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Kinetic Studies of the Electron-Transfer Reaction in Iron(II) and Iron(III) Systems. V. The Reaction in Mixed Solvents of Methanol and Water[1]

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The electron-transfer reaction between Fe(II) and Fe(III) species in mixed solvents of methanol and water was investigated by the use of Fe-59 as the radioactive tracer. The hydrolysis constant of Fe^{3+}, $K_{\rm H}$, in the mixed solvent decreases gradually as the mole faction of methanol, $x_{\rm M}$, increases. At very high acidities, ionic association between Fe^{3+} and ClO_4^- ions occurs, thus forming an ion-pair in the mixed solvent. The apparent rate constant, $k_{\rm app}$, of the electron-transfer reaction is a function with respect to $x_{\rm M}$; $k_{\rm app}$ does not vary much in the concentration range $x_{\rm M} \leqq 0.3$, but it decreases as $x_{\rm M}$ grows higher than 0.3. $k_{\rm app}$ is also dependent upon $[H^+]$ and in a linear relationship with $[H^+]^{-1}$. Thus, the two reaction paths, Fe^{2+}-Fe^{3+} (k_0) and Fe^{2+}-$FeOH^{2+}$ ($k_{\rm H}$), are deduced to be prevailing. Both rate constants, k_0 and $k_{\rm H}$, decrease with an increase in $x_{\rm M}$. The constancy of $k_{\rm app}$ at $0 \leqq x_{\rm M} \leqq 0.3$ is a result of compensation between the increasing $K_{\rm H}$ value and the decreasing k_0 and $k_{\rm H}$ values. By taking into account the values of $\Delta H_{\rm H}^{\ddagger} = 7.6$ kcal/mol and $\Delta S_{\rm H}^{\ddagger} = -19.1$ e.u. at $x_{\rm M} = 0.2$, both of which do not differ greatly from those in pure water, the reaction is concluded to proceed through the hydrogen-atom-transfer mechanism in the mixed solvent, the inhibiting effect of methanol being due to the reduction of the hydrogen bondings between water molecules.

The electron-transfer reaction between the hydrated species of iron(II) and iron(III) in aqueous media, $Fe^{2+}_{aq} + {}^*Fe^{3+}_{aq} \rightarrow Fe^{3+}_{aq} + {}^*Fe^{2+}_{aq}$, was early deduced by several authors[2-4] to proceed *via* the hydrogen-atom-transfer mechanism. This mechanism was supported by the finding that the rate of the reaction decreased upon the addition of some substances in the reaction systems, such substances as nitromethane,[5] 2-propanol,[6] and other alcohols.[7] These added substances were supposed to act as breakers of chains of the hydrogen bondings between water molecules, through which the hydrogen-atom-transfer would have occurred. When dimethyl sulfoxide[1] is added to the reaction system, it is strongly associated with water molecules and, hence, lowers the water activity to a considerable extent, thus, suppressing the reaction rate. On the other hand, both mono- and dimethyl acetamides[8] rather accelerate the reaction, in which cases their partial coordination to iron(III) ion enables the reaction to proceed faster than in the absence of the acetamides without altering the reaction mechanism.

In the present investigation, a quantitative determination of the reaction rate was performed in the mixed solvents of methanol and water in order to find out how the molecules of methanol participate in the electron-transfer process both as solvent and as ligand, and how they affect the reaction mechanism through hydrogen-atom-transfer.

Experimental

Commercial methanol of a guaranteed reagent grade was distilled and used. The preparation of the other chemical materials used and the procedure of the kinetic measurements have been described previously.[9,10] The temperature and the ionic strength of the reaction systems were kept at 25°C and $\mu = 0.5$ M respectively, unless otherwise noted.

