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# Conductance Stopped-Flow Study of Polyelectrolyte Catalysis on the $Ni^{2+}$-Murexide Reaction

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## ABSTRACT

Conductance stopped-flow study was carried out for a polyelectrolyte-catalysed complexation reaction of $Ni^{2+}$ with murexide. The result was compared with the ordinary stopped-flow method and excellent agreement was obtained, showing reliability of the conductance method.

## INTRODUCTION

As is well known, almost of all studies on fast reactions have been so far restricted to spectrophotometric observation of the time change of concentrations of reactants and/or products (Friess et al., 1963). However, there exist a variety of association processes and chemical reactions which cannot be followed by the spectrophotometric detection. The electrical conductance method is convenient for kinetic study of phenomena between ionic species. Sirs (1958) and Prince (1958) constructed for the first time a conductance stopped-flow(κ-SF) apparatus and measured the rate of the reaction of carbon dioxide with hydroxide ion in water and of the hydrolysis of triphenylchlorosilane in aqueous acetone. However, no reports have been published on further application of the κ-SF technique. In this report, we describe preliminary results on a polyelectrolyte-catalysed reaction between $Ni^{2+}$ and negatively charged murexide obtained by a κ-SF apparatus constructed in our laboratory.

## EXPERIMENTAL

Nickel (II) nitrate (G.R.grade) and murexide (ammonium purpurate, $C_8H_8N_6O_6 \cdot H_2O$) were purchased from Wako Pure Chemicals, Osaka, and Dojindo Co., Kumamoto, respectively. Sodium polyethylenesulfonate (NaPES) was obtained from Polysciences, Inc. Warrington, PA. Deionized water obtained with cation- and anion-exchange resins was further distilled for the pre-

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paration of solutions. The specific conductance of the purified water was smaller than $5 \times 10^{-7} \Omega^{-1} cm^{-1}$ at 25°C.

The detail of the $\kappa$-SF apparatus was described elsewhere (Okubo et al., 1975). The platinum plates (2 mm x 10 mm) were fixed on inside opposing walls (2 mm apart) of the observation cell made of epoxy resins. The mixer, which was made of Teflon, was of a four-jet type. The dead time of the apparatus was estimated to be 1 msec. For each individual run, about 0.2 $cm^3$ of solution was required. A value of 1.30 $cm^{-1}$ was obtained for the cell constant. The time change of the deviation of the solution conductance from its equilibrium value was amplified in two steps and monitored by a memoriscope and/or a digital memory and an X-Y recorder after rectification. The polarization effects caused by electrolysis was concluded to be negligible except at high concentrations of electrolyte above 0.1 $mol.l^{-1}$.

Comparative measurements were carried out using a stopped-flow spectrophotometer (UV-SF, Union Giken Co. Type RA1100). The detail of the apparatus was described elsewhere (Ise et al., 1975). The dead time was 1 msec by the flow-speed measurements.

## RESULTS AND DISCUSSION

By using the $\kappa$-SF apparatus, clear relaxation traces were obtained by mixing of $Ni(NO_3)_2$ solution with a murexide solution (Figure 1).

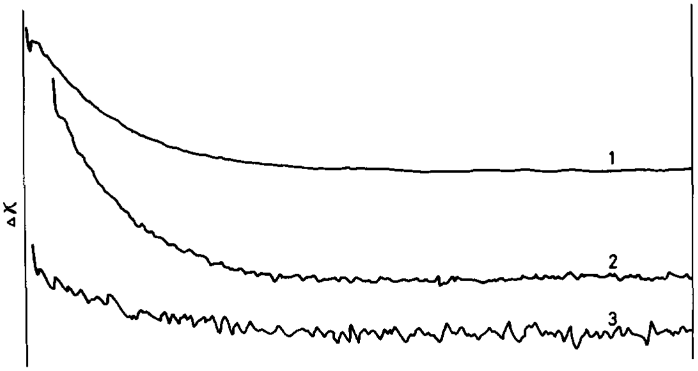

Fig.1 Typical Traces of Concentration-Jump Relaxation for $Ni^{2+}$-Murexide Reaction at 25°. $[Ni^{2+}]$=3 mM, [Murexide]=50 $\mu$M, full scale=500 msec, Curve 1: $[KNO_3]$=0 M, after mixing, Curve 2: $[KNO_3]$= 0.01 M, Curve 3: $[KNO_3]$=0.1 M, pH=4.

The reproducibility of the traces was satisfactory especially for lower concentrations of $KNO_3$. The linearity of the first-order plots of the relaxation traces was obtained with a correlation coefficient of 0.999 between a $\Delta\kappa$ range from 40 % to the equilibrium. Excellent agreement was obtained between the relaxation times, $\tau$, from the $\kappa$-SF method and those from spectrophotometric T-jump technique (Geier, 1968) as is seen in Table I.

Table I Comparison of the Relaxation Times of $Ni^{2+}$-Murexide Reaction from the $\kappa$-SF Method with Those from T-jump Method at 25°C.
[Murexide]=50 μM, pH=4

| | $\tau$ (msec) | | | | |
|---|---|---|---|---|---|
| | $[Ni^{2+}]$=0.001M | 0.002 | 0.003 | 0.005 | 0.007 |
| $\kappa$-SF ($[KNO_3]$=0 M) | 150 | 90 | 65 | 32 | 26 |
| $\kappa$-SF (0.01 M) | 130 | 78 | 57 | 40 | 28 |
| $\kappa$-SF (0.1 M) | 140 | 91 | 81 | 35 | 29 |
| T-jump(0.1M)[a] | 166 | 108 | 83 | 50 | - |

[a] taken from Geier (1968).

