Augmented BACK Equation of State II: Polar Fluid Mixtures

The augmented BACK equation of state for polar fluids is extended to mixtures by introducing mixing rules separately for the nonpolar and polar interactions. Fluid phase equilibria are calculated for polar + nonpolar, and polar + polar mixtures including mixtures of hydrogen-bonding substances. Enthalpy calculations are illustrated with enthalpy of H_2S + N_2 and heats of mixing of steam mixtures, and carbon dioxide mixtures.

Cross interaction coefficients are adjusted for the correlation of data on binary mixtures. Both phase equilibrium and enthalpy data are correlated at the same time with two such coefficients for each binary. The cross interaction coefficients are constants, invariant with temperature, density, or phase state.

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Introduction

Polar substances are characterized by the existence of localized electric charges or poles in their molecules. The poles interact by Coulombic law, giving rise to polar pressure that is in addition to the nonpolar pressure generated by the dispersion interaction of the electronic clouds. While nonpolar interaction is present in all molecules, polar interaction exists only in polar fluids, which explains the anomalous behavior of polar fluids such as water, alcohols, ketones, and others. Although polar fluids are commonly encountered in chemical and industrial processes, they are not well described by equations of state.

In the preceding part of this work (Lee and Chao, 1988) a new equation of state was proposed for polar fluids by adding a new polar pressure term to the Boublik-Alder-Chen-Kreglewski (BACK) equation which accurately expresses the pressure of nonpolar fluids. The new polar pressure was obtained by decoupling the pressure of water according to the model of the water molecule developed by Jorgensen et al. Equation constants were reported for 26 substances, and calculated vapor pressure and pVT behavior were compared with data. Phase equilibria and pVT relationship of mixtures of water + nonpolar fluids were calculated with temperature-independent interaction coefficients.

In this paper we present calculations of fluid phase equilibrium of aqueous and nonaqueous mixtures of polar + nonpolar and polar + polar substances. Enthalpy and heat of mixing are calculated for 19 example mixtures.

Dipole Moment for the Characterization of Polar Interaction

The quantity q has been used to characterize the polar interaction of a component in the augmented BACK equation. It is defined by

$$q_i = T_{ci}/T_{cw} \tag{1}$$

where T_c is the characteristic temperature of the polar interaction of a component. Subscript i designates the component of interest; w designates water. The characteristic temperature of a dipole is

$$T_c = \mu^2/(kv^{oo}/N) \tag{2}$$

where μ is the dipole moment, v^{oo} is the hard core volume at 0 K, and N is Avogadro's number.

Values of q for the polar substances reported in part 1 were determined by a numerical search for the fitting of the equation of state to experimental data on the saturated liquid density and vapor pressure. The other equation of state parameters were determined by the search procedure at the same time. Figure 1 shows $[q(v^{oo}/v_w^{oo})]^{0.5}$ obtained from the equation fitting and (μ/μ_w) based on dipole moments in the literature. The two quantities for a substance are close to being the same, except for the higher alcohols and for m-cresol. The good correlation suggests that q can be estimated from the dipole moment for use in the

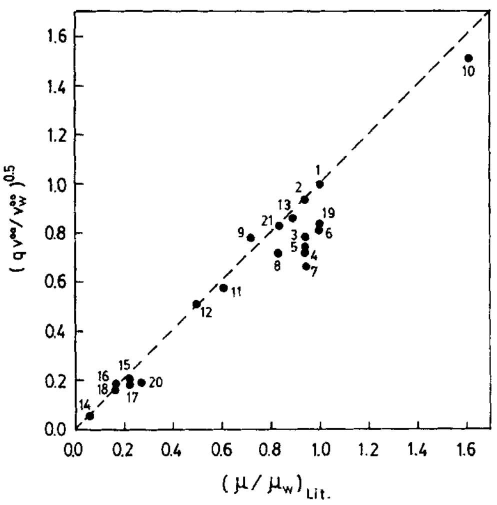

Figure 1. Fitted reduced effective dipole moments vs. literature values.

1. Water 2. Methanol 3. Ethanol. 4. 1-propanol 5. 2-propanol 6. Butan-1-ol 7. Butan-2-ol 8. Ammonia. 9. Diethyl ether 10. Acetone 11. HCl 12. H_2S 13. SO_2 14. CO 15. Propylene 16. 1-butene 17. Toluene 18. *m*-Xylene 19. *m*-Cresol 20. 1-methylnaphthalene 21. Propionic acid

equation of state. The good correlation also suggests that the polar pressure expression in the augmented BACK equation mainly represents dipolar pressure, although its derivation from the pressure of water implies that higher poles are included.

Mixing Rules

Mixing rules are separately introduced in the nonpolar and polar pressure terms. As shown by statistical mechanical simulation of polar fluids, no interaction is allowed between the nonpolar and polar modes.

