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A NEW CUBIC EQUATION OF STATE FOR FLUIDS AND FLUID MIXTURES

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Abstract—A new cubic equation of state for pure fluids is presented in this work. The new equation requires the critical temperature and pressure, as well as two additional parameters to characterize each particular fluid. These parameters have been evaluated by minimizing deviations in saturated liquid densities while simultaneously satisfying the equality of fugacities along the saturation curve. Thus, good predictions of volumetric properties in the liquid region are obtained, while accuracy in vapour–liquid equilibrium calculations is maintained. Parameters for polar as well as nonpolar fluids are presented in this paper. In the case of nonpolar fluids, the two parameters required can be correlated with the acentric factor. No such relationship with independently measured quantities could be found for polar fluids. It is shown that the new equation reproduces many of the good features of the Soave and Peng–Robinson equations of state for nonpolar fluids, whilst overcoming some of the limitations of these equations for polar fluids. Applications of the equation of state to the correlation of phase equilibria are demonstrated.

INTRODUCTION

Since the time of van der Waals, many equations of state have been proposed for the representation of the volumetric properties of pure liquids. These equations have ranged in complexity from simple expressions containing two or three constants to complicated forms containing more than fifty constants. Although the many-constant equations have been utilized for precise representation of volumetric data, they are not generally preferred for phase equilibuium calculations and in process simulation studies, partly because they require excessive computer time and partly because it is difficult to obtain generalized forms of these equations suitable for mixture calculations. In many situations, therefore, the use of simple cubic equations of state represents a satisfactory compromise between accuracy and speed of computation.

Probably the most successful cubic equations for phase equilibuium calculations have been those proposed by Soave[1] and Peng and Robinson[2]. Both the Soave (RKS) and the Peng-Robinson (PR) equations assume a particular (fixed) value of the critical compressibility factor and, as a result, the predicted densities of the saturated liquids and the predicted critical volumes differ considerably from their experimental values (especially for substances whose critical compressibilities are significantly different from the values assumed by these equations). Fuller[3] and, more recently, Schmidt and Wenzel[4] among others, introduced a substance dependent critical compressibility which allowed them to accurately reproduce the experimental saturated liquid volume at a particular temperature. Schmidt and Wenzel[4], in particular showed that the optimum value of this substance dependent critical compressibility was not, in general, equal to the experimental critical compressibility of the fluid of interest.

The present work is an extension of the works of Soave, Peng and Robinson and of Schmidt and Wenzel. The equation of state proposed here uses, in addition to the critical temperature T_c and critical pressure P_c, two substance dependent parameters ζ and F as input parameters. For non-polar fluids, these parameters can be related to the acentric factor ω, so that with suitable assumptions, the equation reduces to those of Soave, Peng and Robinson and Schmidt and Wenzel. The new equation thus reproduces many of the good features of these three equations and, in addition, it can be applied to polar fluids such as water, ammonia and the alcohols. The extension of the equation to mixtures is also demonstrated below.

THE NEW EQUATION OF STATE

The equation of state proposed in this work has the following form:

$$P = \frac{RT}{v-b} - \frac{a[T]}{v(v+b)+c(v-b)} \tag{1}$$

where R is the universal gas constant, "a" is a function of temperature and b and c are constants. The form of the cubic equation chosen is not new, similar forms having been chosen earlier by Harmens[5] and

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Mollerup[6] among others. By making certain assumptions, two well-known cubic equations of state can be obtained from eqn (1). When $c = b$, eqn (1) reduces to the Peng–Robinson expression and when $c = 0$, it reduces to the Redlich–Kwong or Soave equations.

Acceptable prediction of both low and high pressure behavior requires at the very least that the critical compressibility factor implied by the equation of state be treated as an empirical parameter, different in general from the experimental value of Z_c [7–9]. It is also well-known that the predicted value of the critical compressibility factor (denoted by ζ_c below) is not an important indicator of the overall performance of any equation of state[10]. For these reasons, the new equation of state was constrained to satisfy the following conditions:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \qquad (2)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \qquad (3)$$

$$\frac{P_c V_c}{RT_c} = \zeta_c. \qquad (4)$$

Instead of letting ζ_c have a value equal to the experimental value of the critical compressibility factor, an arbitrary value was chosen. Thus, ζ_c was treated as an empirical parameter, our treatment so far being identical to that of Schmidt and Wenzel[4]. It should be noted that if $\zeta_c = 0.3074$, eqn (1), together with constraints (2) and (3), reduces to the Peng–Robinson equation. Similarly, if $\zeta_c = 0.3333$, eqn. (1) reduces to the Soave or Redlich–Kwong equations.

Application of constraints (2–4) to eqn. (1) yields:

$$a[T] = \Omega_a(R^2T_c^2/P_c)\,\alpha[T_R] \qquad (5)$$

$$b = \Omega_b(RT_c/P_c) \qquad (6)$$

$$c = \Omega_c(RT_c/P_c) \qquad (7)$$

where

$$\Omega_c = 1 - 3\zeta_c \qquad (8)$$

$$\Omega_a = 3\zeta_c^2 + 3(1-2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c \qquad (9)$$

and Ω_b is the smallest positive root[4] of the cubic:

$$\Omega_b^3 + (2-3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \qquad (10)$$

For $\alpha[T_R]$, we chose the same function of reduced temperature as that used by Soave and Peng and Robinson. It is given by:

$$\alpha = [1 + F(1 - T_R^{1/2})]^2. \qquad (11)$$

Both Soave and Peng and Robinson correlated the slope F to the acentric factor ω of a substance. Recently, Grabowski and Daubert[11] found that eqn (11) failed to give accurate results for hydrogen and they recommend:

$$\alpha = C_1 \exp(-C_2 T_R). \qquad (12)$$

A similar function was recommended by Heyen[12]

$$\alpha = \exp[C(1 - T_R^n)]. \qquad (13)$$

We have used both eqns (13) and eqn (11) in our equation of state, although it should be noted that eqn (13) contains one more constant than eqn (11). For the 38 substances studied in this work, we found that eqn (13) offered no advantages over eqn (11). We therefore recommend the use of eqn (11), with F being treated as an empirical parameter. The equation proposed by us therefore contains two parameters ζ_c and F, in addition to T_C and P_c.

