Role of ionic competition in the binding of a dye to poly(vinylimidazole)

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The binding of an arylazonaphthol dye to a quaternized basic polymer is dependent on the nature of the counterions. This is observed as a strong temperature dependence of the binding constants. The binding of the dye to the corresponding unquaternized polymer in the presence of salts containing the same anions show similar but much smaller effects. In both cases, the dye is in competition with the anion for the binding site; the presence of charged sites on the quaternized polymer produces stronger competition.

INTRODUCTION

A large number of investigations of substrate binding to both synthetic polymers and biological macromolecules have been reported. The most studied systems are poly(vinyl pyrollidone), (PVP)[1,2,3,4,5]; and serum albumin[6,7,8]; others include poly(ethylene imine)[9], poly(vinyl pyridine)[10], poly(lysine) and derivatives[11,12]. By following the temperature dependence of the binding, it has been possible to estimate thermodynamic data from which the binding mechanisms have been elucidated.

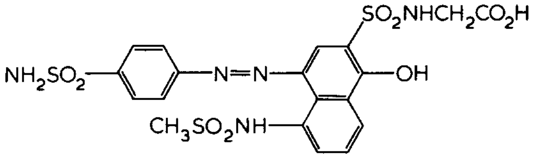
In virtually all these investigations, the structure of water both in the solvent and attached to the solute[13] has been invoked as the driving force in polymer binding. The 'iceberg' concept[1] assumes that a sheath of water molecules, with a reduced number of degrees of freedom, surrounds alkyl groups in aqueous solution. On formation of the polymer substrate complex, some of these molecules are released into the bulk phase, resulting in an overall increase in entropy. This mechanism, *hydrophobic bonding*, has often been used as an explanation of entropy-controlled reactions. The effect of urea, a 'water structure breaker', on co-solute binding[14,15,16,17,18,19] and its thermodynamics[8] has been used to identify hydrophobic interactions.

Little work has been published on binding studies, either on poly(vinylimidazoles) or polymers with a known regular charged site i.e. a charged synthetic polymer Natural proteins, although they do have charged sites, have much less well-defined structures. Little study of the counterion accompanying charged polymers has been made. The work reported here is a study of dye binding to poly(vinylimidazoles) both charged and uncharged. For charged polymers, their backbone was kept constant in terms of quaternization while the nature of the counterion was changed.

EXPERIMENTAL

Materials

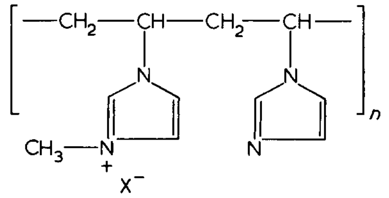
The dye used throughout was a magenta arylazonaphthol compound[26]:



It was chosen for its high solubility and good binding characteristics.

The polymers studied (see *Table 1*) were unquaternized (PVI) and 50% quaternized poly(vinylimidazoles) where the quaternizing compounds were methyl iodide (PVIMeI), dimethyl sulphate (PVIMe$_2$SO$_4$) and methyl ethyl sulphate (PVIMeEtSO$_4$), respectively, The unquaternized polymer was prepared by solution polymerization in water using azobiscyanovaleric acid as initiator; the polymer was isolated by precipitation into acetone and dried. The dimethyl sulphate-quaternized polymer was prepared by copolymerization of n-vinyl imidazole and dimethyl sulphate-quaternized n-vinyl imidazole, by a similar method. The methyl iodide polymer was prepared by simple quaternization of the uncharged polymer in dimethyl formamide and precipitation in ether. The methyl ethyl sulphate polymer was prepared by addition of excess sodium ethyl sulphate to an aqueous solution of the methyl iodine quaternized polymer followed by dialysis

Table 1 Structure and codes of polymers studied



X$^-$	Code
Unquaternized	PVI
I$^-$	PVIMeI
MeSO$_4^-$	PVIMe$_2$SO$_4$
EtSO$_4^-$	PVMeEtSO$_4$

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in Visking tubing. Elemental analysis showed that the polymers were consistent with the proposed structures (*Table 1*).

Ethyl potassium sulphate and methyl potassium sulphate (Eastman Chemicals) were used as supplied.

All other chemicals e.g. potassium iodide and buffer salts were Analar grade and were used as supplied.

