p = pressure of the fluid, N/m^2
T = temperature of the fluid, °K
u = velocity component in x direction, m/s
U = velocity of upper plate, m/s
x = streamwise coordinate, m
y = transverse coordinate, m

Greek Letters

λ = eigenvalue
κ = fluid consistency, N s^n/m^2
ρ = fluid density, kg/m^3
θ = dimensionless temperature, $(T - T_0)/(T_1 - T_0)$
τ = shear stress in fluid, N/m^2

Dimensionless Groups

Ec = Eckert number, $U^2/c_p(T_1 - T_0)$
M = Kummer's function
n = flow behavior index
Nu = Nusselt number, $-a(\partial T/\partial y)_0/(T_0 - T_b)$
Pe = Peclet number, $\rho c_p U\, a/k$
Re = Reynolds number, $\rho\, U^{2-n}\, a^n/\kappa$

Subscripts

0 = lower (stationary) plate
1 = upper (moving) plate
i = entrance at $x = 0$

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Second Virial Coefficients of Water Pollutants

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The major pollutants other than oil in petroleum refinery wastewater streams were identified in a recent paper on ionization constants (Tsonopoulos et al., 1976). They are the following electrolytes: ammonia, hydrogen sulfide, phenols, chlorides, cyanides and thiocyanates, and alkyl mercaptans. With the exception of the chlorides and thiocyanates, these pollutants are volatile and can therefore be removed from the wastewater, to a lesser or greater extent, by vaporization. To predict the vaporization of the volatile pollutants we must know, in addition to their ionization constants and Henry's constants in water, their fugacity coefficients. These fugacity coefficients can be calculated if, in turn, the second virial coefficients are known. This paper presents the second virial coefficients of the volatile water pollutants and their mixtures in terms of an empirical correlation (Tsonopoulos, 1974).

Fugacity coefficients correct for the deviation from vapor phase ideality and are therefore needed in any vapor-liquid equilibrium calculations, especially those at superatmospheric pressures. As long as the density of the vapor mixture is not greater than one fourth its critical value, the following equation can be used to determine the value of ϕ_i, the fugacity coefficient of component i (in a binary mixture):

$$\ln \phi_i = \frac{2}{v_M}\,(y_i\, B_{ii} + y_j\, B_{ij}) - \ln z_M \qquad (1)$$

v_M and z_M are the molar volume and the compressibility factor of the vapor mixture, and y_i is the vapor mole fraction of component i. B_{ii} is the second virial coefficient of pure i, and B_{ij} is the second virial cross coefficient. Since

$$z = Pv/RT = 1 + B/v \qquad (2)$$

ϕ_i can be determined once B is known. This, in turn, can be obtained from experimental data or calculated with a correlation. The latter approach is taken here.

Complete information on the equations will be found in the 1974 paper. Similarly, the references given in 1974 will not be repeated here.

PURE COMPOUNDS

The B correlation involves three terms that are functions of the reduced temperature:

$$\frac{BP_c}{RT_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + f^{(2)}(T_R) \qquad (3)$$

$f^{(2)}$, which is the polar contribution to B, involves two parameters, although of the components considered here only water requires both of them (owing to hydrogen bonding):

$$f^{(2)}(T_R) = \frac{a}{T_R^{\,6}} - \frac{b}{T_R^{\,8}} \qquad (4)$$

a depends strongly on μ_R, the reduced dipole moment, but not through a universally applicable relationship. The following relationship applies to ketones, aldehydes, alkyl nitriles, and ethers (Tsonopoulos, 1974):

TABLE 1. *B* OF PURE COMPOUNDS

Compound	ω	μ_R*	a	Average value of *B*, cm³/gmole	Root-mean-square deviation of *B*, cm³/gmole (No. points)	References
Ammonia	0.257†	147.8†	−0.02370	−93.9	0.95 (12)	Lee et al. (1970)
Hydrogen sulfide	0.100	56.0	−0.0140	−145	2.79 (6)	Reamer et al. (1952)
Phenol	0.443	24.6	−0.0136	−756	16.2 (8)	Opel (1969)
Hydrogen cyanide	0.373**	204.0**	(−0.0566)††	−1 049	16*† (2)	Cottrell et al. (1965)
Ethyl mercaptan	0.189	53.7	(0.0)	−934	24*† (3)	McCullough et al. (1952)
n-Propyl mercaptan	0.237	37.3	(0.0)	−1 195	20*† (3)	Pennington et al. (1956)

* $\mu_R = 10^5 \mu^2 P_c/T_c^2$; the units are Debyes²-atm-°K⁻². Dipole moment data taken from McClellan (1963).
† Calculated with $P_c = 112.5$ atm, as recommended by Edwards (1964).
** Calculated with $P_c = 48.9$ atm, also as recommended by Edwards (1964).
†† Value predicted with Equation (5); see also Figure 1.
*† Average deviation of *B*.