For the nonpolar pressure parameters, following Simnick (1979)

$$u_m/k = \sum_i \sum_j x_i x_j (u/k)_{ij} (v^o_{ij}/v^o_m) \tag{3}$$

$$v^o_m = \sum_i \sum_j x_i x_j v^o_{ij} \tag{4}$$

$$\alpha_m = \sum_i \sum_j x_i x_j \alpha_{ij} \tag{5}$$

where the cross interaction parameters are given by

$$(u/k)_{ij} = (1 - k_{uij}) [(u/k)_i (u/k)_j]^{0.5} \tag{6}$$

$$v^o_{ij} = (1 - k_{vij}) (v^o_i + v^o_j)/2 \tag{7}$$

$$\alpha_{ij} = (\alpha_i + \alpha_j)/2 \tag{8}$$

For the polar attractive pressure, the formalism of dipolar interaction is adopted to combine the dipole moment μ_i obtained from q_i by Eqs. 1 and 2.

$$\mu^4_m = \sum_i \sum_j x_i x_j \mu^4_{ij} \tag{9}$$

The scaling volume and pressure are combined with a weighting factor

$$v^{oo}_m = \sum_i \sum_j x_i x_j v^{oo}_{ij} (\mu_{ij}/\mu_m)^2 \tag{10}$$

$$p_{c,m} = \sum_i \sum_j x_i x_j p_{cij} (\mu_{ij}/\mu_m)^2 \tag{11}$$

The cross interaction parameters are given by

$$\mu_{ij} = (1 - k_{\mu ij}) (\mu_i \mu_j)^{0.5} \tag{12}$$

$$v^{oo}_{ij} = (v^{oo}_i + v^{oo}_j)/2 \tag{13}$$

$$p_{c,ij} = (p_{ci} p_{cj})^{0.5} \tag{14}$$

Three cross interaction coefficients k_{uij}, k_{vij}, and $k_{\mu ij}$ have been introduced, but not all three are adjusted in the correlation of any one mixture. In part 1, for mixtures of water + nonpolar

Table 1. VLE Calculations for Polar + Nonpolar Mixtures

Mixture (1) + (2)	T K	p bar	k_{uij}	k_{vij}	K_1 AAD %	K_2 AAD %	No. Data Pts.	Data Source*
$H_2O + H_2$	311–477	3–138	−1.160	0.283	2.2	8.4	18	1
$H_2O + N_2$	366–589	3–138	−0.924	0.263	0.8	9.8	10	1
MeOH + Tetralin	521–580	16–113	0.173	0.168	4.1	4.3	25	2
EtOH + C_3	325–425	8–48	−0.023	0.063	11.5	2.8	17	3
Acetone + C_3	325–425	4–47	−0.010	−0.110	13.7	8.9	19	3
NH_3 + Argon	298–374	25–823	0.082	0.104	7.4	9.3	36	4
$NH_3 + N_2$	277–344	35–414	0.035	0.113	3.4	4.1	36	5
$H_2S + C_1$	277–344	28–131	0.036	0.009	0.8	2.6	52	6
$H_2S + n\text{-}C_7$	311–477	2–96	0.193	0.015	3.7	14.5	39	7
$CO_2 + n\text{-}C_7$	310–477	2–133	0.239	0.038	3.3	6.1	63	8
$CO_2 + n\text{-}C_{10}$	462–583	20–52	0.270	−0.005	2.5	4.9	16	9
$CO_2 + n\text{-}C_{16}$	462–663	20–51	0.330	−0.006	8.3	12.3	16	9

AAD: absolute average deviation.

*1. Gillespie and Wilson (1980)
2. Watanasiri et al. (1986)
3. Gomez-Nieto (1977)
4. Michels et al. (1961)
5. Reamer and Sage (1959)
6. Reamer et al. (1951)
7. Ng et al. (1980)
8. Kalra et al. (1978)
9. Sebastian et al. (1980a)

substances, $q = 1$ for water, $q = 0$ for nonpolar substances, and

$$\mu_n = \mu_{nw} = p_{c,n} = p_{c,nw} = 0 \tag{15}$$

where n refers to the nonpolar component. It follows that $k_{\mu ij}$ is not required.

Vapor-Liquid Equilibrium (VLE) of Polar + Nonpolar Mixtures

A fugacity formula has been derived from the augmented BACK equation based on the mixing rules of Eqs. 3 to 14. The formula is lengthy and is presented in the appendix. In part 1 eight mixtures of water + an n-paraffin were studied, and the hydrophobic character of the paraffins was shown to be the result of a lack of polar-polar interaction between the water molecule and the paraffin molecules. We extend the study here to nonaqueous mixtures. As a class the polar + nonpolar mixtures have been the most difficult to describe because of the large differences in the character of their molecular interactions. In the augmented BACK equation this interaction is characterized by a lack of the polar-polar component, the only cross interactions being nonpolar-nonpolar, which is generally quite weak.

Table 1 presents the cross interaction coefficients and summary comparisons of the equation with experimental data for 12 polar + nonpolar mixtures. Both hydrogen-bonding and nonhydrogen-bonding substances are represented in these mixtures. There being no poles in one component of the binary mixture and consequently no polar-polar cross interaction, Eq. 15 applies and $k_{\mu ij}$ is irrelevant. The two cross interaction coefficients k_{uij} and k_{vij} are adjusted for the fitting of K values of each binary system. Both coefficients are independent of temperature.

