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A cubic equation of state for vapor–liquid equilibrium calculations of nonpolar and polar fluids

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Abstract

A cubic perturbed hard body (CPHB) equation of state (EOS) was developed and applied for vapor–liquid equilibrium (VLE) calculations in this study. The repulsive part of this EOS was investigated in our previous work. It is a simplified expression of hard body equation which yielded satisfactory agreement to the molecular simulation data of hard molecules from a single sphere to long chain fluids. An empirical attractive term was combined with the repulsive contribution, and the total EOS was written in a cubic form. This EOS has three parameters for each real pure fluid. Pure fluid parameters were regressed in this study for nonpolar and polar fluids. Satisfactory calculated results of the saturated properties of pure fluids were obtained. The accuracy of the CPHB EOS is better than that of other two- or three-parameter cubic MSRK, CCOR, PT or PRSV2 EOSs. VLE calculations on fluid mixtures were also investigated using the van der Waals mixing rules. The CPHB EOS again gave good results, which are comparable to those from other cubic EOSs. © 1997 Elsevier Science B.V.

Keywords: Equation of state; Cubic; Vapor–liquid equilibria; Method of calculation; Nonpolar and polar

1. Introduction

Equation of state (EOS) models, especially cubic type EOSs, have been extensively employed in phase equilibrium calculations for chemical process design. A cubic EOS comprises two parts due to the repulsive and attractive forces between molecules. Various applications of the simplified forms of the Carnahan–Starling hard sphere EOS ([1]) for the repulsive part of a cubic EOS have been presented in literature. Examples are the CCOR EOS ([2]) and the perturbed hard sphere EOS (e.g., [3,4]). For nonspherical hard cores, an extra parameter is needed to describe their shapes. For example, Boublik [5] used a nonspherical factor α for hard fused bodies in his improved scaled

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particle theory (ISPT). Walsh and Gubbins [6] developed the modified thermodynamic perturbation theory (MTPT) of polymerization, which can suitably simulate the thermodynamic properties of hard chain molecules of various shapes ([7]). Chen et al. [8] used a simplified form of the Walsh–Gubbins equation as the repulsive part of an EOS. A non-spherical shape parameter was employed for hard molecules of various shapes and geometries. Compressibility factors of tangent and fused hard fluids from a single sphere to a hard chain of 201 tangent spheres were calculated, and the results are in good agreement with the computer simulation data from literature. Chen et al. [8] have used this repulsive equation and an empirical attractive part to develop a cubic perturbed hard body (CPHB) EOS. They have shown good calculation results for nonpolar fluids and their mixtures. In this study, we extended the CPHB EOS to calculations on both nonpolar and polar fluids. This EOS has a good theoretical basis for the repulsive part and can describe well the phase behavior of fluids with appropriate real fluid parameters. New EOS parameters were correlated and comparisons of the calculated results with other cubic type EOSs were presented.

2. Development of the CPHB EOS

Walsh and Gubbins [6] had developed their hard-body EOS, which expressed the compressibility factor as a function of the packing fraction and a nonspherical factor. Chen et al. [8] applied the Walsh–Gubbins EOS and simplified it into the following form:

$$Z^{\text{rep}} = \frac{V + k_1 b}{V - k_2 b} \quad (1)$$

where b is the hard core volume and b/V represents the packing fraction. k_1 and k_2 are two parameters which are functions of the shapes of hard molecules that vary from a single sphere to chainlike molecules. These k parameters were determined by regression of molecular simulation data of hard fluids. According to our previous work, they were correlated as:

$$k_1 = 4.8319\alpha - 1.5515 \quad (2)$$

$$k_2 = 1.8177 - 0.1778\alpha^{-1.3686} \quad (3)$$

where α is a nonspherical factor that characterizes various shapes of molecules. For a single hard sphere, α is unity and Eq. (1) reduces to approximate the Carnahan–Starling EOS ([1]). Chen et al. [8] have shown that Eq. (1) represented well the compressibility factors for various nonspherical hard molecules with different α values. To complete the EOS, an empirical attractive term was added to Eq. (1):

$$P = \frac{RT(1 + k_1 b/V)}{V - k_2 b} - \frac{a}{V(V + c)} \quad (4)$$

where a , b and c are EOS parameters that are determined from the critical properties of pure fluids. At the critical point, the CPHB EOS satisfies the following conditions:

$$(\partial P / \partial V)_c = (\partial^2 P / \partial V^2)_c = 0 \quad (5)$$

$$P_c V_c / (RT_c) = \zeta_c \quad (6)$$

Applying the above criteria, the EOS parameters a , b and c were then determined by:

$$a = \frac{\Omega_{ac} R^2 T_c^2}{P_c} F_1(T) \quad (7)$$

$$b = \frac{\Omega_{bc} R T_c}{P_c} F_2(T) \quad (8)$$

$$c = \frac{\Omega_{cc} R T_c}{P_c} \quad (9)$$

Parameters a and b are treated as temperature-dependent and F_1 and F_2 are two functions of the reduced temperature. Ω_{ac} , Ω_{bc} and Ω_{cc} were determined from the following equations:

$$k_2^3 \Omega_{bc}^3 + (2k_1 k_2 + 2k_2^2 - 3k_2^2 \zeta_c) \Omega_{bc}^2 + (k_1 + k_2 - 3k_1 \zeta_c - 3k_2 \zeta_c + 3k_2 \zeta_c^2) \Omega_{bc} - 3\zeta_c = 0 \quad (10)$$

$$\Omega_{cc} = 1 + k_2 \Omega_{bc} - 3\zeta_c \quad (11)$$

$$\Omega_{ac} = \frac{\zeta_c^3 - k_1 \Omega_{bc} \Omega_{cc}}{k_2 \Omega_{bc}} \quad (12)$$

