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Manuscript received July 14, 1982; revision received and accepted January 31, 1983.

Excess Second Virial Coefficients and Critical Temperatures: Acetone + Methyl Acetate

For the system acetone + methyl acetate measurements are reported of excess second virial coefficients (at 75 and 100°C) and critical temperatures for nine different compositions. The efficacy of the correlations due to Tsonopoulos and to Hayden and O'Connell are discussed and the former correlation (with one modification) is shown to give a better prediction of unlike interaction terms. The implication of the results for excess Gibbs Free Energy estimation is discussed.

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SCOPE

This study is part of a continuing program of measurement of unlike interaction second virial coefficients B_{ij} of a series of mixtures sufficiently diverse that procedures for the prediction of B_{ij} may be tested and the most successful methods identified. B_{ij} values are required in the determination of the PVT properties of gas mixtures at moderate pressure and in particular in the estimation of activity coefficients from vapor pressure studies. The enormous number of possible mixtures precludes measurement on all systems and so prediction is essential.

Most predictive techniques are variations on the principle of corresponding states and require "reduction" of temperature by a characteristic temperature, usually the pseudocritical temperature for unlike interaction, T_{12}^c. Preferably T_{12}^c is obtained from independent measurements such as the measured critical temperatures used here.

The particular system, acetone + methyl acetate, introduces two additional functional groups into the series studied. Also a recent liquid-vapor equilibrium investigation requiring B_{12} values exposed large differences in two of the most widely used predictive methods.

CONCLUSIONS AND SIGNIFICANCE

The unlike interaction second virial coefficient of the system, acetone + methyl acetate, has been measured and the inability of the correlations due to Tsonopoulos and to Hayden and O'Connell to accurately predict the results is demonstrated. Critical temperatures of this system have also been measured and employed to give an estimate of the unlike interaction pseudocritical temperature T_{12}^c. It is argued that a significant test of the predictive equations is only possible when T_{12}^c is not simply an adjustable fitting parameter but is independently estimated from measurements such as critical temperature. The fact that the Hayden-O'Connell correlation is superior in pure virial coefficient prediction but inferior in unlike interaction prediction suggests that the existing combining rules are inadequate.

INTRODUCTION

For mixing of two components, 1 and 2, in the gas phase, the pressure change, Δp, at constant volume and temperature is for moderate or low pressures simply related to the second virial coefficients (Knobler, 1967) B_{11}, B_{22} (for the pure substances) and B_{12} (for unlike interaction).

$$RT\Delta p/p^2(1 + \Delta p/p)2x_1x_2 = B_{12} - \tfrac{1}{2}(B_{11} + B_{22}) = \epsilon \quad (1)$$

ϵ we will call the excess second virial coefficient.

One advantage of this method is that since ϵ may be measured more accurately than B_{ii} it is possible to estimate B_{12} with an error, δB, comparable to that in B_{11} and B_{22}. Estimation of B_{12} from the mixture second virial coefficient, B_m, must always result in an error of the order $3\delta B$.$^{(2)}$

The quantity ϵ is also the required quantity in the calculation of the fugacity coefficients, ϕ_i, necessary in calculation of liquid vapor equilibria. The common expression

$$ln\ \phi_i = \left(2 \sum_j^m y_i B_{ij} - Bm\right) p/RT \tag{2}$$

may also be written for two components

$$ln\ \phi_1 = (B_{11} + 2y_2^2 \epsilon) p/RT \tag{3}$$

It is thus possible to estimate $RTp^{-1}\ ln\ \phi_i$ with an uncertainty little greater than δB compared to approximately $5\delta B$ when ϕ_i is obtained from B_{ii} and B_m measurements.

Apart from the direct use of ϵ and B_{ij} in gas-phase PVT and liquid-gas equilibrium calculations, accurate values of these quantities are required to test combining rules for the estimation of properties of other two-component or multicomponent systems which are too numerous to be individually studied.

Most of the correlations applied to virial coefficients are extensions of the "principle of corresponding states" for which the "reduced" B is expressed as a function of temperature, itself reduced by a critical or pseudocritical temperature. The pseudocritical temperature T_{12}^c, applicable to the unlike interaction second virial coefficient B_{12}, has been estimated in a number of ways, none of which are particularly satisfactory.

