On the Diffusivity of Nonelectrolytes in Infinitely Dilute Solution

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The validity of the plot, isoviscous diffusion coefficient $D_1\eta_2$ *vs.* molar volume V_2, where D_1 is the diffusion coefficient of solute at infinite dilution, η_2 the viscosity coefficient of solvent, and V_2 the molar volume of solvent, proposed by Hammond and Stokes for carbon tetrachloride, was examined and confirmed with several solutes. General features of the behavior of diffusivity in dilute solution are discussed in terms of solvent association, complex formation and other factors. The experimental results for iodine are given.

The diffusivity of solute in dilute solution has been the subject of many studies primarily because of its practical importance. From a theoretical point of view, this quantity is of fundamental importance in describing transport properties of fluid systems. If the interdiffusion coefficients measured as a function of concentration in dilute solution are extrapolated to infinite dilution, the limiting value, D_1, represents the motion of a single particle in a medium having uniform but different intermolecular force field from that exerted by itself. Thus, the physical meaning of this quantity can be regarded to be almost the same as that of self-diffusion coefficient.

Stokes and co-workers[1,2] carried out extensive studies on the diffusion of carbon tetrachloride and iodine diluted with various organic solvents. An interesting result is a plot of the viscosity-reduced diffusion coefficient $D_1\eta_2$ (η_2; viscosity coefficient of solvent) of carbon tetrachloride against the molar volume, V_2, of the solvent. For the sake of convenience, the plot will be referred to hereafter as the HS (Hammond-Stokes) plot.[2] There are three linear relationships, each corresponding to a group of solvents, namely, spherical molecules, alcohols and the homolog of normal paraffins. All these plots have a positive slope and converge to a common point when extrapolated to $V_2=0$. This is the Stokes-Einstein limit where large particles diffuse in an essentially continuous medium.

The purpose of this paper is to examine the HS plot for other diffusates which sometimes show more complex interactions with solvents. New data are presented for iodine in six organic solvents.

Experimental

Apparatus and Procedure. The diffusion coefficient of iodine in six organic solvents was determined by the capillary cell method. The procedure was reported previously.[3] The diaphragm cell method was also used in part of the measurements. The apparatus and procedure were similar to those given by Hammond and Stokes[2] and Mills and Woolf.[4] The solution-filled procedure was adopted throughout the measurement. The diaphragm used was a micropore glass filter, No. 4. In order to determine the cell constant of the diaphragm, several runs were performed with aqueous KCl solutions. The cell constant was found to be 0.315 cm^2. The concentration changes in two compartments of the cell were determined by measuring the density of solution. A precision vibration-type densimeter (Shibayama Sci. Instr. Co., Model SS·D 200) was used. The concentration change of iodine in the diaphragm cell experiment was determined by titration using sodium thiosulfate solution. The methods of calculation of diffusion coefficient from these two types of measurement have been described.[3,4]

Table 1. Diffusion coefficients of iodine dilute in six organic solvents at 298.15 K

Solvent	D_1 10^5 cm^2 s^{-1}	η_2 cP[a)]	$D_1\eta_2$ 10^{10} dyn[b)]
Heptane	3.40±0.10	0.395	1.34
2,2,4-Trimethylpentane	2.93±0.04	0.484	1.38
1,4-Dioxane	0.96±0.03	1.190	1.14
Tetrahydrofuran	2.35±0.08	0.480	1.09
1-Propanol	1.07 1.00[c)]	1.95	2.03
2-Propanol	0.89 0.84[c)]	2.10	1.83

a) cP = centipoise = 0.01 P. 1P = 0.1 Pa s throughout this paper. b) 1 dyn = 10^{-5} N throughout this paper. c) Data obtained by the diaphragm cell method.

