Augmented BACK Equation of State for Polar Fluids

The pressure of water is decoupled into a polar pressure and a nonpolar pressure, the latter being obtained from the BACK equation based on the size and nonpolar energy of the water molecule determined by Jorgensen and coworkers. The polar pressure is obtained upon subtracting the nonpolar pressure from the total pressure given by the steam table equation of Keenan et al. The polar pressure function thus obtained for water is generalized to augment the BACK equation for the general description of polar fluids.

Equation constants are reported for 26 substances. Calculated vapor pressure, liquid molal volume, and pressure-volume-temperature (PVT) behavior are compared with data. Mixing rules are introduced to express poles interacting with poles and dispersion modes interacting with dispersion modes, but not poles interacting with dispersion modes. PVT relationship, vapor-liquid equilibrium, and liquid-liquid equilibrium in mixtures of water and nonpolar substances are calculated.

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Introduction

Methods for the description of thermodynamic properties and phase equilibria of fluids are of interest in science and are needed in chemical engineering. For nonpolar fluids the methods are highly advanced, and a number of equations of state have proved generally useful. The methods are not as highly developed for polar fluids. The description of phase equilibria of polar fluids depends mainly on activity coefficients at low pressures where the gas imperfection is either insignificant or is described by the two-term virial equation. Polar fluids at higher pressures are generally not well described by equations of state and the activity coefficient method becomes unsuitable. In this work an equation of state that accurately describes nonpolar fluids is extended to polar fluids.

For nonpolar fluids, the extended virial equation of Benedict et al. (1940) was enlarged by Cox et al. (1971) and subsequently generalized by Starling and Han (1972) and Lee and Kesler (1975). Brule et al. (1982) further extended the equation on the basis of the conformal solution model.

Much success has been achieved by the perturbation-type equations. Following van der Waals, cubic equations have been developed by Redlich and Kwong (1949), Soave (1972), Peng and Robinson (1976), and Lin et al. (1983). Chen and Kreglewski (1977) developed a more complex perturbation equation by combining Boublik's (1975) hard convex body equation for the repulsive pressure with Alder et al.'s (1972) polynomial for the attractive pressure. The Boublick-Alder-Chen-Kreglewski (BACK) equation, employing molecular parameters, is highly accurate and has been used in the preparation of thermodynamic property tables of the American Petroleum Institute Research Project 44 (API-44). (Marsh et al., 1987) Since the BACK equation will be employed as a basis of this work, it is presented below.

$$\begin{aligned} z &= z_{rep} + z_{att} \\ &= 1 + \frac{(3\alpha + 1)y + (3\alpha^2 - 3\alpha - 2)y^2 + (1 - \alpha^2)y^3}{(1 - y)^3} \\ &\quad + \sum_{n=1}^{4} \sum_{m=1}^{9} m D_{nm} (u/kT)^n (v^o/v)^m \end{aligned} \qquad (1)$$

Where $y = 0.74048\, v^o/v$ is a reduced density; α is a nonsphericity parameter; v^o is the close-packed volume; and u is an interaction energy parameter. Both v^o and u are temperature-dependent:

$$v^o = v^{oo}[1 - C \exp(-3u^o/kT)] \qquad (2)$$

$$u = u^o(1 + \eta/kT) \qquad (3)$$

Table 1. BACK Equation Universal Constants D_{nm}

	n			
m	1	2	3	4
1	−8.804300	2.9396000	−2.8225000	0.3400000
2	4.164627	−6.0865383	4.7600148	−3.1875014
3	−48.203555	40.1379560	11.2571770	12.2317960
4	140.436200	−76.2307970	−66.3827430	−12.1106810
5	−195.233390	−133.7005500	69.2487850	0.0
6	113.515000	860.2534900	0.0	0.0
7	0.0	−1535.3224000	0.0	0.0
8	0.0	1221.4261000	0.0	0.0
9	0.0	−409.1053900	0.0	0.0

The universal constants D_{nm} have been determined from PVT and residual energy data of argon (Chen and Kreglewski, 1977), and are presented in Table 1. For each substance five parameters are required: u^o/k, v^{oo}, α, η/k, and C. Chen and Kreglewski suggested that $C = 0.12$ in general, thus leaving in effect four constants for a substance.

Progress has been made in statistical theoretical investigation of polar fluids. The perturbation theory of Barker and Henderson (1967) was applied to polar fluids by Masuoka et al. (1977). Gubbins and Twu (1978) developed a perturbation theory for mixtures of polar fluids. The perturbed-hard-chain theory was extended to strongly polar fluids by Gmehling et al. (1979) by means of a dimerization equilibrium theory. Yao et al. (1982) simulated dipolar interaction by the Monte Carlo method. Masuoka and Chao (1984) developed a dipolar pressure equation from Yao's results and used it to augment the chain-of-rotator equation of Chien et al. (1983) to obtain an equation for polar fluids.

Wu and Stiel (1985) developed a four-parameter generalized equation of state by using the Lee-Kesler (1975) equation to describe the nonpolar contribution and taking water as the reference fluid for polar substances. A fourth parameter, polarity factor, Y, was introduced to be determined from PVT data. By retaining the acentric factor as the third parameter, their method does not achieve the intended separation of polar and nonpolar contributions.

In this work we obtain an equation of state for polar substances by augmenting the BACK equation with a polar pressure derived from studies of water.

