lem is indicated, and a more careful definition of equilibrium for systems of this type from a statistical point of view is desirable.

The adsorption of polystyrene on porous alumina is limited by the ability of the polymer molecules to penetrate the pore structure of the adsorbent. Such penetration is limited by the dimensions of the polymer molecule in solution. This result is in accord with the results of Moore[33] who used the differential diffusion rates in cross-linked polymers as the basis of molecular weight fractionation in gel-permeation chromatography.

Kiselev and Eltekov[16,17] have drawn conclusions similar to ours regarding the possibilities of estimating molecular dimensions of polymer molecules and of effecting fractionation by adsorption on porous polymers. These authors, however, characterize the porosity of their adsorbents by a single parameter, a "predominant size of pore openings." It is preferable to obtain the distribution of pore sizes, as in Figure 1 of the present work.

In a recent investigation[15] Howard and McConnell have presented results for the adsorption of polyethylene oxide onto porous adsorbents (charcoal and nylon) from a variety of solvents and conclude, as we have done, that with a porous adsorbent the area of surface available to solute molecules has no unique value but depends on the size of the adsorbate molecule. Furthermore, they measured the pore-size distributions of their adsorbents. However, whereas we find that the absorbance of polystyrene on Al_2O_3 decreases with increasing molecular weight, Howard and McConnell find that for most of their solvent systems that there is no molecular weight dependence of the adsorbance of polyethylene oxide when charcoal was used as the absorbent. The molecular weights of all except one of their polymers are less than 20,000; furthermore, they do not appear to have fractionated their samples. Thus it is difficult to compare their work directly with ours.

Acknowledgment. This work was supported by Grant G-12885 from the National Science Foundation.

(33) J. C. Moore, *J. Polym Sci., Part A*, **2**, 835 (1964).

Specific Counterion Effects on the Viscosity Behavior of Protonated Poly(ethylenimine)

Kang-Jen Liu

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan.

Received April 22, 1968

ABSTRACT: The viscosity of poly(ethylenimine), PEI, was measured as a function of the degree of protonation, α, in aqueous solutions of sodium chloride, sodium nitrate, and sodium perchlorate. The intrinsic viscosities of protonated PEI in solutions containing chloride or nitrate ions are not surprising; they may be explained by the compensating effects of the modified electrostatic repulsion of the polyelectrolyte chain and the decrease of the solvent power for the polyion. However, the intrinsic viscosities of protonated poly(ethylenimine) in aqueous perchlorate solutions are peculiar; $[\eta]$ decreases to a minimum and then increases with increasing α. An intramolecular association of the polymer chain in these aqueous perchlorate solutions is believed to be the cause for the contraction of the polymer coil. This intramolecular association appears to be the result of hydrogen bonding of two nitrogens on polymer chain by a proton; the role of the anion here is to stabilize the complex. Viscosity measurements were also made on protonated poly(ethylenimine) in mixed ethanol–water media. The only counterion present was introduced by the acid used (hydrochloric or perchloric acid) in the protonation process; no salt was added. The results are completely consistent with those obtained in aqueous systems in the presence of excess salts. This excludes the possibility that the intramolecular contraction might be caused by the induced intramolecular hydrophobic associations of the polymer chain. This study shows that, in the presence of simple counterions, a physical picture of polyelectrolytes in solution may sometimes be difficult to obtain in terms of electrostatic interactions of structureless charged units only, but often requires a detailed consideration of all specific counterion effects on the charged macromolecules. This includes, not only the electrostatic repulsion of the polyion and the decrease of solvent power for the polymer, but also the possiblity of induced intramolecular associations of the polyelectrolyte.

It is well known that introduction of ionized groups into uncharged polymer chains results in chain expansions because of electrostatic repulsion. These electrostatic effects, which are much greater than those resulting from solvent effects, are markedly reduced by the addition of simple monovalent ion (counterions). A number of polyelectrolyte theories using purely electrostatic models have been developed to explain this behavior.[1] With the exception of the analysis given by Flory,[1g] these theories neglect effects which are nonelectrostatic in nature.[2] As Flory has pointed out, such effects may contribute to chain expansion, but they may also render chain expansion more difficult.[1g] An extreme example of such nonelectrostatic effects is given by the "polysoaps,"[3-6] where the polyions carry long aliphatic hydrocarbon side chains, that tend to