Results. In connection with the study of diffusion in mixed solvents, the values for the diffusion coefficients of iodine diluted in nine pure solvents have been reported.[3,5,6] The six new data obtained with capillary and diaphragm cell methods are summarized in Table 1. Whenever measurements are duplicated by the two methods, both results agree fairly well with each other. The datum for iodine in heptane agrees with the literature value,[1] while there is a small discrepancy between the two data for iodine in 1,4-dioxane.[1]

Hammond-Stokes Plot for a Solute in Different Solvents

Our literature survey indicates that the diffusion coefficients of a solute in a variety of solvents are available only for limited solutes at 298.15 K. We have tested the validity of the HS plot for these solutes. In the case of CCl_4 and I_2, additional data have been reported since the original works by Stokes *et al.* The HS plots for these two solutes are shown in Figs. 1a and 1b. Other typical examples are also given in Figs. 2a—2f.

We see that the product $D_1\eta_2$ increases when V_2 becomes large. In a limited range where V_2 is between 50 and 200 cm^3 mol^{-1}, $D_1\eta_2$ *vs.* V_2 relation may be approximated by three straight lines. The line with the largest slope is associated with alcohols, aniline, and other associated solvents. Sometimes water can be included in this category. The other two lines are respectively for spherical molecules and for normal paraffins and related chain-like molecules. Extrapolation of these three straight lines may converge to a

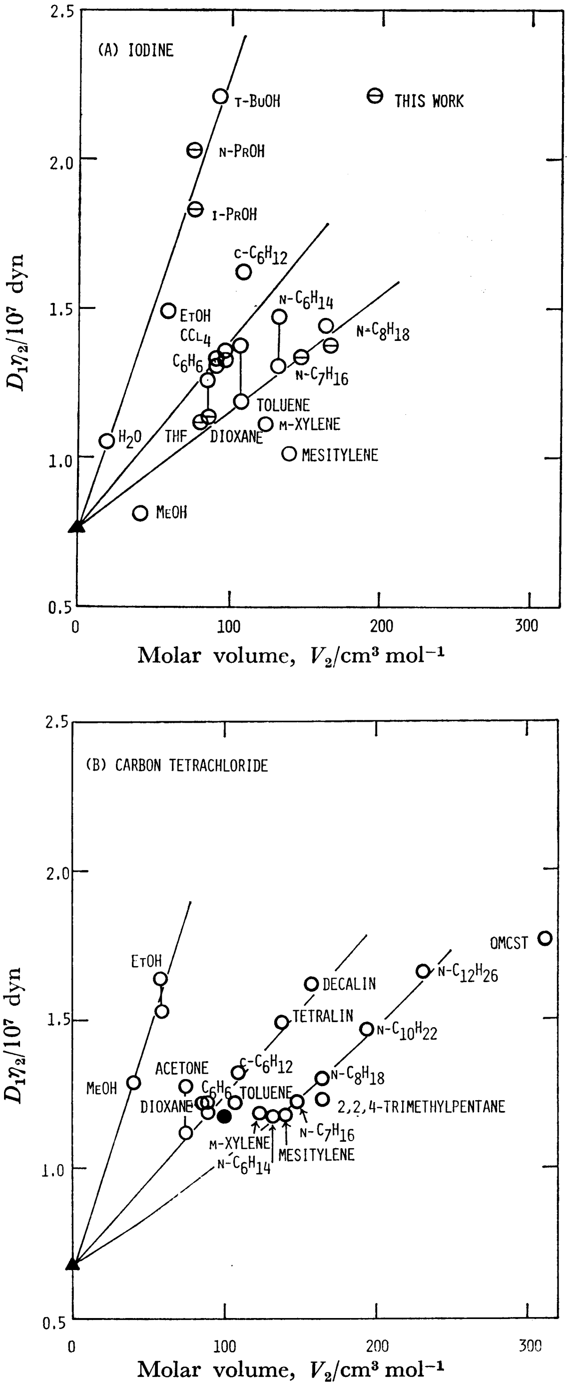

Fig. 1. Hammond-Stokes plot for the diffusion of iodine and carbon tetrachloride in various solvents at 298.15 K. (A) Iodine, (B) carbon tetrachloride. ○, ⊖: $D_1\eta_2$, ●: $(D_1)_{\mathrm{self}}\eta_2$, ▲: $D_1\eta_2$ at the Stokes-Einstein limit. Perpendicular lines connect two or more data for the same solvent from different sources.

