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Received for review April 16, 1973. Accepted August 20, 1973. The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U.S. Atomic Energy Commission. Teflon is a registered trademark for polytetrafluoroethylene resin assigned to E. I. du Pont de Nemours & Co., Wilmington, Del. 19898.

Carbon Dioxide Solubility in Aqueous Carbopol Solutions at 24°, 30°, and 35°C

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Solubilities for carbon dioxide in 0.25, 0.75, and 1.00 wt % aqueous Carbopol (carboxy polymethylene) solutions are determined at 24°, 30°, and 35°C. The rheological behavior of these solutions can be described by the Ostwald-de Waele power-law model with the flow behavior index varying between 0.916 and 0.594. The solubilities are expressed in terms of Henry's Law and decrease with increasing Carbopol concentration and temperature.

Aqueous Carbopol-934 (carboxy polymethylene) solutions are often used as model nonNewtonian fluids since their rheological behavior is well characterized by the power-law relationship. For interphase gas-liquid mass-transfer studies, with nonNewtonian fluids, carbon dioxide is a convenient choice as the solute to be transferred since large mass-transfer rates can be achieved owing to its relatively high solubility in aqueous solutions.

Another advantage with the use of carbon dioxide in aqueous solutions is that concentrations may be measured in a straightforward manner by wet chemistry techniques. To experimentally determine interphase mass-transfer coefficients it is necessary to know equilibrium solubilities for the binary gas-liquid system. In the work described here, solubilities for carbon dioxide in 0.25, 0.75, and 1.00 wt % aqueous Carbopol solutions were determined for partial pressures near atmospheric and for temperatures of 24°, 30°, and 35°C. The Carbopol solutions were pseudoplastic with the flow behavior index varying from 0.916 to 0.594.

Experimental

A schematic drawing of the experimental apparatus is shown in Figure 1. The solutions were saturated by bubbling "bone-dry" grade carbon dioxide through a fritted-glass disc in a gas-washing bottle for approximately 1 hr. Initially, several runs were made lasting 2 hr, and these showed no differences with runs lasting 1 hr. Thus, the majority of the runs were made with a 1-hr bubbling period. A liquid seal was provided for the saturation vessel by placing a 500-ml Erlenmeyer flask in series with the saturation vessel as shown in Figure 1.

After turning the gas to the bubbler off, a sufficient period of time, usually about ½ hr, was allowed to elapse to ensure that the pressure which initially was slightly in excess of atmospheric was reduced to atmospheric. The saturation vessel was shaken manually at 5-min intervals during this period. The initial excess pressure was approximately 1 in. of water. The temperature was controlled to within ±0.1°C by placing the saturation vessel in a constant-temperature water bath. The use of low gas flow rates minimized evaporation losses of water which would have altered the solution compositions.

A 50-ml pipet was used to transfer samples out of the saturation vessel for concentration measurements. Carbon dioxide concentrations were determined by precipitation as barium carbonate from standard barium hydroxide solutions with the excess hydroxide determined by titration with hydrochloric acid to a phenolthalein end point. Since Carbopol solutions are acidic, it was necessary to perform blank titrations on carbon dioxide-free solutions. Care was taken to avoid the loss of carbon dioxide to the atmosphere during the transfer of samples from the saturation vessel and to prevent the introduction of carbon dioxide from the atmosphere during the titrations. The