Determination of the Hydrolysis Constant, $K_{\rm H}$, of Fe^{3+} in Methanol-water Mixed Solvents. The hydrolysis constant, $K_{\rm H} = [FeOH^{2+}][H^+]/[Fe^{3+}]$, in mixed solvents of methanol and water at various mole fractions of methanol, $x_{\rm M}$, was determined at a total concentration of iron(III) of 2×10^{-4} M and at a concentration of perchloric acid of 10^{-3}—10^{-2} M by spectrophotometry at wavelengths of 330, 340, and 350 nm. A Hitachi-Perkin-Elmer UV-VIS spectrophotometer, Model 139, with a thermostated cell compartment was used for the optical density determination. In this compartment was used for the optical density determination. In this connection, the optical densities of the solutions of iron(III) at high acidities up to 4 M were determined in order to show the probable occurrence of ionic association between the iron(III) ion and the perchlorate ion with an increase in the mole fraction of methanol, that is, with a decrease in the dielectric constant of the medium.

Since the values of pK for the second-step hydrolysis of the iron(III) ion in aqueous solutions, $FeOH^{2+} \rightleftarrows Fe(OH)_2^+ + H^+$, were found to be as small as 4.70[11] and 4.59[12] at 25°C, the contribution of the presence of $Fe(OH)_2^+$ in the reaction system could be ignored, the pK value in the mixed solvents not being determined.

Results and Discussion

Hydrolysis Constant of the Fe^{3+} Ion, $K_{\rm H}$, in Mixed Solvents. Considering the balance relations:

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[8] G. Wada and R. Yoshihara, *Kogyo Kagaku Zasshi*, **73**, 2309 (1970).

[9] G. Wada, N. Yoshizawa, and Y. Sakamoto, This Bulletin, **44**, 1018 (1971).

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$$A = \varepsilon_0[\mathrm{Fe^{2+}}] + \varepsilon_\mathrm{H}[\mathrm{FeOH^{2+}}] \tag{1}$$

$$[\mathrm{HClO_4}] = [\mathrm{H^+}] - [\mathrm{FeOH^{2+}}] \tag{2}$$

$$[\mathrm{Fe(III)}] = [\mathrm{Fe^{3+}}] + [\mathrm{FeOH^{2+}}] \tag{3}$$

an equation is established as follows:

$$\frac{1}{A_\mathrm{H}} = \frac{1}{\varepsilon_\mathrm{H}[\mathrm{Fe(III)}]} + \frac{[\mathrm{H^+}]}{\varepsilon_\mathrm{H}K_\mathrm{H}[\mathrm{Fe(III)}]} \tag{4}$$

in which [Fe(III)] and [$HClO_4$] are the total concentrations of iron(III) and perchloric acid, and ε_0 and ε_H, the molar extinction coefficients of Fe^{3+}_{aq} and $FeOH^{2+}$, respectively. A stands for the observed optical density of an aqueous solution containing iron(III) perchlorate, perchloric acid, and methanol, and A_H, for the calculated optical density of a solution simply containing $FeOH^{2+}$, which is equal to $\varepsilon_H[FeOH^{2+}]$. Eq. (4) suggests a linear relationship between A_H^{-1} and [H^+]. Since A_H and [H^+] are not known at first, A and [$HClO_4$] are respectively used instead as a first approximation; they give a rough straight line. The intercept and slope of the approximate straight line give a rough value of K_H, which also gives an approximate value of [$FeOH^{2+}$]. By using this value, more precise A_H and [H^+] values are obtained. By repeating the procedure of this successive approximation, the final relation between A_H^{-1} and [H^+] is reached. A typical relation is plotted in Fig. 1. The values of K_H at various mole fractions of methanol, x_M, at μ=0.5 M and 25°C observed at the wavelengths of 330, 340, and 350 nm are listed in Table 1; the table indicates a clear trend for K_H to increase monotonously as x_M increases because of the lowering of the dielectric constant of the mixed solvent.[13] The observed values of K_H are almost reasonably compared with those appearing in the literature, 1.59×10^{-3} M at $x_M=0$[14] and 1.70×10^{-2} M at $x_M=0.52$.[15]

