

Diffusion of Carbon Dioxide in Tetradecane

Li-Sheng Wang* and Chang-Yu Sun

School of Chemical Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

The binary diffusion coefficients of CO₂ in tetradecane were measured at 311 K and 1.905 MPa by dissolution of CO₂ in liquid tetradecane. On the basis of the constant diffusivity diffusion theory of Reamer et al., the diffusion coefficients were first obtained from the injected CO₂ volume vs time data and the solubility of CO₂ in liquid tetradecane. An uncertainty function F_t , similar to the data analysis of Liu et al. for uptake curves of gases in zeolite, was introduced to describe the diffusion process, and a linear relationship has been deduced for the evaluation of the diffusion coefficients at different diffusion times from the dissolution data. The diffusivity variation during the diffusion process can be represented by a concentration/time-dependent diffusivity D_t . The applicability of the new method has been tested in the binary diffusion of the CO₂-tetradecane system measured in this work and for the diffusion data of the methane-hydrocarbon systems of Reamer et al. The concentration-dependent diffusion coefficients obtained were compared with the existing diffusion coefficient data.

Introduction

In the development of numerical simulation technology of tertiary displacements of reservoir crude oil by CO₂, molecular diffusion is considered to play an important role in determining the concentration front. The traditional method for measuring the diffusion coefficients of a gas in a liquid (such as methane in liquid hydrocarbons) was developed by Reamer et al. (1956). A computer-aided system has been developed by Wang et al. (1996) for measuring the injected CO₂ volume vs time data and the solubility of CO₂ in liquid hydrocarbons, which can be used to obtain the diffusion coefficient based on Reamer's analysis method. However, according to this method, the diffusion coefficient was supposed constant at the specified temperature and pressure. This kind of data cannot satisfy the needs for the knowledge of concentration dependency of the diffusion coefficients in a reservoir simulation.

Much work have been done in the past years for determining concentration-dependent Fick diffusion coefficients. In the early theories, a concentration distribution function was required, but it was difficult to determine such a function. Liu et al. (1994) recognized that though the diffusion coefficient is a function of concentration, the \sqrt{t} law is usually valid for short time region. On the basis of the kinetic theory for pure gas adsorption in zeolites, they proposed that the solution of the concentration-dependent diffusion equation could be represented by the combination of an uncertainty function with the solution for a constant-diffusion coefficient. In this paper, by combination with Reamer's analysis method, Liu's method is extended to a gas-liquid binary diffusion system. Examples of concentration-dependent diffusion coefficients obtained over a range of concentrations from a single dissolution test based on the new method and that assuming a constant diffusion coefficient for the CO₂-tetradecane system are both be tested.

Experimental Section

The experimental method involved the introduction of CO₂ in the gas phase into either a quiescent CO₂-hydrocarbon liquid mixture or a pure hydrocarbon. To start the test, CO₂ from the storage cylinder was injected at constant temperature and pressure into the diffusion cell in contact with the liquid, and the quantity of CO₂

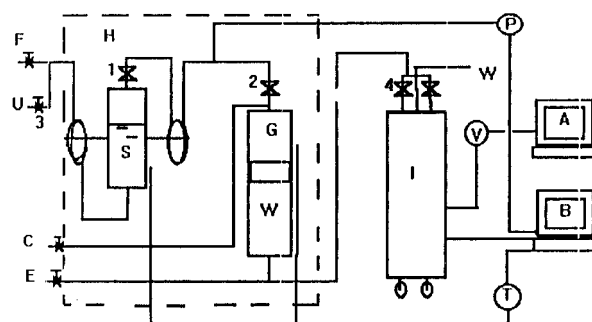


Figure 1. Schematic flow diagram of the diffusion coefficient measurement system: (A) computer-controlled data logger, (B) computer control of pressure/temperature, (C) CO₂ cylinder, (E) effluent water reservoir, (F) flash separator, (G) injection gas cylinder, (H) constant temperature bath, (I) metering pump for water injection, (P) pressure transducer, (S) diffusion cell, (T) temperature transducer, (U) vacuum pump, (V) linear position transducer, (W) water (pressure transmitting agent), (1–4) computer-controlled valves.

necessary to maintain a constant pressure was determined as a function of time.

