MOLECULAR BASIS OF ACTIVITY COEFFICIENTS
(ISOBARIC-ISOTHERMAL ENSEMBLE APPROACH)

G.ALI MANSOORI [*]

*Department of Energy Engineering, University of Illinois at Chicago Circle,
(Box 4348) Chicago, Illinois 60680 (U.S.A.)*

ABSTRACT

Through the application of isobaric-isothermal (NPT) ensemble theory, molecular rela-tions for thermodynamic properties of mixtures are derived with pressure and tempera-ture as the independent variables. Use of the NPT-ensemble approach has made it possible to derive exact molecular thermodynamic relations for activity coefficients of mixtures in the form of the Redlich—Kister power series. It has also become possible to examine the fundamental implications of some of the approximation correlations for the activity coefficient.

INTRODUCTION

In fluid phase equilibria the chemical potential μ_i of a component in liquid solution is defined with respect to the activity coefficient γ_i of that component through (Prausnitz, 1969; Prigogine and Defay, 1954)

$$\mu_i(P, T, x_i\text{'s}) \equiv \mu_i^0 + RT \ln[x_i\gamma_i(P, T, x_i\text{'s})] \qquad (1)$$

In this equation μ_i^0 is commonly called the standard state chemical potential of i which may be chosen equal to the chemical potential of i in the pure state at the temperature and pressure of the solution

$$\mu_i^0 \equiv g_i(P, T) \qquad (2)$$

where g_i is the molar Gibbs free energy of pure component i.

It has been the general practice to use the canonical or the grand canonical theories of statistical thermodynamics to express the chemical potential and activity coefficient with respect to the molecular properties of matter (Prigogine and Defay, 1954; Hill, 1956; Wojtowicz et al., 1957). However, the major problem in application of canonical and grand canonical theories is that the resulting thermodynamic functions are dependent on volume and temperature rather than pressure and temperature which are preferable in

Email addresses: *mansoori@uic.edu, gali.mansoori@gmail.com*

fluid phase equilibria calculations. To derive molecular thermodynamic relations for activity coefficients or chemical potentials which are dependent on P and T, one should use the isobaric-isothermal ensemble theory of statistical thermodynamics.

In the discussion presented here, the use of the isobaric-isothermal partition function allows the derivation of a molecular thermodynamic relation for the activity coefficient. The resulting relation has made possible the molecular interpretation of a number of correlations for the activity coefficient.

ISOBARIC-ISOTHERMAL (NPT) ENSEMBLE THEORY

According to statistical thermodynamics, for an assembly of N particles of different kinds at a temperature T and pressure P in equilibrium at the classical limit the partition function Δ is (Hill, 1956)

$$\Delta(N,\, P,\, T) = \prod_{i=1}^{c} \left(\frac{1}{N_i!\, \Lambda_i^{3N_i}} \right) \int_0^\infty \mathrm{d}\left(\frac{V}{V^*} \right) e^{-PV/NkT} \int_V \ldots N \ldots \int_V e^{-\phi/kT}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N \tag{3}$$

In this equation ϕ is the total intermolecular potential energy function of the assembly of particles, $\Lambda_i = h/[(2\pi m_i kT)^{1/2}]$, V^* is a reference volume, N_i is the number of particles of species i and c is the total number of species (or components) of the system. The total Gibbs free energy of the assembly can then be defined with respect to Δ by

$$G(P,\, T) = -kT \ln \Delta(N,\, P,\, T) \tag{4}$$

with the use of eqns. (3) and (4) other thermodynamic properties, such as volume, enthalpy and internal energy, can be expressed with respect to pressure, temperature and intermolecular interactions as

$$V(P,\, T) = (\partial G/\partial P)_{T,N} = -kT(\partial \ln \Delta/\partial P)_{T,N} = \langle V \rangle \tag{5}$$

$$H(P,\, T) = -T^2 \left(\frac{\partial (G/T)}{\partial T} \right)_{P,N} = kT^2 \left(\frac{\partial \ln \Delta}{\partial T} \right)_{P,N} = H^{ig}(T) + P\langle V \rangle + \langle \phi \rangle \tag{6}$$

$$\Delta U = U(P,\, T) - U^{ig}(T) = \langle \phi \rangle \tag{7}$$

In the above relations, the angled brackets stand for the expectation value of the function inside the bracket over the NPT-ensemble, i.e.

