The Interaction of Methyl Viologen with Anionic Polyelectrolytes

A Study by a Fluorescence Quenching Method

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The interactions between methyl viologen (MV^{2+}) and sodium poly(styrene sulfonate) (PSS) and sodium poly(vinyl sulfonate) (PVS) were studied by means of the fluorescence quenching of a probe molecule (1-naphthylamine) not bound to the polymer. The results can be interpreted in terms of atmospheric binding of MV^{2+} to PVS and PSS. In the latter case, there is also some specific binding, manifested by a change in the absorption spectrum of MV^{2+}.

INTRODUCTION

Polyelectrolytes can change the rates of reaction of organic and inorganic substrates by electrostatic or by hydrophobic interactions (1, 2). For reactions involving ionic substrates the effect of a charged polymer depends largely on its electrostatic potential, which in turn determines the surrounding ionic atmosphere (2). The same principles apply to the effect of polyions on the efficiency with which the fluorescence of ionic species is reduced by ionic quenching agents (3).

In recent years, media effects on photochemically induced electron transfer reactions have been studied in order to find systems in which the overall efficiency of the conversion of light energy to chemical energy is improved (4–6).

Due to their ability to separate unlike charged ions, polyelectrolytes have been used in these types of studies (7–9). Among the more commonly used polyelectrolytes are poly(vinyl sulfonate) (PVS) and poly(styrene sulfonate) (PSS).

As methyl viologen (MV^{2+}) has a suitable redox potential for reducing water to hydrogen (10), it has been widely used as an electron acceptor in photochemically stimulated electron transfer reactions.

Based on results obtained by electrochemical techniques a strong interaction between MV^{2+} and the sulfonate group in PSS was previously reported. It was postulated to be not only electrostatic, but also chemical in nature (11).

In this paper we report another approach for studying the interaction between MV^{2+} and anionic polyelectrolytes. This is based on measurements of fluorescence quenching of a probe molecule not bound to the polymer by MV^{2+}, which finds itself in the macromolecule domains.

EXPERIMENTAL

1-Naphthylamine (1NA) (Fluka, pure) was recrystallized at least three times from ethanol–water and subsequently vacuum sublimed. Methyl viologen dichloride was obtained from a commercial solution and was recrystallized from methanol. Sodium poly(vinyl sulfonate) (Hoechst), sodium poly(styrene sulfonate) (Dow), sodium poly-

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(acrylate) (PA; Rohm & Haas), and sodium poly(methacrylate) (PMA; Hydrum) were used after recrystallization. Sodium chloride (Merck) and urea (BDH) were used as received.

Absorption spectra were obtained with a Cary 17 spectrophotometer. Fluorescence measurements were performed in an Aminco SPF 125 spectrofluorometer. The fluorescence lifetime apparatus was composed of a nitrogen laser 5 ns FMHW as the excitation source, a TRW 75-A filterfluorometer, and a TRW 32-A decay time unit.

RESULTS AND DISCUSSION

When the absorption spectrum of an aqueous solution of PSS containing MV^{2+} is compared with the spectrum of a MV^{2+} solution free of PSS, a red shift of the tail of the absorption band is observed (Fig. 1). The absorbance of this band, measured at 330 nm, depends on both MV^{2+} and PSS concentration. Plots of absorbance versus MV^{2+} or PSS concentration are shown in the inset of Fig. 1. These plots are typical of systems in which association between two species occurs.

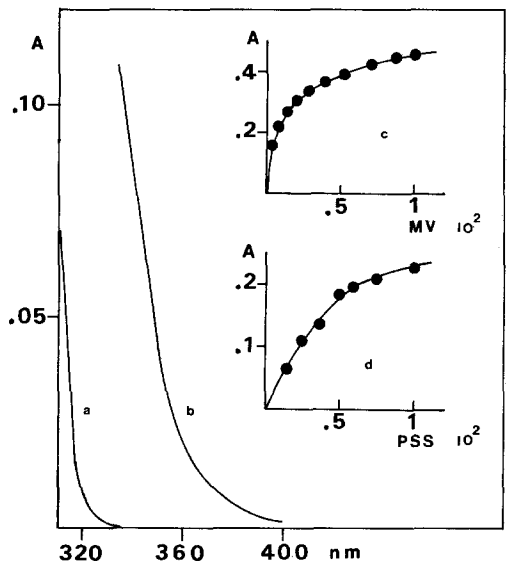

FIG. 1. Absorption spectra of 0.001 *M* MV^{2+} (a) and 0.006 *N* PSS plus 0.001 *M* MV^{2+} (b). Absorbance at 330 nm of a solution of 0.01 *N* PSS versus MV^{2+} concentration (c). Absorbance at 330 nm of a 0.001 *M* MV^{2+} solution versus PSS concentration (d).

It is important to note that the red shift of the absorption band was not observed when other polyelectrolytes such as PVS, PMA, or PA solutions were mixed with MV^{2+}. Sodium toluene-*p*-sulfonate, which might be considered the monomer corresponding to PSS, does not show this red shift either.

