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Isothermal Compressibilities of Carbon Tetrachloride, Methanol, and Isopropyl Alcohol

P. K. KATTI and S. K. SHIL
Department of Physics, Indian Institute of Technology, Delhi, New Delhi, India.

An experimental arrangement for the measurement of isothermal compressibilities of liquids is described. The compressibilities of carbon tetrachloride, methanol, and isopropyl alcohol obtained by using this experimental arrangement in the temperature range of 30° to 70° C. are reported.

DURING the last few years isothermal compressibilities have been receiving increasing attention in studies of the molecular interactions and the behavior of pure liquids and binary liquid mixtures. Measurements of the compressibilities of liquids have been made earlier by Carnazzi (3), Dolezalek and Speidel (6), Drecker (7), Richards and Shipley (16), Rontgen (17), Tyrer (18), Bridgman (2), Philip (14), McKinney (12), and Freyer (9). However, accurate experimental data on the liquids and liquid mixtures in the neighborhood of the atmospheric pressure suitable for obtaining the isothermal compressibilities at zero pressure, which are required for comparison with the results of the various statistical models proposed for describing the properties of liquids and liquid mixtures, are not readily available. Recently, McGlashan and others (5), have made measurements of the compressibilities of binary mixtures of carbon tetrachloride and cyclohexane and have shown that if volume changes on mixing are taken into account, improved agreement between the quasicrystalline model of Guggenheim (10) and experiment can be obtained. Their results also agree well with the cell model proposed by Prigogine (15). Measurements on the molar volumes and compressibilities of biphenyl and m-, o-, and p- terphenyl have been made by Opdycke and others (13). They have compared their results with those predicted by the Eyring-Hirschfelder (11) free volume model adapted to polymers by Flory (8) and also those of corresponding state treatment of Prigogine. The measurement of isothermal compressibilities of pure liquids and binary liquid mixtures containing a polar and a nonpolar molecule is reported in this paper, and an experimental arrangement for the accurate measurement of compressibilities of carbon tetrachloride, methanol, and isopropyl alcohol in the range of temperatures 30° to 70° C. is described.

EXPERIMENTAL PROCEDURE

Purification of Materials. Best available samples of mercury, carbon tetrachloride, methanol, and isopropyl alcohol from Merck's and B.D.H. (British Drug House) used in these investigations were subjected to further purification in the laboratory by usual methods described earlier (4). The purity of the samples used for the experiments was checked by determining their densities with a Desmyter and Chaudhri type pycnometer (4). Table I shows the observed densities of liquids used.

Table I. Densities of Liquids at 40° C.

Substance	Observed Density, G./Ml.	Density Quoted in Literature, G./Ml.
Carbon tetrachloride	1.5550	1.55501
Methanol	0.77230	0.77232
Isopropyl alcohol	0.76900	0.76910

Experimental Arrangement. The experimental setup used in the present experiments is, in general, similar to that used by McGlashan (5) with some modifications as described below.

