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A CONSISTENT CORRECTION FOR REDLICH–KWONG–SOAVE VOLUMES

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ABSTRACT

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If the volumetric and phase behaviour of a fluid mixture is calculated by means of an equation of state, certain translations along the volume axis may be effected that leave the predicted phase equilibrium conditions unchanged. This property may be exploited in the form at a consistent correction to improve volume estimations by the Redlich–Kwong–Soave method. Applications of this improved method to pure liquids, mixtures of liquids or gases, and petroleum fluids show that markedly superior volume estimations are obtained, except in the neighbourhood of the pure-component critical points; nonetheless, critical volumes for mixtures can be estimated correctly.

INTRODUCTION

The Redlich–Kwong–Soave method is the simplest for computing, with good results, vapour–liquid equilibrium conditions (temperature T, pressure P, mole fractions x_i) for fluid mixtures under pressure. Unfortunately, the Soave modification of the Redlich–Kwong equation of state is not satisfactory for P–V–T calculations; when volume estimations are required, the Peng–Robinson method is often preferred. These two methods (Redlich–Kwong–Soave and Peng–Robinson) are described in Appendix I.

We here propose a very simple correction for Redlich–Kwong–Soave volumes, which preserves the consistency of both the above calculations. It is

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founded on the property that certain translations along the volume axis may be effected such that the predicted equilibrium conditions (T, P, x_i) remain unchanged.

EQUATION OF STATE TRANSFORMS BY VOLUME TRANSLATIONS

A system containing p components obeys an equation of state of the form

$$P = E(T, V, n_1, \ldots, n_i, \ldots, n_p) \tag{1}$$

where n_i is the number of moles of component i in the system. Fugacity coefficients ϕ_i are given by

$$\ln \phi_i = \int_0^P (v_i/RT - 1/P)\, \mathrm{d}P \qquad (i = 1, \ldots, p)$$

where v_i is the partial molar volume according to

$$v_i = (\partial V/\partial n_i)_{T,P,n_j} \qquad (j \neq i;\ i = 1, \ldots, p)$$

The equilibrium conditions for two phases, denoted ′ and ″, are given by

$$x_i'\phi_i'(T, P, x_1', \ldots, x_p') = x_i''\phi_i''(T, P, x_i'', \ldots, x''_p) \qquad (i = 1, \ldots, p) \tag{2}$$

The present modification is applied as follows.

Define a "pseudo volume" $\tilde{V}$ according to

$$\tilde{V} = V + \sum_{i=1}^{p} c_i n_i \tag{3}$$

in which the c_i's have constant values. Substitution of $\tilde{V}$ for V in eqn. (1) yields a "pseudo equation of state":

$$P = \tilde{E}(T, \tilde{V}, n_1, \ldots, n_p) \tag{4}$$

"pseudo partial molar volumes":

$$\tilde{v}_i = (\partial \tilde{V}/\partial n_i)_{T,P,n_j} = v_i + c_i \qquad (j \neq i;\ i = 1, \ldots, p)$$

and "pseudo fugacity coefficients":

$$\ln \tilde{\phi}_i = \int_0^P (\tilde{v}_i/RT - 1/P)\, \mathrm{d}P = \ln \phi_i + c_i P/RT \qquad (i = 1, \ldots, p)$$

Thus, the "pseudo equation of state" (4) leads to equilibrium conditions given by

$$x_i'\tilde{\phi}_i'(T, P, x_1', \ldots, x'_p) = x_i''\tilde{\phi}_i''(T, P, x_1'', \ldots, x''_p) \qquad (i = 1, \ldots, p)$$

or

$$x_i'\phi_i'(T, P, x_1', \ldots, x_p') \exp(c_i P/RT) = x''_i\phi''_i(T, P, x_1'', \ldots, x_p'') \exp(c_i P/RT)$$

which is exactly the same result as given by the unmodified equation (2). Thus, translations along the volume axis according to eqn. (3) leave the predicted equilibrium conditions unchanged.

