Liquid Densities of CF_3PCl_2 and CF_3PBr_2

A. D. JORDAN and R. G. CAVELL[1]
Department of Chemistry, University of Alberta, Edmonton, Alta., Canada

Liquid densities of CF_3PCl_2 and CF_3PBr_2 over the temperature range of 20–69°C are reported.

In connection with other work the liquid densities of the trifluoromethylphosphines CF_3PCl_2 and CF_3PBr_2 were required. Since the data were not available in the literature, we measured the liquid densities of these two compounds and herewith report the results.

EXPERIMENTAL

The compounds were prepared from the reaction of carefully purified CF_3PI_2 (*1*) with $HgCl_2$ (*4*) or $HgBr_2$ (*4*) at room temperatures followed by vacuum fractionation of the halogenophosphine. Two successive treatments with a large excess of the mercuric halide were used to ensure complete conversion of the iodo phosphine. The products were purified by vacuum fractionation. Densities were measured by quantitatively transferring in vacuum a weighed quantity of the compound into a calibrated precision bore glass tube which was then sealed under vacuum. The glass tube (i.d. 0.229 cm) had been previously calibrated in terms of the height of liquid in relationship to its volume. The height of liquid in the tube, measured with a cathetometer graduated to 0.01 mm, was determined at a series of temperatures maintained by a water bath thermostat which controlled temperatures to within ±0.05°C.

Temperature was measured by means of a NBS-calibrated thermometer which could be read to the nearest 0.05°C. Since the compounds are relatively volatile, the quantity of liquid lost to the vapor state at each temperature was estimated from the published vapor pressure data (*2*, *5*) and the volume of the vapor assuming ideal gas behavior. The weight of liquid remaining corresponding to the observed volume was used to calculate the density. The results are given in Table I.

The relationship between the height of liquid in the tube and its volume, obtained by measuring the height of a series of known weights of mercury in the tube, was linear over the region of interest. The measured height was taken on the plane tangent to the mercury meniscus.

Since the curvature of the mercury meniscus is opposite to that observed for liquid CF_3PCl_2 and CF_3PBr_2, volume correction of the liquid as obtained from the measured height was necessary. The volume correction owing to the curvature of the mercury meniscus was calculated from the inner diameter of the tube and the measured distance between the point of contact of the meniscus with the wall of the tube and the vertex of the meniscus (*3*). The volume correction owing to the curvature of the liquid meniscus of the phosphine was calculated in the same manner. No estimate of the errors arising from the treatment of the phosphine meniscus in a similar manner to the mercury meniscus was made.

RESULTS

The densities (d_t) fit the linear equations

$$CF_3PCl_2{:}\ d_t(\mathrm{g\ ml^{-1}}) = 1.6065 - (2.58 \pm 0.08) \times 10^{-3}\,t$$

$$CF_3PBr_2{:}\ d_t(\mathrm{g\ ml^{-1}}) = 2.2120 - (2.23 \pm 0.15) \times 10^{-3}\,t$$

---

[1] To whom correspondence should be addressed.

Table I. Variation of Density with Temperature for CF_3PCl_2 and CF_3PBr_2

Temp, °C	Vapor press, torr[a,b]	Ht of liquid, cm	Vol of liquid, ml[c]	Wt of vapor, g × 10^3	Wt of liquid, g	Density obsd, g ml^{-1}	Density calcd, g ml^{-1}
			CF_3PCl_2[d,e]				
20.15	369	4.697	0.1966	0.84	0.3055	1.554	1.554
29.90	520	4.760	0.1992	1.13	0.3052	1.532	1.529
39.40	757	4.841	0.2026	1.59	0.3047	1.504	1.505
51.00	1114	4.934	0.2064	2.22	0.3041	1.473	1.475
59.15	1445	4.994	0.2089	2.76	0.3035	1.453	1.454
69.35	2026	5.064	0.2118	3.69	0.3026	1.429	1.428
			CF_3PBr_2[f,g]				
20.85	64.4	1.736	0.0742	0.29	0.1607	2.166	2.166
30.00	96.2	1.753	0.0749	0.41	0.1606	2.144	2.145
39.40	143.0	1.768	0.0755	0.60	0.1604	2.124	2.124
48.90	208.2	1.784	0.0762	0.84	0.1602	2.102	2.103
59.20	305.2	1.795	0.0766	1.19	0.1598	2.086	2.080
69.00	429.0	1.818	0.0776	1.62	0.1594	2.054	2.058

[a] Vapor pressure of CF_3PCl_2 calculated from equation (*3*) $\log_{10}P = 4.229 - 0.002743\,T + 1.75 \log T - 1516/T$. [b] Vapor pressure of CF_3PBr_2 calculated from equation (*4*) $\log_{10}P = 3.8579 - 0.00206\,T + 1.75 \log T - 1694.74/T$. [c] Volume occupied by a 1-cm height of liquid is 0.04135 ml. To calculated volume a correction of 0.0024 ml is added to correct for volume effect of meniscus. [d] Height of tube was 10.60 cm. [e] Original weight of CF_3PCl_2 taken was 0.3063 (±0.0002) gram. [f] Height of tube was 8.92 cm. [g] Original weight of CF_3PBr_2 taken was 0.1610 (±0.0002) gram.

where t represents the temperature in °C. The densities calculated from the above equations are given in Table I for comparison with observed values.

