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Research Note

Accurate Liquid-Volume Calculations for Pure Polar Compounds Using a Volume-Translated Peng-Robinson Equation of State

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In this paper, the accuracy of Peng-Robinson equation of state for vapor-liquid equilibrium calculations has been studied for pure polar compounds and is compared with some other equations of state. This equation has then been modified using the volume-translation technique to improve saturated liquid-volume predictions in low to intermediate temperature and pressure ranges. Two different generalized forms of the translation parameter have been proposed in terms of critical compressibility factor and the reduced dipole moment multiplied by the acentric factor. The proposed generalized equations demonstrate more accurate results compared with the original Peng-Robinson and other selected equations of state.

INTRODUCTION

Cubic Equations Of State (EOS) are still among the most popular practical tools for the estimation of fluid properties. Numerous efforts have been made for the proposal of more accurate equations or optimization of the previous ones, resulting in a multitude of EOS ranging from the simple van der Waals equation up to very complex multi-parameter ones. However, experience shows that the simpler equations with acceptable accuracy are more preferred in engineering practice. The well-known Peng-Robinson (PR) EOS [1] is such an equation which is still frequently used by design engineers.

On the other hand, generalizations of the parameters in the most popular two and three parameter EOS or their modifications have usually been based on data for non-polar compounds or only few polar compounds. One cannot, therefore, count on using cubic EOS for an accurate prediction of the properties of polar compounds unless complex equations are employed.

In this work, a simple modification of the original PR EOS, based on the consistent volume-translation technique [2], is proposed which yields accurate vapor pressure, liquid-volume and vapor-volume estimates for polar compounds. Furthermore, since one of the major limitations of many recently proposed EOS is the use of critical compressibility factors, an effort has been made to replace the dipole moment as a new parameter in the proposed equation.

PRELIMINARIES

Dipole and Reduced Dipole Moments

Dipole moment is a common measure of the polarity of different compounds and is usually determined from the refractive index. On the other hand, Stockmayers potential energy function [3] is commonly used for modeling the behavior of polar molecules by molecular theories. Through incorporating the molecular theory of corresponding states to this function, a "reduced dipole moment" is obtained; a physical parameter which classifies polar molecules in a way similar to the acentric factor for non-polar molecules. It is defined here as:

$$\mu_R = \frac{10^3 \mu^2 P_C}{T_C^2}, \tag{1}$$

where μ is the dipole moment (in debyes), P_C is the critical pressure (in kPa) and T_C is the critical temperature (in K). It is, therefore, understood that

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parameters in a cubic EOS might well be adjusted in terms of this reduced dipole moment for polar substances in addition to the acentric factor. This idea has been employed before for calculating the second virial coefficients [4], and it is used for developing the proposed equations in this work.

Volume Translation Technique

It has been shown that replacing the saturated liquid and vapor volumes in the EOS (V^1) by the translated volume (V):

$$V = V^1 + c, \tag{2}$$

where c is a component dependent constant, will not change the conditions resulted from the equality of vapor and liquid fugacities and, therefore, the calculated vapor pressures by the EOS are not changed [2]. The translation has also been imposed on the molecular volume parameter:

$$b = b^1 + c, \tag{3}$$

so that the pressure-volume curve is simply shifted along the volume axis. This method is also considered in the present work.

OBSERVATIONS

In order to study the performance of PR and other selected EOS, vapor pressure, saturated liquid volume and saturated vapor volume data for 38 pure components (components 1 to 38 in Table 1) with dipole moments ranging from 0 to 3 debyes were used (846 data points) [5,6]. The data were in the reduced pressure range of between 0.01 to 0.29 and reduced temperatures of between 0.55 to 0.90. The predicted values of vapor pressures, liquid volumes and vapor volumes, calculated by the original two parameter PR EOS, the modified PR EOS (MPR) [7], the three parameter Patel-Teja (PT) EOS [8] and the four parameter Jan-Tsai (JT) EOS [9], were compared with the above experimental data, as shown in Tables 2 to 4. From these tables, it is evident that the original PR EOS provides the best overall results for vapor pressure and saturated vapor volumes compared with the three other selected EOS. Absolute deviations in saturated liquid volume, however, are greater than those for the other two properties.

Table 1. List of studied components.

