Korean J. of Chem. Eng., 8(2), 88-94 (1991)

APPLICATION OF PENG-ROBINSON EQUATION TO HIGH-PRESSURE AQUEOUS SYSTEMS CONTAINING GASES AND SODIUM CHLORIDE

Chul Kwak and Thomas F. Anderson*

Department of Chemical Engineering, Kyungnam University, Masan 630-701, Korea
*Department of Chemical Engineering, University of Connecticut, Storrs, CT USA, 06269
(Received 30 October 1990 • accepted 24 April 1991)

Abstract—A novel approach is proposed for modeling vapor-liquid equilibria in systems containing aqueous NaCl and supercritical gases. The Peng-Robinson equation of state is used for all species, with the salt treated as a hypothetical liquid component. To correctly model the highly non-ideal liquid solution, a two-fluid model is used for the mixing rules in the equation of state. Effective pure-component parameters are reported for NaCl as well as binary interaction parameters for all possible binaries. Representation of high-pressure phase equilibria data show good agreement with experimental data. The principal advantage of this approach is the ability to treat high pressure systems containing non-volatile salts, while maintaining the simplicity of a cubic equation of state.

INTRODUCTION

The description of phase equilibria in aqueous electrolyte solution is necessary to design of a number of industrially important processes such as desalination, evaporation and distillation of solutions containing salts. Similarly, water containing dissolved salts is always found in gas reservoirs. The effects of these salts must be correlated or estimated to correctly model gas production and to properly design surface separation facilities. The nonidealities of aqueous salt solutions can often be described by activity coefficient models. Examples of such efforts include those of Meissner and Tester [1], Bromley [2], Pitzer [3], Kusik and Meissner [4], Cruz and Renon [5], Chen et al. [6], and Anil Kumar and Patwardhan [7]. An extensive review of these works is given by Zemaitis et al. [8].

Although based on molecular thermodynamics, all of the activity coefficient models tend to have an excessive number of empirical parameters. They tend to be difficult to extend to mixed solvents and often break down at high electrolyte concentrations. Their most serious limitation, however, is that they cannot easily be extended to high pressure systems, particularly to systems which include supercritical gases (Prausnitz et al. [9]).

A more consistent description of high pressure phase equilibria can be obtained using a single equation of state. Such equations are commonly used in the petroleum and petrochemical fields. One of the most widely used equations of state is the Peng-Robinson equation (Peng and Robinson [10]). The problem with using this equation or any equation of state with salts is how to correctly represent the salt properties.

There have been recent efforts to apply equations of state to electrolyte systems. These include the works of Copeman and Stein [11], Jin and Donohue [12], Harvey and Prausnitz [13], and Whitson and Soreide [14]. The unique feature of this work is that rather than trying to impose the electrolyte phenomena on the equation of state, we merely consider salt as a unique (nonvolatile) species. The key to applying this method to the Peng-Robinson equation of state (or any other equation of state) is to use sufficiently rigorous mixing rules which can adequately represent very nonideal solution properties.

MODEL DESCRIPTION

The fundamental form of the Peng-Robinson equation is given in the Appendix. Two important modifications are necessary. First, to accurately represent the pure-component vapor pressures of all of the non-salt species, the temperature dependence proposed by Khalil and Anderson [15] is used for attractive term in the equation. As shown in the Appendix, the temperature dependence given by this equation is hy-

Table 1. Optimal values of the adjustable parameters

Pure component	$\mathcal{A}_i$	$\mathcal{B}_i$
Carbon dioxide	2.29858	−0.42563
Nitrogen	1.78215	0.07286
Methane	1.62405	−0.06483
Water	2.44552	−0.84982

Table 2. Parameters and expressions for k_{ij}

System	k_{ij} expression (T:Kelvin)	Temp. range (deg. C)
H_2O-NaCl	0.33295	80.0-300.0
H_2O-CO_2	$-0.26706+6.6137\times10^{-4}\times T$	150.0-300.0
H_2O-N_2	$-1.85920+4.2313\times10^{-3}\times T$	102.5-125.0
H_2O-CH_4	$-1.06800+2.5961\times10^{-3}\times T$	102.5-125.0
NaCl-CO_2	$-1.78445+6.0369\times10^{-3}\times T$	150.0-300.0
NaCl-N_2	$-3.01890+0.010074\times T$	102.5-125.0
NaCl-CH_4	$-2.44529+7.7129\times10^{-3}\times T$	102.5-125.0

perbolic in form. As shown by Khalil and Anderson, this simple equation provides a remarkably good representation of pure-component vapor pressure while giving bounded values for the attractive parameter α at the limits of very high and very low reduced temperatures.

