Density, Viscosity, and Carbon Dioxide Solubility and Diffusivity in Aqueous Ethylene Glycol Solutions

WALTER HAYDUK[1] and VINOD K. MALIK
Chemical Engineering Department, University of Ottawa, Ottawa, Ont., Canada

Results are reported for the densities and viscosities of aqueous ethylene glycol solutions at 25° C. Carbon dioxide solubilities and diffusion coefficients at a temperature of 25° C in the same solutions, measured for the complete range of compositions, are reported and compared with other data when these are available.

In gas absorption experiments, a knowledge of the effect of changes in the liquid viscosity on mass transfer rates is often required. For such experiments, the use of a solvent solution of a viscous, miscible, nonvolatile component—such as ethylene glycol dissolved in water—is indicated. The difficulty in interpreting results from such experiments is that the hydrodynamics of the contacting system are altered as a result of the increased viscosity, and that the molecular diffusivity of the absorbed species is also altered. Therefore, accurate solvent viscosities, as well as diffusivities of the absorbed species, are required for all compositions of the solvent solution. In an attempt to fill such a need, we have chosen the carbon dioxide-ethylene glycol-water system and have measured the density and viscosity at 25° C for various concentrations of solvent solution. We have also measured the carbon dioxide solubilities by chemical analysis of saturated solutions, and the diffusivities in the mixed solvent by means of the steady-state capillary cell method (*7*).

Diffusivities of a dilute species in binary solvent solutions have been successfully correlated by Leffler and Cullinan (*6*) for a number of systems using:

$$(\lim_{x_1 \to 0} D)\eta = (D^0_{12}\,\eta_2)^{x_2}\,(D^0_{13}\,\eta_3)^{x_3} \qquad (1)$$

The diffusion of carbon dioxide in glycol-water is complicated because strong interactions between solvent molecules occur, and because a certain amount of association between solute and solvent molecules is also likely. Thus, experimental data for the diffusivity of carbon dioxide in glycol-water solutions pose a severe test for the applicability of Equation 1.

EXPERIMENTAL

The relatively simple steady-state capillary cell method, found to give reliable diffusivities for a number of gas-liquid systems (*7*), was used in these measurements. This method was considered useful because of its simplicity and particularly because it was an absolute method for measuring diffusivities of gases in liquids and required no prior calibration. The capillary cell consisted essentially of a column of deaerated solvent confined in a capillary. One end of the capillary was exposed to a pool of gas-free solvent, the other, to a small volume of gas which was being absorbed at a steady rate. The volumetric rate of gas absorption was measured by observing the movement of a bead of solvent introduced in a second small capillary, joined to the first capillary. It has been shown (*7*) that, provided the column of liquid confined in the capillary was long enough (in excess of 20 mm), the measured length from the meniscus to the end of the capillary was the actual distance through which molecular diffusion took place. Further, when the cell was purged with gas and then filled with solvent, the cell could be completely flushed with deaerated solvent to ensure that the concentration of dissolved gas within the cell was initially zero. Even after the lapse of time required for steady-state concentrations to be achieved in the capillary, the concentration within the cell was still very low (calculated to be less than 1% of saturation) because of the small rate of diffusion into the cell. If the equilibrium gas solubility was known, the diffusivity could be calculated from the experimental parameters—i.e., the diffusion path length and the rate of gas absorption. In the derivation for the rate of diffusion through the binary liquid solvent solution, it was assumed that the diffusion coefficient for the dilute solute was constant over the compositions encountered along the diffusion path. The pseudobinary diffusion coefficient was then given by:

$$D = \frac{n_1 L}{\rho \ln\left(\dfrac{1+\omega_{10}}{1+\omega_{1L}}\right)} \qquad (2)$$

In the originally reported experiments (*7*) for the diffusivity of carbon dioxide in water, a liquid bead consisting of gas-saturated *s*-octanol was utilized to measure the rate of disappearance of the gas confined in the capillaries. A bead of water tended to stick to the capillary tube wall. We have subsequently found that, provided the bead was relatively short (about 1 mm in length), a water-glycol solvent solution, equivalent in concentration to that in the diffusion cell itself and saturated with carbon dioxide, could be quite successfully utilized. It also avoided any concern about possible contamination of the solution in the capillary.