common point at $V_2=0$. The point given as a triangle represents the D_1 value at the Stokes-Einstein limit and its $D_1\eta_2$ value can be calculated from the Stokes-Einstein equation,

$$D_1\eta_2 = kT/6\pi r_1,$$

where the radius of solute, r_1, is given by

$$r_1 = (3V_1/4\pi N_{\mathrm{av}})^{1/3}.$$

Here V_1 is the molar volume of solute at 298.15 K and N_{av} is the Avogadro number.

Although generalization of the original treatment by Hammond and Stokes[2)] can be fully verified as above, we have made several interesting observations. In the following discussion, the self-diffusion coefficient, $(D_1)_{\mathrm{self}}$, can be included in the correlation. The literature values of $(D_1)_{\mathrm{self}}\eta_2$ are taken mainly from the compilations of Dullien[7)] and Tyn and Calus.[8)]

(1) Whenever a constant slope of $D_1\eta_2$ *vs.* V_2 relation for the same group of solvents can be established, it is almost independent of the solute used. Estimated values for the group of nearly spherical molecules are between 0.95 and 0.55×10^{-9} dyn·mol·cm^3, with the exception of carbon dioxide and other smaller solutes which have a larger slope. This is to be compared with 0.60×10^{-9} for CCl_4 reported by Hammond and Stokes.[2)]

(2) It should be noted that the $D_1\eta_2$ *vs.* V_2 plot for nonpolar liquids deviates upward from linearity as V_2 increases beyond 200 cm^3 mol^{-1} or so. This tendency seems to be evident for smaller solutes such as ethane (Fig. 2a) and carbon dioxide (Fig. 2b). Perhaps the larger difference in molar volume between solute and solvent may be responsible for this deviation.

(3) Benzene, cyclohexane and CCl_4 form a triplet of simple organic liquid. They are all spherical or disk-like molecules and their molar volume is as large as 100 cm^3 mol^{-1}. However, when examined in detail, the molar volume is in the order, $c\text{-}C_6H_{12}>CCl_4>C_6H_6$, while their diffusion coefficient in the same solvent always increases in the order, $C_6H_6>c\text{-}C_6H_{12}>CCl_4$. This indicates that, in spite of larger molar volume, the diffusivity of cyclohexane is somewhat higher than that of CCl_4.

(4) If the diffusing solute has a strong interaction with solvent, that is, there is a solvation between unlike molecules, the product $D_1\eta_2$ takes somewhat lower values.[8,9)] A typical example is the case of acetone in chloroform (Fig. 2e), a classical example of binary solution in which the hydrogen bonding between unlike molecules is a source of negative deviation from the ideal solution law. A similar decrease in $D_1\eta_2$ values is also observed for chloroform in ethers, and esters, and in the present data, I_2 in 1,4-dioxane and THF.

(5) The $D_1\eta_2$ *vs.* V_2 plot for various solutes in aliphatic alcohols has a larger slope.[2)] A similar tendency is observed for the cases of ethylene glycol (Fig. 2b) and aniline (Fig. 2d) as solvents.

(6) The behavior of water as a solute in various kinds of solvents is puzzling. According to Fig. 2f, the $D_1\eta_2$ values for water in hydrophilic solvents such as alcohols, ketones, esters and carboxylic acids are generally small and close to the value at the Stokes-Einstein limit. However, they are higher in nonpolar solvents. No consistent interpretation can be given at the present stage.

