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Boyle temperature from SAFT, PC-SAFT and SAFT-VR equations of state

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ABSTRACT

Second virial coefficient, Boyle temperature and Zeno (unit compressibility) line of some polar, non-polar and associating substances are calculated from SAFT, PC-SAFT and SAFT-VR equations of state (EOS). The results are compared with the corresponding values obtained from published correlations and available data. Our investigation shows that among the three EOSs considered the results obtained from the SAFT EOS are more accurate in predicting the Boyle temperature and the Zeno line. For second virial coefficient prediction, PC-SAFT is superior to SAFT for many substances and, for some alkanols and water; the results of SAFT-VR are more accurate.

A modification on Tsonopoulos correlation for the second virial coefficient is presented for branched-alcohols and amines which has reduced the average absolute percent relative deviation (AAD%) from 13.22 to 3.52 and from 14.55 to 6.00 for four branched-alcohol and two amines, respectively. The proposed modification uses the Boyle temperature obtained from the SAFT EOS as a property of substance.

1. Introduction

The virial expansion of compressibility factor (z) as a power series in terms of molar density (ρ) is:

$$z = 1 + B(T)\rho + C(T)\rho^2 + \dots \tag{1}$$

In this equation B is the second virial coefficient, C is the third virial coefficient, and so on. The virial coefficients are functions of absolute temperature, T, and interaction energy between molecules. The second virial coefficient depends on the pair potential between any two constituent species i and j. The theoretical importance of the virial expansion is well known in statistical thermodynamics [1]. An attractive feature of the virial expansion is that the virial coefficients are given exactly in terms of cluster integrals involving the intermolecular potential between particles [2]. Virial coefficients of real systems can be measured experimentally by different techniques such as PVT measurements [3]. In recent decades various correlations have been developed for second virial coefficient. The correlations proposed by Tsonopoulos [4,5], and, Meng and Duan [6] are perhaps the most popular. A number of experimental data is also available in literature among which we may refer to the second virial coefficient data introduced by Dymond et al. [7] and Smith and Srivastava [8,9].

The Boyle temperature is the temperature at which the second virial coefficient becomes zero and its value is specific for each substance. Any gas at this temperature behaves like an ideal gas, and accordingly, Eq. (1) reduces to:

$$z = 1 + O\left(\rho^2\right). \tag{2}$$

Boyle temperature (T_{Boyle}) can be calculated by different methods. The first procedure utilizes its definition and, therefore, T_{Boyle} is obtained by the following equation from any appropriate correlation representing the second virial coefficient as a function of temperature.

$$B(T) = 0 \rightarrow T = T_{Boyle}. \tag{3}$$

Table 1
Parameters of PC-SAFT EOS for alcohols considering model 2B (Ref. of data [9]), for non-associating fluids, ketones (Ref. of data [8]), and haloalkanes (Ref. of data [9]).

Substance	m	σ (Å)	u^o/k (K)	ε^{AB}/k (K)	κ^{AB}	AAD%	
						P^{sat}	v^l
2-Butanol	3.440	3.313	224.20	2067.63	0.010400	0.35	0.78
2-Methyl-1-propanol	2.020	4.040	287.17	2754.71	0.002503	0.93	0.34
2-Methyl-2-propanol	4.199	3.081	191.47	1727.54	0.029962	0.27	1.05
Phenol	3.982	3.135	276.01	1024.50	0.060662	0.25	3.49
Dichloromethane	2.153	3.383	273.14			0.43	0.24
Trichloromethane	2.177	3.653	284.98			0.38	0.76
Tetrachloromethane	2.200	3.894	292.14			2.43	0.72
Methyl ethyl ketone	2.522	3.615	274.91			0.18	0.09
Methyl n-propyl ketone	2.882	3.677	267.96			0.26	0.03
Diethyl ketone	2.873	3.669	268.67			0.16	0.21

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The other method uses the Zeno line. The temperature and density at which the compressibility factor equals unity are named the Zeno line or Zeno contour. From the temperature–density diagram, the Boyle temperature is determined from extrapolation of the Zeno line to zero density. Several researches have used this method to obtain the Boyle temperature. Among which, we can mention the work of Wagner et al. [10] who also estimated the third virial coefficient at this temperature, and, the interrelationships among virial coefficients presented by Holleran [11].

In some of the published works the Boyle temperature and the second virial coefficient are obtained from different potential functions such as Stockmayer [12], Sutherland [13], Lennard-Jones [14], two center Lennard-Jones quadrupole [15] and dipole [16]. In these works the effect of the potential parameters are investigated and discussed.

Leibovici et al. [17] calculated the Boyle temperature from the Peng–Robinson (PR), Redlich–Kwong (RK), van der Waals (vdW), and Harmens equations of state (EOS) with different alfa functions and compared the results.