EVALUATION OF ζ_c AND F

The following trial and error procedure was adopted for evaluating ζ_c and F. Initially, ζ_c was set equal to 0.307 or $1.1Z_c$, whichever value being closer to the experimental critical compressibility Z_c. Using eqns (8–10), values of Ω_a, Ω_b, and Ω_c were then calculated. Using these values of Ω_a, Ω_b and Ω_c, a value of α was obtained at each temperature along the saturation curve such that the equilibrium condition:

$$f^L = f^V \qquad (14)$$

was satisfied at each point. (The expression for the fugacity is given in the Appendix). F was then calculated by a least squares fit of eqn (11). The following sum was minimized:

$$S = \sum_{i=1}^{m} \{(1 + F\beta_i)^2 - \alpha_{\exp,i}\}^2 \qquad (15)$$

$$\beta_i = 1 - T_{R,i}^{1/2} \qquad (16)$$

Where $T_{R,i}$ is the value of T_R at the ith data point and $\alpha_{\exp,i}$ is the value of α which satisfies eqn (14) at that point.

The condition for a minimum of eqn (15) leads to a cubic equation in F which can be solved analytically and the smallest positive root was taken in the subsequent calculations. Using the values if Ω_a, Ω_b, Ω_c and F, saturated liquid densities were calculated and compared with experimental values obtained from the literature, the average absolute deviation at the chosen value of ζ_c being noted. The value of ζ_c was then changed by 0.001 and new values of Ω_a, Ω_b, Ω_c and F were obtained by solving eqns (8)–(11). The average absolute deviation in saturated liquid densities was obtained and noted. This procedure was repeated until a minimum occurred in the value of the average absolute deviation. After the first iteration, it became clear whether the value of ζ_c should be increased or decreased.

The optium values of ζ_c and F correspond to the minimum deviation in saturated liquid densities and the equilibrium condition of equality of fugacities. The proposed equation using optimum values of ζ_c and F is therefore expected to give good predictions of liquid phase densities and vapor–liquid equilibria (Schmidt and Wenzel adopted a very similar approach, except ζ_c and eqn (11) for nonpolar fluids were determined from a single vapor pressure and density point. They did not extend their procedure to polar fluids such as water and the alcohols or to long molecules such as eicosane). Optimum values of ζ_c and F for 38 pure fluids (including polar substances) are given in Table 1. Experimental saturation pressures and saturated liquid densities were used to obtain ζ_c and F. References to all the data used can be found in Ref. [15].

PURE FLUID CALCULATIONS

The proposed equation of state was used to calculate densities, vapor pressures, enthalpy departures and entropy departures of pure fluids. Calculated values were compared with experimental values (when available) and with values obtained using other equations of state.

Densities

Saturated liquid and vapor densities for the 38 components studied in this work were calculated using the new equation, the Peng–Robinson equation, the Heyen equation, the Redlich-Kwong equation and the BWRS[13] equation. Average absolute deviations in these properties are given in Tables 2 and 3.

The new equation gives lower average deviations in both the vapor and liquid phases than the P–R equation. For polar components and heavy hydrocarbons, the new equation gave consistently better predictions than the P–R equation and the R–K equation. Deviations between experimental and calculated saturated liquid densities are plotted against reduced temperature for *n*-eicosane and ammonia in Figs. 1 and 2. Except in the region close to the critical point, the new equation gives accurate predictions of saturated liquid densities.

Agreement in the critical region ($0.9 < T_R < 1.0$) can be improved if ζ_c is assumed to be a linear function of temperature in this region. The value of ζ_c changes from the calculated value ζ_c' to the experimental value Z_c as T_R changes from 0.9 to 1.0, so that no additional parameters are required if a linear function of temperature is assumed. Thus, for $0.9 < T_R < 1.0$

$$\zeta_c' = \zeta_c - 10(\zeta_c - Z_c)(T_R - 0.9). \tag{17}$$

According to this equation, $\zeta_c' = Z_c$ when $T_R = 1.0$, so that the experimental value of the critical compressibility is reproduced. This resulted in improvement in the average deviations in saturated liquid densities from 11.56% to 3.04%, although the average absolute deviation in saturated vapor densities increased from 2.32% to 5.37%. No cubic equation gives accurate predictions of both these properties in the critical region[4]. Accuracy in the representation of saturated liquid densities in the

Table 1. Parameters of the new equation of state constants F, C, η correspond to eqns (11) and (13)

No.	Component	ζ_c	F	C	η
1	Argon	0.328	0.450751	0.524130	0.895275
2	Nitrogen	0.329	0.516798	0.673567	0.805805
3	Oxygen	0.327	0.487035	0.545990	0.935190
4	Methane	0.324	0.455336	0.526324	0.904570
5	Ethane	0.317	0.561567	0.708265	0.800910
6	Ethylene	0.318	0.554369	0.642236	0.889410
7	Propane	0.317	0.648049	0.763276	0.800655
8	Propylene	0.324	0.661305	0.750739	0.898305
9	Acetylene	0.310	0.664179	0.659602	1.013775
10	n-Butane	0.309	0.678389	0.831715	0.816840
11	i-Butane	0.315	0.683133	0.775633	0.896125
12	1-Butene	0.315	0.696423	0.742573	0.958385
13	n-Pentane	0.308	0.746470	0.851904	0.882260
14	i-Pentane	0.314	0.741095	0.854607	0.875455
15	n-Hexane	0.305	0.801605	0.868581	0.934715
16	n-Heptane	0.305	0.868856	0.890894	0.992105
17	n-Octane	0.301	0.918544	1.057530	0.861175
18	n-Nonane	0.301	0.982750	1.247160	0.759605
19	n-Decane	0.297	1.021919	1.299741	0.755210
20	n-Undecane	0.297	1.080416	1.291079	0.809660
21	n-Dodecane	0.294	1.115585	1.339256	0.602980
22	n-Tridecane	0.295	1.179982	1.319388	0.869635
23	n-Tetradecane	0.291	1.188785	1.427823	0.798090
24	n-Heptadecane	0.283	1.297054	1.354358	0.935665
25	n-Octadecane	0.276	1.276058	1.538739	0.791235
26	n-Eicosane	0.277	1.409671	1.741225	0.763255
27	Carbon dioxide	0.309	0.707727	0.865847	0.816080
28	Carbon monoxide	0.328	0.535060	0.678260	0.799145
29	Sulfur-dioxide	0.307	0.754966	0.871496	0.871745
30	Hydrogen-sulfide	0.320	0.583165	0.855553	0.669095
31	Water	0.269	0.689803	0.987468	0.680260
32	Ammonia	0.282	0.627090	1.425590	0.418730
33	Benzene	0.310	0.704657	0.880633	0.797500
34	Methanol	0.272	0.972708	0.939465	1.064985
35	Ethanol	0.300	1.230395	1.221152	1.001250
36	Propan-1-ol	0.303	1.241347	1.806248	0.629465
37	Butan-1-ol	0.304	1.199787	3.503814	0.298255
38	Pentan-1-ol	0.311	1.242855	2.811893	0.384015