Parameter ζ_c , the nonspherical factor α , and the temperature-dependent functions F_1 and F_2 were determined for each pure fluid. These values were then correlated by generalized equations of pure fluid parameters. To evaluate the EOS parameters, the equal fugacity criterion on each isotherm of the saturation curve was applied in this study:

$$f^V = f^L \quad (13)$$

The fugacity coefficient expression of the CPHB EOS is:

$$\ln \frac{f}{P} = Z - 1 - \ln Z + \frac{k_1 + k_2}{k_2} \ln \frac{Z}{Z - k_2 B} + \frac{A}{C} \ln \frac{Z}{Z + C} \quad (14)$$

where

$$A = Pa / (RT)^2 \quad (15)$$

$$B = Pb / RT \quad (16)$$

$$C = Pc / RT \quad (17)$$

Using the experimental data of saturated vapor pressure and liquid molar volume, ζ_c , α , F_1 and F_2 values were regressed for each pure fluid. The following objective function was minimized in the regressions:

$$Q = \frac{100}{N_P} \sum_i^{NP} \left| \frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right| + \frac{100}{N_V} \sum_j^{NV} \left| \frac{V_j^{\text{cal}} - V_j^{\text{exp}}}{V_j^{\text{exp}}} \right| \quad (18)$$

This EOS was also applied for the VLE calculations of both nonpolar and polar fluid mixtures. In mixture calculations, the following mixing rules were used to determine the mixture parameters from the constituent components:

$$a_m = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (19)$$

$$b_m = \sum x_i b_i \quad (20)$$

$$c_m = \sum x_i c_i \quad (21)$$

$$\alpha_m = \sum x_i \alpha_i \quad (22)$$

The fugacity coefficient of component i in a mixture is expressed as:

$$\begin{aligned} \ln \hat{\phi}_i = & \ln \frac{V}{V - k_2 b} - \frac{a(\partial nc / \partial n_i)}{RT(c^2 + cV)} + \frac{1}{RT} \left(\frac{1}{nc} \frac{\partial n^2 a}{\partial n_i} - \frac{a}{c^2} \frac{\partial nc}{\partial n_i} \right) \ln \frac{V}{V + c} \\ & + \frac{(k_1 + k_2)[k_2(\partial nb / \partial n_i) + nb(\partial k_2 / \partial n_i)]}{k_2 V - k_2^2 b} \\ & - \ln Z + \frac{[(k_1 k_2 + nk_2(\partial k_1 / \partial n_i) - nk_1(\partial k_2 / \partial n_i))]}{k_2^2} \ln \frac{V}{V - k_2 b} \end{aligned} \quad (23)$$

where

$$\frac{1}{n} \frac{\partial n^2 a}{\partial n_i} = 2 \sum_j x_j a_{ji} \quad (24)$$

$$\frac{\partial nb}{\partial n_i} = b_i \quad (25)$$

$$\frac{\partial nc}{\partial n_i} = c_i \quad (26)$$

$$n \frac{\partial k_1}{\partial n_i} = 4.8319(\alpha_i - \alpha) \quad (27)$$

$$n \frac{\partial k_2}{\partial n_i} = 0.2433 \alpha_i^{-2.3686} (\alpha_i - \alpha) \quad (28)$$

For the VLE calculations of fluid mixtures, the fugacity of component i in the equilibrium liquid and vapor phases are equal:

