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An Extended BWR Equation of State for Five Polar Substances

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Abstract

An extended BWR equation of state for polar substances with five polar parameters is proposed. The parameters are determined for popular five polar substances using the second virial coefficient and vapor pressure data. Capability of the equation of state is found to be excellent for water, ammonia and sulfur dioxide, whereas not so excellent for methanol and ethanol.

Introduction

Based on the Pitzer's three-parameter corresponding-state principles¹⁰⁾, various thermodynamic properties of non-polar or slightly polar substances (normal fluids) can be successfully predicted by a BWR equation of state^{5,6,12)}. As for polar substances, the author has already proposed an improved generalized BWR equation of state with three polar parameters⁷⁾ in addition to fifteen non-polar parameters⁵⁾. It is based on the idea of the perturbation method that the dispersion forces represent the main effect and the dipolar interactions produce small deviations^{7,8)}. In the paper⁷⁾, the compressibility factor at the critical point, Z_c , was assumed:

$$Z_c = 0.2923 - 0.093\omega \quad (1)$$

The assumption required by the corresponding-state principles introduces an error in the calculation of pressure for a mixture, because thermodynamic property estimation for a mixture is not based on the reduced variables. Deviations of the experimental Z_c values from those calculated by Eq. (1) are listed in **Table 1**. It indicates that pressure calculation for some polar substances introduces an error of about 5–10 per cent, whereas the deviations for a number of normal fluids are so small as to be within the experimental uncertainty.

The purpose of this paper is to develop an extended BWR equation of state for popular five polar substances using experimental Z_c values instead of Eq. (1).

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Table 1 Deviations of Eq. (1) from experimental Z_C values

Substance	Z_C^{exp}	ω	$\dagger Z_C^{\text{calc}}$	$\dagger\dagger \text{Dev. } [\%]$
normal fluids				
CH ₄	0.2868	0.0072	0.2916	-1.7
C ₃ H ₈	0.2762	0.1454	0.2788	-0.9
C ₈ H ₁₈	0.2582	0.3942	0.2556	1.0
C ₁₀ H ₂₂	0.2461	0.4902	0.2467	-0.2
C ₁₆ H ₃₄	0.2251	0.7418	0.2233	0.8
C ₂₀ H ₄₂	0.2099	0.9065	0.2080	0.9
C ₂ H ₄	0.2677	0.0856	0.2843	-6.2
1-C ₄ H ₈	0.7269	0.1874	0.2749	0.7
Benzene	0.2742	0.2100	0.2728	0.5
Toluene	0.2733	0.2566	0.2684	1.8
CO ₂	0.2747	0.2100	0.2728	0.7
N ₂	0.2917	0.0350	0.2890	0.9
H ₂ S	0.2835	0.1050	0.2825	0.3
C ₂ H ₂	0.2676	0.1860	0.2750	-2.8
polar substances				
H ₂ O	0.2296	0.3440	0.2603	-13.4
NH ₃	0.2452	0.2500	0.2691	-9.7
SO ₂	0.2684	0.2730	0.2660	-2.5
CH ₃ OH	0.2201	0.5560	0.2406	-9.3
C ₂ H ₅ OH	0.2485	0.6350	0.2322	6.1
n-C ₃ H ₇ OH	0.2529	0.6000	0.2365	6.5
Acetone	0.2376	0.3180	0.2627	-10.6
MIPK	0.2596	0.2830	0.2660	-2.5

† Eq. (1): $Z_C = 0.2923 - 0.093\omega$

†† Dev. = $(Z_C^{\text{exp}} - Z_C^{\text{calc}}) / Z_C^{\text{exp}} \times 100$

1. Equation of state

Modification of the previous equation of state with three polar parameters⁷⁾ proved to be a more complex problem than at first be anticipated. It was soon discovered that the three polar parameters could not well fit a vapor pressure curve of a polar substance because of its high sensitivity. Finally, the following equation of state with five polar parameters is obtained:

$$\begin{aligned}
 P = & \rho RT + \left\{ B_0 RT - (A_0 + \Psi_A) - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0 + \Psi_E}{T^4} \right\} \rho^2 \\
 & + \left(bRT - a - \frac{d}{T} - \frac{e}{T^4} - \frac{f}{T^{23}} \right) \rho^3 \\
 & + \alpha \left(a + \frac{d}{T} + \frac{e}{T^4} + \frac{f}{T^{23}} \right) \rho^6 \\
 & + \left(\frac{c}{T^2} + \frac{g}{T^8} + \frac{h}{T^{17}} + T\Psi_s \right) \rho^3 (1 + \gamma \rho^2) \exp(-\gamma \rho^2)
 \end{aligned} \quad (2)$$

where

$$\Psi_s = s_3 + \frac{s_1}{T^{s_2}} \quad (3)$$

Fifteen generalized coefficients (e.g. B_0 , A_0 , C_0 ,) are functions of T_c , V_c and $\omega^{5,6,12}$. Five parameters for polar substances Ψ_A , Ψ_E , s_3 and s_1 are related to reduced quantities Ψ_A^* , Ψ_E^* , s_3^* , s_1^* and s_2 , as follows,

