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The Interaction of the Tris(2,2′-bipyridine)ruthenium(II) Ion with Poly(*p*-styrenesulfonate)

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The interactions of tris(2,2′-bipyridine)ruthenium(II)($[Ru(bpy)_3]^{2+}$) with some polyanions have been studied by means of cation-exchange resins and the luminescence of $[Ru(bpy)_3]^{2+}$. In an aqueous solution of $[Ru(bpy)_3]^{2+}$ in the presence of sodium poly(*p*-styrenesulfonate)(PSS), the adsorbability of $[Ru(bpy)_3]^{2+}$ on the cation-exchange resins is strongly suppressed by the binding of $[Ru(bpy)_3]^{2+}$ to the polyanion. The relative luminescence intensity of $[Ru(bpy)_3]^{2+}$ in an aqueous solution is enhanced by the addition of PSS. With the addition of sodium chloride to an $[Ru(bpy)_3]^{2+}$/PSS solution, the interaction is impeded by the shielding of the electrostatic potential in the polymer domains by the counter ions. A cooperative interaction between PSS and $[Ru(bpy)_3]^{2+}$ is postulated with a view to accounting for the results. A chemical application of the interaction is demonstrated.

The luminescence behavior of $[Ru(bpy)_3]^{2+}$ and its analogous compounds has been well studied using several experimental techniques.[1-8] Meisel and Matheson[9] suggested that the luminescence from the lowest excited state of $[Ru(bpy)_3]^{2+}$, $[*Ru(bpy)_3]^{2+}$, is efficiently quenched by low concentrations of Cu^{2+} ions when poly(vinyl sulfate)(PVS) is present in the solution. The quenching reaction occurs nearly exclusively in the PVS solution. The efficient quenching results from the Cu^{2+} and $[Ru(bpy)_3]^{2+}$ residing in the potential field of the same polymer. They demonstrated a possible utilization of this system in solar-energy conversion and storage systems. The effect of PVS on the luminescence spectrum of $[Ru(bpy)_3]^{2+}$ was also studied by Meisel and Matheson.[9] However, little change in the emission spectrum from $[*Ru(bpy)_3]^{2+}$ was seen when PVS was added to an aqueous solution. This fact indicates that PVS does not affect the energy level of $[*Ru(bpy)_3]^{2+}$ in an aqueous solution.[9]

The results of the luminescence study of $[Ru(bpy)_3]^{2+}$ in an aqueous solution of sodium dodecyl sulfate[3] show that the emission maximum shifts a little to a longer wavelength in a negatively charged micellar solution, although the emission intensity is nearly the same in both micellar solution and pure water. It has been suggested that the micellar effect on the emission spectrum is caused by the hydrocarbon chains and not by the charged sulfonato groups on the surfactant molecules.[10]

The effect of hydrophobic interaction between a polyion and a metal-complex ion has been little studied. In the present study, the interaction between PSS and $[Ru(bpy)_3]^{2+}$, both of which have hydrophobic and charged moieties, has been investigated by means of ion-exchange resins and the luminescence spectrum of $[Ru(bpy)_3]^{2+}$.

