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Excess Second Virial Coefficients and Mixture Critical Temperatures of Diethyl Ether and Methyl Acetate

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Measurements of the unlike-interaction second virial coefficient B_{12} at 30, 50, 70, and 90 °C for the system methyl acetate and diethyl ether are reported. Critical temperatures for 10 compositions of the same system have also been measured. The critical temperature measurements are used in a simple equation of state to solve the critical condition equations for an unlike-interaction critical temperature T^c_{12}. The predictions of B_{12} from the Tsonopoulos equation and from the Hayden and O'Connell correlation both in its original form and in a form incorporating the determined T^c_{12} are tested against the data. Neither equation is found to be satisfactory.

Introduction

The excess second virial coefficients ϵ_{12}, related to the B_{12} values by

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

may be estimated (*3*) from the pressure change of mixing ΔP by using

$$\epsilon_{12} = RT\Delta P/[2x_1x_2(P^2 + P\Delta P)] \qquad (2)$$

where P is the initial pressure.

The unlike-interaction second virial coefficient B_{12} may therefore be determined.

For an equimolar mixture, eq 2 reduces to

$$\epsilon_{12} = 2RT\Delta P/[P^2(1 + \Delta P/P)] \qquad (3)$$

and we have used this expression since the volumes of the gases prior to mixing are equal within 0.1%. It is still possible for the numbers of moles of each component to differ if their B_{ii} values are sufficiently different. We have checked this for the system studied and found that corrections which could be applied are well within uncertainties in ϵ_{12} from other sources.

Equation 3 is derived from the pressure expansion virial equation. The density series virial expansion gives rise to the comparable expression (4). Differences in ϵ_{12} derived by using

$$\epsilon_{12} = 2RT\Delta P/P^2 - 2[(B_{11} - B_{22})^2/4 - \epsilon_{12}(B_{11} + B_{22})/2]P/RT \qquad (4)$$

eqs 4 and 3 are found for this system to be 1 order of magnitude less than the overall uncertainty, and so eq 3 has been used to derive the results.

While there are several correlations of pure-component virial coefficients that are reasonably successful, mixtures require the introduction of combining rules for the equation parameters, which are often less satisfactory. Measurements of B_{12} on a wide variety of mixture types are therefore required to test the effectiveness of current procedures.

For mixtures, correlations based on the Principle of Corresponding States require "reductions" of the variables by using pseudocritical volumes (or pressures) and temperatures T^c_{12}.

Most commonly, estimates of T^c_{12} are obtained from unlike-interaction second virial coefficients. In the absence of an independent experimental source, T^c_{12} is merely a fitting parameter and the correlating equation is not strictly capable of prediction.

In this work, as has been done previously (*1*), measurements of critical temperatures have been undertaken on the same system and, with use of a simple equation of state, an independent measure of T^c_{12} can be obtained.

Experimental Section

Apparatus. The apparatus to obtain ϵ_{12} from ΔP of mixing was unchanged from that described previously (*2*).

The critical temperature measurement on mixtures using the sealed Pyrex tube method was also as previously described (*1*). The tubes were kept to approximately 2 cm in length so as to minimize incomplete mixing in the critical region. The measured critical temperatures were reproducible with both rising and falling temperatures and in tubes of different length, and we conclude that inadequate mixing is not a problem.

Materials. Diethyl ether, "Analytical Reagent" supplied by B.D.H. Chemicals and guaranteed minimum assay of 99.5%, was distilled in a 50-cm spinning band (PTFE) column (Nester Faust Manufacturing Corp., Model S-1179), having been dried over calcium sulfate. The initial and final quarter of the distillate was discarded.

The methyl acetate supplied by May and Baker Ltd. was purified in a similar manner. Gas chromatographic analysis of both liquids indicated greater than 99.95% purity.

Before distillation into the ΔP-of-mixing apparatus or critical-point tubes, all reagents were rigorously degassed by standard procedures.

