Aqueous solution properties of a poly(vinyl imidazolium sulphobetaine)

J. C. Salamone, W. Volksen, A. P. Olson and S. C. Israel
Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854, USA

(Received 30 January 1978; revised 10 April 1978)

In this investigation the aqueous solution properties of an ampholytic poly(vinyl imidazolium sulphobetaine) are discussed. This class of polymer is water insoluble and its solubilization is related to the type and concentration of added salt. Cloud point determinations, intrinsic viscosity and light scattering studies are presented to illustrate the solution behaviour of this polyampholyte as a function of the type of cation and anion present. An explanation of its solubility in certain salt solutions is presented.

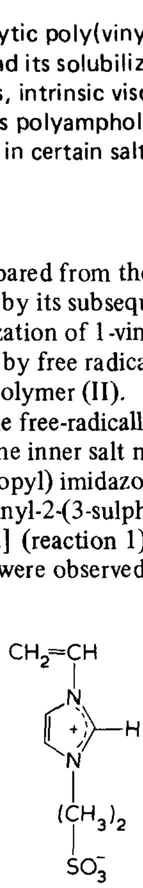
INTRODUCTION

In recent years there has been considerable academic and industrial interest in the preparations and properties of new ionic polymers[1,2]. These studies have involved the areas of cationic and anionic polyelectrolytes, since both classes have certain unique chemical and physical properties.

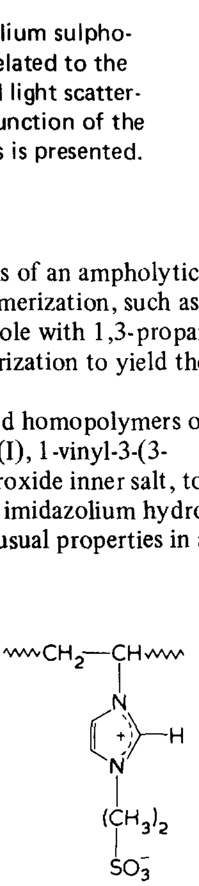
Polyelectrolytes are normally prepared either from the free radical (homo- and co-) polymerization of an ionic monomer or from a subsequent reaction on a preformed, neutral polymer. The first case offers greater control over the structure and properties of the final polyelectrolyte through alteration of the quantities of starting material(s) and conditions employed. In the latter case, reactions on preformed, neutral polymers are considerably more difficult to control because the conversion of a neutral polymer to one of high charge density (either cationic or anionic) becomes considerably more difficult as the amount of charge becomes greater. Consequently, there may be several different rates of ionic charge formation present in these reactions, and most reactions rarely go to completion. For the reasons cited above, control of a polyelectrolyte structure is then most easily obtained by polymerization of a suitable ionic monomer.

In the area of polycations, considerable interest has recently focussed on the spontaneous polymerization of vinyl pyridinium and vinyl imidazolium salts[3–10]. The facile polymerization of these salts under certain conditions has yielded a new method of polycation formation. In general, the preparation of polycations from the homopolymerization or copolymerization of cationic monomers has normally been limited to those of quaternary (meth)acrylate or (meth)acrylamide monomers in which the positive charge was far removed from the double bond in order to facilitate (free radical) polymerization[1]. Few detailed studies have been reported on the polymerizations of cationic monomers in which the positive charge is adjacent to the double bond or on an aromatic ring in resonance with the double bond[11]. We have recently continued our studies on vinyl imidazolium salts by extending our investigation into the area of ampholytic materials. In this regard, ampholytic polymers have been prepared from the synthesis of an ampholytic monomer followed by its subsequent polymerization, such as the quaternization of 1-vinyl imidazole with 1,3-propanesultone followed by free radical polymerization to yield the sulphobetaine polymer (II).