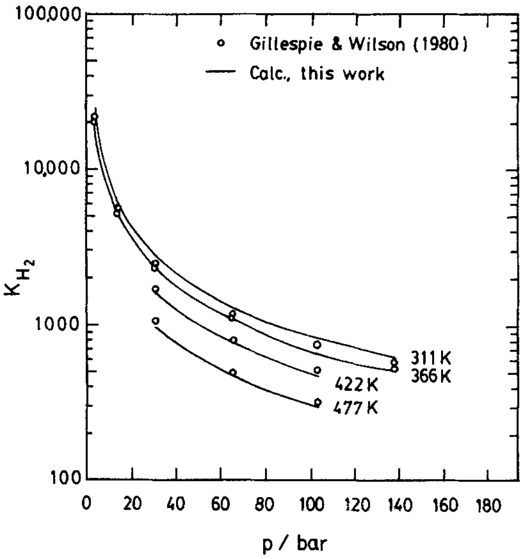

Figure 3. Vaporization equilibrium ratio of hydrogen in $H_2O + H_2$ mixtures.

Figure 2 shows the K value of water in mixtures of hydrogen + water and Figure 3 shows the K value of hydrogen in the same mixtures. While the K values vary over eight decades, the calculation follows the variation with both the temperature and the pressure faithfully. Figure 4 for methanol + tetralin and Figure 5 for ethanol + propane show two mixtures of strongly hydrogen-bonded substances.

VLE of Polar + Polar Mixtures

Table 2 summarizes augmented BACK equation calculations for 14 polar + polar mixtures. These are selected to have repre-

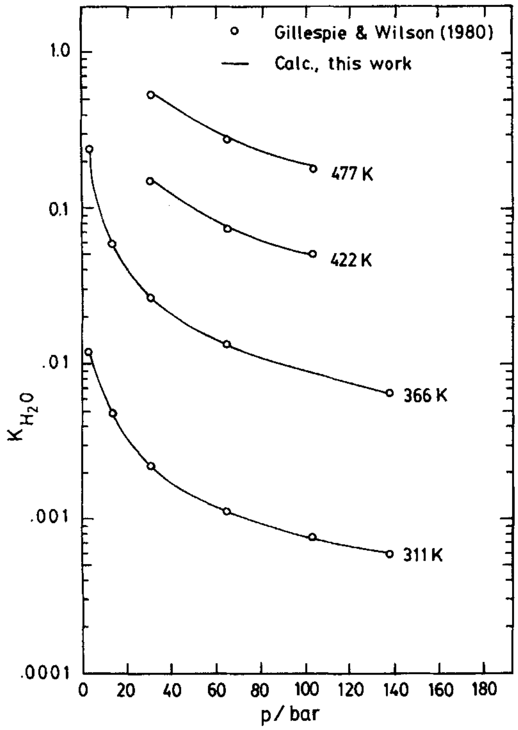

Figure 2. Vaporization equilibrium ratio of water in $H_2O + H_2$ mixtures.

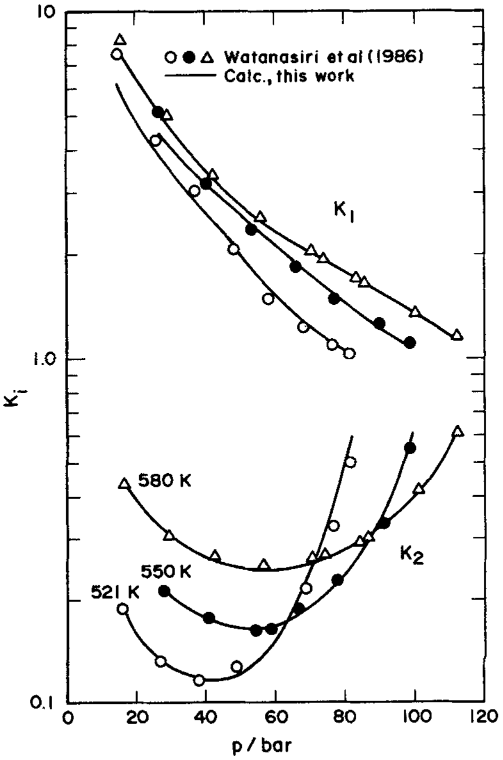

Figure 4. Vaporization equilibrium ratio in methanol(1) + tetralin(2) mixtures.

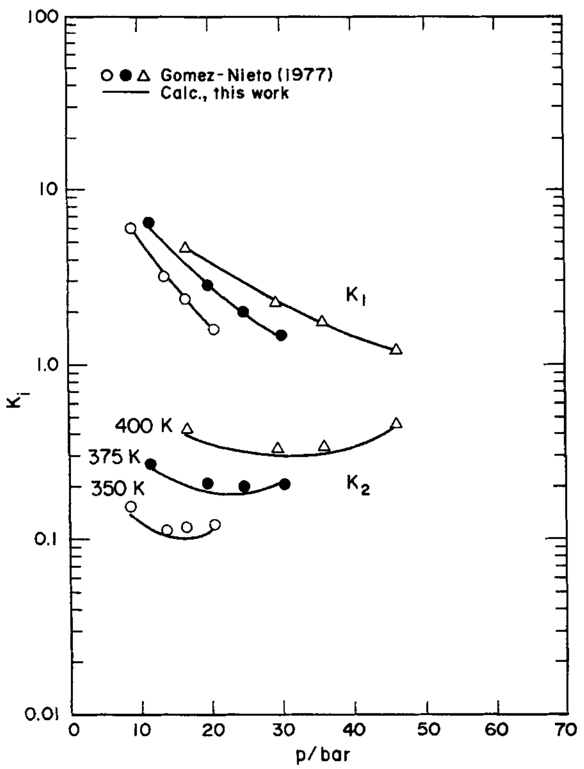

Figure 5. Vaporizaton equilibrium ratio in propane(1) + ethanol(2) mixtures.

