or thereabouts. Because of this concentration effect, presumably related to the dielectric constant of the medium, they assigned that band to an ionic species, not to oxonium ion, however, but erroneously to the hypothetical counterion HF_2^-. On the contrary Huong and Couzi,[33] who extended their measurements to many other solvents, concluded against proton transfer mainly on the basis of electrical conductivity[34] and Raman spectra.[35] Instead, they assigned the bands at about 1850 cm^{-1} to the overtone of the O···H–F bending in molecular complexes. But this also is untenable on the grounds both of intensity (overtones very much stronger than fundamentals) and frequency (large positive anharmonicities). Another objection they invoked had to do with the almost constant frequency of the 1850-cm^{-1} band in widely different organic bases. These objections can be dismissed in terms of proton-transfer complexes, $ROH^+{\cdot}F^-$. The near invariance of the 1850-cm^{-1} frequency (Table I) is a consequence of the strong electrostatic character of the H bond in these complexes. There may also be some partial compensation of the mass effect of the substituent and the strength of the organic base. In fact, the weaker bases, such as acetonitrile and the mercaptans, may be only slightly protonated by HF, hence the lower bending frequency. Besides the OH (or XH) bending there is also the stretching frequency which, generally speaking, varies in the opposite direction.

The elaborate study of Huong and Couzi has yielded some other interesting observations. For instance, in a dilute solution of anhydrous HF (0.015 mol/L) and diethyl ether (0.01 mol/L) in carbon tetrachloride the following characteristic infrared bands appear side by side: (a) 3870 cm^{-1}, of monomeric HF (vs. 3961.64 cm^{-1} in the gas), (b) 3550 cm^{-1} of the dimer $(HF)_2$, (c) 3220 cm^{-1} of the molecular complex $H_2O{\cdot}HF$, and (d) 2700 and 1820 cm^{-1} of $Et_2OH^+{\cdot}F^-$. Significantly, the latter pair of bands is missing in a 1:1 mixture of HF and ether in the same solvent. This confirms that the formation of proton-transfer complexes requires stabilization by solvation. Further evidence to that effect is the recent detection in a solid-argon matrix at 10 K of the $H_3O^+{\cdot}NO_3^-$ complex stabilized by a slight excess (~6%) of water of hydration.[36]

In conclusion, although the above results provide compelling evidence for the new theory, many points remain to be elucidated. Further experimental data are clearly desirable on both the H_2O–HF and D_2O–DF systems. In that connection NMR spectroscopy would be particularly useful. Also desirable are quantum-chemical calculations on the stabilizing effect of solvation similar to those of Newton on the hydrates of H_3O^+[37] and of Morokuma on the $NH_4^+{\cdot}F^-$ complex.[38]

Acknowledgments. The experimental work could be carried out thanks to a grant from the National Research Council of Canada.

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Luminescence Quenching in the Cluster Network of Perfluorosulfonate Membrane[1]

Plato C. Lee and Dan Meisel*

Contribution from the Chemistry Division, Argonne National Laboratory,
Argonne, Illinois 60439.
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Abstract: The effects of the morphology of a perfluorosulfonate membrane (Nafion 120) on the kinetics of quenching of excited states were studied. The charge transfer excited state of $Ru(bpy)_3^{2+}$ was used as a probe and its luminescence quenching by various metal cations and by methylviologen measured. Linear Stern–Volmer behavior was observed when the quenching rate constant was small. When the quenching rate constant approaches the diffusion-controlled limit, deviations from such behavior are observed. Under these conditions, the situation is very similar to nonhomogeneous quenching in micellar systems. A kinetic analysis of the decay curves similar to the one used for the latter systems was then adapted. This analysis can yield detailed information on the microstructure and interactions prevailing in the membrane. The possible implications of such membranes for energy conversion and storage systems are outlined.

