Determining Densities of Solutions of Gases in Liquids under Pressure

Apparent Molal Volumes of Nitrogen and Argon in Organic Solvents at 100 Atm.

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OVER THE past few years, the authors have accumulated a considerable amount of data on the surface tensions of gas-liquid systems at gas pressures of from 1 to 130 atm. (8). Surface tensions were measured by the capillary rise method. A problem arose as to the values to be substituted in the familiar capillary rise equation for the density of the liquid phase. In systems such as nitrogen-water, where the solubility of the gas even at high pressures is relatively small, the density of the liquid solution is very nearly equal to that of the pure liquid at the same pressure. However, in systems such as nitrogen–n-hexane, where the solubility of the gas is much higher, the density of the solution may be expected to differ significantly from that of the pure liquid.

The purpose of this investigation was to develop a general method for determination of densities of saturated solutions of gases in liquids at elevated pressures. A limited number of experimental approaches to the problem have been described (6, 7). None of these appeared to yield data of sufficient accuracy for the authors' purpose. It is believed that with the method described below, densities of gaseous solutions can be measured with an accuracy of at least $\pm 0.05\%$. This method has been applied to four gas-liquid systems for which capillary rise data were available.

EXPERIMENTAL

Apparatus. The float (Figure 1) was made by sealing a glass rod approximately 7 cm. long and 3 mm. in O.D. to a thick-walled glass bulb of 13-ml. volume. The mass of the float was adjusted by adding mercury to bring the top of the rod to a point about 1 cm. above the surface of a liquid of density 0.65 gram per ml. In all the systems investigated, the density of the liquid phase exceeded this value. For solutions of density greater than about 0.67 gram per ml., it was necessary to add copper wire to the float to keep the bulb below the liquid surface.

The saturation cell (Figure 1) was made by sealing a piece of glass tubing 7 mm. in I.D. to a Büchner-type funnel 45 mm. in I.D. containing a coarsely porous, sintered-glass filter. The top of the cell was covered by a smoothly fitting aluminum plate 3 mm. thick. A hole 4 mm. in diameter passing through the center of this plate was covered by a thin glass disk. When gas was introduced into the system, a slight pressure differential was set up, sufficient to force the gas to enter through the side arm and bubble through the liquid. In this way, rapid saturation was achieved at a series of increasing pressures ranging from 1 to 130 atm. At the end of a run, the pressure was quickly released, blowing off the glass disk and allowing gas to escape through the hole in the aluminum plate.

The cell and float were contained in a steel bomb 6 cm. in I.D., and 15 cm. long, equipped with Plexiglas windows, appropriate high pressure fittings, and a Heise pressure gage graduated at 5-p.s.i. intervals. The entire apparatus was surrounded by a constant temperature air bath maintained at $30.0° \pm 0.1°$ C. Preliminary experiments showed that temperature equilibrium between the bomb and the liquid in the cell was established within a maximum of 30 minutes after the pressurizing gas was admitted.

Method. Densities of liquid solutions were calculated from Equation 1, which is readily derived by equating the buoyant forces acting on the float to the sum of the forces of gravity and surface tension tending to pull the float into the liquid.

$$d_L = \frac{m + 2\pi r \gamma/g - Ah\,d_G}{V - Ah} \tag{1}$$

where d_L = liquid density, m = mass of float (including any copper wire added), r = radius of rod, γ = surface tension of liquid, g = 980.3 cm./sec.², A = cross-sectional area of rod = πr^2, h = height of top of rod above liquid surface, d_G = gas density, V = volume of float (including any copper wire added).

Of the various quantities which must be known to calculate d_L from Equation 1, d_G was calculated from the Beattie-Bridgman equation corrected for the effect of solvent vapor on gas density.