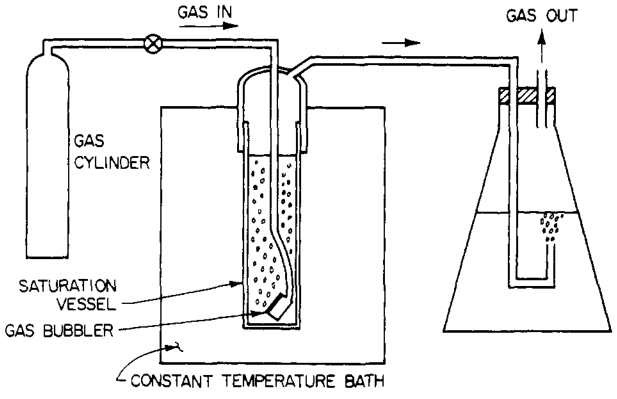

Figure 1. Solubility apparatus

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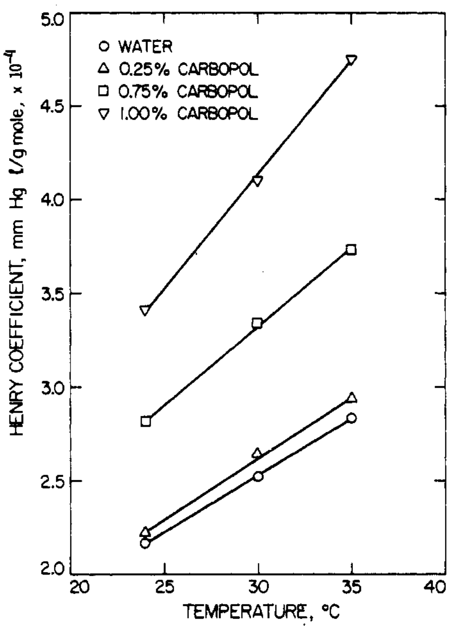

Figure 2. Henry coefficients for carbon dioxide in aqueous Carbopol solutions as function of temperature

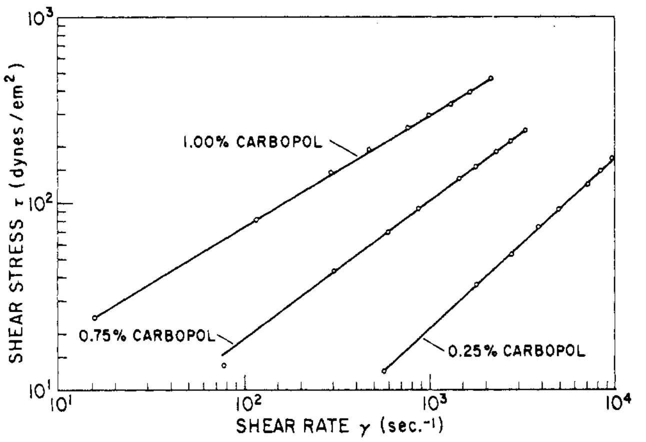

Figure 3. Shear stress vs. shear rate for Carbopol solutions at 30°C

Table I. Henry Coefficients for Carbon Dioxide in Aqueous Carbopol Solutions

Carbopol, wt %	Temp, °C	Henry coefficient, H (mm Hg l./g-mol) $\times 10^{-4}$	No. of measurements	SD, %
0.0	24.0	2.171 (2.176)[a]	3	0.17
	30.0	2.522 (2.545)[a]	4	0.30
	35.0	2.843 (2.858)[a]	3	0.05
0.25	24.0	2.222	3	0.75
	30.0	2.639	3	0.67
	35.0	2.943	3	0.41
0.75	24.0	2.816	3	0.73
	30.0	3.337	3	0.52
	35.0	3.732	3	0.61
1.00	24.0	3.407	3	1.01
	30.0	4.096	3	1.03
	35.0	4.751	3	0.94

[a] Values from Perry (*2*).

Table II. Constants for the Equation, $H + at + b$

Carbopol, wt %	a (mm Hg l./g-mol °C) $\times 10^{-2}$	b (mm Hg l./g-mol) $\times 10^{-3}$
0.00	6.101	7.023
0.25	6.565	6.539
0.75	8.336	8.222
1.00	12.19	4.675

Table III. Power-Law Parameters for Aqueous Carbopol Solutions

Carbopol, wt %	Temp, °C	Flow behavior index, n	Consistency index, K (g/cm sec^{2-n})
0.25	24	0.916	0.04277
	30		0.03794
	35		0.03546
0.75	24	0.773	0.5071
	30		0.4833
	35		0.4691
1.00	24	0.594	5.288
	30		4.835
	35		4.123

solubility determinations are estimated to be accurate to within a maximum experimental error 1.9%.

Solution densities were determined at 24°C to within ±0.001 g/ml and were identical within experimental accuracy to the density of water. Vapor pressures of the aqueous solutions were taken to be those of pure water. Shear stress-shear rate measurements on the nonNewtonian Carbopol solutions were made by use of a capillary-tube viscometer. Further details of these measurements are given elsewhere (*1*).

Results and Discussion

The solubility data are given in terms of Henry coefficients in Table I. The form of Henry's Law used to express the data is

$$p = Hc \tag{1}$$

The solubility data for water are compared to the data in Perry (*2*) in Table I, and the agreement is well within the estimated maximum experimental error of 1.9%. The data are shown plotted as a function of temperature in Figure 2. Since the Henry coefficients show a linear relationship with temperature over the temperature range investigated, they were fitted by a least-squares procedure to the equation

$$H = at + b \tag{2}$$

The constants a and b for Equation 2 are given in Table II. To interpolate the solubilities for intermediate Carbopol compositions, a third-order polynomial satisfactorily represents the isothermal data.

