1278 © 1980 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **53**, 1278—1282 (1980) [Vol. 53, No. 5

Kinetic Studies of the Electron Transfer Reactions in Iron(II) and Iron(III) Systems. IX. Electron Transfer Reactions between Iron(II) and Iron(III) in Water Mixed with Ethanol, 1-Propanol, Ethylene Glycol, Glycerol, and Pentaerythritol

Goro Wada,* Youko Ohta, Sachiko Hayashida, Harumi Sugino,
Toyomi Mizui, and Yumiko Aihara
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

(Received August 9, 1979)

The rate constants of the electron transfer reactions between Fe(II) and Fe(III) were determined in mixed solvents of water and alcohols, such as ethanol, 1-propanol, ethylene glycol, glycerol, and pentaerythritol. From the acid concentration dependence of the rate, the predominant path of the reaction was estimated to be Fe^{2+}-$Fe(OH)^{2+}$ path with a rate constant k_H. The rate constant k_H increases with increase in the mole fraction x of ethanol and 1-propanol, and decreases with increase in x of methanol, ethylene glycol, glycerol, and pentaerythritol. A straight line is obtained when $\ln k_H$ is plotted against the reciprocal dielectric constant D^{-1} of the mixed solvents for the latter group of alcohols. From the slope of the straight line the distance between Fe^{2+} and $Fe(OH)^{2+}$ is estimated to be 7.8 Å at the intermediate stage of the reaction. Therefore, the reaction is mostly controlled by the electrostatic repulsive force, being influenced by D of the mixed solvents.

The electron transfer reactions between iron(II) and iron(III) in aqueous media proceed by a mechanism of hydrogen-atom transfer in the absence of catalyzing ligands which would make the reactions occur by either inner-sphere or outer-sphere mechanism.[1] In the hydrogen-atom transfer mechanism, an electron is transferred by a hydrogen atom, which can be regarded to behave as a proton carrying an electron, along a chain of hydrogen bondings between OH radicals of water or alcohol, with the oxidant and the reductant species at both ends.

If a foreign substance is added to the reaction system and the chain of hydrogen bondings is broken to some extent, the reactions by this mechanism would be retarded, causing a slowering of the reaction rate. This is what happens when substances such as nitromethane,[2] and some alcohols[3,4] are added. The effect of addition of methanol to the reaction system of the electron transfer between iron(II) and iron(III) was investigated in aqueous solutions.[5] In the present investigation, alcohols other than methanol, such as ethanol, 1-propanol, ethylene glycol, glycerol, and pentaerythritol were used for the purpose of clarifying the influence of the number of OH groups, the hydrophobicity of alkyl groups and the dielectric constants of the alcohols on the reaction rates, and confirming the reaction mechanism. The experimental results are discussed including data of the case of methanol.

Experimental

Materials. Alcohols of specially pure grade were purified as follows: ethanol and 1-propanol were redistilled under ordinary pressure, ethylene glycol and glycerol were redistilled under reduced pressures, and pentaerythritol was twice recrystallized from its aqueous solution. The method of preparation and purification of other materials used were the same as those already reported.[5,6)

Procedures. The hydrolysis constants of Fe^{3+} ion, $K_H=[Fe(OH)^{2+}][H^+]/[Fe^{3+}]$ and the rate constants of the electron transfer reaction, k, in mixed solvents of water and alcohols were determined in the same manner as reported.[5—7] The ionic association between Fe^{3+} ion and ClO_4^- ion was also checked in mixed solvents.[5] For the determination of optical densities, a Hitachi-Perkin-Elmer UV-VIS spectrophotometer Model 139 was used. The ionic strengths of the solutions were adjusted at 0.5 M by use of $NaClO_4$.