Polarography

Binding was measured using a standard polarograph in a phosphate buffer at pH 11.5 (to ensure good solubility of all the components) containing 1% sodium sulphite as background electrolyte and antioxidant. Dye aliquots were added from a micrometer syringe in dimethyl formamide solution (1%). The concentration of polymer was approximately 10 times that of the dye, to ensure that the drop in dye concentration due to binding could be followed accurately. A calibration plot was made for each set of conditions (in the absence of polymer) and used to calibrate the polarographic output in the binding experiments where the concentration of dye was increased by regular additions.

One problem associated with binding studies is that of polymer concentration. In common with some previous workers[1,4,20] the concentration was used in terms of a 'base-mol'. Thus, the molecular weight determining unit of the polymer was taken as a dimer. This allowed useful comparisons to be made between 50% quaternized polymers and the homopolymer. The concentration of polymer used was ~ about 5×10^{-3} mol l^{-1}.

Experiments were carried out in the pH 11.5 buffer with and without 6M urea over the temperature range 25°–50°C for all four polymers.

Viscosity

Measurements were made at 25°C using an Ostwald viscometer (Type BS/UC) with an efflux time of 32.5 s for the pH 11.5 buffer, rising to over 300 s with polymer and urea. All solutions were filtered and the densities were measured at 25°C. The results were plotted in the form of reduced viscosity defined as:

$$\eta_{red} = \frac{(\eta/\eta_0)-1}{C}$$

where η and η_0 are the viscosities of the solution and solvent, respectively, and C is the polymer concentration in g 100 ml^{-1}.

Conductance

Measurements were made at 26.5°C using a Wayne Kerr conductance bridge and plotted as equivalent conductance *versus* concentration$^{1/2}$. All solutions were made in triply distilled water.

RESULTS

Dye binding

By considering binding as a succession of dye–polymer equilibria:

$$MD_{i-1} + \text{D} \overset{k_i}{\rightleftharpoons} \text{MD}_i$$

Klotz[21] has shown, on application of the law of mass action, that the relationship between the polymer, free and bound dye is given by:

$$\frac{1}{r} = \frac{1}{Kn}\,\frac{1}{f} + \frac{1}{n} \tag{1}$$

where r is the number of moles of bound dye per mol polymer, f the free dye concentration, n the maximum number of bound dye molecules per molecule of polymer and K the intrinsic binding constant which is an average over all the specific binding constants:

$$k_i = \left[\frac{n-(i-1)}{i}\right] K \tag{2}$$

e.g. $K_1 = nK$

The extrapolation required to obtain n is such as to render it unreliable[2,22]. Thus, the parameter k_1 (see equation (2), the first specific binding constant) was used to analyse the data, since it could be accurately obtained from the slope of the plot of equation (1): this involves no extrapolation and utilizes only the data obtained. k_1 has been used successfully in previous temperature studies of polymer–substrate binding[2,3,7,8,21].

Quaternized polymers

The first specific binding constants have been measured for the dye on the three quaternized polymers PVIMeI, $PVIMe_2SO_4$ and $PVIMeEtSO_4$ at pH 11.5 with an without 6 M urea over the temperature range 25–50°C. These are plotted as $\log_{10}k_1$ in *Figure 1*. In the absence of urea, the temperature sensitivity of the binding constants increases on changing only the counterion i.e. $I^- < MeSO_4^- < EtSO_4^-$. On addition of urea, no binding could be detected for $PVIMeEtSO_4$, and for the other two polymers the binding was much reduced.

The equations used to calculate the thermodynamics of binding from the experimental data are:

$$\Delta F = RT \ln k_1 \tag{3}$$

$$\Delta H = RT^2 \frac{\mathrm{d}\ln k_1}{\mathrm{d}T} \tag{4}$$

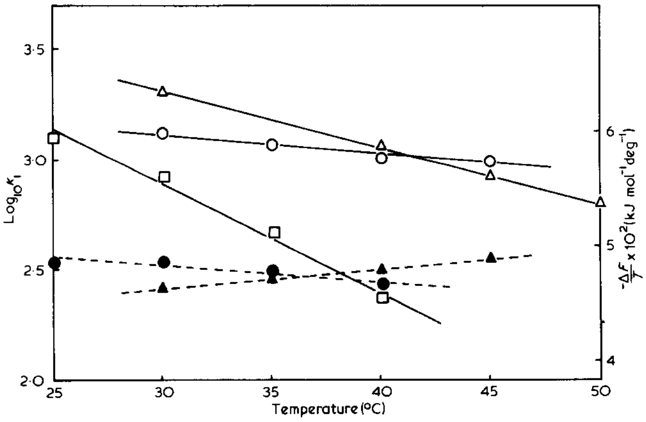

Figure 1 Variation of $\log_{10}k_1$ and $-\Delta F/T$ with temperature for quaternized polymers. ○, ——, PVIMeI; ●, – – –, PVIMeI + urea; △, ——, $PVIMe_2SO_4$; ▲, – – –, $PVIMe_2SO_4$ + urea; □, ——, $PVIMeEtSO_4$

