HYDROGEN ION EQUILIBRIA IN AQUEOUS SOLUTIONS OF HYDROPHOBIC POLYELECTROLYTES

DESMOND EDGAR JOYCE, B.Sc.(Hons.), Dip.Ed.

Department of Physical and Inorganic Chemistry
University of Adelaide.

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To my wife, Carol, for her love and tolerance,
and my father, for his desire to see me succeed.

I waited patiently for the Lord's help;
then he listened to me and heard my cry.
He taught me to sing a new song,
a song of praise to our God . . .

Psalms 40 : 1 and 3

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Summary

A potentiometric study of aqueous solutions of some weak polyacids and polybases was made at two temperatures, 25.0 and 80.0°C. Viscosity measurements were done to complement the potentiometric results. Cross-linked gels and resins of the polybases were also studied potentiometrically. One of the primary aims of this study was to deduce some of the effects that hydrophobic groups have on the hydrogen ion equilibria and conformations of the polymers concerned.

The series of weak polyacids, poly(acrylic acid), poly(methacrylic acid) and poly(ethacrylic acid), was used as a preliminary test for the effect of temperature and hydrophobic substituents on the acidity and conformations of polyacids. Values for the free energy change of conformation for PMA and PEA were calculated from the potentiometric titration curves. No significant temperature effects on the conformational transition were observed, but there was a decrease in the acid strength of PMA at 80.0°C, compared to both PAA and PEA, for which there was no change in acidity with temperature.

Polyelectrolytes and polysoaps were prepared by quaternising various percentages of the pyridine nitrogen atoms of poly-4-vinylpyridine (P4VP) with ethyl and dodecyl bromides, whilst leaving a significant percentage of the pyridine nitrogens 'free'. The chloride forms were subsequently used for titration. At both temperatures, the transition from polyelectrolyte to polysoap was reflected in changes in the magnitude of apparent p*K* values. No confirmational transitions were induced in individual samples with increased ionisation or temperature. The magnitudes of the apparent p*K* values were then used for comparison with those of hexyl and octyl chloride derivatives of P4VP. Dodecyl chloride derivatives of poly-N-vinylimidazole were prepared, and the potentiometric properties compared with the P4VP derivatives.

A new type of polybase was prepared in which aliphatic amine groups are pendant to a P4VP backbone, resulting in polyelectrolyte and polysoap structures in solution, depending upon the length of the alkyl chain. The potentiometric titration curves of these polymers were more characteristic of aliphatic amines than polyamines. Viscosity measurements showed that the polysoap structure was disrupted with ionisation of the amine groups.

Potentiometric properties of the cross-linked P4VP ethyl and dodecyl chloride derivatives were similar to those of the linear polymers. However, the cross-linked octylamine and dodecylamine resins exhibited a decrease in basicity at 80.0°C that was over and above that observed for the linear polymers and for the cross-linked butylamine resin. The butylamine results were unaffected by cross-linking. An attempt at a molecular explanation for this phenomenon is proposed.

To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma at any university, except where due reference is made in the text.

D.E. Joyce

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D.E. Joyce

Department of Physical and Inorganic Chemistry,
The University of Adelaide,
South Australia.

February, 1978.

CHAPTER I

Introduction

1. GENERAL FRAMEWORK

A large group of polymers consists of the polyelectrolytes, those polymers whose repeating units incorporate ionic or, at least, ionisable groups. Naturally occurring polyelectrolytes are extremely diverse; from the pectic acids of fruit jellies, to the polypeptides involved in enzymatic reactions, to the polyions in cell membranes. The synthetic linear polyelectrolytes are numerous, as evidenced by the many different derivatives prepared from the vinyl monomers alone. One of the reasons for the upsurge in research into synthetic polyelectrolytes is their close relationship with the naturally occurring polyelectrolytes, but relative simplicity of structure of the former compared with the latter. This means that the synthetic forms, which in some respects can be "tailor-made", are more suitable for extensive physico-chemical research.

Polyelectrolytes (excluding the strong electrolyte 'polysalts') may be subdivided according to their electrochemical properties as polyacids, polybases or polyampholytes. Although the polyampholytes form a very important class of polyelectrolytes, they are beyond the scope of this study. The polyacids may possess carboxylic, sulphonic or phosphoric functional groups, while the polybases usually have free or substituted amino groups. Depending upon the degree of ionisation of these ionisable groups, polyelectrolytes may exhibit compact, random or extended conformations in solution. Counterions and coions tend to reduce the electrostatic interactions between the fixed ionised groups on the polymer and consequently the ionic strength of simple, added electrolytes is important.

Hydrophobic polyelectrolytes are those polyelectrolytes which, due to the characteristics displayed by portions of the chain or groups attached to the chain, exhibit hydrophobic properties. The concept of hydrophobic *bonding* was first introduced by Kauzmann (1959) to explain the tendency of the non-polar groups in proteins to aggregate in aqueous environments, and so stabilise the folded configuration in many native proteins. Since then, the debate has raged as to the validity of the bonding idea and as to the origin of the stabilisation energy, but generally there has been widespread acceptance of its existence.

In general, any significant degree of hydrophobic interaction leads to more compact structures for polyelectrolytes than predicted on the basis of electrostatic repulsions and random coil considerations. Major research efforts have accordingly been directed at the effects that such forces have on polyelectrolyte conformations in aqueous solutions. Probably the most attractive goal in this regard is the production of mechanical energy, by transforming chemical energy into mechanical work, the basis of all mechanical performances of the living body.

Water, with its unique solvent properties, plays an essential role in the properties of hydrophobic polyelectrolytes. Firstly, its ability to provide an ionising solvent medium of high dielectric constant accounts for the high solubility of polyelectrolytes in water, as compared with say methanol. Secondly, the driving force for hydrophobic bonding is the rearrangement of the surrounding water molecules upon the introduction of non-polar solutes into water (Némethy and Scheraga, 1962c); the water molecules form a higher order state than is present in bulk water (Frank and Evans, 1945). Consequently, hydrophobic polyelectrolytes in aqueous solution owe their unusual behaviour to the unique properties of water as a solvent.

The experimental techniques used for the investigation of polyelectrolyte phenomena have been numerous. Basically, there are two different types of properties of importance, the equilibrium and the transport properties (Armstrong and Strauss, 1969). The equilibrium properties have been measured by potentiometry (anion and cation reversible), osmotic pressure, membrane equilibrium (dialysis), potentiometric titration (hydrogen ion reversible), solubility, light scattering and dilatometry. The transport properties are those determined from viscosity, sedimentation and diffusion, electrophoresis, conductance and transference, and anisotropy of polarisability.

For hydrophobic polyelectrolytes, the equilibrium properties have been used much more extensively than the transport properties for experimental investigation, although the latter type are essential to the interpretation of many of the phenomena. Equilibrium measurements have involved light scattering, solubilisation of hydrocarbons and dyes, calorimetry, potentiometry (cation and hydrogen ion reversible), surface tension, electric permittivity and U.V.-visible spectroscopy. (For examples of the above techniques, respective references are: Strauss and Williams, 1961; Strauss and Gershfeld, 1954; Anufrieva et al., 1968; Crescenzi et al., 1972; Gekko and Noguchi, 1975; Braud et al., 1974; Jorgensen and Strauss, 1961; Muller, 1974a; Mandel et al., 1967). The transport properties have been characterised mainly by viscosity (e.g. Strauss and Williams, 1961; Braud et al., 1974), with some conductance and electrophoresis (Varoqui and Strauss, 1968). The experimental techniques used in this study have been limited to the correlation of potentiometric titrations with viscosity measurements, as these are two of the recognised methods for determination of conformational transitions of hydrophobic polyelectrolytes in aqueous solution.

Theories of polyelectrolyte conformation in aqueous solution have been reasonably well developed and are based on the existence of long-range electrostatic interactions between the charged groups attached to different segments of the chain. These forces are modified by counterion association and specific ion binding, together with the influence of coions. The two basic models for polyelectrolytes are a spherical model and a chain model (rodlike) (Armstrong and Strauss, 1969). For hydrophobic polyelectrolytes, the theory is less well developed and is still more or less at a qualitative stage. In this field, the most notable attempts at quantification of hydrophobicity are by Tanford (1973) and Nakagawa and Inoue (1964). Although only a minor aspect of this study, some qualitative conclusions are made for a model for hydrophobic polyelectrolytes.

2. SOME TOPICS RELATED TO HYDROPHOBIC POLYELECTROLYTES

In this project, the potentiometric titration characteristics of a number of polyacids and polybases were determined at 25.0 and 80.0°C, and these were correlated with viscosity measurements for some of the polybases. There were several aims and questions posed at the outset:

i) What effect does hydrophobic bonding have on the acidity and basicity of weak polyacids and polybases respectively?

ii) What are the temperature effects on hydrophobic bonding?
and hence

iii) Can large differences in acidity/basicity between the two temperatures be produced by molecular engineering?

iv) Can conformational transitions as a function of ionisation and/or temperature be induced for the production of a mechanochemical energy system?

v) What, if any, are the effects of cross-linking on the basicity of weak polybases?

These questions arose out of the joint problems encountered in the following three topics: a) compact polymer systems, b) the thermal regeneration of ion-exchange resins, and c) mechanochemical energy conversion.

2.1 Compact Polyelectrolytes

The number of synthetic polyelectrolytes known to exhibit a compact conformational state is reasonably large. Quite a number also undergo conformational transitions as a function of ionisation or changes in other conditions.

Biopolymers such as poly-L-glutamic acid, PGA (Wada, 1960; Nagasawa and Holtzer, 1964) and a polycondensate between L-lysine and 1,3-benzenedisulfonyl chloride, PLL (Fenyo, 1974; Muller, 1974a) undergo a helix to coil transition in aqueous solution as a function of ionisation. The compact α-helical structure in PGA is stabilised by interpeptide hydrogen bonds, side-chain carboxyl-carboxyl hydrogen bonds and configurational entropy; hence the expansion to a random coil as the fraction of ionised carboxylate groups increases beyond approximately 30 per cent. However, the compact structure of PLL is most likely stabilised by non-electrostatic forces related to the hydrophobic interactions between the non-polar portions of the chain, and not hydrogen bonds (Fenyo et al., 1974; Muller et al., 1974). The break-up of the compact structure to a random coil at approximately 20 to 30 per cent neutralisation occurs as the electrostatic repulsions counteract the hydrophobic stabilisation energy.

The potentiometric properties of polysaccharides such as carboxymethyldextran, Cm-dextran, and carboxymethylbenzyldextran, Cm-bzl-dextran, give no indication of a compact state, nor a conformational transition (Gekko and Noguchi, 1975). However, the intrinsic p*K* of Cm-bzl-dextran increases with increasing degree of substituted benzyl group. This was interpreted in terms of the change in surrounding water structure caused by the hydrophobic benzyl group. Hence there is a noticeable effect on acidity by hydrophobic interactions, even if there is no observable change of conformation.

The classical conformational transition with ionisation is for poly(methacrylic acid), PMA. The compact structure of PMA at low charge density appears to be stabilised by short-range hydrophobic forces (non-electrostatic). There is also the possibility of some hydrogen bond stabilisation. This compactness leads to anomalous potentiometric and viscometric behaviour for PMA, compared to poly(acrylic acid), PAA, which has no hydrophobic side group (Crescenzi, 1968). Poly(ethacrylic acid), PEA, also displays a conformational transition with ionisation in aqueous solution. The stabilisation energy is proportionately greater for PEA (Fichtner and Schönert, 1977). The stability of the compact state in PMA has also been increased by copolymerising methacrylic acid with increasing proportions of styrene (Conio et al., 1976). (See Chapter III for more details.)

Hydrolysed copolymers of maleic anhydride and butyl/hexyl vinyl ether exist in a compact state at low ionisation and undergo a conformational transition to an expanded, random coil configuration at higher degrees of neutralisation (Dubin and Strauss, 1967 and 1970). Stabilisation of the compact state is due to the hydrophobic interactions between the hydrocarbon side chains. Similar results were found for an alternating copolymer of styrene and maleic acid (Ferry et al., 1951; Ohno et al., 1973), although there is some evidence for secondary stabilisation due to hydrogen bonds in this case (Demchenko and Boiko, 1973).

For all of the polyelectrolytes mentioned, there are two predominant forces operating: i) the long-range interactions due to electrostatic forces, and ii) the shorter-range interactions which are of a non-electrostatic origin, like hydrogen bonds, Van der Waals forces or hydrophobic interactions. There is a balance between these two effects, such that at low charge, the short-range interactions stabilise a compact structure. The electrostatic effects predominate at higher charge densities and hence the structure is that of a random coil. Note that the effect of charge may be reduced by modification of the water structure (e.g. the addition of an organic solvent), and hence the anomalies in the titration curves may disappear under special conditions.

No corresponding anomalous potentiometric titration curves have been reported for any polybases, although hydrophobic interactions do exist in polybases, e.g. a copolymer of styrene and 2-vinylpyridine (Muller et al., 1970). In other words, polyanions undergo conformational transitions which affect their potentiometric properties, but no similar results have been observed for polycations.

Nevertheless, there are many derivatives of both polyanions and polycations that exhibit compact conformations in aqueous solution. These are the polysoaps, the first of which was a dodecyl bromide addition compound of poly-2-vinylpyridine, P2VP (Strauss and Jackson, 1951). Polysoaps have compact structures and display micellar properties, with hydrophobic aggregation of the long chain aliphatic groups, surrounded by the charged or polar groups on the periphery. Octyl bromide addition compounds of P2VP with greater than 25% quaternisation also exhibit polysoap-like structures in aqueous solution. However, hexyl side chains are too short to overcome the electrostatic forces and form compact states (Inoue, 1964 a & b).

More polysoaps were prepared from poly-4-vinylpyridine and dodecyl and ethyl bromide (Strauss et al., 1952), and subsequently a polyelectrolyte to polysoap transition was demonstrated as a function of dodecyl group content (Strauss and Gershfeld, 1954). This was later refined by Woermann and Wall (1960). These results are confirmed in Chapter IV. Anionic polysoaps have also been prepared from weak polyacids. One such example is a morpholine salt of the copolymer between maleic acid and dodecyl vinyl ether (Ito et al., 1964) and the decyl analogue (Varoqui and Strauss, 1968). Numerous other examples of polysoaps have been prepared but are not of particular relevance to this study (e.g. Sinha and Medalia, 1957; Medalia et al., 1959; Cooper, 1971).

There have been no reported conformational transitions in any of these polysoap molecules, either as a function of ionisation or temperature. This seemed a logical point of departure for the investigation of the potentiometric properties of some cationic polysoaps.

2.2 Thermal Regeneration of Ion-exchange Resins

A study of the temperature dependence of weak electrolyte resins by CSIRO has resulted in the production of the 'Sirotherm' resins*, which have the simplicity of thermal, rather than chemical dosing, regeneration. A brief outline of the Sirotherm process follows, from the résumé of Bolto and Weiss (1977).

A mixture of weak acid and weak base resins with specific structural features can be used to adsorb significant amounts of salt (low salinity waters containing up to 3000 mg dm^{-3} of salts can be reduced to the potable limit of 500 mg dm^{-3}), and then the resins regenerated by eluting the bound salt with water at 80 - 90°C. The adsorption step involves the transfer of protons from the carboxylic acid groups of the weak acid resin to the amino groups of the weak base resin, to form the cation and anion exchange sites:

$$\overline{R'CO_2H} + H_2O + Na^+ + C\ell^- \rightleftharpoons \overline{R'CO_2^-Na^+} + H_3O^+ + C\ell^-$$

$$\overline{R''NR_2} + H_3O^+ + Na^+ + C\ell^- \rightleftharpoons \overline{R''NR_2H^+C\ell^-} + H_2O + Na^+$$

$$\overline{R'CO_2H} + \overline{R''NR_2} + Na^+ + C\ell^- \rightleftharpoons \overline{R'CO_2^-Na^+} + \overline{R''NR_2H^+C\ell^-}$$

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*Sirotherm is an ICI Aust. Ltd. trade mark for thermally regenerable ion-exchange resins.

where the bars indicate groups bound to the resin. The equilibria are favourable in the forward direction at ambient temperature, but at 80 - 90°C, in the reverse direction.

It is postulated that the major effect on the reversal of the equilibrium is the temperature coefficient of the ionisation constant of water ($\partial pK_w/\partial T$) (e.g. there is a 25-fold increase in K_w, in other words a 5-fold increase in the concentration of protons and hydroxyl ions, when the temperature of water is raised from 25 to 80°C). Therefore, the hot water provides the acidic and basic regenerants. A simple model has been proposed (Hamann, 1971 a & b), in which K_a and K_b are assumed to be constant, with K_w the only temperature dependent variable. Despite the fact that this theory satisfactorily describes the general features of the thermal regeneration of ion-exchange resins, it cannot predict the magnitude of the "thermal effect" (the decrease in acidity/basicity with heat), but simply ascribes the primary effect to ($\partial pK_w/\partial T$). Even though the changes in K_a and K_b with temperature may only be small, they can have significant effects on the exchange capacities of the resins.

The resin equilibria are influenced by resin structure, K_a and K_b (and their temperature dependence), the ratio of acidic to basic groups, the pH, ionic strength and temperature. These factors make the practical application of a simple concept more difficult than perhaps expected. In order to predict resin behaviour, the equilibrium titration curves of the separate resins at both temperatures are determined, and then the best matching pair, in suitable proportions, can be selected (see Bolto and Weiss, 1977, for specific procedures).

Two features of the titration curves of the resins are particularly important for this study: a) the slope of the curves, and

b) the magnitude of the thermal effect. The buffering capacity of a resin increases as the slope of the titration curve decreases and hence flat, plateau-shaped curves are most suitable. Large thermal effects increase the overlap between the pairs of acid and base titration curves and so increase the exchange capacities. As a result of many unsuccessful attempts to find a more suitable weak acid resin than crosslinked poly(acrylic acid), and the fact that reasonably large variations in the thermal effects were observed for the weak base resins, attention has been focussed on the development of large thermal effects in weak base resins. In this study, the decrease in basicity with increasing temperature of weak base resins with hydrophobic interactions, has been measured (see Chapter V). The aim is to produce resins with large, real changes in basicity (changes in K_b).

2.3 Mechanochemical Energy Conversion

For many years, the possibilities of mechanochemical energy conversion have been appreciated and positively demonstrated for a limited number of crosslinked polymer filaments and gels (e.g. Kuhn et al., 1950; Kuhn and Hargitay, 1951 a & b). By harnessing the solution conformational properties of linear polyelectrolytes in the form of crosslinked networks (e.g. poly(acrylic acid) and poly(methacrylic acid)), it is possible to convert the free energy decrease of the contraction during an isothermal chemical change (uptake of protons), into mechanical work. Hence for the polyacids mentioned, the decrease in molecular chain dimensions associated with the equilibrium,

$$\mathrm{RCOO^- + H^+ \rightleftharpoons RCOOH}$$

can be used to perform mechanical work (e.g. lift a weight). This phenomenon is a manifestation of the balance between long-range electrostatic interactions within the molecule and short-range intramolecular attractive forces (Katchalsky, 1964). This particular sort of working system is aptly called a 'homogeneous pH-muscle' (Kuhn et al., 1960).

A novel mechanochemical system has recently been reported (Osada and Saito, 1975) in which thermo-reversible polymer-polymer complexation provides the working structure. A reversible complexation-dissociation process between poly(oxyethylene), PEG, of molecular weight 2000, and poly(methacrylic acid) operating through cooperative hydrogen bonding, forms a membrane capable of lifting a load of 100 times its own weight. Contractions of up to 40% of membrane length over a 10°C temperature interval, and 70% in the 10 to 65°C range have been reported. By changing the embedding solution (addition of non-polar solvent) the contraction with temperature is reversed. This supports the interpretation that the contraction with increasing temperature is due to the hydrophobic interactions between the methyl side groups of PMA and the oxyethylene backbone in PEG; the small temperature gradient is the driving force for the macroscopic contraction.

In the transition region from polyelectrolyte to polysoap for P4VP derivatives, there exists the possibility that under one set of conditions, the polymer may act as an extended polyelectrolyte, and under another, a compact polysoap (Strauss et al., 1956). If the change in environment necessary to produce such a conformational change in a cross-linked system of this type is small, then a much more efficient mechanochemical energy conversion would be possible.

An extension of this idea is possible if the results of Woermann (1959) are also considered. Cross-linked P4VP and dodecyl halide P4VP polysoap gels undergo large changes in water content in a narrow range of the degree of ionisation of pyridine nitrogen groups. Furthermore, ion selectivity for bromide and chloride ions causes this dramatic change in water content to occur at different values of ionisation. Therefore, if this water content corresponds to molecular dimensions, under particular conditions these gels form the basis for a mechanochemical system, by counter ion exchange (Br^- for $C\ell^-$ and reverse) at constant pH. If there is a true correspondence between water content and molecular dimensions, then this effect should be revealed in the potentiometric properties of such resins. The potentiometric titration curves of resins of this type were determined in this project and a study made of the effects of high temperature (see Chapter V). The hydrophobic interactions should be strengthened at higher temperatures and perhaps affect the degree of ionisation significantly. This is the point of coincidence for conformational changes in polyelectrolytes, thermal regeneration of ion-exchange resins and mechanochemical energy conversion.

2.4 Structure of the Thesis

The theories of potentiometric titration of polyelectrolytes and the temperature dependence of pH are presented in Chapter II, along with some general considerations of polyelectrolyte and polysoap models. Temperature effects on the titration curves of the linear polyacids, PAA, PMA and PEA, together with the effects on the conformational transitions for PMA and PEA, are recorded in Chapter III. Chapter IV contains the potentiometric evidence to support the polyelectrolyte to polysoap transition, as well as minor studies on the effects of alkyl chain length and changes in basic group. The aqueous solution properties of a new type of polybase are also contained in Chapter IV.

In Chapter V, the more obvious effects of cross-linking on the potentiometric properties of the polybases used in Chapter IV are presented. Chapter VI summarises the main conclusions and their general importance. Finally, the experimental details are contained in Chapter VII. SI units have been used throughout this thesis, except where indicated (McGlashan, 1971).

CHAPTER II

Theory and Background

3. POTENTIOMETRIC TITRATIONS

The treatment of the theory of potentiometric titrations that follows is strictly for linear polymers, although a few aspects of the theory of titration of gels and resins are covered in section 3.4.

3.1 Titration of Weak Polyacids and Polybases

Hydrogen ion equilibria for weak acids and bases are conventionally represented in terms of dissociation constants (Bates, 1973). The two general forms for a weak monoprotic acid and a weak monobasic base are respectively:

$$\mathrm{AH} + \mathrm{H_2O} \overset{K_a^{HA}}{\rightleftharpoons} \mathrm{A^-} + \mathrm{H_3O^+} \qquad (\text{e.g. } \mathrm{AH} \equiv \mathrm{RCOOH})$$

$$\mathrm{BH^+} + \mathrm{H_2O} \overset{K_a^{B}}{\rightleftharpoons} \mathrm{B} + \mathrm{H_3O^+} \qquad (\text{e.g. } \mathrm{B} \equiv \mathrm{R'NH_2})$$

where K_a^{HA} and K_a^{B} are the respective acidic dissociation constants. (Strictly speaking, K refers to the thermodynamic dissociation constant, expressed in terms of the activities of species involved. In practice, the conventional dissociation constants measured are defined in terms of the concentration of the species involved, and hence are not always true constants. The dissociation constants to follow refer to the conventional dissociation constants.) The derivation of the classical Henderson-Hasselbach equation follows directly from the definition of K_a:

$$\mathrm{pH} = \mathrm{p}K_a \pm \log\left(\frac{1-\alpha}{\alpha}\right) \qquad (3.1)$$

where + for bases, - for acids and α, the degree of ionisation, is defined as

$$\alpha \equiv \frac{c_{A^-}}{c_{A^-} + c_{AH}} \quad \text{for acids}$$

$$\text{and} \quad \alpha \equiv \frac{c_{BH^+}}{c_{BH^+} + c_B} \quad \text{for bases} \tag{3.2}$$

However, the ionisation of polymers is a highly cooperative process (Manning, 1972), in that the work required to ionise each group is dependent on the polyelectrolyte charge density, and hence the dissociation constant of each ionisable group depends on the state of ionisation of every other ionisable group. Therefore it is convenient to define an *apparent dissociation constant*, K_{app}, of an average ionisable group:*

$$K_{app} = c_H \frac{\alpha}{(1-\alpha)} \quad \text{for acids}$$

$$K_{app} = c_H \frac{(1-\alpha)}{\alpha} \quad \text{for bases} \tag{3.3}$$

where K_{app} is a function of α. This apparent dissociation constant differs from the intrinsic dissociation constant, K_o (the polymeric analogue of K_a^A and K_b^B), due to the work required to remove protons from the increasing strength of the electrostatic field surrounding the polyion, as the ionisation proceeds. Hence, if the electrostatic free energy for the removal of an equivalent of protons at a particular degree of ionisation, α, is $\Delta G_{el}(\alpha)$, then

$$pK_{app} = pK_o \pm 0.434 \frac{\Delta G_{el}(\alpha)}{RT} \tag{3.4}$$

where K_o is the intrinsic dissociation constant characteristic of the ionisable group in the absence of electrostatic interactions with other

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*The treatment here follows closely that of Morawetz, 1965, p. 350.

ionisable groups, and + for acids, - for bases. $\Delta G_{el}(\alpha)$ is quite clearly dependent on α and is related to the electrostatic free energy of the polyion, G_{el}, having ν ionised groups, by

$$\Delta G_{el}(\alpha) = N_A \left(\frac{\partial G_{el}}{\partial \nu} \right) \tag{3.5}$$

where N_A is the Avogadro constant. Equation (3.4) is only strictly valid if non-electrostatic effects are of secondary importance i.e. contributions to pK_{app} from such factors as hydrogen bonding, hydrophobic interactions and configurational entropy have been ignored (Armstrong and Strauss, 1969).

If the polymer analogous Henderson-Hasselbach equation from equation (3.3) is combined with equation (3.4), then

$$\mathrm{pH} = \mathrm{p}K_o \pm \log \left(\frac{\alpha}{1 - \alpha} \right) \pm 0.434 \frac{\Delta G_{el}(\alpha)}{RT} \tag{3.6}$$

where + for acids, - for bases. This is the relationship between pH and α derived originally by Katchalsky and Gillis (1949), and Arnold and Overbeek (1950). For practical considerations, this is normally rewritten:

$$\mathrm{pH} + \log \left(\frac{1 - \alpha}{\alpha} \right) \equiv \mathrm{p}K_{app} = \mathrm{p}K_o \pm 0.434 \frac{\Delta G_{el}(\alpha)}{RT} \tag{3.7}$$

where + for acids, - for bases.

Because of the increase in the electrostatic ionisation energy with increasing charge, pK_{app} would be expected to monotonically increase/ decrease with α. However, complicating factors such as increasing chain expansion and ion pair formation tend to reduce the electrostatic potential surrounding the polyion, with the result that $\Delta G_{el}(\alpha)$ increases less rapidly than in proportion to the charge of the polymer chain. Hence poly(acrylic acid) shows an approximately linear relationship between pK_{app} and α for $0.3 \lesssim \alpha < 0.7$, but at higher degrees of ionisation, there is deviation from linearity that is dependent on the ionic strength. Generally though, for polyacids $dK_{\mathrm{app}}/d\alpha < 0$, due to attraction between the polyanion and hydrogen ions, while the reverse is true for polybases, because the acid strength of a polybase increases with ionisation (base strength decreases) as a result of the repulsive forces between the polycation and hydrogen ions.

The effect of added simple electrolyte is to decrease the electrostatic potential term, $\Delta G_{\mathrm{el}}(\alpha)$, quite drastically (Armstrong and Strauss, 1969). Hence the apparent acidity of a polyacid increases and that of a polybase decreases (basicity increases) with increasing ionic strength. Specific counterion binding also significantly affects the apparent strengths of polyacids and polybases.

An empirical relationship between pK and α, a modified Henderson-Hasselbach equation, was developed by Katchalsky and Spitnik (1947) in which, for polyacids,

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{m}} - n \log\left(\frac{1-\alpha}{\alpha}\right) \tag{3.8}$$

where pK_{m} and n are experimental constants determined from plots of pH versus $\log[(1-\alpha)/\alpha]$, which are approximately linear over much of α ($0.3 \lesssim \alpha < 0.7$). The deviation of n from unity is a measure of the magnitude of the electrostatic effects. However, this relation is strictly empirical and hence of limited application.

3.2 Conformational Transitions

There have been many publications concerning a number of polyacids that exhibit conformational transitions as a function of ionisation; e.g. poly(methacrylic acid) (Leyte and Mandel, 1964;

Nagasawa et al., 1965), copolymers of maleic acid and styrene (Ferry et al., 1951), copolymers of maleic acid and butyl/hexyl vinyl ether (Dubin and Strauss, 1970) and poly-L-glutamic acid (Nagasawa and Holtzer, 1964). The conformational transition in synthetic polypeptides such as PGA, is from an α-helical configuration at low pH (pH < 5) to a random coil at higher pH (pH $\gtrsim$ 5.8, depending upon the ionic strength) (Wada, 1960). This transition has been explained in terms of a breakdown of hydrogen bonding as the carboxylic acid groups become ionised. Although there is a definite conformational transition for the other polyacids mentioned, there is much debate as to the nature of the stabilisation forces, especially for poly(methacrylic acid). However, it seems reasonable that hydrophobic interactions account for most of the stabilisation energy of the compact states.

For polyions that undergo a helix-coil transition, Zimm and Rice (1960) developed a theoretical analysis of the titration curves of Wada (1960), to calculate the free energy change for the helix-coil transition at a hypothetical zero charge. A much simpler thermodynamic argument was proposed by Nagasawa and Holtzer (1964) to give equivalent results. This has since been extended to apply to any conformational transition that manifests itself in the potentiometric titration characteristics.

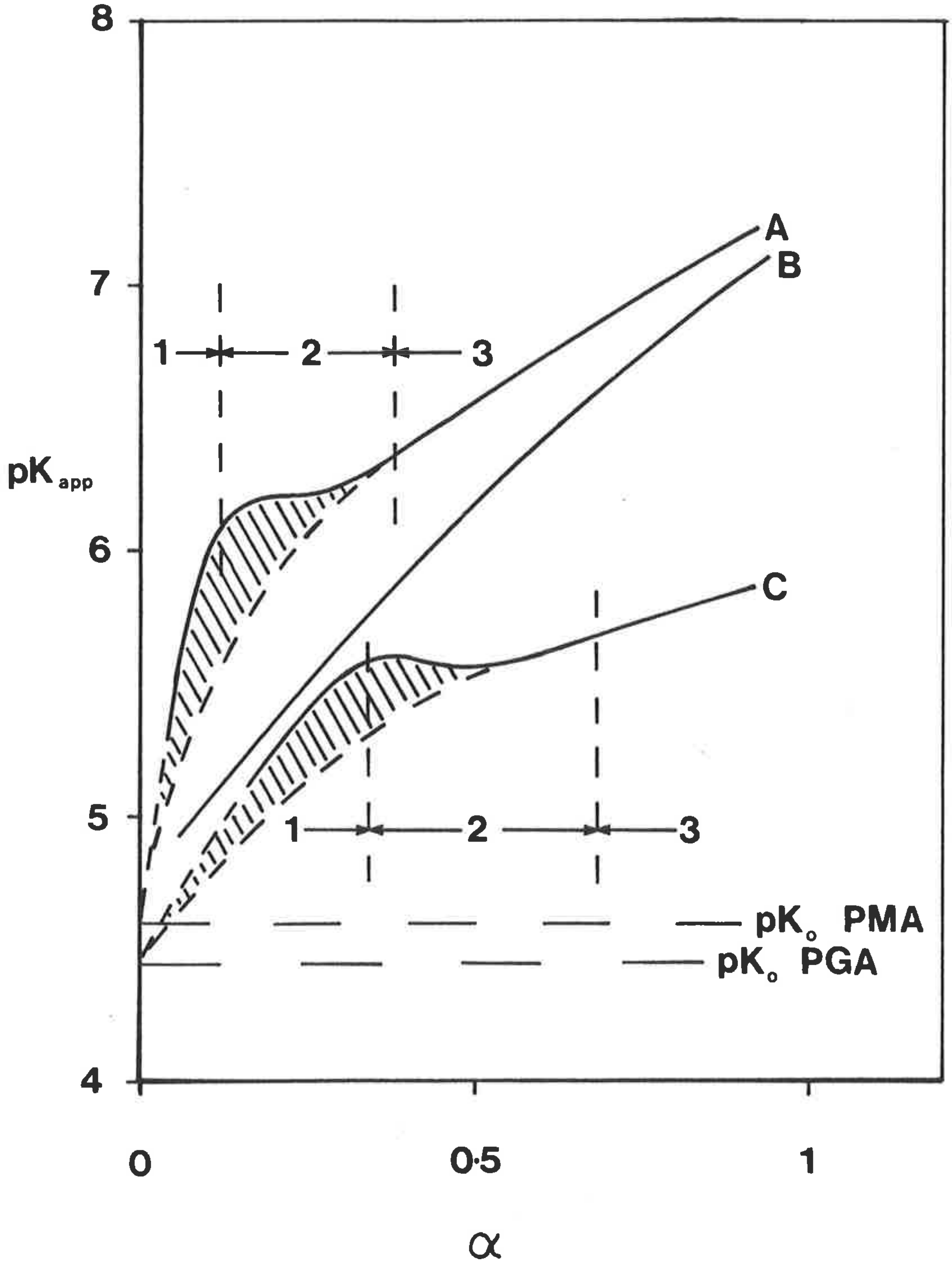
Figure 3.1 shows the typical shapes of titration curves for PAA, PMA and PGA, plotted as pK_{app} versus α. The PAA curve is characteristic of a simple polyelectrolyte that does not undergo a decisive conformational change as a function of ionisation. Both the PMA and PGA results illustrate how the titration curves of any polyacid that undergoes a conformational transition may be characterised by three distinct regions. In region 1, there exists a stabilised, compact configuration, while region 3 is dominated by a highly charged, random

Fig. 3.1 TYPICAL TITRATION CURVES OF WEAK POLYACIDS : EFFECT OF CONFORMATIONAL TRANSITIONS ON CURVE SHAPES

Curve A : PMA Conc. of polymer ≡ 0.00829 monomol dm^{-3} in 0.0100 mol dm^{-3} NaCℓ at 23°C. (Nagasawa et al., 1965).

Curve B : PAA Conc. of polymer ≡ 0.00829 monomol dm^{-3} in 0.0100 mol dm^{-3} NaCℓ at 15°C. (Nagasawa et al., 1965).

Curve C : PGA Conc. of polymer ≡ 0.0188 monomol dm^{-3} in 0.0200 mol dm^{-3} NaCℓ at 25°C. (Nagasawa and Holtzer, 1964).


8
7
6
5
4
pK$_{app}$
0
0·5
1
α
A
B
C
1
2
3
1
2
3
pK$_o$ PMA
pK$_o$ PGA

coil configuration. The middle region, region 2, is that portion representing the compact to expanded state transition. Extrapolation of the experimental data to $\alpha = 0$ yields the intrinsic dissociation constant, pK_o.

In order to calculate the standard free energy change of transition per residue, ΔG_t^o, both the electrostatic and the conformational free energy contributions must be considered, and hence instead of equation (3.6), equation (3.9) is used for polyacids:

$$\mathrm{pH} = \mathrm{p}K_o + \log\left(\frac{\alpha}{1-\alpha}\right) + \frac{0.434}{kT}\left(\frac{\partial G_{ion}}{\partial \alpha}\right) \tag{3.9}$$

where G_{ion} includes electrostatic free energy plus any other free energy changes that accompany ionisation (Nagasawa and Holtzer, 1964), and k is Boltzmann's constant. Hence ΔG_t^o for the process:

(uncharged compact form) ⟶ (uncharged random coil form)

is given by the integral, $\oint \mathrm{d}G_{ion}$, taken over the hypothetical charge cycle:

(compact form at $\alpha = 0$) ⟶ (coil form at value of α above region 2, α_x)

a state

↓

(hypothetical coil form at $\alpha = 0$)

b state

(Zimm and Rice, 1960; Nagasawa and Holtzer, 1964; Dubin and Strauss, 1970.)

$$\text{i.e.} \qquad \Delta G_t^o = 2.303\, RT \int_{\alpha=o}^{\alpha_x} [\mathrm{p}K_{app}(a) - \mathrm{p}K_{app}(b)]\,\mathrm{d}\alpha$$

$$= 2.303\, RTA \tag{3.10}$$

where A is the area bounded by the low α region of the a state curve, the experimental data, and the b state curve (the hatched areas in Figure 3.1).

The procedure for extrapolation of b state titration curve data to low α (hypothetical b state) has been described by Leyte and Mandel (1964). Henderson-Hasselbach plots of pH versus $\log[(1-\alpha)/\alpha]$ yield two linear portions if the polyacid exists in the a state for an appreciable range of α before transition to the b state. Extrapolation of these straight portions into the transition region enables pH(b) values to be obtained, from which $\mathrm{p}K_{\mathrm{app}}(b)$ values can be calculated.

3.3 Temperature Dependence of pH

The treatment of this topic follows that contained in the authoritative text by Bates (1973), "determination of pH: THEORY AND PRACTICE". The currently accepted definition of pH is in terms of the activity of hydrogen ions:

$$\mathrm{p}a_{\mathrm{H}} \equiv -\log a_{\mathrm{H}} = -\log m_{\mathrm{H}}\gamma_{\mathrm{H}} = -\log c_{\mathrm{H}}y_{\mathrm{H}} \qquad (3.11)$$

where m_{H} and c_{H} are molal and molar concentrations and γ_{H} and y_{H} are the activity coefficients on the two concentration scales. This is then directly related to the operational definition of pH through a number of primary buffer standards:

$$\mathrm{pH(S)} \equiv \mathrm{p}a_{\mathrm{H}}$$

for dilute aqueous solutions of low ionic strength. For a quantitative interpretation of pH, "this requirement excludes all nonaqueous media, suspensions, colloids, and aqueous solutions of ionic strength greater than 0.2" (Bates, 1973, p. 103). Nonetheless, semiquantitative interpretations and comparisons in solutions of this kind are still valid.

For strong acids and bases of the 1:1 valence type, at constant pressure and concentration:

for strong acids,

$$\left(\frac{\partial \mathrm{p}a_{\mathrm{H}}}{\partial T}\right)_{P,m} = -\left(\frac{\partial \log \gamma}{\partial T}\right)_{P,m} \tag{3.12}$$

and for strong bases,

$$\left(\frac{\partial \mathrm{p}a_{\mathrm{H}}}{\partial T}\right)_{P,m} = -\left(\frac{\partial \log K_{\mathrm{w}}}{\partial T}\right)_{P} + \left(\frac{\partial \log \gamma}{\partial T}\right)_{P,m} \tag{3.13}$$

Now, for buffer solutions, where the changes in concentration with temperature are neglected due to their insignificant contribution, for a weak acid and its salt,

$$\frac{\partial \mathrm{p}a_{\mathrm{H}}}{\partial T} \approx -\frac{\partial \log K_{\mathrm{a}}}{\partial T} - (2z+1)\,\frac{\partial \log \gamma}{\partial T} \tag{3.14}$$

and for a weak base and its salt,

$$\frac{\partial \mathrm{p}a_{\mathrm{H}}}{\partial T} \approx -\frac{\partial \log K_{\mathrm{w}}}{\partial T} + \frac{\partial \log K_{\mathrm{b}}}{\partial T} - (2z+1)\,\frac{\partial \log \gamma}{\partial T} \tag{3.15}$$

For the preceding equations (3.14) and (3.15), the following equilibria apply:

$$\mathrm{H_2O} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-} \qquad K_{\mathrm{w}} = a_{\mathrm{H}}a_{\mathrm{OH}}$$

$$\mathrm{HA}^{z+1} + \mathrm{H_2O} \rightleftharpoons \mathrm{A}^{z} + \mathrm{H_3O^+} \qquad K_{\mathrm{a}} = \frac{a_{\mathrm{A}}a_{\mathrm{H}}}{a_{\mathrm{HA}}}$$

$$\mathrm{B}^{z} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH}^{z+1} + \mathrm{OH^-} \qquad K_{\mathrm{b}} = \frac{a_{\mathrm{BH}}a_{\mathrm{OH}}}{a_{\mathrm{B}}}$$

where K_{w}, K_{a} and K_{b} are the thermodynamic dissociation constants of water, acid and base,

a_{X} are the activities of species X,

and γ is the activity coefficient of the "average" ion.

The effect of temperature on the activity coefficient, $(\partial \log \gamma/\partial T)$, is small in comparison to that on the dissociation constant, $(\partial \log K/\partial T)$, and hence the variation in pa_H with temperature is very similar to that of pK with temperature. Consequently, the parabolic form of the pK versus temperature curves, which generally have a minimum value in the range 0 to 60°C, largely determines the variation of pa_H with temperature, the minimum being shifted to higher or lower temperatures by the variation in $\log \gamma$ with temperature.

Of particular interest to this study is the difference between the acid and base temperature variation.

> "Most striking, perhaps, is the contrast between the effect of temperature changes on the pa_H of strong acids and on that of strong bases. The pa_H of the former increases slightly with increase of temperature through the influence of the small $\partial \log \gamma/\partial T$ term, whereas the latter reflects the large negative temperature coefficient of pK_w, the water constant. Indeed, as the pa_H value rises above and progressively beyond the neutral point, the ionisation of water with its large heat effect plays an increasingly important part in the equilibria that fix the pa_H value. Hence the pa_H of alkaline solutions usually falls with rising temperature, whereas that of acid solutions usually increases." (Bates, 1973, p. 126)

The situation is not as clear cut for weak acids and bases. However, it is essential to remember that because pa_H is the quantity being measured, and not pa_{OH}, then the dissociation constants obtained from pH titration curves are acid dissociation constants, K_a^{HA} and K_a^B (see Section 3.1). As a consequence of this, any differences in pK_a^{HA} with temperature are direct measures of the change in acid strength of HA, whereas temperature effects on pK_a^B incorporate the increasingly important change in pK_w as pa_H increases. This means that changes in pK_a^B with temperature do not give a direct measure of the change in basic strength of B, but must be corrected to changes in pK_b^B, by subtracting them from the change in pK_w. These values are then directly comparable to those obtained for pK_a^{HA}. In other words, if

$$\Delta pK_a^{HA} = \left(pK_a^{HA}\right)^{T_1} - \left(pK_a^{HA}\right)^{T_2}$$

and $$\Delta pK_a^{B} = \left(pK_a^{B}\right)^{T_1} - \left(pK_a^{B}\right)^{T_2}$$ where $T_1 < T_2$, are the two temperatures

then ΔpK_a^{HA} is not comparable with ΔpK_a^{B}, but rather with $\Delta pK_b^{B} = \Delta pK_w - \Delta pK_a^{B}$.

3.4 Potentiometric Titration of Gels and Resins

Polyacid and polybase gels and resins can be titrated with base and acid respectively by equilibration of an external solution with the insoluble gel phase. In the same way as for a solution, the neutralisation can be followed by measurement of the pH of the supernatant solution as a function of added titrant. These pH titration curves can be used to calculate the capacity of the gel or resin as well as the pK values. The dissociation constants are usually lower than those of a corresponding linear polyelectrolyte and the slopes of the titration curves usually differ. Addition of neutral salt generally produces a change in the acidity or basicity in the direction of the linear parent polymer.

For lightly cross-linked gels in which there is a high degree of swelling, specific interactions between polymeric groups and between fixed and free ions are suppressed to the extent that the gels resemble dilute polyelectrolyte solutions in many characteristics. Katchalsky (1954; Michaeli and Katchalsky, 1957) has proposed a model in which the gel is a matrix of fixed ionic groups; a cross-linked network of chains which are composed of rigid, rod-shaped segments carrying one charged group each. Every chain, which is defined as a network unit between two cross-links, consists of Z segments (on the average); therefore Z characterises the degree of cross-linking. The chains coil statistically.

This theory leads to a relation between the pH of the external solution and the intrinsic pK value, pK_o of a weak acid gel, analogous to equation (3.6) for polyelectrolytes in solution:

$$\mathrm{pH} = \mathrm{p}K_o - \log\left(\frac{1-\alpha}{\alpha}\right) + \frac{0.434}{kTn_m}\left(\frac{\partial G_{el}}{\partial\alpha}\right)_{\overline{V},\overline{K}} + \log\frac{a_{an}}{\overline{a}_{an}} \tag{3.17}$$

where k = Boltzmann constant, T = absolute temperature,

n_m = number of segments in the gel, $\overline{V}$ = gel volume,

$\overline{K}$ = reciprocal of Debye-Hückel ionic radius,

a_{an} = activity of any small univalent anion, quantities with bars refer to interior of gel,

G_{el} is the electrostatic free energy of the gel,

and α = degree of ionisation.

Note that this theory includes the effects of the electrostatic forces acting upon the free energy and entropy of the polymer network, as well as the configurational entropy of the matrix, both of which affect the value of α. This means that pK_o values can be calculated from measurements of the pH of the external solution at various α, provided G_{el} is taken into account; this has been confirmed experimentally (Michaeli and Katchalsky, 1957).

However, this theoretical treatment is limited to weakly cross-linked resins. A more convenient method is to calculate apparent dissociation constants, pK_{app} (Helfferich, 1962). For a weak acid resin titrated with sodium hydroxide,

$$\mathrm{p}K_{app} = \mathrm{pH} + \log[\mathrm{Na}^+] - \log\frac{\boxed{X}}{2} \qquad (\alpha = 0.5) \tag{3.18}$$

and for a weak base resin titrated with hydrochloric acid,

$$pK_{app} = pH - \log[C\ell^-] + \log\frac{[\overline{X}]}{2} \qquad (\alpha = 0.5) \qquad (3.19)$$

where pH ≡ pH in supernatant solution

$[Na^+]$, $[C\ell^-]$ ≡ concentrations of ions in solution

$[\overline{X}] \equiv [\overline{RH}] + [\overline{R^-}]$ is the total concentration of dissociated and undissociated ionogenic groups in the resin.

Hence from a knowledge of the pH, the counterion solution concentration and the concentration of ionogenic groups in the resin, all at 50% conversion, the apparent p*K* value can be computed.

4. THEORETICAL MODELS

There are four types of models that must be discussed in order to set a framework for the discussion of experimental results. These are the polyelectrolyte and polysoap models, the structure of water and the theory of hydrophobic interactions. The model for the structure of water will only be discussed in so far as it relates to hydrophobic bonding.

4.1 Polyelectrolyte and Polysoap Models

Synthetic polyelectrolytes tend to adopt a randomly coiled configuration in aqueous solution that is modified by the mutual interactions of charged groups on the polymer backbone. There are two generally accepted classes of model for polyelectrolytes in solution; a) spherical models, and b) chain models (Armstrong and Strauss, 1969).

The spherical models can be classified into two sub-groups also. Firstly, the polyion is envisaged as being a penetrable sphere through which the charge is uniformly and continuously dispersed. The second type pictures the polyion as an impenetrable sphere with the charge smeared over the surface. Neither model is very realistic in that the charges in a real polyion are much more shielded than the theories predict; hence they overestimate the repulsive forces, leading to polyion expansions that are too great and electrostatic potentials that are too low.

The chain models provide much better predictions of solution behaviour. The polyion is pictured as a stretched rod which is very long compared to its diameter, with the fixed charges either uniformly smeared over the surface of the cylinder, or uniformly dispersed within its volume. Regardless of the conformations of the chain as a whole, this model provides fairly accurate first approximations to the electrostatic behaviour of a real polyion chain segment. Figure 4.1 is an attempt at a diagrammatic representation of this model. At high ionic strength, the surrounding ionic atmosphere is very thin ("sausage" diameter small), when the polyion would be highly coiled. With decreasing ionic strength, the polyion expands and the ionic atmosphere increases in size; in the limit, a rodlike polyion would result. There are also coiled-chain models in which discrete charges are superimposed along a randomly coiled chain at uniform intervals.