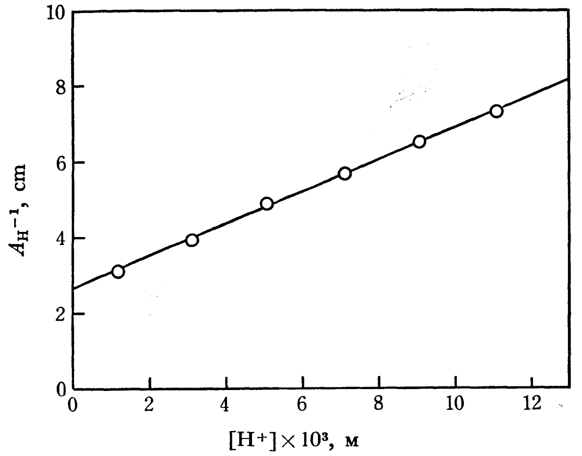

Fig. 1. Linear relation of A_H^{-1} with respect to [H^+] at 330 nm, μ=0.50 M, and 25°C.
[Fe(III)]=2×10^{-4} M, x_M=0.20.

Table 1. Hydrolysis constants K_H and dielectric constants at various mole fractions of methanol x_M at μ=0.50 M and 25°C

x_M	K_H $\times10^3$ M	Dielectric constant
0	2.2	82.6
0.04	2.4	80.0
0.08	3.0	76.4
0.12	3.3	73.1
0.20	6.2	67.6
0.25	8.7	64.1
0.31	9.4	59.9

The dependence of K_H upon the temperature is shown in Table 2, at x_M=0.20. By plotting log K_H against T^{-1}, the enthalpy of the hydrolysis of Fe^{3+}_{aq} is obtained as ΔH_H=11.6 kcal/mol at x_M=0.20, which, for reference, is compared to a value of 13.7 kcal/mol for the enthalpy associated with the ionization process of the water molecule in the liquid state, $H_2O \rightarrow H^+ + OH^-$.

Table 2. Temperature dependence of K_H at x_M=0.2 and μ=0.50 M

Temperature, °C	K_H $\times10^3$, M
15.5	3.0
20	4.7
25	6.2
30.5	8.3

Ionic Association Between Fe^{3+} and ClO_4^- Ions. The determination of K_H values was carried out at concentrations of perchloric acid of 10^{-3}–10^{-2} M. As the acid concentration is raised within this concentration range, the apparent molar extinction coefficient of the iron(III) solution at 330 nm, ε (which is equal to A/[Fe(III)]), decreases because ε_0 is smaller than ε_H. However, when the acid concentration is raised higher than 10^{-2} M up to as high as 4 M, ε begins rather to increase through a broad minimum in the mixed solvents of methanol and water, although this is not the case in pure water, where the line is horizontal. The observations over the whole concentration range at various x_M's are depicted in Fig. 2. The higher the mole fraction of methanol, the steeper the slope of the curve in the concentrated acid media. The phenomena can reasonably be understood by the possible occurrence of the ionic association between Fe^{3+} and ClO_4^-,[16] as follows.

When an ion-pair between Fe^{3+} and ClO^{4-} is represented by $Fe\cdot ClO_4^{2+}$, the total optical density of the solution is expressed in the following form, the ionic association being taken into account:

$$A = \varepsilon[\mathrm{Fe(III)}]$$

$$= \varepsilon_0[\mathrm{Fe^{3+}}] + \varepsilon_\mathrm{H}[\mathrm{FeOH^{2+}}] + \varepsilon_\mathrm{a}[\mathrm{Fe\cdot ClO_4^{2+}}] \tag{5}$$

$$[\mathrm{Fe(III)}] = [\mathrm{Fe^{3+}}] + [\mathrm{FeOH^{2+}}] + [\mathrm{Fe\cdot ClO_4^{2+}}] \tag{6}$$

where ε_a is the molar extinction coefficient of the ion-pair.

