BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (6), 1639—1643 (1978)

Diffusion Coefficients of Argon in Aqueous Ethanol and 1,4-Dioxane Solutions and of Methane in Aqueous Ethanol Solutions*

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(Received October 24, 1977)

The diffusion coefficients of argon in water-rich regions of aqueous solutions of ethanol and of 1,4-dioxane and those of methane in aqueous solutions of ethanol have been measured by using a diaphragm cell apparatus, designed after Hildebrand *et al.*, for dissolved gases in liquid. The diffusivity of gases was found to show much anomaly which might be ascribed to the structural change of water due to the addition of another solvent. The viscosity reduced diffusion coefficient $D\eta$ (D: diffusion coefficient, η: viscosity coefficient) has a maximum value in dilute aqueous solution of both ethanol and 1,4-dioxane.

Studies have been made recently on the diffusivity of dilute solute in a variety of mixed solvents.[1—4] Iodine was used as a solute and the influence of its specific interaction with the solvents upon diffusivity was examined. Among the mixed solvents examined so far, aqueous alcohol solutions exhibit anomaly in diffusivity which is reverse in direction to that in other solvent systems.[1] It was pointed out that this anomaly may have close connection with the destruction or stabilization of water structure as revealed by solubility and other thermodynamic data.[5]

The purpose of the present study is to elucidate this phenomenon through the determination of diffusion coefficient of inert solute in aqueous solutions. Nakanishi *et al.* measured the diffusion coefficient of various gases dissolved in liquid by diaphragm cell method.[6] A diffusion apparatus has been constructed by utilizing the same diaphragm as employed previously. The diffusion coefficients of argon in water-rich regions of aqueous solution of ethanol and of 1,4-dioxane and those of methane in water-rich region of aqueous solutions of ethanol have been measured. In this paper are given the results of these measurements and a discussion based on the effect of structural change in water on gas diffusivity.

Experimental

Gases and Other Materials. Argon and methane of 99.998 and 99.95% purity were used. The gases were introduced into the apparatus after passing through a column of dehydrating agent $CaCl_2$. Guaranteed ethanol and 1,4-dioxane were used as solvent. Water was deionized and distilled three times.

Apparatus. The fundamental design of the diffusion apparatus shown in Fig. 1 is similar to that used by Hildebrand and co-workers.[6,7] The apparatus consists of three main parts, diffusion cell, gas buret and degassing device. Each of the valves used to separate the parts of the apparatus is a high vacuum glass stopcock, except for the Teflon greaseless needle valve (valve 9) used to avoid the contact of grease with solvent. The diffusion cell consists of two glass bulbs between which the diaphragm is placed. The diaphragm was cut from that prepared by Hildebrand and co-workers,[6,7b] the cross section being the same 5.65 cm^2 and the length 1.00 cm.

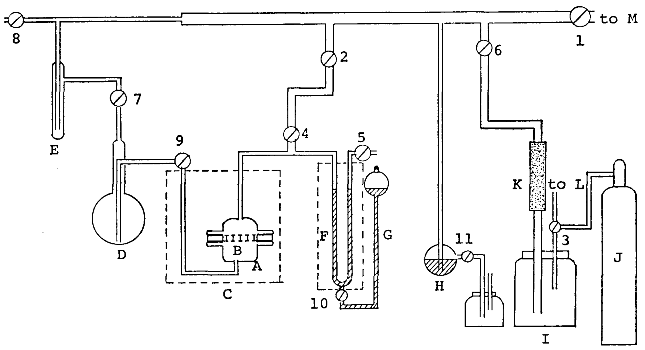

Fig. 1. Schematic diagram of diffusion apparatus.
A: Diffusion cell, B: diaphragm, C: water thermostat, D: degassing flask, E: trap, F: gas buret, G: mercury reservoir, H: open manometer, I: gas reservoir, J: cylinder, K: column of dehydrating reagent, L: gas bag, M: rotary pump, 1—11: valve or stopcock.

During the course of measurements the diffusion cell was immersed in a water thermostat kept at 25.00±0.05 °C. The gas buret was covered with a jacket in which thermostatted water (25.0±0.1 °C) was circulated.