Results and Discussion

Hydrolysis Constants of Fe^{3+} Ion, K_H, in Mixed Solvents. In an aqueous solution containing iron(III) perchlorate and perchloric acid, Fe^{3+}_{aq} is partly hydrolyzed to $Fe(OH)^{2+}$ with a hydrolysis constant $K_H=[Fe(OH)^{2+}][H^+]/[Fe^{3+}]$, the following relation being established:[5]

$$\frac{[Fe(III)]}{A_H}=\frac{1}{\varepsilon_H}+\frac{[H^+]}{\varepsilon_H K_H} \tag{1}$$

where ε_H and A_H denote the molar absorption coefficient of $Fe(OH)^{2+}$ and the optical density due to $Fe(OH)^{2+}$ being equal to $\varepsilon_H[Fe(OH)^{2+}]$, respectively. [Fe(III)] and $[H^+]$ are the total concentration of iron(III) which is equal to the sum of $[Fe^{3+}]$ and $[Fe(OH)^{2+}]$ and the concentration of hydrogen ion which is also equal to the sum of the total concentration of perchloric acid added $[HClO_4]$ and the concentration of hydrolyzed species of iron(III), $[Fe(OH)^{2+}]$, respectively. The plot of $[Fe(III)]/A_H$ against $[H^+]$ would give a straight line with an intercept $1/\varepsilon_H$ and a slope $1/\varepsilon_H K_H$. First, the total optical density of the solution A was used instead of A_H, not known empirically, in order to obtain an approximate K_H, and the precise value of K_H could be obtained by means of successive approximations.

In order to determine A_H necessary for Eq. 1, the value of the molar absorption coefficient of Fe^{3+}, ε_0, should be known, since A_H has to be calculated by an equation $A_H=A-\varepsilon_0[Fe^{3+}]$. When acid concentration is varied from 0.01 M to 4 M, the apparent molar absorption coefficient $\varepsilon(=A/[Fe(III)])$ decreases abruptly, passes a broad minimum, and then increases approximately linearly. An example is shown in Fig. 1, for the case of 1-propanol, the curves being quite similar to the case of methanol.[5] The abrupt di-

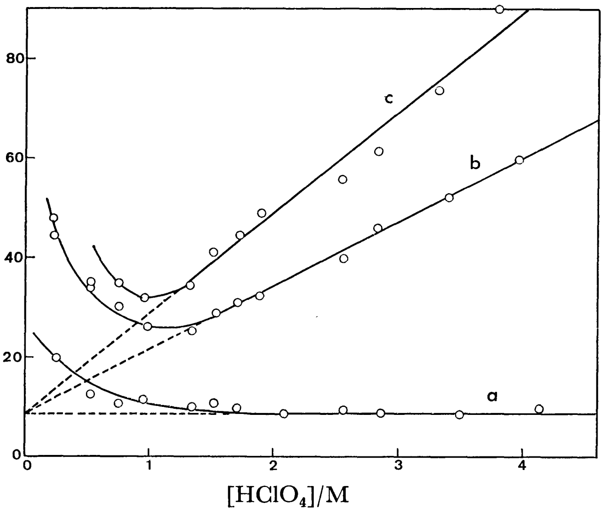

Fig. 1. Variation in apparent absorption coefficient ε of 1-propanol and water mixtures with perchloric acid concentration at $[\mathrm{Fe(III)}]=1.5\times10^{-3}$ M, 330 nm, and 25 °C.
a: $x=0$, b: $x=0.10$, c: $x=0.18$.

minution of ε in the lower acid concentration range is due to the decrease in the concentration of hydrolyzed species of $\mathrm{Fe^{3+}}_{\mathrm{aq}}$, since ε_{H} is much larger than ε_0. On the other hand, the growth of ε in the higher acid concentration range is due to ionic association between $\mathrm{Fe^{3+}}$ and $\mathrm{ClO_4^-}$ ions, which does not occur in the absence of alcohol, this being observed more markedly at higher mole fraction of alcohol. Thus, ε is expressed by

$$\varepsilon=\frac{\varepsilon_0+\varepsilon_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H^+}]^{-1}+\varepsilon_{\mathrm{a}}K_{\mathrm{a}}[\mathrm{H^+}]}{1+K_{\mathrm{H}}[\mathrm{H^+}]^{-1}+K_{\mathrm{a}}[\mathrm{H^+}]}, \tag{2}$$

where ε_{a} and K_{a} are the molar absorption coefficient and the formation constant of ion-pair, respectively.[5]