For the free-radically prepared homopolymers of the sulphobetaine inner salt monomer (I), 1-vinyl-3-(3-sulphopropyl) imidazolium hydroxide inner salt, to II, poly [1-vinyl-2-(3-sulphopropyl) imidazolium hydroxide inner salt] (reaction 1), very unusual properties in aqueous solution were observed[9,10].



(I)



(II)

The polymers were insoluble in water and had hydrogel characteristics: however, the polymers could be dissolved in certain aqueous salt solutions. It was found that the solution properties were related to the type and concentration of salt employed. In contrast to normal polyelectrolytes, it was observed that the reduced viscosity increased with increasing salt concentration, and that the greater the site binding ability of either the anion or the cation, the greater the reduced viscosity[10]. Although the solution properties of polyampholytes has received limited investigation, our studies appeared to agree with previously reported studies in this area, which have employed a variety of ampholytic structures[12–19].

In this investigation are reported further studies of the solution behaviour of the poly(vinyl imidazolium sulphobetaine) II, PVISB, derived from the homopolymerization of I.

0032–3861/78/101157–06$02.00

Table 1 Minimum salt concentration of PVISB in salt solutions with a common cation

Electrolyte	Minimum salt concentration
KF	Insoluble
KCl	0.38 M
KNO_3	0.17 M
KBr	0.13 M
KI	0.05 M
$KClO_4$	0.03 M

EXPERIMENTAL

Sample preparation

Poly[1-vinyl-3-(3-sulphopropyl) imidazolium hydroxide inner salt] (PVISB) was prepared as described earlier[20]. The polymer was then dialyzed against distilled water for several days and dried under vacuum at 100°C for 12 h. An amber coloured material was obtained which was brittle and hydroscopic.

In the case of the light scattering experiments, a large quantity of polymer was dissolved in a 1.50 M aqueous KCl solution and fractionated by the addition of distilled water.

Cloud point titrations

Cloud point titrations to determine the point at which the homopolymer becomes insoluble in the aqueous salt solution of interest were performed by dissolving the material in an aqueous salt solution of sufficient salt content and titrating the stirred solution with distilled water to the first indication of turbidity. Cloud points occurring at high salt concentrations were definite and sharp, whereas cloud points occurring at low salt concentrations were less definite and slow to appear.

Viscometric measurements

Viscometric measurements were performed with an Ubbelohde viscometer (size 50) in a constant temperature bath maintained at 25.00° ± 0.02°C. The polymer samples were dissolved in the salt solution of interest to yield stock solutions of approximately 1.0 g per 100 ml of solvent. Dialysis of all polymeric solutions against solvent was omitted due to the large excess of salt present.

Viscosity data were evaluated by the Huggins equation (1). In relation to the light scattering measurements, the intrinsic viscosity, $[\eta]$, was correlated to the molecular weight by the Mark–Houwink equation (2):

$$\frac{\eta - \eta_0}{\eta_0 c} = \frac{\eta_{sp}}{c} = [\eta] + k[\eta]^2 c \qquad (1)$$

$$[\eta] = K\bar{M}_v^a \qquad (2)$$

Light scattering measurements

The light scattering measurements were carried out on a Brice–Phoenix Universal Light Scattering Photometer using a cylindrical cell and unpolarized light of 4360 Å wavelength. Measurements were made on solutions which were previously dialysed against solvent and filtered through a 0.22 μm Millipore filter. All solutions were checked for optical clarity by viewing at low angles in front of a narrow beam of u.v. light.

The instrument was calibrated with an opal glass reference standard furnished by the manufacturer. Depolarization measurements were made for each system. The lowest concentration used gave no depolarization and the Cabannes factor was taken as unity. The specific refractive index increment, d*n*/d*c*, was determined on a Brice–Phoenix differential refractometer calibrated with KCl solutions of known refractive indices.