While T_{12}^c is commonly obtained by forcing B_{12} to fit a particular correlation, this is useless in testing the correlation and an independent estimate of T_{12}^c is essential.

In this study critical temperatures of mixtures have been measured and estimates of T_{12}^c are obtained from this source.

EXPERIMENTAL

The apparatus for measurement of ϵ from pressure change on mixing has been described previously by McElroy et al. (1980).

Critical temperatures were measured using the sealed glass capillary tube method. Mixtures were formed by distillation of each component from degassed samples in ampoules with teflon-sealed valves and aluminum gasket couplings to the vacuum line.

Care was taken that no significant vapor remained in the distillation lines and then the "pyrex" capillary was sealed off at a point such that the volume was greater than that estimated for critical density in the tube. The preweighed ampoules were removed and weighed and the mass of each component determined by difference.

The temperature for disappearance and reappearance (T decreasing) of the two-phase interface was measured. A miniscus which moved down the tube confirmed a density less than critical. The tube was subsequently decreased in volume in stages by immersing all but the upper end of the tube in liquid nitrogen ensuring that all the mixture was removed from the end which was then collapsed slightly using a "glass-blowing" torch.

After each collapse the temperature of miniscus disappearance was measured. When the critical point was approached, as indicated by no discernable movement of the miniscus up or down the tube prior to disappearance; a mark was made at the midpoint of the tube. The critical temperature was taken as that corresponding to miniscus disappearance at midpoint of the tube, which in the absence of significant gravitational effects should represent the true critical point (Rowlinson, 1969).

The tube length (commonly about 3 cm) was not so short that gravitational effects were ruled out. However, other indications such as maximum opalescence, equality of refractive index of the phases (Saikawa et al., 1979), and more significantly identical temperature readings for densities adjacent to this density confirmed observation of the critical point temperature.

Temperature control was achieved by placing the sealed tube in the center of a solid aluminum cylindrical block of height 35 cm and diameter 18 cm. The surrounding heating mantle in conjunction with an electronic proportional controller with thermistor detector maintained the temperature to better than ±0.01 K. Temperature was measured using a platinum resistance probe and "Rosemount Engineering Co. Ltd. model VLF 5IA" a.c. resistance bridge (or a mercury in glass thermometer regularly calibrated against it).

Final determination of the critical point (or dew or bubble point for noncritical density) was made by controlling the temperature for some hours approximately 0.01 K below the estimated temperature and then resetting the proportional controller to a point 0.01 K above the estimated temperature. This procedure (and subsequently its reverse) caused a very steady transition from two-phase to one-phase region (and back) and enabled highly reproducible readings to be made.

A horizontal hole in the block, plugged with glass rod to obviate cool points, enabled the miniscus to be viewed using a long focal length microscope with back lighting.

THEORY

Pseudocritical Temperature

The critical temperature of two-component mixtures may be related to the unlike interaction pseudocritical temperature using an equation of state and the thermodynamic condition for a critical point that the second and third derivatives of Gibbs Free Energy with respect to mole fraction be zero.

$$\left(\frac{\partial^2 G}{\partial Y_1^2}\right)_{T,P} = \left(\frac{\partial^3 G}{\partial Y_1^3}\right)_{T,P} = 0 \tag{4}$$

The Redlich-Kwong equation

$$p = RT/(V - b) - a/T^{1/2}V(V + b) \tag{5}$$

has been successfully used for this purpose in conjunction with the parameter combining rules

$$a_m = Y_1^2 a_{11} + Y_2^2 a_{22} + 2Y_{11}Y_{22}a_{12} \tag{6}$$

$$b_m = Y_1^2 b_{11} + Y_2^2 b_{22} + 2Y_{11}Y_{22}b_{12} \tag{7}$$

relating the mixture parameters to the pure component and unlike interaction parameters.