$$\langle \xi \rangle = (1/\Delta_c) \int_0^\infty e^{-PV/NkT}\, \mathrm{d}V \int_V \ldots N \ldots \int_V e^{-\phi/kT}\, \xi\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N \tag{8}$$

where Δ_c stands for the configurational partition function

$$\Delta_c \equiv \int_0^\infty e^{-PV/NkT}\, \mathrm{d}V \int_V \ldots N \ldots \int_V e^{-\phi/kT}\, \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N \tag{9}$$

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Similarly, the following molecular thermodynamic relations can be derived for isothermal compressibility κ, isobaric compressibility β and heat capacity at constant pressure C_P

$$\kappa \equiv (1/V)(\partial V/\partial P)_T = (1/VRT)[\langle v^2 \rangle - \langle v \rangle^2] \tag{10}$$

$$\beta \equiv (1/V)(\partial V/\partial T)_P = (P/T)\kappa + (1/VRT)[\langle v\phi \rangle - \langle v \rangle \langle \phi \rangle] \tag{11}$$

$$\Delta C_p = C_p - C_p^{ig} = RZ(2T\beta - P\kappa) + (1/RT^2)(\langle \phi^2 \rangle - \langle \phi \rangle^2) \tag{12}$$

where $Z = PV/NkT$, $R = N_A k$ and N_A is Avogadro's number.

When the total number of particles in the system equals Avogadro's number N_A, the molar Gibbs free energy g can be defined with respect to Δ in the following form

$$g(P, T, x_i\text{'s}) = -kT \ln \Delta(N_A, P, T); \qquad N_A = \sum_{i=1}^{c} N_i \tag{13}$$

Having the molar Gibbs free energy of the solution, the chemical potential of any component i can be derived through

$$\mu_i = g + (1 - x_i)(\partial g/\partial x_i)_{P,T,x_j/x_k}; \qquad i \neq j \neq k \tag{14}$$

In the present discussion we will only consider binary solutions. As a result, for the chemical potential of component one, we will have

$$\mu_1(P, T, x_1) = g + x_2(\partial g/\partial x_1)_{P,T} = -kT\{\ln \Delta - x_2(\partial \ln \Delta/\partial x_1)_{P,T}\} \tag{15}$$

From the definition of activity coefficient given by eqn. (1), and using eqn. (15) the following relation for activity coefficient of component one can be derived

$$\ln \gamma_1(P, T, x_1) = -(1/N_A)\{\ln(\Delta_c/\Delta_{c_1}) + x_2(\partial \ln \Delta_c/\partial x_1)_{P,T}\} \tag{16}$$

where Δ_{c1} is the molar configurational integral of pure component one

$$\Delta_{c1}(P, T, N_A) = \int_0^\infty e^{-PV/NkT} dV \int_v ... N_A ... \int_v e^{-\phi_1/kT} d\mathbf{r}_1 ... d\mathbf{r}_{N_A} \tag{17}$$

and ϕ_1 is the total potential energy function of pure component one.

Using a Taylor series expansion we can write

$$\ln \Delta_c = \ln \Delta_{c1} + x_2 \left(\frac{\partial \ln \Delta_c}{\partial x_2}\right)_{P,T,x_2=0} + \sum_{n=2}^{\infty} \frac{x_2^n}{n!} \left(\frac{\partial^n \ln \Delta_c}{\partial x_2^n}\right)_{P,T,x_2=0} \tag{18}$$

Similarly,

$$\left(\frac{\partial \ln \Delta_c}{\partial x_1}\right)_{P,T} = \left(\frac{\partial \ln \Delta_c}{\partial x_1}\right)_{P,T,x_2=0} + \sum_{m=1}^{\infty} \frac{x_2^m}{m!} \frac{\partial^m}{\partial x_2^m} \left(\frac{\partial \ln \Delta_c}{\partial x_1}\right)_{P,T,x_2=0} \tag{19}$$

By replacing eqns. (18) and (19) in eqn. (16) the following power series for

activity coefficient results

$$\ln \gamma_1(P,\ T,\ x_1) = \frac{1}{N_A} \sum_{n=2}^{\infty} x_2^n \frac{(n-1)}{n!} \left(\frac{\partial^n \ln \Delta_c}{\partial x_2^n}\right)_{P,T,x_2=0} \tag{20}$$

