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Luminescence Probe Studies of Nafion Polyelectrolytes

by

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We have recently described a procedure for dissolving perfluorosulfonate ionomer membranes. This allows, for the first time, for a study of the inherent chemical properties of the polyperfluorosulfonate molecule. Such studies of the free polyelectrolyte molecule in solution should give insight into the chemical properties of the solid state membranes obtained from these polyelectrolytes.

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20. ABSTRACT (continued)

The work described here focusses on investigations of the nature of the interactions between the polyperfluorosulfonates and their counterions. Clearly an electrostatic interaction is extant but because hydrophobic interactions have been implicated in various studies of perfluorosulfonate membranes, it was of interest to see if evidence for such interactions could be observed in solutions of the polyelectrolytes. Luminescence probe studies were used to investigate the nature of the interactions between the polyperfluorosultonates and their counterions.

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Luminescence Probe Studies of Nafion
Polyelectrolytes

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Introduction.

Perfluorinated ionomers[1] have been used in a variety of electrochemi-
cal applications including use in chlor-alkali cells,[2,3] water electro-
lyzers,[4] zinc-bromine cells,[5] hydrogen-halogen cells,[6] hydrogen-oxygen fuel
cells[7] and as agents for the preparation of chemically modified elec-
trodes.[8] These ionomers also have a number of non-electrochemical
uses.[9,10] Because of their remarkable versatility, much current research
effort is being devoted to studying the morphological and chemical proper-
ties of these inomers.[1] We have recently described a procedure for dissol-
ving perfluorinated ionomer membranes[11]. This allows, for the first time,
for a study of the intrinsic chemical properties of the poly(perfluorosul-
fonate) (PFS) molecule itself. Such studies should allow for a more thor-
ough understanding of the chemical and perhaps the morphological features
of ionomer membranes. We report at this time results of various lumines-
cence probe studies of the polyelectrolytes obtained by dissolving the 1100
and 1200 equivalent weight versions of DuPont's Nafion[1]. The primary
objective of this work is to study the interactions between these anionic
polyelectrolytes and their counterions.

Experimental.

Materials. Samples of 1100 and 1200 equivalent weight Nafion were kindly
donated by E. I. DuPont de Nemours and Company. These were dissolved using
the procedure of Martin et al.[11] which uses 50:50 ethanol-water as the sol-
vent. The alcohol was removed from these solutions, immediately before
use, by heating. The Na^+ form of the polyelectrolytes (Na-PFSs) were
obtained by adding carefully measured quantities of NaOH to the polymer
solutions. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (bpy=2,2'-bipyridine) (G. F. Smith), 1,1'-

dimethyl-4,4'-bipyridinium dichloride hydrate (methylviologen) (Aldrich), and 1,1'-diheptyl-4,4'-bipyridinium dibromide (heptylviologen) (Aldrich) were used without further purification. Tris(2,4-pentanedione)Cobalt(III), Co(acac)$_3$, (Alfa) was recrystallized from benzene, washed with diethyl ether and dried at 60°C.[12] Auramine O (4,4'-(imidocarbonyl)bis(N,N'-dimethyaniline)monohydrochloride) (the cation is abbreviated AO$^+$) (Sigma) was recrystallized from NaCl.[13] 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (the cation is abbreviated (6-In-11$^+$)[14]) was donated by N. J. Turro. All other reagents were ACS reagent grade and were used without further purification. Triply distilled water was used throughout this work. The 1100 and 1200 equivalent weight versions of Nafion gave essentially identical results. Only the 1100 data is reported.

Emission Intensity and Absorbance Measurements.

Emission spectra were obtained using a Spex Fluorolog 2 spectrofluorometer. Ru(bpy)$_3{}^{2+}$, AO$^+$ and 6-In-11$^+$ were excited at 455 nm, 435 nm and 290 nm, respectively. Emission intensity was monitored at 600 nm for the Ru(bpy)$_3{}^{2+}$* quenching studies. Absorption spectra were taken using a Beckman Model 26 spectrophotometer.

The solutions for the luminescence intensity measurements were prepared by adding aliquots of stock solutions of the polymer (1 (wt/vol) %) to Ru(bpy)$_3{}^{2+}$ (2 x 10^{-5} M), AO$^+$ (5 x 10^{-5} M) or 6-In-11$^+$ (2 x 10^{-5} M) solutions in quartz cuvettes. Hamilton microliter syringes were used. The cuvette solution was mixed thoroughly after each addition of polymer solution, and intensities were corrected for dilution. The addition of salt solution or quencher to a PFS/Ru(bpy)$_3{}^{2+}$ or PFS/AO$^+$ solution followed a similar procedure.

Lifetime Measurements.

Ru(bpy)$_3{}^{2+}$* lifetime measurements were done at the Center for Fast Kinetics Research at the University of Texas at Austin.

Lifetimes for $Ru(bpy)_3^{2+}*$ in pure water, in a solution 0.01% in H-PFS (proton form of the polyelectrolyte) and in a solution of 0.01% Na-PFS were obtained (all solutions were 2×10^{-5} M in $Ru(bpy)_3^{2+}$). Solutions were degassed with prepurified nitrogen. A Quantrel YG 481 Nd:YAG Q-switched dye laser (535 nm, ca. 10 ns pulse) was used as the excitation source. Luminescence emission was monitored at 650 nm with an RCA R928 photomultiplier tube and processed with a Biomation (Gould) multichannel analyzer and a PDP-11/70 minicomputer. Metal screens were used to attenuate the incident laser intensity.

Results and Discussion.

The Luminescence Probe Studies.

