J. Braz. Chem. Soc., Vol. 6, No. 2, 185-189, 1995.
Printed in Brazil.

0103 – 5053 $5.00 + 0.00

Excimer Formation of 1-Pyrenebutyltrimethylammonium Incorporated into Nafion Film

Marcelo H. Gehlen*, Mariselma Ferreira and Silmara F. Buchwiser

Instituto de Química de São Carlos, Universidade de São Paulo, C. P. 780

13560-780 São Carlos - SP, Brazil

Received: November 23, 1994; February 17, 1995

Fluorescência resolvida no tempo e medidas fotoestacionárias são utilizadas para o estudo das propriedades fotofísicas da sonda 1-butiltrimetilamônio pireno incorporado em filmes de nafion. Em sistemas com baixa concentração de sonda, observa-se um decaimento biexponencial que pode ser atribuído à partição da sonda em diferentes microfases da membrana de nafion. Com o aumento da concentração, observa-se a formação de excímero, e a análise da superfície de decaimento revela a presença de três tempos de vida. O valor da constante de velocidade de formação de excímero da ordem de 2.7×10^8 s^{-1} indica uma distribuição não-aleatória da sonda na estrutura da membrana, provavelmente induzida pela solubilização preferencial de mais de uma molécula na região dos microcanais hidrofílicos da estrutura do nafion hidratado.

The photophysical properties of 1-pyrenebutyltrimethylammonium incorporated into swelled nafion-H membrane is investigated by means of time-resolved and stationary fluorescence measurements. Distribution analysis of decay rates at different temperatures indicates that the observed biexponential decay of the probe at very low concentration (0.02 molecules per ionic cluster) where excimer formation is not detected, is a result of probe solubilization in two distinct microenvironments. At a higher concentration of the probe (0.4 molecules per ionic cluster), excimer emission appears, and the decay surface is properly described by a triple exponential decay function. The fast excimer formation process with a rate constant of about 2.7×10^8 s^{-1} indicates a non-random distribution of the probe, but a close localization on increasing its concentration. This could be achieved by the solubilization of more than one probe molecule in the interface of the short channel between water clusters of the nafion.

Keywords: *nafion, excimer, 1-pyrenebutyltrimethylammonium*

Introduction

Nafion membranes have been extensively used as ion-exchange polymer in separation techniques, and as solid electrolytes in fuel cells[1,2]. This class of ionomers has also found application in polymer modified electrodes for chemical analysis[3]. Nafion-H consist of a tetrafluoroethene backbone with a perfluorinated ether side chain and terminal sulphonic acid groups, which are responsible for its ion-exchange capability and swelling properties. Measurements by neutron and light scattering have indicated a characteristic morphology of the hydrated nafion films, in which the charged groups aggregate to form ionic clusters containing a water nanodroplet[4]. The clusters of 40-60 Å diameter are randomly distributed throughout the backbone chain phase, and are eventually interconnected by channels of about 8-10 Å diameter. Thus, the nafion structure resembles a random network of interconnected reverse micelles.

Owing to these characteristics, nafion has been used for immobilization of aromatic compounds and dyes, and the consequent photophysical and photochemical properties of these molecules have been investigated[5-9]. Other probes such as ruthenium tris(2,2'-bipyridine) have also been used to study the nafion structure and solute-matrix interactions[10]. Several dyes and inorganic complexes incorporated into swelled nafion films have luminescence decays which depart from a simple first-order kinetics[10]. The non-exponential decay has been ascribed to static disorder which is related to solubilization of the probe in different microdomains.

Fluorescence quenching of molecular probes including excimer formation of pyrene or pyrene derivatives has been extensively study in microheterogeneous systems like micelles, reverse micelles and microemulsions[11,12]. The

probe confinement in the micelle structure usually enhances the excimer formation due to the concentration effect. In this work the fluorescence decay and excimer formation of 1-pyrenebutyltrimethylammonium bromide are studied by means of time-resolved and stationary fluorescence measurements. This cationic probe has a large affinity with swelled nafion films allowing an easy incorporation into the polymer structure at high concentration. Time-resolved fluorescence spectral data at different concentrations of the probe in nafion film is analyzed by global multiexponential decay as well as with distribution analysis of decay rates. The picture that emerges from this analysis points to the partition of the pyrene cationic probe between two microdomains. At high concentrations of the probe, excimer emission is detected, and a triple exponential decay function describes the decay surface.