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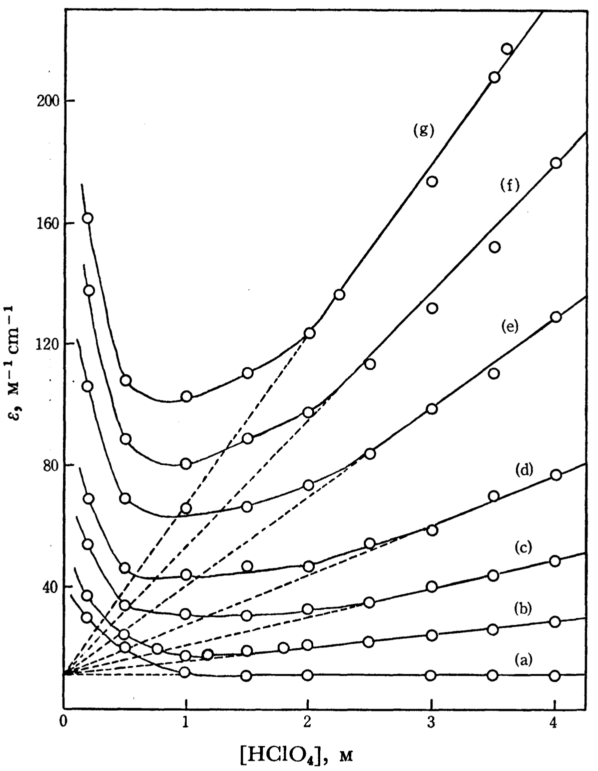

Fig. 2. Apparent molar extinction coefficient of Fe(III) in mixed solvents of methanol and water at 330 nm and 25°C. [Fe(III)]$=2\times10^{-3}$ M
a): $x_M=0$, b): $x_M=0.04$, c): $x_M=0.08$, d): $x_M=0.12$, e): $x_M=0.20$, f): $x_M=0.25$, g): $x_M=0.31$.

Since the formation constant of the ion-pair is defined as $K_a=[\mathrm{Fe\cdot ClO_4}^{2+}]/[\mathrm{Fe}^{3+}][\mathrm{ClO_4}^-]$, ε is given as follows:

$$\varepsilon=\frac{\varepsilon_0+\varepsilon_H K_H/[\mathrm{H}^+]+\varepsilon_a K_a[\mathrm{ClO_4}^-]}{1+K_H/[\mathrm{H}^+]+K_a[\mathrm{ClO_4}^-]} \qquad (7)$$

Considering that perchloric acid is a strong acid and that, therefore, it dissociates completely in aqueous media, $[\mathrm{H}^+]$ is approximately equal to $[\mathrm{ClO_4}^-]$ in the present circumstances. Therefore, Eq. (7) may be rewritten in this form:

$$\varepsilon=\frac{\varepsilon_0+\varepsilon_H K_H/[\mathrm{H}^+]+\varepsilon_a K_a[\mathrm{H}^+]}{1+K_H/[\mathrm{H}^+]+K_a[\mathrm{H}^+]} \qquad (8)$$

When the acidity of the solution is very low as a limiting case, ε will be shown to involve a term in reciprocal proportion to $[\mathrm{H}^+]$:

$$\varepsilon \approx \varepsilon_0+\varepsilon_H K_H/[\mathrm{H}^+] \qquad (9)$$

When the acidity of the solution is very high, as another limiting case, ε will vary under the control of a term proportional to $[\mathrm{H}^+]$:

$$\varepsilon \approx \varepsilon_0+\varepsilon_a K_a[\mathrm{H}^+] \qquad (10)$$

At the intermediate of the two extreme cases, there must occur a minimum nearly at the acid concentration of $[\mathrm{H}^+]=(\varepsilon_H K_H/\varepsilon_a K_a)^{1/2}$, actually occurring at $[\mathrm{H}^+]\sim1$ M, which indicates that $\varepsilon_H K_H \sim \varepsilon_a K_a$ at each x_M.