As noted above, the primary objective of this work is to study the nature of the interactions between the Nafion polyelectrolytes and their counterions. Clearly an electrostatic interaction[15a] will be present, but because hydrophobic interactions[15b] have been implicated in various studies of Nafion membranes,[8,16,17] it was of interest to see if evidence for such interactions could be observed in solutions of the polyelectrolytes. Luminescence probe studies have been shown to be quite effective at characterizing polyion-counterion interactions in other polyelectrolyte systems.[18-24] Two types of luminescence probe experiments were used here. The first involved studies of the effect of addition of the PFSs on the luminescence emission intensities of various cationic probes in aqueous solution. Three structural diverse probes, 6-In-11^{+} [14,22,23], $Ru(bpy)_3^{2+}$ and AO^+ [24] were chosen for these studies. 6-In-11^{+} was chosen because the effect of solvent polarity on its emission characteristics are dramatic and well characterized[14,22,23] and because it has been used to study polyion-counterion interactions in poly(styrene-

sulfonate)(PSS).[23] Ru(bpy)$_3$$^{2+}$ was chosen because Lee and Meisel have sug-
gested that hydrophobic interactions between this ion and the fluorocarbon
chain material occur in 1200 equivalent weight Nafion membranes.[16] AO$^+$ was
chosen because it has proved to be ideally suited for studying polymer-
probe interactions.[24]

The second set of luminescence probe experiments involved studies of
the effect of the PFSs on the rates of quenching of Ru(bpy)$_3$$^{2+}$* by various
electron transfer quenching agents. Ru(bpy)$_3$$^{2+}$ was chosen for these
studies because it strongly binds to the PFSs (vide infra) and because its
luminescence in aqueous solution has been well characterized.[25]

Luminescence Intensity Studies. Figure 1 shows the effect of addition of
an aqueous solution of Na-PFS (1 wt./vol.%) on the emission spectra of 6-
In-11$^+$. A pronounced blueshift in the position of the emission spectrum is
observed (wavelength of maximum emission intensity, λ_{max}, in water is 374
nm, λ_{max} in Nafion solution is 356 nm). A blushift in the emission of a
probe (relative to water) is often indicative of a more hydrophobic envi-
ronment for the probe.[26] (The photochemical mechanism for such a shift is
discussed by Brand and Gohlke.[26]) The observed blueshift, then, suggests
that Nafion is engaging in hydrophobic interactions with 6-In-11$^+$. In this
type of luminescence probe study, however, it is desirable to compare the
emission of the probe from the unknown environment with its emission spec-
trum from some well characterized environment. It is know that PSS can
engage in strong hydrophobic interactions with its counterions.[18,23]
Turro and Okubo observed a pronounced blushift in the emission of 6-In-11$^+$
from aqueous solutions of PSS, which they attributed to hydrophobic binding
of this probe by PSS.[23] The similarity in the responses of this probe to

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the unknown (Nafion) and standard (PSS) environments adds further evidence for hydrophobic interactions between $6\text{-In-}11^+$ and Nafion.

In addition to the shift in λ_{max}, a decrease in emission intensity, with the initial additions of Na-PFS, is observed (Figure 1b) followed by a gradual increase in intensity with further additions (Figure 1c). Similar results were obtained by Turro and Okubo in their investigations of Na-PSS.[23] They suggest that quenching by trace impurities present in the polymer solution may account for the initial decrease in emission intensity.[23]

Further evidence for a strong hydrophobic component to the interaction between $6\text{-In-}11^+$ and PFS is obtained from studies of $6\text{-In-}11^+$ absorption spectra. As shown in Figure 2, the absorbance at 290 nm increases as Na-PFS is added to a solution of $6\text{-In-}11^+$. Turro has shown that the absorbance for this probe increases as the polarity of the environment around the probe decreases;[22,23] furthermore, a similar increase in absorbance was observed with PSS.[23] Figure 2 shows excitation spectra obtained with the fluorometer, but true absorbance spectra (obtained with the spectrophotometer) gave identical results. Finally, it is important to note that while the data shown in Figures 1 and 2 refer specifically to the Na^+ form of PFS, essentially identical results were obtained with the proton form. These studies clearly show that $6\text{-In-}11^+$ engages in strong hydrophobic interations with the PFSs.

Figure 3 shows the effect of concentration of Na-PFS (expressed as the molarity of $-SO_3^-$ sites) on the intensity of emission by $Ru(bpy)_3^{2+}$*. Emission intensity is expressed as the ratio I/I° where I° is the intensity in pure water and I is the intensity after addition of an increment of the Na-PFS solution.[21] Emission intensity increases with increasing concentra-

tion of PFS until a stoichiometrically equivalent amount of $-SO_3^-$ sites have been added to the solution (i.e., until $2 \times [-SO_3^-] = [Ru(bpy)_3^{2+}]$). This increase in intensity is not due to some polymer-induced change in bulk concentration of the $Ru(bpy)_3^{2+}$ because the absorption spectrum (corrected for dilution) is unaffected by the presence of PFS; nor is this intensity increase due merely to a change in the shape of the emission band because an analogous plot of the areas under the emission bands gives an identical curve. When greater than stoichiometric amounts of PFS are added, a leveling in emission intensity is observed (Figure 3).

