Table III. Linear Regression Data and Dipole Moments at 25 °C in Benzene

compd	E_1	a	n_1^2	c	ρ	μ
1	2.2767	24.8345	2.2461	0.5695	0.8721	4.17[a]
	2.2927	23.2203	2.2469	0.5464	0.8727	4.02
2	2.2726	25.5534	2.2464	0.9553	0.8756	4.20[a]
	2.2692	26.1664	2.2464	0.8857	0.8737	4.26
3	2.2666	24.3511	2.2456	1.4573	0.8742	4.06[a]
	2.2627	23.6998	2.2450	1.6300	0.8737	3.98

[a] Determined from data in Table II.

data are given in Table II and the calculated parameters are given in Table III.

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Registry No. 1, 254-60-4; 2, 259-84-7; 3, 260-67-3; benzene, 71-43-2.

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Diffusivities of CO_2 and N_2O in Aqueous Alcohol Solutions

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The molecular diffusivities of CO_2 and N_2O were measured in aqueous solutions of glycerol and 1,5-pentanediol at 25 °C and 1 atm by the laminar-jet technique. Experimental results show that an equation of the form $(D/D_w)_{CO_2} = (D/D_w)_{N_2O}$ can also be applied to the gas-aqueous alcohol solutions studied in this work.

Introduction

Removal of gases from effluents is often encountered in industrial operations and is usually carried out by gas-liquid contacting. The design of gas-liquid contactors requires a knowledge of solubility and diffusivity data of the gas into liquid solution. There are correlations for the estimation of diffusivities of gases into nonreacting liquids, such as the Wilke-Chang (*1*) and the Akgerman-Gainer (*2*) equations, besides several empirical correlations (*3-5*). However, in the case of reacting gases the estimation or experimental measurement of solubilities is not possible because of the difficulty in modeling the simultaneous processes of mass-transfer and chemical reaction.

It has been suggested that the solubility and diffusivity of CO_2 in reacting solutions can be estimated by using the "N_2O analogy" (*6*). In view of the similarities of the CO_2 and N_2O molecules, it has been proven (*7-9*) for aqueous solutions of amines that solubilities and diffusivities of CO_2 and N_2O are related as follows:

$$\log (\alpha/\alpha_W)_{CO_2} = \log (\alpha/\alpha_W)_{N_2O} \qquad (1)$$

$$(D/D_W)_{CO_2} = (D/D_W)_{N_2O} \qquad (2)$$

The N_2O analogy for solubilities has been shown to be valid for alcohol solutions of analogous structures with some previously tested amines such as MEA and DEA (*10*). In the present work diffusivities of N_2O and CO_2 in glycerol and 1,5-pentanediol solutions were measured at 25 °C and it has been shown that a modified form of eq 2 also holds for alcohol solutions.

Experimental Section

Aqueous solutions of alcohols were prepared from distilled water and reagent grade alcohols, glycerol, and 1,5-pentanediol. All solutions used in absorption experiments were previously degassed by stirring under vacuum. The gases N_2O and CO_2 were supplied from commercial cylinders with purities of 99.5% and 99.998%, respectively.

Diffusivities were measured by the laminar-jet technique. The experimental setup was similar to the apparatus described by Scriven and Pigford (*11*). The laminar-jet chamber consists of a 36 cm long, 4 cm i.d. glass vessel with a hole in the bottom that allows draining of any liquid overflow. It is placed inside a constant temperature air bath, provided with a 500-W heating element, a small fan, and an electronic temperature controller. The solution is preheated to the desired temperature and fed to the capillary nozzle through a glass tube (30 cm long, 0.8 cm i.d.) with a bell-shaped entrance to the capillary of 0.14 cm i.d., similar to that used by Raimondi and Toor (*12*). The liquid from the nozzle flows to a capillary receiver (2 cm long, 0.18 cm i.d.) connected to a glass tube (30 cm long, 0.8 cm i.d.). The downstream end was connected to a constant-level overflow. The jet length was measured with a vernier caliper with an accuracy of ±0.005 cm. The gas was preheated to the experimental temperature and saturated with the solution. The liquid flow rate was obtained by measuring the volume of effluent liquid from the system as a function of time.

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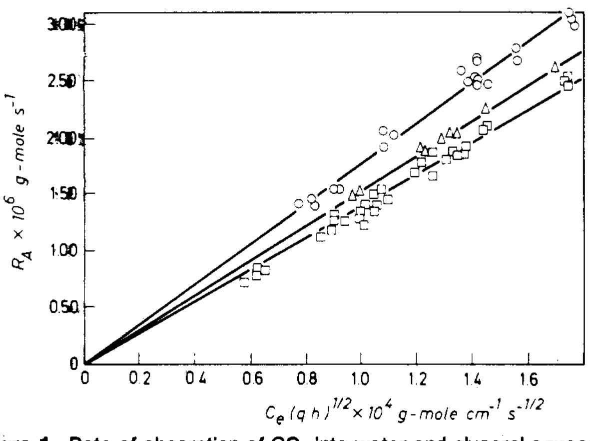

Figure 1. Rate of absorption of CO_2 into water and glycerol aqueous solutions at 25 °C: (○) CO_2/H_2O; (△) CO_2/glycerol 2%; (□) CO_2/glycerol 4%.

