Glossary

K	number of data
M	molecular mass, kg mol^{-1}
x	liquid mole fraction
ν	kinematic viscosity, μm^2 s^{-1}

Subscripts

calcd	calculated
exptl	experimental
i	pure-component property
$iijk$	four-body interaction parameter
mix	mixture property

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Diffusion Coefficients and Solubilities of Carbon Dioxide in Binary Mixed Solvents

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The diffusion coefficients and the solubilities of carbon dioxide in binary systems of miscible solvents over the full range of liquid compositions were determined simultaneously from the relationship between the transient rate of gas absorption and the contact time in a modified diaphragm cell. The binary mixtures studied were selected from various systems on the basis of their viscosity behavior: *n*-propyl alcohol–ethyl alcohol, carbon tetrachloride–benzene, *n*-propyl alcohol–benzene, *n*-octyl alcohol–carbon tetrachloride, methyl alcohol–water, ethyl alcohol–water, *n*-propyl alcohol–water, and isobutyl alcohol–formamide. The results obtained are also discussed in terms of semiempirical correlations.

Introduction

Liquid-diffusion coefficients of gases have both practical and theoretical importance. In order to determine the liquid-diffusion coefficient by using a liquid-jet column (gas–liquid system) or a conventional diaphragm cell (liquid–liquid system), it is necessary to know the solubility or the concentration of gases in the liquid. However, there are few data on the solubility of gases in mixed solvents, and also it is difficult to evaluate the solubilities for mixed solvents from those for their pure-solvent components (*1*).

According to Takeuchi et al. (*2*), on the other hand, from the relationship between the transient absorption rate and the contact time for gas absorption in a modified diaphragm cell the diffusion coefficient and the solubility of a gas in liquids can be determined simultaneously with an accuracy suitable for engineering purposes. In this work, by means of such a simultaneous determination, the diffusion coefficients and the solubilities of CO_2 in various systems of two miscible solvents were obtained, the results being discussed in terms of semiempirical correlations.

Experimental Section

The experimental apparatus shown schematically in Figure 1 is identical with that described in previous papers (*2*, *3*). The geometric interfacial area of the diaphragm and the volume of the lower compartment of a diaphragm cell (1) are 5.81 cm^2 and 53.5 cm^3, respectively. A Millipore filter (mean pore size: 10.0 μm; thickness: 125 ± 15 μm; porosity: 0.68) made of Teflon (labeled LC) was used as the diaphragm after being wetted well with a mixed solvent as the absorbent. A stirrer (2) was rotated by a magnet (3) at the same 1.33 rotations/s as in the previous works (*2*, *3*).

Carbon dioxide was introduced from a gas cylinder (7) into the upper compartment of the cell through two saturators (8). A U-type glass tube (4) fitted with a mercury bottle (5) was used for measuring the absorption rate of CO_2 into the mixed solvents. All parts of the apparatus were set in a water bath (6), whose temperature was controlled at 298 ± 0.1 K. The experimental procedure has been described elsewhere (*2*, *3*).

Binary mixed solvents were selected from various systems by a classification procedure proposed by Ishikawa (*4*) on the basis of viscosity–composition curves, which has taken the chemical properties of the liquids into consideration, that is, the ideal systems (*n*-propyl alcohol–ethyl alcohol and carbon tetrachloride–benzene), the system with a minimum in the liquid viscosity (*n*-propyl alcohol–benzene), the system with a concave type of viscosity–composition curve (*n*-octyl alcohol–carbon tetrachloride), the systems with a maximum in the liquid viscosity (methyl alcohol–water, ethyl alcohol–water, and *n*-propyl alcohol–water), and the system with a minimum and a maximum in the liquid viscosity (isobutyl alcohol–formamide). The chemicals used were of special grade. Solutions of the binary mixtures studied were prepared and degassed by refluxing at total reflux for 5 h; their compositions were determined by measuring their densities or refractive indexes.