Theory

Unlike-Interaction Critical Temperature. Given the critical-point conditions that the second and third derivatives of the Gibbs free energy with respect to composition are zero, a two-parameter (a and b) equation of state plus random mixing combining rules for the coefficients a_m and b_m

$$a_m = a_{11}y_1^2 + a_{22}y_2^2 + 2y_1y_2a_{12} \qquad (5)$$

can be solved for unlike-interaction terms a_{12} and b_{12}. From a_{12} the unlike-interaction critical temperature T^c_{12} can be obtained.

In this work, as before (*17*), the following composite equation employing the Jager (*18*) hard-sphere term and the Redich–Kwong attractive term was used:

$$PV/RT = (1 - b/4V)^{-4} - a[RT^{1.5}(V + b)]^{-1} \qquad (6)$$

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

$$a_{ij} = 1.463RT_{ij}^{c\,1.5}V^c_{ij} \qquad (7)$$

and

$$b_{ij} = 0.3087V^c_{ij} \qquad (8)$$

An alternative procedure is to use the Lorenz–Berthelot rule

$$V^c_{12} = [V_1^{c\,1/3} + V_2^{c\,1/3}]^3/8 \qquad (9)$$

to obtain V^c and then simply solve the equation for a_{12} and hence T^c_{12}. This procedure was found to give a considerably

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Table I. Pure-Component Parameters

	T^c/K	P^c/MPa	μ/D	R_D/nm	ω
methyl acetate	506.1	4.6	1.7	0.2862	0.309
diethyl ether	466.7	3.64	1.3	0.31395	0.281

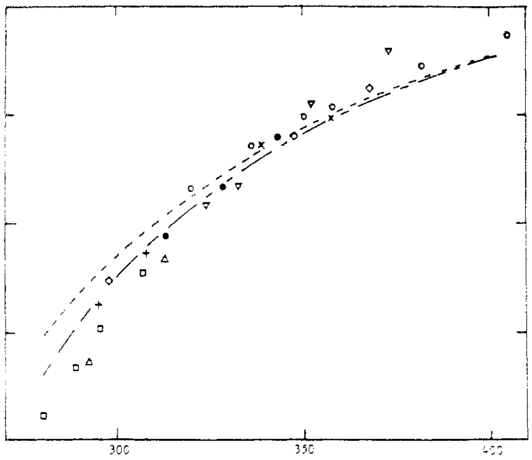

Figure 1. Second virial coefficient of diethyl ether: (- -) Hayden and O'Connell (*5*); (– –) Tsonopoulos (*6*); (○) Lambert et al. (*9*); (▽) Knoebel and Edmister (*10*); (◇) Stryjek and Kreglewski (*11*); (×) Zaalishvili (*12*); (●) Zaalishvili (*13*); (△) Ratzsch and Bittrich (*14*); (+) Bottomley and Reeves (*15*); (□) Counsell et al. (*16*).

more consistant value for T^c_{12}, and so this method was employed here.

Virial Coefficients

The predictions of the Hayden and O'Connell (*5*) correlation and that of Tsonopoulos (*6*) have been compared with the experimental observations.

The Hayden and O'Connell correlation for second virial coefficients requires values of critical temperature and pressure, dipole moment μ, radius of gyration R_D, association parameters η_{ii}, and for unlike interaction, solvation parameters η_{ij}.

The Tsonopoulos modification of the Pitzer and Curl equation has been used in the original form except that B, as before (*1*), has been reduced by using T^c_{12}/P^c_{12} as follows:

$$T^c_{12}/P^c_{12} = \{[T^c_1/(P^c_1(8 + 3\omega_1))]^{1/3} + [T^c_2/(P^c_2(8 + 3\omega_2))]^{1/3}\}^3\{1 + 3(\omega_1 + \omega_2)/16\} \quad (10)$$

The pure-component values required for application of both equations are listed in Table I. The Hayden and O'Connell η terms are zero except that for methyl acetate, which is taken as $\eta_{ii} = 0.85$.

