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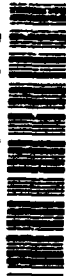Jorge L. Colón and C. R. Martin

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Measurements of the luminescence lifetime of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) in Nafion were used to probe the heterogeneity of $-SO_3H$ sites in the Nafion membrane. The decay kinetics of the probe ion are shown to depart from simple first-order behavior. Alber's model of a continuous distribution of rate constants is used to explain the decay kinetics. The results of these and related investigations indicate that the probe ions reside in sites with different local water activities.

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LUMINESCENCE PROBE STUDIES OF IONOMERS. 3. DISTRIBUTION OF DECAY RATE CONSTANTS FOR TRIS BIPYRIDYL RUTHENIUM(II) IN NAFION MEMBRANES

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Abstract

Measurements of the luminescence lifetime of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) in Nafion were used to probe the heterogeneity of $-SO_3H$ sites in the Nafion membrane. The decay kinetics of the probe ion are shown to depart from simple first-order behavior. Albery's model of a continuous distribution of rate constants is used to explain the decay kinetics. The results of these and related investigations indicate that the probe ions reside in sites with different local water activities.

Introduction

Ion-containing polymers (ionomers) have a wide variety of applications including uses in electrochemistry, chemical synthesis, and separation science.[1-13] Nafion, a family of perfluorosulfonate ionomers marketed by Du Pont, has proven to be an extremely useful and versatile ion-containing polymer. Nafion and other ionomers have an unusual morphology in which the charged groups aggregate to form domains called ionic clusters. These clusters resemble reversed micelles and are randomly distributed throughout the backbone chain material phase.[14,15]

Information on the structural and dynamic nature of Nafion is a prerequisite for the future utilization of this material. Specifically, information about the chemical microenvironment and diffusion of ions and molecules within the ionic clusters is required. Luminescence probe techniques can provide photophysical and photochemical information about the properties of this system. For this reason, we and others[16-27] have been using luminescence probe techniques to study the morphology and chemical characteristics of the ionic cluster phases in ionomers.

The specific luminescent probe molecule used in this study is tris(2,2'-bipyridyl) ruthenium (II), $Ru(bpy)_3^{2+}$, an extensively studied metal complex.[28-30] Lee and Meisel reported luminescence quenching studies of $Ru(bpy)_3^{2+}$ in Nafion.[16] Lee and Meisel observed that the luminescence decay of $Ru(bpy)_3^{2+}$ in Nafion was monoexponential; in contrast, we have always obtained nonexponential decays for the luminescence of $Ru(bpy)_3^{2+}$ in

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Nafion. Possible reasons for the discrepancies between our results and those of Lee and Meisel will be presented here.

We have used Albery's model for dispersed kinetics to analyze the luminescence of $Ru(bpy)_3^{2+}$ in Nafion membrane.[31] The fits of the experimental data to the dispersed kinetics model are better than the fits to the more conventional biexponential decay model. This data analysis shows that the decay of $Ru(bpy)_3^{2+}$ in Nafion can be described by a Gaussian distribution of the energy of activation for the decay. Information about the chemical distribution and nature of the ion exchange sites in the polymer phase can be obtained from this analysis. These and related results are presented in this paper.

Experimental Section

MATERIALS. Nafion 117 membrane (proton form) was obtained from the E.I. Du Pont Company. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ was obtained from G. F. Smith and was used as received. Water was circulated through a Milli-Q water purification system (Millipore Corp.) or was pyrolytically triply distilled. All other reagents and solvents were of the highest available grade and were used without further purification.

PROCEDURES. As-received Nafion membrane was cut into ca. 10 X 30 mm rectangles. The precut membranes were then cleaned by ultrasonicating in several portions of pyrolytically triply distilled water (PTD-H_2O), and then ultrasonicating in 50:50 EtOH-PTD-H_2O (0.5 hr.). The membranes were then boiled in PTD-H_2O for 2 hr. and rinsed ultrasonically in PTD-H_2O. The

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membranes were changed to the Na⁺ form by soaking overnight in 1M
NaOH, and finally rinsed ultrasonically in PTD-H_2O. The wet
membranes were weighed separately and placed in glass vials. Two
of the membranes were used to determine the equilibrium membrane
water content. These two membranes were dried in vacuo overnight
at 115°C and reweighed. The water content was calculated as
percent by weight.