Light scattering data were evaluated by the Zimm technique in terms of equations (3) and (4):

$$Kc/R_\theta = 1/\bar{M}_w + 2A_2c\ldots \qquad (3)$$

$$\lim_{c \to 0} Kc/R_\theta = 1/\bar{M}_w(1 + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2 \theta/2 \qquad (4)$$

RESULTS AND DISCUSSION

Cloud point determinations

With the aim of studying the solution behaviour of the poly(vinyl imidazolium sulphobetaines) and the fact that they readily dissolved in certain aqueous salt solutions of sufficient salt content, it was necessary to measure the lower critical salt concentration (minimum salt concentration) needed for solubilization of the polymer. Utilizing salt solutions containing a common cation but different anions, the data show a definite increase in the solubility of poly[1-vinyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt] (PVISB) in aqueous salt solution in the order $F^- < Cl^- < NO_3^- < Br^- < I^- < ClO_4^-$ for KF, KCl, KNO_3, KBr, KI, and $KClO_4$, respectively, as shown in *Table 1*. These data are consistent with those for the sulphobetaine derived from poly(4-vinyl pyridine)[19] and appear to follow the site binding ability of the anion[21–23].

In a related experiment, the cloud points of polymer solutions containing salts with a common anion but different cations were studied. *Table 2* is a compilation of the data obtained from this investigation. For the chloride salts, the data indicate an increase in the solubility of the polymer in the order $NH_4^+ < Li^+ < Na^+ < K^+$. For the perchlorate salts an order is not observed. A similar tendency has been observed for the binding of these cations to polyelectrolytes containing pendant sulphonate groups, with the potassium ion being bound the strongest and lithium ion being bound weakest[24–26].

For the solubilization of PVISB by aqueous salt solution, the anions and cations of the low molecular weight electrolyte could be considered to enter the ionically crosslinked network of the polymer through osmotic forces, and it would be these forces which caused the polymer to swell when placed in water. The reason that the polymer does not dissolve in water could therefore be that the osmotic force

Table 2 Minimum salt concentration of PVISB in salt solutions with a common anion

Electrolyte	Minimum salt concentration
KCl	0.38 M
NaCl	0.37 M
LiCl	0.50 M
NH_4Cl	0.52 M
$KClO_4$	0.03 M
$NaClO_4$	0.03 M
NH_4ClO_4	0.03 M

Table 3 Minimum salt concentrations of PVISB in salt solutions containing divalent cations

Electrolyte	Minimum salt concentration
$Mg(ClO_4)_2$	0.06 M
BaI_2	0.09 M
$BaCl_2$	0.24 M
$MgCl_2$	0.25 M
$CaCl_2$	0.28 M

Table 4 Total molality and chloride ion molality at the cloud point of PVISB in various salt solutions

Electrolyte	Molarity at cloud point	Total molality	Molality of Cl^-
$BaCl_2$	0.24	0.61	0.37
$CaCl_2$	0.28	0.73	0.44
$MgCl_2$	0.25	0.67	0.41
LiCl	0.50	0.98	0.47
KCl	0.38	0.69	0.31
NaCl	0.37	0.68	0.31

which tends to draw solvent into the polymer is not of sufficient strength to rupture the ionic crosslinks. This would be the typical case of swelling of a crosslinked material in which the polymer swells until the osmotic forces are balanced by the elastic forces of the network. In the case of PVISB, as the solvent is drawn into the material, also bringing in mobile ions, the polymer swells as usual. However, the elastic forces which tend to oppose the continued swelling are constantly being decreased due to the fact that the mobile ions of the added salt are able to neutralize a portion of the ionic crosslinks. As a result, the swelling continues until the gel finally dissolves.