Experimental

Nafion-117 membrane in the H form obtained from du-Pont, Inc. was treated and purified according to the method described by Ticianelli *et al.*[13]. The probe, 1-pyrenebutyltrimethylammonium bromide (Molecular Probes), was used as received. The probe was incorporated into swelled nafion membrane by keeping the membrane for several days in a water solution containing the required concentration of the probe. Milli-Q pure water was used to prepare all solutions. After loading, and prior to measurements, the membranes were rinsed with water. The concentration of the probe in the membrane was estimated from absorption measurements, assuming an extinction coefficient similar to that in ethanol (ε (340 nm) = 4.0 x 10^4 cm^{-1} M^{-1}), and considering an optical path of 0.178 mm, equal to the thickness of the membrane. The amount of probe loaded was maintained very low; between 0.5 and 0.02 % of the ionic sites in the nafion membrane were exchanged with the fluorescent probe.

The absorption measurements were performed on a Hitachi U-2000 spectrophotometer. Fluorescence spectra were recorded on a CD-900 Edinburgh spectrofluorimeter. The membrane of appropriate size was placed diagonally in a quartz cuvette (filled with water) in order to be positioned in the cell compartment at 45 to the axis of excitation. Time-resolved spectra (TRES) were recorded on a CD-900 Edinburgh single photon counting spectrometer operating with nanosecond H_2 flash lamp at 30 kHz pulse frequency. Global multiexponential analysis and distribution analysis of the fluorescence decay traces were done with the software provided by Edinburgh Instruments. All measurements were taken with the membrane system in air equilibrated condition.

Results and Discussion

The fluorescence spectra of the 1-pyrenebutyltrimethylammonium cation incorporated into swelled nafion membranes at low and medium concentrations did not show the presence of excimer emission. Only at a high load ratio equivalent to a concentration of 4.22 mM, excimer emission is detected. It appears as a broad, structureless, red-shifted emission band centered at 477 nm (see Fig. 1). To study the dynamic aspect of the fluorescence deactivation and excimer formation, TRES measurements (with decays collected from 376 nm to 530 nm of the emission spectra) are performed for different probe concentrations in nafion membranes. The decay surface was analyzed with global multiexponential decay (2 or 3 exponential components) with linked lifetimes. In this procedure, several fluorescence decays are analyzed simultaneously in order to fit a biexponential or a triple exponential decay function with the lifetime parameters linked along the decay curves. The linking of the lifetime parameter allows a more precise determination. The lifetimes and pre-exponential factors are computed by a global iteratively reweighted reconvolution program based on the Marquardt algorithm for non-linear least squares. The results of the four series of experiments are shown in Table 1.

For samples with probe concentrations less or equal to 2.06 mM, which are equivalent to probe average occupancy per ionic cluster less or equal to 0.19, the decay surfaces were adequately fitted with a biexponential decay function. The average occupancy is estimated by dividing the probe analytical concentration by the cluster concentration. The swelled nafion membrane contains water equivalent to a 18.33 molar analytical concentration[4]. It has in average 10 water molecules per SO_3^- group and 1690 water molecules per cluster[4]. The cluster average concentration is about 10.85 mM[4].

Along the series with different probe concentrations, the longest lifetime (τ_3) is practically constant while the intermediate one (τ_2) decreases with probe concentration.

