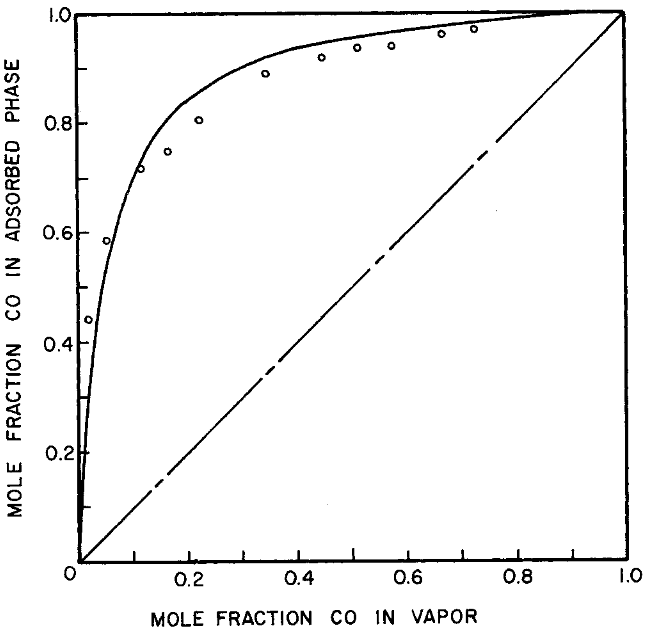

Fig. 3. Phase diagram for adsorption of carbon monoxide and nitrogen on molecular sieve 5A at —200°F. Circles: experimental data. Solid line: theory of ideal adsorbed solutions.

spreading pressure of carbon monoxide. Spreading pressures of carbon monoxide and nitrogen calculated by Equation (1) and the integration constant at one atmosphere are shown as a function of pressure on Figure 2.

Calculation of phase equilibria for adsorption at a particular pressure requires adsorption data on the more volatile adsorbate (here, nitrogen) at higher pressure. Unfortunately Danner and Wenzel failed to measure the adsorption of nitrogen at pressures greater than atmospheric. However, the selectivity may be calculated at lower pressure. On Figure 3, adsorbed and gas compositions predicted by the theory of ideal adsorbed solutions at 100 mm Hg are compared with experimental points of Danner and Wenzel at atmospheric pressure. It is known that selectivity decreases weakly with increasing pressure (Myers, 1968). The theoretical curve should shift somewhat closer to the 45° line, and therefore closer to the experimental points, at atmospheric pressure. Even if differences in pressure are ignored, these data can be explained quantitatively by activity coefficients in the adsorbed phase no larger than 1.5 at infinite dilution. We picked the CO—N_2—zeolite 5A system for discussion because the discrepancy between theory and experiment is greatest. For other mixtures (CO + O_2, N_2 + O_2) adsorbed on zeolites 5A and 10X the theory of ideal adsorbed solutions predicts the observed selectivity (x_1y_2/x_2y_1) within ± 10%.

LITERAURE CITED

Danner, R. P., and L. A. Wenzel, "Adsorption of Carbon Monoxide—Nitrogen, Carbon Monoxide—Oxygen, and Oxygen—Nitrogen Mixtures on Synthetic Zeolites," *AIChE J.*, **15**, 515 (1969).

Myers, A. L., "Adsorption of Gas Mixtures," *Ind. Eng. Chem.*, **60**, 45 (1968).

———, and J. M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.*, **11**, 121 (1965).

Van Ness, H. C., "Adsorption of Gases on Solids," in *Chemistry and Physics of Interfaces*," p. 121, Am. Chem. Soc., Washington, D.C. (1971).

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The Diffusivity of Carbon Dioxide in Some Organic Liquids at 25° and 50°C

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The influence of diffusivity on the mass transfer of gases into both nonturbulent and turbulent liquids is now well established (Davies, 1972) so accurate diffusivity values are needed for the interpretation and calculation of mass transfer rates. Recently Akgerman and Gainer (1972a,b) showed that previously developed diffusivity correlations did not entirely satisfactorily predict the diffusivities of gases in liquids and proposed an improved equation based on significant liquid structure and absolute rate theory. However, only 41 of the 268 data points used to test their equation were for gases in organic liquids and the majority of these values were at temperatures between 20° and 30°C (Akgerman and Gainer, 1972a); this shows the need for diffusivity data for gases in organic liquids over a range of temperatures. As part of a study of mass transfer into turbulent liquids (Davies, 1972, Chapter 4) the diffusivity of carbon dioxide was determined in the following organic liquids at the temperatures in parentheses: toluene (25°, 50°C), decahydronaphthalene (25°, 50°C), tetradecane (25°, 50°C), 4-methyl-2-pentanone (25°, 50°C), fluorocarbon FC 75 (fully fluorinated C_8 compound) (25°C), and octyl alcohol (25°C). The diffusivity of carbon dioxide has previously been determined in water (6.5° to 75°C) (Unver

