Second Virial Coefficients of Polar Haloalkanes

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A recently proposed empirical correlation of second virial coefficients (Tsonopoulos, 1974) is applied here to polar haloalkanes. This is done to show how the correlation can be extended to cover a different class of compounds; to present values for the polar parameter a and the binary characteristic constant k_{ij}; and, most importantly, to re-emphasize a point made in the earlier paper: that although a depends strongly on the reduced dipole moment, the functional dependence is different for each family of compounds—unless the reduced dipole moment is very large.

The equations and the notation, as well as most of the references, are given in the 1974 paper and, with a few exceptions, will not be repeated here.

PURE COMPOUNDS

In reduced form, the correlation is written as

$$\frac{BP_c}{RT_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + f^{(2)}(T_R) \qquad (1)$$

$f^{(2)}$ is the polar term; for nonhydrogen bonding compounds, such as the haloalkanes, it is given by

$$f^{(2)}(T_R) = \frac{a}{T_R^6} \qquad (2)$$

Apparently, only the *mono*haloalkanes, which are more commonly known as alkyl halides, require a polar correction to their B, given by $f^{(2)}$. Even dichloromethane, which has a $\mu = 1.58$ Debyes ($\mu_R = 57.6$), behaves like a nonpolar gas, as shown in Figure 1. (In the O'Connell-Prausnitz correlation, which fits the data equally well, both the polar and the association terms are being used; if neither had been used, the fit would have been just as good.) A more striking example is offered by 1,1-difluoroethane; although it has a dipole moment of 2.27 Debyes ($\mu_R = 153$), the nonpolar correlation fits its B (Mears et al., 1955) with an average deviation of 8.8 cc/gmol; the B values range between -337 and -207 cc/gmol.

The results for the alkyl halides are listed in Table 1. As shown, the absolute value of a drops sharply with decreasing μ_R. The fit of the data is illustrated in Figure 2, where the B of methyl chloride has been plotted. In spite of the slight bias above 200°C, the new correlation provides an excellent fit of the data. On the other hand, the O'Connell-Prausnitz correlation is fairly poor up to its inherent discontinuity (at $T_R = 0.95$), above which it agrees with the new correlation.*

Both for *n*-propyl chloride ($\mu_R = 75.8$) and methyl iodide ($\mu_R = 70.1$), $a = 0.0$, that is, no polar contribution to B, leads to a satisfactory fit. (A better fit results with slightly positive values for a; see Notes d and f in Table 1.)

The results of Rätzsch and Bittrich (1965) for methyl bromide are too positive and have been discarded. For example, Rätzsch (1968) reports the value -483 cc/gmol at 40°C, while Rätzsch and Bittrich give the much more positive value -402 cc/gmol. (At the same temperature, Haworth and Sutton (1971) report -482 cc/gmol.) The apparent substantial positive bias in the measurements of Rätzsch and Bittrich was also noted in the case of ethyl bromide ($\mu_R = 87.5$) for which the calculated values (with $a = 0.0$) were too negative by 130 and 90 cc/gmol—at 19.9 and 40°C, respectively.

The expressed confidence in the calculated values, in preference to the measurements of Rätzsch and Bittrich, is further supported by Figure 3, where the results for alkyl halides are superimposed on the results for ketones, ethers, etc. (Tsonopoulos, 1974). This plot of a versus μ_R helps to further emphasize the strong correlation between a and μ_R. However, as already noted, the polar contribution to B cannot be given for all polar compounds by a unique function of μ_R ~~at least~~ for $\mu_R < 200$. Figure 3 presents a strong case for making a a unique function of μ_R only for nonhydrogen bonding compounds with $\mu_R \gtrsim 200$.