Ru(bpy)$_3^{2+}$ was incorporated (loaded) into the remaining
Nafion membranes by stirring each membrane in a separate vial
containing the required concentration of Ru(bpy)$_3^{2+}$. (The aqueous
solution of Ru(bpy)$_3^{2+}$ used to load Ru(bpy)$_3^{2+}$ into the membranes
is called the "loading solution"; each membranes was placed in a
loading solution containing the precise concentration of
Ru(bpy)$_3^{2+}$ needed to load the membrane to the desired Ru(bpy)$_3^{2+}$
level.) As will be discussed in detail later, because diffusion
of the probe into the polymer phase is slow, the membranes were
equilibrated with their respective loading solution for 1 month
before use. The quantity of Ru(bpy)$_3^{2+}$ loaded was maintained very
low; between 0.8 and 0.01% of the ionic sites in the Nafion
membranes were exchanged with the luminescent probe. After
loading, and prior to measurement, the membranes were rinsed with
water.

Some experiments were performed on oxygen-free Nafion
membranes. Oxygen was removed from the Nafion membranes as
follows: After loading with Ru(bpy)$_3^{2+}$ the membrane was placed in
a 12.5 mm X 12.5 mm X 45 mm rectangular cuvette filled with

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water. The cuvette was sealed with a rubber septum, and nitrogen was bubbled into the solution for one and a half hours while the solution was ultrasonicated.

SPECTROSCOPY. Steady-state emission spectra were obtained with a Spex Fluorolog 2 spectrofluorometer. The samples were excited with a 450-W xenon lamp. Slits were set at 1.25 mm; the excitation wavelength was 452 nm. Luminescence was detected perpendicular to the incident radiation. Luminescence lifetime measurements were obtained using a time-correlated single photon counting spectrometer (Edinburgh Instruments Model 199). The spectrometer is fitted with a nitrogen flashlamp (337 nm) and a microcomputer (IBM PS/2 Model 30 with a 8087 microprocessor). The $Ru(bpy)_3^{2+}$-loaded membranes were sandwiched between two quartz slides. This assembly was positioned in the spectrometer at 45 degrees to the axis of excitation. Emission was detected from the opposite side of the membrane at 45 degrees to the axis of the detector. This orientation (and the emission filter) minimizes the detection of scattering from the membranes.

Data Analyses. The general approach for obtaining kinetic parameters from the luminescence decay curves was described previously.[32] We fitted the experimental intensity vs. time transients to specific decay models using the method of nonlinear least-squares[33,34] (Marquardt algorithm); the Edinburgh Instrument's or MTR Software Inc.'s nonlinear least-squares software was used. Monoexponential, biexponential, and dispersed kinetics[31] decay models were used to fit the decay curves. The

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dispersed kinetics model[31,35-48] assumes that a continuous

dis ibution of decay rates exits within the heterogeneous

system. This continuous distribution of decay rates results from

a continuous distribution of chemical microenvironments within

the system; each microenvironment has a distinct decay rate

constant and each rate constant is first-order. We have

described this model in detail in a previous paper.[32]

Albery's dispersed kinetics model provides the "most

probable" rate constant, $\bar{k}$, which is the first-order rate

constant associated with the average chemical microenvironment

within the medium. This rate constant can be studied in the

normal fashion as if the process was exponer `. (i.e., normal

kinetic analysis can be performed with this "most probable" rate

constant value). The dispersion of k (the γ value) is a measure

of the disorder of the medium; this provides information about

the local structure of the medium and the dependence of the rate

process on energetic and structural parameters.[48]

Results and Discussion

Previous Investigation of Ru(bpy)$_3$$^{2+}$ Emission from Nafion. Lee

and Meisel[16] observed monoexponential decay curves for the

emission of Ru(bpy)$_3$$^{2+}$ in Nafion. We have repeated this

experiment numerous times over the last 8 years and have never

observed monoexponential decays. Recently, Kaneko and Hayakawa[49]

also observed that the decay of Ru(bpy)$_3$$^{2+}$ in Nafion films cannot

be describe by a monoexponential decay model. Figure 1 shows

typical decay curves for Ru(bpy)$_3$$^{2+}$ in Nafion at various loading

levels; note that these are semilogarithmic plots. The nonlinearity observed in Figure 1 clearly shows that a monoexponential decay model is not appropriate.[33]

We believe that it is possible that Lee and Meisel's results were affected by a nonequilibrium distribution of luminescent probe ions in the Nafion membrane. Lee and Meisel stirred their membranes in the $Ru(bpy)_3^{2+}$ loading solution for only 12 hours. A simple calculation shows that equilibrium times well in excess of 12 hours are required if probe-membrane equilibrium is to be achieved. The distance, Δ, a diffusing species moves in time, t, is given by $\Delta = (2Dt)^{1/2}$ where D is the diffusion coefficient.[50] Assuming D for $Ru(bpy)_3^{2+}$ in Nafion is 2 X 10^{-10} cm^2/s,[7] a $Ru(bpy)_3^{2+}$ ion moves, on average, only 0.004 cm into a Nafion membrane during a 12 hour equilibrium period. In order to achieve equilibrium the ion must move half-way through the membrane (0.0125 cm). Thus, after 12 hours, a nonhomogeneous distribution of $Ru(bpy)_3^{2+}$ is extant in the membrane; electron microprobe analyses have experimentally confirmed such nonhomogeneous distributions.[51]

