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Kinetics of the Reactions of Ni(II) with Several Ligands in Water-*t*-Butyl Alcohol Mixtures

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The kinetics of the complex-formation reactions of Ni(II) with 4-phenylpyridine, isoquinoline, 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′: 6′,2″-terpyridine in water–*t*-butyl alcohol mixtures were investigated by means of stopped-flow measurement. With an increase in the *t*-butyl alcohol content of mixtures for all ligands, the rate constants for the reactions decrease monotonically, while the activation parameters, $\Delta H_f^{\neq}$ and $\Delta S_f^{\neq}$, pass through distinct minimum values, and the minima occur at the same concentration of *t*-butyl alcohol. The results are briefly discussed in terms of the stability of the outer-sphere complex of Ni(II) with the ligands, and the structural properties of the solvents.

In an aqueous solution, the rate constants and activation parameters for the complex-formation reactions of many metal ions depend only slightly on the nature of ligand and are approximately equal to those quantities for the exchange of the water molecule from the first coordination sphere of metal ions. In such a case, the reaction is best represented by the Eigen dissociative mechanism (I_d), in which the rate-determining step of the reaction is the dissociation of a water molecule from the coordination sphere of the metal ions.[1,2] On the other hand, it was found that the kinetic parameters in certain nonaqueous solutions exhibit a marked ligand dependence, and some solvent properties influencing the kinetic behavior have been discussed.[3-6] Meanwhile, it may be expected that the change from a single-to a two-component solvent increases the number of factors influencing the kinetic behavior. In fact, a few studies[7-9] have revealed that the kinetic behavior of a mixed solvent depends on the composition of the inner-sphere of the metal ions, the steric requirement of the ligands, and the structures of the solvents.

As a part of an investigation aiming at identifying the mixed solvent properties influencing the kinetics, we wish to report here the results of the complex-formation reactions of Ni(II) with pyridine-type ligands in water–*t*-butyl alcohol mixtures.

Experimental

Materials. *t*-Butyl alcohol (Baker analyzed reagent) was purified by distillation from sodium metal (Baker) through a 25 mm ID × 1219 mm-long glass column packed with 6 mm OD × 6 mm-glass tubes. Ni(II) was introduced as the perchlorate. Ni(II) solutions were standardized by EDTA titration, using Murexide as the indicator. Isoquinoline (Eastman) was distilled alone under a vacuum in a Perkin Elmer Model 251 Auto Annular Still with a Teflon spinning band at a reflux ratio of 200 : 1, with a pot temperature of 126 °C and a head temperature of 62 °C. All the other chemicals used were of reagent quality.

Instrumentation and Experimental Procedure. The kinetic measurements were made with a Dionex Corporation (Sunnyvale, Calif.) Model D-110 stopped-flow spectrophotometer equipped with a Kel-F flow system, observing the precautions necessary for adequate temperature control (±0.5 °C). The reactions were monitored at wavelengths where the complexes and free ligands show the largest difference in absorptivity, *viz.*, 272—275 nm, 322—325 nm, 305—310 nm, 270—275 nm, and 334—338 nm for 4-phenylpyridine, isoquinoline, 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′:6′,2″-terpyridine respectively. All the measurements were made under pseudo-first-order conditions with the total ligand concentration (C_L, after mixing) kept constant at 2.5×10^{-5} mol dm^{-3} for 2,2′-bipyridine and 2,2′:6′,2″-terpyridine, and 10^{-4} mol dm^{-3} for 1,10-phenanthroline, while the Ni(II) concentrations (C_{Ni}) were varied in the range from 1×10^{-3} to 5×10^{-3} mol dm^{-3}. In the cases of 4-phenylpyridine and isoquinoline, the complexes are relatively unstable, so that it was necessary to increase C_L to 2.1×10^{-4} mol dm^{-3}, and C_{Ni} to 0.8—2.4×10^{-2} mol dm^{-3} for isoquinoline, and C_L to 2.5×10^{-5} mol dm^{-3}, and C_{Ni} to 0.6—2.0×10^{-2} mol dm^{-3} for 4-phenylpyridine. The absorbancy measurements were made with a Shimadzu Model UV-200 double-beam recording spectrophotometer equipped with temperature control to ±0.5 °C.

