Further Simplification of the Augmented BACK Equation of State

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An equation of state called the augmented Boublik-Alder-Chen-Kreglewski (ABACK) equation was proposed by Lee and Chao (1988a,b) for polar fluids and mixtures. This equation has been found to offer a good account of the phase equilibria, volumetric and enthalpic properties of polar fluids and mixtures, including mixture of water + hydrocarbons in spite of the hydrophobic nature of hydrocarbons that makes their mixtures with water a daunting challenge.

Unfortunately the ABACK equation is complex and not convenient to use, as it is made up of 107 terms. The complexity is compounded when derivation is made for fugacity, enthalpy, and other thermodynamic quantities.

The complexity of the ABACK equation is due mainly to the expression for the polar pressure of water $p_{att,p,w}$ that is part of the equation. This expression is made up of three parts:

$$p_{att,p,w} = p_w - p_{rep,p,w} - p_{att,np,w} \tag{1}$$

where p_w is the pressure of water by the 55-constant steam table equation of Keenan et al. (1969). The last two terms in Eq. 1 together are represented by the 26-constant Boublik-Alder-Chen-Kreglewski (BACK) equation.

We present in this note a new expression for the polar pressure of water that is obtained by fitting values generated according to Eq. 1 as a function of T and ρ. The new equation is much simpler than the three functions combined in Eq. 1:

$$p_{att,p,w} = \frac{RT}{v}\rho[\pi_1(T) + (\rho - 0.6)\pi_2(T) + (\rho - 1.0)^2\pi_3(T)] \tag{2}$$

where

$$\begin{aligned}
\pi_1(T) &= 106.5 - 90.0 \exp[470/(T + 1{,}770)] \\
\pi_2(T) &= 2{,}880.4 - 5716/T - 2{,}998 \exp[-162/(T + 3{,}300)] \\
\pi_3(T) &= 69.54 - 4{,}450/T - 115 \exp[-258{,}623/(T + 20)^2 \\
&\quad - 559/(T - 100)]
\end{aligned}$$

To obtain Eq. 2, the polar pressure of water is calculated for 126 states of p-ρ-T according to Eq. 1 from 273-811 K. In addition, 42 vapor pressure points of water from 273 to 647 K are taken from Keenan et al. (1969). A nonlinear regression procedure is employed to fit the combined data. The result, Eq. 2, turns out to give a good quantitative representation of the data employed. In Figure 1, the saturated densities of water and steam from Keenan et al. are compared with Eq. 2 combined with the BACK equation.

Previously we reported a simplified form of the polar pressure of water $p_{att,p,w}$ (Lee and Chao, 1990) obtained by linear regression of the p-ρ-T data that were generated according to Eq. 1 for 1,025 states. Vapor pressure of water was not considered explicitly, but implicitly through the inclusion of ex-

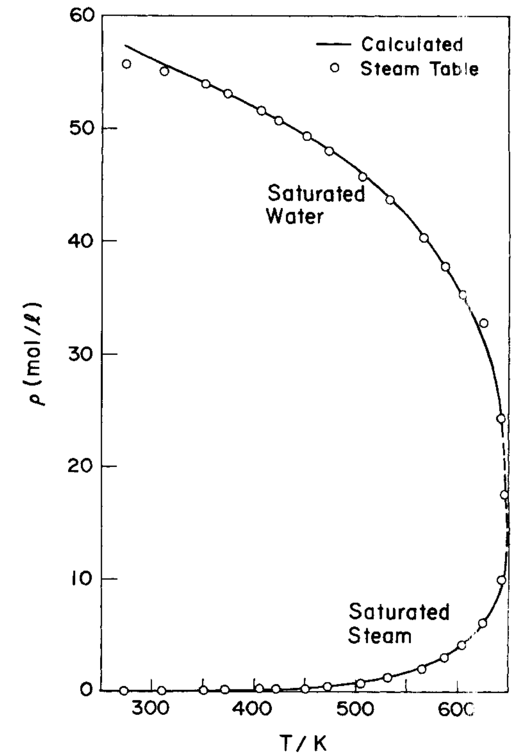

Figure 1. Saturated vapor and liquid densities of water.

perimentally inaccessible states in the condensation range. It was then found necessary to employ an expression containing 57 terms to achieve the quantitative representation of the polar pressure of water. In contrast, Eq. 2 contains eight terms and 16 fitting constants. The nonlinear regression procedure to include vapor pressure data is harder to implement, but the result appears preferable.

