Thermochimica Acta, 145 (1989) 257–264
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CORRELATION OF SECOND VIRIAL COEFFICIENT FOR POLAR FLUIDS

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(Received 10 October 1988)

ABSTRACT

A new empirical correlation of second virial coefficients for pure polar gases has been developed by extending the Mak–Lielmezs correlation for non-polar fluids. The proposed extension requires the availability of the critical pressure and temperature, the Pitzer acentric factor ω, the dipole moment and the knowledge of an empirical substance-dependent factor x. The compounds correlated include acetaldehyde, acetone, acetonitrile, alcohols, ethers, ketones, phenol and water. Predictions agree very well with the experimental data and the values obtained by means of the Tosonopoulos correlation.

INTRODUCTION AND THEORETICAL DEVELOPMENT

In the analysis of vapour–liquid equilibrium behaviour, non-ideality of the vapour phase should be taken into consideration. Often for calculations at low to moderate pressures, the density is less than half the critical density and the virial equation of state truncated after the second term provides an excellent estimate of the vapour phase fugacity coefficient. As a matter of fact, a number of outstanding methods have been developed [1–12] for predicting the second virial coefficient of non-polar and polar gases. Recently, Mak and Lielmezs [12], using a cubic equation of state, developed an expression for the calculation of second virial coefficient of gaseous non-polar substances as follows

$$\frac{BP_c}{RT_c} = \Omega_b - \Omega_a \frac{\alpha}{T_r} \tag{1}$$

Solving eqn. (1) for α, we have

$$\alpha = \left[\frac{\Omega_b}{\Omega_a} - \frac{B_r}{\Omega_a}\right] T_r \tag{2}$$

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0040-6031/89/$03.50

where

$$B_r = \frac{BP_c}{RT_c} \tag{3}$$

Following the Pitzer–Curl [1] and Tsonopoulos [6] development of the three parameter theorem of corresponding states and utilizing the Shaw–Lielmezs [13] model of generalized F function for the Redlich–Kwong-type equation of state, Mak and Lielmezs [12] suggested that the α function (eqns. (1) and (2)) be set for normal fluids as

$$\alpha(T_r, \omega) = \alpha^{(0)}(T_r) + \omega\alpha^{(1)}(T_r) \tag{4}$$

where

$$\alpha^{(0)}(T_r) = \sum_{i=1}^{l} c_{i0} T_r^{(1-i)} \tag{5}$$

$$\alpha^{(1)}(T_r) = \sum_{i=1}^{m} c_{i1} T_r^{(1-i)} \tag{6}$$

Equation (5) represents the α function of simple fluids while eqn. (6) corrects for the deviation of normal fluids from simple fluids. Mak and Lielmezs [12] expanded eqns. (5) and (6) as follows

$$\begin{aligned}\alpha^{(0)} = {} & -1.4524905 + 14.360017/T_r - 45.000285/T_r^2 \\ & + 14.078304/T_r^6 + 1.7835426/T_r^7\end{aligned} \tag{7}$$

$$\begin{aligned}\alpha^{(1)} = {} & -4.3816022 + 15.205023/T_r - 20.874489/T_r^2 \\ & + 12.697209/T_r^3 - 2.5851848/T_r^4\end{aligned} \tag{8}$$

To account for the behaviour of polar and associating fluids [6], the α function has been extended (eqn. 4) to include a correcting term, $\mu_r^x\alpha^{(2)}(T_r)$ consisting of the reduced dipole moment μ_r raised to the power of x and an $\alpha^{(2)}(T_r)$ function, so that the enlarged α function is given by

$$\alpha(T_r, \omega, \mu_r) = \alpha^{(0)}(T_r) + \omega\alpha^{(1)}(T_r) + \mu_r^x\alpha^{(2)}(T_r) \tag{9}$$

where

$$\mu_r = 10^5\mu^2 P_c/T_c^2 \tag{10}$$

with

$$\alpha^{(2)}(T_r) = \sum_{i=1}^{n} c_{i2} T_r^{(-6-i)} \tag{11}$$

and x is a substance-dependent coefficient.

To determine the numerical values of coefficients c_{i2} and the number of terms appearing in eqn. (11), the criterion of minimum variance of the curve fit was used following Mak and Lielmezs [12].

