Hydrophobic polyelectrolytes and polysoaps. Ionization of weakly basic groups and conformation in aqueous solution of some derivatives of poly(4-vinyl pyridine)

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Two different types of cationic polysoaps were prepared in order to study the ionization equilibria of weakly basic groups incorporated in such polymers. A major concern in this work has been an exploration of the effect of temperature on the intrinsic basicity of the ionizable groups, a question of considerable relevance, for example, in the development of thermally regenerable ion exchange resins. The results lead to models that should be helpful in elucidating trends in the basicity of functional groups in polyelectrolytes incorporating hydrophobic residues. A basic resin with greatly enhanced thermal effect has been prepared which provides support for present models of the hydrophobic effect.

INTRODUCTION

Polysoaps are polymers with soap groups attached covalently to their chain structures. Soaps form micelles in aqueous solution; for this process 'the attractive force arises from the hydrophobic effect acting upon the hydrocarbon chains'[1]. Polysoaps also form micellar structures in water as their molecular compactness and ability to solubilize hydrocarbons demonstrate[2]. Our major concern here is the ionization of weakly basic polysoaps that may have potential application as thermally regenerable ion exchange resins in water desalination processes[3].

At present, thermal regeneration of ion exchange resins may be taken to be primarily the consequence of the large temperature dependence of the self-ionization of water[4]. Changes in the magnitudes of the acidic and basic dissociation constants, K_a and K_b, with temperature, may be considered to be second order effects. Thus, the efficiency of the thermal regeneration process would be much improved if a significant drop in the basicity with temperature of the active groups could be achieved.

The broad assumptions that formed the basis of this work were as follows. Hydrophobic interactions in aqueous media are more stable at high than at low temperature; ionizable groups incorporated into an hydrophobic environment have much lower basicities than those in aqueous media. Thus, in principle it should be possible to achieve a transfer of such groups from aqueous to hydrophobic environments by an increase in temperature with a consequent significant reduction in the ionization constants of the ionizable groups.

We prepared and studied, from this point of view, two types of cationic polysoaps. We shall describe polysoap types where the hydrophilic end of the soap is attached to the polymer backbone. Also we shall describe polysoaps that consist of soap molecules with their hydrophobic ends attached to the polymer and whose hydrophilic ends consist of the ionizable amino groups. It will be seen that the basic model referred to above has led to useful results.

EXPERIMENTAL

Poly(4-*vinyl pyridine*) and its alkyl derivatives were prepared according to methods published previously[5-8].

Polymerization was carried out in methanol using the initiator α,α′-azodiiso butyronitrile (~2.5% w/v of monomer). The product was redissolved in methanol and the sample used for the bulk of the work reported here was a large fraction obtained by reprecipitation with ethyl acetate. The sample was redissolved in t-butanol followed by freeze drying and vacuum drying; its viscosity number in 95% ethanol was 8300 cm^3g^{-1}. Amberlite IRA-400 resin was used to convert the quaternary bromide salts to the corresponding chlorides. We determined free-base pyridine nitrogens by titration in glacial acetic acid[9].

Poly(N-*vinyl imidazole*) was a gift of Badische Anilin and Soda Fabrik A. G. (Ludwigshafen, Germany): its dodecyl chloride derivatives were prepared in a manner analogous to that used with poly(4-vinyl pyridine).

The viscosity number of the parent polymer in water was 58 cm^3g^{-1}.

Poly(4-*vinyl*-N-1-*aminoalkyl-pyridinium chloride*) samples were prepared in two steps. The pyridine nitrogens of poly(4-vinyl pyridine) were quaterinized by heating in sulfolane solution using 1-bromo-*n*-phthalimide alkanes[10]. The isolated product was then hydrolysed by a 100-fold excess of 6 mol dm^{-3} hydrochloric acid at reflux temperature lasting about 1 week. On completion of the hydrolysis the solutions were neutralized with 6 mol

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dm^{-3} sodium hydroxide solution followed by exhaustive dialysis against water to remove sodium chloride.

