CONFORMAL-SOLUTION THEORY OF POLAR FLUIDS: THE STATISTICAL MECHANICAL BASIS OF SHAPE FACTORS

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The formalism of conformal-solution theory (CST) has been extended to pure and mixed polar fluids with consideration of dipolar, quadrupolar and induced dipolar forces. The total potential energy is reduced to a form similar to that for neutral molecules by statistical averaging over orientations. The temperature dependences of the conformal parameters f_{aa} and h_{aa} are derived and it is found that the temperature variations are in opposite directions. These conformal parameters are related to Leland's shape factors θ_{aa} and ϕ_{aa}, for which similar trends in temperature variations are observed. Following the theory of Byers-Brown for neutral molecular fluid mixtures, with the random-mixing approximation, an expression is derived for the excess Gibbs free energy of a binary polar mixture, using a generalized mixing-rule approximation.

INTRODUCTION

In the calculation of fluid-phase equilibria, an equation of state can in principle predict both the pure-component and mixture thermodynamic properties of fluids. However, most of the equations of state used in industrial applications are unable to predict phase equilibria when polar molecules are present (Rowlinson, 1979; Chao and Robinson, 1979). These equations are of an empirical nature, and their applicability to a variety of substances is limited. It is desirable to have a formalism based on molecular theories of liquids and liquid mixtures which would allow these equations of state to be extended to polar compounds.

In recent years there has been substantial interest in the thermodynamics of polar fluids (Stell et al., 1974; Rasiah et al., 1975;). The conformal-solution theory (CST) originally developed by Longuet-Higgins (1951) and Byers-Brown (1957a,b) for simple fluids can be used in either the equation-

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of-state or the activity-coefficient approach to the calculation of vapor–liquid equilibria. It is well known that existing semi-empirical models for conformal solutions, such as the average-potential model and van der Waals CST, are inapplicable when tested on highly polar mixtures. The main obstacle to a wider application of CST is a lack of theoretical mixing rules allowing the thermodynamic properties of polar mixtures to be predicted with sufficient accuracy. In this report we extend the formulation of CST to pure and mixed polar fluids with consideration of dipolar, quadrupolar and induced dipolar forces. This formulation of the theory is consistent with the existing experimental data of molecular shape factors as introduced by Leland and co-workers (Leland et al., 1962; Leach et al., 1966; Leach, 1967).

INTERMOLECULAR POTENTIAL OF POLAR FLUIDS

The CST treatment of fluids composed of polar molecules is more complicated than that of nonpolar fluids. This is due mainly to the presence of electrostatic interactions in the former case which cause a departure of the intermolecular potential from spherical symmetry. An electrostatic potential between two otherwise neutral molecules arises from permanent asymmetry in the charge distribution within the molecules. For any pair of localized charged distributions, the mutual electrostatic interaction energy can be written in terms of an infinite series of inverse powers of the separation of any two points. For no overlap between the charge distributions, i.e., when the separation between molecules is large relative to charge separation distances within the same molecules (Jackson, 1975), the series converges. The coefficients of the series are products of dipoles and higher moments of charge distribution. Thus the true pair-potential of polar molecules is orientation-dependent and is the sum of dispersion-force as well as electrostatic interactions:

$$U(r,\theta_i,\theta_j,\phi) = U_{disp} + U_{dip} + U_{quad} + U_{ind,dip} \tag{1}$$

where θ_i, θ_j are the angles between the axes of molecules i and j and the line joining their centers, respectively, and ϕ is the azimuthal angle between the planes containing these areas and the line of centers.

The dispersion interaction potential U appearing in eqn. (1) is spherically symmetric. For a pair of molecules i and j it may be taken to be represented by the Mie (n,m) potential function, i.e.,

$$U_{disp}(r) = K\epsilon_{i,j}\left[(\sigma_{i,j}/r)^n - (\sigma_{i,j}/r)^m\right] \tag{2}$$

with

$$K = [n/(n-m)](n/m)^{m/n-m}$$

The most widely used form of this potential is the Lennard–Jones ($n = 12$, $m = 6$) potential.

The dipole–dipole interaction potential U_{dip} has the form (Hirschfelder et al., 1964, p. 27)

$$U_{dip} = - \left(\mu_i \mu_j / r^3 \right) g\left(\theta_i, \theta_j, \phi \right) \tag{3}$$

where $g(\theta_i, \theta_j, \phi) = 2 \cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos\phi$, and μ_i is the dipole moment of the molecule i.

The quadrupolar interaction potential U_{quad} appearing in eqn. (1) has the form

$$U_{quad} = \left[3(\mu_i Q_j + \mu_j Q_i)/4r^4 \right] f(\theta_i, \theta_j, \phi) + \left[3Q_i Q_j / 4r^5 \right] h(\theta_i, \theta_j, \phi) \tag{4}$$

where $h(\theta_i, \theta_j, \phi) = 1 - 5 \cos^2\theta_i - 5 \cos^2\theta_j - 15 \cos^2\theta_i \cos^2\theta_j + 2[\sin\theta_i \cdot \sin\theta_j \cos\phi - 4\cos\theta_i \cos\theta_j]^2$; $f(\theta_i, \theta_j, \phi) = [\cos\theta_i(3\cos^2\theta_i - 1) - 2\sin\theta_i \sin\theta_j \cos\theta_j \cos(\phi_i - \phi_j)]$; and Q_i is the quadrupole moment of the molecule i. The first term on the right-hand side of eqn. (4) represents the dipole–quadrupole interaction and the second term the quadrupole–quadrupole interaction.