We have found, however, that after loading, the wavelength of maximum emission intensity for $Ru(bpy)_3^{2+}$ blueshifts for periods of up to one month. This blue shift results from a gradual partitioning of the probe from domains with high local water activity to domains with high local fluorocarbon chain material activity (vide infra and ref. 19). These data suggest that $Ru(bpy)_3^{2+}$ in freshly-loaded films, is predominately present

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in an aqueous-like environment. Since only this aqueous-like environment is populated at short equilibration times, a monoexponential decay (as observed by Lee and Meisel) might be anticipated. In contrast, for long equilibration periods a variety of microenvironments become populated (aqueous-like and fluorocarbon-like) and this produces the nonexponential decay observed in our experiments.

Biexponential Decay Model. The biexponential decay model assumes that there are two distinct populations of emitters (or two distinct chemical microenvironments) within the membrane phase. As a result of these populations, two distinct decay rate constant or decay lifetimes are observed. Figure 1 shows that our data can be fitted to a biexponential decay model. The lifetimes, standard deviations, and χ^2 values[32] obtained from these fits are shown in Table I.

The kinetic data obtained from the biexponential decay model (Table I) may be summarized as follows. At loading levels less than 0.07%, both the long and the fast lifetimes increase with the quantity of $Ru(bpy)_3^{2+}$ loaded into the membrane. Furthermore, the data in Table I suggest that the microenvironment yielding the long lived species is preferentially occupied. (At low loading levels 84 to 98% of the emitters occupy sites in this microenvironment, while at higher loading levels, only 68 to 84% of the emitters are in this long lifetime environment.) Above 0.07% loading, the lifetimes and relative sizes of the two populations remain more or less constant (Table I).

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The kinetic data in Table I suggest that the biexponential decay model is not appropriate for this system. The first problem with this model concerns the changes in both the short and long lifetimes, observed at low loading levels. If two distinct non-interacting populations exist in the membrane, the two lifetimes obtained from the kinetic analysis should be the same regardless of the loading level; the relative numbers of emitters in each population might change with loading, but there is no a priori reason to expect that the lifetime will. The change in lifetimes observed in Table I suggest that more than two distinct environments are being populated.

The data obtained from the biexponential model also contradicts evidence obtained from steady-state emission experiments. Table II shows that the wavelength of maximum emission intensity (λ_{max}) is strongly blue shifted (relative to emission from water) at low loading levels; λ_{max} shifts to more aqueous-like values at higher loading levels. The blue-shifted λ_{max} clearly shows that the first $Ru(bpy)_3^{2+}$ ions which enter the membrane occupy sites with high local fluorocarbon chain material activity (and low local water activity).[52] When these sites are occupied the subsequently-loaded $Ru(bpy)_3^{2+}$'s enter sites with higher local water activities; this produces the shift in λ_{max} to more aqueous-like (and less fluorocarbon-like[52]) values.

While the lifetime data obtained from the biexponential decay model (Table I) show evidence for preferential occupancy of one environment over the other, the lifetimes are reversed. The

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results from the biexponential model (Table I) suggest that at low loading the long (aqueous-like) lifetime is preferentially occupied. This is in direct contradiction to the steady-state data which suggest that the nonaqueous or fluorocarbon-like environment is preferentially occupied (Table II). The bottom line is that the bulk of the evidence suggests that the biexponential decay model is not appropriate here. Furthermore, as will be shown below, the dispersed kinetics model provides statistically better fits to the experimental data.

Dispersed Kinetics Model. The data in Tables I and II suggest that more than two chemical microenvironments are present in Nafion; this has been confirmed by a host of other spectroscopic methods.[53-56] Faulkner and Bartolo have recently proposed that a continuous distribution of chemical microenvironments exists, for $Ru(bpy)_3^{2+}$, within poly(styrenesulfonate) (PSS).[57] These authors used the dispersed kinetics model[31] to analyze $Ru(bpy)_3^{2+}$ emission data for PSS. Figure 2 shows that this model can be fitted to the experimental $Ru(bpy)_3^{2+}$ decay data obtained here. Two independently adjustable parameters k, the average decay rate constant and γ, the width of the distribution, were used to obtain these fits. These kinetic parameters, as well as the χ^2 values for the fits, are shown in Table III.