The density measurements were performed by means of a 25-ml vacuum-jacketed pycnometer bottle whose volume was calibrated with distilled water at 25 (±0.1) °C. It is estimated that the maximum error in the density measurements is ±0.0001 g/ml. The viscosities were measured using calibrated Cannon-Fenske viscometers immersed in a constant temperature (±0.02° C) bath and with efflux times in excess of 100 sec. Based on a check

---

[1] To whom correspondence should be addressed.

of the viscosity of distilled water, the maximum error in the viscosity measurements is about 0.25%.

The carbon dioxide solubility was measured by saturating the solution at 25°C and atmospheric pressure using a fritted glass bubbler in a sealed, water-jacketed contactor. Samples of solution were allowed to drain by gravity into a 50-ml pipet for analysis. The analysis consisted of reacting the sample with standard excess sodium hydroxide and back-titrating with standard acid to the phenolphthalein end point. Care was taken to avoid loss of carbon dioxide during analysis.

For the accurate measurement of solubility and diffusivity, it was necessary to ensure complete deaeration of the solvent solution. For the solubility measurements, the solvent was stripped of air by means of the carbon dioxide gas which was bubbled through it. Hence, as the bubbling was continued, the solution was not only completely stripped of air, but also saturated with the gas. Initially, we had considered that the solvent might become concentrated because of the preferential evaporation of water. We placed a carbon dioxide saturator (containing a solution of the same concentration as that in the solubility apparatus) in series with the solubility apparatus. Subsequently, we discovered that, because of the relatively low bubbling rate (about 30 ml/min) and relatively high volume of solution (about 250 ml), the amount of water that could possibly be evaporated by the gas during the period of about 2 hr was negligibly small for all solvent concentrations. For most experiments, therefore, dry gas was utilized in the solubility apparatus. A small correction for the reduction in volume of the glycol-rich (viscous) solution that was discharged from the 50-ml sampling pipet was necessary. Mainly as a result of possible errors in sampling and analysis, the maximum error in the solubilities is estimated to be 1.5%.

A supply of deaerated solvent solution was required for the diffusivity measurements. Solvent solution was boiled under vacuum for at least 1½ hr while stored in a long glass tube 12 mm in diameter. Heat was applied by means of a heating tape. After deaeration, the tube was cooled and connected by Tygon tubing to the diffusion cell which was then filled and purged. A sample of the solvent solution in the tube was withdrawn and its viscosity measured. The solvent composition was determined from the previously established viscosity-composition curve. As a result of boiling, a measurable increase in the glycol content of the solvent solution was usually observed.

The solution confined in the capillary of the diffusion cell was exposed to the gas for a prolonged period of time (about 24 hr) until a steady-state concentration profile was established. Because of the possibility of evaporation of water from the small column of solution with resulting concentration change, steps were taken to prevent it. A saturator for the gas passing across the end of the small capillary of the diffusion cell was employed. The saturator for the gas was also utilized as the source of gas-saturated bead for introduction into the small capillary.

The diffusivity measurement is essentially directly proportional to the solubility, so that any uncertainty of the latter is reflected in the former. Additional uncertainties are the measurement of the rate of descent of the bead, the diameter of the small capillary, and the diffusion path length. It is estimated that the reported diffusivities are accurate to within 3%.

MATERIALS

Carbon dioxide of a commercial grade, having a specified minimum purity of 99.5%, was obtained from the Matheson Co. and used as received. Ethylene glycol, obtained from Fisher Chemicals, was of a certified reagent grade, with a specified maximum water content of 0.2 wt % and an actual lot analysis of 0.1 wt % water. It was assumed that no other impurities were present in the glycol and both the density and viscosity measurements were linearly extrapolated to 100% glycol, assuming the presence of the small amount of water.