Table 2. Comparison of saturated liquid densities

Component	No. of Points	T_r Range	New EQ. $\zeta_c' = \zeta_c$ AAD (%)	New EQ. $\zeta_c' = f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)	BWRS AAD (%)
Argon	34	0.556-0.981	4.27	2.45	1.80	8.72	5.06	-
Nitrogen	32	0.501-0.983	4.10	2.32	1.20	8.88	4.76	-
Oxygen	36	0.530-0.983	4.30	2.37	1.99	8.16	5.74	-
Methane	32	0.524-0.976	4.59	3.03	1.52	7.66	5.72	0.50
Ethane	28	0.563-0.982	6.25	3.63	2.65	7.12	13.32	0.05
Ethylene	24	0.550-0.983	4.82	2.72	1.46	6.07	11.79	-
Propane	33	0.570-0.984	5.58	2.86	1.63	5.98	14.51	0.23
Propylene	27	0.563-0.974	4.35	2.27	5.99	7.17	9.97	-
Acetylene	21	0.624-0.972	4.91	1.83	2.40	5.30	24.91	-
n-Butane	28	0.627-0.980	5.57	3.39	2.26	5.61	19.36	0.13
i-Butane	29	0.578-0.980	2.29	2.61	3.82	3.40	15.64	-
1-Butene	26	0.651-0.966	3.80	1.45	1.19	4.52	16.88	-
n-Pentane	30	0.638-0.981	3.96	3.11	5.22	4.00	20.12	0.05
i-Pentane	21	0.579-0.965	4.83	2.24	1.91	5.43	23.66	-
n-Hexane	32	0.613-0.974	3.11	2.24	0.62	3.22	24.02	0.12
n-Heptane	23	0.637-0.987	4.44	2.04	3.23	4.69	29.56	0.15
n-Octane	23	0.586-0.972	3.91	1.34	3.96	6.55	31.40	-
n-Nonane	27	0.525-0.760	0.53	0.53	-	3.62	-	-
n-Decane	27	0.536-0.771	0.62	0.62	-	5.85	-	-
n-Undecane	27	0.545-0.781	0.63	0.63	-	5.81	-	-
n-Dodecane	27	0.576-0.790	0.70	0.70	-	7.47	-	-
n-Tridecane	27	0.563-0.799	0.70	0.70	2.41	6.81	-	-
n-Tetradecane	27	0.569-0.806	0.76	0.76	1.11	8.95	-	-
n-Heptadecane	27	0.592-0.832	0.94	0.94	1.76	14.82	-	-
n-Octadecane	27	0.598-0.839	1.07	1.07	-	18.89	-	-
n-Eicosane	27	0.615-0.850	1.04	1.04	-	18.42	-	-
Carbon dioxide	44	0.712-0.987	4.48	1.78	5.70	5.22	23.00	-
Carbon monoxide	21	0.542-0.960	3.81	2.10	2.70	8.48	4.97	-
Sulfur dioxide	33	0.593-0.989	4.46	1.71	1.70	4.49	35.14	-
Hydrogen sulfide	29	0.565-0.982	3.47	1.57	0.83	5.84	10.29	-
Water	29	0.546-0.978	3.99	1.57	2.69	26.33	64.88	-
Ammonia	22	0.698-0.986	3.21	2.44	6.19	15.90	45.83	-
Benzene	39	0.553-0.988	3.87	1.69	0.77	4.05	20.95	-
Methanol	22	0.588-0.695	0.51	0.51	0.55	20.05	-	-
Ethanol	26	0.575-0.719	0.51	0.51	0.96	4.33	-	-
Propan-1-ol	30	0.536-0.726	0.66	0.66	7.09	3.06	-	-
Butan-1-ol	23	0.609-0.730	0.28	0.28	10.09	2.18	-	-
Pentan-1-ol	30	0.542-0.736	0.53	0.53	7.11	1.32	-	-
Overall Average (%)			2.94	1.69	2.98	7.75	20.02	

Table 3. Comparison of saturated vapor densities

Component	New EQ. $\zeta_c' = \zeta_c$ AAD (%)	New EQ. $\zeta_c' = f[T_r]$ AAD (%)	Heyen AAD (%)	P-R AAD (%)	R-K AAD (%)	BWRS AAD (%)
Argon	0.36	1.15	4.32	1.42	0.33	-
Nitrogen	0.55	1.32	3.32	1.20	0.75	-
Oxygen	0.70	1.23	3.58	0.91	0.94	-
Methane	0.88	1.50	4.20	1.66	0.51	0.58
Ethane	0.99	2.12	4.03	1.38	1.97	0.20
Ethylene	0.71	1.60	3.72	1.04	1.70	-
Propane	0.86	2.22	4.03	1.23	2.91	0.22
Propylene	2.43	2.71	3.10	1.68	3.91	-
Acetylene	2.09	2.11	2.86	1.87	5.05	-
n-Butane	0.73	1.62	3.98	0.78	3.23	0.15
i-Butane	1.30	2.30	4.39	1.73	1.30	-
1-Butene	1.41	2.31	4.84	1.71	2.65	-
n-Pentane	0.59	1.78	5.27	0.62	3.30	0.14
i-Pentane	0.88	1.99	4.01	1.13	1.97	-
n-Hexane	0.87	1.70	3.48	0.88	4.10	-
n-Heptane	0.67	1.32	3.54	0.63	3.54	-
n-Octane	2.49	3.08	3.85	2.86	4.62	-
Carbon dioxide	0.71	2.13	6.20	2.00	4.53	-
Carbon monoxide	3.93	3.24	3.39	3.45	4.14	-
Sulfur dioxide	1.04	2.00	3.70	1.11	5.11	-
Hydrogen sulfide	2.58	3.36	6.37	3.38	1.27	-
Water	1.26	2.36	4.47	3.76	7.11	-
Ammonia	4.49	3.00	3.64	6.81	11.31	-
Benzene	2.18	3.27	4.80	2.23	4.21	-
Overall average (%)	1.44	2.14	4.14	1.89	3.35	0.26

