Modeling Phase Equilibria in Mixtures Containing Hydrogen Fluoride and Halocarbons

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Recently, much attention has been focused on the production of environmentally acceptable refrigerants, which not only offer desirable physico-chemical properties, but do not deplete the ozone layer and do not cause the greenhouse effect. The production of such refrigerants involves the separation of multicomponent mixtures containing hydrogen fluoride, hydrogen chloride, and various chlorinated and fluorinated hydrocarbons (Knapp et al., 1991). Therefore, it is indispensable to know the phase behavior of these mixtures. While the phase behavior of refrigerant mixtures can be adequately modeled in the absence of HF (hydrogen fluoride) using standard thermodynamic techniques, hydrogen fluoride drastically increases the complexity of the mixture because of its unusually strong association. The association of HF manifests itself in its significantly reduced gas-phase compressibility factor and the strong nonideality of mixtures containing HF and hydrocarbons or halocarbons.

In this work, we develop an accurate, yet simple, association model for hydrogen fluoride and compare it with simulation data. The model is combined with a simple equation of state to yield a closed-form expression that is applicable to both pure fluids and mixtures. In addition to representing the pure-component data for HF, the theory accurately predicts phase equilibria in HF + halocarbon systems.

Theory

A general framework for combining the chemical theory with simple van der Waals-type equations of state has been presented earlier (Anderko, 1990, 1991). It has been shown that the compressibility factor Z can be decomposed into a physical ($Z^{(ph)}$) and a chemical ($Z^{(ch)}$) contributions:

$$Z = Z^{(ph)} + Z^{(ch)} - 1 \tag{1}$$

where the $Z^{(ch)}$ contribution is defined as the ratio of the total number of moles of all species in an associated mixture (n_T) to the number of moles of all species that would exist in the absence of association (n_o):

$$Z^{(ch)} = \frac{n_T}{n_o} \tag{2}$$

The $Z^{(ph)}$ contribution is equivalent to an equation of state for nonreacting monomeric species and can be expressed by a simple cubic EOS.

In this study, we focus on the calculation of the $Z^{(ch)}$ term for the special case of HF. For the consecutive self-association reactions:

$$A_j + A_1 = A_{j+1} \quad j = 1,2,\ldots\infty \tag{3}$$

the equilibrium constants depend, in general, on j and can be expressed as:

$$K_{j,j+1} = f(j)\, K \tag{4}$$

where $f(j)$ is a distribution function that depends on the nature of the associating compound. It is convenient to assume that $f(1) = 1$. Then, K is the dimerization constant. The equilibrium constants of the i-merization reactions

$$i\, A_1 = A_i \quad i = 2,3,\ldots\infty \tag{5}$$

can be related to the consecutive association constants (Eq. 4) by:

$$K_i = \left[\prod_{j=1}^{i-1} f(j)\right] K^{i-1} \tag{6}$$

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The $Z^{(ch)}$ term (Eq. 2) can be calculated if the K_i constants are known. For a pure associating component, Eq. 2 becomes (Anderko, 1991):

$$Z^{(ch)}=\frac{\sum_{i=1}^{\infty}K_i\left(Z^{(ch)}\frac{R\,T}{v}z_{A_1}\right)^i}{\sum_{i=1}^{\infty}i\,K_i\left(Z^{(ch)}\frac{R\,T}{v}z_{A_1}\right)^i} \tag{7}$$

where $K_1=1$, K_i $(i=2,3,\ldots,\infty)$ are given by Eq. 6, and z_{A_1} is the true mole fraction of the monomer. The product $(Z^{(ch)}(R\,T/v)z_{A_1})$ is calculated by inverting the mass balance series:

$$\frac{R\,T}{v}=\sum_{i=1}^{\infty}i\,K_i\left(Z^{(ch)}\frac{R\,T}{v}z_{A_1}\right)^i \tag{8}$$

As shown by Anderko (1991), the solution of Eqs. 7-8 yields in general:

$$Z_{\text{pure}}^{(ch)}=F\left(\frac{R\,T\,K}{v}\right) \tag{9}$$

where F is an algebraic function which depends on the distribution function $f(j)$ (Eq. 4). For mixtures containing one associating component A and r nonassociating components B_k $(k=1,\ldots.r)$, Eq. 9 is modified to:

$$Z^{(ch)}=x_A\,F\left(\frac{R\,T\,K\,x_A}{v}\right)+\sum_{k=1}^{r}x_{B_k} \tag{10}$$

where x is the analytical (apparent) mole fraction and F is the same algebraic function as in Eq. 9. Thus, the distribution function $f(j)$ (Eq. 4) is crucial for the application of the above formalism to the modeling of real fluid data.