The last term on the right-hand side of eqn. (1), $U_{ind,dip}$, is the induced dipole interaction. The induced-dipole interaction term of the potential-energy function has the form (Hirschfelder et al., 1964, p. 27)

$$U_{ind,dip} = - (1/2r^6)\left[\alpha_i \mu_j^2 (3 \cos^2\theta_i + 1) + \alpha_j \mu_i^2 (3 \cos^2\theta_j + 1) \right] \tag{5}$$

where α_i and μ_i are respectively the polarizability and dipole moment of molecule i.

In order to formulate CST for polar fluids in a form similar to that for nonpolar fluids it would be necessary to reduce the intermolecular potential-energy function for polar fluids to an angle-independent form. This may be achieved through statistical averaging of the Helmholtz free energy as originally proposed by Onsager (1933) and Rushbrooke (1940) and implemented by Cook and Rowlinson (1953) for polar fluids. The resulting angle-averaged potential-energy function will then be related to the angle-dependent potential-energy function according to

$$U^*(r, T) = -kT \ln\left[(1/8\pi) \int_0^\pi \int_0^\pi \int_0^{2\pi} \exp\left[- U(r, \theta_i, \theta_j, \phi)/kT \right] \right.$$
$$\left. \sin\theta_i \sin\theta_j \, d\theta_i d\theta_j d\phi \right] \tag{6}$$

Now, in order to obtain the angle-averaged version of the intermolecular potential-energy function, eqn. (1) is substituted into the right-hand side of eqn. (6). Integration of the right-hand side of eqn. (6) may then be carried out by expansion of the exponential factor in powers of $1/kT$. The resulting angle-averaged, pair-interaction, intermolecular potential-energy function is

found to have the form

$$U^*(r, T) = K\epsilon_{ij}\left[(\sigma_{ij}/r)^n - (\sigma_{ij}/r)^m\right] - \mu_i^2\mu_j^2/3(kT)r^6 + 7\mu_i^4\mu_j^4/450(kT)^3r^{12}$$

$$- (1/2kT)\left(\mu_i^2Q_j^2 + \mu_j^2Q_i^2\right)/r^8 - (7/5)Q_i^2Q_j^2/(kT)r^{10}$$

$$- \left(\alpha_i\mu_j^2 + \alpha_j\mu_i^2\right)/r^6 \tag{7}$$

This angle-averaged potential represents the first-order contribution to the anisotropic forces. In this approximation the dipole–dipole-interaction expansion terms up to second order in $1/(kT)$ are retained, while for the other interactions only the lowest-order terms of their respective power-series expansions are considered. From the convergence point of view it should be mentioned that eqn. (7) is valid so long as the following conditions are satisfied:

$$\mu_i^2\mu_j^2/3(kT)^2r^6 < 1 \tag{8}$$

$$\left(\mu_i^2Q_j^2 + \mu_j^2Q_i^2\right)/2(kT)^2r^8 < 1 \tag{9}$$

$$Q_iQ_j/(kT)r^5 < 1/6 \tag{10}$$

and

$$\left(\alpha_i\mu_j^2 + \alpha_j\mu_i^2\right)/kTr^6 < 1 \tag{11}$$

When the temperature is not too low (for example at $T > 200$ K for $\mu \leqslant 3$), the above conditions are satisfied.

CONFORMAL-SOLUTION THEORY OF PURE POLAR FLUIDS

Conformal solution refers to substances whose intermolecular potential-energy functions are all related to each other and to that of a reference substance, usually designated by subscript zero, according to

$$U_{aa}(r) = f_{aa}U_{00}(r/g_{aa}) \tag{12}$$

For substances whose intermolecular potential-energy function can be represented by an equation of the form

$$U_{ij}(r) = E_{ij}\left[(\Gamma_{ij}/r)^n - (\Gamma_{ij}/r)^m\right] \tag{13}$$

and for which the exponents m and n are the same as for the reference substance, the conformal parameters f_{aa} and g_{aa} will be defined by the following relations with respect to the intermolecular potential-energy parameters E_{ij} and Γ_{ij}:

$$f_{aa} \equiv E_{aa}/E_{00}$$

$$g_{aa} = \Gamma_{aa}/\Gamma_{00} \tag{14}$$

Consequently, potential-energy functions (U_{ii}, U_{ij}, etc.) for conformal substances may be obtained from a common reference-substance potential U_{00} by selecting appropriate conformal parameters f_{ii} and g_{ii}.