Experimental

Materials. Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate, $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$,[11] and tris(1,10-phenanthroline)cobalt(III) chloride octahydrate, $[Co(phen)_3]Cl_2 \cdot 8H_2O$,[12] were prepared and purified by the methods described elsewhere. The other inorganic reagents were of a reagent-grade purity and were used without further purification. $CuSO_4 \cdot 5H_2O$ was used for the preparation of the stock solution of Cu^{2+}. Poly(*p*-styrenesulfonic acid) was prepared by the radical polymerization of *p*-styrenesulfonic acid. Freshly distilled *p*-styrenesulfonic acid was used for the polymerization. *p*-Styrenesulfonic acid was dissolved in 50 cm^3 of dimethyl sulfoxide at a total concentration of 2 mol dm^{-3}. To the solution in a 100-cm^3 flask were added a 1.0×10^{-3} mol portion of azobisisobutyronitrile; the flask was shielded after three freeze-evacuation cycles, and then the mixture was kept at 60 °C for 5 h. The resulting polymer was collected by precipitation from diethyl ether. The white powder was dissolved in aqueous dilute hydroxide and dialyzed in water for 50 h. Sodium poly(*p*-styrene sulfonate), PSS, was obtained by the evaporation of the dialyzed solution under reduced pressure. The specific-viscosity number of the PSS in 0.1 mol dm^{-3} KCl solution was 0.51 dl g^{-1} at 25 °C. Sodium poly(vinyl sulfate)-(PVS)($\overline{M}n$ 2×10^5: $\overline{M}n$ is number-average molecular weight) was prepared by the established method.[13] Poly(acrylic acid)($\overline{M}n$ 4×10^5) and poly(methacrylic acid)($\overline{M}n$ 5×10^5) were prepared by the $K_2S_2O_8$–$Na_2S_2O_3$-initiated radical polymerization of acrylic acid and methacrylic acid, respectively, in water at 30 °C. Sodium salts of poly(acrylic acid)-(PAA) and poly(methacrylic acid)(PMA) were prepared by the dialysis of the corresponding poly acid in dilute hydroxide for 50 h. The dialyzed solutions were evaporated under reduced pressure. These poly acid salts were obtained as a white powder. The concentrations of the polyions are represented by those of the monomer units.

Column-exchange Chromatography. A 2-cm^3 portion of aqueous polyelectrolyte or benzenesulfonate, BS, if necessary, sodium chloride were poured onto a water-jacketed column of cation-exchange resins (Dowex 50 W X-8, 100—200 mesh, the H form, 1 cm × 5 cm); then, an aliquot of water was passed through the column with 0.8 cm^3 min^{-1} at 25 °C. The concentrations of $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ were determined spectrophotometrically using a Hitachi Model 320 spectrophotometer, while that of Cu^{2+} was determined by means of the atomic absorption spectra using a Hitachi Model 170-40 atomic absorption spectrometer.

Luminescence Study. Oxygen was removed from the sample solutions by bubbling a nitrogen gas which had been purified by passing it through an acidic solution of

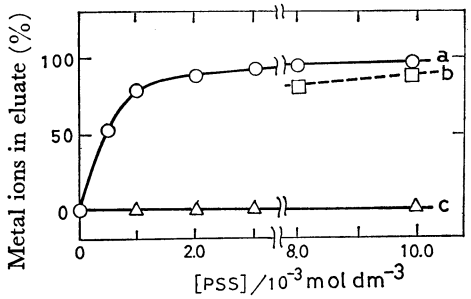

Fig. 1. Plots of the percentage of the metal ions in eluant *vs.* concentration of PSS in aqueous solution at 25 °C.
a: 1.0×10^{-4} mol dm^{-3} $[Ru(bpy)_3]^{2+}$, b: 1.0×10^{-4} mol dm^{-3} $[Co(phen)_3]^{2+}$, c: 1.0×10^{-4} mol dm^{-3} Cu^{2+}.

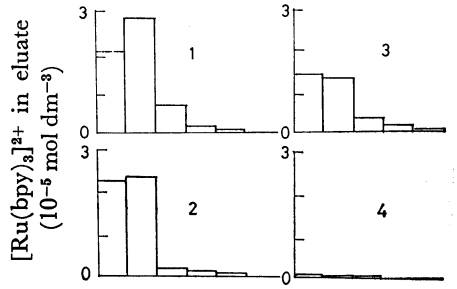

Fig. 2. Cation-exchange column chromatograms of 1.0×10^{-4} mol dm^{-3} $[Ru(bpy)_3]^{2+}$/3.0×10^{-3} mol dm^{-3} PSS/NaCl at 25 °C.
[NaCl]/mol dm^{-3}: 1; 0, 2; 1.0×10^{-4}, 3; 1.0×10^{-3}, 4; 1.0×10^{-2}.