Association Model for HF

Early measurements of gas-phase volumetric data (Simons and Hildebrand, 1924; Long, 1943) suggested the monomer-hexamer model for hydrogen fluoride. These measurements, however, covered only a very limited range of temperatures and densities. Briegleb and Strohmeier (1953) interpreted the more comprehensive data of Strohmeier and Briegleb (1953) and Fredenhagen (1934) using a continuous association model with $1 \le j \le 9$ and found that the $K_{j,j+1}$ constants (Eq. 4) reach a flat maximum at $j=5$. Similarly, Spalthoff and Franck (1957) suggested a continuous association model with a preferential formation of cyclic hexamers. Redington (1982) developed an elaborate association model that included consecutive, linear or cyclic, multimers extending through the dodecamer and found that the association constants show a maximum for $j = 6$. Also, discontinuous association models such as monomer-trimer-hexamer (Beckerdite et al., 1983) and monomer-dimer-hexamer-octamer (Schotte, 1980) were used to facilitate the fitting of empirical equations to gas-phase data. For the liquid phase, chain-like multimers have been also suggested on the basis of neutron diffraction, NMR and dielectric measurements (Cole, 1973). The above models, however, contain numerous empirically determined parameters and, more importantly, their application to mixtures would be very cumbersome.

Molecular simulation data are especially valuable for understanding the structure of HF, because they are free from the ambiguities that arise from fitting equations to experimental data. The work of Zhang et al. (1989) is particulary pertinent, because it gives thermodynamic properties of HF clusters ranging in size from $j = 1$ to 6 (Eq. 3) calculated from Monte Carlo simulations with a fairly realistic potential. Zhang et al. showed that the $K_{j,j+1}$ equilibrium constants at ambient temperatures first increase from $j = 1$ to 3 and then decrease. However, the uncertainty of these results rapidly increases for $j > 3$.

The above survey of data on the association of HF indicates that the distribution function $f(j)$ (Eq. 4) should smoothly cover a wide spectrum of j values and should show a maximum for a small value of j, most probably for $3 \le j \le 6$. After reaching the maximum, it should decay for increasing values of j. These criteria are satisfied by a one-parameter Poisson-like *distribution function:*

$$f(j)=\frac{\kappa^{j-1}}{(j-1)!} \tag{11}$$

where the parameter κ roughly indicates the location of the maximum. Thus, Eqs. 4, 6-8 and 11 completely determine the chemical contribution $Z^{(ch)}$ (cf. Eq. 1). For the physical contribution $Z^{(ph)}$ (cf. Eq. 1) the Peng-Robinson (1976) equation has been used because of its simplicity and popularity in engineering calculations:

$$Z^{(ph)}=\frac{v}{v-b}-\frac{a(T)\,v}{R\,T[v(v+b)+b(v-b)]} \tag{12}$$

The equation-of-state parameters for pure HF have been established in a three-step procedure.

1. First, the parameter κ was determined by fitting the EOS to isothermal one- and two-phase vapor density, saturated liquid density and vapor pressure data. The sources of these data are listed in Table 1. In this step, the $Z^{(ch)}$ contribution was calculated numerically for each density by solving Eqs. 7 and 8 with the K_i constants calculated from Eqs. 6, 4 and 11. On the isothermal basis, the equation contains four parameters: κ (Eq. 11), K (Eq. 4), a, and b (Eq. 12). Among these parameters, κ is very sensitive to the vapor density vs. pressure dependence. The value $\kappa=4.43$ was found to give optimum results for temperatures ranging from approximately 200 to 500 K.

2. Once κ and, hence, the association model have been determined, an analytical expression has been established for the $Z^{(ch)}$ contribution to avoid the repetitive numerical solving of Eqs. 7 and 8 in further calculations. For this purpose, the function $F(q)=Z_{\text{pure}}^{(ch)}$ (Eq. 9) was found by numerically solving

Table 1. Experimental Data Used to Establish the Equation of State for Pure HF

Vapor Pressure	Liquid Volume	Vapor Volume
Simons (1924)	Simons and Bouknight (1932)	Fredenhagen (1934)
Franck and Spalthoff (1957)	Franck and Spalthoff (1957)	Long et al. (1943)
Sheft et al. (1973)	Sheft et al. (1973)	Jarry and Davis (1953)
		Strohmeier and Briegleb (1953)
		Franck and Spalthoff (1957)
		Spalthoff and Franck (1957)