The leveling of the emission intensity at the stoichiometric equivalence point implicates a role for electrostatic interactions in the observed increase in emission intensity. However, if a hydrophilic, divalent metal ion (e.g., Mg^{2+}) is added to a $Ru(bpy)_3^{2+}$/PFS solution, a huge excess of the hydrophilic ion is required to return I/I^o back to 1 (Figure 4, the ratio (moles Mg^{2+}/moles $Ru(bpy)_3^{2+}$) to make I/I^o 1 is ca. 1000). If the increase in emission intensity (Figure 3) resulted from purely electrostatic interactions, the ability of Mg^{2+} to replace $Ru(bpy)_3^{2+}$ as the counterion of the polyelectrolyte would not be so severely retarded, that is, one might expect the ratio (moles Mg^{2+}/moles $Ru(bpy)_3^{2+}$) required to make I/I^o ca. 1 to be close to unity. Given the hydrophobic nature of $Ru(bpy)_3^{2+}$, the results in Figure 4 indicate that there is also a strong hydrophobic interaction between this counterion and the PFSs. The binding of $Ru(bpy)_3^{2+}$ to the PFSs is via a conserted hydrophobic/electrostatic interaction.

When $Ru(bpy)_3^{2+}$ is used as a luminescence probe of hydrophilic poly-ion where only electrostatic interactions are extant, emission intensity does not change with the concentration of the polyion.[27] This suggests

that the increase in emission intensity in Figure 3 is caused by the hydrophobic part of the interaction. Kurimura et al. saw a similar increase in emission intensity when PSS was added to a $Ru(bpy)_3^{2+}$ solution and they also concluded that this increase was due to hydrophobic interactions.[21] A consideration of the effect of water on the non-radiative rate constant provides a possible explanation for the observed increases in $Ru(bpy)_3^{2+}*$ emission intensity. As recently noted by Caspar and Meyer,[28] water is particularly effective at promoting non-radiative decay in $Ru(bpy)_3^{2+}*$. It seems likely, then, that any interaction which shields $Ru(bpy)_3^{2+}*$ from water will increase its quantum yield (the radiative rate constant is relatively insensitive to solvent[28]). Since it is the incompatibility of water and the hydrophobic solute which promotes hydrophobic bonding,[15b] it is reasonable to assume that when bound to PFS, $Ru(bpy)_3^{2+}$ minimizes its contact with water. Therefore, a quantum yield increase would be expected.

The final luminescence probe used was AO^+. In nonviscous solvents electronic excitation energy in AO^+ is dissipated as heat via rotation of its phenyl rings.[24] For this reason, AO^+ does not fluoresce in water (Figure 5) or other non-viscous solvents.[24] Binding of AO^+ to polyanions hinders phenyl ring rotation and fluorescence can be observed.[24] Figure 5 shows that Na-PFS can induce fluorescence in AO^+. As was the case with $Ru(bpy)_3^{2+}$, fluorescence intensity is proportional to $[-SO_3^-]$ until a stoichiometrically equivalent quantity of polymer is added. Furthermore, huge excesses (ca. 1000 fold) of Na^+ are required to return the emission intensity to background levels, indicating that AO^+ also binds via a concerted hydrophobic/electrostatic interaction.

Quenching Studies. It is well known that quenching reactions between an electronically excited cation and a cationic quencher are accelerated in

the presence of a polyanion.[19,27,29] This acceleration is due to the
concentration of the cations in the domain around the polyion chains (i.e.,
the local concentrations of both emitter and quencher are higher than the
bulk concentrations).[19,27,29] It was of interest to see if accelera-
tion of quenching reactions between cationic quenchers and $Ru(bpy)_3^{2+}*$
could be observed in the presence of the PFSs. Furthermore, given the
strongly hydrophobic nature of the PFSs (vide supra), it was of particular
interest to see if a contribution from hydrophobic interactions[18] could be
discerned in any acceleration observed.

Quenching rate constants were determined using the emission intensity
form of the Stern-Volmer equation.[30] Typical Stern-Volmer plots are shown
in Figure 6. We have obtained apparent quenching rate constants from such
plots for hydrophilic cation, hydrophobic cation, and neutral quenchers in
the presence of both Na-PFS and H-PFSs (Table 1). Measured $Ru(bpy)_3^{2+}*$
lifetimes of 640±10 ns (Na-PFS) and 590±10 ns (H-PFS) were used for calcu-
lation of these rate constants. They are called apparent quenching rate
constants because they have been calculated assuming the bulk quencher con-
centrations. To obtain real quenching rate constants, the values shown in
Table 1 would have to be normalized as described by Meisel et al.[19] Since
it is the magnitude of the rate constant enhancement which is of interest
here, normalization was not attempted.

Table 1 shows that quenching rate constants are enhanced for all of
the cationic quenchers. The amount of enhancement can be described quanti-
tatively by the enhancement factor, α, which is the ratio of the apparent
rate constant in the presence of the polymer to the rate constant observed
in pure water. Enhancement factors (Table 2) for the hydrophobic cations
(methylviologen and heptylviologen) are seven to ten times larger than the

enhancement factors for the hydrophilic cations. As in the previous set of experiments, these data show that hydrophobic interactions can play an important role in the binding of counterions to the PFSs. Again, however, the importance of the electrostatic component of the interaction is demonstrated because quenching by neutral $Co(acac)_3$ is not changed appreciably by the presence of the polyanion. As was indicated by the data obtained in the intensity studies, a concerted hydrophobic/electrostatic interaction is required to produce strong binding.

Conclusions. This work has shown that strong binding to the Nafion polyelectrolytes occurs when both electrostatic and hydrophobic interactions are possible. This helps to explain why a Nafion film on an electrode surface retains hydrophobic counterions (e.g., $Ru(bpy)_3^{2+}$, MV^{2+})[8] when the film is immersed in a solution containing high (e.g., 0.1 M) salt concentrations and none of the hydrophobic ion. Nafion shows very different selectivity than the polyelectrolytes investigated by Anson[31] which apparently bind only via electrostatic interactions. We are currently investigating ion exchange selectivity in cationic analogs of Nafion to see if hydrophobically driven ion exchange is a general phenomenon.