Critical Temperatures

Chueh and Prausnitz (*7*) proposed that mixture critical temperatures could be represented by

$$T^c_m = \theta_1{}^2T^c_1 + \theta_2{}^2T^c_2 + 2\theta_1\theta_2T^{c'}_{12} \quad (11)$$

where T^c_{12} is a function of the pure-component T^c values and θ a "surface fraction" based on $V_i^{c2/3}$. T^c_m can therefore be expressed solely in terms of pure-component quantities. This procedure is often superior to the common expression in which θ in eq 11 is replaced by the mole fraction and $T^{c'}_{12}$ is simply a fitting parameter. Both procedures have been applied to the results.

Pure-Component Second Virial Coefficients

Diethyl Ether. Eight sets of measurements reported in the literature on this system are plotted in Figure 1. Reasonable agreement within the data exists. The Tsonopoulos correlation appears to represent a superior fit to the data, although this equation and the Hayden and O'Connell correlation appear to give values that are too positive at low temperatures. Measurements at low temperature, however, are subject to larger uncertainties due to the low vapor pressure of the ether.

Values of B_{11} and B_{22} required for estimation of B_{12} from ϵ_{12} were obtained from a best fit of a third-order polynomial in reciprocal temperature.

Methyl Acetate. The available data for this compound has been commented on previously (*8*).

Results and Conclusions

Critical Temperatures. The results are listed in Table II along with the calculated unlike-interaction critical temperature T^c_{12}. While there is some variation in T^c_{12}, there is no significant trend with composition and a weighted mean (weighting factor, y_1y_2) is found to be T^c_{12} = 479.2 K.

Table II. Mixture of Critical Temperatures for Methyl Acetate (1) + Diethyl Ether (2)[a]

y_1	T^c_m/K	T^c_{12}/K	y_1	T^c_m/K	T^c_{12}/K
0.099	501.27	478.1	0.481	478.58	478.8
0.201	496.01	478.1	0.574	475.12	479.6
0.23	491.12	480.8	0.59	472.03	478.1
0.255	486.58	481.1	0.689	469.29	480.2
0.356	482.4	477.6	0.734	466.93	478.9

[a] y_1 = mole fraction; T^c_m = measured value; T^c_{12} = calculated value.

Table III. Experimental Results: Pressure Change on Mixing of Diethyl Ether (2) + Methyl Acetate (1)

T/K	P/Pa	ΔP/Pa	T/K	P/Pa	ΔP/Pa
302.79	26820	19.0	344.97	92883	68.7
302.93	28376	20.4	344.96	87280	75.7
322.75	47717	41.3	363.26	89566	55.6
322.75	47499	40.7			

Table IV. Second Virial Coefficients, Pure and Excess

	pure-component virial coeff/(cm^3 mol^{-1})		excess virial coeff/(cm^3 mol^{-1})			
			Hayden and O'Connell		Tsonopoulos	
T/K	diethyl ether	methyl acetate	*b*	*c*	*a*	expt
302.79	-1116	-1542	389	282	208	133 ± 5
302.93						128 ± 5
322.75	-923	-1259	286	208	164	97 ± 3
322.74						97 ± 3
344.97	-757	-1029	211	129	116	68.7 ± 4
344.96						75.5 ± 4
363.26	-654	-887	171	92	80	55.5 ± 1.5

[a] Calculated from the predicted value for B_{12} and literature values of B_{11} and B_{22}. [b] Using standard procedures. [c] Incorporating T^c_{12} derived from T^c_m.

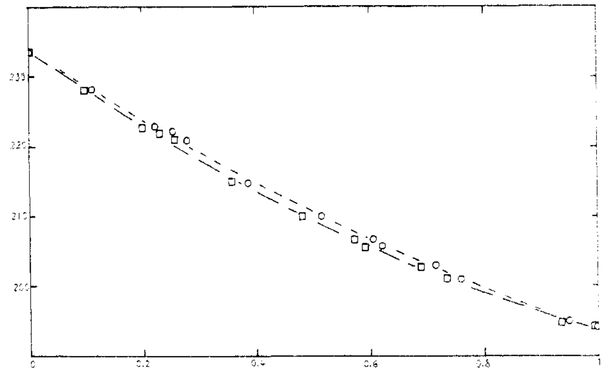

Figure 2. Critical temperatures for methyl acetate + diethyl ether: (○) mole fraction; (□) surface fraction.