Introduction

The photophysical and photochemical processes occurring in a system consisting of a molecule in an excited state and a quencher will often depend not only on the quenchee–quencher pair but also on their immediate environment. Thus, intensive studies have been directed at elucidating the effects of the hydrocarbon–water interface in micellar solutions on such processes.[2-5] In these micellar systems, both the hydrophobic interactions and the interfacial electrostatic interactions are utilized to enhance electron transfer and charge separation in model systems for solar energy conversion and storage. Effects similar to those observed in micellar solutions have been recently observed in ion-exchange resins[6] or polyelectrolytes.[7] In these studies, the thoroughly investigated metal-to-ligand charge transfer state of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) was quenched by metal ions, such as Cu^{2+} or Fe^{3+}, in the presence of Sephadex-SP cation

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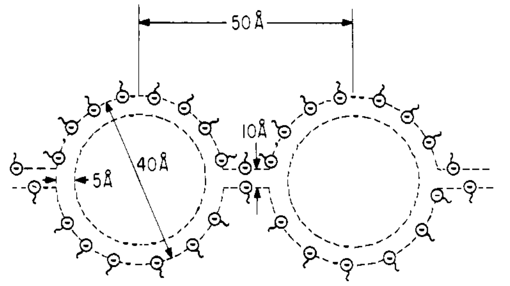
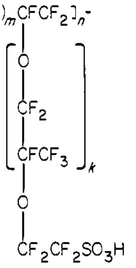


Figure 1. Schematic structure of clustering in Nafion membrane (following ref 10).

exchange beads[6] or poly(vinyl sulfate).[7] In both cases, the apparent increase in the quenching rate was attributed to the high local concentration of the donor excited state, $Ru(bpy)_3^{2+*}$, and the acceptor quenchers in the potential field of the polymer. It was further concluded that the quenching reaction is a dynamic process and not static quenching in these environments. In the present study, we present some results on the quenching of $Ru(bpy)_3^{2+*}$ by various cations in a water-swollen perfluorinated ion exchange membrane.

The membrane of choice is Nafion,[8] which has the structure 1. The exceptional chemical stability of this perfluorinated membrane is bound to be a desirable property in a system where excited states or free radicals abound. Furthermore, the morphology of the membrane may supply a framework for the organizational requirements that an energy conversion system might impose. Small-angle X-ray scattering studies of Yeo and Eisenberg[9] laid the foundation for the detailed model of the morphology of the swollen membrane as developed by Gierke.[10] In this model, hydrated $-SO_3^-$ head groups and counterion clusters (~40 Å in diameter) are interconnected by short channels (~10 Å in diameter) all immersed in the fluorocarbon backbone network. A schematic representation of this model, as adopted from ref 10, is given in Figure 1. The analogy between this biphasic structure and the structure of reversed micelles has been pointed out and was substantiated by ^{23}Na magnetic resonance studies.[11] Further analogy with micellar systems will be presented here.



$$-[(CF_2CF_2)_mCFCF_2]_n-\ \text{with side chain}\ [O-CF_2-CFCF_3]_k-O-CF_2CF_2SO_3H$$

$m = 5-13.5$
$n =$ ca. 1000
$k = 1, 2, 3, \ldots$

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Experimental Section

Materials. Ion-exchange membranes in their H form were Nafion 120 (Du Pont) with nominal capacity of 0.83 mequiv/g and thickness of 0.025 cm. Densities of the swollen membrane were calculated from measurements of weights and dimensions. The IR spectra of the membrane were essentially the same as those reported by Lopez et al.[12] Tris(2,2′-bipyridine)ruthenium(II) chloride ($Ru(bpy)_3Cl_2 \cdot 6H_2O$) (G. F. Smith), nickel sulfate ($NiSO_4 \cdot 6H_2O$) (Mallinckrodt, analytical grade), chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) (J. T. Baker Chemical Co., Baker Analyzed grade), cupric sulfate ($CuSO_4 \cdot 5H_2O$) (Fisher Scientific, Certified A.C.S. grade), europium perchlorate ($Eu(ClO_4)_3 \cdot 6H_2O$) (Research Organic/Inorganic Chemical Corp., 99.9%), and *N,N′*-dimethyl(4,4′-bipyridine) dichloride (methylviologen) (Aldrich) were used without further purification. Triple-distilled water was used throughout this work.