Diffusivity of Different Solutes in the Same Solvent

Let us examine a variation of the diffusion coefficient of different solutes in the same solvent with the molar

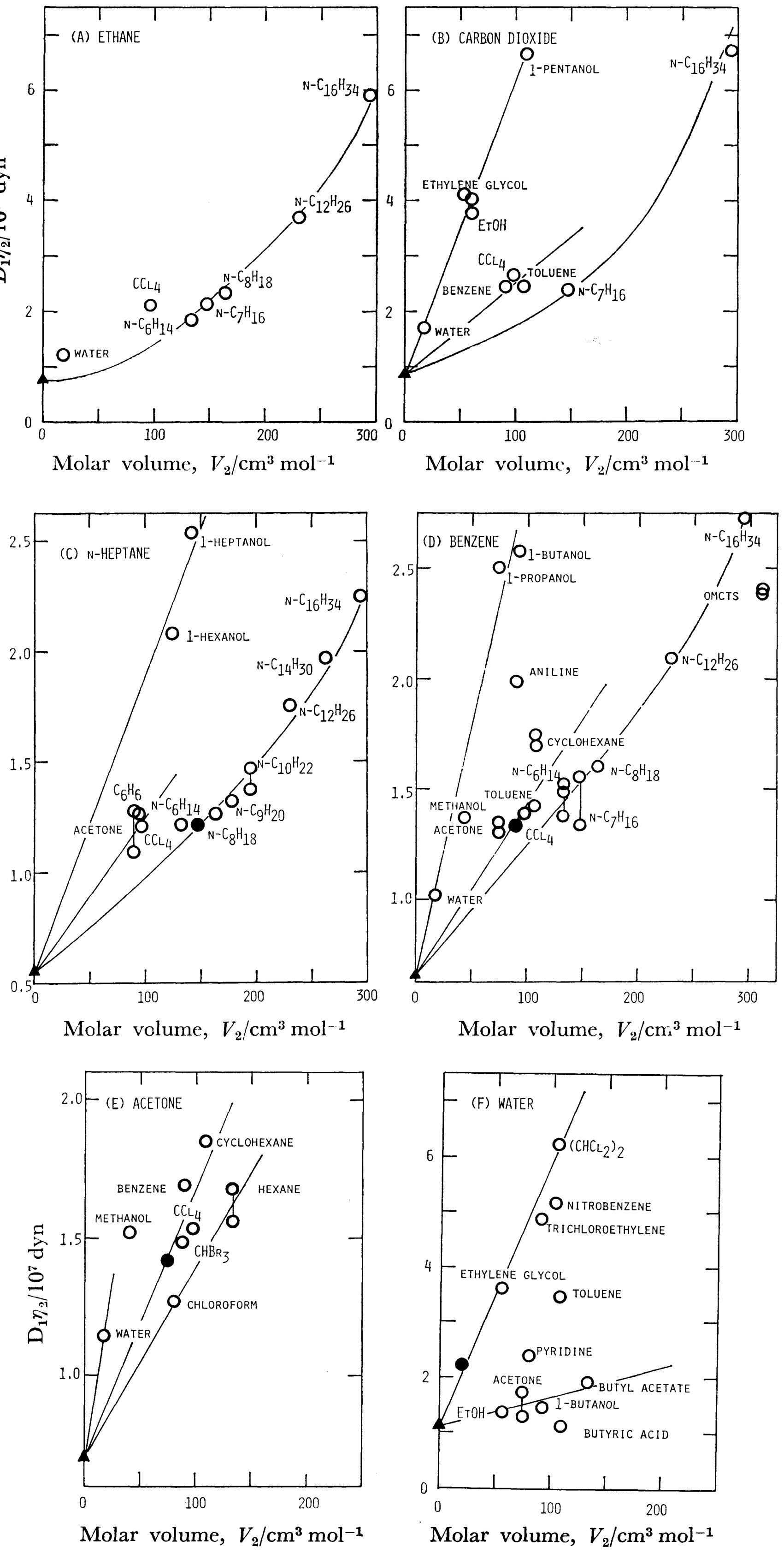

Fig. 2. Hammond-Stokes plot for six solutes at 298.15 K. (A) Ethane, (B) carbon dioxide, (C) heptane, (D) benzene, (E) acetone, (F) water. The notations are the same as those in Fig. 1.

