**Literature Cited**

(1) Schouten, J. A.; Michels, J. P. J.; Ten Seldam, C. A. Updating the GERG Equation Based on Full Gas Analysis; GERG Report No. 8709; Van der Waals Laboratory, University of Amsterdam: Amsterdam, Oct 1987; available on request.

(2) Michels, J. P. J.; Schouten, J. A.; Jaeschke, M. *Int. J. Thermophys.* **1988**, *9*(6), 985.

(3) Biswas, S. N.; Trappeniers, N. J.; Hoogland, J. H. B. *Physica* **1984**, *126A*, 384.

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# Excess Second Virial Coefficients and Critical Temperatures of Methyl Acetate and Diethyl Sulfide

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**For the system methyl acetate and diethyl sulfide, measurements are reported of excess second virial coefficients (at 50, 75, and 100 °C) and critical temperatures for 11 compositions. The efficacy of the correlations due to Tsonopoulos and to Hayden and O'Connell, both in its original form and incorporating a pseudocritical temperature, are discussed.**

## Introduction

The following equation relates the excess second virial coefficient, $\epsilon$, to the change in pressure, $\Delta P$, when equal volumes of two pure gases 1 and 2 at equal pressure are mixed at constant temperature (*1*).

$$\epsilon = 2RT\Delta P/(P^2 + P\Delta P) \qquad (1)$$

$$\epsilon = B_{12} - \tfrac{1}{2}(B_{11} + B_{22}) \qquad (2)$$

This method renders possible estimation of the unlike interaction second virial coefficient $B_{12}$ with uncertainty comparable with that of $B_{11}$ and $B_{22}$.

The fugacity coefficient $\phi_i$ for two components may be expressed in terms of virial coefficients.

$$\ln \phi_1 = (B_{11} + 2Y_2^2\epsilon)P/RT \qquad (3)$$

$B$ values are thus required directly for $PVT$ calculations and for liquid/vapor equilibrium estimations.

Of greater importance is the use of the results to test the efficacy of correlations that have been proposed for the prediction of $PVT$ behavior of mixtures since only a small proportion of all possible mixtures can be studied.

Almost all correlations are of the "corresponding states" type and require that $B$ and $T$ be "reduced" with use of critical or pseudocritical temperatures, pressures, and sometimes volumes.

While pseudocritical temperature has often been used as a fitting parameter for second virial coefficient correlations, as has been previously described (*2*), in this work an independent estimate of $T^c_{12}$ (unlike interaction) has been obtained from the measurement of mixture critical temperatures as a function of composition.

## Experimental Section

***Apparatus.*** The apparatus for measurement of $\epsilon$ from the pressure charge on mixing was unchanged from that described previously (*3*).

The procedure for measurement of critical temperatures using the sealed-tube method has been described by McElroy et al. (*2*). Possible decomposition of the compounds at elevated temperatures was diminished by maintaining temperatures near critical for the minimum time needed for stable readings. No evidence of decomposition was noted, and no drift in critical temperature with increasing exposure to elevated temperatures was observed.

***Materials.*** "Pure"-grade diethyl sulfide supplied by Koch-Light Laboratories, Ltd., was dried over calcium sulfate and distilled in a 50-cm spinning band (PTFE) column (Nester/Faust Manufacturing Corp. Model S-1179).

The methyl acetate supplied by May and Baker, Ltd., was purified in a similar manner, central cuts from the distillation being used in both cases. Gas chromatographic analysis indicated greater than 99.95% purity.

All reagents were thoroughly degassed and then distilled directly into either the virial coefficient apparatus or critical point tubes.