Instrumentation and Procedure. The absorption spectra were taken on a Cary 14 spectrophotometer. Emission spectra and intensities were monitored on a Perkin-Elmer Model MPF-2 fluorescence spectrophotometer, equipped with a 150-W xenon lamp. Emission lifetimes were measured by the single photon counting technique, using a TRW nanosecond spectral source with a pulsed N_2 lamp (5-ns half-width). A combination of cutoff and interference filters was used to isolate the emitted light from that of the excitation source. Kinetic analyses were done on a Sigma V computer, using a deconvolution technique. Whenever emission yields were compared on this instrument, all experimental conditions were kept constant and yields calculated by extrapolation to the middle of the pulse. Small corrections for changes in pulse rate (<5%) were applied. In the case of Cr^{3+} as a quencher, emission intensity was either monitored at 700 nm, where Cr^{3+} does not absorb, or at 592 nm, where some correction for the inner filter effect has to be applied. Both led to similar results. No such difficulties were encountered with the other cations.

All membrane samples (of constant 0.162-g weight) were equilibrated with the well-stirred desired solution for at least 12 h. The amount of uptake of the cations was determined spectrophotometrically from the solution spectrum after equilibration. The "loaded" samples were then sandwiched between two wetted quartz slides which fit tightly into the sample holder and analyzed on either of the instruments described above. For emission spectra and lifetime measurements the samples were positioned at 45° to the axis of the excitation light and emission was detected from the opposite side of the membrane at 45° to the axis of the detector photomultiplier. This configuration was found to reduce greatly the amount of scattered light when compared with direct front-face illumination.

Results and Discussion

I. Absorption and Emission Spectra of the Membrane. Although the chemical structure of the Nafion membrane does not contain any chromophore, the slightly tinted membrane does show two absorption bands, one around 240 nm and the other, weaker band around 320 nm. No change in absorbance could be observed following treatment of the samples with 1 M hot acid for several hours. Excitation of the film in the UV region gives an emission band at 390 nm. The emission spectrum is independent of the excitation wavelength while the excitation spectrum of the 390-nm band clearly reflects the absorption spectrum of the sample. These spectra evidently indicate the presence of some nonexchangeable impurity in the membrane. The amount of this impurity varies from batch to batch as supplied by the manufacturer. All the following measurements were therefore conducted on samples obtained from the same batch. At any rate, since all excitation and emission measurements were carried out at higher wavelengths and since the absorption and emission of the probe molecule, $Ru(bpy)_3^{2+}$, are much stronger than those of the membrane, no effect of this impurity on any of the observations described below is to be expected.

The IR spectra of the dry and acid-treated Nafion show total opacity below 3700 cm^{-1}, as previously reported,[12] indicating that the commercial material is actually in the H form with some residual water. When the membrane is totally exchanged with the divalent or trivalent cations, the IR spectra clearly show the water OH stretch mode at 3500 cm^{-1}, the CF stretch at 2350 cm^{-1}, and the water scissor mode at 1600 cm^{-1} similar to those reported for the Na form.[12]

II. Adsorption of Cations into the Membrane. The inorganic cations Ni^{2+}, Cu^{2+}, Cr^{3+}, and Eu^{3+} were found to quantitatively adsorb into the membrane under the present experimental conditions (~10 mL of $[M^{n+}] = 1-10 \times 10^{-3}$ M). No effect of the membrane on their absorption spectra could be observed. The concentration of M^{n+} in the membrane was calculated from the amount of M^{n+} uptake and the measured dimensions of the swollen membrane. These in turn yield for the extinction coefficients of M^{n+} in the membrane $\epsilon_{810}(Cu^{2+}) = 10$, $\epsilon_{720}(Ni^{2+}) = 2.0$, and $\epsilon_{575}(Cr^{3+}) = 14\ M^{-1}\ cm^{-1}$. These values are very close to those reported for M^{n+} in aqueous solutions, but are appreciably larger than those reported for their hydrated crystalline state.[13] Thomas and co-workers[14] have shown, from ^1H and ^{23}Na magnetic reso-