LITERATURE CITED

(1) Bennett, F. W., Eméleus, H. J., Haszeldine, R. N., *J. Chem. Soc.*, **1953**, p 1565.
(2) Burg, A. B., Griffiths, J. E., *J. Amer. Chem. Soc.*, **82**, 3514 (1960).
(3) "International Critical Tables of Numerical Data," Vol I, McGraw-Hill, New York, N.Y., 1928, p 72.
(4) Nixon, J. F., Cavell, R. G., *J. Chem. Soc.*, **1964**, p 5983.
(5) Peterson, L. K., Burg, A. B., *J. Amer. Chem. Soc.*, **86**, 2587 (1964).

RECEIVED for review January 28, 1971. Accepted June 22, 1971. We thank the National Research Council of Canada for financial support.

Heterogeneous Phase Behavior of Carbon Dioxide in *n*-Hexane and *n*-Heptane at Low Temperatures

UN K. IM[1] and FRED KURATA
Center for Research in Engineering Science, University of Kansas, Lawrence, Kan. 66044

The phase behavior of carbon dioxide in *n*-hexane and *n*-heptane was determined from 216.56°K to the eutectic point. Both systems exhibited partial miscibility phenomena in the upper range of the solubility curve. In the carbon dioxide–*n*-hexane system, the miscibility gap was metastable, and the upper critical solution temperature was determined as 213.7°K by careful subcooling. In the carbon dioxide–*n*-heptane system, the miscibility gap was stable and extended approximately 7°K above the normal solubility curve. The conjugate phase loci were intersected by the normal solubility curve, where L_1-L_2-S_1-V quadruple point was obtained. At the lower ends of the normal solubility curves, another quadruple point (L_2-S_1-S_2-V) or eutectic point was found for both systems. Normal solubility curves as well as the conjugate phase loci were correlated with the Wilson equation with a good predictive accuracy.

Experimental solubility of solid carbon dioxide in light hydrocarbons determined by Jensen (*5*) and in heavy hydrocarbons investigated by Im (*4*) shows that a definite tendency toward partial miscibility with heavier hydrocarbon solvents, as indicated by the increasingly flat solubility curve in the upper range, is characteristic of partially miscible systems as pointed out by Ricci (*8*). Francis (*2*) determined that *n*-heptane forms a stable miscibility gap with carbon dioxide and has an upper critical solution temperature of −51°C. He also predicted a miscibility gap for the carbon dioxide–*n*-hexane system by extrapolating the locus of critical solution temperatures of carbon dioxide–*n*-hexane–acetone system to zero acetone concentration and, in this manner, estimated its critical solution temperature as −61°C. However, no liquid-liquid equilibrium data have been reported for these systems.

That partial miscibility phenomenon was found in the methane–*n*-heptane system by Kohn (*6*) lends strong support to the likelihood that these two systems would form two partially miscible liquid phases in some portion of the solubility curves.

EXPERIMENTAL

A detailed description of the experimental equipment and procedure is given elsewhere (*4*). Briefly, phase boundaries along the miscibility gap as well as solid-liquid-vapor loci were determined by analyzing phase samples withdrawn from an equilibrium cell maintained at a given temperature, or when phase sampling was impracticable, by measuring the equilibrium temperature of a mixture of known composition. A schematic view of the phase equilibrium apparatus is shown in Figure 1. Constant temperature was provided in an air bath with liquid nitrogen as the refrigerant. The bath temperature was measured by a calibrated platinum resistance thermometer. Although the calibration accuracy of the thermometer was better than ±0.1°K, the maximum uncertainty in temperature measurements was reported as ±0.2°K owing to a small thermal gradient present in the bath.

Pressure was measured by a calibrated Heise gage whose accuracy was ±0.03 atm. Phase samples were analyzed on an F&M Model 720 gas chromatograph by use of a 1/4-in. diameter, 5-ft long column packed with 5% squalane on Chromosorb W. To prevent two-phase formation during sample injection, a minute amount of sample was withdrawn into a sample trap under the equilibrium pressure and subsequently flashed into a bigger copper bomb attached to the sample trap. To assure complete vaporization of the sample, the whole sampling apparatus was heated in a conditioning oven connected to the carrier gas line so that sample injection could be carried out without a temperature change in the sample.

Hydrocarbons used were research grades furnished by Phillips Petroleum Co., and the carbon dioxide was Coleman Instrument grade obtained from Matheson Gas Products, Inc. Stated purity for all fluids was better than 99.9 mol %, confirmed by a laboratory analysis.

System fluids were charged into a glass equilibrium cell. After temperature control was obtained, 1 to 2 hr were allowed to attain equilibrium conditions. For the miscibility gap locus determination, the liquid phase to be sampled

---

[1] Present address, Research and Development Department, Amoco Chemicals Corp., Naperville, Ill. 60540. To whom correspondence should be addressed.