Equation (20) is equivalent to the Redlich—Kister correlation for the activity coefficient

$$\ln \gamma_1 = a_1^{(1)} x_2^2 + a_2^{(1)} x_2^3 + \ldots \tag{21}$$

with

$$a_n^{(1)} = \frac{1}{N_A} \frac{n}{(n+1)!} \left(\frac{\partial^{n+1} \ln \Delta_c}{\partial x_2^{n+1}}\right)_{P,T,x_2=0} \tag{22}$$

Using the Gibbs—Duhem equation for activity coefficients

$$x_1\ \mathrm{d} \ln \gamma_1 + x_2\ \mathrm{d} \ln \gamma_2 = 0 \tag{23}$$

it can be shown that

$$\sum_{n=0}^{\infty} \frac{1}{n!} \left\{ x_2^n \left(\frac{\partial^{n+2} \ln \Delta_c}{\partial x_2^{n+2}}\right)_{P,T,x_2=0} - x_1^n \left(\frac{\partial^{n+2} \ln \Delta_c}{\partial x_1^{n+2}}\right)_{P,T,x_1=0} \right\} = 0 \tag{24}$$

In order to calculate the coefficients $a_n^{(1)}$ presented in eqn. (22) the configurational integral Δ_c for the liquid solution must be known. Using the conformal solution theory of mixtures, analytical relations for the first few terms in the expansion of eqn. (20) can be derived with respect to the thermodynamic properties of component one.

According to the conformal solution theory, when the total potential energy function of the mixture is assumed to be pairwise-additive it becomes

$$\phi(r_{ij}) = \bar{\epsilon} \psi(r_{ij}/\bar{\sigma}) = \bar{\epsilon} \sum_{j>i=1}^{N} \sum f(r_{ij}/\bar{\sigma}) \tag{25}$$

where $\bar{\epsilon}$ and $\bar{\sigma}$ are called the conformal solution (or pseudo-potential) parameters of the mixture such that

$$\begin{cases} \bar{\epsilon} = \bar{\epsilon}(\epsilon_{ij},\ \sigma_{ij},\ x_i\text{'s}) \\ \bar{\sigma} = \bar{\sigma}(\epsilon_{ij},\ \sigma_{ij},\ x_i\text{'s}) \end{cases}$$

Using eqns. (24) and (25), Δ_c can be written as

$$\Delta_c(P,\ T,\ N_A) = N_A\ \bar{\sigma}^{3N_A+3} \Delta_c^*(\Pi,\ \theta,\ N_A) \tag{26}$$

where

$$\Delta_c^*(\Pi,\ \theta,\ N_A) = \int_0^{\infty} \mathrm{d}X\ e^{-\Pi X} \int_X \ldots N_A \ldots \int_X e^{-\theta \psi}\ \mathrm{d}X_1 \ldots \mathrm{d}X_{N_A} \tag{27}$$

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with $X \equiv V/N_A \bar{\sigma}^3$, $\Pi \equiv P\bar{\sigma}^3/kT$, $\theta = \bar{\epsilon}/kT$ and $dX_i = d\mathbf{r}_i/\bar{\sigma}^3$.

Substituting eqn. (26) into eqn. (20) produces

$$\ln \gamma_1 = \sum_{n=2}^{\infty} \frac{n-1}{n!} x_2^n \left\{ \left(\frac{d^n \ln \bar{\sigma}^3}{dx_2^n} \right)_{x_2=0} + \frac{1}{N_A} \left(\frac{\partial^n \ln \Delta_c^*}{\partial x_2^n} \right)_{P,T,x_2=0} \right\} \tag{28}$$

From eqns. (27) and (28) it can be shown that the first two terms of expansion (21) will be

$$a_1^{(1)} = \frac{1}{2} \left(\frac{d^2 \ln \bar{\sigma}^3}{dx_2^2} \right)_{x_2=0} + \frac{1}{2N_A}$$

$$\times \{ \langle [\Pi'(X - \langle X \rangle) + \theta'(\psi - \langle \psi \rangle)]^2 \rangle - (\Pi'' \langle X \rangle + \theta'' \langle \psi \rangle) \} \tag{29}$$