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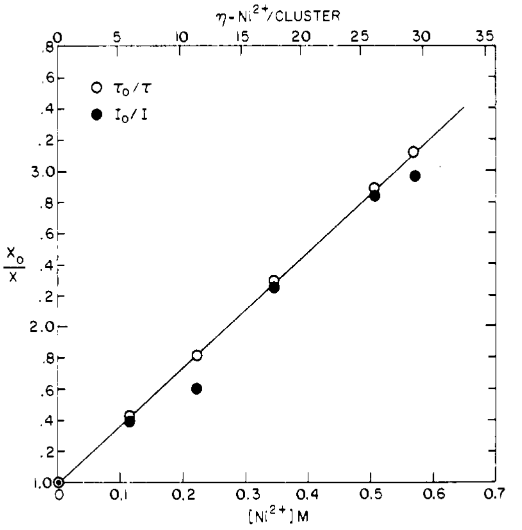

Figure 2. Stern–Volmer plots for quenching of $Ru(bpy)_3^{2+*}$ by Ni^{2+} in Nafion 120 membrane: ●, I_0/I; ○, τ_0/τ. Lower scale; $[Ni^{2+}]$ assuming total volume of membrane is available. Upper scale: number of Ni^{2+} ions per cluster (see text).

nance and absorption and fluorescence studies, that when the radius of water clusters in reversed micelles approaches ca. 23 Å the dipole–dipole and the ion–dipole interactions between the water molecules themselves and between them and the charged head groups are similar to those in bulk water. Since the radius of the water clusters in Nafion is ~21 Å[10] the structure and mobility of the water in these clusters are expected to be similar to those in bulk water and thus the spectroscopic properties of the inorganic cations should resemble those obtained in aqueous solutions.

The absorption spectrum of $Ru(bpy)_3^{2+}$ was also very similar to that in aqueous solution, although it was slightly blue shifted (ca. 3 nm). The quantitative uptake of $Ru(bpy)_3^{2+}$ into the membrane (from ~10 mL of 10^{-4} M solutions) allowed the calculation of its extinction coefficient to be 1.46×10^4 M^{-1} cm^{-1} at λ_{max} 447 nm as compared to 1.42×10^4 M^{-1} cm^{-1} at 450 nm in aqueous solutions. (In all experiments described in this report $[Ru(bpy)_3^{2+}]$ was chosen to yield a final OD in the membrane of 1.0–1.2 at λ_{max}.)

A more pronounced effect of Nafion on the emission spectrum of $Ru(bpy)_3^{2+*}$ could be observed (12-nm blue shift and ca. 10-nm narrowing of the width at half-height as compared to aqueous solutions). Notably this shift is in the opposite direction to the one observed in sodium dodecyl sulfate (SDS) micellar solutions[15] while no effect of condensation along poly(vinyl sulfate) chains on the emission spectrum has been observed.[7b] Similar blue shift and narrowing of the emission spectrum of $Ru(bpy)_3^{2+*}$ were, however, observed in the presence of sodium perfluorooctanoate (SPFO) micelles.[16] It seems, therefore, that, once absorbed into the Nafion membrane, $Ru(bpy)_3^{2+}$ has a molecular environment which differs from that in plain water as well as from that in SDS micelles. However, the environment in the membrane is quite similar to that in SPFO micelles. These similarities indicate, therefore, that the spectral shifts in Nafion stem from the interaction of $Ru(bpy)_3^{2+}$ with the fluorocarbon chain rather than with the sulfonate head groups. The most probable location for the $Ru(bpy)_3^{2+}$ is thus in the Stern layer or the fluorocarbon–head group–water interface which allows electrostatic interaction with the head groups as well as interaction with the fluorocarbon chains.