NO	Component
1	Methane (C_1)
2	Propane(C_3H_8)
3	Normal pentane (C_5H_{12})
4	Acetone (C_3H_6O)
5	2-Heptanone ($C_7H_{14}O$)
6	Fluoromethane (CH_3F)
7	Trichloromethane ($CHCl_3$)
8	Chlorodifluoromethane ($CHClF_2$)
9	Dichlorodifluoromethane (CCl_2F_2)
10	Chloroethane (C_2H_5Cl)
11	1-1-Difluoroethane ($C_2H_4F_2$)
12	1-Chloro-1-1-Difluoroethane ($C_2H_3ClF_2$)
13	1-1-Difluoroethene ($C_2H_2F_2$)
14	I-Butane (C_4H_{10})
15	2-Methyl butane (C_5H_{12})
16	Chloromethane (CH_3Cl)
17	Dichloromethane (CH_2Cl_2)
18	Difluoromethane (CH_2F_2)
19	Dichlorofluoromethane ($CHCl_2F$)
20	Trifluoromethane (CHF_3)
21	Bromotrifluoromethane ($CBrF_3$)
22	Trichlorofluoromethane (CCl_3F)
23	Chlorotrifluoromethane ($CClF_3$)
24	1-1-1-Trifluoroethane ($C_2H_3F_3$)
25	1-2-Dichloro-tetrafluoroethane ($C_2Cl_2F_4$)
26	Chloropentafluoroethane (C_2ClF_5)
27	Chloroethene (C_2H_3Cl)
28	Methanol (CH_3OH)
29	Ethanol (C_2H_5OH)
30	1-Propanol (C_3H_7OH)
31	2-Propanol (C_3H_7OH)
32	1-Butanol (C_4H_9OH)
33	2-Butanol (C_4H_9OH)
34	2-Methyl-1-propanol (C_4H_9OH)
35	2-Methyl-2-propanol (C_4H_9OH)
36	1-Pentanol ($C_5H_{11}OH$)
37	Water (H_2O)
38	Ammonia (NH_3)
39	Methyl Formate ($C_2H_4O_2$)
40	Dimethyl Ether (C_2H_6O)
41	Ethylmercaptan (C_2H_6S)
42	Dimethyl Sulfide (C_2H_6S)
43	Ethyl Formate ($C_3H_6O_2$)
44	Methyle Ethyl Ether (C_3H_8O)
45	Methylmercaptan (CH_4S)
46	Sulfur Dioxide (SO_2)
47	Ethane (C_2H_6)

To consider the effect of dipole moment on the performance of the EOS in predicting liquid volumes, detailed results for average deviations in predicted liquid volumes from experimental data (Table 3) were analyzed for all the selected components. It can be seen that the deviations can be correlated with the dipole moment. A shift in errors from average negative values towards positive values was observed as the reduced dipole moment (μ_R) multiplied by the acentric factor (ω) increased (Figure 1). The parameter

Table 2. Percent absolute average deviations (%AAD) in predicting vapor pressures by different equations of state (for components used in the derivation of the translation parameters).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
1	0.000	0.706	0.483	1.233	1.831	0.999	0.997	1.030
2	0.083	0.532	0.781	0.570	0.983	0.743	0.750	0.751
3	0.370	1.329	1.597	1.402	2.086	1.511	1.526	1.519
4	2.860	0.541	0.580	0.772	0.664	0.425	0.429	0.451
5	2.610	1.964	2.575	2.836	*	*	1.503	1.420
6	1.820	0.302	0.512	0.470	3.915	0.188	0.216	0.209
7	1.100	0.385	0.860	0.208	4.640	0.894	0.868	0.881
8	1.410	0.405	0.733	0.243	1.121	0.792	0.796	0.799
9	0.540	0.292	0.895	0.379	2.155	0.694	0.648	0.678
10	2.040	0.322	0.413	0.452	1.143	0.323	0.321	0.342
11	2.270	2.414	2.503	2.574	2.980	1.967	1.970	1.956
12	2.140	0.802	0.904	0.967	4.147	0.431	0.459	0.468
13	1.370	2.813	2.727	2.571	0.432	2.859	2.859	2.860
14	0.132	0.578	0.650	0.475	2.285	0.962	0.935	0.961
15	0.120	0.146	0.711	0.238	1.538	0.593	0.619	0.569
16	1.940	0.361	0.885	0.425	1.086	0.770	0.788	0.755
17	1.800	1.588	1.762	1.363	*	*	1.977	1.972
18	1.960	0.691	0.752	0.880	1.893	0.457	0.432	0.456
19	1.330	0.968	1.273	0.799	4.100	1.391	1.408	1.367
20	1.620	0.452	0.545	0.667	2.234	0.413	0.418	0.412
21	0.650	0.302	0.768	0.382	1.428	0.712	0.735	0.713
22	0.490	0.335	0.883	0.295	1.918	0.748	0.761	0.746
23	0.480	0.276	0.730	0.130	1.527	0.673	0.674	0.694
24	2.310	0.392	0.640	0.332	1.433	0.761	0.750	0.781
25	0.520	0.777	1.227	0.657	2.648	1.129	1.104	1.103
26	0.520	0.433	0.485	0.405	1.339	0.741	0.734	0.741
27	1.440	3.271	3.694	3.070	4.013	3.643	3.674	3.671
28	1.700	2.173	1.115	0.787	1.179	2.496	2.487	2.500
29	1.730	1.511	1.120	2.083	2.435	1.993	1.990	1.991
30	1.680	2.577	3.098	3.845	3.057	3.050	3.050	3.027
31	1.660	2.751	3.468	4.284	3.380	3.174	3.158	3.203
32	1.810	3.446	3.937	4.632	3.002	3.880	3.901	3.890
33	1.660	4.109	4.633	5.287	4.179	4.414	4.416	4.455
34	1.640	3.947	4.472	5.174	3.640	4.357	4.386	4.382
35	1.670	4.126	4.782	5.506	3.572	4.514	4.512	4.519
36	1.640	3.469	3.743	4.443	3.014	4.025	4.008	4.081
37	1.800	0.938	0.935	1.152	1.739	0.547	0.555	0.577
38	1.500	0.490	0.929	0.933	7.719	2.000	2.646	2.918
Av.		1.392	1.653	1.656	2.512	1.646	1.626	1.642

