THE DIFFUSION COEFFICIENT OF ^{14}C -LABELLED ETHYLENE IN NORMAL ETHYLENE AT HIGH PRESSURE

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The diffusion coefficient of ^{14}C -labelled ethylene in normal ethylene was measured at temperatures of 25, 50, and 75°C in the range up to $10 \times 10^{-3} \text{ mol/cm}^3$ density and 197 atm pressure. The measurements were made through a plug of porous bronze in a diffusion cell of two-chamber type by using the radioactive tracer technique. The diffusion coefficient-density products decreased slightly with increasing density, and could be predicted by a modified Enskog-Thorne theory. The values obtained in this study agreed fairly well with those calculated from a generalized chart which was prepared from correlation of experimental data.

Introduction

This study is part of a continuing research project to measure the diffusion coefficients of gases at high pressure. The previous studies were made for the diffusion coefficients of $^{14}\text{CO}_2$ in the $\text{CO}_2\text{-Ar}^{13,14}$, $\text{CO}_2\text{-CH}_4^{15}$, $\text{CO}_2\text{-N}_2^{19}$ systems; for those of CTH_3 in the $\text{CO}_2\text{-CH}_4^{16}$ and $\text{CO}_2\text{-Ar}^{17}$ system. This paper presents the diffusion coefficient of ^{14}C -labelled ethylene in normal ethylene, which is related to the self-diffusion coefficient of ethylene by applying the mass correction⁷. The self-diffusion coefficient of gaseous ethylene was measured by Hamann *et al.*⁵, using the nuclear spin-echo technique at temperatures from -5 to 40°C in the density range from 0.14 to 0.30 g/cm³. They concluded that the product of the self-diffusion coefficient and density was constant over the whole range up to critical density. According to their conclusion, however, the self-diffusion coefficient of ethylene extrapolated to 1 atm at 25°C is 20% higher than that observed by Mueller *et al.*¹⁰. In addition, the constancy of the product of diffusion coefficient-density in the density range below 0.14 g/cm³ does not seem conclusive from their experimental results.

1. Experimental

The apparatus and the experimental procedure were the same as those described previously¹³. The diffusion path in the cell was a plug of porous bronze with pores of about 10 μ diameter. The temperature of

the diffusion cell was measured by use of a thermistor thermometer calibrated with a standard mercury thermometer and kept constant within 0.1°C. The error in temperature measurement was within 0.05°C. The pressure was measured by use of Bourdon gauges calibrated with a pressure balance of free-piston type. The errors in pressure measurement were within 0.02 atm up to 20 atm, 0.1 atm for pressures ranging from 20 to 50 atm, and 0.5 atm for pressures ranging from 50 to 250 atm. Radioactive ethylene was supplied from the New England Nuclear Corp. The ethylene content was above 99%; the specific radioactivity was 9.0 Ci/mol. Since 60% of the radioactive ethylene contained two radioactive carbon atoms, ^{14}C , and 40% contained one, a mean molecular weight of 31.24 was assumed for radioactive ethylene. Supplied radioactive ethylene was diluted to 110 $\mu\text{Ci/mmol}$ with normal ethylene. Mole fraction of radioactive ethylene in diluted gas was about 0.0011. Addition of this gas to the ethylene in the cell by about 0.5 vol.% enabled us to obtain the ionization current, 90×10^{-13} amp, required for the determination of diffusion coefficient. Normal ethylene was supplied from the Seitetsu Kagaku Kogyo Co. and its purity was above 99.5%. Measurements were made at temperatures of 25, 50, and 75°C in the range up to $10 \times 10^{-3} \text{ mol/cm}^3$ density and 197 atm pressure.

2. Results

The experimental results are given in Table 1 and Fig. 1. The error in diffusion coefficient determination was estimated to be within 3% by taking into account the accuracy of ionization-current measurement. The scattering of obtained values of diffusion coefficient

Received December 14, 1976. Correspondence concerning this article should be addressed to S. Takahashi, Dept. of Chem. Eng., Tohoku Univ., Sendai 980.