γ was calculated at the various pressures from previous capillary rise measurements carried out in the systems studied. The term $2\pi r \gamma/g$ is always small compared to m. An error of as much as 3% in γ would result in a maximum error in d_L of only 0.0001 gram per ml.

m was determined by weighing in air with appropriate buoyancy corrections. The mass of the float alone was 8.6355 grams.

h was measured with a cathetometer read to ± 0.001 cm. Care was taken to ensure that the recorded heights represented equilibrium values. At each pressure, the system was allowed to stand for at least 30 minutes before taking readings to allow temperature equilibrium to be established. The pressure was then decreased by about 5 to 10 atm. and quickly brought back to its original value in order to obtain bubbling and ensure saturation. This technique was repeated until successive cathetometer readings agreed to at least ± 0.02 cm., which corresponds to an uncertainty in density of about ± 0.0001 gram per ml.

A was determined by placing the float in a liquid of the proper density, slipping successive copper rings of known mass over the rod, and reading the corresponding heights. The mean value of A, calculated from Equation 2, was 0.0798 sq. cm., from which r, the radius of the rod, was calculated as 0.159 cm.

$$A = \frac{M_{Cu}(1 - d_L/d_{Cu})}{(h - h')(d_L - d_{air})} \tag{2}$$

M_{Cu}, d_{Cu} = mass and density, respectively, of the copper ring, d_L = density of liquid, h, h' = successive heights.

V was determined as a function of pressure in a preliminary experiment in which nitrogen was used as a pressurizing gas and water as a solvent. The cell used was one in which contact between gas and solvent was minimized and the amount of nitrogen dissolved at any pressure kept well below the saturation value. Values of V were calculated from Equation 1, using for d_L the density of pure water at 30.0° C. and the corresponding pressure. It can be shown that the density of a saturated solution of nitrogen in water at 130 atm. would not differ from that of pure water by more than 0.05%. The volume of the float itself, calculated from data obtained in two runs, was a nearly linear function of pressure, varying from 13.310 ml. at 1 atm. to 13.253 ml. at 130 atm.

Successive runs on the systems gave no evidence of irreversible float compression. In four consecutive runs in which n-hexane was used as a solvent, the values obtained for its density at atmospheric pressure were: 0.6508, 0.6507,
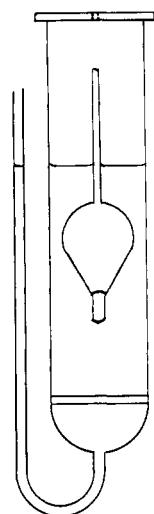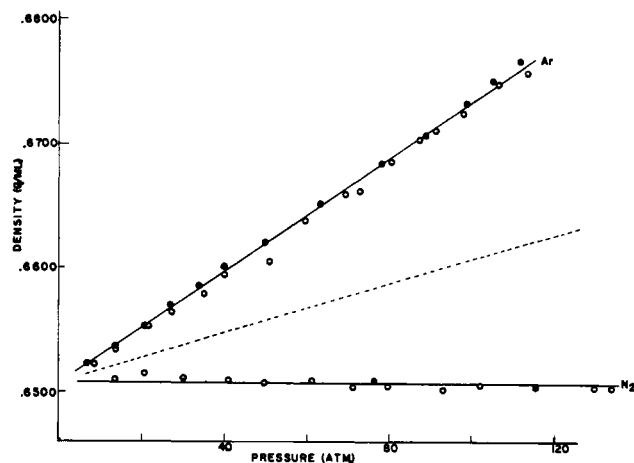
Figure 1. Saturation cell and float

Figure 2. Density of n-hexane solutions
○ Run 1   ● Run 2   ---- Pure n-hexane

0.6514, and 0.6509 gram per ml. using 13.310 ml. for the volume of the float.

Materials. The nitrogen and argon used were of 99.9 mole % purity. The three solvents were of reagent grade and were degassed before use by refluxing. The densities of these solvents at 30.0° C. and atmospheric pressure compared favorably with those calculated from data in the International Critical Tables.

	Gram/Ml.	
Solvent	$d_{obsd.}$ (mean)	$d_{calcd.}$
n-Hexane	0.6509	0.6505
n-Octane	0.6947	0.6940
Methanol	0.7818	0.7818

RESULTS AND DISCUSSION

The density data obtained at 30.0° C. for the four systems studied may be represented by the following linear equations:

$$N_2\text{-}n\text{-hexane:} \quad d = d_0 - 0.000003\,(p - p_0) \qquad (3)$$

$$Ar\text{-}n\text{-Hexane:} \quad d = d_0 + 0.000226\,(p - p_0) \qquad (4)$$

$$Ar\text{-}n\text{-octane:} \quad d = d_0 + 0.000176\,(p - p_0) \qquad (5)$$

$$Ar\text{-methanol:} \quad d = d_0 + 0.000129\,(p - p_0) \qquad (6)$$

where d in gram per ml., p in atm., d_0 = density of solvent at atmospheric pressure p_0.