* Experimental critical compressibility factor not available

$\mu_{R\omega}$ represents, at least to some extent, the combined effect of polarity and acentricity of the molecules. It was, therefore, concluded that the modification of the PR EOS could be based on use of this parameter together with volume-translation technique. It was also deduced that since poor liquid-volume predictions are mainly due to unsatisfactory predictions of the critical compressibility factor (Z_C) [10], this latter parameter must also be related to $\mu_{R\omega}$. Figure 2 depicts variation of Z_C with $\mu_{R\omega}$, from which an accurate correlation relating Z_C to $\mu_{R\omega}$ is obtained for polar compounds.

Table 3. Percent absolute average deviations (%AAD) in predicting saturated liquid volumes by different equations of state (for components used in the derivation of the translation parameters).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
1	0.000	8.400	2.073	2.169	0.946	2.950	2.918	3.142
2	0.083	4.363	0.560	1.783	2.300	1.735	1.994	1.715
3	0.370	3.762	1.761	3.630	2.239	3.709	7.319	4.426
4	2.860	14.357	13.263	14.782	4.242	2.656	2.584	7.141
5	2.610	9.670	11.788	12.131	*	*	15.209	13.657
6	1.820	12.433	15.985	16.759	1.896	1.972	4.459	1.195
7	1.100	6.075	2.711	3.361	4.433	0.517	1.198	3.227
8	1.410	1.610	1.836	2.639	0.711	1.443	1.577	2.740
9	0.540	6.666	2.942	3.536	2.005	2.318	2.162	2.697
10	2.040	4.219	8.187	7.895	7.297	7.961	3.531	2.911
11	2.270	10.401	11.582	12.382	4.390	2.909	1.728	2.103
12	2.140	2.363	1.271	0.971	7.805	3.296	5.945	6.837
13	1.370	5.590	6.165	9.371	3.901	9.240	5.184	2.844
14	0.132	4.317	0.896	1.769	1.698	1.664	2.094	1.068
15	0.120	3.566	1.078	2.184	1.831	2.171	3.404	1.558
16	1.940	1.368	5.873	6.072	0.823	1.529	2.037	4.346
17	1.800	3.728	8.467	7.660	*	*	4.569	2.490
18	1.960	14.033	13.045	15.276	1.262	2.218	2.483	2.260
19	1.330	2.559	0.723	1.818	2.740	1.543	1.586	1.941
20	1.620	4.350	4.707	6.007	0.996	1.526	3.299	5.378
21	0.650	2.645	2.105	1.810	1.457	1.420	3.360	2.126
22	0.490	4.714	1.324	2.034	0.681	1.186	1.506	1.382
23	0.480	5.151	1.414	2.182	1.282	1.426	1.179	1.233
24	2.310	7.819	8.724	9.796	1.884	3.136	4.194	3.219
25	0.520	4.349	3.209	2.820	1.177	1.254	1.832	1.490
26	0.520	5.694	4.836	3.980	4.443	3.288	1.136	2.162
27	1.440	4.970	13.254	11.429	4.850	4.889	9.333	7.304
28	1.700	19.809	11.972	11.544	1.366	3.703	3.795	6.486
29	1.730	9.021	2.036	2.081	2.042	2.646	4.079	2.576
30	1.680	5.790	2.110	2.613	1.317	4.011	3.293	3.317
31	1.660	7.322	2.376	2.402	1.043	3.503	3.134	3.247
32	1.810	4.803	1.994	2.547	1.238	3.391	3.351	3.354
33	1.660	6.688	2.152	2.689	1.063	3.078	4.403	4.147
34	1.640	5.378	2.249	2.750	1.403	3.617	4.148	3.967
35	1.670	4.439	2.157	2.612	1.090	3.142	3.118	3.122
36	1.640	2.470	3.979	4.317	0.942	2.299	2.339	2.291
37	1.800	24.630	3.498	24.010	5.885	6.125	8.782	8.507
38	1.500	13.736	15.912	16.262	7.269	6.931	5.688	6.027
Av.		6.928	5.268	6.318	2.554	3.067	3.388	3.315

