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The Adsorption of Basic Dyes by Poly(Styrene Sulphonate)

Miguel G. Neumann, Fergus Gessner & Geovane L. de Sena

Instituto de Física e Química de São Carlos, Universidade de São Paulo,
Caixa Postal 369-13560 São Carlos SP-Brazil

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ABSTRACT

*The adsorption of basic dyes (Safranine, Neutral Red, Acridine Orange and Proflavine) on poly(styrene sulphonate) has been studied by measuring the amount of free dye in solution using a photochemical method. Adsorption free energies are in the range 7·1–5·3 kcal/mol. Comparing the values of these energies as a function of the structure of the dyes, three different types of interactions can be postulated to contribute to the binding of the dyes to the polymer, viz., electrostatic (*c. *4 kcal/mol), hydrophobic and charge-transfer.*

INTRODUCTION

The study of the interactions between dyes and polymers is of fundamental importance for understanding the processes of fiber dyeing. Although polyelectrolytes are water-soluble, the dye adsorption interactions involving non-electrostatic forces are basically the same as those for insoluble polymers or fibers. On the other hand, chemical reactions in the presence of added polyelectrolytes have been studied for many systems in recent years.[1] Also, in many cases, polyelectrolytes act as catalysts for several reactions by increasing the local concentrations of the reactants,[2] or bringing them together by hydrophobic or electrostatic interactions as in micellar catalysis.[3,4] These effects have been used, for instance, to promote photoinduced electron transfer reactions of xanthenic dyes, avoiding the back-transfer by electrostatic repulsion between the electrolyte charges and the produced ion-radical of the same charge.[5,6]

The presence of oppositely-charged polyelectrolytes,[7-9] improves the aggregation of dyes in aqueous solution. This effect has been claimed to be due to a forced stacking of the dye molecules along the macromolecular chain, involving electrostatic and hydrophobic forces (similar to the metachromatic effect of xanthenic molecules in the presence of biological macromolecules like DNA, carrageenan, etc.).[10,11] On the other hand, assuming a different geometry for the interacting groups, the increased aggregation can be ascribed to a partial cancellation of the electrostatic repulsion.[7]

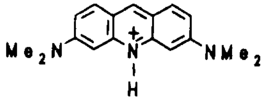
The present study furnishes results that allows a distinction to be made between the electrostatic and hydrophobic contributions to the adsorption of basic dyes to anionic polyelectrolytes, and provides a semiquantitative estimation of the latter contribution in terms of the substituents on the dye molecules.

EXPERIMENTAL

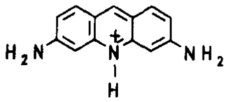
The dyes used were Safranine T (Sf, Merck), Neutral Red (NR, Merck), Acridine Orange (AO, Aldrich) and Proflavine (Pf, Aldrich) (Fig. 1).

The poly(styrene sulphonate) (PSS, Aldrich) was 85% sulphonated and with MW 210 000, as determined by viscometry. Thallium carbonate (C. Erba, p.a.) was used as a non-organic, non-hydrophobic quencher for comparison. The fluorescent probe, sodium 1,4-naphthylamine sulphonate (NAS) was obtained by neutralizing the corresponding naphthionic acid (C. Erba).

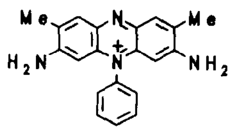
Fluorescence measurements were performed at room temperature (25 ± 1°C) in aqueous solutions prepared in deionized water (Permutit), using an Aminco-Bowman Model J4 spectrofluorimeter. Concentrations



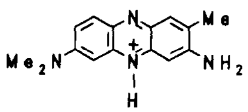
ACRIDINE ORANGE



PROFLAVINE



SAFRANINE



NEUTRAL RED

Fig. 1. Dye structures.

were 10^{-4} M for the probe, 10^{-3} equiv./litre for the polyelectrolyte, and between 0·5 and 10 × 10^{-5} M for the dyes.

RESULTS AND DISCUSSION

The amount of dye adsorbed on the polymer was obtained from the comparison of the quenching of NAS fluorescence by the dye, in the presence and absence of polyelectrolyte, as shown in Fig. 2. Similar plots have been found for the quenching of NAS fluorescence by the other dyes as well as by Tl^+ ions.

The difference in quencher concentrations corresponding to equal I_0/I ratios is ascribed to the amount removed from the bulk solution by adsorption by the polyelectrolyte.[12] The anionic probe will be expelled from the polyelectrolyte domain, due to electrostatic repulsion, and can be considered to be entirely in the aqueous phase.

The adsorption equilibrium can be represented by

$$D^+ + S^- \overset{K}{\rightleftharpoons} [D^{+-}S] \qquad (1)$$

where D^+ stands for a cationic dye molecule, S^- for an anionic site on the polyelectrolyte, $[D^{+-}S]$ is the ion-pair formed between the anionic