Second, to correctly model the extremely nonideal, dense-fluid behavior, better mixing rules must be used. In this work the mixing rules based on two-fluid theory are used for the attractive term, as originally proposed by Vachhani and Anderson [16]. Note that this form is not density dependent. Although not strictly correct in the low pressure limit, this form has the features necessary to account for highly nonideal dense fluid behavior, without introducing the additional complexity of density dependence. The conventional mixing rule is retained for the repulsive constant, b.

The constants a, b, and α for all volatile components are determined in the usual manner. For a salt species α is set to one. The values of a and b for the salt are constants and correspond to it's hypothetical liquid state. They do not depend on the particular solvent in which the salt is dissolved. Note that this analysis effectively ignores the fact that the salt dissociates in solution, and treats the salt as a single hypothetical component in solution; i.e. the microscopic properties are ignored in an attempt to correctly model the macroscopic properties of the solution. Such an analysis not unusual; e.g. it is possible to represent the vapor-liquid equilibria of NaCl and water by treating this as a binary system. The unique feature of this approach is that it allows us to treat all the components in a simple consistent manner.

Since the phase-equilibrium predictions do not appear to be especially sensitive to the value of b, it's values is calculated from the van der Waals radius of a single "molecular" crystal. Phase equilibria properties are, however, sensitive to the constant a. For NaCl the value of a was determined by examining several different ternary systems of water, NaCl and a supercritical gas. For NaCl the values of a and b are 30.0 bar-$(l/\mathrm{mol})^2$ and 0.0384 l/mol, respectively.

Vapor-liquid equilibria calculations are based on the requirement that a component's fugacity must be the same in all of the phases in which it is distributed. This requirement applies to all the components which distributes. NaCl is not assumed to be present in the vapor phase. only the liquid phase. Their vapor mole fractions are always set to zero. In the calculations salts are identified by a value of α equal to one.

In this work, the temperature dependence of the attractive parameter of the Peng-Robinson EOS is represented by a hyperbolic function with two adjustable parameter $\mathcal{A}_i$ and $\mathcal{B}_i$. By requiring the function to become unity at the critical point, the value of the parameter $\mathcal{C}_i$ is constrained to $\mathcal{C}_i=\mathcal{A}_i+\mathcal{B}_i-1$ where $\mathcal{A}_i$ and $\mathcal{B}_i$ are characteristic of each pure component. The parameters are fitted to vapor pressure data each of the pure components. The results are shown in Table 1.

To determine the fugacities of the distributing species, the fugacity coefficients are calculated. The algebraic expressions for the fugacity coefficients are also given in the Appendix for the mixing rule described above. Calculations of phase equilibrium properties follow conventional procedures, e.g. Smith and Van Ness [17].

RESULT AND DISCUSSION

Data for the systems H_2O-NaCl, H_2O-CO_2, H_2O-N_2, and H_2O-CH_4 was first used to determine the binary parameters for each of these systems. Although initially it was hoped that the binary parameters would be temperature independent, this proved to be true only for the H_2O-NaCl system, where a very good fit was obtained from 80℃ to 300℃. The three remaining binary systems were well represented with unique values of ΔU_{ij} and a linear variation of k_{ij} with respect to temperature. The parameters and expressions for k_{ij} for each water binary system are shown in Table 2. The correlation of the binary data is shown in Figure 1-8 and corresponds to the conditions of no salt.