* Experimental critical compressibility factor not available

Figure 3 shows the variations of the 'difference' between predicted and actual liquid volumes (c in Equation 2) for PR EOS as a function of $\mu_R\omega$, for which a similar trend to that of the relative errors is observed. This trend was used to obtain the generalized volume-translation parameter.

DEVELOPMENT OF THE EQUATIONS

The volume-translated PR EOS is given by:

$$P=\frac{RT}{V-b}-\frac{a(T)}{V^2+(2-\frac{4c}{b})bV+(2\frac{c^2}{b^2}-1)b^2}. \qquad (4)$$

Table 4. Percent absolute average deviations (%AAD) in predicting saturated vapor volumes by different equations of state (for components used in the derivation of the translation parameters).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
1	0.000	1.012	1.785	1.051	2.412	1.051	1.048	0.880
2	0.083	1.136	0.613	0.996	1.151	1.241	1.295	1.292
3	0.370	2.979	2.517	3.080	3.733	3.010	2.919	2.975
4	2.860	3.572	3.191	4.069	3.225	3.183	3.181	3.159
5	2.610	2.011	3.372	4.018	*	*	1.186	1.074
6	1.820	4.362	3.482	4.362	4.390	3.999	3.960	3.994
7	1.100	1.042	0.760	1.172	3.851	1.383	1.347	1.336
8	1.410	0.676	0.539	0.641	1.389	0.950	0.952	0.956
9	0.540	0.653	0.940	0.599	2.202	1.034	0.998	1.008
10	2.040	2.100	1.212	2.097	1.341	1.881	1.841	1.855
11	2.270	3.148	3.189	3.350	3.931	2.637	2.637	2.626
12	2.140	1.990	1.224	2.194	3.004	1.844	1.687	1.678
13	1.370	2.904	2.729	3.133	1.597	3.120	2.927	2.856
14	0.132	1.089	1.605	0.998	3.455	1.295	1.262	1.310
15	0.120	0.591	0.810	0.698	2.242	0.767	0.737	0.726
16	1.940	1.734	1.135	1.659	1.349	1.938	1.893	1.782
17	1.800	1.435	1.437	1.362	*	*	1.779	1.755
18	1.960	1.346	0.722	1.694	2.220	1.001	0.998	1.012
19	1.330	1.410	1.523	1.390	4.747	1.844	1.869	1.783
20	1.620	1.061	1.156	1.155	3.826	1.109	1.203	1.246
21	0.650	0.842	0.751	0.686	1.401	1.171	1.236	1.187
22	0.490	0.617	0.675	0.496	2.100	0.927	0.938	0.917
23	0.480	0.641	0.700	0.516	1.940	0.844	0.842	0.861
24	2.310	1.590	1.270	1.898	1.102	1.573	1.566	1.591
25	0.520	1.484	1.956	1.218	3.945	1.693	1.618	1.681
26	0.520	1.750	1.460	1.997	1.143	1.954	2.028	1.981
27	1.440	2.608	3.706	2.828	3.581	2.903	2.924	2.917
28	1.700	1.577	1.490	1.931	1.597	1.889	1.870	1.821
29	1.730	1.038	3.149	2.984	1.687	1.398	1.366	1.399
30	1.680	2.757	4.361	3.874	2.319	2.984	3.052	3.030
31	1.660	3.072	5.105	4.780	2.724	3.244	3.282	3.329
32	1.810	2.448	3.708	3.284	2.256	2.750	2.764	2.756
33	1.660	4.243	5.868	5.358	3.244	4.361	4.461	4.483
34	1.640	3.972	5.655	5.146	2.725	4.241	4.309	4.294
35	1.670	4.452	6.179	5.963	3.026	4.693	4.687	4.690
36	1.640	5.230	6.378	6.284	3.932	5.668	5.679	5.724
37	1.800	2.370	0.511	3.468	2.023	1.904	1.988	1.657
38	1.500	9.281	9.496	9.663	13.663	10.201	10.640	10.937
Av		2.270	2.535	2.687	2.902	2.436	2.394	2.355