Operation. Before the diffusion run, *ca.* 380 ml of solvent was placed in a degassing flask (Fig. 1, D). The flask was then immersed in a Dewar vessel and the liquid was degassed thoroughly by the freeze-and-thaw method *in vacuo.* The number of the times the freeze-and-thaw procedure had to be repeated depended on the sample liquid, but usually five to seven times appeared necessary for complete degassing, which was judged from the disappearance of bubble on thawing. Valve 9 was then closed, and the diffusion cell evacuated.

After degassing was completed, a small amount of sample gas (=1/5 atm) was admitted into the diffusion cell from the gas reservoir. Valves 7 and 8 were then opened to increase the pressure in the degassing flask to ordinary pressure, and the degassed liquid was rapidly transferred to the diffusion cell by opening valve 9. When the surface of liquid layer reached about 1.0 mm above the upper end of the diaphragm, valve 9 was closed in order to complete the introduction of solvent to the diffusion cell. Next, mercury was introduced into the gas buret and the gas was admitted into the vapor space of the diffusion cell. Valve 5 was kept open and the gas pressure in the cell was made to be equal to the atmospheric pressure. The water thermostat placed on a laboratory jack was raised to immerse the diffusion cell in it, and kept at 298.15±0.05 K.

The gas above the liquid surface dissolved in the liquid layer to form a saturated solution and then diffused *via* diaphragm into the liquid phase underneath. After the concentration gradient is established in the diaphragm, diffusion takes place in a steady state and can be followed by the decrease in the

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* Diffusion in Mixed Solvents. Part V.

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amount of gas as measured by the rise of the mercury column in the gas buret F.[8] The pressure of gas was equalized to atmospheric pressure by adjusting the amount of mercury in the gas buret. The rise Δh in mercury level was measured with a cathetometer. Thus Δh can be determined as a function of times Δt and the diffusion coefficient can be calculated from the slope of Δh *vs.* Δt plot.

Calculation of Diffusion Coefficient. For the diaphragm method, Fick's first law of diffusion can be written as

$$\mathrm{d}n/\mathrm{d}t = DA\Delta c/L, \tag{1}$$

where $\mathrm{d}n/\mathrm{d}t$ (mol s^{-1}) is the number of mole of the diffusant which passes through the diaphragm in unit time, A (cm^2) the cross section of diaphragm, L (cm) the length of diaphragm, Δc (mol cm^{-3}) the concentration difference, and D (cm^2 s^{-1}) the diffusion coefficient.[9] If the gas can be assumed to be ideal, then the amount of gas dissolved as a result of steady progress of diffusion is given by

$$\mathrm{d}n/\mathrm{d}t = \mathrm{d}(PV/RT)/\mathrm{d}t = (P/RT)\Delta V/\Delta t, \tag{2}$$

where P is the partial pressure of gas, ΔV the volume decrease of gas due to dissolution, R the gas constant, T the temperature and Δt the time increment. Substitution of Eq. 2 into Eq. 1 gives

$$D = (LP/ART\Delta c)(\Delta V/\Delta t). \tag{3}$$

ΔV can be measured by the change in mercury level Δh in the gas buret as

$$\Delta V = A_{\mathrm{m}}\Delta h, \tag{4}$$

where A_{m} is the cross section of gas buret. The concentration difference $\Delta c(t)$ can be expressed by

$$\Delta c(t) = (c_0P/P_0)\Delta c^*(t), \tag{5}$$

where $c_0 = X/V_1{}^0$ is the concentration of the saturated solution of gas at $P = P_0$ and $\Delta c^*(t)$ a correction term due to the change in concentration difference with the advancement of diffusion of gas into lower vessel of the diffusion cell. Here X is the solubility of gas given in terms of the mole fraction in the liquid phase and $V_1{}^0$ is the molar volume of solvent. P_0 is taken to be the atmospheric pressure so that X is the solubility at 1 atmosphere.