Cross-linked resins of the alkyl derivatives were prepared, with minor modifications, according to the method of Nishide and Tsuchida[11]. We used both α,ω-dibromoalkanes (Fluka) and α,α'-dichloro-*p*-xylene (Fluka purum) as cross-linking agents. The aminoalkyl resins were prepared by cross-linking the phthalimide intermediates followed by hydrolysis.

Potentiometric titrations. An EIL Model 7050 pH meter (Electronics Instruments Ltd., Surrey, England) coupled with a combination glass electrode (121 AP7, Titron Instruments Pty. Ltd., Braeside, Victoria) was used. The precision of the meter is 0.004 pH units. Two separate baths were maintained at 25.0±0.1°C and at 80.0±1°C. The meter-electrode systems were standardized with pH 4 and pH 9 buffers. Titrants were kept at ambient temperature and delivered either from an Agla micrometer syringe or from a Dosimat 10 cm^3 macropiston burette (Metrohm A. G., CH-9100, Herisau, Switzerland). All titrants were either 1 mol dm^{-3} or 0.1 mol dm^{-3} solutions of hydrochloric acid and sodium hydroxide.

Titrations of linear polymers were performed in closed cells at both temperatures under an atmosphere of 'CO_2-free' nitrogen, with 50 cm^3 of sample solution at a concentration calculated to require approximately 1 cm^3 of titrant for neutralization. Each titration consisted of a solvent titration followed in quick succession by a solution titration.

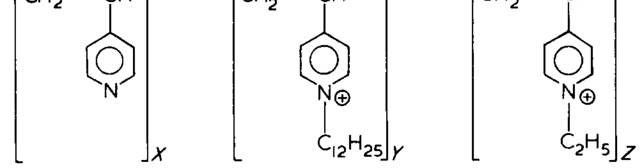
The titration curves of cross-linked resins were determined by a 'point-by-point' method. Known weights of a given resin were equilibrated with different aliquots of the titrants by shaking in sealed tubes at the required temperatures for 24 h; a time found to be sufficient for equilibrium to be attained.

Viscosimetry. An Ubbelohde-type viscometer was used (flow-time of water was 155.1 s at 25°C). Where viscosities were determined as a function of temperature, the same solution was heated and cooled through a series of constant temperatures. Where the viscosities were determined as a function of ionization, progressive additions of acid were made to the solution and samples withdrawn for measuring the pH.

RESULTS

Alkyl derivatives of poly(4-vinyl-pyridine)

The alkyl derivatives of poly(4-vinyl-pyridine) were random copolymers of the type:



where $X+Y+Z=100\%$ and the ionizable groups are the $X\%$ weakly basic pyridine residues. The sum of the $Y\%$ dodecyl-pyridinium and $Z\%$ ethylpyridinium fractions should be kept constant[2] it valid comparisons were to be made between, and meaningful trends to be discovered among, these copolymers. The particular group of polymers to be considered here consisted of the same parent poly(4-vinyl-pyridine) preparation with $Y+Z=51\pm5\%$. A second group of polymers with ~15% higher degree of quaternization was also studied; the results obtained substantiated those to be described below.

We express titration data in terms of $pK_{app}=-\log_{10}K_{app}$, where

$$K_{app}=C_{H}\frac{(1-\alpha)}{\alpha} \text{ with } \alpha \equiv C_{BH^+}/(C_{BH^+}+C_B)$$

Here C_H, C_{BH^+} and C_B refer to the stoichiometric concentrations of the hydrogen ions, of the conjugate acid and base residues in solution, respectively; α may be called the degree of ionization of the base and K_{app} the apparent dissociation constant of an average ionizable group. For polyelectrolytes, in general, K_{app} is a function of α and the form of this dependence is shown in *Figure* 1 for two of the samples studied at two temperatures. The data in *Figure* 1(*a*) refer to a sample that contains no dodecyl groups; the results given in *Figure* 1(*b*) pertain to a sample with $Y=8.7\%$. Extrapolation of the pK_{app} values to $\alpha=0$ seems feasible in these instances, yielding values for the 'intrinsic' dissociation constants, K_0 or pK_0. We note that both the pK_0 values and the slopes of the respective plots differ for the two samples; these two quantities are shown as functions of the dodecyl content of the polymers, at both temperatures of 25° and 80°C, in *Figure* 2.

