

# Binding of (Arylmethyl)ammonium Cations by Polyelectrolytes. Evidence for Hydrophobic and Electrostatic Interactions

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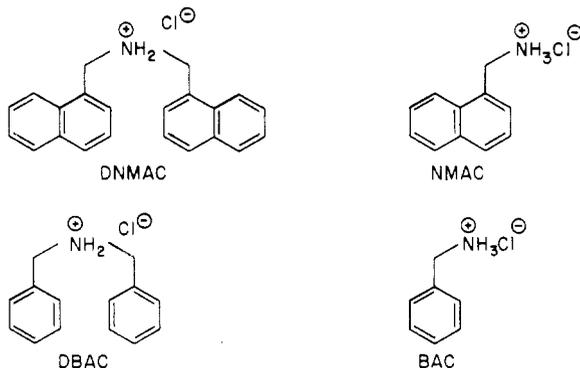
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The associative interactions of several cationic probes, i.e., bis( $\alpha$ -naphthylmethyl)ammonium chloride (DNMAC), ( $\alpha$ -naphthylmethyl)ammonium chloride (NMAC), dibenzylammonium chloride (DBAC), and (benzyl)ammonium chloride (BAC), with anionic polyelectrolytes, i.e., sodium poly(ethylenesulfonate) (PES), sodium poly(styrenesulfonate) (PSS), and sodium poly(2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS), and with a neutral polymer, poly(ethylene oxide) (PEO), have been investigated by fluorescence techniques. Evidence is presented that the probe conformation in both the ground and the excited singlet states depends on the type of interaction (hydrophobic or electrostatic) that dominates in determining the binding strength. For example, the predominately hydrophobic binding of DNMAC and PEO in aqueous solution produces a decrease in the ratio of excimer to monomer emission of the probe, relative to that in aqueous solution. The predominately electrostatic binding of DNMAC and PAMPS in methanol produces a sharp increase in the ratio of excimer to monomer emission of the probe relative to that of the probe in methanol solution. The binding of the probes to the polyelectrolytes PAMPS, PSS, and PES in aqueous solution results in an enhancement of excimer emission of the probe. The dependence of such enhancement of the excimer emission on the probe and/or polyelectrolyte concentration suggests that, in spite of the low effective charge of the probes, electrostatic interactions of the probe and the polyelectrolyte are not negligible with respect to the hydrophobic interactions.

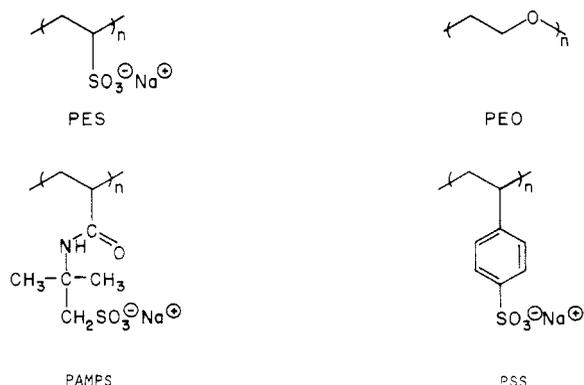
## Introduction

In a previous paper,<sup>1</sup> we reported that the excimer emission of aqueous solutions of bis( $\alpha$ -naphthylmethyl)ammonium chloride (DNMAC) and of ( $\alpha$ -naphthyl-

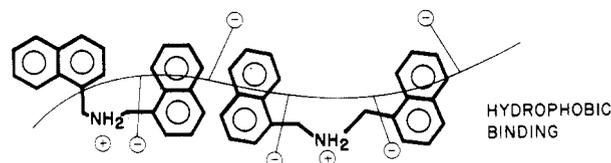
### PROBES



### POLYELECTROLYTES



### Scheme I



methyl)ammonium chloride (NMAC) is enhanced dramatically when the anionic polyelectrolyte sodium poly(styrenesulfonate) (PSS) is added. This result was interpreted as evidence for the formation of a strong polymer-probe associate possessing high local concentrations of probe lumophores gathered in the solvation layers of the polyelectrolyte. The packing of the aromatic rings of the lumophores in these regions of high local concentration evidently favors both inter- and intramolecular excimer formation. It was postulated that the structure of probes in these regions tends to be rich in "dimers" or pairs of aromatic rings possessing a parallel or "face-to-face" disposition.