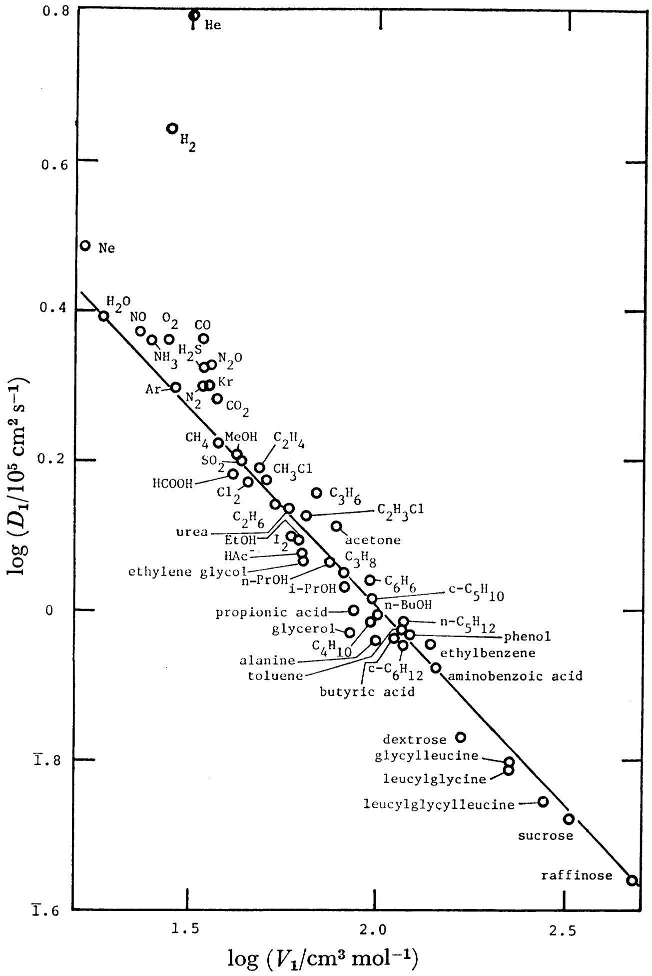

Fig. 3. Log D_1 *vs.* log V_1 plot for various solutes in water at 298.15 K.

volume of solute. Abundant data are available for only limited solvents at 298.15 K. Since no successful procedure has been given for this kind of analysis on diffusivity, we will follow a simple empirical rule proposed by Hildebrand *et al.*[10)]

They claimed that the product $D_1\sigma_1^2$ or $D_1(V_c)_1^{2/3}$ where σ_1 is the diameter of molecule and V_c is the critical volume, is found to be constant for non-quantum gases diffusing in CCl_4 and $(n\text{-}C_4F_9)_3N$. We will therefore examine the log D_1 *vs.* log V_1 plot in some selected solvents at 298.15 K. The results are shown in Figs. 3 and 4.