Polysoaps are defined as water soluble polymers to whose chain structure soap molecules are chemically attached (Strauss and Jackson, 1951; Strauss and Gershfeld, 1954). There have been many qualitative descriptions of polysoap structure, but only one attempt made at a statistical theory on the solution state of polysoaps, by Nakagawa and Inoue (1964). Three different solution states are qualitatively proposed, as in Figure 4.2. If the cohesive power between attached alkyl groups is weak, there is little association to be expected and the polymer would assume an open, extended structure (a). Moderate cohesive power leads to some aggregation with small pockets of micellar aggregates along the polymer backbone, as represented by (b). A compact, highly aggregated micellar state will form if the cohesive forces are strong (c).

The statistical theory involves the introduction of two parameters; s, the tendency of a soap group to be incorporated into an extant, intramolecular micelle, and σ, the tendency of two non-associated soap groups to form an aggregate. Although the theory involves the assumption that association of soap groups occurs only between nearest neighbours, the predictions are borne out by experimental observations; viz., monosoap to polysoap transition and polyelectrolyte to polysoap transition. Also, it is predicted that soap-like groups in the middle

Fig. 4.1 SCHEMATIC DRAWING OF POLYELECTROLYTE IN PRESENCE OF 1:1 SIMPLE ELECTROLYTE.

Symbols

⊖	Fixed charge on polyanion.
⊕	Dehydrated counterion site bound to polyanion.
⊕	Hydrated counterion.
⊖	Coion.

Dashed line is drawn at Debye-Hückel reciprocal shielding length, $1/\mathcal{K}$; R_c denotes the local radius of curvature of the chain.

(from Armstrong and Strauss, 1969, p. 795).

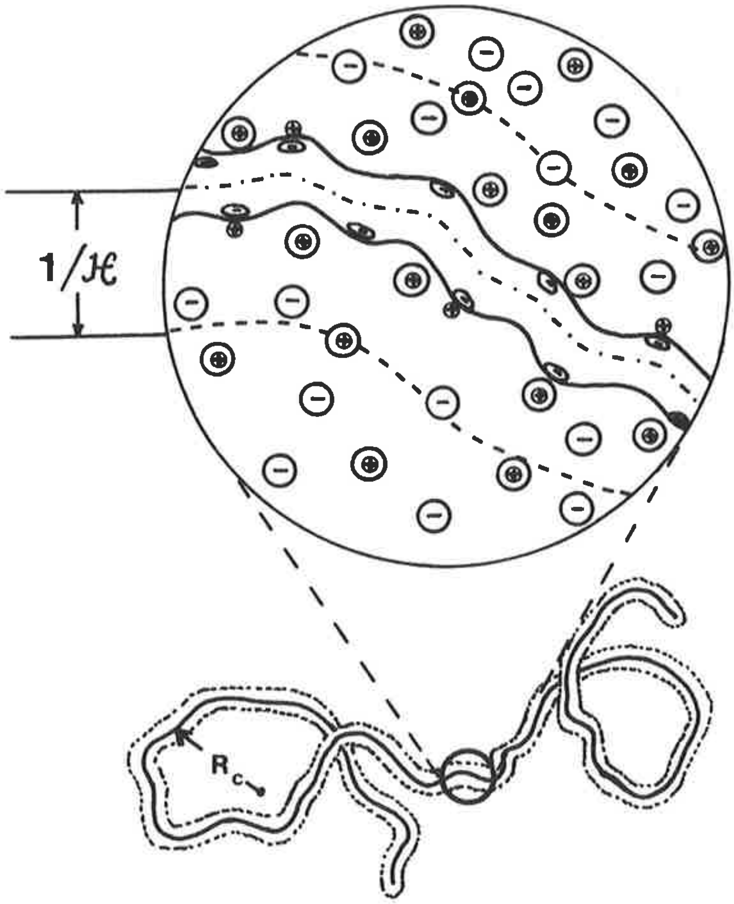
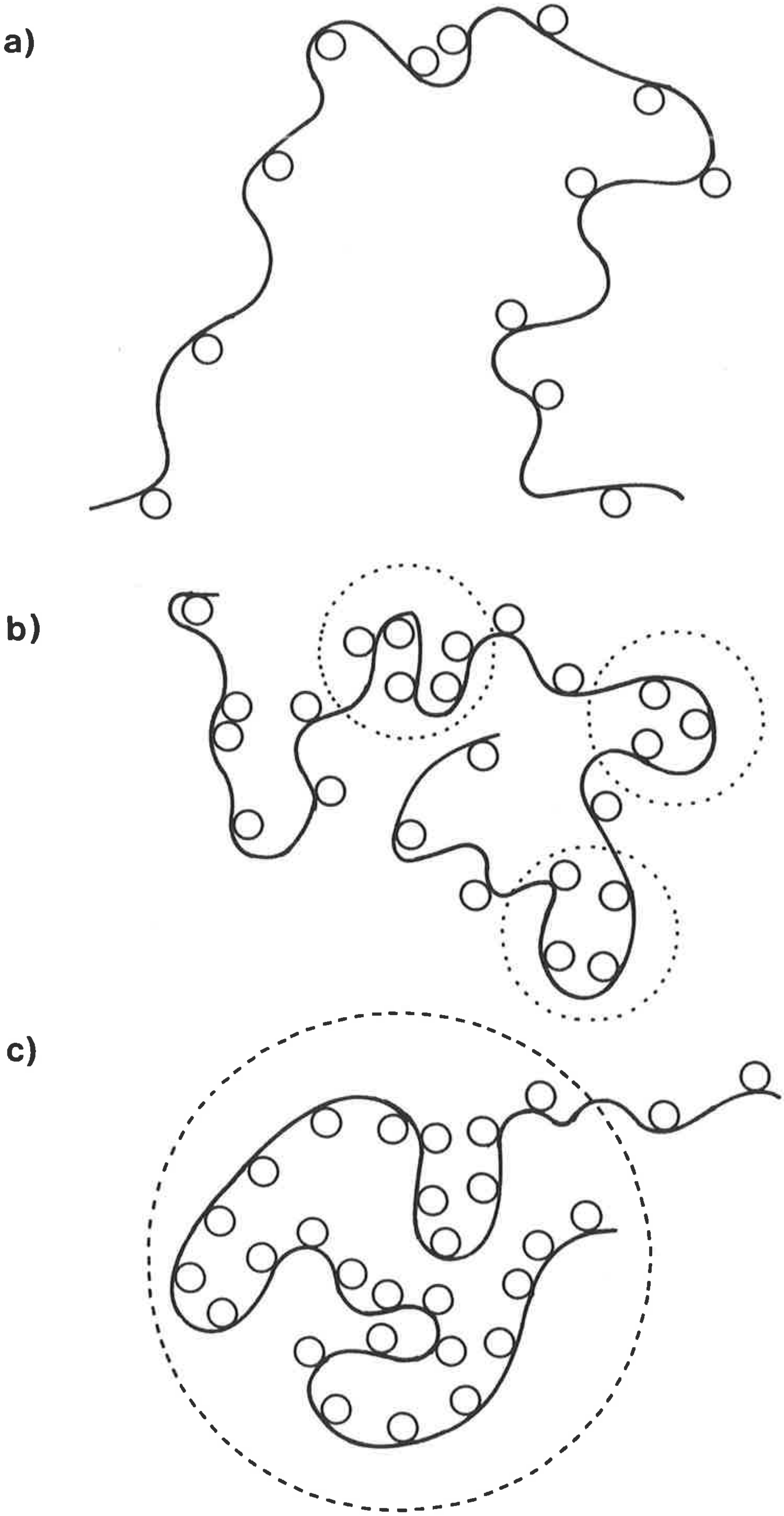

1/ϰ
R_c

Fig. 4.2 SCHEMATICAL ILLUSTRATION FOR SOLUTION STATES OF A POLYSOAP MOLECULE. COHESIVE POWER BETWEEN SOAP-LIKE GROUPS IS a) WEAK, b) MODERATE, c) STRONG.

(from Nakagawa and Inoue, 1964).


a)
b)
c)

of the chain have a stronger tendency to associate than those near the ends.

The most notable qualitative descriptions of the polysoap model have been made by Strauss and coworkers. These are concisely presented in the review of polyelectrolytes by Armstrong and Strauss (1969). Polysoaps exist in solution largely in the form of hypercoiled, intramolecular micelles. Experimental evidence suggests that the polymer resembles a compact coil with a significant fraction of the ionised and ionisable groups buried in the micellar interior, compared to a polyelectrolyte which has essentially all of its ionogenic groups exposed to the solvent. The micellar structure of polysoaps appears to be impermeable to the flow of solvent (nondraining).

4.2 Water Structure and Hydrophobic Interactions

Except where specific reference is made to other authors, the following résumé of the structure of water and hydrophobic bonding is taken from Tanford (1973). The properties of liquid water lead to two types of model, the distorted hydrogen-bond model and the mixture models. The former seems to have gained more acceptance. In either case, there is the unequivocal evidence for the existence of extensive networks of hydrogen bonded water molecules, most of which are arranged in distorted tetrahedra; the average number of nearest neighbours is between 4 and 5, increasing slightly from nearer 4 at low temperatures (approximately 2°C) to nearer 5 at higher temperatures (approx. 80°C). This increase in the average number of nearest neighbours is accompanied by an increase in the average nearest-neighbour distance at higher temperatures; the implication is that there is an average weakening of the hydrogen bond strength (Némethy and Scheraga, 1962a). There is some uncertainty in the validity of either model at higher temperatures, as these authors state that the predictions are not proven at temperatures greater than 70°C.

Hydrophobic substances are defined as those that are very soluble in many non-polar solvents, but only sparingly soluble in water. The tendency of the non-polar groups in hydrophobic substances to adhere to each other in aqueous environments, and in so doing decrease the extent of interaction with the surrounding water, has been called hydrophobic bonding (Kauzmann, 1959). The primary forces responsible for the hydrophobic effect are the strong attractive forces between the isotropically arranged water molecules, which must undergo rearrangements when any solute is dissolved in it; any attractive forces between non-polar groups play a minor role. Rearrangement of the water molecules around non-polar solutes results in a higher degree of order in the surrounding water molecules than in the bulk liquid. Microscopic *"icebergs"* form around the solute, with the water molecules arranged in some sort of quasi-crystalline structure (Frank and Evans, 1945). Hence the stability of hydrophobic interactions is due to the large, favourable entropy effects associated with the changes in the surrounding water structure upon aggregation of these non-polar groups. For the formation of hydrophobic bonds near room temperature, the thermodynamic requirements are that $\Delta G^{o}_{\mathrm{H}\phi} < 0$. The endothermic nature of the transfer of an aliphatic chain from water to a non-polar region ($\Delta H^{o}_{\mathrm{H}\phi} > 0$) is more than compensated by the positive entropy change ($\Delta S^{o}_{\mathrm{H}\phi} > 0$), resulting in a favourable free energy change for hydrophobic bond formation.

Because the formation of hydrophobic bonds is endothermic, the process becomes more favourable with increasing temperature, up to approximately 60°C (Némethy and Scheraga, 1962c). However, at high temperatures, both $\Delta H^{o}_{\mathrm{H}\phi}$ and $\Delta S^{o}_{\mathrm{H}\phi}$ approach zero and tend to negative values at T > 60°C. This is a consequence of the breakdown in water structure at higher temperatures, changing the solubility relationships which are then determined mainly by interaction energies. Under these circumstances, the enthalpy term predominates, producing a large negative $\Delta G^{o}_{H\phi}$.

Although a high degree of ordering of water molecules exists around a non-polar solute, there is no regular variation of $\Delta H^{o}_{H\phi}$ and $\Delta S^{o}_{H\phi}$ with hydrocarbon chain length, indicating that there is no unique arrangement of water molecules favoured. Despite this fact, the enthalpy and entropy terms vary in a mutually compensating manner so that there is a regular variation in the free energy change. "The main conclusion is that the organisation of water at a hydrocarbon-water interface is a makeshift arrangement, subject to alteration as a result of temperature changes as well as changes in hydrocarbon chain length." (Tanford, 1973, p. 21).

When amphiphiles are dissolved in water, that part of the chemical potential arising from solvent-solute interactions, which have a short-range nature, is approximated by the sum of nearly independent contributions from the aliphatic tails and ionic or polar head groups. The hydrophilic head group dominates the junction of itself and the aliphatic tail to the extent that at least one methylene group makes little or no contribution to the hydrophobic effect, while possibly one or two further CH_2 groups may be affected to a lesser degree. However, as the length of the aliphatic chain increases, the hydrophobic effect increases and the solubility decreases. Counteracting this solubility decrease is the tendency of amphiphiles to aggregate cooperatively to form micelles.

Micelles consist of a hydrocarbon core with the polar head groups around the periphery to maintain solubility in the aqueous environment. This micellar core resembles liquid hydrocarbon and may even be more ordered at room temperature than the analogous pure hydrocarbons, depending upon the head group interactions. If the core is highly ordered, the transition to a liquid-like structure may occur at higher temperatures than the corresponding pure hydrocarbon melting point. Even when the interior is liquid-like, it has a higher viscosity than that of a pure hydrocarbon such as dodecane, because of the constraints imposed by aggregation.

In conclusion, there seems to be quite a clear understanding of the factors responsible for hydrophobic bonding and the basic nature of micelle formation at temperatures up to approximately 60 - 70°C. However, there is some uncertainty in the models above this temperature range. Nevertheless, it would be very unlikely that there is a discontinuity in the strength of hydrophobic interactions at higher temperatures than this.

CHAPTER III

Polyacids

5. CONFORMATIONAL TRANSITIONS IN POLYACIDS

As explained in the introduction, those polyelectrolytes that exhibit conformational changes due to hydrophobic bonding are of particular interest. Hence the series of polyacids, poly(acrylic acid), poly(methacrylic acid) and poly(ethacrylic acid) were selected for this study.

5.1 Background

The system which has received a great deal of attention is the PAA, PMA combination. Since it was first recognised that the anomalous titration curve of PMA had significance with respect to polymer conformation and thermodynamics in solution, there has been some dispute as to the correct explanation for this phenomenon. The experimental evidence is overwhelming for the existence of a compact, globular state at low degrees of ionisation ($\alpha < 0.3$) for PMA in aqueous solution (Crescenzi, 1968), whereas PAA exhibits titration curves characteristic of a typical polyelectrolyte. There have been some unconfirmed results, suggesting a conformational transition in PAA (Mathieson and McLaren, 1965; McLaren et al., 1967), although these results were for very high molecular weight samples. As the only difference between PAA and PMA is the methyl side group, there is little doubt that the source of the stabilisation energy is non-electrostatic interaction between these groups. The primary nature of these non-electrostatic interactions was postulated to be either Van der Waals attractions (Leyte and Mandel, 1964; Mandel and Stadhouder, 1964; Mandel et al., 1967) or hydrophobic interactions (Nekrasova et al., 1965; Eliassaf, 1965; Liquori et al., 1966; Nekrasova et al., 1968).

Conclusive evidence has been recently provided (Crescenzi et al., 1972; Braud et al., 1974; Conio et al., 1976) in favour of the hydrophobic bonding, which is primarily responsible for the stabilisation of the compact form at low α. Braud and coworkers show good understanding of Kauzmann's (1959) definition of hydrophobic bonding, in that it reflects the competition between several interactions. It would appear that PMA may be too much of a limiting example to clearly distinguish the features of hydrophobic bonding. The random copolymers of styrene and methacrylic acid (Conio et al., 1976) in water and in water-dioxan mixtures exhibit potentiometric properties that indicate hydrophobic interactions are responsible for the stabilisation of the compact state. Anomalous behaviour for poly(styrene-co-methacrylic acid) and PMA in water is absent for solutions in 40% (v/v) dioxan-water.

As was shown in Section 3.2, the free energy change per residue for the *a* state to *b* state transition, ΔG_t^o, may be calculated from the potentiometric results. The temperature dependence of ΔG_t^o may then be used to evaluate the enthalpy and entropy changes for the transition, ΔH_t^o and ΔS_t^o respectively. This latter quantity is central to the argument in favour of hydrophobic bonding (see Section 4.2). Many values of ΔG_t^o have been calculated, and most of these are summarised in Table 5.1. Although the spread of values is quite large, the standard deviation in the mean ΔG_t^o at 298 K for all ionic strengths is quite good, considering the extrapolation procedures involved in its calculation. The mean value of ΔG_t^o at 298 K is 720 J mol^{-1} (standard deviation = 190 J mol^{-1}), while for all values listed, the mean is 690 J mol^{-1} (s.d. = 180 J mol^{-1}). This indicates that the value of ΔG_t^o is relatively insensitive to ionic strength, temperature and polymer concentration; if there is any variation with temperature, there may be a marginal decrease with increasing temperature.

TABLE 5.1

Summary of Calculated Values of ΔG_t^o for PMA in Aqueous Solutions

ΔG_t^o (J mol^{-1})	T/K	Ionic Strength	Source
920	293	0.1 - 1.0	Nekrasova et al., 1965
507	293	0.003 - 0.1	Leyte and Mandel, 1964
740	278	0.0028	Mandel et al., 1967
645	323		
452	278	0.1	Nekrasova et al., 1968
464	296		
481	308		
498	318		
510	328		
519	338		
552	348		
556	284	0.001	Schäfer and Schönert, 1969
609	291		
718	298		
755	305		
783	312		
770	298	0	Crescenzi et al., 1972
690	298	0.5	
774	298	0	Braud et al., 1974
1004	281	0	Conio et al., 1976
1004	288		
837	308		
753	323		
607	333		

The large scatter in the free energy values means that any derived quantities, namely enthalpy and entropy, are meaningless. Too few values of temperature and lack of constancy of enthalpy and entropy over a defined temperature interval lead to erroneous values of ΔH^o_t and ΔS^o_t. As Crescenzi and coworkers (1972) remarked, this scatter in values cannot be rationalised in terms of ionic strength effects, PMA molecular weight or concentration. A reliable value for ΔH^o_t may be taken from the calorimetric measurements of Crescenzi et al., who have measured ΔH_{diss} values for PMA and PAA for the removal of a proton from the carboxylic acid group. The enthalpy of dissociation for PMA is an increasingly exothermic process which has superimposed on it an endothermic process in a well defined range of ionisation, coincident with the conformational transition. These values of ΔH_{diss} may be approximated to the standard state values of ΔH^o_t. In this way, the ΔS^o_t value may be derived, knowing ΔG^o_t from potentiometry and ΔH^o_t as described. Calculated values were 0.84 J mol^{-1} in water and -0.54 J mol^{-1} in 0.5 mol dm^{-3} sodium chloride at 298 K; in other words, ΔS^o_t is approximately zero at 298 K.

Values of ΔG^o_t for random copolymers of styrene and methacrylic acid (Conio et al., 1976) in the temperature range of 9 to 60°C support the above results for PMA. There is a shallow minimum in ΔG^o_t around 30°C, and thereafter a gradual increase up to 60°C. The calculated entropy of transition is approximately zero below 25°C and decreases gradually to a small negative value at 60°C. These results confirm the existence of hydrophobic interactions, provided that there are two main contributions to the value of ΔS^o_t, the difference of conformational entropy, ΔS_{conf}, and the entropy of formation of the hydrophobic bond, $\Delta S_{H\phi}$. The former contribution is negative, while the latter is positive and a decreasing function of temperature (see Section 4.2). There is a balance between these two contributions that causes the entropy of transition to decrease with increasing temperature.

The simplest test of the validity of the hydrophobic interpretation is to increase the length of the attached alkyl side group. Fichtner and Schönert (1977) have reported preliminary results for poly(ethacrylic acid). A conformational transition occurs over a wider range of ionisation, implying that the mutual interactions stabilising the compact state of PEA are stronger than for PMA. The value of ΔG_t^o was calculated to be 4200 J mol^{-1} monomer^{-1}. The direct implication of the results of PAA, PMA and PEA is that as the length of the attached alkyl side group increases so does the hydrophobic character of the compact state. Hence the stabilisation energy of the compact state at low ionisation increases, as shown by the increasing values of ΔG_t^o; PAA ($\Delta G_t^o \approx 0$), PMA ($\Delta G_t^o \approx 720$ J mol^{-1}), PEA ($\Delta G_t^o \approx 4200$ J mol^{-1}). However, the PEA results must be treated with caution as there may also be a cooperative associational change together with the conformational change, related to the observed cloudiness of solutions.

A physical picture of PAA, PMA and PEA in aqueous solution can be constructed on the basis of experimental evidence. PAA is a flexible, structureless polyelectrolyte which appears to be highly coiled at low α due to random kinking and a degree of hydrogen bonding. With an increase in ionisation, the repulsive electrostatic forces cause chain expansion with a reduction in the entropy of the chain. This expansion is reflected in the increase in viscosity with increasing charge at low α, followed by little change with ionisation at higher α (Braud et al., 1974), as the polymer expands up to approximately 50% charge, after which shielding of charge groups by counterions reduces the repulsive forces. Bak (1962) has postulated that the shape of PAA in solution is such that each -COOH group is surrounded by 8 others in a sphere of radius equal to approximately the separation of two carboxyl groups.

On the other hand, PMA assumes a stabilised, compact globular form in the limit of zero ionisation. This globule expands gradually between $\alpha = 0$ and the degree of ionisation corresponding to incipient transition. Raman spectra (Koenig et al., 1969) of syndiotactic PMA in water indicate that there are progressive changes in the C-COOH motions in the range $0.1 \lesssim \alpha < 0.4$, corresponding to a break-up of the methyl-methyl interactions. This is a progressive transition, and not a cooperative transition as in globular proteins. There are a multiplicity of structures at all degrees of ionisation; at low α they are generally more compact than at high α. The conformation at high degrees of ionisation approaches a random coil, but it is more rigid than the corresponding PAA conformation due to stiffening of the backbone by the methyl groups. The conformational characteristics of PMA and PAA seem to be little affected by temperature (Nekrasova et al., 1968; Schäfer and Schönert, 1969) due to the slight effects of temperature on the hydrophobic interactions.

Finally, PEA must behave in a similar way to PMA except that the polymer backbone would be more rigid. Upon ionisation, the compact structure gradually expands, until at high α values, it exists in a fairly rigid random coil. No temperature dependence studies have been made on PEA.

From the viewpoint of apparent ionisation constants, all three polyacids, PAA, PMA and PEA, behave as typical weak polyacids at high degrees of ionisation. The apparent pK values increase with decreasing ionic strength (e.g. Nekrasova et al., 1965; Schäfer and Schönert, 1969). One unusual feature is that PAA is known to exhibit unusual potentiometric properties in the absence of added, neutral salts, probably as a result of electrostatic repulsions (Miller, 1964). Values of intrinsic dissociation constants, pK_o, of PAA decrease with increasing polymer concentration in the absence of neutral salt, but at concentrations of > 0.01 mol dm^{-3} neutral salt, there is no dependence on polymer concentration (Arnold, 1957). Generally, PAA is a slightly stronger acid than PMA, which is in turn a stronger acid than PEA.

The questions to be answered in this study are:

i) What are the effects of temperature on the acidity of PAA, PMA and PEA?

and ii) What are the effects of temperature on the conformational transitions in PMA and PEA?

5.2 Experimental Results

The potentiometric titration curves of poly(acrylic acid), poly(methacrylic acid) and poly(ethacrylic acid) were determined in aqueous solution at 25.0 and 80.0°C. The relative acid strengths were confirmed, although there were some slight changes at higher temperature.

Weak polyacids are sometimes difficult to titrate in water alone; PAA in particular required abnormally long equilibration times, which resulted in inconsistently high values of pK_{app} at both temperatures. However, in the presence of 0.02 mol dm^{-3} sodium chloride solution, these anomalies were absent. Figure 5.1 shows that the acidity of PAA is independent of temperature. The uniform increase of pK_{app} with α is consistent with the polyelectrolyte theories discussed. Extrapolation of pK_{app} to zero ionisation yields a value of p$K_o \approx 4.9$ at both temperatures.

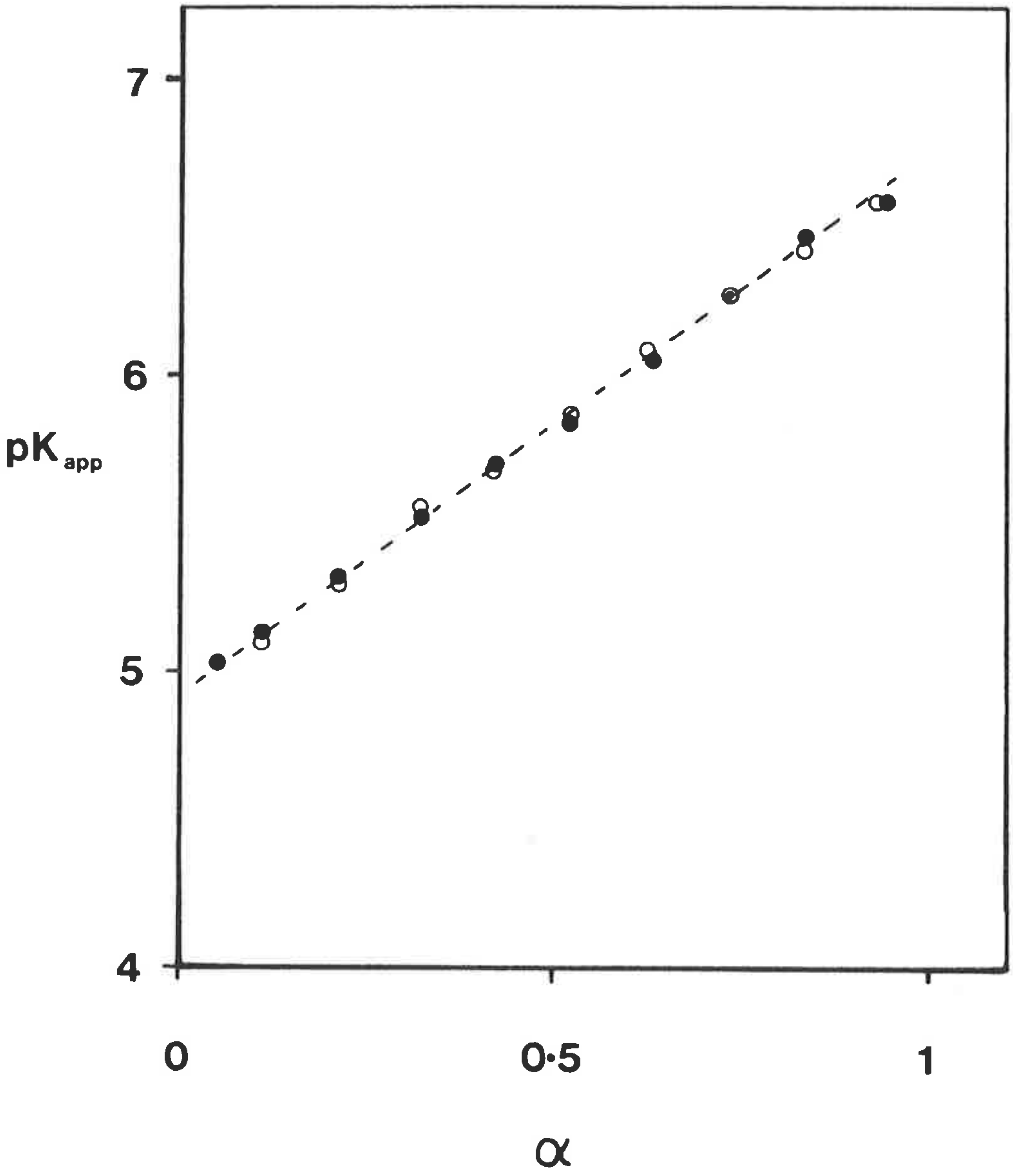
Fig. 5.1 $\mathrm{p}K_{\mathrm{app}}$ vs. α FOR PAA IN AQUEOUS SOLUTION.

Conc. of PAA $\equiv$ 2.00×10^{-2} monomol. dm^{-3} in 0.0200 mol dm^{-3} NaCℓ.

Symbols

● T = 25.0°C

○ T = 80.0°C


7
6
5
4
pK$_{app}$
0
0·5
1
α

The titrations of PAA and PMA were completely reversible in the presence of added sodium chloride. For the purpose of comparison with PEA (the reasons for which will be obvious later), PMA was neutralised with sodium hydroxide, and the sodium poly(methacrylate) then back titrated with hydrochloric acid. Figure 5.2 shows the titration curves obtained in this way together with the hypothetical *b* state titration curves. The obvious feature is that the acidity of PMA decreases with temperature in this 25 to 80°C temperature interval; at half-neutralisation, the apparent acid strength decreases by 0.43 pH units. Although the extrapolations to $\alpha = 0$ are crude, the $\mathrm{p}K_o$ values obtained are 4.2 and 4.4 at 25.0 and 80.0°C respectively. The extrapolated values of $\mathrm{p}K_{\mathrm{app}}$ for the hypothetical random coil have been obtained by the method of Leyte and Mandel (1964), as outlined in Section 3.2. Straight lines in the plots of pH versus $\log[(1-\alpha)/\alpha]$ were obtained by least squares linear regression. The values of ΔG_t^o obtained for PMA are shown in Table 5.2.

TABLE 5.2

Values of ΔG_t^o (J mol^{-1}) for PMA in aqueous solutions at 298 and 353 K

T (°C)	In water	In 0.0200 mol dm^{-3} NaCℓ
25.0	585 ± 20	365 ± 20
80.0	508 ± 25	320 ± 25

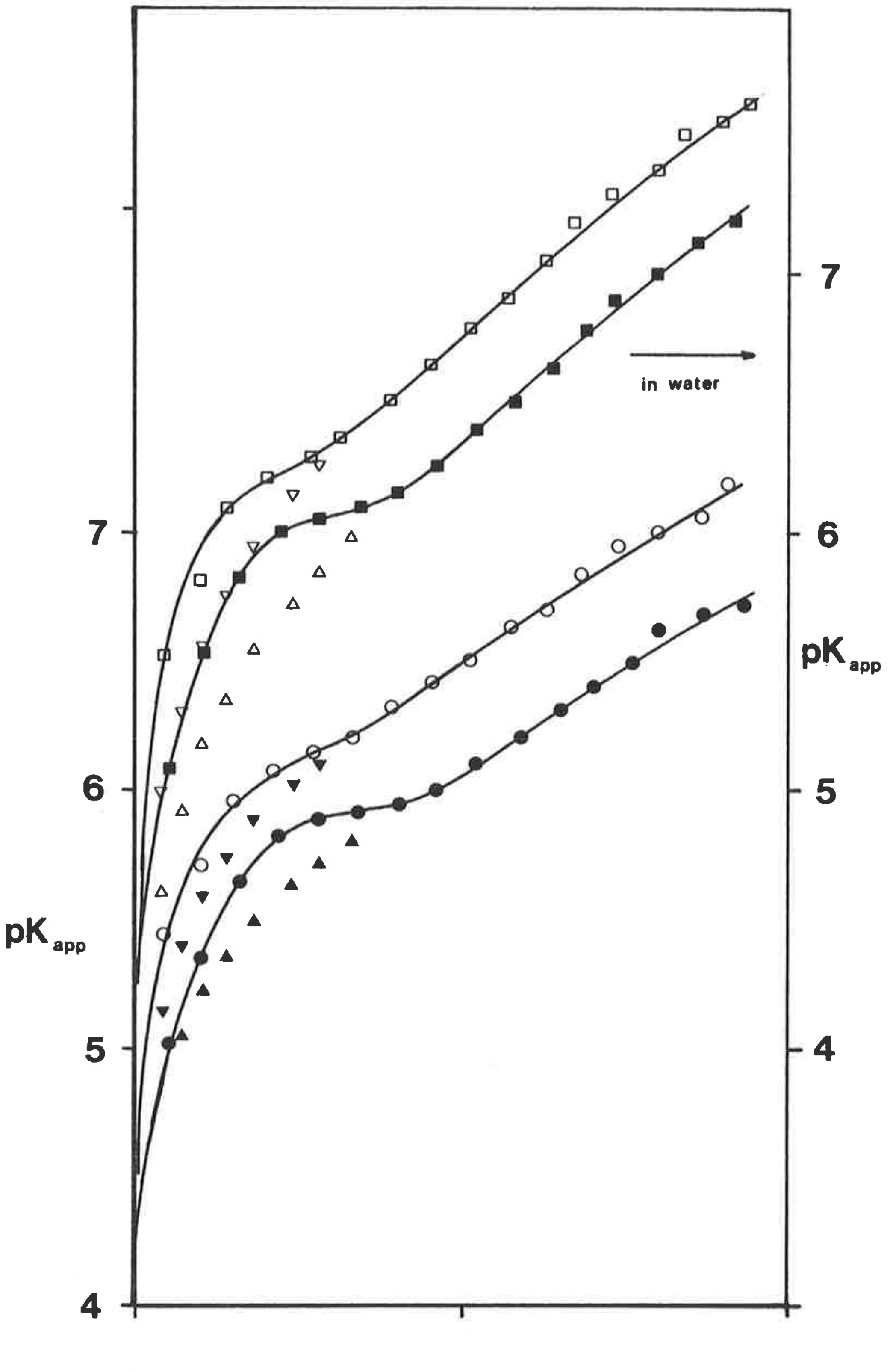
It can be seen that the effect of increased temperature on ΔG_t^o is marginal - there is a slight decrease. The effect of increased ionic strength is to cause a reduction in ΔG_t^o, indicating that the neutral ions shield the fixed charge groups and so reduce the electrostatic

Fig. 5.2 $\mathrm{p}K_{\mathrm{app}}$ vs. α FOR PMA IN AQUEOUS SOLUTION.

Conc. of PMA $\equiv 1.98 \times 10^{-2}$ monomol. dm^{-3}.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
■	T = 25.0°C	●
□	T = 80.0°C	○
	Extrapolated points	
△	T = 25.0°C	▲
▽	T = 80.0°C	▼


pK app
7
6
5
4
0
0·5
1
α
pK app
7
6
5
4
in water

repulsions. These results are in quite good agreement with previously published results.

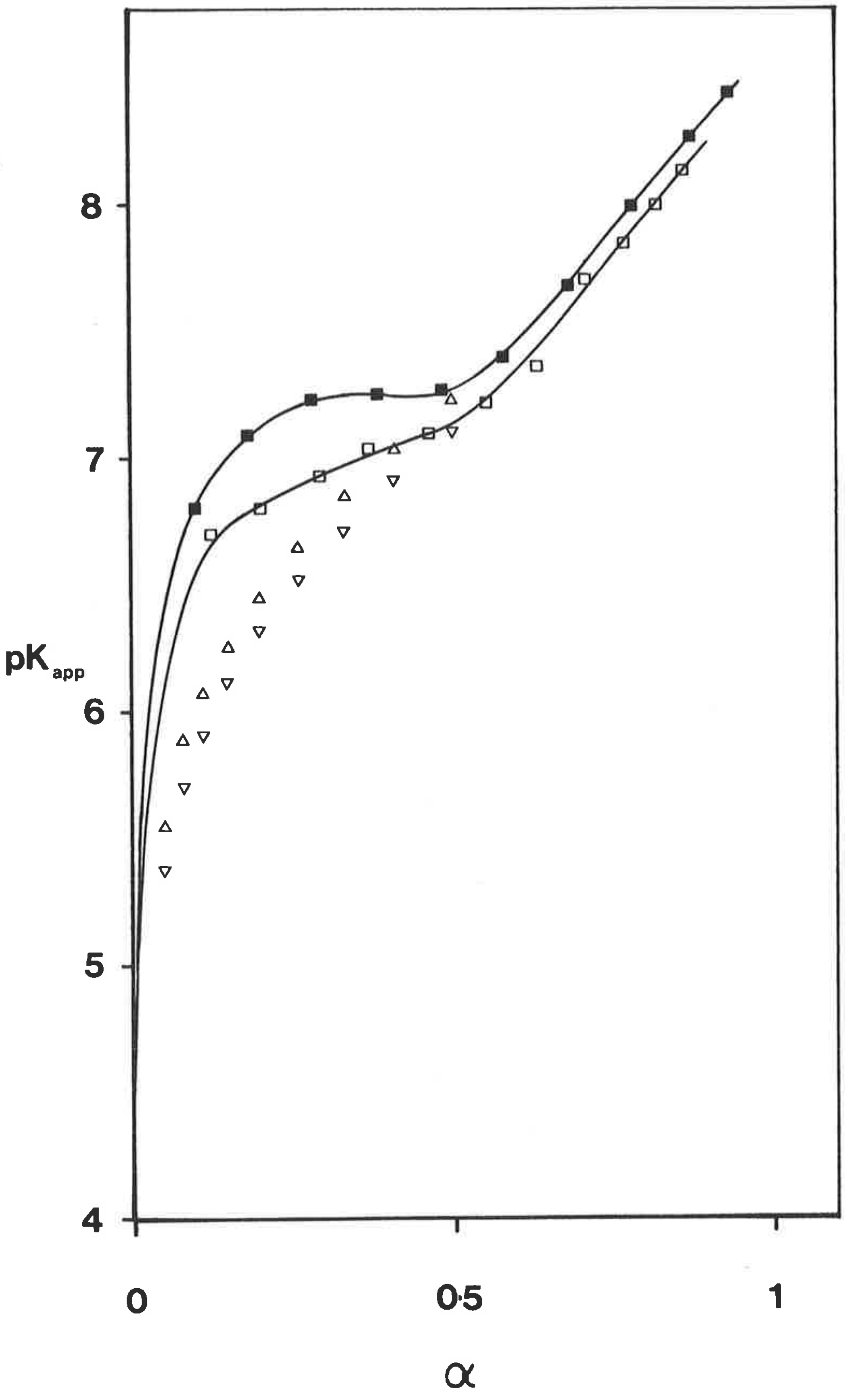
Contrary to the report of Fichtner and Schönert (1977), the sample of PEA prepared for this study did not form a solution in its undissociated form in water. The polymer preparation separated into a dilute solution of PEA in water and solid PEA on standing. Temperature had no noticeable effect on its solubility characteristics. This poor solubility may be explained by the fact that a free radical initiator was used in this preparation, whereas the other authors used a redox initiator; the former type generally produce higher molecular weight polymers. A suspension of PEA in water was titrated with NaOH and a titration curve characteristic of a suspension was obtained. At pH ≈ 8.5 - 9.0 and 7.5 at 25.0 and 80.0°C respectively, the suspension cleared to form a solution which gave a sharp endpoint. Back titration of this sodium poly(ethacrylate) solution with HCℓ was possible over the whole range of neutralisation, without any phase separation. The quantity of base required on the forward titration of the suspension was equivalent to the acid required for back titration of the solution, indicating that all of the suspended polyacid was back titrated as a solution. Figure 5.3 shows the titration curves of PEA obtained for the back titrations together with the extrapolated values of pK_{app} for the transition regions.

Calculated values of ΔG_t^o were 1600 ± 150 J mol^{-1} and 1500 ± 150 J mol^{-1} at 25.0 and 80.0°C respectively. Once again, the free energy change for the transition from compact to random coil form is relatively insensitive to temperature. These values are approximately a third of the magnitude of those reported previously (Fichtner and Schönert, 1977). Consequently, it would appear that an associational change from a two

Fig. 5.3 pK_{app} vs. α FOR PEA IN AQUEOUS SOLUTION.

Conc. of PEA ≡ 1.96 x 10^{-3} monomol dm^{-3} in water.

Symbols	Experimental points	Extrapolated points
T = 25.0°C	■	△
T = 80.0°C	□	▽


8
7
6
5
4
pK_app
0
0·5
1
α

phase to a one phase solution system was responsible for a large part of this previous value. Figure 5.4 illustrates this point, where the titration curves of these authors and of this study at 25.0°C are plotted on the same graph. If the estimate of Dubin and Strauss (1970) for the contribution of one methylene group to the value of ΔG_t^o of approximately 1600 - 1700 J mol^{-1} is correct, then from values of ΔG_t^o for PMA, the predicted value for PEA would be approximately 2200 J mol^{-1}. This means that the value obtained in this study for PEA is very reasonable, and tends to indicate that the increments in contributions to the free energy change of transition for additional methylene groups are not of equal magnitude, but depend on the distance of the particular methylene group from the polymer backbone. In other words, the hydrophobic effect increases disproportionately (at least initially) with increasing alkyl chain length.

In addition to the influence of temperature on the conformational transition, its effects on the acidity of the polyacids is also important. Table 5.3 lists the values of pK_o and pK_{app} at three different degrees of ionisation for PAA, PMA and PEA. If that portion of the titration curve for PMA and PEA concerned with the conformational transition is ignored, then comparison with PAA shows that both PAA and PEA behave quite similarly with respect to acid strength as a function of temperature, whereas PMA shows a marked decrease in acid strength at the higher temperature. This is a real change in acid strength which is completely unrelated to the conformational transition, whereas both PAA and PEA show little change in acid strength with temperature.

Fig. 5.4 COMPARISON OF PEA TITRATION RESULTS IN AQUEOUS SOLUTION AT 25.0°C.

Symbols

△ from Fichtner and Schönert, 1977.

■ from Fig. 5.3.

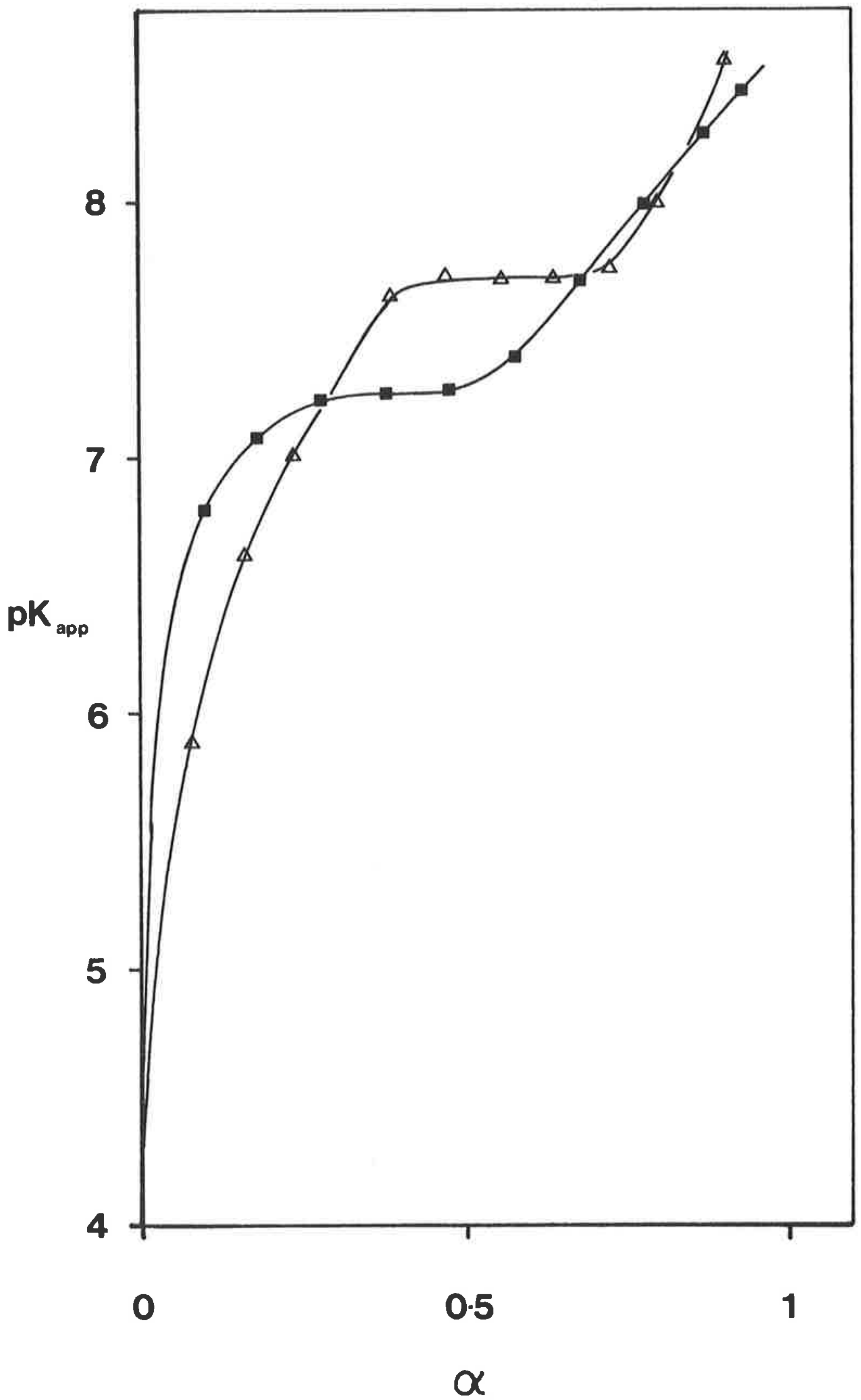

pK_app
4
5
6
7
8
0
0·5
1
α

TABLE 5.3

pK_{app} Values for Polyacids at Three
α Values and Two Temperatures

pK_{app}

Sample	$T = 25.0^\circ C$			$T = 80.0^\circ C$		
	$\alpha = 0$*	$\alpha = 0.50$	$\alpha = 0.75$	$\alpha = 0$*	$\alpha = 0.50$	$\alpha = 0.75$
PAA in 0.02 mol dm^{-3} NaCℓ	4.90	5.83	6.30	4.95	5.83	6.30
PMA in water	4.25	6.33	6.90	4.35	6.76	7.31
PMA in 0.02 mol dm^{-3} NaCℓ	4.25	6.05	6.49	4.50	6.48	6.94
PEA in water	4.35	7.24	7.91	4.25	7.12	7.79

* Extrapolated Values.

5.3 Conclusions

The conformational transitions in PMA and PEA as a function of ionisation have been confirmed potentiometrically, and the results are consistent with the hydrophobic bonding interpretation. An estimate of the contribution to the free energy change of transition for the methylene group penultimate to the backbone of approximately 1000 J mol^{-1} at both temperatures can be made by comparison of PMA and PEA results. This is comparable with previous estimates for this type of contribution, if the reduced effect of groups nearer an ionogenic group is taken into account.

Molecular models of PAA, PMA and PEA were constructed from CPK models. A segment of 19 residues for each polymer was constructed in an atactic sequence, and the photographs of these models are shown in Figures 5.5, 5.6 and 5.7. The segment of PAA was very flexible and could take up a very compact structure or an extended structure. Hence the random coil configuration at zero charge would tend to be compact, whereas that at high charge would be extended. Note that apart from some hydrogen bonding, there are no forces favouring a very compact conformation and hence there is no conformational *transition*. This is in direct contrast to PMA, which has a fairly rigid backbone, with only a limited number of bond rotations possible because of steric hindrances. The aggregation of methyl groups in localised regions is obvious, and there is scope for a reasonable degree of hydrogen bonding. Finally, the backbone of PEA is very rigid; the conformation shown is the only one possible for that sequence without rupturing primary bonds. The aggregation of the non-polar ethyl groups around the carboxyl groups in localised regions is much more extensive than for PMA. (Note also that the 'indented oxygen' atoms had to be used to construct the PEA model, whereas 'full oxygen' atoms were used for PMA, for the doubly bonded

Fig. 5.5 TWO DIFFERENT CONFORMATIONS OF CPK MODEL OF PAA IN ATACTIC SEQUENCE. (19 REPEATING UNITS).

Fig. 5.6 THE ONLY TWO CONFORMATIONS POSSIBLE FOR CPK MODEL OF PMA IN ATACTIC SEQUENCE, FROM DIFFERENT ANGLES. (19 REPEATING UNITS).