$$\Delta S = (\Delta H - \Delta F)/T \qquad (5)$$

For the quaternized polymers, these are given in *Figures 1, 2*, and *3*. On changing the counterion, in the absence of urea, there are regular changes in thermodynamic properties in the order I^-, $MeSO_4^-$ and $EtSO_4^-$. The enthalpy becomes progressively more exothermic and the entropy more negative i.e. there is increasing order on binding. The effect of urea pn PVIMeI binding is relatively small, whereas for PVIMe$_2$SO$_4$ it causes the enthalpy to become endothermic and the entropy to become positive. No binding was detected for PVIMeEtSO$_4$ in the presence of urea.

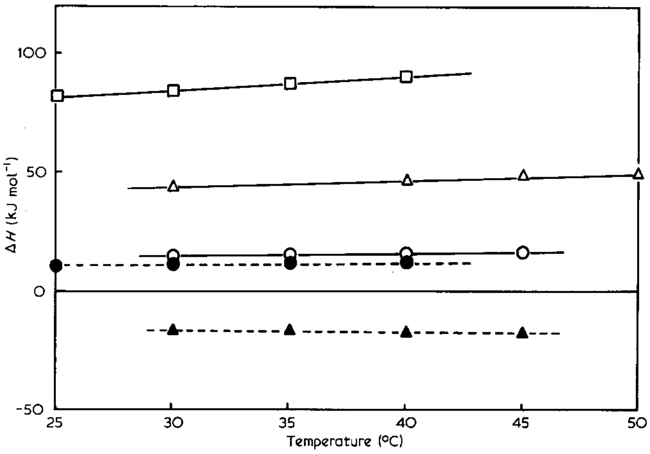

Figure 2 Temperature dependence of enthalpy change for binding to quaternized polymers. ○, ——, PVIMeI; ●, – – –, PVIMeI + urea; △, ——, PVIMe$_2$SO$_4$; ▲, – – –, PVIMe$_2$SO$_4$ + urea; □, ——, PVIMeEtSO$_4$

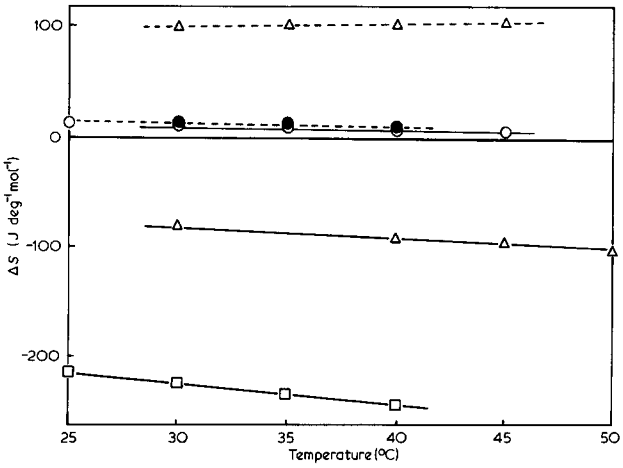

Figure 3 Temperature dependence of entropy change for binding to quaternized polymers: ○, ——, PVIMeI; ●, – – –, PVIMeI + urea; △, ——, PVIMe$_2$SO$_4$; ▲, – – –, PVIMe$_2$SO$_4$ + urea; □, ——, PVIMeEtSO$_4$.

The size of the binding sites ($1/n$) in terms of dimer units per dye molecule are given in *Table 2*. They are very scattered, due to the long extrapolation on the Klotz plot, and show no obvious trend.

Unquaternized polymer

The binding constants for the dye on PVI have been measured alone and in the presence of the salts potassium iodide (KI), methyl potassium sulphate (KMeSO$_4$) and ethyl potassium sulphate (KEtSO$_4$) which were at a concentration 10 times that of the polymer. These experiments were in pH 11.5 buffer with and without 6 M urea over the temperature range 25°–50°C (see *Figure 4*).

In the absence of salt, binding of the dye to PVI is similar to PVIMeI, although the drop in the presence of urea is not as marked as for the latter polymer. Addition of the salts caused a reduction in binding and none could be detected when urea was also present.