In the case of water as solvent, we see that a good correlation can be established in a V_1 range between 16.8 (neon) and 480 (raffinose) (Fig. 3). All the points scatter properly around a straight line; and large deviations, both positive and negative, can be seen. Helium, hydrogen, and deuterium show a large positive deviation which can be ascribed to a mass effect.[10b)] On the other hand, hydrophilic solutes seem to show small negative deviations. We may cite the following solutes: glycerol, ethylene glycol, carboxylic acids, and to a lesser extent, ethanol and 2-propanol The slope of the straight line in log D_1 *vs.* log V_1 plot obtained for water is very close to 2/3, which is equivalent to the rule of the constancy of $D_1\sigma_1^2$ proposed by Hildebrand.[10)]

Water(0.89)–cyclohexane(0.89)–carbon tetrachloride (0.90) forms a triplet of isoviscous solvents (Values in parentheses indicate the viscosity coefficient in centipoise for each solvent). The log D_1 *vs.* log V_1 plot for solutes in the latter two solvents is illustrated in Fig. 4. The points for each solute can be classified into three groups; (i) nearly spherical molecules, (ii) normal paraffins, and (iii) other solutes. The slope of linear relation representing group (i) is slightly larger than that for group (ii). Such a difference in slope is ambiguous in the case of water, and the slope for water as solvent

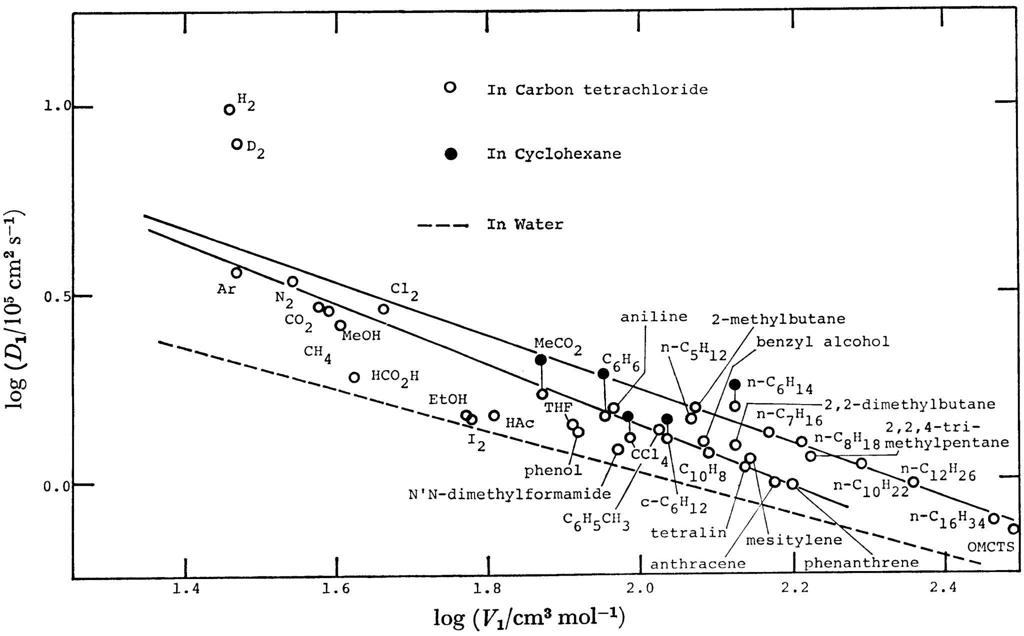

Fig. 4. Log D_1 *vs.* log V_1 plots for various solutes in carbon tetrachloride and cyclohexane at 298.15 K.

being in an intermediate between those for two groups in CCl_4 (dashed line in Fig. 4). The values of diffusion coefficient in water are generally smaller than those in CCl_4 and cyclohexane, indicating that the decrease in diffusivity due to the hydration of each solute cannot be negligible.[11]

The effect of attractive interaction on diffusivity seems to be evident as in the case of the HS plot (Figs. 3 and 4). These observations are supported by recent molecular dynamics calculations on Lennard-Jones liquid mixtures.[12]

In conclusion, the present analysis of the data for the diffusion coefficient in dilute solution reveals general validity of the Hammond-Stokes plot and the presence of the effect of strong specific interaction which causes a decrease in the diffusivity of polar and associated solutes. The analysis will be useful as the basis for empirical methods for predicting the diffusion coefficient in dilute solutions.

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