chromium(II) sulfate for 30 min. Luminescence measurements were made in a 1 cm × 1 cm quartz cell on a Shimadzu RF-500 spectrofluorometer. The temperatures of the samples were adjusted at 25±0.1 °C by means of a thermostated cell holder. The excitation wavelength for $[Ru(bpy)_3]^{2+}$ was 455 nm. A PRA Model 3000-nanosecond fluorometer was used for the determination of the excited state lifetime of $[Ru(bpy)_3]^{2+}$.

Results and Discussion

Studies of the Effect of Polyions by Means of Ion-exchange Resins. The complex cation of $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ and the aquacopper(II) ion, Cu^{2+}, are strongly adsorbed on the cation-exchange resins. The adsorbed $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ ions were hardly eluted with water, dil HCl, and dil NaCl solutions. With the addition of PSS to an aqueous solution of $[Ru(bpy)_3]^{2+}$, however, some interesting effects upon the adsorbability of the metal ions were observed.

In $[Ru(bpy)_3]^{2+}$/PSS, a part or all of the $[Ru(bpy)_3]^{2+}$ passes through the column of the cation-exchange resins: the amount of the adsorbed $[Ru(bpy)_3]^{2+}$ is dependent on the PSS concentration, as is shown in Fig. 1. In the lower concentration region of PSS, the ratio of the amounts of $[Ru(bpy)_3]^{2+}$ in the eluate to the total amounts of $[Ru(bpy)_3]^{2+}$ in the initial solution increased with the increase in the PSS concentration. In the presence of a large amount of PSS (*ca.* 0.1 mol dm^{-3}) in the original solution, the $[Ru(bpy)_3]^{2+}$ ions were completely passed through the column.

In the $[Ru(bpy)_3]^{2+}$/PSS/NaCl systems, the total amount of $[Ru(bpy)_3]^{2+}$ in the eluate decreased with the increase in the NaCl concentration (Figs. 2 and 3). On the other hand, the adsorbability of $[Ru(bpy)_3]^{2+}$ on the resins was unaffected in the presence of a large amount of polyanions, such as PVS, PMA, and PAA and the monomer analogue such as benzenesulfonate.

A similar effect was observed in the $[Co(phen)_3]^{2+}$/PSS system (Fig. 1b). Unfortunately, the precipitate was formed by the addition of PSS to the $[Co(phen)_3]^{2+}$ solution when the PSS concentration was lower than about 6×10^{-3} mol dm^{-3}. The adsorbability of Cu^{2+} on the resins was, however, unaffected in the presence of PSS (Fig. 1c).

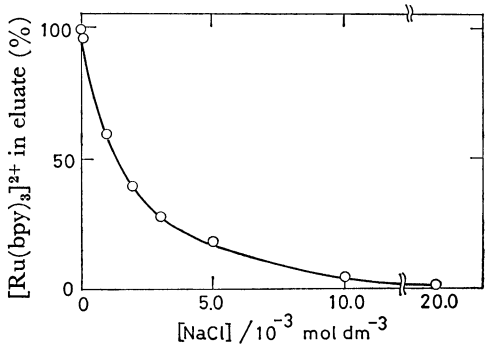

Fig. 3. Plots of the ratio of $[Ru(bpy)_3]^{2+}$ in eluate *vs.* concentration of NaCl at 25 °C.
$[Ru(bpy)_3^{2+}]=1.0\times10^{-4}$ mol dm^{-3}, $[PSS]=3.0\times10^{-3}$ mol dm^{-3}.