The schematic diagram of the experimental system is shown in Figure 1. The apparatus employed included a water injection metering pump (CORE Lab. model 310-FDS) with computer-aided controlling and recording systems (including volume data logger, pressure and temperature controllers, a linear position transducer for injected CO₂ volume measurement, and the temperature and pressure transducer connected to them), a solvent reservoir RUSKA PVT cell contained within a oil bath (accurate to about ± 0.2 °C, the oil was agitated by a stirrer that was located on a base isolated from the oil bath, to avoid vibration that might affect the diffusion rate) was used for diffusion test; it had a volume of 650 cm³, with 5 cm³ pipeline volume from the bottom of the cell to the solvent effluent valve. This cell could be used for vapor-liquid equilibrium tests as well, through a rocking apparatus and a mass transfer test. It can be fixed in a vertical position during the diffusion process and is connected to a variable volume gas sample storage cylinder from the top (the cylinder was contained within a constant temperature air bath to about ± 0.5 °C). The 310-FDS pump was used for injecting water into the lower portion of the gas cylinder

Table 1. Diffusion Results at 311.0 K and 1.905 MPa for the CO₂ + Tetradecane System^a

time (min)	V(CO ₂) added (cc)	time (min)	V(CO ₂) added (cc)
0	0		
20.8	81.5	151.0	317.2
23.7	93.2	169.6	333.5
28.6	108.3	190.6	350.3
38.3	136.2	198.1	353.5
41.6	144.5	213.4	360.1
45.8	153.6	268.8	389.8
49.8	162.0	279.9	395.6
59.2	183.8	318.4	405.4
63.5	194.6	329.8	407.5
68.1	204.6	383.3	419.2
71.9	212.0	427.2	430.3
75.6	217.9	446.3	436.2
83.1	227.3	451.8	437.7
117.3	280.3	466.4	441.7
120.8	286.5	488.3	447.8
137.5	305.0	517.5	456.1
143.8	309.8	541.6	461.0
145.2	311.2	559.3	463.8
147.6	313.5	598.8	466.7
149.8	315.8	611.9	467.0

^a Initial condition: absolute pressure = 0.

to maintain the system at a constant pressure (a constant pressure injection mode was selected for the pump, and the pressure oscillation is within ± 0.5 psig). The diffusion coefficient may be determined from the time/volume data on the basis of the analytical method as described in the next section. Considering total effects of the temperature and pressure oscillation on the obtained time/volume data, the uncertainty of the volume was within 0.4%. The detailed description and calibration for the apparatus and the materials utilized in this study have been reported in the previous paper (Wang et al., 1996). After the diffusion test was completed, the rocking apparatus for the diffusion cell was opened, the temperature and pressure were kept constant at same time, and the accumulative volumes of injected CO₂ were recorded continuously until the injection rate became zero. Then the system was considered to have reached equilibrium, and the total amount of injected CO₂ was used to calculate the solubility. The volumes of injected CO₂ into quiescent liquid *n*-tetradecane vs time data measured at constant pressure and temperature are listed in Table 1.

Method of Analysis Based on a Concentration-Independent Diffusion Coefficient

With the assumption of a constant D , the mass transfer equation of a single-component gas k by diffusion into a one-dimensional quiescent liquid phase is expressed as

$$\frac{\partial C}{\partial t} = D_k \frac{\partial^2 C}{\partial x^2}$$

$$C(x,0) = C_0; \quad C(0,t) = C_{k,e}; \quad C(\infty,t) = C_0 \quad (1)$$

where D_k refers to the Fick diffusion coefficient of gas k in the liquid phase (m²/s), C refers to the concentration of diffusing species i in the liquid phase (kg/m³), and t and x are the diffusion time and distance, respectively. The solution of eq 1 is the concentration as a function of diffusion distance, x , and time, t (Crank, 1975):

$$C(x,t) = C_{i,e} \operatorname{erfc}\left\{\frac{x}{[2(D_k t)]}\right\} \quad (2)$$

An expression for the mass injected into the cell at time t was obtained by Reamer et al. (1956) by integration of