Results and Discussion

The observed pseudo-first-order rate constant, k_{obsd}, is given by Eq. 1:[6]

$$k_{obsd} = k_f[\mathrm{Ni}^{2+}] + k_d, \tag{1}$$

where k_f and k_d are the overall second-order and first-

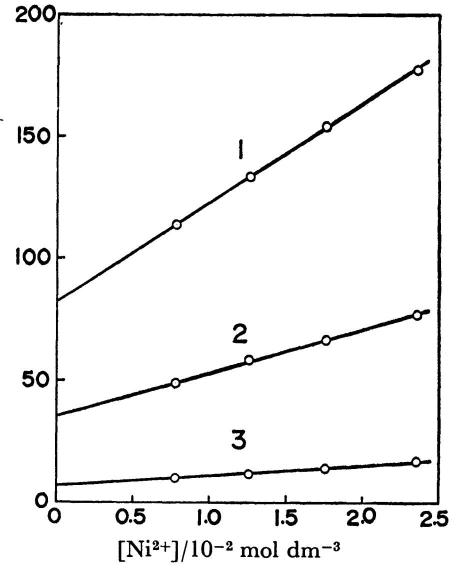

Fig. 1. Pseudo-first-order rate constants for the reaction of Ni(II) with 4-phenylpyridine in water.
Temperature (°C): (1) 35.0, (2) 25.0, (3) 10.0. Concn of 4-phenylpyridine: 2.5×10^{-5} mol dm^{-3}.

order rate constants for a complex-formation reaction and a dissociation reaction respectively. Equation 1 shows that a plot of k_{obsd} *vs.* [Ni^{2+}] should be linear with a slope and an intercept equal to k_f and k_d. A typical result obtained in this study is shown in Fig. 1.

The rate constants at various temperatures for the reactions of Ni(II) with pyridine-type ligands studied in water–*t*-butyl alcohol mixtures are listed in Table 1. In Table 2, the rate constants at 25.0 °C and the activation parameters for the ligands are given for each solvent. The changes in the activation parameters with the solvent composition are shown in Figs. 2 and 3. These are the values of $\Delta H_f^{\ddagger}$, $-T\Delta S_f^{\ddagger}$, and $\Delta G_f^{\ddagger}$ relative to pure water. Figures 2 and 3 show that the minima in $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ for all ligands occur at the same concentration of *t*-butyl alcohol, and that the rate constants decrease with a substantial compensation of the changes in $\Delta H_f^{\ddagger}$ by those in $-T\Delta S_f^{\ddagger}$ over the whole range of solvent compositions studied. Analogous extrema have been found for other properties, such as the partial molal heat of solution of a variety of salts[10] and the limiting cation-transference number[11] in a mixed solvent.

The k_d values can, in principle, be obtained from

TABLE 1. RATE CONSTANTS FOR THE COMPLEX-FORMATION REACTIONS OF Ni(II) IN WATER–*t*-BUTYL ALCOHOL MIXTURES AT VARIOUS TEMPERATURES

		Rate constant (k_f)/10^3 dm^3 mol^{-1} s^{-1}						
Solvent[a)]	Ligand	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
0	2,2′-Bipyridine	0.64_5	0.94_0		2.4_4			7.5_6
2		0.54_3	0.78_0		1.7_1			4.8_5
5		0.41_0	0.59_9		1.2_4			3.3_9
8		0.18_0	0.29_2		0.71_8			1.9_9
0	2,2′: 6′,2″-Terpyridine	0.47_2	0.74_3		1.6_7			5.5_1
2		0.41_3	0.58_1		1.3_4			3.7_5
5		0.18_4	0.26_3		0.53_1			1.3_7
8		0.08_0	0.11_5		0.26_5			0.76_8
0	1,10-Phenanthroline	1.6_2	2.4_6		6.0_1		$12._6$	
5		1.1_9	1.8_7		4.0_7		7.7_7	
0	4-Phenylpyridine	0.4_8	0.7_9	1.1_5	$1._9$	$2._5$	$4._0$	
2		0.4_4	0.6_7		1.3_5			
5		0.3_6	0.4_8	0.6_7	0.8_9			
8		0.2_2	0.3_2	0.4_9	0.6_5			
0	Isoquinoline		1.1_8	$1._9$	$2._6$	$3._8$		
2		0.7_8	1.1_1	1.6_0	$2._2$			
5		0.8_0	1.0_6	1.5_1	$2._0$			
8		0.3_8	0.5_5	0.7_6	$1._1$			

a) Mol % *t*-butyl alcohol.