## Theory

***Pseudocritical Temperature.*** The thermodynamic conditions for a critical point in a binary system is that the second and third derivatives of free energy with respect to mole fraction be zero.

$$\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,P} = 0 \qquad (4)$$

$$\left(\frac{\partial^3 G}{\partial Y^3}\right)_{T,P} = 0 \qquad (5)$$

In the previous study (*2*), the combining rules

$$a_m = a_{11}Y_1^2 + a_{22}Y_2^2 + 2Y_1Y_2a_{12} \qquad (6)$$

and

$$b_m = b_{11}Y_1^2 + b_{22}Y_2^2 + 2Y_1Y_2b_{12} \qquad (7)$$

and the thermodynamic critical point condition were used in conjunction with the Redlich-Kwong equation of state to solve for $a_{12}$ and hence for unlike-interactions critical temperature $T^c_{12}$. The Redlich-Kwong in common with the Peng-Robinson equation and others was developed from the van der Waals equation of state.

$$\frac{RV}{RT} = \frac{1}{V - b} - \frac{a}{V^2} \qquad (8)$$

The first term in this equation is an approximation for the hard-sphere equation of state that was known to be in error by van der Waals himself. The accurate hard-sphere equation of state

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$$PV/RT = 1 + 4\bar{Y} + 10\bar{Y}^2 + 18.36\bar{Y}^3 + 28.2\bar{Y}^4 \quad (9)$$

(where $\bar{Y} = b/4V$) has been known for many years (*4*).

Analytical approximations were developed by Longuet-Higgins and Widom (*5*), Jager (*6*), Carnahan and Starling (*7*), and others. Another representation (*8*)

$$PV/RT = (1 - 1.64\bar{Y}^3 - 5.16\bar{Y}^4)(1 - \bar{Y})^{-4} \quad (10)$$

gives exact agreement up to and including the quartic term, but for our purposes, the simpler Jager equation

$$PV/RT = (1 - \bar{Y})^{-4} \quad (11)$$

is satisfactory.

The composite equation (Jager/Redlich-Kwong)

$$PV/RT = (1 - b/4V)^{-4} - a[RT^{1.5}(V + b)]^{-1} \quad (12)$$

gives a reasonable estimate of the critical compressibility factor, $Z_c = 0.261$, and has been used here to obtain an estimate of the pseudocritical temperature $T_{12}^c$.

The parameters $a$ and $b$ are given by

$$a_{ij} = 1.463RT_{ij}^{c\,1.5}V_{ij}^c \quad (13)$$

and

$$b_{ij} = 0.3087V_{ij}^c \quad (14)$$

where the pseudocritical volume $V_{12}^c$ is estimated by the Lorenz-Berthelot rule.

$$V_{12}^c = [(V_1^c)^{1/3} + (V_2^c)^{1/3}]^3/8 \quad (15)$$

The mixture critical volume was estimated by

$$V_m^c = \phi_1V_1^c + \phi_2V_2^c + 2\phi_1\phi_2V_{12} \quad (16)$$

where $\phi_1$ is the surface fraction and $V_{12}$ an interaction parameter estimated by the procedure described by Schick and Prausnitz (*9*).

The unlike-interaction critical temperature is thus estimated from measurements of the mixture critical temperature and solution of eq 4.

***Virial Coefficients.*** The measured unlike-interaction second virial coefficients have been compared with predictions of two procedures.

Firstly, the Tsonopoulos correlation (*10*)

$$BP_c/RT_c = f^{(0)}(T_r) + Wf^{(1)}(T_r) + f^{(2)}(T_r) \quad (17)$$

with parameters obtained by Tsonopoulos. For unlike-interaction virial coefficient reduced temperature $T_r = T/T_{12}^c$ where $T_{12}^c$ is the pseudocritical temperature described above. $W$ is Pitzer's accentric factor. The $RT_{12}^c/P_{12}^c$ required in eq 17 is estimated by the following expression, which has been previously derived (*2*).

$$T_{12}^c/P_{12}^c = [[T_1^c/P_1^c(8 + 3W_1)]^{1/3} + [T_2^c/P_2^c(8 + 3W_2)]^{1/3}]^3[1 + 3(W_1 + W_2)/16] \quad (18)$$

Secondly, the Hayden and O'Connell correlation (*11*) for second virial coefficients was employed.