Volumes calculated using the Redlich–Kwong–Soave equation of state may be considered as "pseudovolumes" in the sense of eqn. (3); i.e., the Redlich–Kwong–Soave equation may be written as

$$P = RT/(\tilde{v} - \tilde{b}) - a/\left(\tilde{v}(\tilde{v} + \tilde{b})\right) \tag{5}$$

If these values can be improved by some translation along the volume axis that takes the form given in eqn. (3), i.e. by

$$v = \tilde{v} - \sum_{i=1}^{p} c_i x_i \tag{6}$$

then it is possible to apply this correction without changing the vapour–liquid equilibrium conditions determined by the unmodified Redlich–Kwong–Soave method. This procedure leads exactly to the results given by the equation of state

$$P = RT/(v - b) - a/\left((v + c)(v + b + 2c)\right)$$

with

$$c = \sum_{i=1}^{p} c_i x_i$$

$$b = \tilde{b} - c$$

both for equilibrium conditions and for volumes.

Not all forms of volume correction will preserve consistency. For example, consistency is not preserved by the Lin and Daubert (1980) correction, which divides volumes by some factor.

CORRECTIONS FOR REDLICH–KWONG–SOAVE VOLUMES

The Redlich–Kwong–Soave equation gives adequate results for methane and for compounds which have small acentric factors ω. But as ω increases, the calculated volumes become greater than those measured experimentally, and the c-values for correction (6) must be positive. In fact, for the majority of such compounds the best correlating parameter for the pure-component corrections c is not the acentric factor, but the Rackett compressibility factor z_{RA} appearing in Spencer and Danner's (1973) correction of the Rackett equation for saturated liquid volumes:

$$v_s = (RT_c/P_c)\, z_{RA}^{(1+(1-T_r)^{2/7})} \tag{7}$$

The relation between the volume correction c and the Rackett z_{RQ} is

established considering the first ten *n*-alkanes, for which we used critical constants and densities tabulated by the American Petroleum Institute (1973,1974). From eqns. (5)–(7) we determined the values of z_{RA} and thence c that reproduced exactly the correct saturated liquid densities at a reduced temperature $T_r = 0.7$. These values are related according to

$$c = 0.40768(RT_c/P_c)(0.29441 - z_{RA}) \tag{8}$$

Having obtained a series of values for the first ten *n*-alkanes, the mean across the series is then used to calculate saturated liquid densities for each of the alkanes. The mean relative percentage deviation and mean relative percentage bias with respect to the true values can then be calculated (see Appendix II). This process can be repeated for other corrections c, for the original (uncorrected) equation of state, or for other equations of state (e.g., the Peng–Robinson equation), and the deviations and/or biases compared.

We term the correction using adjusted z_{RA} values. Values of z_{RA} from other sources can also be used in eqn. (8); we used values from Spencer and Adler (1978) to generature a further set of data. A third set of data was obtained similarly using compressibility factors $z_{COS} = P_c v^*/(RT_c)$ calculated from the characteristic volumes v^* used for the COSTALD correlation (Hankinson and Thomson, 1979a, b).

TABLE 1

Values of z for volume corrections and mean relative deviations $\overline{\delta_r(\rho)}$ between experimental and predicted saturated liquid densities at $T_r = 0.7$, for the first ten *n*-alkanes (sources of data are given in the text)

Alkane	z_{RA} (RKSc1)	z_c (RKSc2)	z_ω (RKSc3)	z_{RA} Spencer	z_{COS}
Methane	0.2894	0.297	0.2896	0.2894	0.2897
Ethane	0.2803	0.284	0.2820	0.2813	0.2799
Propane	0.2767	0.281	0.2771	0.2766	0.2764
n-Butane	0.2731	0.274	0.2729	0.2733	0.2732
n-Pentane	0.2686	0.263	0.2684	0.2685	0.2688
n-Hexane	0.2636	0.264	0.2642	0.2636	0.2628
n-Heptane	0.2606	0.263	0.2604	0.2607	0.2620
n-Octane	0.2571	0.259	0.2556	0.2568	0.2579
n-Nonane	0.2548	0.254	0.2507	0.2546	0.2565
n-Decane	0.2578	0.253	0.2466	0.2507	0.2603
$\overline{\delta_r(\rho)}$ (%) *	0.14	1.30	0.96	0.50	0.34

* For the unmodified Redlich–Kwong–Soave method, $\overline{\delta_r(\rho)} = 9.30\%$; for Peng–Robinson, $\overline{\delta_r(\rho)} = 4.16\%$.