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE COMPLEX-FORMATION REACTIONS OF Ni(II) IN WATER–*t*-BUTYL ALCOHOL MIXTURES AT 25.0 °C

Solvent[a)]	Ligand	log k_f (dm^3 mol^{-1} s^{-1})	$\Delta H_f^{\ddagger}$ (kJ mol^{-1})	$\Delta S_f^{\ddagger}$ [b)] (J K^{-1} mol^{-1})	$\Delta G_f^{\ddagger}$ (kJ mol^{-1})
0	2,2′-Bipyridine	3.3_9	59.0±1.6	+17	$53._6$
2		3.2_3	51.9±0.5	− 8	$54._4$
5		3.0_9	49.4±0.3	−21	$55._2$
8		2.8_6	56.5±2.3	0	$56._9$
0	2,2′: 6′,2″-Terpyridine	3.2_2	57.7±0.5	+13	$54._8$
2		3.1_3	52.3±1.2	− 8	$55._2$
5		2.7_3	46.9±0.1	−34	$57._3$
8		2.4_2	53.6±0.9	−21	$59._0$
0	1,10-Phenanthroline	3.7_8	57.7±1.2	+21	$51._5$
5		3.6_1	51.9±1.4	0	$52._3$
0	4-Phenylpyridine	3.3	58.0±1.8	+13	$54._4$
2		3.1	49.5±1.4	−21	$55._2$
5		3.0	40.2±0.9	−54	$56._1$
8		2.8	48.8±2.5	−29	$56._9$
0	Isoquinoline	3.4	53.8±2.0	0	$53._6$
2		3.3	46.4±0.5	−25	$54._0$
5		3.2	40.0±1.7	−46	$54._4$
8		3.0	46.1±0.7	−34	$55._6$

a) Mol % *t*-butyl alcohol. b) Reliability is about ±4 J K^{-1} mol^{-1}.

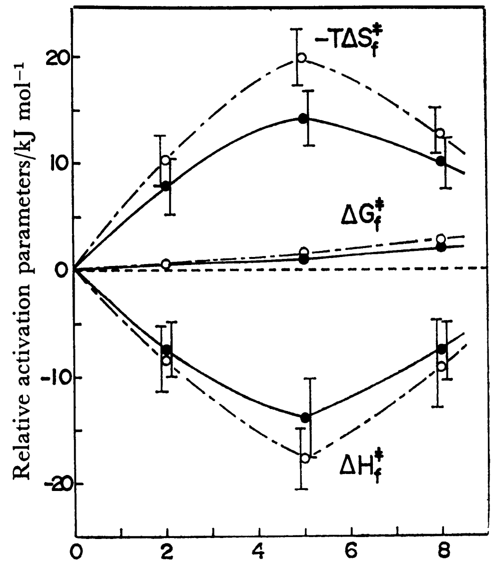

Fig. 2. Activation parameters for the reactions of Ni(II) with 4-phenylpyridine (-○-○-) and isoquinoline (-●-●-) in water–*t*-butyl alcohol mixture, normalized with respect to those in pure water (25.0 °C).

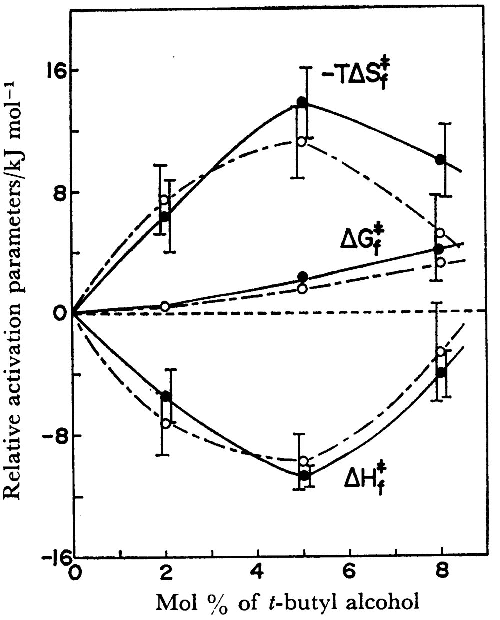

Fig. 3. Activation parameters for the reactions of Ni(II) with 2,2′-bipyridine (-○-○-) and 2,2′:6′,2″-terpyridine (-●-●-) in water–*t*-butyl alcohol mixture, normalized with respect to those in pure water (25.0 °C).