$$\Psi_A = \Psi_A^* RT_c V_c \quad (4)$$

$$\Psi_E = \Psi_E^* RT_c^5 V_c \quad (5)$$

$$s_3 = s_3^* R V_c^2 \quad (6)$$

$$s_1 = s_1^* RT_c^{s_2} V_c^2 \quad (7)$$

2. Determination of Polar Parameters

2.1 Ψ_A^* and Ψ_E^* from the second virial coefficients

Values of the critical properties and of the acentric factor used in this work are listed in Table 2. The second term of right-hand side in Eq. (2) gives the following second virial coefficient B :

$$B = B_0 - \frac{A_0 + \Psi_A}{RT} - \frac{C_0}{RT^3} + \frac{D_0}{RT^4} - \frac{E_0 + \Psi_E}{RT^5} \quad (8)$$

The optimum value of Ψ_E^* for a fixed Ψ_A^* is determined by applying the minimum least squares method to the above equation to fit the second virial coefficient data. The results for water are tabulated from the first to third column in Table 3. The deviation from Kell's experimental data²⁾ indicates that the optimum value for the second virial coefficients is -0.15 and 0.2464 for Ψ_A^* and Ψ_E^* , respectively. Polar parameters, however, are mainly determined to fit vapor pressure data, as will be shown in the following section. Eventually, the values of Ψ_A^* and Ψ_E^* for water are -0.10 and 0.2324 , respectively. Fig. 1 compares the experimental second virial coefficient data²⁾ with the calculated values for the employed parameters. The dotted line indicates a calculated curve for water as a non-polar substance ($\Psi_A = \Psi_E = 0$). It is found that calculated values for a polar substance are always smaller than those as a non-polar one. The difference between a non-polar (dotted line) and a polar (solid line) substance becomes smaller as temperature increases. It coincides with the knowledge of statistical mechanics that polar substances have a tendency to attract each other³⁾.

Table 2 Critical properties and acentric factor

No.	Substance	T_c [K]	P_c [atm]	V_c [l/mol]	ω
1	H ₂ O	647.3	217.6	0.0560	0.344
2	NH ₃	405.6	112.5	0.0725	0.250
3	SO ₂	430.7	77.7	0.122	0.273
4	CH ₃ OH	513.2	78.5	0.118	0.556
5	C ₂ H ₅ OH	516.3	63.0	0.165	0.635

Table 3 Determination of polar parameters for water

Ψ_A^*	Ψ_E^*	dev. of second virial coefficient [cm ³ /mol]	s_3^*	s_1^*	s_2	dev. of vapor pressure [%]
-0.35	0.3623	6.87	-0.4560	0.2968	5.572	4.91
-0.30	0.2883	5.95	-0.4046	0.2893	5.546	4.07
-0.25	0.2743	5.11	-0.3443	0.2804	5.524	3.19
-0.20	0.2604	4.44	-0.2812	0.2709	5.503	2.96
-0.15	0.2464	3.90	-0.2254	0.2632	5.473	1.48
-0.10	0.2324	4.02	-0.1693	0.2549	5.443	1.16
-0.05	0.2184	5.48	-0.1143	0.2473	5.407	1.36
0	0.2044	7.05	-0.0543	0.2382	5.376	2.15
0.05	0.1904	8.62	-0.0018	0.2308	5.332	2.66

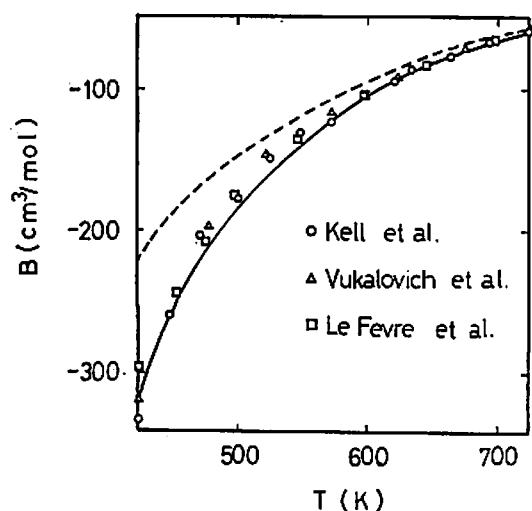


Fig. 1 Correlation of the second virial coefficients of water²⁾: solid line ($\Psi_A^* = -0.10$, $\Psi_E^* = 0.2324$), dotted line ($\Psi_A^* = \Psi_E^* = 0$ for a normal fluid)

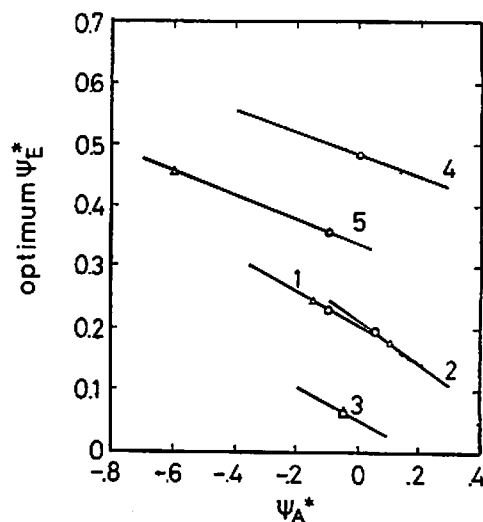


Fig. 2 Relation between Ψ_A^* and optimum Ψ_E^* . Substances are listed in Table 2. Circles and triangles are the optimum values for vapor pressure and the second virial coefficient data, respectively.

