Energy Transfer from Donor to Acceptor Ions in Perfluorosulfonate Membranes[1]

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ABSTRACT: The rare earth metal fluorescence probe technique was applied for elucidation of ion cluster structure in perfluorosulfonate polymer. We studied the fluorescence behavior of the rare metal salts of Nafion, the perfluorinated sulfonate membrane. When Eu^{3+} was bound to Nafion membrane, the fluorescence of Eu^{3+} was greatly enhanced and was observable at Eu^{3+} concentrations as low as 10^{-5} M. This was accounted for by the formation of asymmetric bonding between Eu^{3+} and locally concentrated SO_3^- groups in the Nafion membrane. Nafion Eu^{3+} and UO_2^{2+} salts were prepared. The fluorescence intensities of Eu^{3+} (616 nm) were greatly increased when UO_2^{2+} was present (on excitation of UO_2^{2+}). These results indicated the existence of ion cluster structure in the Nafion membrane in which Eu^{3+} and UO_2^{2+} are close together, facilitating energy transfer between these ions. When Tb^{3+} and Co^{2+} ions were present together in the Nafion membrane, very efficient quenching of the Tb^{3+} fluorescence was observed. This result further supports the existence of ion cluster structure in the Nafion membrane. When Nafion membrane containing Eu^{3+} and UO_2^{2+} was heated, the fluorescence intensity of Eu^{3+} decreased sharply at around 130 °C. This indicated that distances between Eu^{3+} and UO_2^{2+} had increased with increasing temperature due to thermal deformation of the cluster structure of the membrane, decreasing the energy-transfer efficiency from UO_2^{2+} to Eu^{3+}. When Tb^{3+} concentrations were increased in Nafion Na salts, the fluorescence intensities were found to go through a maximum, which was accounted for by concentration quenching. Nafion Tb, showing the concentration quenching, was heated, resulting in an increase in fluorescence intensity of Tb^{3+} at around 130 °C. These results indicated that the structure of the cluster began to deform at around 130 °C and that the average distance between Tb^{3+} ions was increased by about 1.0–1.5 Å. This behavior was reproducible on thermal cycling.

Perfluorosulfonate membranes have found wide use in a variety of applications, many of which involve exchange of cations across membranes that separate solutions of different ionic composition.[2] These membranes show ion selectivity patterns similar to those of cross-linked poly(styrenesulfonate). However, there are several notable differences between the two types of polymers. The differences are partly due to the existence of ionic clusters in the perfluorinated membrane.[3]

A host of techniques, including dielectric relaxation,[4] small-angle X-ray scattering,[5] neutron scattering,[6] electron microscopy,[7] and NMR,[8] IR,[9] and Mössbauer spectroscopy[10,11] have been brought to bear on the elucidation of the ion cluster structure. In the arsenal of spectroscopic techniques, fluorescence measurements offer particular advantages since they are sensitive and can be employed at relatively low concentrations of the luminescent species.[12]

Thus we have been using trivalent lanthanide ions as fluorescent probes to study ion-containing polymers.[13,14]

Experimental Section

Materials. Nafion membrane 117 was obtained from E. I. du Pont de Nemours and Co. (The membrane has an H^+ content of 2.0×10^{-4} mol/g Nafion (1100 equivalent weight).) The thickness is 0.19 mm (7 mil). Europium chloride ($EuCl_3 \cdot 6H_2O$) and terbium chloride ($TbCl_3 \cdot 6H_2O$) were purchased from Ventron. $UO_2(NO_3)_2 \cdot 6H_2O$ was obtained from J. T. Baker Co. These compounds were used without further purification.

Nafion Lanthanide Salts. Various lanthanide-containing membranes were prepared. A typical procedure of the preparations is as follows. A Nafion membrane sheet, 0.20 g, containing about 0.4×10^{-4} mol of ion-exchange sites, was immersed in 15 mL of an aqueous $EuCl_3$ solution (10^{-3} M solution) for several hours at room temperature with stirring. After the sheet was washed thoroughly with deionized water, the film was dried under reduced pressure at 60 °C and kept in a desiccator containing P_2O_5. The total Eu content in the film was determined from the Eu ion remaining in the solution. The Eu concentration was measured by atomic absorption spectroscopy. The fluorescence intensities were recorded on samples taken from different parts of the film, and average values were calculated.

Fluorescence Measurements. A Perkin-Elmer Model MPF-44B fluorescence spectrophotometer was used to measure fluorescence spectra of samples. The film sample was placed in the solid sample holder attached to the instrument, which measured the fluorescence at 90° to the exciting beam. The sample was heated electrically with a Fisher Model 22 proportional temperature control, and the temperature was read from a Fluke 8024A multimeter.