Precautions were taken to avoid excessive exposure of the glycol (or glycol solutions) to air because of the hygroscopic nature of glycol and its solutions. The precautions consisted, essentially, of preparing the solutions rapidly and storing them in 100-ml stoppered (volumetric) flasks. It was calculated, for example, that, provided the air space above a solution was small (less than 100 ml), the change in concentration of a 100-ml solution, even if the water vapor from the air was completely absorbed, was completely negligible. Weighed volumetric flasks containing increasing (weighed) quantities of distilled water were initially prepared. A 100-ml buret fitted with a drying tube was used to dispense the glycol. A predetermined volume of glycol was added to each volumetric flask. Each was sealed and weighed again. The resulting solutions were used for the density and viscosity measurements. The sealed volumetric flasks were immersed in a constant temperature bath before each solution was poured, in turn, into the clean, dry pycnometer bottle for weighing. Solutions of known concentration were charged directly into the clean, dry viscosity pipet for viscosity measurement. It was considered that, during the short time required to achieve thermal equilibrium in the constant temperature bath, absorption of

Table I. Densities and Viscosities at 25° C of Aqueous Ethylene Glycol Solutions

Mole fraction, glycol	Density, g/ml	Viscosity, cps
0.0	0.9971	0.894
0.0414	1.0144	1.22
0.1180	1.0379	1.97
0.1553	1.0477	2.36
0.3385	1.0771	4.73
0.3521	1.0796	4.96
0.4133	1.0860	5.94
0.5333	1.0943	7.96
0.6376	1.0994	9.90
0.7762	1.1044	12.56
0.8769	1.1073	14.49
0.9070	1.1078	15.05
0.9966	1.1097	16.94
1.0000	1.1098[a]	17.01[a]

[a] Extrapolated.

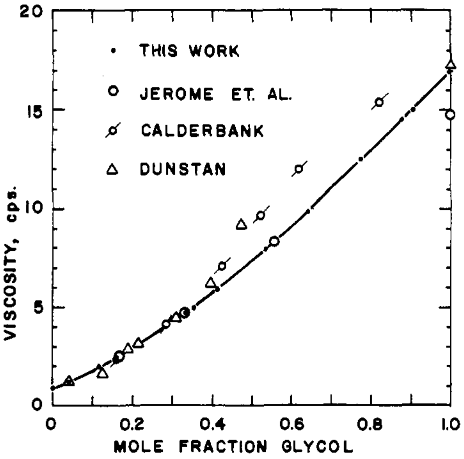

Figure 1. Viscosities of aqueous ethylene glycol solutions at 25° C

water vapor from the air was negligible. This was substantiated because second and third viscosity readings with the same solution almost invariably yielded essentially identical viscosities. Solutions for solubility and diffusion measurements were prepared in larger quantities and charged directly into the solubility apparatus or deaerating tube with similar precautions.

RESULTS AND DISCUSSION

The densities and viscosities of aqueous glycol solutions (Table I) both compare favorably where checks are available with those listed by Curme (*2*). A line representing our viscosity data, along with the data of Calderbank (*1*), Jerome et al. (*4*), and Dunstan (*3*)—whose data were used by Perkins and Geankoplis (*8*)—is shown in Figure 1 for comparison. The viscosities, as reported by Calderbank, are much higher than the rest for solutions rich in glycol; the viscosity of pure glycol as reported by Jerome et al. is much lower. Viscosities of pure ethylene glycol are shown as a function of temperature in Figure 2, using the previously mentioned data (*2-4*), and that of Scott and Hayduk (*9*). It is apparent that the viscosity of Jerome et al. is much too low, and that Dunstan's is somewhat high. A low viscosity is possibly the result of inadequate precaution to prevent water absorption by the highly hygroscopic glycol. In all probability, high viscosities would be caused by higher molecular weight (glycol) contaminants because the probable error of a viscosity measurement itself is usually very small.

The carbon dioxide solubilities, corrected to a gas partial pressure of 760 mm, are listed in Table II and compared with the data of Kobe and Mason (*5*) in Figure 3. Comparisons of data, where possible, are favorable (within 1%).

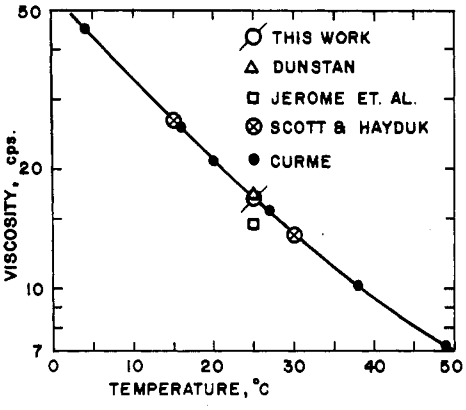

Figure 2. Viscosities of ethylene as a function of temperature

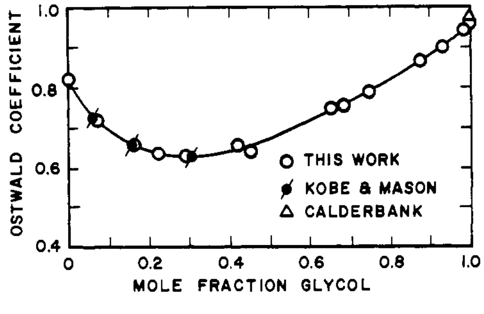

Figure 3. Carbon dioxide solubility in aqueous ethylene glycol solutions at 25° C