Results and Discussion

For the apparatus, in which the so-called film-theory model is applicable to a process of gas absorption (*3*), the transient absorption rate into the finite volume of liquid is given by

$$N_A a = \frac{a}{l} D_A A_i \exp\left\{-\frac{D_A t}{l^2(V/a - 1)}\right\} \qquad (1)$$

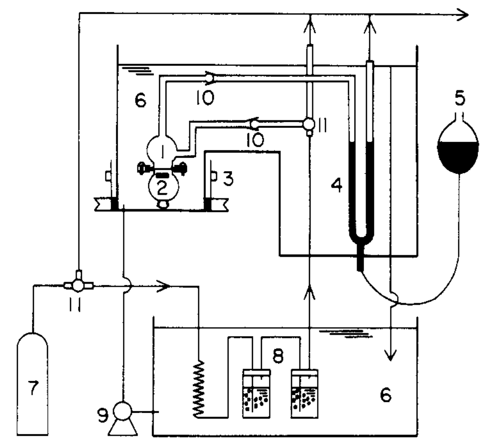

Figure 1. Schematic diagram of experimental apparatus: (1) diaphragm cell, (2) stirrer, (3) rotary magnet, (4) U-type glass tube, (5) mercury bottle, (6) constant-temperature bath, (7) CO_2 cylinder, (8) saturator, (9) pump, (10) ball joint, (11) three-way cock.

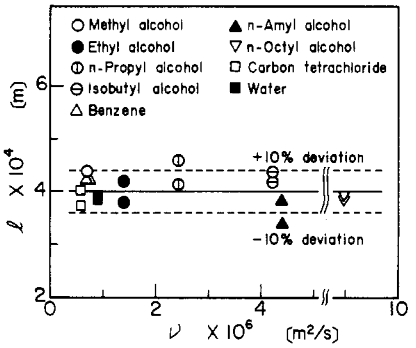

Figure 2. Film thickness for LC diaphragm.

Table I. Diffusion Coefficients and Solubilities of CO_2 for Mixtures with an Ideal Viscosity–Composition Curve at 298 K

	$10^3\mu_m$,[b]	10^9D_A, m²/s		A_i, mol/m³	
x_B[a]	Pa s	obsd	lit. (ref)	obsd	lit. (ref)
	n-Propyl Alcohol (B)-Ethyl Alcohol (C)				
0.00	1.08	3.86	3.66 (*11*)	107	112 (*12*)
0.20	1.24	3.72		88.8	
0.40	1.39	3.50		76.6	
0.60	1.55	3.33		76.5	
0.80	1.71	3.26		71.8	
1.00	1.97	3.06	[3.52][c] (*7*)	62.9	97.8 (*12*)
	Carbon Tetrachloride (B)-Benzene (C)				
0.00	0.60	3.85	4.05 (*11*)	92.9	91.5 (*12*)
0.20	0.64	3.65		86.7	
0.40	0.70	3.60		84.1	
0.60	0.76	3.35		82.2	
0.80	0.82	3.25		72.0	
1.00	0.88	3.17	2.95 (*11*)	91.2	86.0 (*12*)

[a] Mole fraction of B. [b] Reference *4*. [c] At 303 K.

Then, the diffusion coefficient D_A and the solubility A_i of the gas in the liquid are obtained from the slope and the intercept, respectively, of a straight line correlated by plotting log (N_Aa) vs. t, provided that the film thickness l is given.

The value of l for the LC diaphragm was examined by using the slope of the straight line and the values of D_A in the literature (*2*, *5–11*). Figure 2 shows the effect of kinematic viscosity ν on l. As shown in the figure, the behavior of l is almost independent of ν in the same fashion as in the previous work (*2*). Then, the mean value of the effective film thickness is found to be

$$l = 4.00 \times 10^{-4} \tag{2}$$

In this calculation, the geometric area of the diaphragm,

Table II. Diffusion Coefficients and Solubilities of CO_2 for *n*-Propyl Alcohol (B)-Benzene (C) Solutions with a Minimum in the Liquid Viscosity at 298 K

	$10^3\mu_m$,[b]	10^9D_A, m²/s		A_i, mol/m³	
x_B[a]	Pa s	obsd	lit. (ref)	obsd	lit. (ref)
0.00	0.60	3.85	4.05 (*11*)	92.9	91.5 (*12*)
0.20	0.61	3.95		71.4	
0.40	0.62	4.18		69.1	
0.60	0.67	4.20		59.0	
0.80	1.49	3.20		71.0	
1.00	1.97	3.06	[3.52][c] (*7*)	62.9	97.8 (*13*)

[a] Mole fraction of *n*-propyl alcohol. [b] Reference *4*. [c] At 303 K.