Eqs. 4 and 6-8 with $\kappa = 4.43$ for different values of q where $q = RTK/v$. Subsequently, an analytical function was found that accurately reproduces the numerical solution:

$$F(q) = Z_{\text{pure}}^{(ch)} = \frac{1 + \sum_{k=1}^{8} a_k q^k}{(1+q)^8} \tag{13}$$

The parameters a_i ($i = 1,\ldots,8$) are listed in Table 2. The function $F(q)$ is also shown in Figure 1. It reaches an asymptotic value $a_8 = 0.1093$ at $q \rightarrow \infty$. Since Eq. 13 was determined by solving general model equations (Eqs. 4, 6-8 and 11 with $\kappa = 4.43$), it is valid for values of q ranging from zero to infinity.

3. Once an analytical form for the $Z^{(ch)}$ contribution has been established, the final equation (Eqs. 1, 12 and 13) has been fitted to experimental data (Table 1) over the whole temperature range $200 \leq T \leq 500$ K. For this purpose, the temperature dependence of the dimerization constant K is expressed by:

$$\ln K = \frac{-\Delta h^o + \Delta c_p^o T_o}{R\ T} + \frac{1}{R}(\Delta s^o - \Delta c_p^o - \Delta c_p^o \ln T_o) + \frac{\Delta c_p^o}{R} \ln T \tag{14}$$

where Δh^o, Δs^o and Δc_p^o are the standard enthalpy, entropy and heat capacity of association, respectively, and the reference temperature T_o is 273.15 K. These parameters have been determined empirically and their values are $\Delta h^o = -35.069$ kJ/mol, $\Delta s^o = -133.67$ J/mol·K, and $\Delta C_p^o = 52.68$ J/mol·K. The parameters of the $Z^{(ph)}$ contribution (Eq. 12) are:

$$b/(\text{cm}^3\cdot\text{mol}^{-1}) = 9.69 \tag{15}$$

$$a/(\text{bar}\cdot\text{cm}^6\cdot\text{mol}^{-2}) = 10^6\{0.7187 + 0.2734\exp[-0.6232(T/100 - 4.02)^2]\} \tag{16}$$

Table 2. Parameters of Eq. 13

a_1	7.8291	a_5	55.9557
a_2	−27.5821	a_6	−2.9443
a_3	113.5793	a_7	1.6500
a_4	−88.229	a_8	0.10927

Results and Discussion

Figure 2 shows the gas-phase compressibility factors of HF calculated from the equation of state for low reduced temperatures and densities extending from zero to the saturation limit. Under these conditions, the compressibility factors of most fluids differ only slightly from one; hence, Figure 2 illustrates the magnitude of association effects. Figure 3 shows the compressibility factors of coexisting vapor and liquid phases. The compressibility factor of the saturated vapor increases with temperature in a substantial temperature interval, thus showing the unusual behavior of HF. The equation of state represents this behavior with very good accuracy. Besides the properties shown in Figures 2 and 3, the equation reproduces the vapor pressure and liquid volume of HF within 0.7% and 2%, respectively.

The values of association constants $K_{j,j+1}$ (Eq. 4) are influenced almost exclusively by experimental gas-phase data. Therefore, it is worthwhile to compare the standard Gibbs energies of consecutive association reactions $\Delta g_{j,j+1} = -RT\ln K_{j,j+1}$ calculated from the association model (Eqs. 4, 11 and 14) with those obtained by Zhang et al. (1989) from Monte Carlo simulations. As shown in Figure 4, both methods show a fairly rapid decrease of $\Delta g_{j,j+1}$ from $j = 1$ to $j = 3$. At $j > 3$, the Monte Carlo data become much more uncertain,

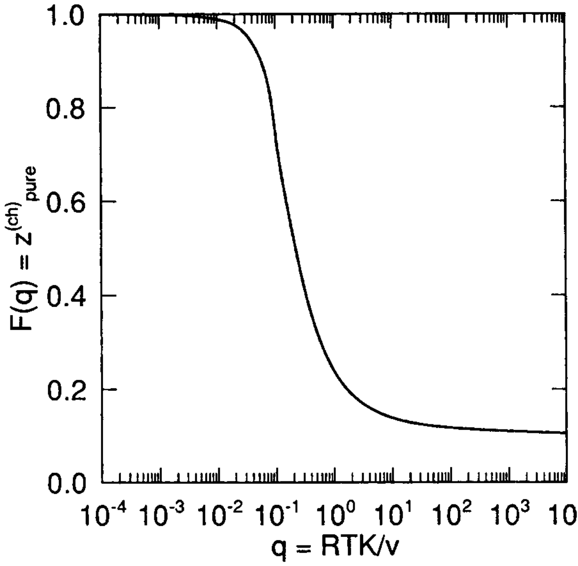

Figure 1. Function $F(q) = Z_{\text{pure}}^{(ch)}$ (Eq. 13) derived from the association model with $\kappa = 4.43$.