For the Redlich-Kwong equation the parameters may be shown to relate to the critical point values as follows:

$$a_{ij} = 3(0.4278)RV_{ij}^c(T_{ij}^c)^{1.5} \tag{8}$$
$$b_{ij} = 3(0.08664)V_{ij}^c$$

The pseudocritical volume V_{12}^c may be estimated using the Lorentz-Berthelot rule

$$V_{12}^c = ((V_1^c)^{1/3} + (V_2^c)^{1/3})^3/8 \tag{9}$$

In the absence of an accurately measured critical volume its value may be estimated from solution of the simultaneous Eqs. 4 or alternatively it may be estimated using

$$V_m^c = \theta_1 V_1^c + \theta_2 V_2^c + 2\theta_1\theta_2\nu_{12} \tag{10}$$

where θ_i, the surface fraction, is given by

$$\theta_i = Y_i(V_i^c)^{2/3}/(Y_1(V_1^c)^{2/3} + Y_2(V_2^c)^{2/3}) \tag{11}$$

and ν_{12} is an interaction parameter estimated as described by Schick and Prausnitz (1968) who developed this procedure.

The measured critical temperature of the mixture may thus be used to estimate T_{12}^c, the unlike interaction pseudocritical temperature. Young and coworkers have previously employed this type of procedure using alternative equations of state (Toczylkin and Young, 1980).

Virial Coefficient

The modification by Tsonopoulos (1974) of the Pitzer and Curl (1957) correlation expresses the second virial coefficient as follows

$$BP_c/RT_c = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + f^{(2)}(T_r) \tag{12}$$

$$f^{(0)}(T_r) = 0.1445 - 0.33\ T_r^{-1} - 0.1385\ T_r^{-2} - 0.0121\ T_r^{-3} - 0.000607\ T_r^{-8} \tag{13}$$

$$f^{(1)}(T_r) = 0.0637 + 0.331\ T_r^{-2} - 0.423\ T_r^{-3} - 0.008\ T_r^{-8} \tag{14}$$

$$f^{(2)}(T_r) = -(2.14 \times 10^{-4}\ \mu_r + 4.308 \times 10^{-21}\ \mu_r^8) \tag{15}$$

for nonhydrogen bonded compounds.

$$\mu_r = \mu^2 p_c T_c{}^{-2}(1.013 \times 10^5) \tag{16}$$

For mixtures Tsonopoulos used the unlike interaction relations

TABLE 1. VALUES OF PARAMETERS FOR APPLICATION OF EQUATIONS

	T_c/K	P_c/bar	ω	μ/Debye	Γ	R_D/nm	ω'
Acetone	508.1	47.0	0.309	2.9	0.90	0.2740	0.146
Methyl Acetate	506.1	46.9	0.324	1.7	0.85	0.2862	0.157

TABLE 2. SECOND VIRIAL COEFFICIENTS/cm^3·mol^{-1}

T/K	Pure Components		Excess, ϵ Acetone + Methyl Acetate		
	Acetone[a]	Methyl Acetate[b]	Hayden & O'C.	Tsonopoulos	Experimental
348.30	−1090	−980	−72.0	100	76.3
373.64	− 830	−820	−41.8	71	49.0

[a] Bottomley and Spurling (1967).

[b] Lambert et al. (1959).

$$T^c_{12} = (T^c_1 T^c_2)^{1/2}(1 - k_{12}) \tag{17}$$

$$\omega_{12} = (\omega_1 + \omega_2)/2 \tag{18}$$

and $p^c_{12} = 4T^c_{12}(p^c_1 V^c_1/T^c_1 + p^c_2 V^c_2/T^c_2)[(V^c_1)^{1/3} + (V^c_2)^{1/3}]^{-3}$ (19)

Equation 19 results from Eq. 9 plus the approximations

$$Z^c_{12} = (Z^c_1 + Z^c_2)/2 \tag{20}$$

$$\text{where } Z = pV/nRT. \tag{21}$$

$$\text{The rule } Z^c = 0.293/(1 + 3\omega/8) \tag{22}$$

relating critical compressibility factor Z^c to Pitzer's accentric factor ω, is reasonably accurate and readily testable unlike the arbitrary combining rules.

What is required to reduce B_{12} is RT^c_{12}/p^c_{12} and employing Eqs. 9, 18, 21 and 22 we obtain

$$T^c_{12}/p^c_{12} = [T^c_1/p^c_1(8 + 3\omega_1)^{1/3} + T^c_2/p^c_2(8 + 3\omega_2)^{1/3}]^3 \times [1 + 3(\omega_1 + \omega_2)/16] \tag{23}$$

We have used this expression to reduce B_{12} since it directly relates T^c_{12}/p^c_{12} to T^c_1/p^c_1 and T^c_2/p^c_2 and avoids the arbitrary Eq. 20.