In order to perform further studies on the binding of MV^{2+} to polyelectrolytes, we used a water-soluble fluorescent probe. This probe should not be bound to the polymer and its fluorescence should be quenched by MV^{2+}. We chose 1NA because its absorption and fluorescence spectra in water are not altered by addition of the polyelectrolytes used in this study; therefore we considered it not to be bound to the polymers. 1NA also fulfills the second condition, as its fluorescence is quenched by MV^{2+} in aqueous solutions, a result that has already been published (12).

The addition of PSS to the aqueous 1NA–MV^{2+} system leads to a decrease in the quenching capability of MV^{2+} on 1NA. This effect becomes more important when the concentration of PSS is increased.

In contrast to the absorption results, when PVS or PMA were used in the quenching studies, results similar to those observed with PSS were obtained.

In order to avoid corrections in the fluorescence intensity measurements due to ground state complexation between 1NA and MV^{2+} (12) and also between MV^{2+} and PSS, we measured the dynamic quenching by determining the fluorescence lifetimes of 1NA as a function of MV^{2+} concentration in the presence of polyelectrolytes.

In Fig. 2, plots of τ_0/τ versus the concentration of MV^{2+} in the absence or presence of PSS or PVS in the 1NA–MV^{2+} system are shown; τ_0 and τ are the fluorescence lifetimes of 1NA in the absence and presence of MV^{2+}, respectively. It can be seen that after an initial region without quenching, the τ_0/τ plots in the presence of polyelectrolytes become almost parallel to the plots in water.

The τ_0/τ plots in the presence of polymers are shifted to higher MV^{2+} concentrations than those in the absence of polymer. These shifts may be related to the plot of absorbance versus MV^{2+} concentrations (inset c, Fig. 1), where the absorbance reaches a plateau. These facts can be interpreted in the following way: as MV^{2+} is added to the solution, it becomes trapped in the polyelectrolyte domains; therefore, it is not able to quench the fluorescence of 1NA, which is distributed uniformly over the solution. Only after the domains are saturated with MV^{2+} will the excess added be free to reduce the fluorescence.

This can be interpreted as an indication that the quenching, when observed, is taking place in the aqueous region and not in the domain of the polymer.

The net result of the addition of PSS or PVS to the 1NA–MV^{2+} system is therefore to reduce the MV^{2+} concentration needed to quench 1NA fluorescence. The quenching experiments clearly show that an interaction between an anionic polyelectrolyte and MV^{2+} is always present, but only PSS produces a change in the absorption band of MV^{2+} as a consequence of this association.

The binding constant of MV^{2+} to PSS can be defined as

$$K_b = [MV_b^{2+}]/[[PSS] - [MV_b^{2+}]][[MV_t^{2+}] - [MV_b^{2+}]], \quad [I]$$

where MV_b^{2+} and MV_t^{2+} refer to methyl viologen bound to the polymer and total MV^{2+}, respectively. This binding constant was calculated by curve-fitting of plots of absorbance versus concentration at a fixed MV^{2+} value by an iterative procedure (13). The best fit was obtained with a binding constant of 180 ± 20 M^{-1}, assuming a 1:1 complex.

An estimate of the binding constant may be obtained from fluorescence data if it is accepted that the fluorescence quenching rate constant of 1NA by MV^{2+} is essentially the same in aqueous and in polyelectrolyte solutions. By assuming this, MV_b^{2+} can be estimated from the fluorescence quenching results

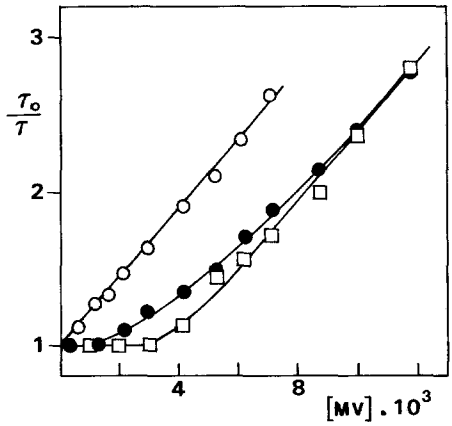

FIG. 2. Stern volmer plots of 1NA fluorescence lifetimes versus MV^{2+} concentration: ○, water; ●, 0.01 *N* PSS; □, 0.01 *N* PVS.

(Fig. 2) by a graphic procedure. In this figure, the τ_0/τ values in the absence of polymers measure the concentration of MV^{2+} that is free to quench dynamically 1NA fluorescence, $[MV_f^{2+}]$. Given a τ_0/τ value, the same amount of MV^{2+} free to quench 1NA is reached at a higher MV^{2+} concentration, $[MV_t^{2+}]$, when polyelectrolyte is present. Therefore, the difference between $[MV_t^{2+}]$ and $[MV_f^{2+}]$ is the amount of MV^{2+} bound to the polymer at the specified τ_0/τ, $[MV_b^{2+}]$.

In Fig. 3, plots of MV_b^{2+} versus MV_t^{2+} obtained from the fluorescence quenching experiments for PSS and PVS are shown.