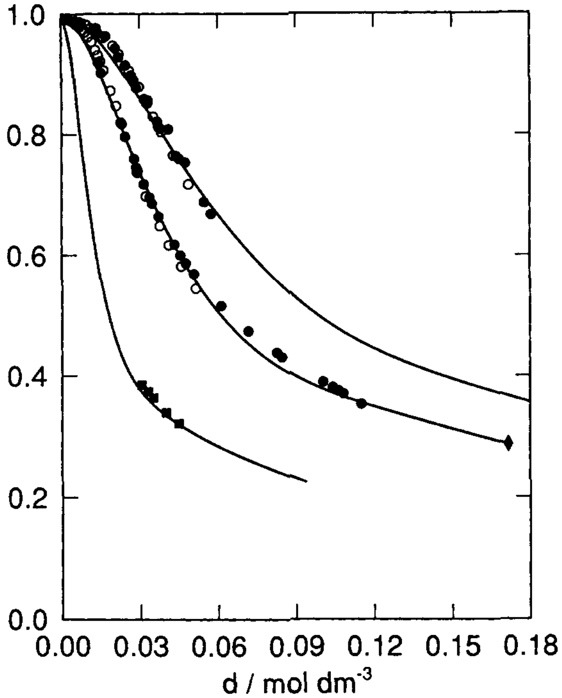

Figure 2. Gas-phase compressibility factors of pure hydrogen fluoride at 273.15 K (lower curve), 299.15 K (middle curve) and 311.15 K (upper curve).

Experimental data: ■, Long et al. (1943); ◆, Jarry and Davis (1953); ●, Fredenhagen (1934); and ○, Strohmeier and Briegleb (1953). The lines denote the results obtained from the EOS.

but indicate an increasing tendency. The association model obtained in this study shows a flat minimum of $\Delta g_{j,j+1}$ around $j = 5$ and an increasing tendency at higher values of j. In view of the uncertainties involved, the agreement between the association model and simulations is satisfactory and indicates that the distribution function (Eq. 11) is physically realistic.

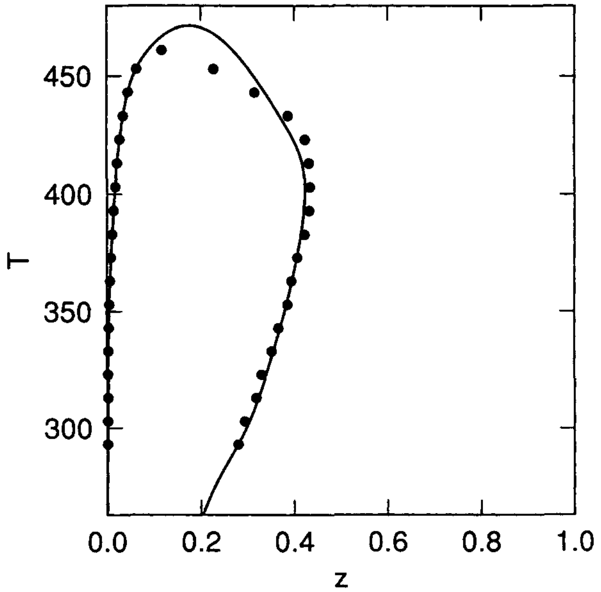

Figure 3. Vapor-liquid coexistence curve of pure HF calculated from the EOS (lines) and measured by Franck and Spalthoff (1957, circles).