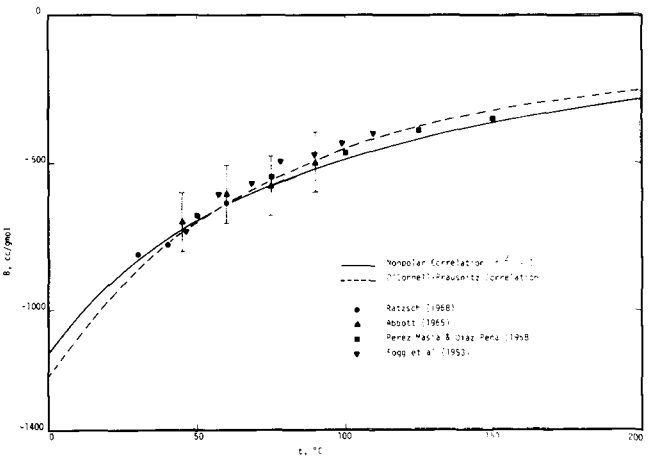

Fig. 1. Second virial coefficient of dichloromethane.

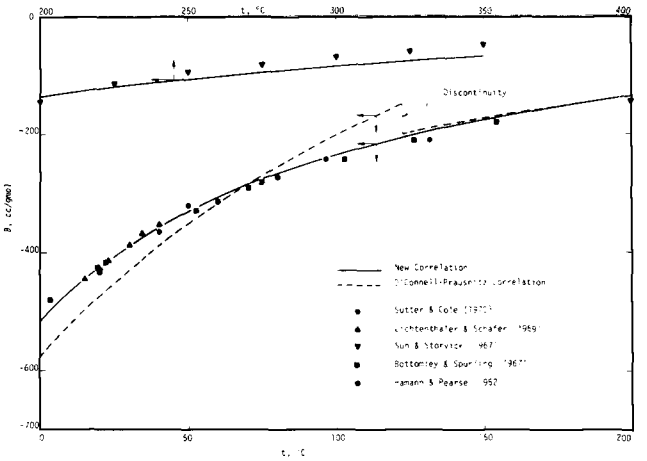

Fig. 2. Second virial coefficient of methyl chloride.

* The O'Connell-Prausnitz correlation is used as the basis of comparison, here as well as in the 1974 paper, because it probably is the best (and the most widely used) of the correlations available in the literature.

TABLE 1. ALKYL HALIDES

Compound	ω	μ_R[a]	a	Root mean square deviation of B cc/gmol (no. points)	References[b]
Methyl fluoride	0.191	190.2	−0.04223	6.35[c] (23)	Cawood and Patterson (1932, 1937); David et al. (1952); Hamann and Pearse (1952); Michels et al. (1952); Sutter and Cole (1970)
Methyl chloride	0.155	143.2	−0.009025	9.96 (29)	Bottomley and Spurling (1967); Hamann and Pearse (1952); Lichtenthaler and Schäfer (1969); Suh and Storvick (1967); Sutter and Cole (1970)
Ethyl chloride	0.192	102.1	−0.006595	21.7 (32)	Bohmhammel and Mannchen (1971); Haworth and Sutton (1971); Lambert et al. (1949); Rätzsch (1968)
n-Propyl chloride	0.230	75.8	(0.0)	37.4[d] (24)	Bohmhammel and Mannchen (1971); Perez Masiá and Diaz Peña (1958); Rätzsch (1968)
Methyl bromide	0.175[e]	106[e]	−0.005392	21.7 (26)	Fogg et al. (1953); Hamann and Pearse (1952); Haworth and Sutton (1971); Kappallo et al. (1963); Lichtenthaler and Schäfer (1969); Rätzsch (1968)
Methyl iodide	0.202	70.1	(0.0)	36.1[f] (10)	Fogg et al. (1953); Zaalishvili and Kolysko (1962)

[a] $\mu_R = 10^5\mu^2P_c/T_c^2$; the units are Debyes^2 − atm − °K^{-2}. Dipole moment data taken from McClellan (1963).
[b] Only those used in the regression analysis are listed.
[c] A better fit (RMSD of B = 3.55 cc/gmol) results with $f^{(2)} = -0.05065/T_R^4$.
[d] The calculated values are more negative than the experimental results. With a = 0.003690, the RMSD of B decreases to 22.1 cc/gmol, but a $f^{(2)} > 0$ is probably unacceptable.
[e] For P_c = 71 atm, which was estimated by analogy with the other alkyl halides. Lydersen's method gives an unacceptably high value (P_c = 83.4 atm).
[f] With a = 0.003888, the RMSD of B decreases to 19.3 cc/gmol (see Note *d*).

