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Application of a volume-translated Peng–Robinson equation of state on vapor–liquid equilibrium calculations

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Abstract

A volume-translated Peng–Robinson (VTPR) equation of state (EOS) is developed in this study. Besides the two parameters in the original Peng–Robinson equation of state, a volume correction term is employed in the VTPR EOS. In this equation, the temperature dependence of the EOS energy parameter was regressed by an improved expression which yields better correlation of pure-fluid vapor pressures. The volume correction parameter is also correlated as a function of the reduced temperature. The VTPR EOS includes two optimally fitted parameters for each pure fluid. These parameters are reported for over 100 nonpolar and polar components. The VTPR EOS shows satisfactory results in calculating the vapor pressures and both the saturated vapor and liquid molar volumes. In comparison with other commonly used cubic EOS, the VTPR EOS presents better results, especially for the saturated liquid molar volumes of polar systems. VLE calculations on fluid mixtures were also studied in this work. Traditional van der Waals one-fluid mixing rules and other mixing models using excess free energy equations were employed in the new EOS. The VTPR EOS is comparable to other EOS in VLE calculations with various mixing rules, but yields better predictions on the molar volumes of liquid mixtures. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Equation of state; Volume translation; Nonpolar component; Polar component; Vapor–liquid equilibria

1. Introduction

Modifications of equations of state are important to the design and simulation of chemical processes. Taking the cubic-type EOS for example, many efforts have been devoted to improve the temperature dependence of the energy parameter (e.g., Refs. [1–3]). This approach results in accurate

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Table 1

Calculated results of saturated vapor pressures and liquid molar volumes of nonpolar and polar pure fluids using the VTPR equation of state

Compounds	Temperature range (K)		Data points		<i>N</i>	<i>k</i> ₃	This work		Data sources
	<i>P</i> ^V	<i>V</i> ^L	<i>P</i> ^V	<i>V</i> ^L			AAD (<i>P</i>)%	AAD (<i>V</i> ^L)%	
Argon	84–149	84–148	68	67	0.03877	0.25486	0.70	0.90	[14]
Krypton	116–208	116–206	47	46	0.05519	0.21040	0.64	1.00	[14]
Oxygen	66–152	72–152	88	82	0.09137	0.25742	0.85	1.02	[14]
Nitrogen	63–125	63–124	64	63	0.09967	0.24086	0.46	1.01	[14]
Carbon dioxide	217–302	217–298	42	33	0.11333	0.28996	0.29	1.46	[14]
Sulfur dioxide	203–428	338–423	31	15	0.21833	0.26345	1.14	1.02	[14]
Hydrogen chloride	159–240	170–230	11	8	0.07253	0.07685	0.89	0.05	[15]
Ammonia	200–406	200–360	22	16	0.15327	0.01978	0.40	1.07	[14]
Methane	91–190	91–187	45	44	0.08248	0.20978	0.53	1.19	[16]
Ethane	163–304	163–295	30	28	0.11292	0.20077	0.47	0.89	[16]
Propane	173–357	173–357	30	30	0.16846	0.22685	0.84	1.05	[16]
Butane	217–392	217–392	28	28	0.15546	0.25370	0.83	0.55	[16]
Isobutane	200–401	213–369	32	25	0.18381	0.25559	1.07	0.47	[16]
Pentane	240–454	240–454	30	30	0.16851	0.26392	0.77	0.94	[16]
2-Methyl butane	236–447	236–440	29	28	0.14908	0.27640	0.58	0.96	[16]
2,2-Dimethyl propane	257–433	261–425	45	42	0.14564	−0.27786	0.46	1.37	[16]
Hexane	282–492	267–492	28	31	0.16397	0.27558	1.05	1.06	[16]
2-Methyl pentane	289–497	289–480	25	22	0.15545	0.27999	0.50	1.01	[16]
3-Methyl pentane	283–504	273–494	43	42	0.16917	0.28046	0.78	1.09	[16]
2,2-Dimethyl butane	236–488	274–463	41	31	0.17424	0.27632	0.84	0.68	[16]
2,3-Dimethyl butane	259–499	275–489	45	39	0.16302	0.27750	0.74	1.04	[16]
Heptane	304–507	280–523	25	31	0.17822	0.26154	1.17	1.08	[16]
2-Methyl hexane	284–524	284–512	41	40	0.19917	0.28434	0.67	1.16	[16]
3-Methyl hexane	283–529	288–518	44	41	0.19433	0.27525	0.52	1.15	[16]
3-Ethyl pentane	300–532	300–523	28	26	0.18450	0.29840	0.64	1.15	[16]
2,2-Dimethyl pentane	286–512	286–503	28	27	0.18038	0.29821	0.67	0.70	[16]
2,3-Dimethyl pentane	260–529	297–522	37	30	0.20322	0.30495	0.58	1.02	[16]
2,2,3-Trimethyl butane	290–525	273–513	41	42	0.16463	0.30112	0.64	0.93	[16]

Table 1 (continued)

Compounds	Temperature range (K)		Data points		N	k_3	This work		Data sources
	P^V	V^L	P^V	V^L			AAD (P)%	AAD (V^L)%	
2,2,4-Trimethyl pentane	291–535	291–527	30	29	0.18330	0.31944	0.90	1.01	[16]
Octane	320–544	312–552	29	30	0.19773	0.24145	0.98	1.06	[16]
n-Decane	283–588	333–443	44	12	0.25192	0.17726	1.20	0.28	[16–19]
n-Undecane	348–499	353–473	30	13	0.24055	0.13471	0.61	0.53	[16,18,20]
n-Dodecane	353–588	373–483	13	12	0.28162	0.08256	0.91	0.51	[16–18]
n-Tridecane	380–540	393–513	30	13	0.23996	0.03898	0.81	0.62	[16,18,20]
n-Tetradecane	373–588	413–523	16	12	0.29092	−0.02270	0.74	0.40	[16–18]
n-Pentadecane	435–577	423–543	28	13	0.17570	−0.06416	0.80	0.42	[16,18,20]
n-Hexadecane	393–583	443–553	20	12	0.32062	−0.12198	0.60	0.29	[16,17,18,20]
n-Heptadecane	461–609	453–573	28	13	0.21106	−0.18978	0.84	0.57	[18,20]
n-Octadecane	413–588	473–583	17	12	0.33351	−0.19293	0.74	0.60	[17,18]
n-Nonadecane	423–588	463–593	16	15	0.34965	−0.20808	1.10	0.74	[17,18]
n-Eicosane	388–583	473–613	41	15	0.39354	−0.20140	1.76	0.78	[17–19]
n-Docosane	453–523	473–750	12	33	0.44472	0.02619	1.89	1.21	[17,18]
n-Tetracosane	453–533	460–774	9	36	0.51055	0.26662	1.68	1.69	[17,18]
n-Octacosane	503–533	535–635	10	13	0.76902	1.85456	1.87	1.23	[17–19]
Ethene	120–281	128–277	41	37	0.14312	0.19916	0.86	1.06	[16]
Propene	163–364	176–364	33	30	0.15774	0.25091	0.87	1.19	[16]
1-Butene	215–413	215–388	40	35	0.14186	0.24347	0.56	0.77	[16]
1-Pentene	221–463	221–443	37	34	0.18205	0.23578	0.84	0.94	[16]
1-Hexene	283–353	283–334	33	45	0.18829	0.23050	0.14	0.10	[16]
Benzene	284–543	284–543	41	41	0.19292	0.22169	0.90	0.90	[16]
Ethylbenzene	297–616	297–487	33	20	0.19837	0.24148	0.88	0.57	[16]
Toluene	301–546	282–546	27	29	0.16898	0.28740	0.93	0.92	[16]
<i>o</i> -Xylene	303–630	312–612	38	35	0.18030	0.25739	0.98	1.11	[16]
<i>m</i> -Xylene	302–616	302–582	37	33	0.17577	0.22372	0.79	0.78	[16]
<i>p</i> -Xylene	296–616	296–491	42	26	0.17247	0.21869	0.97	0.52	[16]
Cyclopropane	203–397	197–386	35	32	0.12271	0.18443	0.96	1.41	[16]
Cyclobutane	203–285	203–273	41	35	0.13612	0.29062	0.54	0.97	[16]
Cyclopentane	229–510	229–496	40	38	0.18433	0.26814	0.81	1.28	[16]
Cyclohexane	279–541	279–535	43	42	0.19138	0.26575	0.83	0.94	[16]
Cycloheptane	283–604	297–575	45	39	0.19322	0.30608	0.55	0.96	[16]
Propyne	217–401	217–387	40	37	0.16686	0.23182	0.80	0.79	[16]
1-Butyne	212–282	242–282	36	21	0.50745	0.03694	1.19	0.05	[16]
Fluoromethane	132–288	144–292	38	34	0.12077	−0.03299	0.57	1.16	[16]
Dichlorofluoro methane	245–450	207–439	38	42	0.20585	0.23148	0.61	1.03	[16]
Trifluoro methane	141–298	191–298	45	27	0.15225	0.16622	0.86	0.99	[16]

$$\text{AAD } (\%) = \frac{100}{n} \sum [|X^{\text{exp}} - X^{\text{cal}}| / X^{\text{exp}}]; \quad X = P \text{ or } V^L.$$

prediction of saturated vapor pressures. It, however, does not necessarily yield the accurate volumetric behavior of fluids and their mixtures. On the other hand, a volume translation can be adopted in the EOS. Martin [4] has pointed out that with the volume translation, an EOS can be made more realistic.

