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Correlation of Second Virial Coefficients of Polar Gases by Redlich-Kwong Equation of State

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In order to describe and accurately predict phase equilibria at superatmospheric pressures, it is usually necessary to take vapor phase nonideality into account. Nonidealities of vapor phase are pictured by the fugacity coefficients. The virial equation of state truncated after the second virial coefficient provides reliable estimates of the fugacity coefficients for conditions up to moderate densities. It is written as an expansion of the inverse powers of volume

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

The second virial coefficient B can be determined from experimental data mostly compiled by Dymond and Smith (1968) or calculated with a suitable correlation. It is well known that accurate procedures are required for the calculation of second virial coefficient of gases. However, it is difficult to establish corresponding correlations for this property of polar gases. Approximate estimations are based on the various approaches (Black, 1958; O'Connel and Prausnitz, 1967; Kreglevski, 1969; Halm and Stiel, 1971; Polak and Lu, 1972; Nothnagel et al., 1973; Tsonopoulos, 1974, 1975; Hayden and O'Connell, 1975; Tarakad and Danner, 1977; Lin and Stiel, 1977; Tsonopoulos, 1978). One of the proposals of the correlations used to compute the second virial coefficient is that based on semiempirical equations. When theoretical approaches are tedious, this semiempirical estimation has the major advantage. The Berthelot and the original and modified Redlich-Kwong (RK) equations have been used (Black, 1958; de Santis et al., 1974; Simonet and Behar, 1976) to calculate the second virial coefficients of some nonpolar and polar gases. Since the original RK equation (Redlich and Kwong, 1949) has only two constants, it is not able, generally speaking, to give a highly accurate representation of the second virial coefficients. The note presented here provides a reasonable method for making the best estimates.

In our previous papers (Djordjević et al., 1977; Mihajlov-Duduković et al., 1978; Djordjević et al., 1979) we have demonstrated the capability of the RK equation to correlate and predict the thermodynamic properties of some nonpolar, slightly polar and polar substances using the optimal values of constants for each available isotherm. The objective of this study is to extend the same method to the correlation of second virial coefficient of polar gases. From extensive comparisons with other more frequently used analytical methods for predicting values of second virial coefficients of polar gases, the present method was found to be superior.

RESULTS AND DISCUSSION

The RK equation of state is given by

$$Z = \frac{v}{v-b} - \frac{a}{RT^{1.5}(v+b)} \tag{2}$$

The constants a and b can be related to the critical properties by

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \tag{3}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{4}$$

The numerical values $\Omega_a = 0.4275$ and $\Omega_b = 0.0867$, as universal constants valid for all temperature and pressures, were found by applying $(\partial P/\partial v)_{Tc} = (\partial^2 P/\partial v^2)_{Tc} = 0$ at the critical point.

The method used in this investigation is already described (Djordjević et al., 1977) as follows. The parameters Ω_a and Ω_b have been determined from experimental P-v-T data of polar gases at each available isotherm. For each temperature, the optimal values of Ω_a and Ω_b were found by Newton-Raphson method (Rosenbrock and Storey, 1966). The objective function is given by

$$\sum_{1}^{N} (Z_{\text{exp}} - Z_{\text{cal}}) \to \text{min} \tag{5}$$

Z_{cal} is calculated from Equation (2). As shown in our cited work, in all cases the proposed method is preferred to the results of other applied modifications of the RK equation.

The second virial coefficient B is defined by

$$B = \lim_{\substack{P \to 0 \\ v \to \infty}} (Z-1)v \tag{6}$$

Prediction of the second virial coefficient B_{RK} is obtained when Equation (6) is applied to the RK equation

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TABLE 1. COEFFICIENTS OF EQUATIONS (8) TO (13)