The average deviation of an experimentally determined density from the value predicted by the above equations is ± 0.0002 gram per ml. The precision of the method is indicated by the excellent reproducibility of the data obtained from duplicate runs on the same system (Figure 2).

The apparent molal volumes reported in Table I were calculated at 100 atm. using the relation:

$$\phi v_2 = \frac{M_2}{d} + \frac{X_1 M_1}{X_2}\left(\frac{1}{d} - \frac{1}{d'}\right) \qquad (7)$$

where M_2 and M_1 are the gram molecular weights of solute and solvent, respectively, X_2 and X_1 the mole fractions of solute and solvent, d the density of the saturated solution, and d' the density of the pure solvent at 100 atm.

Table I. Apparent Molal Volumes of Ar and N_2 at 100 Atm. and 30.0° C.

Solute	Solvent	ϕv_2, Ml.
Nitrogen	n-Hexane	58 ± 2
Argon	n-Hexane	50 ± 2
Argon	n-Octane	48 ± 2
Argon	Methanol	46 ± 1

The densities of the solvents at 100 atm. were calculated from densities at atmospheric pressure and compressibilities. Mole fractions at 100 atm. were calculated from reported solubilities at 1 atm. (1, 2, 3) using Henry's law. The uncertainties in the reported values of ϕv_2 arise almost entirely from the difficulty of accurately estimating values of X_2 and X_1 at 100 atm.

The values of ϕv_2 for argon and nitrogen are slightly smaller than those reported for these gases in similar solvents at atmospheric pressure (4, 5). The apparent molal volume of argon shows a steady decrease with increasing internal pressure of the solvent as one passes from n-hexane through n-octane to methanol. This same trend has been noted with other gas-liquid systems (4, 5).

By rearranging Equation 7 and assuming the validity of Henry's law in the form $X_2 = kp$, it is possible to arrive at an expression for Δd, the difference between the densities of solution and pure solvent at pressure p:

$$\Delta d = \frac{kp\,\phi v_2\,d'}{M_1}\left[\frac{M_2}{\phi v_2} - d\right] \qquad (8)$$

To a first approximation, Δd should be a linear function of pressure, since ϕv_2, d and d' are relatively pressure-independent. This behavior was observed with each of the systems studied.

Equation 8 further predicts that the sign of the density difference should depend on the relative magnitudes of the quantity $M_2/\phi v_2$, which might be loosely interpreted as a "solute density," and d, the density of the solution. For solutions of argon in hexane, where $M_2/\phi v_2$ is greater than d (0.79 vs. 0.67 gram per ml.), it is found that all pressures, the density of the solution is greater than that of pure hexane. On the other hand, the density of hexane is lowered by dissolved nitrogen, since in this case $M_2/\phi v_2$ is smaller than d (0.48 vs. 0.66 gram per ml.).

LITERATURE CITED

(1) Boyer, F.L., Bircher, L.J., J. Phys. Chem. 64, 1330 (1960).
(2) Clever, H.L., Battino, R., Saylor, J.H., Gross, P.M., Ibid., 61, 1078 (1958).
(3) Gjaldebaek, J.C., Hildebrand, J.H., J. Am. Chem. Soc. 71, 3147 (1948).
(4) Ibid., 72, 1077 (1950).
(5) Jolly, J.E., Hildebrand, J.H., Ibid., 80, 1050 (1958).
(6) Krischevski, I.R., Efremova, S., Zhur. Fiz. Khim. 22, 1116 (1940).
(7) Sage, B.H., Lacey, W.H., Ind. Eng. Chem. 26, 163 (1934).
(8) Slowinski, E.J., Jr., Gates, E.E., Waring, C.E., J. Phys. Chem. 61, 808 (1957).