* Experimental critical compressibility factor not available

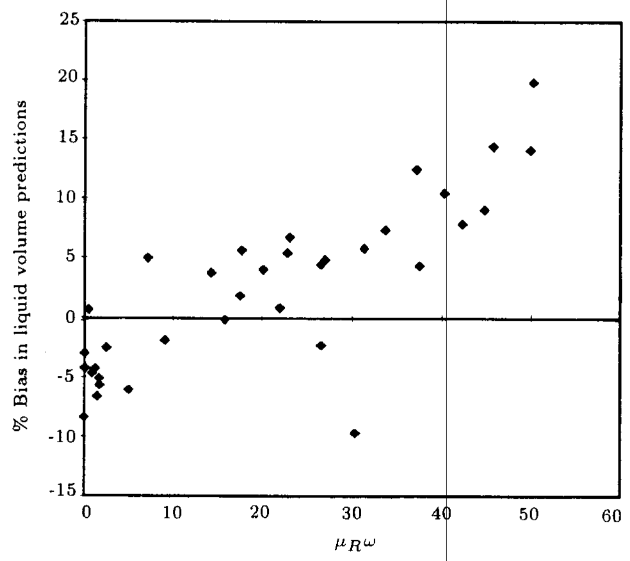

Figure 1. Average percent deviation in liquid volume predictions using Peng-Robinson EOS as a function of $\mu_R\omega$.

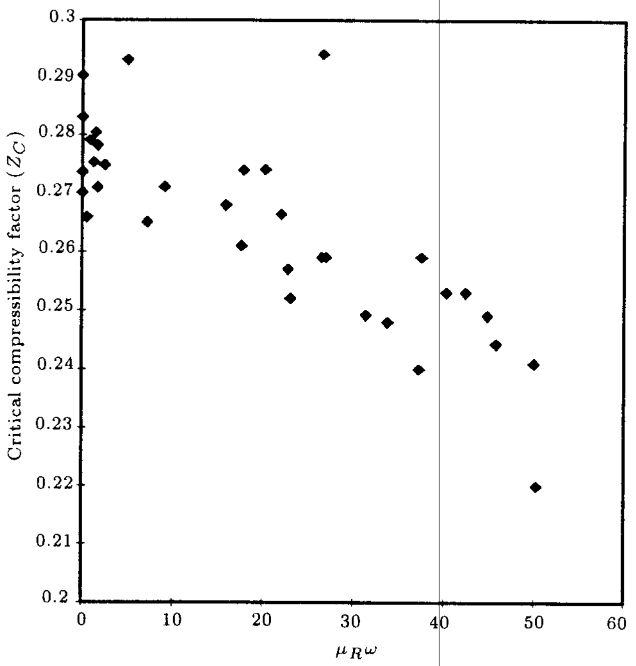

Figure 2. Critical compressibility factors as a function of $\mu_R\omega$.

In order to obtain this equation, the values for molar volume and the molecular volume parameter in the original equation (V^1 and b^1) have been replaced by V and b, respectively, as explained in Equations 2 and 3. Imposing the following conditions at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = 0, \tag{5}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0, \tag{6}$$

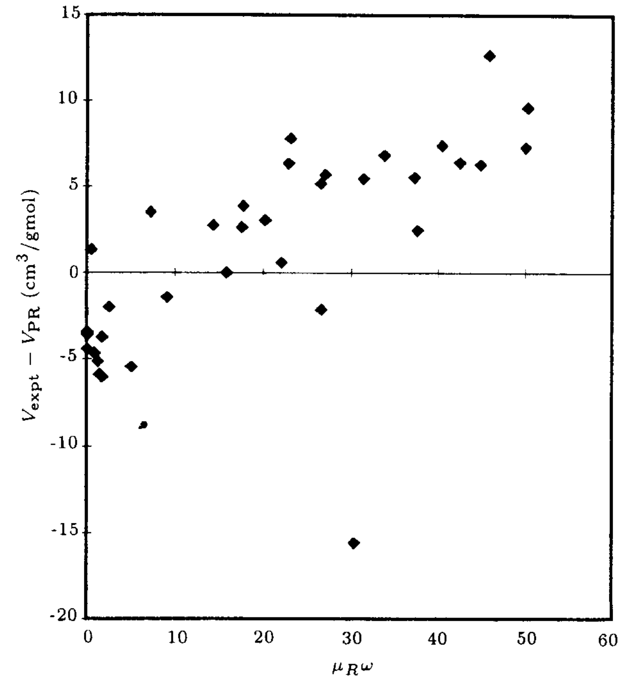

Figure 3. Difference between experimental and predicted saturated liquid volumes as a function of $\mu_R\omega$.