---

(1) For examples, see (a) W. Kuhn, O. Kunzle, and A. Katchalsky, *Helv. Chim. Acta.*, **31**, 1994 (1948); (b) A. Katchalsky, O. Kunzle, and W. Kuhn, *J. Polym. Sci.*, **5**, 283 (1950); (c) A. Katchalsky and S. Lifosn, *ibid.*, **11**, 409 (1956); (d) R. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725, 733 (1954); (e) J. J. Hermans and J. T. G. Overbeek, *Rec. Trav. Chim.*, **67**, 761 (1948); (f) G. E. Kimble, M. Cutler, and H. Samelson, *J. Phys. Chem.*, **56**, 47 (1952); (g) P. J. Flory, *J. Chem. Phys.*, **21**, 162 (1953); (h) M. Nagasawa, *J. Amer. Chem. Soc.*, **83**, 300 (1961).

(2) H. Morawetz, "Macromolecules in Solution," Interscience Publishers, Inc., New York, N. Y., 1966, p 328.

(3) U. P. Strauss and N. L. Gershfeld, *J. Phys. Chem.*, **58**, 747 (1954).

(4) U. P. Strauss, N. L. Gershfeld, and E. H. Crook, *ibid.*, **60**, 577 (1956).

(5) D. Woermann and F. T. Wall, *ibid.*, **64**, 581 (1960).

(6) U. P. Strauss and A. G. Boyes, *J. Polym. Sci.*, **22**, 463 (1956).

remain in contact with one another in spite of the repulsive forces between the fixed charges.

Although many studies of counterion effects on the solution properties of polyacids have been carried out,[7] relatively little attention has been paid to the behavior of polybases,[8] especially to the specific influence of the chemical nature of the interaction between the polyion and simple monovalent counterions. Recently, we reported the specific influence of chloride, bromide, and nitrate ions on the solution properties of protonated poly-N-vinylimidazole.[9] This type of specific interaction probably is important for understanding the behavior of many biopolymers, which frequently involves not only the electrolytic properties of the polymer molecule but also the highly specific nature of these polyelectrolytes. In this report, specific influences of simple monovalent counterions on the viscosity behavior of protonated poly(ethylenimine), a polybase, in aqueous as well as in mixed water–ethanol solutions are presented.

Experimental Section

The poly(ethylenimine), PEI, used in this study was obtained from the Chemirad Corp., East Brunswick, N. J. The sample was an aqueous solution containing about 50% of water; its molecular weight was estimated by the supplier to be in the range of 30,000 to 40,000. The concentration of the stock solution was determined by titration with standard hydrochloric acid in the presence of excess neutral salt. The polymer sample solutions were made from the same stock solution by dilution with various nominal stoichiometric degree of protonation (α), and with different neutral salts. Triple distilled water and absolute ethanol–water mixtures were used as solvent.

A three-bulb Ubbelohde dilution viscometer was used for all measurements. This viscometer permits dilution to be effected directly in the bulb without affecting the pressure gradient. The solvent flow time was such that kinetic energy corrections were negligible. Viscometric measurements were taken at 30° in aqueous system and at 25° in ethanol–water solutions. Routinely, viscosity measurements were made by first flushing with CO_2-free nitrogen, adding the desired solution, and bringing the system to the desired thermostat temperature. Efflux time measurements were repeated three times with each solution. In aqueous systems, the viscosity of PEI at different concentrations of sodium chloride, sodium nitrate, and sodium perchlorate was measured as a function of α with hydrochloric, nitric, and perchloric acid; no neutral salt was added.

Results and Discussion

In Aqueous Solutions. The reduced viscosities, η_{sp}/C, of PEI at different α values in the presence of various excess counterions in aqueous solutions have been extrapolated linearly to zero polymer concentration, yielding intrinsic viscosities, $[\eta]$. These $[\eta]$ values are summarized as a function of α in Figure 1. From these plots, it is seen that the viscosity of protonated PEI is affected differently by each of the monovalent counterions.