and

$$a_2^{(1)} = \frac{1}{3} \left(\frac{d^3 \ln \bar{\sigma}^3}{dx_2^3} \right)_{x_2=0} - \frac{1}{3N_A} \{ \langle [\Pi'(X - \langle X \rangle) + \theta'(\psi - \langle \psi \rangle)]^3 \rangle$$

$$+ 3[\Pi'\Pi'' \langle (X - \langle X \rangle)^2 \rangle + \theta'\theta'' \langle (\psi - \langle \psi \rangle)^2 \rangle$$

$$- (\Pi'\theta'' + \Pi''\theta')(\langle X\psi \rangle - \langle X \rangle \langle \psi \rangle)] - (\Pi''' \langle X \rangle + \theta''' \langle \psi \rangle) \} \tag{30}$$

where

$$\Pi^{(n)} \equiv 3 \frac{P}{kT} \left(\frac{d^n \bar{\sigma}^3}{dx_2^n} \right)_{x_2=0} ; \qquad \theta^{(n)} \equiv \frac{1}{kT} \left(\frac{d^n \bar{\epsilon}}{dx_2^n} \right)_{x_2=0} \tag{31}$$

Using eqns. (5)—(12) coefficient $a_1^{(1)}$ can be expressed with respect to thermodynamic functions as the following

$$a_1^{(1)} = \frac{3}{2} \left(\frac{d^2 \ln \bar{\sigma}^3}{dx_2^2} \right)_{x_2=0} + RT^2 \left\{ \kappa Z \left[\left(\frac{\Pi'}{N_A \bar{\sigma}^3} \right) \frac{1}{P} + \left(\frac{\theta'}{\bar{\epsilon}} \right) P - 2 \left(\frac{\Pi'}{N_A \bar{\sigma}^3} \right) \left(\frac{\theta'}{\bar{\epsilon}} \right) \frac{1}{T} \right] \right.$$

$$- 2\beta Z \left[\left(\frac{\theta'}{\bar{\epsilon}} \right)^2 T - \left(\frac{\Pi'}{N_A \bar{\sigma}^3} \right) \left(\frac{\theta'}{\bar{\epsilon}} \right) \frac{1}{P} \right] + \Delta C_p \left(\frac{\theta'}{\bar{\epsilon}} \right)^2 \right\}_{x_2=0}$$

$$- \left[\left(\frac{\Pi''}{N_A \bar{\sigma}^3} \right) V + \left(\frac{\theta''}{\bar{\epsilon}} \right) \Delta U \right]_{x_2=0} \tag{32}$$

A similar, but lengthier, relation can be derived for $a_2^{(1)}$.

There exist a number of conformal solution mixing rules for $\bar{\sigma}$ and $\bar{\epsilon}$, but the ones due to van der Waals have a sound theoretical basis with a proven accuracy (Leland et al., 1968). According to van der Waals

$$\bar{\sigma} = \{ \sum_{i,j=1}^{c} x_i x_j \sigma_{ij}^3 \}^{1/3} \tag{33}$$

and

$$\bar{\epsilon} = \sum_{i,j=1}^{c} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \Big/ \sum_{i,j=1}^{c} x_i x_j \sigma_{ij}^3 . \tag{34}$$

Using the van der Waals conformal solution mixing rules, eqn. (28) for activity coefficients can be written in the following form

$$\ln \gamma_1 = \sum_{n=2}^{\infty} \frac{n-1}{n!} x_2^n \left\{ -\left[1 - \left(\frac{\sigma_{22}}{\sigma_{11}} \right)^3 \right]^n + \frac{1}{N_A} \left(\frac{\partial^n \ln \Delta_c^*}{\partial x_2^n} \right) \right\}_{P,T,x_2=0} \tag{35}$$

and the first term of this expansion, $a_1^{(1)}$ will be

$$a_1^{(1)} = \tfrac{1}{2} \left\{ (1-r)^2 (PZ_1 \kappa_1 - 1) + E_1^2 (1+r)^2 \left[\frac{\Delta C_{p1}}{R} + Z_1 (P\kappa_1 - 2\beta_1 T) \right] \right.$$

$$\left. + 2E_1 (1-r^2) Z_1 (\beta_1 T - P\kappa_1) - 2r(E_1 r + E_2) \frac{\Delta U_1}{RT} \right\} \tag{36}$$

with

$$r \equiv (\sigma_{22}/\sigma_{11})^3 , \qquad E_1 \equiv 1 - \epsilon_{12}/\epsilon_{11} \quad \text{and} \quad E_2 \equiv (\epsilon_{22}\epsilon_{12})/\epsilon_{11} .$$