The amount of MV^{2+} bound to PSS increases regularly and an apparent binding constant of 800 ± 100 M^{-1} can be obtained by curve-fitting. This value is significantly larger than the binding constant obtained by absorption spectrometry.

On the other hand, when the binding results of MV^{2+} to PVS are analyzed, the plot shows a slope of unit at low MV_t^{2+}, then a small transition zone and, finally, a saturation region depicted by a plateau. This kind of behavior is typical of strong binding, and a constant higher than 8000 M^{-1} can be estimated by curve-fitting for the association of MV^{2+} with PVS. This value is in agreement with the strong binding of MV^{2+} to PMA (14) which has recently been reported.

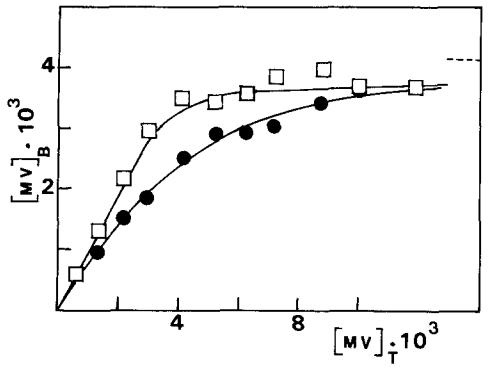

FIG. 3. Concentration of MV^{2+} bound to the polyelectrolyte, obtained from fluorescence lifetimes, versus total MV^{2+} concentration: □, 0.01 *N* PVS; ●, 0.01 *N* PSS.

Furthermore, when our results of fluorescence quenching in the presence of PVS are compared with the values for MV^{2+} quenching of $Ru(bpy)_3^{2+}$ bound to PVS (15), a strong correspondence is observed in both sets of data. In both studies it was found that the MV^{2+} saturates PVS at almost the same concentration.

The fact that the MV^{2+} binds more strongly to PVS than to PSS may be rationalized on the basis that the charge density in PVS is higher than that in PSS. Although the linear distance between charged groups, measured along the backbone of the polyion is the same for both polyelectrolytes (0.25 nm), the actual distance between charges is larger for PSS than PVS, because the groups are situated on side chains, which tend to be on opposite sides of the backbone (16).

The addition of sodium chloride to the 1NA–MV^{2+}–polyelectrolyte system tends to reverse the effect of polyelectrolyte on the quenching of 1NA by MV^{2+}; that is, results similar to those in water are obtained. This behavior is observed when the effect of the addition of NaCl on the absorption band of the MV^{2+}–PSS system is studied. It can be seen in Fig. 4 that the absorbance decreases when increasing amounts of NaCl are added.

These effects can be explained by the fact that the MV^{2+} ions become excluded from the polymer domains when the concentration of NaCl is increased. This happens because the shielding of the potential field of the polyion domains by the Na^+ ions reduces the electrostatic attraction for the MV^{2+} ions. In the higher concentration region of NaCl, MV^{2+} would be completely excluded from the domain.

The absorbance of the PSS–MV^{2+} band also decreases with an increase in the concentration of urea, possibly due to the reduction of a hydrophobic interaction.

This absorption band appears only when the polyelectrolyte used is PSS and not when PVS, PMA, or PA is mixed with MV^{2+}, because these polyelectrolytes have no moieties such as phenyl rings which may interact with MV^{2+} ions. We believe that the association constant measured by absorption spectrometry reflects an electron donor–acceptor type complex formed between the phenyl rings of PSS and MV^{2+}. Since electron donor–acceptor complexation requires some degree of coplanarity between the phenyl ring and MV^{2+}, certain conformations of the polymer would be responsible for the interaction.

The apparent binding constant obtained by fluorescence lifetime measurements in PSS–MV^{2+} is probably the result of a more complicated situation because this experimental technique takes into account the formation of specific interactions plus electrostatic interactions. In the case of the system PVS–MV^{2+},

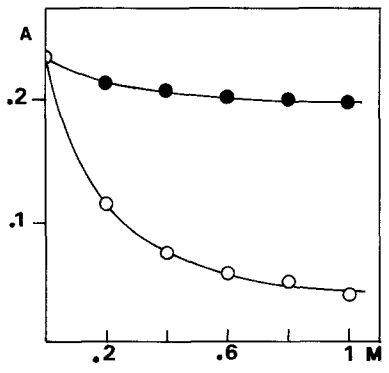

FIG. 4. Absorbance at 330 nm of a 0.001 *M* MV^{2+} plus 0.01 *N* PSS solution as a function of added NaCL (○) and urea (●).

this technique, like others such as potentiometry, conductivity, diffusion, etc., does not permit us to distinguish between the various kinds of counterions found in polyelectrolyte solutions (16).

In conclusion, the results presented in this paper indicate that MV^{2+} ions are primarily concentrated in the domain of the polyelectrolyte as a result of an electrostatic interaction. As a result of this interaction, MV^{2+} is able to interact with the phenyl rings of PSS forming electron donor–acceptor complexes.

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