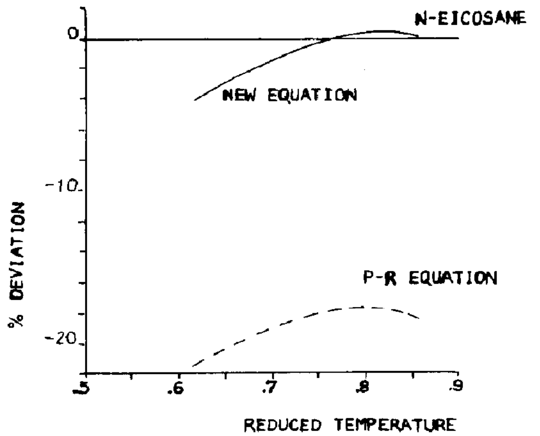

Fig. 1. Comparisons of calculated and experimental saturated liquid densities of n-eicosane.

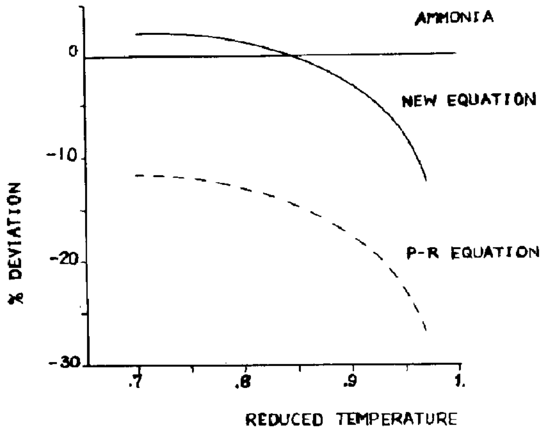

Fig. 2. Comparisons of calculated and experimental saturated liquid densities of ammonia.

critical region always leads to a loss of accuracy in the representation of saturated vapor densities and vice versa. Nevertheless, the use of eqn (17), represents a good compromise.

Overall, the eleven constant BWRS equation gives excellent predictions of both saturated liquid and vapor densities. However, the use of this equation is restricted to normal alkanes from methane to n-octane, for which the equation of state constants have been reported[12].

Densities in regions other than the saturation region have also been calculated. Overall, predictions using the new equation are better than those obtained using other cubic equations of state (Average deviations of 2.4% compared with 3.3% for the PR equation for 3175 data points including available data for methane through n-decane).

Vapor pressures

The vapor pressures of pure fluids were calculated by the simultaneous solution of the following equations:

$$P^L = P^V = P \tag{18}$$

$$f^L = f^V \tag{19}$$

where L and V refer to the liquid and vapor, respectively. Except for n-propanol, n-butanol and n-pentanol, the overall average deviation between calculated and experimental vapor pressure for the 38 substances was found to be 0.86%. For the three alcohols, the deviations were of the order of 5%.

Enthalpy and entropy departures

Enthalpy and entropy departures for saturated liquids calculated from the new equation were compared with values calculated using the BWRS equation for 8 light hydrocarbons. The BWRS equation predicts the enthalpy and entropy departures for these fluids within experimental error (deviations less than 1%). Values from the new equation compare very favorably with the BWRS equation for these fluids, as shown in Table 4.

GENERALIZATION OF EQUATION OF STATE PARAMETERS ζ_c AND F

One way of extending the equation of state to new substances is to generalize the equation of state constants. In order to apply the new equation of state to substances not studied in this work, the values of the parameters ζ_c and F have been correlated with the acentric factor. The resulting correlations are given by

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2 \tag{20}$$

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2. \tag{21}$$

However, as expected, the generalized equations apply to nonpolar substances only (3 parameter CSP). The values of F and ζ_c for water, ammonia and the alcohols did not lie on the curves predicted by eqns (20) and (21). The loss in accuracy in predicting compressibilities of nonpolar fluids using the generalized constants was less than 1% and, often, less than 0.1%.

USE OF AN EXPONENTIAL FUNCTION FOR α

It has been pointed out by many authors[11–14] that the temperature function for α used by Soave and Peng and Robinson does not reproduce the correct temperature behavior of the constant "a" at high temperatures. This is mainly because the function becomes zero at finite T_R and then starts to rise with temperature. The approach of real gas behavior to that of an ideal gas at high temperatures requires that $a \to 0$ as $T_R \to \infty$. Heyen therefore proposed eqn (13) which has the required characteristics but contains one additional constant. Constants C and n have been evaluated for the 38 substances and are given in Table 1. Both eqn (11) and eqn (13) are plotted for methane and n-decane in Figs. 3 and 4. The functions are almost identical upto $T_R = 12$ for methane and $T_R \simeq 2.0$ *for* n-decane and yield almost identical values of densities upto these conditions. Since higher temperatures are unlikely to be encountered for

Table 4 Enthalpy and entropy departures of saturated liquid

Substance	No. of Points	T_r Range	ΔH New Eq. AAD (%)	ΔS New Eq. AAD (%)
Methane	32	0.524-0.976	2.11	1.07
Ethane	28	0.563-0.982	2.53	1.16
Propane	33	0.570-0.984	2.52	1.21
n-Butane	28	0.627-0.980	2.41	1.24
n-Pentane	30	0.638-0.981	1.70	0.92
n-Hexane	32	0.613-0.974	2.55	1.44
n-Heptane	23	0.637-0.987	1.53	0.85
n-Octane	24	0.586-0.972	1.13	0.79
Overall average (%)			2.06	1.09

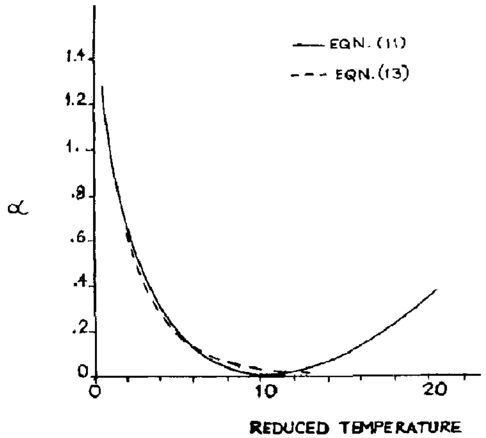

Fig. 3. α as a function of the reduced temperature for methane.