Simplified Augmented BACK Equation of State

The simplified augmented BACK equation (SABACK) is obtained by combining Eq. 2 with the BACK equation:

$$z = 1 + \frac{(3\alpha+1)y + (3\alpha^2 - 3\alpha - 2)y^2 + (1-\alpha^2)y^3}{(1-y)^3} + \sum_{n=1}^{4} \sum_{m=1}^{9} mD_{nm}(u/kT)^n (v^0/v)^m + \frac{v}{RT}\bar{p}p_{\mathrm{att},p,w}(T_w,\rho_w) \quad (3)$$

where

$y = 0.74047v^0/v$

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

The augments of $p_{\mathrm{att},p,w}$ in the last term of Eq. 3 are T_w and ρ_w, corresponding states variables for water given by $T_w = T/q$ and $\rho_w = 18.015v^{00}/(vv^{00}{}_w)$. Five parameters are required in Eq. 3 for each substance: $u^0/k, v^{00}$, η/k, α, and q. The first four appear in the BACK equation. Only q is introduced with the augmented equation to express the polarity of the substance relative to that of water. Table 1 presents the parameter for 26 polar substances. Though they are close to those reported previously for the ABACK equation, they are redetermined for the best accuracy for use with Eq. 3.

Testing the SABACK Equation

When tested with pure fluid data, the calculated vapor pressure and saturated liquid density from Eq. 3 are generally within 1% in average absolute deviation from the experimental value. The results are no worse than the ABACK equation.

For testing Eq. 3 with mixtures, the same mixing rules previously described by Lee and Chao (1988a,b) are employed, except for a simplification of the characterizing pressure of pole-pole interaction. Instead of the previous quadratic form, a linear combination is used here:

$$p_{\mu c,m} = \sum_i x_i p_{\mu c,i} \quad (4)$$

Three adjustable binary nonpolar interaction coefficients, k_{vij}, k_{uij}, and $k_{\alpha ij}$, are introduced for fitting mixture data. Generally, k_{uij} and $k_{\alpha ij}$ are adjusted, and $k_{\alpha ij} = 0$. For mixtures of water and aromatic hydrocarbons, $k_{\alpha ij}$ is adjusted in place of k_{vij}. The adjusted parameters are independent of temperature. No adjustable parameters are introduced for pole-pole interactions.

Table 2 shows the comparison of calculated phase equilibrium ratios with experimental data. Most of the states examined are at vapor-liquid equilibrium; states at liquid-liquid equilibrium are included in two mixtures: H_2O + propane and + n-pentane. A hydrocarbon-rich liquid exists in place of hydrocarbon-rich gas when the pressure exceeds the three-phase co-

Table 1. Simplified Augmented BACK EOS Constants for Polar Fluids

Substance	v^{00} cm³/mol	u^0/k K	η/k K	α	μ_e^*
Water	12.720	99.15	0.00	1.000	1.000
Methanol	24.7312	381.2437	249.7319	1.1393	0.9025
Ethanol	36.7363	357.3845	317.0078	1.0632	0.7515
1-Propanol	47.3984	379.9761	313.9844	1.0855	0.8401
2-Propanol	47.9979	341.1213	327.4009	1.0611	0.8461
1-Butanol	58.7611	397.5173	316.9700	1.0703	0.8777
2-Butanol	56.6310	396.7986	291.9487	1.1394	0.7325
Ammonia	15.2872	319.8269	67.7275	1.0691	0.7218
Diethyl Ether	60.3801	412.5701	87.3801	1.0197	0.7840
Acetone	43.5435	430.0000	111.7200	1.1529	1.496
HCl	17.8486	317.9221	17.6447	1.0675	0.5552
H_2S	21.2921	377.0730	13.4638	1.0223	0.1258
SO_2	25.4531	368.0000	83.0000	1.0891	0.8975
CS_2	36.1800	529.0100	37.9500	1.0324	0.0600
CO	19.6926	131.6316	3.9002	1.0178	0.0567
CO_2	19.8927	283.2488	40.1459	1.0415	0.0293
Ethylene	27.8200	380.8701	12.1121	1.0378	0.0239
Propylene	38.7074	345.1865	33.9489	1.0255	0.2032
1-Butene	50.8684	389.4500	50.1268	1.0200	0.2150
Benzene	54.3390	528.8296	70.0000	1.0413	0.0107
Toluene	67.1512	551.5010	89.3658	1.0482	0.0491
m-Xylene	79.0000	563.0625	123.2500	1.0763	0.0500
Ethylbenzene	78.8000	572.5000	111.0000	1.0181	0.0150
m-Cresol	69.7400	638.8535	192.7502	1.1255	0.8443
Quinoline	82.5600	703.8501	158.3500	1.0657	0.1142
1-Methylnaphthalene	89.8900	746.9299	136.9800	1.1202	0.1907
Propionic acid	48.6962	549.0876	179.7202	1.1066	0.8349