The $\Psi_A^* - \Psi_E^*$ values for five polar substances are plotted as shown in Fig. 2. It reveals that they can be correlated as straight lines and that the slope of a line may be approximated as -0.2 except for ammonia.

2. 2 s_1^* , s_2 and s_3^* from vapor pressures

The values s_1^* , s_2 and s_3^* are correction terms for a liquid phase, whereas Ψ_A^* and Ψ_E^* are for a vapor phase. First, the values of Ψ_s at various temperatures are determined to fit vapor pressure data using newly determined Ψ_A^* and Ψ_E^* . Second, the values of s_1^* and s_2 for a fixed s_3^* are obtained by applying the minimum least squares method to the following equation:

$$\log \{\Psi_s(T) - s_3^*\} = \log s_1^* - s_2 \log T \quad (9)$$

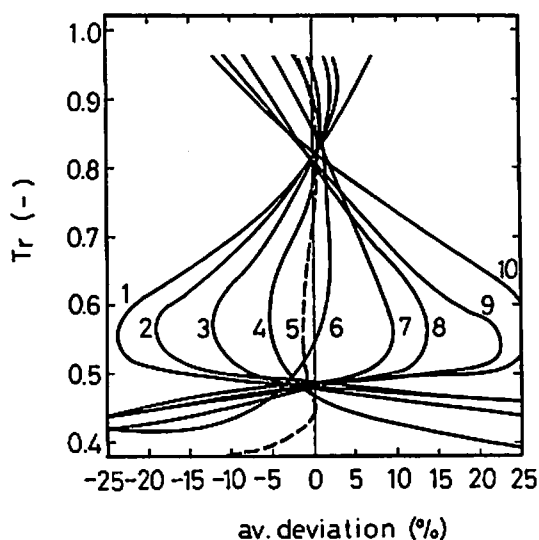


Fig. 3 Influence of s_3^* on vapor pressure deviations of water at $\Psi_A^* = -0.10$ and $\Psi_E^* = 0.2324$ (1: $s_3^* = -0.10$, 2: -0.12 , 3: -0.14 , 4: -0.16 , 5: -0.1693 , 6: -0.18 , 7: -0.20 , 8: -0.22 , 9: -0.24 , 10: -0.26)

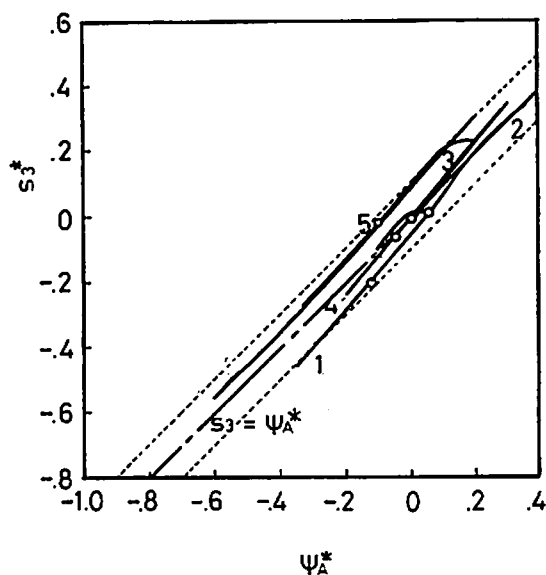


Fig. 4 Relation between Ψ_A^* and s_3^* . Substances are shown in Table 2.

Table 4 Polar parameters for five polar substances

Substance	Ψ_A^*	Ψ_E^*	s_3^*	s_1^*	s_2	Av. dev. of B [cm ³ /mol]	Av. dev. of vapor pressure [%]
H ₂ O	-0.10	0.2324	-0.1693	0.2549	5.443	4.0	1.2
NH ₃	0.05	0.1945	0.0138	0.2451	5.325	3.1	2.3
SO ₂	-0.05	0.0652	-0.0746	0.0851	5.174	4.0	2.0
CH ₃ OH	0	0.4841	-0.0002	0.5144	5.425	130.5	0.7
C ₂ H ₅ OH	-0.1	0.3585	-0.0385	0.3544	5.420	138.4	1.0

Fig. 3 shows the effect of s_3^* change on deviation of vapor pressures for water at various temperatures. The optimum value of s_3^* is obtained by the Powell method. The dotted line (No. 5) shows the optimum value for vapor pressures of water. The results for water are given in Table 4. Fig. 4 shows that the value s_3^* is between $(\Psi_A^* - 0.1)$ and $(\Psi_A^* + 0.1)$. If a set of polar parameters minimizes either deviations, one for vapor pressure is chosen. The determined values based on this criterion are circled in Figs. 2 and 4.