Maghari et al. [18,19] used the Zeno line approach. They calculated the Zeno line and the Boyle temperature of simple hydrocarbons using Kubic–Martin, Adachi–Lu–Sugie, Yu–Lu, Trebble–Bishnoi, Iwai–Margerum–Lu, Twu–Coon–Cunningham, modified Patel–Teja [18], and

Table 2
Parameters of SAFT-VR EOS for associating and non-associating substances.

Substance	m	λ	σ (Å)	ε/k (K)	ε^{AB}/k (K)	K^{AB} (Å^3)	AAD%	
							P^{sat}	v^l
Alcohols(3B), Ref. of data [9]								
2-Propanol	3.176	1.413	3.106	331.34	1904.70	0.006297	1.40	3.52
2-Butanol	2.614	1.408	3.593	373.66	2221.40	0.012076	2.31	3.36
2-Methyl-1-propanol	1.412	1.773	4.503	235.86	2961.80	0.054526	1.99	2.22
2-Methyl-2-propanol	2.773	1.436	3.510	322.82	2246.80	0.015059	0.79	2.65
Phenol	2.697	1.396	3.578	472.64	948.09	0.013206	3.96	1.34
1-Pentanol	2.608	1.345	3.844	476.56	1881.90	0.019673	2.38	2.83
1-Heptanol	3.185	1.334	3.916	487.55	1188.90	0.006406	1.92	1.40
1-Nonanol	3.339	1.352	4.165	488.66	1157.40	0.006487	2.09	1.48
Amines(3B), Ref. of data [35,36]								
Methanamine	1.489	1.417	3.399	358.30	705.94	0.072472	0.88	0.25
Ethanamine	1.682	1.444	3.667	339.54	785.86	0.079761	1.32	0.35
1-Propanamine	1.853	1.416	3.811	356.18	750.86	0.056705	0.21	1.94
1-Butanamine	2.110	1.440	3.912	353.01	742.63	0.075485	0.73	1.55
Dimethylamine	1.675	1.403	3.716	354.46	629.21	0.100022	0.86	0.21
Diethylamine	1.459	1.429	4.573	416.58	370.98	0.097006	2.66	0.23
Ketones, Ref. of data [8]								
Methyl ethyl ketones	2.969	1.612	3.336	227.94			0.12	0.33
Methyl n-propyl ketones	3.317	1.634	3.407	218.44			0.37	0.48
Diethyl ketones	3.202	1.609	3.450	232.41			0.11	0.47
Ethers, Ref. of data [37,38]								
Dimethyl ether	1.849	1.578	3.425	222.20			3.36	0.54
Methyl ethyl ether	2.518	1.771	3.301	152.39			2.55	1.23
Methyl n-propyl ether	2.829	1.644	3.453	190.45			0.03	0.39
Diethyl ether	2.636	1.637	3.320	202.92			0.11	0.42
Haloalkanes, Ref. of data [9]								
Chloromethane	2.205	1.696	2.968	170.36			0.58	0.94
Dichloromethane	2.780	1.675	2.993	193.72			2.41	1.74
Trichloromethane	3.048	1.761	3.112	168.68			1.67	2.47
Tetrachloromethane	3.200	1.800	3.244	159.64			4.43	3.20
Chloroethane	2.332	1.689	3.223	187.61			0.28	2.52
Esters, Ref. of data [37,38]								
Methyl methanoate	2.674	1.632	2.987	207.25			0.04	1.13
Ethyl methanoate	2.974	1.648	3.157	200.67			0.13	1.08
n-Propyl methanoate	3.343	1.674	3.247	193.20			0.47	1.11
Methyl ethanoate	3.070	1.646	3.116	200.02			0.18	1.04
Ethyl ethanoate	3.145	1.660	3.292	199.53			3.06	2.81
n-Propyl ethanoate	3.381	1.590	3.463	223.35			1.47	2.47
n-Butyl ethanoate	3.657	1.649	3.545	213.07			0.09	0.89
Methyl propanoate	3.145	1.707	3.292	188.46			2.56	1.04
Ethyl propanoate	3.381	1.587	3.459	232.09			0.30	0.85
n-Propyl propanoate	4.944	2.048	3.036	98.66			0.71	3.18
Methyl butanoate	3.179	1.587	3.535	242.03			0.96	0.81
Ethyl butanoate	3.748	1.595	3.523	226.90			1.75	0.91
Aromatics, Ref. of data [8]								
Ethyl benzene	3.512	1.745	3.474	191.49			1.15	1.98
n-Propyl benzene	3.802	1.723	3.562	199.26			0.80	1.31
Cycloalkanes, Ref. of data [8]								
Cyclopentane	2.545	1.691	3.486	197.30			1.22	2.69
Methyl cyclopentane	2.552	1.654	3.730	220.50			0.90	2.03
Ethyl cyclopentane	2.735	1.648	3.847	232.90			0.56	1.47
Cyclohexane	2.624	1.684	3.651	213.50			1.10	2.05
Methyl cyclohexane	2.745	1.695	3.797	213.90			1.14	2.88
Ethyl cyclohexane	3.576	1.763	3.630	179.10			0.32	1.05