Table 2

Calculated results of saturated vapor pressures and liquid molar volumes of nonpolar and polar pure fluids using the VTPR equation of state

Compounds	Temperature range (K)				k_3	This work		Data sources	
	P^V	V^L	P^V	V^L		AAD (P)%	AAD (V^L)%		
Trichloromethane	244–431	259–524	27	38	0.16945	0.31307	0.76	0.98	[16]
Dichloromethane	220–503	212–414	39	28	0.25264	0.10812	0.92	0.49	[16]
Tetrafluoromethane	89–227	107–183	45	25	0.17605	0.31695	0.97	0.91	[16]
Trichlorofluoromethane	226–465	219–465	37	38	0.16940	0.26791	0.72	1.30	[16]
Dichlorodifluoromethane	177–383	182–378	40	38	0.16366	0.26461	0.92	1.21	[16]
Chloromethane	193–398	193–398	40	39	0.14825	0.11442	0.55	1.00	[16]
Chlorodifluoromethane	183–365	203–357	45	38	0.17359	0.20674	0.50	1.10	[16]
1,1-Difluoroethane	215–382	232–357	44	31	0.01995	0.09867	1.42	0.93	[16]
1,2-Dichloro-1,1,2,2-tetra fluoroethane	245–413	214–403	31	38	0.21240	0.32566	1.15	1.07	[16]
Chloroethane	217–460	244–383	45	19	0.13881	0.07090	0.78	1.23	[16]
1,2-Dichloroethane	279–403	261–349	35	25	0.12569	0.26278	0.83	1.03	[16]
Fluoroethane	169–375	173–234	45	14	0.13388	0.13826	0.32	0.77	[16]
1,1,2-Trichloro-1,2,2-tri fluoroethane	304–482	281–465	33	34	0.16091	0.31131	0.23	1.04	[16]
1,1,1-Trifluoroethane	173–346	200–315	45	26	0.17242	0.12161	0.32	1.45	[16]
1,1,1-Trichloroethane	251–371	243–336	42	33	0.19610	0.23948	0.63	1.10	[16]
Methanol	235–511	220–474	34	28	0.03221	−0.04426	1.45	1.38	[16]
Ethanol	271–511	239–463	31	26	0.20761	0.02687	0.73	1.17	[16]
1-Propanol	280–525	280–492	30	26	0.40666	0.11811	0.72	1.01	[16]
2-propanol	279–480	265–376	30	17	0.45120	0.04776	0.64	0.08	[16]
1-Butanol	295–556	295–523	32	31	0.54197	0.16820	0.41	0.75	[16]
2-Butanol	281–525	281–488	34	29	0.61833	0.15436	0.60	0.54	[16]
2-Methyl-1-propanol	300–543	300–526	29	26	0.55775	0.16725	0.52	1.19	[16]
2-Methyl-2-propanol	304–443	304–443	35	35	0.64017	0.14725	0.37	0.28	[16]
1-Pentanol	319–401	336–557	11	28	0.66083	0.19857	0.27	0.71	[16]
1-Hexanol	324–428	310–532	9	31	0.72399	0.22577	1.12	0.92	[16]
1-Heptanol	351–445	351–595	12	32	0.68053	0.22027	1.10	0.72	[16]
1-Octanol	372–524	364–617	18	31	0.57262	0.19203	1.44	1.09	[16]
1-Nonanol	366–481	366–653	12	36	1.00074	0.19903	1.03	0.94	[16]
1-Decanol	379–509	327–622	13	33	0.53213	0.07796	1.54	1.09	[16]
Phenol	391–446	368–449	18	26	0.15996	0.50681	1.05	0.89	[16]
Cyclohexanol	364–489	305–430	18	18	0.45851	0.06946	1.18	0.19	[16]
Acetone	253–508	253–463	35	26	0.14457	0.05648	0.66	1.20	[16]
2-Butanone	272–536	272–319	35	7	0.16786	0.14610	0.85	0.17	[16]
2-Pentanone	282–353	282–353	11	11	0.19851	0.18962	0.85	0.25	[16]
3-Pentanone	285–544	285–347	43	11	0.22913	0.18669	0.27	0.30	[16]
3-Methyl-2-butanone	276–500	288–319	37	6	0.18722	0.25482	0.62	0.53	[16]
2-Hexanone	299–427	299–332	40	11	0.19036	0.23240	0.70	0.35	[16]
3-Hexanone	312–394	299–324	34	11	0.20545	0.22667	0.53	0.25	[16]
3,3-Dimethyl-2-butanone	295–405	295–353	41	22	0.19793	0.31412	0.58	0.53	[16]
2-Heptanone	335–432	310–408	25	25	0.03938	0.47751	0.90	0.86	[16]
5-Nonanone	324–485	301–356	36	13	0.24216	0.08138	0.82	0.18	[16]
4-Methyl-2-pentanone	286–500	286–373	33	14	0.25880	0.23928	0.96	0.52	[16]

Table 2 (continued)

Compounds	Temperature range (K)		Data points		N	k_1	This work		Data sources
	P^V	V^L	P^V	V^L			AAD (P)%	AAD (V^L)%	
Cyclohexanone	322–511	308–350	28	7	–0.03808	0.10161	0.86	0.13	[16]
Dimethylether	177–248	200–338	12	56	0.14752	0.25491	1.54	0.57	[21]
Diethylether	250–467	239–374	59	45	0.19306	0.23807	0.73	1.05	[22,23]
Isopropylether	422–494	245–440	14	60	0.32629	0.35998	0.39	0.77	[21]
Methylpropylether	254–333	245–401	22	47	0.17155	0.27569	0.52	1.05	[21,24]
Isopropylmethylether	250–325	242–374	20	42	0.18563	0.26986	0.45	0.99	[21,24]
Dipropylether	293–388	272–431	23	52	0.15101	0.43450	0.41	1.01	[21,24]
Vinylethylether	366–472	269–416	20	47	0.05679	0.71583	0.73	0.65	[21]
Butylmethylether	266–367	257–413	25	49	0.17890	0.28760	0.52	0.98	[21,24]
Ethanoic acid	304–391	293–440	22	10	0.06516	–0.07838	0.68	0.79	[25]
Propanoic acid	308–347	293–443	13	17	0.06602	–0.06286	1.44	0.92	[25]
Butanoic acid	363–396	298–483	13	20	0.17767	0.04272	1.53	0.58	[25]
Pentanoic acid	377–405	298–483	11	20	0.17233	0.03134	1.46	0.76	[25]
Benzene acid	436–523	403–453	6	6	0.46639	0.69242	0.99	0.08	[14]
Methylacetate	260–351	273–493	25	23	0.18823	0.18493	1.13	1.12	[26]
Ethylacetate	271–523	273–473	29	21	0.22821	0.18793	0.67	0.53	[14,26]
Propylacetate	290–399	297–373	28	10	0.23291	0.18416	0.75	0.12	[26,27]
Butylacetate	326–405	273–383	15	13	0.22433	0.27146	0.47	0.89	[27]
Methyl formate	294–305	273–443	9	19	0.06879	0.17135	1.05	0.68	[18]
Ethyl formate	277–323	273–463	12	21	0.20279	0.18477	1.08	0.61	[18]
Propyl formate	308–355	273–513	13	26	0.19834	0.21727	1.01	0.67	[18]
1-Propylamine	296–330	233–431	7	64	0.08544	0.27094	1.92	1.14	[21,28]
2-Propylamine	277–334	230–431	9	64	0.15897	0.31352	1.67	1.26	[21,28]
Trimethylamine	221–276	200–413	16	72	0.13887	0.23705	1.18	0.91	[21,28]
Diethylamine	305–334	230–431	13	68	0.39534	0.17017	0.64	0.50	[21,28]
Water	273–647	289–578	97	60	0.11560	0.01471	0.97	1.69	[14]
Grand average			4182	3995			0.78	0.92	

$$\text{AAD (\%)} = \frac{100}{n} \sum |X^{\text{exp}} - X^{\text{cal}}| / X^{\text{exp}}; X = P \text{ or } V^L.$$

Translation along the volume axis affects the saturated density calculations, and leaves vapor pressure conditions unchanged. Peneloux et al. [5] used a linear volume translation in the SRK EOS [6] and correlated the volume translation parameter as a function of the Rackett compressibility factor. This method gives satisfactory results on nonpolar systems while large errors exist for polar fluids. Yu and Lu [7] also applied the volume translation technique to the Peng–Robinson EOS and presented the translated PR (TPR) EOS. Carrier et al. [8] used a volume translated cubic EOS to hydrocarbon systems and presented the parameters in a group contribution form. Their work was further extended to high pressure calculations by Rogalski et al. [9]. Watson et al. [10] employed the volume translation concept to the VDW-711 EOS and correlated the volume translation parameter as functions of the critical constants, the acentric factor and the reduced temperature. Magoulas and Tassios [11] presented a translated modified Peng–Robinson (t-mPR) EOS and showed obvious improvements on the liquid density calculations of alkanes. Satyro and Trebble [12] showed that the volume translation parameter for alkane molecules can be correlated as a function of their molecular weight. Very