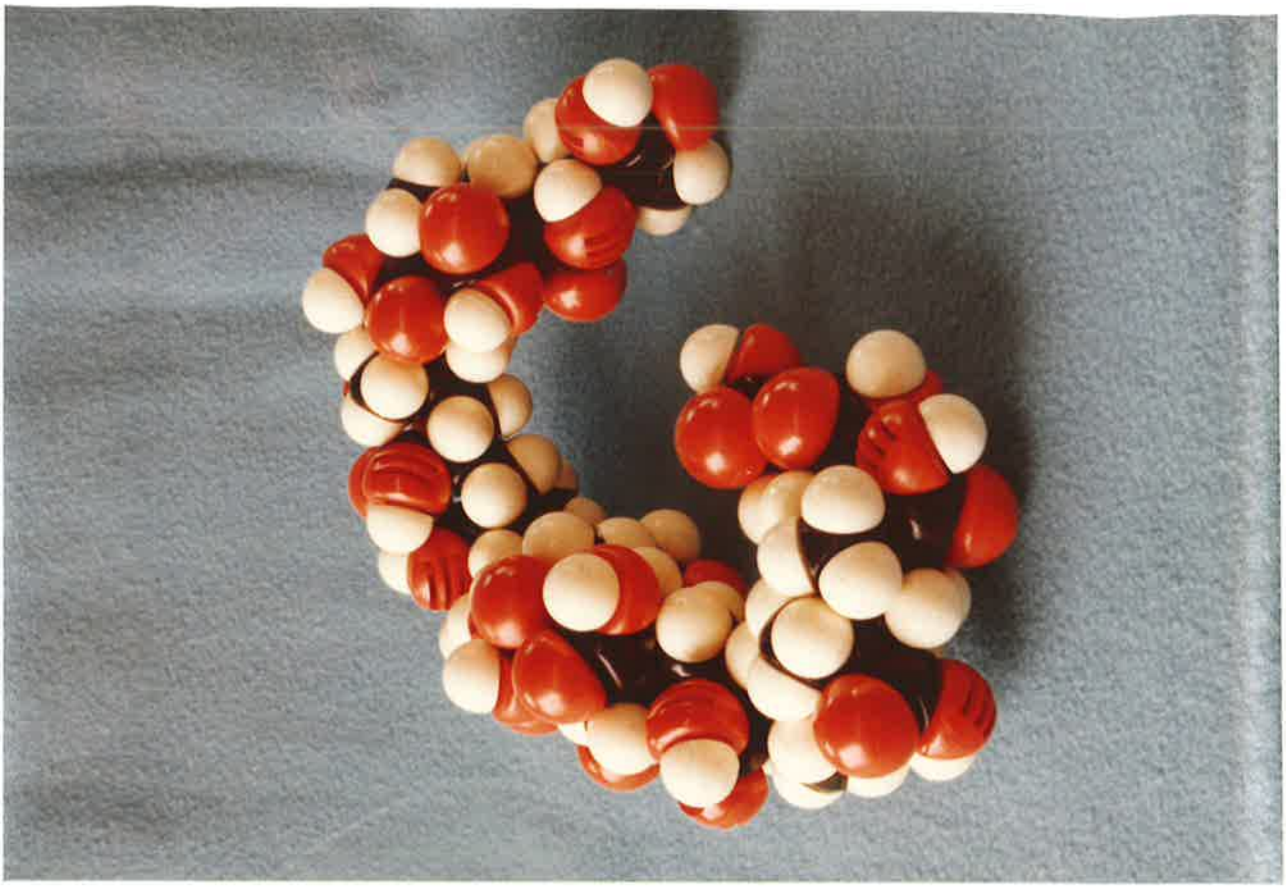


Fig. 5.7 THE ONLY CONFORMATION POSSIBLE FOR CPK MODEL OF PEA IN ATACTIC SEQUENCE, FROM DIFFERENT ANGLES.

(19 REPEATING UNITS).

oxygen atom.) There seems to be less chance for hydrogen bonding in PEA than PMA.

These observations on limited segments of the polyacids titrated may provide the clue to the explanation for the unexpected difference in acidity of PMA at 80.0°C. If PMA can take up a stabilised conformation (by hydrophobic interactions) which is also conducive to the formation of extensive hydrogen bonding between carboxylic acid groups at low temperature, then the effect of temperature will be to enhance the hydrophobic forces slightly, but drastically reduce the hydrogen bonding networks. This effect of increased temperature on hydrogen bonding is well known e.g. poly(glutamic acid). Hence, the reduction in hydrogen bonding between carboxylic acid groups at high temperature leads to a reduced acid strength. The absence of this effect in either PAA or PEA can be explained respectively by the fact that PAA has no stabilisation forces to enhance hydrogen bonding and PEA has such a rigid structure that most hydrogen bonding is precluded by steric factors. This argument is consistent with the molecular models and with the fact that hydrogen bonding is destabilised with increased temperature (Nekrasova et al., 1968).

CHAPTER IV

Polybases

6. POLYSOAPS

Cationic polysoaps have been prepared from the weak polybases, poly-4-vinylpyridine and poly-N-vinylimidazole, by quaternisation with long chain alkyl bromides. The sections to follow are subdivided according to alkyl chain length (Sections 6.2 and 6.3) and parent polymer (Section 6.4).

6.1 Background

Polysoaps are polymers to whose chain structure soap groups are chemically attached; the distance between points of attachment may be varied. As for ordinary soaps, the 'head' groups may be cationic, anionic or non-ionic and the hydrocarbon 'tail' may vary from 10 to 20 methylene groups. In addition, either the hydrophilic or hydrophobic end may be attached to the polymer backbone. (Strauss and Jackson, 1951). For examples of the different types of polysoap structures, see Table 6.1.

The general properties of polysoaps are similar in many ways to those of ordinary soaps. The major feature of all soaps is their ability to form micelles in aqueous solution. Polysoaps also form micellar structures in water, as their molecular compactness and ability to solubilise hydrocarbons demonstrate (Strauss and Gershfeld, 1954). Strauss and coworkers have prepared n-dodecyl bromide derivatives of P2VP as well as a series of P4VP derivatives that were quaternised with n-dodecyl bromide and ethyl bromide. Polysoaps of n-dodecyl bromide derivatives of PVI have been prepared by Salamone et al. (1974). Viscosity measurements have been used to demonstrate the compactness of the polysoap molecules in aqueous solution, while light scattering and solubilisation of hydrocarbons have confirmed these results.

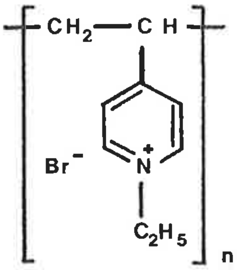
TABLE 6.1

Examples of Polysoaps

Charge	Examples
a) Hydrophilic end attached to polymer backbone.	
Cationic	P4VP, P2VP dodecyl derivatives (Strauss et al., 1952; Strauss and Jackson, 1951)
Anionic	Copolymer of maleic anhydride and dodecyl vinyl ether (Ito et al., 1964)
Non-ionic	poly[methoxy polyoxyethylene 10-(p-styryl)-undecanoate] (Medalia et al., 1959)
b) Hydrophobic end attached to polymer backbone,	
Cationic	poly(diethylaminoethyl methacrylate hydrochloride) (Shatkay and Michaeli, 1966)
Anionic	copolymer of styrene and potassium styrylundecanoate (Medalia et al., 1959)

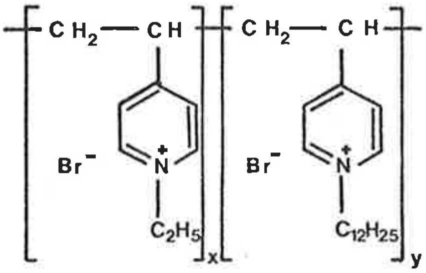
Amphiphiles in aqueous solution tend to aggregate to form micelles only above a certain concentration range known as the critical micelle concentration (cmc). However, polysoaps do not have a cmc, but exist in a micellar state at all concentrations (or in other words, display a zero cmc). (Strauss and Jackson, 1951; Strauss et al., 1952; Sinha and Medalia, 1957; Salamone et al., 1974). This has been explained by considering the restricted movement of soap groups attached to a common polymer backbone; the local concentration of soap groups is greater than any critical concentration at all times (Strauss et al., 1956). Despite the fact that polysoaps do not have a cmc, Strauss and coworkers (1956) have demonstrated that there is a direct analogy between this value for ordinary soaps and the polyelectrolyte to polysoap transition.

Two types of P4VP derivatives were prepared:



where n is large

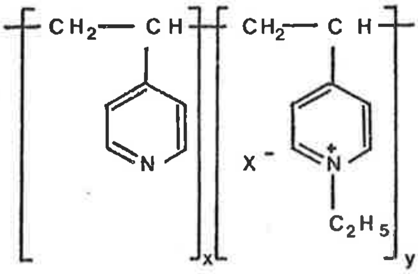
and



where x and y are
large
(random alternation).

The latter type was shown to exhibit either polyelectrolyte or polysoap properties, depending on the degree of dodecyl group quaternisation. This transition from typical polyelectrolyte to typical polysoap behaviour was in the region 6.7 to 13.6% dodecyl group content, and has since been refined by Woermann and Wall (1960) to the range of 5.8 to 8.1% dodecyl group content. In addition, they have demonstrated that the transition occurs at slightly higher values of quaternisation for polymers with chloride counterions compared to those with bromide counterions. Figure 6.1 shows this dependence of viscosity on dodecyl group content. In direct analogy with the cmc for ordinary amphiphiles, this was explained by a 'critical dodecyl group content'. Hence the discontinuity in viscosity as a function of dodecyl group content is interpreted in a similar way to the measured discontinuities in conductance, electrical transport and e.m.f. as a function of concentration for ordinary soaps.

In order to maintain a constant charge density along the polymer backbone, Strauss and coworkers quaternised all available pyridine nitrogen atoms with either ethyl or dodecyl groups. However, for a potentiometric study of the polybase properties, a reasonable percentage (⩾ 30%) of the pyridine nitrogen atoms must be left 'free'. Sufficient charge density is required for water solubility and in practice, this means that approximately 25% of groups must be quaternised with ethyl groups. Consequently, a series of polymers of two basic structures was prepared:



where x and y are
large
(random copolymer)

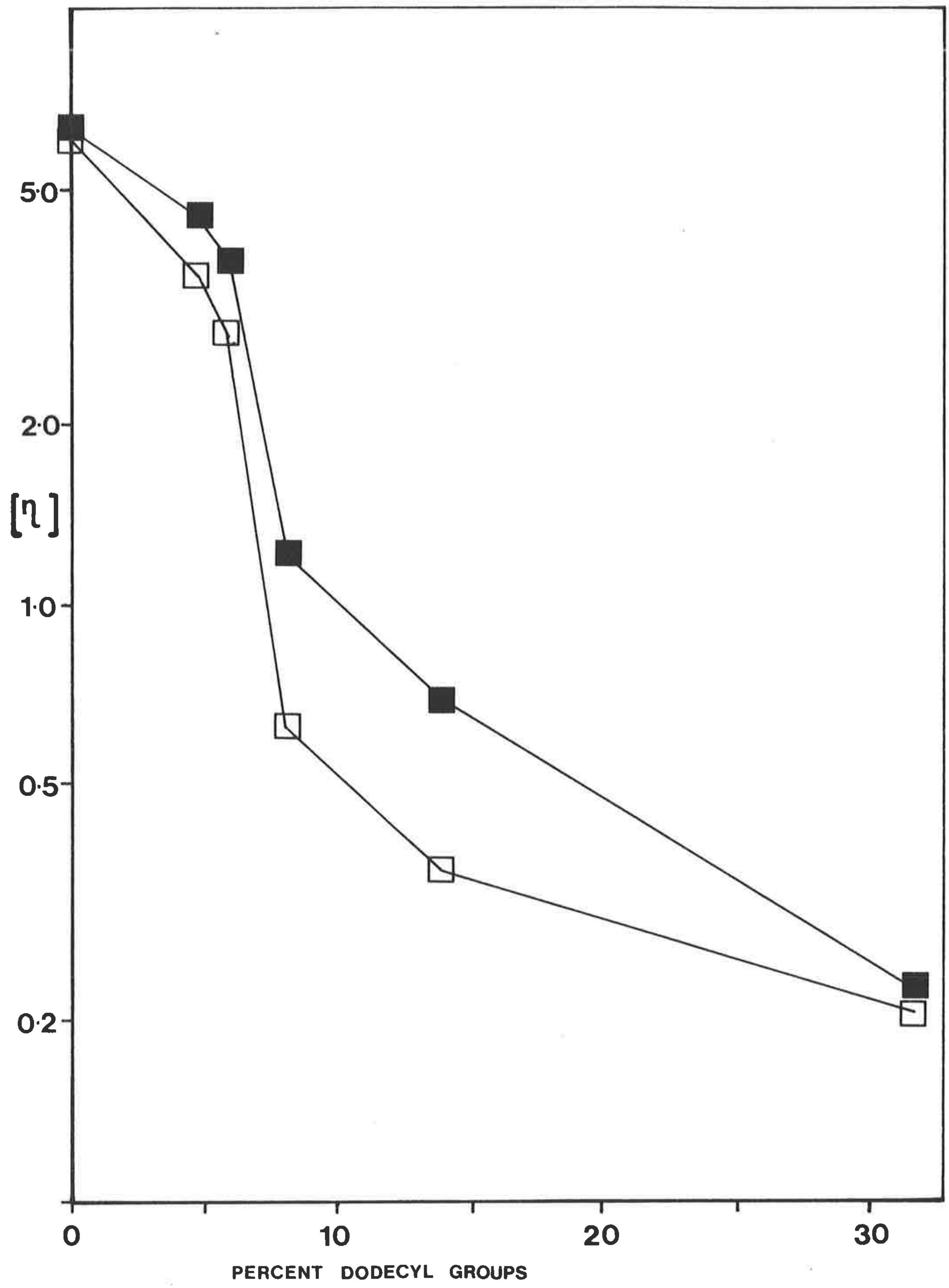
Fig. 6.1 LIMITING VISCOSITY NUMBER AS A FUNCTION OF DODECYL GROUP CONTENT FOR ALKYL DERIVATIVES OF P4VP, WITH DIFFERENT COUNTERIONS, AT 25°C.

Symbols

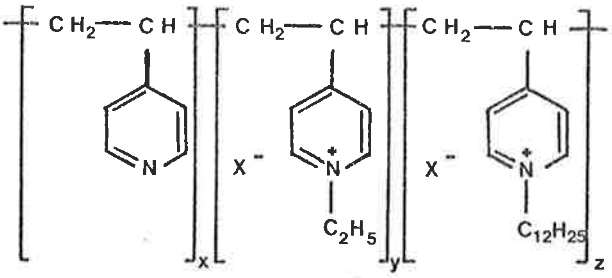
■ Chloride counterions in 0.0223 mol dm^{-3} KCℓ

□ Bromide counterions in 0.0223 mol dm^{-3} KBr

(from Woermann and Wall, 1960).


5·0
2·0
[η]
1·0
0·5
0·2
0
10
20
30
PERCENT DODECYL GROUPS

and



where x, y and z are large (random copolymers)

$X^{-} \equiv$ halide counterion.

Potentiometric and viscosity measurements on these two types of polyelectrolytes were made at 25.0 and 80.0°C in aqueous solutions. Results are presented in Section 6.2.

Not only does the formation of micelles depend on the concentration of amphiphiles, but also on chain length. The shorter the chain length, the smaller is the reduction in the free energy of the system as a result of aggregation and hence the cmc tends to a higher value. It is for this reason that no micelles form for chains of less than four carbon atoms in length (Shinoda et al., 1963). A polymer analogous study has been performed on P2VP alkyl derivatives, from butyl to dodecyl (Inoue, 1964a). Figure 6.2 shows these results in a plot of limiting viscosity number (intrinsic viscosity) versus per cent alkyl quaternisation. The butyl and hexyl derivatives are polyelectrolytes, regardless of the degree of quaternisation, while the octyl and dodecyl derivatives may be either polyelectrolytes or polysoaps, depending on the degree of quaternisation. The transition for the octyl derivatives is in the 14 to 28% region, while the dodecyl derivatives change in the 4.5 to 15% range. Notice that there is close correlation between these

Fig. 6.2 LIMITING VISCOSITY NUMBER AS A FUNCTION OF ALKYL GROUP CONTENT FOR ALKYL DERIVATIVES OF P2VP AT 30°C. (in 0.16 mol dm^{-3} KBr).

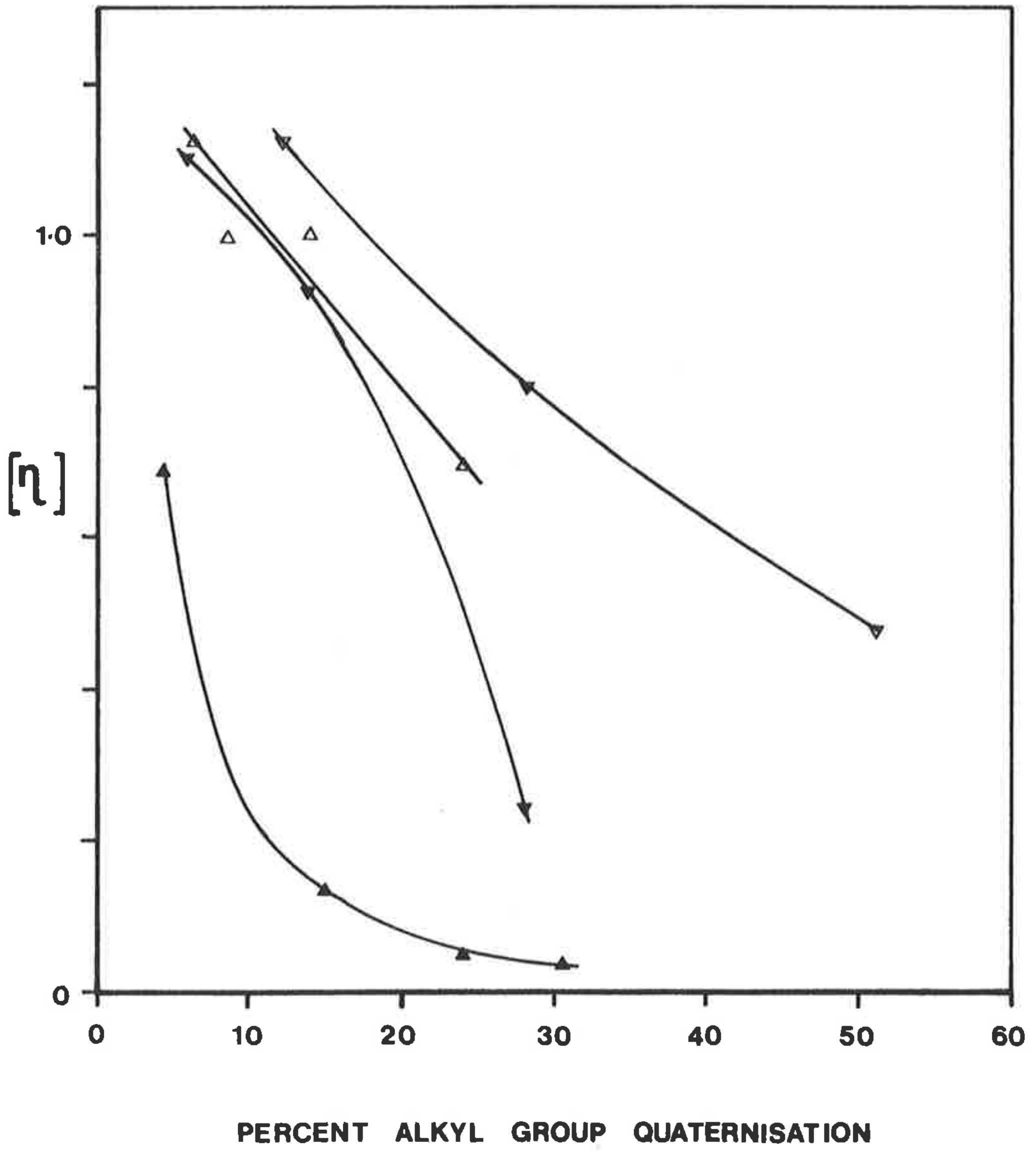
Symbols

▲ Dodecyl

▼ Octyl

△ Hexyl

▽ Butyl



1·0
0
[η]
0
10
20
30
40
50
60
PERCENT ALKYL GROUP QUATERNISATION

results and those for P4VP derivatives. No hexyl or octyl derivatives of P4VP have been studied for possible compact structures. The results of potentiometric and viscosity measurements on derivatives of this type are presented in Section 6.3.

A series of poly-3-n-alkyl-1-vinylimidazolium iodides has been used to demonstrate the effect of attached alkyl chain length on the formation of polysoaps in aqueous solution (Salamone et al., 1974). By means of conductance and viscosity measurements, the authors have demonstrated that methyl and n-propyl derivatives are typical polyelectrolytes, while n-dodecyl and n-hexadecyl derivatives are polysoaps. The interpretation of results for n-hexyl and n-heptyl derivatives was complicated by the fact that these were insoluble in water. Hence some dodecyl derivatives of PVI with some free imidazole base groups were prepared and the potentiometric properties studied in aqueous solution. These results are presented in Section 6.4.

In summary, there is much evidence for the polyelectrolyte to polysoap transition as a function of long chain alkyl group content and length of the attached alkyl group. However, there has been no study on the effects on polysoap and polyelectrolyte conformation of ionisation of the polybases. Nor has there been any investigation of the temperature effects on such systems.

6.2 Ethyl and Dodecyl Derivatives of P4VP

Viscosity measurements have been correlated with the potentiometric measurements on a series of ethyl and dodecyl derivatives of P4VP.

6.2.1 Potentiometric Titrations

The compositions of the samples that were titrated with hydrochloric acid are listed in Table 6.2. The titrations were performed

TABLE 6.2

Compositions of Ethyl and Dodecyl Derivatives

of P4VP that were Titrated

Percentage of pyridine N quaternised with dodecyl chloride	Percentage of pyridine N quaternised with ethyl chloride	Percentage of pyridine N 'free'
4.4	43.9	51.7
-	60.9	39.1
6.6	60.9	32.5
-	40.7	59.3
8.7	40.7	50.6
-	47.0	53.0
9.0	47.0	44.0
17.6	29.7	52.7
-	29.5	70.5
38.8	29.5	31.7
16.4	-	83.6

in water and in 0.0200 mol dm^{-3} sodium chloride solution at 25.0 and 80.0°C. For simplicity, all poly-4-vinyl-N-ethylpyridinium chloride samples shall be referred to as "y% ethyl", and all ethyl and dodecyl derivatives designated "z% dodecyl", where y and z are the percentages of pyridine nitrogen atoms quaternised with ethyl and dodecyl chloride respectively.

Polyelectrolyte titration curves all exhibit the same basic shape as that of the 29.5% ethyl sample shown in Figure 6.3. The effect on polybases of the addition of simple electrolytes is to increase the basicity slightly, whereas, the increase in temperature has a greater effect in the opposite direction. The pH of the solution monotonically decreases with increasing ionisation at both temperatures. These values can then be converted to pK_{app} values, which are plotted versus α in Figure 6.4. This sample exhibits the typical weak polybase characteristics of uniformly decreasing pK_{app} values with increasing α and increased basic strength with increasing ionic strength.

Values of intrinsic dissociation constants, pK_o, may be found by extrapolation of pK_{app} to $\alpha = 0$. These values are plotted against the ethyl group content in Figure 6.5, and considering the errors involved in the determination of pK_o, the trends are quite clear. In water, there is a dramatic decrease in basic strength above 50% quaternisation due to electrostatic repulsions. The effect is diminished in the presence of added sodium chloride, due to shielding of charged groups. There appears to be a slight decrease in basicity above 50% quaternisation. This is consistent with polyelectrolyte theory, for as the charge density on the polymer backbone increases, so the uncharged pyridine groups become more difficult to protonate.

The concentration range for solutions was selected on the basis

Fig. 6.3 TITRATION CURVES OF 29.5% ETHYL DERIVATIVE OF P4VP IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
○	T = 25.0 C	●
×	T = 80.0 C	+

Conc. of polymer ≡ 1.181 g/100 cm^{3}

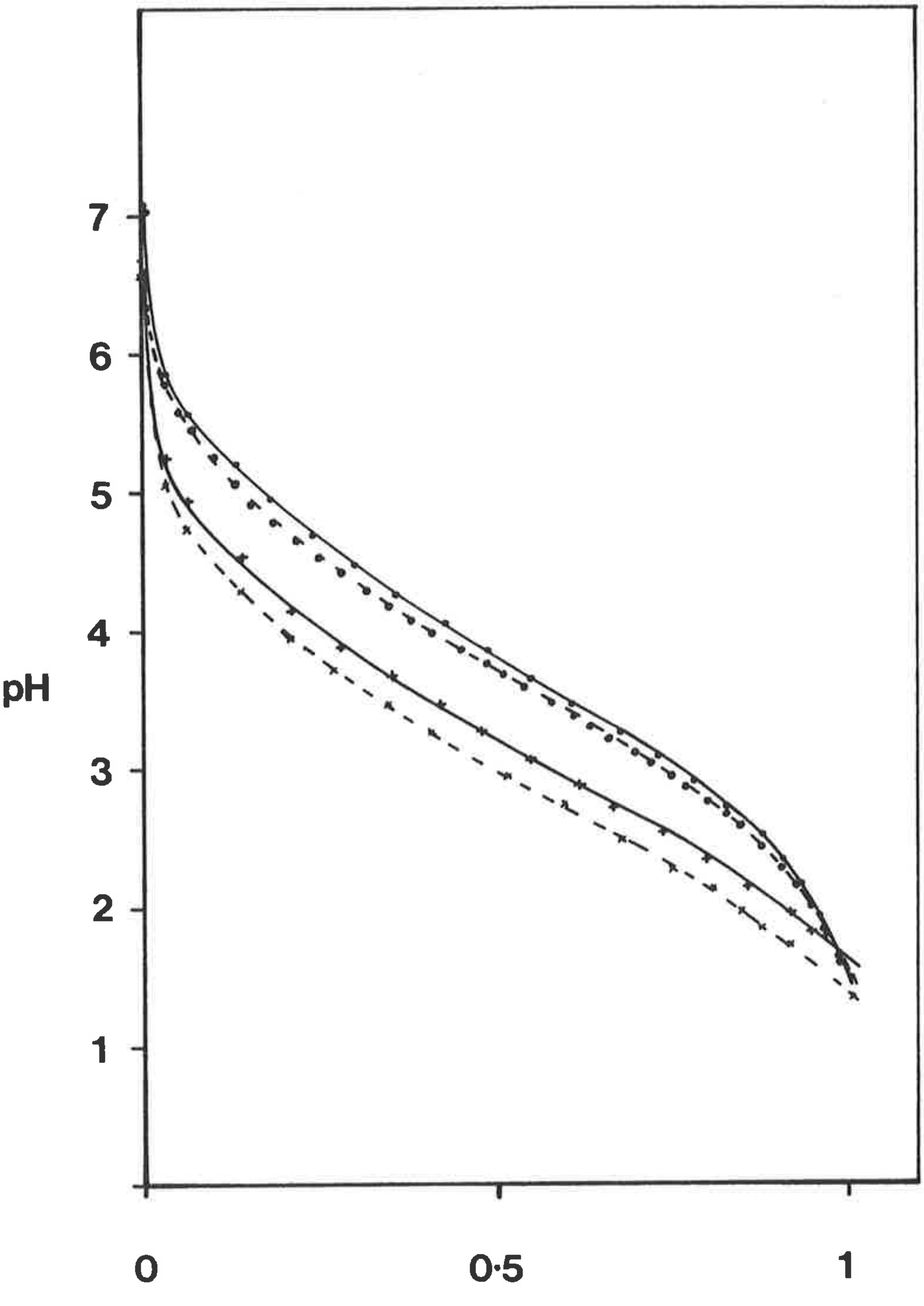

pH
7
6
5
4
3
2
1
0
0·5
1
α

Fig. 6.4 pK_{app} vs. α PLOTS FOR 29.5% ETHYL DERIVATIVE OF P4VP IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
○	T = 25.0°C	●
×	T = 80.0°C	+

Conc. of polymer ≡ 1.181 g/100 cm^3

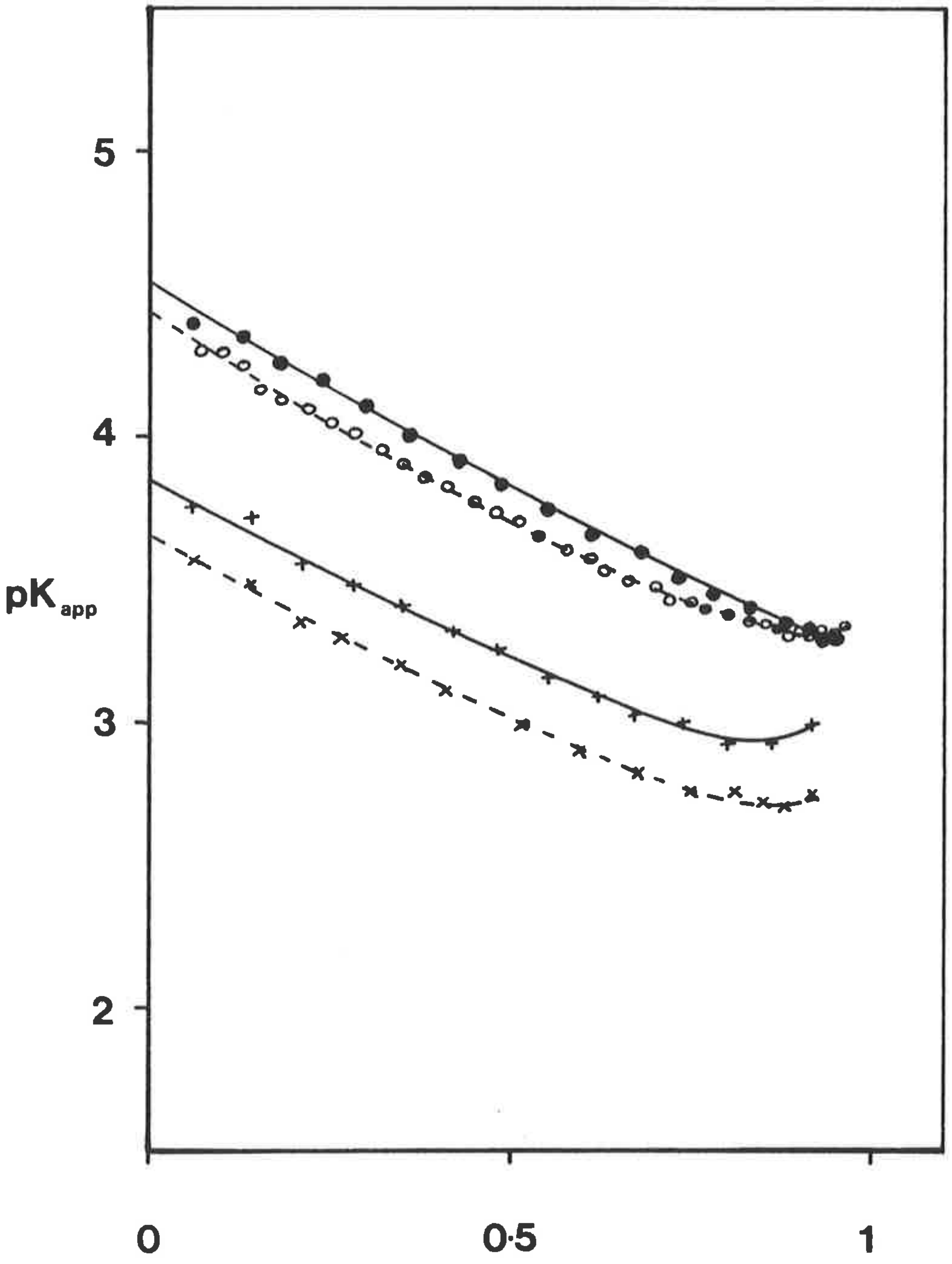

5
4
3
2
pK$_{app}$
0
0·5
1
α

Fig. 6.5 pK_o VALUES FOR ETHYL CHLORIDE DERIVATIVES OF P4VP AS A FUNCTION OF ETHYL GROUP CONTENT.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
●	T = 25.0°C	■
○	T = 80.0°C	□

Conc. of polymers: $1.1 < C < 1.3$ (g/100 cm^3)

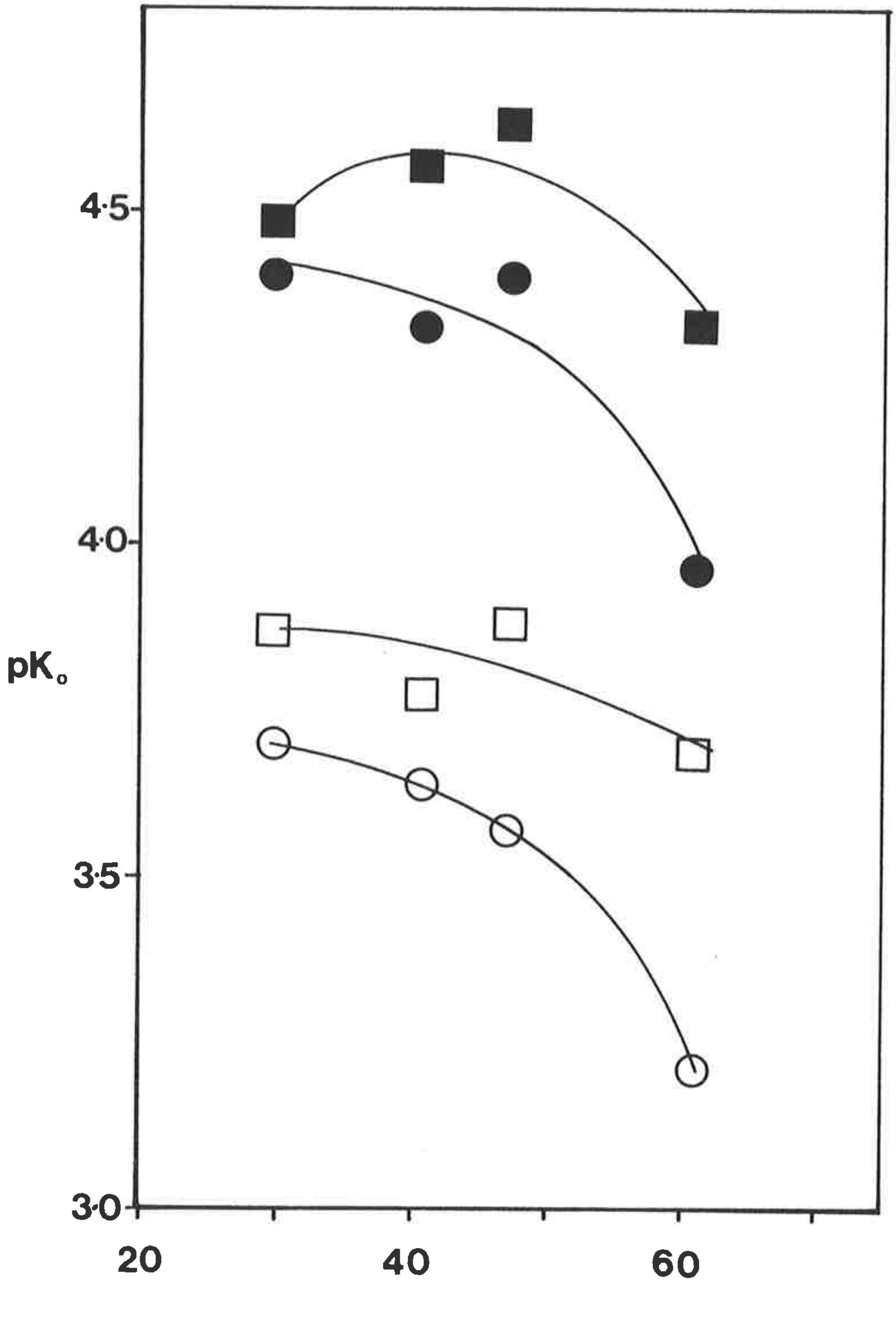
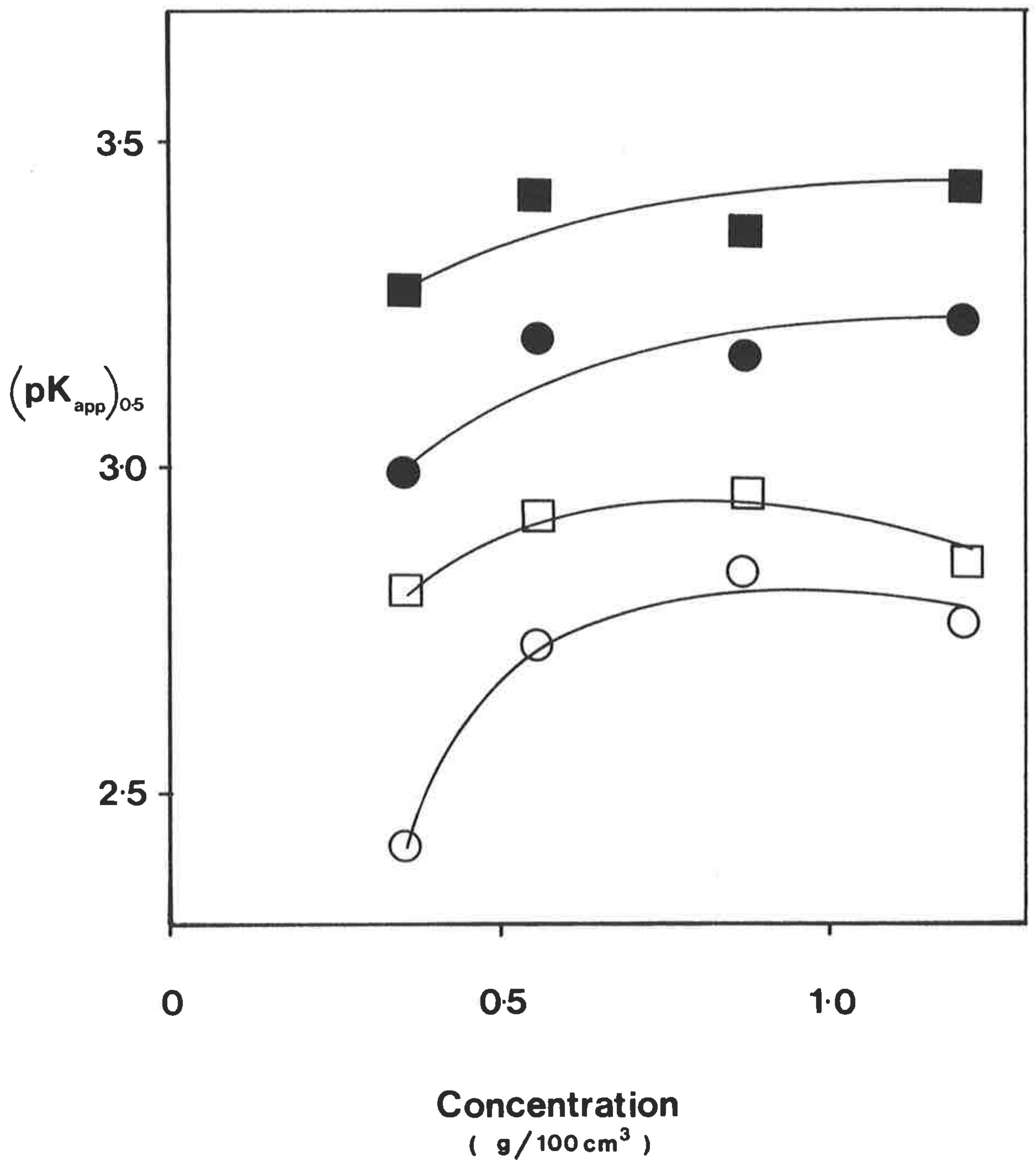

4·5
4·0
3·5
3·0
pK$_o$
20
40
60
PERCENT ETHYL QUATERNISATION

Fig. 6.6 CONCENTRATION DEPENDENCE OF $(\mathrm{p}K_{\mathrm{app}})_{0.5}$ VALUES FOR 17.6% DODECYL DERIVATIVE OF P4VP IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
●	T = 25.0°C	■
○	T = 80.0°C	□


3·5
$(pK_{app})_{0\cdot5}$
3·0
2·5
0
0·5
1·0
Concentration
(g/100 cm^3)

of reasonable titre values; concentrations of approximately 1 g/100 cm^3 satisfied this criterion. However, the basic strength of polybases increases with increasing concentration. Therefore, to resolve any uncertainty in the effect of concentration on basic strength, the 17.6% dodecyl sample was selected as a typical sample and titrated at four different concentrations. The values of pK_{app} at half neutralisation were arbitrarily selected as an indicator of basic strength and plotted against concentration. Figure 6.6 shows the results, which show a very gradual increase in basicity up to approximately 0.7 g/100 cm^3, and thereafter no real change up to 1.2 g/100 cm^3. Consequently most titrations were performed on samples in this concentration range. A few samples were titrated at a concentration of approximately 0.3 g/100 cm^3 in order to confirm the results at the higher concentration. Comparisons are made only between samples in the same concentration range.

A typical set of polysoap titration curves is shown in Figure 6.7 and the corresponding pK_{app} versus α plots in Figure 6.8 for the 8.7% dodecyl sample. The basicity of the free pyridine nitrogen atoms of the polysoaps is less than that of the polyelectrolytes. In addition, the slope of the pH versus α curve in mid-range is less for the polysoaps. Figure 6.9 shows that with a large dodecyl group content, the basicity of free groups approaches a constant value over the whole range of ionisation (38.8% dodecyl sample). This implies that the charge density does not change much with increased ionisation and hence the conformation is little affected. All plots of pK_{app} versus α for the P4VP derivatives show no anomalies, and hence there is little likelihood of a conformational transition with ionisation or temperature.