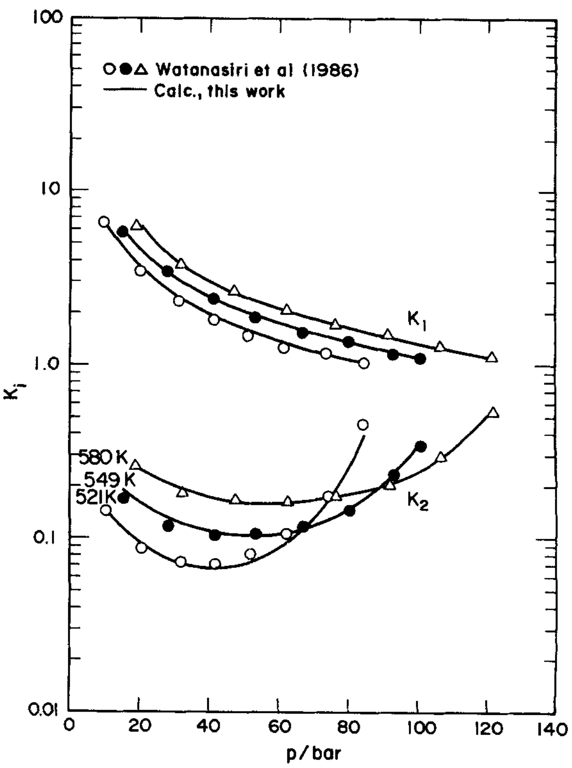

Figure 6. Vaporization equilibrium ratio in methanol(1) + quinoline(2) mixtures.

Table 2. VLE Calculations for Polar + Nonpolar Mixtures

Mixture (1) + (2)	T K	p bar	k_{uij}	k_{vij}	K_1 AAD %	K_2 AAD %	No. Data Pts.	Data Source*
H_2O + EtOH	473–598	25–157	−1.366	−0.197†	7.2	7.7	51	10
H_2O + 2—C_3OH	523–573	59–124	−1.313	−0.302†	3.7	8.5	20	10
H_2O + CO	366–589	3–138	−1.475	0.189	2.4	13.7	13	1
H_2O + CO_2	348–477	7–101	−1.299	−0.005	3.5	8.9	19	11
MeOH + EtOH	373–413	2–11	−0.018	−0.013	3.0	4.0	9	12
MeOH + *n*-Butanol	433–541	14–69	0.020	0.018	3.0	5.2	36	13
n-Butanol + Diethyl ether	413–553	14–41	0.019	−0.004	4.9	2.1	38	13
MeOH + Quinoline	521–560	11–122	0.073	0.176	3.0	5.2	24	2
MeOH + 1-methylnaphthalene	519–570	41–118	0.145	0.168	2.2	6.7	17	14
H_2S + Toluene	311–477	5–116	0.070	0.077	6.0	11.6	21	7
Acetone + CO_2	298–313	39–74	0.104	−0.168	7.5	0.7	14	15
Diethyl ether + CO_2	298–313	7–49	0.123	0.004	6.7	2.7	9	16
2-C_3OH + CO_2	316–394	41–124	0.136	0.011	5.0	2.0	21	17
1-methylnaphthalene + CO_2	463–703	21–51	0.236	0.026	4.9	6.7	15	18

AAD: absolute average deviation.
†K_{uij} instead of K_{vij}.
*1–9. see Table 1 notes.
10. Barr-David and Dodge (1959)
11. Gillespie and Wilson (1982)
12. Niesen et al. (1986)
13. Kay and Doham (1955)
14. Thies et al. (1984)
15. Katayama et al. (1975)
16. Ohgaki and Katayama (1975)
17. Radosz (1986)
18. Sebastian et al. (1980b)

sented:

- A variety of aqueous mixtures
- Several mixtures of alcohols
- Mixtures of highly asymmetric sizes
- A number of CO_2 mixtures

These mixtures are characterized by the presence of cross polar-polar interaction, which is particularly strong for water + alcohol mixtures, for which k_{uij} and $k_{\mu ij}$ are adjusted for data correlation, leaving $k_{vij} = 0$. The rest of the mixtures are correlated by adjusting k_{uij} and k_{vij}, leaving $k_{\mu ij} = 0$ just as for polar + nonpolar mixtures. Figure 6 shows the methanol + quinoline mixture as an example of this class.

Enthalpy

Enthalpy calculations are required in process simulation and design. The Lee-Kesler (1975) equation of state has been recommended to estimate the enthalpy of nonpolar mixtures by Reid et al. (1987), but no such recommendation could be made for polar fluid mixtures.