it is obtained that:

$$a_C = \frac{0.45724 R^2 T_C^2}{P_C}, \tag{7}$$

$$b_C = \frac{0.0778 R T_C}{P_C} + c, \tag{8}$$

$$\xi_C = 0.3074 + \Omega_C, \tag{9}$$

$$\Omega_C = \frac{c P_C}{R T_C}. \tag{10}$$

ξ_C is the predicted critical compressibility factor. The value of b was held constant, as in the original PR EOS, and the temperature functionality of $a(T)$ was also unchanged:

$$a(T) = a_C \alpha(T_R), \tag{11}$$

$$\sqrt{\alpha(T_R)} = 1 + m(1 - \sqrt{T_R}), \tag{12}$$

where m is a function of the acentric factor. Optimum values for c were obtained from the average differences between the predicted and actual liquid volumes. Using these optimum values, the values for m in Equation 12 were calculated by minimizing the differences between the experimental and calculated vapor pressures.

Since this type of volume translation has a very little effect on the predicted vapor pressures, generalization of m in terms of the acentric factor resulted in the same relations that were developed in the original PR EOS:

$$m = 0.37464 + 1.54226\omega + 0.26992\omega^2. \tag{13}$$

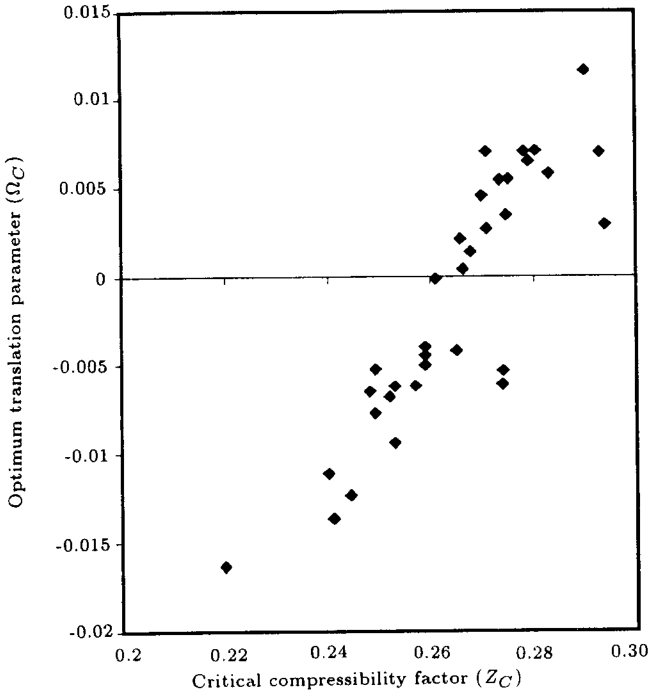

Figure 4. Optimum translation parameter Ω_c as a function of the critical compressibility function Z_C.

The values of c and Ω_C were generalized in terms of $\mu_{R}\omega$ and Z_C, respectively. Generalization of Ω_C in terms of Z_C has also been conducted in order to be able to replace μ_R by Z_C, by preference. Variation of Ω_C versus Z_C is illustrated in Figure 4. The resulting correlations are:

$$c = 5.074566 - 5.366751 \times 10^{-1}(\mu_R.\omega) + 9.425019\times10^{-3}(\mu_R.\omega)^2 - 6.46159 \times 10^{-5}(\mu_R.\omega)^3, \quad (14)$$

$$\Omega_c = 3.097079 - 37.37821\ Z_C + 147.568820\ Z_C^2 - 191.445990\ Z_C^3. \quad (15)$$

Equations 4 to 15 complete the definition of this modified PR EOS. Correlations for the fugacity coefficient are given in the Appendix.

The following correlation was also developed for predicting values of Z_C for polar substances:

$$Z_C = 0.287042 - 2.121481 \times 10^{-3}(\mu_R\omega) + 6.013579\times10^{-5}(\mu_R\omega)^2 - 7.747805\times10^{-7}(\mu_R\omega)^3. \quad (16)$$

RESULTS AND DISCUSSION

Percent relative errors for predicting vapor pressures, saturated liquid volumes and saturated vapor volumes using the proposed equations are presented in Tables 2 to 4. In these tables, MOD.PR-1 refers to calculations using Equation 15 with critical compressibility factors from the literature, MOD.PR-2 refers to calculations using Equation 15 with Z_C's from Equation 16 and MOD.PR-3 refers to calculations using Equation 14.

