Activity Coefficient from a Generalized van der Waals Equation

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The design of separation processes such as distillation, absorption, and extraction requires quantitative estimates of partial equilibrium properties of fluid mixtures. Most of the fluid mixtures are nonideal and we must calculate activity coefficients to describe the phase equilibrium. When limited vapor-liquid equilibrium data are available, the activity coefficients in moderately nonideal mixtures can be estimated reasonably by some empirical or semiempirical correlations, such as Margules, van Laar, Wilson, NRTL, or UNIQUAC equations. When no vapor-liquid equilibrium data are available, it is necessary to estimate activity coefficients from some suitable correlations. Unfortunately few such correlations have been established. Often the Scatchard-Hildebrand theory or the UNIFAC model must be employed.

Frequently, activity coefficient models are derived from models describing only the excess properties. Van Laar derived his equation for excess Gibbs energy from the van der Waals equation of state, and so did Hildebrand et al., (1970). Unfortunately, due to various approximations and assumptions these models have a limited use. In this communication it is shown that it is possible to develop a workable model for activity coefficients using a molecular basis. The main aim of this communication is to arrive at a model which is sufficiently realistic and yet simple with regard to mathematical tractability that it may easily be extended beyond the scope of its original application.

In a recent review Anderson and Pransuitz (1980) have used a generalized van der Waals partition function for prediction of pure- and multicomponent phase equilibria and have shown that very good agreement with experimental results can be obtained for a variety of systems. While our understanding of pure liquids and liquid mixtures has increased considerably in the last few years, primarily due to computer simulation results, it is still not possible to calculate activity coefficients with reasonable accuracy starting from realistic intermolecular potentials. Thus, it is natural to consider whether the generalized van der Waals partition function can be used for predicting the activity coefficients. In this paper a simple equation for predicting activity coefficient as a function of intermolecular potential is proposed. The equation has been successfully used to correlate activity coefficients of benzene-cyclohexane and *n*-hexane–benzene binary systems.

Generalized van der Waals Partition Function

Following Vera and Prausnitz (1972), we can write the Carnahan-Starling canonical configurational partition function Q_c for a hard sphere as

$$Q_c = V^N \left\{ \exp\left[\frac{\xi(3\xi - 4)}{(1 - \xi)^2}\right]\right\}^N \left[\exp\left(-\frac{aN}{VkTN_A}\right)\right]^N \quad (1)$$

Here ξ is the reduced density $b/4v$ ($b/4$ is the volume of one mole of hard-sphere molecules and v is the molar volume); $V = Nv$; a is the characteristic attraction constant; T is the temperature; k is the Boltzmann constant; and N_A is the Avogadro number. We also use the empirical relations of Anderson and Prausnitz (1980) for a and b:

$$a = \frac{\alpha + \beta T_R^2}{1 + T_R^2} \qquad (T_R = T/T_c) \quad (2)$$

$$b = \frac{\gamma + \delta T_R^2}{1 + T_R^2} \quad (3)$$

along with their values for the pure-fluid parameters α, β, γ, δ.

The usual mixing rules allow extension to mixtures.

$$a = \Sigma\, a_{ij} x_i x_j \quad (4)$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \quad (5)$$

with k_{ij} as an adjustable binary parameter and

$$b = \Sigma\, x_i b_i \quad (6)$$

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Mansoori (1980) has related the isothermal-isobaric (N, P, T) ensemble partition function of a mixture to the component activity coefficients. To exploit this theory, the NPT ensemble configurational integral, Δ_c, needs to be evaluated. Evidently this is a nontrivial task for realistic intermolecular potentials. However, working with the generalized van der Waals partition function within the canonical ensemble, it is possible to calculate the activity coefficient.

The chemical potential μ_i of the ith component in a liquid solution is defined with respect to the activity coefficient γ_i of that component through (Mansoori, 1980)

$$\mu_i = g_i + RT \ln (x_i \gamma_i) \tag{7a}$$

where g_i is the molar Gibbs free energy of component i. Since only binary solutions are considered in this communication, Eq. 7 may be rewritten as

$$\mu_1 = g_1 + RT \ln (x_1 \gamma_1) \tag{7b}$$

the chemical potential can also be written as

$$\mu_1 = g + x_2 \left(\frac{\partial g}{\partial x_1}\right) P, T \tag{8a}$$

A canonical ensemble partition function leads to residual Helmholtz free energy but not to the residual Gibbs free energy. In the case of a liquid at low pressures, the residual pressure due to mixing is negligible. Hence, for liquids the Gibbs free energy and Helmholtz free energy are assumed to be equal (Scatchard, 1937). Hence

$$g^r = h^r = -kT \ln Q_c \tag{9}$$

Equations (7b) and (8a) in terms of the residual properties are written as:

$$\mu_1^r = g_1^r + RT \ln \gamma_1 \tag{7c}$$

and

$$\mu_1^r = g^r + x_2 \left(\frac{\partial g^r}{\partial x_1}\right) \tag{8b}$$

μ_1^r in terms of partition function is

$$\mu_1^r = -kT\left(\ln Q_c + x_2 \frac{\partial \ln Q_c}{\partial x_1}\right) \tag{10}$$