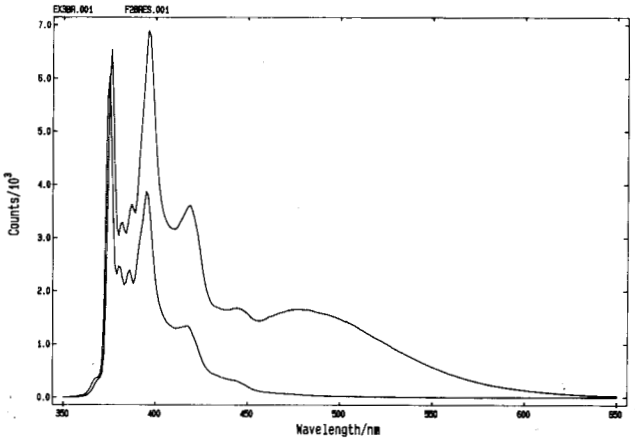

Figure 1. Fluorescence spectra of 1-pyrenebutyltrimethylammonium incorporated into nafion membrane. a) 1.36 mM. b) 4.22 mM ; T = 28 °C. Excitation wavelength, 338 nm.

Table 1. Decay times from simultaneous analysis of TRES data of 1- pyrenebutyltrimethylammonium incorporated into nafion membranes.

Series	[Probe] mM	<n>	τ_1	τ_2	τ_3	χ^2
I	0.24	0.02		36.8 ± 8.9	145.9 ± 3.9	1.170
II	1.36	0.12		55.9 ± 14.9	152.3 ± 6.5	1.212
III	2.06	0.19		63.2 ± 19.4	187.7 ± 5.0	1.145
IV	4.22	0.39	3.7 ± 2.4	69.9 ± 3.6	168.9 ± 14.2	1.058

Global analysis of 5-8 decay curves in the region of 376-530 nm of the probe emission spectra. Excitation at 338 nm. Temperature = 28 °C. <n> is the average number of probe molecules per ionic cluster.

Similar trends of the decay times of Ru tris(2,2' bipyridine) with probe concentrations were observed by Colón and Martin[10]. Even at very low probe occupancy, as in series I where excimer emission is absent, the decay is not monoexponential, suggesting that the probe may be partitioned between two different microdomains. At a very low probe average occupancy, intracluster mutual diffusion to form an excimer complex may be neglected because the probability of finding a micelle cluster containing more than one probe is practically null.

The possibility of partition of the probe between different microdomains giving rise to different lifetimes is investigated by means of the distribution analysis of decay times. Figure 2 shows the distribution of decay times of the sample of series I at different temperatures. At low temperature (5.2 °C), the fluorescence decay is described by a distribution with two well-separated components with mean lifetimes centered at 22.6 ns and 178.6 ns. As the temperature increases, the components approach (27.7 ns and 153.3 ns at 20.2 °C), and finally the distribution becomes bimodal (maximum at 33.2 ns and 118.2 ns at 43.6 °C). The standard deviation of the longest lifetime component decreases as temperature increases. The values obtained in the distribution analysis treatment are summarized in Table 2. These results point out to the presence of two distinct microenvironments in the probe solubilization and this is the main reason for a biexponential decay process at low probe concentration. As temperature increases, the heterogeneity of the probe's sites in nafion membrane becomes smaller. In pure water, the probe has a monoexponential decay with lifetime of 105.7 ns at 28 °C.

However, in the analysis of the temperature dependence of the decay parameters, one has to take into account that decay rate constants may be temperature dependent. Other effects like changes in solvent viscosity with temperature also affect the decay rate constants.

On the other hand, the experiment at the highest probe concentration (series IV in Table 1) corresponding to 0.39 probe molecules per cluster, presents excimer emission, and the decay surface is properly fitted by a triple exponential function. The very short component with a lifetime of 3.7 ns can be ascribed to the excimer formation process. In the monomer emission region it appears as a fast decay transient while in the region of excimer emission it is related to a fast growing with the same decay time but with a negative pre-exponential factor. Figure 3 gives a typical example of monomer and excimer transients obtained at a high concentration of probe in nafion film.