$$\hat{f}_i^v = \hat{f}_i^l \quad (29)$$

Table 1
Pure fluid parameters and comparison of pure fluid calculation results

Compound	Temp. Range (K)		No. of data pts.		C_1	C_2	C_3	AAD (%)		Data ref.
	P^V	V^L	P^V	V^L				P^V	V^L	
Argon	83–148	94–148	67	55	2.88480	1.29716	0.26406	1.79	3.56	[30]
Krypton	116–208	116–208	47	46	2.61571	1.09862	–0.02402	1.34	3.73	[30]
Oxygen	74–152	89–152	80	65	2.10809	1.46570	–0.71923	1.87	2.71	[30]
Nitrogen	63–125	68–125	64	59	1.45165	1.61732	–1.28579	1.30	2.76	[30]
Carbon dioxide	217–302	217–302	42	42	–0.56727	3.58918	–4.71014	0.08	1.02	[30]
Sulfur dioxide	203–428	323–431	31	20	–1.10328	3.45813	–4.38037	0.69	0.55	[30]
Hydrogen chloride	159–240	170–230	11	8	1.05583	1.47471	–0.93925	0.69	2.03	[27]
Ammonia	200–406	200–390	22	20	0.55909	1.98982	–1.80059	0.23	2.13	[30]
Water	273–647	273–647	97	97	0.28111	2.18987	–2.03823	0.17	3.11	[30]
Methane	91–187	111–185	44	34	2.24945	1.25414	–0.40022	1.73	2.5	[29]
Ethane	163–300	163–300	29	29	1.15111	1.93724	–1.59748	0.91	2.83	[29]
Propane	173–363	173–363	31	31	0.26010	2.35833	–2.60292	0.55	2.26	[29]
Butane	217–392	217–392	28	28	–0.68396	2.92231	–3.55943	0.29	1.03	[29]
Isobutane	187–401	213–369	34	25	–0.51955	2.91328	–3.66925	0.62	0.92	[29]
Pentane	240–454	240–454	30	30	–1.24179	3.31679	–3.96418	0.08	0.57	[29]
2-Methylbutane	236–447	236–447	29	29	–1.12959	3.15123	–3.70518	0.24	0.97	[29]
2,2-Dimethylpropane	257–433	261–429	45	43	–0.90309	3.00982	–3.60081	0.10	1.11	[29]
Hexane	267–492	267–492	31	31	–1.12066	3.60780	–3.62742	0.28	0.82	[29]
2-Methylpentane	289–497	289–480	25	23	–1.15511	3.51122	–3.53593	0.59	1.06	[29]
3-Methylpentane	283–504	273–494	43	43	–1.19541	3.53845	–3.82397	0.18	0.79	[29]
2,2-Dimethylbutane	236–488	274–463	41	31	–1.18724	3.17705	–3.50889	0.27	0.43	[29]
2,3-Dimethylbutane	259–499	275–489	45	40	–1.20558	3.28965	–3.56648	0.33	0.71	[29]
Heptane	280–507	280–507	29	29	–0.66819	3.65474	–2.57040	0.24	1.23	[29]
2-Methylhexane	284–524	284–512	41	40	–0.75177	3.62326	–2.77636	0.53	1.03	[29]
3-Methylhexane	283–529	288–523	44	42	–0.79082	3.39884	–2.42917	0.68	0.82	[29]
3-Ethylpentane	300–532	300–523	28	27	–0.83184	3.69644	–3.06484	0.43	1.15	[29]
2,2-Dimethylpentane	286–512	286–503	28	27	–0.93326	3.47375	–2.96623	0.43	0.66	[29]
2,3-Dimethylpentane	260–529	297–522	37	31	–0.90001	3.49629	–2.85731	0.94	1.00	[29]
2,2,3-Trimethylbutane	290–525	273–513	41	42	–1.06114	3.19238	–2.86120	0.23	0.53	[29]
Octane	312–544	312–544	30	30	–0.18867	3.76582	–1.56481	0.66	1.04	[29]
Nonane	333–503	313–423	34	12	0.16220	3.41296	0.63763	0.92	0.83	[28]
<i>n</i> -Decane	353–523	333–443	33	12	0.41578	3.07020	2.86173	1.54	0.53	[28]
<i>n</i> -Undecane	371–498	353–473	28	13	0.54595	2.65026	5.14323	1.72	0.68	[28]
<i>n</i> -Dodecane	405–510	373–483	24	12	0.52746	2.12014	6.96426	1.50	0.86	[28]
<i>n</i> -Tridecane	422–529	393–513	24	13	0.45078	1.75135	7.71931	1.80	1.04	[28]
<i>n</i> -Tetradecane	438–548	413–523	24	12	0.24487	1.58747	6.09753	1.53	0.73	[28]
<i>n</i> -Pentadecane	409–577	423–543	30	13	–0.20370	1.35564	2.79036	1.59	0.42	[28]
<i>n</i> -Hexadecane	462–573	443–553	24	12	–0.22827	2.32076	–4.39664	1.91	1.01	[28]
Ethene	120–281	120–277	41	40	1.22085	1.76200	–1.58983	1.68	4.10	[29]
Propene	163–364	188–364	33	29	0.50218	2.47508	–2.68570	0.98	2.57	[29]
1-Butene	215–413	215–388	40	35	–0.52298	2.81798	–3.33942	0.19	1.99	[29]
1-Pentene	221–463	221–443	37	34	–1.17322	3.14751	–3.88858	0.21	0.43	[29]
1-Hexene	283–353	283–334	45	33	–1.23842	3.36936	–3.63016	0.09	0.03	[29]
Benzene	284–550	284–550	42	42	–1.06972	2.94098	–3.54694	0.20	0.51	[29]
Ethylbenzene	297–616	297–487	33	20	–0.86490	3.30361	–2.34217	0.82	0.53	[29]
Toluene	282–546	282–546	29	29	–1.15521	3.08131	–2.78948	0.16	1.15	[29]

Table 1 (continued)

