A Group Contribution Method for Second Virial Coefficients

A semitheoretical group contribution method for predicting pure-compound second virial coefficients is proposed. An expression for the second virial coefficient, expressed as the product of a nonpolar and a polar contribution, is derived using statistical thermodynamic concepts and an approximate form for the radial distribution function. For polar compounds the nonpolar contribution is assumed to be given by the Tsonopoulos correlation with the nonpolar acentric factor defined by Thompson and Braun. The polar contribution is represented by an energetic term expressed in terms of group contributions. Second virial coefficient predictions for strong polar and associating systems are comparable with those obtained with the correlations of Tsonopoulos and Hayden and O'Connell. Cross-second virial coefficients for mixtures obtained using well-defined molecular mixing rules compare well with literature values.

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Introduction

The study of phase equilibria has shown that most systems deviate from ideal behavior, and gas-phase imperfections are usually expressed by means of the fugacity coefficients. For moderate gas densities, the virial expansion truncated after the second virial coefficient is a useful equation of state:

$$\frac{Pv}{RT} = 1 + \frac{B}{v} \tag{1}$$

where P is the total pressure, T the absolute temperature, v the molar volume, and B is the second virial coefficient, a function of temperature and composition only. Since Eq. 1 has a strong theoretical basis, it can be extended to multicomponent mixtures without any assumption. For a mixture of n components the mixture second virial coefficient, B_m, is given by

$$B_m = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j B_{ij} \tag{2}$$

where the interaction second virial coefficient $B_{ij(i \neq j)}$ depends only on temperature for each pair of compounds.

From Eqs. 1 and 2 the fugacity coefficients take the form (Prausnitz, 1969)

$$\ln \phi_i = \frac{2}{v} \sum_{j=1}^{n} y_j B_{ij} - \ln Z \tag{3}$$

The values of B_{ii} and B_{ij} are not always available. Therefore when required they must either be determined experimentally or obtained by means of a correlation. The former method is unfortunately expensive and time consuming; thus the use of correlations is preferred. In order to fulfill this need, many correlations for pure and interaction second virial coefficients have been proposed in the literature (Pitzer and Curl, 1957; O'Connell and Prausnitz, 1967; Kreglewski, 1969; Nothnagel et al., 1973; Tsonopoulos, 1974; Hayden and O'Connell, 1975; Tarakad and Danner, 1977; McCann and Danner, 1984; Malijevsky et al., 1986). While practically all of them can predict fairly well the second virial coefficients for hydrocarbons and weakly polar compounds, they are not so successful for strongly polar and associating compounds. The predictions for these systems have been made possible by introducing parameters accounting for polar and association effects.

In this work we present a group contribution method to predict pure-compound second virial coefficients, which has been derived from statistical thermodynamics using an approximate representation of the radial distribution function. It consists in a nonpolar part given by the Tsonopoulos (1974) correlation with the nonpolar acentric factor defined by Thompson and Braun (1968), and a polar and associating part expressed in terms of energetic group contributions. The extension to mixtures is done in molecular terms through well-defined mixing rules.

Development of the method

The theoretical expression for the second virial coefficient can be represented (Hill, 1956) by

$$B = \frac{-2\pi N_A}{3k_BT}\int_0^\infty r^3\frac{du(r)}{dr}\exp\left[-u(r)/k_BT\right]dr \qquad (4)$$

where $u(r)$ is the intermolecular potential, r is the radial distance, N_A is Avogadro's number, and k_B is Boltzmann's constant.

Equation 4 can be rewritten as follows:

$$B = \frac{2\pi N_A}{3}\int_0^\infty r^3\left(\frac{d}{dr}\{\exp\left[-u(r)/k_BT\right]\}\right)dr \qquad (5)$$

At low densities, the intermolecular potential is related to the radial distribution function, $g(r)$ (Hill, 1956), by

$$g(r) = \exp\left[-u(r)/k_BT\right] \qquad (6)$$

Consequently, Eq. 5 becomes

$$B = \frac{2\pi N_A}{3}\int_0^\infty r^3\left[\frac{dg(r)}{dr}\right]dr \qquad (7)$$

As shown in Figure 1, the radial distribution function can be approximated by step functions (Abusleme and Vera, 1985), which may be expressed in terms of the unit step function $f_u(r)$.

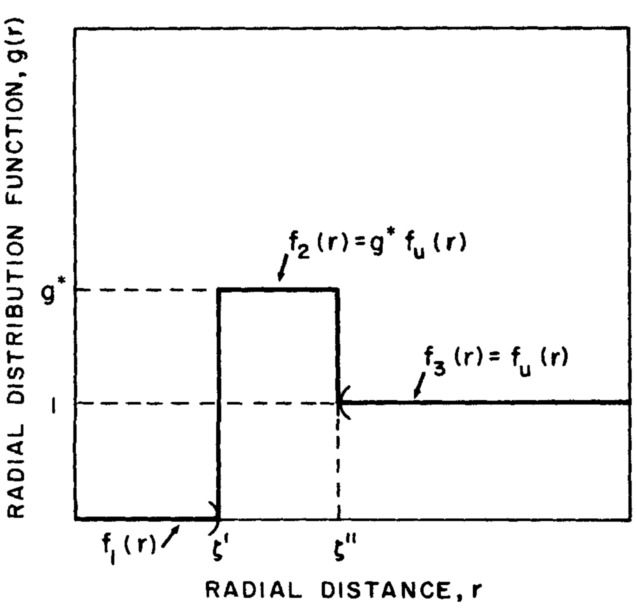

Figure 1. Approximate representation of pair distribution function $g(r)$.

