Activity Coefficients in Multicomponent Systems

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Equations for excess free energy and activity coefficients of binary, ternary, and quaternary liquid systems have been presented by several authors (*1* to *7*). These include the van Laar and Margules equations for binary systems extending to the five-suffix terms and for ternary systems extending to the four-suffix terms (*6*). An extension of the four-suffix Margules equation to quaternary systems has also been made (*3, 4*), and a generalization of this equation to multicomponent systems is given here.

The general expansion of the Margules equation to include two-, three-, and four-suffix terms and applied to a system containing n components results in

$$\frac{\Delta G^{xs}}{RT} = \sum_{j=1}^{n} \sum_{i=1}^{n} x_i x_j a_{ij} + \sum_{k=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} x_i x_j x_k a_{ijk} + \sum_{l=1}^{n} \sum_{k=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} x_i x_j x_k x_l a_{ijkl} \quad (1)$$

which is simplified to

$$\frac{\Delta G^{xs}}{RT} = \sum_{j>i}^{n} \sum_{i=1}^{n-1} x_i x_j (A_{ji} x_i + A_{ij} x_j - D_{ij} x_i x_j)$$
$$+ \sum_{k>j}^{n} \sum_{j>i}^{n-1} \sum_{i=1}^{n-2} x_i x_j x_k (A_{ijk} - C_{iijk} x_i - C_{ijjk} x_j - C_{ijkk} x_k)$$
$$+ \sum_{l>k}^{n} \sum_{k>j}^{n-1} \sum_{j>i}^{n-2} \sum_{i=1}^{n-3} x_i x_j x_k x_l (E_{ijkl} - C_{ijkl}) \quad (2)$$

where

$$A_{ij} = 2a_{ij} + 3a_{ijj} + 4a_{ijjj} \; (\neq A_{ji})$$
$$D_{ij} = 4a_{iiij} + 4a_{ijjj} - 6a_{iijj} \; (= D_{ji})$$
$$2C_{iijk} = \sum_{\substack{n=i,j,k \\ \neq m}} \sum_{m=i,j,k} (3a_{mmn} + 4a_{mmmn}) - 12a_{ijk} + 8a_{iiij} + 8a_{iiik} - 24a_{iijk}$$
$$E_{ijkl} = 1/3 \sum_{\substack{n=i,j,k,l \\ n\neq m}} \sum_{m=i,j,k,l} 8a_{mmmn} - \sum_{\substack{p=i,j,k,l \\ \neq n,m \\ >n}} \sum_{\substack{n=i,j,k,l \\ \neq m}} \sum_{m=i,j,k,l} 4a_{mmnp} + 24a_{ijkl}$$
$$2A_{ijk} = A_{ij} + A_{ji} + A_{ik} + A_{ki} + A_{jk} + A_{kj}$$

and

$$3C_{ijkl} = \sum_{\substack{p=i,j,k,l \\ \neq m,n \\ >n}} \sum_{\substack{n=i,j,k \\ \neq m}} \sum_{m=i,j,k,l} C_{mmnp}$$

In Equation (2) all of the coefficients (except the A_{ij}) are unchanged when the order of subscripts is changed. This symmetry results in equations for activity coefficients which are more convenient (*3, 7*).

Equations for activity coefficients can be obtained by differentiating Equation (2):

$$\ln \gamma_i = \frac{\partial}{\partial n_i} \left[\frac{(\Sigma\, n_i)\, \Delta\, G^{xs}}{RT} \right]_{T,P,n_j}$$

$$\ln \gamma_i = \sum_{\substack{j=1 \\ \neq i}}^{n} x_j^2 \left[A_{ij} + 2x_i (A_{ji} - A_{ij} - D_{ij}) + 3x_i^2 D_{ij}\right]$$
$$+ \sum_{\substack{k>j \\ \neq i}}^{n} \sum_{\substack{j=1 \\ \neq i}}^{n-1} x_j x_k \left[(1 - 2x_i) A_{ijk} + 2x_i (A_{ji} + A_{ki}) - 2x_j A_{kj} - 2x_k A_{jk} + 3x_j x_k D_{jk} - x_i(2 - 3x_i) C_{iijk} - (1 - 3x_i)(x_j C_{ijjk} + x_k C_{ijkk}) \right]$$
$$- \sum_{\substack{l>k \\ \neq i}}^{n} \sum_{\substack{k>j \\ \neq i}}^{n-1} \sum_{\substack{j=1 \\ \neq i}}^{n-2} x_j x_k x_l \left[2A_{jkl} - 3x_j C_{jjkl} - 3x_k C_{jkkl} - 3x_l C_{jkll} + C_{ijkl} - E_{ijkl}\right]$$
$$+ 3 \sum_{m>l}^{n} \sum_{l>k}^{n-1} \sum_{k>j}^{n-2} \sum_{j=1}^{n-3} x_j x_k x_l x_m (C_{jklm} - E_{jklm}) \quad (3)$$

An alternate form of Equation (3) eliminates some of the summations which do not include i. This is easier to use in some cases and is given here.

