International Journal of Thermophysics, Vol. 7, No. 2, 1986

Group Contributions to Activity Coefficients from the Hard Sphere Expansion Corresponding States Theory[1]

D. E. R. Quock[2] and T. W. Leland[2]

A new method has been developed for predicting liquid activity coefficients in ternary mixtures from group contributions. In this method, activity coefficients are obtained from the excess Gibbs free energy of mixing at constant temperature and pressure. In calculating this excess function, the constituent and mixture Gibbs free energies are each represented by an expansion about a pure reference fluid in powers of ratios of hard-sphere diameters and molecular attraction parameters. When the pure component differs from the reference by a single structural group, these ratios represent, respectively, the size contribution and the attraction contribution of this group to the thermodynamic property of the pure fluid. Contributions of intermolecular repulsion to the excess Gibbs free energy are calculated directly from hard-sphere equations of state for the mixture and pure components. The effect of polar contributions calculated by a Padé approximant is also examined. Results indicate that the method developed from the hard-sphere expansion corresponding-states theory is useful for predicting activity coefficients in ternary mixtures when unlike-pair interaction parameters are fitted to binary activity coefficient data. Furthermore, the method shows promise in providing a theoretical basis for applying group contributions to activity coefficients.

KEY WORDS: Activity coefficients; corresponding states; group contributions; hard-sphere theory; polar contributions.

1. INTRODUCTION

In any homogeneous fluid phase at a temperature below the critical temperature of each constituent i, the activity coefficient γ_i can be related to

---

[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] Department of Chemical Engineering, Rice University, Houston, Texas 77251, U.S.A.

the molar excess Gibbs free energy for mixing at constant temperature and pressure. The relation is[3]

$$RT\ \ln(\gamma_i) = \left[\frac{\partial(nG^{\mathrm{E}})}{\partial n_i}\right]_{T,P,n_j} \tag{1}$$

Several methods have been developed for determining the molar excess Gibbs free energy as a function of composition. Three well-known examples are those of the Wilson, NRTL, and UNIQUAC procedures. The development of a new theoretically based method for molecular group contributions is the major concern of this work.

The nonpolar attraction contribution to the Gibbs free energy of a pure or multicomponent fluid can be approximated by an expansion in powers of ratios of the pair potential parameters in the fluid to the analogous parameters of a pure reference.

This new method for predicting activity coefficients is called the "hard-sphere expansion corresponding-states theory" (HSECST). It requires the pressure, density, heat of vaporization, constant-pressure heat capacity, and dipole and higher-order moments of each component and the reference. Experimental binary activity coefficient data are used to fit unlike interaction pair parameters. Activity coefficients for several ternary mixtures are determined from the unlike-pair coefficients of their constituent binaries and compared with experimental results.

2. HARD-SPHERE EXPANSION CORRESPONDING-STATES THEORY

In the hard-sphere expansion method, repulsion interactions between molecules are modeled as hard-sphere repulsions. The attraction contribution, X^{Attr}, is defined as the excess over its hard-sphere value such that

$$X = X^{\mathrm{HS}} + X^{\mathrm{Attr}} \tag{2}$$

where X is any dimensionless residual thermodynamic property. In Eq. (2), X is assumed to be a function of two reduced variables, ε/kT and ρd^3. The ε and d terms are symetrically averaged parameters in a pair potential with a hard-sphere repulsion which may depend on temperature and density.

3. PURE-COMPONENT GIBBS FREE ENERGY EXPANSION

In terms of the two reduced variables ε/kT and ρd^3, the total residual Gibbs free energy G_i' of a fluid i can be obtained by expanding about the

---

[3] For an explanation of symbols, see Nomenclature at end of article.

residual Gibbs free energy G_0' of a reference fluid by the method of Brown [1] as follows:

$$
\begin{aligned}
G_i'(T, P, \varepsilon_{ii}, d_{ii}^3) = G_0'(T, P, \varepsilon_{00}, d_{00}^3) &+ U_0' f_{ii} + (PV_0 - RT)\, h_{ii} \\
&+ \tfrac{1}{2}(2PTV_0\alpha_0 - T(C_p')_0 + P^2 V_0 \kappa_0)\, f_{ii}^2 \\
&+ \tfrac{1}{2}(RT - P^2 V_0 \kappa_0)\, h_{ii}^2 + (P^2 V_0 \kappa_0 - PTV_0\alpha_0)\, f_{ii} h_{ii}
\end{aligned}
\tag{3}
$$

where

$$
f_{ii} = \frac{\varepsilon_{ii}}{\varepsilon_{00}} - 1 \qquad \text{and} \qquad h_{ii} = \frac{d_{ii}^3}{d_{00}^3} - 1 \tag{4}
$$

In Eq. (3), primes indicate a residual property. Properties of the pure reference fluid in Eq. (3) are as follows: U_0' is the molar residual internal energy, V_0 is the molar volume, $(C_p')_0$ is the molar residual heat capacity, α_0 is the volume expansivity, and κ_0 is the isothermal compressibility, all evaluated at T and P.