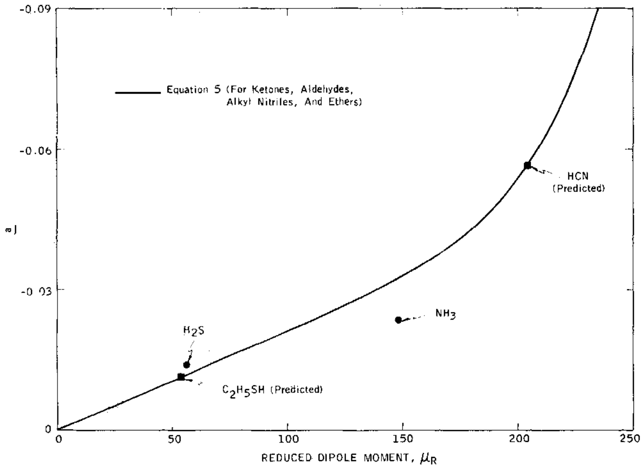

Fig. 1. Dependence of *a* on reduced dipole moment.

$$a = -2.140 \times 10^{-4}\ \mu_R - 4.308 \times 10^{-21}\ (\mu_R)^8 \quad (5)$$

Equation (5) is plotted on Figure 1, along with some *a* values for the water pollutants being investigated. The complete results of the data analysis are summarized in Table 1 and discussed below.

Lee et al. (1970) have reviewed the literature data for the *B* of ammonia and presented smoothed values between 50° and 325°C. These values were fitted extremely well with $a = -0.0237$, as shown in Table 1. This value is in fair agreement with that predicted by Equation (5) (see Figure 1). More interestingly, the excellent fit of *B* without the need of the *b* term suggests that, at least as far as *B* is concerned, hydrogen bonding can be neglected.

The *B* of hydrogen sulfide was calculated from the P-V-T data of Reamer et al. (1950) in the temperature range 4.4° to 171.1°C (40° to 340°F). The fit with $a = -0.0140$ was very good (RMSD of $B = 2.8$ cm³/gmole). Furthermore, this optimum value, perhaps surprisingly, is in very good agreement with the predicted −0.0120 (see Figure 1).

Phenol was included in the original work on the *B* correlation, where it was noted that the data of Opel (1969) were superior to those of Andon et al. (1970). (The latter reference also reports the *B* of *o*-cresol at two temperatures.)

The available information for hydrogen cyanide is both limited and of uncertain quality. Therefore, it was decided to predict the value of *a* rather than obtain it by fitting *B* data. Since Equation (5) applies to acetonitrile, it can also be used for hydrogen cyanide; the resulting *a* value for hydrogen cyanide is given in Table 1 (and in Figure 1). As shown, the predicted *B* for hydrogen cyanide is in excellent agreement with values calculated from ultrasonic measurements (Cottrell et al., 1965).

When the same approach was used for ethyl mercaptan, the results were less satisfactory. Although the generalized relationship works well for hydrogen sulfide, and hence it would be expected to also apply to ethyl mercaptan, the predicted *B* values (with $a = -0.0115$) are 125

TABLE 2. ANALYSIS OF MIXTURE DATA

i/j	Average deviation of B_M ($y \cong 0.5$) or B_{ij}, cm³/gmole	k_{ij}	*t* range, °C (No. points)	References
Ammonia/hydrogen	1.4 (B_M)	−0.45	150-300 (4)	Kazarnovskii et al. (1940)
Ammonia/nitrogen	0.4 (B_M)	0.25	150-300 (4)	Kazarnovskii et al. (1940)
	1.6 (B_{ij})	0.25	350-450 (3)	Lee et al. (1970)*
Ammonia/argon	0.4 (B_{ij})	0.16†	25 (1)	Michels (1958)
Ammonia/krypton	0.3 (B_{ij})	0.26	25 (1)	Michels (1958)
Ammonia/methane	2.3 (B_M)	−0.09	150-300 (4)	Kazarnovskii and Levchenko (1944)
	4.6 (B_{ij})	−0.09	150-300 (4)	Lee et al. (1970)
Ammonia/ethylene	4.8 (B_{ij})	−0.13	30-41 (2)	Rätzsch and Freydank (1971)
Ammonia/acetylene	3.3 (B_{ij})	−0.24	50-150 (5)	Cheh et al. (1966); Khodeeva (1964)
Hydrogen sulfide/ethane	9.3 (B_{ij})	0.06**	50-125 (5)	Khoury and Robinson (1971)
Phenol/water	2.8 (B_M)	0.15	175-250 (6)	Opel et al. (1969)