A further correction, termed "RSKc2", was obtained by substituting for z_{RA} in eqn. (8) the critical compressibility factors z_c calculated from the experimental critical volumes. Finally, by substituting z_ω from the Yamada and Gunn (1973) correlation for z_c, a correction termed "RSKc3" was obtained. In this case $c = 0.40768\ (RT_c/P_c)\ (0.00385 + 0.08775\omega)$

Values of z for the first ten n-alkanes and the resulting mean percentage deviations in predicted saturated liquid densities are given in Table 1 for each of the corrections listed above.

APPLICATIONS

We now discuss further applications of the modified equation of state presented above. The deviations used to compare calculated and experimental volumes or densities for the cases considered here are defined in Appendix II.

Pure liquids at low pressure

Figure 1 shows that a constant volume-translation cannot remove the large discrepancy between measured and calculated saturated liquid densities near the critical temperature. However, when the calculated saturated liquid density is exact at $T_r = 0.7$, great deviations will not occur at lower temperatures; it is thus possible to obtain good results for pure-liquid densities at low pressure.

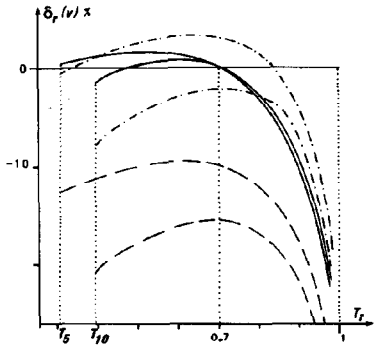

Fig. 1. Relative percentage deviations from American Petroleum Institute, (1973, 1974) data for saturated liquid molar volumes, versus reduced temperature T_r, for n-pentane and n-decane, from the respective triple-points T_5 and T_{10} to $T_r = 0.98$: - - - - - -, Redlich–Kwong–Soave; ————, RKSc1; ·–·–·, Peng–Robinson.

TABLE 2

Mean relative deviations $\overline{\delta_r(\rho)}$ (%) between experimental and predicted saturated liquid densities for 233 compounds, using data from Reid et al. (1977)

Compounds	Number of compounds in set	Method *				
		RKSc1	RKSc2	RKSc3	RKS	PR
Alkanes	49 [a]	1.47	3.39	3.26	10.86	4.47
Alkenes	39 [b]	0.90	2.17	2.44	10.04	3.14
Cycloalkanes	14 [c]	2.11	3.85	4.69	8.06	5.80
Aromatic compounds	22 [d]	1.12	2.48	3.30	14.52	5.28
Chloroalkanes	16 [e]	2.08	5.88	5.01	10.16	5.51
Amines	12 [f]	1.74	3.03	5.49	9.70	3.68
Aldehydes, ketones, esters, ethers	37 [g]	1.52	2.54	5.03	13.68	4.56
Alcohols	15 [h]	3.80	3.35	16.76	10.93	4.25
Inorganic compounds	29 [i]	2.68	3.55	6.17	6.98	10.79

* RKS, Redlich–Kwong–Soave; PR, Peng–Robinson. For RKSc1, RKSc2, RKSc3, see text.

[a] From C_1 to C_{17}.

[b] From C_2 to C_{10}.

[c] Cyclopropane, cyclobutane, cyclopentane, alkylcyclopentanes, cyclohexane, alkylcyclohexanes and cycloheptane, from C_3 to C_8.

[d] Benzene, alkylbenzenes, naphthalene, alkylnaphthalenes and diphenyl, from C_6 to C_{12}.

[e] From C_1 to C_4.

[f] From C_1 to C_8.

[g] From C_2 to C_{12}.

[h] From C_2 to C_8.

[i] Ar, Br, ClNO, Cl_2, Cl_4Si, F_2, F_6S, HBr, HCl, HI, H_2, H_2O, H_2S, H_3N, H_4N_2, He, Kr, NO, N_2, N_2O, Ne, O_2, O_2S, O_3, O_3S, Xe, CCl_2O, CO and CS_2.

The results for 233 compounds are presented in Table 2. Critical constants, acentric factors and liquid densities were taken from data compiled by Reid et al. (1977). These liquid densities were also used for fitting z_{RA} in eqn. (8).