Ternary data for each of the gaseous systems containing N_2, CO_2, and CH_4 were then used to obtain the optimum parameters for NaCl-N_2, NaCl-CO_2, and

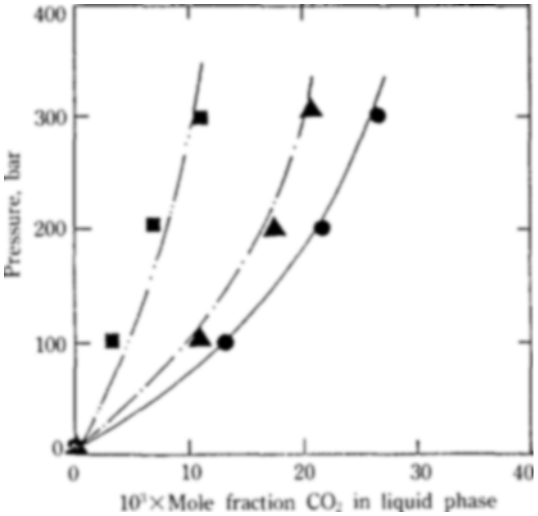

Fig. 1. Comparison of experiment data (Takenouchi and Kennedy [18]; ●: no salt, ▲: 6 wt% NaCl, ■: 20 wt% NaCl) with calculated value (—: no salt, - · -: 6 wt% NaCl, - ·· -: 20 wt% NaCl) at 150°C.

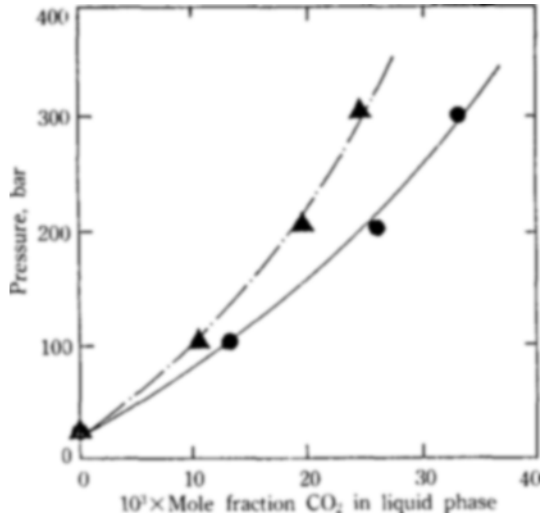

Fig. 2. Comparison of experiment data (Takenouchi and Kennedy [18]; ●: no salt, ▲: 6 wt% NaCl) with calculated value (—: no salt, - · -: 6 wt% NaCl) at 200°C.

$NaCl$-CH_4, systems. These parameters are also reported in Table 2. The corresponding fit to the ternary data is illustrated in Figures 1-8.

Figures 1-4 illustrate the "salting out" of carbon dioxide by sodium chloride. Very good results are found at 150°C and 200°C. The experimental data were reported by Takenouchi and Kennedy [18]. The total pressures at 250°C and 300°C tend to be slightly underpredicted.

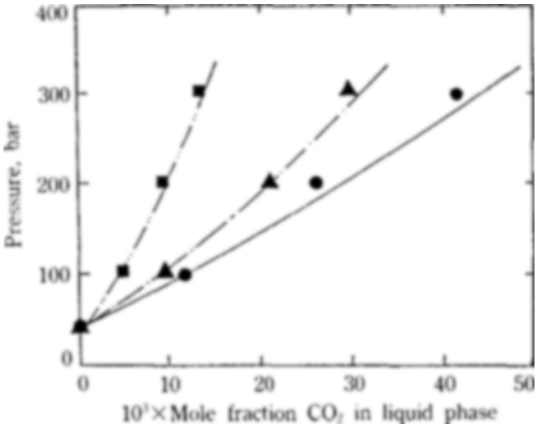

Fig. 3. Comparison of experiment data (Takenouchi and Kennedy [18]; ●: no salt, ▲: 6 wt% NaCl, ■: 20 wt% NaCl) with calculated value (—: no salt, - · -: 6 wt% NaCl, - ·· -: 20 wt% NaCl) at 250°C.