Polar Pressure of Water

The common occurrence and life-supporting role of water have assured it of a special place in scientific enquiries. Perhaps more is known of water than any other fluid. The structure of water has been the subject of numerous investigations, of which the recent work by Ben-Naim and Sillinger (1972), Sillinger and Rahman (1974), Jorgensen (1982), Jorgensen et al. (1985), and Jorgensen and Masura (1985) is particular notable. The charges and locations of the electric poles as well as the size and *nonpolar energy* of the water molecule have been determined. Jorgensen et al. (1983) and Jorgensen and Madura (1985) reported a positive charge of 0.52 *e* on each of the hydrogen atoms and a negative charge of 1.04 *e* in the oxygen atom at a point on the HOH bisector. The nonpolar interaction is represented as a Lennard-Jones potential with $\sigma = 3.15358$ Å and $\epsilon = 0.648694$ kJ/mol. A small, light, argon-like molecule is described that interacts mainly by means of Coulombic forces of the poles rather than by dispersion forces. From correlation of known Lennard-Jones parameter values for the light substances Ar, N_2, and light hydrocarbons we have

$$v^{oo} = 0.6735\, N\sigma^3 \tag{4}$$

$$u^o/k = 1.270\, \epsilon/k \tag{5}$$

Thus we determine the BACK equation parameters of water: $v^{oo} = 12.72$ cm^3/mol, and $u^o/k = 99.15$ K. Furthermore, $\alpha = 1$, $\eta/k = 0$, and $C = 0.12$ for this small, light molecule. The five parameters enable the calculation of the repulsive and nonpolar attractive pressures of water ($p_{rep,w}$ and $p_{att,np,w}$) by the BACK equation.

By van der Waals' theory and perturbation theory, the pressure of a fluid may be expressed as the sum of a repulsive pressure and an attractive pressure,

$$p = p_{rep} + p_{att} \tag{6}$$

For a polar fluid, the attractive pressure is made up of nonpolar interaction and polar interaction contributions. Equation 4 becomes

$$p = p_{rep} + p_{att,np} + p_{att,p} \tag{7}$$

The polar attractive pressure of water is evaluated by turning Eq. 7 around:

$$p_{att,p,w} = p_w - p_{rep,w} - p_{att,np,w} \tag{8}$$

where subscript *w* denotes water. The last two terms of Eq. 8 are found from the BACK equation as described above. To find the pressure of water, p_w, we turn to the steam table equation of Keenan et al. (1969),

$$z = 1 + \rho Q + \rho^2 \left(\frac{\partial Q}{\partial \rho}\right) T \tag{9}$$

where

$$Q = (\beta - 1.544912) \sum_{j=1}^{7} \left\{ \left(\beta - \beta_{aj}\right)^{j-2} \left[\sum_{i=1}^{8} A_{ij} (\rho - \rho_{aj})^{i-1} + e^{-4.8\rho} (A_{9j} + A_{10j}\rho) \right] \right\} \tag{10}$$

$$\beta = 1{,}000/T \tag{11}$$

The constants ρ_{aj}, β_{aj}, and A_{ij} are given in Table 2. The Keenan equation calculates thermodynamic properties of water at temperatures from 260 to 1,600 K and pressures to 2,200 atm.

Figure 1 shows the polar attractive compressibility factor of water $z_{att,p,w} = p_{att,p,w}v/RT$ obtained from Eq. 8 for some gas and liquid states. The $z_{att,p,w}$ value is always negative and increases in absolute magnitude with increasing density and decreasing temperature. It is a lengthy function of ρ and T containing 89 constants. This is the function we use in this work. Simplified fitting of the function will be desirable for routine use in the future.

Table 2. Keenan Equation Constants

i	A_{i1}	A_{i2}	A_{i3}	A_{i4}	A_{i5}	A_{i6}	A_{i7}
1	29.4929370	−5.1985860	6.8335354	−0.15641040	−6.3972405	−3.9661401	−0.69048554
2	−132.1391700	7.7779182	−26.1497510	−0.72546108	26.4092820	15.4530610	2.74074160
3	274.6463200	−33.3019020	65.3263960	−9.27342890	−47.7403740	−29.1424700	−5.10280700
4	−360.9382800	−16.2546220	−26.1819780	4.31258400	56.3231300	29.5687960	3.96360850
5	342.1843100	−177.3107400	0.0	0.0	0.0	0.0	0.0
6	−244.5004200	127.4874200	0.0	0.0	0.0	0.0	0.0
7	155.1853500	137.4615300	0.0	0.0	0.0	0.0	0.0
8	5.9728487	155.9783600	0.0	0.0	0.0	0.0	0.0
9	−410.3084800	337.3118000	−137.4661800	6.78749830	136.8731700	79.8479700	13.04125300
10	−416.0586000	−209.8886600	−733.9684800	10.40171700	645.8188000	399.1757000	71.53135300

$\beta_{a1} = 1.544912$; $\beta_{aj} = 2.5$ $(j > 1)$; $\rho_{a1} = 0.634$; $\rho_{aj} = 1.0$ $(j > 1)$

Generalization of the Polar Pressure

The polar pressure of water is generalized to describe other polar fluids by appealing to the principle of corresponding states (PCS). The electric poles of polar molecules interact by Coulombic forces, by which the potential energy is the same function of distance for all such interactions. A primary condition of PCS is satisfied. However, as the multipoles of real molecules are made up of different relative contributions of dipoles and quadrupoles, the PCS of the polar pressure is not exact, but is a useful approximation. The first term in the multipole expansion, the dipole of a charge distribution usually makes the main contribution. Adopting the formalism of dipole interaction, we define a characteristic temperature by

$$T_c = \mu^2/(kv^{\infty}/N) \tag{12}$$

where μ is the effective dipole moment, v^{∞} is the hard core volume at $T = 0$ K in the BACK equation, and N is Avogadro's number. Subscript c denotes a characteristic quantity. We further define $v_c = v^{\infty}$, and $p_c = RT_c/v^{\infty}$.