The correction RKSc1 gives good results except for associated compounds such as alcohols, hydrogen fluoride, iodine, etc. This correction was therefore retained for further studies. The RKSc2 results are of inferior quality, owing to uncertainties in the experimental values of the critical volumes. The correction RKSc3 is valid only for normal alkanes from C_1 to C_{10}, and gives grossly inaccurate results for polar or associated compounds.

Pure fluids over the entire P–V–T range

We have previously published (Péneloux and Rauzy, 1979) "error maps" which give comparisons between accurate and approximate equations of

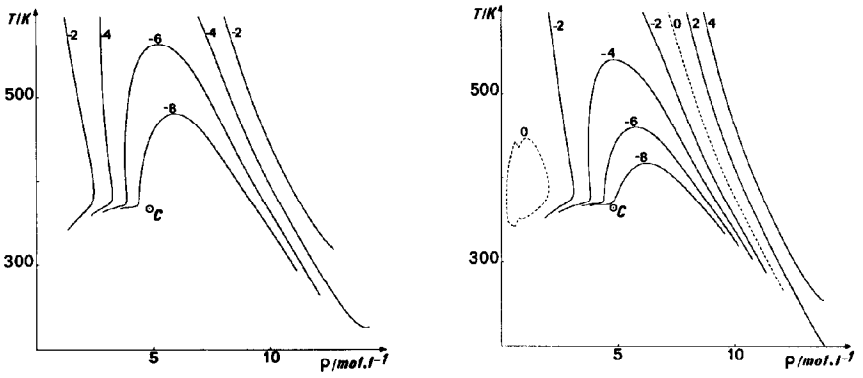

Fig. 2. Comparison between the unmodified Redlich–Kwong–Soave equation of state and the exact equation of Goodwin (1977) for propane. Curves of constant percentage relative deviations in density.

Fig. 3. Comparison between the corrected Redlich–Kwong–Soave equation of state (RKScl) and the exact equation of Goodwin (1977) for propane. Curves of constant percentage relative deviations in density.

state in a summarised form. Here we compare the results of the accurate Goodwin (1977) equation for propane with those of the Redlich–Kwong–Soave equation (Fig. 2), RKScl (Fig. 3), and the Peng–Robinson equation (Fig. 4). On the temperature–density diagrams, curves are plotted that correspond to constant relative deviations in density of −8, −6, −4, −2, 0, 2, 4,

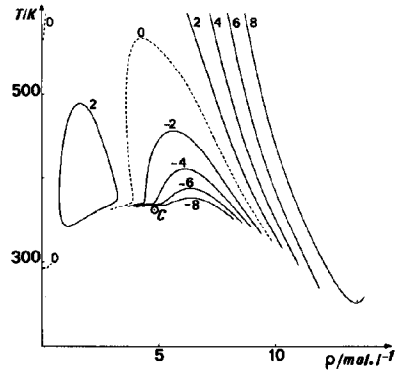

Fig. 4. Comparison between the Peng–Robinson equation of state and the exact equation of Goodwin (1977) for propane. Curves of constant percentage relative deviations in density.

TABLE 3

Mean relative biases $\overline{\beta_r(\rho)}$ (%) between experimental and predicted high-pressure ($300 \leqslant P \leqslant 1200$ kg cm^{-2}) liquid densities, using data from Boelhouwer (1960)

Liquid	Temperatures (°C)	Number of points	Method *		
			RKScl	RKS	PR
n-Heptane	0, 30, 60, 90, 120	49	4.00	−10.78	−0.55
n-Octane	30, 60, 90, 120	39	3.72	−12.69	−2.69
n-Nonane	30, 60, 90, 120	40	3.38	−14.18	−4.36
n-Dodecane	30, 60, 90, 120	16	1.63	−19.48	−10.33
n-Hexadecane	60, 90, 120	30	2.26	−23.76	−15.12

* RKS, Redlich–Kwong–Soave; PR, Peng–Robinson. For RKScl, see text.

and 8%. These curves are bounded on their upper extremities by an isotherm, on the right-hand side by the isobar $P = 700$ bar, and on their lower extremities by the saturation curve.

The correction RKScl to the Redlich–Kwong–Soave equation of state yields (Fig. 3) a zero-deviation line starting on the saturation curve at $T_r = 0.7$. The results are thus improved compared with those obtained using the unmodified Redlich–Kwong–Soave or the Peng–Robinson equation, except for the liquid phase at very high pressures (on the right-hand side of the diagram). However, Table 3 shows that, in the case of the heavier alkanes, predictions of high-pressure liquid densities are also greatly improved by the correction. Note that in this pressure range the Peng–Robinson equation of state gives its best results for normal alkanes from C_5 to C_{10}.