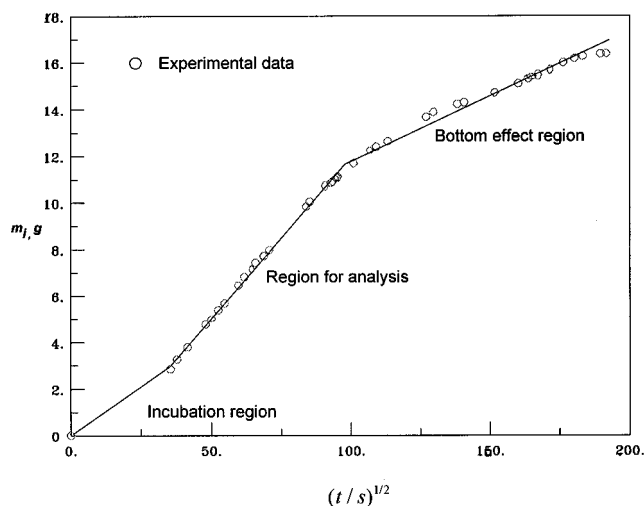


Figure 2. Mass of CO₂ injected vs square root of time for constant diffusion measurement of the CO₂ + tetradecane system at 311.0 K and 1.905 MPa.

eq 2 over the given time t and diffusion distance x :

$$m_i = \frac{2A\Delta C_{k,e}}{\sqrt{F_1 F_2 \pi}} \sqrt{D_k t} \quad (3)$$

in which A is diffusion area (m²), $\Delta C_{k,e} = C_{k,e} - C_0$, where $C_{k,e}$ and C_0 are the concentration at equilibrium and the initial concentration (concentration at $t = 0$ in the diffusion test) of component k in the liquid phase, respectively. The weight correction factor and volume correction factor, F_1 and F_2 , are defined in the Appendix. From the linear relationship of the mass injected into the cell, m_i , and the square root of time, the diffusion coefficient can be obtained from the slope. The data of Table 1 correspond to those presented in Figure 2. To correct the volume data masses, the density data of CO₂ at the test temperature and pressure from Vagafik (1975) have been employed.

At the beginning and end times, the three assumptions made in the Appendix could not be satisfied. As expected, there is a significant deviation from the linear relationship predicted by eq 3 at the beginning and near the end of the diffusion operation. As indicated earlier by Reamer et al., the curvature at the beginning represents an "incubation region" during which CO₂ dissolves in the liquid phase at the gas/liquid interface, thereby establishing the boundary condition. The deviation at the end is caused by concentration changes at the bottom of the diffusion cell becoming important (at this time the assumption of $C(\infty,t) = C_0$ is not true), so it is called the "bottom effect region". Only the linear relation in the middle part, termed "region for analysis", can be used for obtaining the diffusion coefficient. Therefore, the applicability of the theory is limited to a particular range of concentration.

In addition, to correct the obtained diffusion coefficient, F_1 and F_2 have to be calculated first, which requires the average concentration \bar{C} during the process to be estimated by integration of eq 2 (in this case, D_k is the diffusion coefficient with neglect of F_1 and F_2 in the eq 3) over the time t and diffusion distance x . The mixture volume properties of the CO₂/hydrocarbon system were then calculated according to the equation of state, with the partial specific volume $V_{k,l}^*$ or $V_{k,g}^*$ of component k being calculated from a method illustrated in the literature (Zhu, 1991). In this work, a cubic simplified perturbed hard chain equation of state (Wang and Guo, 1993) was used to predict the volume correction factors F_1 and F_2 for diffusion coefficients at high pressure.

Table 2. Concentration-Dependent Diffusion Coefficients of CO₂ in Tetradecane at 311.0 K and 1.905 MPa