According to CST (Rowlinson, 1969, Chaps, 7, 8;) for substances whose intermolecular potentials have the same values of m and n, the configurational partition function Z_a for molecules of type a can be related to the configurational partition function Z_0 for the reference substance according to

$$Z_a(V, T) = h_{aa}^N Z_0(V/h_{aa}, T/f_{aa})$$ (15)

where

$$Z = \int \ldots \int e^{-U/kT} \, dr_1, \ldots, dr_N$$ (16)

and

$$h_{aa} = g_{aa}^3$$ (17)

Thus the configurational thermodynamic properties of the substance of type a are related to those of the reference substance according to the following relations:

configurational Helmholtz free energy:

$$F_a(V, T) = f_{aa} F_0(V/h_{aa}, T/f_{aa}) - NkT \ln h_{aa}$$ (18)

pressure:

$$P_a(V, T) = (f_{aa}/h_{aa}) P_0(V/h_{aa}, T/f_{aa})$$ (19)

volume:

$$V_a(P, T) = h_{aa} V_0(f_{aa} P/h_{aa}, T/f_{aa})$$ (20)

configurational entropy:

$$S_a(V, T) = S_0(V/h_{aa}, T/f_{aa}) + Nk \ln h_{aa}$$ (21)

configurational Gibbs free energy:

$$G_a(P, T) = f_{aa} G_0(P h_{aa}/f_{aa}, T/f_{aa}) - NkT \ln h_{aa}$$ (22)

and, finally, configurational enthalpy:

$$H_a(P, S) = f_{aa} H_0(P h_{aa}/f_{aa}, S)$$ (23)

According to eqns. (18)–(23) all the thermodynamic properties of substance a can be expressed in terms of the conformal parameters h_{aa} and f_{aa}. For nonpolar substances, whose intermolecular potential-energy function can be represented by eqn. (2), the conformal parameters $f_{aa} = E_{aa}/E_{00}$ and $h_{aa} = (\sigma_{aa}/\sigma_{00})^3$ can be determined readily from experimental intermolecular

potential-energy data. For polar substances, whose intermolecular potential-energy function can be represented by eqn. (7), it can be shown that the conformal parameters f_{aa} and h_{aa} have the forms

$$f_{aa} = E_{aa}(T,r)/E_{00}(T,r) \tag{24}$$

$$h_{aa} = \left[\Gamma_{aa}(T,r)/\Gamma_{00}(T,r) \right]^3 \tag{25}$$

where

$$E_{ij}(T,r) = K\epsilon_{ij}A_{ij}(T,r)\left[G_{ij}(T,r) \right]^{n/m} \tag{26}$$

$$\Gamma_{ij}(T,r) = \sigma_{ij}\left[G_{ij}(T,r) \right]^{-1/m} \tag{27}$$

$$G_{ij}(T,r) = \left[B_{ij}(T,r)/A_{ij}(T,r) \right]^{m/(n-m)} \tag{28}$$

$$A_{ij}(T,r) = 1 + 7\mu_i^4\mu_j^4/1800(kT)^3\sigma_{ij}^n K\epsilon_{ij}r^{12-m} \tag{29}$$

and

$$\begin{aligned} B_{ij}(T,r) = 1 &+ \mu_i^2\mu_j^2/12(kT)\sigma_{ij}^m K\epsilon_{ij}r^{6-m} \\ &+ (7/20kT)Q_i^2Q_j^2/\sigma_{ij}^6 K\epsilon_{ij}r^{10-m} \\ &+ \left(\mu_i^2Q_j^2 + \mu_j^2Q_i^2 \right)/8kT\sigma_{ij}^m\epsilon_{ij}Kr^{8-m} \\ &+ \left(\alpha_i\mu_j^2 + \alpha_j\mu_i^2 \right)/4\sigma_{ij}^m\epsilon_{ij}Kr^{6-m} \end{aligned} \tag{30}$$

Eqns. (24)–(30) indicate that for the present formulation of CST for polar fluids, the conformal parameters f_{aa} and h_{aa} are generally dependent on temperature and on intermolecular separation. This makes direct determination of polar-fluid conformal parameters rather formidable. However, a number of useful conclusions can be deduced from these general relations which are of significance in the CST treatment of polar fluids. Also, there exist special circumstances under which conformal parameters for polar substances may be determined from intermolecular potential-energy data, as discussed below.

By substituting eqns. (26)–(28) into eqns. (24) and (25), the following expressions are derived for the conformal parameters:

$$\begin{aligned} f_{aa}(T,r) = (\epsilon_{aa}/\epsilon_{00})\left(A_{aa}(T,r)/A_{00}(T,r) \right)^{-m/(n-m)} \\ \times \left(B_{aa}(T,r)/B_{00}(T,r) \right)^{m/(n-m)} \end{aligned} \tag{31}$$

$$\begin{aligned} h_{aa}(T,r) = (\sigma_{aa}/\sigma_{00})^3\left(A_{aa}(T,r)/A_{00}(T,r) \right)^{3/(n-m)} \\ \times \left(B_{aa}(T,r)/B_{00}(T,r) \right)^{-3/(n-m)} \end{aligned} \tag{32}$$

According to eqns. (29) and (30) the temperature dependence of A_{aa}/A_{00} is

much smaller than that of B_{aa}/B_{00}. So to a first approximation, A_{aa}/A_{00} can be taken to be constant. Thus, according to eqns. (31) and (32), if the temperature is increased then f_{aa} and h_{aa} will vary in opposite directions: that is, h_{aa} increases while f_{aa} decreases. This observation is physically plausible, since as the temperature increases the system is expected to become more repulsive: that is, the "effective repulsive diameter" increases; and f_{aa}, which measures the depth of the attractive part of the potential, decreases. This observation can more readily be made if the second-order term in the dipole–dipole interaction is neglected (i.e., $A_{aa} = A_{00} = 1$).