On the assumption that the vapor phase is an ideal gas at low pressures and the liquid molar volume is negligible compared to that of the vapor, the molar residual internal energy U_0' of the reference reduces to

$$
U_0' = -\Delta H_{\text{vap}} + RT \tag{5}
$$

When species i differs from the reference species by only one structural group, f_{ii} and h_{ii} represent, respectively, the attraction contribution and the size contribution of this group to the residual Gibbs free energy of pure fluid i. The f_{ii} and h_{ii} terms for species i relative to a specified reference are determined from experimental data for pure component i and for the reference. The residual Gibbs free energies of pure fluid i and of the reference fluid are obtained by assuming that at low pressures, the fugacity of a pure liquid is equal to its saturated vapor pressure at the temperature of the system.

By taking the negative partial derivative of the Gibbs free energy expansion equation with respect to temperature, a second independent equation is obtained in terms of the entropy of both species. Parameters f_{ii} and h_{ii} are obtained by simultaneous solution of the entropy and Gibbs free energy equations.

4. MIXTURE GIBBS FREE ENERGY EXPANSION

Equation (3) is derived for a pure fluid, but it can be used to predict the Gibbs free energy of a mixture when ε_{ii} and d_{ii}^3 are replaced by properly selected pseudoparameters, $\bar{\varepsilon}$ and $\bar{d}^3$. Mansoori and Leland [2] defined pseudoparameters $\bar{\varepsilon}$ and $\bar{d}^3$ applicable to the attraction portion of a mixture residual property consisting of a term in $1/T$ and another in $1/T^2$. With these pseudoparameters for attraction, Eq. (3) becomes

$$\begin{aligned} G_{\text{mix}}'(T, P) = {} & G_0'(T, P) + U_0'\bar{f} + (PV_0 - RT)\,\bar{h} + \tfrac{1}{2}(2PTV_0\alpha_0 - T(C_p')_0 \\ & - P^2V_0\kappa_0)\,\bar{f}^2 + \tfrac{1}{2}(RT - P^2V_0\kappa_0)\,\bar{h}^2 + (P^2V_0\kappa_0 - PTV_0\alpha_0)\,\bar{f}\bar{h} \\ & - A_0^{\text{HS}}(\rho_{\text{mix}}\bar{d}^3) + A_{\text{mix}}^{\text{HS}}(\rho_{\text{mix}}, x_i, d_i^3) \end{aligned} \tag{6}$$

where

$$\bar{f} = \frac{\sum_i \sum_j x_i x_j (1 + h_{ij})(1 + f_{ij})^2}{\sum_i \sum_j x_i x_j (1 + h_{ij})(1 + f_{ij})} - 1 \tag{7}$$

$$\bar{h} = \frac{[\sum_i \sum_j x_i x_j (1 + h_{ij})(1 + f_{ij})]^2}{\sum_i \sum_j x_i x_j (1 + h_{ij})(1 + f_{ij})^2} - 1 \tag{8}$$

Values for unlike-pair interaction parameters f_{ij} and h_{ij} are obtained from fitting Eq. (6) to experimental binary activity coefficient data.

The Gibbs free energy in Eq. (6) can be regarded as the result of a mixture equation of state in which

$$P = RT\rho(Z^{\text{HS}} + Z^{\text{Attr}}) \tag{9}$$

The density in Eq. (9) is obtained by assuming additive volumes in forming the mixture. Consequently, it is convenient to express mixture properties in terms of temperature and volume instead of temperature and pressure. For example, the residual Helmholtz free energy can be defined

$$A'(T, V) = A^{\text{HS}}(T, V) + A^{\text{Attr}}(T, V) \tag{10}$$

Furthermore, since the excess volume of mixing is assumed to be negligible, the total residual Helmholtz free energy of a fluid evaluated at T and V can be approximated by the total residual Gibbs free energy of a fluid evaluated at T and P.

$$A'(T, V) \simeq G'(T, P) \tag{11}$$

$G_{\text{mix}}'(T, P)$ in Eq. (6) approximates the Helmholtz function, $A_{\text{mix}}'(T, V)$. Because the mixture pseudoparameters $\bar{\varepsilon}$ and $\bar{d}^3$ are valid only for attraction properties, it is necessary to calculate Helmholtz repulsion contributions separately from hard-sphere equations of state.