In ammonium bases of sufficiently large size, the effective charge is often small so as to contribute little to the forces determining the equilibrium properties of the system.<sup>2</sup> It is expected that, as the "organic" size of such ammonium salts increases, the strength of potential hydrophobic interactions will increase. It has been proposed that interactions of quaternary ammonium cations with carboxylic polyelectrolytes are predominately of the hydrophobic type.<sup>2-6</sup> The energetic basis of the hydrophobic effect is generally attributed to the tendency to preserve hydrogen bonding in the water structure in the vicinity of a hydrophobic portion of a solute in an aqueous solution.<sup>7</sup>

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Scheme II

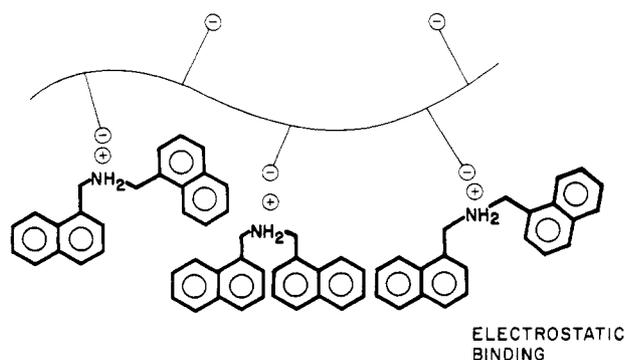


TABLE I: Enhancement ( $Q$ ) of the Excimer Emission for Aqueous Solutions of DNMAC and Interaction Areas ( $A$ ) of Polyelectrolytes with Different Hydrophobic Surfaces Calculated with Parameters Given in Ref 9<sup>a</sup>

	PES	PSS	PAMPS
$Q$	2.1	5.4	2.5
$10^9 A$ , cm <sup>2</sup> /mol	1.9	6.6	10.0

<sup>a</sup> DNMAC concentration is  $5 \times 10^{-5}$  M and polymer concentration is  $6 \times 10^{-5}$  M in all cases.

TABLE II: Enhancement of the Excimer Emission ( $Q$ ) of Different Probes and Their Hydrophobic Surfaces ( $A$ )<sup>a</sup>

	DNMAC	NMAC	DBAC	BAC
$Q$	4.8	1.8	1.3	1.0
$10^9 A$ , cm <sup>2</sup> /mol	18.2	9.1	13.4	8.7

<sup>a</sup> Reference 9. The polyelectrolyte is PES; both polyelectrolyte and probe concentrations are  $7 \times 10^{-4}$  M in water.

An important consequence of this driving force is the formation of thermodynamically stable, but structurally dynamic, microheterogeneous systems composed of a hydrophobic interior core covered by a hydrophilic skin (Scheme I). When electrostatic forces predominate in the formation of an associate between a polyelectrolyte and its counterion, either a structurally "loose" (atmospheric binding) or a more stoichiometric and structurally specific binding (site binding) will occur via interactions of the hydrophilic portions of polyelectrolyte and probe (Scheme II). Thus, rather different structures are expected, depending on whether hydrophobic or electrostatic forces are dominant in the binding mechanism.

Experimental support for information concerning the driving force of the<sup>8-11</sup> macroion-counterion interactions usually derives from techniques that monitor macroscopic properties of the system such as the degree of binding (e.g., conductimetry) or the strength of the binding (e.g., calorimetry). However, information concerning the microscopic structure generally is derived from the use of spectroscopic techniques which are capable of probing local structure.<sup>9</sup> In this paper, we employ the fluorescence probe technique to investigate the contributions of the several interactions mentioned above to the total driving force which determines the equilibrium structure of polyelectrolyte-arylammonium cation systems. In a companion paper<sup>12</sup> we deal with the mechanisms of formation and the

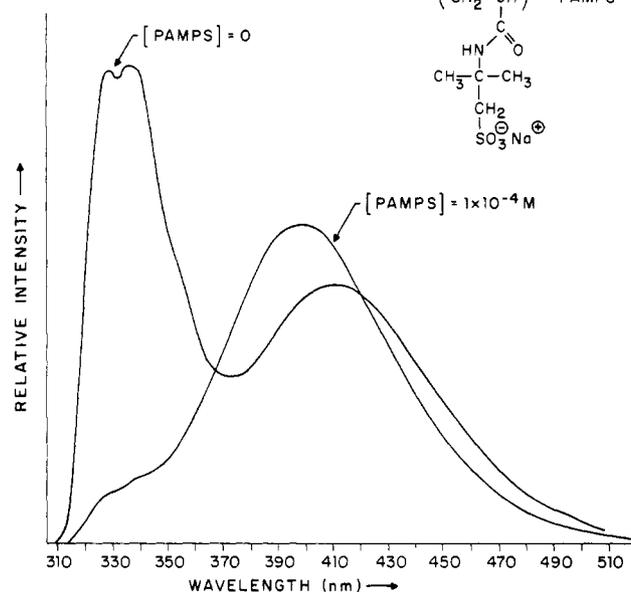
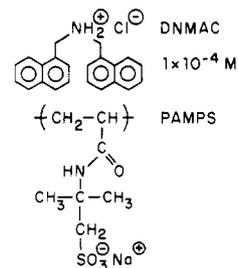


Figure 1. Emission spectrum of aqueous solutions of DNMAC in the presence and absence of PAMPS.

