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The System Carbon Dioxide–Methylene Chloride

Solubility, Vapor Pressure, Liquid Density, and Activity Coefficients

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Static equilibrium measurements were made using a cell design at 70°, 100°, and 130° F., covering a pressure range from the vapor pressure of methylene chloride to 300 p.s.i.a. at each temperature. Curves of total vapor pressure and liquid density *vs.* weight per cent CO_2 in liquid are presented for these isotherms. Henry's Law was found true up to about 5.8 weight per cent CO_2 and 125 p.s.i.a. at 70° F., 5.1 weight per cent CO_2 and 156 p.s.i.a. at 100° F., and 4.4 weight per cent CO_2 and 190 p.s.i.a. at 130° F. Henry's Law constant in p.s.i.a. over these ranges is 1085 at 70°, 1505 at 100°, and 2015 at 130° F. Corresponding activity coefficient for CO_2 is 1.28 at 70°, 1.23 at 100°, and 1.18 at 130° F.

ALTHOUGH the carbon dioxide-methylene chloride system has possible propellant applications in aerosol packaging, the only equilibrium values of total vapor pressure, liquid composition, and liquid density available in the literature are those at 70° F. from 15 to 300 p.s.i.a. (*1*).

As an extension of this work, the system was investigated at 100° F. and 130° F. from the vapor pressure of pure methylene chloride to 300 p.s.i.a. at each temperature. The experimental apparatus and technique developed in the earlier work (*1*) were used in these determinations with only minor modifications.

The vapor-liquid system was brought to equilibrium in a steel chamber, or equilibrium cell, which was rocked in a constant temperature bath until constant system pressure was obtained. The construction of the cell allowed an all-liquid sample of known volume to be isolated at equilibrium conditions, and liquid densities were determined from the weight and volume of this sample. For composition determination, the liquid sample was analyzed by vaporizing it, passing the vapor through sodium hydroxide solutions which absorbed the carbon dioxide, and then titrating with standardized hydrochloric acid.

RESULTS

The liquid composition variation with total system vapor pressure is shown in Figure 1 for the 100° and 130° F. isotherms investigated. For comparison, the previously reported data at 70° F. is also included. The solubility of carbon dioxide was found to vary linearly with pressure up to approximately 5.1 weight % carbon dioxide at 100° F. and to 4.4 weight % carbon dioxide at 130° F., corresponding to total pressures of 156 and 190 p.s.i.a., respectively. Above these pressures the rate of change in carbon dioxide dissolved with increasing pressure steadily increases—i.e., the solubility of carbon dioxide increases more rapidly than predicted by Henry's Law. The experimental curves should well represent the solution characteristics since the individual data points deviated from the smoothed curve values by a maximum of only 0.2 weight %. The values of the pure methylene chloride vapor pressure indicated by extrapolation to zero weight % carbon dioxide were in close agreement with literature values. Extrapolated values: 14 p.s.i.a. at 100° F., 25 p.s.i.a. at 130° F.; literature values: 14.2 p.s.i.a. at 100° F., 25.7 p.s.i.a. at 130° F. (*2*).

The approximately linear variation of liquid density with liquid composition is shown in Figure 2. The individual data points vary a maximum of only 0.002 g./cc. from the smoothed curve values, and the density values found for pure methylene chloride, which are included in these curves, are in close agreement with literature values. Experimental values: 1.297 g./cc. at 100° F., 1.266 g./cc. at 130° F;

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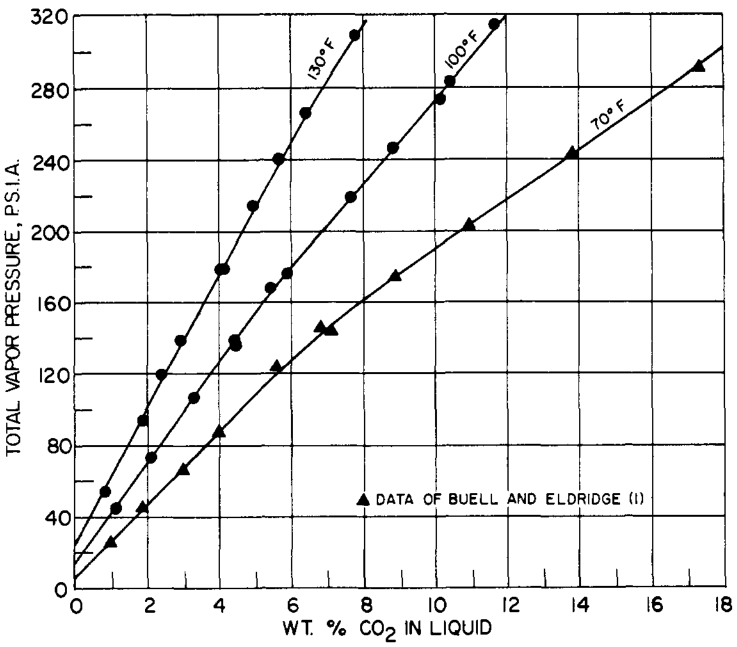