To make enthalpy calculations for polar fluid mixtures we derive the formula for residual enthalpy from the augmented BACK equation. The result is lengthy and is presented in the appendix.

The enthalpy of a mixture of H_2S (25 mol %) + N_2 at 200–339 K and pressures to 138 bar has been calculated. The calculated values agree with data with an absolute average deviation of 0.32% without any parameter adjustment, $k_{uij} = k_{vij} = 0$.

Table 3 presents the comparison of calculated excess enthalpies of mixtures with data. Excess enthalpy is experimentally the heat of mixing with a change of sign and is given by

$$H^E = H_m - \Sigma x_i H_i \tag{13}$$

$$= H_{r,m} - \Sigma x_i H_{r,i} \tag{14}$$

where superscript E denotes excess and subscript r denotes residual; subscript m is mixture, subscript i is component i. Excess enthalpy, being the difference between residual enthalpies of the mixture and the pure components gives a sensitive test of residual enthalpy calculation.

In the residual enthalpy calculation with the equation of state the cross interaction coefficients k_{uij} and k_{vij} are taken from Table 6 of part 1, and Tables 1 and 2 of this paper, where they were adjusted for the fitting of VLE data. No adjustment of any

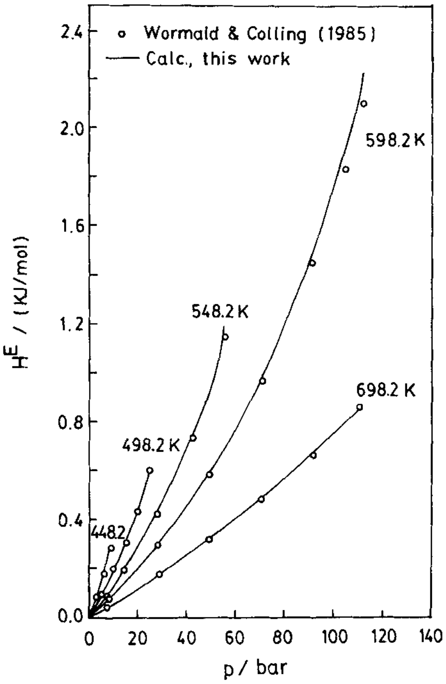

Figure 7. Excess enthalpy of water + hydrogen mixtures.

Table 3. Enthalpy Calculations for Polar-Containing Mixtures at Elevated Pressures

Mixture (1) + (2)	T K	p bar	x_1	k_{uij}	k_{vij}	H^E AAD %	No. Data Pts.	Data Source*
$H_2O + C_1$	448–698	3.5–126	0.5	−0.584	0.342	12.7	62	1
$H_2O + C_2$	448–698	5.5–122	0.5	−0.400	0.463	9.9	86	2
$H_2O + C_2^=$	448–648	4.6–66	0.5	−1.268	0.000	10.3	32	2
$H_2O + C_3$	448–698	5.3–137	0.5	−0.298	0.573	13.2	102	3
$H_2O + n$—C_4	448–698	6.3–130	0.5	−0.148	0.642	15.7	53	3
$H_2O + n$—C_5	448–698	5.5–118	0.5	−0.119	0.678	21.5	67	4
$H_2O + n$—C_6	448–698	3.8–126	0.5	−0.236	−0.356	11.1	54	4
$H_2O + n$—C_7	448–698	4.1–126	0.301–0.701	−0.176	−0.120	7.5	72	4
$H_2O + n$—C_8	498–648	3.4–146	0.363–0.799	−0.269	−0.267	17.8	183	4
$H_2O + CO$	473–698	7.6–122	0.5	−1.475	0.189	21.5	22	5
$H_2O + CO_2$	448–698	4–134	0.5	−1.299	−0.005	16.9	137	5
$H_2O + N_2$	448–698	3.5–126	0.5	−0.924	0.263	8.3	74	6
$H_2O + H_2$	448–698	3.6–112	0.3–0.704	−1.160	0.283	4.4	57	7
$NH_3 + C_1$	313–333	8.1–14.2	0.088–0.925	0.414	0.000	8.1	52	8
$CO_2 + n$—C_5	308–323	76–125	0.005–0.990	0.189	−0.066	22.7	127	9
$CO_2 + n$—C_6	470–573	75–125	0.024–0.992	0.238	−0.017	7.2	272	10
CO_2 + Toluene	358–573	80–166	0.037–0.990	0.184	−0.020	15.1	131	11
CO_2 + Cyclo-C_6	553–573	75–125	0.039–0.990	0.226	0.000	4.9	168	12

AAD: absolute average deviation.