Binary mixtures: saturated liquid and vapour

We based our comparisons for binary mixtures containing saturated liquid and vapour on measurements reported by Shipman and Kohn (1966) for the methane–*n*-nonane binary system. The comparisons were made using two different methods, as follows.

A. Without vapour–liquid equilibrium estimations. Densities were calculated using experimental values for temperature, pressure, and liquid and vapour compositions.

B. With vapour–liquid equilibrium estimations. Here experimental temperatures and liquid compositions were used to calculate liquid densities as a function of estimated pressure and saturated-vapour densities for the estimated equilibrium compositions under the estimated pressure. These estimations were performed using k_{12} values of 0.0495 for the Redlich–Kwong–Soave and 0.0530 for the Peng–Robinson equation.

TABLE 4

Mean relative deviations $\overline{\delta_r(\rho)}$ (%) between experimental and predicted saturated liquid densities for the methane–*n*-nonane system, using data from Shipman and Kohn, (1966): *A*, without equilibrium calculations; *B*, with equilibrium calculations

T(°C)	Number of points	Pressure range (atm.)		Method *		
				RKSc1	RKS	PR
−50	10	10–100	*A*	0.71	15.94	5.78
			B	0.84	16.03	5.90
−25	10	10–100	*A*	0.39	15.83	5.61
			B	0.48	15.90	5.70
0	23	10–318(P_c)	*A*	0.80	13.44	3.88
			B	1.15	14.39	4.20
25	23	10–318(P_c)	*A*	0.85	13.16	3.60
			B	1.20	14.29	3.88
50	23	10–318(P_c)	*A*	0.96	13.00	3.43
			B	1.13	14.09	3.59
75	22	10–313(P_c)	*A*	1.21	13.05	3.47
			B	1.30	13.98	3.61
100	10	10–100	*A*	0.91	13.52	2.66
			B	0.82	13.59	2.72
150	10	10–100	*A*	0.89	14.03	3.17
			B	0.96	14.08	3.19

* RKS, Redlich–Kwong–Soave; PR, Peng–Robinson. For RKSc1, see text.

The results of the comparisons for liquid densities are presented in Table 4; the RKSc1 correction leads to great improvement over both the Redlich–Kwong–Soave and the Peng–Robinson results. Table 5 shows the results for the saturated-vapour densities: for such low values the correction by volume translation results in only slight improvement. The calculation of densities simultaneously with the estimation of liquid equilibria involves certain difficulties: when a mixture contains methane with a heavy hydrocarbon, neither Redlich–Kwong–Soave nor Peng–Robinson vapour–liquid estimations would be expected to give full agreement with the measured values, especially in the critical range. Although the mean relative deviations for both the liquid and the saturated-vapour phases are less satisfactory than in the cases considered above, the liquid densities estimated using RKSc1 are still much better than provided by the uncorrected equations of state (Table 4).

Although the volume correction RKSc1 does not remove the large discrepancies between predicted and experimental densities near the critical points for pure components, it gives adequate estimations for the critical

TABLE 5

Mean relative deviations $\overline{\delta_r(\rho)}$ (%) between experimental and predicted saturated vapour densities for the methane–*n*-nonane system, using data from Shipman and Kohn (1966): *A*, without equilibrium calculations; *B*, with equilibrium calculations

T(°C)	Number of points	Pressure range (atm.)		Method *		
				RKScl	RKS	PR
−50	10	10–100	*A*	1.43	1.62	2.93
			B	4.61	4.87	2.16
−25	10	10–100	*A*	0.64	0.80	2.76
			B	0.97	0.91	2.93
0	15	10–200	*A*	1.63	1.97	2.14
			B	1.59	1.48	5.32
25	12	10–140	*A*	0.87	1.09	1.95
			B	5.33	5.30	7.31
50	11	10–120	*A*	0.68	0.86	1.66
			B	3.89	3.69	6.81
75	11	10–120	*A*	0.67	0.82	1.44
			B	5.11	4.92	8.31
100	10	10–100	*A*	1.55	1.74	0.35
			B	1.28	1.47	1.88
150	10	10–100	*A*	5.36	5.39	5.21
			B	6.87	6.89	8.30

* RKS, Redlich–Kwong–Soave,; PR, Peng–Robinson. For RKScl, see text.