Substance		$T_r < 1$				$T_r \geqslant 1$		
		Ω_a		Ω_b		Ω_a		Ω_b
	s^{2*}	C_i	s^{2*}	C_i	s^{2*}	C_i	s^{2*}	C_i
Propylene	(12)[+]	−6.524891	(9)	−1.41398	(10)	−6.524891	(13)	0.08303786
	$0.25\cdot10^{-2}$	24.49115	$0.83\cdot10^{-2}$	2.281383	$0.22\cdot10^{-3}$	24.49115	$0.14\cdot10^{-4}$	0.00043466
		−21.10112		−0.7753928		−21.10112		0.000015628
		3.566014		−0.02955507		3.566014		0.00000007
Ammonia	(10)	28.26877	(13)	0.09012947	(12)	0.4278759	(12)	0.08664171
	$0.49\cdot10^{-3}$	−77.01449	$0.58\cdot10^{-3}$	−0.00564711	$0.2\cdot10^{-4}$	−0.6958895	$0.115\cdot10^{-6}$	−0.1510731
		57.15391		0.0005032		−0.4225502		−0.1160938
		−7.974042		−0.0000058		0.9300377		0.2343126
Sulfur dioxide	(8)	4.204483	(13)	0.08275584	(9)	5.801057	(13)	0.08627893
	$0.14\cdot10^{-2}$	−3.935886	$0.119\cdot10^{-3}$	0.001380228	$0.27\cdot10^{-3}$	−12.56892	$0.75\cdot10^{-4}$	0.5774925
		6.892952		−0.00007193		8.063751		0.1667383
		−1.693905		0.000001096		−0.8316025		−0.5084222
Methyl chloride	(9)	8.797737	(11)	0.08684059	(12)	0.4277658	(12)	0.08664029
	$0.48\cdot10^{-2}$	−17.46539	$0.50\cdot10^{-2}$	12.26391	$0.13\cdot10^{-5}$	−0.4475567	$0.53\cdot10^{-9}$	−0.9920525
		9.582134		2.279562		−0.5502152		−0.694962
		−0.4697991		−10.83521		1.04849		1.662988

* $s^2 = \sum_{i=1}^{n} (\Omega_{\mathrm{cal}} - \Omega_{\mathrm{cor}})_i^2$

[+]All brackets refer to the correlation Equations (8) to (13).

$$B_{\mathrm{RK}} = b - \frac{a}{RT^{1.5}} \tag{7}$$

To calculate the second virial coefficient of some polar gases by means of the our method, the parameters Ω_a and Ω_b were considered in two ways: as established values at available isothermal conditions for each isotherm separately (Ω_{cal}), and as temperature dependent parameters given by suitable temperature relations (Ω_{cor}). It should be mentioned that those temperature relations can be used in cases where experimental values of second virial coefficients are often not available at desired temperatures.

Ω_{cor} parameters are correlated in terms of T_r for each gas individually in terms of two ranges of temperature: $T_r < 1$ and $T_r \geq 1$. The following correlation equations are used for Ω_a and Ω_b:

$$\Omega = C_0 + \frac{C_1}{T_r} + \frac{C_2}{T_r^2} + \frac{C_3}{T_r^3} \tag{8}$$

$$\Omega = \frac{C_0}{T_r} + \frac{C_1}{T_r^2} + \frac{C_2}{T_r^3} + \frac{C_3}{T_r^6} \tag{9}$$

$$\Omega = C_0 T_r + C_1 T_r^2 + C_2 T_r^3 + C_3 T_r^6 \tag{10}$$

$$\Omega = C_0 + C_1(1-T_r) + C_2(1-T_r)^{1/3} + C_3(1-T_r)^{2/3} \tag{11}$$

$$\Omega = C_0 + C_1\left(1-\frac{1}{T_r}\right) + C_2\left(1-\frac{1}{T_r}\right)^{1/3} + C_3\left(1-\frac{1}{T_r}\right)^{2/3} \tag{12}$$

$$\Omega = C_0 + \frac{C_1}{1-T_r} + \frac{C_2}{(1-T_r)^2} + \frac{C_3}{(1-T_r)^3} \tag{13}$$

The coefficients C_0, C_1, C_2 and C_3 were determined using the least-squares method. For investigated gases (propylene, ammonia, sulfur dioxide and methyl chloride) values of these coefficients are listed in Table 1. For the P-v-T data of these gases, see Djordjević (Djordjević et al., 1977).

A comparison of the evaluation study was made to the original RK equation, where the constants a and b are determined from Equations (3) and (4). The results are presented in Tables 2 and 3. Experimental data are selected from Dymond and Smith (Dymond and Smith, 1969). In Table 2, our method is presented by means of second virial coefficients (B_{cal}) estimated using Ω_{cal} parameters as optimal values calculated from Z [condition given by Equation (4)]. All comparisons in Table 2 are realized for the same available isotherms of volumetric and second virial coefficient data.

A summary of the predicted results, when second virial coefficients (B_{cor}) are computed using Ω_{cor}, is presented in Table 3. Ω_{cor} is taken from correlation Equations (8) to (13). Deviations between the calculated and literature values of second virial coefficients in Table 3 are obtained for a representative number of data points selected from cited literature.