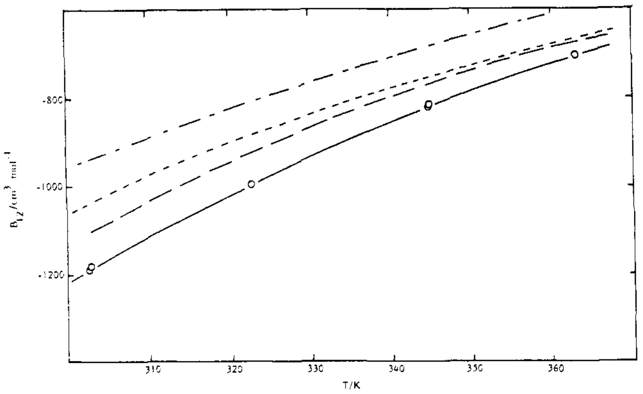

Figure 3. Unlike-interaction second virial coefficient for methyl acetate + diethyl ether: (- - -) Hayden and O'Connell (*5*); (- -) Hayden and O'Connell using T^c_{12}; (— —) Tsonopoulos (*6*); (O) this work.

Second Virial Coefficients. In Tables III and IV, the results obtained and the prediction of the two correlations are tabulated.

Attempting to predict ϵ_{12} values is a demanding test of correlating functions for second virial coefficients and, as illustrated in Figure 1, neither equation is particularly successful.

Prediction of B_{12} is what the equations were devised to do, but again, as evidenced in Figure 3, neither provides a satisfactory representation of the data obtained. As has been observed for other systems (*1*), the Hayden and O'Connell correlation is improved by incorporating the independent T^c_{12} value but not sufficiently. The Tsonopoulos equation is only marginally better.

Notation

B_{11},B_{22}	pure-substance second virial coefficients
B_{12}	unlike-interaction second virial coefficient
ϵ_{12}	excess second virial coefficient
P	pressure
ΔP	pressure change of mixing
T	temperature
T^c_{11},T^c_{22}	pure-substance critical temperatures
T^c_{12}	unlike-interaction critical temperature
T^c_m	mixture critical temperature
y	mole fraction
V^c_{ii}	critical volume
V^c_{ij}	unlike-interaction critical volume
ω	accentric factor
P^c	critical pressure

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Vapor Pressures of the Water–Lithium Bromide–Lithium Iodide System

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The vapor pressures of the water–lithium bromide–lithium iodide system (salt mole ratio 4:1) were measured in the range of temperatures from 280.85 to 383.05 K and in the range of absorbent concentrations from 10.0 to 64.5 wt %. The vapor pressure measurements were made with separate experimental apparatuses by a boiling point method for pressure above 2800 Pa and a static method for pressure below 2800 Pa. The experimental data measured with two experimental apparatuses were separately correlated by means of two Antoine-type equations. The calculated values from these equations were in good agreement with the experimental data.

Introduction

The vapor pressure data for the working medium–absorbent system are one of the important properties for the research and the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. The vapor pressures of the water–lithium bromide–lithium iodide system (salt mole ratio 4:1) were measured with separate experimental apparatuses by a boiling point method and a static method at various temperatures and absorbent concentrations. The vapor pressure measurements above 2800 Pa were made with the usual experimental apparatus (*1*) used for a boiling point method. It is difficult to measure low vapor pressure below 2800 Pa with the usual experimental apparatus used for a boiling point method. Therefore, the vapor pressure measurements below 2800 Pa were made with a special apparatus devised for low-pressure measurements (*2*) by a static method. Accurate vapor pressure data for the working medium–absorbent system at low temperatures are particularly important for the design of the absorber. The experimental data measured with two experimental apparatuses were separately correlated by means of two Antoine-type equations.

Experimental Section

Materials. The lithium bromide and lithium iodide used in this work were from the Honjo Chemical Co., Ltd., analytical reagent

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