The diffusion coefficient D can be calculated by the following equation, obtained from Eqs. 3, 4, and 5:

$$D = (LA_{\mathrm{m}}P_0/ARTc_0)(\Delta h/\Delta c^*\Delta t), \tag{6}$$

$$= K(\Delta h/\Delta c^*\Delta tc_0), \tag{7}$$

where K is the apparatus constant and K/c_0 is also a constant for the combination of gas and solvent. Thus we can calculate D from the slope of linear relation between $\Delta h/\Delta c^*$ and Δt.

In order to use Eq. 7 for the calculation of D, it is necessary to apply some corrections to Δh and Δc^*. Since Δh is influenced by the change in atmospheric pressure, a correction should be made by means of the equation

$$\Delta h = \Delta h_0 - (V_{\mathrm{g}}/A_{\mathrm{m}})(\Delta P/P), \tag{8}$$

where V_{g} is the volume of vapor phase, ΔP the fluctuation of atmospheric pressre and Δh_0 the manometer (gas buret) reading. On the other hand, the correction for the concentration change can be estimated by

$$\Delta c^* = 1 - (P/RT)(A_{\mathrm{m}}/V_1)(\Delta h^*(\Delta t)/c_0), \tag{9}$$

where V_1 is the volume of degassed solvent and $\Delta h^*(\Delta t)$ is the change in mercury level after the steady state was attained. The relation is somewhat ambiguous as the amount of gas dissolved before the establishment of steady state of diffusion is unknown. When V_1 is sufficiently large, the correction is negligible.

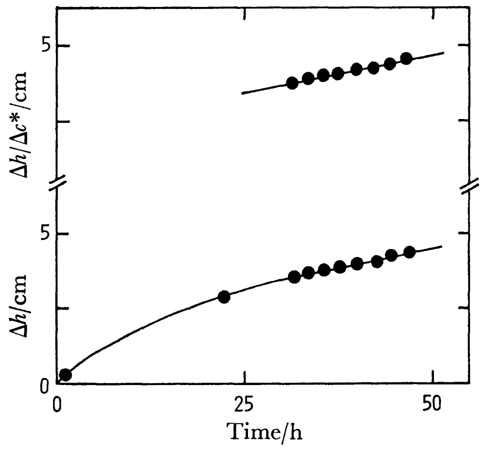

Fig. 2. Plot of height change in buret against time.

The present technique is an absolute method for the measurement of D without use of any apparatus constant determined by calibration with a gas of known D. It is in contrast to the conventional diaphragm cell technique for which the determination of cell constant is indispensable.

An example of $\Delta h/\Delta c^*$ *vs.* Δt plot is given in Fig. 2. The plot shows a downward curvature in the initial stage indicating gradual attainment of the steady concentration gradient and linearity. It requires about one day to establish a stationary state of diffusion in aqueous solutions.[10] The diffusion coefficient can be calculated from the slope of the straight line.

Apparatus Constants and Physical Constants Used. Instead of carrying out calibration measurement with a gas of known D, several apparatus constants should be determined in advance. The values of each constant used in most measurements with gases of unknown D are as follows.

$$A = 5.65\ \mathrm{cm}^2,\quad L = 1.00\ \mathrm{cm},\quad A_{\mathrm{m}} = 0.326\ \mathrm{cm}^2,$$

$$V_1 = 257\ \mathrm{cm}^3,\ \text{and}\ V_{\mathrm{g}} = 144\ \mathrm{cm}^3.$$

Somewhat different values of V_1 and V_{g} were used in part of the measurements since it was necessary to overhaul and reconstruct the apparatus during the course of the present study.