Combining eqns. (31) and (32),

$$f_{aa} \cdot h_{aa}^{n/3} = (\epsilon_{aa}/\epsilon_{00})(\sigma_{aa}/\sigma_{00})^n (A_{aa}/A_{00}) \tag{33}$$

Provided that a reference substance is chosen that has no dipole moment ($A_{00} = 1$), eqn. (33) indicates that $f_{aa} \cdot h_{aa}^{n/3}$ should be a slowly decreasing function of temperature. For nonpolar substances and for polar substances having zero dipole moment (quadrupolar substances, such as carbon dioxide and benzene), $f_{aa} \cdot h_{aa}^{n/3}$ will be independent of temperature.

To separate the temperature dependence of the conformal parameters which arises from nonsphericity of the molecules, Leland and co-workers (Leland et al., 1962; Leach et al., 1966; Leach, 1967) introduced the concept of shape factor. Although the definition of shape factors is phenomeno-logical in nature, their values being determined in terms of macroscopic thermodynamic properties, they have been used quite successfully in corre-lating the thermophysical properties of polar substances. The molecular shape factors Θ_{aa} and Φ_{aa} for a pure substance are related to the conformal parameters f_{aa} and h_{aa} according to the relations

$$\Theta_{aa} = (T_0^c/T_a^c) f_{aa} \tag{34}$$

$$\Phi_{aa} = (V_0^c/V_a^c) h_{aa} \tag{35}$$

where T_i^c and V_i^c are respectively the critical temperature and critical volume of substance i. As $T_a^c/T_0^c = \epsilon_{aa}/\epsilon_{00}$ and $V_a^c/V_0^c = (\sigma_{aa}/\sigma_{00})^3$, the molecular shape factors take the forms

$$\Theta_{aa} = (A_{aa}/A_{00})^{-m/(n-m)} (B_{aa}/B_{00})^{n/(n-m)} \tag{36}$$

$$\Phi_{aa} = (A_{aa}/A_{00})^{3/(n-m)} (B_{aa}/B_{00})^{-3/(n-m)} \tag{37}$$

Using the same arguments as for eqns. (31) and (32), on increasing the temperature Θ_{aa} and Φ_{aa} will vary in opposite directions. Also,

$$\Theta_{aa} \Phi_{aa} = A_{aa}/A_{00} \tag{38}$$

should be a slowly decreasing function of temperature.

All the formulations and discussions presented above are based on the

assumption that the dispersion part of the intermolecular potential energy is the generalized Mie (n, m) potential function. However, the Lennard–Jones function ($m = 6$, $n = 12$) is the most commonly used form of the dispersion potential. Using the Lennard–Jones function, the dependence of the conformal parameters (and the shape factors) on intermolecular separation is minimal:

$$f_{aa} = (\epsilon_{aa}/\epsilon_{00})\Theta_{aa} = (\epsilon_{aa}/\epsilon_{00})(A_{00}/A_{aa})(B_{aa}/B_{00})^2 \tag{39}$$

$$h_{aa} = (\sigma_{aa}/\sigma_{00})^3\Phi_{aa} = (\sigma_{aa}/\sigma_{00})^3(A_{aa}/A_{00})^{1/2}(B_{aa}/B_{00})^{-1/2} \tag{40}$$

with

$$A_{aa} = 1 + 7\mu_a^8/1800(kT)^3\sigma_{aa}^{12}\epsilon_{aa} \tag{41}$$

and

$$B_{aa} = 1 + \mu_a^4/12\,kT\sigma_{aa}^6\epsilon_{aa} + 7Q_a^4/20\,kT\sigma_{aa}^6\epsilon_{aa}r^4$$
$$+ \mu_a^2Q_a^2/4kT\sigma_{aa}^6\epsilon_{aa}r^2 + \alpha_a\mu_a^2/2\sigma_{aa}^6\epsilon_{aa} \tag{42}$$

In this case only the two terms of eqn. (42) which include the quadrupole moments are r-dependent. In order to remove the r-dependence in these terms, the following approximation may be used:

$$Q_a/r \simeq \delta_{aa}Q_a/r_{aa}^* \equiv Q_a^{eff}/r_{aa}^* \tag{43}$$

where r_{aa}^* is the mean effective radius at which the potential makes the greatest contribution. It can be taken equal to the intermolecular distance, when the potential is at its minimum.

On the basis of the concept of shape factor, a great deal of computation has been performed to predict the thermophysical properties of polar fluids. There also exist a large number of empirical correlations of the shape factors for various substances (Leland et al., 1962; Leach et al., 1966; Leach, 1967). The available literature is indicative of the fact that the concept of shape factor has been quite successful in the correlation and prediction of thermophysical properties of polar fluids. The shape-factor correlations available in the literature are all based on vapor-pressure correlations and empirical equations of state, mostly the Benedict–Webb–Rubin equation and its branches. This has resulted in empirical shape-factor correlations which are usually expressed as functions of temperature and density. The CST results presented here consider only the temperature dependence of the shape factors; i.e., the shape factors are density-independent. This may be due to the averaging performed in eqn. (43) to make a quadrupole fluid conformable with a nonpolar reference fluid, and/or to the absence of a three-body potential in the total potential-energy function.