This predictive equation has the form

$$B_{ij} = (B_{\mathrm{nonpolar}}^{\mathrm{F}} + B_{\mathrm{polar}}^{\mathrm{F}} + B_{\mathrm{metastable}}^{\mathrm{D}} + B_{\mathrm{bound}}^{\mathrm{D}} + B_{\mathrm{chemical}}^{\mathrm{c}}) \quad (19)$$

and as well as critical temperature and pressure, dipole moment, mean radius of gyration, and an association or solution parameter are required for its application. The values used for the systems here are tabulated in Table I.

**Table I. Pure Component Parameters**

| | $T^c$/K | $P^c$/MPa | $\mu$/D | $R$/nm | $W$ |
|---|---|---|---|---|---|
| methyl acetate | 506.1 | 4.6 | 1.7 | 0.2862 | 0.309 |
| diethyl sulfide | 557.0 | 3.9 | 1.6 | 0.3207 | 0.324 |

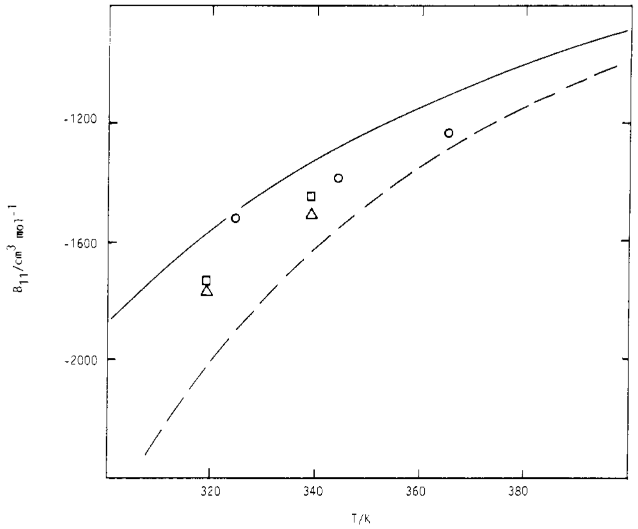

**Figure 1.** Second virial coefficients of diethyl sulfide: ○, Scott et al. (*12*); □, McCullough et al. (*14*); △ Bottomley and Coopes (*13*); —, Hayden and O'Connell (*11*); --, Tsonopoulos (*10*).

The Hayden and O'Connell correlation has been applied in its original form, and in addition, we have employed the relation incorporating the independently estimated unlike-interaction critical temperature $T_{12}^c$.

In the Hayden and O'Connell correlation for pure components, the required quantity $\epsilon_{ij}/k$ is given by

$$\epsilon_{ij}/k = T_i^c[0.748 + 0.91W_{ii} - 0.4\eta_{ii}/(2 + 20W_{ii})] \quad (20)$$

For unlike interaction virial coefficients, $\epsilon_{kj}/k$ is expressed in terms of a function of $\epsilon_{ii}$ and $\epsilon_{jj}$. In the alternative procedure as previously described, $\epsilon_{ij}$ is obtained from the pseudocritical temperature $T_{ij}^c$ with

$$\epsilon_{ij}/k = T_{ij}^c[0.748 + 0.91W_{ij} - 0.4\eta_{ij}/(2 + 20W_{ij})] \quad (21)$$

where

$$W_{ij} = (W_{ii} + W_{jj})/2 \quad (22)$$

***Pure-Component Second Virial Coefficients. Diethyl Sulfide.*** The three sets of measurement on this system are illustrated in Figure 1. The values obtained are in reasonable agreement. The Tsonopoulos and the Hayden and O'Connell correlations bracket the results, neither being a good fit.

***Methyl Acetate.*** It has been shown previously (*2*) that the considerable number of experimental points obtained by Lambert et al. (*15*) are well fitted by the Hayden and O'Connell correlation. Three experimental points obtained by Connet et al. (*16*) from enthalpy measurements are also in good agreement.