In order to calculate the diffusion coefficient, it is necessary to use physical constants such as gas solubility, vapor pressure, and density of solvent. Gas solubility data given by Ben-Naim and Baer[11] and Cargill and Morrison[12] (argon in ethanol+water solutions), Ben-Naim and Moran[13] (argon in 1,4-dioxane+water solutions) and Ben-Naim[14] (methane in ethanol+water solutions) were used. The density and vapor pressure of all the solvents have been taken from the compilation of Timmermans.[15]

Results and Discussion

Diffusion Coefficient of Argon and Methane in Water. In order to confirm the reliability of the apparatus, comparison has been made between the present data for pure solvents and those in literature. The diffusion coefficients of argon and methane have been studied extensively. Figures 3 and 4 show both data as a function of temperature. We have found that the diffusion coefficient of argon in water is 2.22×10^{-5} cm^2 s^{-1}. Literature values scatter a great deal. However, the reliable data by Duda[16] and Baird and Davidson[17] seem to converge to about 2.0×10^{-5} cm^2 s^{-1} at 25 °C. The agreement between both data is reasonable, though the present value is about 10% higher. The results for

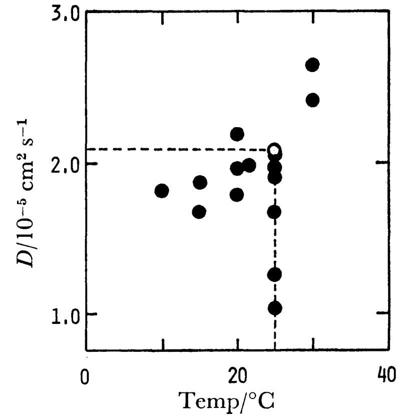

Fig. 3. Diffusion coefficient of argon in water as a function of temperature. ○: This work, ●: literature value.

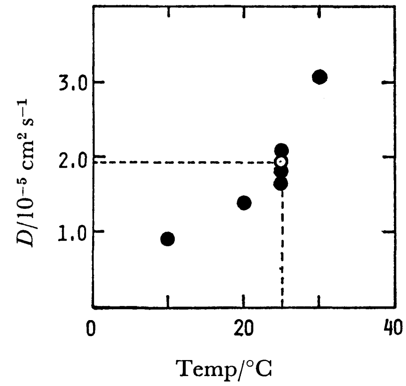

Fig. 4. Diffusion coefficient of methane in water as a function of temperature. ○: This work, ●: literature value.

methane do not scatter much, the representative datum due to Witherspoon and Saraf[18] being 1.88×10^{-5} cm^2 s^{-1} at 25 °C, in perfect agreement with the present data. It is thus concluded that the present data can be regarded as reliable.

Diffusion Coefficients in Aqueous Solutions. The diffusion coefficients of argon in aqueous solution of ethanol and in aqueous solution of 1,4-dioxane and of methane in aqueous solution of ethanol have been measured at 298.15 K. The measurements are restricted to water-rich regions. The results are given in Table 1, the values being an average of the results of two or three runs. Reproducibility is satisfactory, deviation being less than ±4%. The diffusion coefficients and the viscosity coefficient η of the mixed solvents are plotted against the mole fraction of ethanol or 1,4-dioxane in Figs. 5—7.

TABLE 1. DIFFUSION COEFFICIENTS OF ARGON AND METHANE IN AQUEOUS SOLUTIONS AT 298.15 K

Ar–H_2O+EtOH		Ar–H_2O+$C_4H_8O_2$		CH_4–H_2O+EtOH	
x_{EtOH}	$D^{a)}$	$x_{dioxane}$	D	x_{EtOH}	D
0	2.22	0	2.22	0	1.88
0.045	1.87	0.015	2.19	0.045	1.61
0.090	1.53	0.060	2.09	0.090	1.04
0.150	1.02	0.150	1.35	0.150	0.43
0.250	1.12	0.200	1.54	0.200	0.52
		0.250	1.85	0.250	0.54

a) 10^5 cm^2 s^{-1}.

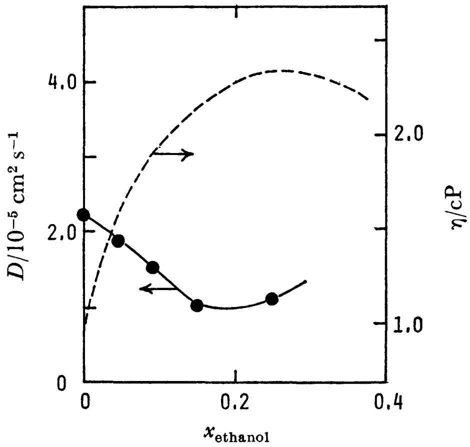

Fig. 5. Diffusion coefficients of argon in aqueous solutions of ethanol at 298.15 K.