In order to calculate coefficients $a_n^{(1)}$ from statistical thermodynamics one has to solve the configurational integral Δ_c as given by eqns. (9) or (26). The rigorous solution of the configurational integral requires application of Monte Carlo and molecular dynamics computer techniques. There exist also a number of approximation techniques through which the configurational integral can be calculated. In any circumstance, it is necessary to truncate the activity coefficient power series as given in different forms by eqns. (20), (28) or (34). In the following sections the molecular implications of some of the correlations of activity coefficients and their relationships with truncated activity coefficient power series is discussed.

MARGULES TWO-SUFFIX CORRELATION

This correlation is equivalent to the case when the power series for the activity coefficient is truncated after the first term. According to eqn. (35) in this case

$$\ln \gamma_1 = \frac{1}{2N_A} \left(\frac{\partial^2 \ln \Delta_c}{\partial x_2^2} \right)_{P,T,x_2=0} x_2^2$$

$$= \tfrac{1}{2} \left\{ -\left[1 - \left(\frac{\sigma_{22}}{\sigma_{11}} \right)^3 \right]^2 + \frac{1}{N_A} \left(\frac{\partial^2 \ln \Delta^*}{\partial x_2^2} \right)_{P,T,x_2=0} \right\} x_2^2 \tag{37}$$

Since $\ln \gamma_2$ will also have a form similar to eqn. (37) the Gibbs—Duhem consistency relation, eqn. (23) will require that

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$$-\left[1-\left(\frac{\sigma_{22}}{\sigma_{11}}\right)^3\right]^2 + \frac{1}{N_A}\left(\frac{\partial^2 \ln \Delta_c^*}{\partial x_2^2}\right)_{P,T,x_2=0} = -\left[1-\left(\frac{\sigma_{11}}{\sigma_{22}}\right)^3\right]^2$$
$$+ \frac{1}{N_A}\left(\frac{\partial^2 \ln \Delta_c^*}{\partial x_1^2}\right)_{P,T,x_1=0} \qquad (38)$$

For eqn. (38) to hold at all conditions of pressure and temperature we should have

$$\sigma_{11} = \sigma_{22} \qquad (39)$$

$$\left(\frac{\partial^2 \ln \Delta_c^*}{\partial x_2^2}\right)_{P,T,x_2=0} = \left(\frac{\partial^2 \ln \Delta_c^*}{\partial x_1^2}\right)_{P,T,x_1=0} \neq 0 \qquad (40)$$

and

$$\left(\frac{\partial^n \ln \Delta_c^*}{\partial x_2^n}\right)_{P,T,x_2=0} = \left(\frac{\partial^n \ln \Delta_c^*}{\partial x_1^n}\right)_{P,T,x_1=0} = 0 \qquad \text{for } n \geqslant 3 \qquad (41)$$

The first condition, eqn. (39), implies that the Margules two-suffix correlation is good for mixtures of components with equal molecular sizes. For eqns. (40) and (41) to hold it is necessary to have

$$\ln \Delta_c^* \propto x_2^2 \qquad (42)$$

One special case for which the configurational integral of the mixture satisfies eqn. (42) is when the lattice theory of liquids with uniform potential inside each cell can be assumed for the mixture. According to the Lennard-Jones and Devonshire lattice theory of liquids (Lennard-Jones and Devonshire, 1937), Δ_c^* can be written as

$$\Delta_c^* = \exp(-N_A \bar{\epsilon}/kT) \int_0^\infty e^{-\Pi X} v_f^{*N_A} \, dX$$

where v_f^* is the cell free volume

$$v_f^* = 2\sqrt{2}\,\Pi(X) \int_0^{0.30544} r^{1/2} \exp\{-[y(r)-y(0)]/kT\} \, dr$$

For cells with uniform potential fields and molecules of equal sizes

$$v_f^* = 2.6867\,X$$

and

$$\Delta_c^* = (2.6867)^{N_A} \exp(-N_A \bar{\epsilon}/kT) \frac{N_A!}{\Pi^{N_A+1}}$$