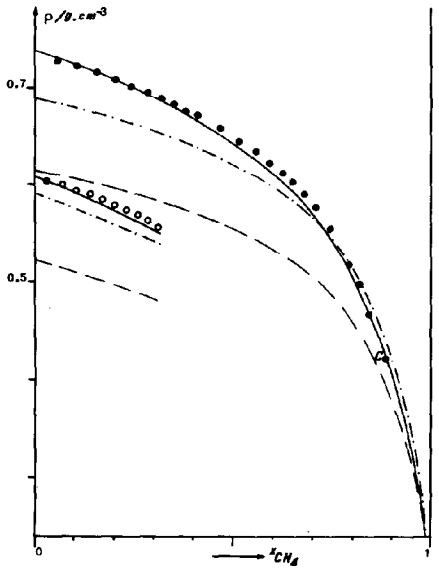

Fig. 5. Densities of saturated methane–*n*-nonane mixtures at 0 and 150°C. Calculated curves: - - - - -, Redlich–Kwong–Soave; ————, RKScl (see text); ·–·–·, Peng–Robinson. Experimental points (Shipman and Kohn, 1966: ●, 0°C; ○, 150°C.

TABLE 6

Data for the methane(1)–propane(2)–*n*-decane(3) ternary system (Sage and Berry, 1971)

Mixture *	Molar fractions		Pressure range (atm.)	Number of points
	x_1	x_2		
1	0.1803	0.0000	39.8–680.5	82
2	0.3152	0.0000	78.3–680.5	66
3	0.4999	0.0000	143.0–680.5	59
4	0.6806	0.0000	195.3–680.5	48
5	0.8184	0.0000	187.8–680.5	43
6	0.0000	0.1805	1.0–680.5	89
7	0.0000	0.3195	1.8–680.5	86
8	0.0000	0.5000	2.8–680.5	86
9	0.0000	0.6806	3.7–680.5	83
10	0.0000	0.8194	4.5–680.5	72
11	0.1528	0.1530	30.8–680.5	78
12	0.1312	0.5912	26.6–680.5	73
13	0.2431	0.2420	51.3–680.5	69
14	0.5917	0.1305	168.8–680.5	50
15	0.7555	0.1663	205.9–680.5	41
16	0.7880	0.1737	187.1–680.5	41
Total				1066

* For all mixtures, the temperature range is 277.6–510.9 K.

densities of mixtures, as is shown in Fig. 5. When vapour–liquid estimations are performed, it should be borne in mind that the vapour–liquid equilibrium estimations are performed on the basis of critical densities calculated using temperatures and compositions that are probably incorrect, as explained above.

Gas mixtures

We made our comparisons for gas mixtures using the data of Sage and Berry (1971) for the ternary system methane–propane–*n*-decane. The experimental results are summarised in Table 6. Table 7 shows the great improvement in predicted densities when RKSc1 is used to correlate the data rather than the unmodified Redlich–Kwong–Soave or Peng–Robinson equation.

Heavy hydrocarbons

As an aid to thermodynamic computations for petroleum fluids, Robinson and Peng (1978) calculated correlations giving critical reduced temperatures

TABLE 7

Mean biases $\overline{\beta(v)}$ ($cm^3\ mol^{-1}$) and mean deviations $\overline{\delta(v)}$ ($cm^3\ mol^{-1}$) between experimental and predicted volumes for each of the mixtures listed in Table 6 (data of Sage and Berry (1971) for the methane–propane–*n*-decane ternary system), and resulting mean relative deviations $\overline{\delta_r(v)}$