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and Himmelblau, 1964; Thomas and Adams, 1965), ethyl alcohol (6.4° to 30°C) (Onda et al., 1961; Tang and Himmelblau, 1965; Davies et al., 1967), decahydronaphthalene (21.5° to 40°C) (Vielstich, 1956), hexadecane (25°, 50°C) (Hayduk and Cheng, 1971), benzene (25°C), toluene (25°C), carbon tetrachloride (25°C) (Tang and Himmelblau, 1965), ethylene glycol (25°C) (Hayduk and Malik, 1971), heptane (25°C), isobutyl alcohol (25°C), pentyl alcohol (25°C), some oils and kerosene (25°C) (Davies, et al., 1967), and ethyl, heptyl, and octyl alcohols (25°C) (Dim et al. 1971). So this work extends the variety of liquids and the temperature range for organic liquids.

EXPERIMENT

The diffusivities were measured by an unsteady state capillary cell technique similar to that used for hydrocarbon gases in water by Witherspoon and Saraf (1965). An advantage of this method is that no solubility data are required. A small diameter (less than 1 mm) capillary tube closed at one end, which had previously been brought to the experimental temperature, was filled with a saturated solution of carbon dioxide in the solvent at the same temperature, then immersed vertically with the open end upwards in a vessel containing the solvent (at the experimental temperature) and allowed to stand in a thermostat controlled to ±0.05°C for sufficient time for the average carbon dioxide concentration in the tube to decrease to 30 to 50% of its initial value (except for the fluorocarbon, where the decrease was to 40 to 80% of the initial value). The contents of the capillary tube were then transferred to the vacuum extractor of a gas chromatograph unit, the carbon dioxide completely desorbed from the liquid and the quantity determined chromatographically (Woollen, 1968). For the determinations with toluene at 25°C and the fluorocarbon, the capillary cell was formed from a microsyringe similar to that of Witherspoon and Saraf (1965); for the other liquids, precision bore capillary tubes sealed with a flat bottom at one end were used and the solutions were removed by a microsyringe with a fine needle while the tubes were immersed in the solvent. As the needle was moved down the capillary tube, solution was drawn into the syringe so that none was displaced out of the tube by the needle and, eventually, more than three times the volume in the tube was drawn into the syringe to ensure that all the solution was removed from the tube.

The diffusivity was calculated from the solution of the equation for one-dimensional diffusion (Witherspoon and Saraf, 1965)

$$\frac{M}{M_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \pi^2 \left(\frac{Dt}{4L^2} \right) \right]$$

The quantity of carbon dioxide initially in the solution in the tube M_0 was determined after each diffusion run by filling the capillary tube with saturated solution, immersing it briefly in the solvent, then transferring its contents to the vacuum extractor for analysis. If the atmospheric pressure was different from that when the tube was filled at the start of the diffusion run, the concentration was corrected for this by Henry's law. As a test of this method, the diffusivities of carbon dioxide in water and toluene at 25°C were determined; the values found (accuracy, ±3%) were 1.99×10^{-9} m^2/s for water (recent literature values are between 1.85×10^{-9} (Unver and Himmelblau, 1964) and 2.0×10^{-9} (Jeffreys and Bull, 1964) and 4.6×10^{-9} m^2/s for toluene (4.38×10^{-9}, Tang and Himmelblau, 1965). Also the value for octyl alcohol agrees with that found by Dim et al. (1971). However, the value found in this work for decahydronaphthalene at 25°C is 1.5 times that obtained by interpolation between the results of Vielstich (1956) using a laminar jet method for which solubility data are required.

The toluene, 4-methyl-2-pentanone, and octyl alcohol were Analar reagent quality and the decahydronaphthalene was technical grade; all were distilled before use. The tetradecane had been separated from a stock of straight chain paraffins by vacuum distillation and chromatographic analysis showed that its purity was at least 99.9%. Both it and the fluorocarbon were used without further purification. The densities and viscosities of the liquids were measured by a density bottle and U-tube viscometer, calibrated with water at the two temperatures. Table 1 contains the physical properties and diffusivity values obtained in this work. The precision shown for the diffusivities is the standard deviation of the arithmetic mean and the figure in parentheses after each value is the number of determinations made.