τ (min)	m_1^t/m_∞ (%)	$\bar{C}/C_{k,e}$ (%)	$(at^{1/2} - b)$				F_t	$D_k^t \times 10^9$ (m ² /s)
			$a \times 10^3$	$b \times 10^1$	r	$(b/a)/\tau^{1/2}$		
20.8	11.63	12.97	6.041	2.125	0.9997	0.996	1.096	1.706
23.7	13.30	14.83	6.049	2.296	0.9996	1.006	1.096	1.711
28.6	15.45	17.24	6.082	2.529	0.9996	1.004	1.098	1.723
38.3	19.43	21.68	5.977	2.872	0.9986	1.002	1.093	1.681
41.6	20.62	23.00	5.786	2.880	0.9986	0.996	1.082	1.608
45.8	21.92	24.45	5.735	2.977	0.9988	0.990	1.078	1.591
49.8	23.12	25.78	5.586	2.996	0.9988	0.981	1.068	1.536
59.2	26.23	29.25	5.398	3.170	0.9990	0.985	1.055	1.472
63.5	27.77	30.97	5.336	3.273	0.9992	0.994	1.050	1.453
68.1	29.20	32.56	5.217	3.327	0.9991	0.998	1.041	1.412
71.9	30.25	33.74	5.176	3.400	0.9988	1.000	1.038	1.398
75.6	31.09	34.68	5.152	3.466	0.9983	0.999	1.036	1.391
83.1	32.43	36.18	5.002	3.473	0.9960	0.983	1.023	1.344
117.3	40.00	44.61	4.278	3.556	0.9985	0.991	0.956	1.126
120.8	40.88	45.60	4.022	3.401	0.9988	0.993	0.931	1.048
137.5	43.52	48.54	3.714	3.367	0.9965	0.998	0.902	0.954
143.8	44.21	49.31	3.411	3.138	0.9953	0.990	0.872	0.861
145.2	44.41	49.53	3.302	3.044	0.9964	0.988	0.860	0.828
147.6	44.73	49.90	3.062	2.825	0.9936	0.980	0.835	0.755
151.0	45.26	50.49	2.884	2.681	0.9922	0.977	0.815	0.703
198.1	50.44	56.26	2.147	2.287	0.9900	0.977	0.724	0.494
213.4	51.38	57.31	2.067	2.269	0.9900	0.970	0.713	0.472
268.8	55.62	62.04	1.960	2.531	0.9902	1.017	0.697	0.444
279.9	56.45	62.96	1.788	2.343	0.9978	1.011	0.670	0.401
318.4	57.85	64.52	1.824	2.532	0.9962	1.010	0.675	0.411
329.8	58.15	64.86	1.914	2.707	0.9964	1.005	0.689	0.434
383.3	59.82	66.72	1.976	2.979	0.9974	0.994	0.700	0.448
427.2	61.40	68.49	2.087	3.329	0.9987	0.996	0.719	0.474
451.8	62.46	69.66	2.108	3.471	0.9980	1.000	0.723	0.478

The solubility of CO₂ in tetradecane was measured and corrected from the accumulative volumes of CO₂ injected continuously during the experiment until the injection rate approaches zero, when the system is considered at equilibrium state. The solubility at 311.0 K and 1.905 MPa for the CO₂ + nC₁₄ system is 5.527×10^{-2} g·cm⁻¹. From these data, a constant diffusion coefficient $D = 1.933 \times 10^{-9}$ m²·s⁻¹ can be determined on the basis of eq 3.

Solution of the Concentration-Dependent Diffusion Equation

In the case of single-component gas k diffusion into a quiescent liquid phase, the concentration dependent diffusion equation can be expressed as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D^k \frac{\partial C}{\partial x} \right)$$

$$C(x,0) = C_0; \quad C(0,t) = C_{k,e}; \quad C(\infty,t) = C_0 \quad (4)$$

Equation 4 cannot be solved because of the unknown function $D(C)$. It has been found that there are some similarities between the concentration-dependent diffusion and constant diffusivity diffusion, with both processes showing a concentration variation as $M_t/M_\infty = k\sqrt{t}$ for a small time range. In the case of single-component gas diffusion into a quiescent liquid phase, the solution of the concentration-dependent diffusion equation can be expressed as a solution of a constant diffusivity diffusion with initial and boundary conditions and an uncertainty function F_t . So eq 3 can be expressed as:

$$1 - \frac{m_1^t}{m_\infty} = F_t \left(1 - \frac{2A\Delta C_{k,e}}{m_\infty \sqrt{F_1 F_2 \pi}} \sqrt{D_k^t t} \right) \quad (5)$$

in which m_1^t, m_∞ are the mass of gas injected into the diffusion cell at time t and the mass absorbed by the liquid