Table 3
Comparison of the calculated results of nonpolar pure fluids using various cubic equations of state

Compounds	Temperature range (K)	P^V	V^L	Data points				MSRK				CCOR				t-mPR				This work		Data sources	
				P^V		V^L		P^V		V^L		AAD		AAD		AAD		AAD		AAD			
				(p)%		(V ^L)%		(p)%		(V ^L)%		(P)%		(V ^L)%		(P)%		(V ^L)%		(P)%			
Argon	84–149	84–148	68	67	0.91	9.18	0.40	3.94	0.81	1.38	1.95	1.85	0.70	0.90	[14]								
Oxygen	66–152	72–152	88	82	0.41	9.60	0.41	3.59	1.36	1.63	1.64	2.08	0.85	1.02	[14]								
Carbon dioxide	217–302	217–298	42	33	0.03	4.36	0.26	15.40	0.28	1.29	0.56	1.46	0.29	1.46	[14]								
Methane	91–190	91–187	45	44	0.29	8.15	0.25	4.99	1.03	1.42	1.14	0.70	0.53	1.19	[16]								
Ethane	163–304	163–295	30	28	0.17	5.85	0.21	7.85	0.71	0.95	0.86	0.42	0.47	0.89	[16]								
Propane	173–357	173–357	30	30	0.46	5.20	0.52	8.86	0.95	1.03	1.52	0.77	0.84	1.05	[16]								
Butane	217–392	217–392	28	28	0.30	3.87	0.31	9.56	0.87	1.00	1.31	1.14	0.83	0.55	[16]								
Pentane	240–454	240–454	30	30	0.20	3.29	0.26	12.74	0.68	1.25	1.05	0.84	0.77	0.94	[16]								
Hexane	282–492	267–492	28	31	0.32	2.91	0.65	14.59	0.92	1.63	1.49	1.11	1.05	1.06	[16]								
3-Methylpentane	283–504	273–494	43	42	0.27	3.55	0.44	13.07	0.73	1.90	1.06	1.39	0.78	1.09	[16]								
Heptane	304–507	280–523	25	31	0.31	3.19	0.69	16.70	0.89	1.37	1.52	0.88	1.17	1.08	[16]								
2,2,3-Tri-methylbutane	290–525	273–513	41	42	0.21	4.37	0.31	11.01	0.66	2.49	1.07	2.20	0.64	0.93	[16]								
Octane	320–544	312–552	29	30	0.33	4.60	0.50	18.34	0.72	1.31	1.55	0.85	0.98	1.06	[16]								
n-Decane	283–588	333–443	44	12	0.13	5.01	0.48	18.55	0.46	1.63	1.95	0.66	1.20	0.28	[16,17,19]								
n-Dodecane	353–588	373–483	13	12	0.06	7.81	0.18	21.76	0.30	0.73	1.50	0.40	0.91	0.51	[16,17]								
n-Tetradecane	373–588	413–523	16	12	0.18	10.38	0.34	24.71	0.64	0.84	1.82	0.30	0.74	0.40	[16–18]								
n-Hexadecane	393–583	443–553	20	12	0.12	13.03	0.43	27.71	0.87	3.39	1.79	0.38	0.60	0.29	[16–18]								
n-Octadecane	413–588	473–583	17	12	0.14	15.50	0.35	30.50	0.84	7.01	2.10	0.36	0.74	0.60	[17,18]								
n-Nonadecane	423–588	463–603	16	15	0.39	16.91	0.87	32.01	1.45	9.17	2.53	0.32	1.10	0.74	[17,18]								
n-Eicosane	388–583	473–613	41	15	0.34	18.06	0.36	33.34	1.22	11.79	2.09	0.16	1.76	0.78	[17–19]								
n-Docosane	453–573	473–749	12	33	0.16	8.63	0.23	22.65	0.66	4.73	1.73	2.72	1.89	1.21	[17,18]								
n-Tetracosane	453–533	460–774	9	36	0.07	12.02	0.09	26.40	0.38	10.85	1.49	2.96	1.68	1.69	[17,18]								
n-Octacosane	483–533	535–635	10	13	0.35	14.43	0.36	29.22	0.40	34.96	1.79	3.31	1.23	1.23	[17–19]								
Grand average			725	690	0.32	7.45	0.39	13.75	0.84	3.26	1.50	1.14	0.87	1.00									

$$\text{AAD} (\%) = \frac{100}{n} \sum [|X^{\text{exp}} - X^{\text{cal}}| / X^{\text{exp}}] ; X = P \text{ or } V.$$

Table 4
Comparison of the calculated results of polar pure fluids using various cubic equations of state

Compounds	Temperature range (K)				Data points				MSRK				CCOR				PRSV2				This work				Data sources	
	P^V		V^L		P^V		V^L		AAD		AAD		AAD		AAD		AAD		AAD		AAD					
			(P)%		(P)%		(P)%		(P)%		(P)%		(P)%		(P)%		(P)%		(P)%		(P)%		(P)%			
Ammonia	200–406	200–360	22	16	1.64	0.79	0.28	27.90	0.22	14.4	0.30	13.20	0.40	1.07	[16]											
Water	273–647	289–578	97	60	0.49	0.78	0.40	34.52	0.63	16.6	0.12	19.31	0.97	1.69	[16]											
Methanol	235–511	220–474	34	28	3.49	0.84	3.49	0.84	3.31	8.99	1.32	19.21	1.45	1.38	[16]											
Ethanol	271–511	239–463	31	26	1.81	1.01	1.81	1.01	2.16	2.72	0.12	7.71	0.73	1.17	[16]											
1-Propanol	280–525	280–492	30	26	5.07	1.34	2.09	17.02	1.87	5.71	0.59	3.78	0.72	1.01	[16]											
1-Butanol	295–556	295–523	32	31	7.86	1.04	1.41	15.66	2.40	6.04	0.10	2.48	0.41	0.75	[16]											
1-Hexanol	324–428	310–532	9	31	0.91	1.62	0.37	9.77	0.31	11.39	0.30	3.41	1.12	0.92	[16]											
1-Octanol	372–524	364–617	18	31	6.60	1.19	0.61	14.33	6.29	9.15	1.20	2.69	1.44	1.09	[16]											
1-Decanol	379–509	327–622	13	33	7.65	1.18	0.73	16.55	0.86	6.66	1.34	3.31	1.54	1.09	[16]											
Phenol	391–446	368–449	18	26	0.22	4.96	0.04	0.99	0.05	15.21	0.09	10.48	1.05	0.89	[16]											
Cyclohexanol	364–489	305–430	18	18	5.33	0.58	0.61	25.46	0.86	2.15	1.04	11.34	1.18	0.19	[16]											
Acetone	253–508	253–463	35	26	1.41	0.98	0.19	28.73	0.32	12.55	0.35	13.93	0.66	1.20	[16]											
3-Pentanone	285–544	285–347	43	11	2.71	0.44	0.91	18.80	0.38	3.26	0.09	5.34	0.27	0.30	[16]											
Cyclohexanone	322–511	308–350	28	7	4.56	0.30	0.53	26.99	0.28	6.40	0.62	12.74	0.86	0.13	[16]											
Diethyl ether	250–467	239–374	59	45	1.23	1.28	0.44	13.00	0.70	0.65	0.38	1.45	0.73	1.05	[21,23]											
Isopropyl methyl ether	250–325	242–374	20	42	0.65	1.49	0.11	10.60	0.08	1.94	0.09	2.76	0.45	0.99	[21,24]											
Vinyl ethyl ether	366–472	269–416	20	47	0.83	11.07	1.11	4.68	6.41	6.17	1.63	13.75	0.73	0.65	[21]											
Ethanoic acid	304–391	293–440	22	10	1.45	1.06	0.18	45.54	0.08	21.94	0.60	29.05	0.68	0.79	[25]											
Butanoic acid	363–396	298–483	13	20	1.19	1.06	0.12	22.86	0.12	0.75	1.39	8.86	1.53	0.58	[25]											
Benzene acid	436–523	403–453	6	6	3.49	0.28	1.15	18.51	1.11	5.29	1.05	5.25	0.99	0.08	[14]											
Ethyl acetate	271–523	273–473	29	21	2.08	1.00	0.24	20.27	0.11	2.92	0.15	6.44	0.67	0.53	[14,16]											
Butyl acetate	326–405	273–383	15	13	1.01	1.13	0.05	14.18	0.03	3.66	0.26	1.60	0.47	0.89	[27]											
Ethyl formate	277–323	273–463	12	21	1.66	2.39	0.05	18.12	5.61	3.34	0.17	4.11	1.08	0.61	[18]											
Trimethylamine	296–330	233–431	7	64	0.74	1.64	0.07	11.06	5.79	1.70	0.20	3.35	1.92	1.14	[21,28]											
2-Propylamine	305–334	230–431	13	68	1.42	0.84	0.01	10.31	0.12	2.81	1.52	2.65	0.64	0.50	[21,28]											
Grand average			644	727	2.44	1.92	0.77	15.25	1.32	6.5	0.48	7.61	0.83	0.93												

$$\text{AAD} (\%) = \frac{100}{n} \sum [|X^{\text{exp}} - X^{\text{cal}}| / X^{\text{exp}}] ; X = P \text{ or } V^L.$$