Compound	Temp. Range (K)		No. of data pts.		C_1	C_2	C_3	AAD (%)		Data ref.
	P^V	V^L	P^V	V^L				P^V	V^L	
<i>o</i> -Xylene	303–630	303–612	38	36	–0.80773	3.35803	–2.15722	0.58	1.34	[29]
<i>m</i> -Xylene	302–616	302–582	37	33	–0.76506	3.25647	–1.94749	0.88	0.69	[29]
<i>p</i> -Xylene	296–616	296–491	42	26	–0.79954	3.19317	–1.87191	0.64	1.01	[29]
Cyclopropane	174–397	197–386	40	34	0.71588	2.07302	–1.97358	1.71	1.88	[29]
Cyclobutane	203–285	203–273	41	35	–0.33404	2.58199	–2.94394	0.32	1.62	[29]
Cyclopentane	229–510	229–503	40	39	–0.79429	2.89539	–3.48003	0.12	1.22	[29]
Cyclohexane	279–491	279–491	35	35	–1.12371	3.16102	–3.79000	0.13	0.52	[29]
Cycloheptane	283–604	290–575	45	40	–1.12610	3.26814	–3.21087	0.69	0.68	[29]
Propyne	217–401	217–387	40	37	–0.14506	2.97974	–3.55069	0.31	1.69	[29]
1-Butyne	202–282	242–282	41	21	1.34082	1.53164	–2.07124	0.34	0.11	[29]
Methanol	227–511	220–482	39	36	–1.73089	4.55337	–7.42214	1.02	0.96	[29]
Ethanol	231–511	231–503	36	35	–1.20047	7.36221	–13.2154	1.83	1.07	[29]
1-Propanol	280–525	280–517	30	29	–0.62505	8.21378	–13.9506	1.38	0.84	[29]
2-Propanol	279–500	230–494	33	39	–0.48940	8.56535	–15.6307	0.95	1.20	[29]
1-Butanol	295–556	295–548	32	31	–0.25057	8.00124	–12.9622	0.69	1.83	[29]
2-Butanol	281–525	281–488	34	29	–0.31623	7.17247	–11.7186	0.49	2.61	[29]
2-Methyl-1-propanol	300–543	300–535	29	28	–0.25259	7.82728	–12.7573	0.97	2.01	[29]
2-Methyl-2-propanol	304–443	304–443	35	35	–0.18159	8.45516	–14.5657	0.45	2.16	[29]
1-Pentanol	278–508	278–508	29	29	0.12884	7.60194	–11.0150	0.18	1.12	[29]
1-Hexanol	310–428	310–428	17	17	0.66938	10.8773	–12.9516	0.28	1.32	[29]
1-Heptanol	351–445	351–445	13	13	0.60239	6.42386	–6.55448	0.40	0.35	[29]
1-Octanol	364–549	364–549	23	23	0.77058	5.76596	–4.06642	0.90	0.13	[29]
1-Nonanol	366–481	366–481	15	15	0.82941	4.94632	–1.47716	0.26	0.05	[29]
1-Decanol	327–526	327–526	24	24	0.85601	4.35481	–0.43164	0.46	0.41	[29]
Acetone	253–508	253–493	35	33	–1.49247	2.54349	–3.10093	0.97	2.64	[29]
2-Butanone	272–536	272–319	35	7	–1.40259	3.30402	–3.87178	0.06	0.15	[29]
2-Pentanone	282–353	282–353	11	11	–1.05362	3.09769	–2.60213	0.07	0.20	[29]
3-Pentanone	282–353	282–353	11	11	–1.11238	3.91647	–4.29502	1.12	0.05	[29]
3-Methyl-2-butanone	276–549	288–319	45	6	–1.08925	3.64100	–3.55369	0.60	0.02	[29]
2-Hexanone	299–427	299–332	40	11	–0.56396	3.80167	–2.67369	0.04	0.31	[29]
3-Hexanone	299–407	297–324	44	12	–0.63368	3.74362	–2.73628	0.07	0.20	[29]
3,3-Dimethyl-2-butanone	284–405	295–353	45	22	–0.82022	3.92052	–3.27888	0.06	0.45	[29]
2-Heptanone	274–452	310–428	45	30	0.33118	5.29518	–2.25655	0.80	3.37	[29]
5-Nonanone	319–453	301–356	30	13	0.27963	2.19627	4.48415	2.82	0.41	[29]
Propylene oxide	361–478	–	22	–	–3.15125	–1.79198	–0.20938	0.26	–	[19]
Diethyl ether	250–467	293–370	59	8	–1.30277	3.47539	–4.15299	0.48	0.10	[14,22]
Methyl propyl ether	254–333	–	22	–	–1.11464	3.68290	–3.90947	0.08	–	[15]
Isopropyl methyl ether	250–325	–	20	–	–1.50462	2.76848	–3.61444	0.04	–	[15]
Butyl methyl ether	266–367	–	25	–	–1.19490	3.27202	–3.25247	0.07	–	[15]

Table 1 (continued)