If the linear part of a curve is extended to $[\mathrm{HClO_4}]=0$ the intercept of the extended straight line would give the value of ε_0 in the alcoholic solution. According to the extrapolation (broken lines in Fig. 1), ε_0 seems to have a constant value independent of the mole fraction of alcohol. In the cases of polyhydric alcohols, however, convergence to a common intercept does not generally take place; ε_0 seems to increase gradually with the increase in x. This might be due to the partial solvation of alcohol molecules into the hydration sphere of iron(III). At any rate, the ε_0 values estimated by this back extrapolation of the curves of ε against acid concentration were used for the calculation of A_{H}. In the present investigation, the acid concentration was so small that the occurrence of ion-pair formation was ignored.

The linearity of A_{H}^{-1} *vs.* $[\mathrm{H^+}]$ is shown at constant $[\mathrm{Fe(III)}]=1.0\times10^{-4}$ M at various mole fractions x of ethanol in Fig. 2. The values of K_{H} thus obtained are given in Table 1 for various mole fractions of alcohols. The value of K_{H} increases with the increase in x for all the alcohols studied.[5]

The Rate of Electron Transfer Reaction. The reaction proceeds with an apparent second-order rate constant k_{app} according to McKay's equation[8]

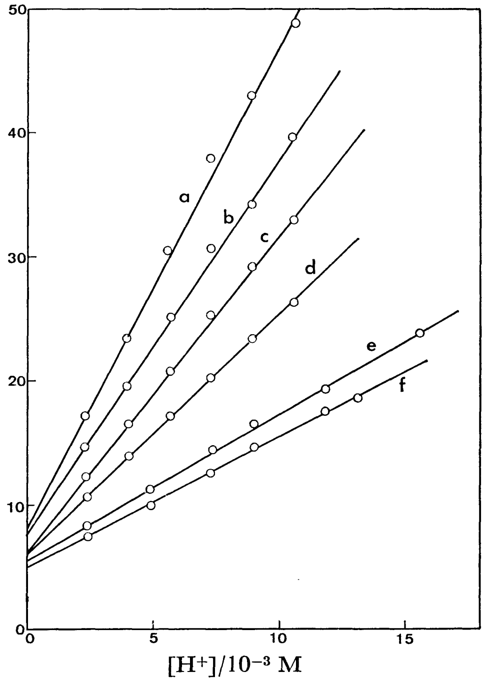

Fig. 2. Linear relationship of A_{H}^{-1} *vs.* $[\mathrm{H^+}]$ at various mole fractions of ethanol x at $[\mathrm{Fe(III)}]=1.0\times10^{-4}$ M and 25 °C.
a: $x=0$, b: $x=0.04$, c: $x=0.09$, d: $x=0.14$,
e: $x=0.21$, f: $x=0.30$.

TABLE 1. HYDROLYSIS CONSTANTS K_{H} AND RATE CONSTANTS k_{H} AT MOLE FRACTIONS OF ALCOHOLS x AND DIELECTRIC CONSTANTS OF MIXED SOLVENTS D AT $\mu=0.5$ M AND 25 °C

Alcohol	x	D	$\frac{K_{\mathrm{H}}}{10^{-3}\,\mathrm{M}}$	$\frac{k_{\mathrm{H}}}{10^{3}\,\mathrm{M^{-1}\,s^{-1}}}$
Ethanol	0	78.5	1.9	2.7
	0.04	72.8	2.0	3.1
	0.09	66.6	2.5	3.5
	0.14	61.0	3.2	3.7
	0.21	54.5	4.8	3.8
	0.30	47.8	4·7	3.7
1-Propanol	0.10	59.0	3.3	3.7
	0.18	48.5	4.7	3.9
Ethylene glycol	0.039	75.9	4.0	1.49
	0.085	72.7	4.9	1.40
	0.145	69.5	7.7	0.98
	0.206	66.0	10.8	0.76
	0.289	61.4	20.7	0.60
	0.394	56.0	32.2	0.33
Glycerol	0.027	75.0	2.8	—
	0.058	71.6	6.2	1.1
	0.096	68.6	8.9	—
	0.141	65.4	9.2	0.94
	0.198	61.6	13.4	—
	0.270	57.8	17.5	0.54
Pentaerythritol	0.00091	—	2.4	2.3
	0.00181	—	2.9	2.1
	0.00542	—	5.1	1.2