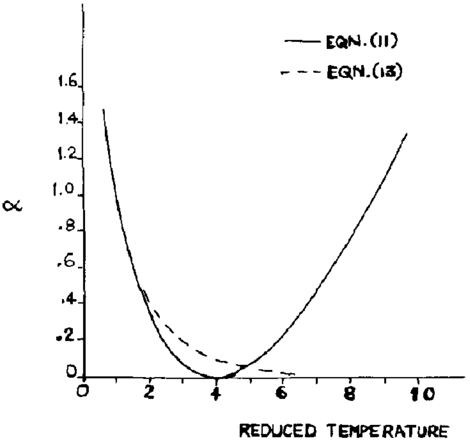

Fig. 4. α as a function of the reduced temperature for n-decane.

these substances (especially in phase equilibrium calculations), it appears that the use of the exponential function for α does not lead to much improvement (except for substances such as hydrogen which are normally at high reduced temperatures).

COMMENTS ON THE VALUES OF ζ_c AND F

The new equation of state proposed in this work requires two parameters ζ_c and F, in addition to T_c and P_c, for each pure substance. For nonpolar substances, however, ζ_c and F can be correlated with the acentric factor ω, so that only three constants (T_c, P_c and ω) are needed for such fluids.

For all substances considered, ζ_c was found to be greater than Z_c. This was also found to be true by Schmidt and Wenzel using a similar equation of state. For light nonpolar substance ($\omega = 0$, $\zeta_c = 0.329$), the new equation is comparable to the S-R-K equation and for components whose acentric factors are close to 0.3 ($\omega = 0.3$, $\zeta_c = 0.307$) the proposed equation is comparable to the P-R equation. Thus, characteristics of both the SRK and PR equation are implicit in the new equation. However, the application of the new equation extends to heavy hydrocarbons (upto n-eicosane) and polar substances.

EXTENSION TO MIXTURES

Equation (1) can be used for the calculation of mixture properties if the constants a,b,c are replaced by the mixture constants a_m, b_m, c_m as follows:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad (22)$$

$$b_m = \sum_i x_i b_i \qquad (23)$$

$$c_m = \sum_i x_i c_i. \qquad (24)$$

The choice of this model is completely arbitrary, the only justification being the success with which analogous equations have been used with other equations of state such as the Soave and the Peng–Robinson equations. It is also possible to reduce eqn (1) to the Soave and the Peng–Robinson equation by setting $c_m = 0$ and $c_m = b_m$ respectively as in the case of pure fluids. This would not be possible if a different mixture model (in particular, a different combining rule for c_m) is used.

The cross-interaction term a_{ij} in eqn (22) evaluated using the following mixing rule:

$$a_{ij} = \xi_{ij}(a_{ii}a_{jj})^{1/2} \qquad (25)$$

where ξ_{ij} is a binary interaction coefficient which must be evaluated from experimental data. Compared with vapor–liquid equilibrium (VLE) predictions, the sensitivity of predicted bulk mixture properties such as density and enthalpy to the value of ξ_{ij} is small. Therefore it is common practice to use binary VLE data for the determination of ξ_{ij} values. In principle, no further information is required to predict the properties of ternary and higher systems.

In this study, the optimum value of ξ_{ij} for each binary pair was obtained by minimizing the absolute average deviation in the bubble point pressures at selected temperatures. The determination of the bubble point pressure or vapor-liquid equilibrium in general, requires that the following equalities be satisfied:

$$f_i^V = f_i^L \; (i = 1,2,\ldots .m) \qquad (26)$$

where f_i denotes the fugacity of component i and the superscripts V and L denote the vapour and liquid phases respectively. An equation for the fugacity of component i is given in the Appendix.

EVALUATION OF THE BINARY INTERACTION COEFFICIENT

A number of criteria may be chosen for evaluating the optimum value of ξ_{ij}. Among these criteria are[11]:

(1) minimization of deviations in bubble point pressures;

(2) minimization of deviations in flash volumes.

Grabowski and Daubert[11] used both criteria with the Soave equation and found that convergence problems were encountered with the second criterion for close-boiling mixtures because the correct value of ξ_{ij} was needed in advance to "find" the two phase region. The application of the first criterion, on the other hand, produced no convergence problems and led to good results for both flash and bubble point calculations.

In this study, the optimum value of ξ_{ij} was obtained by minimizing the absolute average deviation in the pressure at a selected temperature for each binary mixture. The absolute average deviation is defined as:

$$\Delta P(\%) = \frac{1}{m}\sum_{1}^{m}\left|1 - \frac{P_{\text{calc}}}{P_{\text{exp}}}\right| \times 100.$$

Generally, ξ_{ij} is assumed to be independent of temperature, pressure, density and composition[11, 16]. In practice, however, this is not strictly true and ξ_{ij} should be determined at conditions of interest. In our work, values of ξ_{ij} were obtained at a single temperature for each binary pair—the temperature being carefully selected to lie in the middle range of reported experimental data. It should be added that the temperature dependence of ξ_{ij} was found to be small, and the optimum values of ξ_{ij} may be used to predict VLE at other temperatures.

VLE RESULTS

Optimum value of ξ_{ij} had been evaluated using the Soave, the Peng-Robinson and the proposed equation and are given Table 5. The three equations were used for VLE calculations for 32 binary systems containing the light hydrocarbons, carbon dioxide and hydrogen sulfide. The new equation was also used for calculations involving an additional 20 systems containing the heavy hydrocarbons, water and the alcohols. The results are shown in Table 6.