5. HARD-SPHERE EQUATIONS

The Helmholtz hard-sphere free energy for a pure fluid is obtained from the equation developed by Carnahan and Starling [3]. This equation is

$$A^{\mathrm{HS}}=\frac{1}{(1-\eta)^2}+\frac{2}{(1-\eta)}-3 \tag{12}$$

where $\eta=(\pi/6)\,\rho d^3$.

Properties of hard-sphere mixtures can be derived from the equation of state of Mansoori et al. [4]. The results for the residual Helmholtz function are

$$A^{\mathrm{HSM}}=-3\alpha+\frac{3\alpha-\gamma}{1-y}+\frac{\gamma}{(1-y)^2}+(\gamma-1)\ln(1-y) \tag{13}$$

where

$$y=\frac{\pi}{6}\rho_{\mathrm{mix}}\sum_i^m x_i d_i^3$$

$$\alpha=\frac{\langle d\rangle\langle d^2\rangle}{\langle d^3\rangle}$$

$$\gamma=\frac{\langle d^2\rangle^3}{\langle d^3\rangle^2}$$

$$\langle d^k\rangle=\sum_i^m x_i d_i^k$$

To use Eq. (13), it is necessary to know the hard-sphere diameter of the reference. From this value, the hard-sphere diameter of each component in the mixture can be obtained from Eq. (3) after h_{ii} is obtained by a fit to experimental data. In this manner, each component in the mixture is forced to be conformal with the reference substance.

The hard-sphere diameter of the reference species is obtained from an expansion of the dimensionless residual Gibbs free energy in powers of reciprocal temperature [5]. By defining the temperature-independent terms of this expansion as the hard-sphere Gibbs free energy, the following result is obtained.

$$\begin{aligned}\left[\frac{T}{P_i^s}\left(\frac{\partial P_i^s}{\partial T}\right)+\ln\left(\frac{P_i^s}{P}\right)-\frac{1}{2}\frac{C_p'}{R}\right]\\ =\frac{1}{(1-\eta)^2}+\frac{2}{(1-\eta)}-4+\left(\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right)\\ -\ln\left(\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right)\end{aligned} \tag{14}$$

6. POLAR CONTRIBUTION

The attraction contribution to a residual thermodynamic property can be considered to be made up of a symmetrical part and an asymmetrical part. The asymmetrical part is generated by permanent and induced polar moments. The dimensionless residual thermodynamic property of a gas or liquid mixture can be redefined as follows:

$$X = X^{\mathrm{HS}} + X^{\mathrm{Sym}} + X^{\mathrm{Asym}} \tag{15}$$

It was assumed previously in the method of calculating Gibbs free energy that molecular potentials are independent of relative orientation. By evaluating the asymmetrical attraction contribution separately from the symmetrical attraction contribution, any error that may have been created by this assumption should be minimized. The total Gibbs free energy of the mixture is then

$$G_{\mathrm{mix}}(T, P) = G_{\mathrm{mix}}{}^{\mathrm{Sym}} + A_{\mathrm{mix}}{}^{\mathrm{HS}}(\rho_{\mathrm{mix}}, x_i, d_i^3) + A_{\mathrm{mix}}{}^{\mathrm{Asym}}(\mu_i, \rho_{\mathrm{mix}}, x_i, d_i^3) \tag{16}$$

Asymmetrical contributions due to multipole effects developed by Larsen et al. [6] and Hang [7] are used here to obtain Helmholtz free energy asymmetrical values. In Larsen's theory, Helmholtz free energy is defined as a perturbation to a nonpolar reference system. In terms of the dimensionless residual Helmholtz free energy, this perturbation expansion is extrapolated by a Padé approximant as follows:

$$\left[\frac{A_{\mathrm{Asym}} - A^*}{RT}\right] = \beta f_2 (1 - f_3/f_2)^{-1} \tag{17}$$

where

$$\beta f_2 = -\frac{\rho \mu^4}{6(kT)^2 d^3} I_6{}^{\mathrm{HS}}(\rho d^3)$$

$$\beta f_3 = \frac{\rho^2 \mu^6}{54(kT)^3 d^3} I_{\mathrm{TD}}{}^{\mathrm{HS}}(\rho d^3)$$

The terms $I_6{}^{\mathrm{HS}}$ and $I_{\mathrm{TD}}{}^{\mathrm{HS}}$ are integrals over hard-sphere distribution functions tabulated by Larsen, Rasaiah, and Stell. Due to a lack of sufficient data, multipole moments higher than dipole moments have been set equal to zero in this work, although they should probably be replaced with fitted parameters.