The titration results shown in *Figures* 1 and 2 were obtained in aqueous solution without added salt. All titrations were also repeated in 0.02 mol dm^{-3} sodium chloride solutions resulting in higher overall pK_{app} values at both temperatures compared with the salt-free solutions. However, since no additional significant features or trends were revealed by these data they will not be reported here.

Viscosity measurements as a function of dodecyl content confirmed previously published results[12]; a rapid drop in viscosity with dodecyl group content takes place between about $6\% \leqslant Y \leqslant 8\%$ with relatively minor changes beyond this transition region. *Figure* 3 shows the temperature dependence of the viscosity of two samples, with $Y=0\%$ and 17.6%, respectively, at both $\alpha=1$ and $\alpha=0$.

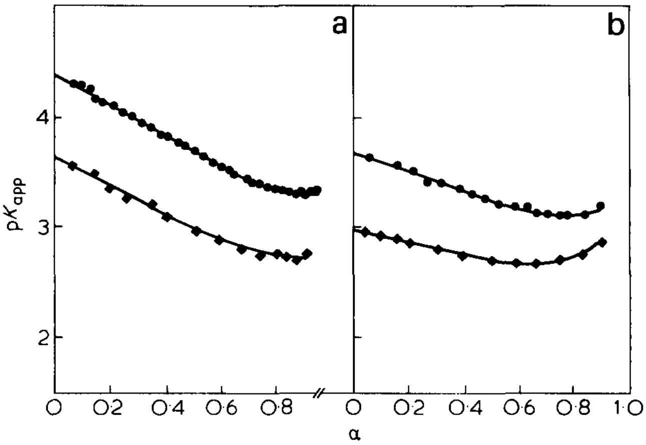


Figure 1 pK_{app} as a function of α for two samples of partially quaternized poly(4-vinyl-pyridine). The percentage of dodecyl content is denoted by Y. (a) $Y=0$, (b) $Y=8.7$. ●, 25°C, ◆, 80°C

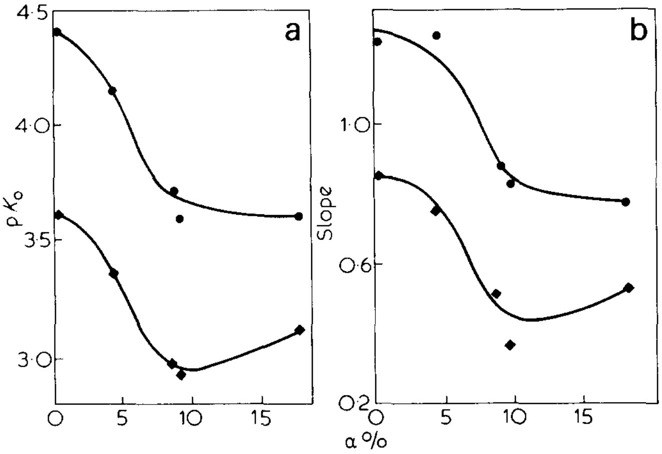


Figure 2 Characteristic titration parameters as functions of the dodecyl content of partially quaternized poly(4-vinyl-pyridine) derivatives. (a) pK_0, (b) initial slope of pK_{app} *vs.* α. ●, 25°C, ◆, 80°C

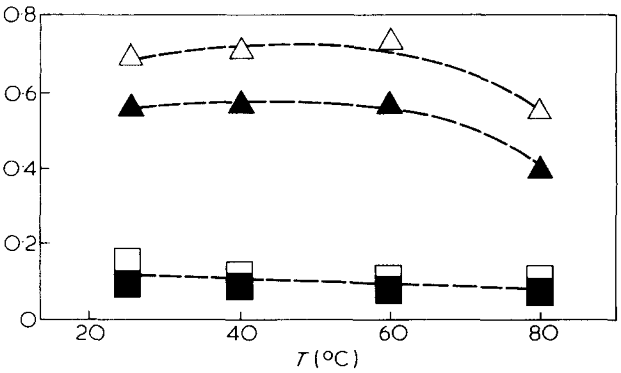


Figure 3 Temperature dependence of the viscosity of two partially quaternized poly(4-vinyl-pyridine) samples. △, Y = 0%; □, Y = 17.6%. In each case empty and filled symbols refer, respectively, to α = 0 and α = 1