Our results for the different groups of binary systems studied in this work can be summarized as follows:

(a) *Light hydrocarbon binaries (upto* n-decane)

In general, the three equations of state correlate data for these systems equally well. Moreover, except for binaries containing methane, values of ξ_{ij} for these systems were found to be close to 1.0. This is true for all three equations and supports Soave's conclusion that no binary interaction coefficients are needed for VLE calculations involving light hydrocarbon binaries not containing methane. For systems containing methane, the new equation gives ξ_{ij} values which are closer to unity than those obtained using the Soave or Reng-Robinson equations. In general, the Soave and Peng-Robinson equations give very similar values of ξ_{ij} for such systems.

(b) CO_2-*light hydrocarbon, and* H_2S-*light hydrocarbon binaries*

The optimum values of ξ_{ij} obtained from the three equations are slightly different from each other, but are usually in the range 0.84–0.90 for systems containing CO_2 and 0.91–1.0 for systems containing H_2S.

(c) *Light hydrocarbon-heavy hydrocarbon binaries*

These systems include binaries such as methane-*n*-eicosane, ethane-*n*-eicosane etc. Only the new equation gave acceptable deviations in bubble point pressures for these systems. Most of the optimum ξ_{ij} values were found to lie in the range 1.0–1.08.

(d) *Alcohol-water binaries*

Only the new equation of state was used to calculate ξ_{ij} for these binaries. The methanol–water system could be correlated with an optimum value of ξ_{ij} of 1.083 and the ethanol-water binary could be correlated with a value of 1.075.

Typical predicted P vs x curves for CO_2-*n*-butane, methane-*n*-eicosane and water–methanol are shown in Figs. 5–7. Predicted P vs x curves for light hydrocarbon

Table 5. Optimum values of ξ_{ij} and bubble point correlation using three different equations of state

No.	System	No. of Points	Temperature K	Optimum ξ_{ij} EQ. (1)	Optimum ξ_{ij} P-R	Optimum ξ_{ij} S-R-K	EQ. (1) ΔP (%)	EQ. (1) ΔY_1	PR ΔP(%)	PR ΔY_1	S-R-K ΔP(%)	S-R-K ΔY_1
1.	Methane-Ethane	6	250.0	0.995	0.989	0.991	0.59	0.0039	0.45	0.0044	0.65	0.0038
2.	Methane-n-Butane	8	211.0	1.008	0.986	1.000	8.65	0.0190	8.31	0.0189	8.30	0.0195
3.	Methane-i-Butane	7	311.0	0.986	0.976	0.977	0.43	0.0067	0.63	0.0117	0.58	0.0149
4.	Methane-n-Pentane	9	273.2	0.980	0.959	0.964	6.16	0.0015	4.97	0.0025	5.41	0.0021
5.	Methane-n-Hexane	9	373.2	0.990	0.954	0.952	0.88	0.0150	0.56	0.0149	0.47	0.0073
6.	Ethane-Propane	7	277.6	0.996	0.994	0.998	0.42	0.0019	0.46	0.0023	0.53	0.0020
7.	Ethane-Propylene	6	283.2	0.994	0.992	0.997	0.34	0.0036	0.24	0.0026	0.44	0.0040
8.	Ethane-n-Butane	9	310.4	0.999	0.994	0.997	2.20	0.0093	2.19	0.0093	2.44	0.0093
9.	Ethane-n-Pentane	10	311.0	1.001	0.994	0.998	1.02	0.0040	1.02	0.0039	1.12	0.0044
10.	Ethane-n-Heptane	5	366.5	1.015	0.999	0.999	1.31	0.0038	1.15	0.0040	1.21	0.0015
11.	Ethylene-Methane	9	150.0	0.974	0.971	0.973	1.36	0.0043	0.97	0.0060	1.26	0.0040
12.	Ethylene-Ethane	9	255.4	0.992	0.990	0.994	0.22	0.0056	0.18	0.0053	0.33	0.0053
13.	Ethylene-Propane	10	273.1	0.981	0.979	0.982	0.21	0.0020	0.32	0.0014	0.18	0.0015
14.	Ethylene-n-Butane	7	322.0	0.938	0.932	0.930	1.37	0.0237	1.41	0.0241	1.34	0.0184
15.	Propane-i-Butane	10	299.8	0.987	0.987	0.944	0.90	0.0075	0.96	0.0072	0.60	0.0048
16.	Propane-n-Pentane	11	361.0	0.987	0.976	0.979	0.46	0.0141	0.49	0.0144	0.51	0.0129
17.	Propane-i-Pentane	10	373.2	0.979	0.978	0.980	0.63	0.0166	0.60	0.0168	0.80	0.0166
18.	Propylene-Propane	9	311.0	0.970	0.993	1.000	1.51	0.0132	0.25	0.0029	0.41	0.0034
19.	Propylene-1-Butene	7	294.3	1.002	0.998	1.000	0.44	0.0021	0.18	0.0013	0.43	0.0017
20.	n-Butane-n-Decane	9	377.6	0.995	0.986	0.988	1.24	0.0007	0.94	0.0010	1.86	0.0006
21.	1-Butene-n-Butane	9	411.0	1.003	1.000	1.000	0.14	0.0161	0.39	0.0013	0.76	0.0013
22.	CO_2-Methane	8	241.5	0.907	0.902	0.899	3.26	0.0145	3.19	0.0129	3.27	0.0118
23.	CO_2-Ethane	10	253.0	0.872	0.870	0.870	1.15	0.0066	1.17	0.0070	1.18	0.0074
24.	CO_2-Ethylene	10	231.6	0.943	0.942	0.944	0.39	0.0107	0.50	0.0122	0.50	0.0095
25.	CO_2-Propane	9	294.3	0.869	0.874	0.868	0.67	0.0048	0.70	0.0050	0.55	0.0045
26.	CO_2-n-Butane	10	273.2	0.891	0.875	0.886	1.77	0.0084	3.81	0.0082	3.19	0.0085
27.	CO_2-i-Butane	9	311.0	0.873	0.884	0.874	1.23	0.0036	1.11	0.0038	0.99	0.0039
28.	CO_2-n-Pentane	9	377.6	0.865	0.866	0.849	2.64	0.0270	2.70	0.0271	2.43	0.0242
29.	H_2S-Methane	8	277.6	0.920	0.927	0.931	2.76	0.0138	3.00	0.0122	3.51	0.0129
30.	H_2S-Ethane	9	283.2	0.911	0.910	0.909	0.67	0.0099	0.78	0.0102	0.76	0.0095
31.	H_2S-i-Butane	8	344.4	0.954	0.952	0.950	0.99	0.0205	0.90	0.0210	0.97	0.0210
32.	H_2S-n-Heptane	9	311.0	0.947	0.936	0.928	3.27	0.0019	2.92	0.0020	3.27	0.0018