Table 2. Comparison of Phase Equilibrium Ratios

mixture (1) + (2)	T K	p bar	k_{uij}	k_{vij}	K_1 AAD %	K_2 AAD %	Data Pts. No.	Data Source
Polar + Nonpolar								
H_2O + Methane	423-633	49-980	−0.874	0.246	3.6	5.6	65	[1]
H_2O + Ethane	523-629	200-1000	−0.754	0.325	3.1	6.2	15	[2]
H_2O + *n*-Propane	344-394	7-206	−0.465	0.508	11.2	8.4	53	[3]
H_2O + *n*-Butane	411-511	4-206	−0.259	0.611	8.0	9.3	41	[4]
H_2O + *n*-Pentane	463-477	34-103	−0.272	0.631	10.2	4.3	11	[5]
H_2O + *n*-Hexane	473-493	20-$p_{3\Phi}$	−0.259	−0.308	7.6	1.4	11	[6]
H_2O + *n*-Octane	498-538	20-$p_{3\Phi}$	−0.324	−0.455	4.5	3.1	12	[6]
H_2O + *n*-Decane	423-563	5-$p_{3\Phi}$	−0.321	−0.056	3.9	6.5	13	[6]
Methanol + Tetralin	1-580	16-113	0.215	0.095	2.6	2.4	26	[7]
H_2S + Methane	277-344	28-131	0.063	−0.016	0.8	2.8	52	[8]
H_2S + *n*-Heptane	311-477	2-96	0.219	0.012	2.7	8.0	39	[9]
CO_2 + Ethane	223-293	6-63	0.093	0.115	2.2	2.4	30	[10]
CO_2 + *n*-Heptane	310-477	2-133	0.238	0.056	3.4	7.1	63	[11]
CO_2 + *n*-Decane	462-583	20-52	0.254	0.055	2.7	4.5	16	[12]
CO_2 + *n*-C_{16}	462-663	20-51	0.335	0.026	7.2	11.9	16	[12]
Polar + Polar								
H_2O + NH_3	370-420	1-4	−1.249	0.198	1.6	8.8	9	[13]
H_2O + Ethanol	473-598	25-157	−1.540	−0.274	4.3	7.7	51	[14]
H_2O + H_2S	477-589	55-207	−1.409	−0.222	3.3	5.2	9	[5]
H_2O + CO_2	347-477	7-101	−1.192	0.129	6.7	7.7	19	[5]
Methanol + Ethanol	373-413	2-11	−0.002	−0.086	2.2	2.1	9	[15]
Methanol + Quinoline	521-560	11-122	0.153	0.124	1.8	3.6	24	[7]
H_2S + Toluene	311-477	5-116	0.119	−0.023	2.9	11.6	21	[10]
Aceetone + CO_2	293-313	39-74	0.087	−0.068	5.1	1.4	14	[16]
Diethyl ether + CO_2	298-313	7-49	0.131	0.041	5.2	1.6	9	[16]
2-Propanol + CO_2	316-394	41-124	0.137	0.005	2.8	1.7	21	[17]
1-Methylnaphthalene + CO_2	463-703	21-51	0.245	0.033	4.4	5.6	15	[18]

1 = Sultanov et al. (1972a)
2 = Danneil et al. (1976)
3 = Kobayashi and Katz (1953)
4 = Sage and Lacey (1955)
5 = Gillespie and Wilson (1982)
6 = Sultanov and Skripka (1972b)
7 = Watanasiri et al. (1961)
8 = Reamer and Sage (1959)
9 = Reamer et al. (1951)
10 = Ng et al. (1980)
11 = Kalra et al. (1978)
12 = Sebastian et al. (1980a)
13 = Polak and Lu (1975)
14 = Barr-David and Dodge (1959)
15 = Niesen et al. (1986)
16 = Kotayama et al. (1975)
17 = Radosz (1986)
18 = Sebastian et al. (1980b)

existence value at a below critical temperature. The equilibrium ratio is then the mole fraction in the hydrocarbon-rich phase to that in the water-rich phase. The comparisons show that