Results and Discussion

Energy transfer occurs from a donor to an acceptor when the fluorescence spectrum of the donor overlaps the absorption spectrum of the acceptor.[15] The emission of UO_2^{2+} ion extends from 480 to about 570 nm. The absorptions of Eu^{3+} observed at room temperature lie within this range. It was suggested that energy transfer from UO_2^{2+} to Eu^{3+} ion involves an electric dipole transition or electron-exchange interaction.[16] In both cases the transfer is short range—of the order of collision diameters.

We have previously shown that UO_2^{2+} transfers energy to Eu^{3+} in ionomers such as methyl methacrylate–methacrylic acid copolymers, resulting in a 20–30-fold increase in the Eu^{3+} fluorescence intensity.[14] This phenomenon was accounted for by the proximity of the two ions in the ionic cluster of the polymer. When Eu^{3+} and UO_2^{2+} were introduced into poly(methacrylic acid), no enhancement in the Eu^{3+} fluorescence intensity was observed. The poly(methacrylic acid) metal salt has no ion clusters, and Eu^{3+} and UO_2^{2+} were expected to be distributed throughout the polymer system so that the distances between Eu^{3+} and UO_2^{2+} were far beyond the energy-transfer range.

In order to apply this fluorescence probe technique to the elucidation of ion cluster formation in the perfluorosulfonate polymer, we studied the rare earth metal salts of Nafion, the perfluorinated sulfonate membrane, registered trademark of E. I. du Pont de Nemours and Co.

When the Nafion membrane (H^+ form) was soaked in Eu^{3+} solution, the exchange between H^+ and Eu^{3+} occurred relatively rapidly. It was observed that the fluorescence of Eu^{3+} was enhanced when Eu^{3+} was bound to the Nafion membrane. The fluorescence was observable at Eu^{3+} concentrations as low as 10^{-5} M. At similar concentrations, fluorescence of the aqueous solution was not detectable. The fluorescence intensity of rare earth metal ions is

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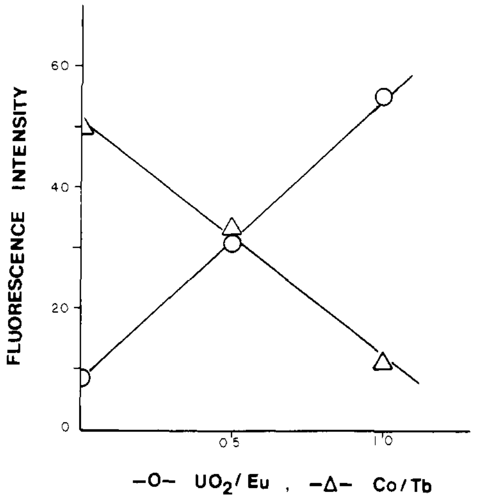

Figure 1. (O) Energy transfer from UO_2^{2+} to Eu^{3+} in Nafion membrane at room temperature: membrane, 0.19 g; 0.4 × 10^{-4} mol of SO_3^-; $[Eu^{3+}] = 0.5 \times 10^{-5}$ mol. Emission at 616 nm, excitation at 320 nm. (Δ) Energy transfer from Tb^{3+} to Co^{2+} in Nafion membrane at room temperature: membrane, 0.27 g; 0.54 × 10^{-4} mol of SO_3^-; $[Tb^{3+}] = 1.5 \times 10^{-5}$ mol. Emission at 545 nm.

known to be sensitive to the environment. Particularly, asymmetric bonding to the ion would greatly enhance the fluorescence intensity.[17] Thus the enhancement of the fluorescence of the Eu^{3+} in the Nafion membrane may be due to the formation of asymmetric bonding between Eu^{3+} and locally concentrated SO_3^- groups. Similar results were also obtained when Tb^{3+} was bound to the Nafion membrane.

Nafion Eu^{3+} and UO_2^{2+} salts were prepared by immersing the membrane in an aqueous solution that contained both Eu^{3+} and UO_2^{2+} ions. The fluorescence intensities of Eu^{3+} at 616 nm were found to be greatly increased when UO_2^{2+} was present, as shown in Figure 1. These results support the existence of ion cluster structure in the Nafion membrane in which Eu^{3+} and UO_2^{2+} are close together, facilitating energy transfer between these ions.

The spectral overlap between Tb^{3+} fluorescence and Co^{2+} absorption is sizeable. We have found previously that when Tb^{3+} and Co^{2+} ions were present in ionomers having ion cluster structure, the energy transfer from Tb^{3+} to Co^{2+} was detected by the quenching of Tb^{3+} fluorescence.[13] Thus when the Tb^{3+} and Co^{2+} ions are present together in the Nafion membrane, very efficient quenching of Tb^{3+} fluorescence is observed, as shown in Figure 1.