This work also raises important points concerning the transport properties of Nafion. The permeability of a material to a solute species is proportional to the product of the partition constant and the diffusion coefficient for that species in the material. In most of the electrochemical applications of Nafion, high permeability to cations is desired. Because of the affinity of the polymer for hydrophobic cations (i.e., high partition constant), these ions could show higher permeabilities than smaller alkali metal ions, if the membrane is in contact with a solution con-

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taining both types of cations. Finally, these data corroborate results obtained previously in this laboratory which showed that rates of ionic diffusion through Nafion films can be affected by hydrophobic interactions.[32]

Table 1. Apparent second order rate constants ($M^{-1}S^{-1}$) for quenching of $Ru(bpy)_3^{2+}$* emission by various quenchers. Effect of the PFSs on the rate constants.

Quenchers

Media	Cu^{2+}	Fe^{3+}	MV^{2+}[a]	HV^{2+}[b]	$Co(acac)_3$[c]
Water	7.7×10^7[d]	2.1×10^8[e]	4.5×10^8[f]	4.2×10^8[g]	1.1×10^9[h]
H-PFS[1]	2.4×10^9	2.2×10^9	1.5×10^{11}	9.7×10^{10}	1.5×10^9
Na-PFS[1]	3.9×10^9		4.5×10^{11}		

[a] Methylviologen

[b] Heptylviologen

[c] acac = acetylacetone

[d] Meisel et al., J. Am. Chem. Soc., 100, 117 (1978).

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[g] M.A.J. Rodgers and J.C. Becker, J. Phys. Chem., 84, 2762 (1980).

[h] Reference 12

[1] Solution was 2×10^{-5}M in $Ru(bpy)_3^{2+}$ and 0.05% in polymer.

Table 2. H-PFS induced enhancement factors, α (α = apparent rate constant in the presence of polymer divided by pure water rate constant) for various quenchers.[a]