From the data which were obtained it seems apparent that the effect of the anion on the solution properties of these polymers is much greater than the effect of the cation. Also, among the anions, it has been observed that salts containing anions having a small charge/radius ratio are better solvents than are salts containing anions having a high charge/radius ratio. This may be due to the extent of hydration of the anions and their ability to approach closely to the cationic imidazolium ring, thus effectively neutralizing the charge. It is also conceivable that the charge/radius ratio may be the reason that the cationic effect is small. The hydration shell of a positvely charged ion in water is generally fairly large, leading to a distance of closest approach which is not sufficient to neutralize effectively the charge on the sulphonate group. Once the imidazolium ring has bound the anion, the sulphonate group is then surrounded by water molecules and cations from the salt. With regard to the effect of the cation being small, it may be seen from *Table 3* that divalent cations, known to precipitate anionic polyelectrolytes from aqueous solution even at low concentrations, did not precipitate the PVISB under investigation. In fact, as may be seen from *Table 4,* which is a compilation of the chloride ion concentrations at the precipitation points, the divalent metal chlorides are at least as good as LiCl for dissolving the polymer. *Table 4* also lends support to the proposal that the polymer is soluble because of the interaction of the chloride anion with the imidazolium ring. However, the effect of the cation may also be observed. If it is assumed that the polymer precipitates at a certain chloride concentration for monovalent cationic species, then it can be observed that there is a tendency for divalent cations to precipitate the polymer at higher chloride ion concentrations.

Viscosity measurements

It is generally accepted that the intrinsic viscosity is a measure of the hydrodynamic volume of the polymer molecule for samples containing polymer of the same molecular weight. Thus, determination of the intrinsic viscosity of PVISB in the presence of different electrolytes should reflect the influence of these salts on the hydrodynamic volume of the polymer chain. Conducting the viscosity study along similar lines as the cloud point determinations, the first stage of this investigation was to determine the influence of different electrolytes, having a common cation, K^+, on the intrinsic viscosity of PVISB. Therefore, the reduced viscosities of the polyampholyte in aqueous KCl, KBr and KI solutions of the same added salt concentration were studied, as illustrated in *Figure 1.*

An analogous viscosity experiment was conducted employing a common anion, Cl^-. The results obtained are shown in *Figure 2* and *Table 5.* It is observed that the viscosity behaviour for the potassium and sodium salts are very similar, whereas that for LiCl is different. This is probably due to the fact that at the concentration used in this experiment (i.e. 0.5 M), the LiCl is acting as a θ solvent, as may be seen from the cloud point titrations (*Table 2*). It is also interesting to note that the anion and cation effects which are observed in the viscosity experiments are the same as those observed in the cloud point determination experiments. Furthermore, as may be seen in *Table 5,* the value for the Huggins constant, k', decreases as the intrinsic viscosity increases. This decrease in the Huggins constant may be associated with an increased polymer–solvent interaction, a proposal which is reaffirmed by the cloud point titrations (*Tables 2 and 3*).

As mentioned previously, divalent cations do not precipitate the polyampholyte, which is contrary to the behaviour

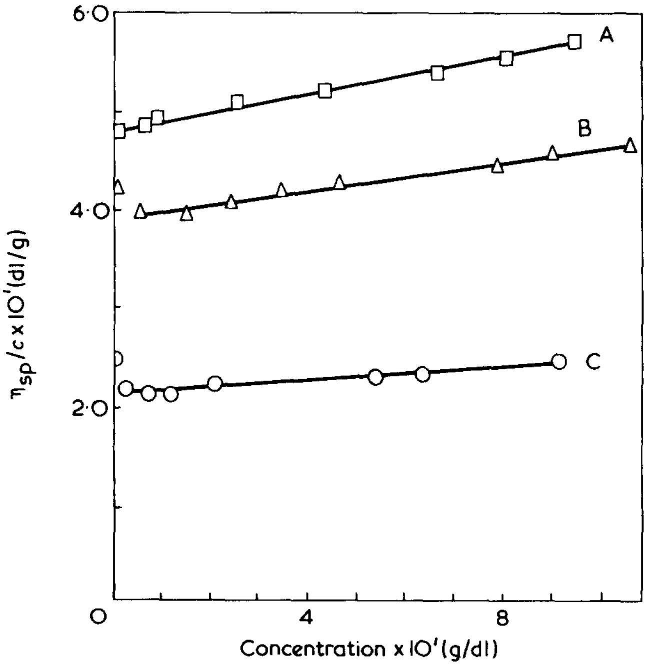


Figure 1 Reduced viscosities of PVISB as a function of concentration for salts containing a common cation. A, 0.50 M KI; B, 0.50 M KBr; C, 0.50 M KCl