Mixture	RKSc1 *		RKS *	PR *	
	$\overline{\beta(v)}$	$\overline{\delta(v)}$	$\overline{\beta(v)}$	$\overline{\beta(v)}$	$\overline{\delta(v)}$
1	0.28	2.99	−28.98	−6.28	6.38
2	−0.65	2.76	−25.07	−5.45	5.54
3	−0.84	1.95	−18.96	−3.23	3.36
4	−0.77	1.40	−12.60	−0.80	1.26
5	−0.81	1.02	−7.80	1.14	1.19
6	1.29	3.66	−28.78	−5.37	5.47
7	0.58	3.60	−25.28	−4.10	4.43
8	−0.40	3.75	−20.79	−2.42	3.18
9	−1.00	4.15	−15.92	−0.46	2.73
10	−0.42	4.18	−11.13	1.91	3.70
11	0.58	2.86	−25.01	−4.25	4.41
12	−0.85	3.07	−13.91	0.25	1.92
13	−0.50	2.64	−20.24	−2.87	3.11
14	−0.83	1.51	−11.80	−0.17	0.76
15	−0.22	1.05	−4.39	3.32	3.32
16	−0.72	1.27	−3.54	3.52	3.52
$\overline{\delta_r(v)}$ (%)	1.84		12.37	2.47	

* RKS, Redlich–Kwong–Soave; PR, Peng–Robinson. For RKSc1, see text. For the RKS method, $\delta(v)=|\beta(v)|$.

and pressures, acentric factors, and densities at equilibrium for paraffins, naphthenes (alkylcyclohexanes), and aromatic compounds (alkylbenzenes). We used these densities and critical properties to fit z_{RA} values in eqn. (8). For members up to C_5, these values may be expressed as a function of the

TABLE 8

Parameters Z_j for calculating z_{RA} according to eqn. (9), for application with Robinson–Peng correlations

Compounds	Z_0	Z_1 ($\times 10^3$)	Z_2 ($\times 10^4$)	Z_3 ($\times 10^5$)	Z_4 ($\times 10^7$)	Z_5 ($\times 10^9$)
Paraffins	0.26461	−4.0597	2.6801	−1.1970	2.7563	−2.4443
Naphthenes	0.27540	−5.3180	3.1085	−1.1087	2.0743	−1.5444
Aromatic compounds	0.27289	−5.0685	3.2782	−1.3579	2.9975	−2.6441

TABLE 9

Mean relative deviations $\overline{\delta_r(\rho)}$ (%) between "experimental" and predicted Robinson–Peng heavy-hydrocarbon densities, form C_6 to C_{45}

Compounds	Method *		
	RKSc11	RKS	PR
Paraffins	1.92	27.90	19.47
Naphthenes	2.10	26.53	18.43
Aromatic compounds	1.90	26.44	18.13

* RKS, Redlich–Kwong–Soave; PR, Peng–Robinson. For RKSc11, see text.

number N of carbon atoms for each series of compounds considered:

$$z_{RA} = \sum_{j=0}^{5} Z_j (N-6)^j \tag{9}$$

The values of Z_j are presented in Table 8.

Used together with the Robinson–Peng (Robinson and Peng, 1978) correlations, these z_{RA} values enable the Redlich–Kwong–Soave method to be corrected and satisfactory estimates to be obtained for the densities of heavy hydrocarbons (Table 9). This method of correction for heavy hydrocarbons, together with the correction RKScl for other components, may be applied to a mixture containing a range of compounds: the following section discusses such an application to petroleum fluids. We term this combined correction method "RKSc11".

Petroleum fluids

Bergman et al. (1975) listed compositions and densities for 113 liquid deposits in natural-gas pipelines. Analysis of these deposits showed that they were typically 17-component mixtures containing nitrogen, carbon dioxide, ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane and fractions containing C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12} and C_{13} compounds. Using the data of Bergman et al. (1975) we calculated densities for such mixtures according to three alternative hypotheses concerning the C_6–C_{13} fractions, which were assumed to be either exclusively paraffins, exclusively naphthenes or exclusively aromatic compounds.

The correction RKSc11 yields estimated densities within a reasonable range about the experimental values (Fig. 6). The hypothesis that the C_6–C_{13} fractions are exclusively paraffins would not, of course, be expected to give