Table 1 Titration results on salt-free solutions of poly(*N*-vinyl-imidazole) and two of its dodecyl derivatives

	25°C		80°C	
Y %	pK_0	slope	pK_0	slope
0	5.75	2.9	4.78	2.6
9.3	5.17	2.1	4.50	2.3
27.3	5.22	2.2	4.25	1.9

*Dodecyl derivatives of poly(*N*-vinyl imidazole)*

The samples, described in the experimental section, were titrated at 25°C and 80°C in salt-free and in 0.02 mol dm^{-3} sodium chloride solution. The data for the salt-free solutions are summarised in *Table* 1. The pK_0 values are seen to conform to the trends observed for the poly(4-vinyl-pyridine) derivatives. The slopes of the pK_{app} vs. α curves are considerably steeper than for the previous group of polymers; they are, however, similarly reduced with dodecyl content.

*Poly(4-vinyl-*N*-1-aminoalkylpyridinium)chlorides*

In these derivatives we titrated the amino groups attached via hydrocarbon chains to the quaternary nitrogens of the pyridinium residues. The ionization of the much weaker remaining free pyridine bases may be neglected in the pH region of concern. In *Figure* 4 are shown plots of pK_{app} vs. α for two samples at both 25 and 80°C. The 16% aminododecyl derivative had an additional 40% of pyridine nitrogen atoms quaternized with ethyl chloride. Thus the overall degree of quaternization of the two samples is of comparable magnitude.

Viscosities of the samples were found to increase with α. However, as shown in *Figure* 5, the rate of increase was greater for the aminododecyl derivative, particularly at 80°C, than that for the aminobutyl compound. In *Table* 2 a comparison is made between the viscosity numbers of three polyelectrolyte samples all prepared from the same poly(4-vinylpyridine) fraction with approximately the same degree of quaternization. The polymer concentrations were 1.43–1.51 g/100 cm^3, the solutions contained no added salt or acid ($\alpha = 0$).

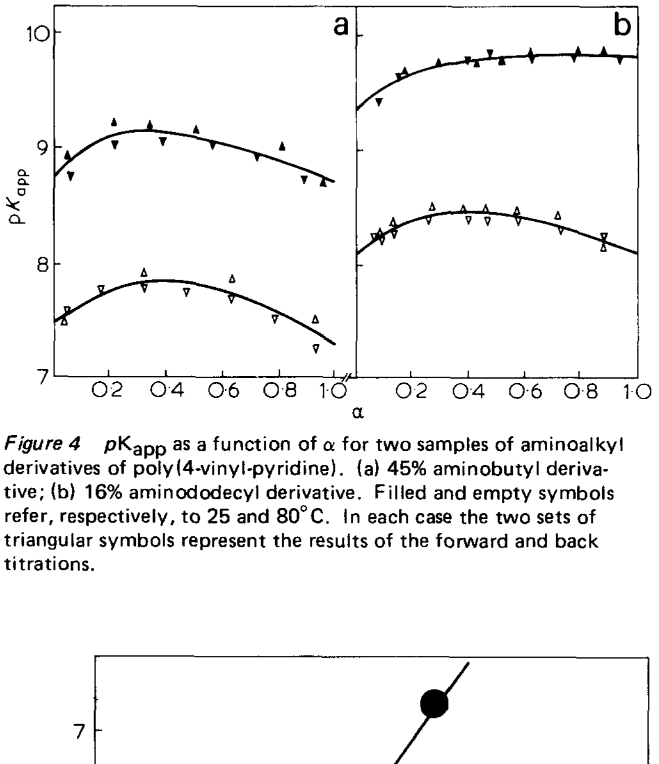


Figure 4 pK_{app} as a function of α for two samples of aminoalkyl derivatives of poly(4-vinyl-pyridine). (a) 45% aminobutyl derivative; (b) 16% aminododecyl derivative. Filled and empty symbols refer, respectively, to 25 and 80°C. In each case the two sets of triangular symbols represent the results of the forward and back titrations.