$$\ln \gamma_i = \sum_{\substack{j=1 \\ \neq i}}^{n} x_j (x_j A_{ij} + 2x_i A_{ji} - 2x_i x_j D_{ij})$$
$$+ \sum_{\substack{k>j \\ \neq i}}^{n} \sum_{\substack{j=1 \\ \neq i}}^{n-1} x_j x_k (A_{ijk} - 2x_i C_{iijk} - x_j C_{ijjk} - x_k C_{ijkk})$$
$$+ \sum_{\substack{l>k \\ \neq i}}^{n} \sum_{\substack{k>j \\ \neq i}}^{n-1} \sum_{\substack{j=1 \\ \neq i}}^{n-2} x_j x_k x_l (E_{ijkl} - C_{ijkl})$$
$$- \sum_{k>j}^{n} \sum_{j=1}^{n-1} x_j x_k (2x_j A_{kj} + 2x_k A_{jk} - 3x_j x_k D_{jk})$$
$$- \sum_{l>k}^{n} \sum_{k>j}^{n-1} \sum_{j=1}^{n-2} x_j x_k x_l \left[2A_{jkl} - 3(x_j C_{jjkl} + x_k C_{jkkl} + x_l C_{jkll}\right]$$
$$- \sum_{m>l}^{n} \sum_{l>k}^{n-1} \sum_{k>j}^{n-2} \sum_{j=1}^{n-3} x_j x_k x_l x_m \, 3(E_{jklm} - C_{jklm}) \quad (4)$$

For a quaternary system this equation is equivalent to and an improvement on Equation (1) presented by Lu and Wang (*3*). The coefficient E_{ijkl} is here defined to include only four-suffix terms, while the E used by Lu and Wang includes also three-suffix terms. The difference

$(E_{ijkl} - C_{ijkl})$ presented here is equal to the E used by Lu and Wang (3). This has the advantage that in the absence of quaternary data, the corresponding E_{ijkl} may be set to zero to obtain a better approximation than by setting $(E_{ijkl} - C_{ijkl})$ to zero.

NOTATION

a = interaction coefficient
A = binary two- and three-suffix coefficient
C = ternary coefficient
D = binary four-suffix coefficient
E = quaternary coefficient
ΔG^{xs} = molar excess Gibbs free energy
i, j, k, l, m, n, p = index representing components
n = moles
P = pressure
R = gas constant
T = absolute temperature
x = mole fraction
γ = activity coefficient

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A Generalized Method for Predicting the Minimum Fluidization Velocity

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In a recent article Narsimhan (*18*) presented a generalized expression for the minimum fluidization velocity by extending the correlation proposed by Leva, Shirai, and Wen (*14*) into intermediate and turbulent flow regions. Based on a similar approach by employing the fixed-bed pressure drop equation of Ergun (*7*), an expression for the minimum fluidization velocity quite different from that of Narsimhan has been obtained (*23*).

It is the purpose of this communication to compare these two correlations and to examine the validity and applicability of each.

The generalized expression given by Narsimhan consists of three equations [Equations (6), (9), and (11) in his communication (*18*)].

The correlation obtained by Wen and Yu (*23*) can be represented by

$$(N_{Re})_{mf} = \sqrt{(33.7)^2 + 0.0408\, N_{Ga}} - 33.7 \qquad (1)$$

For nonspherical particles, the particle diameter d_p is defined as the equivalent diameter of a spherical particle with the same volume. As an approximation, the particle diameter may be calculated from the geometric mean of the two consecutive sieve openings without introducing serious errors (*26*).

The major differences between the two correlations are the minimum fluidization voidage ϵ_{mf} and the shape factor ϕ_s.

1. Narsimhan considered that for spherical particles, ϵ_{mf} has the value of 0.35 and is independent of the particle diameter, provided that the wall effect can be neglected. From the literature data (*16, 20, 24*), as well as from the experimental data of the present investigation (*23*), ϵ_{mf} for spherical particles can be shown to vary from 0.36 to 0.46. Different average values of ϵ_{mf} have

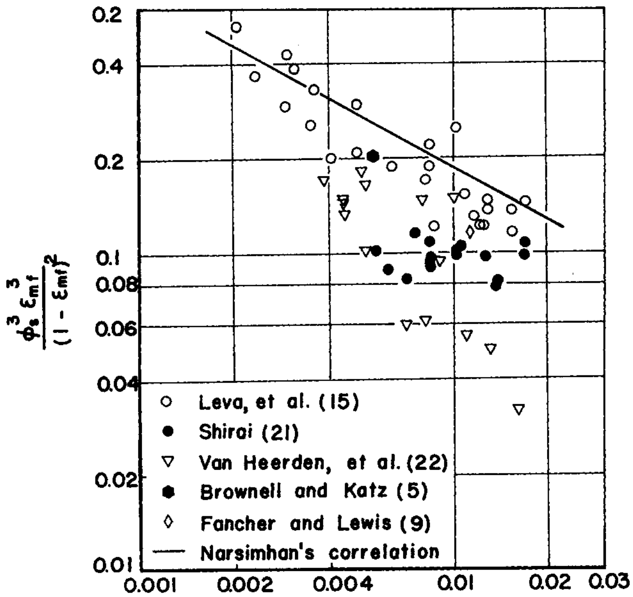

Fig. 1. Correlation of voidage shape factor function $\frac{\phi_s^3\,\epsilon_{mf}^3}{(1-\epsilon_{mf})^2}$.