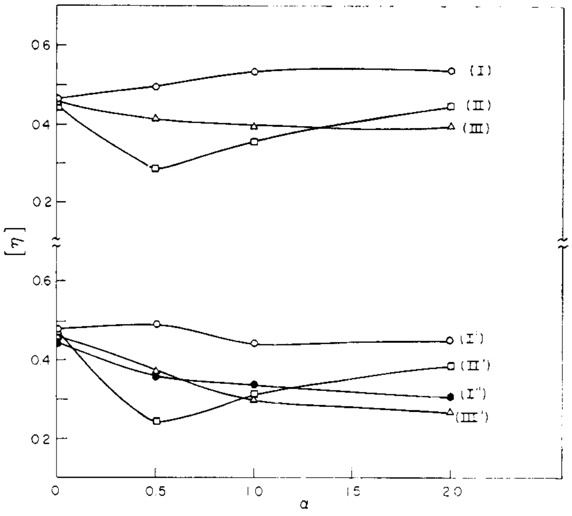

Figure 1. Plots of intrinsic viscosity (η) of protonated poly(ethylenimine) in water as a function of α with various counterions at 30°: (I) 0.5 M chloride, (II) 0.5 M perchlorate, (III) 0.5 M nitrate, (I′) 1.0 M chloride, (II′) 1.0 M perchlorate, (III′) 1.0 M nitrate, and (I″) 4.0 M chloride.

According to our general knowledge about polyelectrolyte solutions, the present $[\eta]$ results in systems containing chloride or nitrate ions are not surprising. It is known that, in the absence of neutral salt, $[\eta]$ rises rapidly with α at low α values (*e.g.*, $\alpha < 0.5$), and increases only slowly with further increasing α.[9] In the presence of simple salt ions, two effects are known to be important, one of which causes the viscosity to increase, the other causes the viscosity to decrease. This may be understood in the following way. The polyelectrolyte expands with increasing α because of electrostatic repulsion even though the salt reduces this to a smaller magnitude than that found in the absence of added salt. The opposing tendency is often referred as the familiar "salting out" process.[10] The solvent power for the polyelectrolyte is reduced when the concentration of added salt is high and the polymer tends to coil more tightly because of reduced solvent power. Therefore, the protonation of a polybase in the presence of appreciable counterions may cause $[\eta]$ to increase or decrease depending upon the compensating effects of the modified electrostatic repulsion of the polyelectrolyte chain (which increases the viscosity) and the decrease of the solvent power for the polyion (which reduces the viscosity). When the former effect plays a predominant role, $[\eta]$ increases with α, such as the results of PEI in 0.5 M chloride solutions. On the other hand, when the latter effect is the predominant factor, $[\eta]$ decreases consistently with α, as is seen for PEI in 0.5 and 1.0 M nitrate or 4.0 M chloride solutions. The $[\eta]$ results of PEI in 1.0 M chloride solutions may be classified as an intermediate case (See Figure 1).

The results of protonated PEI in perchlorate solutions

---

(7) For examples, see (a) U. P. Strauss, D. Woodside, and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1959); (b) D. T. F. Pals and J. J. Hermans, *Rec. Trav. Chim.*, **71**, 447 (1955); (c) N. S. Schneider and P. Doty, *J. Phys. Chem.*, **58**, 765 (1954); (d) T. A. Orofino and P. J. Flory, *ibid.*, **63**, 283 (1959); (e) P. J. Flory and J. E. Osterheld, *ibid.*, **58**, 653 (1954); (f) J. C. Leyte and M. Mandel, *J. Polym. Sci., Part A-2*, **2**, 1879 (1964); (g) M. Mandel, J. C. Leyte, and M. G. Stadhouder, *J. Phys. Chem.*, **71**, 603 (1967).

(8) C. Tanford, "Physical Chemistry of Macromolecules," John Wiley and Sons, Inc., New York, N. Y., 1962, p 506.

(9) K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, **69**, 1248 (1965).

(10) See ref 8, p 243.

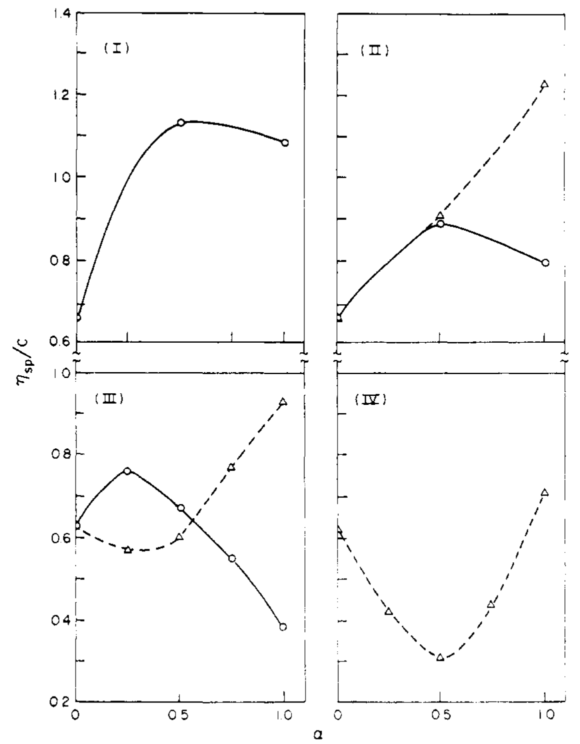

Figure 2. Plots of reduced viscosity, η_{sp}/C, of protonated poly(ethylenimine) (1%) as a function of protonation with perchloric acid (broken line) and hydrochloric acid (solid line) in various water–ethanol mixtures: (I) 1:1, (II) 1:2, (III) 1:3, and (IV) 19:81.

