Fluorescence Studies of Self-Assembly in Aqueous Solutions of Poly(ethylene-*co*-methacrylic acid) Ionomers

Ewa Szajdzinska-Pietek,*,†,‡ Marian Wolszczak,† Andrzej Plonka,† and Shulamith Schlick*,‡

Contribution from the Institute of Applied Radiation Chemistry, Technical University of Lodz, Wroblewskiego 15, 93-590 Lodz, Poland, and Department of Chemistry, University of Detroit Mercy, Detroit, Michigan 48219-0900

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Abstract: Steady-state and time-resolved fluorescence measurements were performed on aqueous solutions of poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers using pyrene (P) and 1,3-bis(1-pyrenyl) propane (P3P) as the luminophores and the nitroxide radical 5-doxylstearic acid methyl ester (5DSE) as the fluorescence quencher. The ionomers contained 7.5 mol % methacrylic acid and were neutralized (90%) with KOH. The fluorescence spectra of P and P3P together with the electron spin resonance (ESR) spectra of 5DSE indicate that all probes are located in an environment of low polarity and high viscosity that was identified as the hydrophobic micellar core of EMAA aggregates. The local polarity was estimated from the intensity ratio of the third to the first vibronic peaks (I_{III}/I_I) in the fluorescence spectrum of P. The critical micelle concentration (CMC) of the ionomer, CMC = 0.02% (w/w) EMAA, was deduced from the dependence of I_{III}/I_I on the ionomer concentration. The spectroscopic data (ESR and fluorescence) point to the existence, *below* the CMC, of intramolecular (unimeric) micelles, which are in equilibrium with large aggregates *above* the CMC. The microviscosity of the micellar core, η, was estimated to be ≥230 cP at ambient temperature on the basis of the fluorescence spectra of P3P, from a calibration curve of the intensity ratio of the excimer to monomer emissions, I_E/I_M, vs viscosity in 14 nonaqueous solvents of known viscosities. The fluorescence decay of P in EMAA in the presence of 5DSE as the quencher was analyzed with two kinetic models, the Infelta−Tachiya model based on a Poisson distribution of the quencher and the luminophore in the micelles and the general approach of dispersive kinetics that introduced the time-dependent rate coefficient, k_{qm}, for intramicellar quenching. The second model gives a better fit to the experimental data, and the low value of the dispersive parameter, $\alpha = 0.30$ (compared to unity for classical kinetics), indicates a broad distribution of the quenching rate constants. The results obtained in this study add important structural details to the recent models for self-assembly of EMAA ionomers, which were deduced from spin probe ESR spectroscopy and small-angle neutron scattering.

Introduction

Analysis of emission spectra from fluorescent probes has provided important details on the structure, dynamics, and transport in organized assemblies,[1] including the amphiphilic polymers known as ionomers. The ionic groups in the ionomers are typically carboxylic or sulfonic acids, but their number is small, usually <15 mol %, and most ionomers, even when in the salt form, do not dissolve in polar solvents at room temperature. Bulk ionomers have a separated morphology consisting of polar and nonpolar domains; in the presence of polar solvents such as water or alcohols, solvent clusters are formed, which contain the counterions and the ionic headgroups.[2] Fluorescent probes such as metal ions, metal complexes, and polycyclic aromatic hydrocarbons have been examined in ionomers, and the intensity, lifetime, and quenching of their emission have been interpreted in terms of the size and polarity of the solvent clusters depending on the type of solvent and counterion, and the diffusion coefficients of the counterions; the variation of the fluorescence wavelength with temperature has been linked to rearrangements of the solvent cluster.[3−14]

Several fluorescence studies of ionomer membranes have been performed with pyrene (P) and its cationic derivatives as fluorescent probes.[6−9,12−14] The rich vibronic structure in the fluorescence spectrum of pyrene is normally resolved in solutions and depends on the local polarity: the intensity ratio of the third to the first vibronic bands, I_{III}/I_I, is 2 in a saturated perfluorinated solvent, 0.53 in dimethyl sulfoxide, and 0.63 in

* To whom correspondence should be addressed. E-mail: espietek@mitr.p.lodz.pl and schlicks@udmercy.edu, respectively.

† Technical University of Lodz.

‡ University of Detroit Mercy.

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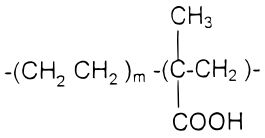
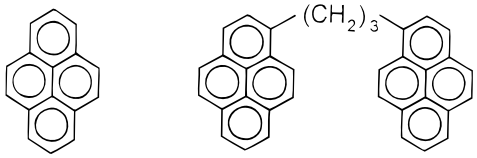
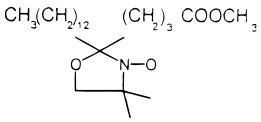
Chart 1. The Ionomer and the Probes



Poly(Ethylene-*co*-Methacrylic Acid) (EMAA) Ionomers



Pyrene (P) 1,3-bis(1-pyrene) propane (P3P)



5-doxylstearic acid methyl ester (5DSE)

water.[15,16] Data for pyrene in perfluorinated ionomers (PFI) containing sulfonic groups such as Nafion have indicated, however, a *range* of I_{III}/I_I values; most values vary between 0.68 and 0.78 in Nafion neutralized by Na^+ swollen by water, suggesting a *hydrophilic* environment,[14] a surprising result for a hydrophobic probe. A different result has been reported when the probe was introduced in Nafion membranes by methanol as carrier: in this case $I_{III}/I_I = 1.6$,[7] a *hydrophobic* environment comparable to that in *n*-hexane. A recent study has reported that the I_{III}/I_I ratio increases for prolonged contact (over several months) of Nafion with solutions of pyrene.[14] These findings seem to suggest that an equilibrium site for the probe is only slowly achieved, and methanol, which is known to *plasticize* the Nafion membranes, is needed to intercalate the probe inside the polymer aggregates.