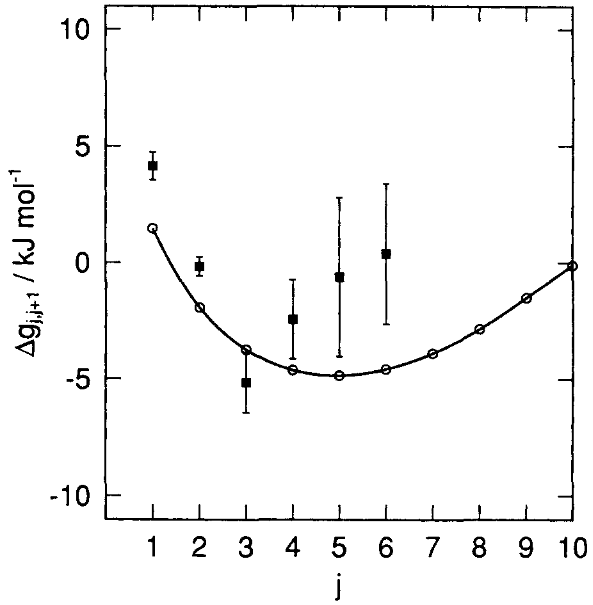

Figure 4. Standard Gibbs-free energies of the reactions $(HF)_j$ + HF = $(HF)_{j+1}$ obtained from the proposed association model (lines) and Monte Carlo simulations of hydrogen fluoride clusters (Zhang et al., 1989).

The equation of state has been applied to mixtures using the classical quadratic mixing rules for the $Z^{(ph)}$ contribution (Eq. 12):

$$a = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j \, (a_i a_j)^{1/2} (1 - \theta_{ij}) \tag{17}$$

$$b = \sum_{i=1}^{\infty} x_i b_i \tag{18}$$

where θ_{ij} is the only binary parameter needed. The pure component parameters a and b for compounds other than HF have been calculated from critical temperature, critical pressure, and vapor pressure using an expression for the temperature dependence of a proposed by Melhem et al. (1989).

Vapor-liquid equilibria have been calculated for three binary systems related to the separation of refrigerants. The binary parameters are listed in Table 3 and the quality of reproducing the VLE data is illustrated in Figures 5 and 6. Two versions of calculations are shown in Figures 5 and 6; the dotted lines represent the prediction of VLE with $\theta_{ij} = 0$ and the solid lines denote the results obtained by fitting θ_{ij} to the data.

In the case of HF + halocarbon mixtures, the binary parameters are very small (cf. Table 3). Therefore, the equation not only accurately represents the data with a single adjustable parameter but it is also useful for predicting the phase behavior without any mixture information, that is, from pure component data alone. The binary parameter is significantly different from zero for the HF + HCl mixture because cross-association

Table 3. Binary Parameters Used for Mixture Calculations and Deviations between Experimental and Calculated Pressures

Mixture	Ref.	θ_{12}	δP^*
HF-CHF_2Cl	Wilson et al. (1989)	−0.01	1.0
HF-CF_3CCl_3	Knapp et al. (1991)	−0.01	1.9
HF-HCl	Gillespie et al. (1985)	0.04	2.7

$^*\delta P = \frac{100}{N} \Sigma \, |(P_i^{cal} - P_i^{exp})/P_i^{exp}|$

between HF and HCl has not been explicitly taken into account. Equation 10 is based on the assumption that only one self-associating component is present and the remaining ones are inert. Although HCl shows a negligible self-association, the assumption that it is inert is crude. However, we did not deem it necessary to explicitly introduce specific HF − HCl interactions because the self-association of HF remains dominant even in the HF + HCl mixture.

The above results show that the combination of a realistic association model with a simple equation of state has produced an accurate and predictive model for mixtures containing HF and halocarbons. Since the combined model is only slightly more computationally demanding than van der Waals type equations of state, it can be useful for practical calculations.

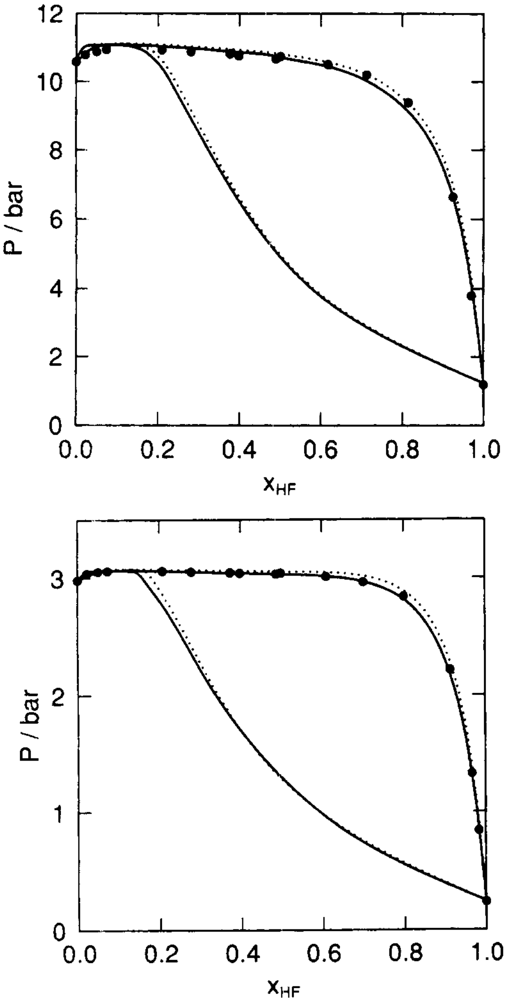

Figure 5. Vapor-liquid equilibria in the system HF-CHF_2Cl at 258.15 K (lower graph) and 298.15 K (upper graph).