III. Quenching by M^{n+} in the Nafion Membrane. The quenching of $Ru(bpy)_3^{2+}$ emission by M^{n+} was determined by both steady state emission intensity and lifetime measurements. In the steady-state measurements the dependence of intensity on $[M^{n+}]$ followed a Stern–Volmer behavior. The decay of the emission followed a single exponential rate law. A typical dependence of I_0/I and of τ_0/τ on $[M^{n+}]$ for $M^{n+} = Ni^{2+}$ is shown in Figure 2 (where I_0, τ_0, I, and τ are the intensity and lifetime of the emission in the absence and presence of the quencher, respectively). Both are seen to follow the Stern–Volmer dependence:

Table I. Quenching Rate Constants of $Ru(bpy)_3^{2+*}$ by $M^{n+} = Ni^{2+}, Cu^{2+}, Cr^{3+}$, and Eu^{3+} in Nafion

M^{n+}	K_{SV}- (Nafion)[a]	k_q(Nafion) × 10^{-7}, M^{-1} s^{-1}	k_q(aqueous) × 10^{-7}, M^{-1} s^{-1}
Ni^{2+}	3.7	0.21	0.06[b]
Cu^{2+}	9.8	0.64	0.67,[b] 5.4[c]
Cr^{3+}	7.2	0.43	1.2[d,e]
Eu^{3+}	<0.02	<0.0014	≤0.008[d,f]

[a] Calculated assuming 35.7% of the total volume of swollen membrane is available. Accuracy ±10%. [b] Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* 1976, *98*, 5800, at infinite dilution. [c] Hoselton, M. A.; Lin, C-T.; Schwarz, H. A.; Sutin, N. *ibid.* 1978, *100*, 2383, at 0.5 M H_2SO_4 at 16.9 °C. [d] Lin, C-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *Ibid.* 1976, *98*, 6563. [e] *d* at ionic strength of 1 M. [f] *d* at ionic strength ~2.7 M.

$$I_0/I = 1 + K_{SV}[M^{n+}]; \qquad \tau_0/\tau = 1 + K_{SV}[M^{n+}]$$

where the Stern–Volmer constant $K_{SV} = k_q/k_0$ and k_q and k_0 are the rate constants for the quenched and unquenched reactions. Since the slopes of both curves (Figure 2) are practically identical we can conclude that the quenching reaction is a dynamic process with negligible, if any, contribution from static quenching. Furthermore, initial intensity of emission in the lifetime measurements remained constant throughout the range of $[M^{n+}]$ used here as would be expected for a dynamic quenching process. The values of K_{SV} could be calculated from the slopes of plots similar to those in Figure 2, assuming that 35.7% of the total volume of the swollen membrane is available to $Ru(bpy)_3^{2+}$ and M^{n+}; i.e., the quenching processes take place only in the clusters and channels occupied by water. From the value of k_0 (1.7×10^6 s^{-1} as measured in the membrane) the values of k_q for the different M^{n+} were calculated; these are summarized in Table I and are compared to k_q values in aqueous solutions. Since the quenching reactions involve highly charged cations, we expect an appreciable primary salt effect on their rate constants. The ionic strength inside the cluster can be estimated to be several moles/liter. This may explain the differences between the rate constants measured at low ionic strength in homogeneous solution and those measured in the membrane. As can be seen in Table I, when the rate constants were measured at high ionic strength, similar results were obtained in both media. We therefore believe that the course of the reaction is the same in the membrane and the homogeneous phase.

The number of head groups in a single cluster, η_{max}, can be calculated by using the equation

$$\eta_{max} = \frac{N_0 \rho}{E_w} \frac{d^3}{1 + \Delta V} \tag{1}$$

where $\rho = 1.98$ g/cm³ is the density of the dry polymer, $E_w = 1200$ is its equivalent weight, $d = 47.3$ Å is the Bragg spacing,[10] and $\Delta V = 0.556$ cm³ is the water volume absorbed by 1 cm³ of dry polymer. For the membrane used in the present study $\eta_{max} = 67$ head groups in a cluster and at full capacity $67/n$ M^{n+} ions could be loaded into a cluster.