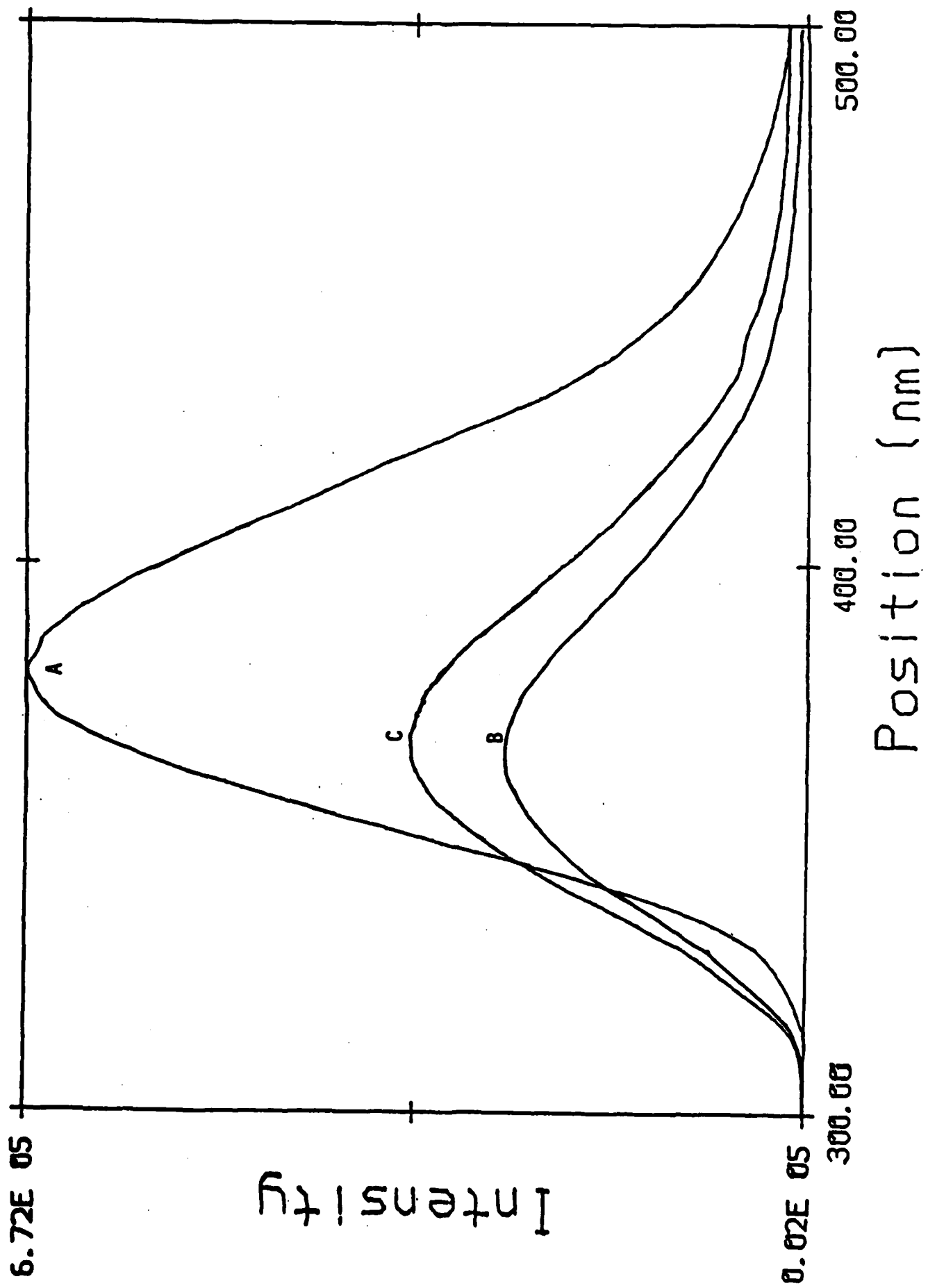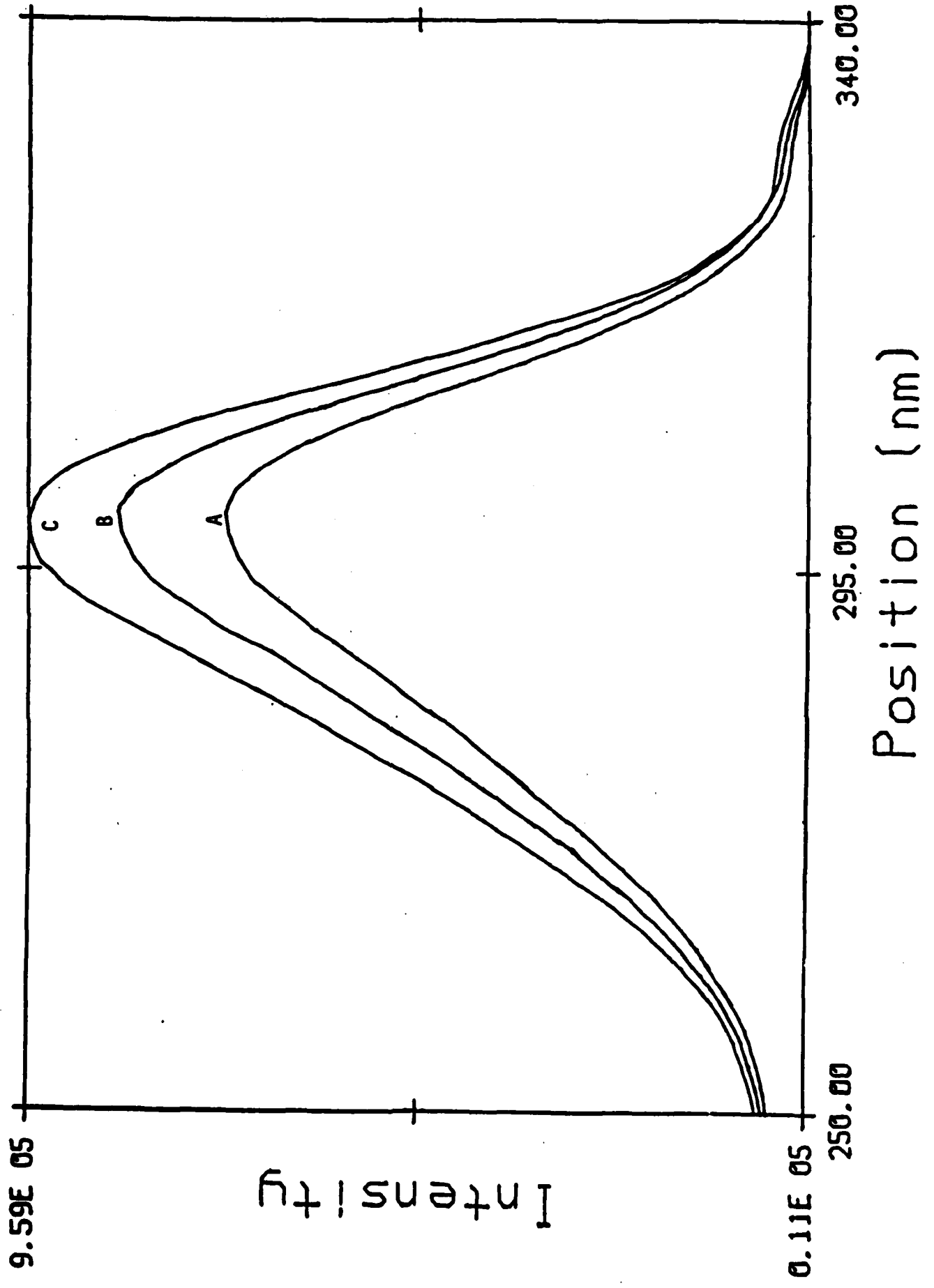| Quencher	Cu^{2+}	Fe^{3+}	MV^{2+}	HV^{2+}	$Co(acac)_3$
α	31	10	330	230	1.4

[a] See Table 1.