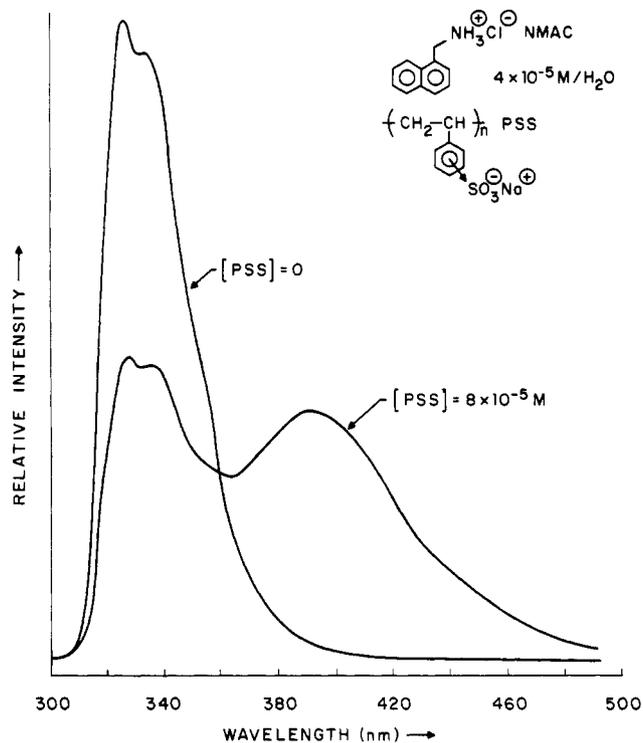


Figure 2. Emission spectrum of aqueous solutions of NMAC in the presence and absence of PSS.

structure of the probe-polyelectrolyte complex that is formed.

## Results

Figures 1 and 2 and Tables I and II demonstrate the relative enhancement of the excimer emission of aqueous solutions of the ammonium probes upon addition of polyelectrolyte. A convenient measure of the enhancement of excimer emission is the quantity  $Q$ , which is defined in eq 1, where  $I_E/I_M$  is the ratio of intensities of the maximum

$$Q = (I_E/I_M)/(I_E/I_M)_0 \quad (1)$$

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TABLE III: Excimer to Monomer Intensity Ratios ( $I_E/I_M$ ) of the DNMAC Emission in the Presence of Aqueous Solutions of PEO

[DNMAC], M	[PEO], M	$I_E/I_M$
$6.8 \times 10^{-5}$	0	0.59
$6.5 \times 10^{-5}$	$2.6 \times 10^{-5}$	0.39
$6.5 \times 10^{-5}$	$6.5 \times 10^{-5}$	0.61
$8.5 \times 10^{-5}$	$6.5 \times 10^{-4}$	0.40
$8.5 \times 10^{-5}$	$6.5 \times 10^{-3}$	0.31

of the excimer and monomer emission, respectively. The subscript 0 refers to the excimer/monomer emission ratio in the absence of polyelectrolyte.

For the systems studied, the maximum enhancement is found for the associate of DNMAC with PSS. The "hydrophobic surface",  $A$ , of the probe and the polyelectrolyte may be evaluated by a literature method.<sup>13</sup> This method takes the standard covalent radii of atoms in their typical geometries as the basis for evaluating volumes and areas occupied by groups of atoms. We found no correlation between  $Q$  and the value of  $A$  for the polymers or of the probe (Tables I and II). These results provide significant evidence *against* hydrophobic interactions as the predominant forces that contribute to the binding of the probes by the polyelectrolytes in water.

An enhancement of excimer formation, although a smaller one than observed in aqueous solution, is found for methanol solutions of the DNMAC-PAMPS aggregate. It is expected that, in the latter system, the electrostatic interactions between the polyion and its counterions are larger because of the smaller dielectric constant of methanol compared with water. The observed intensity difference in the two solvents is understandable in terms of the interplay of several factors: (a) the different viscosity of the two probe environments; (b) the different requirements for reorganization of solvent structure as the probe attempts to achieve a conformational shape appropriate for excimer formation; and (c) the absence of hydrophobic interactions in methanol. Qualitatively, however, when probe-polymer interactions are predominately electrostatic, an increase in the relative degree of excimer formation is expected on the basis of the model of Scheme II, and is observed.