The concentration of clusters, m (in units of mol/cm³), can then be calculated by using the equation

$$m = \rho / E_w \eta_{max} \tag{2}$$

to be 2.5×10^{-5} mol/cm³. From the total concentration of M^{n+} ions in the membrane we can calculate the average number of M^{n+} ions in a cluster, η, at each $[M^{n+}]$, using $\eta = [M^{n+}]/1000m$. In Figure 2, $[M^{n+}]$ is transformed to this η scale (upper scale).

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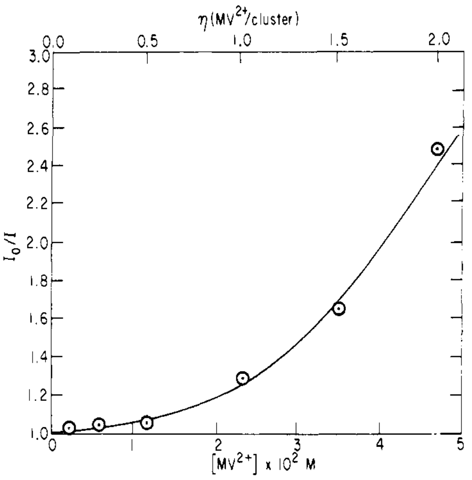

Figure 3. Stern–Volmer plot for quenching of $Ru(bpy)_3^{2+*}$ by MV^{2+} in Nafion 120 membrane. Scales are the same as in Figure 2.

Because of the relatively low values of k_q for the metal cations in Table I, rather high η values had to be used before any quenching could be observed (cf. Figure 2). Under such conditions inhomogeneity effects are not likely to be apparent. In order to check such effects, quenchers of higher k_q have to be investigated (see below).

IV. Inhomogeneity in Quenching by Methylviologen. The rate constant for quenching of $Ru(bpy)_3^{2+}$ by methylviologen dication (MV^{2+}) in homogeneous solutions

$$Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+} \qquad (3)$$

was measured to be $k_3 = 4.5 \times 10^8$ M^{-1} s^{-1}, in close agreement with the value 5×10^8 M^{-1} s^{-1} previously obtained for this reaction.[17] This reaction, although slower than the diffusion-controlled limit, is much faster than the quenching reactions by metal cations previously discussed. The probable inhomogeneity effects of clustering in the membrane were probed, therefore, with this reaction. The positively charged MV^{2+} is quantitatively adsorbed into the Nafion membrane. No appreciable change in the UV absorption spectrum of MV^{2+} on adsorption into the membrane could be detected.

In Figure 3 we show the intensity Stern–Volmer plot for the quenching of $Ru(bpy)_3^{2+*}$ luminescence by MV^{2+} in Nafion. In sharp contrast to the quenching by M^{n+}, this Stern–Volmer plot strongly deviates from the linearity observed in the pseudohomogeneous case. The nonhomogeneous behavior is further evidenced in the nonexponential decay of the luminescence as shown in Figure 4. The decay curves show a rather fast component followed by a slower decay component. The fraction of the excited states that decay in the fast component increases on increasing [MV^{2+}], while the slow component decreases. It can also be seen in Figure 4 that the lifetime corresponding to the slow component is practically the same as that of the unquenched decay.

The appearance of a two-component decay, one of which is of the same rate as the unquenched decay, indicates that the diffusion of the quencher (and quenchee) from one cluster to another is significantly hindered. We thus can assume that during the lifetime of the excited state the quencher ions are confined to a particular cluster which may or may not contain the emitting probe. The quencher ions, however, are free to diffuse inside that cluster in which they happen to reside at the time of excitation and thereby may encounter the excited emitter. This behavior resembles the features observed for the quenching of solubilized excited probes in micellar systems by quenchers confined to the micellar–water interface.[18,19] To rationalize quantitatively the details of this dynamic quenching we therefore adapt the same treatment[18,19] to the present system. In particular, we follow the approach of Rodgers and Wheeler.[19] In view of the size of the cluster and the nonspecific interactions involved, we assume a Poisson distribution of quenchers among the clusters, i.e.,