CROSS-COEFFICIENTS FOR MIXTURES

The most sensitive mixing rule in the calculation of B_{ij} is that for T_{cij}, which is given by

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

k_{ij} is a characteristic constant for each binary, and its optimum value can be determined by analyzing B_{ij} or B_M data.

Table 2 summarizes the results of the analysis of B_M data (at $y = 0.5$)* for binaries of polar haloalkanes. The comparison with the O'Connell-Prausnitz correlation, in which k_{ij} is set equal to zero, underlines the need for a nonzero k_{ij}.

The negative k_{ij} value for chloroform/carbon tetrachloride may not be significant, but the value −0.13 for dichloromethane/acetone is. It suggests the formation of a complex between dichloromethane and acetone. (O'Connell and Prausnitz add a specific interaction constant to account for such a cross-dimerization.) The complex is probably due to hydrogen bonding between dichloromethane's hydrogen(s) and acetone's oxygen. Since the three chlorine atoms in chloroform make the hydrogen atom much more readily available for hydrogen bonding, the chloroform-acetone complex should be even stronger.

The available B_M data confirm this expectation, and this is illustrated in Figure 4. The optimum k_{ij} values needed to fit the B_M of chloroform/acetone (Zaalishvili and Kolysko, 1961) and of the similarly behaving chloroform/ethyl ether (Fox and Lambert, 1952; Zaalishvili and Kolysko, 1960) are very negative at low temperatures, but become more positive as the temperature is raised (and the complex becomes weaker. Such a temperature dependence should have also been observed for dichloromethane/acetone). A more tentative result is that the two binaries have essentially the same k_{ij} values above 90°C.

As a conclusion, the reader is reminded that the correlation is an empirical one. Therefore, it (and Figure 3 in particular) should not be used to explain the nature

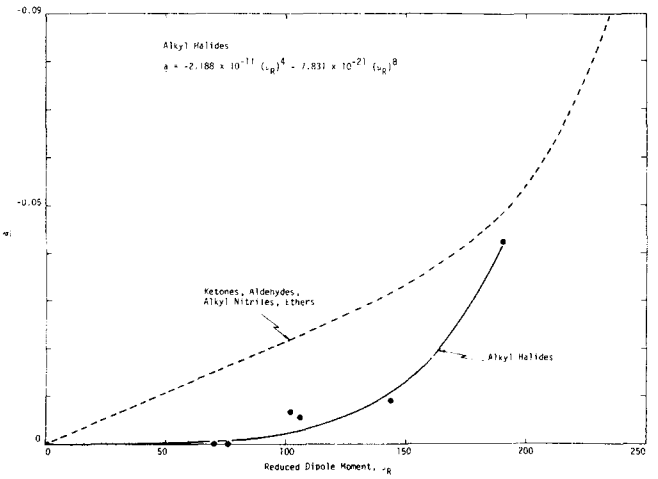

Fig. 3. Dependence of a on reduced dipole moment.

* In a few cases, as noted in Table 2, the comparison was made with B_{ij}, either because B_{ij} was obtained directly from solubility measurements or because the experimental information did not allow back-calculation of B_M.