Both tables indicate that data calculated by our procedure are to be preferred to the results of the original RK equation. However, the interesting quality of results of these predictions is that B_{cal} is slightly remote from experimental values in all cases, while B_{cor} gives fair results for sulfur dioxide and propylene. Also, satisfactory agreement is obtained for ammonia and methyl chloride.

TABLE 2. DEVIATIONS OF SECOND VIRIAL COEFFICIENTS CALCULATED USING Ω_{cal} FROM EXPERIMENTAL VALUES*

Substance	No. pts[+]	Avg** B	Redlich-Kwon Avg[++]	Redlich-Kwon Bias[*+]	This Work Avg	This Work Bias
Propylene	10	235.15	10.73	+4.082	6.28	6.00
Ammonia	6	153.3	32.77	+31.36	7.79	+7.79
Sulfur dioxide	5	278.18	52.59	+52.59	8.27	−5.91
Methyl chloride	4	350	80.66	+80.66	12.58	+0.45

*All deviations are in cubic centimeters mole^{-1}.

[+]n is the number of same isotherms for which experimental P-v-T data and experimental second virial coefficients of mentioned substances exist.

**Avg B is defined as $\Sigma |B_{\mathrm{exp}}|/n$.

[++]Avg is defined as $\Sigma |B_{\mathrm{cal}} - B_{\mathrm{esp}}|/n$.

[*+]Bias is defined as $\Sigma (B_{\mathrm{cal}} - B_{\mathrm{exp}})/n$.

TABLE 3. DEVIATIONS OF SECOND VIRIAL COEFFICIENTS CALCULATED USING Ω_{cor} FROM EXPERIMENTAL VALUES*

Substance	No. pts⁺	Avg** B	Redlich-Kwon Avg⁺⁺	Redlich-Kwon Bias*⁺	This Work Avg	This Work Bias
Propylene	21	188.92	8.86	−3.18	2.84	−0.99
Ammonia	13	213.15	68.95	+67.99	28.40	−10.97
Sulfur dioxide	17	358.48	93.86	+93.86	8.62	+7.59
Methyl chloride	17	306.65	54.84	+54.84	21.50	−16.65

*All deviations are in cubic centimeters mole^{-1}.
⁺n is the number of tested points for which experimental second virial coefficients exist.
**Avg B is defined as $\Sigma|B_{exp}|/n$.
⁺⁺Avg is defined as $\Sigma|B_{cor}-B_{esp}|/n$.
*⁺Bias is defined as $\Sigma(B_{cor}-B_{exp})/n$.

Besides the original RK equation, the following methods were also included in the analysis: O'Connell-Prausnitz (1967), Hayden-O'Connell and Tsonopoulos (1975).

For propylene, results obtained by Hayden-O'Connell (Avg = 5 cm^3/mole) and Tsonopoulos methods (Avg = 5) are better than those of Tarakad and Danner (Avg = 6) and Nothnagel (Avg = 8). These comparisons are carried out for Avg B = 224 (Tarakad and Danner, 1977). Our Avg B is similar, and our results are excellent as shown in Tables 2 and 3. Figure 1 indicates slightly worse results obtained with B_{cor} for lower temperature.

Ammonia is firstly correlated by Black (1958). For Avg B = 167, according to Tarakad and Danner (1977), results of other authors are Tarakad and Danner, Avg = 10; Nothnagel et al., Avg = 15; Tsonopoulos, Avg = 24; Hayden and O'Connell, Avg = 36. Lin and Stiel (1977) in the temperature range 243° to 523°K for eight experimental data points obtained Avg = 0.25. Lee et al. (1970) presented smoothed values for the second virial coefficient of ammonia between 50° and 325°C. Tsonopoulos (1978) fitted these values very well. Our results of B_{cal} for Avg B = 153.3 and six experimental data points show good agreement with Avg = 7.79. As shown in Figure 2, in the region $T_r > 1$ agreement of B_{cor} with experiments is not as good as that in B_{cal} because the data are not correlated as well. But in both cases, representation with our procedure is better than with other used analytical methods.

