac{\partial \ln \gamma_i}{\partial n_i} \right)_{n_j, n_k} + n_j \left(\frac{\partial \ln \gamma_j}{\partial n_j} \right)_{n_i, n_k} + n_k \left(\frac{\partial \ln \gamma_k}{\partial n_k} \right)_{n_i, n_j} \right] dn_i +$$

$$\left[n_i \left(\frac{\partial \ln \gamma_i}{\partial n_j} \right)_{n_i, n_k} + n_j \left(\frac{\partial \ln \gamma_j}{\partial n_i} \right)_{n_i, n_k} + n_k \left(\frac{\partial \ln \gamma_k}{\partial n_i} \right)_{n_i, n_k} \right] dn_j +$$

$$\left[n_i \left(\frac{\partial \ln \gamma_i}{\partial n_k} \right)_{n_i, n_j} + n_j \left(\frac{\partial \ln \gamma_j}{\partial n_k} \right)_{n_i, n_j} + n_k \left(\frac{\partial \ln \gamma_k}{\partial n_k} \right)_{n_i, n_j} \right] dn_k = 0$$

... (11)

as all three bracketed dn_i , dn_j and dn_k coefficients do not independently equal zero. For notational simplicity constant T and P subscripts are dropped from Eq. 11 and only the first coefficient will be considered. Partial derivatives are taken with respect to n_i ,

$$RT(\partial \ln \gamma_i / \partial n_i)_{n_j, n_k} =$$

$$- (1/\rho)^2 [V_i n_j V_j A_{ij} f_{ij} + n_k V_k V_i A_{ik} f_{ik}] \dots (12)$$

$$RT(\partial \ln \gamma_j / \partial n_i)_{n_j, n_k} =$$

$$(1/\rho)^2 [(n_j + n_k)(V_j + V_k)V_i A_{ij} f_{ij} - V_i n_k V_k A_{jk} f_{jk}]$$

... (13)

$$RT(\partial \ln \gamma_k / \partial n_i)_{n_j, n_k} =$$

$$(1/\rho)^2 [(n_j + n_k)(V_j + V_k)V_i A_{ik} f_{ki} - V_i n_j V_j A_{jk} f_{kj}]$$

... (14)

while holding T, P and the remaining two mole numbers constant. Substitution of these three partial derivatives into the Gibbs-Duhem equation, followed by suitable mathematical manipulations, yields the following expression,

$$[n_i (\partial \ln \gamma_i / \partial n_i) + n_j (\partial \ln \gamma_j / \partial n_i) + n_k (\partial \ln \gamma_k / \partial n_i)] dn_i =$$

$$- (V_i / \rho^2) [n_i n_j V_j A_{ij} f_{ij} + n_i V_k n_k A_{ik} f_{ik} + n_j n_k V_k A_{jk} f_{jk}$$

$$- n_j (n_j + n_k)(V_j + V_k)A_{ij} f_{ji} - n_k (n_j + n_k)(V_j + V_k)$$

$$\times A_{ik} f_{ki} + n_j n_k V_j A_{jk} f_{kj}] (RT)^{-1} dn_i \dots (15)$$

which equals zero only under the very trivial condition that the ternary solution behaves ideally, i.e., $f_{ij} A_{ij} = f_{ik} A_{ik} = f_{jk} A_{jk} = 0$, etc. To eliminate this particular criticism the authors could either obtain all three expressions via the appropriate differentiation of \bar{G}_{ijk}^E or integrate the Gibbs-Duhem equation for the third component's activity coefficient after assuming that any pair of Eqs 1-3 is correct. Both methods, however, would still give an incorrect description of the solute's activity coefficient in a pure solvent. For example, Eqs 1 and 10 contain the molar volume of component *j* whenever $x_j = 0$.

Singh, Maken and Bhatia's Eqs 1-4 are inconsistent with conventional thermodynamics, and

these inconsistencies must cast considerable doubt upon the general applicability of the basic solution model, the topological relationships derived and/or molecular interpretations based therefrom. The preceding comments, which concern a specific solution model, should in no way be construed as a criticism of the three authors. I have great personal respect and admiration for Prof. Singh as he has published a large number of excellent papers. His present paper on topological investigations of nonelectrolyte solutions represents an important first step in developing a coherent, consistent thermodynamic description of aqueous-organic systems. Solution modeling is extremely difficult, often controversial, and most thermodynamicists (myself included) must invoke simplifying approximations to arrive at a tractable model. Careful examination of the limitations and applic-

ations of any model, of which testing and critiquing play important roles, point out our inability to thermodynamically model certain systems. Deficiencies, once recognized, will prompt the future development of better thermodynamic solution models.

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