phase at equilibrium, respectively. In the case of constant D diffusion, $F_t = 1$. For the concentration-inhibited diffusion, the value of F_t will be in the range of $1 > F_t > 0$, so at equilibrium condition $F_{t=\infty} = 0$. In fact, the value of F_t is not limited in a range of 0–1, as shown later in Table 2. Equation 5 can be simplified as the following

$$1 - \frac{m_1^t}{m_\infty} = F_t (1 - \beta \sqrt{D_k^t t}) \quad (6)$$

with

$$\beta = \frac{2A\Delta C_{k,e}}{m_\infty \sqrt{F_1 F_2 \pi}} \quad (7)$$

During the whole process of diffusion, we can fix a specified test time (limited to the region of analysis) as τ . At the time τ , eq 5 can be expressed as

$$1 - \frac{m_1^\tau}{m_\infty} = F_\tau (1 - \beta \sqrt{D_k^\tau \tau}) \quad (8)$$

From eqs 6 and 8, we obtain

$$\frac{m_1^t - m_1^\tau}{m_\infty} = \beta F_t \sqrt{D_k^t} t^{1/2} - \beta F_\tau \sqrt{D_k^\tau} \tau^{1/2} = at^{1/2} - b \quad (9)$$

where a and $-b$ are the slope and intercept of the line $(m_1^t - m_1^\tau)/m_\infty \sim t^{1/2}$ based on the experimental data. From eq 8, F_t can be expressed as

$$F_t = 1 - \frac{m_1^t}{m_\infty} + \beta F_\tau \sqrt{D_k^\tau} \tau^{1/2} = 1 - \frac{m_1^t}{m_\infty} + b \quad (10)$$

Because b has been obtained from the intercept of the line $(m_1^t - m_1^\tau)/m_\infty \sim t^{1/2}$ (eq 9 at $t = 0$), then F_t can be calculated from eq 10. The concentration-dependent dif-

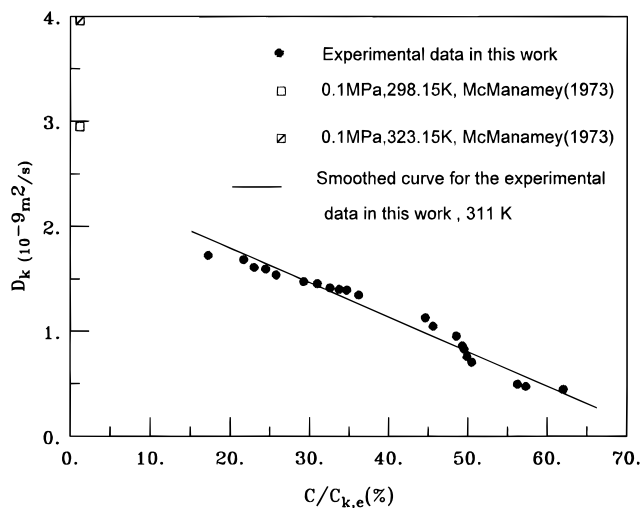


Figure 3. Concentration dependency of diffusion coefficients of the CO₂ + tetradecane system.

fusivity D_k^f can then be determined from the intercept b on the basis of the experimental data without any assumption. A series of D_k^f values could be evaluated by altering the τ value and repeating the operation from the $(m_i^t - m_i^\tau)/m_\infty \sim t^{1/2}$ data.

Results and Discussion

There are some differences between this method to that of Liu et al. (1994). The following limitations exist in the method of Liu et al.: (1) only pure gas diffusion can be treated; (2) the adsorption curves obtained for pure gas in zeolite vs $t^{1/2}$ were not straight: this means that not all data points are used for determining D . The present paper has clarified this problem using the theory of Reamer et al. The concentration-dependent diffusion coefficients of the CO₂–tetradecane system obtained in this work have been listed in Table 2 and the concentration dependency of the D is shown in Figure 3, where \bar{C} refers to the average concentration of diffusing species i at time t in liquid phase and $C_{k,e}$ refers to the concentration of component i in the liquid phase saturated at the test pressure. A relative concentration $\bar{C}/C_{k,e}$ (%) has been used. However, not all the D data in the Table 2 were included because the data from $\tau \geq 318.4$ min belong to the bottom effect region, as shown in Figure 2. In Table 2, the data in bold type stand for those significant concentration-dependent diffusion coefficients obtained in this work.