Gierke and Hsu investigated the cluster morphology of Nafion alkali salts (1200 EW) and showed that the cluster does exist in the dry polymer and that the diameter is ~19 Å, containing about 26 ion-exchange sites.[18] When the H^+ of Nafion was exchanged mostly with equimolar concentrations of Tb^{3+} and Co^{2+} ions, the fluorescence intensity of Tb^{3+} was found to decrease by 80% (Figure 1). Exact calculation of the distances between these metal ions is a rather complex problem. However, according to Förster,[15] the quenching of fluorescence owing to dipole–dipole radiationless energy transfer is given by

$$\frac{F}{F_0} = \frac{1}{1 + (R_0/R)^6} \tag{1}$$

where R is the distance between donor and acceptor and R_0 is the critical distance for 50% energy transfer, given by

$$R_0^6 = 8.78 \times 10^{-25} K^2 Q n^{-4} J \quad \mathrm{cm}^6 \tag{2}$$

In eq 2, K is the dipole–dipole orientation factor, Q is the donor quantum yield in the absence of energy transfer, n is the refractive index of the intervening medium, and J is the spectral overlap integral, given by

$$J = \int_0^\infty F(\nu)\epsilon(\nu)\nu^{-4}\, d\nu \tag{3}$$

where $F(\nu)$ is the spectral distribution of the donor emission normalized to unity, $\epsilon(\nu)$ is the molar extinction coefficient of the acceptor in units of $cm^{-1}\ M^{-1}$, and ν is the frequency in cm^{-1}. We calculated, according to eq 2, the critical distance R_0 for our donor–acceptor pairs as 19.4 Å,[13] using the refractive index 1.35 (Teflon) as a first approximation. The fluorescence yield in the presence and absence of acceptor, F/F_0, was 0.2. Thus, using eq 1, we calculated the average Tb and Co distance in this case as 15.4 Å. This value is comparable to the cluster diameter obtained by Gierke and Hsu.

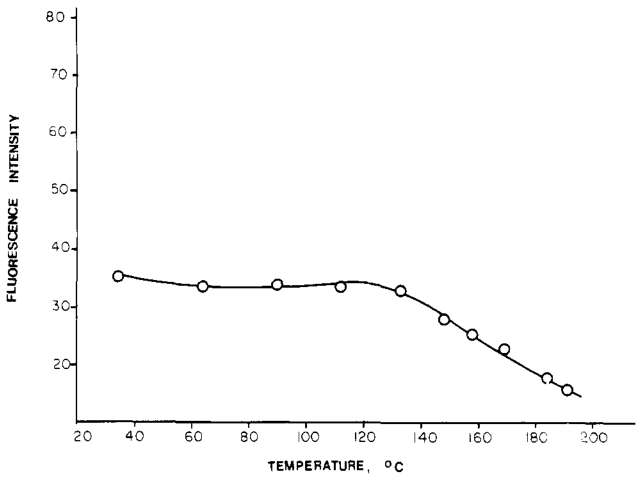

Figure 2. Effect of temperature on the fluorescence intensity of Nafion Eu^{3+} and UO_2^{2+} salts. $[Eu^{3+}] = 0.5 \times 10^{-4}$ mol; $[UO_2^{2+}] = 0.5 \times 10^{-4}$ mol. Emission at 616 nm, excitation at 320 nm.

When samples of Nafion Eu^{3+} (or Tb^{3+}) and UO_2^{2+} salts were heated, the fluorescence intensities of Eu^{3+} (or Tb^{3+}) decreased sharply at around 130 °C (Figure 2). This indicated that the distance between Eu^{3+} and UO_2^{2+} was increased, and as a result the energy-transfer efficiency from UO_2^{2+} to Eu^{3+} ion was decreased.

Nafion Na salt containing a small amount of Tb^{3+} (5.6 × 10^{-6} mol/g of Nafion) was prepared and heated gradually to 200 °C. The fluorescence intensities of Tb^{3+} (at 545 nm) were found to decrease with increasing temperature (Figure 3). This may be due to thermal quenching of Tb^{3+} fluorescence. However, Nafion Na salt containing a higher concentration of Tb^{3+} (4.0 × 10^{-5} mol/g of Nafion) was heated similarly, and the fluorescence was found to increase sharply beginning around 130 °C. This behavior was also reproducible on thermal cycling of the sample, as shown in Figure 4. We have found previously that when Eu^{3+} or Tb^{3+} were introduced into ionomers having ion aggregates, the fluorescence intensities reached a maximum at certain concentrations of these ions and decreased with further increase in these ion concentrations. These results were accounted for by concentration quenching.[13] The Eu^{3+} or Tb^{3+} ions in the aggregate would create locally high ion concentrations whose interactions lead to concentration quenching.