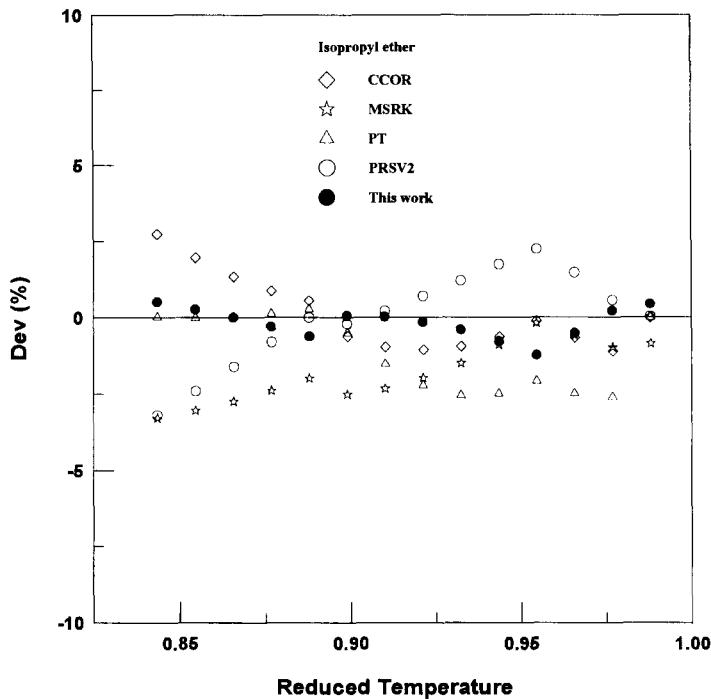


Fig. 1. Error distributions of the calculated saturated vapor pressures of isopropyl ether by various equations of state.

recently, Kenney et al. [13] developed a hard-sphere volume translated van der Waals EOS to model the supercritical water oxidation process. It is observed that the volume translation technique yields improved volume calculation results and previous investigations are usually limited to the nonpolar hydrocarbon systems. In this study, we apply the volume translated Peng–Robinson EOS to both nonpolar and polar fluids. Optimal pure fluid parameters are presented and their volumetric and phase equilibrium calculations are compared with those from other EOS methods.

1.1. Development of the VTPR EOS

Applying the volume translation technique, the VTPR EOS is written as:

$$P = \frac{RT}{V + t - b} - \frac{a}{(V + t)(V + t + b) + b(V + t - b)} \quad (1)$$

where t is the translated volume parameter with which the volume calculated by this EOS approaches the experimental value:

$$V_{\text{exp}} = V_{\text{EOS}} + t \quad (2)$$

The EOS parameters a and b are determined by the critical properties:

$$\left(\frac{\partial P}{\partial V} \right)_c = \left(\frac{\partial^2 P}{\partial V^2} \right)_c = 0 \quad (3)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (4)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (5)$$

Various expressions of α had been presented in literature. In this study, it is also correlated as a function of temperature. To determine the pure fluid parameters, the equal fugacity criterion was employed:

$$f^V = f^L \quad (6)$$

The fugacity coefficient of the VTPR EOS is:

$$\ln \phi = (Z + T^* - 1) - \ln(Z + T^* - B) - \frac{A}{2\sqrt{2}B} \ln \left[\frac{Z + T^* + (1 + \sqrt{2})B}{Z + T^* + (1 - \sqrt{2})B} \right] \quad (7)$$

where

$$A = \frac{Pa}{R^2 T^2} \quad (8)$$

$$B = \frac{Pb}{RT} \quad (9)$$

$$T^* = \frac{Pt}{RT} \quad (10)$$

Regressions of the saturated properties of pure fluids were carried out along the saturation curve with the following objective function:

$$OF = \frac{100}{n} \sum_i^n \frac{|P_i^{\text{exp}} - P_i^{\text{cal}}|}{P_i^{\text{exp}}} + \frac{100}{n} \sum_i^n \frac{|V_i^{\text{exp}} - V_i^{\text{cal}}|}{V_i^{\text{exp}}} \quad (11)$$

The VTPR EOS was also employed in VLE calculations where the following mixing rules were used:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (12)$$

$$a_{ij} = \sqrt{a_i a_j} (l - k_{ij}) \quad (13)$$

$$b_m = \sum_i x_i b_i \quad (14)$$

$$t_m = \sum_i x_i t_i \quad (15)$$

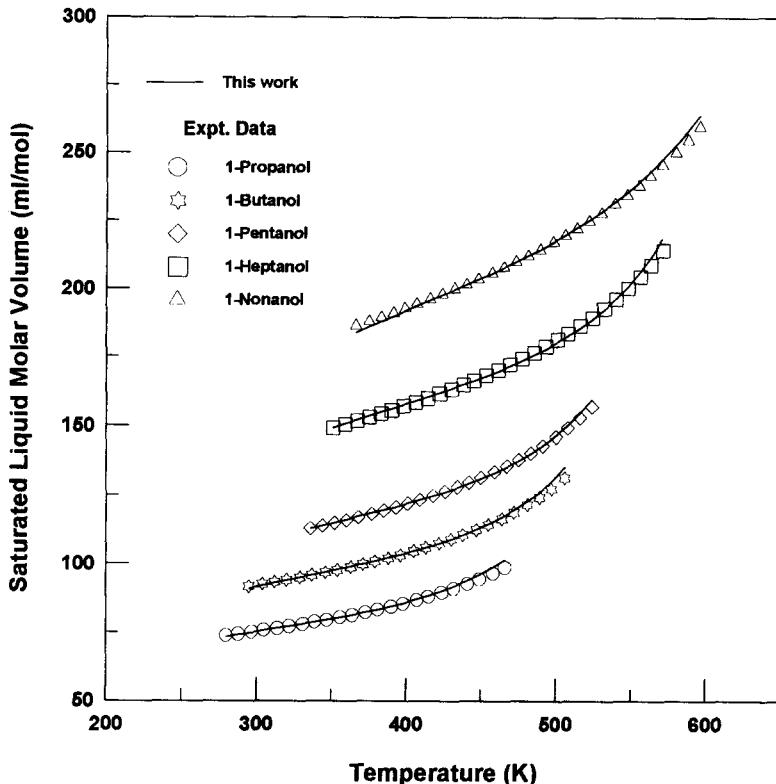


Fig. 2. Comparison of the calculated saturated liquid molar volumes of selected alcohols with experimental data [16].

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

$$\ln \bar{\phi}_i = \frac{b_i}{B} (Z + \bar{t} - 1) - \ln(Z + \bar{t} - 1) - \frac{A}{2\sqrt{2}B} \left[\frac{2 \sum_j x_j a_{ij}}{A} - \frac{b_i}{B} \right] \ln \left[\frac{Z + \bar{t} + (1 + \sqrt{2})B}{Z + \bar{t} + (1 - \sqrt{2})B} \right] \quad (16)$$

A and B are defined as shown in Eqs. (8) and (9) for a fluid mixture and

$$\bar{t} = \frac{P t_m}{R T} \quad (17)$$

One binary interaction parameter k_{ij} was used in VLE calculations of fluid mixtures. The optimal values of k_{ij} were obtained using the following objective function:

$$OF' = \frac{100}{n} \sum_i^n \left[\left| \frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right| + \left| y_i^{\text{cal}} - y_i^{\text{exp}} \right| \right] \quad (18)$$

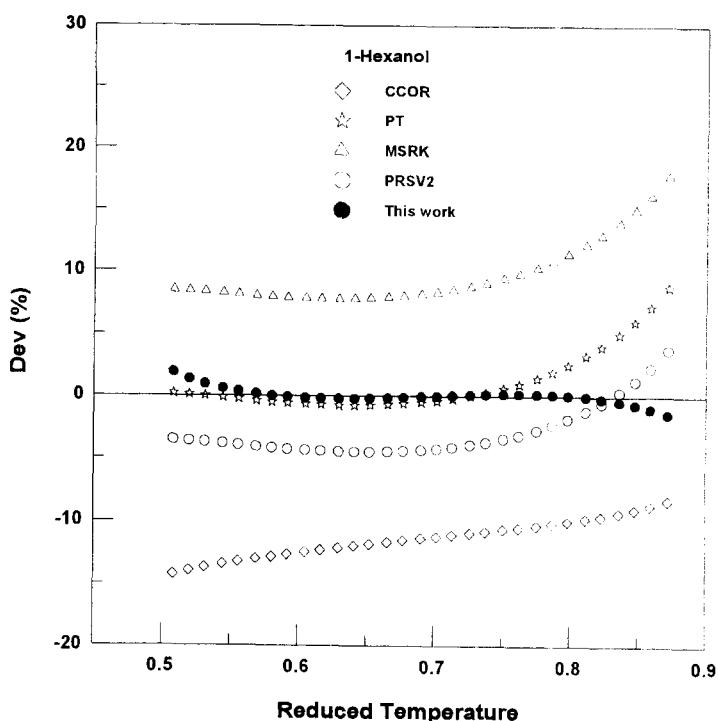


Fig. 3. Comparison of the calculated saturated liquid molar volumes of 1-hexanol from various equations of state. Data source: Ref. [16].