When values for the dissociation constants of polybases are compared, one of the obvious factors that influences the magnitude of such constants is the fixed charge density along the polymer backbone

Fig. 6.7 TITRATION CURVES OF 8.7% DODECYL DERIVATIVE OF P4VP IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
○	$T = 25.0^{\circ}C$	●
×	$T = 80.0^{\circ}C$	+

Conc. of polymer ≡ 1.178 g/100 cm^3

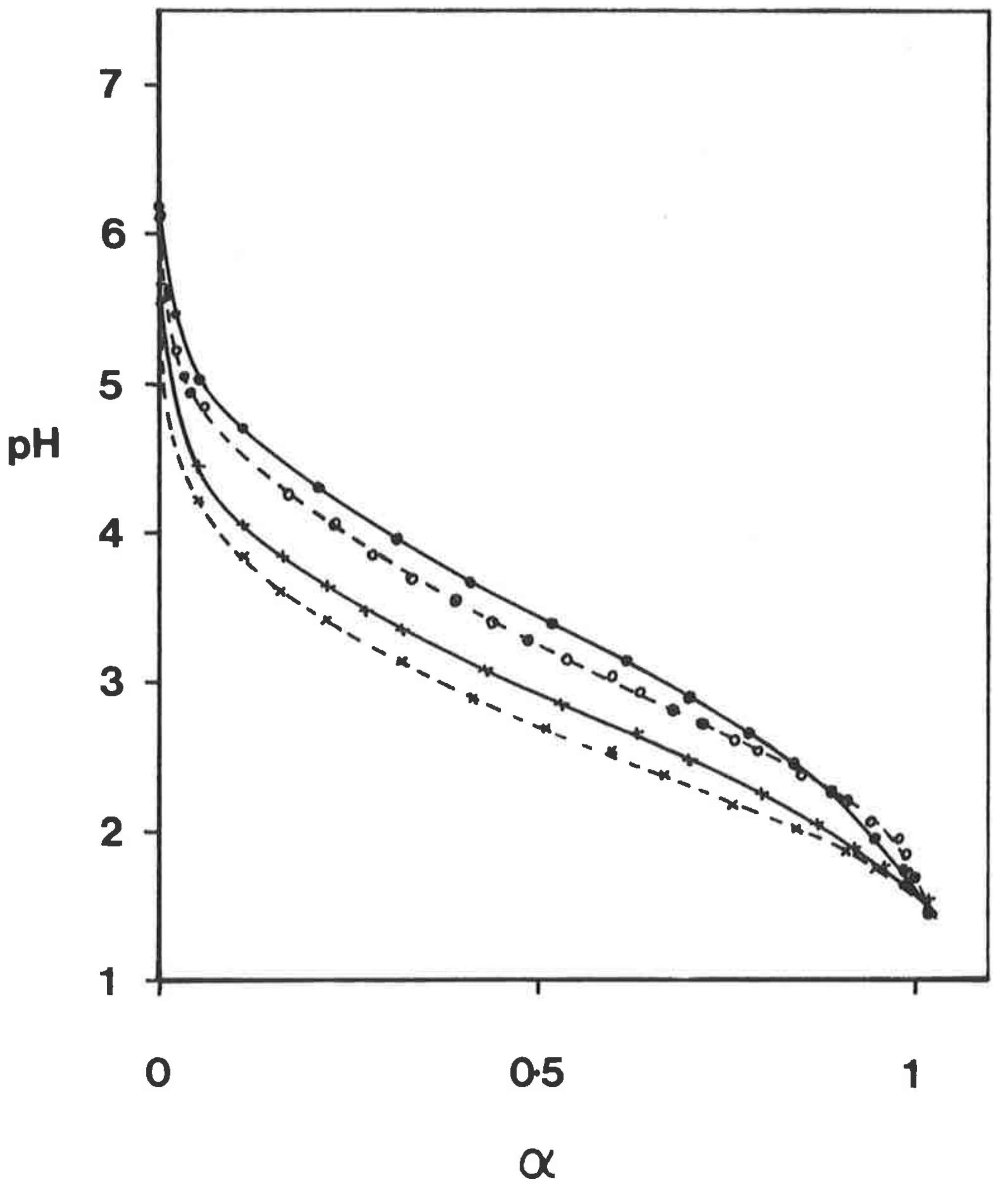

pH
7
6
5
4
3
2
1
0
0·5
1
α

Fig. 6.8 pK_{app} vs. α PLOTS FOR 8.7% DODECYL DERIVATIVE OF P4VP IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
○	T = 25.0°C	●
×	T = 80.0°C	+

Conc. of polymer ≡ 1.178 g/100 cm^3

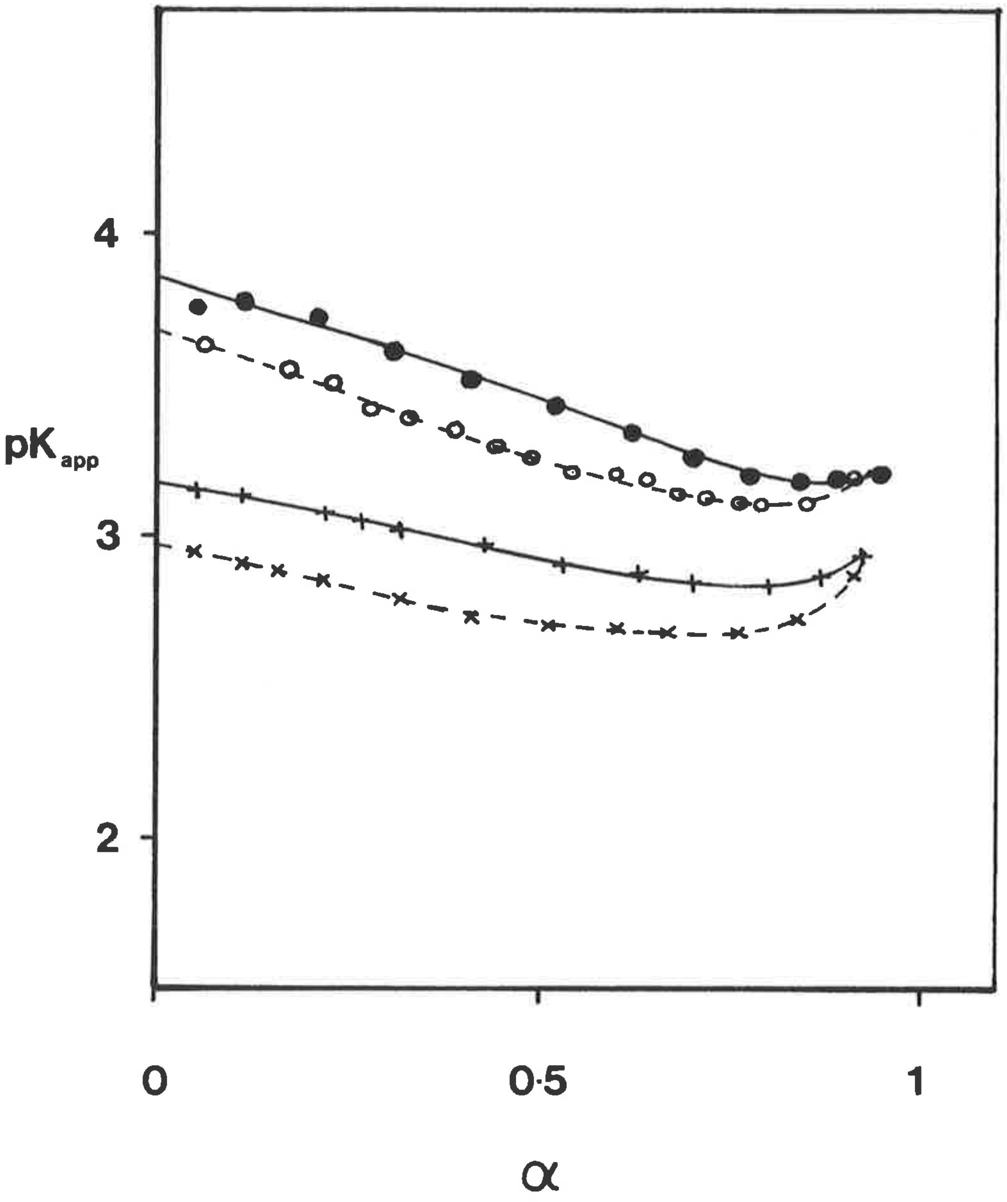
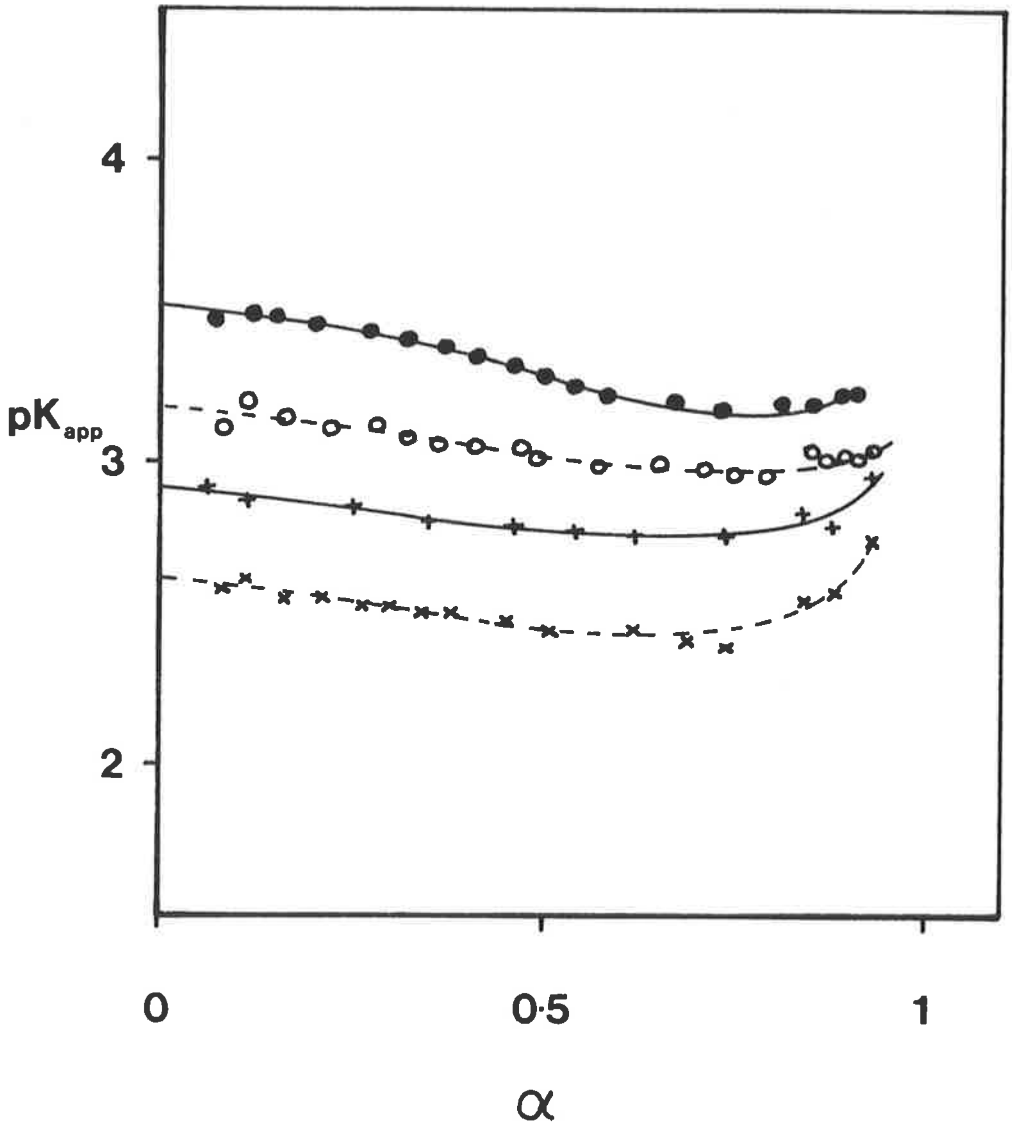

pK_app
4
3
2
0
0·5
1
α

Fig. 6.9 pK_{app} vs. α PLOTS FOR 38.8% DODECYL DERIVATIVE OF P4VP IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
○	T = 25.0°C	●
×	T = 80.0°C	+

Conc. of polymer ≡ 1.217 g/100 cm^3


4
pKapp
3
2
0
0·5
1
α

(see Figure 6.5). Therefore in order to discriminate between the effects of soap group content and fixed charge, the total degree of quaternisation (or charge) must be constant. For this reason, the polyelectrolytes and polysoaps have been divided into two groups:

a) group 1 - percentage of pyridine nitrogen atoms quaternised with alkyl groups $\equiv 51 \pm 5\%$,

b) group 2 - percentage of pyridine nitrogen atoms quaternised with alkyl groups $\equiv 65 \pm 5\%$.

There are two dissociation constants that are often used for the discussion of polyacids and polybases, the intrinsic dissociation constant, $\mathrm{p}K_{\mathrm{o}}$, and the dissociation constant at half neutralisation, $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ (the polymeric analogue of $\mathrm{p}K_{\mathrm{a}}$). Figures 6.10, 6.11, 6.12 and 6.13 show these values plotted as a function of dodecyl group content for groups 1 and 2. The polyelectrolyte to polysoap transition is clearly evident, with the 4.4% dodecyl derivative behaving potentiometrically as a typical polyelectrolyte, and the rest of the dodecyl derivatives as polysoaps. There is a distinct drop in $\mathrm{p}K_{\mathrm{o}}$ and $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ values at both temperatures between 5 and 8% dodecyl group content. This is in excellent agreement with the viscosity measurements of previous workers. Another feature of these diagrams shows that there is no difference in the trends obtained from $\mathrm{p}K_{\mathrm{o}}$ values and $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ values. This removes then the necessity to determine $\mathrm{p}K_{\mathrm{o}}$ values which are inherently less certain due to the extrapolations involved. In all subsequent discussions where there are no anomalies observed, the use of $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ values is justified. The values of both $\mathrm{p}K_{\mathrm{o}}$ and $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ are tabulated in Appendix A, together with the results for group 1 polymers in the concentration range of approximately 0.3 g/100 cm^3.

Fig. 6.10 pK_o VALUES FOR ETHYL AND DODECYL CHLORIDE DERIVATIVES OF P4VP AS A FUNCTION OF DODECYL GROUP CONTENT:

GROUP 1

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
●	T = 25.0°C	■
○	T = 80.0°C	□

Conc. of polymers: $0.9 < C < 1.3$ (g/100 cm^3)

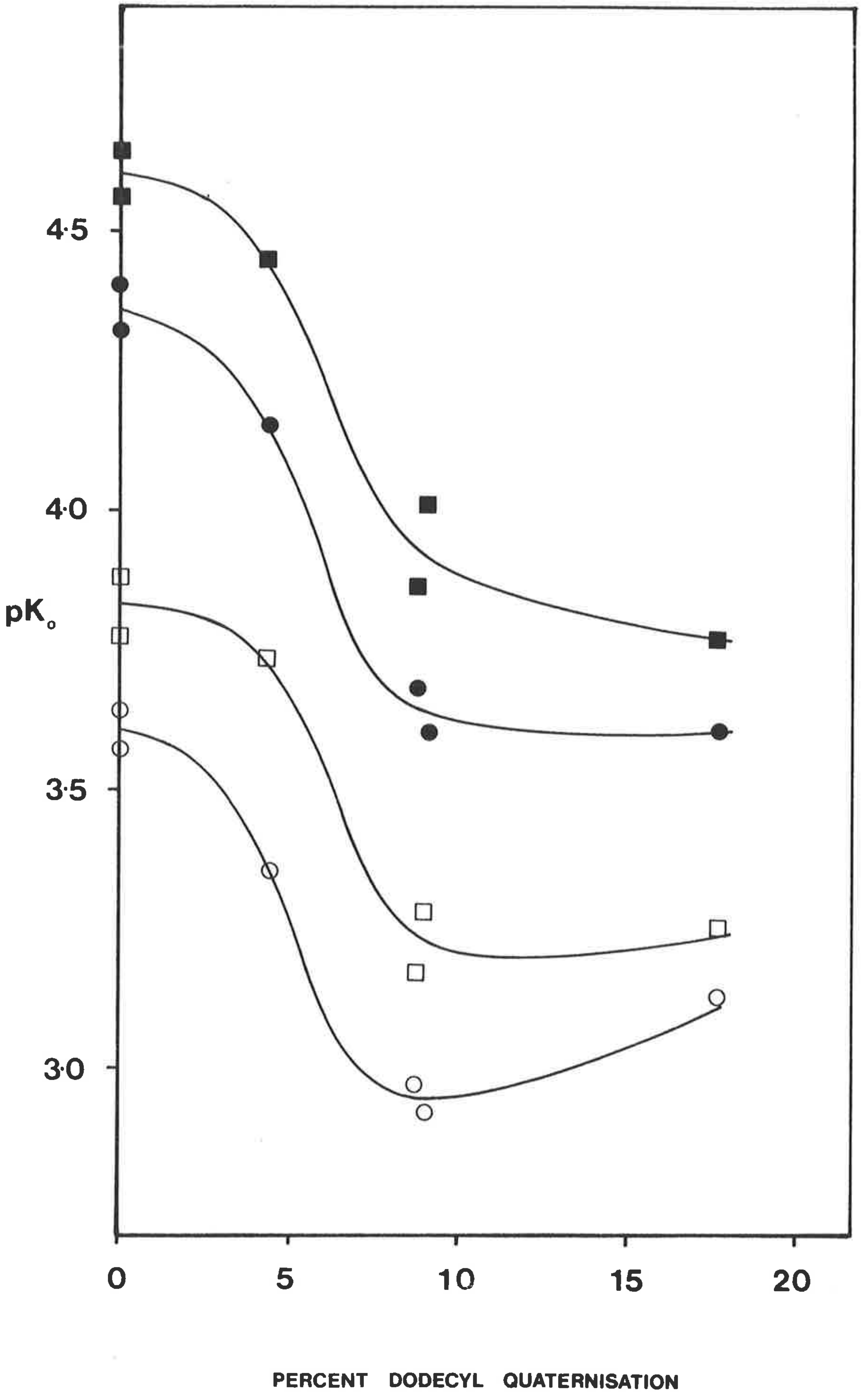

4·5
4·0
3·5
3·0
pK$_0$
0
5
10
15
20
PERCENT DODECYL QUATERNISATION

Fig. 6.11 $(pK_{app})_{0.5}$ VALUES FOR ETHYL AND DODECYL CHLORIDE DERIVATIVES OF P4VP AS A FUNCTION OF DODECYL GROUP CONTENT: GROUP 1

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
●	T = 25.0°C	■
○	T = 80.0°C	□

Conc. of polymers: $0.9 < C < 1.3$ (g/100 cm^3)

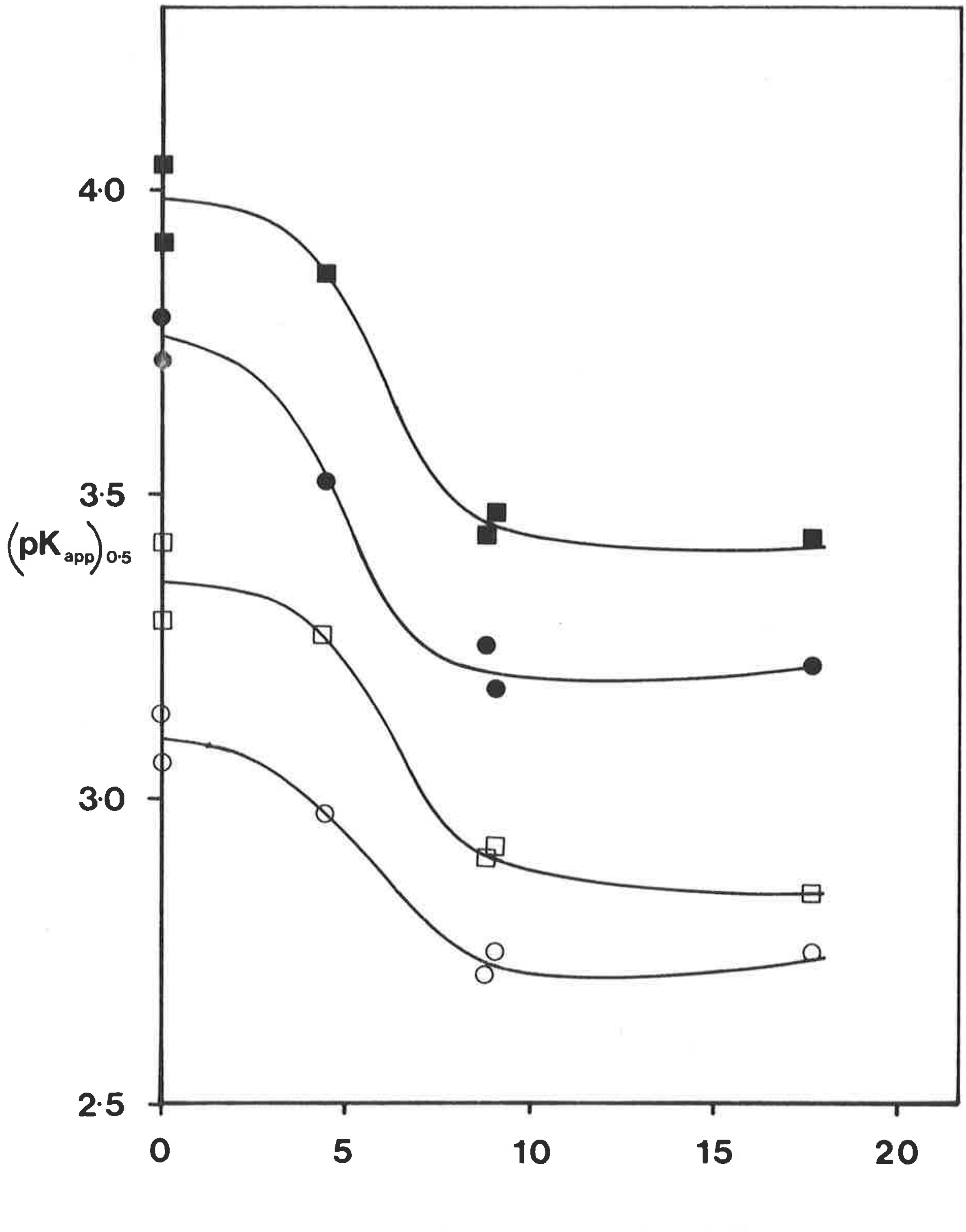

4·0
3·5
3·0
2·5
$(pK_{app})_{0\cdot5}$
0
5
10
15
20
PERCENT DODECYL QUATERNISATION

Fig. 6.12 pK_o VALUES FOR ETHYL AND DODECYL CHLORIDE DERIVATIVES OF P4VP AS A FUNCTION OF DODECYL GROUP CONTENT:

GROUP 2

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
●	T = 25.0°C	■
○	T = 80.0°C	□

Conc. of polymers: $0.9 < C < 1.3$ (g/100 cm^3)

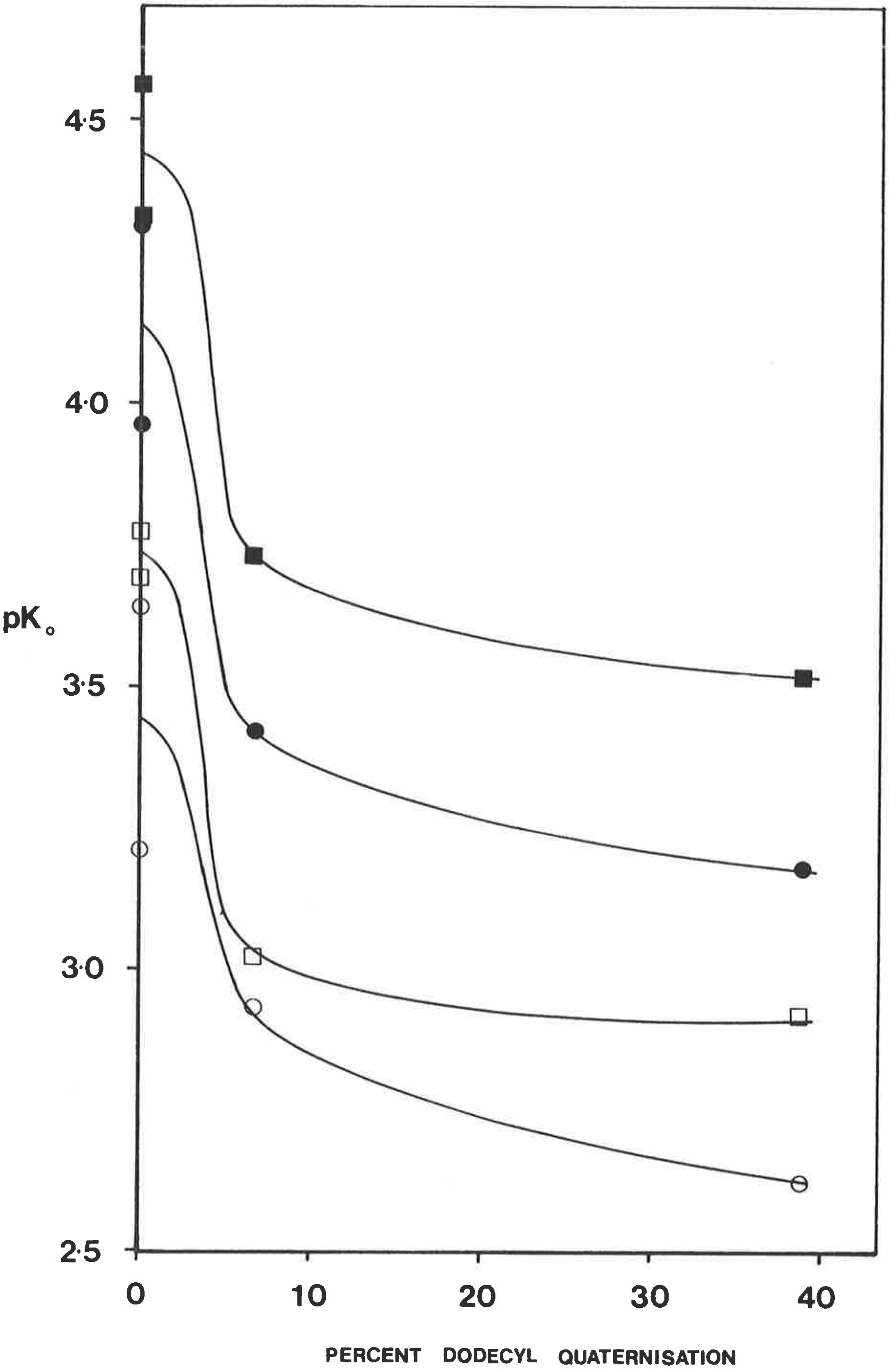
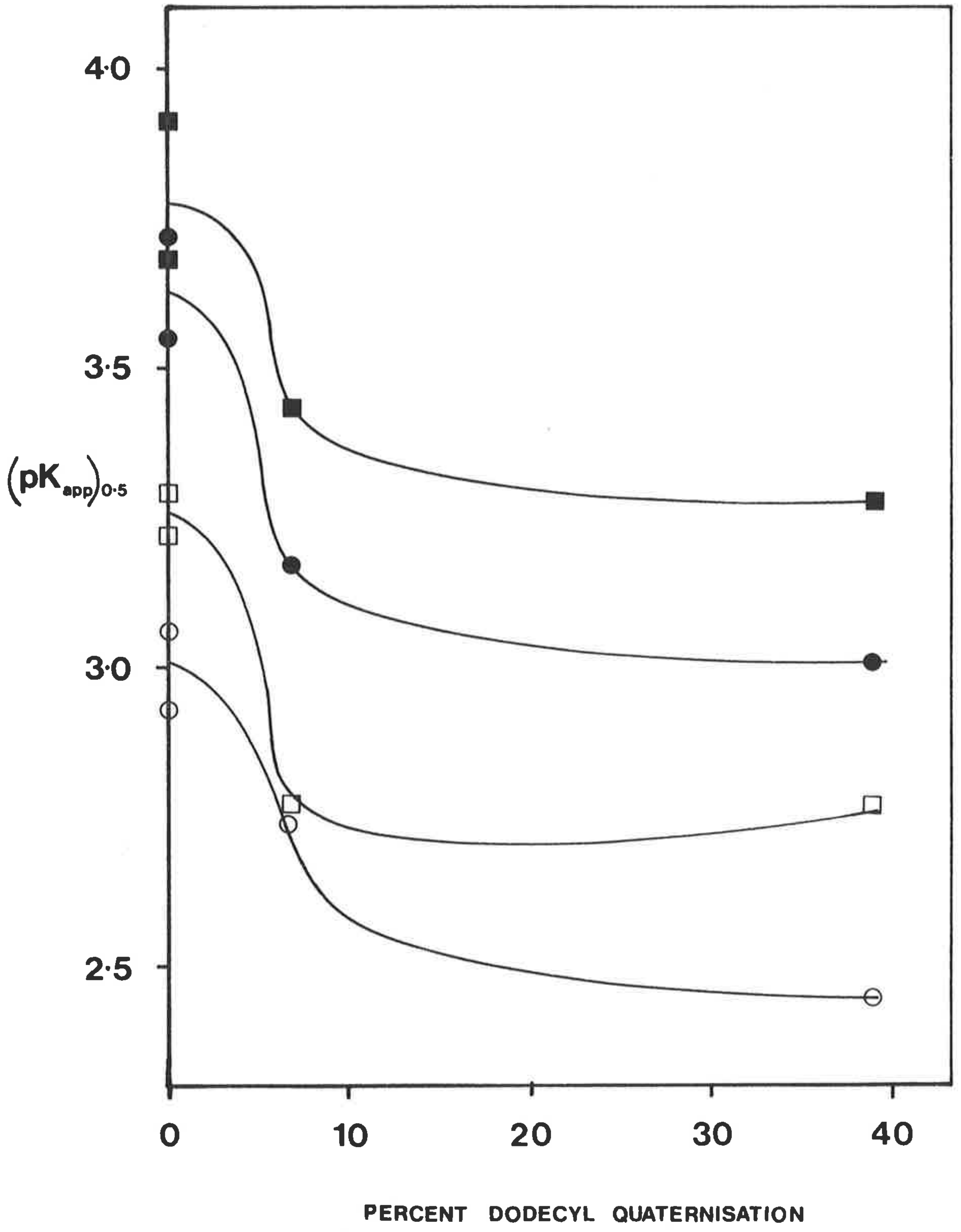

4·5
4·0
3·5
3·0
2·5
pK$_o$
0
10
20
30
40
PERCENT DODECYL QUATERNISATION

Fig. 6.13 $(pK_{app})_{0.5}$ VALUES FOR ETHYL AND DODECYL CHLORIDE DERIVATIVES OF P4VP AS A FUNCTION OF DODECYL GROUP CONTENT: GROUP 2

Symbols

In water		In 0.0200 mol dm^{-3} $NaC\ell$
●	T = 25.0°C	■
○	T = 80.0°C	□

Conc. of polymers: $0.9 < C < 1.3$ (g/100 cm^3)


4·0
3·5
3·0
2·5
$(pK_{app})_{0\cdot5}$
0
10
20
30
40
PERCENT DODECYL QUATERNISATION

To show whether the presence of ethyl groups has any effect on the polysoap conformation, a sample labelled PD7 was prepared with only 16.4% of pyridine nitrogen atoms quaternised with dodecyl chloride (no ethyl chloride). This polysoap was titrated in aqueous solution from $\alpha \approx 0.30$ to $\alpha = 1.0$, and as a 0.5% (w/v) suspension in 10% v/v ethanol: water from $\alpha = 0$ to $\alpha = 1.0$. The behaviour in aqueous solution was identical to that of the other polysoaps except that the basicity was higher due to the lower charge density. Values of $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ are tabulated in Appendix A. However, the suspension displayed a more interesting behaviour. At 25.0°C, the suspension cleared to become a solution at $\alpha \approx 0.20$, corresponding to a flat portion of the titration curve, which thereafter is similar to the aqueous solution results. Figure 6.14 shows this titration curve in sodium chloride (the same shape was observed in the absence of NaCℓ). Upon heating the suspension to 80.0°C, it cleared to become a solution without the addition of any acid. This sample illustrates two important points; firstly that a phase transition is accompanied by an anomalous titration curve, and secondly that the increased ionisation of the solvent at 80.0°C can have a noticeable effect on the solubility of polysoaps.

Generally, the effect of temperature on the basicity of polybases can be gauged by the change in $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ values at the two temperatures; $\Delta\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5} \equiv \left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=25} - \left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=80}$. This is called the *thermal effect*. All of the P4VP derivatives displayed a decrease in basic strength with increased temperature. The mean value of this thermal effect is 0.57 pH units (standard deviation = 0.08 pH units) for 22 readings (see the Appendix A for tabulated values), for both polyelectrolytes and polysoaps. Hence for this system, the structure of the polymer in solution has no noticeable differences at 25.0 and 80.0°C with respect to the overall changes in the potentiometric properties.

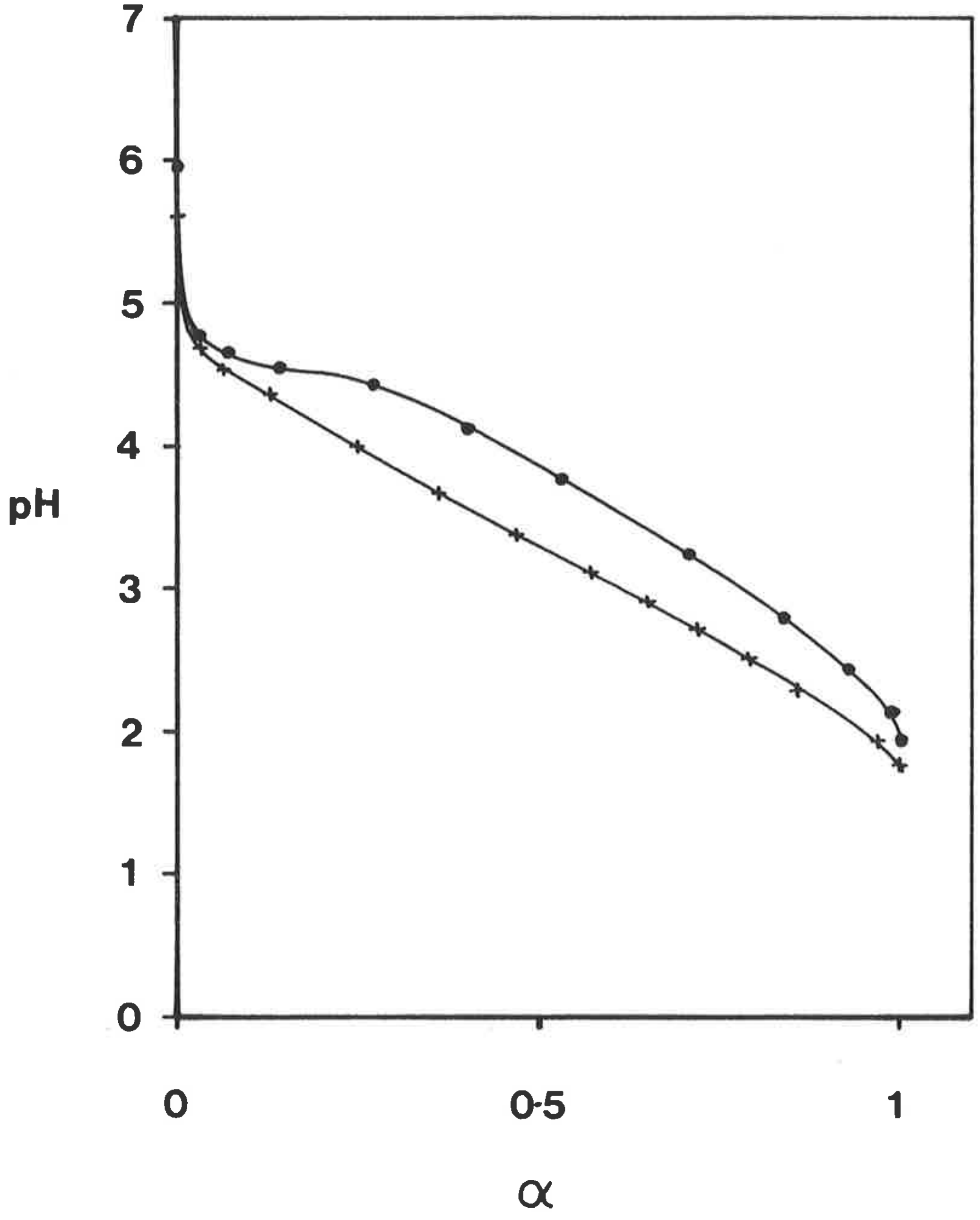
Fig. 6.14 TITRATION CURVES OF 16.4% DODECYL DERIVATIVE OF P4VP IN 10% ETHANOL: WATER (V/V).

Symbols

● T = 25.0°C

+ T = 80.0°C

Conc. of polymer ≡ 0.50 g/100 cm^3 in 0.0200 mol dm^{-3} NaCℓ.


7
6
5
4
3
2
1
0
pH
0
0·5
1
α

Finally, it should be noted that many studies have shown that the potentiometric properties of polymers are independent of molecular weight, provided that the molecule is large enough for end effects to be ignored (e.g. Katchalsky and Spitnik, 1947). Figure 6.15 confirms this observation for this system, where two polysoaps of different parent polymer molecular weights are shown to have identical potentiometric titration curves.

6.2.2 Viscosity Measurements

The polymers in this study were prepared primarily for potentiometry and hence there was no need for fractionated polymer samples. This presented severe limitations for the viscosity measurements. However, derivatives prepared from the same parent polymer sample are suitable for viscosity measurements, provided that semi-quantitative conclusions only are satisfactory. This is the case for distinguishing between polyelectrolytes and polysoaps, as the viscosity of a polysoap is orders of magnitude less than that of a polyelectrolyte.

The first question concerns that of molecular conformation as a function of temperature and ionisation. The viscosities of 29.7% ethyl and its polysoap derivative 17.6% dodecyl are shown at four different temperatures as η_{sp}/C versus temperature in Figure 6.16. Both samples were compared at zero and complete ionisation. These results indicate quite clearly that there is no conformational change for either the polyelectrolyte or the polysoap as a function of temperature or ionisation. The viscosity of both types of polymer decreases slightly with increased temperature.

The other requirement from viscosity measurements is to show that

Fig. 6.15 POTENTIOMETRIC PROPERTIES INDEPENDENT OF MOLECULAR WEIGHT: TITRATION CURVES OF 8.7% DODECYL AND 17.6% DODECYL DERIVATIVES OF P4VP IN 0.0200 mol dm^{-3} NaCℓ.

Symbols

8.7% dodecyl		17.6% dodecyl
○	T = 25.0°C	●
×	T = 80.0°C	+
1.178	Conc. (g/100 cm^3)	1.212

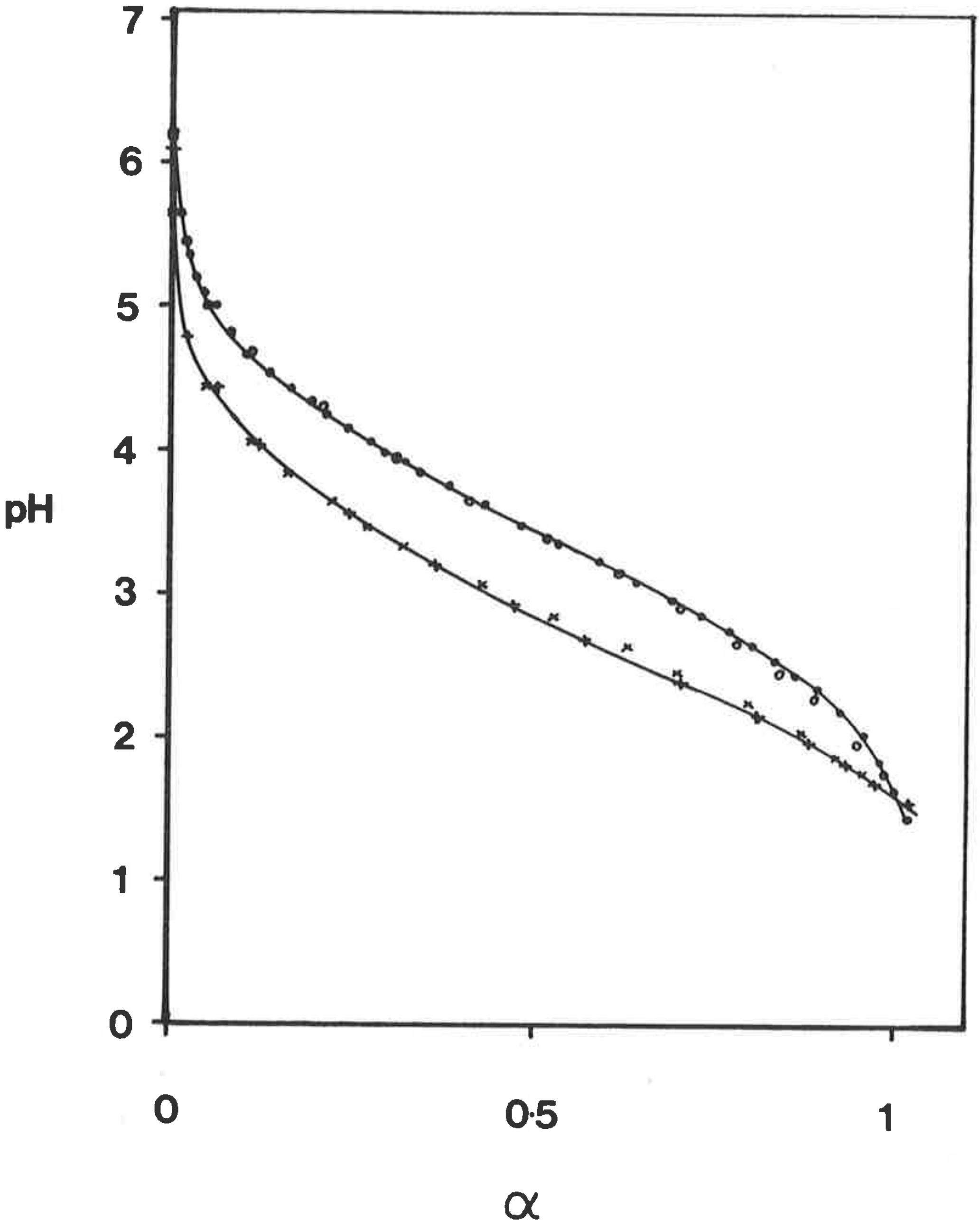
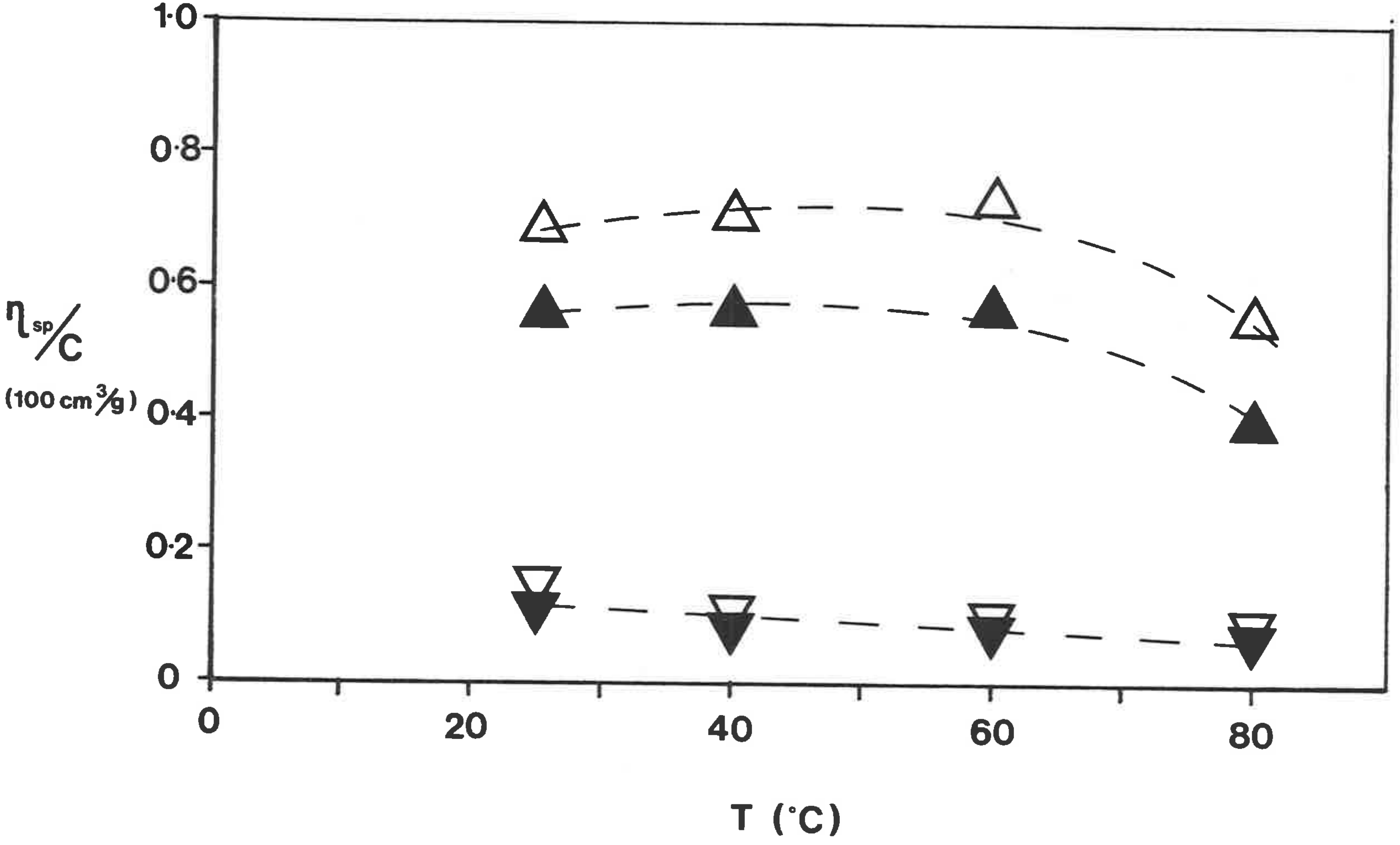

7
6
5
4
3
2
1
0
pH
0
0·5
1
α

Fig. 6.16 VISCOSITY NUMBER OF TYPICAL POLYELECTROLYTE AND TYPICAL POLYSOAP IN AQUEOUS SOLUTION AT $\alpha = 0$ AND $\alpha = 1.0$ AS A FUNCTION OF TEMPERATURE FOR P4VP DERIVATIVES.

Symbols

29.5% ethyl		17.6% dodecyl
△	$\alpha = 0$	▽
▲	$\alpha = 1.0$	▼
1.380	Conc. (g/100 cm^3)	1.583



1·0
0·8
0·6
0·4
0·2
0
η_{sp}/C
(100 cm³/g)
0
20
40
60
80
T (°C)

the polysoaps are actually more compact in aqueous solution than the polyelectrolytes. The values of η_{sp}/C for the derivatives of P4VP sample 4P2', at 25.0 and 80.0°C are listed in Table 6.3 for $\alpha = 0$ and $\alpha = 1.0$. There is no difference in behaviour with either temperature or ionisation. The general trends are shown in Figure 6.17 for zero ionisation at both temperatures. A note must be made on the unexpectedly low value for the 4.4% dodecyl sample. The viscosity is very dependent on total fixed charge, as shown by the two ethyl derivatives. Hence the viscosity of the 4.4% dodecyl sample must be corrected (increased by at least 0.4) in order to validly compare it with the other samples, as this sample has a lower fixed charge than the others. This is precisely why Strauss and Gershfeld (1954) stressed the necessity for constant electrolyte density along the polymer backbone. With this in mind, the viscosity values show that there is a change in conformation that correlates with the potentiometric results. One feature of the viscosity results that is misleading is the decrease in viscosity at full ionisation. This is partly due to the screening of charged groups by small ions as the ionic strength at $\alpha = 1.0$ is quite high for such weak polybases. As a control experiment, the viscosities of 60.9% ethyl were determined in water and in a sodium chloride solution equivalent in ionic strength to that at $\alpha = 1.0$. Values of η_{sp}/C in water and sodium chloride at 25.0°C are 2.42 and 0.30 respectively, comparable to those values in Table 6.3.

6.3 Hexyl and Octyl Derivatives of P4VP

6.3.1 Potentiometric Titrations

Since no conformational transitions were observed for any of the dodecyl derivatives of P4VP, it was concluded that the hydrophobic interactions were too strong to be disrupted by the electrostatic repulsions provided by increased charge. Hence the length of the alkyl

TABLE 6.3

Viscosity Numbers of P4VP Derivatives from 4P2'

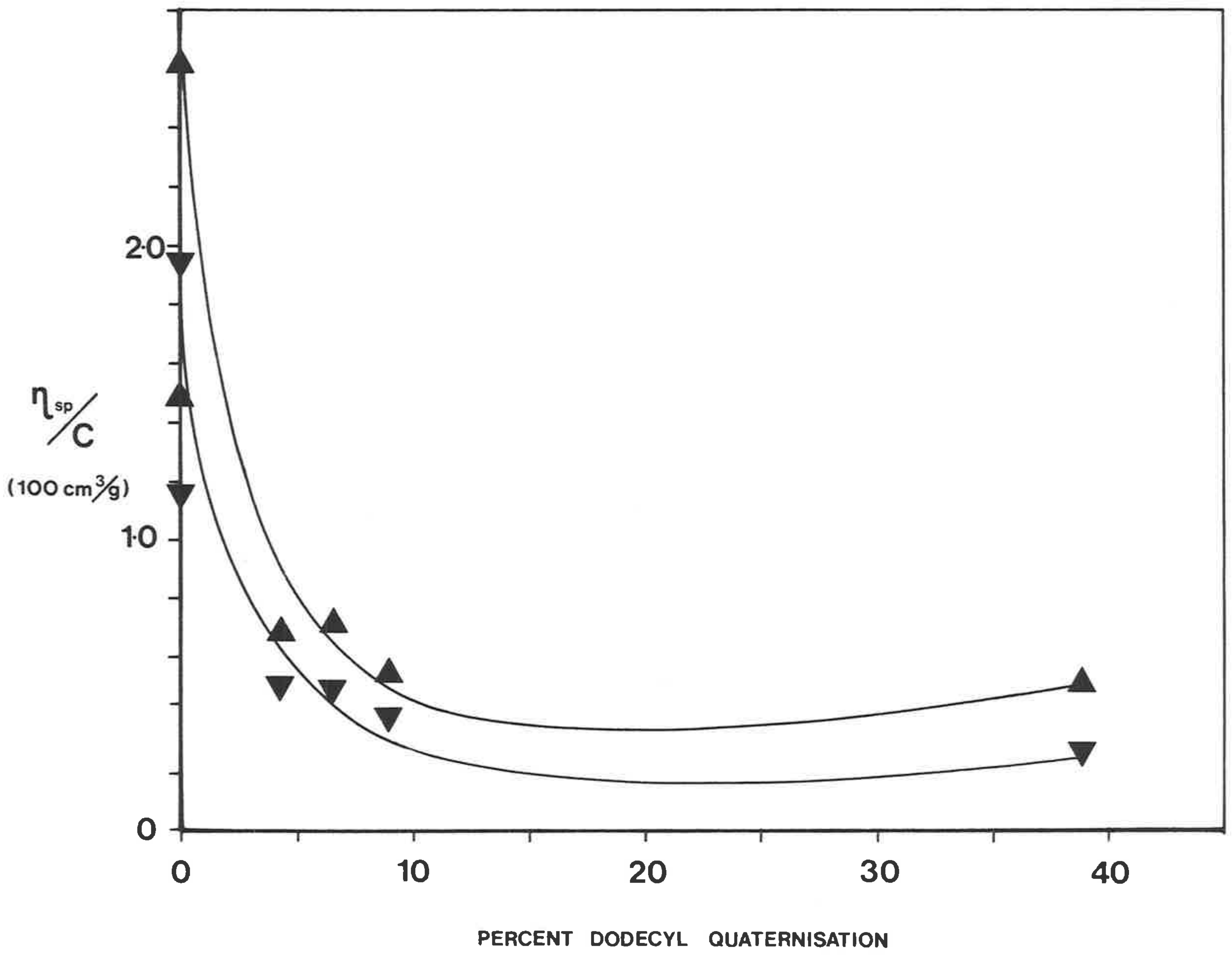
Sample	Conc. (g/100 cm^3)	$\alpha = 0$ η_{sp}/C (100 cm^3/g)		Conc. (g/100 cm^3)	$\alpha = 1.0$ η_{sp}/C (100 cm^3/g)	
		$T = 25.0$°C	$T = 80.0$°C		$T = 25.0$°C	$T = 80.0$°C
29.5% ethyl	1.389	1.49	1.15	1.263	0.60	0.40
60.9% ethyl	1.428	2.62	1.94	1.298	0.52	0.36
4.4% dodecyl	1.453	0.69	0.50	1.298	0.26	0.16
6.6% dodecyl	1.464	0.72	0.49	1.362	0.13	0.10
9.0% dodecyl	1.458	0.55	0.40	-	-	-
38.8% dodecyl	1.418	0.51	0.28	1.319	0.22	0.10

Fig. 6.17 VISCOSITY NUMBER FOR ETHYL AND DODECYL CHLORIDE DERIVATIVES OF P4VP at $\alpha = 0$ AS A FUNCTION OF DODECYL GROUP CONTENT, IN WATER.