A: from Eq. (3) C: from Eqs. (12)–(14)
B: from Eqs. (6) and (7) D: observed by Hamann *et al.*

Fig. 1 Comparison of the observed values with Enskog-Thorne theory

Table 1 Experimental results

P [atm]	$\rho \times 10^3$ [mol/cm ³]	$D_{12} \times 10^3$ [cm ² /sec]	P [atm]	$\rho \times 10^3$ [mol/cm ³]	$D_{12} \times 10^3$ [cm ² /sec]
25°C					
20.52	0.9630	5.12*	72.6	4.5645	1.23
20.61	0.9672	5.17*	84.5	6.0267	0.891
49.00	3.1791	1.59*	98.5	7.8371	0.644
49.5	3.2503	1.56*	117.1	9.5829	0.539
59.8	5.0255	0.971	138.4	10.833	0.467
50°C					
67.6	7.7376	0.626	20.45	0.7732	7.47*
77.1	9.8137	0.480	20.45	0.7732	7.54*
86.2	10.907	0.394	51.1	2.2158	2.55*
75°C					
20.36	0.8496	6.48*	51.2	2.2199	2.63*
20.65	0.8631	6.33*	87.1	4.5623	1.28
50.0	2.5343	2.06	121.0	7.2603	0.752
51.3	2.6286	2.07	158.8	9.5317	0.579
			196.5	10.777	0.504

* These values were used to estimate the scattering of data.

was 1.0% on the average and 1.3% at maximum for the 5 experimental conditions: two runs were carried out for each condition, as shown in Table 1. The density of gas, ρ , was obtained from the compressibility factor recommended by Date *et al.*²⁾. The error in density determination was estimated to be within 0.5% by taking into account the uncertainty of reported data and of interpolation.

As can be seen from Fig. 1, the diffusion coefficient-

Table 2 Comparison of the values extrapolated to 1 atm, $D_{12, \text{extra}}$, with those observed by Mueller *et al.*, $D_{12, \text{obs}}$, and the theoretical ones, $D_{12, \text{theor}}$

t [°C]	$D_{12, \text{extra}}$ [cm ² /sec]	$D_{12, \text{obs}}$ [cm ² /sec]	$(D_{12})_{\text{diff}}^{\text{a)}}$ [cm ² /sec]	$(D_{12})_{\text{vis}}^{\text{b)}}$ [cm ² /sec]
25.0	0.123	0.122	0.124	0.115
50.0	0.144		0.144	0.135
75.0	0.165		0.166	0.155

a) The force constants determined from diffusion coefficient data for the Lennard-Jones 12-6 potential, $\sigma_1 = \sigma_2 = 4.046 \text{ \AA}$, $\epsilon/k = 212^\circ \text{K}$ (Ref. 10), were used.

b) The force constants determined from viscosity data, $\sigma_1 = \sigma_2 = 4.232 \text{ \AA}$, $\epsilon/k = 205^\circ \text{K}$ (Ref. 6, p. 1112), were used.

density product, $D_{12}\rho$, decreases slightly with increasing density. The values of diffusion coefficient at 1 atm obtained through the extrapolation of the $D_{12}\rho$ at high density agree fairly well with the experimental values obtained by Mueller *et al.*¹⁰⁾, as shown in Table 2. It should be noted that the values of D_{12} obtained in the measurements of Hamann *et al.*⁵⁾ were 20% higher than those obtained in this study in the density range from 5×10^{-3} to $8 \times 10^{-3} \text{ mol/cm}^3$, and no remarkable decrease of $D_{12}\rho$ at the critical density of about $7.75 \times 10^{-3} \text{ mol/cm}^3$, as suggested by Hamann *et al.*, was observed in this study. The values denoted by $\square$ and dotted lines (D) were obtained through the application of mass correction to the experimental self-diffusion coefficients of ethylene in the literature.

3. Discussion

3.1 Chapman-Enskog theory

The values of diffusion coefficient at 1 atm obtained through the extrapolation of the $D_{12}\rho$ at high pressure to 1 atm were compared with the theoretical values calculated from the following equation⁸⁾, as given in Table 2.

$$(D_{12})^0 = 0.002628 \frac{\sqrt{T^3(M_1 + M_2)/2M_1M_2}}{P\sigma_{12}^2 Q_{12}^{(1,1)*}} \quad (1)$$

Here, $(D_{12})^0$ is the first approximation to D_{12} and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, $\sigma_1 = \sigma_2$. Table 2 shows that the extrapolated values, $D_{12, \text{extra}}$, agree fairly well with the experimental values, $D_{12, \text{obs}}$, and the theoretical ones, $(D_{12})_{\text{diff}}^0$, obtained by use of the force constants determined from diffusion coefficient data; however, the theoretical values, $(D_{12})_{\text{vis}}^0$, obtained by use of the force constants determined from viscosity data, are 6% lower than $D_{12, \text{extra}}$. Such a deviation of $(D_{12})_{\text{vis}}^0$ from observed values is similar to those in other systems¹¹⁾.