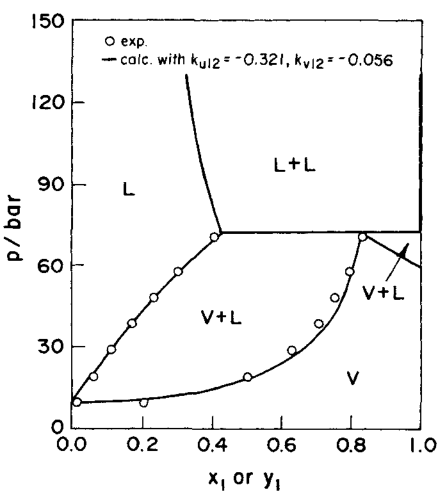

Figure 2. *p-x-y* diagram for water (1) + *n*-decane (2) mixture at 548 K.

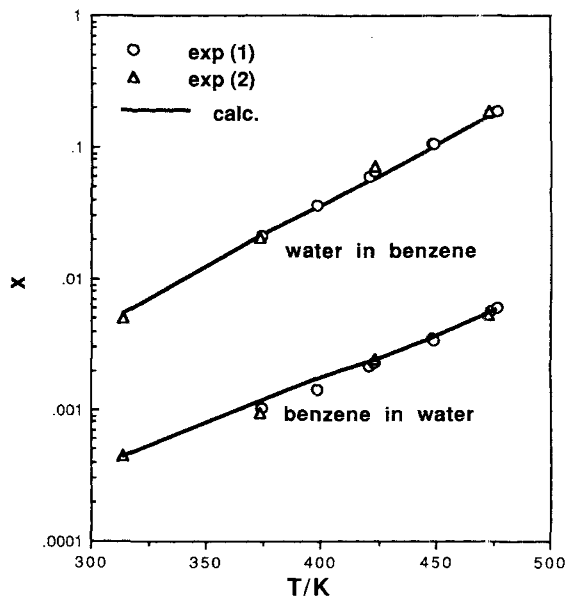

Figure 3. Mutual solubilities of water and benzene.

Data source: 1. Anderson and Prausnitz (1986); 2. Tsonopoulos and Wilson (1983)

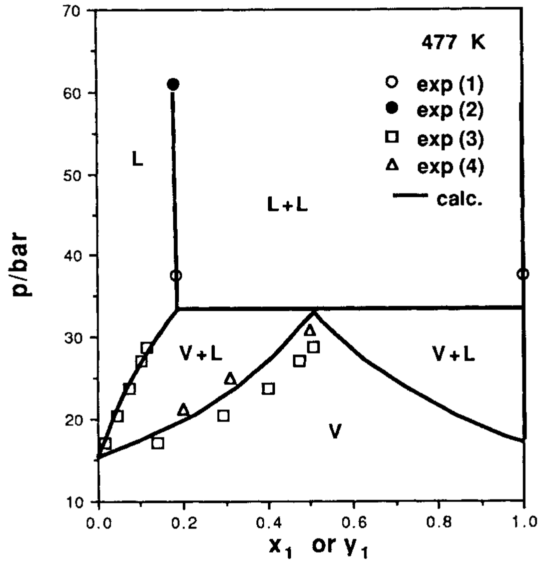

Figure 4. *p-x-y* diagram for water (1) + benzene (2) mixture at 477 K.

Data source: 1. Anderson and Prausnitz (1986); 2. Thompson and Snyder (1964); 3. Burd and Braun (1968); 4. Rebert and Kay (1959)

the SABACK equation is hardly distinguishable from the ABACK equation of Lee and Chao.

There is a rich variation in the phase behavior of water + hydrocarbon mixtures that is of both practical and theoretical interest. Figure 2 shows the *p-x-y* diagram for *n*-decane mixture at 548 K. The SABACK equation is in good agreement with the observed VLE data. The calculation also shows the existence of VLE at a separate region with high *n*-decane concentrations and LLE at higher pressures which have not been observed.