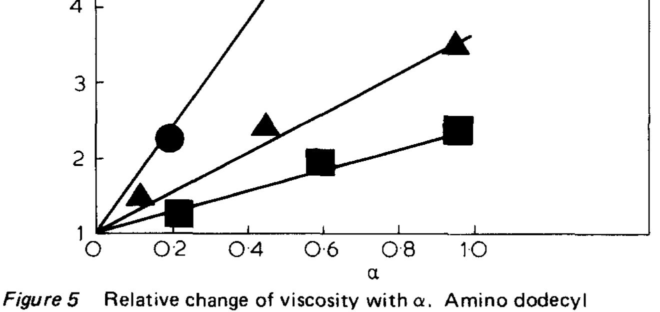


Figure 5 Relative change of viscosity with α. Amino dodecyl derivative at ●, 80°C and ▲, 25°C, ■, aminobutyl derivative at 25°C

Table 2 Viscosity numbers (η_{sp}/c) of quaternized derivatives of a poly(4-vinyl-pyridine) sample

Derivative	η_{sp}/c	
	25°	80°
60.9% ethyl	2.62	1.94
47% ethyl, 9% dodecyl	0.55	0.40
40% ethyl, 16% aminododecyl	0.33	0.07

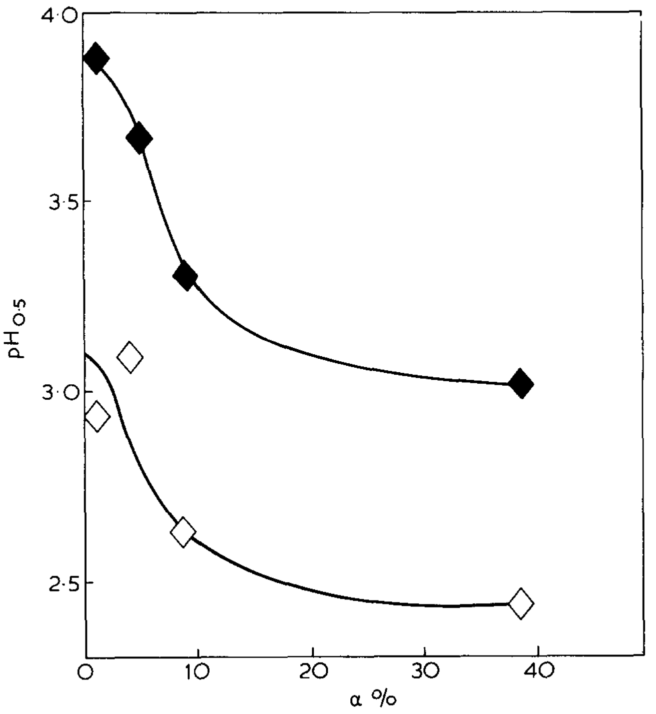


Figure 6 pH at α = 0.5 as a function of dodecyl content of cross-linked quaternized derivatives of poly(4-vinyl-pyridine). ♦, 25°C; ◇, 80°C

Cross-linked resins

No attempt was made to calculate values of pK_{app}[13]. Values of the pH at $\alpha = 0.5$, $pH_{0.5}$, are plotted against dodecyl content of the cross-linked alkyl derivatives in *Figure* 6. Finally, *Figure* 7 shows the titration results for a cross-linked amino-butyl and an aminododecyl derivative.

DISCUSSION

Our primary aim has been to test the validity of the assumption that by judicious molecular engineering, and on the basis of our present understanding of the hydrophobic effect, improved thermally regenerable ion exchange resins may be prepared. Accordingly, we were looking for large effects and we shall be considering the broad features only of relevant polyelectrolyte and polysoap models.