Figure 1. Total vapor pressure of solutions of CO_2 in methylene chloride

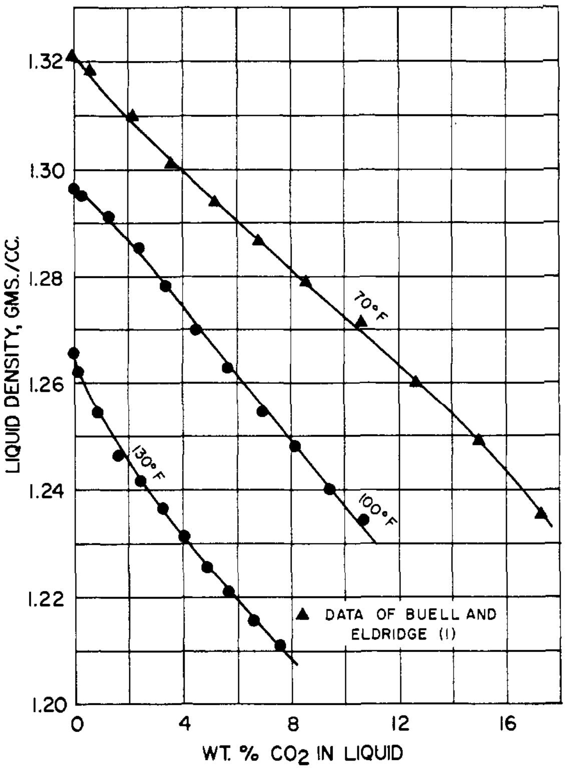

Figure 2. Density of solutions of CO_2 in methylene chloride

literature values: 1.295 g./cc. at 100° F., 1.265 g./cc. at 130° F. (*2*).

At each temperature, for the range over which the data followed Henry's Law, the constant, *H*, was calculated based on the equation:

$$H = \frac{\text{partial pressure of } CO_2 \text{ in vapor, p.s.i.a.}}{\text{mole fraction of } CO_2 \text{ in liquid}} \tag{1}$$

Applying Raoult's law to the solvent and Dalton's law to the vapor phase, the Henry's law constant may be calculated from total pressure and liquid composition data through the relationship

$$P_t = HX_{CO_2} + P_{M.C.}(1 - X_{CO_2}) \tag{2}$$

where

P_t = total pressure, p.s.i.a.
H = Henry's law constant, p.s.i.a.
X_{CO_2} = mole fraction carbon dioxide in liquid
$P_{M.C.}$ = vapor pressure of pure methylene chloride, p.s.i.a.

These values of *H* are presented in Table I, which also includes the Henry's Law constant for the previously reported data at 70° F.

The partial pressure exerted by a dissolved gas may also be expressed in terms of its activity coefficient in the solution, as

$$\bar{p} = \gamma x p \tag{3}$$

where

$\bar{p}$ = partial pressure of solute gas
x = mole fraction of solute gas in liquid
P = vapor pressure of pure solute gas at temperature of solution
γ = activity coefficient

Comparing Equations 1 and 3 it is seen that

$$\gamma = H/P \tag{4}$$

Using this equation, the activity coefficient of carbon dioxide in the liquid solution was calculated for each temperature from the corresponding value of *H* and the vapor pressure. Above the critical temperature a hypothetical vapor pressure was used, obtained by a slight extrapolation of the vapor pressure curve above the critical point.

The values of the activity coefficients so obtained, which are, of course, valid only in the dilute solution range where Henry's Law holds, are given in Table I.

Table I. Henry's Law Constant and Activity Coefficient for CO_2 Dissolved in Methylene Chloride

Temp., ° F.	*H*, P.S.I.A.	Activity Coeff.
70	1085	1.28
100	1505	1.23
130	2015	1.18

The activity coefficient changes in the direction of unity as the temperature increases, indicating that the solutions become more nearly ideal at higher temperatures.

From the standpoint of rigorous thermodynamics the activity coefficient (Equation 3) represents a choice of standard state of unit activity for CO_2 as the pure compound at the temperature and total pressure of the system in the hypothetical liquid state having a fugacity equal to the actual vapor pressure of pure CO_2 at the same temperature. It also involves the assumption that fugacity of CO_2 in the vapor phase is equal to the Dalton's Law partial pressure. This assumption proves to be only 1 to 2% in error at the low pressures of CO_2 for which Henry's Law was found to hold in this work.

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