Our group has recently studied the morphology and local structure in Nafion and related perfluorinated ionomers,[17] and in poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers (Chart 1).[18] At ambient temperature these ionomers are insoluble in water and organic solvents, due to the cross-links formed by crystallization of the perfluorinated chains in Nafion and of the polyethylene component in the EMAA ionomers. For this reason, most fluorescence studies to date have been performed on bulk or solvent-swollen membranes. Dissolution of Nafion and EMAA ionomers in an autoclave has been achieved recently and has enabled the study of the self-assembly of the chains in solutions, and comparison of results obtained for the protiated EMAA system and the perfluorinated ionomers.[18,19]

A recent study of EMAA solutions in D_2O by small-angle neutron scattering (SANS) has suggested the presence of ellipsoidal or cylindrical aggregates with short semiaxes in the range 55−135 Å, depending on the type of the counterion and the degree of neutralization.[19] EMAA solutions have also been studied by the nitroxide spin probe ESR method.[18] The model for self-assembly that has emerged from the analysis of ESR spectra for six spin probes has proposed aggregates that consist of three main regions: a hydrophobic core, an intermediate layer that contains both ionomer chains and some ions, and a hydrophilic region where most of the ions are located.

We have initiated a study of EMAA solutions using pyrene and 1,3-bis(1-pyrenyl) propane (P3P) as fluorescent probes and the nitroxide radical 5-doxylstearic acid methyl ester (5DSE) as the fluorescence quencher, to obtain details on the self-assembly of the chains that prove or refute the model proposed in the ESR spin probe study. The choice of the quencher is based on the ESR study, which has indicated that a similar probe, 10-doxylstearic acid methyl ester (10DSE), is located in the nonpolar core of the aggregates.[20] It was thus expected that the probe and the quencher be in the same region of the aggregates; their limited solubility in water could remove complications in the interpretation of the results. In this study we have determined the critical micellar concentration (CMC) of EMMA in aqueous solution from the fluorescence spectra of pyrene, estimated the local viscosity from the fluorescence spectra of 1,3-bis(1-pyrenyl) propane (P3P) using a series of solvents of known viscosities to build a calibration curve, and evaluated the detailed kinetic model of Infelta and Tachiya[21] and the general approach of dispersive kinetics[22] to rationalizing the results of the time-resolved fluorescence quenching (TRFQ) experiments for the EMAA/P/5DSE system. The results presented below provide support for the presence of a highly nonpolar and viscous core in the multichain aggregates, and for the existence of unimeric micelles.

Dilute solutions of ionomers in organic solvents such as toluene have been studied by fluorescence, and the results have answered important questions on the rate of counterion exchange, the extent of ion pair aggregation, and the diffusion of counterions.[3] To the best of our knowledge the study presented here is the first application of fluorescence methods for the determination of the CMC and the aggregation process in an aqueous solution of an ionomer; the results emphasize the different behavior of ionomeric micelles compared to the small micelles formed from aggregation of monomeric surfactants.[23]

Experimental Section

The starting material, poly(ethylene-*co*-methacrylic acid), had a melt index of 60 g/10 min, $M_n = 20\,500$, and $M_w = 84\,900$; the content of methacrylic acid was 7.5 mol %, so in Chart 1 $m = 12.5$. Aqueous solutions were prepared from EMAA pellets suspended in deionized water in the presence of KOH in an autoclave at 150 °C for ∼30 min. After dissolution, the autoclave was cooled to 25 °C in 90 min while the solution was stirred. The ionomer content of the solution, 25.5% (w/w), was determined from the weight loss of the samples after drying in a vacuum at ∼440 K for 20 min. This aqueous solution was prepared in the laboratories of Du Pont-Mitsui Polychemicals Co. Ltd., Japan. Less concentrated solutions, in the range 1.6−0.0016% (w/w), were prepared by diluting the original solution with Millipore deionized water and stirring overnight. Additional details have been published.[18,25]

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(20) The spin probe 5DSE was used in this study because the spin probe 10DSE used in the ESR study (ref 18 above) was not available commercially.

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Pyrene (P) from Aldrich was purified by column chromatography; 1,3-bis(1-pyrenyl)propane (P3P) from Molecular Probes, 5DSE from Sigma (Chart 1), and hexadecyltrimethylammonium chloride (HTAC) as a 25% (w/w) solution from Aldrich were used as received. Dodecyltrimethylammonium chloride (DTAC) from Eastman Kodak was purified by repeated crystallizations from a mixture of spectral grade ethanol and acetone.

The EMAA solutions were added to vials lined with a pyrene film obtained by evaporating a proper amount of the pyrene stock solution in ethanol with a stream of argon or nitrogen. By magnetic stirring and heating at 50−60 °C, the luminophore was readily dissolved in concentrations of 10^{-6}−10^{-5} M, increasing with EMAA concentration. P3P was introduced (in a concentration of $\sim 10^{-5}$ M) to the EMAA solution as a stock solution in dioxane, and the amount of added dioxane was 1.96% (v/v). The spin probe 5DSE as quencher was dissolved to a known concentration in chloroform, and films were prepared in separate vials, as for pyrene. The 5DSE films were stirred at ∼40 °C with the EMAA/P solution containing 0.5% or 1.6% (w/w) EMAA. Stirring for ≤10 h was occasionally followed by sonication for a few minutes (20 kHz sonicator; total sonication time 0.15 min) to help incorporate the probe in the ionomer aggregates; the maximum 5DSE concentration was 1mM. Prior to the spectroscopic measurements, the samples were deaerated by bubbling with H_2O-saturated argon or nitrogen for 20 min at least.