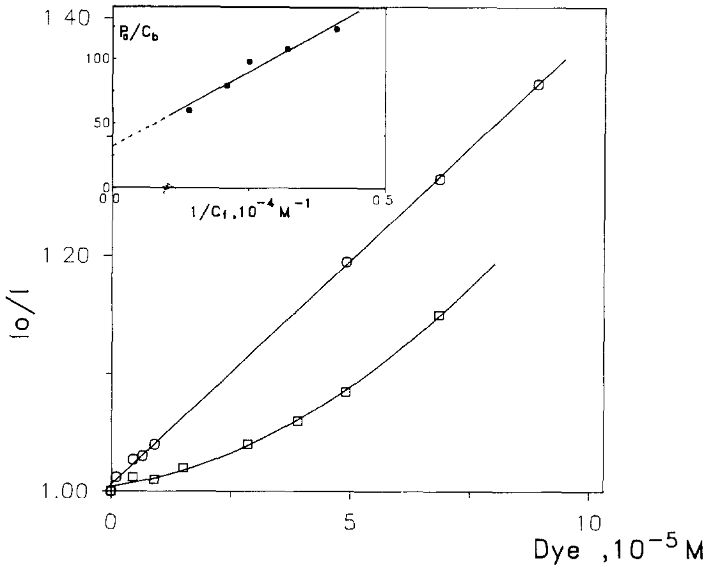


Fig. 2. Stern–Volmer plots for the fluorescence quenching of 1,4-naphthylaminosulphonate (10^{-4} M) by Acridine Orange in aqueous solution (○) and in the presence of PSS 10^{-3} equiv./litre (□). Insert: corresponding Klotz plot.

site and the dye, i.e. an adsorbed dye molecule, and K is the adsorption equilibrium constant. This constant can be determined from the Klotz relationship[13]

$$P_o/C_b = \left[\frac{n}{K}\right]\cdot\left[\frac{1}{C_f}\right] + n \qquad (2)$$

where P_o is the total number of anionic sulphonic groups: C_f and C_b are the concentrations of free and bound dye; and $1/n$ is the number of sulphonic groups per binding site. The plot of eqn (2) is shown as an insert in Fig. 2, and the equilibrium constants and adsorption free energies for all the studied systems are presented in Table 1. The extrapolated n values obtained from these plots are in the range 20–30 corresponding to site saturations of 3–5%.

The values in Table 1 are within the range of those found previously. AO on PSS has been reported[14] to have a binding equilibrium constant of 15 × 10^5, and also as being higher than 10^5.[10] The interaction of the anionic dyes Methyl Orange with quaternized derivatives of poly(vinylimidazol) has been found[15] to correspond to free energies of 4·2–4·6 kcal/mol in 0·01 M salt solutions, which corresponds to 5·5 kcal/mol in solution without added electrolyte. As the dyes used in this work have a more hydrophobic structure, that value can be considered to be compatible with those of Table 1. The adsorption of Methylene Blue on poly(acrylic acid) homologues has been reported[16] to be in the range of 10^5.

From the data in Table 1, it can be seen that the dyes with more substitution on the aromatic ring system interact more strongly with the polyelectrolyte than the less substituted dyes, whereas the interaction energy for Tl^+ is lower than those of the dyes.

Thus, considering the behaviour of the Tl^+ ion to be representative of

TABLE 1

Equilibrium Constants and Adsorption Free Energies for the Interaction of Poly(Styrene Sulphonate) with Basic Dyes and the Tl^+ Ion

	K	$-\Delta G^0$ (kcal/mol)
Safranine	1 46 × 10^5	7·1
Acridine Orange	3·40 × 10^4	6·3
Neutral Red	7·47 × 10^4	6·7
Proflavine	6·62 × 10^3	5·3
Tl (I) ion	7 39 × 10^2	3·9

Errors in ΔG have been estimated at ±0·4 kcal/mol, corresponding to a factor ≈2 in the K values.

electrostatic (or simple ion-exchange) interactions, the difference between the adsorption free energies of the dyes and the thallium ion has to be attributed to other types of interaction, mainly hydrophobic and charge-transfer type. The substitution on the dye ring system will increase the former contribution in the order Safranine (one phenyl group and two methyl groups), Acridine Orange and Neutral Red (four and three methyl groups, respectively) and Proflavine (no alkyl groups). This order matches that of the equilibrium constants and interaction free energies for the dyes on the polymer. The same trend is also followed by the constants for the partition of these dyes between benzene and water: Sf (2·25) > NR (0·66) > AO (0·52) > Pf (0·06). In a similar way, the difference in interaction free energies between Methyl Orange and N-methyl- and N-benzyl-poly(vinylimidazol) has been attributed partially to a larger hydrophobic contribution in the latter.[16]

Charge-transfer interactions have been postulated for the interaction of tris-(2,2'-bipyridine)ruthenium(II) with PSS, as well as with poly(vinyl sulphate).[17] The shifts in the spectra of Methylene Blue in Nafion membranes have been explained by the delocalization of the π-system, which promotes charge-transfer interactions.[18] On the other hand, as the charge on the basic dye Safranine is quite localized, its ability to form charge-transfer complexes will be reduced, as found for protonated Methylene Blue in sodium lauryl sulphate.[19] Thus, it can be expected that the charge-transfer contribution to the adsorption free energy in Safranine will be lower than on the other dyes, in spite of the presence of a N-phenyl group on the dye.

CONCLUSIONS

The adsorption of basic dyes on polyelectrolytes can be explained assuming three types of interactions: (a) An electrostatic interaction between the charge on the dye and the sulphonic group on the polyelectrolyte (contributing about 4·0 kcal/mol to the adsorption energy), similar for all the cationic dyes and independent of the nature of the polymer: (b) an hydrophobic contribution, mainly entropic, which increases with the amount of substitution on the dye structure; and (c) a charge-transfer contribution which depends on the degree of delocalization of the π-system of the dye.

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