The second correlation, developed by Hayden and O'Connell (1975), is widely used and is often preferred in phase calculation computational procedures. In common with the Tsonopoulos correlation it is an extension of the "principle of corresponding states" incorporating an accentric factor derived from mean radius of gyration, the dipole moment, plus an association parameter or solvation parameter. The virial coefficient is expressed as

$$B_{ij} = (B^F_{\text{nonpolar}})_{ij} + (B^F_{\text{polar}})_{ij} + (B^D_{\text{metastable}})_{ij} + (B^D_{\text{bound}})_{ij} + (B^D_{\text{chemical}})_{ij} \tag{24}$$

where superscript F denotes relatively "free" molecules (weak physical forces), and D denotes relatively "bound" or dimerized molecules (chemical forces). The extensive detailed equations for estimation of each term as a function of temperature are listed by Hayden and O'Connell and in a clearer form (but with a sign error in Eq. A4) by Prausnitz et al. (1980). The values of the parameters used in application of both equations are listed in Table 1.

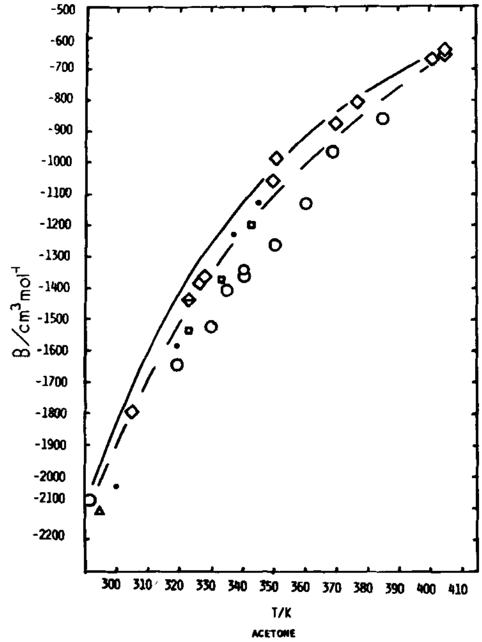

Figure 1. Acetone second virial coefficients. ◇ Bottomley and Spurling (1967); ○ Lambert et al. (1949); ∘ Pennington and Kobe (1957); □ Zaalishvili and Kolysko (1964); △ Bottomley and Spurling (1967). Correlations: — — Hayden and O'Connell (1975); ——— Tsonopoulos (1974).

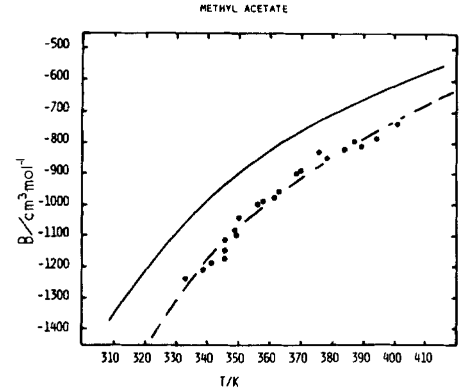

Figure 2. Methyl acetate second virial coefficients. ○ Lambert et al. (1959). Correlations: — — Hayden and O'Connell (1975); ——— Tsonopoulos (1974).

PURE COMPONENT SECOND VIRIAL COEFFICIENTS

Acetone

Figure 1 shows that there are considerable discrepancies among measurements on this system (Dymond and Smith, 1969). The Hayden-O'Connell correlation appears to provide a reasonable fit to the data while that of Tsonopoulos gives negative values somewhat insufficient in magnitude. Best fit values at the temperature of this study are given in Table 2.

Methyl Acetate

The measurements of Lambert et al. (1959), the only ones for this system, are plotted in Figure 2. The Hayden-O'Connell correlation is again superior. The uncertainty in these measurements, however, may well be approaching ±100 cm^3·mol^{-1}.

RESULTS AND CONCLUSIONS

The measured critical temperatures are listed in Table 3 along with the T^c_{12} values calculated using the procedure previously

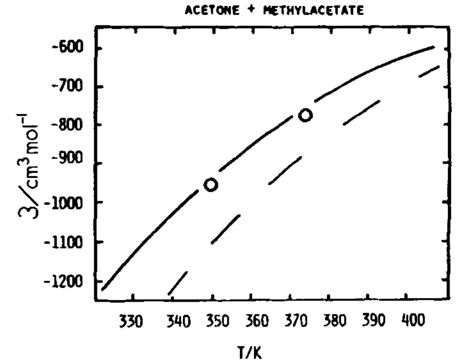

Figure 3. Unlike interaction second virial coefficient acetone + methyl acetate. ○ experimental; Correlations: ——— Tsonopoulos (1974); — — Hayden and O'Connell (1975).