Figure 2 also indicates that the slope of the line, $\varepsilon_a K_a$, grows larger as x_M becomes higher, although it is not known whether this is due to the increase in

Table 3. Apparent second-order rate constants at various mole fractions of methanol x_M at $\mu=0.50$ M and 25°C

[HClO$_4$] M	x_M	[Fe(II)] $\times10^4$, M	[Fe(III)] $\times10^5$, M	$t_{1/2}$ sec	k_{app} M^{-1}sec^{-1}
0.035	0.20	0.39	0.60	94	166
0.04	0.20	0.74	1.63	60	128
0.05	0	1.14	1.58	47	114
	0	0.52	1.41	87	121
	0	1.07	8.69	55	109
	0.04	0.69	1.58	73	112
	0.08	0.76	1.74	60	124
	0.08	0.80	1.63	67	108
	0.12	0.71	1.63	75	106
	0.15	1.02	1.63	55	107
	0.20	1.15	1.52	44	121
	0.20	0.93	1.68	62	102
	0.20	0.84	0.43	72	109
	0.25	0.83	1.74	64	108
	0.31	1.02	1.58	54	110
	0.35	0.66	1.90	77	106
	0.38	0.97	1.52	62	99.8
	0.42	0.96	2.39	58	99.5
	0.47	0.78	2.77	85	76.9
	0.51	0.77	1.63	101	73.0
	0.58	0.80	2.44	121	55.1
	0.62	0.98	1.79	140	42.7
	0.68	1.47	2.17	154	26.6
0.07	0.20	1.34	1.79	57	80.0
0.10	0.20	1.01	1.63	108	54.8
0.15	0.20	1.16	1.74	145	35.7
0.20	0	1.50	1.58	135	30.8
	0	1.09	1.58	173	32.0
	0.04	1.34	1.68	138	33.2
	0.04	1.60	1.68	121	32.0
	0.08	1.43	1.68	138	31.4
	0.12	1.23	1.74	157	31.3
	0.15	1.85	1.85	111	30.6
	0.20	1.32	1.68	154	30.4
	0.25	2.13	1.90	98	30.5
	0.31	1.52	1.90	134	30.2
	0.35	1.26	1.85	157	30.6
	0.35	2.11	2.06	103	29.1
	0.35	1.64	2.39	131	28.3
	0.37	1.43	1.74	155	28.0
	0.39	2.27	1.74	102	27.8
	0.39	1.99	2.12	109	28.9
	0.42	1.53	1.96	161	24.9
	0.42	1.79	1.85	130	27.1
	0.48	2.47	1.85	111	23.4
	0.49	1.80	2.28	143	23.9
	0.51	1.83	2.23	174	19.4
	0.56	1.60	1.74	182	21.4
	0.56	1.24	2.39	251	18.6
	0.58	2.31	2.71	159	16.9
	0.58	1.94	2.23	213	15.0
	0.62	2.02	1.74	230	13.8
	0.62	2.46	2.23	174	14.8
	0.68	1.86	2.55	302	10.8
	0.68	3.25	2.34	246	8.1
0.30	0.20	1.38	1.79	246	18.1

ε_a, to that in K_a, or to both. Another interesting indication is that all of the straight lines expressed by Eq. (10) converge on the same point on the axis, giving a common value of $\varepsilon_0 = 11\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$ regardless of the concentration of methanol. Therefore, the Fe^{3+} ion might not be coordinated at all with methanol below $x_M = 0.3$ at least, or might exhibit a constant value for ε_0, regardless of whether or not it is partially coordinated with methanol. At any rate, the value of K_a is not known at this time.

Rate of Electron-Transfer Reaction. Since the electron-transfer reaction between iron(II) and iron(III) has been recognized to be of the first order with respect to both [Fe(II)] and [Fe(III)],[1,7,8] the apparent second-order rate constant, k_{app}, can be calculated by the following equation:

$$k_{app} = \frac{0.693}{([\mathrm{Fe(II)}]+[\mathrm{Fe(III)}])t_{1/2}} \tag{11}$$

The experimental results obtained at various mole fractions of methanol, mainly at $[HClO_4] = 0.05$ and $0.20\ \mathrm{M}$ at $\mu = 0.50\ \mathrm{M}$, and 25°C are shown in Table 3. A survey of k_{app} depending upon x_M is made in Fig. 3. k_{app} seems to be almost constant at $x_M < 0.3$, over which point it begins to diminish abruptly. This trend can be noticed more clearly at a lower acid concentration.