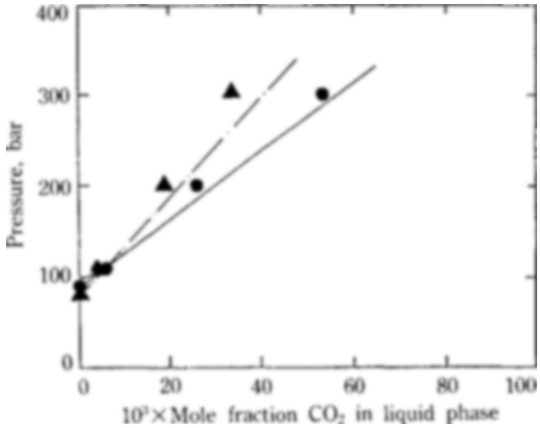

Fig. 4. Comparison of experiment data (Takenouchi and Kennedy [18]; ●: no salt, ▲: 6 wt% NaCl) with calculated value (—: no salt, - · -: 6 wt% NaCl) at 300°C.

Data for the system H_2O-$NaCl$-N_2 are shown in Figures 5 and 6. The experimental data for this system were reported by O'Sullivan and Smith. Here, the temperature range is smaller, but the calculations with the proposed model are quite good. Data for the system H_2O-$NaCl$-CH_4 are shown in Figures 7 and 8. These data were also reported by O'Sullivan and Smith. Again the temperature range is not great, however, the agreement with the experimental data is very good.

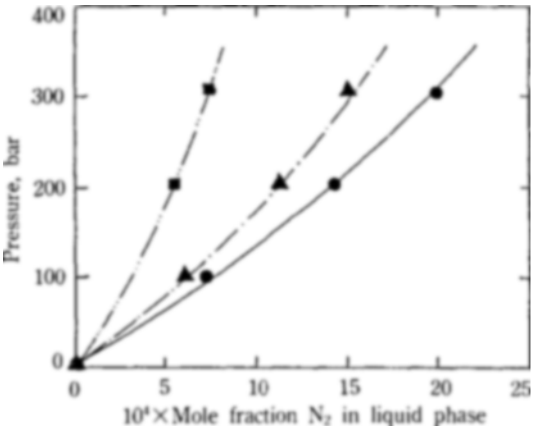

Fig. 5. Comparison of experiment data (O'Sullivan and Smith [19]; ●: no salt, ▲: 1 m NaCl, ■: 4 m NaCl) with calculated value (—: no salt, -·-: 1 m NaCl, -··-: 4 m NaCl) at 102.5°C.

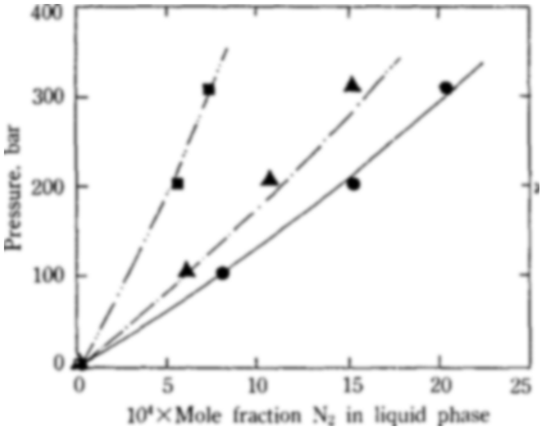

Fig. 6. Comparison of experiment data (O'Sullivan and Smith [19]; ●: no salt, ▲: 1 m NaCl, ■: 4 m NaCl) with calculated value (—: no salt, -·-: 1 m NaCl, -··-: 4 m NaCl) at 125°C.