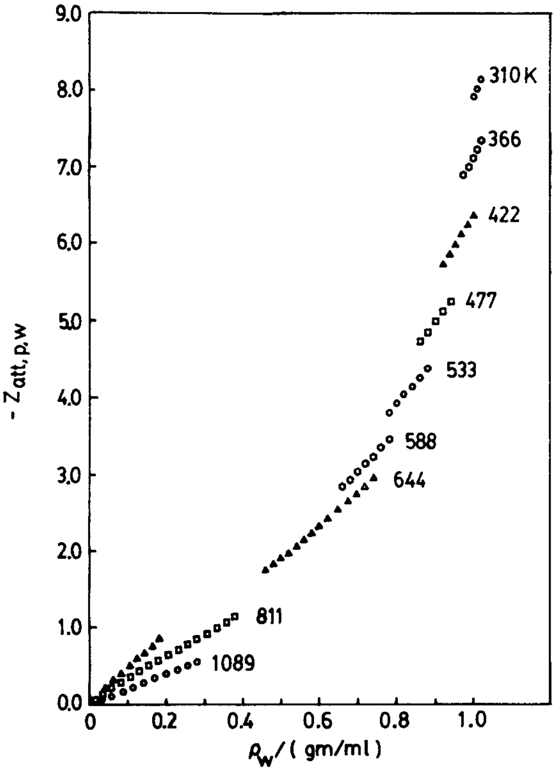

Figure 1. Polar compressibility factors of water.

The polar pressure of a fluid i when reduced is equal to the polar pressure of water also reduced, both being at the same reduced temperature and reduced density:

$$\frac{p_{att,p,i}}{p_{c,i}} = \frac{p_{att,p,w}}{p_{c,w}} \tag{13}$$

The polar pressure of fluid i is therefore given by the polar pressure of water, upon being suitably scaled:

$$p_{att,p,i} = \left(\frac{p_{c,i}}{p_{c,w}}\right) p_{att,p,w} \tag{14}$$

The scaling factor is reexpressed in T_c and v^{∞}:

$$p_{att,p,i} = \left(\frac{T_{c,i}}{T_{c,w}}\right)\left(\frac{v_w^{\infty}}{v_i^{\infty}}\right) p_{att,p,w} \tag{15}$$

In Eqs. 14 and 15 the temperatures of i and w must be corresponding, and the volumes must be likewise. Let T and v be the state of fluid i of interest. Then

$$p_{att,p,i}[T, v] = \left(\frac{p_{c,i}}{p_{c,w}}\right) p_{att,p,w}\left[\left(\frac{T_{c,w}}{T_{c,i}}\right) T, \left(\frac{v_w^{\infty}}{v_i^{\infty}}\right) v\right] \tag{16}$$

or

$$p_{att,p,i}[T, v] = \left(\frac{T_{c,i}}{T_{c,w}}\right)\left(\frac{v_w^{\infty}}{v_i^{\infty}}\right) p_{att,p,w}\left[\left(\frac{T_{c,w}}{T_{c,i}}\right) T, \left(\frac{v_w^{\infty}}{v_i^{\infty}}\right) v\right] \tag{17}$$

where the square brackets express functional dependence.

Let $q_i = T_{c,i}/T_{c,w}$ be the ratio of the characteristic temperature of the charge distribution of molecule i relative to that of water. Then q_i characterizes the polar energy of a polar molecule in Eq. 17:

$$p_{att,p,i}[T,v] = q_i\left(\frac{v_w^{\infty}}{v_i^{\infty}}\right) p_{att,p,w}\left[\frac{T}{q_i}, \left(\frac{v_w^{\infty}}{v_i^{\infty}}\right) v\right] \tag{18}$$

The calculation of polar pressure of fluid i by using the polar pressure equation of water requires one new equation of state parameter, q_i, in addition to the scaling volumes v_i^{oo} and v_w^{oo} of the BACK equation.

The corresponding states expression, Eq. 18, has been obtained by considering the polar interaction to be dipolar. The same results are obtained by considering quadrupolar interaction, to lead to a different meaning for q. In this work q will be taken as an equation of state parameter. It will be found to be related to the dipole moment, and quadrupole moment, but the exact value will be determined by fitting the equation of state.