For sulfur dioxide, Hayden and O'Connell (1975) gave root-mean-square deviations for second virial coefficients and those obtained using the methods of Black (1958), O'Connell and Prausnitz (1967), Kreglevski (1969), Nothnagel et al. (1973) and Tsonopoulos (1974). It is shown that their method and that of Black are similar but significantly better than other ones. For Avg B = 302, Tarakad and Danner (1977) show that method of Hayden and O'Connell (Avg = 8) is better than theirs (Avg = 9), Nothnagel et al. (Avg = 15) and Tsonopoulos (Avg = 28). From Figure 3 it can be seen that literature data are excellent represented by B_{cal}, slightly better than those of Hayden and O'Connell (1975).

Methyl chloride was investigated by Black (1958), Tsonopoulos (1975) and Lin and Stiel (1977). Tsonopoulos (1975) compared his results with the O'Connell-Prausnitz correlation (1967). For twenty-nine experimental data points, Tsonopoulos provides excellent fit of available

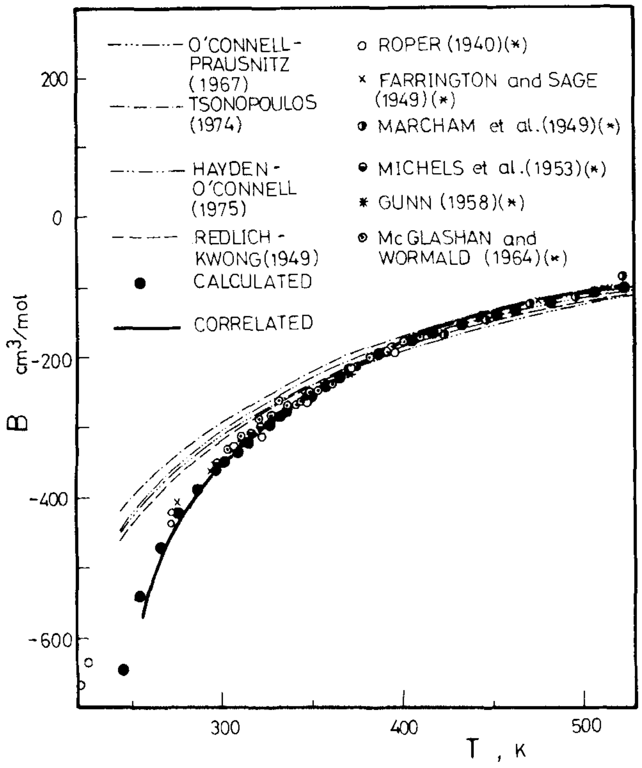

Figure 1. The second virial coefficients of propylene. References denoted with an asterisk are selected from Dymond and Smith (1969).

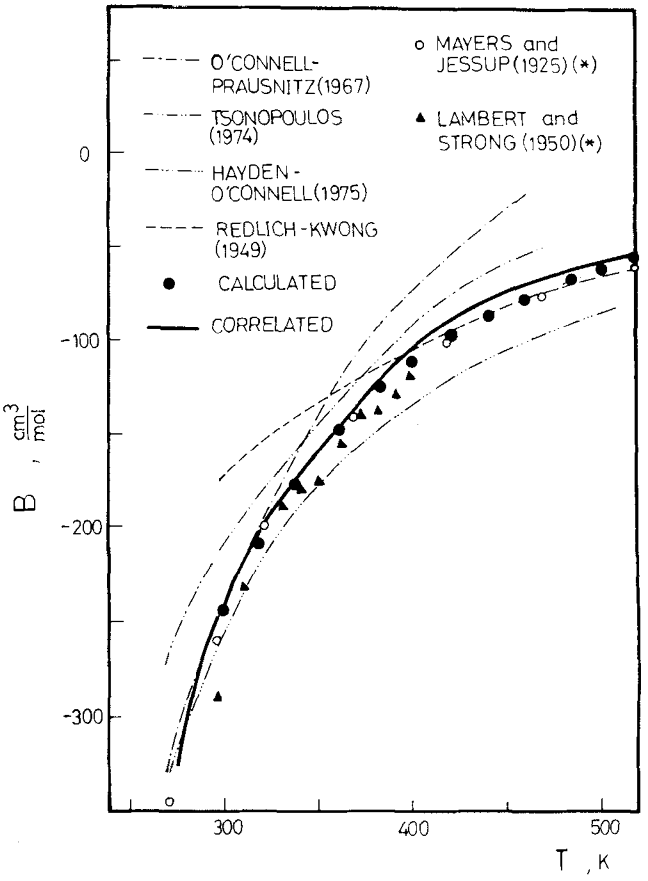

Figure 2. The second virial coefficients of ammonia. References denoted with an asterisk are selected from Dymond and Smith (1969).