Alkyl derivatives

The existence of a polyelectrolyte to polysoap transition which occurs on increasing the long chain alkyl content of polyelectrolytes is well known and the analogy between this transition and the critical micelle concentration of ordinary soaps has been demonstrated[14]. Our results on the alkyl derivatives of both poly(4-vinyl-pyridine) and poly(*N*-vinyl-imidazole) shown in *Figure* 2 and *Table* 1 established that the basicity of ionizable groups in such materials is equally dependent on the long chain alkyl content. Moreover, on the basis of these data, augmented by those shown in *Figures* 3 and 6, we may assert that no major conformational transitions take place as a function of either ionization or temperature in these materials irrespective of whether the alkyl derivatives studied were polyelectrolytes or polysoaps. We note that even those dodecyl derivatives of poly(4-vinyl-pyridine) which are very near the critical region of the polyelectrolyte to polysoap transition with $Y = 4.4\%$ and $Y = 8.7\%$, respectively, were found to exist as polyelectrolytes and as polysoaps, respectively, under all conditions of ionization and at both temperatures studied.

We conclude that the positions of the potential charged groups (free pyridine nitrogens) are such that, upon ionization, they do not disrupt the hydrophobic effect operating between the non-polar hydrocarbon chains. A model that would conform to the above conclusion is shown schematically in *Figure* 8; the titratable pyridines

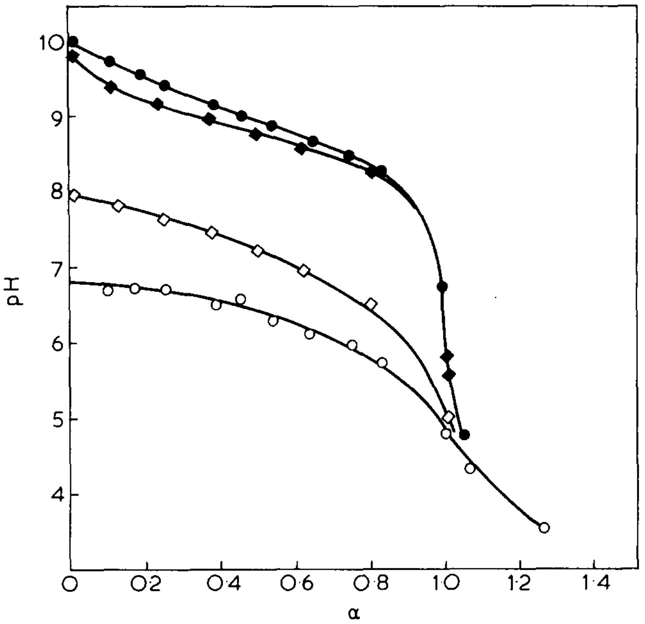


Figure 7 pH as a function of α for crosslinked aminoalkyl resin derivatives of poly(4-vinyl-pyridine). ○, aminododecyl derivative; ◇, amino-butyl derivative. Filled and empty symbols refer to temperatures of 25 and 80°C, respectively

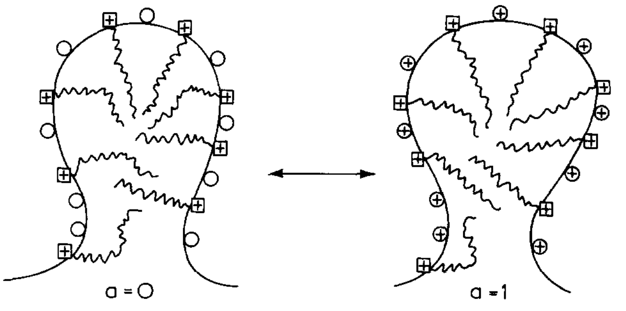


Figure 8 Schematic representation of the conformational changes upon ionization of dodecyl derivatives of poly(4-vinyl-pyridine). □, quaternized pyridinium nitrogens; ○, titratable nitrogens

are shown as being situated on the external boundaries of micellar aggregates produced by the long chain alkyl residues along the polysoap chain. Firstly, the ionization of the pyridine groups tend to enhance the hydrophobic effect, rather than disrupt it, by increasing the hydrophilic nature of the water/micelle interface. Secondly, compared with a corresponding random-coil polyelectrolyte, the charge density near a pyridine group due to the quaternary nitrogens would be higher in the polysoap and, correspondingly, the basicity of the group lower. Thus the trend in pK_0 values shown in *Figure* 3 and that in $pH_{0.5}$ of *Figure* 7 could be rationalized as well. Thirdly, according to the model the ionizable groups are in close proximity to hydrophobic pockets. Upon ionization an increase in polarity and dielectric constant near the micellar interface would occur providing a possible explanation, as suggested by Hamann[4], for the significant flattenning of the polysoap titration curves observed.