Equations (3), (4) and (5) have been used to calculate the thermodynamic changes on binding to the uncharged polymer (*Figures 4, 5* and *6*). In the absence of salt, binding to PVI shows a slightly exothermic enthalpy change and positive entropy change; urea causes the enthalpy change to become endothermic and the entropy change more positive. The presence of the salts gives a regular variation in enthalpy change from endothermic for KEtSO$_4$ to exothermic for KI, KMeSO$_4$ being intermediate. Similarly binding gives increasing disorder as follows: KEtSO$_4$ < KMeSO$_4$ < KI. This is

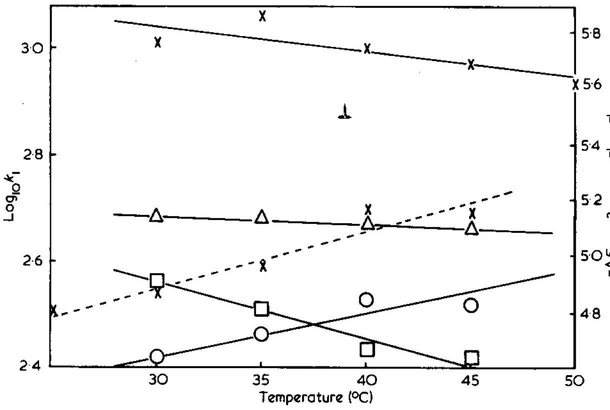

Figure 4 Variation of $\log_{10}k_1$ and $-\Delta F/T$ with temperature for unquaternized polymer with added salts. X, ——. no added salt; X, – – –, no added salt + urea; ○, ——, KI added; △, —— KMeSO$_4$ added; □, ——, KEtSO$_4$ added

Table 2 The number of dimer units in binding sites of quaternized polymers

	pH 11.5 buffer			+6 M urea	
Temperature (°C)	PVIMeI	PVIMe$_2$SO$_4$	PVIMeEtSO$_4$	PVIMeI	PVIMe$_2$SO$_4$
25	–	–	1.7	1.9	–
30	2.4	7.6	2.7	2.5	1.7
35	2.9	–	1.0	4.6	3.3
40	3.1	8.2	1.8	4.6	2.7
45	3.6	3.9	–	–	4.9
50	–	14.5	–	–	–

Mean = 4.0 ± 3.1

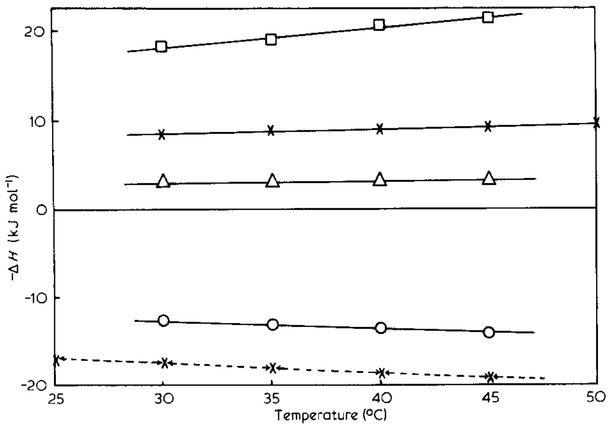

Figure 5 Temperature dependence of enthalpy change for binding to unquaternized polymer with added salts. X, ——, no added salt; X, – – –, no added salt + urea; ○, ——, KI added; △, ——, $KMeSO_4$ added; □, ——, $KEtSO_4$ added

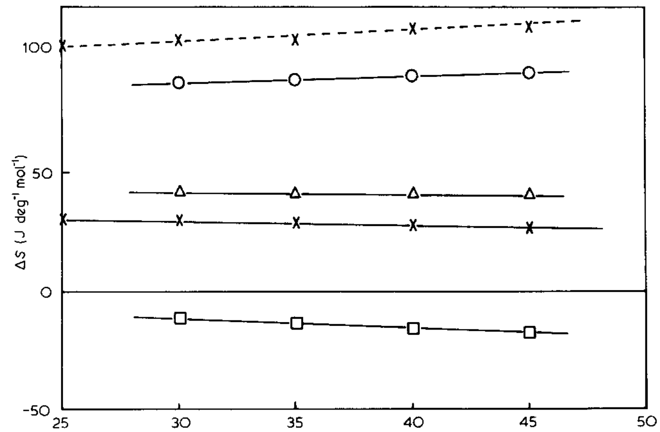

Figure 6 Temperature dependence of entropy change for binding to unquaternized polymer with added salts. X, ——, no added salt; X, – – –, no added salt + urea; ○, ——, KI added; △, ——, $KMeSO_4$ added; □, ——, $KEtSO_4$ added

the same trend (but the effect is much smaller in magnitude) as that cuased by varying the counterions associated with the charged polymer.