Table 5

Comparison of saturated vapor molar volumes of pure fluids using various cubic equations of state

Compounds	Temperature range (K)	Data points	AAD(V^V)%				
			PT	MSRK	CCOR	PRSV2	This work
Methane	91–176	39	1.23	0.49	6.68	0.89	0.96
Octane	312–504	25	1.63	1.44	4.29	1.67	1.26
Benzene	284–517	37	1.74	1.10	4.41	2.30	1.14
Chloromethane	193–372	35	1.60	3.61	3.39	1.48	1.48
Sulfur dioxide	323–378	12	3.00	2.44	6.38	1.85	1.87
Ammonia	200–406	13	2.93	2.88	1.59	4.02	1.86
Methanol	227–459	32	5.20	3.55	9.41	12.62	1.48
Ethanol	231–423	20	2.14	5.28	3.86	2.31	1.49
1-Propanol	280–475	24	5.72	3.52	5.16	7.94	1.18
1-Butanol	295–506	26	7.92	2.71	5.42	9.80	1.09
1-Nonanol	366–440	10	40.63	47.30	4.54	0.84	0.82
Acetone	253–335	12	2.98	1.68	0.38	3.00	1.60
Water	273–598	80	2.15	1.72	4.48	9.54	1.59
Grand average		365	3.97	3.54	4.93	5.45	1.36

Data source: Ref. [16]

$$\text{AAD}(\text{V}^{\text{V}})\% = \frac{100}{n} \sum [|\text{V}^{\text{V exp}} - \text{V}^{\text{V cal}}|] / \text{V}^{\text{V exp}}$$

2. Results and discussion

The VTPR EOS has been used to correlate the saturated properties of pure nonpolar and polar fluids. A new temperature-dependent function of α is obtained:

$$\alpha(T) = [1 + M(1 - T_R) + N(1 - T_R)(0.7 - T_R)]^2 \quad (19)$$

where M and N are two parameters for each pure fluid. It is found that M can be correlated as a function of the acentric factor:

$$M = 0.20473 + 0.83548\omega - 0.18470\omega^2 + 0.16675\omega^3 - 0.09881\omega^4 \quad (20)$$

No suitable correlation for N was obtained and it is left as a pure fluid parameter for the VTPR EOS. The translated volume parameter t has been examined for various pure fluids. At reduced temperatures less than 0.8, a constant value of t is simple enough to result in satisfactory improvement of the calculated saturated liquid molar volumes. At higher reduced temperatures, t is better treated as a temperature-dependent parameter. In this study, t is taken as the following temperature-dependent form in correlating the saturated properties:

$$t = \frac{RT_c}{P_c} \left[k_1 + k_2(1 - T_R^{2/3}) + k_3(1 - T_R^{2/3})^2 \right] \quad (21)$$

Further regression of the k parameters in the above equation has been investigated. It is found that k_1

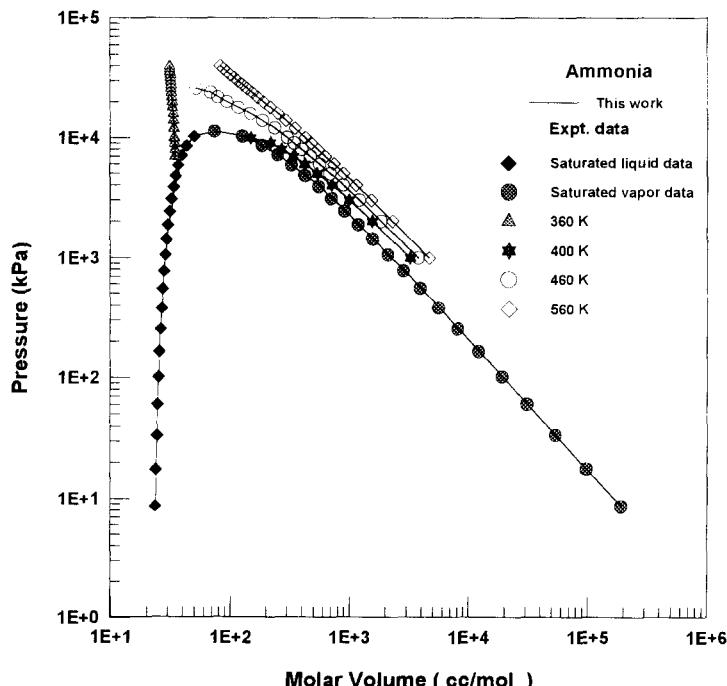


Fig. 4. Comparison of the calculated PVT data from the VTPR EOS for ammonia with experimental data [14].

Table 6

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

System (compound 1 + compound 2)	Temperature range (K)	Pressure range (kPa)	Data AAD(PV_i)				Data Dev(V_i/V_i^*)						
			points	PT	MSRK	CCOR	PRSV ₂	This work	PT	MSRK	CCOR	PRSV ₂	This work
methanol + ethanol	293–373	6.48–318.37	54	1.91 (-0.0009) ^a	2.09 (-0.0092)	2.27 (-0.0170)	1.95 (-0.0088)	1.96 (-0.0104)	0.91	0.85	1.01	0.86	0.90
methanol + 1-propanol	293–333	3.25–79.06	45	1.98 (-0.0009)	1.60 (0.0011)	2.46 (-0.0191)	1.72 (-0.0023)	1.65 (-0.0040)	1.97	0.71	1.52	1.17	1.13
methanol + 2-pentanone	337–345	101.32	7	1.33 (-0.0050)	1.72 (0.0026)	1.21 (-0.0451)	1.84 (0.0119)	1.74 (0.0011)	3.37	2.68	2.39	2.69	2.74
methanol + water	308–373	7.33–337	66	4.15 (-0.0988)	2.98 (-0.0925)	2.74 (-0.0490)	2.64 (-0.0892)	2.74 (-0.0896)	2.15	1.98	2.10	1.99	1.98
ethanol + 1-propanol	323–353	14.40–103.98	36	1.12 (0.0136)	0.59 (0.0134)	1.10 (0.0006)	0.60 (0.0145)	0.64 (0.0126)	0.62	0.44	1.14	0.60	0.67
acetone + ethanol	305–321	13.69–73.81	42	0.71 (0.0183)	1.29 (0.0225)	1.27 (0.0166)	1.10 (0.0219)	1.37 (0.0221)	0.52	0.39	0.52	0.48	0.38
ethanol + 2-pentanone	351–356	101.32	9	2.18 (0.0270)	2.54 (0.0259)	3.29 (-0.0175)	1.73 (0.0273)	1.93 (0.0275)	1.73	1.58	1.39	1.61	1.66
ethyl acetate + ethanol	313–343	18.21–94.95	43	1.44 (0.0260)	1.99 (0.0295)	1.87 (0.0085)	1.86 (0.0292)	1.72 (0.0208)	1.41	1.61	1.30	1.57	1.48
ethyl formate + 1-propanol	323	28.46–81.97	9	1.56 (0.0539)	0.46 (0.0513)	4.87 (0.0666)	0.39 (0.0496)	1.31 (0.0533)	0.27	1.07	0.82	0.54	0.32
methyl acetate + 1-propanol	24.14–61.17	11	0.60 (0.0475)	1.04 (0.0466)	1.62 (0.0438)	0.71 (0.0464)	0.66 (0.0499)	0.56	1.39	0.85	0.70	0.51	
1-propanol + propyl acetate	371–367	101.32	11	0.59 (0.0241)	1.26 (0.0175)	3.37 (-0.0124)	1.19 (0.0181)	1.22 (0.0179)	1.08	0.88	2.27	0.88	0.89
dichloro methane + acetone	298–398	31.04–99.91	57	2.55 (-0.0335)	2.13 (-0.0373)	0.61 (0.0409)	0.76 (-0.0422)	0.62 (-0.0409)	0.94	0.83	0.61	0.34	0.37
acetone + trichloromethane	298–323	21.76–79.43	89	1.11 (-0.0673)	0.98 (-0.0692)	1.09 (-0.0647)	0.98 (-0.0656)	0.96 (-0.0635)	1.05	1.05	1.14	1.06	1.07
acetone + cyclohexane	298–328	26.09–106.96	54	3.63 (0.1005)	2.40 (0.1128)	2.93 (0.1027)	18.99 (0.0621)	2.42 (0.1076)	1.98	2.24	1.97	3.05	1.75
acetone + benzene	298–318	15.55–67.89	31	2.37 (0.0222)	1.10 (0.0283)	1.20 (0.0267)	1.18 (0.0279)	1.06 (0.0279)	1.13	0.76	0.74	0.79	0.71
acetone + methyl acetate	313	53.60–57.50	15	0.51 (0.0067)	0.70 (0.0046)	0.62 (0.0049)	0.46 (0.0062)	0.88 (0.0061)	0.51	0.38	0.35	0.33	0.37
Grand average			579	2.03	1.71	1.83	3.03	1.51	4.27	4.15	1.24	1.21	1.08

^a Optimal k_{ij} : $\text{AAD}(PV_i) = \frac{1}{n} \sum_i |PV_i - P^{\text{exp}}|$; $\text{Dev}(V_i/V_i^*) = \frac{1}{n} \sum_i |V_i/V_i^* - V_i^{\text{exp}}|$.