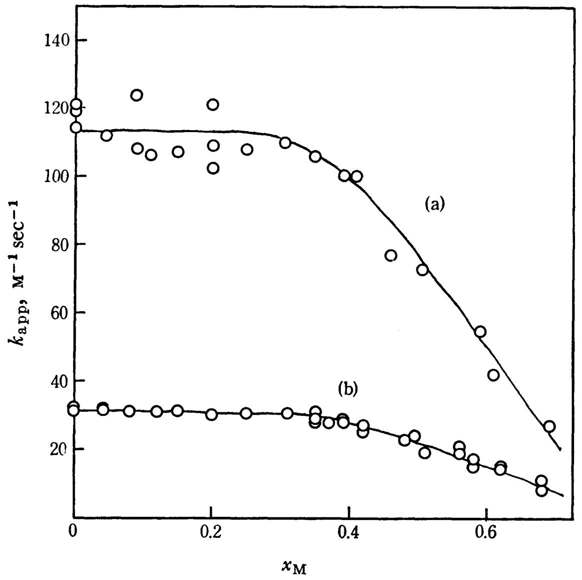

Fig. 3. Plot of k_{app} *vs.* x_M at $\mu = 0.50\ \mathrm{M}$ and 25°C.
a) $[H^+] = 0.05\ \mathrm{M}$, b) $[H^+] = 0.20\ \mathrm{M}$

The dependence of k_{app} upon the acidity of the solution at a constant mole fraction of methanol, at $x_M = 0.2$ for instance, which belongs to the plateau portion in Fig. 3, was observed; it is shown in Fig.4. The plot of k_{app} *vs.* the reciprocal $[H^+]$ indicates that there may be a linear relationship between them, passing the vicinity of the origin of the coordinates.

Reaction Mechanism. When the facts revealed in Figs. 3 and 4 are taken into account, the following two paths of the electron-transfer reaction can most convincingly be considered to actually occur:

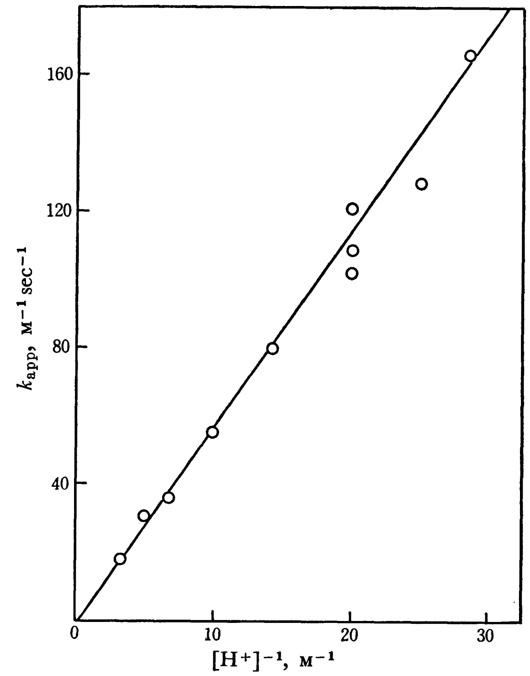

Fig. 4. Plot of k_{app} *vs.* $[H^+]^{-1}$ at $x_M = 0.20$, $\mu = 0.50\ \mathrm{M}$ and 25°C.

$$Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+} \qquad (k_0) \tag{12}$$

$$Fe^{2+} + {}^*FeOH^{2+} \rightarrow FeOH^{2+} + {}^*Fe^{2+} \qquad (k_H) \tag{13}$$