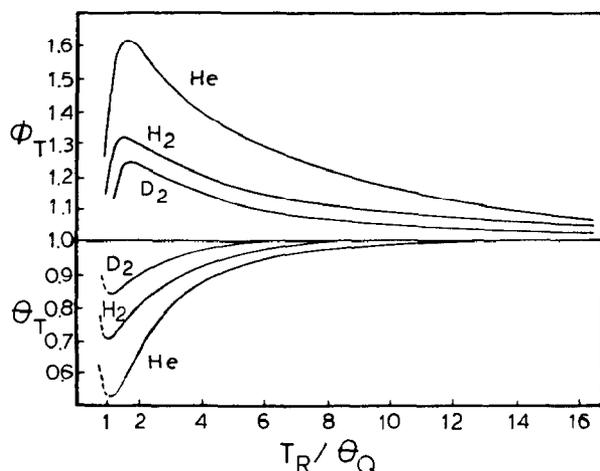However, it should be pointed out that the theoretical temperature-varia-

Fig. 1. Temperature dependence of shape factors at low density.

tion trends indicated by eqns. (36)–(38) and discussed above are all observed in the available empirical correlations of shape-factors. One such example is the low-density temperature-dependence of the shape factors of helium, hydrogen and deuterium, as reported by Leland and co-workers (Leland et al., 1962; Leach et al., 1966; Leach, 1967) and demonstrated in Fig. 1. According to this figure, Θ and Φ always have opposite slopes, as indicated by eqns. (36) and (37). Also, our computations indicate that when $n = 12$ (which is a reasonable value for simple molecules), $\Theta \cdot \Phi^4$ is a slowly decreasing function of temperature, as indicated by eqn. (38).

CONFORMAL SOLUTION THEORY OF MIXTURES

The basic concept of the CST of mixtures is the same as for pure fluids, with similar formulations, except that f_{aa} and h_{aa} in eqs. (18)–(23) should be replaced with f_{xx} and h_{xx}, the mixture conformal parameters, as given below

$$f_{xx}(T, X_i) = f_{xx}(f_{ij}, h_{ij}, X_i) \tag{44}$$

$$h_{xx}(T, X_i) = h_{xx}(f_{ij}, h_{ij}, X_i) \tag{45}$$

with

$$f_{ij} = E_{ij}/E_{00} \tag{46}$$

and

$$h_{ij} = \left(\Gamma_{ij}/\Gamma_{00} \right)^3 \tag{47}$$

where E_{ij} and Γ_{ij} have already been given by eqns. (26) and (27). Eqns. (44) and (45) are the mixture conformal-solution mixing rules. The functional forms of eqns. (44) and (45) will be different for different theories of mixtures. For example, according to the van der Waals theory (Leland et al., 1968), f_{XX} and h_{XX} for a multicomponent mixture may be expressed as

$$f_{XX} = \sum_{i=1}^{c} \sum_{j=1}^{c} X_i X_j f_{ij} h_{ij}^3 \Big/ \sum_{i=1}^{c} \sum_{j=1}^{c} X_i X_j h_{ij}^3 \tag{48}$$

and

$$h_{XX} = \sum_{i=1}^{c} \sum_{j=1}^{c} X_i X_j h_{ij} \tag{49}$$

where c is the number of components in the mixture. A variety of other mixing rules exist in the literature, in addition to the van der Waals mixing rules, discussion of which is beyond the scope of the present report.

In the formulation of a mixture theory it is also necessary to know the combination rules for the interaction parameters ϵ_{ij} and σ_{ij}, which are usually expressed with respect to ϵ_{ii}, ϵ_{jj}, σ_{ii} and σ_{jj} according to the expressions

$$\sigma_{ij} = \left(\sigma_{ii} + \sigma_{jj} \right)/2 \tag{50}$$

$$\epsilon_{ij} = \left(1 - k_{ij} \right)\left(\epsilon_{ii}\epsilon_{jj} \right)^{1/2} \tag{51}$$

where k_{ij} is an empirical coefficient to be calculated from macroscopic thermodynamic data. Eqns. (44)–(51), when combined with the preceding formulation of CST, will satisfy the requirements of extension of CST to the case of mixtures of polar fluids.

In order to derive workable expressions for the conformal parameters and excess thermodynamic properties of mixtures, it is necessary to redefine A_{ij} and B_{ij} (eqns. (41) and (42)) in the forms

$$A_{ij} = 1 + A_{ij}^{(1)} / (kT)^3 \tag{52}$$

and

$$B_{ij} = 1 + B_{ij}^{(1)} + \left[B_{ij}^{(2)} / (kT) \right]\left(1 + B_{ij}^{(3)} \right) \tag{53}$$

where

$$A_{ij}^{(1)} = 7\mu_i^4\mu_j^4 / 1800\, \sigma_{ij}^{12}\epsilon_{ij} \tag{54}$$

$$B_{ij}^{(1)} = \left(\alpha_i\mu_j^2 + \alpha_j\mu_i^2 \right)/4\sigma_{ij}^6\epsilon_{ij} \tag{55}$$

$$B_{ij}^{(2)} = \mu_i^2\mu_j^2 / 12\sigma_{ij}^6\epsilon_{ij} \tag{56}$$

and

$$B_{ij}^{(3)} = -15/28 + \left(15/28 + B_{ii}^{(3)}\right)^{1/2}\left(15/28 + B_{jj}^{(3)}\right)^{1/2} \tag{57}$$

with

$$B_{ii}^{(3)} = 3\left(Q_i^{\mathrm{eff}}/\mu_i r_{ii}^*\right)^2\left[1 + (7/5)\left(Q_i^{\mathrm{eff}}/\mu_i r_{ii}^*\right)^2\right] \tag{58}$$

and a similar expression for $B_{jj}^{(3)}$ obtained by replacing subscript i in eqn. (58) by j.