Solid lines denote the results obtained from the EOS by fitting one binary parameter θ_{12}, dotted lines obtained with $\theta_{12} = 0$, and circles represent the data of Wilson et al. (1989).

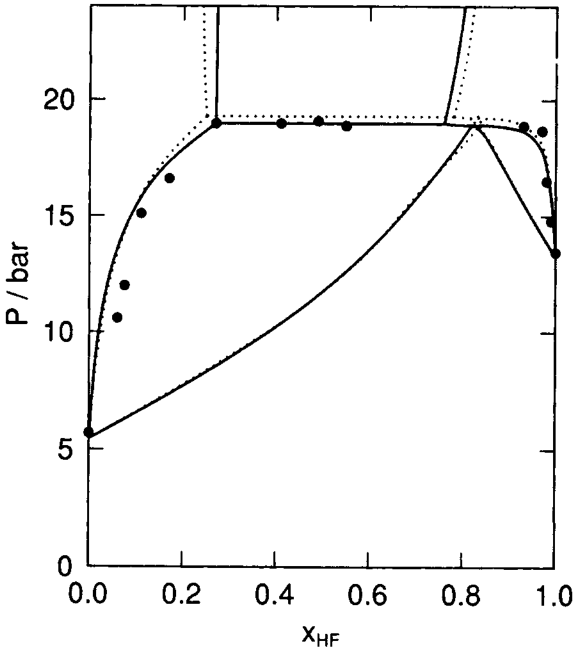

Figure 6. Vapor-liquid-liquid equilibria in the system HF-CF_3CCl_3 at 383.15 K.

Solid lines denote the results obtained from the EOS by fitting one binary parameter θ_{12}, dotted lines obtained with $\theta_{12} = 0$, and circles represent the data of Knapp et al. (1991).

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Notation

a, b = parameters of the Peng-Robinson EOS (Eq. 12)
A = associating component
f = distribution function (Eq. 4)
K = dimerization constant ($K = K_2$)
K_i = i-merization constant (Eq. 6)
$K_{j,j+1}$ = consecutive association constant (Eq. 4)
n = number of moles
q = $RTKx_A/v$
R = gas constant
T = temperature, K
v = molar volume
x = analytical (nominal) mole fraction
z = true mole fraction
Z = compressibility factor

Greek letters

κ = parameter of the distribution function (Eq. 11)
θ = binary parameter (Eq. 17)

Superscripts

(ch) = chemical contribution
(ph) = physical contribution

Subscripts

A = associating component
B = inert component

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Errata

◆ In the article titled "Effects of Protein Aggregation in Isocratic Nonlinear Chromatography" (April 1991, p. 555) by Whitley et al., the y axis of Figure 3 was incorrect. The values of the y axis should be rescaled by multiplying by 0.70. The simulation parameters are correct as shown; figure shape and conclusions are unaffected.

◆ In the article titled "Steric Mass-Action Ion Exchange: Displacement Profiles and Induced Salt Gradients," (December 1992, p. 1969) by Brooks and Cramer, the following corrections are made:

The term "nonsterically hindered" in the subcaption of Figure 1 (p. 1970) should be changed to "sterically nonhindered."

Equation 13 (p. 1971) should read:

$$\alpha_{i1} \equiv \frac{Q_i/C_i}{\bar{Q}_1/C_1} = K_{1i}\left(\frac{\bar{Q}_1}{C_1}\right)^{\nu_i - 1} \qquad i = 1, 2, \ldots, n+1 \quad (13)$$

"Δ" in Eqs. 32, 37, 40 and 41 should read "δ".

Equation 49 (p. 1975) should read:

$$\delta_{a,b} = \left(\frac{K_{1a}{}^{\nu_b}}{K_{1b}{}^{\nu_a}}\right)^{\frac{1}{\nu_b - \nu_a}} \qquad (49)$$