Furthermore, it is known (Coughanowr and Koppel, 1965) that $f_u(r)$ and the Dirac function $\delta(r)$ are related by

$$\delta(r) = \left[\frac{df_u(r)}{dr}\right] \qquad (8)$$

where $\delta(r)$ satisfies

$$\int_{-\infty}^{\infty}\delta(r)\,dr = 1 \qquad (9)$$

The lower limit of Eq. 9 may be replaced by the value of the variable for which the unit step function becomes unity. Thus, using the approximate representation for $g(r)$ given in Figure 1, Eq. 7 takes the form

$$B = \frac{2\pi N_A}{3}\left(\int_0^{r\leq\zeta'} r^3\left[\frac{df_1(r)}{dr}\right]dr + \left\{\int_{r=\zeta'}^{\infty} r^3\left[\frac{df_2(r)}{dr}\right]dr - \int_{r=\zeta''}^{\infty} r^3\left[\frac{df_2(r)}{dr}\right]dr\right\} + \int_{r\geq\zeta''}^{\infty} r^3\left[\frac{df_3(r)}{dr}\right]dr\right) \qquad (10)$$

The first and last integrals are zero because $f_1(r)$ and $f_3(r)$ are independent of r. The second and third integrals may be expressed in terms of the unit step function as

$$\int_{r=\zeta}^{\infty} r^3\left[\frac{df_2(r)}{dr}\right]dr = g^*\int_{r=\zeta}^{\infty} r^3\left[\frac{df_u(r)}{dr}\right]dr = g^*\zeta^3 \qquad (11)$$

We now define the size parameter σ_Q, a function of temperature, as

$$\sigma_Q^3 \equiv \zeta''^3 - \zeta'^3 \qquad (12)$$

and the nonpolar second virial coefficient B_o as

$$B_o \equiv \frac{2\pi N_A\sigma_Q^3}{3} \qquad (13)$$

Then, Eq. 10 may be written as a product of an energetic contribution represented by g^*, and a nonpolar contribution represented by B_o as

$$B = B_o g^* \qquad (14)$$

which is the solution of Eq. 7 under the simplifying assumption for $g(r)$ shown in Figure 1.

Equation 14 suggests that the second virial coefficient may be expressed as a product of a nonpolar contribution and an exponential factor representing polar and associating energetic effects. As can be seen from Eq. 13 and from Figure 1, Eq. 14 gives only positive values of the second virial coefficients. In this work, Eq. 14 is used as the model equation and the above limitation is relaxed as described below.

Nonpolar contribution

To evaluate the nonpolar contribution to the second virial coefficient we generalize the correlation of Pitzer and Curl

(1957) for nonpolar compounds, B_o, and write

$$B_o = \frac{RT_c}{P_c}\left[f^{(0)}_{(T_R)} + Wf^{(1)}_{(T_R)}\right] \tag{15}$$

where $f^{(0)}_{(T_R)}$ and $f^{(1)}_{(T_R)}$ are taken from the work of Tsonopoulos (1974):

$$f^{(0)}_{(T_R)} = 0.1445 - 0.330/T_R - 0.1385/T_R^2 - 0.0121/T_R^3 - 0.000607/T_R^8 \tag{16}$$

$$f^{(1)}_{(T_R)} = 0.0637 + 0.331/T_R^2 - 0.423/T_R^3 - 0.008/T_R^8 \tag{17}$$

In this work the term W, introduced to correct for the acentricity of the molecules, is considered differently depending whether the compound is polar or nonpolar. In the case of nonpolar compounds the generalized acentric factor W coincides with the definition given by Pitzer et al. (1955):

$$W = \omega = -\log_{10}\left(\frac{P_o}{P_c}\right)_{T_R=0.7} - 1.000 \tag{18}$$

Since for nonpolar compounds, by definition $g^* = 1$, the value of B obtained from Eq. 14 is identical to the value given by the Tsonopoulos (1974) correlation for these compounds.

When dealing with polar and associating molecules there are several ways of calculating a representative nonpolar contribution to the second virial coefficient. If the form of Eq. 15 is preserved, the alternatives can be grouped in three categories:

1. To use actual values of T_c and P_c and to identify W with ω defined by Eq. 18
2. To use representative nonpolar values of T_c, P_c, and W based on the homomorph or other similar concepts;
3. To use a combination of the above based on purely pragmatic considerations of simplicity vs. accuracy

Since the purpose of this work is to provide a better correlation for second virial coefficients, we have followed the third option. After trying various alternatives, we recommend using the actual values of T_c and P_c of the polar or associating compound to evaluate $f^{(0)}_{(T_R)}$, $f^{(1)}_{(T_R)}$, and (RT_c/P_c), and to use W equal to the value of the acentric factor, ω_H, as defined by Thompson and Braun (1968). This value of W is calculated from the mean radius of gyration, R_H, using Eq. 15 of the work of Hayden and O'Connell (1975), namely,

$$W = \omega_H = 0.006\,R_H + 0.02087\,R_H^2 - 0.00136\,R_H^3 \tag{19}$$

Therefore, B_o is evaluated using Eqs. 15 through 19, choosing either Eq. 18 or 19, depending on the case.