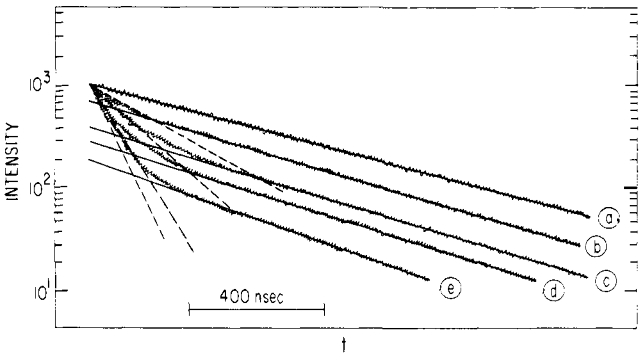

Figure 4. Decay curves for the decay of $Ru(bpy)_3^{2+*}$ in Nafion in the presence of MV^{2+}. [MV^{2+}] for a–e: 0, 0.012, 0.024, 0.036, 0.048 M in the membrane calculated assuming that the total volume is available.

$$P_i = (\eta^i/i!)e^{-\eta}$$

where P_i is the probability that a cluster will contain i quencher ions and η is the average number of quenchers in a cluster as calculated in the previous section. (In view of the low average number of $Ru(bpy)_3^{2+}$ in a cluster, $\eta_{Ru} < 0.1$, the probability of a cluster containing more than one $Ru(bpy)_3^{2+}$ in a cluster is extremely small.) The rate of decay of the excited molecules in clusters containing i quencher ions is then

$$dR_i^*/dt = (k_0 + ik')R_i^*$$

where R_i^* is the concentration of excited states in a cluster that contains i quencher molecules and k' is the pseudo-first-order rate constant (s^{-1}) for the quenching reaction.

The above relation assumes therefore that the rate of quenching is directly proportional to the number of quenchers in the cluster. The time dependence of R_i^* is then given by $(R_i^*)_t = (R_i^*)_{t=0}e^{-(k_0+ik')t} = (R^*)_{t=0}(\eta^i/i!)e^{-\eta}e^{-(k_0+ik')t}$ where R^* is the total concentration of excited states and the subscript t denotes the particular time. It follows therefore that the time dependence of the total concentration of R^* is given by

$$(R^*)_t = (R^*)_{t=0}\sum_{i=0}^{\infty}(e^{-\eta}(\eta^i/i!)e^{-(k_0+ik')t})$$

which after rearrangement will give

$$(R^*)_t = (R^*)_{t=0}e^{-\eta}e^{-k_0t}\sum_{i=0}^{\infty}((\eta e^{-k't})^i/i!)$$

and since the sum of the series above converges to $\exp(\eta_e{}^{-k't})$, one gets

$$(R^*)_t/(R^*)_{t=0} = \exp(\eta e^{-k't} - \eta - k_0t)$$

or in the semilogarithmic form of Figure 4

$$\ln((R^*)_t/(R^*)_{t=0}) = \eta(e^{-k't} - 1) - k_0t \qquad (4)$$

Equation 4 adheres to the features of the kinetics observed in Figure 4. At relatively long times eq 4 reduces to a single exponential decay with the unquenched rate constant:

$$\ln((R^*)_t/(R^*)_{t=0}) = -(\eta + k_0t) \qquad (5)$$

On the other hand, at times close to the time of excitation a single exponential decay, proportional to the average number of quenchers in the clusters, is to be expected:

$$\ln((R^*)_t/(R^*)_{t=0}) = -(\eta k' + k_0)t \qquad (6)$$

This latter equation describes also the situation when k' is very

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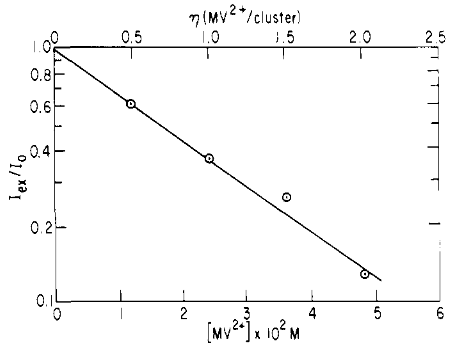

Figure 5. Comparison of the fraction of clusters containing no quencher with the predictions of the cluster-network model. I_{ext}/I_0 were obtained from the extrapolations of Figure 4; solid line is P_0, the probability that a cluster will contain no MV^{2+}, using η calculated from the model.

small, i.e., the case described above for M^{n+}.