The pressure chamber, (Figure 1) which can be used for pressures up to 50 atm., is made of a steel cylinder A open at one end, 10 inches high, 4 inches in I.D., 1-inch wall thickness. The upper end could be closed by means of a lid B which could be screwed to the upper threaded portion of chamber A. Leakage of air through the sides of the lid was prevented by O ring C fixed between the concentric grooves on lid B and the top of cylinder A. Visual observations on the piezometer capillary inside the chamber were made through a vertical perspex window, D, 5 inches high, 1¼ inches wide, and 1½ inches thick fitted to the cylinder by a steel frame with nuts and bolts as shown in Figure 1,b. A rubber gasket between the steel frame and the perspex sheet prevented the leakage of air through the sides of the window. The piezometer was held vertical in a brass stand E mounted on a heavy circular steel plate resting on the bottom of the cylinder, A. The chamber was nickel plated both outside and inside to avoid rusting. The entire pressure chamber up to mark L, in Figure 1, was held under water in a thermostat. The steel chamber ensured a quicker thermal equilibrium between the thermostat and the inside of the chamber. The perspex window could stand pressures up to 50 atm. without showing any signs of strain. Pressure was applied to the chamber by connecting it through pressure leads of copper S to a nitrogen cylinder. The pressures were regulated through a needle valve and measured on a bourdon standard test gage with an accuracy of ±0.07 atm. Temperature control inside the chamber during the periods of measurement as observed on a 1° Beckmann thermometer divided into parts was better than 0.001° C. Temperatures were measured on
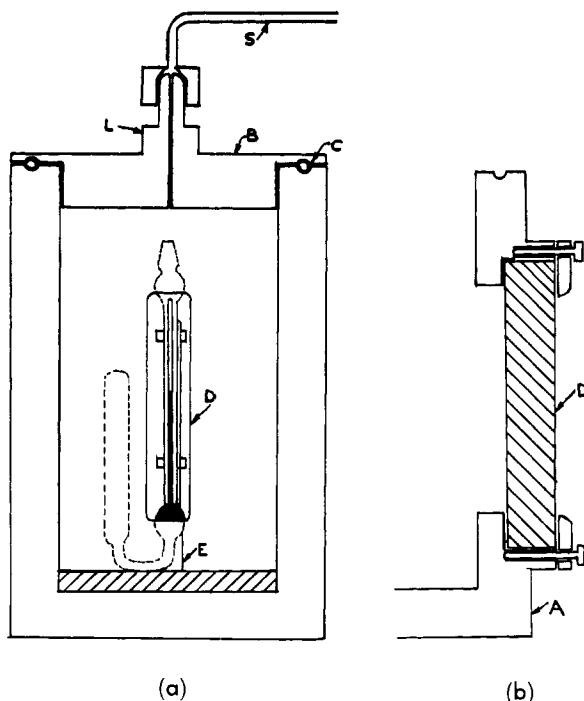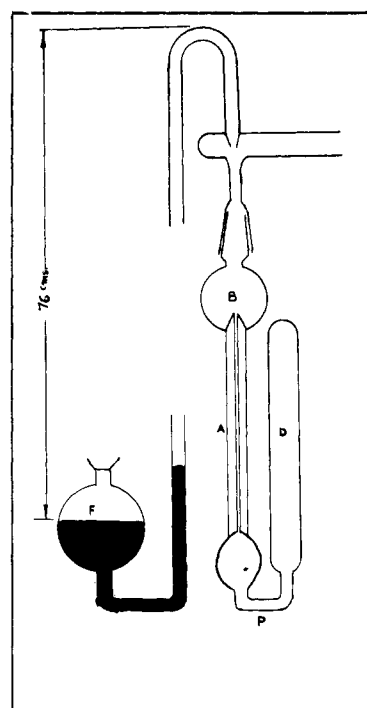
Figure 1. Pressure chamber

Figure 2. Apparatus for filling
piezometer with mercury

the international scale with calibrated thermocouple and a Pye-type precision vernier potentiometer.

Filling the Piezometer. The single piezometer, P, (Figure 2) similar to that used by McGlashan, was made of a calibrated capillary tube of 11 cm. in height and 1 mm. in average diameter, fused to arm D containing the liquid over mercury. The piezometer was cleaned with hot chromic acid and rinsed several times with doubly distilled water and dried for several hours in an air oven at about 150° C. It was then connected to the high vacuum line (10^{-6} mm. of mercury) and the mercury reservoir containing cleaned and degassed mercury, through the B_{10} ground glass joint. The piezometer was heated to about 250° C., and maintained for about 2 hours at this temperature under vacuum to remove the last traces of adsorbed gases on its inner walls. The piezometer then was allowed to cool, still keeping in contact with the vacuum line. The mercury reservoir then was raised sufficiently high to enable the mercury to flow into the piezometer. The whole piezometer could, thus, be filled completely with mercury with no traces of air present in arm D above the level of mercury. Then a known quantity of freshly distilled and degassed sample of liquid specimen was introduced over the mercury in arm D of the piezometer by means of a hypodermic syringe by a method similar to that used by Adcock and McGlashan (1) in their heats of mixing calorimeter.