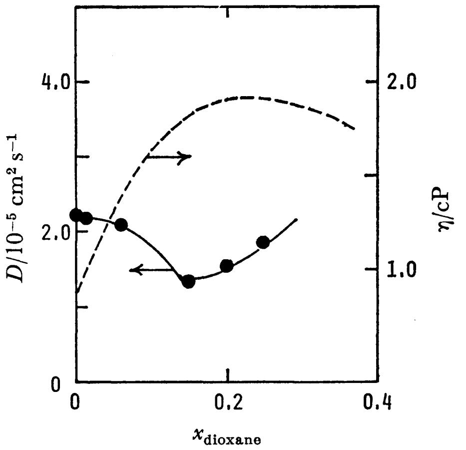

Fig. 6. Diffusion coefficients of argon in aqueous solutions of 1,4-dioxane at 298.15 K.

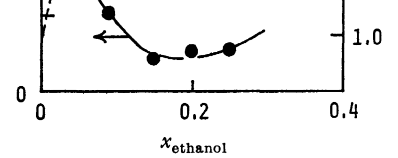

Fig. 7. Diffusion coefficients of methane in aqueous solution of ethanol at 298.15 K.

The viscosity of solvent increases with the addition of ethanol until the mole fraction of ethanol x_{EtOH} exceeds 0.25, at which the viscosity becomes maximum. A similar tendency can be seen for 1,4-dioxane solutions. On the other hand, the diffusion coefficient decreases rapidly with the addition of ethanol or 1,4-dioxane, becoming minimum near $x=0.2$, and then increasing. Thus D and η are inversely proportional with each other.

Anomaly in $D\eta$ vs. x Plot. It is common practice to reduce the D value with η to examine the behavior of the product $D\eta$ as a function of the composition of mixed solvents. We have recently studied the diffusion in mixed solvents using iodine as a solute and found that $D\eta$ value of iodine becomes maximum in aqueous alcohol (ethanol and *t*-butyl alcohol) solutions near $x_{\text{alcohol}}=0.1$ to 0.2.[1] A similar anomaly has been reported by Perkins and Geankoplis[19] for acetic acid in aqueous ethanol solutions. The minimum diffusion coefficient does not necessarily correspond to maximum viscosity. It is thus of interest to examine the relation $D\eta$ *vs.* x. Figure 8 shows the plot of $D\eta$ against x for argon and methane in aqueous ethanol solutions. It should be noted that a small peak appears in the region $x_{\text{EtOH}}<0.1$. This may be characteristic of aqueous alcohol solutions and aqueous solutions of all the compounds acting as a structural maker. Although 1,4-dioxane has been regarded often as a structural breaker, it may act as a structural maker as far as diffusivity concerned.

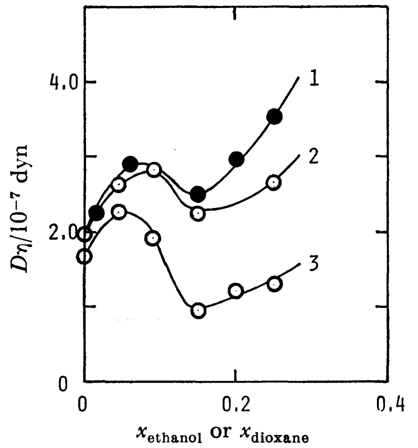

Fig. 8. Isoviscous diffusion coefficients as a function of mole fraction of ethanol or 1,4-dioxane in aqueous solutions. 1: Argon in 1,4-dioxane solutions, 2: argon in ethanol solutions, 3: methane in ethanol solutions.

Comparison between Ar and CH_4 and between Ethanol and 1,4-Dioxane Solutions. The diffusivity of gases in aqueous ethanol solution has been studied extensively.[20,21] The dependence of diffusion coefficient on the molar composition is complicated, varying with gas. In view of the complicatedness of the problem, we confine our attention to a comparison only between the three data obtained in the present study.