cannot be adequately explained by the previous considerations. An additional specific mechanism must be involved. Here, the decrease in the viscosity at the early stage of protonation is probably the consequence of significant intramolecular association which causes polymer coil contraction, as we have pointed out previously for certain polyvinylimidazole solutions.[6] At present, it appears to be more likely that this intramolecular association is the result of hydrogen bonding of two nitrogens on the polymer chain by a proton; the role of the anion here is merely to stabilize the complex. Therefore, this association might be expected to diminish when the functional groups of the polymer are either not protonated or all protonated. This consideration is consistent with the experimental results (see Figure 1).

The specific effects of counterions on the viscosity behavior of protonated PEI are mainly due to the ionic interaction of simple ions with the charged groups of the polyion, and therefore, they should be expected to be less pronounced for the uncharged PEI ($\alpha = 0$). This is indeed true as shown in Figure 1.

In Mixed Ethanol–Water Solutions. An alternative explanation of intramolecular contractions induced by the partial protonation of PEI might be described as the result of induced intramolecular hydrophobic associations of the polymer chain. In order to discriminate between this possible explanation and that given above, and also to avoid the use of excess of neutral salts in in solution, viscosity measurements were made on protonated PEI in mixed ethanol–water solvents. The only counterion present was introduced by the acid used in the protonation process; no salt was added. Under these conditions, it is not practical to extrapolate the viscosity results to zero polymer concentration, because then there will be no counterion in the solution. In the present systems, the results of reduced viscosity at a finite polymer concentration (1%) are adequate to serve the purpose of demonstrating the specific counterion effect on the viscosity behavior of the polyelectrolyte. These results are summarized in Figure 2. Again, it is not surprising that the viscosity of PEI in all ethanol–water mixtures increased with α at the early stage of protonation with hydrochloric acid, and then decreased with α as more hydrochloric acid was added. They may all be explained as a consequence of the compensating effects of electrostatic repulsion and the decrease of solvent power during the protonation process. The former effect played a predominant role at the early stage of protonation, and then it was overcome by the latter effect at high α values.

The reduced viscosity of PEI increased monotonically with α as the polyelectrolyte was protonated with perchloric acid in a 2:1 mixed ethanol–water medium. It appears that electrostatic repulsion is the predominant factor which determines the viscosity behavior of all protonated PEI in this medium. When the ethanol content was increased to 75 and 81% in the solvent mixtures, the reduced viscosity of PEI decreased with the increasing α at the early stages of protonation with perchloric acid, and then increased with α as more perchloric acid was added. This is a case (Figure 2-III) which exactly reverses the results found when hydrochloric acid is used for protonation of the polymer. An intramolecular association is again believed to be the cause for the contraction of the polymer coil in these high ethanol content perchlorate media. Evidently, the intramolecular contraction is not due to the induced intramolecular hydrophobic associations of the polymer chain, because hydrophobic associations of the polymer chain could not be promoted by increasing the ethanol content in a mixed ethanol–water medium. Therefore, the intramolecular association of the polymer must be ionic in nature. When the polymer is highly protonated, the intramolecular association is reduced and the electrostatic repulsion becomes the predominant factor in the expansion of the polymer coil.

Conclusion

The viscosity results obtained in ethanol–water solutions without added salts are completely consistent with those obtained in aqueous solutions in the presence of excess salts. The experiments in both solvent systems indicated the specific effects of counterions on the viscosity behavior of the protonated PEI. The protonation of the polybase may cause the polymer coil to expand or contract depending upon the specific effects of simple monovalent counterions. These effects are sensitive to the charge density of the polymer, the solvent power, the concentration of the counterion, and moreover, the specific nature of the interaction between the polyion and the simple counterions.