Consequently for a binary mixture

$$\ln \Delta_c^* = -N_A(x_1^2 \epsilon_{11} + x_2^2 \epsilon_{22} + 2x_1 x_2 \epsilon_{12})/kT$$

$$+ \ln[(2.6867)^{N_A}(N_A!/\Pi^{N_A+1})] \tag{43}$$

which is equivalent to eqn. (42). From eqn. (43) it can be shown that

$$(\partial^2 \ln \Delta_c^*/\partial x_2^2)_{P,T} = -2N_A(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/kT$$

and the relations for activity coefficients will be

$$\begin{cases} \ln \gamma_1 = [(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/kT]x_2^2 \\ \ln \gamma_2 = [(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/kT]x_1^2 \end{cases} \tag{44}$$

The discussion presented above indicates that the Margules two-suffix correlation for the activity coefficient is valid for mixtures of molecules with equal molecular sizes and at the ranges for which eqn. (42) holds. It is clear that in the limit, when intermolecular energy differences vanish, the Margules two-suffix correlation can be expected to approximate very well the actual properties of solutions.

It should be pointed out that the Margules three-suffix correlation in principle is equivalent to the Redlich—Kister power series, eqn. (21), when it is truncated after the second term and will not be discussed here any further.

VAN LAAR CORRELATION

In calculating the activity coefficient from eqns. (20), (28) or (35) it is generally possible to calculate coefficients of the first two terms of the expansion with the use of the molecular properties of pure components or through the principle of statistical thermodynamics. The resulting truncated power series

$$\begin{cases} \ln \gamma_1 = a_1^{(1)}x_2^2 + a_2^{(1)}x_2^3 + O(x_2^4) \\ \ln \gamma_2 = a_1^{(2)}x_1^2 + a_2^{(2)}x_2^3 + O(x_1^4) \end{cases} \tag{21}$$

can then be used for calculation of activity coefficients. However, according to the Padé approximation theory (Wall, 1948) when the first two terms of a power series are known, a better approximation to the power series than eqns. (21) will be

$$\begin{cases} \ln \gamma_1 = a_1^{(1)}x_2^2/[1 - (a_2^{(1)}/ma_1^{(1)})x_2]^m, \\ \ln \gamma_2 = a_1^{(2)}x_1^2/[1 - (a_2^{(2)}/ma_1^{(2)})x_1]^m, \end{cases} \quad m \geqslant 1 \tag{45}$$

with the value of exponent m being at our disposal. This exponent should be chosen such that the Gibbs—Duhem equation as given by eqn. (23) is satisfied. The Gibbs—Duhem condition will result with $m = 2$ and consequently

$$\begin{cases} \ln \gamma_1 = a_1^{(1)}x_2^2/[1 - a_2^{(1)}/2a_1^{(1)}x_2]^2 \\ \ln \gamma_2 = a_1^{(2)}x_1^2/[1 - a_2^{(2)}/2a_1^{(2)}x_1]^2 \end{cases} \tag{46}$$

with

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$$\begin{cases} a_1^{(2)} = -a_1^{(1)}/(a_2^{(1)}/2a_1^{(1)} - 1)^3 \\ a_2^{(2)} = -a_2^{(1)}/(a_2^{(1)}/2a_1^{(1)} - 1)^4 \end{cases} \tag{47}$$

Equations (46) are equivalent to the van Laar correlation for the activity coefficient. In the original derivation of the van Laar correlation the regular solution approximation ($V^E = S^E = 0$) together with the van der Waals equation of state for mixtures was used (Prausnitz, 1969). In the derivation presented here, it is shown that the van Laar correlation is actually a Padé approximation to the exact power series of the activity coefficient when only two terms of the series are retained.

CONCLUSION

In the discussion presented in this paper, it is demonstrated that isobaric-isothermal (NPT) ensemble theory is a powerful tool for predicting thermodynamic properties applicable to fluid-phase equilibria calculations. Through the NPT-ensemble, one is able to develop molecular thermodynamic relations for chemical potential and activity coefficient with pressure and temperature as independent variables, as required in fluid-phase equilibria calculations. The molecular thermodynamic relations developed for the activity coefficient, eqns. (20), (28) and (35), allow us to evaluate different correlations of the activity coefficient from a statistical thermodynamics point of view. This would also allow a better understanding of the molecular nature of activity coefficients and possibly allow development of more accurate relations for activity coefficients than the existing correlations.

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