Energetic contribution

From Eq. 6 and Figure 1 we can express g^* as follows

$$g^* = \exp(-\epsilon/T) \tag{20}$$

where the Boltzmann constant has been absorbed in the energetic parameter ϵ, which is closely related to the intermolecular potential. The ϵ term is assumed to be zero for nonpolar compounds and to be given by a summation of group contributions for a polar molecule. In this work we postulate that ϵ may be expressed by:

$$-\epsilon = \sum_{k}^{NG}\sum_{l=k}^{NG}\theta_k\theta_l\epsilon^G_{kl} \tag{21}$$

where θ_k is the group surface area fraction of group k; $\epsilon^G_{kl} = \epsilon^G_{lk}$ is the k–l group interaction parameter and NG is the number of groups composing the molecule. The group surface area fraction, θ_k, is given by

$$\theta_k = \frac{\nu_k(zQ_k)}{\sum_l \nu_l zQ_l} \tag{22}$$

where Q_k is the surface area of group k, z is the coordination number, and ν_k is the number of groups k in the molecule. The coordination number value is irrelevant in the calculations since zQ_k is calculated directly (Abusleme and Vera, 1985) by

$$zQ_k = 0.4228\,V_k^* + (2 - J_k) \tag{23}$$

where V_k^* is the van der Waals volume of group k and J_k is the number of groups bonded to group k. These values are listed in Table 1 according to the group definitions used in this work.

In this work two expressions for the temperature dependence of ϵ^G_{kl} were tested. The first satisfies the zero limit at high temperature, but $-\epsilon$ might become negative because in some cases Eq. 15 fails to represent properly the nonpolar contribution B_o. This expression for ϵ^G_{kl} is

$$\epsilon^G_{kl} = \frac{T_{ref}}{T^{0.5}}\left\{a_{kl} + b_{kl}\left[\left(\frac{T_{ref}}{T}\right)^{0.5} - 1\right]\right\} \tag{24a}$$

where $T_{ref} = 298.15$ K and a_{kl}, b_{kl} are temperature-independent parameters for the k–l group interaction.

The second expression for ϵ^G_{kl} meets all the limits at the expense of a better fitting of the experimental second virial coefficient data. This expression, which is always positive and has a limiting value of zero at infinite temperature, has the form

$$\epsilon^G_{kl} = a'_{kl}[1 - \exp(b'_{kl}/T)] \tag{24b}$$

where a'_{kl} and b'_{kl} are the temperature-independent parameters for the k–l group interaction. Values of a_{kl} and b_{kl} determined from experimental information on pure-compound virial coefficient are exhibited in Table 2. Values of a'_{kl} and b'_{kl} are not reported here.

Therefore, the pure-compound second virial coefficient may be obtained by using Eq. 14 written as

$$B = B_o\exp(-\epsilon/T) \tag{25}$$

where the nonpolar and the energetic contributions may be calculated by the equations presented above.

Mixtures

The interaction second virial coefficient, B_{ij}, may be expressed as

$$B_{ij} = B_{oij}\exp(-\epsilon_{ij}/T) \tag{26}$$

Table 1. Hard Core Volumes V_k^* and the Term $(2 - J_k)$

No.	Group†	V_k^* $cm^3 \cdot mol^{-1}$	$2 - J_k$
1	$(CH_3)_{al}$	13.67	1
	$(CH_2)_{al}$	10.23	0
	$(CH)_{al}$	6.78	−1
	$(C)_{al}$	3.33	−2
	$(CH_2{=})_{al}$	11.94	1
	$(CH{=})_{al}$	8.47	0
	$(CH_2)_{cy}$	9.92	0
2	$(CH\ {=})_{ar}$	8.06	0
	$(C\ {=})_{ar}$	5.54	−1
3	$(HCOO)_{al}$	15.20	1
	$(C00)_{al}$	15.20	0
4	$[CH_3CH0]°$	—	—
5	$(Cl)_{al}$	11.62	1
6	$(O)_{al}$	10.23‡	0
7	(OH)	4.59‡	1
8	$(CO)_{al}$	11.70	0
9	$[NH_3]°$	—	—
	$(NH_2)_{al}$	10.54	1
	$(NH)_{al}$	8.08	0
	$(N)_{al}$	4.33	−1
10	$[H_2O]°$	—	—
11	$[CH_3CN]°$	—	—
12	$(Br)_{al}$	14.40	1
13	$(F)_{al}$	5.72	1
14	$[S0_2]°$	—	—
15	$(SH)_{al}$	14.81	1
	$(S)_{al}$	10.80	0
16	$(N)_{ar}$	5.20	0
17	$[CH_3I]°$	—	—
18	$[HCl]°$	—	—
19	$[HCN]°$	—	—
20	$[CH_3NO_2]°$	—	—