The present study is exploratory in nature. Therefore, the interpretations given here should be regarded as speculative, although they are consistent with all the experimental results. Many other types of measurements, such as counterion activities, light scattering, and electrophoresis, may also be useful for our understanding of the problem. However, the present experiments indicate that viscosity alone is sufficient to yield a direct demonstration of the specificity of the counterion effects of simple monovalent anions on the solution behavior of a protonated base, poly(ethylenimine). This study shows that, in the presence of simple counterions, a physical picture of polyelectrolytes in solution may sometimes be difficult to obtain in terms of electrostatic interactions of structureless charged units only, but often requires a detailed consideration of all specific counterion effects on the charged macromolecules. This includes not only the electrostatic repulsion of the polyion and the decrease of solvent power for the polymer, but also the possibility of induced intramolecular associations of the polyelectrolyte.

Acknowledgment. The author wishes to express his appreciation to Dr. Robert Ullman for valuable discussions and to Mrs. Libby Zirkin for experimental help.

The Role of Organic Agents in the Stress Crazing and Cracking of Poly(2,6-dimethyl-1,4-phenylene oxide)

G. A. Bernier and R. P. Kambour

General Electric Research and Development Center, Schenectady, New York.
Received March 12, 1968

ABSTRACT: The critical flexural strain ϵ_c for crazing or cracking has been determined for compression molded bars of poly(2,6-dimethyl-1,4-phenylene oxide) in air and in 28 different small molecule organic liquids. Measurements have also been made of equilibrium solubility of liquid in the polymer and in some cases the drop in polymer T_g caused thereby. Studies of the degree of solvent-induced crystallinity and Instron stress–strain behavior of sorption-equilibrated films have also been effected. Both surface energy and plasticization effects are thought to be observable in liquid-induced crazing and cracking. Transformation from cold drawing to crazing as the mode of failure is effected even by liquids of negligible solubility in the polymer suggesting that they act by reducing the surface energy of the holes in the craze making their formation easier. However, the difference in crazing and cracking resistance between good and poor swelling agents correlates well with the solubility parameter, with actual solubilities in the polymer, and with consequent differences in polymer T_g. Such a difference is almost wholly a plasticization phenomenon.

There exist in the general literature no systematic and careful studies of the influence of organic agents on the susceptibility of glassy polymers to crazing and cracking under stress. In fact there is known to the authors only one set of systematic data in this regard.[1] In light of the scarcity of data and the multiplicity of processes known or suspected to take place in a stressed glassy polymer in contact with a liquid, it is not surprising that the role of organic agents in the mechanism of so-called environmental stress crazing and cracking has remained obscure.

Two theories that attempt to rationalize "solvent" crazing and cracking have existed primarily in one form or another for more than a decade. By analogy with certain effects in inorganic systems, the first postulated that organic agents, having generally low surface tensions, spread on polymer surfaces and thus reduce the surface energy for crack formation.[1-3] Upon discovery that crazes were not cracks but rather thin platelike regions of porous polymer of very high specific internal surface area (*e.g.*, 100 m^2/g) and upon development of a "domain" theory of the structure of glassy polymers,[4] it became reasonable to suspect that organic agents could serve to reduce the surface energy of craze internal surface area formation. The best evidence in support of the surface energy hypothesis comes from the poly(methyl methacrylate) study[1]—tensile strength falls in proportion to surface tension decrease in a series of alcohols and alcohol–water mixtures used as immersion fluids. Attempts to extend this correlation to PMMA in other liquids are not very successful.

The second theory holds that the organic agent acts as a plasticizer. Originally it was supposed that solvent crazes (then thought to be cracks) occurred when the combination of stress and plasticizer lowered the polymer T_g to ambient temperature. Because of our present knowledge of the structure and mechanical properties of crazes and because of current concepts about flow in the glassy state under stress,[5] a modern casting of this hypothesis would be that limited plasticization lowers T_g to a limited degree and application of sufficient stress promotes a liquidlike flow of the glass in the stress direction. The lower T_g is the smaller will be the strain energy input required to induce flow.

Lowering of T_g depends directly on plasticizer concentration and to a first approximation the latter is expected to increase directly as the difference between the cohesive energy density, CED, of polymer and environmental liquid decreases. Thus a plot of tensile

---

(1) E. Wieser, Doctoral Thesis, Aachen, Germany, 1959.

(2) L. E. Nielsen, *J. Appl. Polym. Sci.*, **1**, 24 (1959).

(3) H. A. Stuart, G. Markowski, and D. Jeshke, *Kunststoffe*, **54**, 618 (1964).

(4) R. E. Robertson, *J. Phys. Chem.*, **69**, 1575 (1965).

(5) R. E. Robertson, *J. Chem. Phys.*, **44**, 3950 (1966).