$$k_{\mathrm{app}}=\frac{0.693}{([\mathrm{Fe(II)}]+[\mathrm{Fe(III)}])t_{1/2}} \tag{3}$$

where $t_{1/2}$ represents the half period of the reaction, which can be determined from the slope of a straight line obtained by plotting logarithms of the radioactivities caused by one of the reacting species against the reaction time. The variations of k_{app} in mixed solvents at various mole fractions of various alcohols are shown in Figs. 3—7. In the cases of ethanol (Fig. 3) and 1-propanol (Fig. 4), k_{app} increases with increase in x, contrary to the case of methanol,[5] in which k_{app} remains constant in the biginning, decreasing gradually with increase in x. In the cases of ethylene glycol (Fig. 5) and glycerol (Fig. 6), k_{app} first increases in a similar way to the cases of ethanol and 1-propanol, but then decreases. In the case of pentaerythritol (Fig. 7), k_{app} remains almost unchanged as far as its solubility in water permits the experiments. In all the measurements of k_{app} (Figs. 3—7), the values of k_{app} are always larger at lower acid concentrations.

Reaction Paths. Iron(III) might take part in the electron transfer reactions in two forms such as Fe^{3+}_{aq} and $Fe(OH)^{2+}$, the latter being produced in

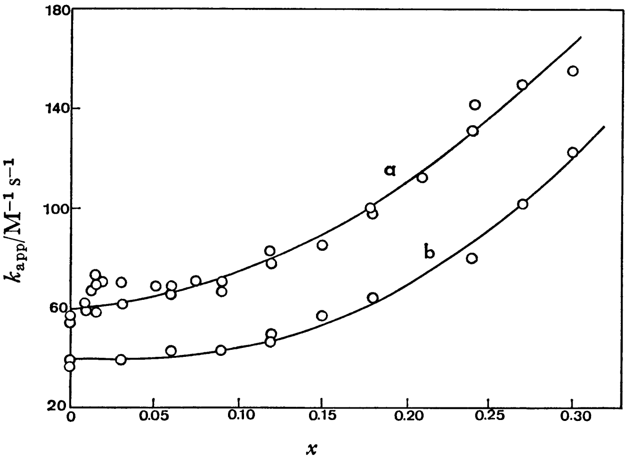

Fig. 3. Variation of k_{app} upon mole fraction of ethanol x at μ=0.5 M and 25 °C.
a: $[H^+]$=0.10 M, b: $[H^+]$=0.15 M.

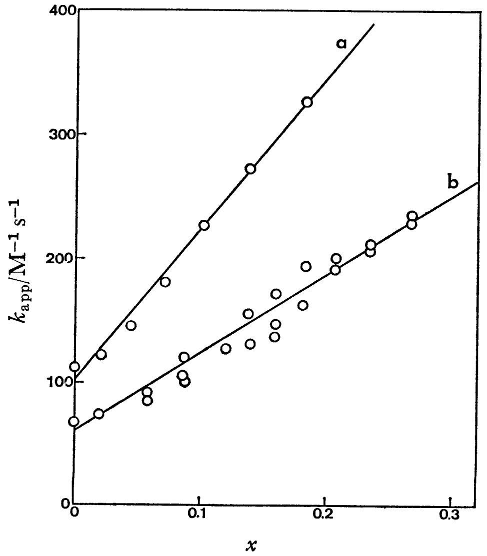

Fig. 4. Variation of k_{app} upon mole fraction of 1-propanol x at μ=0.5 M and 25 °C.
a: $[H^+]$=0.05 M, b: $[H^+]$=0.10 M.