Another advantage of obtaining the diffusion coefficient from the intercept of the line $(m_i^t - m_i^\tau)/m_\infty \sim t^{1/2}$ is that this method can reduce the experimental uncertainty for each data point. The estimated experimental uncertainty was within 0.2% for the diffusion coefficient due to an uncertainty of 0.4% in the injected volume measurement.

The method of Liu et al. for concentration-dependent diffusion is only strictly tenable as diffusion time $t \rightarrow \tau$. If we introduce this assumption, following expressions can be obtained:

$$F_t \rightarrow F_\tau; \quad D_k^t \rightarrow D_k^f \quad (11)$$

$$\frac{m_i^t - m_i^\tau}{m_\infty} = \beta F_\tau \sqrt{D_k^f (t^{1/2} - \tau^{1/2})} \quad (12)$$

If eq 12 is strictly tenable, according eq 9, $(b/a)/\tau^{1/2}$ will be equal to 1. This is shown in Table 2 where most of the

Table 3. Smoothed Results of Concentration-Dependent Diffusion Coefficients of CO₂ in Tetradecane at 311.0 K and 1.905 MPa

$\bar{C}/C_{k,e}$ (%)	D_k^f (10^{-9} m ² /s)	$\bar{C}/C_{k,e}$ (%)	D_k^f (10^{-9} m ² /s)
16	1.883	40	1.156
18	1.823	42	1.095
20	1.762	44	1.035
22	1.701	46	0.974
24	1.641	48	0.914
26	1.580	50	0.853
28	1.520	52	0.792
30	1.459	54	0.732
32	1.398	56	0.671
34	1.338	58	0.611
36	1.277	60	0.550
38	1.217	62	0.489

values $(b/a)/\tau^{1/2}$ are within 1% of unity. Therefore, the features of eq 9 are similar to eq 12. The values of uncertainty function F_τ are also listed in the table. It is clearly shown that the function F_τ describes the concentration effect on the D ; if we set F_τ to unity, a constant D will be obtained.

From Table 2, it can be seen that the correlation coefficients r of $(m_i^t - m_i^\tau)/m_\infty \sim t^{1/2}$ (eq 9) are almost equal to 1, so it shows good linear relationship.

The experimental diffusion coefficient data recorded in bold type in Table 2 were fitted by a linear equation of relative concentration of CO₂

$$10^9 D_k^f / (\text{m}^2 \cdot \text{s}^{-1}) = A_1 + A_2 x \quad (13)$$

in which

$$x = (\bar{C}/C_{k,e})^\tau \quad (14)$$

and where superscript τ denotes the concentration obtained at time τ . The fitted values of the constants A_i in eq 13 are $A_1 = 2.3679$, $A_2 = -0.0303$. The standard deviation of the calculated values based on the smoothing function eq 13 to the experimental data of the CO₂–tetradecane system is 0.077 (10^{-9} m²/s). The results fitted by the least-squares method are shown in Figure 3. The smoothed values are recorded in Table 3. In Figure 3, the diffusion coefficients of CO₂ in tetradecane (at infinite dilution conditions) at 0.1 MPa, 298.15 K, and 323.15 K measured by McManamey and Woolen (1973) using the Taylor–Aris dispersion technique were also shown. The agreement between the data of McManamey and the results of this work shows that such a concentration dependence is reasonable.

Two previously published constant D diffusion data points of methane–decane and methane–white oil systems (mass of gas added to the cell vs time data at constant temperature and pressure) of Reamer et al. (1956) have been treated according to the proposed method. The concentration dependent diffusion coefficient results obtained are listed in Table 4 and Table 5, respectively. In Figure 4, the concentration dependency of diffusion coefficient data at 344.3 K and 2.473 MPa are shown together with the constant D diffusion coefficients obtained by Reamer et al. Each data point shown in Figure 4 obtained by Reamer et al. belongs to a different pressure, and the concentrations were expressed in weight percent (for the data of Reamer et al., averaged weight percentage concentrations of methane in the liquid phase were used). Both the results obtained in this work and the results of Reamer et al. show clear effects of concentration-inhibited diffusion.