The size of the binding sites for all the experiments on the uncharged polymer are given in *Table 3*. The site sizes for the urea experiments are generally smaller than the rest but, on average, the size is larger than for charged polymers.

Viscosity

The reduced viscosity (η red) of PVI in pH 11.5 buffer with and without 6 M urea is given in *Figure 7*. For comparison, the viscosities of $PVIMe_2SO_4$ are also given (over a less extensive range). The intrinsic viscosities i.e. $\lim_{C \to 0} (\eta \text{ red})$ of the polymers (g^{-1})

PVI	0.292
PVI (6 M urea)	0.425
$PVIMe_2SO_4$	0.312
$PVIMe_2SO_4$ (6 M urea)	0.393

A previous study of poly(vinylpyrrolidone)[23] showed that the viscosity of this neutral polymer was not affected by the presence of large concentrations of urea. This is not the case for poly(vinylimidazoles) where there is a significant increase in viscosity on addition of urea; the effect is most marked for the unchanged form.

Conductance

Measurements were made on PVIMeI, $PVIMeETSO_4$, KI, $KEtSO_4$; and KI and $KEtSO_4$ in the presence of twice the concentration of PVI (neutral polymer) see *Figure 8*.

DISCUSSION

Quaternized polymers

The difference in thermodynamic data associated with binding of the dye to the three polymers in aqueous solution (*Figures 2* and *3*) are striking and indicate a regular variation

Table 3 The number of dimer units in binding sites of unquaternized polymer

Temperature °C	PH 11.5 buffer				+6 M urea
	KI	$KMeSO_4$	$KEtSO_4$	No salt	No salt
25	–	–	–	–	1.7
30	6.0	5.6	10.3	3.7	2.8
35	10.8	5.2	10.6	6.0	1.9
40	9.5	4.5	13.8	10.5	2.5
45	11.2	5.2	10.2	7.6	4.0
50	–	–	–	15.9	–

Mean = 7.2 ± 4.1

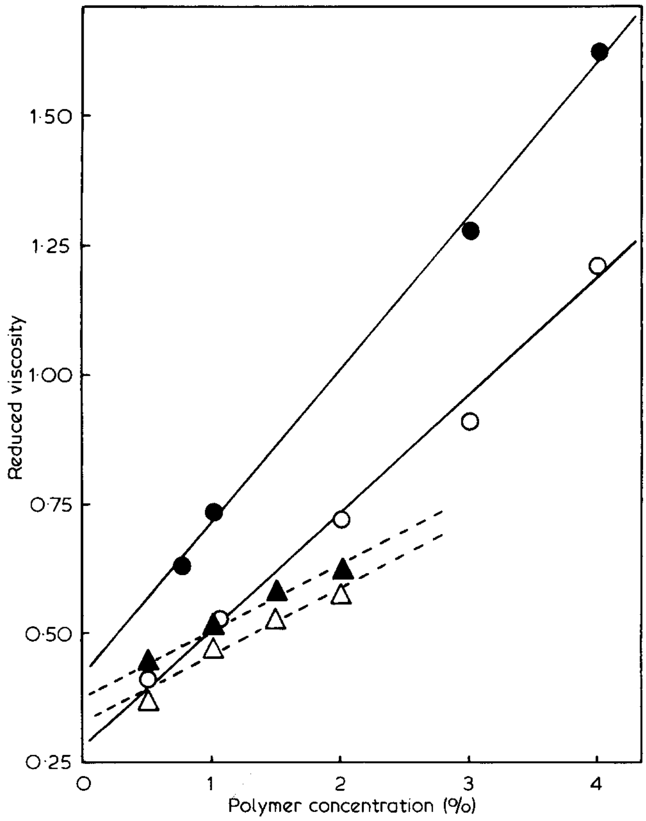

Figure 7 Reduced viscosity of polymers as a function of concentration at 25°C and pH 11.5. ○, ——, PVI; ●, ——, PVI + urea; △, – – $PVIMe_2SO_4$; ▲, – – –, $PVIMe_2SO_4$ + urea