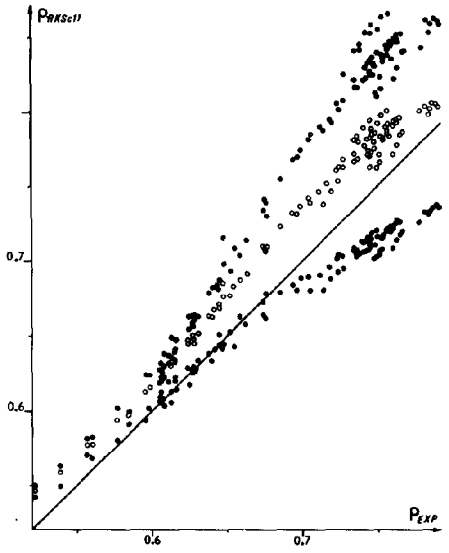

Fig. 6. RKSc11 estimated values (see text) versus experimental values (g cm^{-3}) for densities of pipeline liquid deposits quoted by Bergman et al. (1975), under the three alternative hypotheses that the higher fractions (C_6–C_{13}) are either: ●, exclusively paraffins; ○, exclusively naphthenes; or ⊙, exclusively aromatic compounds.

densities greater than the experimental values: indeed, there are 22 outlying points, with 0.019 g cm^{-3} as the maximum deviation. However, for comparison, the Peng–Robinson method leads to 33 outlying points, with 0.047 g cm^{-3} as the maximum deviation.

The values of the interaction parameters k_{ij} used in the above calculations were taken directly from results published previously (Péneloux and Rauzy, 1979); for interactions between two hydrocarbons, we assumed $k_{ij} = 0$. The results of the volume estimation are not greatly sensitive to the k_{ij} values chosen; however, this is not the case for the estimation of vapour–liquid equilibria.

CONCLUSIONS

The proposed correction to the Redlich–Kwong–Soave equation of state leads to good volume estimations, except for pure components in the neighbourhood of their critical points, and, to a lesser extent, for liquids under very high pressures. The results for mixtures are generally good, and often better than those from the Peng–Robinson equation of state. The use

of the correction will extend the range of applicability of the Redlich–Kwong–Soave method.

Coherent corrections by means of volume translations of the type discussed in this paper constitute a very general method which can be used for improving the results of other equations of state, either for the entire P–V–T range or for some particular region.

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APPENDIX I. THE REDLICH–KWONG–SOAVE AND PENG–ROBINSON METHODS

The Redlich–Kwong–Soave method uses a modification of the Redlich–Kwong equation of state, i.e.

$$P = RT/(v-b) - a(T)/(v(v+b))$$

The Peng–Robinson equation of state is

$$P = RT/(v-b) - a(T)/(v(v+b)+b(v-b))$$

The mixing rules have the same form for both methods, namely

$$b = \sum_{i=1}^{p} x_i b_i$$

$$a = \sum_{i=1}^{p}\sum_{j=1}^{p} x_i x_j (a_i a_j)^{1/2}(1-k_{ij})$$

as do the expressions giving b_i and a_i for each component:

$$b_i = \Omega_b RT_{ci}/P_{ci}$$

$$a_i = \Omega_a\left(1+\left(m_0+m_1\omega_i+m_2\omega_i^2\right)\left(1-(T/T_{ci})^{1/2}\right)\right)^2 R^2 T_{ci}^2/P_{ci}$$

For the five parameters Ω_a, Ω_b, m_0, m_1, m_2, we have used in this work the values given by Soave (1972) and by Peng and Robinson (1976).

APPENDIX II. DEVIATIONS BETWEEN CALCULATED AND EXPERIMENTAL VALUES

For comparisons between calculated and experimental values we used the deviations

$$\delta(v) = v_{\text{exp}} - v_{\text{calc}}$$

$$\delta(\rho) = \rho_{\text{calc}} - \rho_{\text{exp}}$$

in order to obtain the same sign for volume and density deviations.

For the densities, for a data set containing N points, the following measurements of deviation are used:

percent relative deviation: $\delta_r(\rho) = 100(\rho_{calc} - \rho_{exp})/\rho_{exp}$

mean percentage relative deviation: $\overline{\delta_r(\rho)} = (100/N) \sum_{i=1}^{N} |\rho_{calc} - \rho_{exp}|/\rho_{exp}$

mean percentage relative bias: $\overline{\beta_r(\rho)} = (100/N) \sum_{i=1}^{N} (\rho_{calc} - \rho_{exp})/\rho_{exp}$

mean deviation: $\overline{\delta(\rho)} = (1/N) \sum_{i=1}^{N} |\rho_{calc} - \rho_{exp}|$

mean bias: $\overline{\beta(\rho)} = (1/N) \sum_{i=1}^{N} (\rho_{calc} - \rho_{exp})$

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