Steady-state fluorescence spectra were recorded with the Aminco-Bowman spectrofluorimeter and/or with the optical spectrometric multichannel analyzer (OSMA; Princeton Instruments) using excitations at $\lambda_{exc} = 337$ nm or $\lambda_{exc} = 345$ nm. In time-resolved experiments, the samples were kept in 1 cm quartz cuvettes and excited at $\lambda_{exc} = 337$ nm by single light pulses (duration about 300 ps; energy up to 78 μJ) from a nitrogen laser (Laser Photonics, model LN 120C). The cuvette orientation was carefully adjusted in order to reduce the interference with the scattered light from the laser pulse. Appropriate optical filters were used to avoid reflections of the laser light directly onto the monochromator slit. The emitted light through the monochromator (Bausch & Lomb, slit setting 0.1) was detected at $\lambda = 392$ nm or $\lambda = 400$ nm by a Hamamatsu 1P28 or R3896 photomultiplier with ∼2 ns response time. The signal was recorded with a digitizing oscilloscope (Hewlett-Packard 54510 A) and transferred via an HP-IB interface to a personal computer for data storage and analysis. The fluorescence measurements were performed at ambient temperature (∼25 °C).

ESR spectra at the X band of the spin probe 5DSE were measured with a Bruker ECS106 spectrometer equipped with the ESP 3240 data system for acquisition and manipulation, and with the ER4111 VT variable temperature unit. The samples were sealed in capillary tubes made of disposable pipets, and the spectra were recorded with the following parameters: magnetic field modulation, 100 kHz; microwave power, 2 mW; modulation amplitude, 2 G; time constant, 20 ms; conversion time, 41 ms; number of accumulated scans, 10.

Results

Local Polarity and CMC of Aqueous EMAA. The fluorescence spectrum of pyrene in EMAA solutions (Figure 1) exhibits a well-resolved vibronic fine structure. The third and first maxima correspond to the allowed $S_0(\nu{=}1) \leftarrow S_1(\nu{=}0)$ and the forbidden $S_0(\nu{=}0) \leftarrow S_1(\nu{=}0)$ transitions at 385 and 373 nm, respectively. In the range of EMAA concentrations from 1.6% to 0.016% (w/w), the ratio I_{III}/I_I is essentially constant, 1.52 ± 0.05, indicating that the probe resides in EMAA micelles in a region of low polarity. Below a concentration of 0.016% (w/w) EMMA, the intensity ratio sharply decreases and reaches the value of 0.87 at an ionomer concentration of 0.0016% (w/w), as seen in the inset of Figure 1; the decrease

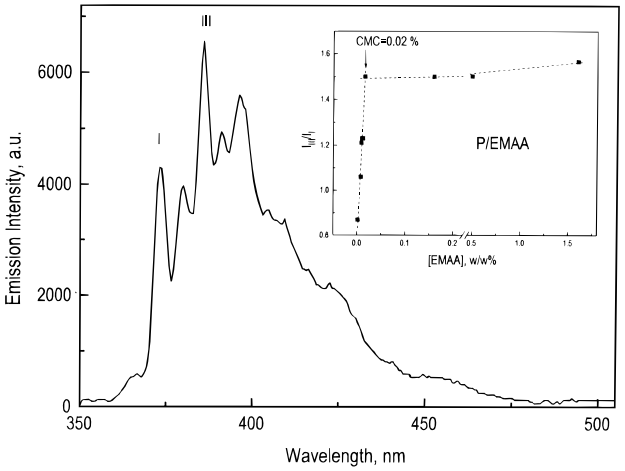

Figure 1. Fluorescence spectrum at ambient temperature of pyrene in an aqueous EMAA solution containing 1.6% (w/w) ionomer. Inset: dependence of the intensity ratio of the third to the first vibronic peaks, I_{III}/I_I, on ionomer concentration.

is assigned to the disappearance of the multichain micellar aggregates. From the intersection of the two linear parts of the I_{III}/I_I vs EMAA concentration plot, we determined the CMC ≈ 0.02% (w/w). This value is significantly lower than that measured for typical surfactants such as sodium dodecyl sulfate (SDS; CMC = 8 mM, or 0.2% (w/v)).[1,15] For the nonionic polymeric surfactants known as Pluronics, which are triblock copolymers poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), $EO_mPO_nEO_m$, the CMC values decrease with increasing temperature; for the polymer with the largest hydrophobic block, P123, the CMC values are in the range 0.03−0.001% (w/v) in the temperature range 25−35 °C.[26] The value deduced for EMAA is therefore in a range that has been measured before in polymeric systems.