The decrease in the adsorbabilities of $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ on the cation-exchange resins on the addition of PSS seems to indicate that the attractive interactions between PSS and $[Ru(bpy)_3]^{2+}$ or $[Co(phen)_3]^{2+}$ are sufficiently large to prevent the cation-exchange reaction between the hydrogen ions on the resins and the metal-complex ions in the solution. In the $[Ru(bpy)_3]^{2+}$/PSS and $[Co(phen)_3]^{2+}$/PSS systems, it is considered that the hydrophobic interaction between the complex ion and the polyanion contributes to the adsorbabilities of the metal-complex ions on the resins since few changes in the adsorbabilities of $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ were observed in the presence of PVS, PAA, PMA, or BS. It may be concluded that a strong interaction between $[Ru(bpy)_3]^{2+}$ and PVS, PAA, PMA, or BS would not occur, since these polyelectrolytes have no hydrophobic moieties such as a phenyl ring on the polymer chains. Intimate multi-site bindings between the pendant phenyl rings, which are bound to the polymer backbone with a high density, and the metal-complex ion may be necessary for such a strong interaction, as has been seen in the cases of the $[Ru(bpy)_3]^{2+}$/PSS and $[Co(phen)_3]^{2+}$/PSS systems, since no change in the adsorbability was observed in the $[Ru(bpy)_3]^{2+}$/BS and $[Co(phen)_3]^{2+}$/BS systems.

The results seem to indicate that the $[Ru(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ ions are concentrated in the polymer domains as a result of the electrostatic attraction,

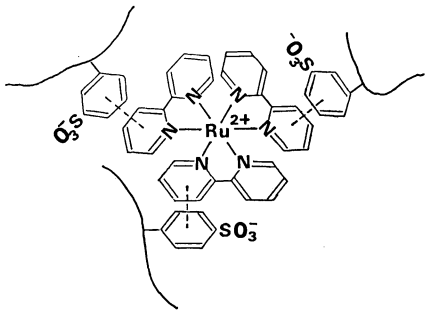

Fig. 4. Proposed structure of PSS bound $[Ru(bpy)_3]^{2+}$ by cooperative interaction.

and that, furthermore, the complex ions are bound tightly to the pendant phenyl groups of PSS by the hydrophobic interaction. The bipyridine rings of $[Ru(bpy)_3]^{2+}$ and the phenanthroline rings of $[Co(phen)_3]^{2+}$ would form intimate bindings to the pendant phenyl groups of PSS by means of hydrophobic interaction with the aid of the electrostatic force. A schematic representation of such coopertive interaction is postulated in Fig. 4. The molecular motion of the complex ions in the domains would be fairly much restricted by such interaction, and hardly none of the complex ions tightly bound to the polyanion chains should be adsorbed on the cation-exchange resins.

In the $[Ru(bpy)_3]^{2+}$/PSS/NaCl system the increase in the adsorbability of $[Ru(bpy)_3]^{2+}$ on the resins with the addition of NaCl can be explained by the fact that the $[Ru(bpy)_3]^{2+}$ ions are successively excluded from the polymer domains with increase in the concentration of the simple salt. The shielding of the potential field of the polyion domains by the counter ions reduces the electrostatic attraction for the complex ions. In the higher concentration region of NaCl, $[Ru(bpy)_3]^{2+}$ in the domains would be completely excluded from the domains. Thus, the $[Ru(bpy)_3]^{2+}$ ions are well adsorbed on the resins.

Effect of PSS on the Luminescence of $[Ru(bpy)_3]^{2+}$. The luminescence spectrum from $[*Ru(bpy)_3]^{2+}$ in an aqueous solution was greatly affected in the presence of PSS: the luminescence intensity at the luminescence maximum increased with the increase in the concentration of PSS (Figs. 5 and 6), while the absorption band in the visible region was not affected. A little change in the luminescence maximum is seen in the presence of PSS (Fig. 5): the luminescence peak of $[Ru(bpy)_3]^{2+}$ in the presence of 4.0×10^{-4} mol dm^{-3} PSS shifts to a wavelength longer by about 4 nm than that in the absence of PSS.