Table III. Diffusion Coefficients and Solubilities of CO_2 for *n*-Octyl Alcohol (B)-Carbon Tetrachloride (C) Solutions with a Concave Viscosity–Composition Curve at 298 K

	$10^3\mu_m$,[b]	10^9D_A, m²/s		A_i, mol/m³	
x_B[a]	Pa s	obsd	lit. (ref)	obsd	lit. (ref)
0.00	0.88	3.17	2.95 (*11*)	91.2	86.0 (*12*)
0.20	1.40	2.70		68.8	
0.40	2.25	2.40		71.7	
0.60	3.55	1.96		73.7	
0.80	5.25	1.80		55.4	
1.00	7.35	1.53	1.46 (*6*)	49.6	74.2 (*6*)

[a] Mole fraction of *n*-octyl alcohol. [b] Reference *4*.

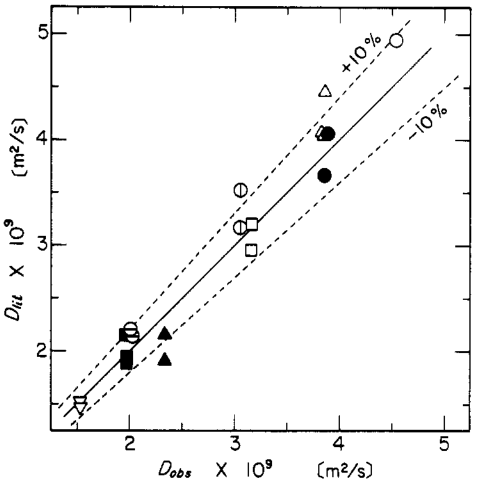

Figure 3. Comparison for diffusion coefficients of CO_2 in pure solvents between experimental results and literature values. Symbols are the same as those in Figure 2.

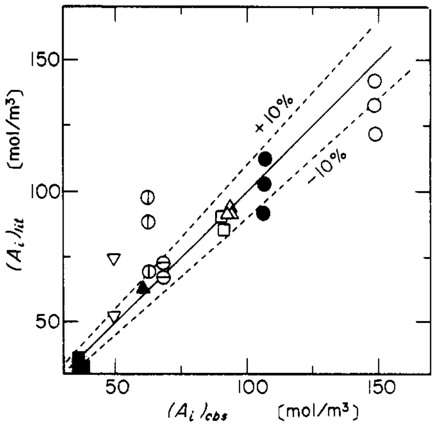

Figure 4. Comparison for solubilities of CO_2 in pure solvents between experimental results and literature values. Symbols are the same as those in Figure 2.

Table IV. Diffusion Coefficients and Solubilities of CO_2 for Alcohol (B)-Water (C) Solutions with a Maximum in the Liquid Viscosity at 298 K

	$10^3\mu_m$,[b]	10^9D_A, m²/s		A_i, mol/m³	
x_B[a]	Pa s	obsd	lit. (ref)	obsd	lit. (ref)
Methyl Alcohol (B)-Water (C)					
0.00	0.89	1.97	1.94 (*9*)	35.6	32.8 (*12*) 32.8[d] (*14*)
0.20	1.50	1.98		36.5	34.7[d] (*14*)
0.40	1.45	2.30		44.9	47.4[d] (*14*)
0.60	1.16	2.76		66.2	71.0[d] (*14*)
0.80	0.85	3.60		107	102[d] (*14*)
1.00	0.55	4.54	8.02 (*8*)	149	122 (*12*) 142[d] (*14*)
Ethyl Alcohol (B)-Water (C)					
0.00	0.89	1.97	1.94 (*9*)	35.6	32.8 (*12*) 32.8[d] (*14*)
0.20	2.34	1.76		29.7	32.1[d] (*14*)
0.40	2.15	2.06		46.8	50.0[d] (*14*)
0.60	1.79	2.60		58.2	68.7[d] (*14*)
0.80	1.44	3.05		72.1	85.9[d] (*14*)
1.00	1.08	3.86	3.66 (*11*)	107	112 (*12*) 103[d] (*14*)
n-Propyl Alcohol (B)-Water (C)					
0.00	0.89	1.97	1.94 (*9*) [2.15][c] (*7*)	35.6	32.8 (*12*) 32.8[d] (*15*)
0.20	2.47	1.76	[1.89][c] (*7*)	35.2	40.8[d] (*15*)
0.40	2.56	2.04	[2.30][c] (*7*)	50.6	57.2[d] (*15*)
0.60	2.35	2.30	[2.71][c] (*7*)	53.8	68.4[d] (*15*)
0.80	2.14	2.69	[3.12][c] (*7*)	58.8	77.6[d] (*15*)
1.00	1.97	3.06	[3.52][c] (*7*)	62.9	97.8 (*12*) 88.7[d] (*15*)

[a] Mole fraction of alcohol. [b] Reference *4*. [c] At 303 K. [d] Interporated value.