Microviscosity at the Probe Site. P3P was chosen as a microviscosity probe. Due to the presence of two pyrenyl moieties in the molecule, this probe forms excimers on excitation, and the process is more efficient in media of low viscosity.[1] We have examined the P3P fluorescence spectra in aqueous EMAA micelles, in 0.1 M aqueous solutions of DTAC and HTAC, and in a number of nonaqueous solvents of known viscosities,[27] and measured the intensity ratio of the excimer to the monomer emission maxima, I_E/I_M. The ratio strongly depends on the presence of oxygen, as the quenching of the excimer band is stronger than that of the monomer. For this reason the aqueous samples were deaerated by bubbling with nitrogen or argon; in the case of the nonaqueous solvents where the oxygen solubility is higher, the samples were deaerated using the freeze−thaw technique. The ratios I_E/I_M were not corrected for changes in the photomultiplier response with the wavelength; such a correction would result in an increase of the I_E/I_M values by a factor of 1.7 and a shift of the excimer maximum absorption to higher wavelength by 20 nm.[28]

A calibration curve for the microviscosity *(*I_E/I_M vs viscosity at 25 °C) is presented in Figure 2. The variation of I_E/I_M with η can be reproduced by eq 1. As seen in the inset of Figure 2,

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(27) The viscosities in cP at 25 °C of the following solvents were used in the calibration curve given in Figure 2: cyclohexanol, ethylene glycol, heptanol, benzyl alcohol, butanol, propanol, dodecane, ethanol, cyclohexane, toluene, methanol, chloroform, heptane, and acetonitrile. Source: *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1995−1996.

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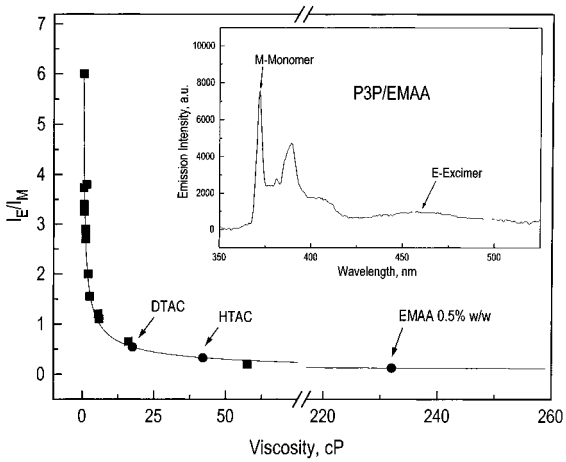


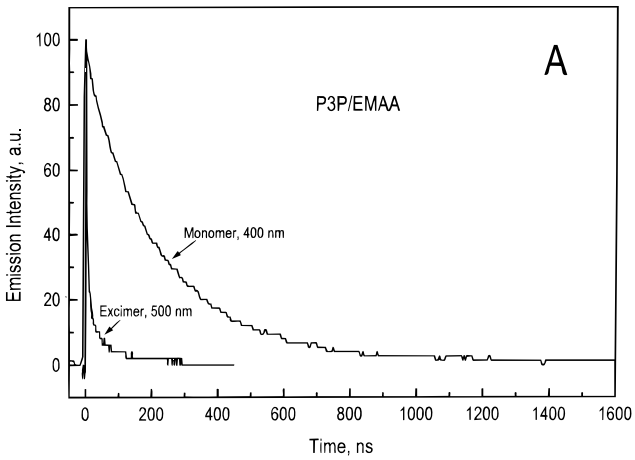
Figure 2. Dependence of the intensity ratio of excimer to monomer fluorescence, I_E/I_M, for P3P on the local viscosity. The full line is the best fit to the viscosity data at 25 °C for 14 organic solvents.[27] Inset: fluorescence spectrum of P3P in aqueous EMAA (0.5% (w/w) ionomer).

$$I_E/I_M = 2.764\eta^{-0.57} \quad (1)$$

emission maxima are observed in the P3P/EMAA system (ionomer concentration 0.5% (w/w)) at $\lambda_M = 373$ nm and $\lambda_E = 480$ nm. For this EMAA micellar solution, the emission from the excimer is weak compared to the intensity of monomer fluorescence ($I_E/I_M = 0.125 \pm 0.015$), and the microviscosity in the P3P environment estimated from the calibration curve is 230 cP ± 25%. Although this value is deduced by extrapolation and has a relatively large margin of error, the viscosity is clearly very large and indicative of a hard core, in agreement with the ESR spectra of 10DSE[18] and 5DSE in EMAA solutions (vide infra). The microviscosity for the EMAA solution is significantly higher than the values for micelles formed from monomeric surfactants that were also deduced from Figure 2: η(DTAC) = 18 cP and η(HTAC) = 42 cP, in agreement with literature results for monomeric surfactants of similar size.[1b] Moreover, the value for DTAC is close to that deduced for SDS micelles, 19 cP, with the same probe.[29]

No growth of the excimer emission (at 500 nm) accompanying the monomer emission (at 400 nm) has been detected, as seen in Figure 3A. In addition, the absorption spectrum of P3P in the EMAA solution is red shifted with respect to that in dioxane (Figure 3B), and the ratio of the absorption intensity of the most intense peak to that of the adjacent minimum at a shorter wavelength is lower for the EMAA solution (2.22) compared to the dioxane solution (2.91). These results suggest[30] that the excimer band in the EMAA system is due, at least in part, to "static excimers" formed from preassociated pyrenyl moieties in the ground state. Therefore, the viscosity estimated for the EMAA solution from the I_E/I_M data is a lower limit value.

ESR of 5DSE (Quencher). Intensity-normalized ESR spectra at 297 K of the 5DSE spin probe are shown in Figure 4. At the examined EMAA concentrations, 0.5% (w/w) and 1.6% (w/w), the spectra consist of two spectral components. The main component (0.98% of the total intensity) is a slow-motional spectrum with an extreme separation $2A'_{zz} = 58.4 \pm 0.3$ G, independent of the EMAA concentration; the line width is markedly larger in the less concentrated EMAA solution. Qualitatively, the slow-motional component is similar to that observed previously for the 10DSE spin probe in EMAA solutions at the same temperature, where the $2A'_{zz}$ value was only slightly higher, 60.3 G.[18] The minor component is the motionally averaged signal whose $m_I = \pm 1$ lines are indicated by arrows.