Symbols

▲ T = 25.0°C

▼ T = 80.0°C



2·0
1·0
0
η_{sp}/C
(100 cm³/g)
0
10
20
30
40
PERCENT DODECYL QUATERNISATION

chain was decreased, and hexyl and octyl derivatives of P4VP were prepared in the belief that there may be aggregation at low ionisation with disruption of this structure at higher charge density. The compositions of the hexyl and octyl derivatives that were titrated at 25.0 and 80.0°C in water and 0.0200 mol dm^{-3} NaCℓ are listed in Table 6.4. None of the prepared polymers was soluble in water. All titrations were performed only in those regions where enough acid had been added for solubilisation. Approximate values of α at which the samples dissolved in water are shown also in Table 6.4.

TABLE 6.4

Hexyl and Octyl Derivatives of P4VP: Compositions

	Percentage of pyridine N quaternised with alkyl groups	Percentage of pyridine N 'free'	Approx. value of α at which water soluble
Hexyl	35.3	64.7	0.35
	63.8	36.2	0.10
Octyl	18.3	81.7	0.45
	44.0	56.0	0.30

All titration curves of these derivatives have the same characteristics as the polyelectrolytes in Section 6.2, the main effect of increased temperature being to decrease the basicity of the pyridine groups by approximately 0.5 pH units, as well as to decrease the value of d pK_{app}/dα. The values of $\left(pK_{app}\right)_{0.5}$ are listed in Appendix A, and values of pK_o were not determined because of the uncertainty in extrapolating to zero ionisation. Titration curves of all samples were also determined in 10% (v/v) ethanol: water in which they were soluble in the free base form. No anomalies were observed in the regions of neutralisation for which the polymers were insoluble in water. Hence no conformational transitions with temperature or ionisation were observed by potentiometry with the hexyl and octyl derivatives of P4VP.

Values of $\left(pK_{app}\right)_{0.5}$ for these derivatives are plotted against the alkyl group content in Figure 6.18. The basicity decreases with increasing alkyl group content, as for other polyelectrolytes. More important is the fact that for corresponding degrees of quaternisation, the octyl derivatives have a lower value of $\left(pK_{app}\right)_{0.5}$. This implies that the octyl derivatives are more compact at high degrees of quaternisation than the hexyl derivatives. The extent to which they approach a polysoap-like conformation is questionable.

6.3.2 Viscosity Measurements

No viscosity measurements were possible for the hexyl derivatives because they were prepared from different samples of P4VP. The two octyl derivatives were prepared from the same parent polymer and hence the viscosities are meaningful. As both samples were insoluble in the free base form in water, and also the amount of added acid required for solubilisation was relatively large, the viscosities were determined in 10% (v/v) ethanol:water, with sufficient added acid to dissolve the polymers. The results are summarised in Table 6.5 below. The decrease in viscosity with increased octyl group content is of a comparable size to that previously observed for the dodecyl derivatives of P4VP. Consequently it can be inferred that the 44.0% octyl derivative exhibits a relatively compact structure in aqueous solution, something similar to that of the dodecyl polysoaps.

Fig. 6.18 $(pK_{app})_{0.5}$ VALUES FOR HEXYL AND OCTYL CHLORIDE DERIVATIVES OF P4VP AS A FUNCTION OF ALKYL GROUP CONTENT.

Symbols

	In water		In 0.0200 mol dm^{-3} NaCℓ
a) hexyl			
	■	T = 25.0°C	◆
	□	T = 80.0°C	◇
b) octyl			
	▼	T = 25.0°C	▲
	▽	T = 80.0°C	△

Conc. of polymers: $0.92 < C < 0.99$ (g/100 cm^3)

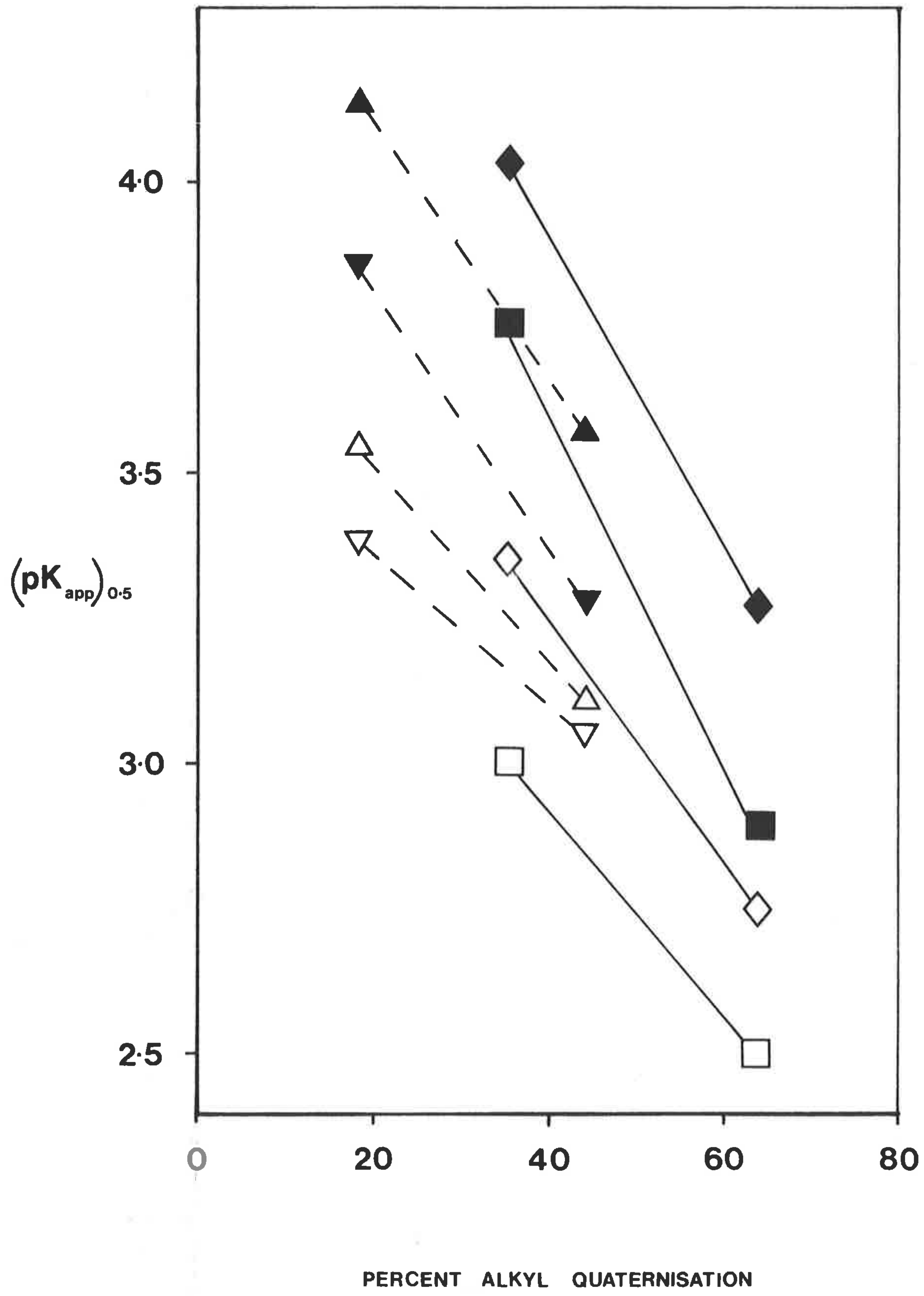

4·0
3·5
3·0
2·5
$(pK_{app})_{0\cdot 5}$
0
20
40
60
80
PERCENT ALKYL QUATERNISATION

TABLE 6.5

Viscosity Numbers of Octyl Derivatives in 10% (v/v) Ethanol : water at 25.0°C

Sample	Conc. (g/100 cm^3)	α	η_{sp}/C (100 cm^3/g)
18.3% octyl	0.230_7	0.22	2.11
44.0% octyl	0.230_7	0.21	0.56

6.4 PVI and Dodecyl Derivatives

Poly-N-vinylimidazole and two dodecyl chloride derivatives of PVI were potentiometrically titrated in water and 0.0200 mol dm^{-3} NaCℓ solution at 25.0 and 80.0°C. The compositions of the two dodecyl derivatives are shown below in Table 6.6.

TABLE 6.6

Compositions of Dodecyl Derivatives of PVI

Percentage of Imidazole N quaternised with dodecyl chloride	Percentage of Imidazole N 'free'
9.3	90.7
23.3	76.7

The potentiometric titration curves of PVI and the two dodecyl derivatives are very similar, the only difference between the parent polymer and its derivatives being that the latter have slightly reduced slopes. This observation can be explained by the reduction in number of distinguishable sites available for protonation. Figures 6.19 and 6.20

Fig. 6.19 TITRATION CURVES OF PVI IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} $NaC\ell$
○	$T = 25.0^\circ C$	●
×	$T = 80.0^\circ C$	+

Conc. of polymer $\equiv 1.84 \times 10^{-2}$ monomol dm^{-3}.

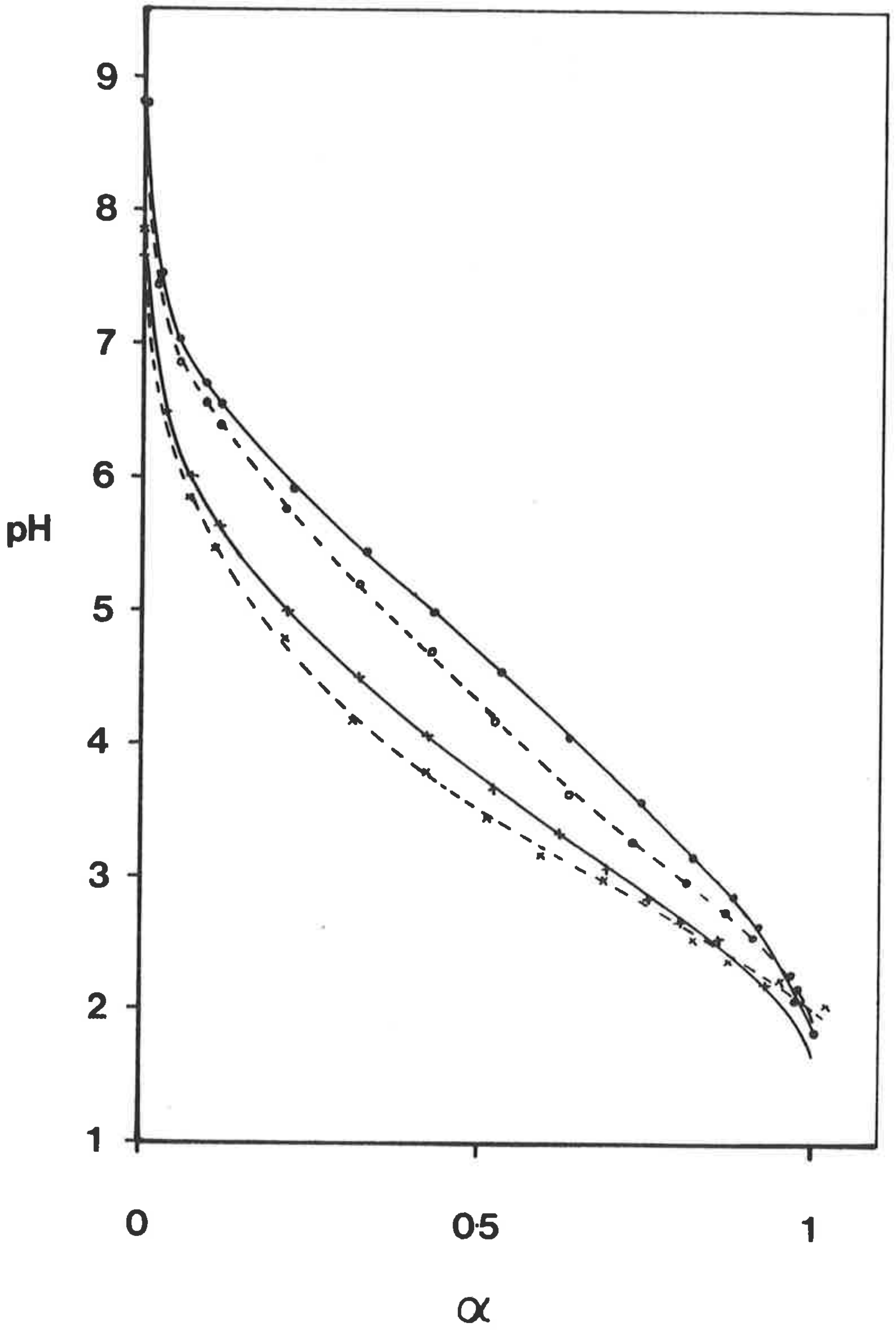
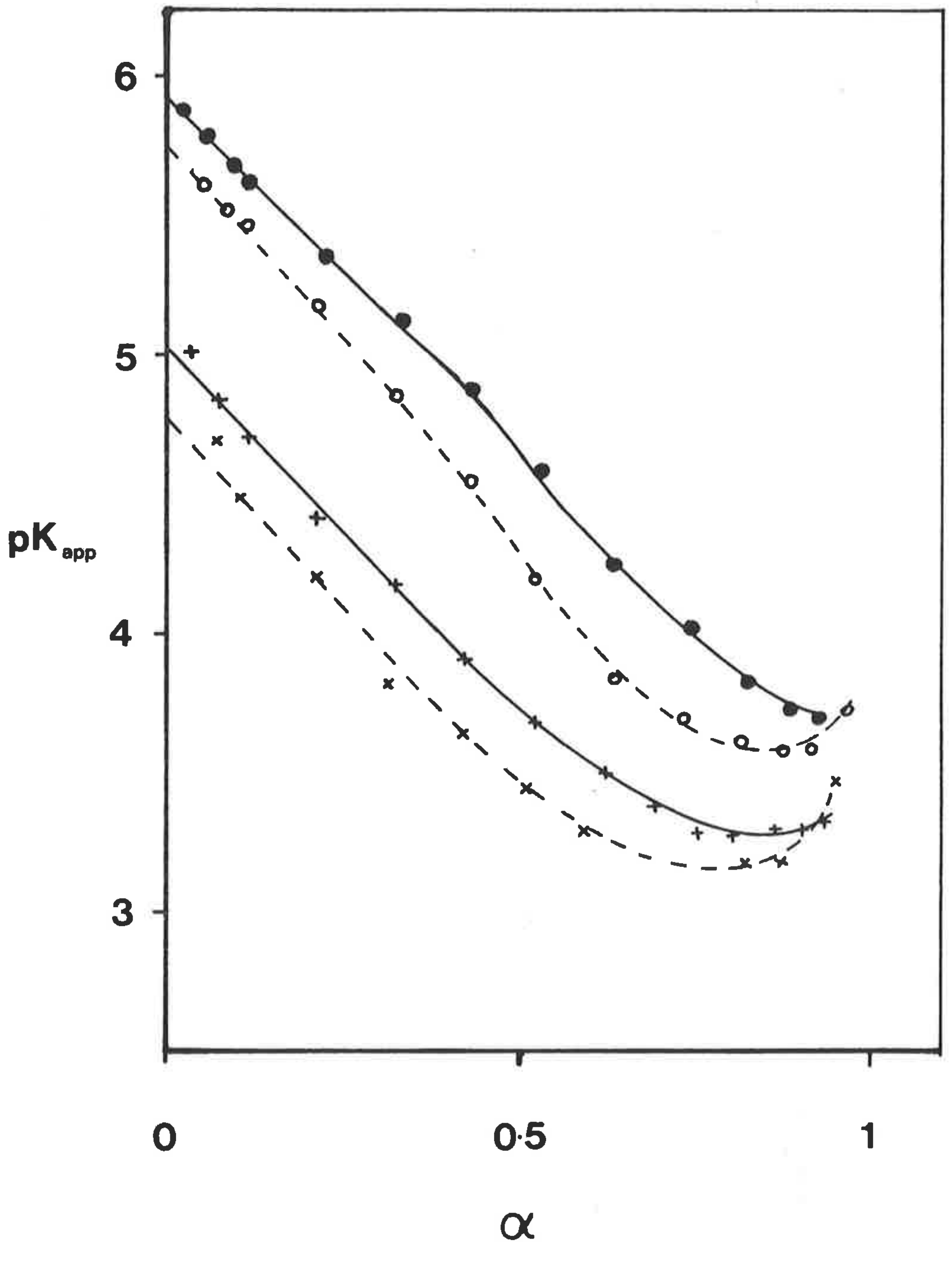

pH
9
8
7
6
5
4
3
2
1
0
0·5
1
α

Fig. 6.20 pK_{app} vs. α PLOTS FOR PVI IN AQUEOUS SOLUTION.

Symbols

In water		In 0.0200 mol dm^{-3} NaCℓ
○	T = 25.0°C	●
×	T = 80.0°C	+

Conc. of polymer ≡ 1.84×10^{-2} mol dm^{-3}


6
5
4
3
pK
app
0
0·5
1
α

show the titration curves of PVI, which displays the typical characteristics of a polybase; the absolute values of pK_{app} compare well with those of previous authors (Gold and Gregor, 1958). The values of pK_o and $\left(pK_{app}\right)_{0.5}$ for all three polymers are listed in Table 6.7. The pK_o values for the 9.3% dodecyl derivative are uncertain as solution was achieved in water at $\alpha \approx 0.10$ and in sodium chloride solution at $\alpha \gtrsim 0.40$. This means that the extrapolation to zero ionisation is very subjective.

Notwithstanding the difficulties mentioned above, the trends in pK_o, $\left(pK_{app}\right)_{0.5}$ and ΔpK values are reasonably clear. There is a significant reduction in the intrinsic dissociation constant when some of the base groups are permanently charged. However, the reduction in $\left(pK_{app}\right)_{0.5}$ values is much smaller. Therefore this reduction in dissociation constant can be ascribed largely to the charging process and not to any increased charge density as a result of increased compactness. This is consistent with the fact that uncharged PVI is relatively compact in solution, probably of a similar configuration to its dodecyl derivatives. Gold and Gregor (1958) have shown that the molecular dimensions of PVI polymer chains increase with ionisation up to $\alpha \approx 0.50$, due to electrostatic repulsions (polyelectrolyte effect), followed by a slight decrease with further ionisation as a result of counterion binding at higher ionic strength. In summary, the potentiometric results of this system are very unproductive as far as conformational changes are concerned.

The thermal effect, $\Delta\left(pK_{app}\right)_{0.5}$, is quite independent of dodecyl group content in the range covered. The average thermal effect is 0.86 pH units (standard deviation = 0.06 pH units), which is significantly larger than that for P4VP derivatives. However, this may in part be due to the fact that PVI is a stronger polybase than P4VP

TABLE 6.7

pK_o and $\left(pK_{app}\right)_{0.5}$ Values for PVI and Dodecyl Derivatives

Sample	Conc. (g/100 cm^3)	In water			In 0.02 mol dm^{-3} NaCℓ		
		$\left(pK_o\right)^{T=25}$	$\left(pK_o\right)^{T=80}$	ΔpK_o	$\left(pK_o\right)^{T=25}$	$\left(pK_o\right)^{T=80}$	ΔpK_o
PVI	0.1956	5.75	4.78	0.97	5.94	5.03	0.91
9.3% dodecyl	0.220	5.17	4.50	0.67	5.52	4.78	0.74
23.3% dodecyl	0.218	5.22	4.25	0.97	5.50	4.70	0.80
		$\left(pK_{app}\right)_{0.5}^{T=25}$	$\left(pK_{app}\right)_{0.5}^{T=80}$	$\left(\Delta pK_{app}\right)_{0.5}$	$\left(pK_{app}\right)_{0.5}^{T=25}$	$\left(pK_{app}\right)_{0.5}^{T=80}$	$\left(\Delta pK_{app}\right)_{0.5}$
PVI	0.1956	4.28	3.46	0.82	4.67	3.73	0.94
9.3% dodecyl	0.220	4.10	3.32	0.78	4.49	3.64	0.85
23.3% dodecyl	0.218	4.17	3.28	0.89	4.52	3.62	0.90

and hence the ionisation constant of water may play a more significant role.

6.5 Conclusions

From the correlation of viscosity with potentiometric measurements on all of the polymers in the foregoing Section 6, it can be concluded that no conformational transitions (i.e. major conformational changes over a narrow range of environment) take place, whether the polymers were polyelectrolytes or polysoaps, as a function of ionisation or temperature. Even those dodecyl derivatives of P4VP in the critical region of polyelectrolyte to polysoap transition (4.4% and 6.6% dodecyl) existed as a polyelectrolyte and a polysoap respectively, under all conditions of ionisation and at both temperatures. This means that the position of the potential charge groups ('free' pyridine nitrogens) is such that, rather than disrupt the hydrophobic interactions of the non-polar hydrocarbon chains, they facilitate polysoap formation upon ionisation. The effect of increased alkyl quaternisation is to lower the basicity of the free base groups. Formation of a polysoap structure has an effect over and above this general polyelectrolyte phenomenon as a result of the increased charge density in such a compact structure.

The magnitude of the thermal effect for both polybase types is of interest. The titration curves of the monomeric analogue of P4VP, 4-ethylpyridine, at 25.0 and 80.0°C are shown in Figure 6.21. Note that the pK_a values are 6.19 and 5.68 respectively; the thermal effect is $\Delta pK_a = 0.51$. This value is practically identical to that mean value for the P4VP derivatives in Section 6.2.1 (0.57 pH units). Hence the thermal effect seems to be independent of the polymeric nature of the polybases. As outlined in Section 3.3, the important value to consider

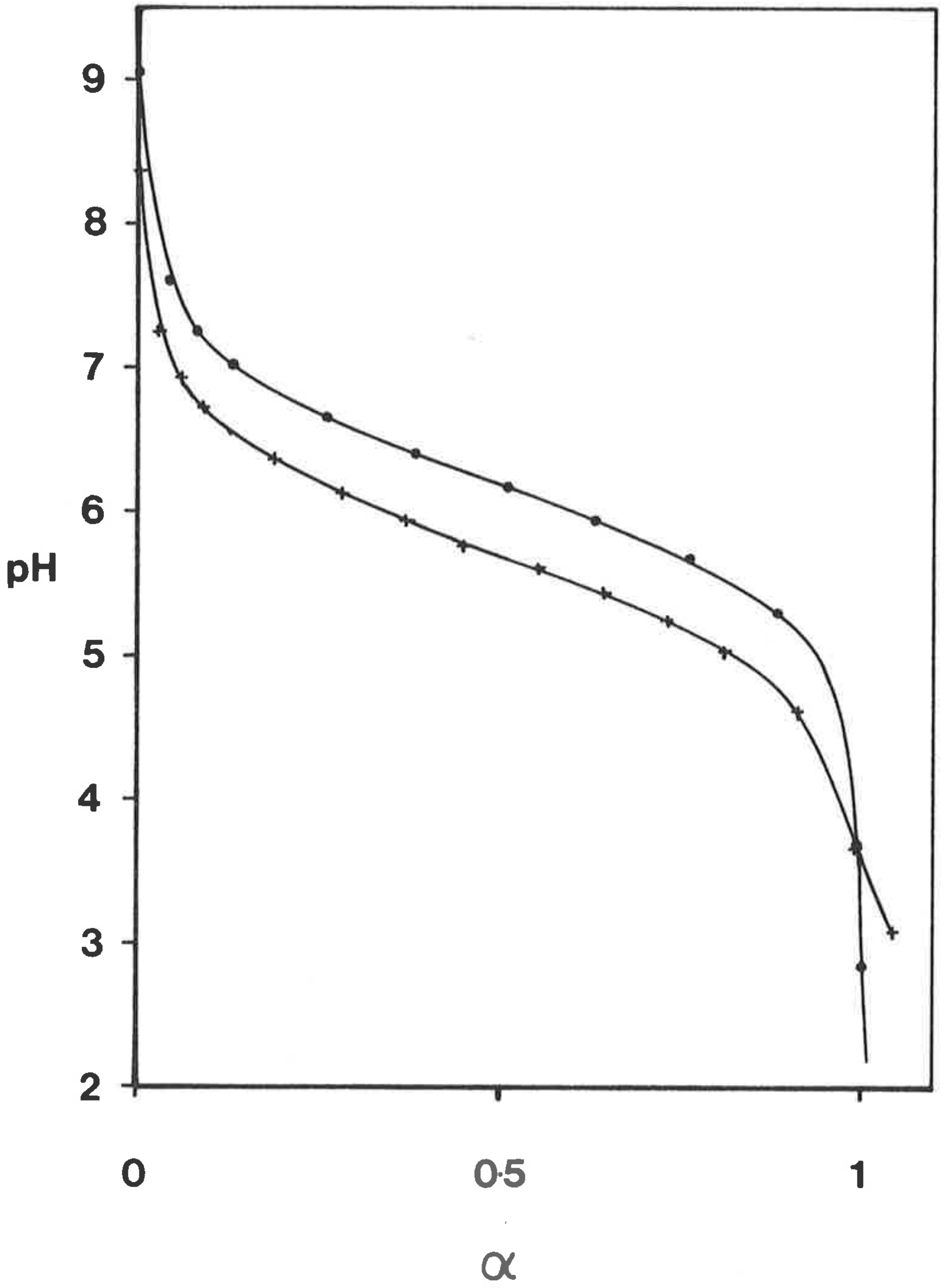
Fig. 6.21 TITRATION CURVES OF 4-ETHYLPYRIDINE IN 0.0200 mol dm^{-3} NaCℓ.

Symbols

● T = 25.0°C

+ T = 80.0°C

Conc. of 4-ethylpyridine ≡ 0.020 mol dm^{-3}


9
8
7
6
pH
5
4
3
2
0
0·5
1
α

for bases is ΔpK_b, and not ΔpK_a. However, this is only a clear argument when the base is such that $pK_a > 7$ at 25°C, as the ionisation of water has an increasingly important role as the pH increases above and beyond neutrality. Nevertheless, if this difficulty is ignored, the polymer analogous values of ΔpK_b are 0.83 pH units for the P4VP derivatives and 0.54 pH units for the PVI and its dodecyl derivatives. The meaning of these values is that the polybases are stronger bases at high temperature than would be the case if the change in the ionisation of water solely determined the magnitudes of the thermal effects. In other words, there is a real change in their basic strength with temperature, but in the opposite direction to that which is of use to Sirotherm. A cautionary comment is that the interpretation is obscured by the fact that the polybases in this section are such weak polybases that their conjugate polyacids are stronger in acid strength than the polybases are in base strength ($pK_{app} < 7$ at 25°C). This means that the increased thermal effect for PVI may in part be due to its higher pK_{app} value.

The results obtained from both potentiometric and viscosity measurements provide some further clues to the physical description that best fits polysoaps in solution. The following observations can be accommodated into the statistical model of polysoaps proposed by Nakagawa and Inoue (1964) and discussed in Section 4.1. The most obvious question raised by the lack of any conformational transition in the polysoaps as a function of ionisation is that, if uncharged basic groups are buried in the non-polar interior of a highly aggregated molecule, why then does the protonation of such groups not disrupt the aggregated state? This can be understood in one of two ways: either, the uncharged groups are not *buried* within such a structure, but are in such close proximity to aggregated hydrophobic pockets along the polymer backbone, that the charge density in the near environment is still high enough to depress the basic strength; or, the protonation of the uncharged groups that are buried within the structure simply causes minor conformational changes in the polymer backbone that place the newly charged groups on the periphery of the micellar structure. Both interpretations seem to fit the experimental results equally well. In actual fact, there is probably some character of both descriptions in the real situation.

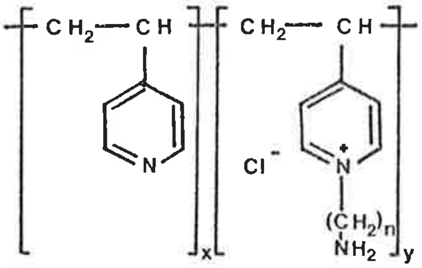
None of the results obtained contradict the enthalpic nature of 'hydrophobic bonds', but nor do they offer positive support. The disappointing feature of the results is that the interpretation of the thermal effect is obscured by the very weak basic strength of both P4VP and PVI and their derivatives. One thing that is reasonably clear is that the thermal effect for P4VP derivatives is apparently unaffected by molecular compactness when the base group is incorporated into the polymer backbone and the compactness results from aggregation of pendant groups. The implication of this work is that the interpretation of results would be much simpler for 'stronger' weak polybases.

7. POLY-4-VINYL-N-1-AMINOALKYLPYRIDINIUM CHLORIDES

7.1 Reasons for Type of Polymer

As a result of the behaviour of the polyacids and polybases presented in Sections 5 and 6, it would appear that there is something unique about the polyacids that exhibit conformational transitions (PMA and PEA, plus other polyacids mentioned), but is absent for the polybases such as the derivatives of P4VP and PVI. The major difference in the general structures is that the carboxylic acid groups are in close proximity to hydrophobic substituents at zero charge, whereas the basic nitrogen atoms are nearer the hydrophilic environment of surrounding charged nitrogen atoms at $\alpha = 0$. There are two basic ways of overcoming this problem. The first is to position the potential charge group (base group) away from the hydrophilic environment of the quaternised nitrogen atoms and into the hydrophobic environment by attaching the base group to the free end of the pendant hydrocarbon chain. The second is to prepare a polymer with the base group as part of a hydrophobic backbone, for example, polybase analogues of PMA and PEA. The first of these alternatives is the subject of this Section, while the latter has been left as an area for further study.

Hence a series of P4VP derivatives was prepared by quaternising the parent polymer with alkyl halides, to the other end of which was attached the potential charge group. The details of the preparations are contained in the Experimental, Section 10.2.4. Polymers prepared were of the general structure:



(random copolymer)

where $n = 4$, 8, 12

and x and y varied according to particular conditions of preparation.

With this series of polybases (actually polydibases), there is the possibility of amine groups being buried within a hydrophobic environment. On the basis of polyelectrolyte and polysoap studies of P4VP derivatives, the conformation of these new derivatives in solution can be tentatively predicted, provided that the amine group does not disrupt hydrophobic interactions. When $n = 4$, the polymer should behave like a polyelectrolyte in solution; $n = 8$, the properties would depend on the degree of quaternisation; $n = 12$, the polymer should be a polysoap for greater than 10% quaternisation. These conformations in solution may, or may not, directly affect the potentiometric properties of the pendant amine groups. Hence potentiometry is correlated with viscosity for the elucidation of the conformations of these polymers in aqueous solution.

7.2 Experimental Results

7.2.1 Potentiometric Titrations

The polymer samples shown in Table 7.1 were titrated in aqueous solution at 25.0 and 80.0°C. The percentages of pyridine N atoms quaternised with aminobutyl, aminooctyl and aminododecyl chloride are shown and the corresponding derivatives are labelled PAB, PAO and PAD respectively. Since the aminobutyl derivatives are quite soluble in water (c.f. poly-4-vinyl-N-n-butylpyridinium bromide; Fuoss and Strauss, 1948), two samples of different degrees of quaternisation were prepared to study the effects of increased charge on the potentiometric properties. The aminooctyl derivative required a high degree of quaternisation to make a water soluble polymer, and the aminododecyl derivative was prepared from poly-4-vinyl-N-ethylpyridinium chloride to make it water soluble. The only requirement for the aminododecyl sample was to quaternise as many pyridine nitrogen atoms with aminododecyl groups as possible, so that a polysoap structure would form (> 8% quaternisation). The higher the degree of quaternisation, the more base groups are present for titration.

TABLE 7.1

Compositions of Aminoalkyl Derivatives of P4VP

Sample	Percentage of pyridine nitrogen quaternised with aminoalkyl chloride
PAB1	34
PAB2	45
PAO	63
PAD*	16

*PAD has 40.7% of pyridine nitrogen atoms quaternised with ethyl chloride also.

The shapes of the titration curves, pH versus α, for PAB1 and PAB2 are similar, the most significant difference being the decrease in basicity with increased degree of quaternisation. Figure 7.1 shows the titration curves of PAB2 in the forward and backward directions. The shape is very similar to the titration curve of a simple aliphatic amine. Figure 7.2 shows quite clearly the relationship between basic strength and ionisation, where at both temperatures there is a slight increase in pK_{app} up to $\alpha \approx 0.25$, followed by a fairly constant value up to $\alpha \approx 0.60$, and thereafter a gradual decrease in pK_{app} up to $\alpha = 1.0$. This can be tentatively explained by an initial chain expansion, followed by an equilibrium chain configuration with amine groups sufficiently separated to titrate like an aliphatic amine with a single dissociation

Fig. 7.1 TITRATION CURVES OF PAB2 IN AQUEOUS SOLUTION (NO ADDED SALTS).

(45% AMINOBUTYL DERIVATIVE OF P4VP).

Symbols

Titration of base		Titration of conjugate acid
○	$T = 25.0^\circ C$	●
×	$T = 80.0^\circ C$	+

Conc. of polymer ≡ 0.220 g/100 cm^3

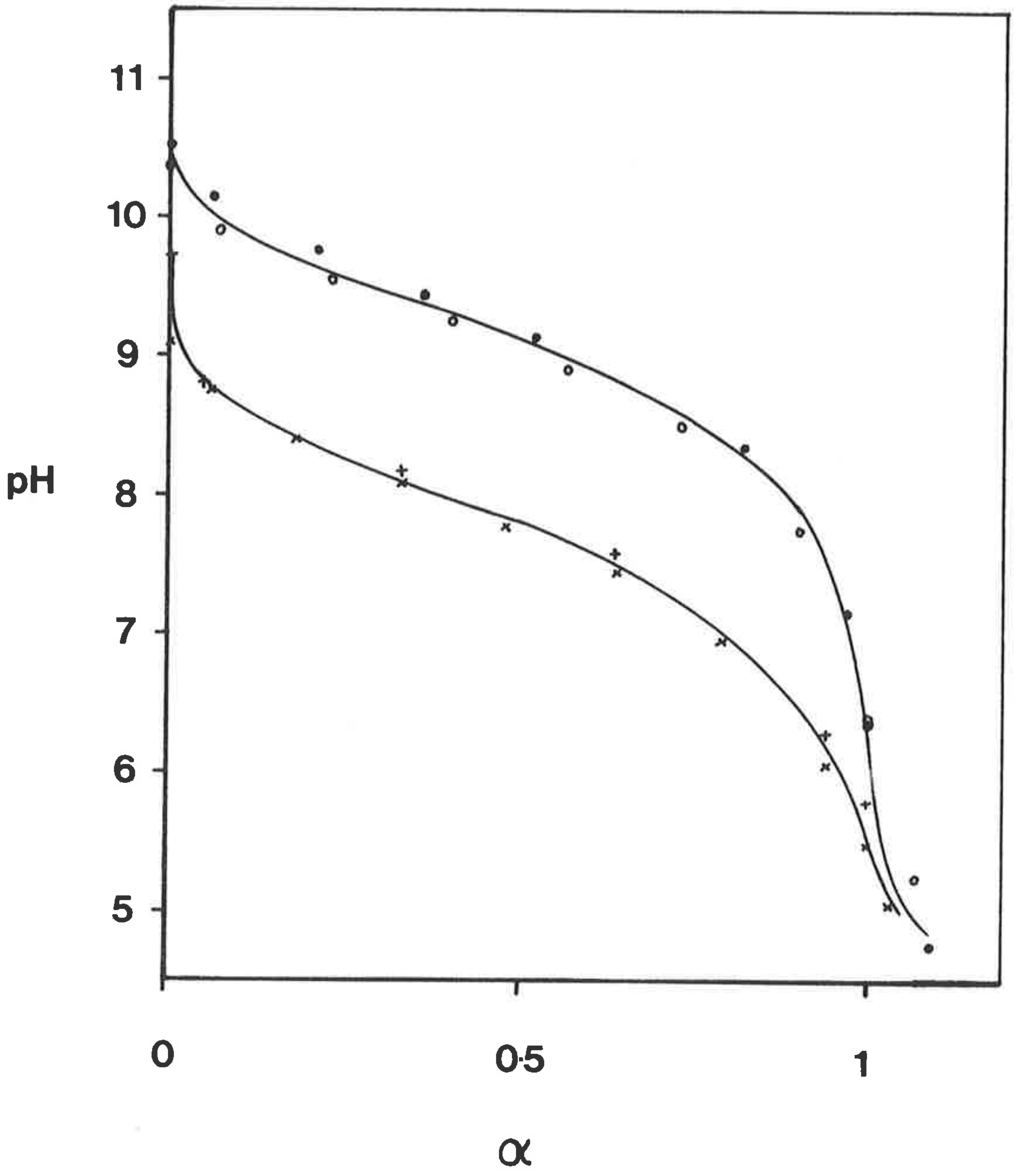

11
10
9
8
7
6
5
pH
0
0·5
1
α

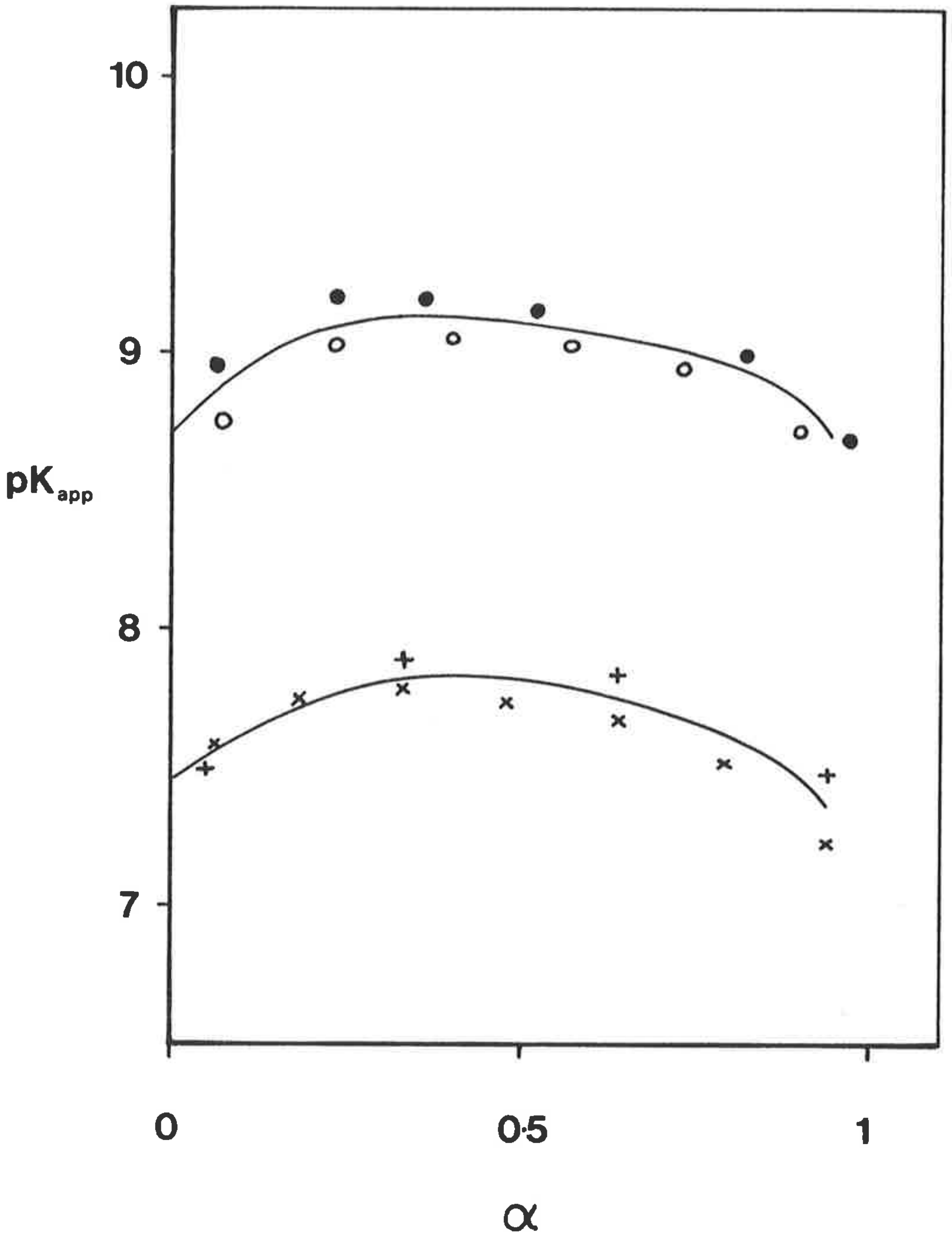
Fig. 7.2 pK_{app} vs. α PLOTS FOR PAB2 IN AQUEOUS SOLUTION (NO ADDED SALTS).

(45% AMINOBUTYL DERIVATIVE OF P4VP).

Symbols

Titration of base		Titration of conjugate acid
○	T = 25.0°C	●
×	T = 80.0°C	+

Conc. of polymer ≡ 0.220 g/100 cm^3


10
9
8
7
pK$_{app}$
0
0·5
1
α

constant, and finally a gradual decrease in basic strength as significant electrostatic interactions between protonated amine groups occur. The results of PAB1 mirror those of PAB2, apart from a less noticeable decrease in pK_{app} at high α due to the lower degree of quaternisation.

The basicity of the amine groups in sample PAO was much higher than that for the PAB samples and the titration curves were more characteristic of polyelectrolytes at $\alpha > 0.40$. Figures 7.3 and 7.4 show the plots of pH versus α and pK_{app} versus α respectively, for two independent titrations at both temperatures. One of the titrations at 25.0°C was performed after the sample had first been heated to 80.0°C; this was to test for any irreversible conformational changes as a function of temperature. As a consequence of the high pH at which the amine groups were first protonated (~11.5 at 25.0°C and ~10.0 at 80.0°C), the titration curve of sample PAO was difficult to obtain accurately, because of hydroxide ion counterion binding. A sample of P4VP fully quaternised with ethyl chloride was titrated as a control. The pH at the inflexion of this plateau-shaped titration curve corresponded to the pH at which there was a small inflexion point in the titration curve of PAO. Hence this point was set as the commencement of titration for the amine groups in PAO ($\alpha = 0$). The equivalence point ($\alpha = 1.0$) was difficult to determine from $\partial pH/\partial \Delta V$ in the forward direction because of the large change in pH over a relatively large range of added acid. Fortunately, the maximum in $\partial pH/\partial \Delta V$ was quite clear in the reverse direction (titrate the protonated amine with base).

Figures 7.5 and 7.6 show the potentiometric titration curves of sample PAD, the shapes of which suggest the titration of an aliphatic amine over much of the range of α. The basic strength lies between that of PAB1 and PAO. There seems to be no evidence for any unusual electrostatic effects associated with the titration of PAD.

Fig. 7.3 TITRATION CURVES OF PAO IN AQUEOUS SOLUTION (NO ADDED SALTS).

(63% AMINOOCTYL DERIVATIVE OF P4VP).

Symbols

Titration 1		Titration 2
○	$T = 25.0^\circ C$	● *
×	$T = 80.0^\circ C$	⊗

Conc. of polymer ≡ 0.230 g/100 cm^3

*Heated to 80.0°C before titrated at 25.0°C.

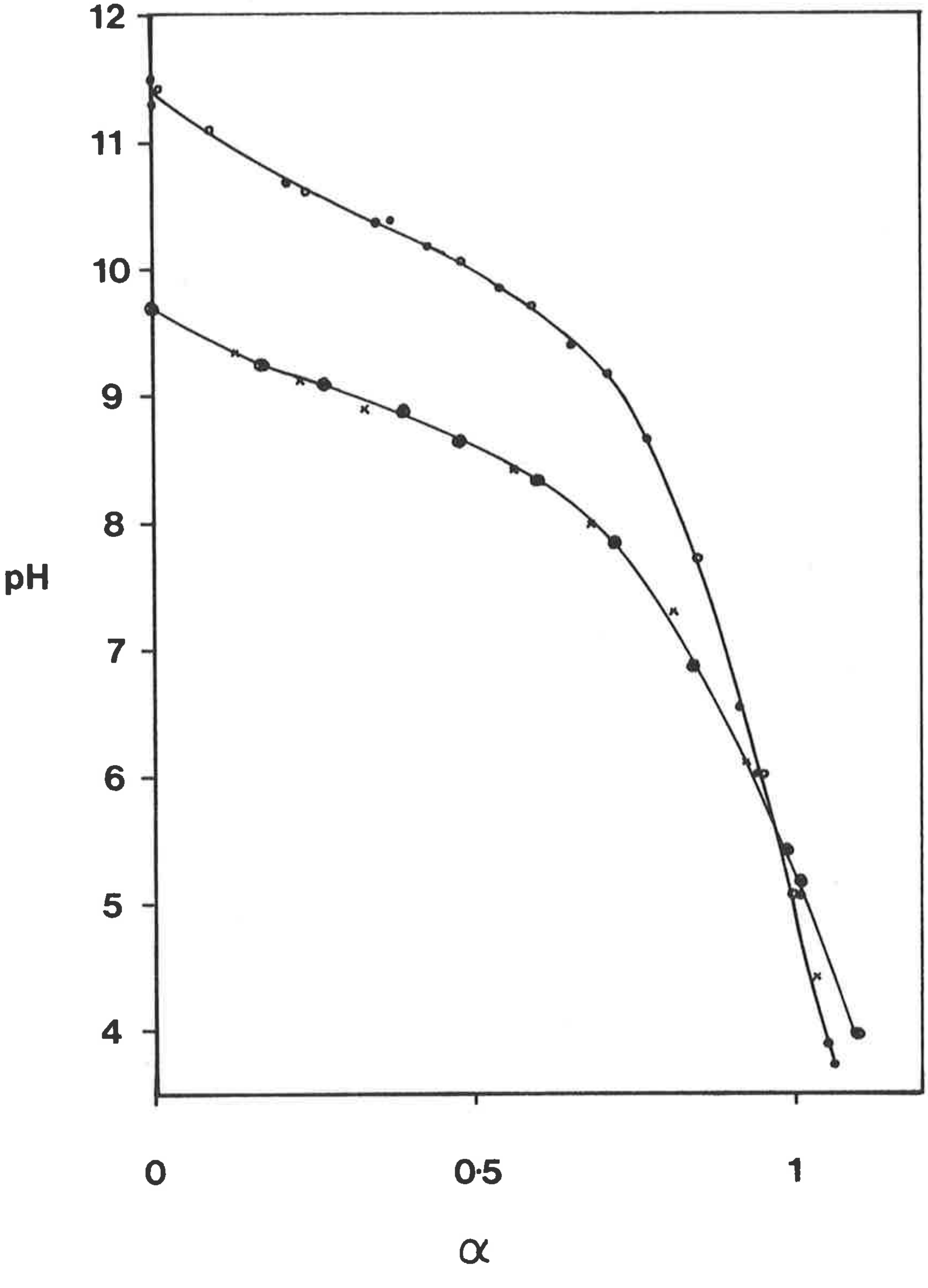

12
11
10
9
8
7
6
5
4
pH
0
0·5
1
α

Fig. 7.4 $\mathrm{p}K_{\mathrm{app}}$ vs. α PLOTS FOR PAO IN AQUEOUS SOLUTION (NO ADDED SALTS).