7. SELECTION OF A REFERENCE FLUID

When polar contributions are not calculated explicitly, the excess over hard-sphere contributions includes both asymmetrical and symmetrical attraction forces. In this case, the reference fluid should be selected on the basis that its polar properties most nearly represent that of the mixture. In the polar Helmholtz free energy equations derived by Larsen, the function $\{\mu^4/d^3\}$ represents a measure of the polarity contribution to the total Helmholtz free energy when only two-body interactions are considered. As a criterion for selecting the optimal reference component, the following expressions were evaluated and compared to computer-generated results with different references.

$$\text{Pure fluid:}\quad \tau_i = \frac{\mu_i^4}{V_{ci}} \tag{18}$$

$$\text{Mixture:}\quad \bar{\tau} = \sum\sum x_i x_j \frac{\mu_i^2 \mu_j^2}{(V_{ci} + V_{cj})/2} \tag{19}$$

where μ_i is the dipole moment of component i and V_{ci} is the critical volume of component i.

8. ACTIVITY COEFFICIENT PREDICTION

Experimental activity coefficients are calculated from vapor–liquid equilibrium data. In this work, only low-pressure systems near 1 atm are considered and the vapor phases of these systems are ordinarily approximated as ideal gases, although in some of the associated molecules considered, gas phase nonideality should be taken into account. With this assumption, the activity coefficient γ_i of component i in a mixture reduces to

$$\gamma_i = \frac{y_i P_{\text{tot}}}{x_i P_i^{\text{sat}}} \tag{20}$$

Experimental activity coefficients for the systems acetone–methanol–ethanol, acetone–methanol–isopropanol, and acetone–methanol–chloroform are calculated from Eq. (20). Experimental activity coefficients for the system ethanol–2-butanone–benzene have been calculated by Ohta et al. [8] from the following equation:

$$\gamma_i = \frac{\psi_i y_i P}{\psi_i^{\text{s}} x_i P_i^{\text{s}} \exp[V_i^{\text{L}}(P - P_i^{\text{s}})/RT]} \tag{21}$$

where ψ_i is the fugacity coefficient of component i.

9. THERMODYNAMIC CONSISTENCY

The computer program for activity coefficient prediction from this theory was tested for binary systems and found to be consistent according to the Redlich–Kister test [9].

10. RESULTS AND CONCLUSIONS

This work shows that separation of dimensionless residual thermodynamic properties into repulsion and attraction contributions is beneficial in the prediction of activity coefficients. With the exception of the mixture acetone–methanol–chloroform, which gave poor results for all of the methods tested, the HSECST method was either comparable to or significantly better than the same method without the hard-sphere correction terms. For example, the mixture ethanol–2-butanone–benzene had an average error of 2.0% calculated with HS terms and an average error of 15.8% without HS terms.

The inclusion of polar contribution terms calculated from a Padé approximant method did not improve activity coefficient prediction. Computer calculations showed that for the mixture acetone–methanol–ethanol, the inclusion of polar contribution terms increased the average error of activity coefficients from 9.1 to 14.8%. While the Padé approximant works well for simple polar systems such as carbon dioxide and propane, as shown by Hang [7], it apparently cannot be used in systems involving hydrogen bonding. For the types of systems studied in this work where hydrogen bonding is important, it is believed that the polar expansion about a nonpolar reference fluid does not converge quickly enough to be accurately approximated by a Padé method. It is probable that terms beyond the third order are significant in hydrogen-bonded systems and cannot be approximated by a Padé technique. Furthermore, the polar terms in this study involved only dipole moments and hydrogen-bonded systems should consider higher-order multipole moments.

The choice of reference fluid has been found to have dramatic effects on the accuracy of predicted activity coefficients. In the case where both symmetrical and asymmetrical attraction effects are incorporated in the Gibbs free energy expansion, the dipole moments alone for the components in the mixture can be used to select the best reference fluid. In a polar mixture, this study has shown that the reference fluid should be chosen on the basis that its polar parameter τ value is nearest to that of the mixture's pseudo average value, $\bar{\tau}$. For example, the selection of methanol as the reference fluid in the mixture acetone–methanol–ethanol resulted in the lowest average error. In comparison, the polar parameter τ values for acetone, methanol, and ethanol are, respectively, 0.338, 0.071, and 0.050, while $\bar{\tau}$ of the mixture varies from 0.074 to 0.212 in the temperature range 70.3 to 56.6°C at 760 mm Hg. The method for selecting the optimal reference fluid in a nonpolar mixture has not been examined and requires further investigation. The molar average acentric factor may, in this case, be the best indicator of the optimal reference fluid.