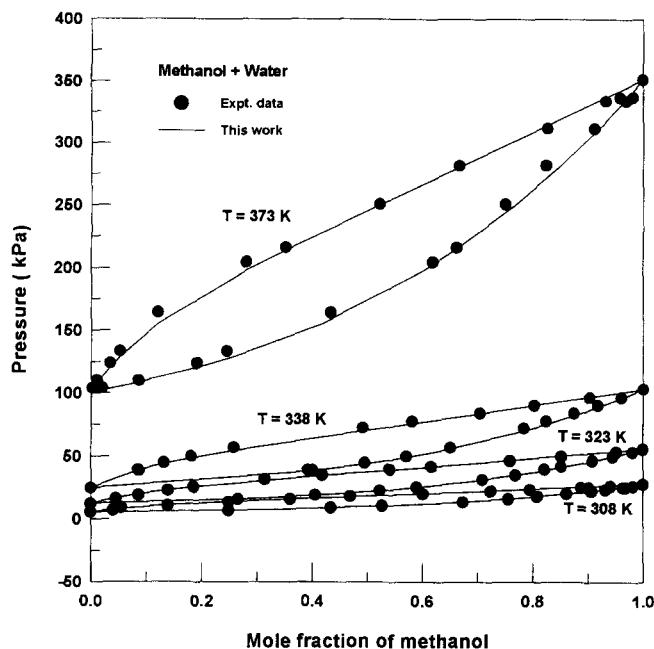


Fig. 5. VLE calculation results from the VTPE EOS and the VDW mixing rules for methanol and water binary mixtures at various temperatures ($k_{ij} = -0.0896$). Data source: Ref. [35].

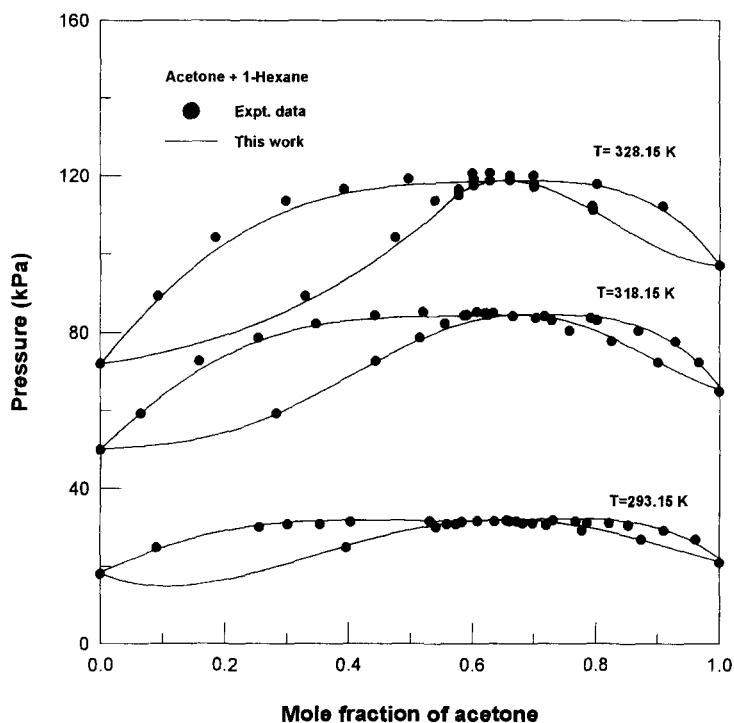


Fig. 6. VLE calculation results from the binary mixtures of acetone and 1-hexane at various temperatures using the VTPE EOS with MHV2 mixing rules. Data source: Ref. [35].

can be expressed as a function of the acentric factor, k_3 is left as another pure fluid parameter, and k_2 can be regressed as a function of k_3 :

$$k_1 = 0.00185 + 0.00438\omega + 0.36322\omega^2 - 0.90831\omega^3 + 0.55885\omega^4 \quad (22)$$

$$k_2 = -0.00542 - 0.51112k_3 + 0.04533k_3^2 + 0.07447k_3^3 - 0.03831k_3^4 \quad (23)$$

Thus the VTPR EOS has two pure fluid parameters N and k_3 , in addition to the critical properties and acentric factors. These pure fluid parameters have been regressed for over 130 pure components and their values are listed in Tables 1 and 2. The overall absolute average deviations in vapor pressure and saturated liquid molar volume are less than 1%. The VTPR EOS has been compared with other cubic EOS (PRSV2 [1,2]; MSRK [29]; PT [30]; CCOR [31,32]; t-mPR [11]). The PRSV2 EOS has three parameters, and each other EOS has two parameters for every pure fluid. The pure fluid parameters of various EOS have been refitted using the same pure fluid data base in the comparisons. The results for saturated property calculations are listed in Tables 3 and 4 for nonpolar and polar pure fluids, respectively. The PRSV2, MSRK, and the CCOR EOS give accurate results for vapor pressures, but relatively larger deviations in saturated liquid molar volumes. The t-mPR EOS yields improved liquid molar volume calculations for nonpolar fluids. The generalized correlations for the nonpolar fluid parameters of the t-mPR EOS can not yield satisfactory results for polar systems. For the polar fluids, it is observed that the PT EOS gives good results on saturated liquid molar volumes, but larger deviations in vapor pressures. The VTPR EOS developed in this study shows satisfactory results for both nonpolar and polar fluids. The absolute average deviations in vapor pressure and saturated liquid molar volume are less than 1%, and the peak deviations are less than 1.5%. Fig. 1 shows an example

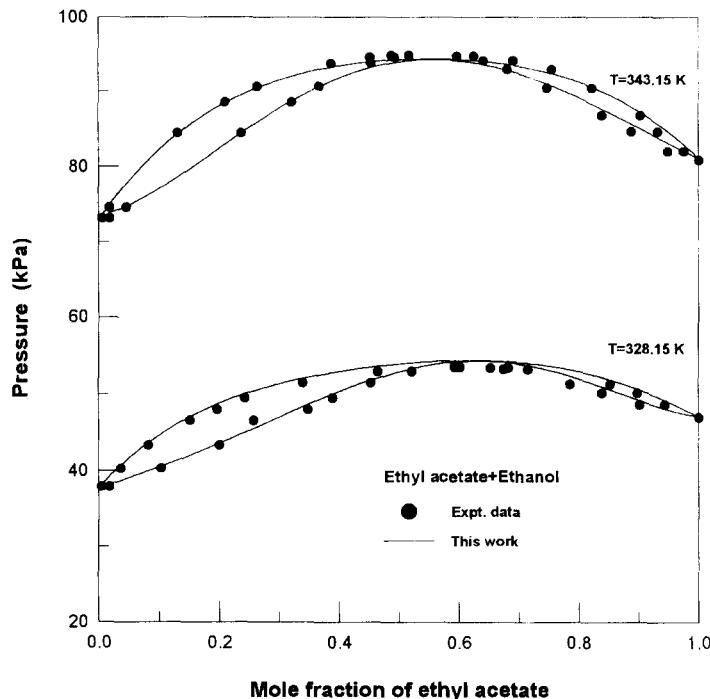


Fig. 7. VLE calculation results from the binary mixtures of ethyl acetone and ethanol at various temperatures using the VTPR EOS with LCVM mixing rules. Data source: Ref. [35]