* The 45°C value has been neglected; with it, the average deviation of B_{ij} is 8.2 cm³/gmole.
† Lee et al. (1970) have concluded that the B_{ij} value at 25°C reported by Michels (1958) is probably 20 cm³/gmole too negative. If that is true, the optimum k_{ij} would be closer to 0.25.
** k_{ij} value recommended by Chueh and Prausnitz (1967); with $k_{ij} = 0.10$, the average deviation was only 1.3 cm³/gmole.

TABLE 3. PREDICTION OF THE B OF ESTERS

Data of Lambert et al. (1959)

Ester (No. points)	ω	μ_R[*]	a from Equation (5)	Average value of B, cm^3/gmole	Average deviation of B, cm^3/gmole
Methyl formate (11)	0.252	80.8	−0.0173	−626	22
Ethyl formate (13)	0.283	65.3	−0.0140	−815	37
n-Propyl formate (18)	0.315	50.0	−0.0107	−1 178	73
Methyl acetate (22)	0.324	52.1	−0.0112	−984	93
Ethyl acetate (18)	0.363	44.7	−0.00957	−1 225	21
Methyl propionate (14)	0.352	40.5	−0.00868	−1 271	56
Overall (96)				−1 044	55

[*] See Table 1, first footnote.

to 150 cm^3/gmole more negative than the experimental results, which are based on vapor pressure and heat of vaporization measurements (McCullough et al., 1952). If no polar contribution is used ($a = 0$), the predicted B is only 18 to 31 cm^3/gmole too positive.

To further test the need for a polar contribution, and in the absence of any data for methyl mercaptan, the B of n-propyl mercaptan was examined. (Lydersen's method had to be used to estimate its critical constants: $t_c = 262.5°\mathrm{C}$ and $P_c = 45.7$ atm.) Again, no polar contribution had to be used; with $a = 0.0$, the average deviation from the B values of Pennington et al. (1956) was only 20 cm^3/gmole. The apparent conclusion, therefore, is that the alkyl mercaptans can be treated as nonpolar compounds.

CROSS COEFFICIENTS FOR MIXTURES

The calculation of B_{ij}, the second virial cross coefficient, is described by Tsonopoulos (1974). As shown there, the critical step in the calculation is the mixing rule for T_{cij} (used in place of T_{ci}):

$$T_{cij} = (T_{ci}\,T_{cj})^{1/2}\,(1 - k_{ij}) \qquad (6)$$

k_{ij} is a characteristic constant for each binary and can be determined by fitting B_{ij} or B_M (B of mixture) data. The results of such an analysis are summarized in Table 2.

The negative k_{ij} for ammonia/acetylene was expected because Cheh et al. (1966) had previously observed that ammonia and acetylene interact weakly; compare with the dichloromethane/acetone binary (Tsonopoulos, 1975). The interaction between ammonia and ethylene would not be as strong, and therefore the k_{ij} should be less negative, as indeed it was found. An even more negative k_{ij} is needed to fit the data for ammonia/hydrogen, the most important of the binaries listed in Table 2.[*] A negative k_{ij} is also needed for ammonia/methane, but $k_{ij} = 0.0$ gives a satisfactory fit (average deviation of $B_M = 4.7$ cm^3/gmole; the probable experimental uncertainty is ±20 cm^3/gmole).