3.2 Generalized chart

For predicting the diffusion coefficients of gases at high pressure generalized charts may be used. At the present time those presented by Slattery *et al.*¹²⁾ and by the author¹⁸⁾ are convenient for practical use.

Hereafter, they are abbreviated to SB- and T-chart. Figure 2 shows that the calculated values from SB-chart deviate from those observed in the lower-pressure region, but agree fairly well in the higher-pressure region; those calculated from T-chart agree well in the lower-pressure region, but deviate in the higher-pressure region. The deviation of the values calculated by use of SB-chart from those observed was 6.8% on the average, and the maximum was 12%; that by use of T-chart was 5.1% on the average and the maximum was 18% for 19 experimental points. The deviation of values calculated by both charts is close together; however, it seems that the pressure dependency of $D_{12}P$ is represented better by T-chart than by SB-chart as a whole.

3.3 Enskog-Thorne theory

According to the Enskog-Thorne theory¹¹ the diffusion coefficient of a trace of radioactive ethylene in normal ethylene, D_{12} , at high pressure is given as follows:

$$D_{12}\rho/(D_{12}\rho)^0 = 1/\chi_{12} \quad (2)$$

$$\chi_{12} = 1 + (\pi/12)n_2\sigma_2^3(5 - 3\sigma_2/\sigma_{12}) + \dots \quad (3)$$

where σ_{12} is assumed to be $(\sigma_1 + \sigma_2)/2$. In this calculation, $\sigma_1 \doteq \sigma_2 = 4.046 \text{ \AA}$ (Ref. 10) was used. The values predicted by use of Eqs. (2) and (3) are represented in Fig. 1 by the dashed lines (A). The deviations from observed values increase with increasing density and are about 35% at $\rho = 10 \times 10^{-3} \text{ mol/cm}^3$.

Since the theoretical values calculated from Eq. (3) deviate largely from those observed, several investigators^{3,9,21} attempted to use the following relations:

$$P + a_0\rho^2 = (RT/V)(1 - b_0\rho\chi) \quad (4)^*$$

$$b_0 = (2/3)\pi N\sigma^3 \quad (5)$$

$$b_0\rho\chi = (V/R)(\partial P/\partial T)_V - 1 \quad (6)^{**}$$

$$b_0 = B + T(dB/dT) \quad (7)^{**}$$

$$\chi_{12} \doteq \chi \quad (8)$$

The results obtained by use of the above relations for the present system also deviate greatly, as represented in Fig. 1 by the dot-dashed lines (B). In this calculation the values of $(\partial P/\partial T)_V$ and B were calculated by use of the following empirical equation of state, proposed for ethylene by Uematsu *et al.*²⁰.

$$\begin{aligned} P = RT\rho + (a_1T + a_2 + a_3T^{-2})\rho^2 + (a_4T - a_5)\rho^3 \\ + (a_6 + a_7T^{-5})\rho^4 + (a_8 + a_9T^{-3})\rho^5 \\ + (a_{10} + a_{11}T^{-1})\rho^6 + (a_{12} + a_{13}T^{-2} + a_{14}T^{-4}) \\ \times (1 + \gamma\rho^2)\rho^3 \exp(-\gamma\rho^2) \end{aligned} \quad (9)$$

where P denotes pressure in MPa. Equation (9) reproduces the compressibility factor recommended by Date *et al.*²¹ with the average deviation of 0.06%. By use of the definition of second virial coefficient

* Ref. 1, p. 286, ** Ref. 1, p. 288, *** Ref. 6, p. 650.