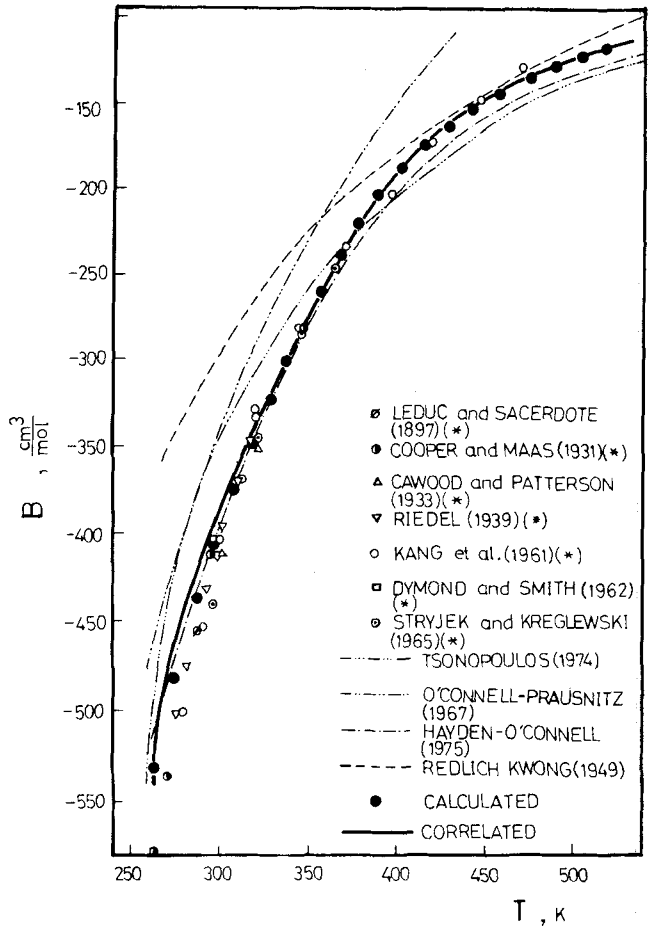

Figure 3. The second virial coefficients of sulfur dioxide. References denoted with an asterisk are selected from Dymond and Smith (1969).

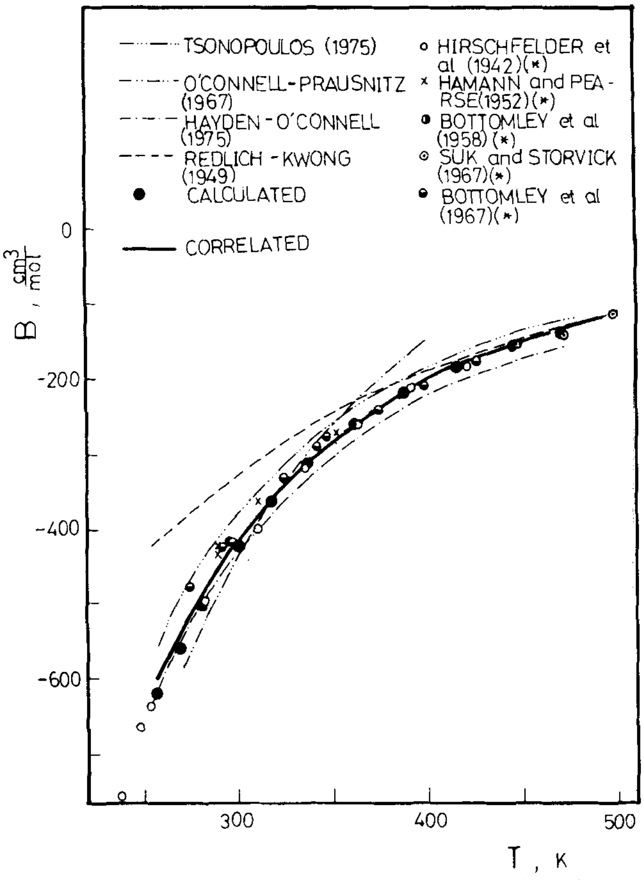

Figure 4. The second virial coefficients of methyl chloride. References denoted with an asterisk are selected from Dymond and Smith (1969).

data with Avg = 1.85. On the other hand, the method of O'Connell and Prausnitz is unsatisfactory in a wide region of temperatures. Lin and Stiel (1977) correlated 7 data points in the temperature range 293° to 498°K with good accuracy (Avg = 1.76). Our results are obtained for a wide range of temperatures with lower temperatures than Lin and Stiel. Figure 4 indicated that good agreement can be obtained for methyl chloride by the method of this study.