†al = in aliphatic compound
cy = in cyclic compound
ar = in aromatic compound.
[ ]° molecular species, $\theta_k = 1$
‡Does not correspond to Bondi's value

where B_{oij} is the nonpolar cross second virial coefficient. Its determination requires mixing rules for the critical pressure, temperature, and acentric factor of the binary interaction. The chosen mixing rules for P_{cij} and T_{cij} of the mixture are the same as those used by Tsonopoulos (1974):

$$T_{cij} = (T_{ci}\, T_{cj})^{1/2}(1 - k_{ij}) \tag{27}$$

$$P_{cij} = \frac{4\, T_{cij}(P_{ci}v_{ci}/T_{ci} + P_{cj}v_{cj}/T_{cj})}{(v_{ci}^{1/3} + v_{cj}^{1/3})^3} \tag{28}$$

where k_{ij} is a characteristic parameter for each binary molecular interaction and v_{ci} is the critical volume of component i. For the acentric factor of the mixture ω_{ij}, we use simply

$$\omega_{ij} = (\omega_i + \omega_j)/2 \tag{29}$$

where ω_i and ω_j are determined with Eq. 18 or 19 according to the characteristics of the compounds. Then, with the above mixing rules and Eqs. 15 through 19 we may calculate B_{oij}.

Table 2. Values for Temperature-Independent Group Parameters

Interaction k/ℓ	Parameter*	
	$a_{k\ell}$ / $K^{1/2}$	$b_{k\ell}$ / $K^{1/2}$
3/1	15.41	20.76
3/3	−2,138.	44.21
4/4	13.25	31.84
5/1	6.22	82.05
5/5	2.47	−26.85
6/1	15.21	277.5
6/6	−38.11	−1,636.
7/1	125.5	724.6
7/2	82.55	216.0
7/7	−324.1	−2,331.
8/1	14.80	−154.9
8/8	78.69	1,307.
9/1	9.74	−5.66
9/9	6.45	23.76
10/10	35.09	109.9
11/11	31.06	58.63
12/1	−13.09	−33.04
12/12	50.39	90.20
13/1	8.97	4.55
13/13	−6.06	71.80
14/14	4.47	14.04
15/1	12.83	56.57
15/15	−49.33	−527.0
16/1	−58.20	−722.1
16/2	36.51	332.0
16/16	−173.4	−2,747.
17/17	−0.04	16.79
18/18	19.14	114.6
19/19	18.84	87.31
20/20	21.20	22.91

*T_{ref} = 298.15 K

In addition, the i-j molecular interaction parameter ϵ_{ij} of Eq. 26 is assumed to be the geometric mean of ϵ_{ii} and ϵ_{jj}:

$$\epsilon_{ij} = (\epsilon_{ii}\, \epsilon_{jj})^{1/2} \tag{30}$$

The term ϵ_{ij} vanishes when one of the components is nonpolar. This agrees with the Tsonopoulos (1974) correlation for second virial coefficients, which assumes no polar term in B_{ij} when one of the constituents of the binary mixture is nonpolar. Should either ϵ_{ii} or ϵ_{jj} be negative, the value of ϵ_{ij} is also set at zero.

Consequently, knowing the nonpolar and energetic contribution to the interaction second virial coefficient B_{ij}, its value may be obtained with Eq. 26.

Results and Discussion

Since the Tsonopoulos (1974) and Hayden and O'Connell (1975) correlations to predict pure-compound and interaction second virial coefficients are the two most successful, they have been used as references to test the correlation developed in this work. Experimental pure-compound and interaction second virial coefficients have been taken from the compilation of Dymond and Smith (1980) and from the data bank of J.P. O'Connell, (1987). On the other hand the parameters used in