Augmented BACK Equation

We obtain the augmented BACK equation for polar substances by combining Eqs. 1 and 18 according to Eq. 7:

$$z = 1 + \frac{(3\alpha + 1)y + (3\alpha^2 - 3\alpha - 2)y^2 + (1 - \alpha^2)y^3}{(1 - y)^3}$$
$$+ \sum_{n=1}^{4} \sum_{m=1}^{9} m D_{nm} (u/kT)^n (v^o/v)^m$$
$$+ q \left(\frac{v_w^{oo}}{v^{oo}}\right) \frac{v}{RT} p_{att,p,w}\left[\frac{T}{q}, \left(\frac{v_w^{oo}}{v^{oo}}\right) v\right] \qquad (19)$$

Six parameters are required for a substance to be described by Eq. 19: u^o/k, v^{oo}, α, η/k, C, and q. Kreglewski suggested that $C = 0.12$ in general, leaving five parameters. For nonpolar substances $q = 0$ and Eq. 19 simplifies to the BACK equation. For water, $q = 1$ and Eq. 19 becomes Eq. 9, the steam table equation of Keenan et al. The augmented BACK equation in effect interpolates (or extrapolates for a very few substances) between the BACK and the Keenan equations for polar fluids.

Table 3. BACK EOS Constants for Some Polar Fluids

Substance	u°/k K	v^{oo} cm³/mol	η/k K	α	q	μ/μ_w
Water	99.15	12.72	0.00	1.0000	1.0000	1.0000
Methanol	374.00	24.20	271.00	1.2450	0.4609	0.9364
Ethanol	353.84	36.75	307.50	1.0950	0.2133	0.7850
1-Propanol	380.00	47.13	314.00	1.1468	0.1378	0.7145
i-Propanol	341.00	48.12	326.91	1.1047	0.1448	0.7401
Butan-1-ol	397.52	58.68	316.97	1.1006	0.1434	0.8133
Butan-2-ol	396.80	56.55	291.95	1.1650	0.0997	0.6660
Ammonia	319.82	15.29	67.65	1.1024	0.4245	0.7144
Diethyl Ether	412.57	60.38	87.38	1.0312	0.1298	0.7850
Acetone	426.46	43.42	111.61	1.1723	0.6747	1.5176
HCl	317.93	17.79	17.65	1.1252	0.2381	0.5771
H_2S	377.13	20.88	14.29	1.1068	0.1593	0.5114
SO_2	357.02	26.10	85.58	1.0703	0.3595	0.8589
CS_2	529.01	36.18	37.95	1.0325	0.0013	0.0600
CO	131.50	19.70	3.90	1.0249	0.0022	0.0584
CO_2	283.25	19.86	40.06	1.0503	0.0006	0.0293
Ethylene	280.87	27.82	12.10	1.0378	0.0003	0.0239
Propylene	345.20	39.33	33.99	1.0353	0.0135	0.2042
1-Butene	390.00	50.86	50.00	1.0356	0.0089	0.1883
Benzene	528.83	54.33	71.90	1.0527	0.0069	0.1720
Toluene	551.50	67.13	89.25	1.0525	0.0065	0.1846
m-Xylene	562.50	79.00	123.25	1.0763	0.0041	0.1600
m-Cresol	638.22	69.74	192.75	1.1475	0.1279	0.8375
Quinoline	703.85	82.56	158.35	1.0748	0.0039	0.1592
1-Methyl-naphthalene	746.93	89.89	136.98	1.1149	0.0052	0.1909
Propionic acid	549.09	48.68	179.72	1.1201	0.1826	0.8359

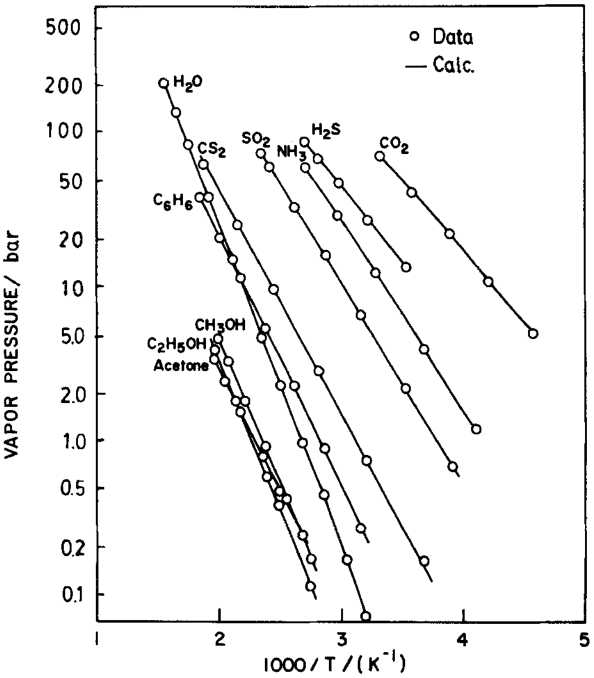

Figure 2. Vapor pressure of some pure polar fluids.

To make fluid-phase equilibrium calculations we derive a formula for fugacity from Eq. 19 according to standard procedures (Chao and Greenkorn, 1975). Table 3 presents the augmented BACK equation constants determined from experimental vapor pressures and saturated liquid densities for 26 polar substances. Figure 2 shows a comparison of the calculated vapor pressures with data for some of the substances. Figure 3 shows a comparison of the calculated saturated liquid and gas densities with data for methanol. Table 4 presents the average absolute deviations (AAD) of calculated vapor pressure and saturated liquid density for the 26 substances of Table 3. The calculated vapor pres-

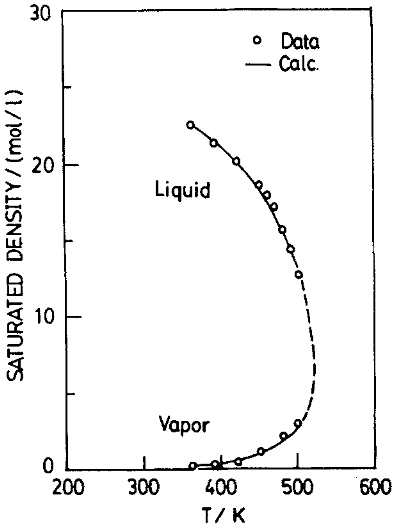

Figure 3. Saturated vapor and liquid densities of methanol.