The rate of the complexation, $\overrightarrow{k}_2$, was derived from the relaxation curve using the $\kappa$-SF method and the polyelectrolyte influence, $\overrightarrow{k}_2/\overrightarrow{k}_2^*$, is shown by the open circle and triangle in Figure 2. The $\overrightarrow{k}_2^*$ values were $6.5 \times 10^3$ $M^{-1}sec^{-1}$ and $2.9 \times 10^3$ $M^{-1}sec^{-1}$ at [NaCl] = 0 and 0.05 M, respectively at 25°C, pH = 4, $[Ni^{2+}]$ = 1.5 mM and [Murexide] = 50 μM. The former value of $\overrightarrow{k}_2^*$ agrees excellently with the literature value reported by Kunugi and Ise (1974), $6.2 \times 10^3$ $M^{-1}sec^{-1}$(at 25°C, pH = 4, $[Ni^{2+}]$ = 2 ~ 10 mM, [Murexide] = 6 ~ 20 μM). Excellent agreement was obtained between the $\kappa$-SF and the UV-SF techniques (cross and solid circle in Figure 2). Clearly, the complexation was strikingly retarded by the anionic polyelectrolyte. This is quite reasonable for reactions between oppositely charged ionic species (Okubo and Ise, 1972). The retardation was calculated by the Brönsted-Bjerrum-Manning theory, which reads for the present reaction :

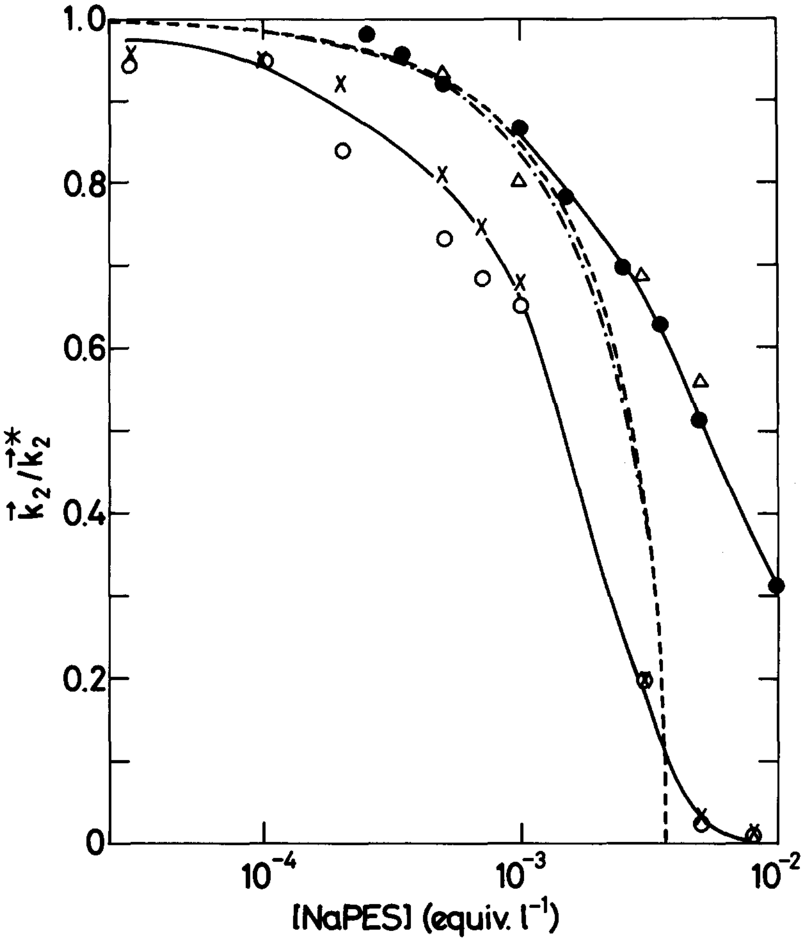

Fig.2 The Influence of NaPES on the $\vec{k}_2$ of the $Ni^{2+}$ Complexation with Murexide Observed by κ-SF Method (o : [NaCl] = 0 M, Δ : 50 mM) and by UV-SF Method (x : 0 M, ● : 50 mM) at 25°C.

$[Ni^{2+}]$ = 1.5 mM, [Murexide] = 50 μM, pH = 4, theory : ---- ([NaCl] = 50 mM), — · — · — : (0 M), $\vec{k}_2^*$ : the $\vec{k}_2$ without polymer.

$$\ln(\vec{k}_2/\vec{k}_2^*) = \frac{1}{2}\ln\left\{\frac{m_A - \frac{1}{2}m_2(1 - \frac{1}{2\xi})}{m_A}\right\} - \frac{3}{8}\,\frac{m_2}{\xi\{m_2+6m_A+2m_B+2m_3\}} \qquad (1)$$

where $\xi$ is the charge density parameter, $m_A$ and $m_B$ denote the molar concentration of $Ni^{2+}$ and murexide, respectively, $m_2$ and $m_3$ are the concentrations of NaPES and 1-1 type salt, respectively. For the derivation of eq.(1) the previous work should be consulted (Mita et al., 1975 ; Ise and Okubo, 1978). The results are shown by the dotted and broken curves in Figure 2. The agreement with the theory and experiment is most satisfactory at low polymer concentration and at higher salt concentration (50 mM).

On the basis of the excellent agreement between the κ-SF and optical methods on the present reaction system and on others described previously (Okubo et al., 1975), it can be concluded that the κ-SF technique would be convenient and reliable for kinetic studies of (polyelectrolyte catalysed) ionic reactions and processes. Further studies on various reactions are in progress, and will be published in forthcoming articles.

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