CORRELATION

Davies et al. (1967) found their results were best represented by Arnold's equation (Arnold, 1930); however, this equation contains empirical abnormality factors for both solute and solvent which limit its application. The present results are compared with values calculated from the Wilke-Chang correlation D_W (Wilke and Chang, 1955), the Lusis-Ratcliff correlation D_L (Lusis and Ratcliff, 1968), which was obtained for organic liquids, and the equation of Akgerman and Gainer D_A (1972b), based on a modified absolute rate theory.

The values of the association parameter in the Wilke-Chang equation were those given by Wilke and Chang (1955), except for octyl alcohol, where the value of 5.1 suggested by Lusis and Ratcliff (1971) for higher alcohols was used. The association number for 4-methyl-2-pentanone was taken to be one. The present results show that the Wilke-Chang equation is satisfactory for liquids with viscosities not exceeding 1×10^{-3} N s/m^2 (1 centipoise), irrespective of temperature and the nature of the liquid, but the predicted values are generally lower than experimental for more viscous liquids. This is similar to the conclusions of other investigators (Hayduk and Cheng, 1971; Akgerman and Gainer, 1972a,b). The correlation of Lusis and Ratcliff (1968) is slightly more satisfactory

TABLE 1. PHYSICAL PROPERTIES AND DIFFUSIVITIES

Liquid	Temp., °C	Density, kg/m^3	Viscosity, $\times 10^3$, Ns/m^2	Diffusivity $\times 10^9$, m^2/s			
				Exp.	D_W	D_L	D_A
Toluene	25	862	0.552	4.6 ± 0.1 (2)	4.64	5.26	3.15
	50	839	0.425	6.69 ± 0.15 (5)	6.58	7.45	4.99
Decahydronaphthalene	25	881	2.42	2.33 ± 0.04 (5)	1.29	1.45	1.80
	50	856	1.392	3.25 ± 0.19 (5)	2.44	2.77	3.23
Tetradecane	25	761	2.04	2.95 ± 0.03 (8)	1.83	2.24	1.76
	50	742	1.293	3.96 ± 0.14 (5)	3.14	3.86	2.94
4-methyl-2-pentanone	25	798	0.540	4.40 ± 0.06 (8)	4.93	5.85	3.50
	50	774	0.405	6.47 ± 0.29 (5)	7.13	8.43	5.12
Fluorocarbon FC75	25	1764	1.36	3.36 ± 0.20 (5)	4.09	3.13	3.55
Octyl alcohol	25	822	7.58	1.46 ± 0.07 (5)	0.90	0.48	1.49

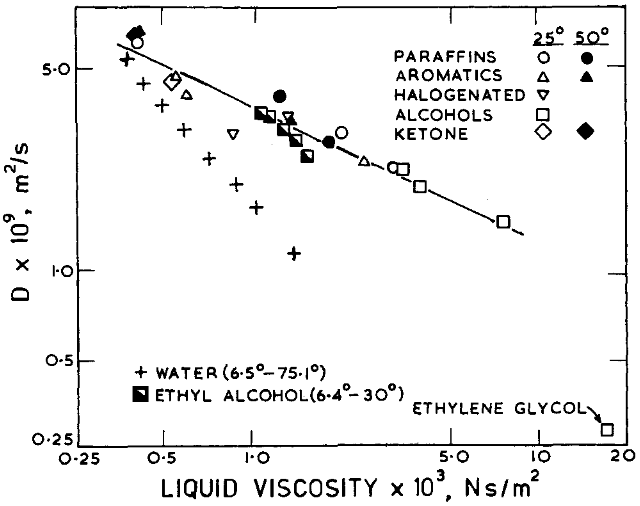

Fig. 1. Carbon dioxide diffusivity versus liquid viscosity, on log-log coordinates. The data sources, other than the present results, are given in the first paragraph.

for the more viscous liquids but does not predict the diffusivities in low viscosity liquids as well as the Wilke-Chang equation. The predictions from the Akgerman and Gainer (1972b) equation are low for the low viscosity liquids but more satisfactory for the liquids with viscosities above 1×10^{-3} N s/m². If the absolute error is defined by

$$\text{absolute \% error} = \left| \frac{\text{calculated} - \text{experimental}}{\text{experimental}} \right| \times 100$$

the average absolute error for the Akgerman and Gainer equation is 19.4%. This equation is more successful for gas diffusivities in water; for carbon dioxide in water the average absolute error is 5.6% (Akgerman and Gainer, 1972a).