The polar parameters determined by the above method are listed in Table 4, together with average absolute deviations of the second virial coefficients and those of vapor pressures. It is preferable that the value of s_2 is between 5.1 and 5.5, because this term does not affect the calculation of thermodynamic properties at higher temperatures than the critical temperature.

3. Discussion

Capability of the extended BWR equation of state with newly determined five polar parameters is discussed below.

3.1 Water

The average absolute deviation between calculated and observed¹³⁾ vapor pressures of water is 1.1% over the temperature range 1.2–365°C (0.424–0.986 in reduced temperature) with a maximum deviation of 3.4% at 120°C as shown in Table 5. Prediction of saturated properties for water in Table 6 results in good agreement with smoothed values¹¹⁾ except for saturated liquid density in the temperature region lower than 40°C and for saturated vapor density and vaporization enthalpy at 350°C.

The volumetric behavior of a vapor phase ranging 100–870°C can be predicted with a deviation of less than 1 per cent for pressures lower than 20 MPa and of less than 3 per cent between 20 and 37 MPa, because the second virial coefficients are well correlated

Table 5 Comparison of predicted vapor pressures of H₂O with experimental values¹³⁾

Tr [–]	Temp. [°C]	$P. cal$ [atm]	$P. exp$ [atm]	Dev. [%]
0.986	365.00	190.72	195.80	2.6
0.974	357.00	174.36	177.80	1.9
0.960	348.00	156.79	159.30	1.6
0.943	337.00	137.27	183.90	1.2
0.924	325.00	118.39	119.00	0.5
0.902	311.00	98.64	98.80	0.2
0.878	295.00	79.10	79.00	0.1
0.849	276.50	60.30	60.00	0.5
0.831	264.70	50.15	50.00	0.3
0.810	251.10	40.22	40.00	0.6
0.784	234.60	30.15	30.00	0.5
0.751	213.10	20.06	20.00	0.3
0.701	180.50	9.97	10.00	0.3
0.657	152.40	4.96	5.00	0.9
0.608	120.10	1.93	2.00	3.4
0.576	100.00	0.98	1.00	2.0
		[mmHg]	[mmHg]	
0.550	83.00	392.72	400.00	1.8
0.525	66.50	197.39	200.00	1.3
0.502	51.60	99.21	100.00	0.8
0.486	41.60	60.01	60.00	0.0
0.475	34.10	40.21	40.00	0.5
0.456	22.20	20.31	20.00	1.5
0.439	11.30	10.23	10.00	2.3
0.424	1.20	5.08	5.00	1.6
			av. abslt. dev.	1.1

as shown in Fig. 1 (4.0 cm³/mol deviation). The P-V-T calculation of a liquid phase gives about 15% bigger density than the experimental values at lower temperatures than 40°C, and deviations of a few per cent at higher temperatures¹¹⁾.

Enthalpy (Fig. 5) and entropy (Fig. 6†) over liquid and vapor phases, the isobaric specific heat capacity for a vapor phase of water (Fig. 7) and the above mentioned results indicate that various kinds of thermodynamic properties of water over wide ranges of temperature and pressure for liquid and vapor phases can be well predicted except for lower temperature than 40°C and near the critical region.

3. 2 Ammonia

Tables 7 and 8 reveal that newly determined five polar parameters for ammonia can

Table 6 Prediction of saturated properties for water¹¹⁾

Temp. [°C]	Absolute deviation [%]		
	Density		Vaporization entropy
	Liquid	Vapor	
10	20.1	1.9	0.5
40	13.8	0.2	1.6
70	9.1	1.6	0.9
100	5.6	2.0	0.1
150	1.5	0.9	0.6
200	1.0	0.1	0.5
250	2.3	0.2	0.5
300	2.4	2.9	1.5
350	3.5	11.9	7.6

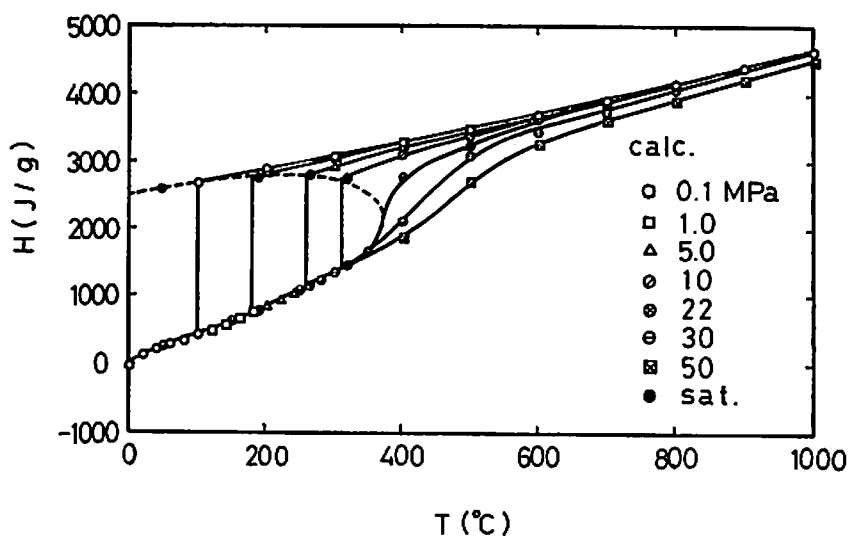


Fig. 5 Comparison of predicted enthalpy of water with smoothed experimental values (solid lines)¹¹⁾