As a result of these redefinitions, f_{ij} and h_{ij} as given by eqns. (46) and (47) become

$$f_{ij} = \left(\epsilon_{ij}/\epsilon_{00}\right)\left[\frac{1 + A_{00}^{(1)}/(kT)^3}{1 + A_{ij}^{(1)}/(kT)^3}\right]\left[\frac{1 + B_{ij}^{(1)} + \left(B_{ij}^{(2)}/kT\right)\left(1 + B_{ij}^{(3)}\right)}{1 + B_{00}^{(1)} + \left(B_{00}^{(a)}/kT\right)\left(1 + B_{00}^{(3)}\right)}\right]^2 \tag{59}$$

and

$$h_{ij} = \left(\sigma_{ij}/\sigma_{00}\right)^3\left[\frac{1 + A_{ij}^{(1)}/(kT)^3}{1 + A_{00}^{(1)}/(kT)^3}\right]^{1/2}\left[\frac{1 + B_{ij}^{(1)} + \left(B_{ij}^{(2)}/kT\right)\left(1 + B_{ij}^{(3)}\right)}{1 + B_{00}^{(1)} + \left(B_{00}^{(2)}/kT\right)\left(1 + B_{00}^{(3)}\right)}\right]^{-1/2} \tag{60}$$

When expanded to the first order in powers of moments divided by kT, i.e., to the same order as the angle-averaging approximation of eqn. (6), eqns. (59) and (60) take the forms

$$f_{ij} = \left(\epsilon_{ij}/\epsilon_{00}\right)\left[1 + 2\left(B_{ij}^{(1)} - B_{00}^{(1)}\right) + (2/kT)\left(B_{ij}^{(4)} - B_{00}^{(4)}\right)\right.$$
$$\left. - \left[1/(kT)^3\right]\left(A_{ij}^{(1)} - A_{00}^{(1)}\right)\right] \tag{61}$$

and

$$h_{ij} = \left(\sigma_{ij}/\sigma_{00}\right)^3\left[1 - (1/2)\left(B_{ij}^{(1)} - B_{00}^{(1)}\right) - (1/2kT)\left(B_{ij}^{(4)} - B_{00}^{(4)}\right)\right.$$
$$\left. + \left[1/(kT)^3\right]\left(A_{ij}^{(1)} - A_{00}^{(1)}\right)\right] \tag{62}$$

with

$$B_{ij}^{(4)} = B_{ij}^{(2)}\left(1 + B_{ij}^{(3)}\right) \tag{63}$$

As for the angle-averaging approximation of the intermolecular potential (eqn. (6)), eqns. (61) and (62) are valid so long as conditions (8)–(11) are satisfied. Eqns. (61) and (62) combined with appropriate mixing rules for f_{XX} and h_{XX}, such as eqns. (48) and (49), provide analytical expressions for the mixture conformal parameters.

Considering mixtures of fluids, the major thermodynamic functions of

interest, which are also experimentally attainable, are the excess properties over the ideal mixture at the same given values of pressure, temperature and composition. In this Section we extend the formulation of the excess Gibbs free energy of nonpolar mixtures developed by Longuet-Higgins (1951) to the case of polar mixtures according to the principles of CST. Expressions for other excess thermodynamic properties then follow. In a similar fashion as for eqn. (22), the corresponding CST expression for the Gibbs free energy of a mixture, $G(T, P, X)$, is

$$G(T, P, X) = f_X G_0(Ph_{XX}/f_{XX}, T/f_{XX}) - RT \ln h_{XX} \tag{64}$$

Following Longuet-Higgins (1951), by selecting a reference substance having conformal parameters close to unity, $G(T, P, X)$ may be expanded in powers of

$$\delta f_{XX} = f_{XX} - 1$$
$$\delta h_{XX} = h_{XX} - 1 \tag{65}$$

about the value G_0 for an isotropic reference mixture of the same composition, as

$$G(T, P, X) = G^0(T, P, X) + U_0(\delta f_X) + (PV_0 - RT)(\delta h_{XX}) + (1/2)(-TC_{P0}$$
$$+ PTV_0\alpha_0 - P^2V_0\kappa_0)(\delta f_X)^2 + (P^2V_0\kappa_0 - PTV_0\alpha_0)(\delta f_X \delta h_X)$$
$$+ (1/2)(RT - P^2V_0\kappa_0)(\delta h_X)^2 + 0(\delta^3) \tag{66}$$

with

$$G^0(T, P, X) = G_0(T, P) + RT\sum_i X_i \ln X_i \tag{67}$$

In eqn. (66) properties with subscript zero are those of a reference pure substance at the same temperature and pressure as the mixture. U_0 is the internal energy, C_{P0} the heat capacity at constant pressure, V_0 the volume, α_0 the coefficient of thermal expansivity, and κ_0 the coefficient of isothermal compressibility for the reference pure substance. Eqn. (66), when written for a pure component i, has the form originally derived by Byers-Brown (1957a,b):