The χ^2 values obtained using the dispersed kinetics model (Table III) are essentially identical, at all loading levels, to the χ^2 values obtained from the biexponential model (Table I). This would seem to suggest that neither model is preferable;

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however, four independently adjustable parameters (Two k's and two B's) were used in the biexponential fit, whereas only two adjustable parameters were used for the dispersed kinetics model. Thus, in addition to the arguments presented above, the principle of "Ockham's Razor"[58] makes the dispersed kinetics model preferable to the biexponential model. More important than the philosophical "Ockham's Razor" argument, the standard deviation for the parameters obtained from the fit to the dispersed kinetics model were always smaller than for the biexponential fit (Table I and III). This provides quantitative statistical evidence that the dispersed kinetics model provides a better fit to the experimental data.

Albery's dispersed kinetics model is a functional mathematical model that can be used to obtain kinetic information. How can this information be translated into a chemical model? A chemical picture can be envisioned in which the clusters of Nafion offer a variety of chemical microenvironments to the $Ru(bpy)_3^{2+}$ ions. These microenvironments arise because different parts of the clusters have different dielectric constants, depending on the amount of water and perfluorocarbon chain material present.

The characteristics of a specific chemical microenvironment can have a significant impact on the $Ru(bpy)_3^{2+}$ decay rate. The lifetime of $Ru(bpy)_3^{2+}$ metal-to-ligand charge transfer (MLCT) excited-state decay is dependent on both radiative and nonradiative modes of deactivation.[28-30] In addition, the excited-

state decay is dependent on thermal activation to, and subsequent decay from, low-lying dd states. These processes are known to be dependent on the chemical microenvironment in which $Ru(bpy)_3^{2+}$ resides.[28-30] Thus, the excited-state lifetime will vary from microenvironment to microenvironment within the membrane.

Recent studies have demonstrated the effects of the properties of the chemical microenvironment on the emission characteristics of $Ru(bpy)_{32+}$. Surridge et al.[59] have observed nonexponential decays for a Ru(II) polypyridyl complex bound to a chlorosulfonated polystyrene film. The observed lifetimes were dependent on the hydrophobicity and structure of the chemical sites within the film. Furthermore, Vining and Meyer[60] have presented electrochemical and spectroelectrochemical evidence for at least three different chemical regions within Nafion films.

The k values obtained from the fits to the dispersed kinetic model can be used to calculate the mean lifetime, τ, values for each $Ru(bpy)_3^{2+}$ loading level. These τ values are shown in Table III. The τ value for the lowest loading level appears to be significantly lower than the other τ's. Applying the standard Q test for rejection of data,[61] we find that at the 99% confidence level, the τ associated with the lowest loading level is significantly less than the τ's obtained at the high loading levels. Furthermore, the average τ value obtained from the higher (0.03 to 0.80%) loading levels (435 ± 8 ns) is identical to the lifetime for $Ru(bpy)_3^{2+}$ in aerated water (434 ns).

The trends in the kinetic parameters obtained from the

dispersed kinetics model (Table III) agree with the trends in the steady-state emission data (Table II). Both data show that an aqueous-like environment is populated at high loading levels whereas a "non-aqueous" environment is preferentially populated at low loading levels. As noted above, this "non-aqueous" environment simply means that the first $Ru(bpy)_3^{2+}$'s which enter the membrane preferentially occupy sites with high local fluorocarbon chain material activities and low water activities; given the known hydrophobicity of $Ru(bpy)_3^{2+}$, this preference for hydrophobic sites is not surprising.[52]

The width of the distribution (γ values in Table III) also follow the trends observed in the τ and λ_{max} values; as the loading level is increased the overall Gaussian distribution is reduced in width. This reduction in width occurs because many of the component lifetimes are similar in the aqueous-like domains and because a relatively smaller number of the fast-decaying species are present. Therefore, at higher loading levels there is a smaller contribution of the ions in the "non-aqueous" sites to the total distribution.

The question which arises, however, is why would a high local fluorocarbon chain material-activity microenvironment yield a diminished lifetime for $Ru(bpy)_3^{2+}$. We believe that part of this diminution in $Ru(bpy)_3^{2+}$ lifetime results from a higher local O_2 activity. It is well known that O_2 is more soluble in fluorocarbon-containing media than in pure water.[62,63] For example, Lee and Rodgers[63] have shown that singlet oxygen is five

times more soluble in the perfluorocarbon region than in the water clusters. Thus, we propose that the "non-aqueous" sites are also sites of high local O_2 activity. Thus, the $Ru(bpy)_3^{2+}$'s which occupy these high fluorocarbon chain material-activity sites have shorter lifetimes due to the higher local quencher concentrations.