the analysis of the plots of Fig. 1. However, it should be noted that the intercept in Fig. 1 does not always give a correct dissociation-rate constant.[3)] At present, it is, therefore, impossible to discuss strictly the solvent dependence on the dissociation reactions of metal complexes using the k_d values obtained by means of Eq. 1. In testing whether or not the complex-formation reaction proceeds through an I_d mechanism, the following equation presented by Chattopadhyay and Coetzee[7)] was used:

$$R_1 = (4/3)k_f/K_{ass}k_s, \qquad (2)$$

where K_{ass} and k_s are the formation constant of the outer-sphere complex and the rate constant for solvent exchange respectively, and where a dimensionless ratio, R_1, should have a value near unity. The log R_1 values calculated for the reactions in water at 25.0 °C are as follows: 4-phenylpyridine, −0.6; isoquinoline, −0.5; 2,2′-bipyridine, −0.5; 1,10-phenanthroline, −0.1; 2,2′:6′,2″-terpyridine, −0.7. The log k_s value for Ni(II) used was 4.5,[12)] and the K_{ass} values were estimated by the Eigen-Fuoss equation.[13,14)] Furthermore, the activation parameters, $\Delta H_s^{\ddagger}$ and $\Delta S_s^{\ddagger}$, for Ni(II) in water were as follows: $\Delta H_s^{\ddagger}=58.6$ kJ mol^{-1} and $\Delta S_s^{\ddagger}=+38$ J K^{-1} mol^{-1}.[12)] From these results, it may be concluded that the complex-formation reactions of Ni(II) in water proceed through an I_d pathway.

It is probable that the Ni(II) species is solvated by only water molecules in the aqueous mixtures containing a small amount of *t*-butyl alcohol, taking into consideration the results on the form of Ni(II) in methyl alcohol–water mixtures.[15)] Moreover, it has been shown that the water structure in mixtures containing a small amount of alcohol is both stiffer and more ordered than in pure water.[3,8,11)] As has been assumed by previous workers,[7,8)] the sharp decrease in the kinetic parameters shown in Figs. 2 and 3 may, therefore, be interpreted with the framework of an I_d mechanism. That is, the decrease in $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ may be caused by the passage of a water molecule from the disordered region near the Ni(II) into a bulk solvent which is more structured than water itself.

The enthalpy of activation should be related to that for solvent exchange as follows:

$$\Delta H_f^{\ddagger} = \Delta H_s^{\ddagger} + \Delta H_{ass}, \qquad (3)$$

where ΔH_{ass} is the standard enthalpy for the formation of the outer-sphere complex and will usually be negligible when the ligand is uncharged. In previous papers,[16–18)] we ourselves reported that the specific interactions between the inner-sphere and the outer-sphere (*e.g.*, hydrogen-bonding) should be considered in the formation of the outer-sphere complex. The decrease in the dielectric constant of media upon the addition of *t*-butyl alcohol will result in a stronger hydrogen-bonding interaction, and the outer-sphere complex is assumed to be stabilized. The increased stability of the outer-sphere complex may cause the remaining coordinated water molecule to be labilized as a result of the partially ionic character imparted to the water molecule involved in the hydrogen bond. The type of interaction introduced here is similar to the "internal conjugate base" mechanism proposed by Rorabacher.[19)] In conclusion, we assume that the decrease in $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ upon the addition of *t*-butyl alcohol to water could arise mainly from the combined effects by stiffening the solvent structure and promoting the specific interaction between the inner-sphere and the outer-sphere. The increase in $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ upon the further addition of *t*-butyl alcohol to water remains unexplained, but a dramatic change in the solvation shell of Ni(II) and a breakdown of the water structure are expected to be of the greatest importance.

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