LETTER TO THE EDITOR

To the Editor:

Several equations have been proposed for the relation between activity coefficient and mole fractions of the components in a multicomponent mixture. These equations use either the concept of local composition (Wilson, 1964; NRTL, Renon and Prausnitz, 1968; UNIQUAC, Abrams and Prausnitz, 1975) or the group contribution model (UNIFAC, Fredeslund et al., 1975; ASOG, Derr and Deal, 1969), and usually contain two adjustable parameters per each possible binary pair in the multicomponent solution.

In a multicomponent mixture, the "primary" interaction parameters a_{ij} are characteristic constants of the interaction between one molecule of i component and that of j component; therefore, a set of three primary parameters (a_{ij}, a_{ii}, and a_{jj}) is required to describe each possible binary pair in the mixture. However, the adjustable parameters currently used for both correlation of experimental data and equilibrium data prediction are the "secondary" interaction parameters A_{ij}, which are defined as functions of the difference between two binary parameters:

$$A_{ij} = f(a_{ij} - a_{ii}) \tag{1}$$

and in this case, only two secondary parameters per binary would be needed to describe the mixture. Nevertheless, this practice is not advisable, as will be proved in this letter.

For a system with n-components or n-groups, the number of adjustable secondary parameters is $N_s = n^2 - n$, but of these only $N_p = (n^2 + n)/2$ is independent, as shown by Eq. 1, since the matrix of a_{ij} primary parameters is symmetrical ($a_{ij} = a_{ji}$). This fact is not normally considered when running correlation or prediction calculations.

Obviously, it is always possible to calculate the secondary parameters from the primary ones by using Eq. 1, but the opposite transformation is not possible, since the $N_p \times N_s$ transformation matrix from the secondary parameters to the primary ones (TMSP) is of $N_p - 1$ rank.

A possible reason for using commonly the A_{ij} set of parameters for these problems may be that the number of adjustable parameters for binary systems is 2 (1 less than when using primary parameters). In this case, the rank of the TMSP is also 2; consequently, secondary parameters are still consistent with theory, although it is obviously impossible to calculate the three primary parameters from them. Nevertheless, for higher-order systems, the secondary parameters are inconsistent with theory, since the rank of the TMSP is always lower than the number of secondary parameters; consequently, additional conditions should be included in the calculations to make the system compatible. This is never done, and parameters are calculated without any restriction.

For ternary systems, for instance, the number of both primary and secondary parameters is 6, but the rank of the TMSP is 5, which means that one additional condition must be satisfied by the system to be compatible. In this case, secondary parameters must satisfy the following equation:

$$A_{12} - A_{21} + A_{13} - A_{31} + A_{32} - A_{23} = 0 \tag{2}$$

This equation is never satisfied by any set of published secondary parameters for ternary systems (either components or groups), except by coincidence. On the other hand, the number of primary parameters is progressively lower than that of secondary parameters, as the number of components or groups in the mixture (n) increases:

n	TMSP Rank	N_p	N_s
2	2	3	2
3	5	6	6
4	9	10	12
5	14	15	20
6	20	21	30
...	...	...	...

and the number of restrictions must, accordingly, increase to make the system compatible when using secondary parameters. All these problems can and should be overcome by using primary parameters.

In conclusion, the secondary parameters are inconsistent with theory, and their number is only lower than that of primary parameters for binary systems and should not be used. Consequently, all published correlations based on secondary parameters should be reviewed, and trials to correlate any parameter with molecular structure or properties should be carried out with primary parameters.

Literature cited

Abrams, D., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly and Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).

Derr, E. L., and C. H. Deal, "Analytical Solution of Groups: Correlation of Activity Coefficients Trough Structural Group Parameters," *Inst. Chem. Eng. Symp. Ser. (London)*, **3**, 40 (1969).

Fredeslund, Aa., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, **21**, 1086 (1975).

Renon, H., and J. M. Prausnitz, "Local Composition in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.*, **14**, 135 (1968).

Wilson, G. M., "Vapor-Liquid Equilibrium: XI. A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, **86**, 127 (1964).

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