$$G_i(T, P) = G_0(T, P) + U_0\delta f_{ii} + (PV_0 - RT)\delta h_{ii} + (1/2)(-TC_{P0} + 2PTV_0\alpha_0$$
$$- P^2V_0\kappa_0)(\delta f_{ii})^2 + (P^2V_0\kappa_0 - PTV_0\alpha_0)\delta f_{ii}\delta h_{ii}$$
$$+ (1/2)(RT - P^2V_0\kappa_0)(\delta h_{ii})^2 + 0(\delta^3) \tag{68}$$

where, as for eqn. (65), δf_{ii} and δh_{ii} are defined as

$$\delta f_{ii} = f_{ii} - 1$$
$$\delta h_{ii} = h_{ii} - 1 \tag{69}$$

Combining eqns. (66) and (67) with the definition of the excess Gibbs free energy,

$$G^{E} = G(T, P, X) - \sum_{i=1}^{c} G_i(T, P) - RT \sum_i X_i \ln X_i \tag{70}$$

the following general expression is derived for the excess Gibbs free energy according to CST:

$$G^{E} = G_f\left(\delta f_x - \sum_i X_i \delta f_{ii}\right) + G_h\left(\delta h_x - \sum_i X_i \delta h_{ii}\right) + G_{ff}\left[(\delta f_x)^2 - \sum_i X_i(\delta f_{ii})^2\right]$$

$$+ G_{hh}\left[(\delta h_x)^2 - \sum_i X_i(\delta h_{ii})^2\right] + G_{fh}\left[\delta f_x \delta h_x - \sum_i X_i \delta f_{ii} \delta h_{ii}\right] + 0(\delta^3) \tag{71}$$

where

$$G_f = U_0 \tag{72}$$

$$G_h = (PV_0 - RT) \tag{73}$$

$$G_{ff} = (1/2)\left(-TC_{P0} + 2PTV_0\alpha_0 - P^2V_0\kappa_0\right) \tag{74}$$

$$G_{hh} = (1/2)\left(RT - P^2V_0\kappa_0\right) \tag{75}$$

$$G_{fh} = \left(P^2V_0\kappa_0 - PTV_0\alpha_0\right) \tag{76}$$

Using the generalized forms of the mixing rules,

$$f_x = \left[\sum_i \sum_j X_i X_j f_{ij}^m h_{ij}^n\right]^{q/(mq-np)} \left[\sum_i \sum_j X_i X_j f_{ij}^p h_{ij}^q\right]^{-n/(mq-np)} \tag{77}$$

$$h_x = \left[\sum_i \sum_j X_i X_j f_{ij}^m h_{ij}^n\right]^{-p/(mq-np)} \left[\sum_i \sum_j X_i X_j f_{ij}^p h_{ij}^q\right]^{m/(mq-np)} \tag{78}$$

in eqn. (70) and following a method similar to that of Byers-Brown (1957a,b), the expansions of eqns. (76) and (77) in powers of δf_{ij} and δh_{ij} are:

$$\delta f_x = \sum_i \sum_j X_i X_j \delta f_{ij} + \left[nq(m-p)/(mq-np)\right]$$

$$\times \left[\sum_i \sum_j X_i X_j \delta f_{ij} \delta h_{ij} - \left(\sum_i \sum_j X_i X_j \delta f_{ij}\right)\left(\sum_i \sum_j X_i X_j \delta h_{ij}\right)\right]$$

$$+ (1/2)[nq(n-q)/(mq-np)]\left[\sum_i \sum_j (\delta h_{ij})^2 - \left(\sum_i \sum_j X_i X_j \delta h_{ij}\right)^2\right]$$

$$+ (1/2)\left\{\left[(m^2q - np^2)/(mq-np)\right] - 1\right\}$$

$$\times \left[\sum_i \sum_j X_i X_j (\delta f_{ij})^2 - \left(\sum_i \sum_j X_i X_j \delta f_{ij}\right)^2\right] + 0(\delta^3) \tag{79}$$

and

$$\delta h_x = \sum_i \sum_j X_i X_j \delta h_{ij} + \left[pm(q-n)/(mq-np) \right]$$

$$\times \left[\sum_i \sum_j X_i X_j \delta f_{ij} - \left(\sum_i \sum_j X_i X_j \delta f_{ij} \right) \left(\sum_i \sum_j X_i X_j \delta h_{ij} \right) \right]$$

$$+ (1/2) \left[mp(p-m)/(mq-np) \right]$$

$$\times \left[\sum_i \sum_j X_i X_j (\delta f_{ij})^2 - \left(\sum_i \sum_j X_i X_j \delta f_{ij} \right)^2 \right]$$

$$+ (1/2) \left\{ \left[(mq^2 - n^2 p)/(mq-np) \right] - 1 \right\}$$

$$\times \left[\sum_i \sum_j X_i X_j (\delta h_{ij})^2 - \left(\sum_i \sum_j X_i X_j \delta h_{ij} \right)^2 \right] \tag{80}$$