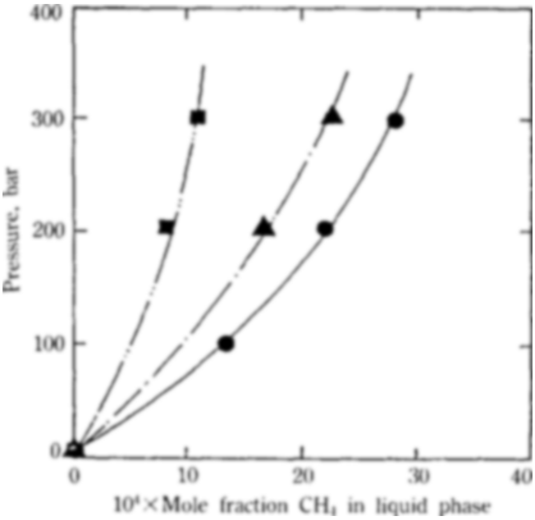

Fig. 7. Comparison of experiment data (O'Sullivan and Smith [19]; ●: no salt, ▲: 1 m NaCl, ■: 4 m NaCl) with calculated value (—: no salt, -·-: 1 m NaCl, -··-: 4 m NaCl) at 102.5°C.

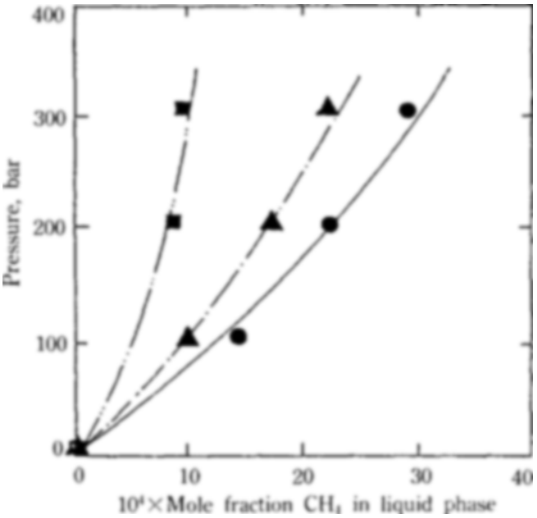

Fig. 8. Comparison of experiment data (O'Sullivan and Smith [19]; ●: no salt, ▲: 1 m NaCl, ■: 4 m NaCl) with calculated value (—: no salt, -·-: 1 m NaCl, -··-: 4 m NaCl) at 125°C.

The results presented above indicate that the proposed model can conveniently describe vapor-liquid of gases in aqueous solutions of NaCl. The values given are suitable for the systems here; however, it is likely that if additional data sets were examined, better values could be obtained, which may cover even wider ranges of temperature and pressure.

In this method, some 300 bar was available, but more than 300 bar has been shown considerably a range of error, with its clearly tendency.

The model proposed here potentially may be extended to systems of solvents, i.e. methanol-water-NaCl with a supercritical gas. It may also be possible to treat systems of mixed electrolytes. This will be the subject of future research.

CONCLUSIONS

A new approach is proposed for calculating vapor-liquid equilibria in systems containing aqueous

NaCl and supercritical gases at high pressure. In this method the salt is treated as a hypothetical liquid component. In the presented systems, the effective pure-component parameters for NaCl are 30.0 bar-(l/mol)^2 for a and 0.0384 l/mol for b. Representation of high-pressure phase equilibria data show good agreement with experimental data. The advantage of this method is the ability to treat high pressure systems with non-volatile salts, while maintaining the simplicity of procedures.

ACKNOWLEDGEMENT

C. Kwak, one of the authors wishes to thank Department of Chemical Engineering, in University of Connecticut for the kindly support.

APPENDIX

The form of the Peng-Robinson equation of state is

$$P=\frac{RT}{(V-b)}-\frac{\alpha a}{V(V+b)+b(V-b)} \tag{A1}$$

which can also be written in terms of the compressibility factor, Z, as

$$Z^3-Z^2(1-B)+Z(A-3B^2-2B)-(AB-B^2-B^3)=0 \tag{A2}$$

where

$$A=\frac{\alpha aP}{(RT)^2} \tag{A3}$$

and

$$B=\frac{bP}{RT} \tag{A4}$$

The values αa and b are properties of the mixture. The mixing rules commonly used are

$$\alpha a=\sum_i^m \sum_j^m y_i y_j (\alpha a)_{ij} \tag{A5}$$

$$(\alpha a)_{ij}=\sqrt{\alpha_i\alpha_j a_i a_j}(1-k_{ij}) \tag{A6}$$

$$b=\sum_i^m y_i b_i \tag{A7}$$

where k_{ij} is a single binary interaction parameter. In this work, the mixing rule for the parameter b is retained. But, as discussed in the paper, the quadratic mixing rule used for αa is replaced by a two-fluid model. The expression for αa is then given by

$$\alpha a=\sum_{i=1}^m \sum_{j=1}^m \frac{y_i y_j (\alpha a)_{ij}}{\sum_{k=1}^m y_k \exp[(\Delta U_{ik}-\Delta U_{ij})/RT]} \tag{A8}$$