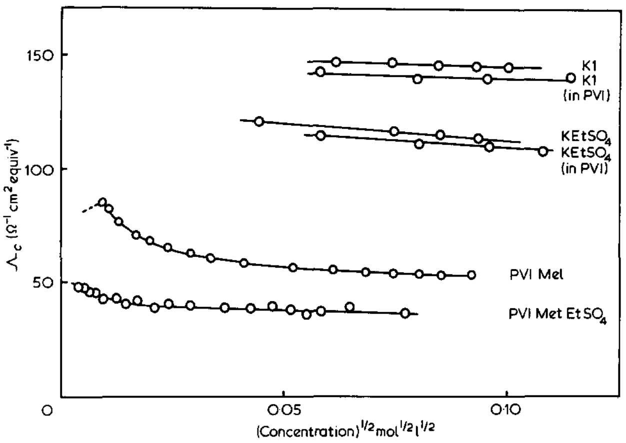

Figure 8 Variation of equivalent conductance with (concentration)$^{1/2}$ for salts and polymers at 26.5°C

in mechanism. The greater binding, invariably observed with charged polymers, has often been considered to derive primarily from ionic interactions between the dye and the charged site. In the present study, the binding to PVIMeI is similar to that of the uncharged polymer, whereas the other two quaternized polymers show large differences. Since the number and position of the charged sites are identical, these differences must derive from the nature of the counterions.

In a number of studies[2,6,7], evidence for hydrophobic interactions between a polymer and substrate can be derived from the relative magnitudes and signs of the enthalpy and entropy changes. These interactions are invariably accompanied by a small exothermic enthalpy change and relatively large positive entropy change. Dye binding to PVIMeI and the uncharged polymer shows this behaviour (*Figures 2, 3, 5* and *6*) but the binding mechanism is different for the charged polymers with the $MeSO_4^-$ and $EtSO_4^-$ counterions as evident by the large exothermic enthalpy change and the negative entropy change (*Figures 2* and *3*). The results from the conductivity measurements (see below) show that the probable explanation of the observed thermodyanmics is that these counterions are bound in the positively charged sites.

If the overall enthalpy change is considered to be the sum of separate contributions[1], an interesting comparison may be made between the polymers. For this comparison it will be assumed that, for example, $EtSO_4^-$ is strongly bound in the site and I^- is very weakly bound, if at all. Thus:

$$\Delta H^o = \Delta H^a + \Delta H^b + \Delta H^c + \Delta H^d$$

where ΔH^o is the overall enthalpy change as measured;

ΔH^a is the enthalpy change for removal of water molecules prior to binding;

ΔH^b is the enthalpy change due to removal of counterions from the site (positive);

ΔH^c is the enthalpy change for binding the dye (negative); and

ΔH^d is the enthalpy change for hydration of the released counterions.

Comparison of the two polymers (*Figure 2*) shows that $(\Delta H^o_{EtSO_4^-} - \Delta H^o_{I^-})$ is negative. Therefore, since the effect of loss of water, i.e. ΔH^a, is approximately equal for both polymers it follows that:

$$(\Delta H^b + \Delta H^d)^{EtSO_4^-} - (\Delta H^b + \Delta H^d)^{I^-} < 0$$

Since I^- is assumed to be weakly bound, $\Delta H^b \sim 0$ for this counterion. Therefore, incorporating the signs for the enthalpy changes gives:

$$\Delta H^d_{EtSO_4^-} > \Delta H^b_{EtSO_4^-} + \Delta H^d_{I^-}$$

Thus, the effect of hydration of $EtSO_4^-$ is greater than the counterion binding of $EtSO_4^-$ or the hydration of I^- i.e. in binding to $PVIMeEtSO_4$ and $PVIMe_2SO_4$, a large proportion of the highly exothermic enthalpy change results from hydration of the released counterions. pH titration has shown the dye to have 2 or 3 negative charges at pH 11.5 ($pK_a \sim 12$), thus this number of counterions will be fully released. Since the binding site has on average four charges, one or two further counterions could be affected if not fully released.

This hypothesis also gives a reasonable account of the entropy changes. The unexpectedly large neagtive values (*Figure 3*) measured in the presence of $EtSO_4^-$ and $MeSO_4^-$ can be explained on the basis that, once released, these counterions are hydrated (producing the large exothermic ΔH). This results in the ordering of water structure. The overall gain in order must be much larger than that lost on hydrophobic association of the dye and polymer.

Further evidence for this is obtained from the studies in the presence of 6 M urea. The enthalpy change on dye binding to $PVIMe_2SO_4$ becomes endothermic in urea (*Figure 2*), whereas there is little change for PVIMeI. Urea is known to disrupt hydrophobic hydration; thus, the advantageous enthalpy change in aqueous solution due to hydration of the released counterion is no longer available, and the positive ΔH derives from the differences in enthalpies of binding of the dye and released counterions. The change in ΔS on addition of urea to $PVIMe_2SO_4$ (*Figure 3*) is also a consequence of counterion binding, since the dye can release up to three of the latter, giving an overall increase of species in solution. For $PVIMeEtSO_4$, where no binding was detected in urea, the counterion is bound so strongly that the energy contribution from the increased entropy is not great enough to remove up to three counterions from the site.