The effect of the local O_2 activity on the lifetime of $Ru(bpy)_3^{2+}$ was confirmed by performing luminescence lifetimes studies of $Ru(bpy)_3^{2+}$ in Nafion membranes that have been deaerated (oxygen removed). Figure 3 compares two luminescence decay curves for the same loading level of $Ru(bpy)_3^{2+}$ in aerated and deaerated Nafion membranes. Figure 3 clearly shows that the luminescence decay for the deaerated membrane is longer lived than the luminescence decay in the aerated membrane.

Conclusions

The dispersed kinetics model used here assumes a Gaussian distribution of the logarithm of the decay rate constant. However, other distribution models are possible (e.g., Lorentzian, which generally gives narrower distributions).[40] The distribution model used in the fitting equations could have also been a Gaussian or Lorentzian distribution of rate constants, or lifetimes, or energies of activation, etc. In addition, there is no reason to believe that the "real" lifetime distribution is symmetric. Finally, it is possible that a second distribution component should be included, making the distribution bimodal. At present there is no theoretical model to predict the exact

distribution and therefore the selection of a particular distribution model is made arbitrarily. However, the key question is whether the decay process is best described by discrete lifetimes or a continuous distribution of lifetimes; in the present case a distribution model is appropriate.

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TABLE I. Kinetic and Statistical Parameters Obtained by Fitting
a Biexponential Decay Model to the Experimental $Ru(bpy)_3^{2+}$
Emission Data

$Ru(bpy)_3^{2+}$, % [a]	τ_{short} (%), ns [b]	τ_{long} (%), ns [b]	χ^2 [c]
0.01	42.8 ± 11 (2.75)	442 ± 20 (97.25)	0.993
0.03	43.7 ± 13 (1.81)	475 ± 9 (98.19)	1.237
0.05	127 ± 48 (6.07)	505 ± 12 (93.93)	1.003
0.07	219 ± 53 (16.20)	613 ± 27 (83.80)	1.266
0.10	222 ± 42 (17.87)	633 ± 25 (82.13)	1.389
0.20	201 ± 24 (15.25)	606 ± 15 (84.75)	1.538
0.30	217 ± 27 (16.73)	608 ± 15 (83.27)	1.724
0.50	284 ± 26 (32.34)	758 ± 36 (67.66)	2.051
0.80	259 ± 24 (23.85)	657 ± 18 (76.15)	2.174

[a] Percent of $-SO_3^-$ sites in Nafion occupied by $Ru(bpy)_3^{2+}$.

[b] Error in lifetime value given as one standard deviation. Value
in parenthesis is the percent of that lifetime component to the
total luminescence decay.

[c] Reduced chi square value. See ref. 32.

TABLE II. Dependence of Emission λ_{max} on the $Ru(bpy)_3^{2+}$ Loading Level in Nafion

$Ru(bpy)_3^{2+}$, %[a]	λ_{max}, nm
0.01	593
0.03	597
0.05	599
0.07	600
0.10	600
0.20	602
0.30	601
0.50	602
0.80	603

[a] Percent of $-SO_3^-$ sites in Nafion occupied by $Ru(bpy)_3^{2+}$.

TABLE III. Kinetic and Statistical Parameters Obtained by Fitting the Dispersed Kinetics Model to the Experimental $Ru(bpy)_3^{2+}$ Emission Data

$Ru(bpy)_3^{2+}$, %[a]	$\overline{k} \times 10^6$, s^{-1}	τ, ns	γ	χ^2[b]
0.01	2.639	379 ± 18	1.226	1.003
0.03	2.241	446 ± 8	0.842	1.204
0.05	2.365	423 ± 6	0.882	1.002
0.07	2.264	442 ± 5	0.826	1.262
0.10	2.292	436 ± 4	0.862	1.384
0.20	2.329	429 ± 3	0.894	1.538
0.30	2.306	434 ± 2	0.826	1.718
0.50	2.332	429 ± 2	0.740	2.066
0.80	2.278	439 ± 2	0.735	2.189

[a] Percent of $-SO_3^-$ sites in Nafion occupied by $Ru(bpy)_3^{2+}$.

[b] Reduced chi square value.

Figure 1. Points- Experimental luminescence decay data for Ru(bpy)$_3^{2+}$ from Nafion membrane. Loading levels were (A) 1 - 0.80%, 2 - 0.50%, 3 - 0.30%, 4 - 0.20%; (B) 1 - 0.10%, 2 - 0.07%, 3 - 0.05%, 4 - 0.03%. The solid curves are best fit curves obtained from the biexponential decay model.

Figure 2. Points - Experimental luminescence decay data for Ru(bpy)$_3^{2+}$ from Nafion membrane. Loading levels are (A) 0.80%, (B) 0.10%, (C) 0.03%. The solid curves are best fit curves obtained from the Albery's dispersed kinetics model.