Table 5. Percent absolute deviation in predicting critical compressibility factors by Equation 16 for components used in the derivation of the equation constants.

Comp. No	DIP. MOM. (Debye)	% Error
1	0.000	1.088
2	0.083	4.926
3	0.370	7.579
4	2.860	1.087
5		*
6	1.820	4.757
7	1.100	5.184
8	1.410	0.927
9	0.540	1.303
10	2.040	4.247
11	2.270	1.770
12	2.140	12.045
13	1.370	3.616
14	0.132	1.376
15	0.120	6.271
16	1.940	1.935
17		*
18	1.960	2.658
19	1.330	0.409
20	1.620	3.039
21	0.650	2.703
22	0.490	2.221
23	0.480	1.977
24	2.310	2.687
25	0.520	3.370
26	0.520	4.675
27	1.440	3.614
28	1.700	6.432
29	1.730	2.413
30	1.680	2.624
31	1.660	2.478
32	1.810	0.244
33	1.660	3.422
34	1.640	1.471
35	1.670	0.142
36	1.640	1.196
37	1.800	5.921
38	1.500	3.610
Av.	Including no. 12	3.295
Av.	Not incling no. 12	2.954

* Experimental critical compressibility factor not available

While predicted vapor pressures and vapor volumes were only slightly affected by this modification, liquid-volume predictions were considerably improved and results were usually similar to, and sometimes even better than, those of the four-parameter JT EOS. Using Equation 15 with actual Z_C's produced the best results, while the given correlation for Z_C (Equation 16) only slightly degrades the results. Absolute errors for predicting Z_C by Equation 16 are shown in Table 5. The relatively high error for component 12 could be due to an incorrect experimental value in the cited reference. Application of Equation 14 also produced very satisfactory results which were similar to those of the other two methods.

In order to test the proposed modification for substances not included in the original database, 9 components were chosen (components 39 to 47 in Table 1) for which VLE data were taken from [11]. Average errors for vapor pressure, saturated liquid volume and saturated vapor volume predictions are given in Tables 6 to 8. It is observed that the proposed modification of the PR EOS produces accurate results for calculating liquid volume, vapor volume and vapor pressures of pure polar compounds. Accuracy of calculations (especially those using Equation 14) are even better than those of the four parameter JT EOS. Percent absolute relative errors for predicting Z_C by Equation 16 for the mentioned components are given in Table 9. Except for nonpolar ethane, predictions have a high degree of accuracy.

Finally, the modified equations were also tested for the prediction of subcooled liquid volumes of water (35 data points for reduced pressures ranging between 0.045 and 45.0) [7]. Results are provided in Table 10. Considering the broad pressure range tested, Equation 15 yields very promising results, while Equation 14 also clearly improves the original predictions.

CONCLUSIONS

Liquid volume calculations for pure polar compounds using PR EOS have been improved by using dipole moment or critical compressibility factor and volume-

Table 6. Percent absolute average deviations (%AAD) in predicting vapor pressures by different equations of state (for components not used in the derivation of the translation parameters).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
39	1.800	0.757	0.597	0.858	1.037	0.882	0.882	0.896
40	1.300	1.296	1.964	1.230	2.074	1.597	1.597	1.591
41	1.500	0.595	1.115	0.816	1.474	0.605	0.605	0.592
42	1.500	2.014	1.400	2.077	1.307	1.708	1.708	1.725
43	2.000	0.897	0.752	1.238	1.222	0.989	0.989	0.996
44	1.200	2.630	2.436	2.631	2.521	2.748	2.748	2.745
45	1.300	0.919	0.847	0.585	1.330	1.200	1.200	1.184
46	1.600	3.660	3.100	3.907	3.213	3.330	3.330	3.356
47	0.000	0.549	0.975	1.143	0.566	0.682	0.682	1.151
Av.		1.480	1.465	1.609	1.638	1.417	1.417	1.582