Finally, the effect of temperature on the basicity of the ionizable groups is of interest. We shall use[15] the value of pK_{app} at half-neutralization to define the thermal effect as:

$$\Delta(pK_{app})_{0.5} = (pK_{app})^{25°}_{0.5} - (pK_{app})^{80°}_{0.5}$$

We found no evidence that the thermal effect differed for corresponding polyelectrolytes and polysoaps. The mean values of the thermal effects are $0.57 \pm .08$ and $0.86 \pm .06$ pH units for the poly(4-vinyl-pyridine) and poly(*N*-vinylimidazole) derivatives, respectively. As defined in the 'Results' section, pK_{app} is related to the dissociation of the conjugate acid and the thermal effect above incorporates that due to the ionization of water. In the first approximation we may write[4] for the thermal effect of the base:

$$\Delta pK_b = \Delta pK_w - \Delta pK_{app}$$

Since $\Delta pK_w \approx 1.40$ we see that the polybases are stronger bases at high temperature than at low temperature.

Aminoalkyl derivatives

The dependence of pK_{app} on α, shown in *Figure* 4, has similar trends for both the aminobutyl and aminododecyl derivatives. The viscosity results shown in *Figure* 5 imply that a substantial expansion of the polymers takes place with increasing degree of ionization of the amino groups. Since the polymers are relatively highly charged due to the quaternary nitrogens even at $\alpha = 0$, chain expansion would reduce the charge density in the vicinity of free amine groups resulting in a gradual increase in their basic strength by 0.2–0.4 pH units in the 0–0.3 range of the degree of protonation. The following flat portions of the pK_{app} vs. α curves would seem to indicate that at this stage the amine groups are sufficiently separated to titrate like an aliphatic amine with a single dissociation constant. At high values of α a gradual decrease in basic strength is observed for the aminobutyl derivative as significant electrostatic interactions between protonated amino groups occur. This last effect is much less significant for the aminododecyl sample due, presumably, to the low percentage of amino groups. However, superficially there appears to be no evidence for any significant differences between the titrations of the two samples at either of the two temperatures studied.

More information may be derived from a consideration of the numerical magnitudes of the pK_{app} values at 25°C. The pK_a values of aliphatic amines[16] is uniformly near 10.65. However, in the polymers the basicity of the amino groups is expected to be depressed by the electrostatic effect of the quaternary nitrogen atoms to which they are attached. A comparison should, therefore, involve the pK_2 values of aliphatic diamines, $NH_2 \cdot (CH_2)_n \cdot NH_2$, provided a correction is made[17] for the statistical factor of $\log_{10} 4 = 0.60$ which is not applicable to the unsymmetrical aminoalkyl derivatives of poly(4-vinyl pyridine). In the absence of any other effects, a value of $pK_a \approx 9.95$ at 25°C is given to the aminobutyl derivative. On the basis of such data it is concluded that with $n = 12$, no electrostatic effect is likely to exist between the two amino groups. Therefore, the pK_a of the aminododecyl derivative is expected to be ~ 0.7 units higher than that of the aminobutyl derivative. Reference to *Figure* 4 shows experimentally that both pK_{app} values are found to be lower than expected at $\alpha = 0$, and the difference between them is only ~ 0.45 of a pH unit. The generally lower basicity of the amino groups in the polymers compared with that of the monomeric analogues may be attributed to the overall polyelectrolyte effect. Since the degree of quaternization of the polymers is of comparable magnitude the comparatively larger loss in the basicity of the aminododecyl derivative implies that it has a more compact conformation resulting in a higher overall charge density and polyelectrolyte effect.

The viscosity data on these polymers fully substantiates the above conclusions. From *Table* 2 is is seen that at $\alpha = 0$ the aminododecyl derivative has a molecular compactness comparable with that of dodecyl polysoaps at both temperatures studied. From *Figure* 5 one sees that upon ionization of the amino groups the molecular compactness gradually diminishes with, presumably, a corresponding gradual transition from polysoap to polyelectrolyte. As the polyelectrolyte state is approached, as expected, the difference in pK_{app} between the aminobutyl and aminododecyl derivatives tends to ~ 0.7, the value predicted for such circumstances.