The fast excimer formation process of 1-pyrenebutyltrimethylammonium probe in a concentration equivalent to

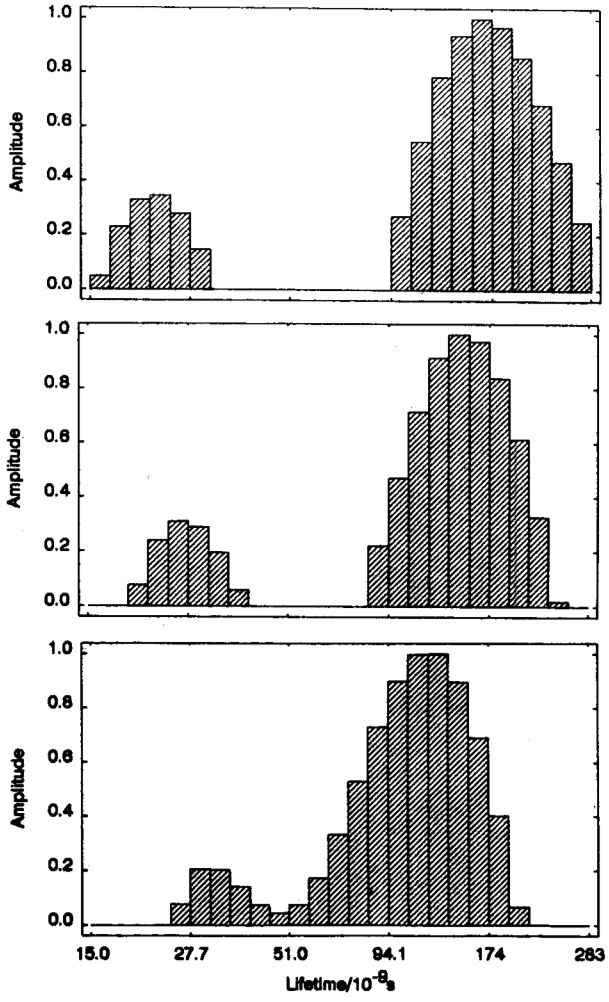

Figure 2. Distribution Analysis at different temperatures. Top to botton, 5,2 ; 20,2 ; and 43,6 °C, (sample series I).

Table 2. Distribution analysis of fluorescence decays at different temperatures (sample series I). λ_{em} = 396 nm.

T (°C)	mean lifetimes ($\tau_{2,3}$) ns	amplitude
5.2	22.6 ± 3.8	0.169
	178.6 ± 51.8	0.831
20.2	27.7 ± 4.5	0.161
	153.3 ± 39.6	0.839
43.6	33.2 ± 4.9	0.093
	118.2 ± 34.8	0.907

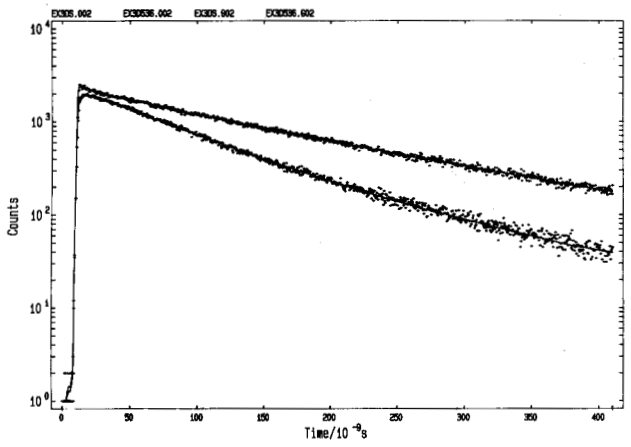

Figure 3. Monomer (λ_{em} = 396 nm) and excimer (λ_{em} = 530 nm) fluorescence decays of sample series IV. Fitting with triple exponential decay function in global analysis (see Table 1 for decay times). T = 28 °C. Excitation wavelength 338 nm.