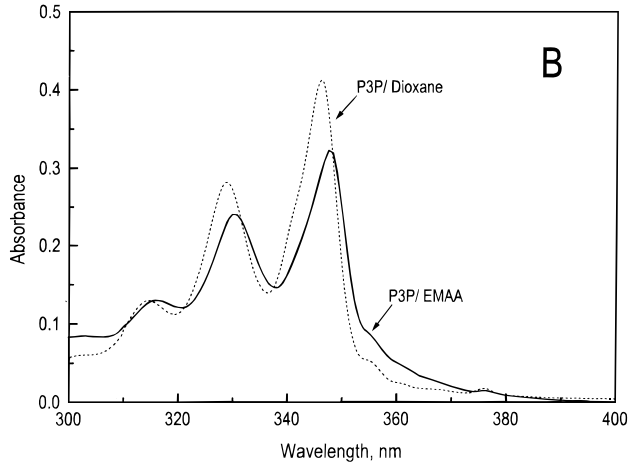


Figure 3. (A) Time-resolved monomer and excimer emissions at ambient temperature of P3P in aqueous EMAA (0.5% (w/w) ionomer). (B) Absorption spectra of P3P in aqueous EMAA (0.5% (w/w) ionomer) and in dioxane solution.

The ESR signal for 5DSE in water, obtained after prolonged stirring (0.48 h) and sonication, is shown in the inset of Figure 4. The motionally averaged signal mentioned above is *not* observed. The weak and broad signal is assigned to undissolved probe particles that could not be removed by centrifugation; indeed, the sample was slightly turbid. This experiment proves that 5DSE is insoluble in water, and that the isotropic triplet detected for 5DSE in the EMAA solutions is due to the association of the spin probe to small aggregates. The extreme separation $2A_{zz}$ for 5DSE at 120 K (in the rigid limit) is 70.0 ± 0.3 G, higher than the corresponding value of 67.6 G for 10DSE, and lower than the value of 71.0 G measured for the spin probe 5-doxylstearic acid (5DSA).[18] The ESR spectra for 5DSE measured in this study suggest a local site where the polarity is *higher* compared to that deduced from spectra of 10DSE and *lower* than that deduced from ESR spectra of 5DSA, in agreement with the polarity profile proposed in the model for the EMAA aggregates.[18]

Kinetics of Fluorescence Quenching in the EMAA/P/5DSE System. In the absence of quencher, the decay of the pyrene fluorescence is first order with rate constants $k_0 = 2.26 \times 10^6$ s^{-1} and $k_0 = 2.15 \times 10^6$ s^{-1} for EMAA concentrations of 0.5% (w/w) and 1.6% (w/w), respectively. In the presence of the quencher the decay curves become nonexponential. Initially,

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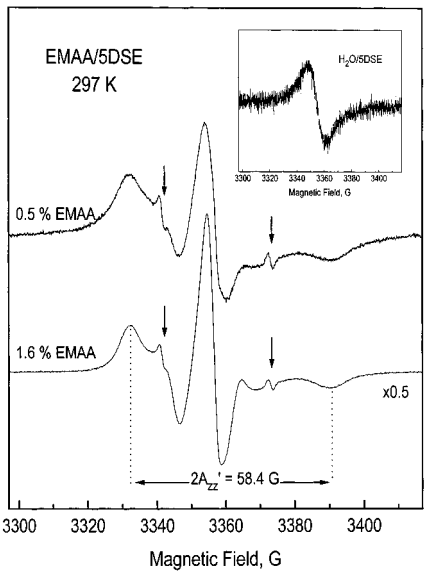

Figure 4. X-band ESR spectra at 297 K for 5DSE in EMAA micellar solutions at the indicated ionomer concentrations. The spectra were normalized to the same total intensity. Vertical arrows indicate the positions of the outermost lines of the motionally averaged component. Also shown is $2A'_{zz}$, the maximum separation for the slow-motional component. Inset: ESR spectrum of aqueous 5DSE at 297 K.

we modeled the fluorescence quenching kinetics on the basis of the Infelta−Tachiya model (eq 2), which assumes monodis-

$$I(\mathrm{t}) = A_1 \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \qquad (2)$$

perse micelles and Poisson statistics for the occupation of micelles by the luminophore and quencher.[21] $A_1 = I(0)$ is the intensity at $t = 0$ (after the laser pulse), and A_2, A_3, and A_4 are parameters.

If the luminophore and quencher do not undergo intermicellar exchange during the lifetime of the excited state, the parameters A_2, A_3, and A_4 are given in eqs 3−5, where τ_0 is the lifetime of

$$A_2 = k_0 = 1/\tau_0 \qquad (3)$$

$$A_3 = \langle n \rangle = [\mathrm{Q}]/[\mathrm{M}] \qquad (4)$$

$$A_4 = k_{\mathrm{qm}} \qquad (5)$$

the excited probe in the absence of the quencher, $\langle n \rangle$ denotes the mean occupancy of micelles M by the quencher Q, k_{qm} (s^{-1}) is the intramicellar quenching rate constant, and the brackets stand for the molar concentrations. Both P and 5DSE are insoluble in water and can be considered immobilized in the micelles. Thus, the micellar aggregation number, N, can be obtained from the A_3 vs [Q] dependence through eq 6.