$\Delta Y_1 = \frac{1}{n} \Sigma\ 1 - (Y_{1calc}/Y_{1exp})$

For data references, see ref. [15]

Y_1 refers to composition of hydrocarbon

Table 6. Values of the deviations in bubble point pressures and vapour phase mode fractions with $\xi_{ij} = 1.0$ and $\xi_{ij} \simeq \xi_{ijopt}$ from equation (1)

No.	System	No. of Points	Temperature K	$\xi_{ij} = 1.0$ ΔP (%)	$\xi_{ij} = 1.0$ ΔY_1	ξ_{ijopt}	$\xi_{ij} = \xi_{ijopt}$ ΔP (%)	$\xi_{ij} = \xi_{ijopt}$ ΔY_1
1.	Methane-propane	5	277.6	2.65	0.0059	0.989	0.68	0.0048
2.	Methane-benzene	7	338.8	2.45	0.0064	0.991	0.92	0.0054
3.	Methane-n-Eicosane	5	313.2	29.26	0.0000	1.080	1.09	0.0000
4.	Ethane-i-butane	8	311.8	3.57	0.0072	1.018	1.62	0.0038
5.	Ethane-n-decane	8	377.6	4.81	0.0455	1.019	0.60	0.0426
6.	Ethane-n-dodecane	9	323.2	5.58	0.0009	1.016	2.26	0.0008
7.	Ethane-n-Eicosane	7	333.2	41.01	0.0002	1.070	9.15	0.0000
8.	Ethylene-n-dodecane	8	298.2	2.92	0.0002	1.006	1.10	0.0000
9.	Propane-benzene	10	377.6	3.58	0.0101	0.988	1.86	0.0086
10.	Propane-n-decane	7	377.6	8.63	0.0008	1.024	0.79	0.0004
11.	Nitrogen-methane	10	155.4	4.22	0.0299	0.968	0.71	0.0217
12.	Nitrogen-propane	6	298.2	11.00	0.0269	0.926	3.80	0.0161
13.	Nitrogen-n-butane	6	311.0	10.83	0.0146	0.969	8.73	0.0151
14.	Nitrogen-n-heptane	5	352.6	17.4	0.0032	0.911	3.30	0.0018
15.	H_2S-n-heptane	5	352.6	10.97	0.0027	0.956	3.41	0.0018
16.	H_2S-n-decane	7	344.3	0.62	0.0004	0.999	0.53	0.0004
17.	CO_2-n-decane	7	344.3	24.74	0.0003	0.903	2.24	0.0020
18.	CO-propane	8	273.2	7.11	0.0170	0.979	6.11	0.0151
19.	Methanol-water	10	373.2	27.45	0.0750	1.083	1.75	0.0081
20.	Ethanol-water	10	423.2	23.75	0.0847	1.075	2.04	0.0213

systems using the Soave, the Peng–Robinson and the new equation were identical. Multicomponent predictions were also found to be comparable for systems of light hydrocarbons.

DENSITIES

Densities of five binary mixtures were calculated and the results are shown in Table 7. Values of ξ_{ij} were not used. Average deviations between calculated and experimental densities were of the order of 2% and compare favorably with deviations obtained using the Chaudron equation[17] with six constants per component. A major advantage of using the new equation is that it gives accurate predictions of saturated liquid volumes as well as other properties of the equilibrium phases. Earlier, we showed that the new equation is superior to the Soave and Peng-Robinson equations in the representation of the saturated liquid densities of pure substances. We found that this improvement extends to mixture saturated liquid densities as well. Results for the n-butane-n-decane system are shown in Fig. 8. As can be seen, the new equation is superior to the Peng-Robinson equation.

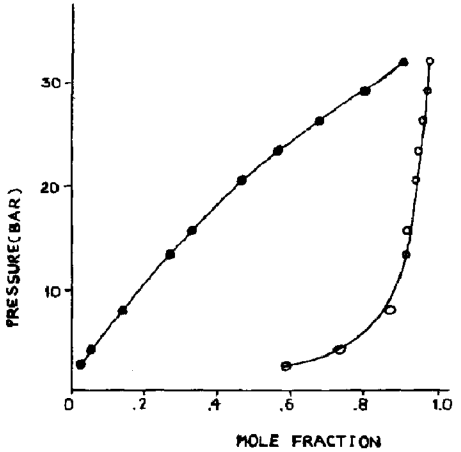

Fig. 5. Vapor-liquid equilibria in the Co_2-n-butane system at 273.2K.

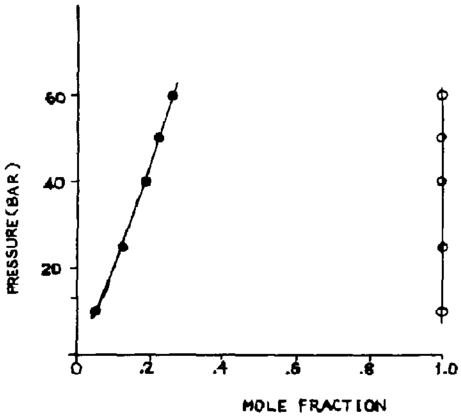

Fig. 6. Vapor-liquid equilibria in the Methane-n-eicosane system at 313.2K.