Between experiments, the jet chamber was purged with the gas. Once steady-state conditions were reached, the gas inlet was closed, and the flow of gas entering the jet chamber was measured with a soap film meter. Under these conditions, the flow of gas entering the chamber is equal to the rate of absorption. Experiments were repeated several times and data reported are based on the average of experiments measurements.

Results and Discussion

The rate of absorption of a slightly soluble, nonreacting gas in a laminar jet, using the penetration theory (*13*), is given by

$$R_A = 4(Dqh)^{1/2}(C_e - C_0) \qquad (3)$$

As $C_0 \simeq 0$, a plot of R_A vs $C_e(qh)^{1/2}$ at constant T and P should give a straight line with a slope of $4D^{1/2}$ and the diffusivity can thus be obtained.

The experimental technique was tested with the CO_2/water system at 25 °C and 1 atm; a plot of R_A vs $C_e(qh)^{1/2}$ is show in Figure 1. The data follow a straight line passing through the origin which proves that the hydrodynamic conditions in the laminar jet are quite ideal (*13*). The solubility of CO_2 under the experimental conditions was taken as 3.34×10^{-5} (g-mol)/cm^3 (*10*) and the diffusivity of CO_2 in water was found to be 1.98×10^{-5} cm^2/s at 25 °C by least-squares regression fitting. This result is within the range of the reported literature values which vary from 1.82 to 2.00×10^{-5} cm^2/s (*14*, *15*).

The rates of absorption of CO_2 into glycerol and 1,5-pentanediol aqueous solutions were also measured; data for the CO_2/glycerol system are shown in Figure 1.

The rates of absorption of N_2O into water and aqueous solutions of glycerol and 1,5-pentanediol were determined at 25 °C and 1 atm. The experimental data are illustrated in Figure 2 for the N_2O/water and N_2O/1,5-pentanediol solutions.

Experimental raw data for absorption of both CO_2 and N_2O into water, glycerol, and 1,5-pentanediol aqueous solutions at 25 °C are available in the supplementary material.

Solubilities of N_2O in water and in the alcohol solutions used in this work have been reported in the literature (*10*). The experimental molecular diffusivity of N_2O in water was found to be 1.61×10^{-5} cm^2/s at 25 °C which is of the same order of magnitude that the rather scatter values reported in the literature ranging from 1.69 to 2.57×10^{-5} cm^2/s (*15*).

The diffusivities at 25 °C and 1 atm for CO_2 and N_2O in dilute aqueous solutions of glycerol and 1,5-pentanediol are listed in Table I. The standard error of diffusivities estimation ranges from 0.001×10^{-5} to 0.005×10^{-5}.

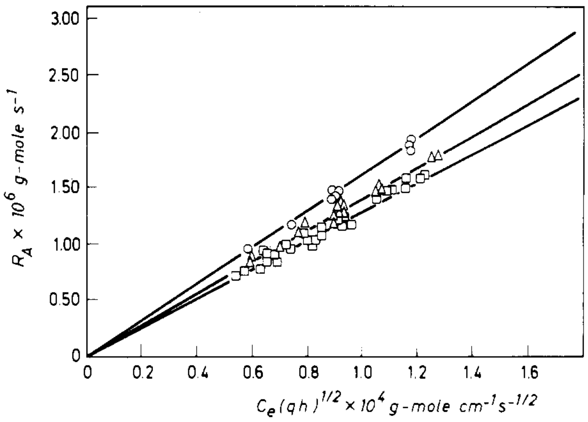

Figure 2. Rate of absorption of N_2O into water and 1,5-pentanediol aqueous solutions at 25 °C: (△) N_2O/1,5-pentanediol 2%; (□) N_2O/1,5-pentanediol 4%, (○) N_2O/H_2O.

Table I. Diffusivities of CO_2 and N_2O in Aqueous Alcohol Solutions at 25 °C

solute	mole fractn of solute	diffusivity, $10^5 \times cm^2/s$		γ
		CO_2	N_2O	
water		1.98	1.61	1.000
glycerol	0.02	1.47	1.29	1.018
	0.04	1.19	0.87	0.936
1,5-pentanediol	0.02	1.57	1.20	0.982
	0.04	1.28	1.02	1.021

Several attempts have been made to correlate diffusivities and viscosities of solutes using equations of the form $D\mu^k$ = constant (*16*, *17*) based on the Stokes-Einstein equation. However, relationships do not hold. The equation proposed by Joosten and Danckwerts (*9*), eq 2, seems to give better results.