Interestingly, the associate of DNMAC with PEO produces an initial decrease in the  $Q$  ratio with respect to the probe alone in water (Table III), then increases until the probe/monomer unit ratio reaches a value of unity, and then decreases again as the ratio of probe/monomer unit increases beyond unity.

The detailed conformation of our probe in the polyelectrolyte associate depends on the nature of its interactions with the polymer and by consequence on the structure of the complex formed. Each probe and each polymer possess different hydrophobic/hydrophilic characteristics which are expected to lead to different interactions and structures that will contribute to binding. Thus, in the case of the DNMAC complex with PEO, the probe structure is probably determined by the driving force to minimally disturb the water structure and to maximize the interaction with the polymer backbone (Scheme I). This could lead to *trans-gauche*, *trans-trans*, or *gauche (+)-gauche (+)* conformation being favored with respect to the *gauche (+)-gauche (-)* conformations that are required for formation of the excimer. The hydrophobic interactions between probe and polymer should lead therefore to the observed decrease in  $Q$ . The situation for polyelectrolytes

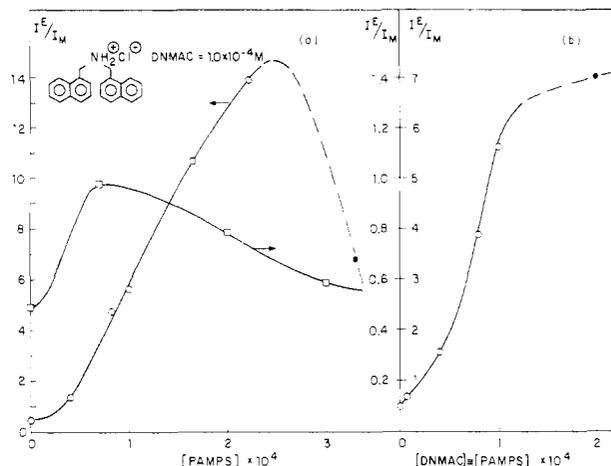


Figure 3. Polyelectrolyte concentration dependence of the excimer to monomer intensity ratios ( $I_E/I_M$ ) of DNMAC. (a) Round points: constant concentration of DNMAC =  $1.0 \times 10^{-4}$  M in aqueous solution. Square points: constant concentration of DNMAC =  $7 \times 10^{-5}$  M in methanol solution. (b) Aqueous solution with concentration of DNMAC equal to the PAMPS concentration in all cases. Filled points represent turbid solutions, but without phase separation.

can be contrasted with that for the association of DNMAC in sodium dodecyl sulfate micelles<sup>14b</sup> or in cyclodextrins<sup>14a</sup> in aqueous solution where the ratio  $Q$  increases by only about 50%. Note that in those cases where the interaction is hydrophobic, but conformation is different, micelles and cyclodextrins are "cavities" and polyelectrolytes are "unidimensional".

The dependence of  $Q$  on the probe and polymer concentrations is displayed in Figure 3. At low concentration of probe or polyelectrolyte, the value of  $Q$  is nearly the same as that of the probe in pure aqueous solution. The value of  $Q$  increases dramatically when either the polyelectrolyte concentration (at fixed probe concentration) or the polyelectrolyte-probe concentration ratio is increased.

A maximum has been previously observed in the  $Q$ -[polymer] profile of the aqueous PSS-DNMAC system at  $10^{-5}$  M probe (concentration fixed).<sup>1</sup> We find a similar tendency to a maximum for the DNMAC-PAMPS system. When the probe and polymer concentrations are approximately the same, a turbidity, indicative of an incipient phase separation, is observed for concentrations just beyond the maximum. For the aqueous DNMAC-PAMPS system, the simultaneous increase of both polymer and probe concentrations (but at a fixed ratio of 1:1) results in an increase in  $Q$  until the metastable region is reached (Figure 3, dashed line). In methanol,  $Q$  reaches a maximum and then decreases to a value tending toward that for zero polyelectrolyte concentration, but the system remains clear throughout the entire concentration range investigated.