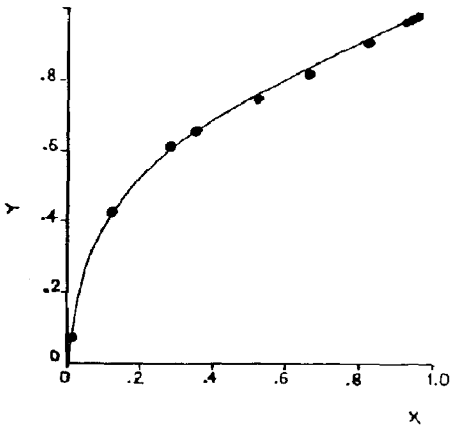

Fig. 7. Vapor-liquid equilibria in the Methanol-water system at 373.2K.

CONCLUSION

This work demonstrates that the new equation of state is capable of accurate and consistent predictions of the thermodynamic properties of mixtures. The most interesting feature of the new equation is its applicability to mixtures containing heavy hydrocarbons and polar substances, and the fact that it is cubic in volume and thus easy to handle. It can reproduce with sufficient accuracy the liquid and vapour phase densities and yield very accurate VLE predictions. Comparisons have shown that

Table 7. Comparison of density predictions of binary mixtures

Mixture	No. of Points	Temp. Range (°R)	Pressure Range (psia)	X_1	EQ. (1) AAD (%)	C-H AAD (%)
Ethane-propene	174	470-858	15-10000	0.4958	2.37	**1.88**
Ethane-n-pentane	152	498-920	200-10000	0.4000	3.72	**3.13**
Propane-n-pentane	44	619-800	20-500	0.2480	0.67	1.27
Propane-n-pentane	28	619-709	20-500	0.6511	0.66	**0.37**
Propene-propane	268	470-858	15-10000	0.6289	1.92	**1.79**
H_2S-n-pentane	123	498-800	200-10000	0.6123	2.95	**2.01**
OVERALL AVERAGE =					2.05	**1.74**

C-H Chaudron et al, [6] equation with fitted constants

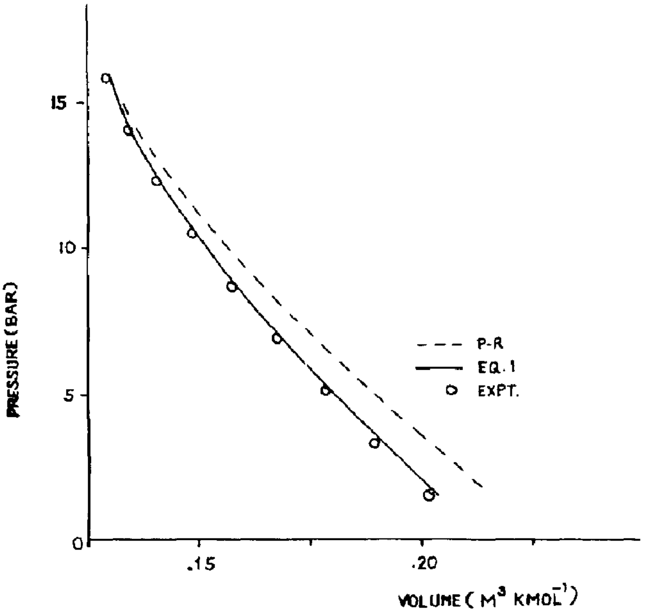

Fig. 8. Comparison of saturated liquid volumes of n-butane-n-decane mixtures at 377.6K.

for VLE calculations, the new equation is as good as the Soave and Peng-Robinson equations for mixtures of light hydrocarbons. For systems containing heavy hydrocarbons and polar substances, the new equation is superior to the Soave and Peng-Robinson equations.

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NOTATION

a, b, c	Constants in eqn (1)
B	$= bP_c/RT_c$
c	constant in eqns (12 and (13)
f	fugacity
F	parameter required in eqn (1)
m	number of components
n	number of moles
P	pressure
R	gas constant
T	temperature
S	entropy
v	molar volume
V	total volume
x	mole fraction
Z	compressibility $= Pv/RT$

Symbols

α	temperature function, eqn (11)
β	temperature function, eqn (16)
ζ_c	value of P_cv_c/RT_c calculated from eqn (1) parameter required in eqn (1)
ξ	binary interaction coefficient
$\Omega_a, \Omega_b, \Omega_c$	constants in eqns (5–7)

Subscripts

c	critical value
calc	calculated value
exp	experimental value
i, j	component i, j
j	jth data point
R	reduced value

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APPENDIX

Derived properties using the new equation of state

Fugacity.

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \ln(Z - B) + \frac{a}{2RTN}\ln\left(\frac{Z+M}{Z+Q}\right)$$

$$B = bP/RT$$

$$M = \left(\frac{b+c}{2} - N\right)\frac{P}{RT}$$

$$N = \left[bc + \frac{(b+c)^2}{2}\right]^{-1/2}$$

$$Q = \left(\frac{b+c}{2} + N\right)\frac{P}{RT}$$

Enthalpy departure.

$$\varphi(H - H^{\circ}) = RT(Z-1) - \left(T\frac{\partial a}{\partial T} - a\right)\left[\frac{1}{2N}\ln\left(\frac{Z+M}{Z+Q}\right)\right]$$

φ = conversion factor; Q, M, N are given above

Entropy departure.

$$\varphi(S - S^{\circ}) = -R\ln\left(\frac{P}{Z-B}\right\} - \frac{\partial a}{\partial t}\left[\frac{1}{2N}\ln\left(\frac{Z+M}{Z+Q}\right)\right]$$

φ = conversion factor; Q, M, N are given above

Fugacity of component i *in a mixture.*

$$RT\ln\left(\frac{fi}{x_iP}\right) = -RT\ln(Z - B) + RT\left(\frac{bi}{v-b}\right) - \frac{\Sigma x_j a_{ij}}{d}\ln\left(\frac{Q+d}{Q-d}\right)$$

$$+\frac{a(b_i + c_i)}{2(Q^2 - d^2)} + \frac{a}{8d^3}\{c_i(3b + c) + b_i(3c + b)\}$$

$$\times\left\{\ln\left(\frac{Q+d}{Q-d}\right) + \frac{2Qd}{Q^2 - d^2}\right\}$$

$$Q = v + \frac{b+c}{2}$$

$$B = bP_c/RT_c$$

$$d = \sqrt{bc + \frac{(b+c)^2}{4}}.$$