Mutual Solubility of Water and Hydrocarbons

Mutual solubility of water and hydrocarbons are calculated with the SABACK equation and compared with the data to provide a severe test of the equation. Figure 3 shows the close agreement of the calculated mutual solubilities of water and benzene with experimental data in a wide temperature range. Figure 4 presents the *p-x-y* phase diagram for water + benzene mixtures at 477 K. The calculated benzene-rich liquid is in close agreement with the data. The coexistent vapor composition is found to be at somewhat different compositions by two groups of investigators, while the calculation falls generally in-between the two. Both coexistent liquid mixtures at higher pressures calculated are in excellent agreement with the data. Figure 5 presents the vapor–liquid–liquid coexistence states calculated with Eq. 3 for water + propane mixtures in comparison with the data. Generally a good agreement is observed except for the mole fraction of water in vapor at higher temperatures approaching the critical state of mixture.

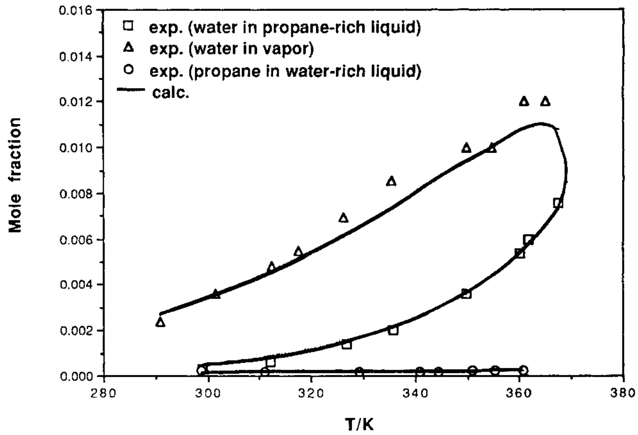

Figure 5. Three coexistent phase compositions for water + propane mixtures.

Data source: Kobayashi and Katz (1953)

Table 3 presents percent deviations of the calculated mutual solubilities from the data for five mixtures of water + paraffin and four mixtures of water + aromatic hydrocarbon. The interaction coefficients, k_{uij} and k_{vij}, are adjusted for mixtures of water + paraffin, k_{uij} and $k_{\alpha ij}$, for water + aromatic hydrocarbon. In view of the different shapes of water and aromatic hydrocarbon molecules, it seems reasonable to adjust $k_{\alpha ij}$ in place of k_{vij}. The values of the interaction coefficients are presented in Table 3.

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Table 3. Calculated Mutual Solubilities of Water and Hydrocarbon vs. the Data

Hydrocarbon	Temp. K	k_{uij}	k_{vij}	Water in HC $\Delta x/10^{-2}$	Water in HC $\Delta x/x$ %	HC in Water $\Delta x/10^{-4}$	HC in Water $\Delta x/x$ %	Data Pts. No.	Data Source
n-Propane	310–366	−0.465	0.508	0.015	10.6	0.408	20.3	8	1
n-Pentane	463–477	−0.272	0.631	1.08	10.6	0.104	3.4	6	2
n-Hexane	370–495	−0.259	−0.308	0.228	17.9	—	—	5	3
n-Octane	421–550	−0.324	−0.455	0.229	27.8	—	—	5	4
n-Decane	573–613	−0.321	−0.056	1.62	2.47	—	—	19	5
		k_{uij}	$k_{\alpha ij}$						
Benzene	373–477	−0.96	−0.117	0.494	6.4	1.377	7.6	8	6
Toluene	373–473	−0.985	−0.284	0.96	9.0	1.497	9.6	6	6
m-Xylene	398–473	−0.902	−0.267	1.70	10.6	0.418	9.0	5	6
Ethylbenzene	423–552	−0.816	−0.137	3.76	11.6	1.69	8.5	4	4

1 = Kobayashi and Katz (1953)
2 = Gillespie and Wilson (1980)
3 = Tsonopoulos et al. (1983)
4 = Brady and Wilson (1982)
5 = Anderson and Prausnitz (1986)

Notation

p = pressure
T = absolute temperature
v = volume per mole
y = dimensionless density, $=0.74048v^0/v$
z = compressibility factor, $=pv/(RT)$
ρ = density, g/cm

Subscripts

att = attractive
m = mixture
p = polar
w = water
i, j = component i, j
np = non-polar
rep = repulsive

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