$$[\mathrm{M}] = ([\mathrm{EMAA}] - \mathrm{CMC})/N \qquad (6)$$

In Figure 5A we present the calculated decay curve of EMAA (0.5% (w/w))/P/5DSE based on eq 1. The agreement is satisfactory, especially if the initial few points corresponding to the fast decay are excluded; similar results were obtained for EMAA (1.6% (w/w))/P/5DSE. However, the resulting parameters lead to an aggregation number of 10 and 20 carboxylic groups per micelle, respectively, for EMAA concentrations of 0.5 and 1.6% w/w, while one polymeric chain contains on average 190 methacrylic acid units. The aggregation number deduced from SANS experiments is 44 chains.[19] We conclude that this approach is not valid for the EMAA system,

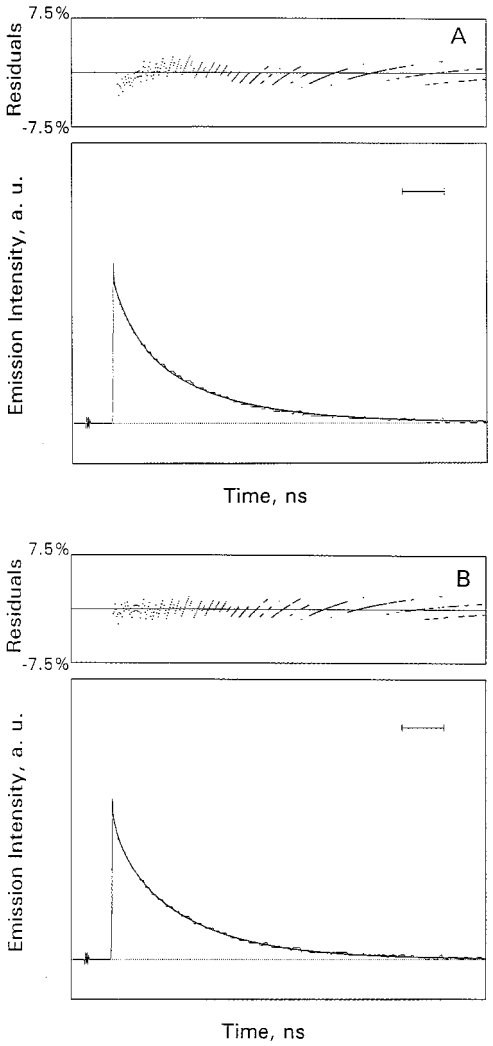

Figure 5. Fitting of the time-resolved fluorescence quenching data for the EMAA (0.5% (w/w))/P/5DSE (0.46 mM) system by the Infelta−Tachiya equation ($A_3 = 0.563$, $A_4 = 4.79 \times 10^6\ \mathrm{s}^{-1}$) in (A), and by the dispersive kinetics approach ($\alpha = 0.3$, $\tau_0 = 1389$ ns) in (B). The smooth calculated curves are superimposed on the experimental data. The corresponding residuals, in percent of the maximum signal intensity, are shown for the calculated curves. The scale bar represents 200 ns.

possibly because the model is based on classical assumptions of kinetics that do not take into account the changes in reactivity for species confined in a highly viscous environment.

We have thus used an alternative approach, the method of dispersive kinetics developed by Plonka with a time-dependent rate coefficient for the pseudo-first-order process of intramicellar quenching[22] where B and α are parameters: $0 < \alpha \leq 1$

$$k_{\mathrm{qm}}(t) = Bt^{\alpha-1} \qquad (7)$$

characterizes the distribution width for the reaction lifetimes, and B is related to the effective lifetime τ_0, as in eq 8. For this model, the observed fluorescence decay curves are described by eq 9.

$$\tau_0 = (\alpha/B)^{1/\alpha} \qquad (8)$$

$$I(t) = I(0) \exp\{-k_0 t - (t/\tau_0)^{\alpha}\} \qquad (9)$$

The decay calculated from eq 9 is in excellent agreement with the experimental decay, as seen in Figure 5B. The best

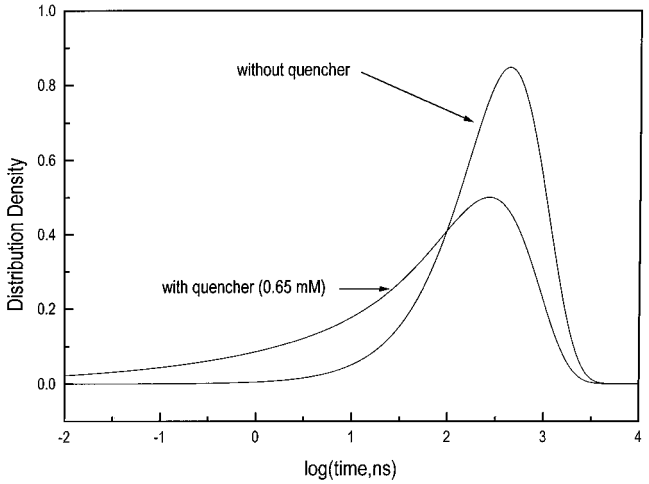

Figure 6. Density distribution functions of the logarithm of the lifetimes for the spontaneous decay of excited P and for intramicellar quenching by 5DSE ($\alpha = 0.3$) in EMAA solutions containing 0.5% (w/w) ionomer.