The variation in the relative luminescence intensity with the concentration of the polyion is given in Fig. 6. In the concentration region of PSS lower than about 2×10^{-4} mol dm^{-3}, where $[PSS]/[Ru(bpy)_3]^{2+}<10$, the relative intensity increases sharply on the addition of the polyion. However, no noticeable change in the CTTL and luminescence bands was observed in the presence of a large amount of PAA, PMA, or BS. Similar results have been reported in the luminescence study of $[Ru(bpy)_3]^{2+}$ in an aqueous PVS solution.[2] These facts seem to indicate that

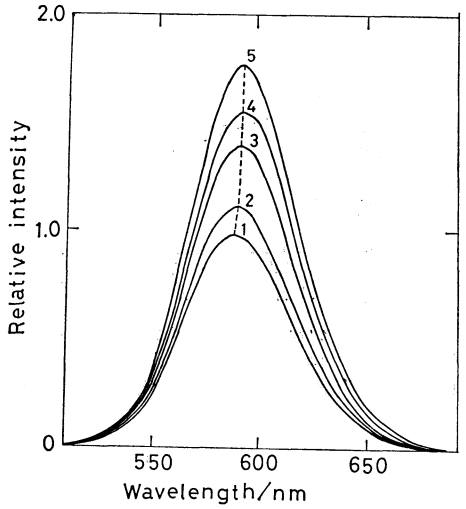

Fig. 5. Luminescence spectra of $[Ru(bpy)_3]^{2+}$ in PSS solution at 25 °C.
$[Ru(bpy)_3^{2+}]=2.0\times10^{-5}$ mol dm^{-3}, [PSS]/mol dm^{-3}: 1; 0, 2; 2.5×10^{-5}, 3; 5.0×10^{-5}, 4; 1.0×10^{-4}, 5; 4.0×10^{-4}.

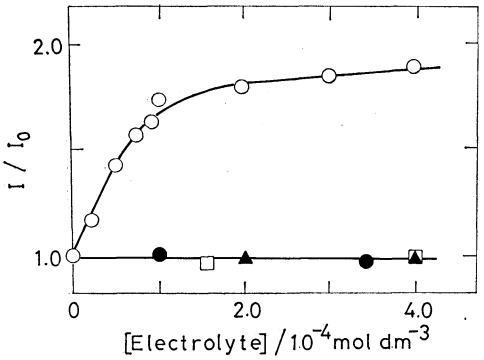

Fig. 6. Dependence of the luminescence intensity on the concentration of electrolyte at 25 °C.
$[Ru(bpy)_3^{2+}]=2.0\times10^{-5}$ mol dm^{-3}, ○: PSS, ●: BS, ▲: PAA, □: PMA.

such electrolytes as PAA, PMA, and BS do not affect the energy levels of $[Ru(bpy)_3]^{2+}$ and that no quenching or quenching reversal of the luminescence by these electrolytes occurs. These facts also suggest that the luminescence spectrum of $[Ru(bpy)_3]^{2+}$ is little affected by binding to the polyanions attributable to only the electrostatic force.

The dependence of the luminescence intensity on the concentration of urea in $[Ru(bpy)_3]^{2+}$/PSS is shown in Fig. 7. The luminescence intensity decreases with an increase in the concentration of urea. This may be due to the reduction of the hydrophobic interaction by the addition of urea. It may be concluded from the results that the enhancement of the luminescence intensity is brought about as a result of a cooperative interaction, which is also suggested by the results of the column-exchange chromatography. An intimate site binding due to the hydrophobic interaction would cause a sharp increase in the luminescence intensity upon the addition of PSS, presumably as a result of the restriction of the molecular motion of the $[Ru(bpy)_3]^{2+}$ bound to the polymer chains.