Measurements. The charged piezometer, with the amount of mercury adjusted to stand about a centimeter below the tip of the capillary in arm A at the lowest temperature from which the observations were to be made, was introduced into the pressure chamber filled with water. The piezometer capillary was illuminated by a beam of light from a torch bulb, entering the pressure chamber through the window in a nearly perpendicular direction. The mercury meniscus in the capillary was viewed through the perspex window and the level of the meniscus, above the nearest reference mark on the capillary, was measured to the nearest 0.01 mm; with a PTI cathetometer. Higher pressures were then applied in steps of 5 kg. per sq. cm. (4.84 atm.), and the changes in the position of the mercury

in the capillary tube were noted. After every change of pressure, an interval of about 45 minutes was allowed to dissipate completely the heat of compression of expansion to ensure that the measurements were truly isothermal. Measurements on the position of the mercury meniscus were made both while the pressure increased and decreased in the range of pressure from 1.032 kg. per sq. cm. to 50 kg. per sq. cm. (1 atm. to 48.4 atm.).

The mercury in the capillary was adjusted next for observations at the next higher temperature. This could be done easily by increasing the temperature of the bath to a temperature slightly above the next temperature of the measurement when the excess mercury overflows into bulb B owing to expansion in the piezometer.

After all the measurements were completed, the piezometer containing the mercury and the sample of the liquid was weighed. The mercury was then removed, dried, and weighed. Finally the dried piezometer was weighed, giving the weight of mercury and that of specimen of liquid used. In all cases, graphs were drawn between height h of the mercury meniscus from a reference mark and corresponding pressure P. The observed points were then fitted to a straight line by using the method of least squares and the value of $[(\partial h)/(\partial p)]$ was determined. In the range of pressures used for these investigations, values of h varied linearly with P within the experimental errors.

The compressibilities were then calculated by adopting McGlashan's procedure using the relation:

$$K_L = - \frac{A}{V_L} \frac{\partial h}{\partial P} - \frac{V_{Hg}}{V_L} K_{Hg} + \left(1 + \frac{V_{Hg}}{V_L}\right) K_s \qquad (1)$$

where K_L is the compressibility of the liquid; A, the area of the cross section of the capillary; V_L, the volume of the liquid at the temperature; $\partial h/\partial P$, the slope of the straight line between h and P; V_{Hg}, the volume of mercury; K_{Hg}, the compressibility of mercury; and K_s, the compressibility of glass. For K_s and K_{Hg} the values of Bridgman and McGlashan, respectively, quoted by McGlashan and

Table II. Isothermal Compressibility of Glass and Mercury

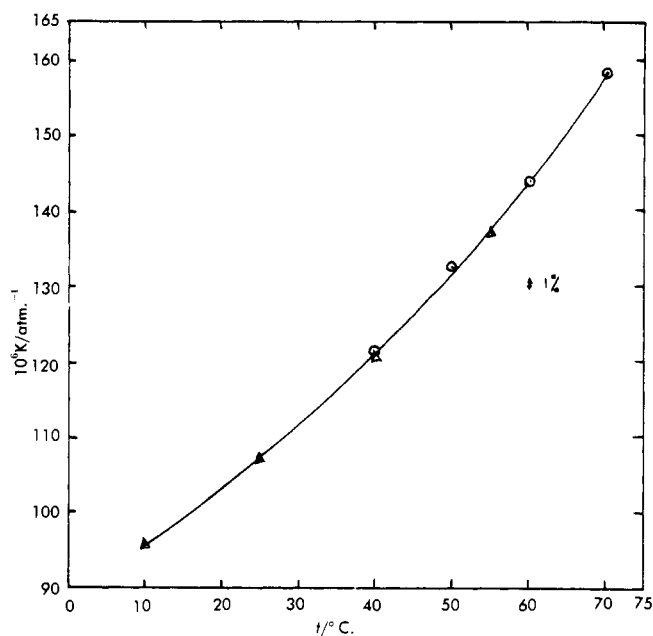| Temperature, °C.	$10^6 K_g$ Atm.$^{-1}$	$10^6 K_{Hg}$ Atm.$^{-1}$
10	2.97	4.04
25	2.98	4.09
40	2.99	4.13
55	3.00	4.23
60	3.00₃[a]	4.25[a]
70	3.10[a]	4.30₄[a]

[a] Extrapolated values.