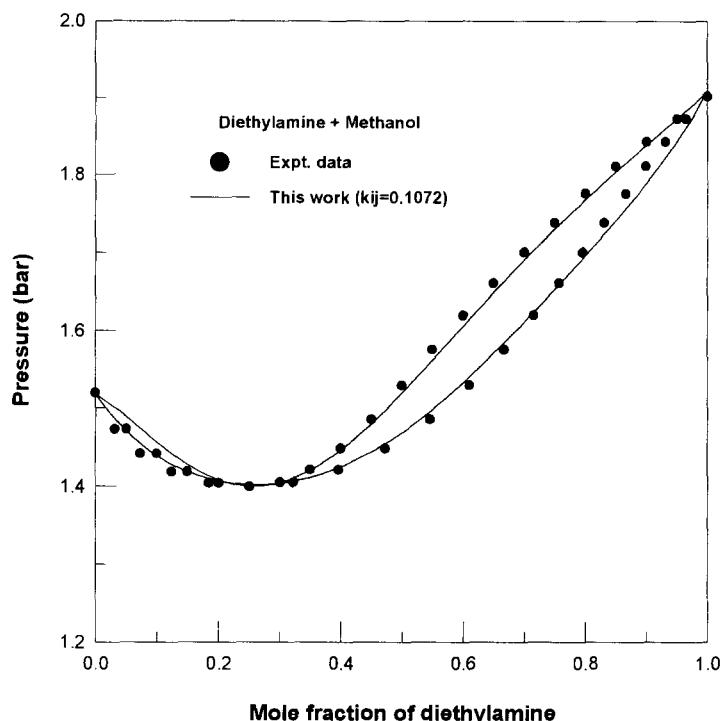


Fig. 8. VLE calculation results from the binary mixtures of diethylamine and methanol at 348.09 K using the VTPR EOS with Wong–Sandler mixing rules. Data source: Ref. [42].

of the error distributions of the vapor pressure calculations of isopropyl ether from various EOS. The VTPR EOS is satisfactory in a wide range of reduced temperature. Fig. 2 shows the calculated results of the saturated liquid molar volumes of alcohols from the VTPR EOS. Good agreement with the experimental data is observed up to the reduced temperatures higher than 0.9. Fig. 3 shows a graphical comparison of the error distribution on the saturated liquid molar volume calculations of 1-hexanol using various EOS. The VTPR EOS gives general good results and the smallest deviation at higher reduced temperature range. The VTPR EOS also yields satisfactory results on the saturated vapor volumes. A comparison of the calculation results with other EOS models is shown in Table 5. It is presented that the grand average absolute deviation from the VTPR EOS is again superior to other EOS. A comparison of the calculated *PVT* data of ammonia is shown in Fig. 4, and the agreement with experimental data is satisfactory. Very recently, we have developed a three-parameter cubic perturbed hard body (CPHB) EOS [33], and have shown satisfactory results for nonpolar and polar fluids. Both the CPHB and VTPR EOS show good results on vapor pressures with absolute average deviation less than 1% for nonpolar and polar pure fluids. The VTPR EOS, with less pure fluid parameters, shows further improvement on liquid volume results than those from the CPHB EOS. Both EOS parameters are obtained by regressing the saturated properties of pure fluids. They may have limitations for direct application to supercritical conditions. For certain compounds without experimental saturated property data, values estimated from correlation equations [34] can be used to regress the EOS parameters. In this case, the predicted results depend on the accuracy of the correlation equations.

Table 7
Comparison of VLE calculations results using VTPR with various mixing models

Component 1	Component 2	Temp. range (K)	Pres. range (kPa)	Data points	MHV2		LCVM		WS		
					(P)%		AAD (%)		AAD (%)		
					AAD	(y)%	(P)%	AAD	(y)%	(P)%	
Acetone	Chloroform	298–323	21.75–79.41	93	1.50	0.45	1.17	0.50	0.045	1.03	0.62
Acetone	Methyl acetate	313	53.60–57.50	15	1.16	0.51	1.15	0.50	0.055	1.04	0.89
Acetone	Benzene	298–318	15.55–67.89	31	3.76	1.14	3.24	1.17	0.130	3.36	1.80
Acetone	Cyclohexane	298–328	26.09–106.96	54	2.51	0.49	4.79	0.78	0.190	3.59	1.04
Acetone	Toluene	318	13.49–63.85	15	7.29	1.11	6.03	0.82	0.08	6.86	0.57
Acetone	Heptane	323	35.02–81.91	7	2.35	1.09	5.65	2.21	0.245	6.10	2.70
Acetone	Ethanol	305–321	13.69–73.79	42	2.93	1.93	1.65	1.53	0.210	6.42	1.80
Chloro	Benzene	313–343	24.66–82.11	30	1.65	1.60	1.45	7.50	0.016	0.98	0.22
methane											
Chloroform	Benzene	308–323	21.89–66.86	24	1.52	0.97	1.45	4.42	−0.030	2.10	2.08
Benzene	Toluene	393	150.88–248.9	6	1.65	0.70	1.77	0.66	0.031	0.90	0.64
Benzene	Cyclohexane	283–343	6.55–80.04	76	5.23	0.59	5.72	0.64	−0.160	3.55	2.71
Methanol	2-Butanone	323	41.71–58.78	13	5.70	3.60	2.33	2.40	0.250	4.35	3.30
Methyl	Ethanol	323–353	32.12–206.6	32	4.05	1.97	3.65	1.69	0.035	2.14	1.75
acetate											
Ethanol	1-Butanol	353–388	101.3	12	0.50	0.43	0.30	0.43	0.039	1.43	1.85
Ethanol	1-Propanol	323–353	14.4–103.98	36	3.68	1.87	3.85	1.68	0.052	1.81	1.76
Ethanol	2-Butanone	328	40.41–49.8	14	0.82	1.11	1.38	0.64	0.030	2.70	1.20
Ethyl	Ethanol	313–343	18.21–94.8	43	3.53	1.41	1.90	1.19	−0.120	6.97	1.90
acetate											
Ethyl	1-Propanol	313–333	11.20–53.58	26	7.32	1.86	5.95	1.58	−0.020	2.56	1.80
acetate											
Grand average				569	3.25	1.13	3.08	1.51	3.14	1.55	
average											

Data source : Ref. [35].

Table 8

Comparison of liquid density calculations of fluid mixtures at atmospheric pressure using various cubic equations of state

System	Temperature (K)	Data points	AAD(ρ^L)%					Data sources
			MSRK	CCOR	PRSV2	PT	This work	
<i>n</i> -hexane + <i>n</i> -decane	298.15	9	9.92	0.574	2.41	1.00	0.22	[43]
<i>n</i> -octane + <i>n</i> -decane	298.15	9	11.23	0.89	3.75	1.39	0.52	[43]
<i>n</i> -nonane + <i>n</i> -decane	298.15	9	11.77	1.21	4.28	1.69	0.73	[43]
toluene + octane	298.15	10	9.42	0.78	1.39	0.62	0.56	[44]
toluene + <i>n</i> -decane	303.15	10	10.68	0.59	2.62	1.14	0.42	[44]
1-hexane + 1-hexanol	298.15	11	6.29	6.47	2.14	0.41	0.25	[45]
octane + 1-hexanol	298.15	11	8.49	5.34	1.23	0.50	0.41	[46]
octane + 1-octanol	298.15	11	9.72	4.60	1.64	1.27	0.96	[46]
water + methanol	298.15	19	23.24	9.26	14.97	1.26	0.98	[47]
water + ethanol	298.15	19	18.75	3.57	10.11	1.91	1.93	[47]
1-propanol + water	303.15	10	17.50	4.71	8.53	1.66	1.57	[48]
acetone + water	298.15	14	21.21	11.02	12.89	2.21	1.79	[48]
methanol + ethanol	323.15	19	15.78	2.56	7.96	0.79	0.67	[48]
1-octanol + methanol	298.15	19	13.37	5.24	5.05	2.34	0.36	[47]
1-octanol + ethanol	298.15	19	11.36	3.06	2.83	2.05	0.38	[47]
Grand Average		199	14.1	4.37	6.19	1.43	0.82	

$$\text{AAD}(\rho^L)\% = \frac{100}{n} \sum [|\rho^L_{\text{exp}} - \rho^L_{\text{cal}}| / \rho^L_{\text{exp}}].$$

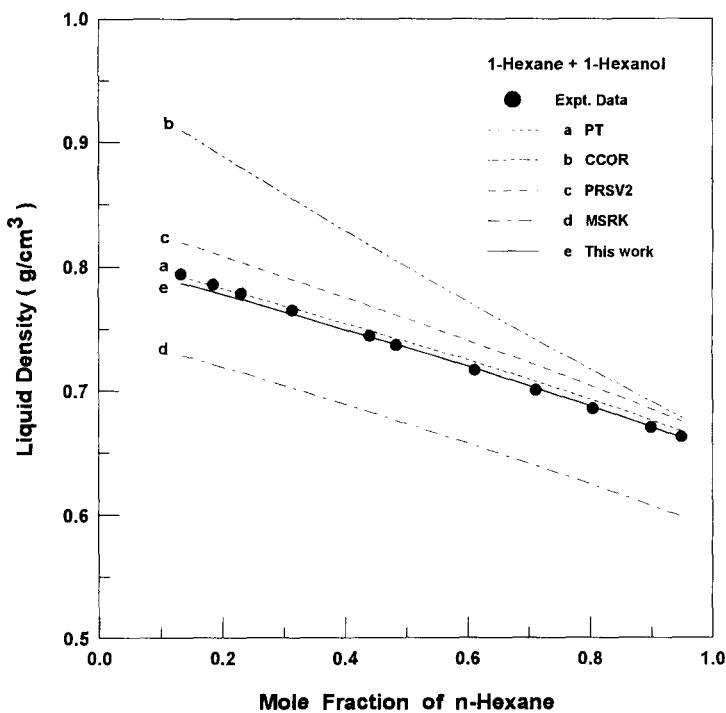


Fig. 9. Comparison of the calculated liquid densities from various equations of state for binary mixtures of 1-hexane + 1-hexanol at 298.15 K and 101.3 kPa. Data source: Ref. [45].