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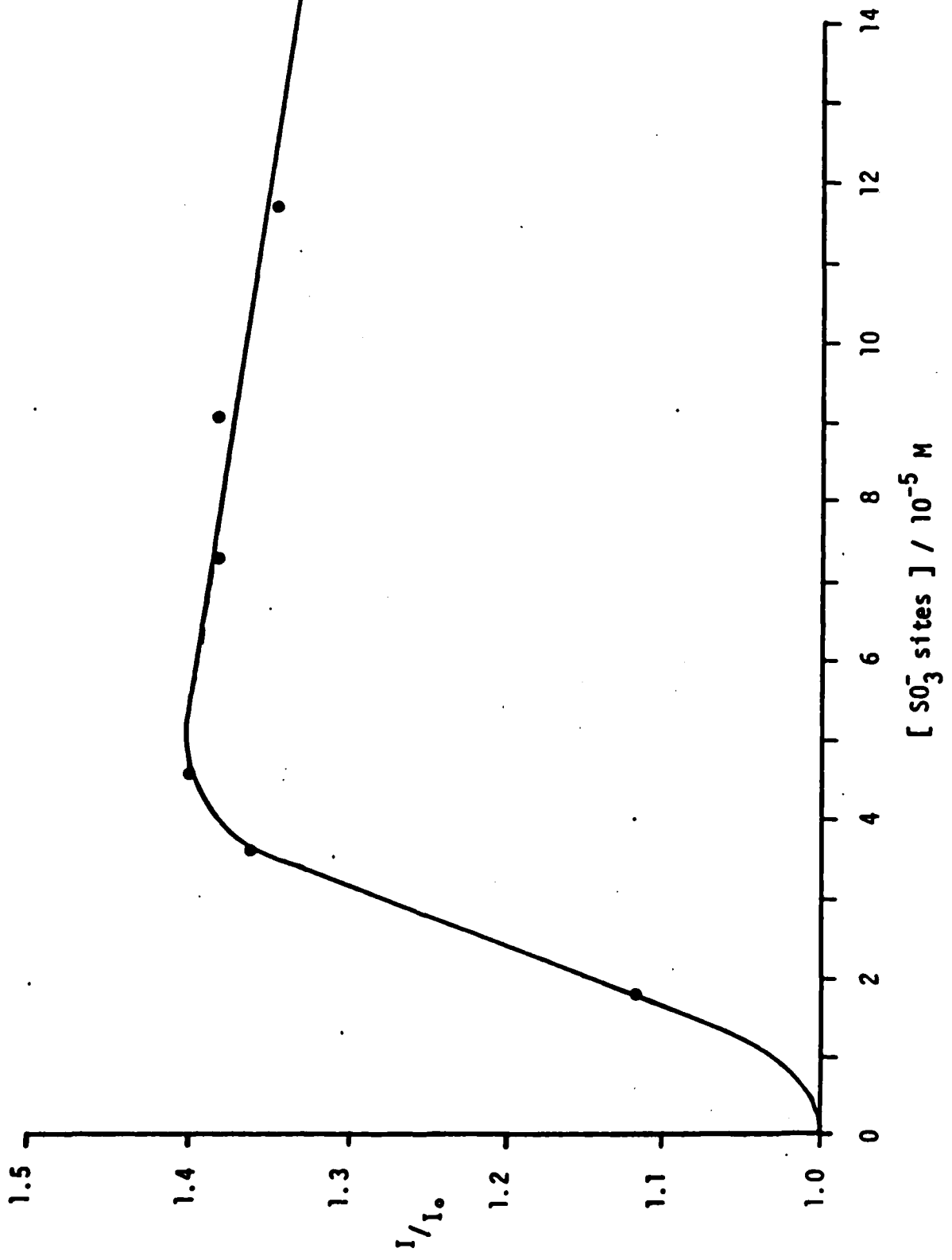18. N. J. Turro and T. Okubo, J. Phys. Chem., 86, 1535 (1982).