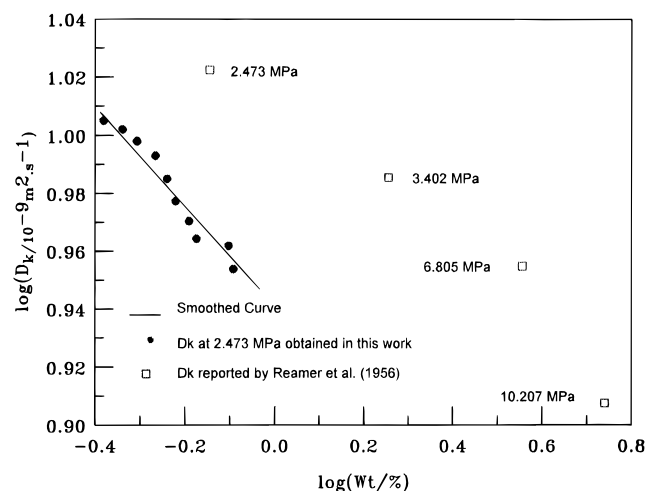
The diffusivity vs relative concentration curves in Figure 3 and Figure 4 both show a sharp decrease of diffusivity in the early stages of absorption and then approach a

Table 4. Concentration-Dependent Diffusion Coefficients of Methane in Decane at 344.3 K and 2.473 MPa^a

τ (min)	m_l^i/m_∞ (%)	$\bar{C}/C_{k,e}$ (%)	$(at^{1/2} - b)$				F_τ	$D_k^\tau \times 10^8$ (m ² /s)
			$a \times 10^3$	$b \times 10^1$	r	$(b/a)/\tau^{1/2}$		
46.2	18.84	28.72	3.887	1.936	0.9999	1.014	1.005	0.977
86.1	26.46	36.34	3.970	2.771	0.9997	1.007	1.013	1.005
100.0	28.46	38.34	3.988	2.993	0.9997	0.999	1.015	1.010
123.8	32.01	41.89	4.001	3.367	0.9997	1.001	1.017	1.012
147.7	35.22	45.10	3.973	3.660	0.9996	0.999	1.014	1.004
170.0	37.90	47.78	3.945	3.897	0.9995	0.996	1.011	0.996
202.8	41.69	51.57	3.899	4.220	0.9993	0.996	1.005	0.984
225.0	44.21	54.09	3.827	4.376	0.9992	0.998	0.995	0.966
245.5	46.19	56.07	3.754	4.470	0.9993	0.993	0.985	0.949
272.5	49.50	59.38	3.686	4.701	0.9993	1.009	0.975	0.934
300.0	51.42	61.30	3.621	4.789	0.9996	0.996	0.965	0.921
420.8	60.72	70.60	3.602	5.691	0.9996	1.001	0.962	0.916
444.0	62.22	72.10	3.515	5.700	0.9997	1.000	0.948	0.899
462.3	63.36	73.24	3.441	5.693	0.9999	1.000	0.936	0.884

^a Experimental data from Reamer et al. (1956).**Table 5. Concentration-Dependent Diffusion Coefficients of Methane in White Oil at 410.9 K and 7.096 MPa^a**