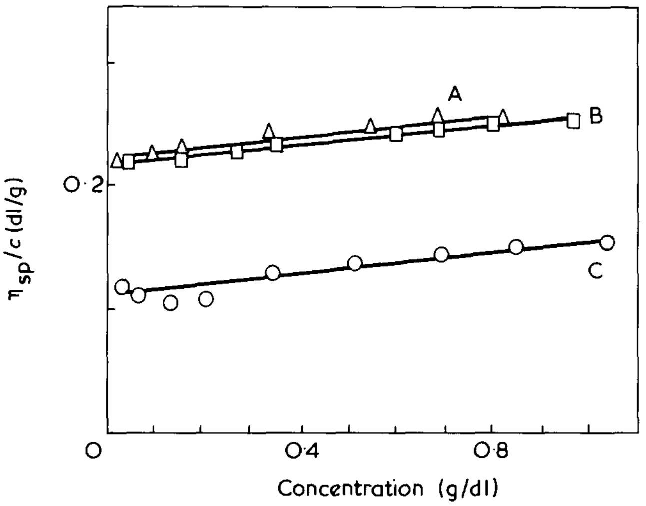


Figure 2 Reduced viscosities of PVISB as a function of concentration for salts containing a common anion. A, 0.50 M KCl; B, 0.50 M NaCl; C, 0.50 M LiCl

Table 5 Effect of anion and cation on the viscosity behaviour of PVISB at 25.0°C

Solvent (0.5 M)	Slope	Intercept, [η]	k'
KCl	0.028	0.217	0.60
KBr	0.064	0.395	0.41
KI	0.085	0.480	0.36
LiCl	0.032	0.190	0.89
NaCl	0.032	0.220	0.67
$CaCl_2$	0.043	0.394	0.27

of normal polyelectrolytes. In *Figure 3* the effect of a divalent cation, Ca^{2+}, on the viscosity behaviour of PVISB is graphically illustrated and compared with the monovalent cation, Na^+. Since the concentration of chloride ion is different in each case, a difference in the intrinsic viscosity of the two solutions is to be expected. We attribute more significance to the observation that the difference in intrinsic viscosity is nearly linearly related to the difference in chloride concentration. This concept was examined more closely in an experiment in which the intrinsic viscosities of solutions of KCl of several different concentrations containing PVISB were determined. The results are shown in *Table 6* and *Figure 4;* the latter is a plot of the intrinsic viscosity *versus* the molality of the chloride ion. This Figure indicates that the intrinsic viscosity is indeed closely related to the chloride ion concentration. It is possible to consider *Figure 4* to be composed of two straight lines. One line extends from approximately 0.70 to 1.50 m. The first line, which has the higher slope, may be due to site binding of the chloride ion by the imidazolium ring. This line is characterized by a relatively rapid change in the intrinsic viscosity as the chloride ion concentration is increased. The second line, which is characterized by a slower rate of change of intrinsic viscosity as the chloride ion concentration is increased, may be due to atmospheric binding of the anion by the polyampholyte. If the assumption is made that a certain portion of the ions of the added electrolyte is closely associated with a corresponding fraction of the charged sites along the polyampholyte and, further, that the portion bound is proportional to the concentration of the added electrolyte, a plausible explanation of the shape of the curve in *Figure 4* may be given. At the lower concentrations shown, site binding of the anion predominates. As the concentration of the salt is increased, more and more of the potential binding sites are occupied, resulting in a decreased tendency for further site building. Since binding will lower the draining capability of the polymer particle, an increase in the viscosity of the solution is expected. The viscosity increases rapidly at first, owing to the rapid decrease in draining, and less rapidly as the tendency to site bind decreases. Atmosphere binding beings to predominate and as a result, the viscosity increase with increasing salt concentrations begins to lessen. This explanation seems to agree with the fact that k' decreases as the salt concentration is increased, or as the power of the solvent is increased (N. B., the Huggins constant, k', is generally considered to be related to the polymer–solvent interaction). It is also consistent with the observation from the light scattering experiments (see above) that the second virial coefficient is more susceptible to changes in the solvent than is the radius of gyration.