Figure 3 shows the shear stress-shear rate data as determined from the capillary-tube viscometer for the Carbopol solutions at 30°C. The power-law model represents the rheological behavior of these solutions well over the shear rate range investigated. The power-law parameters are given in Table III. Since the flow behavior index is relatively insensitive to the temperature, it was assumed to be constant in the regression analysis to fit the shear stress-shear rate data to the equation

$$\tau = K|\gamma|^n \tag{3}$$

Nomenclature

a = constant in Equation 2, mm Hg l./g-mol, °C
b = constant in Equation 2, mm Hg l./g-mol
c = concentration, g mol/l.
H = Henry coefficient, mm Hg l./g-mol
K = consistency index, g/cm sec^{2-n}
n = flow behavior index
p = partial pressure of gas, mm Hg
t = temperature, °C

Greek Letters

γ = shear rate, sec^{-1}
τ = shear stress, g/cm sec

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Received for review April 16, 1973. Accepted September 19, 1973.

Dew-Point Loci for Methane-*n*-Butane Binary System

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The dew-point loci for the binary system of methane and normal butane were determined at 13 temperatures from +40° to −200°F. The pressure range covered from 20 up to near 1900 psia. A constant flow gas saturation technique was developed and used for the experimental study. The existence of triple-valued dew points in a narrow concentration range was observed for isotherms at and immediately below the critical temperature of pure methane.

Equilibrium data for binary systems of methane and heavier alkanes are important both for practical and for theoretical purposes. Accurate *K*-value data are needed for the design of process units in petroleum industries. The data can also be used to extract the interaction coefficients which are often required in the equilibrium computations for multicomponent systems. Earlier studies of equilibrium in the low temperature range for binary systems of methane with other alkanes heavier than propane are either incomplete or inconsistent. This has been caused by the difficulties in the determination of the dew-point concentrations.

The concentration of the heavier component in the vapor phase becomes small as the system temperature goes down. The ordinary chromatographic method will be inaccurate because errors are caused by adsorption on the tube wall. Also, characteristics of the packing material for the chromatographic column and the sampling technique become more significant. Calibration of the chromatographic detector becomes more difficult since it is difficult to prepare a very dilute mixture without appreciable errors.

A constant flow gas saturation technique (*1*) has been developed to measure the dew-point concentration. This method is especially useful to determine the trace amount of the heavier component in the vapor phase.

Experimental Method

The main equipment components which were used in the constant flow saturation method consisted of a 410 stainless-steel windowed cell with a pressure rating of 8000 psi, a cryostatic bath, a carrier gas metering pump, and analytic equipment. For details of the equipment and method, please refer to the earlier paper (*1*) by the authors.

The flow chart of the equipment layout is shown in Figure 1. Pure methane flow is metered by the carrier gas metering pump. The methane flow passes through the bypass line for a period of time to clear out impurities in the system. The equilibrium cell and presaturator are first evacuated, and then charged with normal butane. The cell and presaturator are immersed in a stirred cryogenic bath which is controlled at the desired temperature. After thermal equilibrium is attained, the bypass line is shut off, and the pure methane passes through the precooler to bring the stream temperature to the bath temperature; then it flows through a presaturator made of three 1-ft long sections of ⅛-in. stainless-steel pipes connected in series, packed with Chromopacks which were presaturated with normal butane. Finally, the gas stream enters from the bottom of the equilibrium cell, which is filled with the heavier hydrocarbon and small glass beads to disperse the gas flow through the liquid.

The effluent dew-point gas mixture is expanded to atmospheric pressure and measured continuously by a thermal conductivity cell and recorder. A steady-state condition produces a steady signal on the recorder and a constant cell pressure and pump pressure. After the steady signal voltage on the recorder has been registered, the pure methane flow is again switched to the bypass line to clear out the mixture and to recheck the base line. The concentration of the mixture is determined by a calibration curve from the signal difference between the mixture and pure methane.

The detector was calibrated in a steady flow manner to preserve the similarity to the conditions of obtaining data. A specially designed micropump (*5*) pumped normal butane at a slow rate into the mixing valve, where pure methane was metered by the carrier gas metering pump to mix with the hydrocarbon stream. The mixed gas stream was passed into the thermal conductivity cell where a signal was produced by using pure methane as the reference stream. A pressure transducer was installed at the top of the micropump. When steady state is obtained, the pressure in the carrier gas pump and micropump will stay constant, and the signal from the thermal conductivity cell will also stay at a constant value. The concentration of the mixture can be calculated from the flow rate of both pumps.

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