Table 7. Percent absolute average deviations (%AAD) in predicting saturated liquid volumes by different equations of state (for components not used in the derivation of the translation parameters).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
39	1.800	6.087	6.599	7.981	3.095	3.581	4.379	2.448
40	1.300	2.651	1.273	1.985	1.247	1.919	1.829	2.565
41	1.500	2.232	1.702	2.415	0.733	1.939	1.402	1.886
42	1.500	1.417	4.315	5.302	1.266	2.699	4.097	2.060
43	2.000	5.569	5.027	6.671	0.913	2.111	3.938	2.783
44	1.200	3.332	2.661	4.099	2.089	3.594	4.886	3.792
45	1.300	2.428	3.045	3.172	1.448	2.044	2.155	1.949
46	1.600	9.165	10.429	11.265	3.623	2.514	5.239	1.608
47	0.000	5.178	1.997	3.254	6.654	6.048	2.440	2.039
Av.		4.229	4.117	5.127	2.341	2.704	2.936	2.347

Table 8. Percent absolute average deviations (%AAD) in predicting saturated vapor volumes by different equations of state (for components not used in the derivation of the translation parameters).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
39	1.800	1.864	1.923	1.944	1.412	2.005	2.027	1.987
40	1.300	1.868	2.228	1.832	2.571	2.132	2.122	2.132
41	1.500	*	*	*	*	*	*	*
42	1.500	*	*	*	*	*	*	*
43	2.000	1.602	1.732	1.917	1.177	1.627	1.714	1.677
44	1.200	*	*	*	*	*	*	*
45	1.300	*	*	*	*	*	*	*
46	1.600	9.451	8.784	9.748	8.534	9.185	9.242	9.159
47	0.000	0.550	1.223	0.445	1.130	0.581	0.494	3.320
Av.		3.067	3.178	3.177	2.965	2.781	2.777	3.655

* Experimental value not available in cited reference

Table 9. Percent absolute deviation in predicting critical compressibility factors by Equation 16 for components not used in the derivation of the equation constants.

Comp. No	**DIP. MOM. (Debye)**	**%Error**
39	1.800	0.584
40	1.300	0.378
41	1.500	0.635
42	1.500	1.221
43	2.000	2.239
44	1.200	2.415
45	1.300	1.835
46	1.600	1.977
47	0.000	9.183
Av.		2.274

translation technique. The proposed equations are simple, with a minimum change in the form of the original equation, but the performance is similar to the more complex EOS. The components examined in this study include associating substances, for which results comply very well with experimental values. An accurate correlation has also been developed for the prediction of critical compressibility factors of polar compounds using reduced dipole moments and acentric factors.

Use of the reduced dipole moment in a cubic EOS has produced very satisfactory results, and it is quite probable that including more nonpolar substances in the data-base could result in a single set of equations which provides accurate calculations for numerous varieties of substances using only the critical properties (T_C and P_C), acentric factor and dipole moment. This modification could also be applied to other popular EOS. The proposed correlation using critical compressibility factor also possesses the above mentioned characteristics; it is applicable to polar/nonpolar compounds whenever accurate values for Z_C could be obtained.

NOMENCLATURE

$a(T)$	parameter in Equation 4 (kPa(cm^3 mol^{-1})^2)
b	parameter in Equation 4 (cm^3 mol^{-1})
c	volume-translation parameter in Equation 4 (cm^3 mol^{-1})
m	parameter in Equation 12
P	pressure (kPa)

Table 10. Percent absolute average deviations (% AAD) in predicting subcooled liquid volumes by different equations of state (for water substance).

	%AAD Equation of State							
Comp. No	**DIP. MOM. (Debye)**	**PR**	**MPR**	**PT**	**JT**	**MOD.PR-1**	**MOD.PR-2**	**MOD.PR-3**
37	1.800	20.404	20.116	21.401	7.103	1.226	2.319	16.863

R	universal gas constant (kPa $\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{K}^{-1}$)
T	temperature (K)
V	molar volume ($\mathrm{cm}^3\ \mathrm{mol}^{-1}$)
Z	compressibility factor

Greek Letters

α	parameter in Equation 11
ξ	calculated value of compressibility factor
μ	dipole moment (debye)
Φ	fugacity coefficient
Ω	volume translation coefficient defined in Equation 10
ω	acentric factor

Subscripts

C	critical value
R	reduced property

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APPENDIX

The fugacity coefficient of pure compounds, derived using the proposed EOS is given as:

$$Ln(\Phi) = \frac{b}{V-b} - Ln\left[\frac{P(V-b)}{RT}\right]$$

$$-\frac{a(T)V}{RT(V^2+ubV+wb^2)} - \frac{a(T)}{sRT}Ln\left(\frac{2V+ub+s}{2V+ub-s}\right)$$

$$u = 2 - \frac{4c}{b},$$

$$w = \frac{2c^2}{b^2} - 1,$$

$$s = b\sqrt{u^2-4w}.$$