Light scattering measurements

Although equations (3) and (4) were developed for light scattering from macromolecular solutions comprising a two component system, it has been shown that the equations for a three component system, such as a polymer solution with added low molecular weight electrolyte, are analogous to those of the two component system, by dialysing the three component system against solvent so as to obtain solutions of similar chemical potential[27].

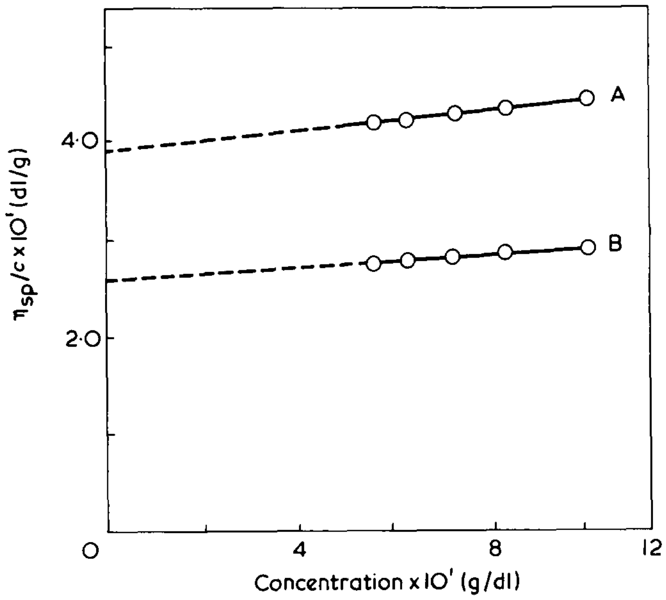


Figure 3 Reduced viscosities of PVISB as a function of concentration for $CaCl_2$ and NaCl. A, 0.50 M $CaCl_2$; B, 0.50 M NaCl

Table 6 Effect of salt concentration on the intrinsic viscosity and Huggins constant of PVISB

KCl concentration	Cl^- molality	[η] (dl/g)	k'
0.50 M	0.39	0.28	0.62
0.60 M	0.47	0.35	0.32
0.70 M	0.54	0.41	0.20
0.80 M	0.62	0.45	0.26
0.90 M	0.69	0.47	0.30
1.00 M	0.77	0.50	0.28
1.50 M	1.16	0.60	0.20
2.00 M	1.54	0.64	0.19