The numerical values of coefficients c_{i2} (eqn. (11)) were determined by means of linear multiple regression methods letting $x = 1$; that is, considering

$$\alpha^{(2)}\left(T_r,\ \omega,\ \mu_r^{x=1}\right) = \frac{\alpha_i - \left[\alpha_i^{(0)} + \omega_i\alpha_i^{(1)}\right]}{ri^{x=1}}$$
$$= \sum_{i=1}^{n} c_{i2} T_r^{(-6-i)} \tag{12}$$

then, using the c_{i2} coefficient valued computed using eqn. (12), the optimum value of the exponent x * (Table 1) was determined in each case for each compound in such a way as to minimize the RMS% error in the calculated value of the second virial coefficient.

The expanded form of the $\alpha^{(2)}(T_r)$ function in terms of the calculated coefficients c_{i2} (Eqn. (12)) is

$$\alpha^{(2)}(T_r) = -0.008019636/T_r^7 + 0.01092317/T_r^8 - 0.003505639/T_r^9 \tag{13}$$

The final expression of the $\alpha^{(2)}(T_r)$ function (eqn. (13)) was obtained from a set of 276 experimental data points representing 19 highly polar and associating fluids (see Table 1) with a variance of 0.00002798. All experimental data used were taken from the recent compilation of second virial coefficients by Dymond and Smith [14]. As the data used were thought to be of sufficient reliability, no further evaluation of their accuracy was made.

DISCUSSION

The second virial coefficients (eqns. (1) and (3)) have been calculated using the proposed correlations (eqns. (7)–(11) and (13)) for 19 polar and associating fluids. Table 1 compares the experimental virial coefficients with the values obtained in this work and those calculated by means of the Tsonopoulos correlation [6]. For normal fluids the proposed method (eqns. (4)–(8) appears to be superior to the Tsonopoulos correlation for the compounds studied [12]. Table 1 indicates that the predictions made by the extended calculation method for polar compounds (eqns. (7)–(11) and (13)) agree very well with the available experimental data and the results obtained by means of the Tsonopoulos correlation [6], the Tsonopoulos method perhaps possessing a very slight edge in the curve-fit accuracy over the proposed correlation (Table 1). Figure 1 shows the second virial coefficient values as calculated by the proposed method (eqns. (7)–(11) and (13) and Table 1) and the Tsonopoulos correlation, and the available experimental

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* As a measure of x stability, the x range over which there is a 10% or less variation (increase) of RMS% error value with respect to the optimum (least) x, is given in Table 1.

TABLE 1

Second virial coefficient (eqns. (1)–(3)): absolute average deviation (AAD%) [a] and RMS% error [b] value comparison

Compound	T_r range	N (number of data points)	x coeff. eqn. (9)	x range [c]	Comparison				Data sources [d]
					Tsonopoulos [6]		This work, eqn. (9)		
					AAD%	RMS%	AAD%	RMS%	
Dimethyl ether	0.683–0.820	13	0.95	0.87, 1.00	3.1	3.9	6.0	7.2	Cawod and Paterson (1933), Kennedy et al. (1941), Tripp and Dunlap (1962), Haworth and Sutton (1971)
Diethyl ether	0.600–0.857	7	0.65	0.0, 0.91	11.7	15.2	9.2	11.9	Dymond and Smith (1980)
Diisopropyl ether	0.622–0.683	3	0.50	0.45, 0.85	1.4	1.5	0.9	1.2	Andon et al. (1974)
Acetone	0.590–0.945	10	0.83	0.81, 0.85	2.9	4.1	5.0	7.0	Dymond and Smith (1980)
Methyl ethyl ketone	0.587–0.692	5	0.71	0.70, 0.72	6.3	6.8	1.7	1.8	Nickerson et al. (1961)
Methyl *n*-propyl ketone	0.594–0.700	5	0.90	0.89, 0.92	4.1	4.7	3.1	4.0	Nickerson et al. (1961)
Diethyl ketone	0.597–0.669	3	0.80	0.80, 0.81	0.1	0.2	0.8	0.9	Hales et al. (1967)
Acetaldehyde	0.625–1.023	16	0.91	0.87, 0.94	3.4	4.5	10.0	13.5	Alexander and Lambert (1941), Prausnitz and Carter (1960)
Acetonitrile	0.592–0.772	39	1.02	1.01, 1.04	5.7	6.9	9.6	12.7	Lambert et al. (1949), Brawn and Smith (1960), Prausnitz and Carter (1960), Zaalishvili et al. (1971), Kolisko et al. (1972)
Methanol	0.623–1.118	57	1.08	1.02, 1.13	12.7	16.8	11.4	14.2	Lambert et al. (1949), Kretschmer, Wiebe (1954), Fox et al. (1954), Bottomley and