Table 3. RMS Deviations F^* for Pure-Compound Second Virial Coefficients

Pure Compound (No. Exp. Points)**	Tsonopoulos (1974)	Hayden & O'Connell (1975)	This Work
Methanol (29)†	$137^{(a)}$	$237^{(a)}$	124
Ethanol (18)	$334^{(a)}$	$455^{(a)}$	270
Propanol (7)	$106^{(a)}$	$146^{(a)}$	72
Butanol (7)	$100^{(a)}$	$186^{(a)}$	143
2-methyl–propanol (4)	$23^{(a)}$	$46^{(a)}$	52
2-butanol (4)	$15^{(a)}$	$15^{(a)}$	22
2-methyl–2-propanol (4)	$33^{(a)}$	$87^{(a)}$	47
Phenol (10)‡	51	881	28
0-cresol (4)	$152^{(c)}$	$278^{(c)}$	118
Acetone (30)†	$29^{(a)}$	$50^{(a)}$	28
Methyl ethyl ketone (5)	$84^{(a)}$	$67^{(a)}$	48
Diethyl ketone (3)	$42^{(a)}$	$71^{(a)}$	79
Dimethyl ether (10)†	$14^{(a)}$	32	14
Diethyl ether (29)	$63^{(a)}$	110	37
Methyl formate (11)	$22^{(a)}$	$24^{(a)}$	30
Ethyl formate (13)	$59^{(a)}$	$28^{(a)}$	73
Propyl formate (18)	$79^{(a)}$	$47^{(a)}$	110
Methyl acetate (22)	$94^{(a)}$	$23^{(a)}$	93
Ethyl acetate (18)	$26^{(a)}$	$44^{(a)}$	27
Methyl propionate (14)	60	$51^{(a)}$	67
Bromomethane (26)	$48^{(a)}$	45	37
Bromoethane (2)	141	139	3
Chloroform (21)†	37	164	50
Chloromethane (24)†	$10^{(a)}$	40	23
Chloroethane (30)†	$22^{(a)}$	25	34
Dichloromethane (13)‡	102	34	64
Chloroethylene (6)†	35	66	73
Fluoroform (20)‡	29	23	29
Fluoromethane (16)†	$5^{(a)}$	3	2
Methyl iodide (10)‡	83	95	$18^{(a,b)}$
Dimethyl sulfide (4)‡	184	24	22
Methyl ethyl sulfide (3)‡	420	223	157
Methyl propyl sulfide (2)‡	394	82	15
Methyl *i*-propyl sulfide (2)‡	308	20	83
Diethyl sulfide (3)‡	437	151	57
Propyl thiol (2)‡	314	$8^{(a)}$	40
i-Propyl thiol (2)‡	294	$5^{(a)}$	22
Butyl thiol (2)‡	454	$19^{(a)}$	71
i-Butyl thiol (2)‡	369	$90^{(a)}$	44
t-Butyl thiol (2)‡	284	$17^{(a)}$	92
Pentyl thiol (2)‡	469	$10^{(a)}$	52
Methylamine (23)	—	$22^{(a)}$	15
Ethylamine (11)	—	$29^{(a)}$	17
Dimethylamine (10)	—	$24^{(a)}$	9
Diethylamine (11)	—	$21^{(a)}$	19
Trimethylamine (8)†	—	$7^{(a)}$	17
α-Picoline (7)‡	272	48	68
β-Picoline (6)‡	478	$58^{(a)}$	99
γ-Picoline (4)‡	410	$13^{(a)}$	35
Pyridine (7)‡	223	122	24
Water (28)†	$4^{(a)}$	$38^{(a)}$	3
Ammonia (22)†	$5^{(a)}$	9	4
Acetonitrile (9)†	$193^{(a)}$	$541^{(a)}$	$70^{(a,b)}$
Hydrogen cyanide (3)‡	$101^{(a)}$	$52^{(a)}$	$3^{(a)}$
Hydrogen chloride (5)‡	3	18	$0^{(a)}$
Acetaldehyde (16)	$35^{(a)}$	$99^{(a)}$	$32^{(a,b)}$
Sulfur dioxide (23)‡	101	10	$10^{(a)}$
Nitromethane (3)‡	854	$296^{(a)}$	$14^{(a)}$
Pyrrolidine (2)‡	390	$4^{(a)}$	60

*$F = \{[\Sigma_{NP}(B_{exp} - B_{calc})^2]/\mathrm{NP}\}^{1/2}$, cm³/mol

**Except as marked † ‡, all data sets compiled by Dymond and Smith (1980) were used

†Only some sets from Dymond and Smith used:

Methanol, 2–5, 8; acetone, 5, 8, 10, 11; dimethyl ether, all sets, set 3 series lb only; chloroform, all sets, set 2 below 343.2 K; chloromethane, 5–8; chloroethane, 1, 3, 4; chloroethylene, 1; fluoromethane, 2a, 3, 4; trimethylamine, 1; water, 5; ammonia, 1, 3, 4; acetonitrile, 3, 5

‡All points from O'Connell (1987) data bank

(a) Specific polar, associating, or group parameter for pure compound

(b) Compound considered as a group due to lack of experimental second virial coefficients for systems of the same family

(c) Compound parameter of phenol used

the Tsonopoulos correlation are those provided by Tsonopoulos (1974, 1975, 1978, 1979). The experimental values of B_{12} of methanol-amine binary systems are those reported by Millen and Mines (1974). The corresponding η's were taken from the work of Stein and Miller (1980).

Since, by definition, Eq. 14 reduces to the form of the correlation of Tsonopoulos (1974) for nonpolar compounds, in this work we do not present results for hydrocarbons, other nonpolar compounds, or their mixtures. For all these cases, results are available (Tsonopoulos, 1974). For polar and associating compounds the group interaction parameters were obtained by minimizing the relative deviation between the experimental and calculated second virial coefficients of compounds pertaining to the same homologous series. Even when we used the relative root mean square deviation to optimize the group parameters, following standard conventions the results are compared with those of other correlations in terms of absolute root mean square deviations.

Table 3 compares the root mean square deviation for polar and associating compounds obtained using Eq. 24a with the values obtained with other available correlations. Overall results per family of compounds and for all the sets considered are compared in Table 4.

Figures 2, 3, and 4 compare the prediction of B using Eq. 24a and experimental measurements for acetone, methylamine, and methanol, respectively. The prediction of B is fairly in the middle of the experimental B values, except in the case of methanol at high temperature, where the predicted second virial coefficients are closer to those given by Kudchadker and Eubank (1970).

The N/N and N/CH_3 interactions present in amines deserve special attention. In this work we have not differentiated between the N group present in ammonia and the one present in a tertiary amine. However, even with this approximation the predictions obtained with the method proposed here are comparable with those obtained by Hayden and O'Connell (1975).