The expression for the activity coefficient of component 1 in a binary mixture is

$$\ln \gamma_1 = -(1/N_A)\left[\ln (Q_c/Q_{c1}) + x_2 \left(\frac{\partial \ln Q_c}{\partial x_1}\right)_{V,T}\right. \tag{11}$$

where Q_{c1} is the value of Q_c for pure component 1. Using a Taylor series expansion for $\ln Q_c$ we have the following expression

$$\ln Q_c = \ln Q_{c1} + x_2 \left(\frac{\partial \ln Q_c}{\partial x_2}\right)_{V,T,x_2=0} + \sum_{n=2}^{\infty} \frac{x_2^n}{n!} \left(\frac{\partial^n \ln Q_c}{\partial x_2^n}\right)_{V,T,x_2=0} \tag{12}$$

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$$\left(\frac{\partial \ln Q_c}{\partial x_1}\right)_{V,T} = \left(\frac{\partial \ln Q_c}{\partial x_1}\right)_{V,T,x_2=0} + \sum_{m=1}^{\infty} \frac{x_2^m}{m!} \frac{\partial^m}{\partial x_2^m} \left(\frac{\partial \ln Q_c}{\partial x_1}\right)_{V,T,x_2=0} \tag{13}$$

Substituting these values in Eq. 11 we have

$$\ln \gamma_1 = (1/N_A) \sum_{n=2}^{\infty} x_2^n \frac{(n-1)}{n!} \left(\frac{\partial^n \ln Q_c}{\partial x_2^n}\right)_{V,T,x_2=0} \tag{14}$$

This equation is similar to the equation derived by Mansoori (1980) for the activity coefficient from an isobaric-isothermal ensemble. Equation 14 is equivalent to the Redlich-Kister correlation for the activity coefficient

$$\ln \gamma_1 = a_1^{(1)} x_2^2 + a_2^{(1)} x_2^3 + \cdots \tag{15}$$

with

$$a_n^{(1)} = \frac{1}{N_A} \frac{n}{(n+1)!} \left(\frac{\partial^{n+1} \ln Q_c}{\partial x_2^{n+1}}\right)_{V,T,x_2=0} \tag{16}$$

Following Mansoori, it can be shown that the Gibbs-Duhem equation for activity coefficient

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0 \tag{17}$$

leads to the relation

$$\sum_{n=0}^{\infty} \frac{1}{n!} \left[x_2^n \left(\frac{\partial^{n+2} \ln Q_c}{\partial x_2^{n+2}}\right)_{V,T,x_2=0} - x_1^n \left(\frac{\partial^{n+2} \ln Q_c}{\partial x_1^{n+2}}\right)_{V,T,x_2=0} \right] = 0 \tag{18}$$

A significant advantage of dealing with a canonical ensemble is that we can evaluate the configuration partition function in terms of realistic intermolecular parameters. The logarithmic partial differential of the configural partition function Q_c, Eq. 1, can be evaluated using the van der Waals mixing rules given by Eqs. 4–6. Substituting the value of the logarithmic partial differential of the configural partition function in Eq. 14, it can be shown that the following expression for the Avogadro number of molecules may be obtained as

$$\ln \gamma_1 = x_2^2 \left\{ \frac{a_1 - 2a_{12} + a_2}{vRT} + \left(\frac{b_2 - b_1}{4v}\right)^2 \left[\frac{2\xi - 5}{(1-\xi)^4}\right]_{x_2=0} \right\} + \sum_{n=3}^{\infty} x_2^n (n-1) \left(\frac{b_2 - b_1}{4v}\right)^n \left[\frac{2\xi - (3+n)}{(1-\xi)^{n+2}}\right]_{x_2=0} \tag{19}$$