*1. Wormald and Colling (1984)
2. Lancaster and Wormald (1987)
3. Wormald and Lancaster (1986)
4. Wormald et al. (1983)
5. Wormald et al. (1986)
6. Wormald and Colling (1983)
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8. Naumowicz and Woycicki (1986)
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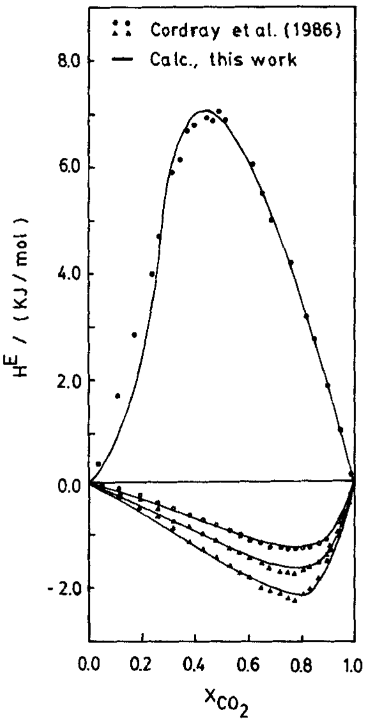

Figure 8. Excess enthalpy of carbon dioxide + toluene.
● 573.15K, 80.1 bar; ○ 358.15K, 166.3 bar
▲ 358.15K, 149.1 bar; △ 358.15K, 138.8 bar).

parameter is made to fit the equation to the enthalpy data, except for water + ethylene and water + *n*-heptane, which were not included in the preceding

Figure 7 shows the excess enthalpy of steam + hydrogen in an equimolal mixture. Figure 8 shows CO_2 + toluene mixtures at different pressures and temperatures. The calculated excess enthalpy changes from negative to positive as the temperature is changed in agreement with experimental data.

Acknowledgment

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Notation

A_{ij} = constants in Keenan EOS
D_{nm} = constants in attractive terms
f = fuacity
H = enthalpy
k = Boltzmann's constant
k_{uij} = binary interaction parameter for u/k
k_{vij} = binary interaction parameter for v^o
$k_{\mu ij}$ = binary interaction parameter for effective dipole moment
K = vaporization equilibrium ratio
n = number of moles
p = pressure, bar
q = ratio of characteristic temperature of charge distribution of fluids relative to that of water
Q = terms in Keenan EOS
R = gas constant
T = temperature
$\overline{T}$ = reduced temperature
u^o = parameter of interaction energy at infinite temperature
v = molal volume, cm^3/mol
$\overline{v}$ = reduced molal volume
v^o = close-packed volume, cm^3/mol
v^{oo} = close-packed volume at 0 K, cm^3/mol
x = molal fraction in liquid phase
y = molal fraction in vapor phase
z = compressibility

Greek letters

α = parameter of nonsphericity
β_{aj} = constants in Keenan EOS
η = parameter in BACK EOS
μ = effective dipole moment
ρ = density, g/cm^3
ρ_{aj} = constants in Keenan EOS
τ = 0.74048
Φ = fugacity coefficient (f/py) or (f/px)

Subscripts

c = characteristic property
i = component i
ij = interaction between i and j components
j = component j
m = mixture
r = residual
w = water

Appendix: Fugacity and Enthalpy Formulas of Augmented BACK Equation

The fugacity f_i of a component i is given through its fugacity coefficient Φ_i, defined as $f_i/(py_i)$ or $f_i/(px_i)$. By the augmented BACK equation,

$$\ln \Phi_i = \ln \Phi_i^{\mathrm{BACK}} + \ln \Phi_i^P \tag{A1}$$

$$\begin{aligned}\ln \Phi_i^{\mathrm{BACK}} &= \frac{(\alpha_m^2 + 3\alpha_m)y - 3\alpha_m y^2}{(1-y)^2} + (\alpha_m^2 - 1)\ln(1-y) \\ &+ \sum_{j=1}^{4}\sum_{m=1}^{9} \frac{D_{jm}}{\overline{T}^j\,\overline{v}^m} + \left(n\frac{\partial \alpha_m}{\partial n_i}\right)\left[\frac{-3y^2 + (3+2\alpha_m)y}{(1-y)^2}\right. \\ &\left. + 2\,\alpha_m \ln(1-y)\right] + \frac{1}{y}\left(n\frac{\partial y}{\partial n_i}\right) \\ &\cdot\left[\frac{-(\alpha_m^2-1)y^3 + (3\alpha_m^2 - 3\alpha_m - 2)y^2 + (3\alpha_m+1)y}{(1-y)^3}\right] \\ &+ \sum_{j=1}^{4}\sum_{m=1}^{9} \frac{D_{jm}}{\overline{T}^j\,\overline{v}^m}\left[\frac{j}{(u/k)_m}\left(n\frac{\partial (u/k)_m}{\partial n_i}\right)\right. \\ &\left. + m\left(1 + \frac{1}{v_m^o}\,n\frac{\partial v_m^o}{\partial n_i}\right)\right] - \ln z\end{aligned} \tag{A2}$$

where

$$\overline{v} = v/v_m^o$$

$$y = 0.74048/\overline{v}$$

$$\overline{T} = T/(u/k)_m$$

Partial derivatives in Eq. A2 are evaluated from the mixing rules.

