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A New Perturbed Hard-Sphere Equation of State

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Abstract: A new equation of state based on hard-sphere perturbed theory was developed. This equation combined the CS repulsive term and Guo-Du attractive term. Parameters of 38 substances were estimated, the pressure-volume-temperature properties were calculated and compared with two other equations. The results show that this equation is more accurate.

Keywords: Equation of state, hard-sphere perturbed theory, thermodynamic properties.

In 1873 van der Waals[1] proposed a two-parameter cubic equation of state (EOS), which provides a rather clear physical picture of molecular interactions in real fluids. Because of its simplicity, it soon was widely used. Other famous equations of state, such as PR[2], Soave[3], have been proposed since then. But all these equations are not accurate enough when applied to liquid phase.

The trend of modeling the properties of fluids is that a single equation of state can be applied to both vapor and liquid phases.

By combining the repulsive term of the Carnahan-Starling[4] hard-sphere equation and the attractive term of Guo-Du equation[5], we proposed the following equation:

$$P = \frac{RT}{v}\left[\frac{1+y+y^2-y^3}{(1-y)^3}\right] - \frac{a(T)}{v(v+c)+c(v-b)} \qquad (1)$$

Where P is the pressure, T is the absolute temperature, v is the molar volume, and R is the gas constant. The other parameters are as follows:

$$\text{AADV\%} = 100 \times \left[\frac{1}{n}\sum_{i=1}^{n}\left|v_i^{cal} - v_i^{\exp}\right| / v_i^{\exp}\right]$$

$$\text{AADP\%} = 100 \times \left[\frac{1}{n}\sum_{i=1}^{n}\left|p_i^{cal} - p_i^{\exp}\right| / p_i^{\exp}\right]$$

(*) Calculate from equation (1), *PVT* data are from Smith[6], ω,*Tc*,*Pc*,*Vc* data are from Reid[7]

(#) Calculate from Mcspt equation[10]

$$y = \frac{b}{4v} \qquad \zeta_c = \frac{P_c V_c}{RT_c}$$

$$a(T) = \Omega_{ac}\alpha(Tr)\frac{R^2 T_c^{\,2}}{P_c}, \quad b = \Omega_b \frac{RT_c}{P_c}, \qquad c = \Omega_c \frac{RT_c}{P_c}$$

$$\alpha(Tr) = [1 + a_1(1-\sqrt{Tr}) + a_2(1-\sqrt{Tr})^2 + a_3(1-\sqrt{Tr})^3]^2$$