Compound	Temp. Range (K)		No. of data pts.		C_1	C_2	C_3	AAD (%)		Data ref.
	P^V	V^L	P^V	V^L				P^V	V^L	
<i>t</i> -Butyl methyl ether	288–351	—	16	—	–2.08811	1.31380	–2.77846	0.05	—	[15]
Ethyl propyl ether	261–359	—	26	—	–0.42389	5.49225	–4.39952	0.01	—	[15]
Dipropyl ether	293–388	—	23	—	–0.39928	4.14864	–2.40607	0.007	—	[15]
Methyl phenyl ether	383–437	—	17	—	–0.87186	4.31379	–4.31540	0.004	—	[15]
Ethyl phenyl ether	391–454	—	18	—	–1.54123	0.30709	–0.01433	0.005	—	[15]
Ethanoic acid	304–415	293–490	27	14	–1.59208	2.20598	–2.69563	0.96	2.49	[22,16]
Propanoic acid	328–438	288–490	28	15	–0.63879	4.76718	–6.20723	0.91	2.44	[22,17]
Butyric acid	350–452	—	26	—	2.81838	22.5235	–19.6192	0.06	—	[17]
Benzene acid	405–523	403–453	8	6	0.55604	5.38674	–5.07857	1.10	0.61	[30]
Methyl formate	294–305	—	10	—	–0.67765	3.42796	–1.91868	0.80	—	[20]
Ethyl formate	277–327	—	13	—	–1.36645	3.30125	–4.08239	0.05	—	[20]
Propyl formate	299–355	—	16	—	–1.55669	2.60912	–3.47168	0.46	—	[20]
Methyl acetate	260–351	—	26	—	–1.49780	3.17459	–4.03031	0.03	—	[17]
Ethyl acetate	253–523	273–503	58	24	–0.95984	3.64834	–3.45716	0.28	0.76	[30,17]
Propyl acetate	290–399	297–373	28	10	–0.55197	3.52582	–2.25033	0.26	0.38	[17,24]
Butyl acetate	326–405	—	15	—	–1.19003	1.51766	–1.28465	0.02	—	[24]
Fluoro methane	132–288	144–296	38	37	0.03942	1.76605	–1.93107	0.50	1.35	[29]
Dichloro fluoro methane	245–450	207–439	38	43	–1.14537	2.87157	–3.00653	0.26	0.56	[29]
Trifluoro methane	141–298	191–298	45	31	–1.34377	3.05069	–3.66627	0.10	1.11	[29]
Trichloro methane	216–431	209–524	31	45	–1.05848	3.36860	–3.13252	0.99	1.24	[29]
Dichloro methane	212–503	212–414	40	28	–1.03726	2.53839	–3.17354	0.39	1.92	[29]
Tetrafluoro methane	89–227	92–183	45	30	–0.89309	2.85818	–3.27113	0.43	1.03	[29]
Trichloro fluoro methane	226–465	180–465	37	44	–0.99064	2.70948	–1.97476	0.53	1.07	[29]
Dichloro difluoro methane	172–383	151–378	41	44	–1.07475	2.75424	–2.57806	0.15	0.90	[29]
Chloro methane	193–398	193–398	40	40	0.31599	2.02707	–2.11970	0.56	1.98	[29]
Chloro difluoro methane	183–365	203–365	45	40	–1.20197	2.90998	–3.27968	0.25	0.88	[29]
1,1-Difluoro ethane	203–382	232–382	44	37	–1.38034	2.62107	–2.99642	1.63	1.06	[29]
1,2-Dichloro-1,1,2,2-tetrafluoro ethane	245–413	214–403	34	38	–0.13756	2.81518	0.85946	1.11	1.20	[29]
Chloro ethane	217–460	244–383	45	26	–0.79618	2.45677	–3.02460	0.40	1.99	[29]
1,2-Dichloro ethane	279–403	243–349	35	30	–1.16597	3.09077	–2.35803	0.03	0.46	[29]
Fluoro ethane	169–375	173–234	45	14	–0.55808	2.39104	–2.75868	0.29	0.19	[29]
1,1,2-Trichloro-1,2,2-trifluoro ethane	304–482	281–465	33	34	0.06220	2.71073	1.83349	1.76	0.84	[29]
1,1,1-Trifluoro ethane	251–371	243–336	43	33	–1.37474	2.65120	–2.88683	0.76	0.17	[29]

Table 1 (continued)

Compound	Temp. Range (K)		No. of data pts.		C_1	C_2	C_3	AAD (%)		Data ref.
	P^V	V^L	P^V	V^L				P^V	V^L	
1,1,1-Trichloroethane	173–346	200–327	45	33	–0.93841	2.56792	–1.23895	0.52	2.80	[29]
Hexafluorobenzene	283–387	—	23	—	18.0081	31.5650	12.1060	1.85	—	[20]
Methyl amine	190–267	—	13	—	–0.70116	2.84724	–4.22465	0.13	—	[20]
Dimethyl amine	201–280	—	13	—	–1.70652	4.80058	–8.95688	0.05	—	[20]
Trimethyl amine	193–277	—	19	—	–0.27031	4.27975	–4.51601	0.03	—	[20]
Diethyl amine	305–334	—	13	—	1.38154	10.2608	–8.24635	0.24	—	[20]
1-Propyl amine	296–351	—	12	—	1.4487	3.84500	–5.57313	0.006	—	[20]
2-Propyl amine	277–334	—	13	—	–1.42340	3.26901	–4.69386	0.005	—	[20]
2-Methyl-2-propyl amine	292–348	—	12	—	–1.11634	4.37654	–5.43046	0.005	—	[20]
<i>n,n</i> -Dimethylformamide	303–363	—	7	—	0.88067	7.55181	–5.22791	—	—	[20]
Aniline	331–699	293–453	16	17	–0.72183	4.00981	–3.52901	3.32	0.21	[30]
Acetonitrile	439–530	—	15	—	2.30928	8.67001	–5.96392	1.04	—	[25]
Tetrahydrofuran	296–373	—	15	—	–1.09099	2.63336	–3.17383	0.003	—	[20]
Pyridine	340–426	—	15	—	–1.29519	3.29104	–4.09374	0.01	—	[20]
2-Furfuraldehyde	329–434	—	34	—	3.45577	15.2371	–6.59535	0.87	—	[20]
<i>p</i> -Nitro toluene	417–512	—	18	—	3.71841	6.86415	5.84124	1.48	—	[18]
<i>m</i> -Cresol	407–594	—	22	—	–1.57900	0.75438	–1.86520	0.84	—	[20,26]
<i>o</i> -Cresol	393–464	—	5	—	0.52861	5.18826	–1.40940	0.22	—	[20]
<i>p</i> -Cresol	401–475	—	6	—	1.23334	6.79198	–2.37839	0.20	—	[20]
Phenol	345–456	329–449	35	38	–0.21334	4.70549	–3.49593	0.49	1.57	[29]
Methyl propionate	294–352	—	15	—	0.59544	7.27903	–4.54050	0.09	—	[20]
Grand Average			4409	3092				0.61	1.19	