τ (min)	m_l^i/m_∞ (%)	$\bar{C}/C_{k,e}$ (%)	$(at^{1/2} - b)$				F_τ	$D_k^\tau \times 10^8$ (m ² /s)
			$a \times 10^3$	$b \times 10^1$	r	$(b/a)/\tau^{1/2}$		
116.2	9.44	60.37	1.217	0.988	0.9996	0.972	1.004	0.483
146.7	10.65	61.58	1.228	1.122	0.9997	0.974	1.006	0.489
161.8	11.14	62.07	1.267	1.215	0.9989	0.973	1.010	0.517
174.5	11.73	62.66	1.304	1.317	0.9979	0.987	1.014	0.543
201.5	12.65	63.49	1.343	1.451	0.9980	0.983	1.020	0.570
218.3	13.26	64.19	1.368	1.554	0.9979	0.992	1.023	0.587
239.2	13.91	64.84	1.399	1.666	0.9983	0.994	1.027	0.609
268.7	14.85	65.78	1.426	1.802	0.9987	0.995	1.032	0.627
289.5	15.41	66.34	1.411	1.885	0.9991	0.993	1.034	0.637
324.0	16.27	67.20	1.440	1.974	0.9989	0.983	1.035	0.636
353.2	17.07	68.00	1.398	1.983	0.9986	0.974	1.028	0.608
395.7	18.53	69.46	1.350	2.044	0.9995	0.983	1.019	0.577
420.8	19.36	70.29	1.330	2.088	0.9998	0.988	1.015	0.563
448.3	20.02	70.95	1.327	2.148	0.9998	0.987	1.015	0.562
517.3	21.76	72.69	1.326	2.319	0.9998	0.993	1.014	0.561
543.7	22.38	73.31	1.305	2.340	0.9995	0.993	1.010	0.548
581.7	23.18	74.11	1.263	2.335	0.9980	0.990	1.002	0.522
679.8	25.12	76.05	1.231	2.457	0.9966	0.988	0.995	0.503
724.0	26.02	76.95	1.128	2.324	0.9952	0.989	0.972	0.442
808.7	27.72	78.65	1.100	2.429	0.9946	1.002	0.966	0.427
867.2	28.66	79.59	1.055	2.414	0.9944	1.003	0.955	0.401
920.2	29.36	80.29	0.965	2.267	0.9975	0.999	0.933	0.351

^a Experimental data from Reamer et al. (1956).**Figure 4.** Concentration dependency of diffusion coefficients of the methane + decane system at 344.3 K.

constant in the high-concentration region. The shape of the curve is very similar to the curves of diffusivities vs concentrations evaluated from the uptake curve of some hydrocarbons in zeolite measured by Liu et al.

Conclusions

A experimental technique similar to that of Reamer et al., modified to include a computer-aided controlling system has been developed to determine the diffusivity of gases in liquids from the linear relationship of gas injection volume vs time data during absorption measurements. A theoretical development for determining the Fick diffusion coefficient of gas in a liquid phase has been proposed and tested for the system CO₂-tetradecane at 311 K and 1.905 MPa.

Appendix. Method of Analysis for Constant Diffusion

The entire system is assumed to be at constant temperature throughout the transport process. The central problem is to solve the following nonsteady-state one-dimensional (limited to the x -direction) diffusion equation for a given horizontal section of the diffusion system.

To simplify the analysis, the following assumptions were made:

(1) The gas/liquid interface is located at $x = 0$, while the bottom of the test liquid is at $x = \infty$. The assumption of a semiinfinite liquid phase is valid as long as CO₂ does not reach the bottom of the diffusion cell during the test.

(2) The liquid is assumed to be saturated with CO₂ at the interface $x = 0$, and interfacial resistance to transport of the gas into the liquid is negligible. This assumption is valid during the test except at the beginning of the measurements.

(3) The gas phase is assumed to be pure CO₂, as tetradecane is relatively nonvolatile under the experimental conditions. The diffusion coefficients and the partial specific volumes of all components are assumed to be constant throughout the composition range encountered during the test.

As defined by Reamer et al., F_1 accounts for the effects of hydrodynamic velocity and the change in the volume of liquid upon mixing. For a binary diffusion (gas k in liquid j)

$$F_1 = \frac{1 + C_k V_{k,l}^* + C_j V_{j,l}^*}{(1 + C_j V_{j,l}^*)(1 + C_k/C_j)}$$

The total mass of component k absorbed in the liquid after time t , $m_{k,l}$, can be calculated from the mass of component k , $m_{k,c}$, injected into the test cell after time t required to maintain the condition of constant pressure. This relationship can be obtained by recognizing the total accumulated volume injected into the cell, $m_{k,c} V_{k,g}^*$, plus the expansion in volume, $m_{k,l} V_{k,l}^*$, resulting from absorption of CO₂. As the volume increase of the liquid phase corresponds to the volume decrease of CO₂ in the cell due to absorption, then

$$m_{k,l} V_{k,g}^* = m_{k,c} V_{k,g}^* + m_{k,l} V_{k,l}^*$$

From this expression the relationship between the quantity of gas injected into the test cell $m_i (m_i = m_{k,c})$ and that

absorbed by the liquid phase can be obtained

$$m_{k,l} = m_i F_2$$

where

$$F_2 = V_{k,g}^* / (V_{k,g}^* - V_{k,l}^*)$$

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