Figure 3. Plot of isothermal compressibility K of carbon tetrachloride against temperature
O Author's results
△ Diaz Pena and McGlashan (5)

Table III. Compressibility of Carbon Tetrachloride

$t°$ C.	40.0	50.0	60.0	70.0
$10^6 K$, atm.$^{-1}$	120.7	132.6	143.9	158.6

Table IV. Compressibility of Methanol

$t°$ C.	29.85	40.00	50.00	55.20	60.00
$10^6 K$, Atm.$^{-1}$	125.8	139.4	157.0	167.0	178.0

others (5), were used (Table II). The values of K_g and K_{Hg} beyond 55° C. were obtained by extrapolation from the graph.

RESULTS AND DISCUSSION

Compressibility of Carbon Tetrachloride. To test the performance of the present experimental setup, measurements were made on the compressibility of carbon tetrachloride at 40°, 50°, 60°, and 70° C.

Figure 3 shows the isothermal compressibilities with temperature of carbon tetrachloride in the range of temperature 10° to 70° C. The observations of Diaz Pena and McGlashan were made with a similar experimental setup under truly isothermal conditions. Throughout the temperature range, the authors' observations and McGlashan's observations lie on a smooth curve. The deviations are less than the estimated 1% accuracy. Table III shows the values of K of carbon tetrachloride, obtained in the temperature range of 40° to 70° C.

Compressibility of Methanol. The observed compressibilities of methanol are recorded in Table IV.

Earlier measurements on compressibilities of methanol have been made by Bridgman (2), Freyer (9), Philip (14), McKinney (12), and Tyrer (18). For comparison, the values obtained by different observers have been plotted in Figure 3. Bridgman has investigated the variations in the volumes with pressure of given quantity of the liquids at intervals of 500 atm. at each temperature. The P-V curves are not linear and assumption of linearity in the first interval— i.e., 1 to 500 atms.—leads to K values which are about 40% less than the values of other workers. Values obtained by the slopes of the tangent to the P-V curve at zero pressure give values of K consistently lower by about 12% than the present values.
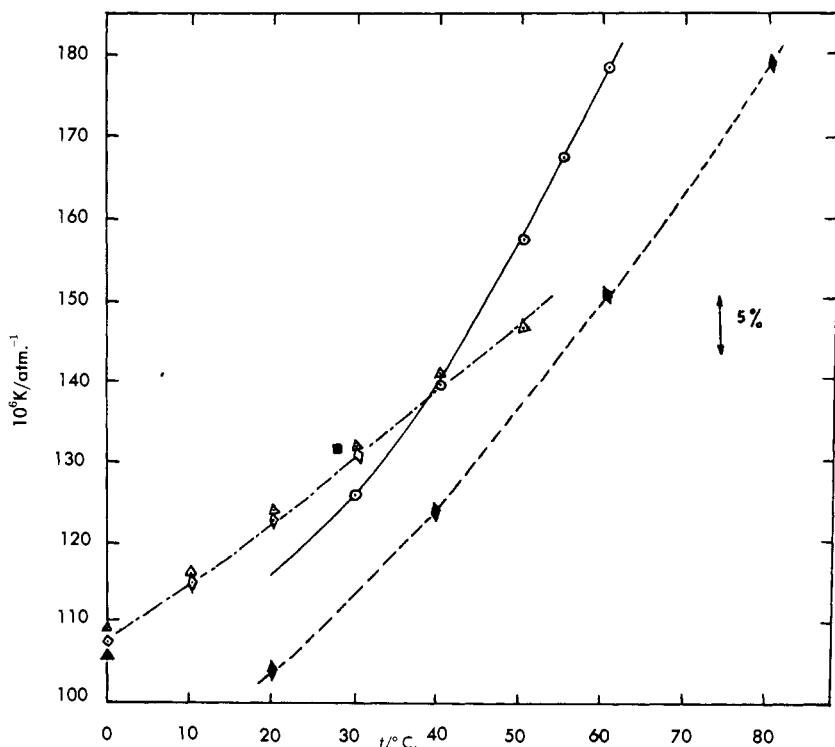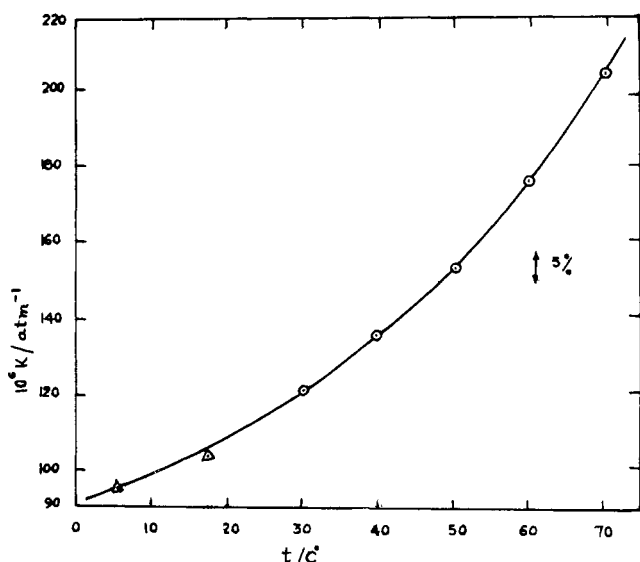