									Spurling (1967), Knoebel and Edmister (1968), Kell and McLaurin (1969), Kudchadkev and Eubank (1970)
Ethanol	0.623–0.774	18	1.13	1.07, 1.18	13.7	17.0	14.4	16.4	Hank and Lambert (1951), Kretschmer and Wiebe (1954), Knoebek and Edmister (1968)
n-Propanol	0.652–0.789	7	0.90	0.66, 0.99	6.9	8.8	9.6	9.8	Fox et al. (1954), Cox (1961)
Isopropanol	0.689–0.731	22	0.96	0.90, 1.05	3.5	4.0	3.4	4.6	Fox et al. (1954), Kretschmer and Wiebe (1954), Cox (1961), Moreland et al. (1967)
1-Butanol	0.622–0.780	7	0.20	0.0, 0.66	5.7	6.6	9.7	12.1	Fox et al. (1954), Cox (1961)
Isobutanol	0.718–0.802	4	0.20	0.0, 0.76	3.3	4.7	4.4	6.7	Cox (1961)
sec-Butanol	0.706–0.790	4	0.68	0.0, 0.82	2.6	3.2	3.4	4.7	Cox (1961)
tert-Butanol	0.747–0.836	4	0.70	0.0, 1.00	5.2	7.4	6.8	9.8	Cox (1961)
Phenol	0.617–0.654	6	0.80	0.77, 0.83	8.1	8.5	2.2	2.6	Andon et al. (1960)
Water	0.500–1.812	55	0.72	0.63, 0.78	6.9	10.0	4.5	7.1	Vukalovichet et al. (1967), Kell et al. (1968)
Total	276								
Average					5.7	7.1	6.1	7.8	

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[a] AAD% = Σ^N |(Experimental − Calculated)/Experimental | × 100/N.

[b] RMS% error = $[\Sigma(\%\ \text{error})^2/N]^{0.5}$; % error = [Exp. − Calc./Exp.] × 100

[c] x range corresponds to a 10% (or less) variation (increase) of RMS% error taken with respect to the optimum value of x.

[d] All experimental data for second virial coefficient taken from Dymond and Smith [14]; all physical property data from Reid, Prausnitz and Sherwood [16], except the acentric factor value for isopropanol which was taken from Reid, Prausnitz and Poling [17].

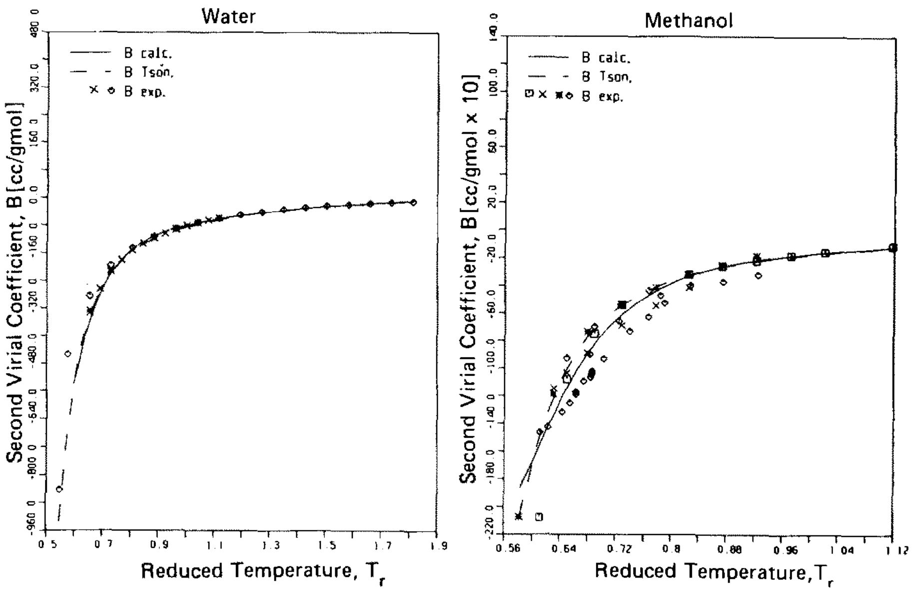

Fig. 1. Second virial coefficient B of water and methanol versus reduced temperature T_r.