† Figure 6 was obtained using a 16-bit micro-computer "MITSUBISHI-MULTI 16"

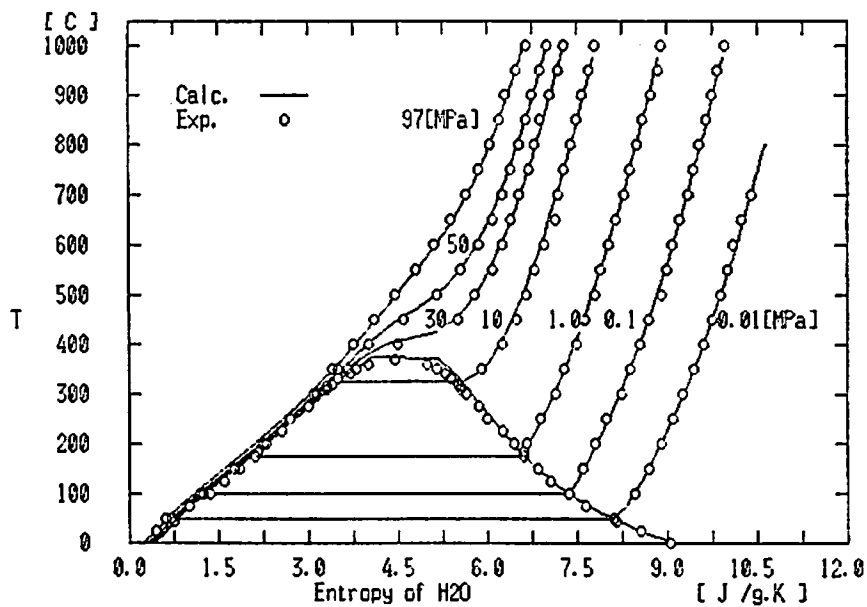


Fig. 6 Comparison of predicted entropy (solid lines)⁹⁾ of water with smoothed values by Perry⁹⁾ (circles)

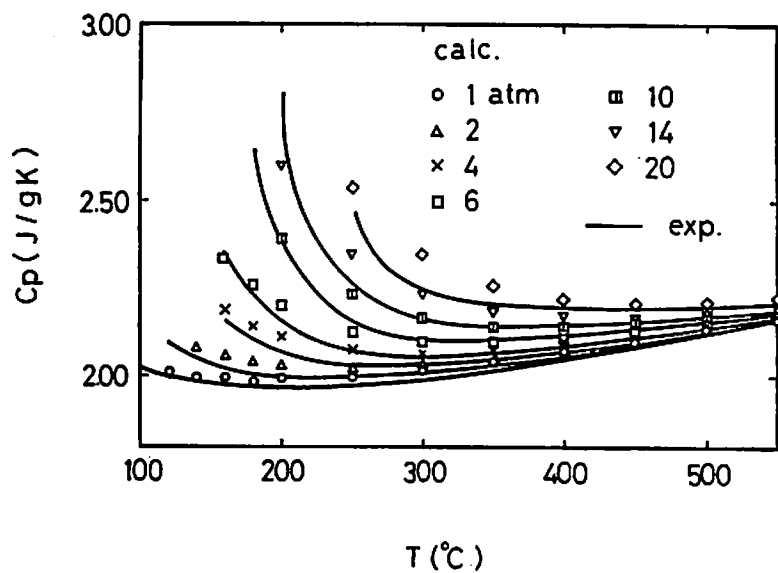


Fig. 7 Comparison of predicted isobaric specific heat capacity of water with smoothed values (solid lines)⁹⁾

be applied to solid-vapor region as well as vapor-liquid equilibrium (the melting point is -77.7°C). The average absolute deviation of the second virial coefficients is only $3.1\text{ cm}^3/\text{mol}$ over the temperature range $273.16\text{--}573.16\text{ K}$. The P-V-T prediction of a vapor phase ranging from 0 to 315°C and up to about 100 MPa gives deviation of less than 1 per cent for pressures lower than 34 MPa and of a few per cent for higher pressures. The deviation of volumetric behavior prediction of a liquid phase over temperature range $25\text{--}100^{\circ}\text{C}$ and up to 50 MPa is 1.5% with a maximum deviation of 4.9% . The proposed correlation gives excellent predictions of enthalpy¹³⁾ (Fig. 8) and the isobaric specific heat capacity of ammonia for a vapor phase¹⁴⁾.