Table 4. Comparison of Calculated Vapor Pressures and Saturated Liquid Densities of Pure Polar Fluids with Data

Substance	Temp. Range K	p AAD** %	v_l AAD %	No. Data Pts. p/v_l	Ref.† p/v_l
Water	313–643	0.16	0.04	34/34	a/a
Methanol	363–493	2.40	1.57	13/13	b/b
Ethanol	364–511 293–455*	2.01	1.46	18/13	c/d
1-Propanol	412–494 414–523*	1.38	3.00	18/10	c/d
i-Propanol	395–493 407–486	1.86	1.58	20/11	e/d
Butan-1-ol	351–398 320–480*	1.38	0.97	18/10	f/d
Butan-2-ol	306–373 303–490*	1.95	1.12	20/12	g/d
Ammonia	255–372	1.75	1.80	22/22	h/h
Diethyl ether	250–456 293–370	1.49	0.76	35/8	i/j
Acetone	374–498	0.90	0.74	27/27	k/k
HCl	170–230	2.96	0.62	8/8	l/l
H_2S	283–369	1.46	2.34	11/11	m/m
SO_2	272–422	1.19	2.01	29/29	h/h
CS_2	288–533	1.75	0.93	21/21	n/n
CO	68–130	1.30	0.33	23/23	h/h
CO_2	227–302	1.53	0.46	28/28	h/h
Ethylene	169–277	1.02	0.57	21/21	h/h
Propylene	225–355	0.59	1.16	25/25	h/h
1-Butene	273–419	2.34	1.03	27/27	h/h
Benzene	316–544	0.67	0.63	43/43	h/h
Toluene	354–568	1.60	0.80	24/20	o/o
m-Xylene	372–591	0.96	0.97	25/23	o/o
m-Cresol	374–542 373–453*	2.34	1.75	28/9	o/o
Quinoline	437–723	2.16	---	41/0	p/-
1-Methyl-naphthalene	396–700	1.60	---	29/0	o/-
Propionic acid	334–438 323–493*	1.18	1.01	25/18	o/o

*Temperature range of the data of saturated liquid densities.

**Average absolute deviation.

†a. Haar et al. (1984)
b. Machado and Streett (1983)
c. Ambrose et al. (1975)
d. Hales and Ellender (1976)
e. Ambrose and Townsend (1963)
f. Ambrose and Sprake (1970)
g. Ambrose et al. (1971)
h. Canjar and Manning (1967)
i. Ambrose et al. (1972)
j. Hales et al. (1983)
k. Campbell and Chatterjee (1968)
l. DaPonte and Staveley (1983)
m. Sage and Lacey (1955)
n. O'Brien and Alford (1951)
o. Marsh et al. (1987) API-44
p. Malanowski (1973)

sure and liquid molal volume generally agree with data to about 1 ~ 2%.

Figure 4 shows four isotherms of the compressibility factor of hydrogen chloride, which is highly polar with a dipole moment of 1.1 Debye. Two isotherms are supercritical and the other two are subcritical compressed liquid states. The calculations agree with the experimental data to 2.76% AAD. The five equation of state constants presented in Table 3 are used in the calculations.

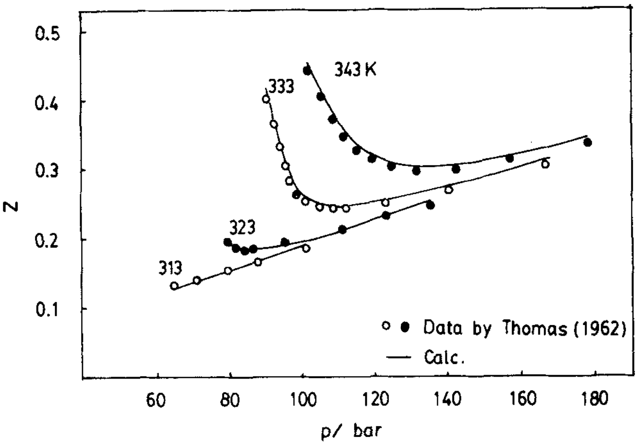

Figure 4. Compressibility factor of hydrogen chloride in sub- and supercritical states.

Mixtures

The augmented BACK equation of state is extended to mixtures with the introduction of mixing rules as follows.