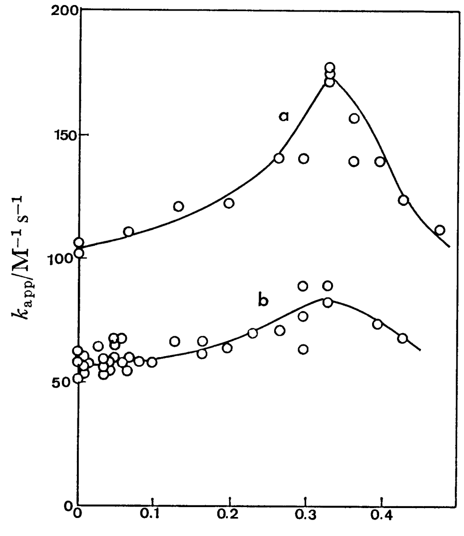

Fig. 5. Variation of k_{app} upon mole fraction of ethylene glycol x at μ=0.5 M and 25 °C.
a: $[H^+]$=0.05 M, b: $[H^+]$=0.10 M.

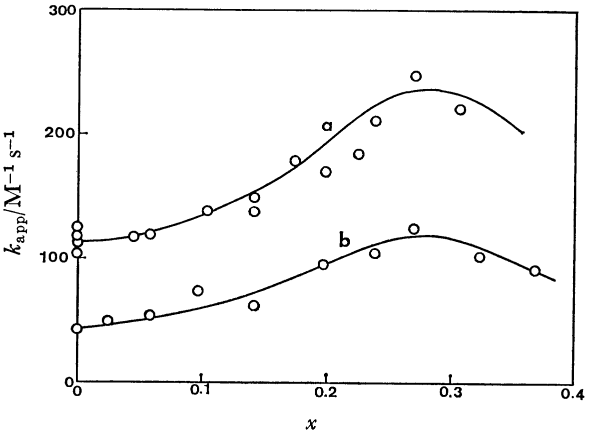

Fig. 6. Variation of k_{app} upon mole fraction of glycerol x at μ=0.5 M and 25 °C.
a: $[H^+]$=0.05 M, b: $[H^+]$=0.15 M.

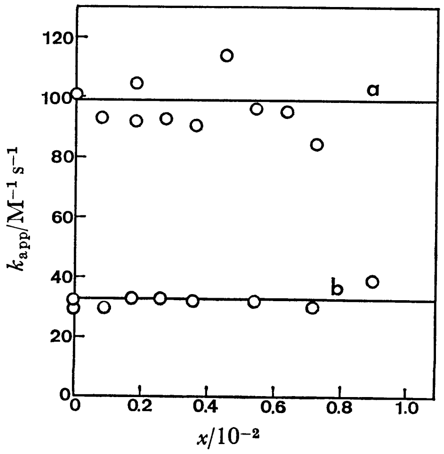

Fig. 7. Variation of k_{app} upon mole fraction of pentaerythritol x at μ=0.5 M and 25 °C.
a: $[H^+]$=0.065 M, b: $[H^+]$=0.20 M.

a greater amount in lower acid concentrations. The main reaction paths are considered to be as follows:

$$Fe^{2+} + {}^*Fe^{3+} \longrightarrow Fe^{3+} + {}^*Fe^{2+} \qquad (k_0) \qquad (4)$$

$$Fe^{2+} + {}^*Fe(OH)^{2+} \longrightarrow Fe(OH)^{2+} + {}^*Fe^{2+} \qquad (k_H) \qquad (5)$$