Table 1. Parameters of a_i for correction of $a(Tr)$

Substance	Tr	a_1	a_2	a_3	AADV%			AADP%		
					(*)	(#)	PR	(*)	(#)	PR
Methane	0.48~0.99	0.14445	1.79545	6.099780	1.06	4.01	8.43	0.37	0.79	0.40
Ethane	0.38~0.95	0.12884	3.68879	6.899390	0.73	2.51	6.24	0.97	1.49	0.70
Propane	0.35~1.00	0.08713	4.46085	8.803020	1.18	1.11	5.50	0.72	0.93	0.37
n-Butane	0.35~1.00	0.15220	4.17665	12.22939	1.15	0.66	4.79	1.50	1.73	0.39
i-Butane	0.34~0.98	0.18617	3.89880	11.52915	0.98	1.14	5.04	0.52	1.62	1.00
n-Pentane	0.31~0.95	0.22832	3.33374	17.13772	0.33	1.33	3.33	0.54	0.76	0.76
2-methylbutane	0.41~0.97	0.23846	3.23491	14.92863	0.89	0.41	4.78	0.35	0.49	0.32
2,2-dimethylpropane	0.59~0.96	0.28350	1.75260	18.28319	1.03	1.19	5.77	0.71	0.90	1.07
2,3-dimethylbutane	0.52~0.98	0.31743	2.58120	19.01501	0.61	0.68	4.18	0.82	1.24	0.54
3-methylpentane	0.56~0.98	0.43195	2.22477	23.14935	0.65	2.13	3.90	0.80	1.39	0.66
2-methylpentane	0.58~0.96	0.37036	2.25064	23.81969	0.41	3.11	3.35	0.78	1.28	0.36
3-methylheptane	0.42~0.97	0.34008	2.33984	24.29490	0.57	1.21	3.96	0.64	0.71	0.41
2-methylheptane	0.42~0.97	0.50959	1.78414	34.66863	0.28	1.18	3.97	0.56	0.98	0.44
n-Hexane	0.35~0.97	0.47202	1.69208	26.08994	0.33	1.99	3.08	0.53	0.93	1.02
Ethylene	0.37~1.00	0.09765	3.02460	8.783980	0.96	2.41	6.58	0.62	0.84	0.45
Propene	0.24~1.00	0.21373	2.76665	10.87821	0.76	3.18	6.40	0.56	0.93	1.59
1-Butene	0.51~0.93	0.21971	2.94036	16.99725	0.65	0.68	3.93	0.70	1.42	0.46
i-butene	0.46~0.84	0.19636	3.84077	14.18608	0.07	1.03	3.87	0.6	1.34	0.55
Cis-2-butene	0.45~0.69	0.19313	3.76382	15.95767	0.004	2.00	3.34	0.29	0.82	0.57
Trans-2-butene	0.45~0.88	0.22507	3.48201	15.32479	0.11	0.36	3.82	0.56	----	2.88
1-pentene	0.42~0.95	0.16809	4.78769	15.67423	0.71	1.97	2.66	0.80	1.18	1.37
1-hexene	0.56~0.70	0.50009	2.05129	25.96779	0.001	4.12	0.46	0.71	0.93	1.15
Benzene	0.51~0.98	0.28048	2.93172	19.15451	0.54	1.52	3.43	0.67	1.23	1.61
Toluene	0.37~1.00	0.19821	4.62070	18.40568	1.41	2.63	3.37	0.87	1.09	0.54
Ethylbenzene	0.43~0.79	0.53801	1.39864	30.62589	0.10	4.23	0.83	0.50	1.08	1.17
O-xylene	0.44~0.97	0.43980	2.45806	27.17071	0.31	2.90	2.90	0.56	1.11	0.76
P-xylene	0.47~0.80	0.41344	2.83473	29.31783	0.046	4.95	2.72	0.62	1.13	0.59
M-xylene	0.43~0.94	0.45552	2.42938	28.55923	0.12	3.51	4.26	0.53	1.06	0.47
Acetone	0.49~0.97	0.31945	0.30711	23.28535	0.36	3.27	15.74	2.13	2.48	1.86
Argon	0.56~1.00	0.06611	1.43081	7.460330	0.91	4.47	8.34	0.64	0.86	0.52
Oxygen	0.35~1.00	0.11226	2.55240	7.467710	0.95	9.67	12.36	0.47	0.50	1.31
Nitrogen	0.50~1.00	0.06856	1.78304	7.585640	1.81	4.71	8.80	0.68	0.80	0.53
Carbon dioxide	0.71~0.98	0.41760	0.20257	31.52609	0.68	0.64	4.81	0.58	1.16	0.44
Carbon monoxide	0.52~0.99	0.12741	1.72376	7.396040	0.92	4.94	9.21	0.92	0.44	0.29
Ammonia	0.50~1.00	0.36133	2.13706	30.85232	1.69	3.94	18.47	2.00	2.49	2.61
R32	0.40~0.90	1.04666	-4.92938	51.63505	1.87	6.87	17.36	0.92	2.33	2.22
R125	0.51~0.99	0.42380	2.27622	25.40940	0.68	1.81	4.30	0.64	1.23	0.49
R152a	0.40~0.91	0.63230	-0.08600	36.60415	0.69	5.00	9.75	0.72	1.60	1.24

where a_1, a_2, a_3 are substance dependant parameters. ζ_c is the pseudo-critical compressibility factor and it is temperature dependent. The value of ζ_c in this work has the following correlation form[8]:

$$\zeta_c = Zc + p_1 \times (1-Tr)^{0.5} + p_2 \times (1-Tr)$$

where P_1 and P_2 are related to acentric factor ω and real compressibility factor Zc

$$p_1 = 3.36666 - 7.03847Zc + 7.43658\times10^{-5}\exp(\omega) - 0.349501/Zc$$

$$p_2 = -0.278403 + 0.0290252\omega\exp(\omega) - 1.34075Zc/Log(Zc)$$

At the critical point equation (1) must satisfy the following conditions rigorously:

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

From equation (2) and equation (1) at P_c,V_c,T_c point， parameter $\Omega_{ac}(\zeta_c)$、$\Omega_b(\zeta_c)$、$\Omega_c(\zeta_c)$ can be obtained by suitable mathematic techniques[8].

To verify the equation of this work, We calculated pressure-volume-temperature properties of 38 typical substances. **Table 1** lists the temperature range, the values of the coefficients α_i, deviations between calculated data and experimental data for vapor pressure and molar volume. The deviations calculated by Mcspt[9] equation, which has similar form with equation (1), are also listed in the **Table 1**. The overall average deviations of liquid molar volume and vapor pressure are respectively 0.70% and 0.74% by equation (1), and 2.27% and 1.17% by Mcspt[9] equation. Guo-Du[5] equation gets an average vapor pressure deviation of 1.84% for light hydrocarbons (C_1-C_7), and the overall average liquid densities deviation of 25 pure hydrocarbons is 1.90%[5].

Figure1. Comparison the deviation of saturated liquid volume of acetone

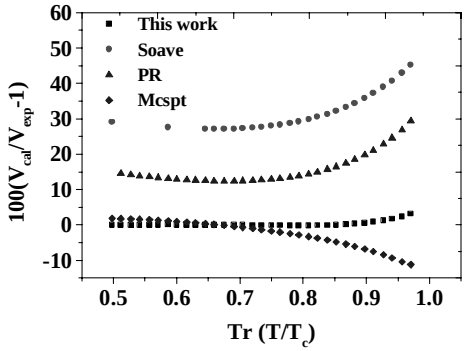

Figure2. Comparison of calculated results for CO_2 along V-L coexistence

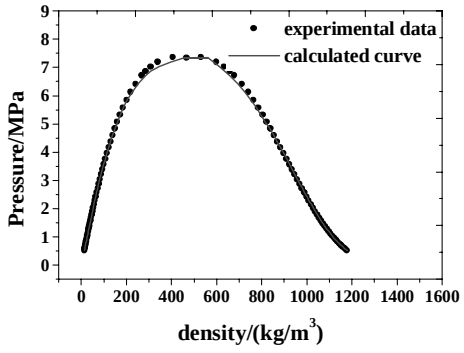

Figure 1 compares the deviations of this work with three other equations for liquid molar volume of acetone. **Figure 2** shows the experimental data[10] and the predicted data along the vapor-liquid (V-L) saturation curve of carbon dioxide. All the results above indicate that equation of this work is more accurate, especially in liquid region.

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References

1. J. D. van der Waal, *Over de continuiteit van gas-en vloeistoftoestand*. Doctoral dissertation, Leiden, The Netherlands. **1873**
2. D.Y. Peng, D.B. Robinson, *Ind. Eng. Chem. Fundls.* ,**1976**, *15*, 59
3. G. Soave, *Chem. Eng. Sci*., **1972**, *27*, 1197
4. N. F. Carnahan, K. E. Starling, *J. Chem. Phys*., **1969**, *51*, 635
5. T.M. Guo, L. Du, *Fluid Phase Equilibra*. **1989**, *52*, 47
6. B. D. Smith, R. Srivastava, *Thermodynamic Data for Pure Compounds*, part A, N.Y. **1986**
7. R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases and Liquids*, 4th, **1987**
8. P. Li, X. Y. Zheng, J. F. Lin, *Fluid Phrase Equilibria*, **1991**, *67*, 173
9. P. Li, Z. H. Xu, *J. Chem. Ind. Eng.* (China), **1993**, *44*(2), 129
10. R. Span, W. Wagner, *J. Phys. Chem. Ref. Data*, **1996**, *25*(6), 1509

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