Table V. Diffusion Coefficients and Solubilities of CO_2 for Isobutyl Alcohol (B)-Formamide (C) Solutions with a Minimum and a Maximum in the Liquid Viscosity at 298 K

	$10^3\mu_m$,[b]	10^9D_A, m²/s		A_i, mol/m³	
x_B[a]	Pa s	obsd	lit. (ref)	obsd	lit. (ref)
0.00	3.30	0.946		75.6	
0.20	3.64	1.15		77.8	
0.40	3.86	1.27		86.7	
0.60	3.68	1.49		87.8	
0.80	3.31	1.76		86.0	
1.00	3.36	2.02	2.20 (*5*)	68.1	72.8 (*12*)

[a] Mole fraction of isobutyl alcohol. [b] Reference *4*.

$\pi d^2\epsilon/4$, was used as the interfacial area a.

The experimental values of D_A and A_i of CO_2 in nine kinds of pure solvents are given in Tables I–V, together with the literature values (*5-9*, *11-15*); the comparisons between those for D_A and A_i are shown in Figures 3 and 4, respectively, wherein the broken lines represent deviations of ±10%.

As for eight of the mixtures, the results obtained are also shown in Tables I–V over the full range of liquid compositions. To obtain these data, the experimental runs were conducted several times for each mixture, and then the respective deviations of N_Aa from the straight line of the log (N_Aa) vs. t plot were less than 10%. This fact suggests good reproducibility of the present work.

For the isobutyl alcohol-formamide solution as a typical example, which shows a complicated behavior of the viscosity, the values of A_i and D_A are plotted in Figure 5 against the mole fraction of isobutyl alcohol (x_B) in the mixture, together with the viscosity data (*4*). The solid lines corresponding to A_i and D_A represent the calculated values from eq 3 and 4, respectively, which will be described later; both of the results for A_i and D_A are in satisfactory agreement with the respective curves, though the deviation for A_i is a little larger than that for D_A.

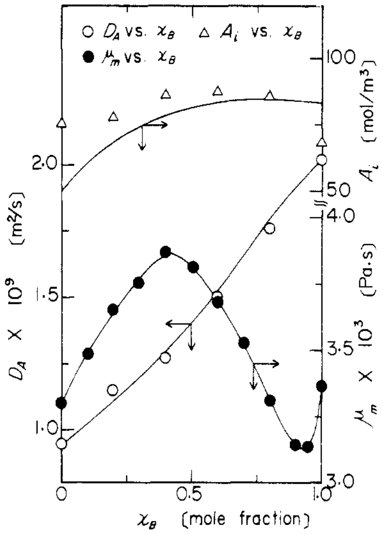

Figure 5. Diffusion coefficients and solubilities of CO_2 in mixture of isobutyl alcohol and formamide, together with viscosities of mixture at 298 K.

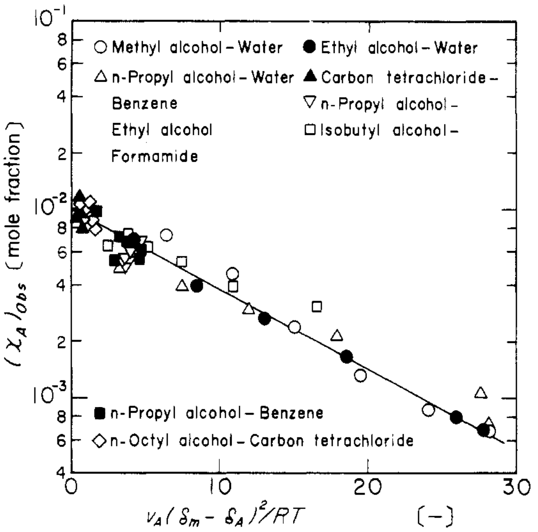

Figure 6. Plots of x_A vs. $v_A(\delta_m - \delta_A)^2/RT$ for binary mixtures.