## Results and Conclusions

***Critical Temperatures.*** The measured critical temperatures and the unlike-interaction critical temperature $T_{12}^c$ calculated as previously described are listed in Table II.

Mixture critical temperatures on a mole fraction plot may be fitted by

$$T_m^c = Y_1^2T_1^c + Y_2^2T_2^c + 2Y_1Y_2\Delta T_{12} \quad (23)$$

or by surface fractions (*17*)

$$T_m^c = \theta_1^2T_1^c + \theta_2^2T_2^c + 2\theta_1\theta_2T_{12}^* \quad (24)$$

The results obtained are plotted against both $Y_2$ and $\theta_2$ in Figure

Table II. Mixture Critical Temperatures of Methyl Acetate (1) + Diethyl Sulfide (2)

| mole fraction $Y_1$ | measured $T^c_m$/K | calculated $T^c_{12}$/K |
|---|---|---|
| 0.15 | 547.35 | 501.85 |
| 0.345 | 536.41 | 507.3 |
| 0.368 | 535.53 | 508.7 |
| 0.503 | 529.75 | 513.4 |
| 0.635 | 522.54 | 513.3 |
| 0.638 | 522.26 | 513.1 |
| 0.706 | 520.11 | 515.9 |
| 0.770 | 515.29 | 512.3 |
| 0.811 | 512.71 | 510.3 |
| 0.905 | 509.71 | 512.0 |
| 0.947 | 507.9 | 508.7 |

Table III. Second Virial Coefficients, Pure Component and Excess

| | pure-component coeff/(cm$^3$ mol$^{-1}$) | | excess virial coeff/(cm$^3$ mol$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | Hayden and O'Connell | | | |
| $T$/K | methyl acetate | diethyl sulfide | $b$ | $c$ | Tsonopoulos[a] | exptl |
| 323.16 | −1250 | −1640 | 391 | 288 | 141 | 154 |
| 348.15 | −980 | −1330 | 280 | 198 | 127 | 115 |
| 373.15 | −820 | −1180 | 260 | 193 | 162 | 107 |

[a] Calculated from the predicted value for $B_{12}$ and literature values of $B_{11}$ and $B_{22}$. [b] Using standard procedure. [c] Using $T^c_{12}$ (pseudocritical).

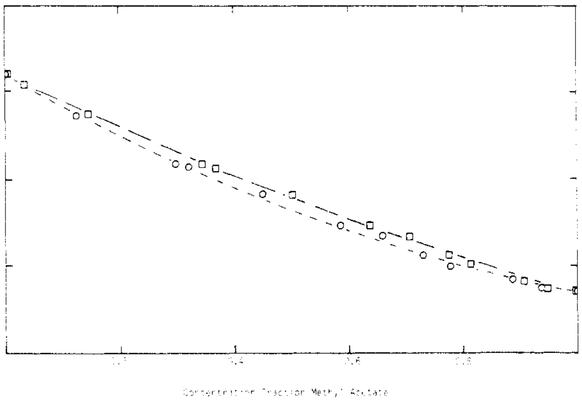

**Figure 2.** Critical temperatures methyl acetate + diethyl sulfide: □, mole fraction; ○, surface fraction.

2. The deviation from a linear relationship is not large, and the mole fraction plot is more nearly linear. Within the experimental uncertainty, neither plot is obviously superior. The surface fraction relationship, however, is predictive rather than simply fitting and predicts the behavior very well. The pseudocritical temperatures calculated as previously described show some drift with composition. Applying a weighting factor of $Y_1Y_2$ results in a weighted mean value of

$$T^c_{12} = 511.8 \text{ K}$$

***Second Virial Coefficients.*** The results are presented in Table III along with the selected $B_{ij}$ values and the predictions of the correlations.