0.4 probe molecules per cluster in average is unexpected if one considers the dimensions of the reaction domain formed by the interface shell and the water nanodroplet of the nafion ionic cluster. In reverse micelles of about 25 Å radius, which is a size similar to the nafion ionic cluster, the average time for a bimolecular encounter in a diffusion process is about 100 ns[12]. In an ideal distribution of the probe among the clusters, an average occupancy of 0.4 generates a fraction of 6.2% of cluster with more than one probe. This rules out the formation of excimers by free diffusion starting from an initial random distribution of the molecules. A possible close localization of the pyrene probe molecules is the only way to explain the fast excimer formation process. The probe solubilization in neighboring sites would allow a fast excimer formation by a molecular rearrangement. Considering the nafion morphology, the fast excimer formation process could be explained by the solubilization of more than one probe in the interface of the short channels between clusters which have about 8-10 Å diameter. The channel diameter is slightly higher than the critical distance of excimer formation in a diffusion controlled process (7.6 Å) which is very close to the sum of the van der Waals radii of two pyrene molecules (7.1 Å)[14].

In the study of fluorescence properties of a polydiprobe system, a halato-telechelic polymer capped at both ends with N,N,N-trimethyl-3-(1-pyrenyl)-1-propanaminium perchlorate, De Schryver *et al.*[15] observed that intramolecular excimer formation occurs in 7.8 ns, mediated by a dipole-dipole interaction which allows a close localization of the probes.

Conclusions

The photophysical properties of 1-pyrenebutyltrimethylammonium incorporated into swelled nafion membranes were investigated by means of time-resolved and stationary fluorescence measurements. Distribution analysis of the decay rates at different temperatures indicates that the observed biexponential decay of the probe at very low concentration, where excimer formation is not detected, is a result of probe solubilization in two distinct microenvironments. Excimer emission appears at a high concentration of the probe, and the decay surface is properly described by a triple exponential decay function. The observed fast excimer formation rate indicates a close localization of the pyrene probe molecules in nafion. This could be achieved by the solubilization of more than one probe molecule in the interface of the short channel between water clusters.

Acknowledgments

Financial support by CNPq and FAPESP (Brazil) is gratefully acknowledged. M. F. thanks CNPq for an undergraduate fellowship. S. F. B. thanks CAPES for a doctoral fellowship. We thank Prof. Dr. M. G. Neumann for helpful discussions.

References

1. A. Eisenberg and H.L. Yeager, *Perfluorinated Ionomer Membranes* (ACS Symposium Series 180, ACS: Washington, DC 1982).
2. E.A. Ticianelli, J.G. Beery and S. Srinivasan, *J. Appl. Electrochem.* **21**, 597 (1991).
3. H.D. Abruña, *Coord. Chem. Rev.* **86,** 135 (1988).
4. S.J. Sondheimer, N.J. Bunce and C.A. Fyfe, *Macromol. Chem. Phys. Rev.* **C26**, 353 (1986).
5. V. Wintgens and J.C. Scaiano, *Can. J. Chem.* **65,** 2131 (1987).
6. H. Mohan, P.N. Moorthy and R.M. Iyer, *Photochem. Photobiol.* **49,** 395 (1989).
7. H. Mohan and R.M. Iyer, *J. Chem. Soc. Faraday Trans.* **88,** 41 (1992).
8. K.I. Priyadarsini, H. Mohan and J.P. Mittal, *J. Photochem. Photobiol., A: Chem.* **69,** 345 (1993).
9. E. Blatt, W.H.F. Sasse and A.W.H. Mau, *J. Phys. Chem.* **92,** 4151 (1988).
10. J.L. Cólon and C.R. Martin, *Langmuir* **9,** 1066 (1993).

11. K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems* (Academic Press, 1987).
12. M.H. Gehlen and F.C. De Schryver, *Chem. Rev.* **93,** 199 (1993).
13. E.A. Ticianelli, C.R. Derouin and S. Srinivasan, *J. Electroanal. Chem.* **251,** 275 (1988).
14. J.M.G. Martinho and M.A. Winnik, *J. Phys. Chem.* **91,** 3640 (1987).
15. F.C. De Schryver, N. Boens, M. Van der Auweraer, L. Viaene, S. Reekmans, B. Hermans, J. Van Stam, M.H. Gehlen, H. Berghmans, M. Berghmans and M. Ameloot, *Pure Appl. Chem.* **67,** 157 (1995).