The solubilities of CO_2 in the binary mixtures were examined on the basis of the thermodynamics for vapor-liquid equilibrium (*16*). The equilibrium concentrations of CO_2 (x_A) in the mixtures at a CO_2 pressure of 1.013 × 10^5 Pa were calculated from the values of A_i given in Tables I–V; the semilogarithmic plots of x_A vs. $v_A(\delta_m - \delta_A)^2/RT$ are shown in Figure 6, where values of the saturated vapor pressures of the mixtures at 298 K were calculated from the vapor pressures of the pure solvents (*17*) and the activity coefficients were estimated from the Wilson equation with the parameters according to Hirata et al. (*18*) and Kojima et al. (*19*). In addition, to determine the solubility parameter of the binary mixtures δ_m, we calculated the heats of vaporization of the mixtures from the literature values for the pure solvents at 298 K (*17*) and the activity coefficients mentioned above. Furthermore, the molar volumes of the mixtures (v_m) were evaluated from the literature (*20*) and/or the observed values of the density at 298 K, whereas a value of 388 kJ/m³ was taken as the solubility parameter of CO_2 gas (δ_A) at 298 K (*21*). As Figure 6 shows, the data points of x_A fall reasonably well on a straight line, which is expressed by

$$\log x_A = -2 - 0.0424v_A(\delta_m - \delta_A)^2/RT \qquad (3)$$

The deviations of data points from eq 3 are within 10% for most of the mixtures used in this work.

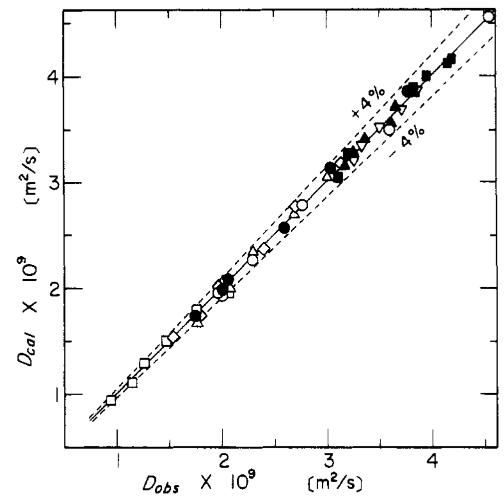

Figure 7. Comparison for diffusion coefficients of CO_2 in binary mixtures between experimental results and calculated values from eq 4 with $n = {}^1/_3$. Symbols are the same as those in Figure 6.

On the other hand, the diffusion coefficients of CO_2 in binary mixtures can be estimated by the same equation as in a previous paper (*22*), that is, eq 4 based on the activated state theory.

$$D_{Am}\mu_m^{\,n} = \sum x_i D_{Ai}\mu_i^{\,n}(v_m/v_i)^{(2/3)-n} \tag{4}$$

Then, the value of n in eq 4 was examined from the viscosity data (*4*).

Figure 7 shows the comparison between the diffusion coefficients D_{Am} calculated from eq 4 with the same $n = {}^1/_3$ as found by Fukushima et al. (*7*) and the results obtained in this work, wherein the deviations are within 4%.

From such examinations, we may conclude that the solubility and the diffusion coefficient of CO_2 in various binary mixtures based on viscosity–composition curves are evaluated with a reasonable accuracy from eq 3 and 4 with $n = {}^1/_3$, respectively.

Glossary

A_i	solubility of gas in liquid, mol/m³
a	gas–liquid interfacial area, m²
D	diffusion coefficient of gas in liquid, m²/s
l	thickness of stagnant liquid film, m
n	constant of eq 4
N_A	absorption rate of gas into liquid, mol/(m² s)
R	gas constant, J/(mol K)
T	temperature, K
t	gas–liquid contact time, s
V	volume of liquid-side cell, m³
v	molar volume, m³/mol
x	mole fraction in liquid phase

Greek Letters

δ	solubility parameter, (kJ/m³)$^{1/2}$
ϵ	porosity of membrane
μ	viscosity, Pa s
ν	kinematic viscosity, m²/s

Subscripts

A	diffusing component
B	B component in mixture (system of B–C)
C	C component in mixture (system of B–C)
i	i component
m	mixture

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Excess Volumes of Binary Mixtures of *o*-Xylene + *n*-Alkanes

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Excess volumes of the binary mixtures *o*-xylene + *n*-hexane, + *n*-octane, + *n*-decane, + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane have been measured at 298.15 K as a function of composition. Measurements were made in a semicontinuous dilution dilatometer.

Introduction

Excess volume measurements of hydrocarbon mixtures have been widely used to check liquid-state theories. Binary mixtures of xylene + *n*-alkanes have been chosen to extend our investigations in order to study the influence of methyl groups and

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