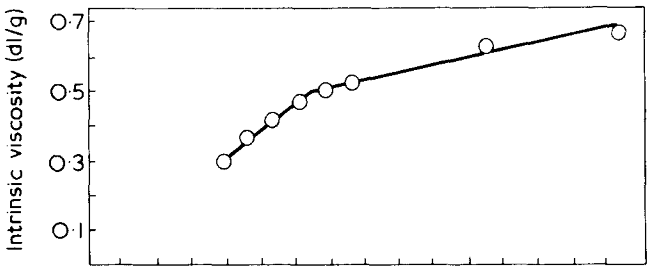


Figure 4 Intrinsic viscosity of PVISB as a function of chloride ion molality

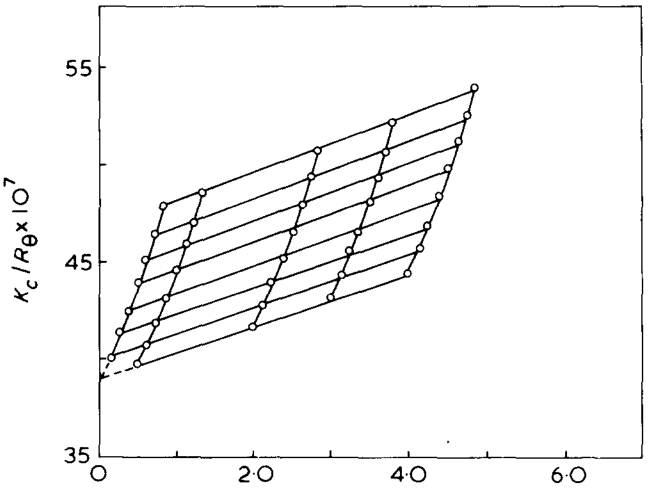


Figure 5 Zimm plot of PVISB in 0.50 M salt, $\overline{M}_w$ = 263000; A_2 = 6.2×10^{-5}; [η] = 0.216

Being able to use this technique effectively for the characterization of the polyampholyte in the presence of added salt, it was decided to investigate further the possibility of an increased polymer–solvent interaction on increased salt concentration and binding capability by light scattering measurements. The Zimm technique which consists of extrapolating both to zero angle and zero concentration is a convenient method of evaluating the polymer molecular weight, the second virial coefficient and the radius of gyration of the polymer chain[28]. *Figure 5* is an illustration of this technique with respect to the polymer under study. Applying this method to 0.50 M aqueous solutions of LiCl, NaCl, KCl, KBr, and KI the data in *Table 7* were compiled. In this study the Zimm plot of the poly(vinyl imidazolium sulphobetaine) in 0.50 M LiCl showed a downward curvature at constant angle and increasing concentration, whereas the other plots illustrated conventional grid patterns. A possible explanation of this effect may be that 0.50 M LiCl is very close to the θ solvent for this polymer (which we have observed as the lower limit for solubility in the cloud point titrations), and the polymer molecules may be forming an aggregate structure.

From *Table 7* it can be noted that the radii of gyration increase with increasing binding ability of the anions (Cl^-, Br^- and I^-) and also the cations (Li^+, Na^+ and K^+). In the case of NaCl and KCl solutions, there was little difference in R_G and A_2 values; however, this is consistent with the cloud point titrations and viscosity measurements which also showed a very slight difference between the two salts. For the salt solutions containing different anions, the radii of gyration and second virial coefficient increase with the generally accepted binding order of these anions to cationic polyelectrolytes.

A comparison of the experimentally determined radii of gyration and second virial coefficients, in *Table 7*, appears to confirm the idea that the increase in intrinsic viscosity is mainly due to an increased polymer–solvent interaction as reflected by the second virial coefficient, rather than to electrostatic repulsive forces, which would appear as a large change in the radii of gyration. This is clearly illustrated for the cases of aqueous KBr and KI solutions where the higher ion binding ability of I^- relative to Br^- leads to a small increase in the radius of gyration, but to a much larger increase in the second virial coefficient.

From *Table 7* it may also be observed that the second virial coefficient and the intrinsic viscosity increase upon proceeding to better solvents. In fact, as shown in *Figure 6*, the relationship between the intrinsic viscosity and the second virial coefficient is linear for the samples studied. This linear behaviour would indicate that there is a close association between the anion of the added salt and the polymer segment That is, for [Cl^-] = 1.00 M, the anion is probably associated with a particular site on the polymer chain rather than being part of a 'mobile' atmosphere of anions. Otherwise, there would appear to be no reason to expect that the excluded volume would be related to the hydrodynamic volume in a linear fashion.