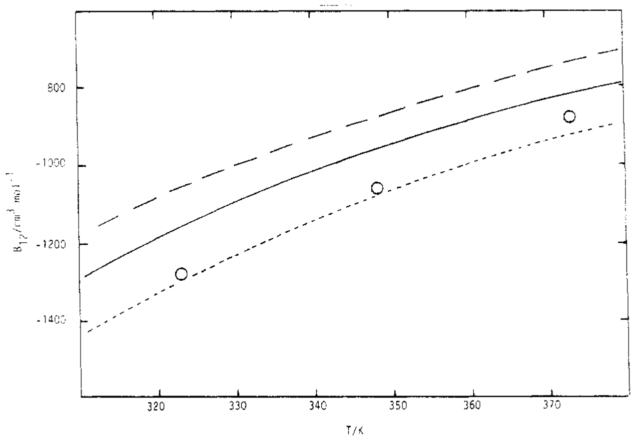

**Figure 3.** Unlike-interaction second virial coefficient for methyl acetate + diethyl sulfide: – –, Hayden and O'Connell (*11*); —, Hayden and O'Connell with $T^c_{12}$; - -, Tsonopoulos (*10*).

None of the correlations generate a good fit to the measured data for $\epsilon$. The Hayden and O'Connell correlation is considerably improved by incorporation of the pseudocritical temperature $T^c_{12}$ determined here, but still the deviation is considerable and greater than that of the Tsonopoulos correlation.

The fitting of $\epsilon$, however, is a severe test as the uncertainties in $B_{11}$ and $B_{22}$ are included.

In Figure 3, the unlike-interaction second virial coefficients calculated from the measured $\epsilon_{12}$ value and the literature $B_{11}$ and $B_{22}$ values are plotted. The Hayden and O'Connell and Tsonopoulos predictions are also plotted. In this presentation, it is evident that the Tsonopoulos correlation represents a good representation of the measured data.

**Registry No.** Methyl acetate, 79-20-9; diethyl sulfide, 352-93-2.

## Literature Cited

(1) Knobler, C. M. *Rev. Sci. Instrum.* **1967**, *38*, 184.
(2) McElroy, P. J.; Hashim, H.; Wong Loke Tatt. *AIChE J.* **1983**, *29*, 1007.
(3) McElroy, P. J.; Shannon, T. W.; Williamson, A. G. *J. Chem. Thermodyn.* **1980**, *12*, 371.
(4) Alder, B. J.; Wainwright, T. E. *J. Chem. Phys.* **1959**, *33*, 369.
(5) Longuet-Higgins, H. C.; Widon, B. *Mol. Phys.* **1965**, *8*, 549.
(6) Jager, G. *Wiem. Ber.* **1986**, *15*, 105.
(7) Carnahan, N. F.; Starling, K. E. *AIChE J.* **1972**, *18*, 1184.
(8) McElroy, P. J. *Proc. Inst. Eng. Aust. Conf.* **1983**, *11*, 449.
(9) Schick, L. M.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 673.
(10) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(11) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(12) Scott, D. W.; Finke, H. L.; Hubard, W. M.; McCullough, J. P.; Oliver, G. D.; Gross, M. E.; Datz, M. E.; Williamson, K. D.; Waddington, G.; Kuffman, M. *J. Am. Chem. Soc.* **1952**, *74*, 4656.
(13) Bottomley, G. A.; Coopes, I. H. *Aust. J. Chem.* **1962**, *15*, 190.
(14) McCullough, J. P.; Hubbard, W. N.; Fraw, F. R.; Hossenlapp, I. A.; Waddington, G. *J. Am. Chem. Soc.* **1957**, *79*, 561.
(15) Lambert, J. D.; Clarke, J. S.; Duke, J. K.; Hicks, C. L.; Lawrence, S. D.; Morris, D. M.; Shane, M. G. T. *Proc. R. Soc. London* **1959**, *A249*, 414.
(16) Connet, J. E.; Counsell, J. F.; Lee, D. A. *J. Chem. Thermodyn.* **1976**, *8*, 1199.
(17) Chueh, P. L.; Prausnitz, J. M. *AIChE J.* **1967**, *13*, 1099.

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