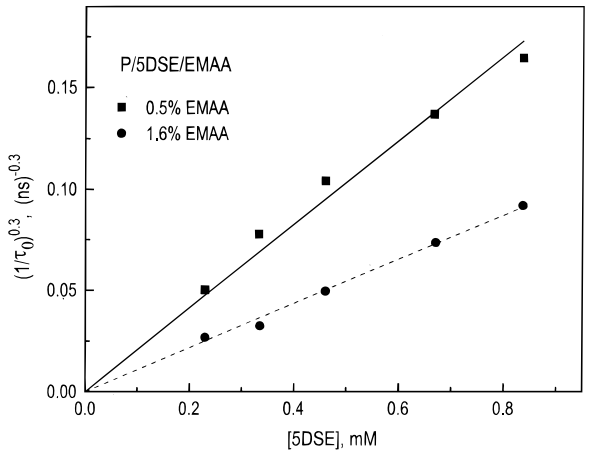

Figure 7. Dependence of $(1/\tau_0)^{\alpha}$ (for $\alpha = 0.3$) on the concentration of 5DSE in EMAA solutions containing 0.5% (■) and 1.6% (●) (w/w) ionomer.

fit is obtained with $\alpha = 0.30 \pm 0.05$, independent of the quencher concentration (up to 0.84 mM) and EMAA concentration (0.5% (w/w) or 1.6% (w/w)). The low value of the dispersion parameter indicates a broad distribution of lifetimes for the intramicellar quenching process. This effect is illustrated in Figure 6, where the density distribution of the logarithms of the lifetime for $\alpha = 0.3$ and $\alpha = 1.0$ are compared. The case of $\alpha = 1.0$ corresponds to the limit of classical kinetics, which is observed in the absence of the quencher. The "dispersive" term in eq 9 can be written as in eq 10, where $k = (s^{-\alpha}M^{-1})$ is

$$(1/\tau_0)^{\alpha} = k'[Q] \qquad (10)$$

a parameter characterizing the bimolecular intramicellar quenching process. It should be stressed that this parameter is related to the *bulk* quencher concentration, not to that in the micellar phase. As seen in Figure 7, the dependence of $(1/\tau_0)^{\alpha}$ on the quencher concentration is linear. From the slope of the straight lines, the values $k' = 1.04 \times 10^5$ M^{-1} $s^{-0.3}$ and $k' = 0.55 \times 10^5$ M^{-1} $s^{-0.3}$ were determined for EMAA contents of 0.5% (w/w) and 1.6% (w/w), respectively.

Discussion

In this section we will define the solubilization site for the fluorescent probes and quencher in the large multichain micellar aggregates, present evidence for the existence of a small amount of unimeric micelles in aqueous solutions of EMAA ionomers at low ionomer concentrations, and consider the significance of the results deduced from the application of the dispersive kinetics model.

Sites of Fluorescent Probes and Quencher. The fluorescence data clearly indicate that in micellar EMAA solutions above the CMC (~0.02% (w/w)), P and P3P reside in a microenvironment of low polarity and high viscosity ($\eta \geq 230$ cP), which we identify as the hydrophobic core of the EMAA aggregates. The observed value of I_{III}/I_I for P (1.52) is significantly higher than that measured in surfactant micelles.[15,23]

The highly anisotropic ESR spectrum observed for 5DSE in EMAA solutions suggests that the quencher is also located in the micellar core. Because the core is highly viscous, only *slow* tumbling of the nitroxide group of the spin probe is possible. This location is consistent with the conclusions of the detailed ESR study of EMAA aqueous solutions and swollen membranes, on the basis of ESR spectra of 5DSA and 10-doxylstearic derivatives in the form of acid (10DSA) and methyl ester (10DSE).[18] Analysis of the temperature dependence of the ESR spectra has indicated that the carboxylic groups of *n*DSA probes are anchored at the surface region of the EMAA micelles, and the nitroxide groups are immersed in the intermediate layer, the nitroxide in 10DSA deeper than in 5DSA. The more hydrophobic 10DSE spin probe penetrates still deeper into the micelles: its carboxylic group is located at the interface between the intermediate layer and the hydrophobic core, while the nitroxide group is buried inside the core. We anticipate a similar location for 5DSE, with the nitroxide group closer to the interface in comparison to 10DSE.

Evidence for the Presence of Unimeric Micelles. At an EMAA concentration 10 times lower than the CMC, the observed intensity ratio of the vibronic bands ($I_{III}/I_I = 0.87$) is higher than that observed in water ($I_{III}/I_I = 0.63$), and close to that in SDS *above* the CMC ($I_{III}/I_I = 0.9$).[15] This finding suggests that even below the CMC pyrene is bound to EMAA chains, which form unimeric micelles by *intra*molecular aggregation. The small contribution of a three-line signal in the ESR spectrum of 5DSE was assigned to the spin probes bound to the unimeric micelles; the signal cannot be due to the free probe in the aqueous phase, since 5DSE is insoluble in water, as seen in the inset of Figure 4. The unimeric aggregates are expected to have an internal molecular packing looser than the larger aggregates, and because they are small, the rotation of the aggregate as a whole may be possible on the time scale of the ESR experiment. Consequently, the 5DSE signal becomes motionally averaged. Thus, the ESR spectra of 5DSE give additional support to the conclusion derived from the fluorescence spectra of pyrene that unimeric micelles are formed in EMAA solutions; above the CMC these micelles remain in equilibrium with the large aggregates.