When Nafion Tb^{3+} salt was heated, the data of the increasing fluorescence intensity suggested that the distances between ions were increasing.

Nakazawa and Shionoya[19] studied energy transfer between trivalent rare earth ions in calcium metaphosphate glass and reported the critical transfer distance R_0 for

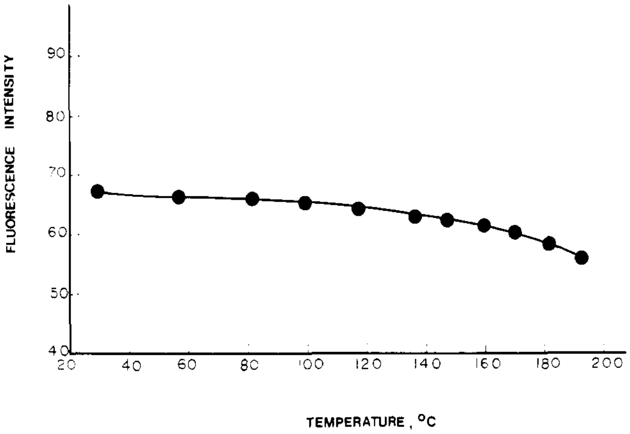

Figure 3. Effect of temperature on the fluorescence intensity of Nafion Tb^{3+} and Na^+ salts. Tb^{3+} content = 5.6×10^{-6} mol/g of Nafion. Emission at 545 nm, excitation at 305 nm.

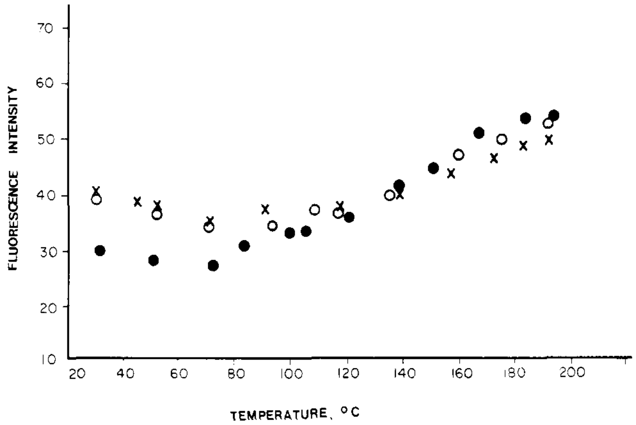

Figure 4. Effect of temperature on the fluorescence intensity of Nafion Tb^{3+} and Na^+ salts. Tb^{3+} content = 4.0×10^{-5} mol/g Nafion.

Tb–Tb as 5.3 Å. R_0 for Tb–Tb in Nafion was estimated as 5.6 Å. The decrease in the fluorescence intensity due to thermal quenching at 130 °C is about 10% (see Figure 3). Thus the increase in the fluorescence intensity due to an increase of Tb–Tb separation would be about 30% at 130 °C (the fluorescence intensity increased from 25 to 55), and this increase corresponds to an increase in the distance between Tb^{3+} ions of ~1.2 Å.

The linear thermal expansion coefficient of Nafion is at most 2×10^{-4} deg^{-1}. Over a 100 °C range, the distance between ions would increase by 2×10^{-2}, 2%, assuming isotropic expansion of the clusters.[20] Thus the increased distance (~1.2 Å) at about 130 °C is greater than that expected from isotropic expansion, and the fluorescence intensity behavior in both Nafion Tb^{3+} and Nafion Eu^{3+}–UO_2^{2+} salts showed some discontinuity at around 130 °C. These results suggest that the cluster structure undergoes a thermal rearrangement that is thermally reversible in the temperature range from 100 to 200 °C (see Figure 4).

Yeo and Eisenberg investigated the dynamic mechanical properties of Nafion alkali salts and found that the mechanical β peak shoulder appeared at around 150 °C in the dry materials and moved to lower temperatures with increasing water content.[4] They suggested that this behavior may be due to the glass transition of a highly polar cluster region in Nafion.

Kawai and co-workers studied the effect of temperature on the structure of cesium perfluorinated sulfonate membranes using small-angle X-ray scattering and reported that intercluster distances in the membrane decreased at around 270 °C.[21] They rationalized the phenomenon by increasing thermodynamic work required for the deformation of a polymer coil to form the cluster. This thermodynamic factor may outweigh the effect of thermal expansion, which tends to make the cluster larger. Eu^{3+} and Tb^{3+} are trivalent ions and may differ in binding properties from the univalent ion Cs^+. We are currently further investigating this difference.

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Registry No. $EuCl_3$, 10025-76-0; $TbCl_3$, 10042-88-3; $UO_2(NO_3)_2$, 10102-06-4; Nafion 117, 66796-30-3.

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