These observations are interpreted to mean that a maximal  $Q$  requires a balance between the need for a high local concentration (which favors excimer formation and increases  $Q$ ) and the tendency to saturate the available sites on the polymer (which forces additional DNMAC into the aqueous phase and causes a decrease in  $Q$ ). When the probe concentration is "concentrated", the probe becomes a disproportionately distributed in the aqueous phase, and the value of  $Q$  decreases because of the low value of  $Q$  for the pure aqueous phase. When the probe substitutes for sodium in the solvation layer of the polymer, the mobility

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of the bound probe becomes restricted, since probe motions and conformational changes will be resisted by the energetically unfavorable changes that would be induced in the water structure that surrounds the polymer chain.<sup>10,11</sup> This increase in the local probe concentration in the surroundings of the polyelectrolyte enhances the probability of attaining the geometric requirements for formation of an excimer intramolecularly (DNMAC and DBAC) and/or intermolecularly (NMAC and BAC). The occurrence in the ground state of conformations that are preferential for excimer formation is corroborated by absorption spectra and time-correlated emission spectra.<sup>1,12</sup>

At sufficiently high concentrations of both components, precipitation occurs. The onset of turbidity or incipient phase separation correlates with the value of  $Q$ : for probes with the highest value of  $Q$ , the concentration at which the onset of turbidity occurs is the lowest. In the case of DNMAC, an initial turbidity occurs at concentrations of probe and electrolyte of the order of  $10^{-4}$  M in each component. In the cases of PES and DNMAC, even when both components are  $10^{-3}$  M, the solutions remain clear. These results suggest a strong binding of the probes and the polyelectrolytes.<sup>3</sup>

### Conclusions

The interactions of the sulfonic macroanions PES, PSS, and PAMPS and the (arylmethyl)ammonium cation photoluminescent probes DNMAC, DBAC, NMAC, and BAC in aqueous solutions result in enhanced excimer emission of the probes. From the data, it is concluded that interactions other than hydrophobic effects operate to contribute to probe-polymer binding and to cause the enhancement of excimer emission. In particular, it is proposed that electrostatic interactions make an important contribution to the binding of probe and polyelectrolyte.

Our conclusions contrast with those derived from studies of carboxylic polyelectrolytes and tetraalkylammonium cations, systems for which hydrophobic interactions appear to be dominant.<sup>2-6</sup> Differences between the latter systems and the ones investigated here can be understood on the basis of the following considerations: (a) in dilute solutions, such as the ones investigated here, the electrostatic field around the charged sites is expected to be significant relative to hydrophobic forces;<sup>15,16</sup> (b) the sulfonate group is generally less hydrophobic than the carboxylate group,<sup>15</sup> so that sulfonate groups are expected to displace water more readily from a hydrophobic associate than a carboxylate group.<sup>8</sup>

We conclude that the excimer/monomer ratio of the probes employed in this study, a readily measured parameter, is a useful interrogator of the nature of the binding of organic salts to polyelectrolytes.

### Experimental Section

The polyelectrolytes are a gift of Prof. H. Gregor (Columbia University) and have been purified as described in ref 1. Probes, synthesis, and purification have also been previously described. Emission spectra have been recorded on a Perkin-Elmer Hitachi spectrometer. Spectra have not been corrected.

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**Registry No.** DNMAC, 17018-62-1; NMAC, 39110-74-2; DBAC, 20455-68-9; BAC, 3287-99-8; PES, 25053-27-4; PSS, 28038-50-8; PAMPS, 55141-01-0; PEO, 25322-68-3.

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## Electron Microscopy Investigation of Platinum Supported on TiO<sub>2</sub> and TiO

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Electron microscopy has been used to examine Pt dispersed on various oxides of titanium. On prerduced TiO<sub>2</sub> that shows bulk Ti<sub>9</sub>O<sub>17</sub> crystallites, Pt particles are polyhedral. Extensive reoxidation removes Ti<sub>9</sub>O<sub>17</sub> and the Pt particles are hemispherical. Pt deposited on TiO is raftlike.

Transition metal/titania systems have recently received considerable attention in areas such as photoassisted catalytic reactions at the gas-solid interface,<sup>1</sup> development of gas sensor systems,<sup>2</sup> and strong metal-support interaction (SMSI) phenomena.<sup>3</sup> The promising potential for

modifying catalyst activity and selectivity<sup>4-6</sup> through control of the oxide character makes transition metal/titania catalysts interesting. One rule for selecting the supporting materials which will show the SMSI property has been proposed by Tauster and Fung<sup>7</sup> and is based on

(1) The published papers are too numerous to cite. For review, refer to: (a) A. J. Bard, *Science*, 207, 139 (1980); (b) K. Rajeshwar, P. Singh, and J. DuBow, *Electrochim. Acta*, 23, 1117 (1978); (c) M. Gratzel, *Acc. Chem. Res.*, 14, 376 (1981).

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