For $i \neq j$, $(\alpha a)_{ij}$ is given by expression above. Note that since $k_{ij}=k_{ij}$, there are three adjustable parameter for each combination of two species, i.e. a two-component mixture will have three adjustable binary parameters, k_{ij}, ΔU_{12} and ΔU_{21}.

For a salt species α is set to one. The values of a and b for a salt are constants and correspond to it's hypothetical liquid state. They do not depend on the particular solvent. The pure-component constants for all non-salt species are calculated from the critical properties by the equations

$$a_i=0.4572\,R^2\,T_{ci}^2/P_{ci} \tag{A9}$$

and

$$b_i=0.0778\,R\,T_{ci}/P_{ci} \tag{A10}$$

In the original Peng-Robinson equation, α_i is a function of the reduced temperature.

$$\alpha_i=[1+S_i(1-\sqrt{T_{ri}})]^2 \tag{A11}$$

where

$$S_i=0.37464+1.54226\omega_i-0.26992\omega_i^2 \tag{A12}$$

In this work, we have used a hyperbolic form for the temperature dependence of α_i.

$$\alpha_i=(\mathcal{A}_i+\mathcal{B}_i T_r)/(1+\mathcal{C}_i T_r) \tag{A13}$$

and

$$\mathcal{C}_i=\mathcal{A}_i+\mathcal{B}_i-1.0 \tag{A14}$$

where $\mathcal{A}_i$ and $\mathcal{B}_i$ are fit to vapor pressure data for each of the pure components.

Using standard thermodynamic relations, the expression for the fugacity coefficient can be derived. Based on the two-fluid mixing rules, the equation for the fugacity coefficient is

$$\ln\varphi_i=\frac{B_i}{B}(Z-1)-\ln(Z-B)-\frac{A}{2\sqrt{2B}}\left(\frac{D_i}{\alpha a}-\frac{B_i}{B}\right)\times\ln[\{Z+(1+\sqrt{2})B\}/\{Z+(1-\sqrt{2})B\}] \tag{A15}$$

where:

$$B_i=\frac{b_iP}{RT} \tag{A16}$$

and

$$D_i = \frac{1}{n}\left(\frac{\partial(n^2\alpha a)}{\partial n_i}\right) \tag{A17}$$

If we let $\theta=\alpha a$ and $\theta_{ij}=(\alpha a)_{ij}$, the expression for D_i is given by the following equations.

$$\begin{aligned} D_i &= \frac{1}{n}\left(\frac{\partial(n^2\theta)}{\partial n_i}\right) \\ &= \sum_{l=1}^{m}{}' \sum_{j=1}^{m}{}' \frac{y_l y_j \theta_{ij}}{(D^{-}_{jli})^2}\left[D^{-}_{jli} - \exp\left(\frac{\Delta U_{jl}-\Delta U_{il}}{RT}\right)\right] \\ &\quad + \sum_{j=1}^{m}{}' \frac{y_j\theta_{ij}}{(D^{-}_{jii})^2}\left[D^{-}_{jii}(1+y_i) - y_i \exp(\Delta U_{ij}/RT)\right] \\ &\quad + \sum_{l=1}^{m}{}' \frac{y_l\theta_{il}}{(D^{-}_{ili})^2}\left[D^{-}_{ili}(1+y_i) - y_i\right] \\ &\quad + \frac{y_i\theta_{ii}}{(D^{-}_{iii})^2}\left[D^{-}_{iii}(2+y_i) - y_i\right] \end{aligned} \tag{A18}$$