In general, the results obtained with both expressions for the temperature dependence of ϵ are reasonably good. Results obtained with Eq. 24b are slightly worse than those obtained with Eq. 24a and are not reported here. Equation 24a fits the experimental data better, since the condition of only positive $-\epsilon$ has been withdrawn. This is so since in some cases the nonpolar contribution to the second virial coefficient becomes smaller than experimental B values. This effect is present in the case of water, where the error given by Eq. 24b is much higher than the error obtained with Eq. 24a. Similar good results are obtained

Table 4. Average RMS Deviation of Second Virial Coefficients for Classes of Compounds

Family (No. Exp. Points, No. of Sets)	Avg. F Dev., cm^3/mol		
	Tsonopoulos (1974)	Hayden & O'Connell (1975)	This Work
Alcohols and phenols (87, 9)	106	259	97
Ketones and ethers (77, 5)	46	66	41
Esters (96, 6)	57	36	67
Halogenated compounds (168, 10)	51	63	33
Sulfides and thiols (26, 11)	357	59	57
Amines (63, 5)	—	21	15
Pyridines (24, 4)	346	60	57
Others (111, 9)	187	119	22
Overall	167	94	50

with the Tsonopoulos correlation, which does not have any theoretical limit in the expressions for the pure-compound parameters as functions of the reduced dipole moment of pure polar compounds.

In addition, Tsonopoulos and Hayden and O'Connell, sometimes use specific parameters for certain compounds. These cases have been indicated in Table 3, since the comparison of the predictions in these cases is unfair. However, in some of those cases the semitheoretical group method proposed here gives better predictions than those obtained with the other two correlations considered in the comparison.

Following Tsonopoulos (1974) for the treatment of mixtures, a binary molecular parameter k_{12} is introduced. Tarakad and Danner (1977), also agree to the need of having at least one adjustable parameter for each binary interaction.

Table 5 lists the root mean square error function F given by this work and the other two correlations for the polar-nonpolar interaction second virial coefficient B_{12}. Results show that the introduction of the mean radius of gyration R_H improves the fit-

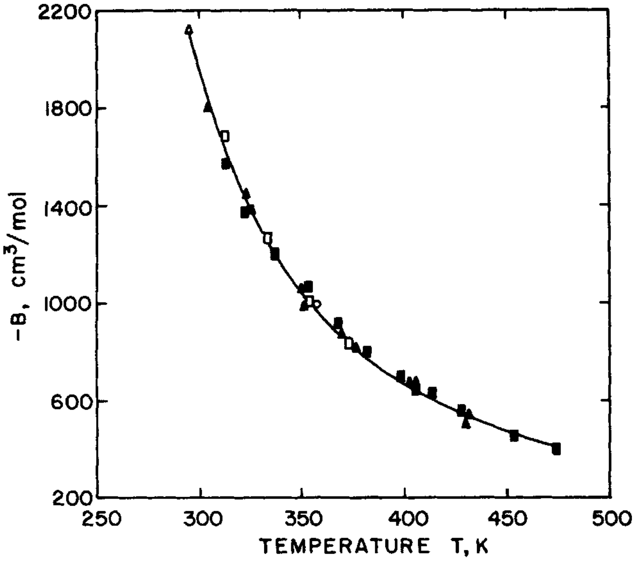

Figure 2. Second virial coefficient for acetone.
—— Prediction with Eq. 26a
Experimental data
△ Bottomley and Spurling (1962)
□ Knoebel and Edmister (1968)
▲ Bottomley and Spurling (1967)
■ Hajjar et al. (1969)
○ Abusleme and Vera (1989)

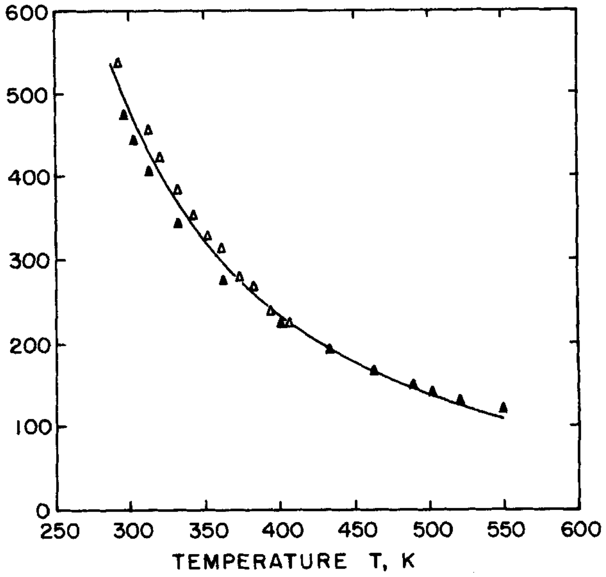

Figure 3. Second virial coefficient for methylamine.
—— Prediction with Eq. 26a
Experimental data
△ Lambert and Strong (1950)
▲ Adam et al. (1976)