Table II. Solubility of Carbon Dioxide in Aqueous Ethylene Glycol at 25° C and Partial Pressure of 760 Mm

Mole fraction, glycol	Wt fraction, glycol	Solubility, Mmol/l.	Ostwald coeff.
0.00	0.00	33.6	0.825
...	0.20	...	0.726 (*9*)
0.072	0.211	29.4	0.721
...	0.40	...	0.654 (*9*)
0.165	0.405	26.9	0.660
0.222	0.496	26.0	0.638
0.291	0.586	25.7	0.630
...	0.60	...	0.627 (*9*)
0.420	0.714	26.9	0.660
0.453	0.741	26.2	0.643
0.651	0.866	30.6	0.751
0.685	0.882	31.0	0.760
0.748	0.911	32.3	0.793
0.874	0.960	35.5	0.871
0.932	0.979	36.8	0.903
0.983	0.995	38.5	0.945
0.997	0.999	39.2	0.962
1.00	1.00	39.4[a]	0.966[a]

[a] Extrapolated.

Table III. Diffusivity of Carbon Dioxide in Aqueous Ethylene Glycol at 25° C and Atmospheric Pressure

Mole fraction, glycol[a]	Solution viscosity, cps	Diffusivity, cm^2/sec ($\times 10^5$)
0.00	0.894	1.98
0.257	3.63	0.894
0.270	3.80	0.808
0.572	8.62	0.554
0.572	8.62	0.582
0.618	9.43	0.549
0.824	13.47	0.408
0.997	16.94	0.280
0.997	16.94	0.283
1.00	17.01[b]	0.279[b]

[a] Solution compositions obtained from composition-viscosity graph. [b] Linearly extrapolated.

The solubility of carbon dioxide in pure glycol as listed by Calderbank (*1*) is equivalent to an Ostwald coefficient of 0.975 and is also within 1% of our value of 0.966. A minimum solubility occurs at a composition of about 30 mol % glycol.

The measured diffusivities of carbon dioxide in aqueous glycol solutions are listed in Table III, and are shown as functions of composition, and solution viscosity, in Figures 4 and 5, respectively. Comparable diffusivities of Calderbank (*1*) are appreciably lower—especially for glycol-rich solutions. The purity of the glycol utilized in Calderbank's experiments was not specified, so it is difficult to assess the accuracy of his results. It would appear possible that the ethylene glycol contained a higher molecular weight glycol (or other impurity) which yielded, in aqueous solution, an increased viscosity, a reduced carbon dioxide diffusivity, and a somewhat higher density than for a two-component aqueous glycol solution.

Calculated diffusivities, based on Equation 1 of Leffler and Cullinan, are also shown in Figure 4. The comparison for the expected highly nonideal behavior is not favorable, suggesting that the use of the equation should be limited to solutions in which molecular interactions are less extreme.

Despite differences in carbon dioxide diffusivity as a function of solvent composition, the data of Calderbank compare much better with ours when plotted as a function of the solution viscosity (Figure 5). Figure 5 suggests that the viscosity of a solvent largely determines the solute diffusivity regardless of the actual composition of the sol-

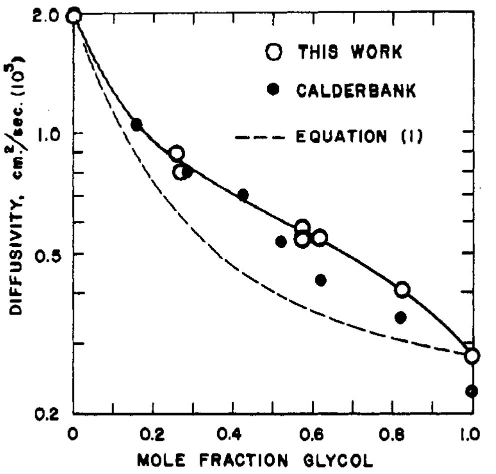

Figure 4. Diffusivity of carbon dioxide in aqueous ethylene glycol solutions at 25° C