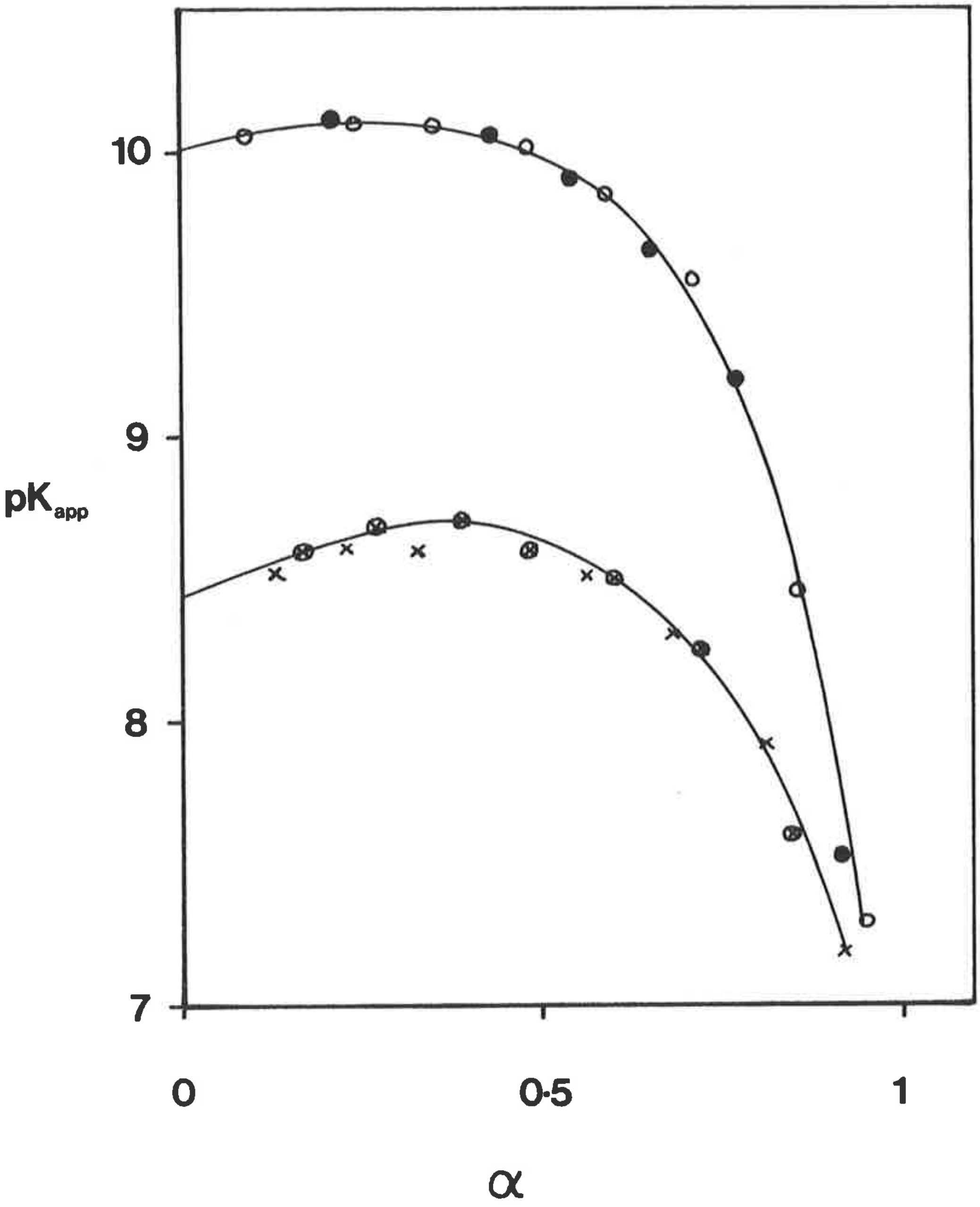
(63% AMINOOCTYL DERIVATIVE OF P4VP).

Symbols

Titration 1		Titration 2
○	T = 25.0°C	● *
×	T = 80.0°C	⊗

Conc. of polymer ≡ 0.230 g/100 cm^3

*Heated to 80.0°C before titrated at 25.0°C.



10
9
8
7
pK$_{app}$
0
0·5
1
α

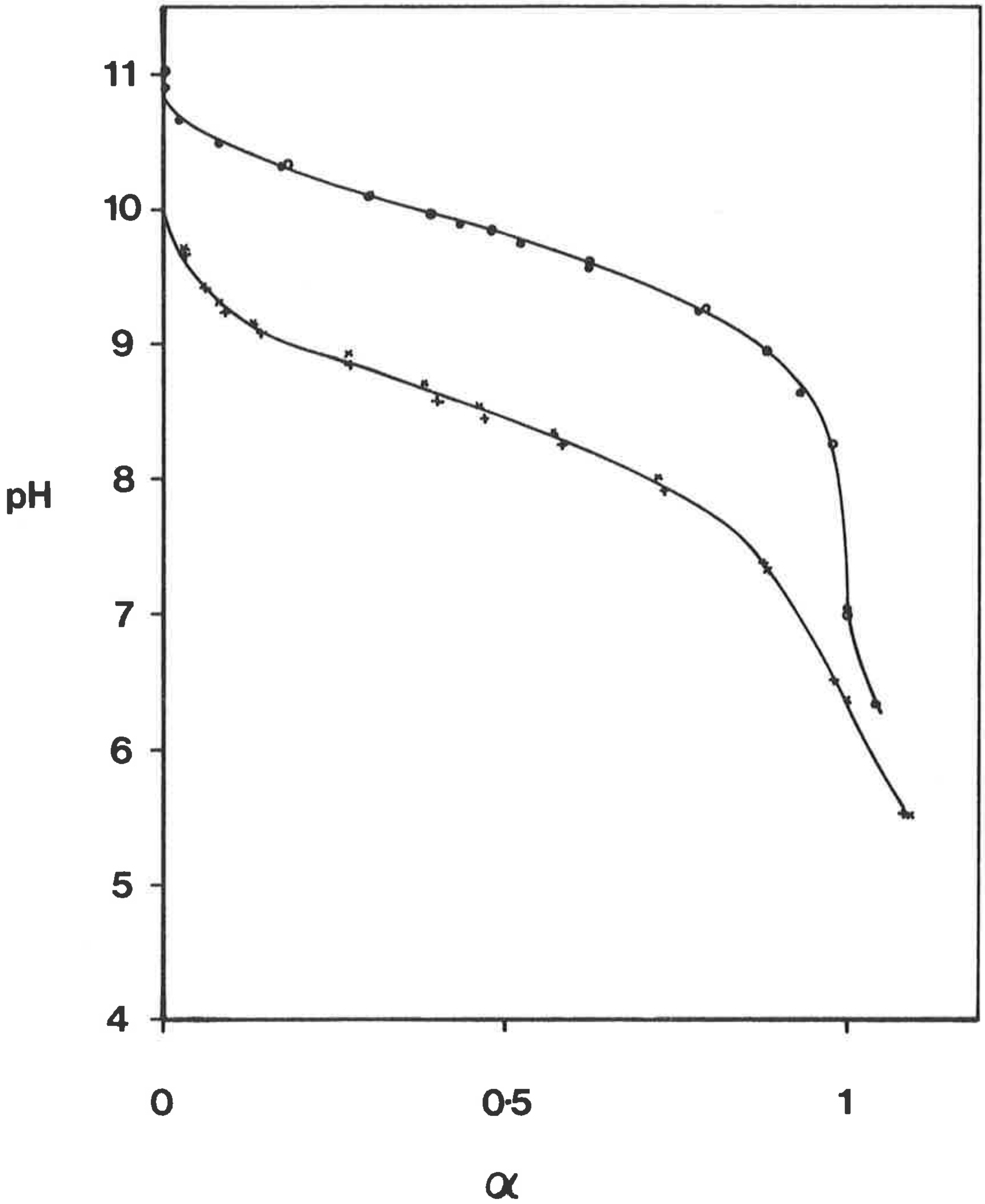
Fig. 7.5 TITRATION CURVES OF PAD IN AQUEOUS SOLUTION (NO ADDED SALTS).

(16% AMINODODECYL DERIVATIVE OF P4VP).

Symbols

Titration 1		Titration 2
○	T = 25.0°C	●
×	T = 80.0°C	+

Conc. of polymer $\equiv$ 0.405 g/100 cm^3



pH
11
10
9
8
7
6
5
4
0
0·5
1
α

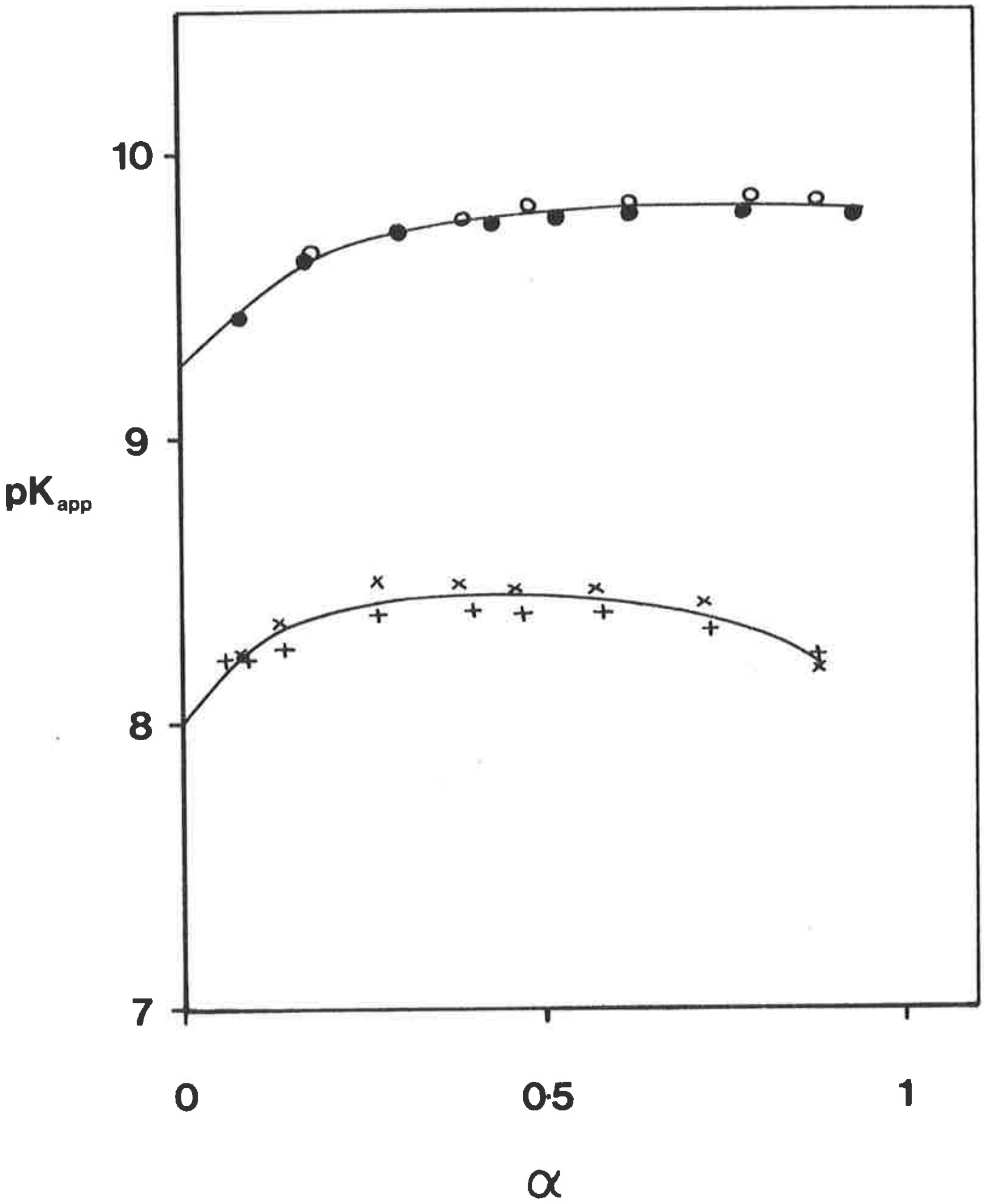
Fig. 7.6 pK_{app} vs. α PLOTS FOR PAD IN AQUEOUS SOLUTION (NO ADDED SALTS).

(16% AMINODODECYL DERIVATIVE OF P4VP).

Symbols

Titration 1		Titration 2
○	$T = 25.0^{\circ}\text{C}$	●
×	$T = 80.0^{\circ}\text{C}$	+

Conc. of polymer ≡ 0.405 g/100 cm^3


10
9
8
7
pK_app
0
0·5
1
α

Values of pK_o and $\left(pK_{app}\right)_{0.5}$ for all samples at both temperatures are tabulated in Table 7.2, together with the difference values for the thermal effect. Although the extrapolation of pK_{app} to $\alpha = 0$ is a little subjective, there seems to be a confirmation of the trends in $\left(pK_{app}\right)_{0.5}$ values.

TABLE 7.2

Titration Constants for Aminoalkyl Derivatives of P4VP in Water

Sample	$\left(pK_o\right)^{T=25}$	$\left(pK_o\right)^{T=80}$	ΔpK_o	$\left(pK_{app}\right)_{0.5}^{T=25}$	$\left(pK_{app}\right)_{0.5}^{T=80}$	$\left(\Delta pK_{app}\right)_{0.5}$
PAB1	9.05	7.75	1.30	9.59	8.26	1.33
PAB2	8.80	7.50	1.30	9.04	7.74	1.30
PAO	10.00	8.45	1.55	10.02	8.56	1.46
PAD	9.25	8.00	1.25	9.79	8.43	1.36

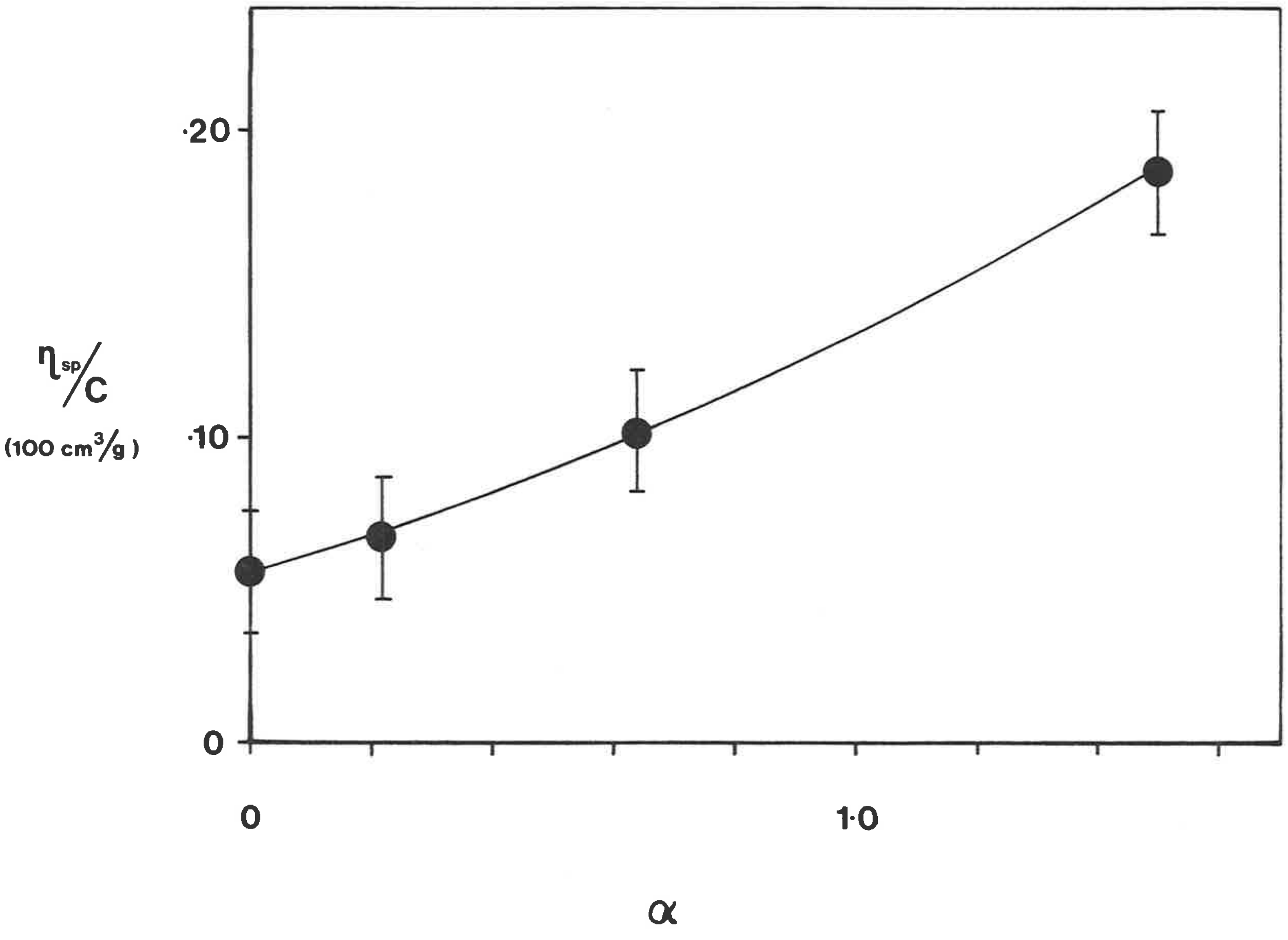
The mean values of ΔpK_o and $\left(\Delta pK_{app}\right)_{0.5}$ are 1.35 (standard deviation = 0.14) and 1.36 (standard deviation = 0.07) pH units respectively. Since the value of ΔpK_w is 1.40 pH units over this temperature interval, and the bases are relatively 'strong' weak polybases, then the implication is that the basicity of the amine groups is unaffected by temperature ($\Delta pK_b \approx 0$). Hence the discussion of results in Section 7.3 centres around the differences between the 'polymeric' and monomeric alkylamines in basic strength, rather than any temperature effects.

7.2.2 Viscosity Measurements

The viscosity of sample PAB2 in aqueous solution was determined as a function of pH at 25.0°C, as being representative of both PAB1 and PAB2. Figure 7.7 shows the variation in the viscosity number, η_{sp}/C, with

Fig. 7.7 VISCOSITY NUMBER FOR PAB2 AS A FUNCTION OF IONISATION IN AQUEOUS SOLUTION AT 25.0°C (NO ADDED SALTS).

Conc. of polymer $\equiv$ 0.2200 g/100 cm^3 at $\alpha = 0$.



η_{sp}/C
(100 cm^3/g)
·20
·10
0
0
1·0
α

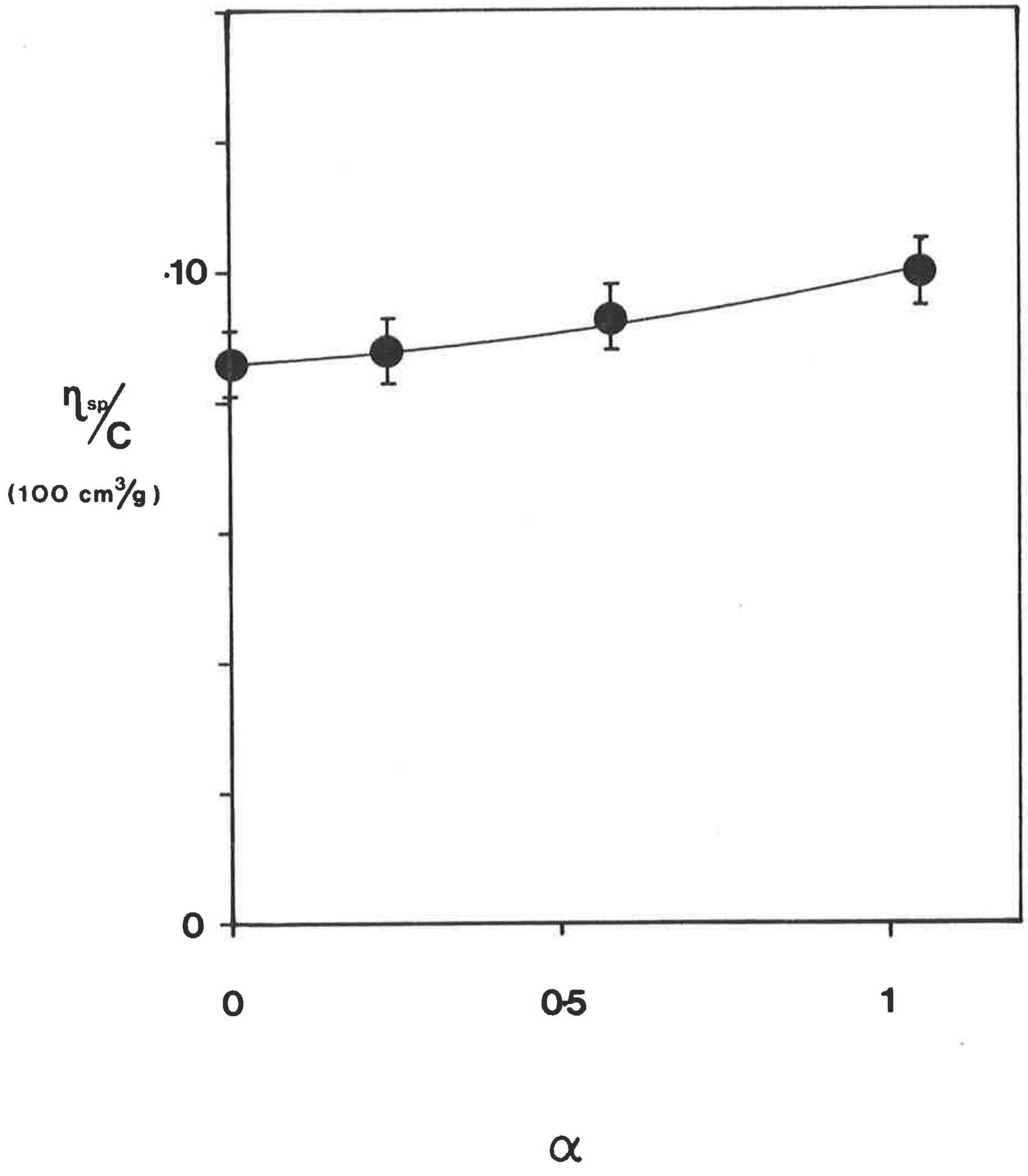
estimated α values (the α values were interpolated from the potentiometric titration curve of PAB2). The value of $\alpha > 1.0$ is arbitrarily expressed in terms of the equivalents of amine groups, whereas it actually refers to the titration of the unquaternised pyridine nitrogen atoms. There is a definite chain expansion with increasing protonation as expected intuitively. The increased electrostatic repulsions introduced by the protonated amine groups, which are in close proximity to, but not on the backbone, causes gradual chain expansion over the full range of ionisation. After the titration of all the amine groups, the protonation of the free pyridine groups causes further chain expansion as the polymer backbone is further stiffened. This interpretation is also consistent with the potentiometric properties displayed by these derivatives.

Figure 7.8 shows the viscosity of PAO as a function of α in water at 25.0°C. There is only a small, but gradual, increase in the viscosity with protonation of the aminooctyl groups. This would tend to indicate that there is no change from a compact conformation at $\alpha = 0$ to an expanded configuration at higher α. Obviously the polymer is reasonably extended at $\alpha = 0$ because of the high degree of quaternisation of pyridine groups. The polyelectrolyte-like behaviour of the potentiometric properties at higher α is reflected in the increased viscosity; in other words, the electrostatic repulsions cause a slight chain expansion, but not as great as that for the aminobutyl derivatives. This would be a manifestation of the great flexibility of the longer, pendant octyl chain.

The viscosity of PAD as a function of pH was determined in water at 25.0 and 80.0°C, by titrating the free base with $HC\ell$ at 25.0°C and then back titrating the conjugate acid with NaOH at 80.0°C. This accounts for some of the decrease in viscosity at 80.0°C. As sample

Fig. 7.8 VISCOSITY NUMBER FOR PAO AS A FUNCTION OF IONISATION IN AQUEOUS SOLUTION AT 25.0°C (NO ADDED SALTS).

Conc. of polymer $\equiv$ 0.2308 g/100 cm^3 at $\alpha = 0$.



·10
0
η_{sp}/C
(100 cm^3/g)
0
0·5
1
α

PAD was prepared from the same poly-4-vinyl-N-ethylpyridinium chloride sample as was the 8.7% dodecyl polysoap (Section 6.2.1), the viscosity number, η_{sp}/C, of PAD can be compared with the values obtained for the polyelectrolyte and polysoap derivatives of P4VP in Section 6.2.2. The viscosity numbers of PAD at $\alpha = 0$ and $\alpha = 1.00$ for both temperatures are plotted on the graph showing the viscosity as a function of per cent dodecyl group content for the ethyl and dodecyl derivatives of P4VP, in Figure 7.9. Quite clearly, PAD exhibits a compact, polysoap structure in aqueous solution at $\alpha = 0$ at both temperatures. However, the viscosity of PAD as a function of α shows quite a different behaviour to that observed for the 'conventional' P4VP polysoaps, which showed a slight decrease at full ionisation. Figure 7.10 shows this variation of η_{sp}/C versus α, where once again, α was interpolated from the titration curve of PAD and the measured pH of the solutions. At 25.0°C, there is a rapid expansion with ionisation up to approximately half neutralisation, followed by a fairly constant expansion up to full ionisation. The values of $\alpha > 1$ are arbitrarily expressed relative to the moles of amine groups, but represent the titration of pyridine groups. The viscosity at 80.0°C shows similar characteristics, although the initial increase may not be as great. Hence at both temperatures, the polysoap structure is disrupted by ionisation to form an expanded polyelectrolyte structure at full protonation of the amine groups. The transition is of a continuous chain expansion and hence there are no unusual potentiometric properties of the linear polymer, as shown in Section 7.2.1, apart from a slight initial increase in pK_{app} at low α.

7.3 Discussion

The thermodynamic values of the dissociation constants of the aliphatic amines, 1-aminobutane, 1-aminooctane and 1 aminododecane are

Fig. 7.9 VISCOSITY NUMBER FOR PAD AT $\alpha = 0$, PLOTTED ON THE GRAPH OF VISCOSITY NUMBER VERSUS DODECYL GROUP CONTENT FOR ETHYL AND DODECYL DERIVATIVES OF P4VP (FROM Fig. 6.17); AT 25.0 AND 80.0°C (NO ADDED SALTS).

Symbols

		Conc. (g/100 cm^3) at $\alpha = 0$
◆	T = 25.0°C	1.5100
◇	T = 80.0°C	1.473

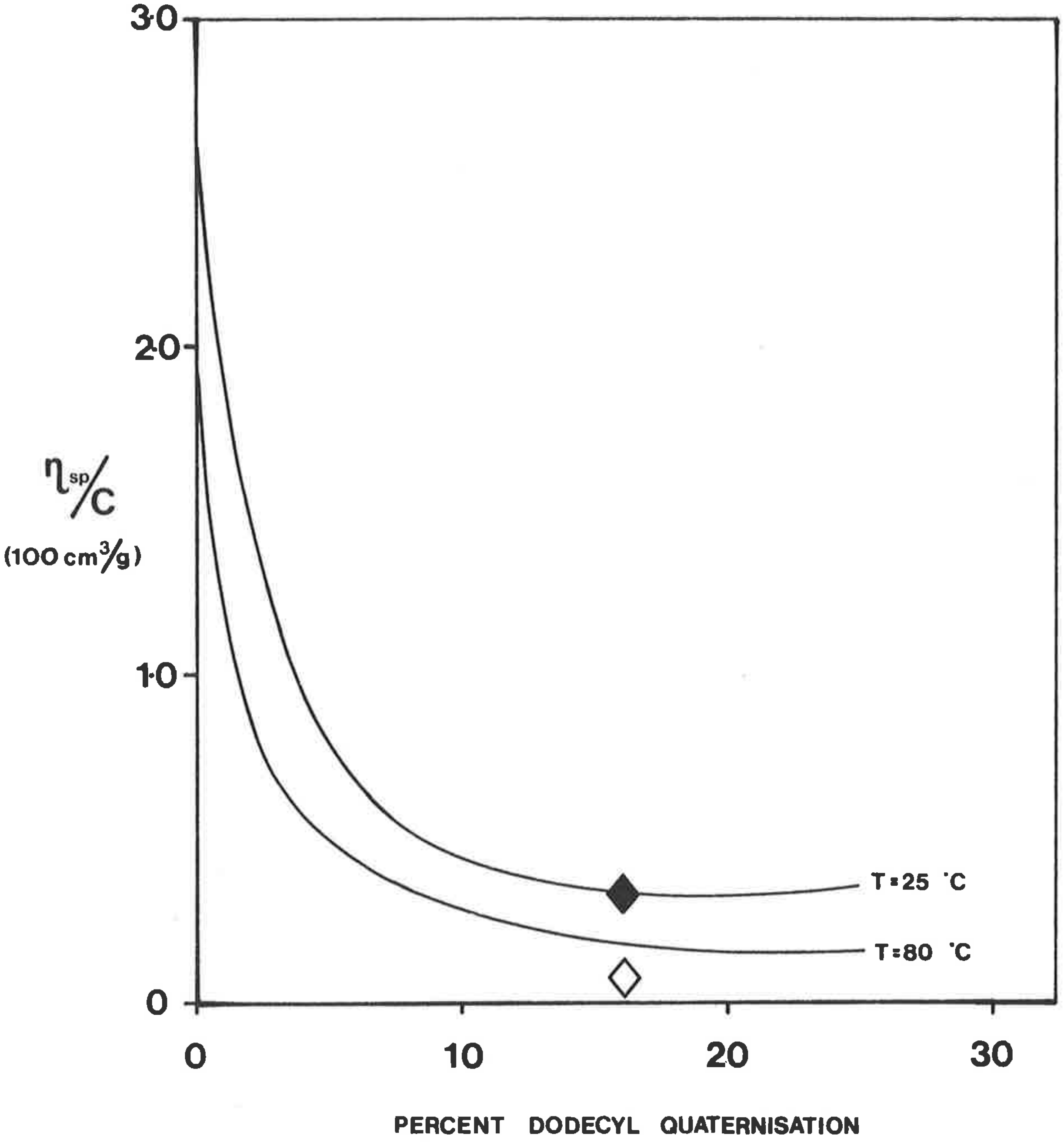
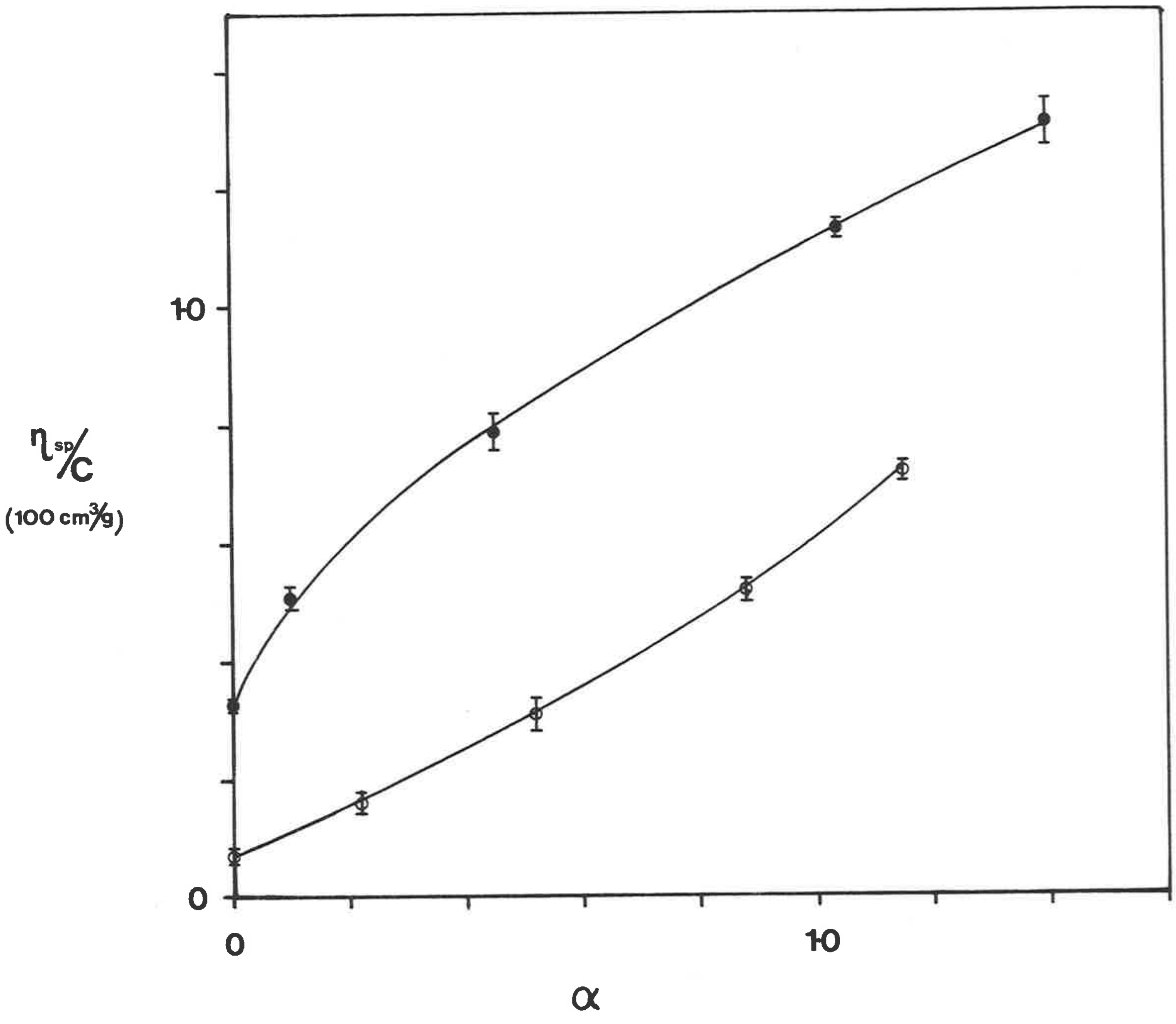

3·0
2·0
1·0
0
η_{sp}/C
(100 cm^3/g)
T=25 °C
T=80 °C
0
10
20
30
PERCENT DODECYL QUATERNISATION

Fig. 7.10 VISCOSITY NUMBER FOR PAD AS A FUNCTION OF IONISATION IN AQUEOUS SOLUTION AT 25.0 AND 80.0°C (NO ADDED SALTS).

Symbols

	Conc. (g/100 cm^3) at $\alpha = 0$
● T = 25.0°C	1.5100
○ T = 80.0°C	1.473



η_{sp}/C
(100 cm³/g)
1·0
0
0
1·0
α

very similar; pK_a values at 25.0°C are 10.66 (0.01 mol dm^{-3}), 10.65 (0.02 mol dm^{-3}) and 10.63 (0.01 mol dm^{-3}) respectively (Perrin, 1965). The effect of temperature on pK_a values is likely to be very similar for all three. The value of pK_a for the n-butylammonium ion is 10.640 (Robinson and Stokes, 2nd edition, 1970) at 25°C, from which the value at 80°C can be calculated to be 9.045 (by use of $pK_a = -\log K_a = A_1/T - A_2 + A_3T$). Hence the thermal effect is $\Delta pK_a = 1.595$. The corresponding value for the ammonium ion is 1.415. Hence the large temperature effect on the ionisation of water ($\Delta pK_w = 1.402$ over this temperature range) is the dominant part of the thermal effect for the above aliphatic amines. There is little change in the value of K_b with temperature. In this respect then, the polymeric species PAB, PAO and PAD behave in a similar manner to the simple aliphatic amines as a function of temperature.

To give a rigorous treatment of the effect on the basicity of the amine group by being attached to a polymer, the monomeric analogues with which to compare the results would be the N-1-aminoalkyl-4-ethylpyridinium chlorides. This is because there are two main factors influencing the basic strength of the amine groups:

i) the proximity of the $-NH_2$ group to the charged pyridinium group,

and ii) the proximity of each $-NH_2$ group to neighbouring $-NH_2$ groups and charged pyridinium groups, i.e. the degree of quaternisation.

The second aspect can be assessed from the fact that the $\left(pK_{app}\right)_{0.5}$ value for PAB2 is approximately 0.5 pH units lower than that for PAB1. This is clearly an effect due to the increased degree of quaternisation. Hence at least part of the decreased basicity of PAB2 can be related to the close proximity of other amine groups. Nevertheless, there is still a large effect due to the close proximity of the charged pyridine group.

This decrease in basicity of the amine group can be quite simply related to the charged pyridine group to which it is attached by comparison with the values of pK_1 and pK_2 of the simple aliphatic diamines, $NH_2(CH_2)_nNH_2$. Table 7.3 lists the values of pK_1, pK_2 and $pK_1 - pK_2$ for the diamines for n = 2 to n = 8 (from Perrin, 1965), all at 20°C, except n = 5, which is at 25°C. The values of $pK_1 - pK_2$ tend toward the statistical figure of log 4 = 0.60 (see e.g. Robinson and Stokes, 1970, p. 348) for n > 8. For the unsymmetrical case, which exists in the aminoalkyl derivatives of P4VP, there is no statistical depression of pK. Hence, for n = 4, the decrease in basicity relative to pK_1 due to the fixed charge group should be 0.85 (= 1.45 - 0.60) i.e. the value of $\left(pK_{app}\right)_{0.5}^{T=25}$ for PAB1 should be approximately 9.9. This is in excellent correlation with the value obtained (9.59), as there is likely to be a small polyelectrolyte effect on the basic strength as well.

TABLE 7.3

Dissociation Constants of Diamines

$NH_2(CH_2)_nNH_2$ (Perrin, 1965)

n	pK_1	pK_2	$pK_1 - pK_2$
2	10.08	6.99	3.09
3	10.62	8.64	1.98
4	10.80	9.35	1.45
5	10.25	9.13	1.12
6	11.10	10.01	1.09
8	11.0	10.1	0.9

On the basis of the values of pK_1 and pK_2 of the diamine for n = 8, the decrease in pK for the unsymmetrical case should be approximately

0.3(= 0.9 - 0.6) pK units i.e. the value of $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=25}$ for PAO should be approximately 10.7 (very close to the pK_a for 1-aminooctane). However, the value obtained was about 0.7 pH units lower than this predicted value. Hence there is a decrease in basic strength of the aminooctyl groups as a result of being attached to a common polymer backbone. This may be caused by either the high charge density as a result of molecular compactness, or relative closeness of amine groups as a result of the high degree of quaternisation. The molecular compactness would most likely cause most of the reduction in basic strength, while the high degree of quaternisation causes the sharp drop in basic strength at high degrees of ionisation ($\alpha > 0.5$). There are extensive electrostatic interactions between the charged groups as the polymer behaves as a polyelectrolyte. If the results for PAO are correlated with those of the octyl derivatives of P4VP in Section 6.3, then at $\alpha = 0$ for PAO, the possibility exists for a polymer molecule composed of pockets of aggregated micellar-like structures along the backbone. As the amine groups are protonated, these pockets are progressively disrupted. This model is consistent with the basic strength of the amine groups, the polyelectrolyte effect at high α, and the small increase in viscosity with protonation.

On the basis of the diamine pK values for n = 2 to n = 8, the value of $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=25}$ for the aminododecyl derivative of P4VP would be predicted to be similar to the pK_a value for 1-aminododecane. However, the actual value for PAD is approximately 0.8 pH units lower than this predicted value. As was shown by the viscosity measurements, the aminododecyl derivative does have a polysoap-like structure when all of the amine groups are in the free base form. This molecular compactness would account for the decreased basic strength of the amine groups because of the high charge density around the non-polar groups. This effect is even more striking when the degrees of quaternisation of PAD and PAO are compared. Upon protonation, the very compact structure is disrupted as the electrostatic repulsions outweigh the hydrophobic bonding - this effect is made obvious by the increase in viscosity from $\alpha = 0$ to $\alpha = 1.0$. The fact that there is no dramatic change in the basicity at any particular value of α suggests that this is not an all or none process, but that the hydrophobic interactions are gradually reduced in importance with ionisation. This explanation is consistent with a gradual change from a highly aggregated, compact molecule, through a state in which there are pockets of hydrophobic groups, to an extended, open structure. From the shape of the titration curve at $\alpha \gtrsim 0.3$, wherefrom it resembles that of an aliphatic amine, it would appear that the amine groups are exposed to the solvent in a similar way to those of a monomeric, aliphatic amine.

One feature of the potentiometric titration curves that is common to all three types of polymer is the gradual increase in basic strength of 0.2 to 0.4 pH units (as shown by pK_{app}) in the 0 to 0.3 range of the degree of protonation. This would correspond to at least some form of chain expansion, hence reducing the charge density in the vicinity of free amine groups. Thereafter the primary effect on the titration curve is amine-amine group interactions. Note that these are virtually absent for the aminododecyl sample due to the low degree of quaternisation. A conclusion to be drawn from these results is that conformational changes in polymers need not be reflected in obviously anomalous potentiometric properties.

In summary, it has been demonstrated that the electrostatic repulsions between like charged groups are sufficient to disrupt the hydrophobic interactions in compact structures, provided that the potential charge group is initially buried within the hydrophobic environment. This does not necessarily lead to anomalous titration behaviour. Also, there is evidence for the possibility of pockets of hydrophobic groups along a polymer backbone for the aminooctyl derivative, whereas the aminododecyl could be interpreted more in terms of a highly aggregated, compact molecule.

CHAPTER V

Cross-linked Polybases

8. POLYBASE GELS AND RESINS

8.1 Background

At the outset, one of the aims of this project was to prepare linear polybases that would provide fundamental information about the temperature dependence of potentiometric titrations of weak anionic exchange resins. However, in order to correlate this information from linear systems with that of the cross-linked resins, some knowledge about the effects of cross-linking on polymers of this type had to be obtained. Is there something unique about cross-linked resins in general, or is it only that particular resins have unusual properties?

In this context, a preliminary study of the general effects of cross-linking on some of the linear polybases of Sections 6.2 and 7 was made. No attempt was made at a systematic study of the effects of different types or degrees of cross-linking; this aspect was outside the scope of the present investigations. Representative samples of the ethyl and dodecyl derivatives of P4VP, and the aminoalkyl derivatives of P4VP, were cross-linked and potentiometrically titrated to determine if there were any departures from the properties of the corresponding linear polymers.

The 'pH titration curves' were obtained by measuring the pH of the supernatant solution which was in equilibrium with the resin phase at 25.0 and 80.0°C. Direct comparisons were then made with the linear polymer titration curves, despite the fact that errors are inherent in this procedure because of slightly increased degrees of quaternisation and differences between the pH of the supernatant solution and solution inside the resin. The individual titration curves (pH versus acid fraction) of resins have been shown to be of great predictive assistance in the selection of resins for Sirotherm (Bolto, 1976). Therefore in this study it was not considered necessary to calculate values of pK_{app} at half neutralisation, as this would have required measurements of the water content of the resins (see Helfferich, 1962, pp. 84-88, and in particular equ. 4-17), an unnecessary procedure when only large effects are the subject of interest. (Some preliminary measurements of the water contents and swelling volumes of the aminoalkyl derivatives of P4VP were made, and are recorded in Appendix B.) Instead, values of pH at half neutralisation, $pH_{0.5}$, are used as an approximate measure of the magnitudes of pK_{app} at half neutralisation. As well as this, values of pH at several different degrees of neutralisation were used to calculate the thermal effect (usually at acid fractions of 0.25, 0.50 and 0.75) for comparisons with the corresponding linear polymers.

Generally, the polyelectrolyte and polysoap gels may be considered as the insoluble base derivatives of their linear counterparts, but with the ability to interact with water and exchange ions. As Helfferich (1962) has noted, in many respects the resins act like their soluble counterparts, especially in their potentiometric properties. Nevertheless, this is only a generalisation, and it is usually the exceptions that are of most interest.

8.2 Potentiometric Titrations

8.2.1 Ethyl and Dodecyl Derivatives of P4VP

The compositions of the cross-linked materials prepared are listed in Table 8.1. For the purposes of simplicity, the particular resins will be referred to as "y/z% alkyl X", where y and z refer to the degree of quaternisation with ethyl and dodecyl chloride respectively, and the X signifies that it is cross-linked.

TABLE 8.1

Composition of Resins of Ethyl and Dodecyl Chloride Derivatives of P4VP

Sample No.	Percentage ethyl chloride quaternisation	Percentage dodecyl chloride quaternisation	Approx. degree of cross-linking
XPE6	29.5	-	5
XPED1	43.9	4.4	5
XPED3	40.7	8.7	5
XPED6	29.5	38.8	5
XPD7	-	16.4	10

The general shapes of the titration curves were all very similar to those of the corresponding linear polymers. With increasing dodecyl group content, the slopes of the curves decreased. Also, at 80.0°C, the slopes were less than those at 25.0°C. These two observations are independent of the presence of ethyl chloride, as the resin 16.4% dodecyl X contained no ethyl quaternisation, yet conformed to the behaviour of the other resins. The implication of the above observations is that the p*K* values of basic groups in these resins become more uniform with increasing hydrophobicity and increasing temperature. A typical titration curve is shown in Figure 8.1, where the results for the 4.4% dodecyl X sample are shown.

The values of $\mathrm{pH}_{0.5}$ for the resins are very similar to the $\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ values for the corresponding linear polymers. Figure 8.2 shows these values of $\mathrm{pH}_{0.5}$ plotted against the dodecyl group content, where the same trends are obvious as observed for the linear polymers. Hence the effect that hydrophobic bonding has on the magnitude of $\mathrm{p}K_{\mathrm{app}}$ for linear polymers is still evident in their cross-linked derivatives. The hydrophobic aggregation leads to molecular compactness of the resins

Fig. 8.1 TITRATION CURVES OF 4.4% DODECYL X RESIN OF P4VP IN $0.0200 \text{ mol dm}^{-3}$ NaCℓ.