Table 7 Comparison of predicted vapor pressures of NH_3 with experimental values¹³⁾

Tr [—]	Temp. [$^{\circ}\text{C}$]	$P. cal$ [atm]	$P. exp$ [atm]	Dev. [%]
0.986	126.70	101.46	100.70	0.8
0.972	121.10	91.47	91.40	0.1
0.958	115.60	82.37	82.80	0.5
0.945	110.00	75.70	74.90	1.1
0.920	100.00	64.24	61.65	4.2
0.858	75.00	37.21	36.58	1.7
0.797	50.00	20.07	20.05	0.1
0.772	40.00	15.29	15.34	0.3
0.760	35.00	13.25	13.32	0.5
0.747	30.00	11.43	11.51	0.7
0.735	25.00	9.81	9.89	0.8
0.723	20.00	8.38	8.46	0.9
0.710	15.00	7.12	7.19	0.9
0.698	10.00	6.01	6.07	0.9
0.686	5.00	5.04	5.09	0.9
0.673	0.	4.20	4.24	0.8
0.661	-5.00	3.48	3.50	0.7
0.649	-10.00	2.85	2.87	0.5
0.636	-15.00	2.32	2.33	0.3
0.624	-20.00	1.88	1.88	0.0
		[mmHg]	[mmHg]	
0.591	-33.60	758.02	760.00	0.3
0.562	-45.40	407.60	400.00	1.9
0.533	-57.00	204.16	200.00	2.1
0.505	-68.40	93.36	100.00	6.6
0.490	-74.30	59.04	60.00	1.6
0.478	-79.20	39.04	40.00	2.4
0.462	-85.80	21.07	20.00	5.3
0.447	-91.90	11.02	10.00	10.2
0.433	-97.50	5.59	5.00	11.8
0.404	-109.10	0.94	1.00	5.6
			av. abslt. dev.	2.2

Table 8 Prediction of saturated properties for ammonia¹⁾

Temp [°C]	Absolute deviation [%]		
	Density		Vaporization entropy
	Liquid	Vapor	
-100		0.1	4.6
-80	10.3	2.2	0.9
-60	7.4	2.2	1.0
-40	5.2	1.5	1.7
-20	3.7	0.7	1.9
0	2.6	0.0	1.7
20	1.9	0.5	1.2
40	1.6	0.8	0.7
60	1.4	0.8	0.2
80	0.9	0.6	0.4
100	4.5	0.2	0.9
120	49.1	0.4	1.2

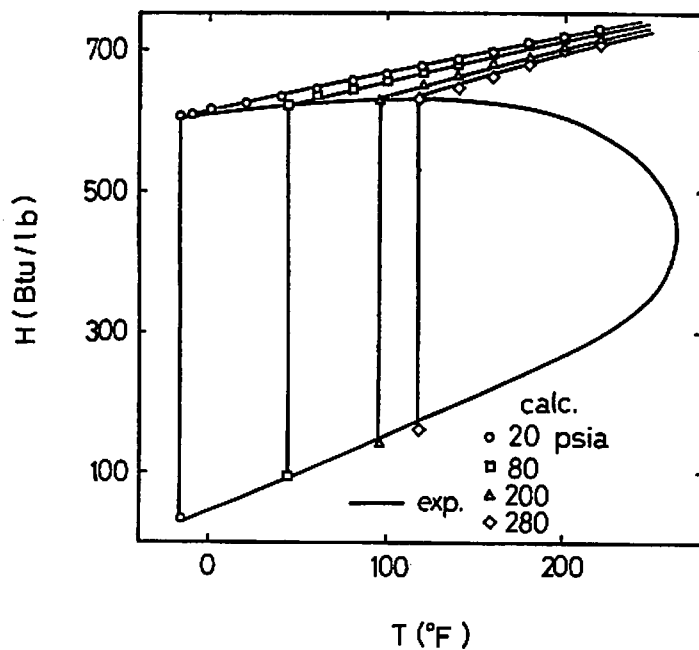


Fig. 8 Comparison of predicted enthalpy of ammonia with smoothed values¹⁾

3.3 Sulfur dioxide

Tables 9 and 10 show that the correlation in this work gives the excellent prediction of saturated thermodynamic properties (the melting point is -73.2°C). The average absolute deviation of the second virial coefficients is $4.1 \text{ cm}^3/\text{mol}$ ranging from 283.16 to 473.16 K. The P-V-T calculation gives the deviations of less than 1 per cent for a vapor phase ($0\text{--}250^{\circ}\text{C}$ and up to 30 MPa) and of less than 4 per cent for a liquid phase ($-20\text{--}20^{\circ}\text{C}$ and up to 16 MPa).