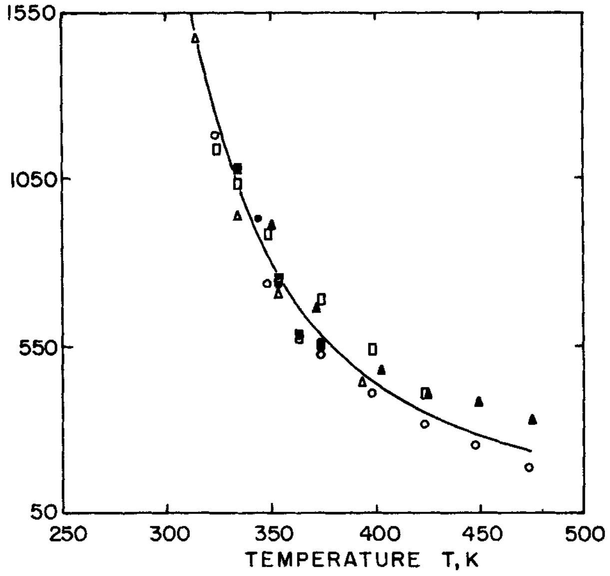

Figure 4. Second virial coefficient for methanol.
—— Prediction with Eq. 26a
Experimental data
△ Kretschmer and Wiebe (1954)
□ Bottomley and Spurling (1967)
▲ Foz et al. (1954)
■ Knoebel and Edmister (1968)
○ Kudchadker and Eubank (1970)
● Abusleme and Vera (1989)

Table 5. RMS Deviations F^* for Polar-Nonpolar Interaction Second Virial Coefficients

System (No. Exp. Points)**	Tsonopoulos (1974)	Hayden & O'Connell (1975)	This Work (k_{12})
Water–argon (4)	2	10	3 (0.39)
Water–carbon dioxide (4)	20	31	27 (0.15)
Water–nitrogen (4)	3	3	3 (0.33)
Water–nitrous oxide (4)	8	16	13 (0.15)
Water–methane (4)†	4	7	5 (0.37)
Water–ethane (7)	8	16	12 (0.40)
Methanol–argon (5)	3	18	4 (0.1)
Methanol–carbon dioxide (6)†	15	24	20 (−0.04)
Methanol–nitrogen (9)†	2	19	2 (0.08)
Methanol–nitrous oxide (5)	8	34	13 (0.1)
Methanol–methane (5)	4	11	4 (0.14)
Methanol–ethane (5)	9	54	13 (0.08)
Methanol–pentane (2)†	353$^{(a)}$	523	15 (−0.08)
Methanol–ethene (5)	9	17	17 (0.04)
Methanol–benzene (4)†	69	65	71 (0.22)
Ethanol–argon (2)	40	33	36 (0.18)
Ethanol–nitrogen (1)	—	38	0 (0.39)
Ethanol–methane (3)†	4$^{(a)}$	12	3 (0.18)
Ethanol–ethane (3)†	18$^{(a)}$	25	16 (0.16)
Ethanol–benzene (3)	55	64	52 (0.15)
2-propanol–argon (2)	—	13	7 (0.21)
Butanol–methane (1)†	1	23	3 (0.20)
Butanol–ethane (1)†	2	25	4 (0.14)
Diethylether–hexane (2)†	185	28	11 (−0.01)
Diethylether–benzene (3)	73	100	47 (0.04)
Acetone–argon (1)	—	5	1 (0.19)
Acetone–carbon dioxide (1)	—	46	0 (0.25)
Acetone–butane (4)	628	42	46 (0.12)
Acetone–benzene (4)‡	218$^{(b)}$	30	24 (−0.03)
Acetonitrile–Cyclohexane (2)	195	33	31 (0.26)
Ammonia–argon (4)	15	28	10 (0.26)
Ammonia–krypton (1)	0	37	1 (0.27)
Ammonia–nitrogen (4)	15	8	11 (0.21)
Ammonia–methane (4)	10	19	7 (−0.15)
Ammonia–ethene (2)	5	7	6 (−0.16)
Chloroform–argon (2)	—	42	7 (0.25)
Chloroform–carbon dioxide (1)	—	51	2 (0.17)
Chloroform–nitrogen (1)†	—	66	0 (0.41)
Chloroform–benzene (4)	34	93	15 (−.05)
Methylchloride–argon (6)	13	45	7 (0.44)
Methylchloride–propane (5)	—	149	31 (−0.01)
Methylbromide–propane (13)	35	97	18 —
Overall	61	49	15

*$F = \{[\Sigma_{NP}(B_{12,exp} - B_{12,calc})^2]/NP\}^{1/2}$, cm^3/mol

**Except as marked † ‡, all data sets taken from O'Connell (1987) data bank

†Dymond and Smith (1980); ‡ set 1, Dymond and Smith (1980)

(a) $k_{12} = 0.15$, Tsonopoulos (1974) for alcohol-hydrocarbon interactions when the particular value is not available

(b) Constant $k_{12} = 0.12$ assumed

ting of B_{12} values. In this case the energetic term vanishes since $\epsilon_{12} = 0$. Some of the Tsonopoulos (1974) predictions may not be as good as expected because we have assumed either a characteristic k_{12} for the compound type interaction (no specific k_{12} available) or a representative k_{12} in the temperature range of the experimental values for the binary mixture. The binary parameters k_{12} obtained in this work are reported in Table 5. In some cases these k_{12} values are less than zero, which is reasonable for systems presenting dimerization due to hydrogen bonding (Tsonopoulos, 1975). Negative k_{12} exhibited in Table 5 for polar-nonpolar systems are due only to failures in the estimation of $B_{\omega ij}$. The dimerization phenomena cannot be used in this case as an argument to explain a negative k_{12} value because the energetic term vanishes and therefore the temperature dependence for ϵ is irrelevant.