By the usual means of calculation, the apparent rate constant, k_{app}, is given as follows, where k_0 and k_H are the rate constants for the (12) and (13) reaction paths respectively:

$$k_{app} = \frac{k_0 + k_H K_H/[H^+]}{1 + K_H/[H^+]} \tag{14}$$

If the denominator on the right-hand side of Eq. (14) is regarded approximately as unity, k_{app} must show a linear trend, as has been seen in Fig. 4. When the denominator is precisely computed and multiplied by k_{app}, a more regular straight line than that in Fig. 4 is obtained between $k_{app}(1+K_H/[H^+])$ and $[H^+]^{-1}$, which is again reproduced in Fig. 5. The straight line in the figure passes near the point of origin, pointing out that k_0 is almost zero at $x_M = 0.20$. By the use of the K_H values in Table 1, the k_0 and k_H values at different x_M's are similarly obtained from the intercepts and slopes of the respective straight lines; they are collected in Table 4.

The values of k_0 in Table 4 are very approximate, but it can be safely said that k_0 is almost zero at mole fractions of methanol over 0.2. The values of k_H in the table, on the other hand, more regularly decrease with an increase in x_M. The range of x_M values adopted in the table, $x_M = 0-0.3$, corresponds to that exhibiting the plateau portion of the curve in Fig. 3.

It can be concluded, therefore, that although both k_0 and k_H decrease as x_M increases, k_{app} holds an approximate constancy, because the increase in K_H cancels the decrease in k_0 and k_H to make k_{app} almost unchanged, by chance. Table 4 also lists the prod-

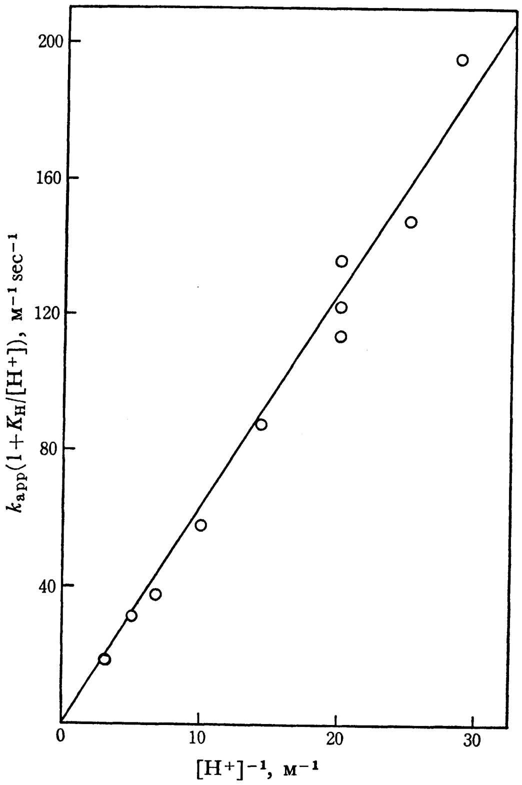

Fig. 5. Plot of $k_{app}(1+K_H/[H^+])$ *vs.* $[H^+]^{-1}$ under the same conditions as in Fig. 4.

Table 4. k_0 and k_H at different x_M at μ=0.50 M and 25°C

x_M	k_0 M^{-1}sec^{-1}	k_H $\times10^{-3}$, M^{-1}sec^{-1}	$k_H K_H$ sec^{-1}
0	~2	2.7	6.0
0.04	~4	2.3	5.5
0.08	~2	2.0	6.0
0.12	~5	1.6	5.3
0.20	~0	1.1	6.7
0.25	~0	0.73	6.3
0.31	~0	0.70	6.6

ucts of k_H and K_H; they suggest the apparent constancy of k_{app} within the whole range of x_M values far observed.

Activation Parameters for Reaction. The values of k_H at x_M=0.20 were obtained at different temperatures in the same way as at 25°C; the correlation of log (k_H/T) against T^{-1} is drawn in Fig. 6, from which the activation enthalpy, $\Delta H_H^{\ddagger}$=7.6 kcal/mol, and the activation entropy, $\Delta S_H^{\ddagger}=-19.1$ e.u., are calculated. A comparison with the activation parameters in pure water is made in Table 5.