When the respective rate constants of Paths 4 and 5 are denoted by k_0 and k_H, the apparent second-order rate constant of the electron transfer reaction would be given by[5]

$$k_{app} = \frac{k_0 + k_H K_H [H^+]^{-1}}{1 + K_H [H^+]^{-1}}. \qquad (6)$$

In order to confirm the mechanism, the values of $k_{app}(1+K_H[H^+]^{-1})$ were plotted against $[H^+]^{-1}$, linearity being obtained in each case. An example is shown in Fig. 8, where ethanol is adopted as a cosolvent in the $[H^+]$ range 0.03—0.3 M. The values of k_0 and $k_H K_H$ were obtained from the intercepts and the slopes. By using the values of K_H listed in Table 1, the values of k_H were obtained. The values of k_0 are usually very small and, consequently, inaccurate as compared with those of k_H. Therefore, the reaction rate via Path 5 is overwhelmingly greater than that via Path 4, except for the case in which very high acid concentration was used. The following discussion is thus restricted to Path 5.

The variation of k_H with x of various alcohols is shown in Fig. 9, along with that of methanol.[5] The k_H value decreases with increase in x of individual alcohol, the order of the depression effect being methanol<ethylene glycol<glycerol<pentaerythritol, in line with the order mono-<di-<tri-<tetra-hydric alcohols; k_H increases with increase in x in the cases of ethanol and 1-propanol.

Discussion. Both K_H and k_H vary with x (Table 1 and Fig. 9). However, when their logarithms are plotted against the reciprocals of dielectric constants of the mixed solvents,[9] the points lie on a straight line independent of the kind of alcohol with a positive and a negative slope corresponding to the plots of ln K_H and ln k_H respectively (Figs. 10 and 11). There are two exceptions: ethanol and 1-propanol. They give another straight line in Fig. 10 and deviate a great deal from linearity in Fig. 11.

Except for the cases of ethanol and 1-propanol,

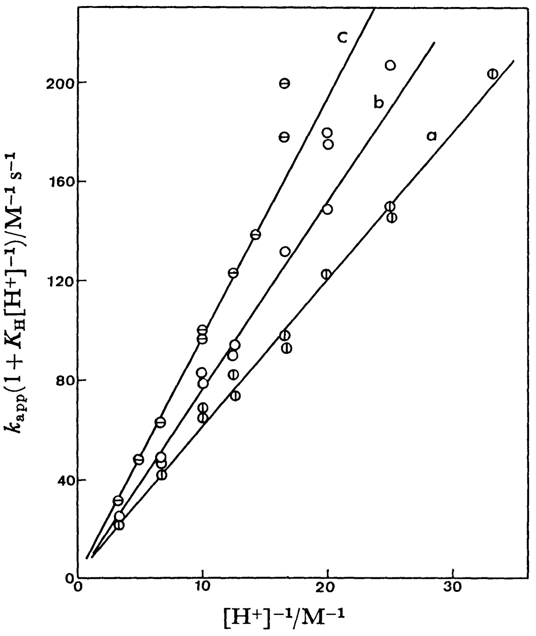

Fig. 8. Linear relation of $k_{app}(1+K_H[H^+]^{-1})$ with $[H^+]^{-1}$ at various ethanol mole fractions x at μ=0.5 M and 25 °C.
a: x=0.04, b: x=0.09, c: x=0.14.

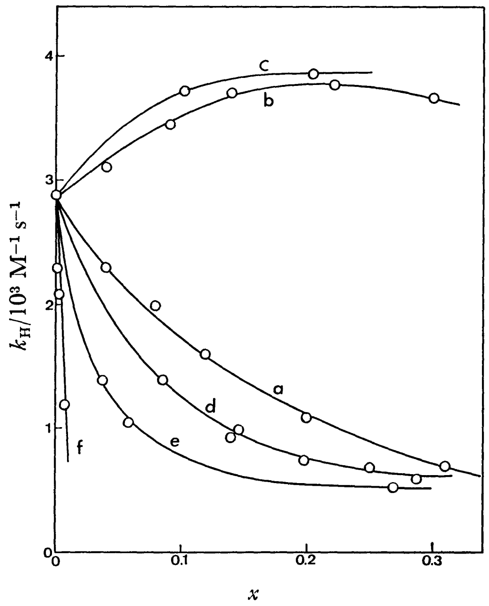

Fig. 9. Variation of k_H upon mole fraction of alcohols x at μ=0.5 M and 25 °C.
a: Methanol, b: ethanol, c: 1-propanol, d: ethylene glycol, e: glycerol, f: pentaerythritol.