One binary interaction parameter k_{ij} was employed in the VLE calculations of fluid mixtures. The objective function used in the VLE calculations to determine the optimal binary interaction parameters was:

$$Q' = \frac{100}{N} \sum \left[\left| \frac{P^{\text{cal}} - P^{\text{exp}}}{P^{\text{exp}}} \right| + |y^{\text{cal}} - y^{\text{exp}}| \right] \quad (30)$$

3. Results and discussion

For each pure fluid, α , ζ_c , and two temperature functions F_1 and F_2 were determined by regressing the saturated properties of pure compounds. Their values were then generalized as functions of pure fluid properties, such as the molecular weight (MW), acentric factor and the normal

Table 2

Comparison of calculated pure fluid vapor pressures and saturated liquid molar volumes by various EOS models

EOS models	No. of data points		AADP (%)		AADV ^L (%)	
	P^V	V^L	A	B	A	B
MSRK (A)/CPHB (B)	3150	2433	1.12	0.62	15.2	1.17
PRSV2 (A)/CPHB (B)	2109	1340	0.63	0.68	6.61	1.23
PT (A)/CPHB (B)	1735	1349	2.92	0.79	1.93	1.38
CCOR (A)/CPHB (B)	2726	2121	2.06	0.73	1.79	1.27

boiling temperature. Over 140 pure nonpolar and polar fluids were examined in the regression and the following generalized correlations were obtained:

$$\alpha = 1.0003 - 0.2719M + 3.7311M^2 - 1.0827M^3 + 0.1144M^4 - 4.1276 \times 10^{-3}M^5 \quad (31)$$

where

$$M = \frac{MW \times \omega}{39.948} \quad (32)$$

MW is the molecular weight and the constant 39.948 is the MW of argon. The acentric factor of argon is 0.001 and the α value of argon is zero, evaluated from the above equations. The physical significance of α is the nonspherical shape of a molecule. For fluids other than the simple spherical

Fig. 1. Comparison of saturated vapor pressures of benzene calculated by various equations of state.

molecules, the numerical values of α are always greater than unity. The temperature functions F_1 and F_2 were correlated by the following forms:

$$F_1 = \left[1 + C_1(1 - \sqrt{T_R}) + C_2(1 - T_R) \right]^2 \quad (33)$$

$$F_2 = \left[1 + C_3(1 - T_R^{2/3}) + C_4(1 - T_R^{2/3})^2 + C_5(1 - T_R^{2/3})^3 \right]^2 \quad (34)$$

In the last two equations, parameters C_2 and C_5 were generalized by the following functions of pure fluid properties:

$$C_2 = -1.4671 + 3.6889 \left(\frac{T_c}{\alpha T_b} \right) - 2.0005 \left(\frac{T_c}{\alpha T_b} \right)^2 + 5.2614 \sqrt{\omega Z_c} \quad (35)$$

$$C_5 = 7.9885 - 4.3604 e^{\omega} + 1.4554 MW \omega^{3.063} - 21.395 \alpha (\zeta_c - Z_c) - 4.0692 Z_c \alpha^{1.667} \quad (36)$$

The critical properties were either taken from literature or estimated by group contribution method ([9]). Parameter ζ_c was correlated by the following equation:

$$\zeta_c = 0.2974 + 0.1123 \omega - 0.9585 \omega Z_c + 7.7731 \times 10^{-4} \omega MW \left(\frac{T_b}{T_c} \right) \quad (37)$$

For the pure fluids investigated in this study, ζ_c values are close to their critical compressibility factors Z_c . The numerical values of ζ_c are always between 0.215 and 0.312. From the above correlations, it is concluded that for each pure fluid, there are three individual EOS parameters: C_1 , C_3 , and C_4 . Table 1 lists the pure fluid parameters of the CPHB EOS, and the deviations of the calculated saturated properties. Generally, the results are satisfactory where the absolute average

Fig. 2. Comparison of saturated liquid molar volumes of benzene calculated by various equations of state.

Fig. 3. Comparison of saturated vapor pressures of ethanol calculated by various equations of state.

calculated errors in vapor pressure and saturated liquid molar volume are about 1%. We have compared the calculated results from the CPHB EOS with those from other EOS models (MSRK, [10]; PRSV2, [11]; CCOR, [12]; PT, [13]). There are three parameters for the PRSV2 EOS, and other EOS models have two parameters for each pure fluid. The comparison of pure fluid calculations is shown in Table 2. The CPHB EOS has shown good calculation results on both vapor pressures and

Fig. 4. Comparison of saturated liquid molar volumes of ethanol calculated by various equations of state.