The activation enthalpy and entropy for the electron-transfer reaction between Fe^{2+} and $FeOH^{2+}$ do not greatly differ from each other in pure water and in methanol-water mixtures. This fact indicates that the hydrogen-atom-transfer mechanism[2-4] may still be active even in methanolic media. The effect of methanol on the rate of the reaction is the partial destruction and breaking of the hydrogen bondings in the chains between water molecules by substituting the methanol molecules for water in the bulk solvent.

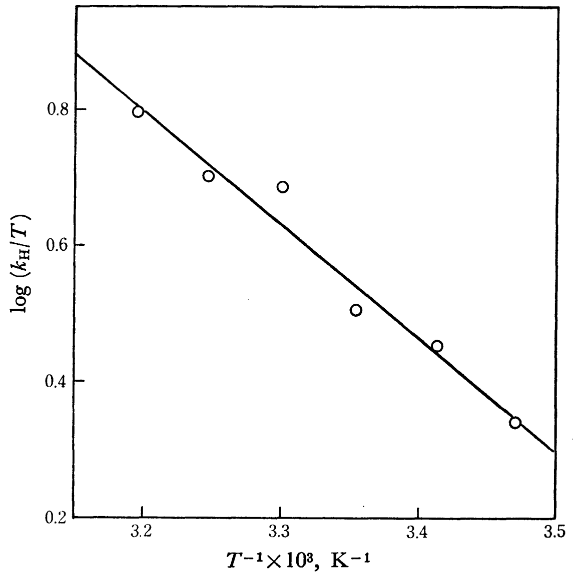

Fig. 6. Plot of log (k_H/T) *vs.* T^{-1} at x_M=0.2 and μ=0.50 M.

Table 5. Activation parameters for the reaction Fe^{2+}-$FeOH^{2+}$

x_M	$\Delta H_H^{\ddagger}$ kcal/mol	$\Delta S_H^{\ddagger}$ cal/deg·mol	Ref.
0.20	7.6	−19.1	Present work
0	6.9	−18	17)
0	8.4	−14.4	18)

In the case of a mixed solvent of DMSO and water,[1] the effect of DMSO is so great that it forms a molecular associate with water, thus lowering the activity of water. In the present case of methanol, its effect on the rate constant is not so markedly clear as to influence it explicitly, as a result of compensation for the growth of K_H.

According to the conductivity measurements,[19] Walden's ionic radius and the activation energy for the ionic migration for simple ions are nearly unchanged when the mole fraction of methanol is varied in methanol and water mixtures within the range of its mole fractions of 0—0.3. This suggests no possible occurrence of mixed solvation of methanol around the central ions in this mole fraction range. We have described above the constant molar extinction coefficient of the Fe^{3+} ion, ε_0=11 M^{-1}cm^{-1}, in the same mole fraction range of methanol. We attributed this either to the constancy of light absorption by the ions, regardless of the composition of their coordination sphere, or to the constancy of the composition sphere, or to the constancy of the composition of the coordination sphere itself, regardless of the surrounding medium. Now we can obviously decide that the latter is the case. In this concentration range, Fe^{3+}

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18) S. Fukushima and W. L. Reynolds, *Talanta*, **11**, 283 (1964).

19) G. Wada, C. Ito, and K. Horie, *J. Electrochem. Soc. Jap.*, **28**, 58 and E-32 (Overseas Edition) (1960).

may be preferentially solvated only with water molecules. The decrease in the rate of the electron-transfer reaction is, therefore, brought about, not by the reaction species themselves, but by the decrease in the ease of the hydrogen-atom-transfer along the chains of hydrogen bondings between the reacting species, by the insertion of methanol molecules in place of water ones, although the composition of the coordination sphere does not alter upon the addition of methanol.