First we deal with the difference in the diffusivity of argon in aqueous ethanol solution and in aqueous 1,4-dioxane solution. When ethanol or 1,4-dioxane is added to water, viscosity increases a great deal to the same extent. However, the decrease in diffusivity is fairly large in ethanol solution, while that in 1,4-dioxane solution is small. This may be interpreted as follows. There should be various kinds of cavities in three dimensional hydrogen bonding structure in water. The size of these cavities is thought to be *ca.* 5.8—6.6 Å.[22] Since 1,4-dioxane shows no self-association, the cavity can be occupied by 1,4-dioxane molecule dissolved in water. In fact, the self-diffusion of 1,4-dioxane decreases distinctly with the increase in x_{dioxane} in aqueous solution.[23] When argon diffuses in aqueous 1,4-dioxane solution, capture of argon molecule in the water cavity is reduced. Rapid diffusion may be energetically favorable. In spite of a large viscosity increase, the diffusion of argon would not decrease much. On the other hand, the addition of ethanol to water may enlarge and stabilize the cavity in water. Therefore, in aqueous ethanol solution, argon can be easily trapped in the cavity and its diffusion coefficient will decrease a great deal with the addition of ethanol into water.

The diffusion coefficient of methane in aqueous ethanol solutions is always smaller than that of argon in the same solutions. This reflects the difference in the size of diffusant. For the size effect on diffusivity, Ross and Hildebrand[7] have proposed an empirical relation, $D\sigma^2 = \text{constant}$, where σ is the diameter of diffusant. Witherspoon and Saraf[18] showed that a relation, $D\sigma = \text{constant}$, seems to be also valid for the diffusion of gaseous hydrocarbons in water. In the present case, it can be shown that the latter gives a better fit. Thus

$$D_{\text{Ar}}\sigma_{\text{Ar}} = D_{\text{CH}_4}\sigma_{\text{CH}_4}, \tag{10}$$

seems to be valid in water. It is of interest to examine whether $D_{\text{Ar}}/D_{\text{CH}_4}$ is a constant in aqueous ethanol solutions. Figure 9 shows $D_{\text{Ar}}/D_{\text{CH}_4}$ *vs.* x_{EtOH} plot. The ratio becomes maximum near $x_{\text{EtOH}}=0.1$—0.15. This indicates that the capture of solute in the cavity of water enlarged by the introduction of ethanol depends appreciably on the kind of solute and the effect can be clearly seen in the composition range where the anomaly of aqueous ethanol solution is often observed.[5] The characteristics of the diffusivity of solutes in dilute aqueous solutions is too complicated to deduce a clear-cut interpretation. It seems necessary to accumulate experimental data for various solutes in aqueous mixed solvents at different temperatures.

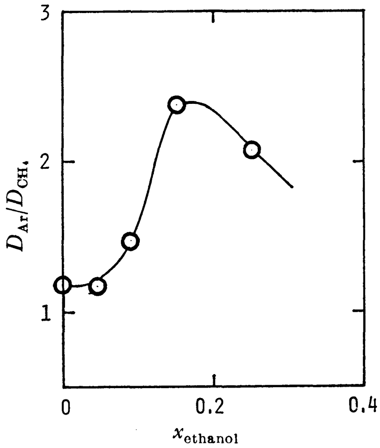

Fig. 9. Ratio of diffusion coefficient between argon and methane as a function of mole fraction of ethanol in aqueous solution.

The authors thank Mr. Soto Asakura for his cooperation in the earlier stage of the work. They are grateful to Prof. Nobuatsu Watanabe for his interest and discussion.

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8) It is possible that a stagnant layer is formed just below the diaphragm if no stirring is applied in the degassed liquid phase. However, no retardation of diffusion was observed in the experiment carried out with the same diaphragm as that used here.6) No stirrer was attached to the diffusion cell in the present experiment.

9) The method of calculation of diffusion coefficient described here is based on the one established by Hildebrand and co-workers.6,7) No detailed description of this method has been given.

10) The time required for the establishment of steady state diffusion seems to be longer than expected.

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