Under the same experimental conditions, from eq 3 and making use of the "N_2O analogy", it would be possible to obtain the following relationship:

$$(C_eD^{1/2})_{CO_2}/(C_eD^{1/2})_{N_2O} = \text{constant} \qquad (4)$$

The ratio defined by eq 4 is equal to 1.523 when pure water is used as solvent and, hence, a parameter γ which is a measure of deviation of aqueous solutions from water may be defined as

$$\gamma = 1.523(C_eD^{1/2})_{N_2O}/(C_eE^{1/2})_{CO_2} \qquad (5)$$

For the dilute solutions studied in this work, γ values are close to unity, as shown in Table I. Further, diffusivities can be predicted with an average deviation of 3% when γ is assumed equal to unity, as compared with the 6.7% deviation obtained when eq 2 is used.

Glossary

C	liquid concentration of the gas species, (g-mol)/cm^3
D	diffusivity, cm^2/s
h	jet length, cm
q	liquid volumetric flow rate, cm^3/s
R_A	rate of absorption of solute A, (g-mol)/s
α	Bunsen absorption coefficient, cm^3 of gas/cm^3 of solution
μ	viscosity of the liquid solution, cP
γ	parameter defined in eq 5

Subscripts

e	equilibrium
0	initial
w	in water

Registry No. N_2O, 10024-97-2; CO_2, 124-38-9; glycerol, 56-81-5; 1,5-pentanediol, 111-29-5.

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Supplementary Material Available: Experimental raw data for absorption of both CO_2 and N_2O into water, glycerol and 1,5-pentanediol aqueous solutions at 25 °C (4 pages). Ordering information is given on any masthead page.

Heats of Mixing of Binary Systems of *n*-Butylamine with Toluene and Methylcyclohexane at 288.15, 298.15, and 308.15 K

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Heats of mixing of *n*-butylamine with toluene and with methylcyclohexane were measured at three temperatures in an isothermal dilution calorimeter. Experimental results were fitted with a Redlich–Kister polynomial. Both the experimental data and the Redlich–Kister coefficients for the smoothing of the data are reported.

Recent studies of the quasi-chemical group approach to model liquid mixtures (*1*, *2*) have confirmed the importance of accurate heat-of-mixing data for the evaluation of group interaction parameters. A knowledge of the interactions of the amino group with other organic groups may be of potential use for the extension of group models to systems of interest in biochemical studies. Previous studies in our laboratory (*3*, *4*) have concentrated on binary systems containing amines with *n*-alkanes and *n*-alcohols. This work presents heats of mixing data for butylamine with toluene and with methylcyclohexane in an attempt to cover the interactions of the amine group with substituted aromatic and aliphatic rings. Measurements in this study were made at 288.15, 298.15, and 308.15 K.

Materials and Apparatus

The materials used in this work were all supplied by Aldrich Chemical Co. with a stated purity of 99 mol %. The materials were used without further purification. Refractive indices of the chemicals, measured in a Bausch and Lomb refractometer, are compared with literature values in Table I.

The heats of mixing measurements were made in an isothermal semicontinuous dilution calorimeter of Van Ness type described in detail previously (*3*). In this work, the calorimeter was used in its endothermic mode of operation and perfluoroelastometer O-rings were used for the work with amine (*4*). The performance of the calorimeter was checked periodically by measuring the system 1-pentanol + *n*-heptane at 298.15 K (*5*). Its accuracy is believed to be within 1%, judging by the

Table I. Refractive Indices of the Pure Compounds at 298.15 K

compound	refractive index: this work	refractive index: lit. value	ref
toluene	1.4939	1.49405	*6*
methylcyclohexane	1.4210	1.4206	*7*
n-butylamine	1.3985	1.3991	*8*

Table II. Experimental Heats of Mixing Values for the System *n*-Butylamine (1) + Toluene (2)

x_1	ΔH, J/mol	x_1	ΔH, J/mol	x_1	ΔH, J/mol
		$T = 288.15$ K			
0.0449	117.4	0.4134	586.8	0.7594	411.7
0.1237	291.5	0.4581	592.1	0.8079	346.7
0.1587	352.6	0.5083	589.0	0.8634	261.2
0.2199	441.6	0.5459	582.2	0.8939	209.3
0.2730	502.8	0.5977	558.2	0.9266	149.9
0.3196	538.9	0.6432	527.9		
0.3604	563.3	0.6965	480.9		
		$T = 298.15$ K			
0.0429	104.4	0.4037	554.4	0.7588	392.6
0.0827	189.4	0.4481	564.8	0.8073	331.3
0.1530	316.8	0.5019	564.8	0.8626	249.8
0.2130	403.2	0.5576	552.6	0.9259	145.4
0.2652	462.0	0.6117	523.7	0.9610	79.3
0.3108	503.2	0.6595	490.4		
0.3512	530.6	0.7156	439.8		
		$T = 308.15$ K			
0.0411	93.3	0.4074	527.1	0.7827	350.7
0.0788	170.0	0.4495	535.6	0.8341	283.8
0.1470	288.1	0.5077	536.5	0.8624	241.0
0.2053	369.8	0.5581	523.6	0.9260	138.9
0.2561	427.9	0.6120	500.2	0.9619	73.3
0.3007	467.4	0.6776	457.0		
0.3584	506.0	0.7159	421.9		

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