The VTPR EOS has been employed on the VLE calculations of binary mixtures. The calculated results using traditional van der Waals one-fluid mixing rules and the comparison with other EOS are presented in Table 6. One optimally fitted binary interaction factor was used for the energy parameter of each EOS. It is shown that all EOS models give satisfactory VLE calculation results, except for certain mixtures as alcohol + normal hydrocarbon systems, with their optimally fitted parameters. A graphical presentation for the VLE calculation results using the VTPR EOS and the van der Waals mixing rules is shown in Fig. 5 for the binary mixture of methanol + water. Satisfactory agreement with the experimental data has been obtained with single temperature-independent binary interaction parameter. The VTPR EOS has also been combined with the excess free energy models in the VLE calculations. In these calculations, a group contribution UNIFAC model [37] was employed and no empirical parameter was included in the MHV2 [38,39] and LCVM [40] mixing rules. Examples are shown in Figs. 6 and 7 for the binary systems of acetone + 1-hexane and ethyl acetate + ethanol where the MHV2 and the LCVM models are employed, respectively. It is shown that the VTPR EOS yields good results for these systems from either group contribution mixing model. The azeotropic behavior can be correctly determined as shown in these figures. The Wong–Sandler mixing rules [41] were also used in the VTPR EOS, where one empirical binary interaction parameter l_{ij} was included in the second virial coefficient of the mixture. Fig. 8 shows an example for the VLE calculation results from the VTPR EOS and the Wong–Sandler mixing rules for the diethylamine + methanol binary system. It is again demonstrated that the VTPR EOS with the Wong–Sandler mixing rules yields good results for this nonideal mixture with one empirical parameter. VLE calculation results using VTPR EOS + GE mixing rules are also presented in Table 7 for more binary mixtures.

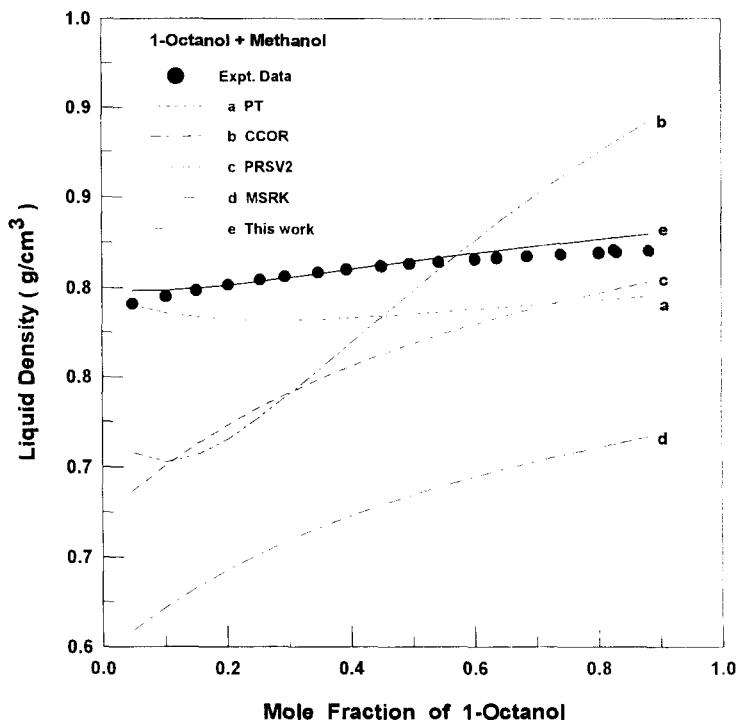


Fig. 10. Comparison of the calculated liquid densities from various equations of state for binary mixtures of 1-octanol + methanol at 298.15 K and 101.3 kPa. Data source: Ref. [47].

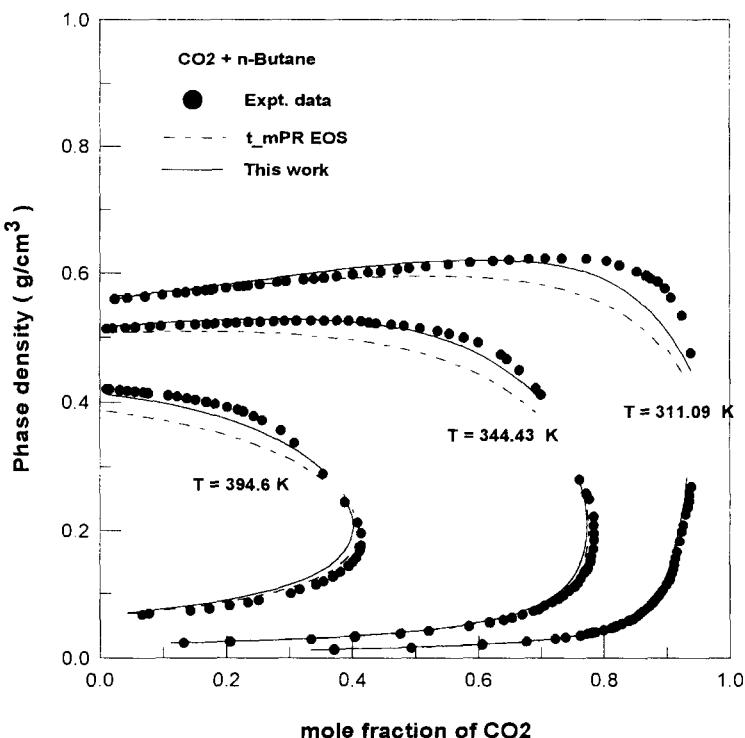


Fig. 11. Comparison of saturated densities for carbon dioxide and *n*-butane binary mixtures calculated from t-mPR and VTPR EOS. Data source: Ref. [50].

The volume translated EOS gives improved calculated results on the liquid densities of binary mixtures at atmospheric pressure, as shown in Table 8. Five EOS models are compared for the liquid density calculations of various fluid mixtures. No binary interaction parameter was used in these calculations and all EOS were compared at a predictive basis. It is observed that the VTPR EOS yields the best accuracy. Graphical comparisons are shown in Figs. 9 and 10 for the binary mixture of 1-hexane + 1-hexanol and 1-octanol + ethanol, respectively. Generally, the PT and VTPR EOS give good agreement with the experimental data, where the VTPR EOS has the best overall accuracy. The VTPR EOS has been tested in calculating the saturated vapor and liquid molar volumes at high pressures for several binary mixtures of carbon dioxide + alkanes. Comparing to those calculated from the t-mPR EOS [49], the VTPR EOS has slightly better saturated liquid molar volume and better saturated vapor molar volume results. The calculated results for $\text{CO}_2 + n\text{-butane}$ are shown in Fig. 11 at various temperatures. The pressure range in this calculation is from 5 to 80 bars. The VTPR EOS gives satisfactory results where the absolute average deviations in saturated vapor and liquid molar volumes are less than 2%. It is also demonstrated that the VTPR EOS presents improvement in the saturated molar volume calculations than the original PR EOS without volume translation.

3. Conclusion

A volume translated Peng–Robinson (VTPR) EOS is developed in this study. Pure fluid parameters are presented over 130 nonpolar and polar compounds. The VTPR EOS shows satisfactory calculated

results of both the vapor pressures and the saturated liquid and vapor molar volumes. VLE calculations are satisfactorily carried out using the VTPR EOS and various mixing rules. The VTPR EOS gives comparable VLE calculation results to other cubic type EOS models. The VTPR EOS, however, shows superior results on the liquid density calculations of fluid mixtures.

4. List of symbols

<i>a</i>	equation of state energy parameter
<i>b</i>	equation of state excluded volume parameter
<i>f</i>	fugacity for pure component <i>i</i>
<i>k_{ij}, l_{ij}</i>	binary interaction parameters
<i>k₁, k₂, k₃</i>	parameters in Eq. (21)
<i>n</i>	number of data points
<i>N, M</i>	parameters in Eq. (19)
<i>P</i>	pressure
<i>R</i>	gas constant
<i>t</i>	volume-translation parameter
<i>T</i>	temperature
<i>V</i>	molar volume
<i>x</i>	mole fraction in the liquid phase
<i>y</i>	mole fraction in the vapor phase
<i>Z</i>	compressibility factor
<i>Greek letters</i>	
α	temperature-dependent function
ρ	density
ϕ	fugacity coefficient for a pure fluid
ϕ_i	fugacity coefficient for component <i>i</i> in a mixture
ω	acentric factor
<i>Subscripts</i>	
<i>c</i>	critical value
<i>i, j</i>	component <i>i</i> or <i>j</i>
<i>m</i>	mixture property
<i>R</i>	reduced property
<i>Superscripts</i>	
cal	calculated value
exp	experimental value
L	liquid phase
V	vapor phase

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