Additional studies on the solution properties of PVISB were undertaken by determining the Mark–Houwink K and a values using a series of polymer fractions of known molecular weights and intrinsic viscosities. The solvents used

Table 7 Molecular characteristics of PVISB in various salt solutions at 30°C

Electrolyte (0.50 M)	R_G (Å)	$A_2 \times 10^5$	$M_w \times 10^{-5}$	[η] (dl/g)
LiCl	172	−5.2	2.40	0.17
NaCl	210	6.2	2.63	0.22
KCl	207	3.0	2.56	0.21
KBr	259	28.0	2.78	0.39
KI	261	37.0	2.67	0.44

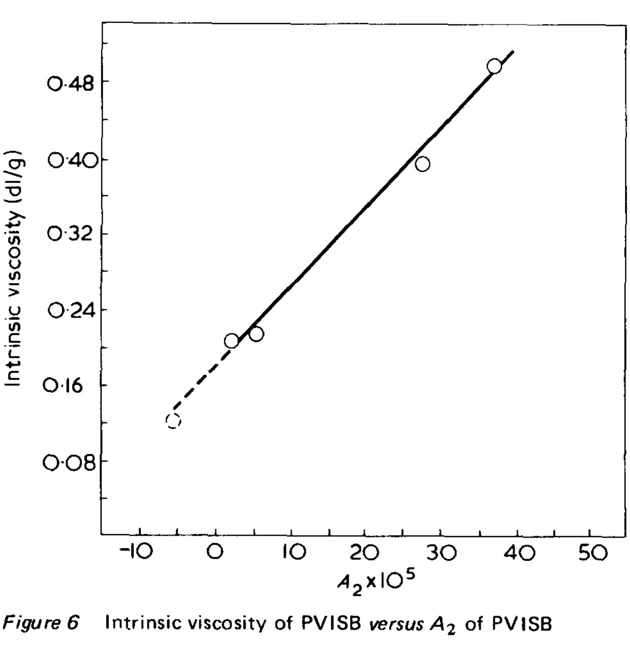


Figure 6 Intrinsic viscosity of PVISB *versus* A_2 of PVISB

were 0.20 M KSCN and 0.50 M $NaClO_4$. It was found that K and a values were 5.7×10^{-5} and 0.67 for 0.20 M KCN and 1.3×10^{-5} and 0.84 for 0.50 M $NaClO_4$. These a values indicate that the polymer chain behaves as a flexible coil in both salt solutions, being more tightly coiled in the KSCN solution and more expanded in the $NaClO_4$ solution. In the latter case of a very good solvent, it is doubtful that the polymer chain could approach the dimensions of a rod-shaped macromolecule by using a higher salt concentration, since this would require large repulsive interactions between the ionic sites on the polymer chain. Such a large repulsive interaction would only be possible if one charge on the polymer chain could be effectively neutralized, leaving the opposite charge in a relatively unshielded condition. It seems apparent that this condition could not be achieved with a polyampholyte, since neutralization of one charge, for example the cationic charge by strongly binding anions, would leave the oppositely charged anionic pendant groups in a large concentration of cations and, therefore, in a relatively shielded condition.

CONCLUSIONS

In this investigation it has been shown that the poly(vinyl imidazolium sulphobetaines) are dependent on a lower critical salt concentration needed for dissolution. This lower critical salt concentration is strongly dependent on the nature of the salt and may be related to the ion binding capabilities of the anions and cations of the electrolyte.

Light scattering studies in conjunction with viscosity determinations of the polyampholyte in the presence of different low molecular weight electrolytes provided a conformational model of the polymer chain in aqueous salt solutions. It appears that the presence of the inorganic salts disrupts the intramolecular and/or intermolecular interactions of the imidazolium and sulphonate groups, which causes the insolubility of the polyampholyte in the first place, thus allowing the solvation by water molecules. The large concentration of ions needed to cause this dissolution prevents the polymer chain from expanding drastically due to the shielding of like charges by these ions.

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