$$n\frac{\partial y}{\partial n_i} = \frac{0.74048\,v_m^o}{v}\left[1 + \frac{1}{v_m^o}\left(n\frac{\partial v_m^o}{\partial n_i}\right)\right] \tag{A3}$$

$$n\frac{\partial \alpha_m}{\partial n_i} = 2\left(\sum_j x_j\alpha_{ij} - \alpha_m\right) \tag{A4}$$

$$n\frac{\partial v_m^o}{\partial n_i} = 2\left(\sum_j x_j v_{ij}^o - v_m^o\right) \qquad (A5)$$

$$n\frac{\partial (u/k)_m}{\partial n_i} = 2\left[\frac{\sum_j x_j v_{ij}^o (u/k)_{ij}}{v_m^o} - (u/k)_m\right] - \frac{(u/k)_m}{v_m^o}\left(n\frac{\partial v_m^o}{\partial n_i}\right) \qquad (A6)$$

The fugacity coefficient from polar pressure terms is

$$\begin{aligned}\ln \Phi_i^P = \frac{18.015}{v v_{c,w}} \Bigg\{ & 2\bar{p} Q v_{c,m} + Q v_{c,m}\left(n\frac{\partial \bar{p}}{\partial n_i}\right) \\ & + \bar{p} v_{c,m}\left[\left(\frac{\partial Q}{\partial \rho_w}\right)\left(n\frac{\partial \rho_w}{\partial n_i}\right) + \left(\frac{\partial Q}{\partial \beta}\right)\left(n\frac{\partial \beta}{\partial n_i}\right)\right] \\ & + \bar{p} Q\left(n\frac{\partial v_{c,m}}{\partial n_i}\right)\Bigg\} - \left(\bar{p} + n\frac{\partial \bar{p}}{\partial n_i}\right) \\ & \cdot \left[\frac{4y_w - 3y_w^2}{(1-y_w)^2} + \sum_{j=1}^{4}\sum_{m=1}^{9}\frac{D_{jm}}{\overline{T}_w^j \bar{v}_w^m}\right] \\ & - \bar{p}\left(n\frac{\partial y_w}{\partial n_i}\right)\left[\frac{4 - 6y_w}{(1-y_w)^2} + \frac{8y_w - 6y_w^2}{(1-y_w)^3}\right] \\ & + \bar{p}\left[\sum_{j=1}^{4}\sum_{m=1}^{9}\frac{mD_{jm}}{\overline{T}_w^j \bar{v}_w^{m+1}}\left(n\frac{\partial \bar{v}_w}{\partial n_i}\right)\right. \\ & \left. + \sum_{j=1}^{4}\sum_{m=1}^{9}\frac{jD_{jm}}{\overline{T}_w^{j+1}\bar{v}_w^m}\left(n\frac{\overline{T}_w}{\partial n_i}\right)\right] \qquad (A7)\end{aligned}$$

where $\bar{p} = p_{c,m}/p_{c,w}$

$$\bar{v}_w = \frac{v v_{c,w}}{v_w^o v_{c,m}}$$

$$y_w = 0.74048/\bar{v}_w$$

$$\rho_w = \frac{18.015 v_{c,m}}{v v_{c,w}}$$

$$\overline{T}_w = \frac{T}{(u/k)_w q_m}$$

$$\beta = 1{,}000/T_w = 1{,}000 q_m/T$$

and partial derivatives in Eq. A7 are expressed as

$$n\frac{\partial \bar{p}}{\partial n_i} = \frac{1}{p_{c,w}}\left(n\frac{\partial p_{c,m}}{\partial n_i}\right) \qquad (A8)$$

$$n\frac{\partial \rho_w}{\partial n_i} = \frac{18.015}{v v_{c,w}}\left(v_{c,m} + n\frac{\partial v_{c,m}}{\partial n_i}\right) \qquad (A9)$$

$$n\frac{\partial y_w}{\partial n_i} = \frac{0.74048 v_w^o}{v v_{c,w}}\left(v_{c,m} + n\frac{\partial v_{c,m}}{\partial n_i}\right) \qquad (A10)$$

$$n\frac{\partial \bar{v}_w}{\partial n_i} = \frac{-v v_{c,w}}{v_w^o v_{c,m}}\left[1 + \frac{1}{v_{c,m}}\left(n\frac{\partial v_{c,m}}{\partial n_i}\right)\right] \qquad (A11)$$

$$n\frac{\partial \overline{T}_w}{\partial n_i} = \frac{-T}{(u/k)_w q_m^2}\left(n\frac{\partial q_m}{\partial n_i}\right) \qquad (A12)$$

$$n\frac{\partial \beta}{\partial n_i} = \frac{1{,}000}{T}\left(n\frac{\partial q_m}{\partial n_i}\right) \qquad (A13)$$

$$n\frac{\partial q_m}{\partial n_i} = \frac{v_{c,w}\bar{\mu}_m}{v_{c,m}}\left[2\left(n\frac{\partial \bar{\mu}_m}{\partial n_i}\right) - \frac{\bar{\mu}_m}{v_{c,m}}\left(n\frac{\partial v_{c,m}}{\partial n_i}\right)\right] \qquad (A14)$$

where $\bar{\mu} = \mu/\mu_w$

$$n\frac{\partial p_{c,m}}{\partial n_i} = 2\left(\frac{\sum_j x_j p_{c,ij}\mu_{ij}^2}{\mu_m^2} - p_{c,m}\right) - 2\frac{p_{c,m}}{\mu_m}\left(n\frac{\partial \mu_m}{\partial n_i}\right) \qquad (A15)$$

$$n\frac{\partial v_{c,m}}{\partial n_i} = 2\left(\frac{\sum_j x_j v_{c,ij}\mu_{ij}^2}{\mu_m^2} - v_{c,m}\right) - 2\frac{v_{c,m}}{\mu_m}\left(n\frac{\partial \mu_m}{\partial n_i}\right) \qquad (A16)$$

$$n\frac{\partial \mu_m}{\partial n_i} = \frac{1}{2\mu_m^3}\left(\sum_j x_j \mu_{ij}^4 - \mu_m^4\right) \qquad (A17)$$

