Thermal Pressure Coefficients of Di-*n*-alkyl Ethers

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The thermal pressure coefficients of four di-*n*-alkyl ethers are reported over the temperature range 20–35°C.

The thermal pressure coefficient γ defined by $\gamma = (\partial P/\partial T)_V$ is of interest both in the study of the liquid state and in relating the readily measured isobaric heat of mixing H_p^E to the theoretically interesting energy of mixing U_v^E (*5*, *7*, *8*). This relationship is to a first approximation

$$U_v^E = H_p^E - T\gamma V_p^E \tag{1}$$

where V_p^E is the volume of mixing at constant pressure.

The value of γ often has been estimated from the coefficients of thermal expansion α and the isothermal compressibility β via the expression (*10*):

$$\gamma = \alpha/\beta \tag{2}$$

However, even when values of α and β are available, the direct measurement of γ is usually more accurate. The present work was undertaken to provide data in conjunction with studies of the mixing properties of ethers with halocarbons.

EXPERIMENTAL

The apparatus was similar to that described by Malcolm and Ritchie (*9*). The sample is contained in a cylindrical vessel (Figure 1) in a pressure vessel which is, in turn, placed in an aluminum block fitted with a heater and a thermometer set in an unpressurized duplicate of the experimental vessel. The symmetrical nature of the arrangement ensures that the temperature behavior of the duplicate pressure vessel closely approximates that of the experimental vessel. The arrangement of the sample cell in the pressure vessel is described by Williamson (*11*). The temperature of the apparatus is controlled via a solid-state relay by the expansion of the experimental liquid. Thus the temperature of the apparatus automatically adjusts to maintain the liquid volume constant at any pressure.

The apparatus was pressurized with nitrogen. Temperatures were measured with a mercury-in-glass thermometer which had been calibrated by the National Physical Laboratory to ±0.01°C and which could easily be read to ±0.02°C. Pressures were measured with a Budenberg Bourdon-type gage which had been calibrated by the manufacturers against a deadweight tester and which carried a calibration certificate to ±2 psi over its range, 0–1000 psi.

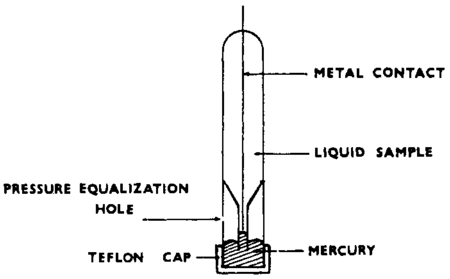

Figure 1. Sample cell

By slightly altering the amount of liquid in the cell, a series of isochores can be measured at different densities. A typical set of isochores is shown in Figure 2. The observed slopes of $(\partial P/\partial T)$ were corrected for thermal and pressure effects on the sample vessel using the relationship (*10*) of

$$\gamma = (\partial P/\partial T)_{\text{obsd}} \left(1 + \frac{\alpha_g}{\alpha_l} - \frac{\beta_g}{\beta_l}\right) \tag{3}$$

where α_g, α_l are the coefficients of thermal expansion of the glass and of the experimental liquid, and β_g, β_l are the isothermal compressibilities of the glass and of the liquid. The values used for the correction were

$$\beta_g = 3.03 \times 10^{-6}\ \text{atm}^{-1}\ (3)$$
$$\alpha_g = 1.04 \times 10^{-5}\ {}^\circ\text{C}^{-1}\ (4, 6) \tag{4}$$

α_l was estimated from the known density (*1*) of each ether and β_l was estimated from γ and α by successive approximations.

Materials. The following materials were used without further treatment. Carbon tetrachloride: BDH spectroscopic grade ($d_4^{10} = 1.592$). Diethyl ether: DHA anesthetic grade. Di-*n*-butyl ether: BDH laboratory reagent grade ($d_4^{20} = 0.768$). Di-*n*-amyl ether: BDH laboratory reagent grade. Di-*n*-hexyl ether: Schuehart laboratory reagent grade.

Infrared spectra of the ethers showed that the major impurity in each ether was the corresponding alcohol and that there were only trace quantities of aldehyde and ketone. The ethers were free from water. Gas-liquid chromatography using a 6-ft column of neopentyl glycol sebacate indicated that the alcohol