For the repulsive and nonpolar attractive pressures

$$u_m/k = \sum_i \sum_j x_i x_j (u/k)_{ij} (v^o_{ij}/v^o_m) \tag{20}$$

$$v^o_m = \sum_i \sum_j x_i x_j v^o_{ij} \tag{21}$$

$$\alpha_m = \sum_i \sum_j x_i x_j \alpha_{ij} \tag{22}$$

where the cross-interaction parameters are given by

$$(u/k)_{ij} = (1 - k_{uij})[(u/k)_i (u/k)_j]^{0.5} \tag{23}$$

$$v^o_{ij} = (1 - k_{vij})(v^o_i + v^o_j)/2 \tag{24}$$

$$\alpha_{ij} = (\alpha_i + \alpha_j)/2 \tag{25}$$

For the polar attractive pressure of a mixture, we adopt the formalism of dipolar interaction and combine the dipole moment μ_i obtained from the temperature scaling factor q_i to form the mixture μ_m:

$$\mu^4_m = \sum_i \sum_j x_i x_j \mu^4_{ij} \tag{26}$$

The dipole moments μ_i, being obtained from the equation of state parameter q_i, are "effective" dipoles as they can contain quadrupolar or higher polar components. The scaling volumes are combined with a weighting factor

$$v_{c,m} = \sum_i \sum_j x_i x_j v_{c,ij} \left(\frac{\mu_{ij}}{\mu_m}\right)^2 \tag{27}$$

The characteristic temperature $T_{c,m}$ of the mixture follows upon substitution in Eq. 12.

The characteristic pressure $p_{c,m}$ for Eq. 16 is obtained by also

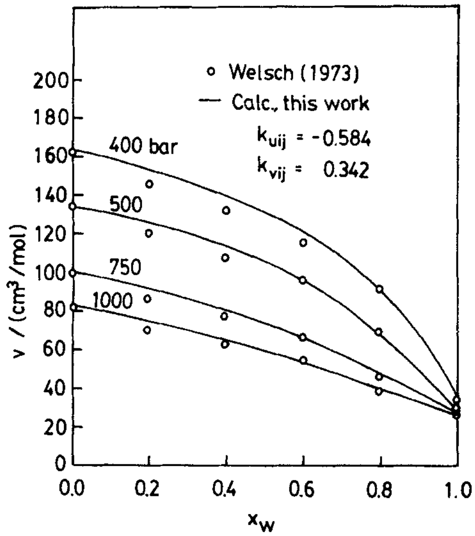

Figure 5. Molal volume of steam plus methane mixtures at 673 K and pressure up to 1,000 bar.

combining the $p_{c,i}$ with a weighting factor:

$$p_{c,m} = \sum_i \sum_j x_i x_j p_{cij} \left(\frac{\mu_{ij}}{\mu_m}\right)^2 \tag{28}$$

By these mixing rules a dispersion mode interacts with other dispersion modes, and a pole interacts with other poles, but a dispersion mode and a pole do not interact.

Mixtures of water and nonpolar substances have resisted systematic description with equations of state, and with solution theories, and have posed a special challenge and severe test that to a large extent motivated the present work. We address these mixtures in the remaining part of this work.

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

$$\mu_n = \mu_{nw} = p_{c,n} = p_{c,nw} = 0 \tag{29}$$

where the subscript n denotes a nonpolar component.

There being no poles on a nonpolar molecule, the only interaction it has with water is with the nonpolar dispersion mode of water, and this mode is weak in energy. Thus, the equation of state explains the hydrophobic behavior of the nonpolar substances.

Two mixture parameters, k_{uij} and k_{vij}, are adjustable for fitting of data on a binary mixture. Only the nonpolar interaction is adjusted.

Figure 5 shows the calculated molal volume of steam plus methane mixtures at 673 K and pressures up to 1,000 bar in comparison with data by Welsch (1973). The comparison shows an AAD of 2.7% and bias of 1.6%. Similarly steam plus argon and steam plus xenon mixtures at pressures up to 1,000 bar are studied. We summarize the results in Table 5.

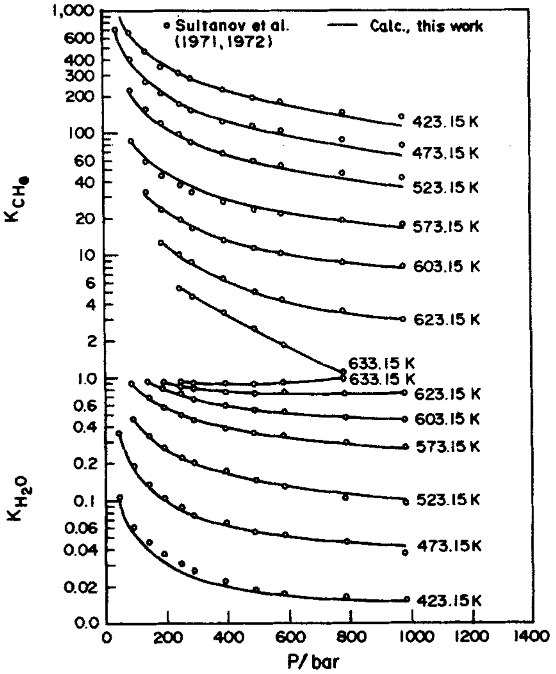

Figure 6. Vaporization equilibrium ratio in water plus methane mixtures.

To calculate vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) we derive a fugacity equation from the augmented BACK equation and the mixing rules. The fugacity equation will be presented in a second paper on this work together with the complete mixing rules.

Figure 6 shows the calculated vaporization equilibrium ratios $K_i = \Phi_{iL}/\Phi_{iv}$ in water plus methane mixtures in comparison with experimental data $K_i = y_i/x_i$ of Sultanov et al. (1971, 1972). The full range of states of the data is included, with temperature from 423 to 633 K and pressure up to 1,000 bar. With two constant interaction parameters k_{uij} and k_{vij}, the calculation shows an AAD of 2.7% for the K value of water and 4.7% for methane.