TABLE 2. MIXTURE SECOND VIRIAL COEFFICIENTS AT $y = 0.5$

i/j	Average deviation of B_M ($y = 0.5$), cc/gmol: New	New (k_{ij})	O'Connell-Prausnitz	t range, °C (no. points)	References
Methyl fluoride/nitrogen[a]	0.2	(0.08)	11	25 (1)	Michels (1958)
Methyl fluoride/carbon dioxide[a]	0.2	(0.00)	1.2	25 (1)	Michels (1958)
Methyl chloride/argon	6.8	(0.30)	27	15-157 (10)	Bottomley and Spurling (1967); Lichtenthaler and Schäfer (1969)
Methyl chloride/carbon disulfide	8.1	(0.05)	17	50-157 (6)	Bottomley and Spurling (1967)
Methyl chloride/acetone	6.4	(0.00)	15	50-155 (6)	Bottomley and Spurling (1967)
Methyl chloride/methyl bromide[a]	2.4	(0.07)	4.0	23-50 (3)	Lichtenthaler and Schäfer (1969)
Ethyl chloride/dichloromethane	6.4	(0.07)	12	30-60 (3)	Rätzsch (1968)
Ethyl chloride/*n*-propyl chloride	3.1	(0.02)	157[b]	30-60 (3)	Rätzsch (1968)
Ethyl chloride/methyl bromide	1.5	(0.07)	21	40, 60 (2)	Rätzsch (1968)
Dichloromethane/acetone	7.5	(−0.13)	159[c]	45-90 (4)	Abbott (1965)
Chloroform/*n*-hexane	1.8	(0.06)	67	53, 78 (2)	Fox and Lambert (1952)
Chloroform/benzene	26	(0.00)	40	43-76 (5)	Francis and McGlashan (1955)[d]
Chloroform/carbon tetrachloride	24	(−0.03)	67	37-70 (6)	Francis and McGlashan (1955)
Methyl bromide/argon[a]	5.4	(0.20)	40	15-50 (4)	Lichtenthaler and Schäfer (1969)
Methyl bromide/propane[a]	17	(0.05)	30	−29 to 48 (4)	Kappallo et al. (1963)
Methyl bromide/*n*-butane	5.3	(0.05)	34	−29 to 48 (4)	Kappallc et al. (1963)
Methyl iodide/ether ether	34	(0.05)	222[e]	40-85 (4)	Zaalishvili and Kolysko (1962)

[a] Comparison was made with B_{ij} rather than B_M ($y = 0.5$) data.
[b] The predicted B of pure *n*-propyl chloride is 240 cc/gmol too positive.
[c] A specific association constant must be added to account for complex formation.
[d] Zaalishvili et al. (1965) have presented data in the range 80° to 110°C that are inconsistent with those of Francis and McGlashan—which are considered as the more reliable. A $k_{ij} = -0.13$ is needed to fit Zaalishvili's data.
[e] The predicted B of pure methyl iodide is 250 cc/gmol too positive.

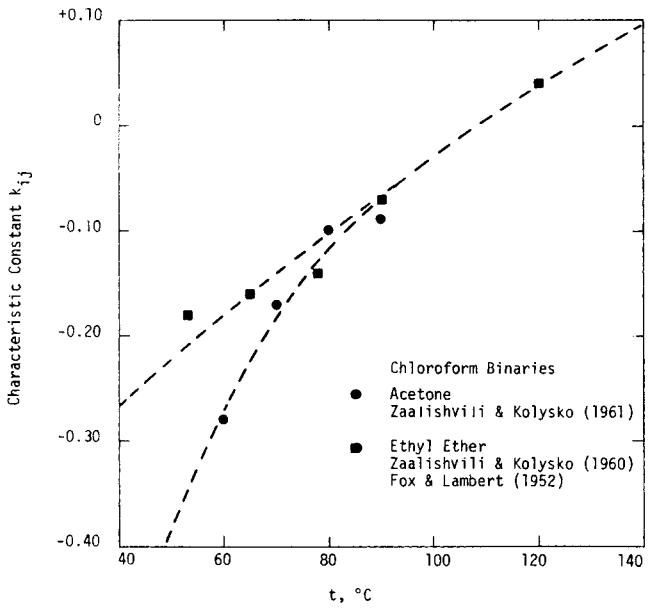

Fig. 4. Optimum k_{ij} values for strongly cross-dimerizing binaries.

of the intermolecular forces in polar gases. An appreciation and some understanding of what these forces are, however, can be very helpful (if not essential) in developing a correlation. They may even provide some support for what Figure 3 says about the relationship between a and μ_R.

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