Symbols

● T = 25.0°C

○ T = 80.0°C

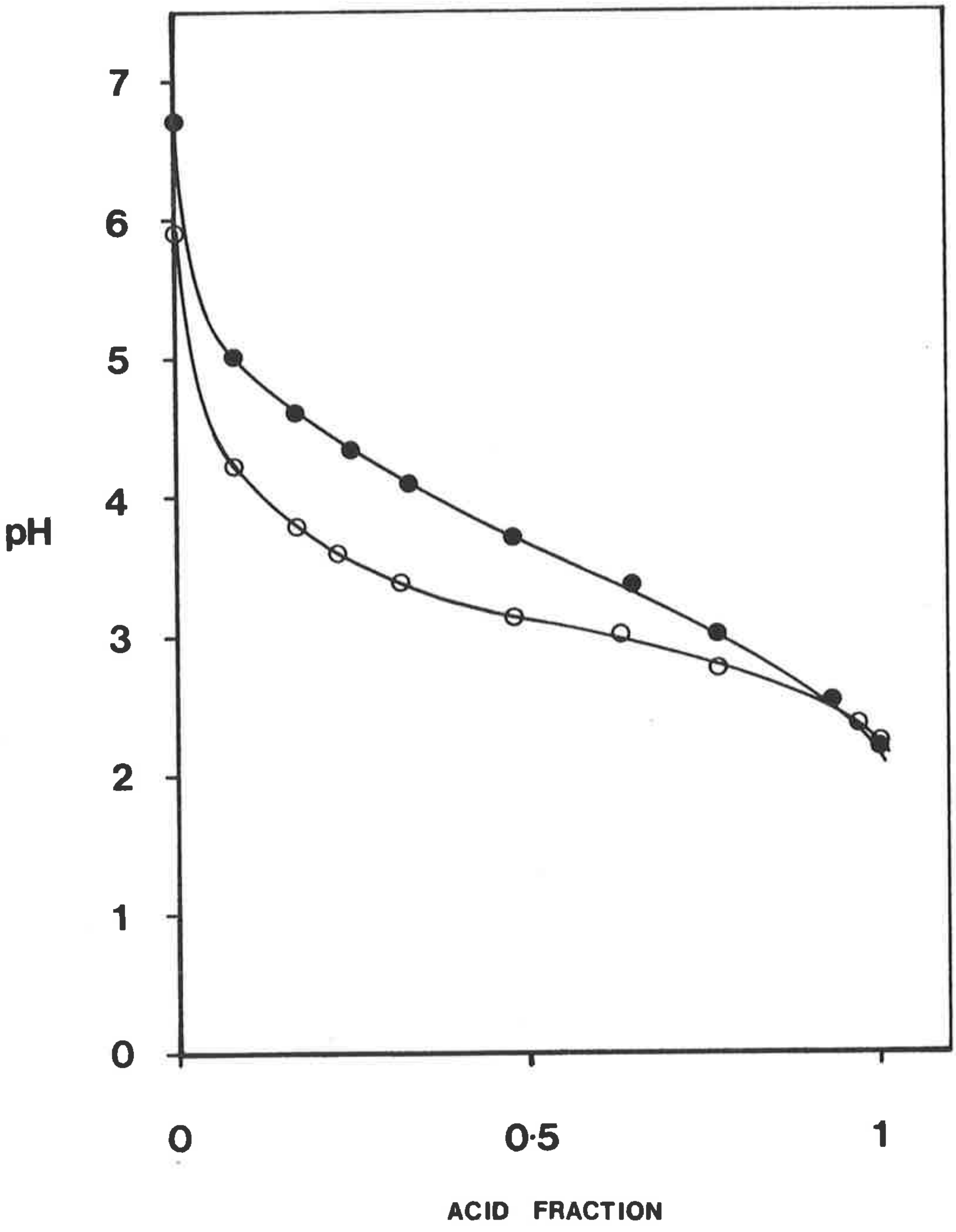
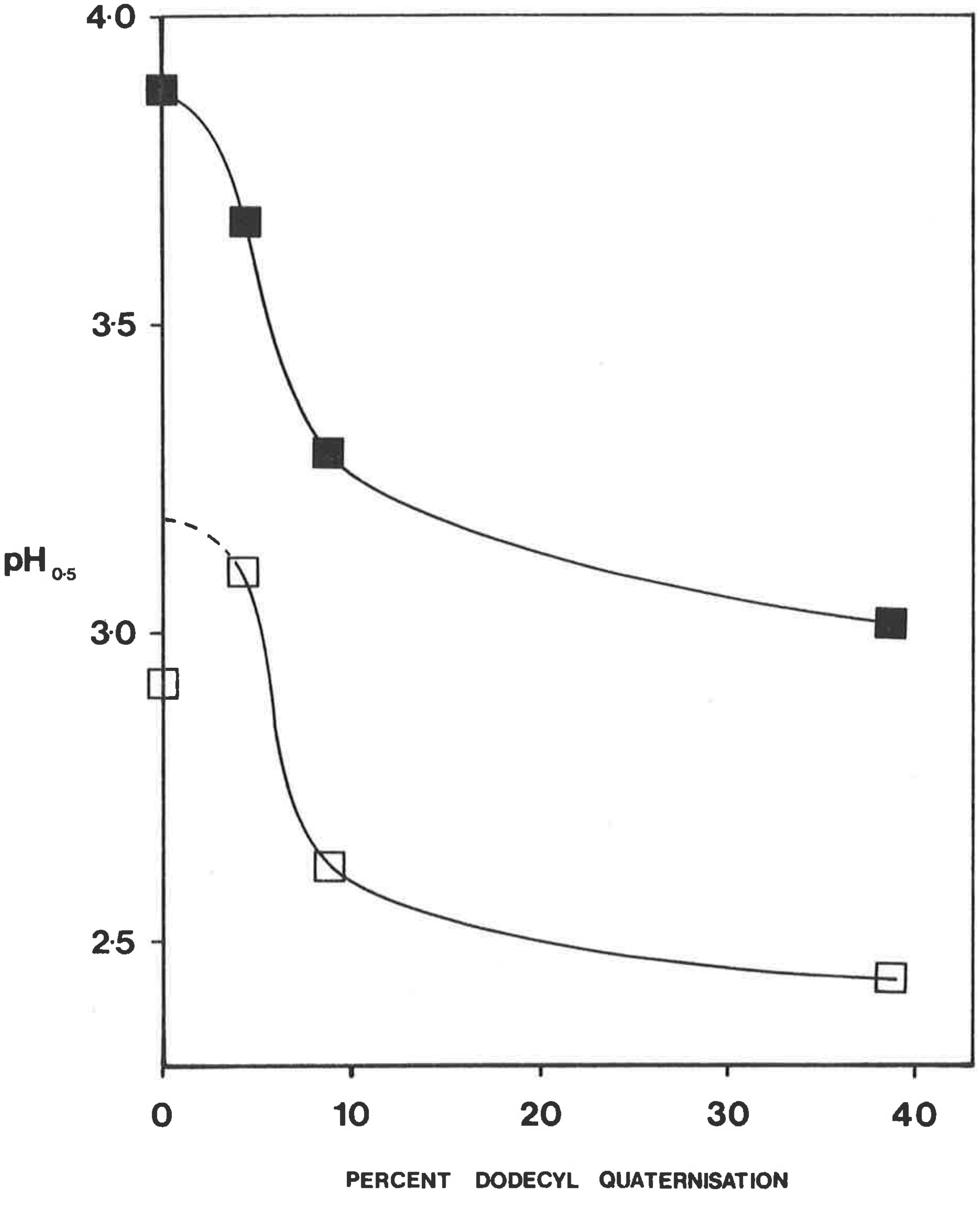

7
6
5
4
3
2
1
0
pH
0
0·5
1
ACID FRACTION

Fig. 8.2 pH$_{0.5}$ VALUES FOR CROSS-LINKED DERIVATIVES OF P4VP AS A FUNCTION OF DODECYL GROUP CONTENT IN 0.0200 mol dm^{-3} NaCℓ.

Symbols

■ T = 25.0°C

□ T = 80.0°C


4·0
3·5
3·0
2·5
pH 0·5
0
10
20
30
40
PERCENT DODECYL QUATERNISATION

and as a result, the increased charge density depresses the basic strength. The one anomalous result is the $pH_{0.5}$ value for 29.5% ethyl X at 80.0°C, in that it is approximately 0.30 pH units lower than expected. This may be due to hydrophobic aggregation of the non-charged portions of the resin at high temperature, causing a decrease in the basic strength, as this sample has a relatively low degree of quaternisation (Woermann, 1959). The pH values at acid fractions of 0.25 and 0.75 support the results shown for $pH_{0.5}$. The values of $pH_{0.5}$ and the thermal effects, $\Delta pH_{0.5}$, are listed in Table 8.2

TABLE 8.2

$pH_{0.5}$ Values for Resins at 25.0 and 80.0°C
in 0.0200 mol dm^{-3} NaCℓ Solution

Sample	$pH_{0.5}^{T=25}$	$pH_{0.5}^{T=80}$	$\Delta pH_{0.5}$
29.5% Ethyl X	3.88	2.92	0.96
4.4% Dodecyl X	3.67	3.10	0.57
8.7% Dodecyl X	3.29	2.62	0.67
38.8% Dodecyl X	3.02	2.44	0.58
16.4% Dodecyl X	3.57	2.96	0.61

Temperature affects these cross-linked polymers in the same way as it does the linear samples. The average value of the thermal effect, $\Delta pH_{0.5}$ ($\equiv pH_{0.5}^{T=25} - pH_{0.5}^{T=80}$), is 0.68 (standard deviation = 0.16) pH units; this is well within one standard deviation of the value for the linear samples (0.57 pH units). The mean value of $\Delta pH_{0.5}$ is 0.61 (standard deviation = 0.05) pH units if the 29.5% ethyl X value is excluded. This implies that the effect of temperature on the cross-linked samples is negligibly different to its effect on the linear parents. There is one exception in that cross-linked poly-4-vinyl-N-ethylpyridinium chloride resins of a low degree of quaternisation may exhibit enhanced hydrophobic aggregation of the uncharged portions of the resin matrix, sufficient to depress the basic strength noticeably at 80.0°C.

In conclusion, the effects of cross-linking on these dodecyl chloride derivatives of P4VP are negligible in respect of the titration characteristics of the unquaternised pyridine nitrogen atoms. This may be due to the relatively fixed position of the potential charge group that forms part of the resin matrix by being in the polymer backbone. Undue restrictions may be imposed upon the basicity of the free pyridine groups by this close proximity to charged groups.

8.2.2 Aminoalkyl Derivatives of P4VP

Contrary to the observations for titration of the very weak pyridine nitrogen base in cross-linked networks, as compared with the linear samples, the results for the cross-linked aminoalkyl system exhibit some remarkable differences to those for the linear polymers. Furthermore, the results imply that there is a significant difference in the potentiometric properties of cross-linked resins where the potential charge group is part of (or very close to) a hydrophobic resin matrix and those in which it is pendant to the hydrophobic matrix.

The approximate compositions of the three resins are shown in Table 8.3. The samples shown are cross-linked portions of the corresponding linear polymers of the same label. Figure 8.3 shows the titration curves of the 34% aminobutyl X (XPAB1) resin at 25.0 and 80.0°C. Cross-linking has caused the dissociation constants to decrease at both temperatures, the decrease at 80.0°C being slightly greater than that at 25.0°C. Hence the thermal effect, $\Delta pH_{0.5}$ = 1.51 pH units, is marginally greater than that for PAB1 at $\alpha = 0.5$ (0.18 pH units difference).

TABLE 8.3

Compositions of Cross-linked Aminoalkyl

Derivatives of P4VP

Sample	Per cent Aminoalkyl quaternisation	Approx. degree of cross-linking
XPAB1	34% aminobutyl	< 5
XPAO	63% aminooctyl	< 5
XPAD*	16% aminododecyl	10

*XPAD has 40.7% ethyl chloride quaternisation as well.

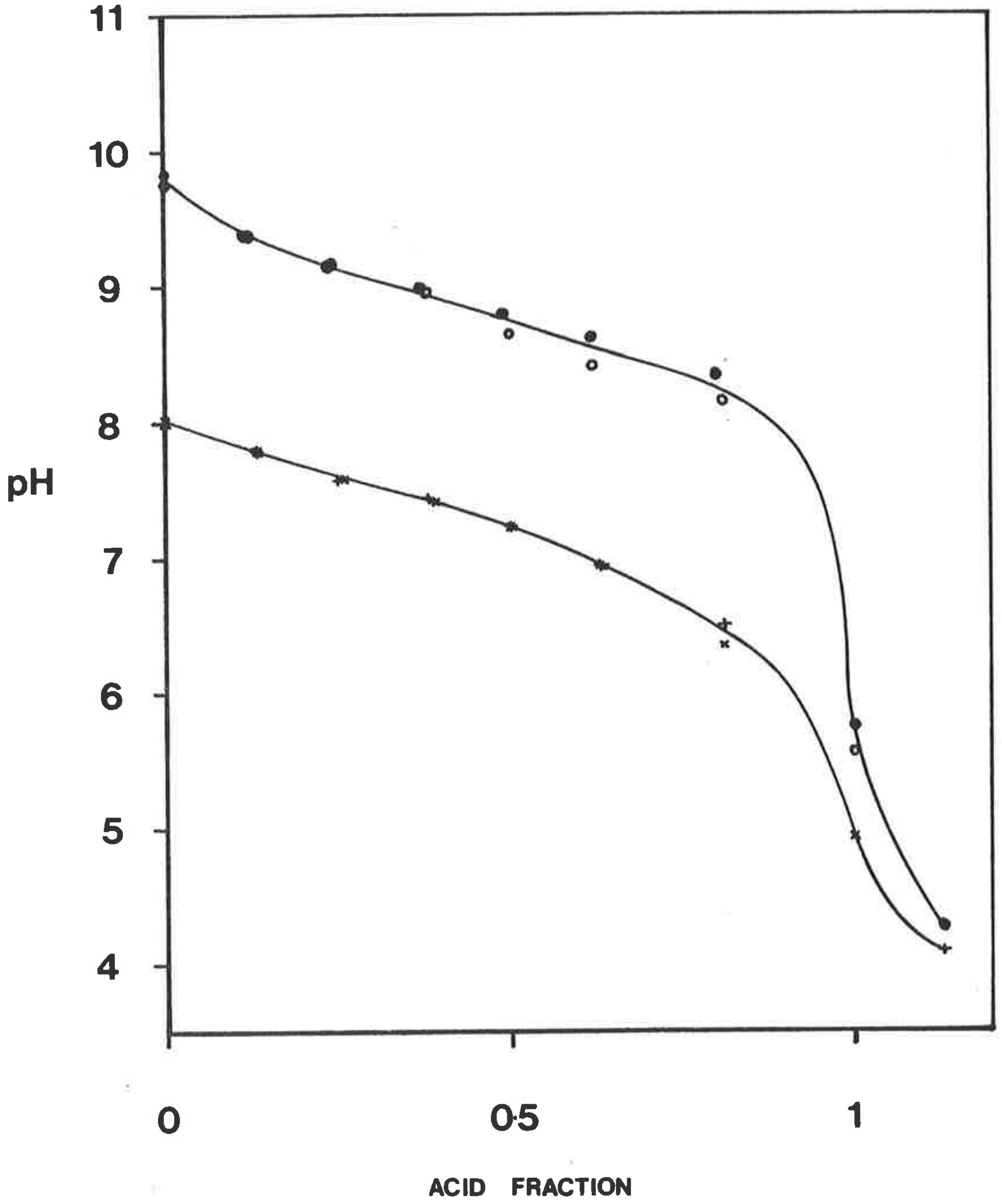
Consequently there is no drastic change in the thermal effect with cross-linking, although the small change that does occur is such that the basicity decreases to a greater extent at high temperature in a cross-linked network. At 25.0°C, the value of $pH_{0.5}$ is 0.85 ± 0.05 pH units lower than $\left(pK_{app}\right)_{0.5}$ for PAB1. This may in part be due to the increased charge in the cross-linked resin, but there is also a genuine change in basic strength. By being fixed in a charged matrix, each aminobutyl group is less likely to be able to aggregate with other aminobutyl groups and hence will experience a higher surrounding charge density.

Spectacular changes in the basicity of the amine groups were observed for the aminooctyl and aminododecyl cross-linked systems. The titration curves of XPAO and XPAD at 25.0 and 80.0°C are shown in Figures 8.4 and 8.5 respectively. In like manner to the results for XPAB1, the basic strength of both XPAO and XPAD at 25.0°C is less than the respective linear samples. In particular, the value of $pH_{0.5}$ at 25.0°C for XPAO is 0.54 pH units less than $\left(pK_{app}\right)_{0.5}$ for PAO. However, the basic strength is much less at 80.0°C than for PAO; the thermal

Fig. 8.3 TITRATION CURVES OF XPAB1 (CROSS-LINKED 34% AMINOBUTYL DERIVATIVE OF P4VP) IN WATER.

Symbols

Titration 1		Titration 2
○	T = 25.0°C	●
×	T = 80.0°C	+



11
10
9
8
pH
7
6
5
4
0
0·5
1
ACID FRACTION

Fig. 8.4 TITRATION CURVES OF XPAO (CROSS-LINKED 63% AMINOOCTYL DERIVATIVE OF P4VP) IN WATER.

Symbols

○ T = 25.0°C

× T = 80.0°C

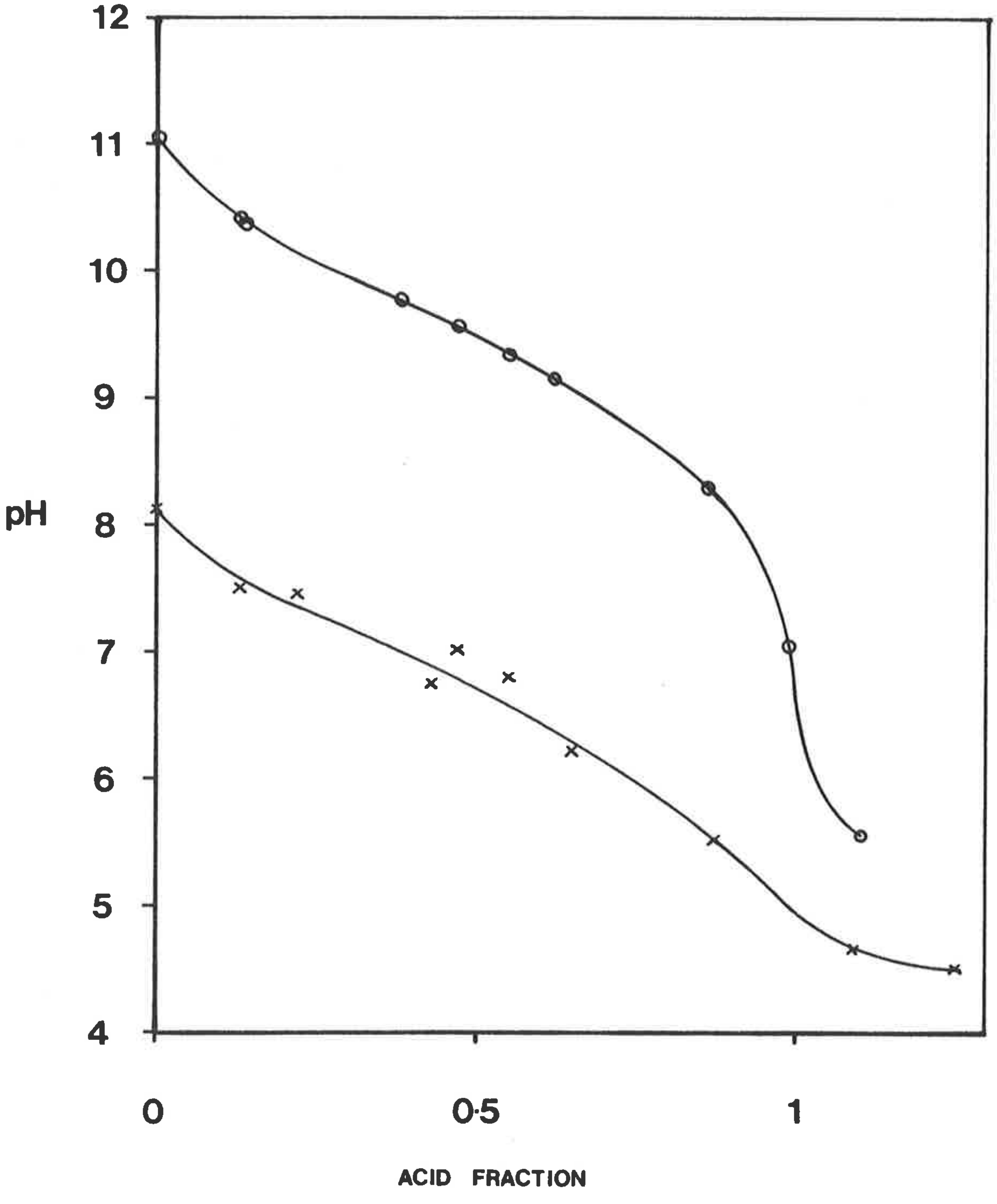
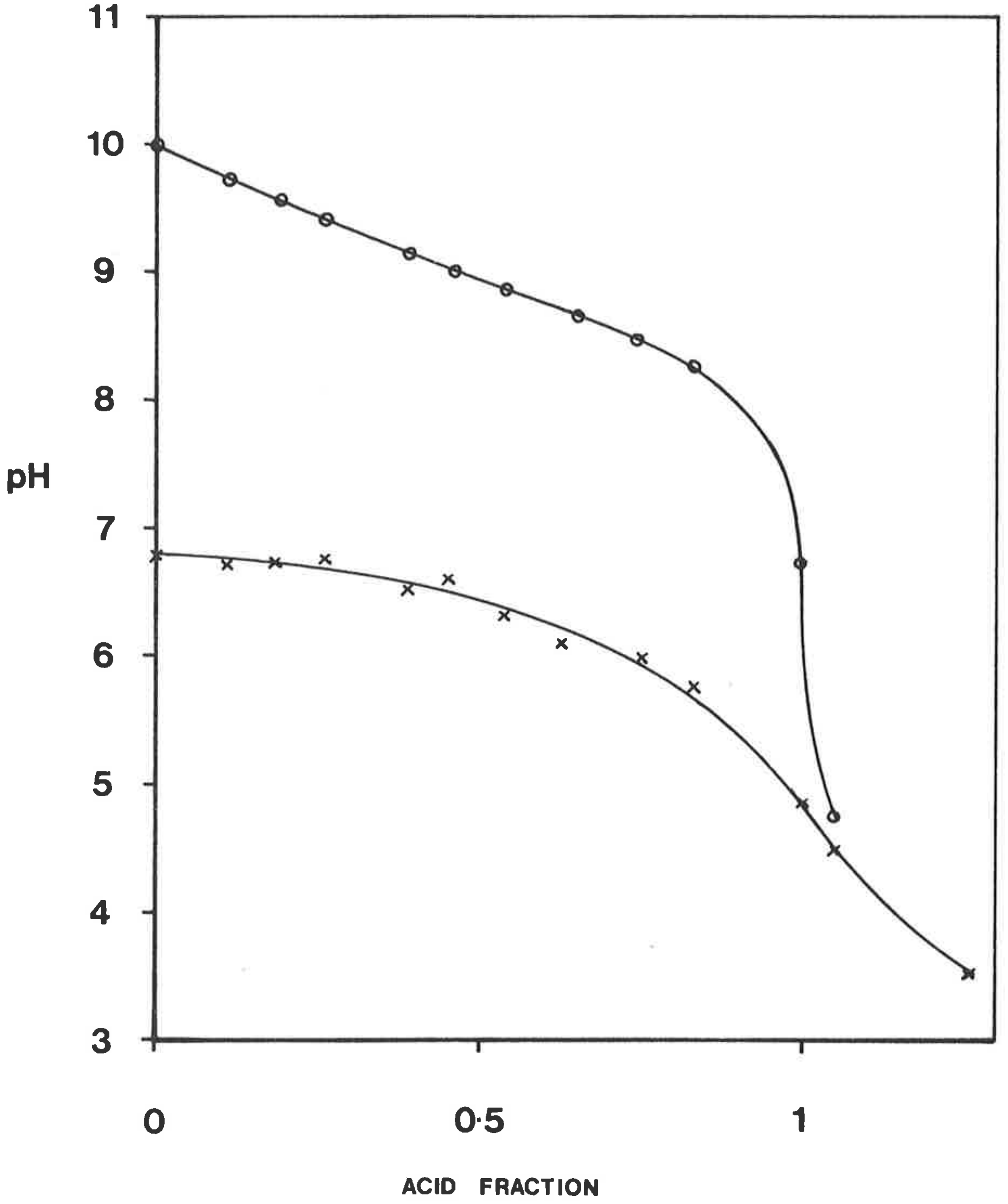

12
11
10
9
8
7
6
5
4
pH
0
0·5
1
ACID FRACTION

Fig. 8.5 TITRATION CURVES OF XPAD (CROSS-LINKED 16% AMINODODECYL DERIVATIVE OF P4VP) IN WATER.

Symbols

○ T = 25.0°C

× T = 80.0°C


11
10
9
8
7
6
5
4
3
pH
0
0·5
1
ACID FRACTION

effect, $\Delta pH_{0.5}$ = 2.75 pH units, is much larger than $\left(\Delta pK_{app}\right)_{0.5}$ = 1.46 for PAO. Hence there is a real change in basic strength of the amine groups in XPAO of approximately 1.35 pH units at 80.0°C (analogous to ΔpK_b for monomeric bases). For XPAD, the value of $pH_{0.5}$ at 25.0°C is 0.86 pH units lower than $\left(pK_{app}\right)_{0.5}$ for PAD, but at 80.0°C, the basic strength of amine groups in the resin is much lower than for the linear samples. The thermal effect, $\Delta pH_{0.5}$ = 2.48, represents a decrease in basicity of approximately 1.08 pH units of the amine groups at 80.0°C, at half neutralisation.

A summary of results for the three resins at an acid fraction of 0.50 is given in Table 8.4.

TABLE 8.4

pH Values at Half Neutralisation

for 'Aminoalkyl Resins'

Sample	$pH_{0.5}^{T=25}$	$pH_{0.5}^{T=80}$	$\Delta pH_{0.5}$
XPAB1	8.74	7.23	1.51
XPAO	9.48	6.73	2.75
XPAD	8.93	6.45	2.48

The larger value for XPAO compared with that for XPAD of $\Delta pH_{0.5}$ may be partly because of the fact that XPAO is a lightly cross-linked gel, whereas XPAD is a resin. This would permit greater changes in internal resin structure as a function of ionisation and hence slightly greater changes in conformations that affect the basic strength of amine groups in the gel. One interesting feature of the titration behaviour of XPAD is that at 80.0°C, there is a plateau-shaped curve over most of the range of neutralisation, even at acid fractions less than 0.10. This is not the case for XPAB1 and XPAO, which both exhibit similar titration curve characteristics at both temperatures. Hence the thermal effect of XPAD is greater at low degrees of neutralisation, increasing up to a value of 3.20 pH units at acid fraction = 0.

The explanation for the large change in basicity of the amino-octyl and dodecyl resins compared to that of the aminobutyl resin must be related to the increased length of the pendant aliphatic chain, as this is the only systematic variable. In other words, there must be hydrophobic interactions between the amino- octyl and dodecyl groups that are absent for the aminobutyl groups. These hydrophobic interactions, which are endothermic in nature, are significantly strengthened at 80.0°C, causing the amine groups to become more inaccessible to solvent molecules and solvated protons. This causes a real reduction in basic strength. The flatter titration curve of XPAD at 80.0°C indicates that the hydrophobic bonding is stronger for the longer aliphatic chain (as has been previously observed). The fact that there is no discontinuity in the potentiometric properties of either XPAO or XPAD supports the model of small pockets of hydrophobic groups, rather than a highly aggregated polymer molecule as a whole, as the hydrophobic groups are themselves restricted in space by being fixed to a three-dimensional matrix.

8.3 Comparisons of Linear with Cross-linked Results

Firstly recall that no unusual potentiometric results were observed for any of the linear polybases prepared, despite the fact that the aminododecyl derivative of P4VP displayed a conformational change as a function of ionisation. In addition, the thermal effects were dependent on the basic strength of the weak polybase, such that with increasing values of $\left(pK_{app}\right)_{0.5}$, the values of $\left(\Delta pK_{app}\right)_{0.5}$ approached the value of ΔpK_w over the 55.0°C temperature interval.

When the weak basic group forms part of a hydrophobic backbone, no amount of hydrophobic aggregation of pendant groups will affect the basic strength to a greater degree at high temperature than at low temperature (viz. dodecyl chloride derivatives of P4VP). However, if hydrophobic aggregation of the polymer backbone is a possibility, then there may be an enhanced thermal effect (viz. 29.5% ethyl X). However, cross-linked polymers with a long, aliphatic chain, to the end of which is attached the potential charge group, pendant to the polymer backbone, exhibit large changes in basic strength at high temperature (viz. XPAO and XPAD). This effect is absent if the attached aliphatic chain is too short (viz. XPAB1).

The general conclusions that can be drawn from these limited observations are as follows:

i) cross-linking appears to be essential to produce any significant changes in basic strength with temperature (although it is not in itself a sufficient condition);

ii) if the potential charge group cannot experience different environments, then no unusual potentiometric effects will be observed (polar versus non-polar environments);

iii) the endothermic nature of hydrophobic interactions has been confirmed up to 80.0°C;

iv) the cross-linked systems show titration characteristics that favour the model of small pockets of hydrophobic groups;

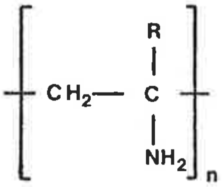
and v) there appears to be a quite delicate balance between the two primary forces in resins of this type. The hydrophobic interactions of the non-polar groups are counter-balanced by the electrostatic repulsions of the fixed charge groups, such that the positions with respect to one another and the number and size of each type of group are critical to the conformation of the polymer network.

CHAPTER VI

Conclusions

9. CONCLUSIONS

Although this study has been very restricted in scope, a number of vitally important, fundamental questions have been answered. In relation to the area of hydrophobic bonding in amphiphilic polymers, it has been clearly demonstrated that the position of the potential charge group (acidic or basic) with respect to the hydrophobic sections of the molecule, is of crucial importance. If the potential charge group is incorporated in the hydrophobic aggregate, then upon ionisation, there is a change in conformation. However, this is not sufficient in itself to produce dramatic changes in acid or base strength. This can be illustrated by the solution potentiometric properties of the alkyl as compared to the aminoalkyl derivatives of P4VP. It was shown that cross-linking can have a large effect on the potentiometric properties of some polymers by restricting the movement of the hydrophilic and hydrophobic groups. Hence the pyridine nitrogen atoms in a cross-linked ethyl chloride derivative of P4VP (29.5% ethyl X) showed a decrease in basic strength at high temperature because of the enhanced hydrophobic aggregation of the non-polar resin matrix and the backbone of P4VP. This effect is absent if the backbone is too hydrophilic (total charge $\gtrsim$ 40% e.g. 4.4% dodecyl X). Consequently there is a very delicate balance between the hydrophobic and hydrophilic interactions. The implication of these results is that the polybase analogues of PAA, PMA and PEA would be a suitable system for producing an enhanced thermal effect in a cross-linked network: polyvinylamine and the polyalkylvinylamines,



$$\left[-CH_2-\underset{NH_2}{\overset{R}{C}}- \right]_n$$

where R = H, CH_3, C_2H_5, . . .

The large effect of temperature on the basicity of the cross-linked aminooctyl and aminododecyl derivatives of P4VP has implications for Sirotherm, in that it has been shown that enhanced thermal effects can be produced by molecular engineering, once the forces involved, and how they operate, are understood. The exchange capacity of resins of this type can be increased by increasing the aminoalkyl quaternisation and in the case of XPAD, removing the ethyl groups (these were only present to make a water soluble polymer). With vastly increased thermal effects ($\Delta pK \gg \Delta pK_w$) there exist the possibilities of working with resins of lower exchange capacity per unit volume and/or over a smaller temperature interval.

From the viewpoint of a mechanochemical system, it would seem that the potential charge group must be part of the three-dimensional network, i.e. be part of the polymer backbone. This is the implication of the results of the cross-linked aminoalkyl derivatives of P4VP, for although there is a large change in basic strength at high temperature in the resin and a large increase in viscosity of the linear polymers in solution with ionisation, there appears to be a negligible change in the swelling volume of the resins with ionisation (see Appendix B). This type of resin undergoes changes in the internal structure that are not necessarily reflected in changes in external dimensions. Hence cross-linked networks where the potential charge groups are incorporated into the backbone of the polymer and hence resin network, such that they can form part of a hydrophobic aggregate, are more likely to form the basis of a working mechanochemical energy system. The 29.5% ethyl X results and those of Woermann (1959) on cross-linked P4VP gels vindicate this prediction. Hence the polyvinylamine series mentioned above would most likely be a profitable system from this aspect as well, provided hydrophobic aggregation occurs, analogous to that for PMA and PEA.

It may be worth noting that the roles of hydrophobic interactions in the Sirotherm process and mechanochemistry are not necessarily convergent, as was originally supposed.

CHAPTER VII

Experimental

10. MATERIALS

10.1 Polyacids

The poly(acrylic acid) was supplied by Aldrich and used without further purification. Poly(methacrylic acid) was obtained by neutralisation of a sample of sodium poly(methacrylate), followed by dialysis to remove any small molecular weight material and finally recovered from water by freeze drying.

Poly(ethacrylic acid) was prepared by free radical polymerisation of a 5% solution of ethacrylic acid monomer in water. The solution was purged of oxygen by bubbling through it high purity, carbon dioxide-free nitrogen, after which the initiator, azobisisobutyramidine hydrochloride (~0.5% w/w of monomer; supplied by CSIRO, Division of Chemical Technology) was added. After approximately 12 hours at 50 - 60°C, a milky suspension was evident - the reaction mixture was kept in this temperature range for a further 2 days. Small molecular weight material was then removed by exhaustive dialysis against water.

The ethacrylic acid monomer was prepared according to the method of Böhme and Teltz (1955). A suspension of paraformaldehyde (3.2 g; Fluka purum) in diethyl ethylmalonate (18.8 g; Fluka purum) reacted with spontaneous heating upon the addition of 3 to 4 drops of a 10% methanol-sodium methoxide solution (10% w/v of sodium in methanol) with stirring. Excess paraformaldehyde was filtered off and unreacted ester removed by shaking with a little n-hexane. This left diethyl oxymethylethylmalonate (21.6 g) which was heated with concentrated hydrochloric acid (100 cm^3) for 24 hours at 60°C. All volatile components were then removed at 35 - 40°C by evacuation with a water pump and then a high vacuum pump to leave a pinky white solid. This residue was dissolved in absolute ether (20 cm^3) and again the solvent was removed, leaving a white solid. Upon being heated to 143 - 145°C for 25 minutes, this solid changed to an amber liquid after loss of water and carbon dioxide. Immediately prior to use, this was distilled to yield α-ethylacrylic acid (b.pt. = 88°C at 15 mm Hg) or ethacrylic acid, an oil with a pungent odour. NMR and IR spectra confirmed the presence of an olefinic bond and a carboxylic acid group.

10.2 Polybases

10.2.1 Poly-4-vinylpyridine

Several samples of P4VP were used in this work and were prepared according to two basic methods which are described below. The samples used for subsequent quaternisation are listed in Table 10.1, together with the intrinsic viscosities in absolute alcohol at 25.00°C, of those samples that were fractionated. The calculated viscosity average molecular weights, $\overline{M}_v$, are also shown, as per the relationship of Berkowitz et al. (1958); $[\eta] = 2.5 \times 10^{-4} M^{0.68}$.

Sample 4P1 was prepared according to the method of Strauss and Williams (1961), where benzene was the solvent and azobisisobutyronitrile (AIBN) the initiator (0.6% w/w of monomer). Three fractions were obtained using the methanol-toluene, solvent-nonsolvent system (Berkowitz et al., 1958); the highest molecular weight fraction was labelled 4P1, which was dried, freeze-dried from t-butanol and finally vacuum-dried at 60°C and <0.01 mm Hg for at least a day.

Samples 4P2, 4P2', 4P3 and 4P4 were all prepared according to a modification of the methods of Kirsh et al. (1970) and Morcellet-Sauvage and Loucheux (1975). Methanol was used as the solvent and AIBN ($\leq$2.5% w/v of monomer) as the initiator. The reaction mixture was outgassed three times (<0.03 torr) and shaken at 50°C for at least 2 days, after

TABLE 10.1

Characterisation of P4VP Samples

Sample designation	$10^{-2}[\eta]/\text{cm}^3\text{g}^{-1}$	$10^{-6}\bar{M}_v$
4P1	3.4	1.2
4P2	2.0	0.54
4P2'	8.3	>2 *
4P3	-	†
4P4	-	†
R1	~10	>2 *

*Relationship of Berkowitz et al. only valid for $0.102 \leqslant 10^{-6}\bar{M}_v \leqslant 1.85$.

†The viscosities of samples 4P3 and 4P4 were not determined as these samples were not fractionated, but simply were freed of any small molecular weight material.

which the product was recovered by precipitation into excess ethyl acetate at 0°C. Both samples 4P2 and 4P2' are different fractions of the same preparation; ethyl acetate was used to precipitate them from a methanol solution. The fractions obtained were not necessarily of a narrow molecular weight distribution, but simply excluded low molecular weight and cross-linked material. All products were dried to form a glassy solid, redissolved in t-butanol and freeze-dried, followed by vacuum drying as for 4P1.

Sample R1 is that described by Darskus (1962), and is a reasonably high molecular weight sample, which was prepared by an emulsion polymerisation similar to that of Fitzgerald and Fuoss (1950).

10.2.2 Alkyl Derivatives of P4VP

a. Ethyl and dodecyl chloride derivatives. A number of polyelectrolytes and polysoaps were prepared by modifying P4VP with alkyl halides. Various percentages of the pyridine nitrogen atoms were quaternised with ethyl, ethyl and dodecyl, or dodecyl halide groups. Table 10.2 shows the compositions of all samples of this type that were prepared and titrated, together with the parent P4VP sample from which each was derived. The intermediate ethyl chloride polyelectrolytes not listed were prepared only for analytical purposes. The structures of the three different types of polymers are shown in Figure 10.1.

All samples except PD7 were prepared by a combination of the methods described initially by Strauss et al. (1952) and later by Fuoss et al. (1960), and Morcellet-Sauvage and Loucheux (1975). To a 5 - 10% (w/v) solution of P4VP in tetramethylene sulphone (tetrahydrothiophene-1,1-dioxide or sulpholane), the required stoichiometric quantity of ethyl bromide was added, and the mixture heated at 70°C for 3 days with mechanical stirring. After the desired amount of polyelectrolyte had been removed, the required stoichiometric quantity of dodecyl bromide was added to the remainder, and the mixture heated for a further 3 days at 70°C with stirring. Both the polyelectrolyte intermediates and the dodecyl derivatives were recovered from the solvent by precipitation into excess ethyl acetate at 0°C. When the product had settled, it was separated from the ethyl acetate/sulpholane mixture by pouring off the supernatant liquid, followed by filtration. This crude product was then vacuum-dried at 60°C and 0.01 mm Hg for 2 days. Sample PD7 was prepared in the same way except that the ethyl bromide reaction was by-passed.

All of the P4VP derivatives were converted from the bromide form in the crude product to the chloride form by passing a solution of each,

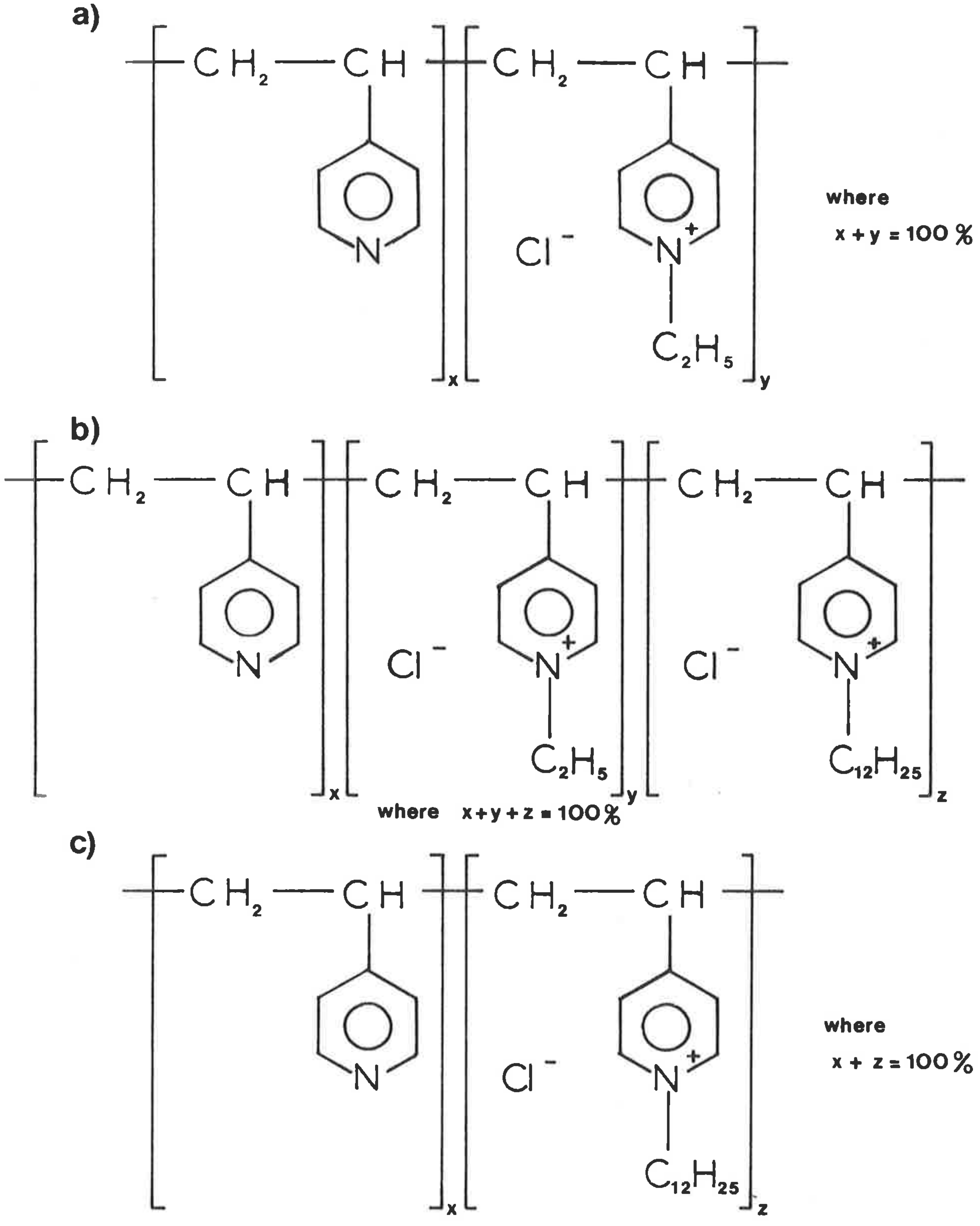
TABLE 10.2

Calculated Compositions of Ethyl and Dodecyl Chloride Derivatives of P4VP

Parent P4VP Sample	Derivative designation	Percentage of pyridine N quaternised with ethyl chloride*	Percentage of pyridine N quaternised with dodecyl chloride*
4P2'	PED1	43.9	4.4
4P2'	PE2	60.9	-
4P2'	PED2	60.9	6.6
4P2'	PE3	40.7	-
4P2'	PED3	40.7	8.7
4P2'	PE4	47.0	-
4P2'	PED4	47.0	9.0
4P2	PED5	29.7	17.6
4P2'	PE6	29.5	-
4P2'	PED6	29.5	38.8
4P3	PD7	-	16.4

*Errors in values are $\leq \pm 0.5$

Fig. 10.1 Types of ethyl and dodecyl chloride derivatives of P4VP.
(random copolymers)



a) where $x + y = 100\%$

b) where $x + y + z = 100\%$

c) where $x + z = 100\%$

where x = percentage of pyridine N unquaternised

y = " " " " quaternised with ethyl chloride

z = " " " " " " dodecyl "

in either water or 50% ethanol/water (v/v), through a column packed with an anion exchange resin (Amberlite IRA-400) in the chloride form. Some of these samples were analysed for bromide ions with a negative result (CSIRO, Melbourne). After this counterion exchange was complete, the solutions were adjusted to pH = 7(±0.5) if necessary, with sodium hydroxide solution. These solutions were then dialysed (Visking tubing 20/32 inch) against water as the external solvent for at least 2 days. The external water was changed frequently during this period. This process removed any sodium chloride as well as small molecular weight polymeric material. Finally, the samples were recovered from solution by freeze-drying and subsequent vacuum drying at 60°C and 0.01 mm Hg for at least 2 days.

A number of samples were initially microanalysed (CSIRO, Melbourne), but, due to a number of factors involved with this type of polymer (Burleigh et al., 1959) plus drying problems, the results were not reproducible. A satisfactory method of analysis was the non-aqueous titration of the unquaternised pyridine nitrogens in glacial acetic acid (Darskus, 1962). Firstly, the polymers were vacuum-dried at 60°C and 0.01 mm Hg over phosphorous pentoxide to constant weight (this usually took several days) and then dissolved in glacial acetic acid. The free pyridine nitrogen atoms were titrated with standardised p-toluene sulphonic acid (0.100_0 mol dm^{-3}) in glacial acetic acid. The e.m.f. of the solutions was monitored by a glass-calomel electrode system, coupled to an EIL Model 7050 pH meter. A break of approximately 200 mV was recorded at the titration end-point. From this titre value, the number of moles of 'free' pyridine nitrogen per gram of polymer was calculated. Since the quaternisation reaction is irreversible under the preparative conditions, and all non-titratable pyridine groups must be quaternised, the compositions of the ethyl and dodecyl derivatives can be calculated.

These calculated compositions are those shown in Table 10.2. The raw data are shown in Appendix A.

b. Hexyl and octyl chloride derivatives. The hexyl and octyl chloride derivatives of P4VP were prepared in a similar manner to the ethyl and dodecyl chloride derivatives. To a 5% solution (w/v) of P4VP in sulpholane was added the required quantity of alkyl bromide, and the mixture was heated at 65 - 75°C for 5 days with mechanical stirring. The product was then precipitated by pouring the reaction mixture into excess ethyl acetate at 0°C. The crude product was filtered off and dried under vacuum, redissolved in 50% (v/v) ethanol/water and the bromide ions exchanged for chloride ions by passage through a column packed with an anionic exchange resin (Amberlite IRA-400 Cℓ). These solutions were reduced in volume, freeze-dried, and the resultant product was dried in a vacuum oven at 60°C for at least 2 days.

The four samples prepared were analysed by non-aqueous titration in glacial acetic acid, as for the ethyl and dodecyl chloride derivatives. The raw data are shown in Appendix A as moles of free pyridine nitrogen atoms per gram of dried polymer. The degree of quaternisation was then calculated assuming 100% purity; these values are shown in Table 6.4.

10.2.3 Poly-N-vinylimidazole and Dodecyl Derivatives

Poly-N-vinylimidazole was obtained through the courtesy of the Badishe Anilin-und Soda-Fabrik A.G. Ludwigshafen, Germany. Gregor and Gold (1957) have shown that pure PVI can be obtained from this product by drying to constant weight at 60°C and 0.01 mm; this is the only pretreatment necessary prior to dissolution in water for titration. Two dodecyl chloride derivatives of PVI were prepared in an analogous manner to the P4VP derivatives in Section 10.2.2. The main difference in the preparation of PVI derivatives was that acetone was used to precipitate them from sulpholane. The final products were creamy-coloured solids. Degrees of quaternisation were determined as for the P4VP derivatives. Non-aqueous titration in glacial acetic acid with p-toluene sulphonic acid was used to determine the number of moles of free imidazole nitrogen atoms per gram of polymer - the raw data are shown in Appendix A and the calculated compositions in Table 6.6.