The residual enthalpy H_r is expressed by the augmented BACK equation in parts,

$$H_r = H_{r,\mathrm{BACK}} + H_{r,\mathrm{Keenan}} - H_{r,w,\mathrm{BACK}} \qquad (A18)$$

where

$$\begin{aligned}H_{r,\mathrm{BACK}} = -RT^2\Bigg(& \frac{1}{v_m^o}\left(\frac{\partial v_m^o}{\partial T}\right)\left[\frac{1+3\alpha_m}{\bar{v}/\tau - 1} + \frac{3\alpha_m^2 + 3\alpha_m}{(\bar{v}/\tau - 1)^2}\right. \\ & \left. + \frac{2\alpha_m^2}{(\bar{v}/\tau - 1)^3}\right] + \sum_{n=1}^{4}\sum_{m=1}^{9} mD_{nm}\left\{\frac{\left(\frac{\partial v_m^o}{\partial T}\right)}{v_m^o \overline{T}^n \bar{v}^m}\right. \\ & \left. - \frac{n\left[\frac{1}{(u/k)_m} - \frac{T}{(u/k)_m^2}\frac{\partial (u/k)_m}{\partial T}\right]}{m\overline{T}^{n+1}\bar{v}^m}\right\}\Bigg) \\ & + RT(z - 1) \qquad (A19)\end{aligned}$$

$$H'_{r,\mathrm{Keenan}} = -RT^2\bar{p}\left[\rho_w\left(\frac{\partial Q}{\partial T}\right)\right] + RT(z_w - 1) \qquad (A20)$$

$$\begin{aligned}H_{r,w,\mathrm{BACK}} = RT\bar{p}\Bigg\{ & \frac{v_w^{oo}}{v_w^o}\frac{0.36u_w^o}{kT}\exp(-3u_w^o/kT)\left[\frac{4}{(\bar{v}_w/\tau - 1)}\right. \\ & \left. + \frac{6}{(\bar{v}_w/\tau - 1)^2} + \frac{2}{(\bar{v}_w/\tau - 1)^3}\right] \\ & + \sum_{n=1}^{4}\sum_{m=1}^{9}\frac{mD_{nm}}{\overline{T}_w^n \bar{v}_w^m}\left[\frac{n}{m} + \frac{v_w^{oo}0.36u_w^o/kT}{v_w^o}\right. \\ & \left. \cdot \exp(-3u_w^o/kT)\right]\Bigg\} + RT(z_w - 1) \qquad (A21)\end{aligned}$$

and

$$\frac{\partial v_m^o}{\partial T} = \sum_i\sum_j x_i x_j\left(\frac{\partial v_{ij}^o}{\partial T}\right) \qquad (A22)$$

$$\frac{\partial v_{ij}^o}{\partial T} = \frac{-0.18(1 - k_{vij})}{T^2}\left[\frac{v_i^{oo}u_i^o}{k}\exp(-3u_i^o/kT) + \frac{v_j^{oo}u_j^o}{k}\exp(-3u_j^o/kT)\right] \quad \text{(A23)}$$

$$\frac{\partial (u/k)_m}{\partial T} = \sum_i \sum_j x_i x_j (1 - k_{uij}) \left\{\frac{v_{ij}^o}{v_m^o}\frac{0.5}{[(u/k)_i(u/k)_j]^{0.5}} \cdot \left[(u/k)_j(u_i^o/k)\left(\frac{-\eta_i}{kT^2}\right) + (u/k)_i(u_j^o/k)\left(\frac{-\eta_j}{kT^2}\right)\right] + [(u/k)_i(u/k)_j]^{0.5}\left(\frac{1}{v_m^o}\frac{\partial v_{ij}^o}{\partial T} - \frac{v_{ij}^0}{v_m^{o2}}\frac{\partial v_m^o}{\partial T}\right)\right\} \quad \text{(A24)}$$

$$\frac{\partial Q}{\partial T} = \frac{-1{,}000Q}{T_w^2 q_m\left(\dfrac{1{,}000}{T_w} - 1.544912\right)} + \left(\frac{1{,}000}{T_w} - 1.544912\right) \cdot \sum_{j=1}^{7}(j-2)\left(\frac{1{,}000}{T_W} - \beta_{aj}\right)^{j-3}\frac{-1{,}000}{T_w^2 q_m}\left[\sum_{i=1}^{8} A_{ij}(\rho_w - \rho_{aj})^{i-1} + \exp(-4.8\rho_w)(A_{9j} + A_{10j}\rho_w)\right] \quad \text{(A25)}$$

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