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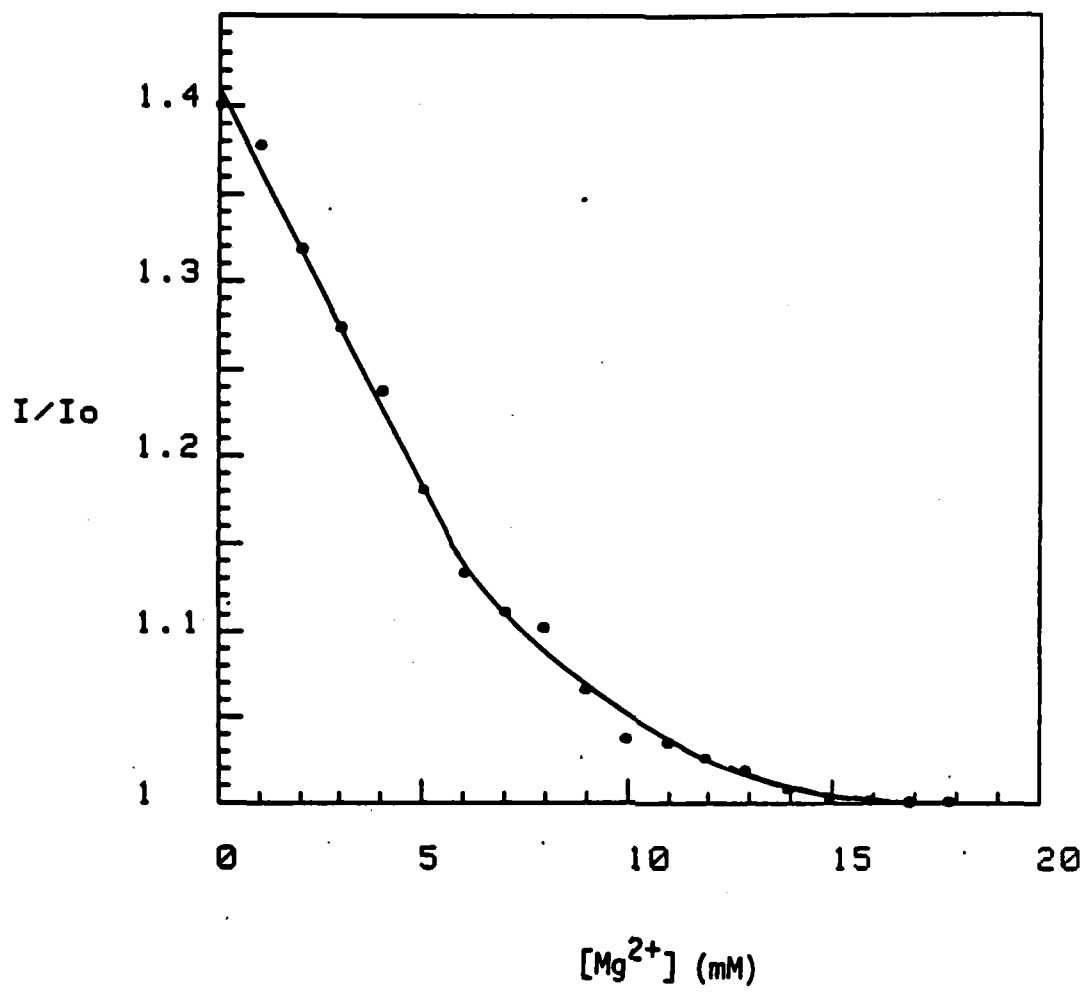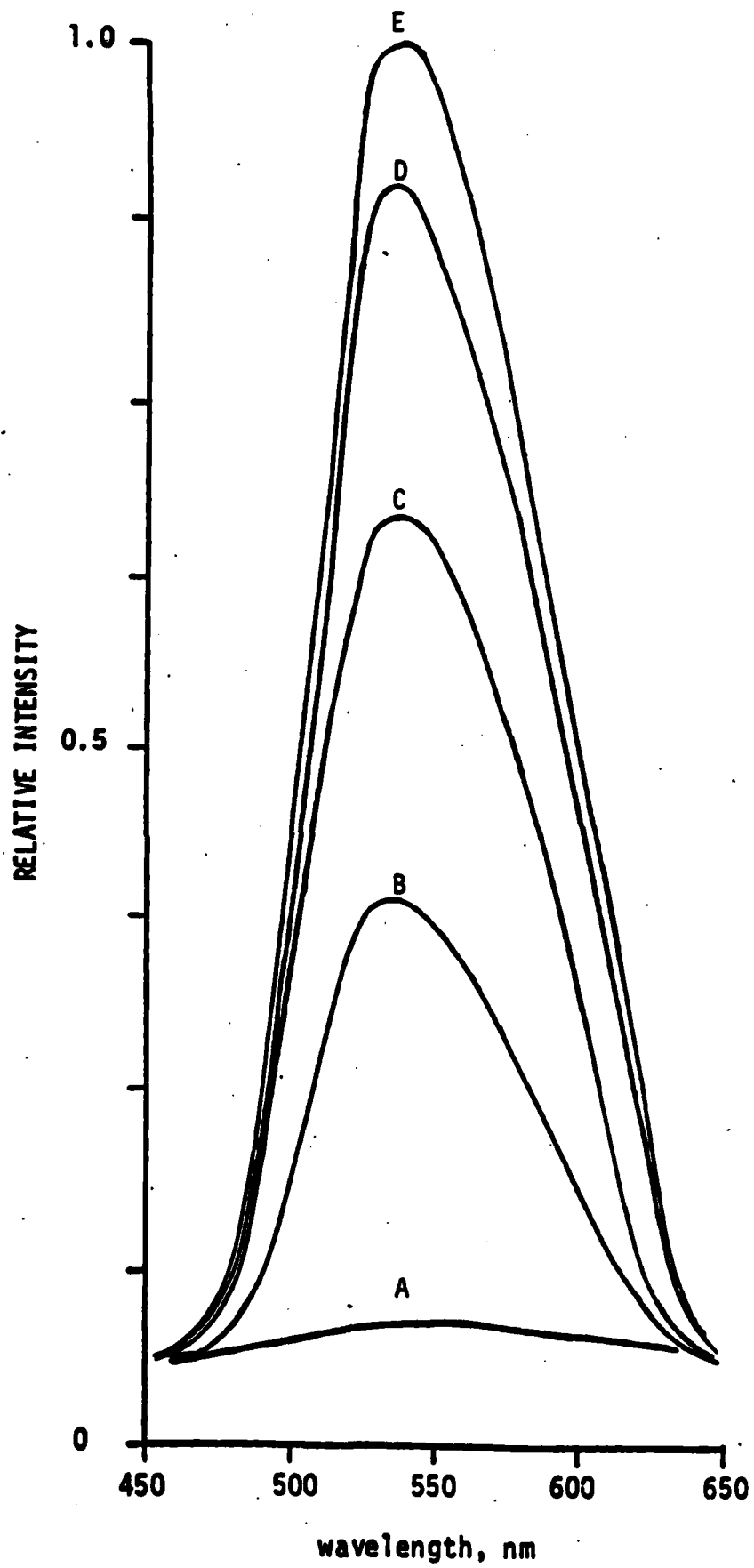32. C. R. Martin and K. A. Dollard, J. Electroanal. Chem., in press.

Figure Captions.

Figure 1. Effect of addition of Na-PFS on fluorescence spectra for 6-In-11$^+$ (2×10^{-5} M). A. No Nafion added. B. After addition of Na-PFS solution. 3.79×10^{-8} moles of $-SO_3^-$ sites added. C. After addition of more Na-PFS solution. 5.05×10^{-7} moles of $-SO_3^-$ sites added.

Figure 2. Excitation spectra of 6-In-11$^+$ (2×10^{-5} M, monitored at 374 nm). A. No Nafion added. B. After addition of Na-PFS solution. 7.26×10^{-8} moles of $-SO_3^-$ sites added. C. After addition of more Na-PFS solution. 1.99×10^{-7} moles of $-SO_3^-$ sites added.