Figure 3. (A) Luminescence decay curves for a deaerated Ru(bpy)$_3^{2+}$ exchanged Nafion membrane. (B) luminescence decay curve for an aerated Nafion membrane.

Fig 1

Fig 2
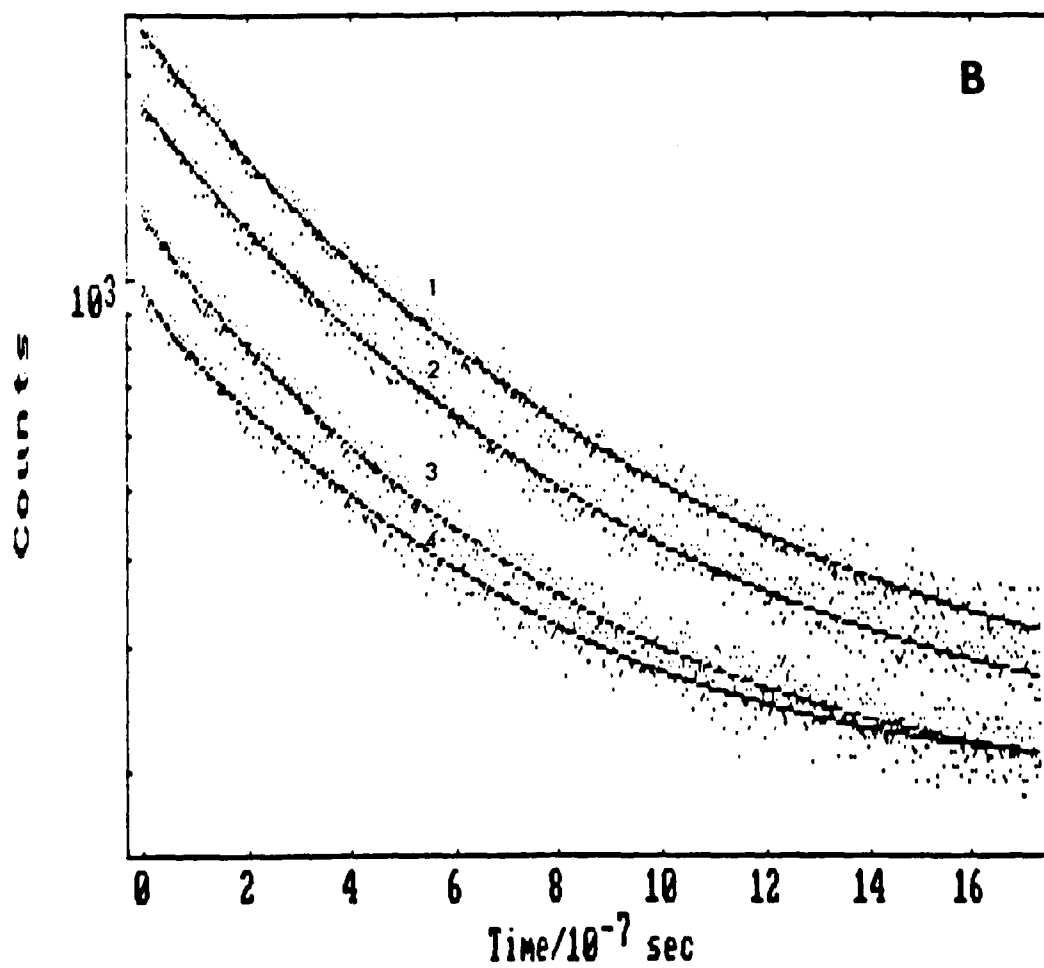