Figure 4. Plot of isothermal compressibility K of methanol against temperature
O Authors' results ◇ Tyrer (18), △ Freyer (9), ■ Philip (14), ▲ McKinney (12), and ◆ Bridgman (2).

Table V. Compressibility of Isopropyl Alcohol

t, °C.	30.25	40.0	50.4	60.0	70.0
$10^6 K$, Atm.$^{-1}$	120.2	135.0	152.5	175.2	206.6

Figure 5. Plot of isothermal compressibility K
of isopropyl alcohol against temperature

O Authors' results
△ Rontgen (17).

Freyer (9) has calculated the isothermal compressibilities in the range of temperature 0° to 50° C. from the measurement on the velocity of ultrasonic waves in methanol taking into consideration the correction term $T\alpha^2 v/c_p$. The correction terms are of the order of 30%. Tyrer (18) has made measurements on the adiabatic compressibility of methanol in the range of temperature 0° to 40° C., and has used them to calculate the isothermal compressibility. His correction terms also are of the order of 30%. Both Freyer and Tyrer's values agree to within 0.5% in the range of temperature common to them. The compressibility of methanol obtained by Philip (14) at 27.6° C. is slightly higher (by about 2%) as seen from Figure 3. The authors' observed values in the temperature range of 30° to 60° C. lie on a curve with a larger slope than those of Tyrer and Freyer's results. These two curves intersect at 40° C. At 30° C., the authors' value is less than theirs by 3%, and at 50° C., higher by 6.5%. Both of them are well above the range of experimental errors.

As pointed out earlier, the poor agreement between the present results and the early results of Bridgman is due obviously to the large intervals of pressures (about 500 atm.) used by Bridgman and the difficulties involved in extrapolating them to zero pressures.

The large deviations from Tyrer and Freyer's results are not surprising in view of the fact that measurements were made under adiabatic conditions and the correction terms $T\alpha^2 v/c_p$ which are as large as 30% of K and depend upon the accuracy in the measurement of the parameters α and c_p are involved in the quantity.

Compressibility of Isopropyl Alcohol. Measurements on the isothermal compressibility of isopropyl alcohol have been made at temperatures of 5.65° and 17.85° C. by Rontgen (17) within the range of 1.032 to 8.256 kg. per sq. cm. (1 to 8 atm.). However, accurate measurements in the range of temperatures 30° to 70° C. and pressures of 1.032 to 30 kg. per sq. cm. (1 to 29.04 atm.) required for these investigations on the statistical properties of binary liquid mixtures are not readily available. Table V shows the values of K obtained by us in the temperature range of 30° to 70° C. Figure 5 shows the plot of compressibilities of isopropyl alcohol with temperature. Rontgen's observations were made under truly isothermal conditions at temperatures 5.65° and 17.85° C. Within the entire range of measurement, all the observed points lie on a smooth curve with deviations less than the estimated experimental error of 1%.

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Allyl- and Vinyl-Substituted Silazanes

R. L. ELLIOTT and L. W. BREED
Midwest Research Institute, Kansas City, Mo.

LITTLE has been published on the preparation and properties of either N-substitued or Si-substituted allyl and vinylsilanes (1-3, 6-8). In the course of a study of the synthesis of silazane polymers, a series of allyl and vinyl-silazanes and silylamines were prepared and characterized. These compounds, which are reported in Table I, could be prepared readily by methods reported previously (3). Yields were usually high except when mixtures of silyl-