Figure 7 shows the calculated phase equilibrium ratio of water in water plus propane mixtures, and Figure 8 shows the phase equilibrium ratio of propane in mixture with water. A propane-rich vapor phase exists in equilibrium with a water-rich liquid at lower pressures. This vapor phase disappears and is transformed into a propane-rich liquid at a transition pressure at

Table 5. Summary Comparison of Molal Volume Calculations with Data for Water (1) plus Nonpolar Fluid (2) Mixtures

Component (2)	T K	p bar	k_{uij}	k_{vij}	v AAD* %	v Bias %	No. Data Pts.	Data Source
Methane	673	400–1,000	−0.584	0.342	2.7	1.6	24	Welsch (1973)
	—	—	−1.430	0.000	2.8	−0.6	—	
Argon	673–713	500–1,000	−1.212	0.000	2.5	1.1	53	Lentz & Franck (1969)
Xenon	673	500–1,000	−1.152	0.000	1.8	0.6	33	Welsch (1973)

*Average absolute deviation.

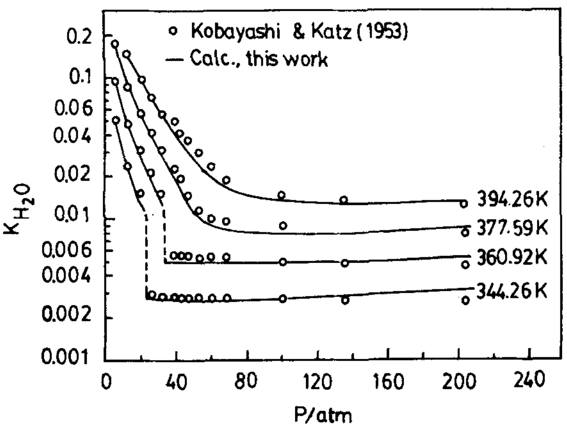

Figure 7. Phase equilibrium ratio of water in mixture with propane.

the lower temperatures 344 and 360 K. Two liquids coexist at pressures above the transition pressure. The transition from VLE to LLE is described by the new equation of state and is shown with a break of the curves at the two lower temperatures. The equilibrium ratio for LLE is calculated by $K_i = \Phi_{iL}/\Phi_{iL'}$ where subscript L' denotes the propane-rich liquid. The calculation of K value for LLE is entirely similar to that of K value for VLE. The K values are also comparable in significance. Therefore no distinction is made between VLE and LLE in comparing calculations with data. The overall AAD of K of water is 10.2%, and of propane 9.5%. The same constants of nonpolar interactions, k_{uij} and k_{vij}, are used in both VLE and LLE calculations.

Figure 9 shows the calculated phase equilibrium ratio of water in mixtures of water plus n-pentane. Similar to water plus propane, a pentane-rich vapor exists in equilibrium with a water-rich liquid at the lower pressures. This vapor phase disappears and is transformed into a pentane-rich liquid at a transition pressure at the lower temperatures 464 and 469 K. Two liquids coexist at pressures above the transition. The K value of water shows a discontinuity at the three-phase equilibria (VLLE) transition pressure.

Figure 10 shows the calculated phase equilibrium ratios of both components in water plus n-decane mixtures. The VLE K_2 isotherms all terminate at the VLLE K_2 curve at the high pressure end. This phenomenon is illustrated with the 548 K isotherm. Table 6 presents a summary comparison of the phase equilibrium calculations for mixtures of water plus an n-paraffin up to C_{10}.

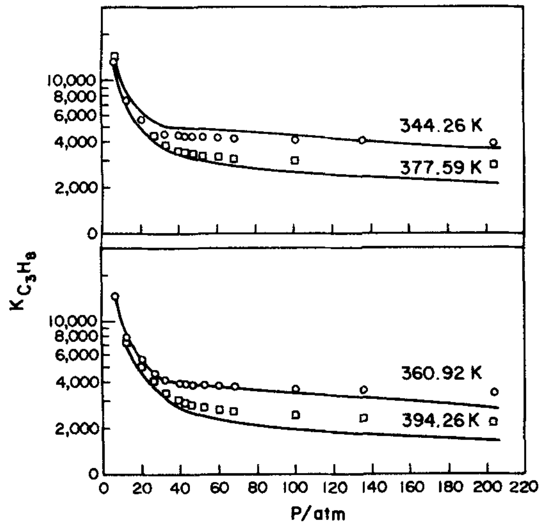

Figure 8. Phase equilibrium ratio of propane in mixture with water.

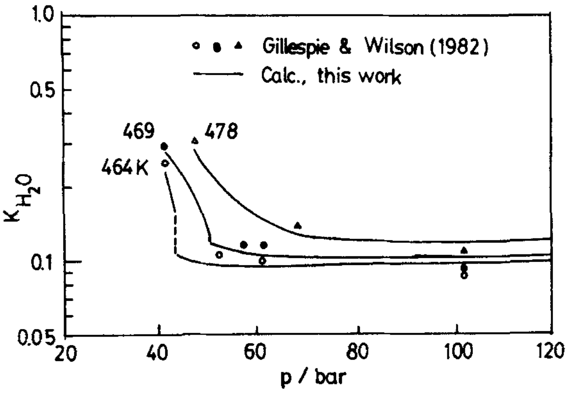

Figure 9. Phase equilibrium ratio of water in mixture with n-pentane.