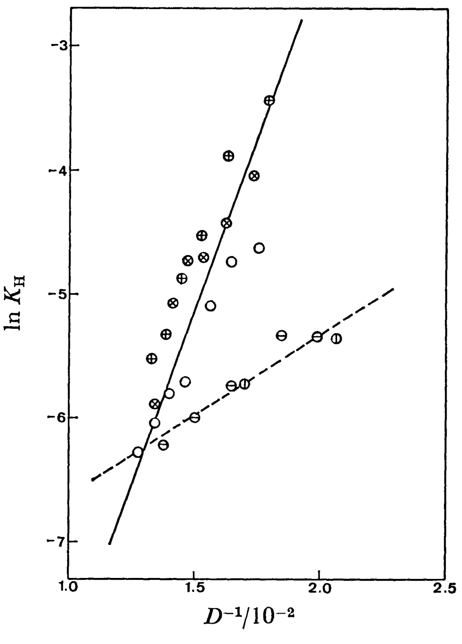

Fig. 10. Relationships between ln K_H and reciprocal dielectric constant D^{-1} in mixed solvents at μ=0.5 M and 25 °C.
○: Methanol, ⊖: ethanol, ⦶: 1-propanol, ⊕: ethylene glycol, ⊗: glycerol.

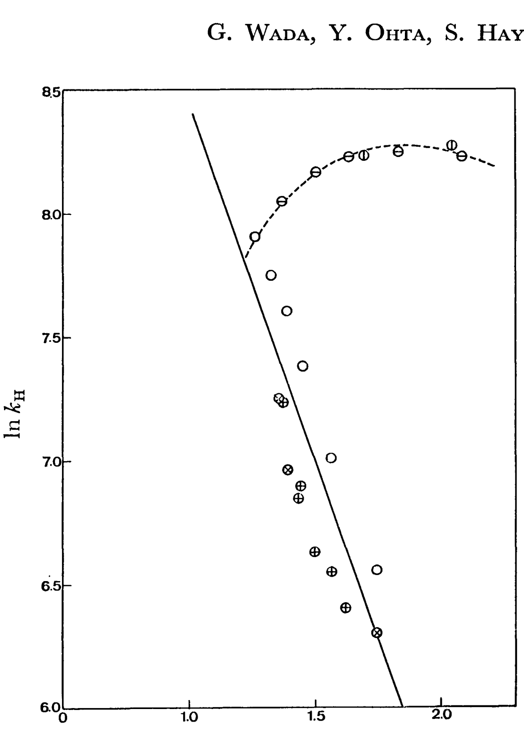

Fig. 11. Relationships between ln k_H and reciprocal dielectric constant D^{-1} in mixed solvents at $\mu=0.5$ M and 25 °C.

○: Methanol, ⊖: ethanol, ⦶: 1-propanol, ⊕: ethylene glycol, ⊗: glycerol.

the fact that the plots of ln K_H and ln k_H *vs.* D^{-1} lie on a straight line indicates that both the hydrolysis reaction $Fe^{3+} \rightleftharpoons Fe(OH)^{2+} + H^+$ and Path 5 in the electron transfer reaction $Fe^{2+} + Fe(OH)^{2+} \rightarrow Fe(OH)^{2+} + Fe^{2+}$ are mostly influenced by electrostatic repulsion between the ions of the same sign, $Fe(OH)^{2+}$ and H^+, and Fe^{2+} and $Fe(OH)^{2+}$ respectively, in mixed solvents of different dielectric constants. According to Scatchard, these linear correlations are expressed by[10)]