A similar expression can be derived for $\ln \gamma_2$ as

$$\ln \gamma_2 = x_1^2 \left\{ \frac{a_1 - 2a_{12} + a_2}{vRT} + \left(\frac{b_1 - b_2}{4v}\right)^2 \left[\frac{2\xi - 5}{(1-\xi)^4}\right]_{x_1=0} + \sum_{n=3}^{\infty} x_1^n (n-1) \left(\frac{b_1 - b_2}{4v}\right)^n \left[\frac{2\xi - (3+n)}{(1-\xi)^{n+2}}\right]_{x_1=0} \right\} \tag{20}$$

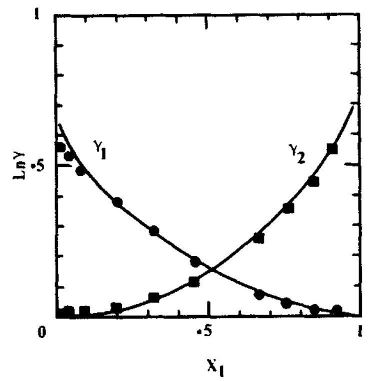

Figure 1. Activity coefficient as a function of composition for benzene(1)-cyclohexane(2) system.
P = 0.06 bar; T = 281.0 K; k_{ij} = 0.03 (data of Aim, 1978)
— calculated values; ● ■ experimental values

From Eqs. 19 and 20 it can be seen that the coefficients in the series are not strictly related as in the Redlich-Kister expression. This is due to the limitations arising from the Taylor series expansion, once starting at $x_2 = 0$ and once starting at $x_1 = 0$. However, the relation between the coefficients in series is striking. This is a significant find since the parameters have a direct interpretation in terms of properties of the molecules and the forces between them. This allows a better understanding to the molecular nature of the activity coefficient.

Results and Discussion

Figures 1 and 2 compare the experimental and the predicted values of the activity coefficient as a function of composition of benzene(1)-cyclohexane(2) and n-hexane(1)–benzene(2) binary systems. The values of molar volumes of mixtures were estimated by the method proposed by Anderson and Prausnitz (1980). It can be seen that the proposed equation fits the data reasonably well. The simplicity of the calculation procedure needs to be stressed. Further, the parameters in the theory have a direct interpretation in terms of properties of the molecules and the forces between them. This allows a better understanding of the molecular nature of the activity coefficient. However, the value of k_{ij} is not known *a priori*. Thus, this procedure is not predictive but can be considered to be a one-parameter model for correlation purposes. The proposed equation appears quite useful for correlation purposes at least for nonpolar and perhaps for weakly polar systems.

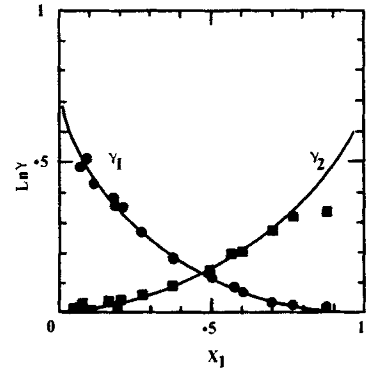

Figure 2. Activity coefficient as a function of composition for n-hexane(1)–benzene(2) system.
P = 0.49–0.64 bar; T = 328.0 K; k_{ij} = 0.110 (data of Yuan et al, 1063)
— calculated values; ● ■ experimental values

The molecular thermodynamic relations developed for the activity coefficient, Eq. 19, allows us to evaluate correlations of the activity coefficients such as those of Margules and van Laar, which are truncated Redlich-Kister power series. Extension to mixtures of polar components and the use of a local composition model to derive the corresponding equations of state should help bridge the gap between equation of state procedure and the excess model procedures.

Notation

a = equation of state constant for mixtures
a_1, a_2 = equation of state constant reflecting attractive forces, bar · L^2/mol^2
a_{ij} = equation of state constant for $i - j$ pair
$b/4$ = volume of one mole of hard-sphere molecules, L/mol
k = Boltzmann's constant, 1.380×10^{-16} erg/K
k_{ij} = binary mixture interaction parameter
N = number of molecules
N_A = Avogadro constant, 6.023×10^{23} molecules/mol
P = pressure, bar
Q = canonical partition function
Q_c = configurational canonical partition function
T = temperature, K
T_c = critical temperature, K
T_R = reduced temperature
V = volume occupied by N molecules, L
v = molar volume, L/mol
x = mole fraction

Greek letters

α, β = characteristic parameters, Eq. 2
$\gamma\delta$ = characteristic parameters, Eq. 3
γ_1 = activity coefficient
Δ = isothermal-isobaric (NPT) configurational partition function
ξ = reduced density

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