By substituting eqns. (79) and (80) into the expression for the excess free energy (eqn. (71)), the result is obtained that

$$G^E = G_f \left[\sum_i \sum_j X_i X_j \delta f_{ij} - \sum_i \sum_j X_i \delta f_{ii} \right] + G_h \left[\sum_i \sum_j X_i X_j \delta h_{ij} - \sum_i \sum_j X_i \delta h_{ij} \right]$$

$$+ (Z_{ff}/2) \sum_i \sum_j X_i X_j (\delta f_{ij})^2 + (1/2)(G_{ff} - Z_{ff})$$

$$\times \left(\sum_i \sum_j X_i X_j \delta f_{ij} \right)^2 - (G_{ff}/2) \sum_i X_i (\delta f_{ii})^2$$

$$+ (Z_{hh}/2) \sum_i \sum_j X_i X_j (\delta h_{ij})^2 + (1/2)(G_{hh} - Z_{hh})$$

$$\times \left(\sum_i \sum_j X_i X_j \delta h_{ij} \right)^2 - (G_{hh}/2) \sum_i X_i (\delta h_{ii})^2$$

$$+ Z_{fh} \sum_i \sum_j X_i X_j \delta f_{ij} \delta h_{ij} + (G_{fh} - Z_{fh})$$

$$\times \left(\sum_i \sum_j X_i X_j \delta f_{ij} \right) \left(\sum_i \sum_j X_i X_j \delta h_{ij} \right) - G_{fh} \sum_i X_i (\delta f_{ii})(\delta h_{ii}) + 0(\delta^3) \tag{81}$$

where

$$Z_{hh} = G_f \left[nq(n-q)/(mq-np) \right] + (G_h/2) \left\{ \left[(mq^2 - n^2 p)/(mq-np) \right] - 1 \right\} \tag{82}$$

$$Z_{ff} = G_f \left\{ \left[(m^2 q - np^2)/(mq-np) \right] - 1 \right\} + G_h mp(p-m) \tag{83}$$

$$Z_{fh} = G_f[nq(m-p)/(mq-np)] + G_h[mp(q-n)/(mq-np)] \qquad (84)$$

Finally, the excess Gibbs free energy G^E (eqn. (80)) for a binary mixture may be computed:

$$
\begin{aligned}
G^E = X(1-X)(eG_f + sG_h) + (1/2)X(1-X)\Big\{ -\Big[\theta^2\big(G_{ff} - (1/2)Z_{ff}\big) \\
+ \phi^2\big(G_{hh} - (1/2)Z_{hh}\big) \\
+ 2\theta\phi\big(G_{fh} - (1/2)Z_{fh}\big)\Big] + (1/4)\Big[e^2\big(G_{ff} + Z_{ff}\big) \\
+ s^2\big(G_{hh} + Z_{hh}\big) + 2\,es\big(G_{fh} + Z_{fh}\big)\Big] \\
+ (1-2X)\Big[e\theta\big(G_{ff} - Z_{ff}\big) \\
+ s\phi\big(G_{hh} - Z_{hh}\big) + s\theta\big(G_{fh} - Z_{fh}\big) + e\phi\big(G_{fh} - Z_{fh}\big)\Big] \\
- (1/4)(1-2X)^2\Big[e^2\big(G_{ff} - Z_{ff}\big) + s^2\big(G_{hh} - Z_{hh}\big) + 2\,es\big(G_{fh} - Z_{fh}\big) \\
+ (1/2)\big(eG_{ff} + sG_{fh}\big)\delta(f_{11} + f_{22}) \\
+ (1/2)\big(eG_{fh} + sG_{hh}\big)\delta(h_{11} + h_{22})\Big]\Big\}
\end{aligned}
\qquad (85)
$$

where

$$e = 2f_{12} - f_{11} - f_{22}$$
$$s = 2h_{12} - h_{11} - h_{22}$$
$$\theta = f_{11} - f_{22} \qquad (86)$$
$$\phi = h_{11} - h_{22}$$

The generalized mixing rules (76) and (77) reduce to van der Waals mixing rules when $m = 1$, $n = 1$, $p = 0$, $q = 1$, and to those of the average-potential model when $m = 1$, $n = 2$, $p = 1$, $q = 4$. All other mixing rules available in the literature can be deduced from eqns. (76) and (77) by appropriate choices of the exponents m, n, p and q.

DISCUSSION

In this report conformal-solution theory (CST) has been extended to polar fluids. This was done by reducing the intermolecular potential energy of polar molecules to a form analogous to that for neutral molecules by the configurational-angle averaging technique. We have been able to derive temperature-dependence expressions for the conformal parameters f_{aa} and h_{aa}, and found that they have opposite trends with respect to temperature variation. These conformal parameters have been related to Leland and

co-workers' notion of shape factors, from which the statistical mechanical basis of shape factors has been found. The theory indicates that molecular shape factors are temperature-dependent only, whereas the available shape-factor data (Leland et al., 1962; Leach et al., 1966; Leach, 1967) are both density- and temperature-dependent. However, the theoretical temperature-variation trends agree with all the empirical correlations of shape factors when density is kept constant. CST has also been extended to polar liquid mixtures. This was done by expanding the conformal parameters in powers of moments over kT. By using a generalized mixing rule, an expression has been derived for the excess Gibbs free energy of polar mixtures. This expression reduces to a simple form for binary mixtures. On the basis of the expression for the excess Gibbs free energy, expressions for activity coefficients and other excess thermodynamic properties can be derived.

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