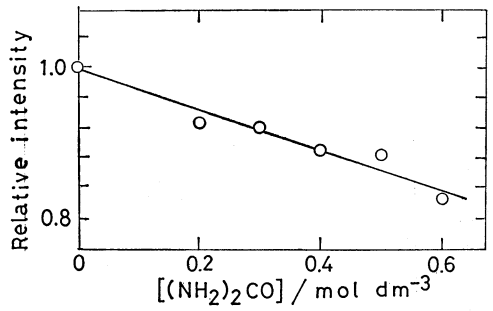

Fig. 7. Effect of urea on the luminescence intensity of $[Ru(bpy)_3]^{2+}$ in aqueous PSS solution at 25 °C. $[Ru(bpy)_3^{2+}]=2.0\times10^{-5}$ mol dm^{-3}, $[PSS]=2.0\times10^{-4}$ mol dm^{-3}.

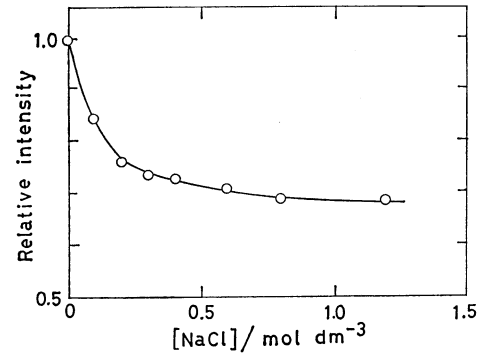

Fig. 8. Effect of sodium chloride on the luminescence intensity of $[Ru(bpy)_3]^{2+}$ in aqueous solutions at 25 °C. $[Ru(bpy)_3^{2+}]=2.0\times10^{-5}$ mol dm^{-3}, $[PSS]=2.0\times10^{-4}$ mol dm^{-3}.

Consequently, the lifetime of the lowest excited state of $[Ru(bpy)_3]^{2+}$ in the presence of 2.0×10^{-4} mol dm^{-3} PSS was longer than that in the absence of PSS: the excited-state lifetime in the presence and absence of PSS were 590±4 nsec and 450±2 nsec respectively at 28 °C.

The effect of sodium chloride on the luminescence of $[Ru(bpy)_3]^{2+}$ in an aqueous PSS solution is shown in Fig. 8. This figure shows that the luminescence intensity decreases with an increase in the salt concentration. Na^+ ions start to displace the $[Ru(bpy)_3]^{2+}$ out of the polymer domains in the higher-concentration region of sodium chloride: therefore, the luminescence intensity should be decreased with the concentration of the salt.

Application of the Cooperative Effect. In an aqueous solution of $[Ru(bpy)_3]^{2+}$ containing an excess of PSS, the $[Ru(bpy)_3]^{2+}$ ions bound to PSS should be hardly replaced by the hydrogen ions. Then, a simple application of the cooperative effect, *e.g.*, the separation of $[Ru(bpy)_3]^{2+}$ from Cu^{2+}, was tested by means of ion-exchange chromatography. To a 2-cm^3 portion of an aqueous solution containing 5.0×10^{-4} mol dm^{-3} $[Ru(bpy)_3]^{2+}$ and 5.0×10^{-4} mol dm^{-3} Cu^{2+} were added 2.0 cm^3 of 5.0×10^{-2} mol dm^{-3} PSS. The solution was poured into the column of the cation-exchange resins. Then, a 100-cm^3 portion of water was passed through the column. The Cu^{2+} ions were completely adsorbed on the resins, whereas more than 99.3% of all the $[Ru(bpy)_3]^{2+}$ ions passed through the column. The adsorbed Cu^{2+} ions could be eluted with dilute hydrochloric acid; more than 99% of the Cu^{2+} ions were recovered with 50 ml of 6 M HCl.

It is considered that the polymer domains with high local densities of negatively charged groups and the hydrophobic groups can usefully be employed as a reaction field in which the complex cations with a hydrophobic nature are concentrated and tightly bound to the polymer chains.

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