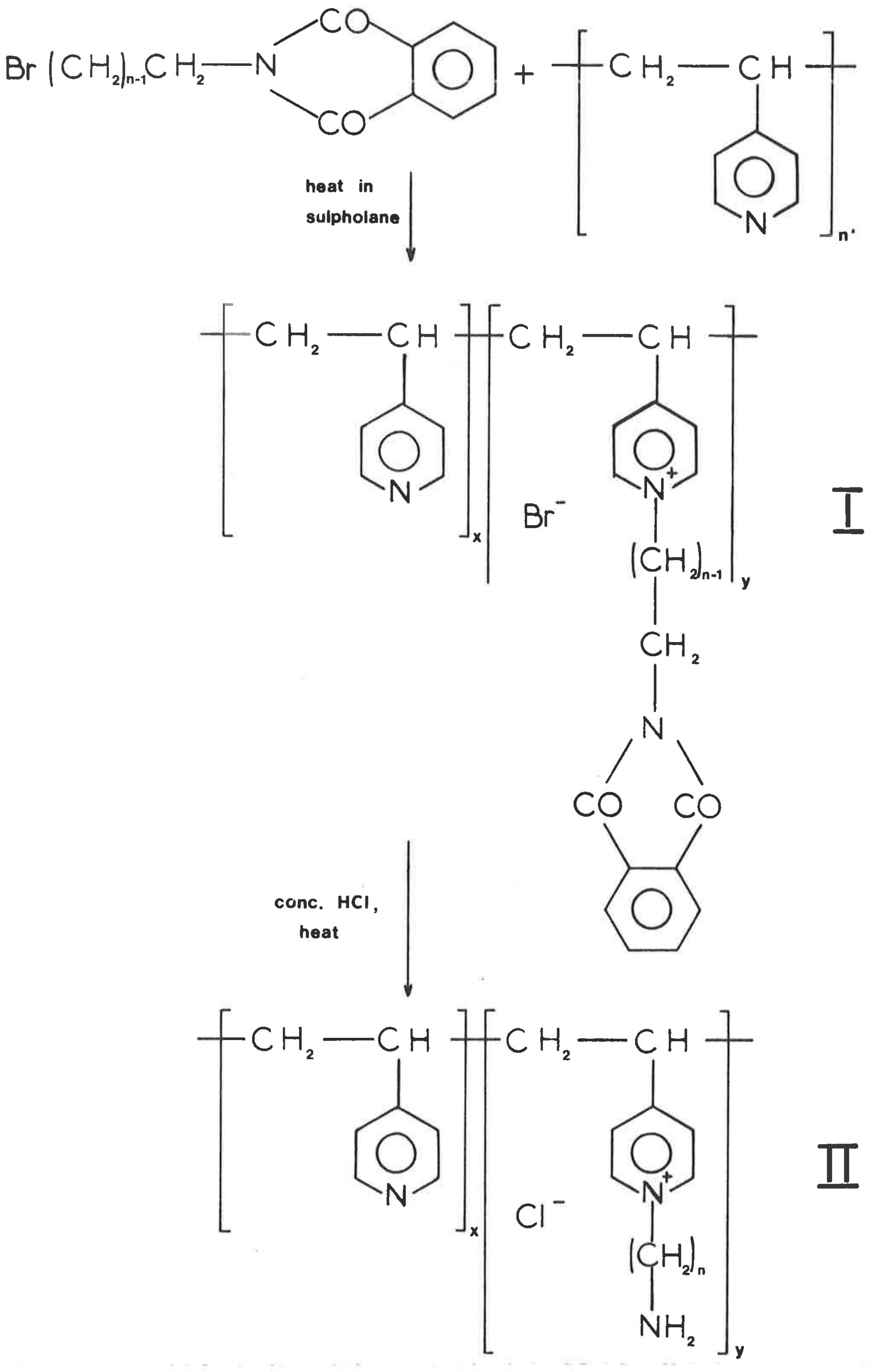
10.2.4 Poly-4-vinyl-N-1-aminoalkylpyridinium chlorides

The preparation of P4VP derivatives with pendant 1-aminoalkyl groups requires the protection of the amino groups until the quaternisation reaction is complete, as the compounds of the type $Br(CH_2)_nNH_2$ (where $4 \leq n \leq 12$) react intramolecularly to form cyclic compounds or intermolecularly to form polymers, depending upon the value of n. Compounds of the type 1-bromo-n-phthalimido-alkane (Delpierre et al., 1966) were used to quaternise the pyridine nitrogens, with subsequent hydrolysis of the phthalimide groups to form the free amine groups. Figure 10.2 shows the general outline of the reaction path. For simplicity, the various derivatives have been labelled as follows:

poly-4-vinyl-N-1-aminobutylpyridinium chloride	PAB
poly-4-vinyl-N-1-aminooctylpyridinium chloride	PAO
poly-4-vinyl-N-ethyl-1-aminododecylpyridinium chloride	PAD.

Polymers of type I were prepared in exactly the same way as the hexyl and octyl derivatives of P4VP. Both PAB1 and PAB2 were prepared from P4VP/4P4; PAO from P4VP/R1 and PAD from poly-4-vinyl-N-ethylpyridinium chloride, sample PE3. The crude dried products of type I were then added to 100 times excess of 6 mol dm^{-3} hydrochloric acid and

Fig. 10.2 Reaction sequence for preparation of aminoalkyl derivatives of P4VP.



the mixture heated to reflux temperature for 1 week. At higher degrees of quaternisation, the phthalimide groups made the type I polymers insoluble in acid. As the hydrolysis reaction proceeded, the polymers gradually became soluble in acid. When the hydrolysis was complete, the solutions were neutralised with 6 mol dm^{-3} sodium hydroxide solution. The final pH was adjusted to pH ≈ 10 for the butyl derivatives and pH ≈ 11 for the octyl and dodecyl derivatives. The solutions were then dialysed exhaustively against water to remove the sodium chloride. After this, the salt-free solutions were reduced in volume and freeze-dried. The resultant polymers were then dried under vacuum at 60°C for at least 2 days.

The degree of quaternisation of pyridine groups with aminoalkyls was calculated from the aqueous potentiometric titration of each sample. It was assumed for these calculations that the polymers were dried to 100% purity. In the case of PAO, only a very small change in pH was observed at the basic end of the titration because of the high basicity. Consequently, potentiometric titration of bound chloride counterions was used to confirm the values obtained. A glass reference electrode and a pure silver wire were used to measure the e.m.f. of the solution with respect to chloride ions, according to the method of Coleman and Fuoss (1955). An aqueous solution of PAO was adjusted to pH = 5.06 ± 0.05 with 0.1 mol dm^{-3} $HC\ell$, the pH at which all amine groups are protonated (determined from the aqueous titrations). A sample of this solution estimated to consume 10 - 15 cm^3 of 0.005 mol dm^{-3} silver nitrate solution was mixed with 45 cm^3 of methanol and 6 cm^3 of 2 mol dm^{-3} H_2SO_4 in a beaker containing a stirrer and the electrodes. The number of moles of titrated chloride ions is equal to twice the amount of free amine present in the polymer. This method gave good agreement with the aqueous titration values. The raw data for all aminoalkyl samples are listed in Appendix A and the calculated compositions are shown in Table 7.1.

All 1-bromo-n-phthalimidoalkanes were prepared by a similar method according to the preparations of 1-bromo-3-methyl-5-phthalimidopentane and 1-bromo-4-methyl-7-phthalimidoheptane as described by Delpierre et al. (1966).

i) <u>1-Bromo-4-phthalimidobutane</u>

A mixture of 1,4-dibromobutane (Merck) and potassium phthalimide (Fluka purum) in the mole ratio of 3.80:1 was heated at 150 - 155°C for 3 hours. Any unreacted 1,4-dibromobutane was recovered by steam distillation in the distillate. The crude product was extracted from the residue with ether, which on evaporation left a yellow solid. Continuous extraction (Sohxlet extraction) with boiling light petroleum spirit (b.p. 60 - 80°C) yielded a light yellow coloured solution which was decanted from a yellow oily gum. The solvent was removed and the crude product then chromatographed on silica gel (BDH, 60 - 120 mesh) in benzene-light petroleum spirit (b.p. 60 - 80°C) (1:1). The polarity of the eluents was gradually increased until the desired product was eluted with ether. This left a creamy white solid after evaporation of the ether. Recrystallisation from light petroleum spirit (b.p. 60 - 80°C) : ether (1:1) yielded long needle-like white crystals (m.p. = 73 - 75°C). (Analysis: found C = 51.19, H = 4.21, N = 4.94; theor. C = 51.09, H = 4.29, N = 4.96%.) Integration of the NMR spectrum revealed the ratio of aromatic to aliphatic protons to be 1:1.95 (expected 1:2). Characteristic carbonyl stretching frequencies were observed in the infra-red: $\bar{\nu}_{max}$ = 1768, 1716, 1610 cm^{-1}.

ii) 1-Bromo-8-phthalimidooctane

1,8-Dibromooctane was distilled prior to use (b.p. = 150°C at 13 mm Hg). A mixture of 1,8-dibromooctane and potassium phthalimide (mole ratio = 3.80:1) was heated at 160°C for 3 hours. Steam distillation was used to recover unreacted 1,8-dibromooctane in the distillate; the steam involatile portion contained the crude product, which was extracted with ether. After evaporation of the ether, the semi-crystalline viscous gum that was left was continuously extracted with boiling light petroleum spirit (b.p. = 60 - 80°C). A creamy yellow solid crystallised out of solution on cooling. The supernatant was decanted off and the solid chromatographed on silica gel with petroleum spirit (b.p. = 60 - 80°C) : benzene (1:3). Once the coloured impurities were washed off the column, the desired compound was eluted with ether. This crude product was then distilled under high vacuum (b.p. = 184 - 192°C at 0.01 mm of Hg) to yield a yellow liquid which crystallised on standing. White needle-like crystals were obtained after recrystallising twice from light petroleum spirit (m.p. = 43 - 45°C). (Analysis: found C = 57.65, H = 6.04, N = 4.05; theor. C = 56.81, H = 5.96, N = 4.14%.) Integration of the NMR spectrum confirmed the structure; the ratio of aromatic to aliphatic protons was found to be 1:4.14 (expected 1:4). The IR spectrum showed the characteristic carbonyl bands: $\bar{\nu}_{max}$ 1768, 1721, 1611 cm^{-1}.

iii) 1-Bromo-12-phthalimidododecane

A mixture of 1,12-dibromododecane (Fluka purum) and potassium phthalimide (in the mole ratio of 3.80:1) were heated at 160 - 165°C for 5 hours. The unreacted 1,12-dibromododecane was recovered by vacuum distillation (b.p. = 107 - 109°C at 0.02 mm of Hg). On standing, the residue formed an oily, yellow solid which was dissolved in light petroleum spirit (b.p. = 60 - 80°C) : ethyl acetate (1:1) and chromatographed on silica gel. The product thus obtained was recrystallised twice from petroleum spirit (m.p. = 60 - 62°C). NMR showed the ratio of aromatic to aliphatic protons to be 1:6.14 (expected 1:6), and the IR spectrum exhibited the characteristic carbonyl bands: $\bar{\nu}_{max}$ 1764, 1721, 1612 cm^{-1}. (Analysis: found C = 60.69, H = 7.19, N = 3.39; theor. C = 60.92, H = 7.16, N = 3.55%.)

Microanalyses of all three 1-bromo-n-phthalimidoalkanes were performed on a Perkin-Elmer 240 Elemental Analyzer (South Australian Institute of Technology). The values shown are the average of two separate determinations (the standard deviations were $\lesssim$0.2%).

10.3 Polybase Gels and Resins

All cross-linked samples of the ethyl and dodecyl derivatives of P4VP were prepared according to the method of Nishide and Tsuchida (1976), with minor modifications in concentration and cross-linking agent. The linear polymer was dissolved in a minimum amount of methanol to form a viscous solution, to which was added the desired amount of cross-linking agent, either 1,6-dibromohexane (Fluka) or α,α'-dichloro-p-xylene (Fluka purum), and the mixture heated at 65°C for 2 days. Additional methanol was added as cross-linking proceeded. The resins obtained in this way were washed repeatedly with methanol and hydrochloric acid (≈0.1 mol dm^{-3}), in order to remove any linear, unreacted material. Finally the resins were washed with water and neutralised to the free base form by adjusting the pH of the supernatant water to pH ≈ 7 over a period of several days until there was no change in the supernatant pH. After excess chloride ions were removed by washing with water, the resins were dried in vacuum at 60°C for several days.

Both XPAO and XPAB1 were prepared from the phthalimide polymer, prior to hydrolysis to free amine, in sulpholane solution. XPAO was cross-linked lightly with 1,8-dibromooctane as a result of the use of unpurified 1-bromo-8-phthalimidooctane which contained traces of 1,8-dibromooctane; a gel resulted. Sample XPAB1 was prepared by the addition of 5% (mole per cent) α,α'-dichloro-p-xylene to the preparative solution of linear poly-4-vinyl-N-1-aminobutylpyridinium bromide. For both XPAO and XPAB1, after 2 days, the cross-linked materials were washed with ethyl acetate to remove sulpholane and subsequently the phthalimide groups were hydrolysed with 100 times excess $HC\ell$ (≈ 6 mol dm^{-3}) under reflux for 1 week. Excess acid was then neutralised with sodium hydroxide solution (≈ 6 mol dm^{-3}) and the pH of the supernatant adjusted to pH ≈ 10 and pH ≈ 9 for XPAO and XPAB1 respectively, over a period of several days. The products were then washed with water until no more chloride ions were detectable, and then dried under vacuum at 60°C for several days.

Sample XPAD was prepared from the phthalimide intermediate of PAD in methanol solution, with 1,8-dibromooctane as the cross-linking agent. One attempt to cross-link with α,α'-dichloro-p-xylene was unsuccessful. This could be due to the steric hindrance of the phthalimide groups. The phthalimide groups were hydrolysed after the cross-linking was achieved, and the resin washed and dried as described for XPAO.

For all cross-linked derivatives of P4VP, the degree of cross-linking is expressed as an approximate mole percentage of pyridine groups present, both quaternised and unquaternised. (If all the pyridine groups in a sample of P4VP were cross-linked, the percentage of cross-linking would be 50.) Calculated percentages of cross-linking agents that were then added to the various solutions were used as the approximate values for the degree of cross-linking. No attempt was made to accurately measure the degrees of cross-linking because of the complexity of most resins produced. The labels attached to the cross-linked samples correspond to the linear samples from which they were derived, the X denoting a cross-linked sample. Table 10.3 shows the capacities of all cross-linked samples prepared, together with the cross-linking agents, the solvent used for the preparation and the approximate degree of cross-linking.

The basic capacities of the cross-linked ethyl and dodecyl derivatives of P4VP were determined by shaking a known weight of dry resin with 20 cm^3 of 0.100 mol dm^{-3} HCℓ for 2 days, then filtering off the resin, washing it with water and subsequently titrating the free acid with 0.100 mol dm^{-3} NaOH. Hence the quantity of free pyridine nitrogen, or the exchange capacity, can then be calculated. Capacities of the cross-linked aminoalkyl derivatives of P4VP were calculated from the aqueous titrations. Table 10.3 lists the exchange capacities of all the resins.

TABLE 10.3

Cross-linked P4VP Derivatives

Sample	Solvent used in preparation	Cross-linking agent	Approx. degree of cross-linking*	Exchange capacities (10^{-3} mol g^{-1})
XPED1	methanol	α,α'-dichloro-p-xylene	5	3.0 ± 0.1
XPED3	"	"	5	2.6 ± 0.1
XPE6	"	"	5	3.7 ± 0.2
XPED6	"	"	5	0.9 ± 0.1
XPD7	"	1,6-dibromohexane	5	2.5 ± 0.1
XPAB1	sulpholane	α,α'-dichloro-p-xylene	<5	2.18 ± 0.07
XPAO	"	1,8-dibromooctane	<5	1.4 ± 0.1
XPAD	methanol	"	10	1.08 ± 0.05

*moles of cross-linking agent per total moles of pyridine groups.

11. EXPERIMENTAL TECHNIQUES

11.1 Potentiometric Titrations

An EIL Model 7050 pH meter, coupled with a Titron 121 AP7 combination glass electrode, was used to measure the pH of all solutions. The precision of the meter is 0.004 pH units. Constant temperature baths were continuously maintained at 25.0 ± 0.1°C and 80.0 ± 0.1°C; water and oil (Shell, Diala BX) were used as the respective working fluids. The thermometers (Hg in glass) were calibrated against a Pt resistance thermometer. Two buffers, kept in stoppered quickfit test-tubes at both temperatures, were used to standardise the meter-electrode system; EIL pH 4 and pH 9 buffers (to NBS specifications: $pH = 4.01 \pm 0.02$ and $pH = 9.19 \pm 0.02$ at 25°C; $pH = 4.16 \pm 0.02$ and $pH = 8.89 \pm 0.02$ at 80.0°C). In order to prolong electrode life, different electrodes were used for the two temperatures. One electrode was kept continuously at 25.0°C. Experience proved that electrode life was short (approximately 4 to 6 weeks) if the electrode was maintained at 80.0°C continuously; the internal $Ag/AgC\ell$ references tended to disintegrate. Consequently, prior to high temperature measurements, an electrode was heated in a beaker of deionised water to 80°C over a period of about 2 hours, and then equilibrated at 80.0°C. At the completion of the day's readings, the electrode was allowed to cool slowly in a beaker of water from 80°C to room temperature overnight. This procedure extended electrode life to at least 3 months. In addition, the response was much better from an electrode treated in this way.

Titrants were kept at ambient temperature and delivered from either an Agla micrometer syringe or a Metrohm Dosimat 10 cm^3 macro piston burette. The precision of the micrometer syringes is 0.002 cm^3 and that of the burette is 0.01 cm^3 with an absolute accuracy of 0.02 cm^3.

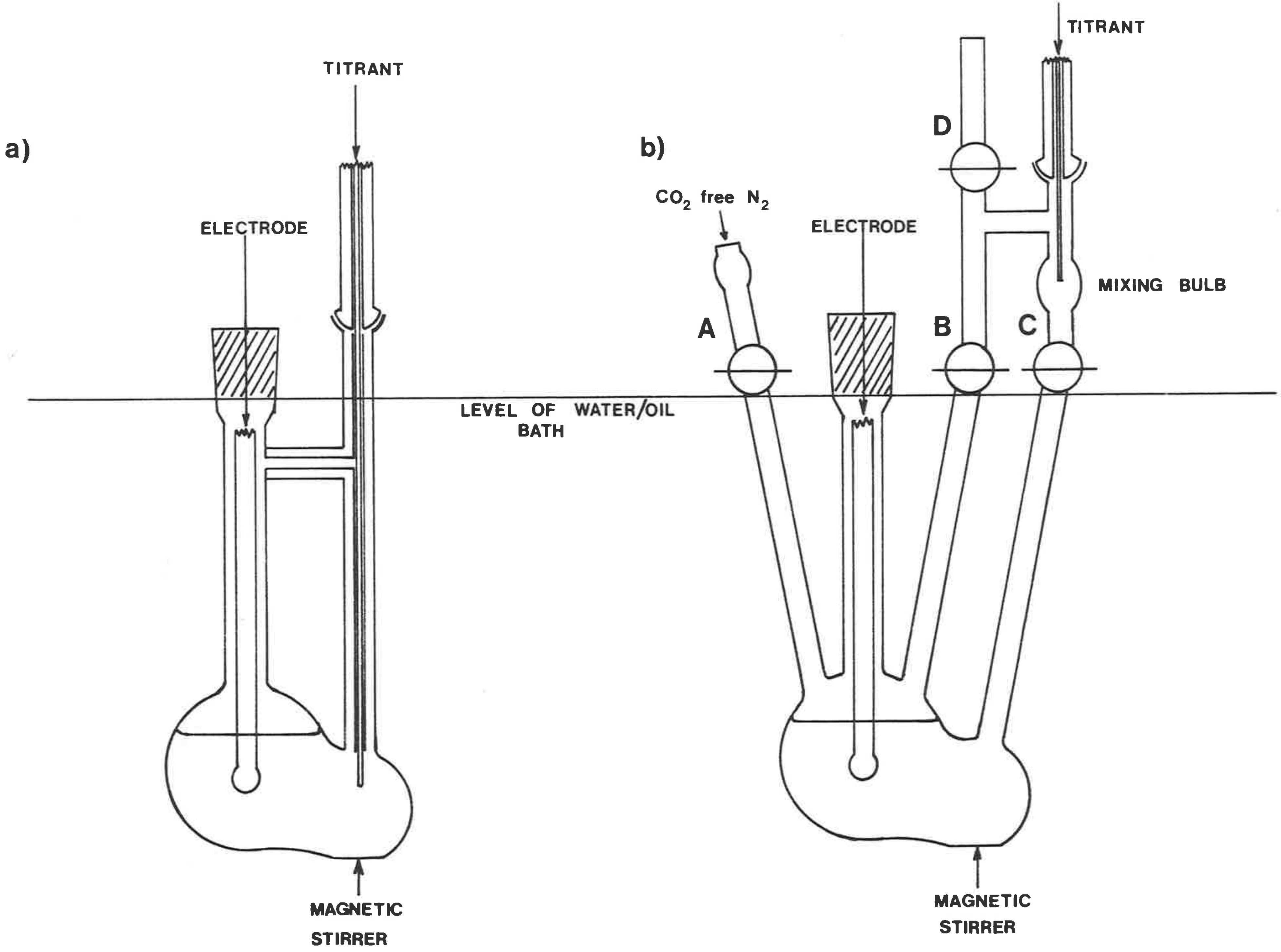
The burette was calibrated by recording the weight of water delivered at ambient temperature. All titrants were either 1 mol dm^{-3} or 0.1 mol dm^{-3} BDH (cvs) solutions of HCℓ and NaOH.

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 at a concentration calculated to require approximately 1 cm^3 of titrant for neutralisation. The solutions were equilibrated at the respective temperatures prior to any measurements being made. Titrant was added to the solution which was then stirred with a magnetic stirrer for a couple of minutes. The pH was recorded with the stirrer off when all meter fluctuations ceased. The cell for measurements at 25.0°C is shown in Figure 11.1a, where the electrode was held in a quickfit joint, the magnetic stirrer was contained in the smaller bulb to protect the electrode from accidental damage, and the titrant was added to the solution just above the stirrer via a fine polythene tube. If this same set-up was used at 80.0°C, the titrant addition could not be controlled because of the expansion in volume with heat. Hence the cell in Figure 11.1b was designed for use at 80.0°C. The solution was forced up into the mixing bulb when taps A, C and D were opened, by applying a positive pressure of 'CO_2-free' nitrogen saturated with water vapour at 80°C through tap A. Then the titrant was added, taps A and D closed, and tap B opened to equalise pressures, allowing the solution to return to the bottom of the cell. Taps B and D were then closed, and the process repeated to wash the mixing bulb. The solution was then stirred for a couple of minutes and the 'steady state' value of the pH recorded with the stirrer off.

Each titration consisted of a blank titration (solvent only), followed in quick succession by titration of the solution, to minimise meter and electrode fluctuations. Raw titration data were corrected for

Fig. 11.1 a. CLOSED CELL USED FOR TITRATION OF SOLUTIONS AT 25.0°C.

b. CLOSED CELL USED FOR TITRATION OF SOLUTIONS AT 80.0°C.


a)
TITRANT
ELECTRODE
LEVEL OF WATER/OIL BATH
MAGNETIC STIRRER
b)
TITRANT
D
CO_2 free N_2
ELECTRODE
MIXING BULB
A
B
C
MAGNETIC STIRRER

the dissociation of water (neglecting the effects of the polymer on the activity coefficients of H^+ and OH^- ions), and its effects on the acid or base dissociation, by titration of the pure solvent. The volume of titrant consumed by the polymer, ΔV_{pH}, is equal to the volume added at any pH, $V_{sample,pH}$, minus the volume added to the blank (solvent) to bring it to the same pH, $V_{blank,pH}$:

$$\Delta V_{pH} = \left\{V_{sample} - V_{blank}\right\}_{pH}$$

The equivalence point, $\Delta V_{equiv.}$, is determined by finding the maximum value of $\partial pH/\partial \Delta V_{pH}$. Hence the degree of ionisation, α, is calculated from the volume of acid consumed by the polymer at any pH divided by the volume of acid consumed at the equivalence point:

$$\alpha \equiv \frac{\Delta V_{pH}}{\Delta V_{equiv.}}$$

For the titration of pyridine nitrogen atoms, the inflexion point at neutralisation was difficult to detect because neutralisation occurred at pH ≈ 2. In this region with 1 mol dm^{-3} HCℓ titrant, the pH is relatively insensitive to large changes in the volume of added acid and hence the blank titration curve is relatively flat. Agreement between $\Delta V_{equiv.}$ and theoretical equivalence points could be obtained within 5% by the following procedure. The observed $\Delta V_{equiv.}$ was used to construct pH versus α plots and compared with those obtained by using theoretical equivalence points. Any differences between the two were detected by anomalies in the plots of pK_{app} versus α near equivalence. Where an anomaly was evident, new equivalence points were obtained from the theoretical plots. These invariably agreed with the experimentally determined values within 5%. All other polybases and polyacids were strong enough to enable accurate determination of the equivalence points from $\partial pH/\partial \Delta V_{pH} \equiv$ maximum, to within < 5% deviation from the theoretical equivalence points.

The titration curves of cross-linked resins and gels were determined by a 'point by point' method. An accurately determined weight of resin (usually 0.15 to 0.20 g) was added to each of 10 to 15 quickfit test tubes. Then 20 cm^3 of water or 0.0200 mol dm^{-3} NaCℓ solution was added, followed by different aliquots of the titrant. These were then sealed and shaken at room temperature for a day (see later for time dependence of pH), equilibrated at 25.0°C and the pH of the supernatant measured. The tubes were then re-sealed and shaken in an air oven at 80°C for 24 hours, after which they were equilibrated at 80.0°C. The pH of the supernatant was recorded, and then the supernatant withdrawn and cooled to 25.0°C before the pH of each sample was again recorded. In this way, the pH values of the supernatant at 25.0°C, 80.0°C and the 80.0°C supernatant at 25.0°C were measured for points across the range of ionisation. Corrections for solvent effects were made in the same way as for titration of the linear polymers. The corrected volume of titrant consumed, ΔV_{pH}, was then converted to a value of *acid fraction* (analogous to the degree of ionisation for solutions) by dividing by the volume of titrant required for equivalence, $\Delta V_{equiv.}$:

$$\text{acid fraction} \equiv \frac{\Delta V_{pH}}{\Delta V_{equiv.}}$$

(The value of $\Delta V_{equiv.}$ was determined either from the titration curve or the exchange capacity.)

The rate of uptake of acid by the resins was measured for the resin XPD7, as being typical of the titration of the ethyl and dodecyl derivatives of P4VP and being slower in uptake than the aminoalkyl derivatives which are a relatively 'strong' weak base. The pH of the supernatant over the whole range of ionisation was measured at 25.0°C after 1, 2 and 5 days and at 80.0°C after 1 and 2 days. The results of this study are shown in Table 11.1. It is quite apparent that the resin had attained equilibrium with the supernatant liquid after 1 day at both 25.0 and 80.0°C. Hence all resins were shaken at the two temperatures for a minimum of 1 day before the pH values were recorded.

11.2 Viscosity Measurements

The viscosities of polyelectrolyte and polysoap solutions were determined in a modified Ubbelohde viscometer (flow time of water, t_o = 155.1 s at 25.0°C), in a constant temperature bath (±0.1°C). Flow times were recorded manually with a stop watch, except for the determination of the limiting viscosity numbers, $[\eta]$, for the P4VP samples, where an automatic timer was used. Prior to the addition of any liquid to the viscometer, all suspended matter was removed by filtration of the liquid through a Swinney adaptor (Millipore). Where the 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 ionisation, progressive additions of acid were made to the solution and samples withdrawn for the purposes of measuring the pH.

11.3 Infra-red and NMR Spectra

All IR spectra were recorded on a Perkin-Elmer 457 Grating Infra-red Spectrophotometer in nujol with $NaC\ell$ plates. The spectra obtained were used only for qualitative purposes of identification. The NMR spectra were recorded on a Varian T-60 NMR Spectrometer System. The solvents used were either deuterated chloroform ($CDC\ell_3$) or deuterium oxide (D_2O).

TABLE 11.1

Rate of Acid Uptake for XPD7

Vol. of 1 mol dm^{-3} HCℓ added (cm^3)	pH after shaking at 25.0°C for			pH after shaking at 80.0°C for	
	1 day	2 days	5 days	1 day	2 days
0	6.38	6.39	6.35	5.55	6.36
0.05	4.78	4.76	4.78	3.96	3.98
0.10	4.32	4.31	4.35	3.54	3.55
0.15	4.04	4.01	4.05	3.28	3.35
0.20	3.80	3.78	3.81	3.10	3.14
0.30	3.42	3.41	3.44	2.82	2.88
0.40	3.02	3.01	3.02	2.60	2.66
0.50	2.78	2.77	2.78	2.48	2.53
0.60	2.48	2.46	2.48	2.35	2.41
0.80	2.14	2.11	2.14	2.18	2.22
1.00	1.91	1.88	1.89	2.06	2.09
1.30	1.69	1.66	1.67	1.91	1.91
1.60	1.55	1.52	1.53	1.81	1.77

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Appendices

APPENDIX A EXPERIMENTAL DATA

TABLE A1

$\text{p}K_o$ Values for Ethyl and Dodecyl
Chloride Derivatives of P4VP

Sample No.	In water			In 0.02 mol dm^{-3} NaCℓ		
	$(\text{p}K_o)^{T=25}$	$(\text{p}K_o)^{T=80}$	$\Delta\text{p}K_o$	$(\text{p}K_o)^{T=25}$	$(\text{p}K_o)^{T=80}$	$\Delta\text{p}K_o$
Group 1						
PED1	4.15	3.35	0.80	4.45	3.73	0.72
* PE3	4.32	3.64	0.68	4.56	3.77	0.79
PED3	3.68	2.97	0.71	3.86	3.17	0.69
PE4	4.40	3.57	0.83	4.64	3.88	0.76
PED4	3.60	2.92	0.68	4.01	3.28	0.73
PED5	3.60	3.13	0.47	3.77	3.25	0.52
Group 2						
PE2	3.96	3.21	0.75	4.33	3.69	0.64
PED2	3.42	2.93	0.49	3.73	3.02	0.71
* PE3	4.32	3.64	0.68	4.56	3.77	0.79
PED6	3.18	2.62	0.56	3.52	2.92	0.60
Neither						
PE6	4.40	3.70	0.70	4.48	3.87	0.61
PD7	4.20	3.72	0.48	4.38	3.91	0.47

* PE3 is intermediate between gps. 1 and 2.

TABLE A2

$\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ Values for Ethyl and Dodecyl Derivatives of P4VP

Sample No.	Conc. (g/100 cm^3)	In water			In 0.02 mol dm^{-3} NaCℓ		
		$\left(\mathrm{p}K_{\mathrm{app}}\right)^{T=25}_{0.5}$	$\left(\mathrm{p}K_{\mathrm{app}}\right)^{T=80}_{0.5}$	$\Delta\mathrm{p}K_{\mathrm{app}}$	$\left(\mathrm{p}K_{\mathrm{app}}\right)^{T=25}_{0.5}$	$\left(\mathrm{p}K_{\mathrm{app}}\right)^{T=80}_{0.5}$	$\Delta\mathrm{p}K_{\mathrm{app}}$
Group 1							
PED1	0.937	3.52	2.97	0.55	3.86	3.27	0.59
* PE3	1.294	3.72	3.06	0.66	3.91	3.29	0.62
PED3	1.178	3.25	2.71	0.54	3.43	2.90	0.53
PE4	1.131	3.79	3.14	0.65	4.04	3.42	0.62
PED4	0.961	3.18	2.75	0.43	3.47	2.92	0.55
PED5	1.212	3.22	2.75	0.47	3.43	2.85	0.58
Group 2							
PE2	1.144	3.55	2.93	0.62	3.68	3.22	0.46
PED2	0.948	3.17	2.74	0.43	3.43	2.77	0.66
* PE3	1.294	3.72	3.06	0.66	3.91	3.29	0.62
PED6	1.217	3.01	2.45	0.56	3.28	2.77	0.51
Neither							
PE6	1.181	3.71	3.01	0.70	3.82	3.23	0.59
PD7	1.101	3.67	3.08	0.59	3.80	3.20	0.60
PD7 susp†	0.50	3.60	3.13	0.47	3.82	3.30	0.52
Group 1							
PE3	0.313	3.52	2.97	0.55	3.98	3.35	0.63
PED3	0.343	3.00	2.58	0.42	3.24	2.74	0.50
PED5	0.350	2.99	2.42	0.57	3.27	2.81	0.46

* PE3 is intermediate between gps. 1 and 2.

† 0.50% suspension in 10% ethanol : water.

TABLE A3

$\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}$ Values for Hexyl and Octyl Derivatives of P4VP

Sample	Conc. (g/100 cm^3)	In water			In 0.02 mol dm^{-3} NaCℓ		
		$\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=25}$	$\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=80}$	$\Delta\mathrm{p}K_{\mathrm{app}}$	$\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=25}$	$\left(\mathrm{p}K_{\mathrm{app}}\right)_{0.5}^{T=80}$	$\Delta\mathrm{p}K_{\mathrm{app}}$
35.3% hexyl	0.925	3.76	3.01	0.75	4.03	3.35	0.68
63.8% hexyl	0.958	2.89	2.50	0.39	3.27	2.75	0.52
18.3% octyl	0.948	3.86	3.38	0.48	4.14	3.55	0.59
44.0% octyl	0.987	3.28	3.05	0.23	3.57	3.11	0.46

TABLE A4

Free Base Units per gram of Polymer for Ethyl and Dodecyl Chloride Derivatives of P4VP

Sample	Titratable Pyridine Nitrogen (10^{-3} mol g^{-1})
PE1	4.24
PED1	4.04
PE2	2.71
PED2	2.05
PE3	4.51
PED3	3.40
PE4	3.91
PED4	2.86
PE5	5.65
PED5	3.28
PE6	5.67
PED6	1.56
PD7	6.03

TABLE A5

Free Base Units per gram of Polymer for Dodecyl Chloride Derivatives of PVI

Sample	Titratable Imidazole Nitrogen (10^{-3} mol g^{-1})
QPVI/1	8.02
QPVI/2	5.41

TABLE A6

Titratable Amine Groups in Aminoalkyl Derivatives of P4VP

Sample	Titratable Amine Nitrogen (10^{-3} mol g^{-1})
PAB1	2.4
PAB2	2.9
PAO	3.0
PAD	0.95

APPENDIX B WATER REGAINS OF AMINOALKYL RESINS

The water regains of the three cross-linked aminoalkyl derivatives of P4VP were measured according to the centrifuge method of Pepper et al. (1952). A sample of resin (≈1 g of wet resin) was placed in a tube with a sintered-glass disc of porosity 4. This was immersed in deionised water at 25°C for about 1 hour and then centrifuged at approximately 2000 r.p.m. for 30 minutes. The centrifuge was cooled during spinning and the tube was covered with a rubber cap to prevent evaporation of water. The tube was weighed and the process repeated. The filter-tube was then heated at 65°C and 0.01 mm Hg in a vacuum oven over P_2O_5 to dry the resins. The dried tube plus resin was then weighed. The results are expressed as weight of water per gram of dry resin, where the weight of water is uncorrected for residual water held between particles of resin. This process was performed for both the free amine forms and the fully charged amine hydrochloride forms of all three samples. Table B1 shows the results obtained.

TABLE B1

Water Contents of Aminoalkyl Resins

Sample	Water Content (g H_2O per g dry resin)
XPAB1	25 - 29
XPAB1 HCℓ	17 - 21
XPAO	2.7
XPAO HCℓ	3.5
XPAD	3.1
XPAD HCℓ	3.8

The extremely large values for XPAB1 suggest that this sample is a lightly cross-linked gel. This correlates with the observation that XPAB1 was very susceptible to basic attack at high pH and 80°C - the cross-linked form tended to be rapidly degraded to a solution of branched polymers under these conditions.

Approximate swelling volumes were also determined for these three derivatives. There was negligible change ($\lesssim 4\%$) in the swelling volume with protonation of the amine groups for all three samples. The results are shown in Table B2 as the volume of resin in the free base form in water per gram of dry resin, as well as the corresponding protonated forms.

TABLE B2

Approximate Swelling Volumes of Aminoalkyl Resins

Sample	Swelling volume (volume of wet resin (cm^3) per g of dry resin)
XPAB1	20.0
XPAB1 HCℓ	20.7
XPAO	10.8
XPAO HCℓ	11.2
XPAD	11.2
XPAD HCℓ	11.4

APPENDIX C THERMAL EFFECTS IN CROSS-LINKED SYSTEMS

The thermal effect in this study refers to the change in pH of the supernatant liquid over the temperature interval, 25.0 to 80.0°C:

$$\Delta pH = pH^{T=25} - pH^{T=80}$$

where the $pH^{T=80}$ is the pH of the supernatant at 80.0°C. However, the thermal effect measured in the Sirotherm process is the difference in the pH of the supernatant at 20°C and the supernatant in equilibrium with the resin at 80°C but cooled to 20°C for measurement of the pH (Weiss et al., 1966a and b):

$$\Delta pH' = pH^{T=20} - pH^{\text{supernatant } 80,\, T=25}$$

Hence there is a difference in the two methods, the latter not showing the real change in pH with temperature. As a means of comparing the results from the two methods, one of the resins used and supplied by Weiss et al. (1966a), De-Acidite G (7 - 9% cross-linked and 2.6% quaternary ammonium content), and all of the resins in Chapter V of this study were treated according to both methods. The titration curves of De-Acidite G are shown in Figure C1, where it is quite clear that the real change in pH is much larger than that measured by cooling the hot supernatant to 25.0°C. The change in pH at an acid fraction of 0.50 is taken as an indicator of the thermal effect for the two methods. Table C1 shows the thermal effects for all resins mentioned for both methods, where $\Delta pH_{0.5}$ refers to the 'real' change and $\Delta pH'_{0.5}$ refers to the change measured by cooling the 80.0°C supernatant to 25.0°C.

As expected, there is a general tendency for the difference between the two methods to increase as the pH increases, because the change in the ionisation constant of water plays an increasingly

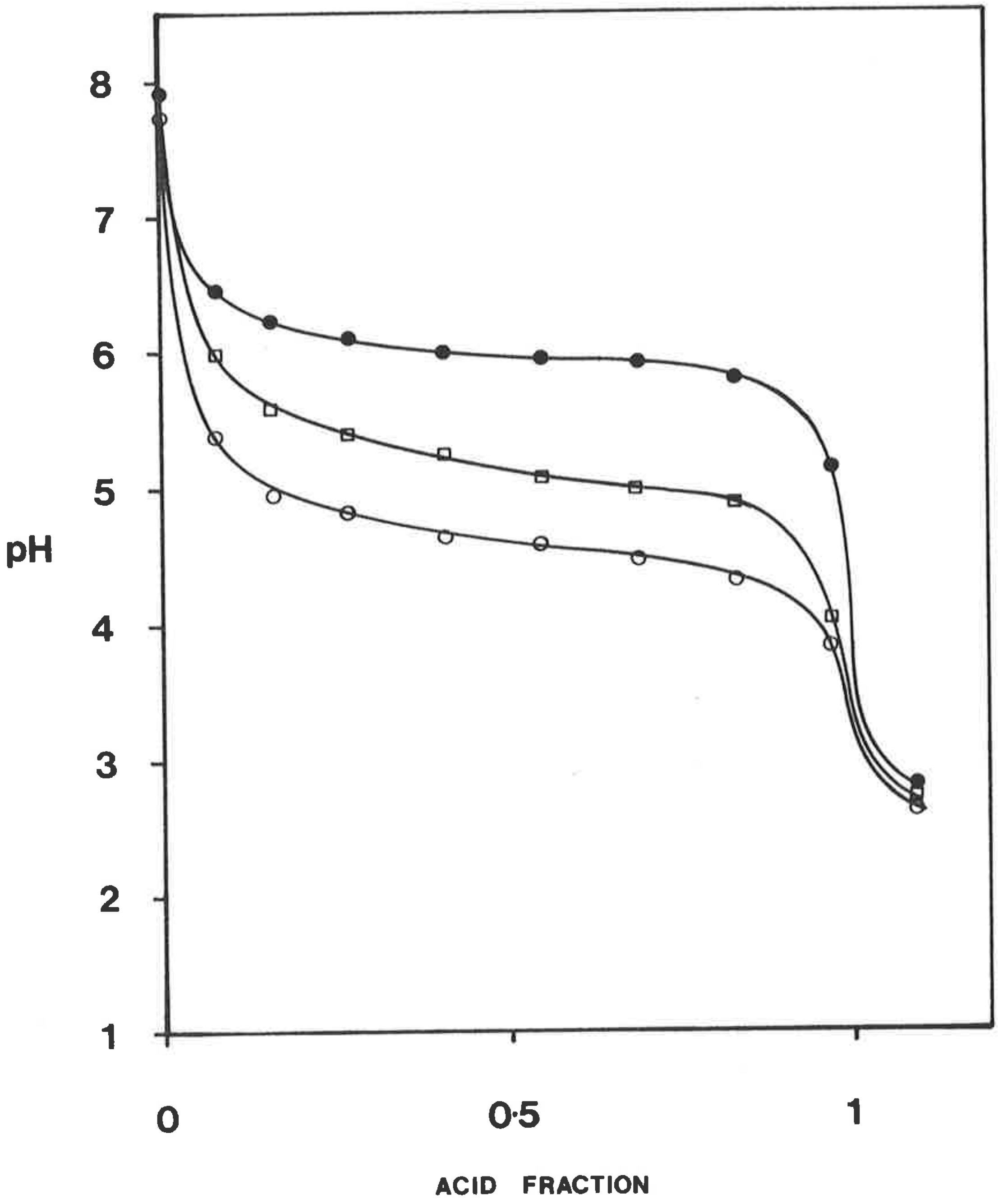
Fig. C1 TITRATION CURVES OF DE-ACIDITE G RESIN (7-9% CROSS-LINKED AND 2.6% QUATERNARY AMMONIUM CONTENT) IN 0.0200 mol dm^{-3} NaCℓ.

Symbols

● T = 25.0°C

○ T = 80.0°C

□ T = 80.0°C supernatant, pH measured at T = 25.0°C


8
7
6
5
4
3
2
1
pH
0
0·5
1
ACID FRACTION

important role at higher pH. However, there does not seem to be any obvious relationship between the differences and the pH. The only clear fact is that the method used in the Sirotherm studies underestimates the real change in pH with temperature.

TABLE C1

Thermal Effects for Selected Resins

Sample	$\Delta pH_{0.5}$	$\Delta pH'_{0.5}$	$pH_{0.5}^{T=25}$
De-Acidite G	1.37	0.86	5.97
XPE6	0.96	0.70	3.88
XPED1	0.57	0.50	3.67
XPED3	0.67	0.56	3.29
XPED6	0.58	0.39	3.02
XPD7	0.61	0.59	3.57
XPAB1	1.51	0.36 *	8.74
XPAO	2.75	2.00	9.48
XPAD	2.48	1.93	8.93

* This value is very doubtful due to the tendency of this gel/resin to disintegrate at high pH and high temperature.

APPENDIX D POLY-2-VINYLPYRIDINE DERIVATIVES

A preliminary study of the potentiometric titration behaviour of three dodecyl chloride derivatives of poly-2-vinylpyridine was undertaken. P2VP was quaternised with dodecyl bromide in the same way as for the P4VP derivatives (see Section 10.2.2). The compositions (determined in the same way as for the P4VP derivatives) are shown in Table D1.

TABLE D1

Compositions of Dodecyl Chloride Derivatives of P2VP

Sample	Titratable pyridine Nitrogen (10^{-3} mol g^{-1})	% Pyridine N quaternised with Dodecyl Chloride	% Pyridine N unquaternised
2PD1	7.18	9.9	90.1
2PD2	6.17	15.5	84.5
2PD3	5.57	19.4	80.6

The potentiometric titration of these derivatives was difficult because of the low solubility in water and the low basicity as a result of steric hindrance (Kirsh et al., 1973), even lower than P4VP derivatives. It is extremely difficult to protonate any more than approximately half of the pyridine nitrogen atoms in P2VP (see e.g. Muller, 1974b). The plots of pK_{app} versus α show that the basicity decreases rapidly with ionisation for all three samples up to $\alpha \approx 0.6$, after which there appears to be negligible uptake of acid. Figure D1 shows the typical shapes of these plots for sample 2PD1 in 10% ethanol:water (v/v) at 25.0°C in the absence of NaCℓ and in 0.02 mol dm^{-3} NaCℓ. The values at 80.0°C showed similar trends, the only differences being a decrease in basicity of approximately

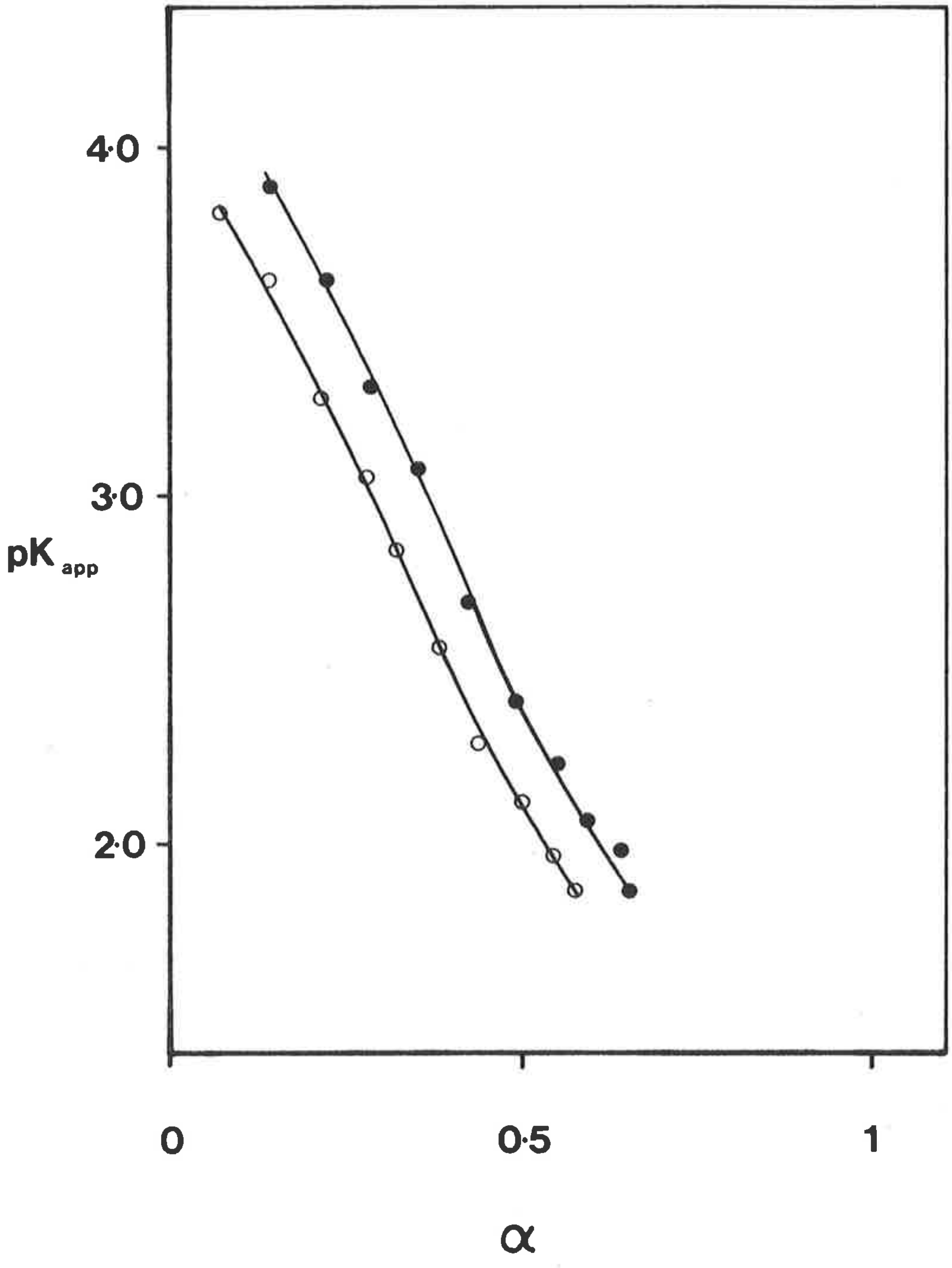
Fig. D1 TITRATION CURVES OF 9.9% DODECYL DERIVATIVE OF P2VP AT 25.0°C IN 10% (V/V) ETHANOL : WATER.

Symbols

○ No added salt

● 0.0200 mol dm^{-3} NaCℓ

Conc. of polymer ≡ 0.373 g/100 cm^3


4·0
3·0
2·0
pK app
0
0·5
1
α

0.4 to 0.5 pH units. The results obtained were only approximate and hence not of sufficient accuracy to justify tabulation here. The general characteristics are in agreement with the results of Kirsh et al. (1973). The major conclusion drawn from these preliminary measurements is that P2VP is not a suitable polymer for potentiometric titration of basic groups.

APPENDIX E ABBREVIATIONS

Abbreviation	Compound
AIBN	azobisisobutyronitrile
Cm-bzl-dextran	carboxymethylbenzyldextran
Cm-dextran	carboxymethyldextran
PAA	poly(acrylic acid)
PLL	polycondensate between L-lysine and 1,3-benzenedisulfonyl chloride
PEA	poly(ethacrylic acid)
PGA	poly-L-glutamic acid
PMA	poly(methacrylic acid)
PEG	poly(oxyethylene)
PVI	poly-N-vinylimidazole
P4VP	poly-4-vinylpyridine
P2VP	poly-2-vinylpyridine