Table 9 Comparison of predicted vapor pressures of SO₂ with experimental values¹³⁾

<i>Tr</i> [-]	Temp. [°C]	<i>P. cal</i> [atm]	<i>P. exp</i> [atm]	Dev. [%]
0.994	155.00	74.39	74.45	0.1
0.982	150.00	68.16	68.20	0.1
0.959	140.00	57.79	57.60	0.3
0.936	130.00	48.49	48.38	0.2
0.913	120.00	40.50	40.25	0.6
0.890	110.00	33.40	33.25	0.4
0.866	100.00	27.32	27.25	0.2
0.843	90.00	22.11	22.10	0.1
0.820	80.00	17.69	17.70	0.1
0.797	70.00	13.97	14.10	0.9
0.774	60.00	10.86	11.00	1.3
0.750	50.00	8.30	8.35	0.6
0.727	40.00	6.23	6.25	0.4
0.704	30.00	4.57	4.60	0.6
0.681	20.00	3.28	3.20	2.5
		[mmHg]	[mmHg]	
0.581	-23.00	412.42	400.00	3.1
0.552	-35.40	210.43	200.00	5.2
0.525	-46.90	103.29	100.00	3.3
0.507	-54.60	60.56	60.00	0.9
0.494	-60.50	38.75	40.00	3.1
0.472	-69.70	17.92	20.00	10.4
0.456	-76.80	9.17	10.00	8.3
0.442	-83.00	4.77	5.00	4.5
0.412	-95.50	1.01	1.00	0.6
			av. abslt. dev.	2.0

Table 10 Prediction of saturated properties for sulfur dioxide¹¹⁾

Temp [°C]	Absolute deviation [%]		
	Density		Vaporization entropy
	Liquid	Vapor	
-50	3.1	3.3	3.8
-30	2.1	0.0	1.2
-10	1.4	1.1	0.2
10	1.0	1.1	1.1
30	0.8	1.2	1.8
60	0.9	2.0	3.2
90	1.5		
120	2.4		
140	0.2		

Table 11 Comparison of predicted vapor pressures of CH₃OH with experimental values¹³⁾

Tr [-]	Temp. [°C]	$P. cal$ [atm]	$P. exp$ [atm]	Dev. [%]
0.969	224.00	58.27	60.00	2.9
0.949	214.00	47.91	50.00	4.2
0.929	203.50	38.66	40.00	3.3
0.896	186.50	28.58	30.00	4.7
0.859	167.80	17.32	20.00	13.4
0.801	138.00	10.10	10.00	1.0
0.751	112.50	4.97	5.00	0.6
0.696	84.00	1.98	2.00	0.8
0.658	64.70	0.97	1.00	3.2
		[mmHg]	[mmHg]	
0.630	49.90	398.77	400.00	0.3
0.600	34.80	199.73	200.00	0.1
0.574	21.20	100.23	100.00	0.2
0.556	12.10	60.72	60.00	1.2
0.542	5.00	40.06	40.00	0.1
0.521	-6.00	20.05	20.00	0.2
0.501	-16.20	9.92	10.00	0.8
0.483	-25.30	5.01	5.00	0.2
0.447	-44.00	1.00	1.00	0.2
			av. abslt. dev.	2.1

3.4 Methanol

The use of the polar parameters gives poor prediction for the saturated density with deviations of 8-40%, whereas vapor pressures can be well correlated as shown in Table 11. Fig. 9 shows correlated results of the second virial coefficients. It is difficult to obtain the best fit because of the scattered experimental data²⁾. The corresponding state principles suggests that the abnormally big value of Ψ_E^* means methanol to attract strongly each other. Since this work is based on additivity between dispersion forces and small polar contribution, this idea may not be available to methanol because of its high nonlinearity.

3.5 Ethanol

The trend is similar to methanol. The equation of state for ethanol gives poor results for the saturated liquid density (5-30% deviation), whereas vapor pressures (Table 12)

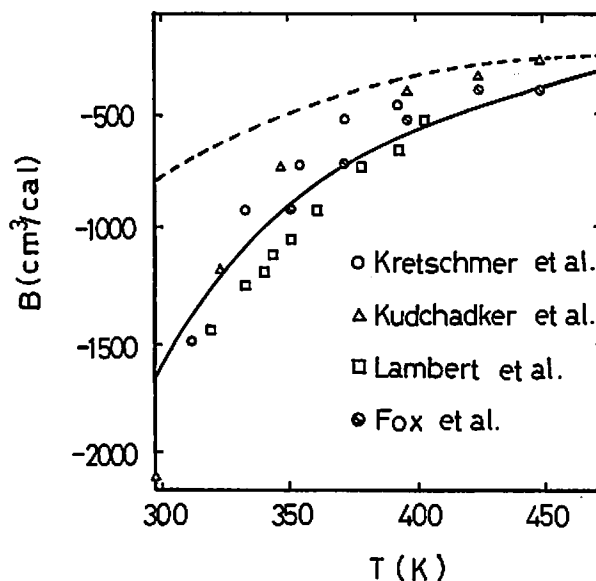


Fig. 9 Correlation of the second virial coefficients of methanol²⁾: solid line ($\Psi_A^*=0$, $\Psi_E^*=0.4841$), dotted line ($\Psi_A^*=\infty$, $\Psi_E^*=0$)

Table 12 Comparison of predicted vapor pressures of C_2H_5OH with experimental values¹³⁾