Based on this evidence we may assert that, in contrast to the alkyl polysoaps, the aminododecyl derivatives studied undergo a polysoap to polyelectrolyte transition with increasing α. However, no dramatic change occurs either in the basicity of the amino groups or in the viscosity of the solutions: the disruption of the compact structure is not a highly cooperative process. *Figure* 9 presents a schematic model consistent with the above considerations. It is envisaged that when $\alpha = 0$ the molecule is relatively compact due to pockets of aggregated hydrophobic groups. The micellar structure is stabilized,

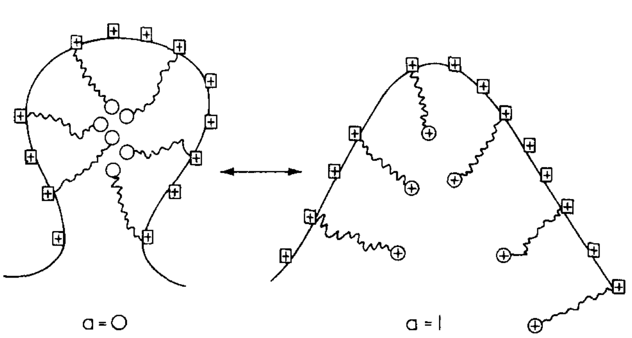


Figure 9 Schematic representation of the conformational changes upon ionization of amino-dodecyl derivatives of poly(4-vinylpyridine). Symbols as in *Figure 8*

as for the model shown in *Figure* 8, by the charged quaternary nitrogens near the periphery of the pockets. The free amino groups are thought to be largely incorporated into the hydrophobic regions. Upon ionization of the amino groups the size of the hydrophobic pockets gradually decreases and the resultant additional hydration is accommodated by a corresponding expansion of the polymer chain.

The magnitude of the thermal effect for both aminoalkyl derivatives was approximately the same, 1.30. Thus, in view of the change in the self-ionization of water over this temperature range, and as explained in the previous section, no significant change occurs in the value of K_b with temperature of the amino groups attached to the polymer backbone. This agrees with our deliberations that led to the model shown in *Figure* 9, which implied that little resistance is offered to the disruption of the hydrophobic pockets by the ionization of the amino groups.

A very different situation may arise in crosslinked aminoalkyl polymers. In *Figure* 7 it may be seen that the titration curve at 25°C of a crosslinked aminobutyl resin and that of an amino dodecyl resin essentially coincide. In view of the discussion presented before one would have expected to find the basicity of the aminododecyl derivative to be higher by about 0.7 units of pK_a than that of the aminobutyl resin. Therefore the results imply that at 25°C the basicity of the amino group in the aminododecyl resin is significantly depressed compared with the aminobutyl resin. At 80°C the difference between the two samples is enormous. The thermal effect observed with the aminobutyl resin is of the same order as that found with the corresponding linear polymer sample; primarily attributable to ΔpK_w that exists between the two temperatures. In contrast $\Delta pH = 3.20$ at $\alpha = 0$ for the aminododecyl resin which, after allowing for $\Delta pK_w \approx 1.40$, corresponds to a more than 60-fold decrease in K_b of the amino group upon an increase of temperature from 25 to 80°C.

According to the model depicted in *Figure* 9 crosslinking of the polymer backbone may aid the preservation of hydrophobic pockets since local chain expansion would be hindered. It would seem that the ease of the ionization and hydration of amino groups incorporated in the pockets is subject to a delicate balance between the magnitude of the hydrophobic effect and polyelectrolyte expansion. The very different basicities of the amino groups found at the two temperatures reflect, accordingly, as sensitive indicators differences in the relative magnitudes of these opposing forces.

CONCLUSIONS

We prepared cationic resins that undergo a significant lowering of their base strengths upon an increase in temperature. The significance of our findings extends beyond the practical potential of such materials as thermally regenerable ion-exchange resins. The results vindicate the models that guided our way of thinking and hence, by implication, currently accepted ideas about the hydrophobic effect.

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