Figure 3. Dependence of $Ru(bpy)_3^{2+}$* luminescence emission intensity on concentration of Na-PFS. $[Ru(bpy)_3^{2+}] = 2\times10^{-5}$ M. $\lambda_{EX} = 455$ nm, $\lambda_{EM} = 610$ nm.

Figure 4. Effect of addition of MgSO$_4$ on emission intensity of $Ru(bpy)_3^{2+}$* from a $Ru(bpy)_3^{2+}$/Na-PFS solution. 2×10^{-8} moles $Ru(bpy)_3^{2+}$, 6×10^{-8} moles Nafion $-SO_3^-$ sites (see Figure 3).

Figure 5. Fluorescence spectra of AO$^+$ as a function of concentration of Na-PFS ([AO$^+$] = 5×10^{-5} M, $\lambda_{EX} = 435$ nm). A. No Na-PFS. B. 9×10^{-9} moles of $-SO_3^-$ sites. C. 1.8×10^{-8} moles $-SO_3^-$ sites. D. 2.7×10^{-8} moles $-SO_3^-$ sites. E. 3.6×10^{-8} moles $-SO_3^-$ sites.

Figure 6. Typical Stern-Volmer plots for quenching of PFS-bound $Ru(bpy)_3^{2+}$* by various quenchers. $[Ru(bpy)_3^{2+}] = 2\times10^{-5}$ M, [Na-PFS] = 0.05%.

[SO$_3^-$ sites] / 10^{-5} M

I/I_o

1.5

1.4

1.3

1.2

1.1

1.0

0   2   4   6   8   10   12   14
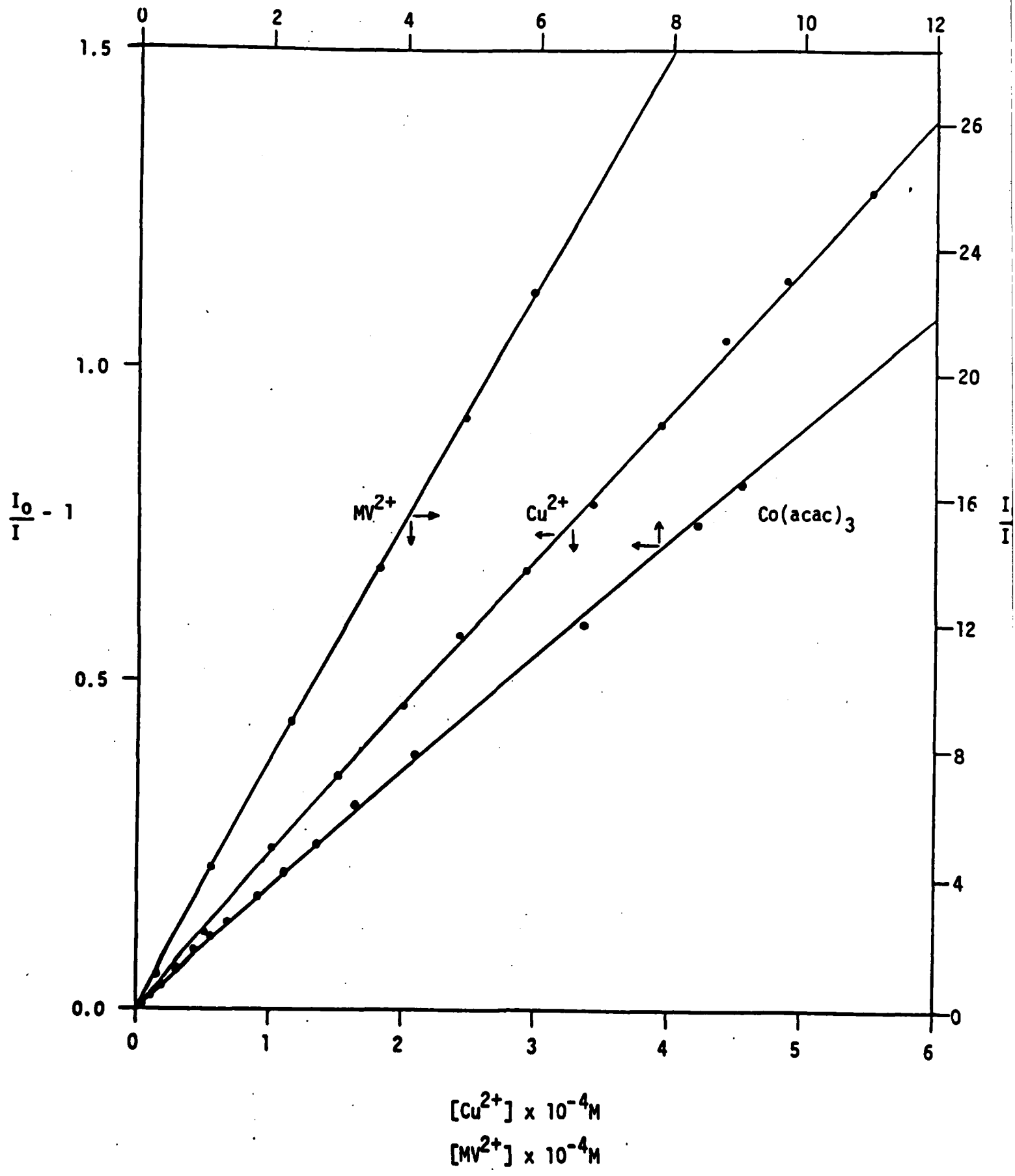
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