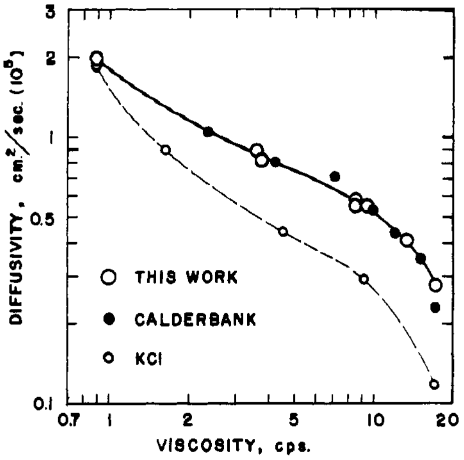

Figure 5. Carbon dioxide diffusivity in aqueous ethylene glycol solutions as a function of solvent viscosity

vent. The diffusivity data of Perkins and Geankoplis (*8*) for KCl in aqueous glycol at 25° C are shown for comparison to indicate the similarity in the viscosity–diffusivity relationship.

NOMENCLATURE

D = diffusivity in binary solvent solution, cm²/sec
D^0_{12}, D^0_{13} = diffusivities of solute in pure solvents, 2 and 3, cm²/sec
L = diffusion path length, cm
n_1 = mass flux of solute, g/cm² sec
x_2, x_3 = mole fraction of components 2 and 3 in solute-free solvent solution

Greek Letters

ρ = solution density, g/cm³
ω_{10} = mass concentration solute at (saturated) solvent interface, g/cm³
ω_{1L} = mass concentration of solute in capillary cell, g/cm³
η = solvent solution viscosity
η_2, η_3 = viscosities of pure solvent components

LITERATURE CITED

(1) Calderbank, P. H., *Trans. Inst. Chem. Engrs.*, **37**, 173 (1959).
(2) Curme, G. O., Johnston, F., Eds, "Glycols," pp 35, 57, Reinhold, New York, N. Y., 1953.
(3) Dunstan, A. E., *J. Chem. Soc. T.*, 87, 11 (1905).
(4) Jerome, F. S., Tseng, J. T., Fan, L. T., *J. Chem. Eng. Data*, 13, 496 (1968).
(5) Kobe, K. A., Mason, G. E., *Ind. Eng. Chem. (Anal. Ed.)*, 18, 78 (1946).
(6) Leffler, J., Cullinan, H. T., Jr., *Ind. Eng. Chem. Fundam.*, 9, 88 (1970).
(7) Malik, V. K., Hayduk, W., *Can. J. Chem. Eng.*, 46, 462 (1968).
(8) Perkins, L. R., Geankoplis, C. J., *Chem. Eng. Sci.*, 24, 1035 (1969).
(9) Scott, D. S., Hayduk, W., *Can. J. Chem. Eng.*, **44**, 130 (1966).

RECEIVED for review June 15, 1970. Accepted November 23, 1970.

Vapor-Liquid Equilibria for Carbon Dioxide–Difluoromethane System

ROBERT A. ADAMS and FRED P. STEIN[1]
Department of Chemical Engineering, Lehigh University, Bethlehem, Pa. 18015

Published data on the phase equilibria of systems containing carbon dioxide as one of the components are abundant, but those containing a fluorocarbon as the second component are rare. Also scarce are studies of fluorocarbon solutions containing difluoromethane. Thus, the combination of carbon dioxide and difluoromethane in this study provides an interesting addition to the available phase equilibrium data on the fluorocarbons.

The flammability of difluoromethane removes it from consideration as a commercial refrigerant. However, in combination with a second refrigerant which is nonflammable, such as carbon dioxide, the fire hazard may be overcome. At the same time, the mixture might produce a refrigerant whose physical-property range would be desirable. Establishment of such properties requires, among other things, accurate data describing the vapor-liquid equilibria of the mixture.

EXPERIMENTAL

An apparatus of the vapor-recirculation type (*9*) was used in this investigation. With this technique vapor was continuously removed from the top of the vapor-liquid equilibrium cell and reintroduced at the bottom of the

---

[1] To whom correspondence should be addressed.