From the urea experiments, the order of binding strength of counterions to the polymer is $EtSO_4^- > MeSO_4^- > I^-$. The regular increase in exothermic ΔH and the decrease in ΔS on dye binding in aqueous medium in the presence of the counterions indicates that they are hydrated hydrophobically in the same order. Thus, a significant portion of the binding ability of the ions is derived not only from their negative charge, but also from their ability to structure water and thus undergo hydrophobic bonding.

Direct evidence for the existence of counterion binding is obtained from the variation of conductance with polymer concentration (*Figure 8*). It is considered that, if the polymers bind a significant proportion of their counterions, these measurements will show a reduced overall conductivity. The equivalent conductances of PVIMeI and $PVIMeEtSO_4$ are very much smaller than their respective potassium salts. Part of this derives from the fact that the cation is a polyelectrolyte, but if, for example, I^- is unaffected by the polymer, then the conductance will at least be equal to that for I^- alone. The specific conductance of I^- (at 25°C and zero concentration) is 77 Ω^{-1} cm^2 equiv^{-1}; this varies little with concentration or increased viscosity due to the presence of uncharged polymer. Now, in the asympototic region for PVIMeI, the equivalent conductance is less than 55 Ω^{-1} cm^2 equiv^{-1}. Thus, the mobility of the I^- ion is influenced strongly by the presence of the polyelectrolyte. Both poly-

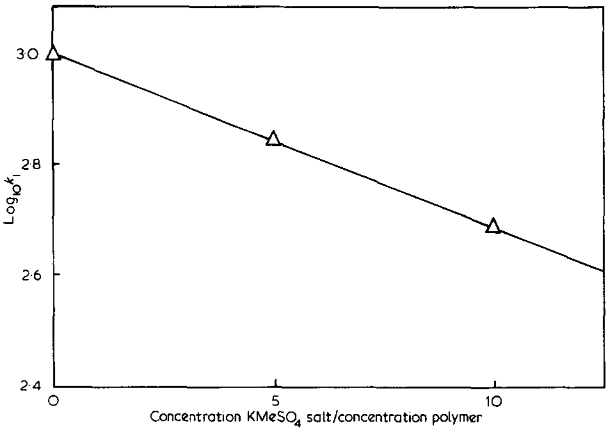

Figure 9 Variation of $\log_{10}k_1$ for dye binding to PVI with concentration of added KMeSO$_4$

mers also show a curvature in their conductance plots (*Figure 8*) normally exhibited by weak electrolytes. Therefore conductance measurements suggest that the counterions are associated with the charged polymers in solution.

Uncharged polymer

The dye binding characteristics of the uncharged polymer (PVI) alone, in pH 11.5 buffer, are typical of a system whose predominant mechanism is hydrophobic interaction. The relatively low but exothermic enthalpy (*Figure 5*) and positive entropy (*Figure 6*) changes have been noted in previous studies of uncharged polymers[1–4]. On addition of urea, binding falls appreciably with an endothermic enthalpy change and the entropy change still positive but becoming larger. A similar study[8] of the binding of butyl orange to bovine serum albumin showed an opposite effect on addition of urea i.e. increasing exothermic enthalpy and decreasing postive entropy changes. The latter result was explained by loss of hydrophobic hydration of the binding moieties, but this cannot be invoked to explain the effect of urea on the present dye and polymer.

A possible explanation of the results can be given by considering that urea interacts with the polymer in solution resulting in changes in configuration or hydrogen bonding. These mechanisms may be invoked to produce the observed changes in the thermodynamic properties. To test these possibilities, the viscosities of PVI in pH 11.5 buffer alone and with 6 M urea were measured (*Figure 7*) by the same method used in previous studies of synthetic polymers[12,23] There is a large increase in viscosity of PVI in the presence of urea, which is in marked contrast to the study of poly(vinyl pyrrollidone) (PVP) where no change in viscosity was noticed for this neutral polymer[23]. However, the effect of urea on the charged polymer formed by condensation between L-lysine and 1,3-benzene disulphonyl chloride[12,24] also gave a large increase in viscosity especially at low levels of ionization. This was considered to be due to a change from a clustered configuration, held together by hydrophobic interactions, to a more extended structure. The explanation could well account for the changes in viscosity with PVI, especially since the effect of urea on the charged polymer is much less. But to account, for the positive ΔH and ΔS in terms of a configurational change only, the dye binding would have to produce a change from a compact to a more extended structure on formation of the dye–polymer complex. Since the viscosity results show that the polymer is already extended, this emchanism is improbable. The other possibility is that urea is associated with the polymer e.g. hydrogen bonded, producing the increased viscosity. Binding of the dye has to overcome this association (hence the positive ΔH) and release urea molecules, producing increased disorder i.e. a positive ΔS. Direct evidence of such an interaction has yet to be obtained.