TABLE 3. MEASURED CRITICAL TEMPERATURES

Acetone (1) + Methylacetate (2)

Mole Fraction Y_1	Measured T^c_m/K	Calculated Pseudocritical T^c_{12}/K
1	508.35	
0.876	507.29	504.26
0.691	507.18	506.28
0.651	507.17	506.49
0.515	507.05	506.72
0.482	506.95	506.61
0.192	506.83	506.75
0.066	506.65	505.34
0	506.65	

TABLE 4. $G^E/RT \times 10^{-3}$ ($x_1 = 0.5021$, $T = 60°C$)

$B_{11} + B_{12}$ Source	ε Source Tsonopoulos Correlation	Hayden & O'Connell Correlation	This Work
Tsonopoulos	35.2		
Hayden & O'Connell		33.3	
Literature[a,b]	37.5	33.2	37.1

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[a] Bottomley and Spurling (1967).
[b] Lambert et al. (1959).

outlined. Applying a weighting factor Y_1Y_2 results in a weighted mean value

$$T^c_{12} = 506.3 \text{ K}$$

with a standard deviation of ±0.7 K.

The measured values of ϵ are listed in Table 2 along with the ϵ values calculated from the best fit pure component values and the Tsonopoulos and Hayden-O'Connell correlations. Evidently the former correlation is in excellent agreement while that of Hayden-O'Connell is significantly in error.

The B_{12} results calculated from the experimental values and the best fit B_{11} and B_{22} values are plotted in Figure 3 along with the two correlations. The discrepancy in the Hayden-O'Connell plot is again large even in this less demanding test. The contrast with the good agreement obtained for pure component results suggests that the combining rules used in this correlation might be improved.

Olson's (1981) study of the PTX and G^E behavior of this system revealed the necessity for accurate B and ϵ values, even at low pressure, particularly in estimation of G^E. This was indeed one reason for the present study. He argued that the Hayden-O'Connell correlation was expected to be superior to that of Tsonopoulos, and his G^E results at 60°C for $x_1 \simeq x_2 \simeq 0.5$ are listed in Table 4. Evidently the best estimate of G^E would have been obtained using previously measured pure component B values and the Tsonopoulos equation estimate of B_{12}. Accurate B_{12} estimation is the primary requirement since pure component B measurements are often available. The success of the Hayden and O'Connell correlation in predicting pure values, however, suggests that it might also be superior in B_{ij} prediction if more successful combining rules can be developed. In particular the relationships

$$e_{ij} = 0.7\,(e_{ii}e_{jj})^{1/2} + 0.6(1/e_{ii} + 1/e_{jj})^{-1} \qquad (25)$$

and

$$\sigma_{ij} = (\sigma_{ij}\sigma_{jj})^{1/2} \qquad (26)$$

which were adopted by Hayden and O'Connell (1975) have the virtue of simplicity but are otherwise arbitrary. There are a number of other rules for estimation of these quantities which have at least equivalent theoretical justification and testing against experiment for a range of systems and establish whether improved correlation can be effected.

NOTATION

B = second virial coefficient
B_{12} = unlike interaction second virial coefficient of components 1 and 2
k = interaction parameter
p = pressure
Δp = pressure change on mixing
R = gas constant
T = temperature
T^c_{12} = pseudocritical temperature for mixture of 1 and 2
V = volume
V^c_{12} = pseudocritical volume for mixture of 1 and 2
z = compressibility factor.
e = characteristic interaction energy

Greek Letters

ϵ = excess second virial coefficient
Γ = association parameter
μ = dipole moment
ξ = pseudocritical volume interaction parameter
ϕ = fugacity coefficient
ω = Pitzer's accentric factor
σ = molecular radius

Subscripts

m = mixture
i or ii = component i
r = reduced

Superscripts

c = critical point value

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Manuscript received January 4, 1982; revision received December 15, and accepted January 6, 1983.