The composition selected in the binary input data to obtain the parameters for ternary systems has a significant effect on activity coefficient prediction. Results have shown that activity coefficients at binary compositions of approximately $x_1 = 0.67$ and $x_2 = 0.33$ should be used when experimental data at varying compositions are available.

Of the mixtures tested, predicted activity coefficients for the system ethanol–2-butanone–benzene had the lowest overall average percentage error. This system was shown by Ohta et al. [8] to have a nearly ideal vapor phase. If the nonideality of the vapor phases in the other mixtures had been calculated, substantial improvement might be obtained in all predicted activity coefficients because liquid-phase activity coefficient predictions were best in the systems with the lowest total pressure. One possible method for obtaining the vapor-phase fugacity coefficients is from second virial coefficients estimated by the method given in *Vapor-Liquid Equilibria Using UNIFAC* by Fredenslund et al. [10].

The HSECST method was found to be comparable to or better than the ternary van Laar equation in all mixture cases except for the system acetone–methanol–chloroform. The most noticeable difference was in the mixture acetone–methanol–ethanol, where the van Laar method has a 34.7% average error and the HSECST method had a 9.1% average error. The average percentage error of the mixture acetone–methanol–chloroform was exceedingly large for both the HSECST and the van Laar methods and is attributed to the existence of a ternary saddle-point azeotrope in this system.

The attractive feature of the HSECST method is its capability for constructing theoretically based group contributions that are approximately independent of changes in the mixture environment around the group. The unlike-pair parameter h_{12} values for the binary pair acetone–methanol in the mixtures acetone–methanol–ethanol, acetone–methanol–isopropanol, and acetone–methanol–chloroform where methanol is the reference are, respectively, 0.3604, 0.3458, and 0.3571. The unlike-pair parameter f_{12} values for the same systems are, respectively, 0.0003, 0.0058, and 0.0044. The deviation of f_{12} among the different mixtures is attributed to calculation inaccuracy at such low molecular potential contributions.

Future work planned in this area is to examine the predictability of group contribution parameters by testing many different kinds of mixtures.

It is concluded that a better method of calculating polar effects when hydrogen bonding is present would help to improve the predictability of unlike-pair parameters. If successful, the method of "activity coefficient prediction by hard-sphere expansion corresponding-states theory" could be expanded to mixtures where no binary data are available.

NOMENCLATURE

A'	Residual Helmholtz free energy
C_p	Constant-pressure heat capacity
ΔH_{vap}	Heat of vaporization
P^{s}	Saturated vapor pressure
R	Gas constant
T	Temperature
U^{HS}	Hard-sphere internal energy
V_{c}	Critical volume
V^{L}	Liquid volume
X	Dimensionless residual thermodynamic property
Z	Compressibility factor
d	Center-to-center distance between two touching molecules
k	Boltzmann constant
n	Moles
x	Liquid mole fraction
y	Vapor mole fraction
α	Volume expansivity
γ	Liquid activity coefficient
ε	Minimum molecular attraction potential
κ	Isothermal compressibility
μ	Permanent dipole moment
π	3.14159...
ρ	Density
ψ	Fugacity coefficient

REFERENCES

1. W. B. Brown, *Proc. R. Soc.* **A250**:175 (1957).
2. G. A. Mansoori and T. W. Leland, *J. Chem. Soc. Faraday Trans. II* **68**:320 (1972).
3. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**(2):635 (1969).
4. G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54**(4):1523 (1971).
5. D. E. R. Quock, *Activity Coefficient Prediction by Hard Sphere Expansion Corresponding States Theory,* M.S. thesis (Rice University, Houston, Tex., 1985).

6. B. Larsen, J. C. Rasaiah, and G. Stell, *Mol. Phys.* **33**(4):987 (1977).
7. T. Hang, *An Improved Hard Sphere Expansion Conformal Solution Theory to Predict Vapor-Liquid Equilibria*, Ph.D. thesis (Rice University, Houston, Tex., 1985).
8. T. Ohta, T. J. Koyabu, and I. Nagata, *Fluid Phase Equil.* **7**:65 (1981).
9. A. T. Kister and O. Redlich, *Ind. Eng. Chem.* **40**:345 (1948).
10. A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC, A Group Contribution Method* (Elsevier, New York, 1977), pp. 6–20.