A reason for the difficulty in representing diffusivities in water and organic liquids by a single equation is suggested by the log-log plot of carbon dioxide diffusivities against viscosity shown in Figure 1. The values for all the organic liquids except ethylene glycol can be represented by one line, but there is a distinctly different relationship for water, tending towards the organic liquids line at low viscosities. This could be caused by the different form of the molecular associations in water, such as hydrogen bonding, which would also apply to ethylene glycol, although on this basis the alcohols would be expected to differ from the other organic liquids. Hayduk and Cheng (1971) suggested a relationship between diffusivity and viscosity having the form $D = A\,\mu^B$, in which both A and B depend on the solute. For carbon dioxide they found $B = -0.44$; the least squares line of best fit of the results for the organic liquids shown in Figure 1 (except for ethylene glycol) is

$$D = 1.41 \times 10^{-10}\,\mu^{-0.47}$$

which agrees well with their value of B and provides more support for their view that a simple relationship between diffusivity and viscosity is useful for correlation and extrapolation purposes in liquids which do not form complexes.

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NOTATION

A, B = constants
D = diffusivity, m²/s
D_A = diffusivity predicted by Akgerman and Gainer equation, m²/s
D_L = diffusivity predicted by Lusis and Ratcliff equation, m²/s
D_W = diffusivity predicted by Wilke and Chang equation, m²/s
L = length of capillary cell, m
M = quantity of carbon dioxide in capillary at time t, moles
M_0 = quantity of carbon dioxide initially in capillary, moles
t = time, s
T = absolute temperature, K
μ = dynamic viscosity, N s/m²

LITERATURE CITED

Akgerman, A., and J. L. Gainer, "Predicting Gas-Liquid Diffusivities," *J. Chem. Eng. Data,* **17,** 372 (1972a).

———, "Diffusion of Gases in Liquids," *Ind. Eng. Chem. Fundamentals,* **11,** 373 (1972b).

Arnold, J. H., "Studies in Diffusion," *J. Am. Chem. Soc.,* **52,** 3937 (1930).

Davies, G. A., A. B. Ponter, and K. Craine, "The Diffusion of Carbon Dioxide in Organic Liquids", *Can. J. Chem. Eng.,* **43,** 372 (1967).

Davies, J. T., *Turbulence Phenomena,* Academic Press, New York (1972).

Dim, A., G. R. Gardner, A. B. Ponter, and T. Wood, "Diffusion of Carbon Dioxide into Primary Alcohols and Methyl Cellulose Ether Solutions," *J. Chem. Eng. Japan,* **4,** 92 (1971).

Hayduk, W., and S. C. Cheng, "Review of Relation between Diffusivity and Solvent Viscosity in Dilute Liquid Solutions," *Chem. Eng. Sci.,* **26,** 635 (1971).

———, and V. K. Malik, "Density, Viscosity and Carbon Dioxide Solubility and Diffusivity in Aqueous Ethylene Glycol Solutions," *J. Chem. Eng. Data,* **16,** 143 (1971).

Jeffreys, G. V., and A. F. Bull, "The Effect of Glycine Additive on the Rate of Absorption of Carbon Dioxide in Sodium Carbonate Solutions," *Trans. Inst. Chem. Engrs.* (London), **42,** T118 (1964).

Lusis, M. A., and G. A. Ratcliff, "Diffusion in Binary Liquid Mixtures at Infinite Dilution," *Can. J. Chem. Eng.,* **46,** 385 (1968).

———, "Diffusion of Inert and Hydrogen-Bonding Solutes in Aliphatic Alcohols," *AIChE J.,* **17,** 1492 (1971).

Onda, K., T. Okamoto, and Y. Yamagi, "Measurement of the Diffusivity of Carbon Dioxide in Liquids by Liquid Jets," *Mem. Fac. Eng. Nagoya Univ.,* **13,** 138 (1961).

Tang, Y. P., and D. M. Himmelblau, "Effective Binary Diffusion Coefficients in Mixed Solvents," *AIChE J.,* **11,** 54 (1965).

Thomas, W. J., and M. J. Adams, "Measurements of the Diffusion Coefficients of Carbon Dioxide and Nitrous Oxide in Water and Aqueous Solutions of Glycerol," *Trans. Faraday Soc.,* **61,** 668 (1965).

Unver, A. A., and D. M. Himmelblau, "Diffusion Coefficients of Carbon Dioxide, Ethylene, Ethane and Butene-1 in Water from 6° to 65°C", *J. Chem. Eng. Data,* **9,** 428 (1964).

Vielstich, W., "The Kinetics of Mass Transfer between Gases and Liquids," *Chem. Ing-Tech.,* **28,** 543 (1956).

Wilke, C. R., and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE J.,* **1,** 264 (1955).

Witherspoon, P. A., and D. N. Saraf, "Diffusion of Methane, Ethane, Propane and *n*-Butane in Water," *J. Phys. Chem.,* **69,** 3752 (1965).

Woollen, J. M., "Basic Processes of Interfluid Mass Transfer," Ph.D. thesis, Univ. Birmingham, England (1968).

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