where

$$D^{-}_{jli} = \sum_{k=1}^{m} y_k \exp[(\Delta U_{jl} - \Delta U_{kl})/RT] \tag{A19}$$

$$D^{-}_{jii} = \sum_{k=1}^{m} y_k \exp[(\Delta U_{ji} - \Delta U_{ki})/RT] \tag{A20}$$

$$D^{-}_{ili} = \sum_{k=1}^{m} y_k \exp[(\Delta U_{il} - \Delta U_{kl})/RT] \tag{A21}$$

$$D^{-}_{iii} = \sum_{k=1}^{m} y_k \exp(-\Delta U_{ki}/RT) \tag{A22}$$

Note: Σ' indicates that species " i " is excluded from the summation and that $\Delta U_{ii}=0$.

NOMENCLATURE

A : constant defined by eq. (A3)
$\mathcal{A}$: constant in eq. (A13)
a : attraction parameter [bar l^2/mol^2]
B : constant defined by eq. (A4)
$\mathcal{B}$: constant in eq. (A13)
b : van der Waals covolume [l/mol]
$\mathcal{C}$: constant in eq. (A14)
D : partial differentiation indicated by eq. (A17)
D^{-} : constant defined by (A19), (A20), (A21), or (A22)
k : interaction parameter
P : pressure [bar]
R : gas constant [l bar/mol K]
S : dimensionless function defined by eq. (A12)
T : temperature [K]
U : binary interaction [cal/mol]
V : molar volume [l/mol]
y : vapor phase mole fraction
Z : compressibility factor

Greek Letters

α : scaling factor in eq. (A1)
θ : αa
φ : fugacity coefficient
ω : acentric factor

Subscripts

c : critical
i : component i
j : component j
k : component k
l : component l
r : reduced property

REFERENCES

1. Meissner, H. P. and Tester, J. W.: *I&EC Process Des. Dev.*, **11**, 128 (1972).
2. Bromley, L. A.: *AIChE J.*, **19**, 313 (1973).
3. Pitzer, K. S.: *J. Phys. Chem.*, **77**, 268 (1973).
4. Kusik, C. L. and Meissner, H. P: *AIChE Symp. Ser.*, **173**, 14 (1978).
5. Cruz, J. L. and Renon, H.: *AIChE J.*, **24**, 817 (1978).
6. Chen, C. C., Britt, H. I., Boston, J. F. and Evans, L. B.: *AIChE J.*, **28**, 588 (1982).
7. Anil Kumar and Patwardhan, V. S.: *Can. J. Chem. Eng.*, **64**, 831 (1986).
8. Zemaitis, J. F., Clark, D. M., Rafel, M. and N. C. Scrivner, N. C.: Handbook of Aqueous Electrolyte Thermodynamics, Design Institute for Physical Property Data, New York (1986).
9. Prausnitz, J. M., Lichtenthaler, R. N. and Azevedo, E. G.: Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ (1986).
10. Peng, D. Y. and Robinson, D. B.: *I&EC Fundam.*, **15**, 59 (1976).
11. Copeman, T. W. and Stein, F. P.: *Fluid Phase Equili.*, **35**, 165 (1987).
12. Jin, G. and Donohue, M. D.: *I&EC Res.*, **27**, 1073 (1988).
13. Harvey, A. H. and Prausnitz, J. M.: *AIChE J.*, **35**, 635 (1989).
14. Whitson, C. H. and Soreide, I.: A book to be published, (1990).
15. Khalil, Y. F., Anderson, T. F. and Lovand, J.: Petroleum Chemistry Division General Poster Session, ACS, Washington Meeting, (1990).
16. Vachhani, H. N. and Anderson, T. F.: 75th Annual AIChE Meeting, Los Angels, November, (1982).

17. Smith, J. M. and Van Ness, H. C.: Introduction to Chemical Engineering Thermodynamics, 4th ed., McGraw-Hill, New York, (1987).
18. Takenouchi, S. and Kennedy, G. C.: *American J. Sci.*, **263**, 445 (1965).
19. O'Sullivan, T. D. and Smith, N. O.: *J. Phy. Chem.*, **74**, 1460 (1970).