Finally, it may be concluded that prediction of second virial coefficients for polar gases such as propylene, ammonia, sulfur dioxide and methyl chloride, by means of the simple Redlich-Kwong equation with temperature dependent parameters, performs as well as or better than other frequently used analytical methods of O'Connell, Prausnitz, Hayden-O'Connell and Tsonopoulos. The procedure employed in this note for correlations of the parameters Ω_a and Ω_b in function of reduced temperature produces only a small loss of accuracy in representation of second virial coefficient in comparison with the second virial coefficient obtained using the optimal values of same parameters for each available isotherm. In all cases, data predicted by the proposed method are to be preferred to the results of the original RK equation.

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NOTATION

a, b = constants of the Redlich-Kwong equation
B = second virial coefficient
C_0, C_1, C_2, C_3 = coefficients of Equations (8) to (13)
P = pressure
R = gas constant
T = absolute temperature
v = molar volume
Z = compressibility factor
Ω_a, Ω_b = dimensionless proportionality parameters

Subscripts

c = critical property
r = reduced

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The Separation of Ethylbenzene from *p*- and *m*-Xylene by Extractive Distillation Using Mixtures of Polychloro Compounds

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The use of a single compound as the agent in modifying the apparent relative volatility in extractive distillation is well known. In the separation of ethylbenzene from para- and meta-xylenes by extractive distillation, it was found that mixtures containing from two to four components were more effective than any known single compound. Hundreds of combinations of extractive agents were investigated in vapor-liquid equilibrium stills, and from these, twenty-seven different combinations of chlorinated organic compounds showed merit. The relative volatility of ethylbenzene to *p*-xylene is 1.06 and to *m*-xylene 1.08. The promising combinations were investigated in three glass perforated plate extractive distillation columns containing twelve, fifteen and nineteen theoretical plates, respectively. Of the twenty-seven different extractive agents tested in the columns, sixteen yielded a relative volatility greater than 1.20. The best one, a mixture of pentachlorophenol, benzene hexachloride and 1,2,4-trichlorobenzene, gave a relative volatility of 1.27. Other combinations approaching this relative volatility are pentachlorophenol, benzene hexachloride and 2,4-dichlorotoluene giving 1.25 and polychlorobenzene, pentachlorophenol, benzene hexachloride and 1,2,4-trichlorobenzene giving 1.26, when used in the ratio of two parts of extractive agent to one part of ethylbenzene-xylene mixture. All the extractive agents boil sufficiently above xylene to make their recovery by distillation easy and complete. Life studies showed no excessive decomposition of any of them while in use.

The separation of ethylbenzene (boiling point 136.15°C.) from *p*-xylene (boiling point 138.4°C.) and *m*-xylene (boiling point 139.2°C.) presents considerable difficulty by reason of the proximity of their boiling points and the accompanying similarity of their vapor pressures as to require the use of fractioning columns containing a great number of plates and high reflux ratios in order to assure effective separation thereof. A major end use for these compounds is in plastics, where high purity is essential; for example, ethylbenzene is converted to styrene and much of *p*-xylene is made into dimethyl terephthalate. As a result, the cost of accomplishing such a separation by conventional rectification is relatively uneconomical. Since ethylbenzene, *p*-xylene and *m*-xylene are all isomers of C_8 aromatic hydrocarbons, their chemical properties are almost identical, and separation by chemical means does not appear to be an attractive route.

Although extractive distillation has fairly wide acceptance in some hydrocarbon separations, toluene from similar boiling nonaromatic hydrocarbons for example, this technique has not been widely investigated in the separation of ethylbenzene from the xylenes. Most of the previous investigators in this field have looked at single compounds as the extractive agent without marked success (Chu, 1954). The relative volatility of ethylbenzene to *p*-xylene is 1.06; to *m*-xylene it is 1.08. To be considered attractive, we believe that the extractive agent should be capable of increasing this value to about 1.20. Amir (1963) reported that *p*-dichlorobenzene increased the relative volatility to 1.116, 2,4,5-trichlorophenol to 1.147 and 2,3,4,5,6-pentachloro-1-butoxybenzene to 1.26. Nixon (1950, 1953) reported that antimony trichloride gave 1.15.

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