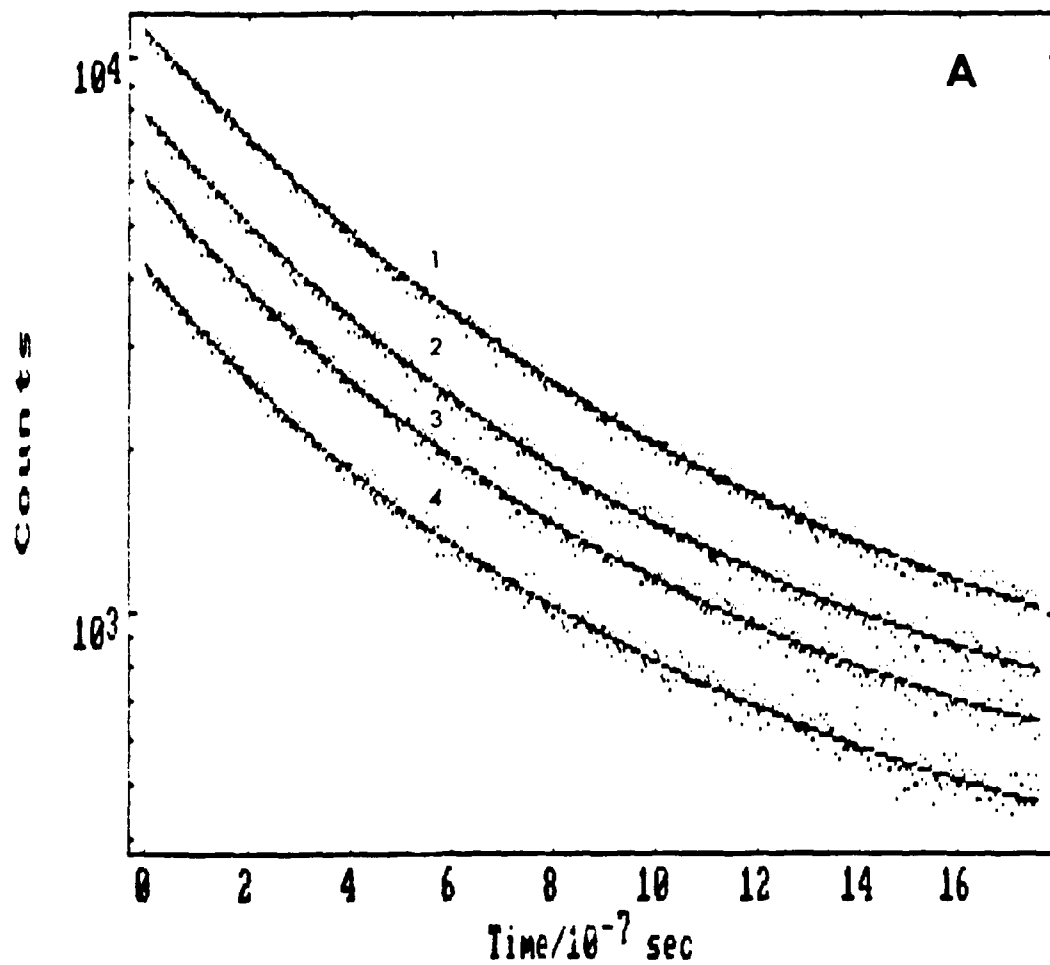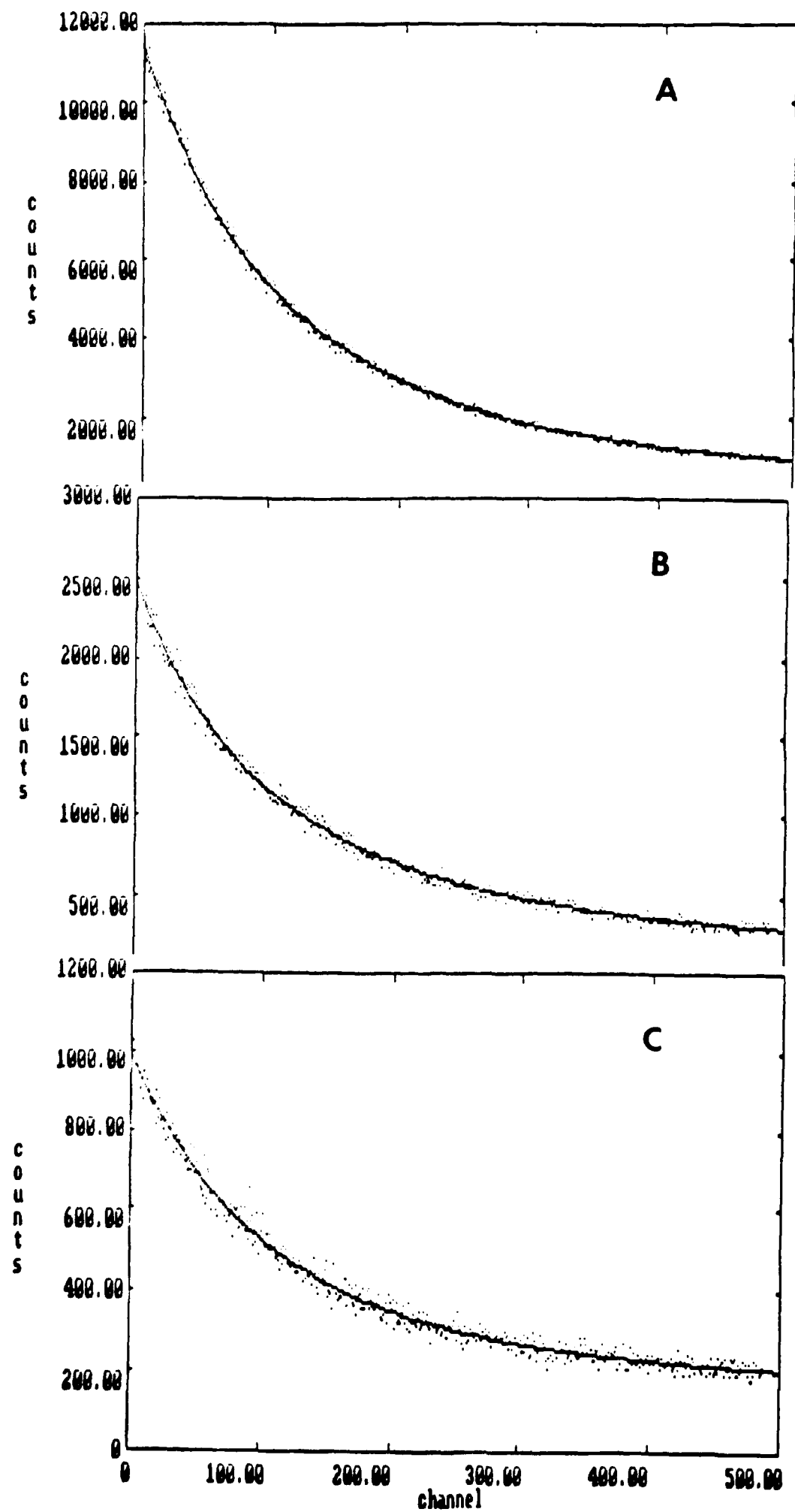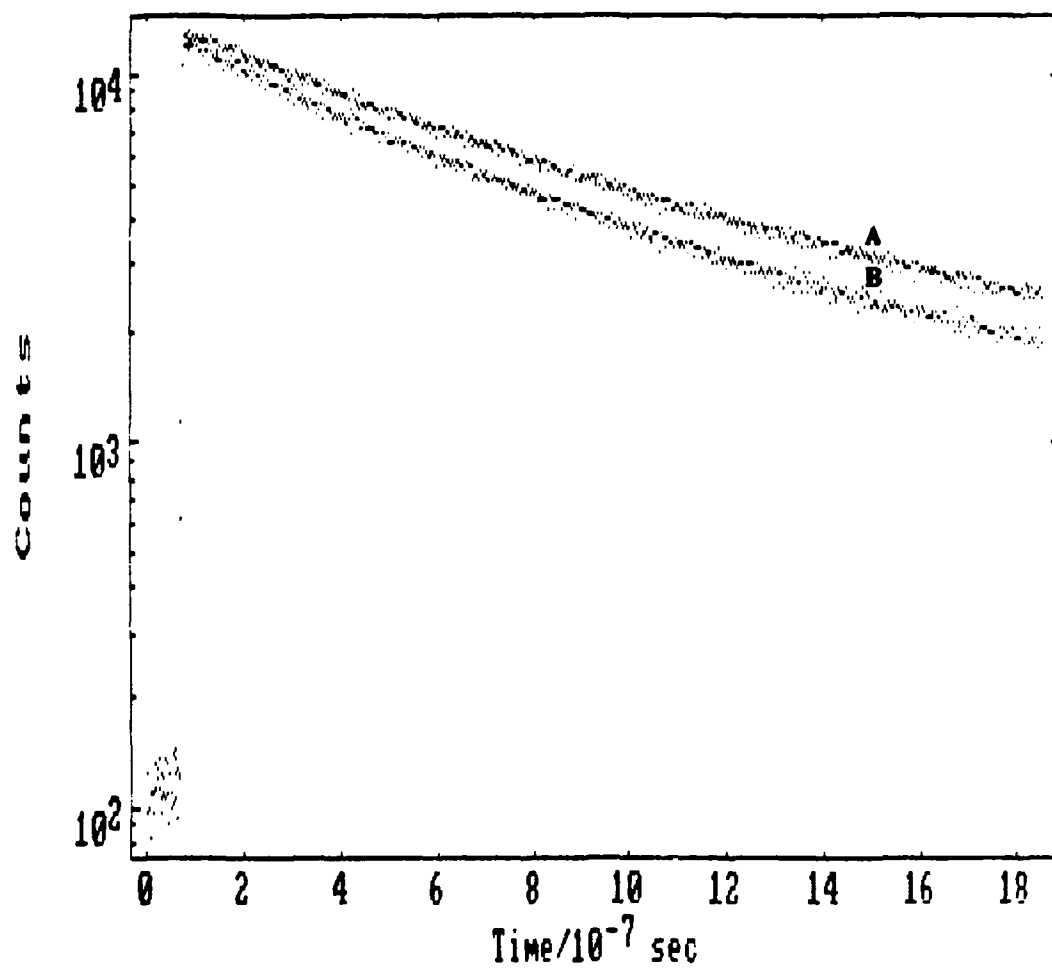
Fig 3