Table 6 exhibits the root mean square deviation of B_{12} for some strongly polar and associating binary systems. The comparison between the results obtained with the method proposed in this work and the other two methods is considered to be fair since all three methods introduce a binary molecular parameter. McCann and Danner (1984) proposed a group contribution

Table 6. RMS Deviations* for Polar-Polar Interaction Second Virial Coefficients

System (No. Exp. Points)**	Tsonopoulos (1974)	Hayden & O'Connell (1975)	This Work (k_{12})
Water–hydrogen chloride (3)	—	39	89 (−0.14)
Methanol–methylamine (5)†	—	327	143 (−0.78)
Methanol–dimethylamine (5)†	—	266	352 (−0.72)
Methanol–trimethylamine (5)	—	255	659 (−0.85)
Acetone–chloroform (4)	—	304	339 (−0.13)
Acetone–diethylether (4)	61	57	26 (0.12)
Acetone–dichloromethane (7)	801	26	134 (−0.57)
Acetone–methylchloride (6)	11	16	26 (−0.06)
Acetonitrile–acetaldehyde (4)‡	803$^{(a)}$	1,709	541 (−0.55)
Ethylchloride–methylbromide (2)	20	99	21 (0.06)
Ethylchloride dichloromethane (3)	414	152	50 (−0.43)
Chloroform–diethylether (5)§	—	95	80 (−0.18)
Chloroform–methylformate (3)§	—	126	21 (−0.10)
Chloroform–propylformate (4)	—	100	64 (−0.14)
Chloroform–methylacetate (3)	—	134	50 (−0.22)
Chloroform–ethylacetate (5)	—	148	51 (−0.20)
Overall	352$^{(b)}$	241	165

*Error function, $F = \{[\Sigma_{NP}(B_{12,exp} - B_{12,calc})^2]/NP\}^{1/2}$, cm^3/mol

**Except as marked † ‡ §, all data sets taken from O'Connell (1987) data bank

†Millen and Mines (1974); ‡Zaalishvili and Kolysko (1961); §Dymond and Smith (1980)

(a) $k_{12} = -0.32$ assumed; (b) only 6 systems method for the prediction of pure-compound second virial coefficients. The authors did not differentiate between polar and nonpolar contributions, and necessarily the latter effects were absorbed in the interaction group parameters. This may be the reason why they had to define a large number of different groups, with up to five constants for the temperature dependence of each specific group. Their treatment was not extended to mixtures.

Conclusions

A group contribution method to predict pure-compound second virial coefficients has been proposed. The nonpolar contribution of empirical nature given by the Tsonopoulos (1974) correlation functions $f^{(0)}_{(T_R)}$ and $f^{(1)}_{(T_R)}$ with the nonpolar acentric factor, ω_H, was found to be the most suitable expression to account for nonpolar effects. The approximation assumed for the radial distribution function $g(r)$ seems to be an appropriate representation of the energetic contribution to the second virial coefficient.

The results obtained with this group method compare favorably with those of the correlations of Tsonopoulos (1974) and Hayden and O'Connell (1975). The predictions obtained for strongly polar and associating compounds are surprisingly good. The case of amines and alcohols is a good example, showing that the group concept approach is useful to represent strong interactions in the gas phase.

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Notation

a, b = temperature-independent parameters, $K^{1/2}$, Eq. 26a
a', b' = temperature-independent parameters, K, Eq. 26b
B = second virial coefficient, cm^3/mol
B_o = nonpolar contribution to the second virial coefficient, cm^3/mol
F = error function, root mean square deviation
f_1, f_2, f_3 = step functions, Figure 1
f_u = unit step function
$f^{(0)}_{(T_R)}, f^{(1)}_{(T_R)}$ = dimensionless terms of Tsonopoulos (1974) correlation
g = pair distribution function
g^* = maximum value of g, Figure 1
J_k = number of groups bonded to group k
k_B = Boltzmann's constant
k_{ij} = characteristic constant for binary interaction i-j
n = number of components
N_A = Avogadro's number
NG = number of groups in molecule
NP = number of experimental points
P = total pressure
P_c = critical pressure
P_o = vapor pressure
Q_k = surface area of group k
r = radial distance
R = gas constant
R_H = mean radius of gyration
T = temperature
T_c = critical temperature
T_{ref} = reference temperature, 298.15 K
T_R = reduced temperature
$u(r)$ = intermolecular potential
v = molar volume
v_c = critical molar volume
V^*_k = van der Waals volume of group k
W = generalized acentric factor
y = vapor phase molar composition
Z = compressibility factor
z = coordination number (number of nearest neighbors to a given group)

Greek letters

$\delta(r)$ = Dirac function
ϵ = energetic parameter
ϵ^G_{kl} = k–l group interaction parameter
ζ', ζ'' = approximate locations for beginning and end of first peak of radial distribution function
σ_Q = size parameter, Eq. 12
θ_k = group surface area fraction of group k
ν_k = number of groups k in molecule
ϕ_i = fugacity of component i in a mixture
ω = acentric factor, Eq. 15
ω_H = nonpolar acentric factor, Eq. 19

Subscripts

i, j = component i, j
ij = interaction between molecules i and j
k, l = groups k, l
m = mixture

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