Addition of salts to uncharged polymer

In the preceding sections, the effect of the counterion on the mechanism of dye binding to charged polymers was discussed. The effectiveness of a particular counterion depends on how strongly it is bound and hydrated on release. This shows that counterion binding can occur by mechanisms other than ionic attraction, the most important being hydrophobic bonding. Thus, a study of dye binding to the uncharged polymer in the presence of these anions should give further evidence of a competitive interaction.

Binding of the $MeSO_4^-$ anion is indicated by the sensitivity of dye binding (at 30°C) to concentration of added KMeSO$_4$ salt (see *Figure 9*). This is in marked contrast to a study of PVP and a range of alkyl orange dyes[25] where the presence of anions Cl^-, ClO_4^- and CNS^- gave increased binding. This was explained in terms of the effect of these ions on water structure, and *not* their competitive binding. When used with PVI, ClO_4^- and CNS^- caused precipitation and Cl^- gave slightly reduced binding (at 30°C and 10x polymer concentration $\log_{10}k_1 = 2.89$ and $1/n = 7.52$).

Comparison of the binding constants for all the added salts (*Figure 4*) shows no obvious trend. But, on consideration of the thermodynamic data, a regular pattern emerges. The enthalpy change (*Figure 5*) varies regularly from endothermic with I^- to exothermic with $EtSO_4^-$; similarly, the entropy change (*Figure 6*) becomes progressively smaller in the order $I^- > MeSO_4^- > O > EtSO_4^-$. Similar to the quaternized polymers, the results may be explained on the basis of anion binding and hydration on removal. Release of I^- is accompanied by an endothermic enthalpy change, since the dye has to remove a number of anions from the site (see *Table 3*) which will not be hydrated. Together with the water released by hydrophobic association of dye and polymer, they add to the number of species in solution, thus giving an entropy change greater than for no added salt. On release, the $MeSO_4^-$ anion becomes fully hydrated (i.e. produces a negative enthalpy change, which, when added to the overall change, cancels the unfavourable effect of binding). The entropy change is approximately the same as for binding with no added salt, because the rise in the number of species in solution due to released $MeSO_4^-$ roughly balances the loss due to their hydration. Since $EtSO_4^-$ is hydrated even more strongly, the enthalpy change is relatively large and exothermic and there is an overall increase in order on dye binding.

This pattern of increasing exothermic enthalpy change and order is analogous exactly to that observed with the quaternized polymers, except that the effects are much smaller. This is because, with the charged polymers, the counterions are strongly bound in the site by ionic as well as hydrophobic interactions and will be only weakly hydrated, if at all; when the ions are bound to the uncharged polymer. it is by hydrophic association only i.e. they will retain a major proportion of their solvent sheaths.

CONCLUSION

In aqueous solutions, the dye has to compete with counterions or added anions for binding to poly(vinyl imidazole)s.

The enthalpy and entropy changes associated with removal of the anions from the binding site strongly influences the binding constant and its temperature dependence. For quaternized polymers, the effect is so large that, at certain temperatures, simple variation in counterion can produce large changes in binding to an otherwise identical polymer chain. A similar effect occurs for the uncharged polymer, where different added anions produce smaller, but nonetheless significant, changes in binding.

The effect of urea on dye binding to the charged polymers is consistent with the view that this compound reduces the degree of structure of the aqueous medium. Thus, urea has a two-fold action: it severely restricts hydrophobic bonding between the alkyl groups of the dye and polymer; and it reduces hydration of any released counterions. For the uncharged polymer, the situation is less clear, since binding produces more disorder than in aqueous solution. A possible explanation is that a polymer–urea interaction is overcome by the dye, thus releasing urea molecules and increasing the entropy; no direct evidence for this interaction has been obtained.

Dye binding to the uncharged polymer in the presence of various anions gives thermodynamic changes that are consistent with those obtained for the analogous quartemized polymers. Thus, competition between the dye and anions for the binding sites also occurs for uncharged polymer; the extent of anion binding is controlled by hydrophobic interaction.

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