Fig. 5. Comparison of saturated vapor molar volumes of 1-pentanol calculated by various equations of state.

saturated liquid molar volumes. It is demonstrated that in over at least 1000 data points, the CPHB EOS yielded overall better results than those from other EOS models. Graphical comparisons are also presented for nonpolar and polar fluids. Figs. 1 and 2 shows the error distributions of the calculated vapor pressures and liquid molar volumes of benzene from various EOS. The CPHB EOS has the

Fig. 6. Comparison of heats of vaporization of ammonia calculated by various equations of state. (Data source: Smith and Srivasta, 1986 [29]).

Table 3
Comparison of the VLE calculation results of fluid mixtures from various cubic equations of state with their optimal binary interaction parameters

Binary System (component 1 + component 2)	Temp. Range (K)	Pressure Range (kPa)	Data pts.	AAD P(%)		MSRK		CCOR		PRSV2		AAD y_1 (%)		Data ref.
				PT	PT	MSRK	MSRK	CCOR	CCOR	PRSV2	PRSV2	PT	PT	
Methanol + water	308–338	7.33–96.96	33	2.56 (–0.087) ^a	2.56 (–0.087) ^a	1.89 (–0.087) ^a	1.89 (–0.087) ^a	2.01 (–0.040)	2.01 (–0.040)	1.97 (–0.085)	1.97 (–0.085)	2.71 (–0.068)	2.71 (–0.068)	[21]
Acetone + methanol	308–328	32.86–101.0	59	1.26 (–0.006)	1.26 (–0.006)	1.31 (–0.003)	1.31 (–0.003)	1.08 (–0.029)	1.08 (–0.029)	1.31 (–0.003)	1.31 (–0.003)	2.41 (–0.006)	2.41 (–0.006)	[21]
Methyl acetate + methanol	293–323	15.63–88.50	35	3.87 (0.020)	3.87 (0.020)	2.91 (0.021)	2.91 (0.021)	1.80 (0.021)	1.80 (0.021)	3.30 (0.020)	3.30 (0.020)	2.71 (0.038)	2.71 (0.038)	[21]
Acetone + ethanol	305–321	13.62–73.81	42	0.71 (0.018)	0.71 (0.018)	1.29 (0.022)	1.29 (0.022)	1.15 (0.022)	1.15 (0.022)	1.10 (0.022)	1.10 (0.022)	1.17 (–0.002)	1.17 (–0.002)	[21]
Ethyl formate + ethanol	318	32.92–73.30	12	3.35 (0.058)	3.35 (0.058)	2.31 (0.057)	2.31 (0.057)	1.40 (0.052)	1.40 (0.052)	2.38 (0.056)	2.38 (0.056)	1.77 (0.030)	1.77 (0.030)	[21]
Ethanol + water	313–343	10.12–72.59	39	4.86 (–0.107)	4.86 (–0.107)	4.35 (–0.108)	4.35 (–0.108)	3.41 (–0.095)	3.41 (–0.095)	4.94 (–0.106)	4.94 (–0.106)	2.57 (–0.097)	2.57 (–0.097)	[21]
Ethanol + 1-propanol	323–353	14.40–104.0	36	1.12 (0.014)	1.12 (0.014)	0.59 (0.013)	0.59 (0.013)	0.51 (0.006)	0.51 (0.006)	0.60 (0.015)	0.60 (0.015)	0.90 (0.009)	0.90 (0.009)	[21]
Benzene + 1-propanol	303–333	8.34–56.64	37	4.39 (0.077)	4.39 (0.077)	4.79 (0.081)	4.79 (0.081)	4.08 (0.070)	4.08 (0.070)	4.86 (0.079)	4.86 (0.079)	3.52 (–0.014)	3.52 (–0.014)	[21]
Ethyl acetate + 1-propanol	313–333	11.20–53.60	26	1.59 (0.018)	1.59 (0.018)	2.09 (0.023)	2.09 (0.023)	1.57 (0.033)	1.57 (0.033)	2.14 (0.021)	2.14 (0.021)	1.81 (0.019)	1.81 (0.019)	[21]
Dichloro methane + acetone	298–398	31.04–999.1	57	2.50 (–0.034)	2.50 (–0.034)	2.13 (–0.037)	2.13 (–0.037)	0.86 (–0.042)	0.86 (–0.042)	0.82 (–0.043)	0.82 (–0.043)	0.93 (–0.036)	0.93 (–0.036)	[23]
Acetone + benzene	298–318	15.55–67.19	31	2.37 (0.022)	2.37 (0.022)	1.10 (0.028)	1.10 (0.028)	1.22 (0.027)	1.22 (0.027)	1.18 (0.028)	1.18 (0.028)	2.52 (0.020)	2.52 (0.020)	[21]
Acetone + toluene	318	13.49–63.87	15	2.79 (0.033)	2.79 (0.033)	5.49 (0.063)	5.49 (0.063)	2.09 (0.027)	2.09 (0.027)	1.88 (0.034)	1.88 (0.034)	1.33 (0.032)	1.33 (0.032)	[21]
Methyl acetate + water	323–333	39.46–110.12	12	7.02 (–0.178)	7.02 (–0.178)	9.62 (–0.225)	9.62 (–0.225)	7.60 (–0.193)	7.60 (–0.193)	6.93 (–0.154)	6.93 (–0.154)	4.01 (–0.099)	4.01 (–0.099)	[21]
Pentane + dichloro methane	298–398	66.08–1186.957	57	0.88 (0.049)	0.88 (0.049)	1.14 (0.050)	1.14 (0.050)	1.42 (0.047)	1.42 (0.047)	0.62 (0.041)	0.62 (0.041)	1.27 (0.034)	1.27 (0.034)	[21]
Dichloro methane + benzene	298–348	14.68–294.8	38	2.53 (–0.001)	2.53 (–0.001)	1.73 (–0.005)	1.73 (–0.005)	0.64 (–0.014)	0.64 (–0.014)	0.32 (–0.008)	0.32 (–0.008)	0.62 (–0.013)	0.62 (–0.013)	[21]
Grand Average			529	2.46	2.46	2.32	2.32	1.73	1.73	1.94	1.94	1.87	1.87	1.98