Fig. 2 Comparison of the observed values with those calculated from the generalized chart

Table 3 The second and third virial coefficient of ethylene

t [°C]	B_U [cm ³ /mol]	B_M [cm ³ /mol]	C_U [cm ⁶ /mol ²]	C_M [cm ⁶ /mol ²]
25.0	-139.86	-140.55	6953	7644
50.0	-117.07	-118.07	5996	6743
75.0	-98.83	-99.90	5312	5999
100.0	-83.91	-85.11	4818	5464
125.0	-71.50	-72.61	4459	4990
150.0	-61.00	-62.07	4191	4670

given by the equation

$$B = (1/RT) \lim_{\rho \rightarrow 0} (z - 1)/\rho \quad (10)$$

the second virial coefficient of ethylene was obtained from Eq. (9) as follows:

$$B_U = (a_1 + a_2T^{-1} + a_3T^{-2})/R \quad (11)$$

The second virial coefficients of ethylene obtained from Eq. (11), B_U , are shown in Table 3 along with the experimental values presented by Michels *et al.*⁴.

Iwasaki⁸ performed with success the theoretical calculation of the viscosity of argon at high pressure by using the following relations:

$$z = PV/RT = 1 + (b_0 - a_0/RT)\rho + b_0\rho(\chi - 1) \quad (12)$$

$$B(T) = b_0(T) - a_0/RT \quad (13)$$

$$C(T_1)/C(T_2) = \{b_0(T_1)/b_0(T_2)\}^2 \quad (14)$$

where $B(T)$, $b_0(T)$, and $C(T)$ imply that B , b_0 , and C are dependent on temperature T . The χ_{12} is obtained from Eqs. (12)–(14) and Eq. (8) by use of the values of z , B , and C . In the present study these values were derived from Eq. (9), that is, the B 's were calculated from Eq. (11); the C 's were determined from the following equation:

$$C_U = \{a_4 + (a_5 + a_{12})T^{-1} + a_{13}T^{-2} + a_{14}T^{-5}\}/R \quad (15)$$

Equation (15) was obtained from Eq. (9) by use of the definition of third virial coefficient given by the following equation:

$$C = (1/2RT) \lim_{\rho \rightarrow 0} \partial^2(PV)/\partial \rho^2 \quad (16)$$

The third virial coefficients obtained from Eq. (15), C_U , are shown in Table 3, along with those presented by Michels *et al.*, $C_M^{(4)}$.

The values of b_0 in the temperature range from 25 to 150°C were determined from Eqs. (12)–(14) by using six sets of $B_U(T)$ and $C_U(T)$ given in Table 3 by means of the least squares method. The theoretical values obtained by this method agree fairly well with those observed as represented in Fig. 1 by the solid lines (C).

Conclusion

The diffusion coefficients of ^{14}C -labelled radioactive ethylene in normal ethylene were measured at 25, 50, and 75°C in the range up to 10×10^{-3} mol/cm³ density and 197 atm pressure. They were reproduced approximately by the generalized chart presented by the author. A modified Enskog-Thorne theory predicts fairly well the diffusion coefficients measured in the present study.

Acknowledgment

The author wishes to express his deep gratitude to Professor Hiroji Iwasaki for his kind direction and encouragement throughout this work.

Nomenclature

a_0	= constant in Eq. (4)	
a_i ($i=1-14$)	= constant in Eq. (9)	
B	= second virial coefficient	[cm ³ /mol]
b_0	= constant in Eq. (4)	
C	= third virial coefficient	[cm ⁶ /mol ³]
D	= diffusion coefficient	[cm ² /sec]
M	= molecular weight	[—]
N	= Avogadro's number	[1/mol]
n	= number of molecules per unit volume	[1/cm ³]
P	= pressure	[atm]
R	= gas constant	[J/°K·mol]
T	= temperature	[°K]
t	= temperature	[°C]
V	= molecular volume	[cm ³ /mol]
z	= compressibility factor	[—]
ϵ/k	= force constant	[°K]
ρ	= density	[mol/cm ³]

σ	= collision diameter	[cm or Å]
χ	= correction factor	[—]
$Q^{(1,1)*}$	= reduced collision integral	[—]

<Subscripts>

1	= radioactive ethylene
2	= normal ethylene

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(This study was presented at the 17th High Pressure Symposium at Sapporo, Oct. 1st, 1976.)