Description of mixtures of water plus hydrocarbons has required temperature-dependent interaction coefficients in previous equations of state. The Soave and Peng-Robinson equations further require two sets of coefficients, one each for the hydrocarbon-rich phase and the water-rich phase. The cubic combination rule of the Cotterman-Prausnitz (1986) equation also requires two sets of interaction coefficients, one of which is temperature-dependent. The use of only two temperature-independent coefficients in this work represents a significant simplification made possible by the separation of the nonpolar and polar forces.

Concluding Remarks

The intense efforts in the study of the microstructure of water as one of the most complex liquids have provided the key to the

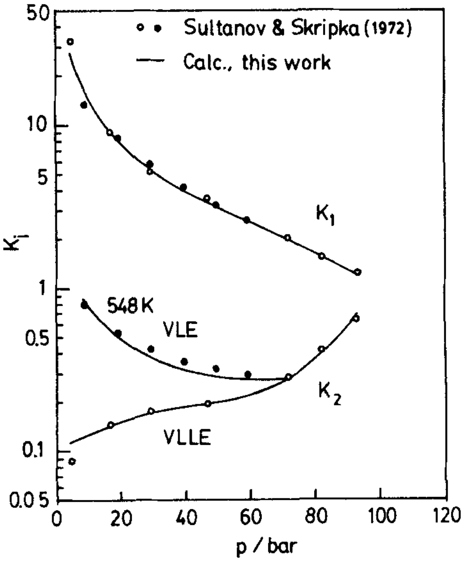

Figure 10. Vaporization equilibrium ratio in water (1) plus n-decane (2) mixtures.

Table 6. Summary Comparision of Phase Equilibria Calculations with Data for Water (1) plus Paraffin (2) Mixtures

Paraffin	Temp. Range, K	Pressure Range, bar	k_{uij}	k_{vij}	K_1 AAD* %	K_2 AAD %	No. Data Pts.	Data Source
Methane	423–633	49–980	−0.584	0.342	2.7	4.7	65	Sultanov et al. (1971, 1972)
Ethane	523–629	200–1,000	−0.400	0.463	2.8	9.8	15	Danneil et al. (1967)
Propane	344–394	7–206	−0.298	0.573	10.2	9.5	53	Kobayashi & Katz (1953)
n-Butane	411–511	4–206	−0.148	0.642	8.5	10.4	41	Sage & Lacey (1955)
n-Pentane	464–478	34–103	−0.119	0.678	9.9	4.1	11	Gillespie & Wilson (1982)
n-Hexane	473–493	$20\text{–}p^{3\phi}$**	−0.232	−0.356	8.1	1.5	11	Sultanov & Skripka (1972)
n-Octane	498–538	$20\text{–}p_{3\phi}$	−0.269	−0.267	3.8	3.0	12	Sultanov & Skripka (1972)
n-Decane	423–563	$5\text{–}p_{3\phi}$	−0.287	−0.014	4.4	6.5	13	Sultanov & Skripka (1972)

*Average absolute deviation.

**$p_{3\phi}$, three-phase equilibria (VLLE) pressure.

thermodynamics of water, mixtures of water, and polar substances. By subtracting a weak nonpolar pressure from the pressure of water, a strong polar pressure is obtained, which is scaled down for the description of most other polar substances.

In the augmented BACK equation separation of the attractive pressure into polar and nonpolar parts is achieved. Such a separation is fundamentally significant in the description of polar mixtures, for poles interact with poles, and dispersion mode interacts with dispersion mode, but the two modes do not (appreciably) interact for large classes of substances. Thus, the immiscibility and solubility of water and hydrocarbons follow as a direct consequence of the separate interactions, and are explained by the equation of state upon separating the interaction pressures.

The lengthy equation for the polar pressure of water remains to be simplified and applied to mixtures of other polar fluids.

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Notation

A_{ij} = constants in Keenan EOS, Table 2
C = parameter in BACK EOS
D_{nm} = constants in attractive term, Table 1
k = Boltzmann's constant
N = Avogadro's number
n = number of moles
p = pressure, bar
q = ratio of characteristic temperature of charge distribution of molecule i relative to that of water
Q = terms in Keenan EOS
R = gas constant
T = temperature, K
$\tilde{T}$ = reduced temperature
u = potential energy
u^o = parameter of interaction energy at infinite temperature
v = molal volume, cm^3/mol
$\tilde{v}$ = reduced molar volume
v^o = close-packed volume, cm^3/mol
v^{oo} = closed-packed volume at 0 K, cm^3/mol
x = molal fraction
y = reduced density
z = compressibility factor

Greek letters

α = parameter of nonsphericity
β = 1,000/T, 1/K
β_{aj} = constants in Keenan EOS
ϵ = molecular potential energy
η = parameter in BACK EOS
μ = effective dipole moment
ρ = density, g/mL
ρ_{aj} = constants in Keenan EOS
σ = molecular diameter, Å
Φ = fugacity coefficient ($= f/xp$)

Subscripts

att = attractive contribution
c = characteristic property
i = component *i*
m = mixture
np = nonpolar contribution
p = polar contribution
rep = repulsive contribution
w = water

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