The details of the cluster network model as well as the validity of the assumptions leading to eq 4 can now be verified. Extrapolation of the unquenched component to the time of the excitation pulse (solid lines, Figure 4) should yield I_{ext}, and according to eq 5 ln (I_{ext}/I_0) = $-\eta$, where I_0 is the emission intensity in the absence of quencher at t = 0 (curve a, Figure 4). Obviously the ratio $I_{ext}/I_0 = e^{-\eta} = P_0$ should give the probability that a cluster will contain no quencher at that particular average number of quenchers per cluster. In Figure 5 we check this prediction in the light of the parameters developed for the Nafion cluster-network model. The experimentally obtained values for ln (I_{ext}/I_0) are plotted as a function of η calculated as described in the previous section. As can be seen in Figure 5 the agreement between the results from the emission quenching and the predictions of the model is quite satisfactory. Clearly this procedure could be reversed; i.e., emission quenching experiments could provide data for estimates of the average number of quenchers in the aqueous microphase of similar ion exchange membranes which in turn could yield detailed information on the morphology of these structures.

The initial portion of the decay curves (dashed lines, Figure 4) according to eq 6 can yield some information on the quenching rate constant inside the cluster. Thus, in Figure 6, the observed rate constant for the initial decay curve is plotted against the average number of quenchers in a cluster. The slope of the line obtained is equal to $k' = 1.4 \times 10^7$ s^{-1}. This is the pseudo-first-order rate constant for the quenching reaction when one quencher molecule is present in the cluster. Using the same parameters of the cluster model as outlined in the previous section, we can transform this rate constant to the second-order rate constant $k_3 = 3.2 \times 10^8$ M^{-1} s^{-1}, somewhat smaller than but in close agreement with the value obtained in homogeneous solutions.

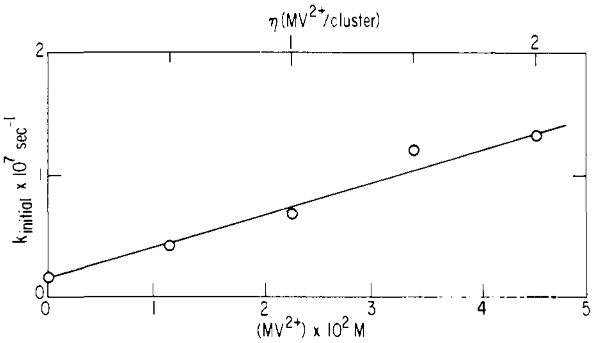

Figure 6. The dependence of the initial pseudo-first-order rate constant for quenching of Ru(bpy)$_3^{2+*}$ by MV^{2+} on η in Nafion.

Conclusions

Structural similarities between the network of the Nafion membrane and micellar systems are shown to affect the kinetics of quenching of excited states in a similar fashion. The microinhomogeneity and the biphasic nature of such systems can cause a rather peculiar kinetic behavior, the study of which may in turn provide further information on the host structure itself. Our own interest in the presently studied system is, however, in conjunction with the search for possible media for energy conversion and storage systems. In that respect, some of the properties of the Nafion membrane are rather attractive. Thus, for example, it is easy to produce metallic colloidal dispersions in the membrane whose aggregate size is determined by the cluster size and concentration of the metal ion used. As previously shown for bulk solutions,[20] these colloids when stabilized by the membrane network can also catalyze hydrogen production from water.[22] For that purpose the perfluorinated backbone provides the necessary stability against hydrogen abstraction from organic colloid stabilizers by hydrogen atoms adsorbed on the colloid surface which may occur with some of these metals.[21] Furthermore, the ion exchange properties of those materials can be utilized to effect charge separation of photoredox products.[22] For this purpose, the slow intercluster diffusion seems to be a hindrance. Methods to overcome such problems are now under investigation.

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