values plotted against temperature for water and methanol, two hydrogen-bonding polar fluids. Figure 2 gives similar second virial coefficient versus temperature plots for two non-hydrogen-bonding polar fluids, diethyl ether

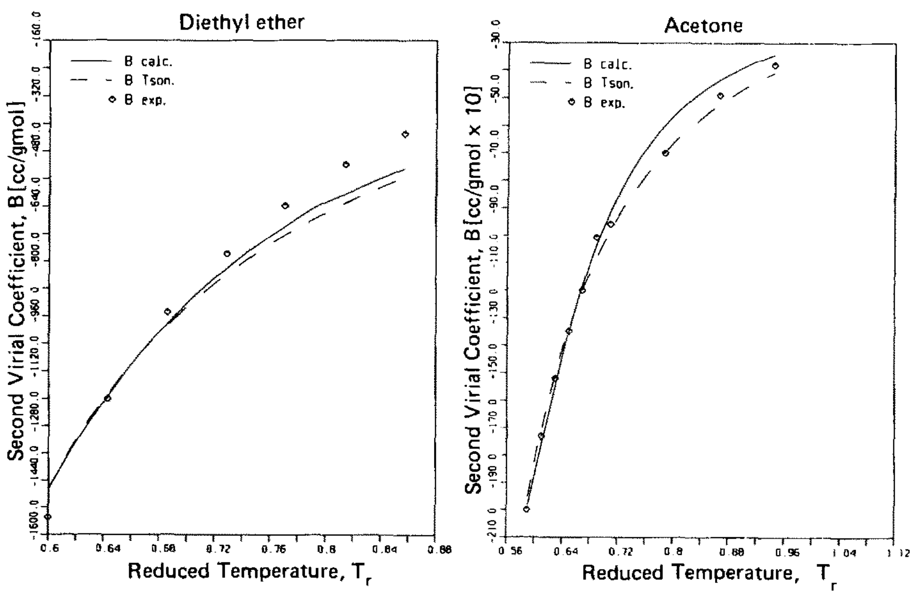

Fig. 2. Second virial coefficient B of diethyl ether and acetone versus reduced temperature, T_r.

and acetone. As can be seen from Figs. 1 and 2, both methods compare very well with the experimental data for all polar compounds for all temperature ranges considered. The Tsonopoulos correlation, in addition to the acentric factor ω, the critical temperature T_c and pressure P_c, and the reduced dipole moment μ_r, is curve-fitted with one substance dependent parameter (non-hydrogen and weakly hydrogen-bonding polar substances) or with two substance dependent parameters (hydrogen-bonding polar substances) while the proposed method, in addition to the same basic parameters (ω, T_c, P_c and μ_r), uses only one curve-fitted substance dependent constant, the optimum x coefficient value (Table 1). It appears, therefore, that the proposed method is altogether simpler to use than the Tsonopoulos correlation (Table 1 and Figs. 1 and 2). Equations (7), (8) and (13) are simple linear polynomials describing the α term as a function of the variable T_r. This power series expansion in T_r for the given α function has a radius of convergence which extends from the point of expansion to the nearest singularity in the function so that a power series expansion becomes useless beyond that point [15]. Because of this weakness in the convergence properties of the given series, we have set the experimentally tested curve-fitting ranges for the state parameter T_r to be: $0.3 < T_r < 14.0$ for normal fluids (eqns. (4)–(8)), and $0.52 < T_r < 2.0$ for all polar fluids (eqns. (4)–(11) and (13), Table 1 and Figs. 1 and 2). Studies to extend the range of application of the proposed correlation to include mixtures have been started. The results obtained and the comparisons made (Table 1, Figs. 1 and 2) strongly support the proposed method.

NOMENCLATURE

B	second virial coefficient
c	power series coefficient defined by eqns. (5), (6) and (11)
N	number of data points
P	pressure
R	universal gas constant
T	temperature
x	substance dependent coefficient, defined by eqn. (9)

Greek letters

α	function defined by eqns. (2) and (9)
ω	Pitzer acentric factor
Ω_a, Ω_b	dimensionless entities
μ	dipole moment

Subscripts

c	critical state
r	reduced state

ACKNOWLEDGEMENTS

The financial assistance of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged. Mrs. H. Aleman is thanked for aiding in the computer work. A. Romero also thanks the University of British Columbia for the financial assistance received by means of a University Graduate Fellowship award.

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