The presence of unimeric micelles has also been proposed in the previous spin probe ESR studies of both EMAA and Nafion solutions.[17,18] These studies have also shown that the relative intensity of the isotropic triplet is small for polymer concentration above 0.4% (w/w) ionomer but measurable for lower concentrations, in the range measured in the present study. The study of the salt effect on ionomer chain aggregation is currently underway in our laboratory,[33] and unpublished light scattering results for aqueous EMAA solutions, which have

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(32) Chu, B.; Zhou, Z. In *Nonionic Surfactants*; Nace, V. M., Ed.; Marcel Dekker: New York, 1996; Chapter 3.
(33) Unpublished data from the Detroit laboratory.

indicated the presence of a bimodal distribution of aggregate size,[31] provide additional support for the presence of the small (unimeric) micelles. In the case of the Pluronic copolymers, plots of the surface tension as a function of polymer concentration show two breaks.[32] The break at the higher polymer content is usually taken as the CMC and as an indication of a transition from unimeric micelles to the larger multichain micelles. The second break observed at much lower polymer contents has been interpreted as a transition between unimeric micelles and single chains solvated by water. Because solvated EMAA chains are not expected to be stable in aqueous systems, it is reasonable to assign the drop in the I_{III}/I_I ratio (inset of Figure 1) to the CMC, and no additional break is expected.

Dispersive Kinetics Model for Ionomer Solutions. The Infelta−Tachiya model is not appropriate for the EMAA system, especially in view of the small aggregation number (10−20 carboxylic groups per micelle) deduced from the model. Low values of the aggregation number were also predicted by this model for HTAC micelles studied with pyrenesulfonic acid (PSA) and pyrenebutyric acid (PBA) as luminophores and *n*DSE derivatives as quenchers; these results are in marked contrast to those for the P/*n*DSE luminophore/quencher pair, which have indicated an aggregation number of $N = 114$ for 0.1 M HTAC, in agreement with other methods. The failure of the Infelta−Tachiya model in the case of PSA/*n*DSE and PBA/*n*DSE systems has been related to the restricted diffusion of luminophore and quencher inside the micelles.[23] A similar explanation can be adopted for the present results. For the 5DSE location proposed above, it is expected that the radial diffusion of the quenching moiety inside the EMAA micellar core be limited. On the other hand, pyrene molecules are most likely distributed evenly in the entire core, but due to the high microviscosity, not all are able to diffuse to the quencher during the lifetime of the excited state. In this case the Infelta−Tachiya model fails as it assumes that the rate of intramicellar quenching is proportional to the number of quencher molecules in the micelle derived from the Poisson distribution for an average occupancy of micelles by the quencher (eq 4).

The picture that provides the rationale for the use of eq 7 for the intramicellar quenching rate constant is as follows. During reaction, the distribution of the reactivities of reactants in condensed media is disturbed, and proximal reactants have a higher probability of reaction. The extent of disturbance depends on the ratio of the rates of reaction to the rate of internal rearrangement in the system; diffusional mixing restores the initial distribution of reactivities. In highly viscous self-assembled systems, the rate of chemical reactions greatly exceeds the rate of internal rearrangements; as a result, the initial reactivity distribution is not preserved during the reaction, and the reaction rate constant becomes time dependent.[22,34]

The parameter k' characterizing the rate of the bimolecular intramiceller process was evaluated from data for different quencher concentrations. As seen in Figure 7, k' decreases by a factor of 2 with a 3-fold increase of ionomer concentration. This result can be rationalized in the following way: 5DSE is anchored by its carboxylic group at the interface of the hydrophobic core and the intermediate layer; a 3-fold increase in volume of the micellar phase corresponds to a 2-fold increase of the core surface, and thus to a 2-fold decrease of the surface concentration of 5DSE. This finding suggests that micelles grow as more EMAA is added to the system. The observed broader ESR lines in 0.5% EMAA solution, in comparison to 1.6% EMAA solution (Figure 4), are in agreement with this conclusion. For a given total quencher concentration, it is expected that the local quencher concentration be higher in small aggregates than in large aggregates, and that spin−spin interactions leading to the line broadening be more important in the former case.

The proposed growth of the EMAA aggregates with increasing EMAA concentration is, however, not in agreement with the SANS experiments, which have indicated that the shape and dimension of the aggregates were independent of EMAA concentration in the range 0.1−25% (w/w). Further ESR and fluorescence quenching experiments with other probes are in progress, to explain the present controversy.

Conclusions

The intensity ratio of the third to the first vibronic bands, I_{III}/I_I, in the fluorescence spectrum of pyrene in aqueous EMAA solutions indicates that the large ionomer aggregates have a highly nonpolar core, comparable in polarity to the environment in *n*-hexane. The microviscosity at the probe site is very high, $\eta \geq 230$ cP, as estimated from the intensity ratio of the excimer to the monomer fluorescence in the spectrum of 1,3-bis(1-pyrenyl)propane (P3P) as the luminophore.

The critical micelle concentration of EMAA chains, 0.02% (w/w), was deduced from the variation of I_{III}/I_I with ionomer concentration in the range 0.0016−1.6% (w/w). Even at the lowest ionomer concentration, however, the ratio I_{III}/I_I is higher than that measured in water, and similar to that in sodium dodecyl sulfate *above* the CMC; this result is taken as evidence for the existence, below the CMC, of unimeric micelles formed by *intra*molecular aggregation.

ESR spectra of the nitroxide spin probe 5-doxylstearic acid methyl ester (5DSE) provided additional evidence for the existence of unimeric micelles and for the existence of the highly viscous micellar core deduced for the multichain aggregates from the fluorescence measurements.

The nonexponential decay of the pyrene fluorescence in the presence of 5DSE as the quencher was well reproduced by the dispersive kinetics approach, and the low value of the dispersive parameter, $\alpha = 0.30$, indicates a broad distribution of lifetimes for the process.

This study emphasized the different behavior of *polymeric* amphiphiles compared to that of *monomeric* surfactants in four important ways: the lower value of the CMC, the higher viscosity of the micellar core, the slower rotational motion, and the broad distribution of lifetimes for fluorescence quenching.

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