Tr [-]	Temp. [°C]	$P. cal$ [atm]	$P. exp$ [atm]	Dev. [%]
0.998	242.00	61.65	60.00	2.8
0.975	230.00	48.82	50.00	2.4
0.951	218.00	38.22	40.00	4.5
0.922	203.00	29.19	30.00	2.7
0.884	183.00	18.58	20.00	7.1
0.823	151.80	10.06	10.00	0.6
0.773	126.00	4.99	5.00	0.3
0.718	97.50	2.00	2.00	0.2
0.681	78.40	0.98	1.00	1.6
		[mmHg]	[mmHg]	
0.652	63.50	401.96	400.00	0.5
0.623	48.40	199.41	200.00	0.3
0.597	34.90	99.51	100.00	0.5
0.579	26.00	60.54	60.00	0.9
0.566	19.00	39.95	40.00	0.1
0.545	8.00	19.86	20.00	0.7
0.525	-2.30	9.81	10.00	1.9
0.506	-12.00	4.81	5.00	3.8
0.468	-31.30	1.02	1.00	1.8
			av. abslt. dev.	1.8

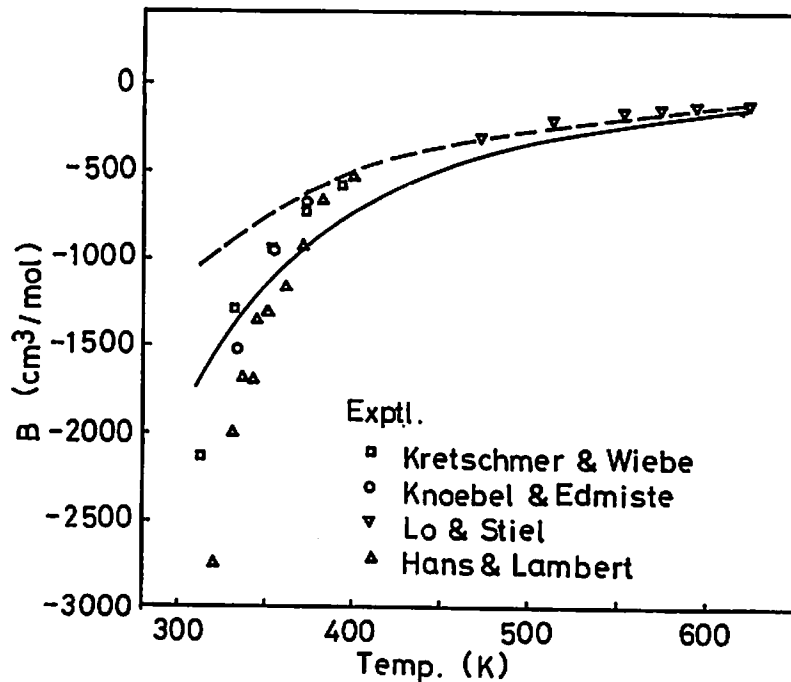


Fig. 10 Correlation of the second virial coefficients of ethanol²⁾: solid line ($\Psi_A = -0.1, \Psi_E^* = 0.3585$), dotted line ($\Psi_A^* = \Psi_E^* = 0$)

and vaporization enthalpy calculation gives excellent values. For the determination of the values of Ψ_A^* and Ψ_E^* , the second virial coefficient data by Kretschmer and Wiebe²⁾, Knoebel and Edmister²⁾ and our estimated values using the P-V-T data at high temperatures by Lo and Stiel⁴⁾ were used (Fig. 10). The P-V-T prediction over the temperature range of 220–350°C and up to 68 MPa gives over 10 per cent deviations for less than 0.6 in the Z value and a few per cent for over 0.6.

Conclusion

The polar parameters proposed in this work are found to be effective over wide ranges of temperature and pressure for water, ammonia and sulfur dioxide, whereas not so effective for methanol and ethanol. The failure for these alcohols may suggest that the perturbation method composed of the main effect of dispersion forces and small contribution of dipole interaction is not valid for methanol and ethanol because of their high polarity.

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Nomenclature

$A_0, B_0, C_0, D_0, E_0, a, b, c, d, e, f, g, h, \alpha, \gamma$ = fifteen coefficients for normal fluids in Eq. (2)

B	=second virial coefficient	[cm ³ /mol]
P	=pressure	[atm]
P_C	=critical pressure	[atm]
R	=gas constant	[1 atm/mol K]
s_1, s_2, s_3	=polar parameters defined in Eq. (3)	
s_1^*, s_3^*	=reduced polar parameters in Eqs. (6) and (7)	[–]
T	=temperature	
T_C	=critical temperature	[K]
V_C	=critical molar volume	[cm ³ /mol]
Z	=compressibility factor	[–]
Z_C	=compressibility factor at a critical point	[–]
ρ	=molar density	[mol/l]
Ψ_A, Ψ_E	=polar parameters defined in Eq. (2)	
Ψ_A^*, Ψ_E^*	=reduced polar parameters defined in Eqs. (4) and (5)	
ω	=Pitzer's acentric factor	

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