$$\ln K_H = \ln K_H^\circ + \frac{Z_A Z_B e^2}{kTd_H D}, \tag{7}$$

$$\ln k_H = \ln k_H^\circ - \frac{Z_C Z_D e^2}{kTd_{Fe} D}, \tag{8}$$

where Z_A, Z_B, Z_C, and Z_D are the numbers of electric charges on the reacting ions, e the elementary electric charge, k the Boltzmann constant, D the dielectric constant of the mixed solvents, and d_H and d_{Fe} the distances of the closest approach between the two reacting ions in the intermediate states during the course of hydrolysis and the electron transfer, respectively. K_H° and k_H° are hypothetical constants in solvents of infinite dielectric constant.

In the case of the hydrolysis, the reaction is the separation of an ion into two ions, $Fe(OH)^{2+}$ and H^+, bearing electric charges $Z_A=+2$ and $Z_B=+1$, while the electron transfer reaction of Path 5 is a collisional encounter of two ions, Fe^{2+} and $Fe(OH)^{2+}$, of $Z_C=Z_D=+2$. From the slopes of the straight lines in Figs. 10 and 11, we obtain the values $d_H=2.1$ Å and $d_{Fe}=7.8$ Å. By taking the approximate values of ionic radii $r(Fe^{2+})=0.8$ Å and $r(Fe^{3+})=0.7$ Å, and of molecular diameter $d(H_2O)=3.0$ Å into account, the values of d_H and d_{Fe} obtained are reasonable, since the intermediate approach in the former reaction might be the direct contact of two ions to each other with d_H nearly equal to the sum of $r(Fe^{3+})$ and $d(H_2O)$, while that in the latter reaction might be the outer-sphere contact of the two with d_{Fe} nearly equal to $r(Fe^{2+})+r(Fe^{3+})+2d(H_2O)$, which would support the plausibility of hydrogen-atom-transfer mechanism between aqua- and hydrolyzed-iron ions.[†]

The abnormal behavior of k_H observed in the cases of ethanol and 1-propanol has not been clarified. It might be related to the hydrophobicity of alkyl groups in alcohol molecules. The hydrophobic groups would promote the ice-like structure of water surrounding them,[11,12)] and increase the hydrogen bondings between water molecules, which would increase the rate of the hydrogen-atom-transfer mechanism, k_H.

References

1) W. L. Reynolds and R. W. Lumry, *J. Chem. Phys.*, **23**, 2460 (1955).

2) A. G. Maddock, *Trans. Faraday Soc.*, **55**, 1268 (1959).

3) N. Sutin, *J. Phys. Chem.*, **64**, 1766 (1960).

4) R. A. Horne, "Exchange Reactions", International Atomic Energy Agency, Vienna (1965), p. 67.

5) G. Wada and A. Endo, *Bull. Chem. Soc. Jpn.*, **45**, 1073 (1972).

6) G. Wada, N. Yoshizawa, and Y. Sakamoto, *Bull. Chem. Soc. Jpn.*, **44**, 1018 (1971).

7) G. Wada, S. Nakago, and Y. Abe, *Bull. Chem. Soc. Jpn.*, **52**, 1381 (1979), Part VIII of this series.

8) H. A. C. McKay, *Nature*, **42**, 997 (1938).

9) G. Åkerlof, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

10) G. Scatchard, *Chem. Rev.*, **10**, 229 (1932); E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York (1966), Chap. 1.

11) G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn.*, **35**, 646 (1962).

12) G. Wada, E. Nagao, N. Kawamura, and K. Kinumoto, *Bull. Chem. Soc. Jpn.*, **51**, 1937 (1978).

[†] An approximate straight line is drawn on the points for ethanol and 1-propanol (broken line, Fig. 10). From the slope $d_H=8.8$ Å is obtained by use of Eq. 7. This seems to correspond to a distance of $r(Fe^{3+})+nd(H_2O)$, n being approximately equal to 2.7. The physical meanings of this apparent distance are not clear. The exceptional characteristics of K_H for these two alcohols would partly reflect on k_H for the same alcohols as the exceptional behavior.