^a Optimally fitted k_{ij} values for various EOS are shown in the parentheses.
Data reference: [21] Gmehling et al. (1978); [23] Khurma et al. (1983).

Table 4

Comparison of binary VLE calculation results using various equations of state

EOS models	No. of data points	AADP (%)		AAD _{y1} (%)	
		A	B	A	B
MSRK (A)/CPHB (B)	1462	3.67	3.25	4.18	3.69
PRSV2 (A)/CPHB (B)	646	3.93	3.66	4.21	3.65
PT (A)/CPHB (B)	630	3.96	3.69	4.12	3.64
CCOR (A)/CPHB (B)	674	2.06	2.20	2.88	2.70

smallest peak and average deviations over the entire reduced density range. Figs. 3 and 4 shows another comparison for the polar fluid of ethanol. It is demonstrated that except the CCOR and CPHB EOS, all other models have relatively larger errors in saturated liquid molar volume calculations. On the other hand, the CPHB EOS has the overall satisfactory results on vapor pressures. The deviations on saturated vapor volumes for 1-pentanol is shown in Fig. 5. It is again observed that the CPHB EOS shows superior results than those from other models. The heat of vaporization was derived from various models and the comparison for ammonia is presented in Fig. 6. It is demonstrated that the CPHB EOS has satisfactory temperature dependence and the heat of vaporization is satisfactorily determined from this EOS. The CPHB EOS gives satisfactory results on the saturated properties of pure fluids. It, however, still has some limitations beyond the saturation envelope. More efforts should be devoted to the application of this EOS to supercritical calculations.

VLE calculations were carried out for nonpolar and polar fluid mixtures. Traditional van der Waals mixing rules with one binary interaction parameter for the energy parameter of various EOS models

Fig. 7. Comparison of the calculated and the experimental VLE results of methanol and water mixture at various temperatures. (Data source: Gmehling et al., 1978 [21]).

Fig. 8. Comparison of the calculated and the experimental VLE results of acetone and methanol mixtures at various temperatures. (Data source: Gmehling et al., 1978 [21]).

were employed. The calculation results and the comparison of various EOS for typical binary mixtures are shown in Table 3. All EOS models show comparable VLE calculation results with their optimally adjusted binary parameters. Table 4 shows the overall comparison of VLE calculation results. The CPHB EOS yielded slightly better deviations than those from other methods. Graphical VLE calculation results are shown in Figs. 7 and 8 for the binary mixtures of methanol + water and acetone + ethanol, respectively. It is found that the CPHB EOS gives good agreement with the experimental Pxy data at various temperatures.

4. Conclusion

A CPHB EOS was developed for VLE calculations of pure fluids and fluid mixtures. The repulsive part of this EOS has good physical significance and it has been shown to be in satisfactory agreement with molecular simulation data. This EOS has been extended to real fluid calculations in this study. Pure compound parameters of the CPHB EOS were determined for extensive pure nonpolar and polar fluids. The CPHB EOS yielded satisfactory results on saturated properties of pure fluids. The absolute average deviations from this EOS are better than those from other commonly used cubic EOS. VLE calculations on fluid mixtures are also successful using this EOS. The overall accuracy for mixture calculations of this EOS is also slightly better compared to those of other EOS with their optimal binary parameters.

Nomenclature

a, b, c	Equation of state parameters
A, B, C	Parameters defined in Eqs. (15)–(17)
f	Fugacity
k	Parameter defined in Eqs. (2) and (3)

m	Binary interaction parameter
M	Parameter defined in Eq. (32)
MW	Molecular weight
n, N	Number of data points
P	Pressure
Q, Q'	Objective functions defined in Eqs. (18) and (30)
R	Gas constant
T	Temperature
V	Volume
x	Mole fraction
Z	Compressibility factor

Greek letters

α	Nonspherical factor
ζ	Parameter defined in Eq. (6)
ω	Acentric factor
Ω	Parameter defined in Eqs. (10)–(12)

Superscripts

L	Liquid phase
V	Vapor phase

Subscripts

b	Normal boiling point
c	Critical property
i, j	Component i or j
m	Mixture parameter
R	Reduced property

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