Whereas the data for the binaries of ammonia with hydrogen, acetylene, ethylene, and even methane suggest some weak interaction,[*] no evidence of that is found in the binaries with nitrogen, argon, and krypton. Indeed, the same k_{ij} can be used for all three (see also Table 2):

$$NH_3 + N_2, + \mathrm{Ar}, \text{ or } + \mathrm{Kr}: \quad k_{ij} = 0.25$$

Unfortunately, no B data are available for the important binary ammonia/water (or for hydrogen sulfide/water). However, this binary exhibits negative deviations from Raoult's law (that is, activity coefficients below one), and this generally suggests that $k_{ij} < 0$. Still, in the absence of any data, it is recommended that k_{ij} be set equal to 0.0. The hydrogen sulfide/water binary exhibits positive deviations from Raoult's law and should have a positive k_{ij}. Comparison with the vapor-liquid equilibrium data of Selleck et al. (1952) suggests that $k_{ij} \cong 0.15$.

Chueh and Prausnitz (1967) have presented optimum k_{ij} values for binaries of hydrogen sulfide with $C_1 - C_5$ hydrocarbons and carbon dioxide. Those k_{ij}'s were meant to be used in calculations with the Redlich-Kwong equation of state, but they should be adequate in the present use. As evidence of this, the B_{ij} data of Khoury and Robinson (1971) on hydrogen sulfide/ethane were fitted satisfactorily with the k_{ij} value recommended by Chueh and Prausnitz (see Table 2; an even better fit was obtained for $k_{ij} = 0.10$).

Finally, the phenol/water binary was examined in the original paper on the B correlation.

CONCLUDING REMARKS ON THE CORRELATION

Although several classes of polar compounds have been examined (in 1974, 1975, and the present paper), no attempt has been made to completely generalize the correlation. On the contrary, it has been emphasized that such a generalization covering all polar compounds is not possible. Instead, one has to work on the basis of similarities. For example, ketones, aldehydes, ethers, and even the nitriles were found in 1974 to behave similarly, at least as far as the relationship between a and μ_R is concerned. But in 1975 it was shown that a very different relationship had to be used for the alkyl halides, unless μ_R is very large.

As a final statement on the development of the correlation, the B of a class of polar organic compounds not yet examined will be predicted with the correlation. The esters of the carboxylic acids are reasonably similar to the ketones, etc., and hence Equation (5) can be used to predict the value of a.

Lambert et al. (1959) have reported the B of six esters. They are listed in Table 3 along with their values for ω, μ_R, and a, which was determined with Equation (5). Since the experimental error is probably within 50 cm^3/gmole (Lambert et al., 1959), the average deviations given in Table 3 are satisfactory. That is, the polar contribution to the B of esters is adequately represented by Equation (5).

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[*] Hydrogen is usually a major component in the gas streams of a number of important petroleum refinery processes, such as hydrodesulfurization processes. In this work, hydrogen is treated as a simple fluid with the following classical constants: $T_c = 43.6°\mathrm{K}$, $P_c = 20.2$ atm, $v_c = 51.5$ cm^3/gmole, $\omega = 0.0$ (Prausnitz, 1969).

[*] The very negative k_{ij} for ammonia/hydrogen, as well as a $k_{ij} = 0.0$ for ammonia/propane, are supported by the fugacity coefficients reported by Antezana and Cheh (1975, 1976).

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Professor Joseph Joffe made the fugacity coefficient calculations on the ammonia/hydrogen and ammonia/propane binaries and compared them with the measurements of Antezana and Cheh (1975, 1976). He also made the calculations on the hydrogen sulfide/water binary. The author is also grateful to Robert H. Johnston for his helpful comments and to Exxon Research and Engineering Company for the permission to publish this paper.

NOTATION

a, b = parameters of polar contribution term to B, $f^{(2)}$; see Equation (4)
B = second virial coefficient
$f^{(0)}, f^{(1)}, f^{(2)}$ = dimensionless terms of Equation (3)
k_{ij} = characteristic binary constant; see Equation (6)
P = pressure
R = gas constant
$t(T)$ = (absolute) temperature
v = molar volume
y_i = vapor mole fraction of component i
z = compressibility factor
μ = dipole moment
ϕ_i = fugacity coefficient of component i
ω = acentric factor

Subscripts

c = critical property
i, j = property of component i, j
ij = characteristic property used in the calculation of the second virial cross coefficient
M = mixture property
R = reduced property

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Reaction Kinetics in Porous Electrocatalysts

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Porous electrocatalytic electrodes offer a high surface area and high activity for current generation, electrochemical processing, and investigation of catalytic surface reactions. However, slow reactant diffusion in the electrode pores can decrease the local reaction rate and can result in apparent experimental electrode-kinetic parameters (rates, orders, and transfer coefficients) which mask the true, intrinsic ones.

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