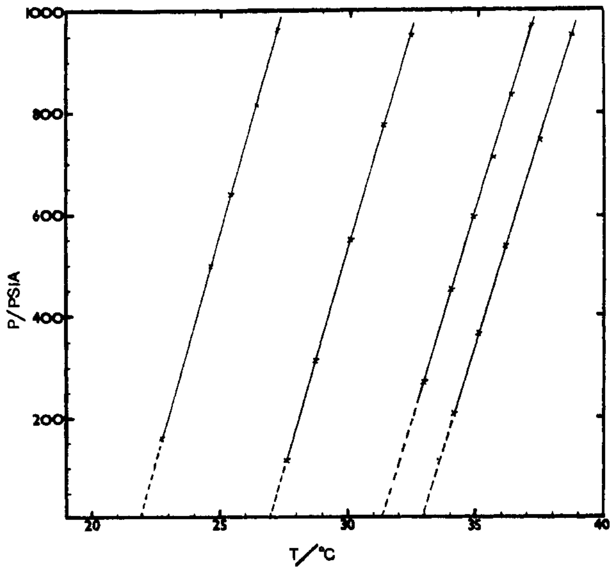

Figure 2. Carbon tetrachloride

Table I. Thermal Pressure Coefficients of Carbon Tetrachloride

Temp (P = 0), °C	$(\partial P/\partial T)_{\text{graph}}$, atm °C^{-1}	γ_{corr}, atm °C^{-1}	γ (2), atm °C^{-1}
21.90	11.84	11.56 ± 0.2	11.45 ± 0.06
27.00	11.48	11.21 ± 0.2	11.08 ± 0.06
31.35	10.95	10.70 ± 0.2	10.78 ± 0.06
32.95	10.73	10.49 ± 0.2	10.60 ± 0.06

Table II. Thermal Pressure Coefficients of Ethers

Substance	Temp (P = 0), °C	$(\partial P/\partial T)_{\text{graph}}$, atm °C^{-1}	γ_{corr}, atm °C^{-1}
Diethyl ether	17.40	9.02	8.93
	22.00	8.61	8.53
	27.15	8.20	8.13
	31.80	7.82	7.76
Di-*n*-butyl ether	21.25	9.68	9.52
	28.35	9.10	8.96
	32.50	8.85	8.72
	37.40	8.67	8.55
Di-*n*-amyl ether	20.90	10.08	9.87
	25.00	9.69	9.51
	30.95	9.36	9.19
	35.15	9.23	9.07
Di-*n*-hexyl ether	20.25	10.50	10.27
	24.90	10.01	9.80
	28.80	9.67	9.48
	33.85	9.29	9.12

Table III. Smoothed Values of Thermal Pressure Coefficients

Substance	Mol wt	$\gamma_{20°\text{C}}$	$\gamma_{25°\text{C}}$	$\gamma_{30°\text{C}}$	$\gamma_{35°\text{C}}$
Diethyl ether	74.1	8.71	8.29	7.90	7.51
Di-*n*-propyl ether	102.1	9.80	8.78	8.41	8.09
Di-*n*-butyl ether	130.1	9.64	9.20	8.85	8.63
Di-*n*-amyl ether	158.2	9.95	9.50	9.23	9.07
Di-*n*-hexyl ether	186.2	10.29	9.78	9.38	9.06

content was under 1% except for the dibutyl ether where it was estimated to be just under 4%.

It was considered that these levels of impurity would not significantly alter the thermal pressure coefficients.

RESULTS

As a test of the apparatus and technique, we have measured γ for carbon tetrachloride. The overall accuracy of the measurements is estimated to be ±0.2 atm °C^{-1}. The agreements between our results and those of Benninga and Scott (*1*) is shown in Table I. Table II shows the experimental data for the ethers. Table III shows values at rounded temperatures obtained by smoothing the experimental data and values for di-*n*-propyl ether obtained by interpolation from the data for other ethers.

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Solubility of H_2O and D_2O in Carbon Tetrachloride, Toluene, and Cyclohexane at Various Temperatures

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The solubilities of H_2O and D_2O in carbon tetrachloride, toluene, and cyclohexane have been determined at various temperatures by means of a Karl Fischer titration. The solubility of both solutes is greatest in toluene and least in cyclohexane. The ratio of solubility H_2O/D_2O at 25°C is 1.19 for toluene, 1.14 for carbon tetrachloride, ane 1.10 for cyclohexane. The heat of solution is greatest for CCl_4, least for cyclohexane. There is no significant difference in $\Delta H°$ for H_2O and D_2O in a given solvent.

In the course of some work on the infrared spectra of D_2O in carbon tetrachloride solution, it became necessary to know the solubility of D_2O in carbon tetrachloride. The data available were limited to two references (*2*, *6*). In the first of these, the data had been obtained for only two samples and only at 25°C. In the second, the value was expressed as having been obtained at "room temperature."

The solubilities of D_2O in carbon tetrachloride were measured at several temperatures using the Karl Fischer method with a "dead stop" end-point determination (*9*). At the same time, the solubility of H_2O in carbon tetrachloride was measured as a check on the procedure.

The study was extended to a measurement of the solubility of D_2O and H_2O in toluene and in cyclohexane because it has