Polyelectrolytes

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"POLYELECTROLYTES" is a term which has been coined to describe substances of high molecular weight which are simultaneously electrolytes. Within the scope of this definition are a number of possible subclasses. According to source, we have, on the one hand, the naturally-occurring polyelectrolytes such as proteins and polysaccharides and, on the other, the synthetic materials which will be described shortly. From the point of view of electrolytic behavior, polyelectrolytes, just like the simple electrolytes of low molecular weight, may be either weak or strong. Very briefly, a weak electrolyte is one for which there exists a neutral molecule, held together by electronic bonds, and which can dissociate into ions; a strong electrolyte is one for which only ions exist. Acetic acid and sodium chloride are, respectively, familiar examples of the two classes. The former is present in liquid acetic acid mostly as the electrically neutral $CH_3 \cdot CO_2H$ molecule, which in water or other basic solvents can dissociate into a negative acetate ion and a positive hydrogen ion; this dissociation involves an electron rearrangement. The latter, however, exists as a lattice of positive sodium ions and negative chloride ions in the crystal; on solution, these ions become solvated and separate, retaining the charges which characterize them. No dissociation, in the sense of breaking electron bonds, is involved; only electrostatic Coulomb forces need to be considered.

The importance of an understanding of the behavior of proteins and polysaccharides need not be emphasized—these are essential building blocks of all living organisms. The biochemist, who might be described as one who studies the chemistry of substances of natural origin, labors under a number of handicaps which do not interfere with his colleague, the chemist, who works with synthetic compounds. The biochemist necessarily must begin his work with substances of unknown chemical structure; before he can even begin a breakdown of the molecule to determine its structure, he must demonstrate that he has succeeded in separating a chemical individual from the biological source material. The chemistry of these compounds is determined by the source and not by the experimenter. Furthermore, the materials are often chemically or biologically unstable and must be handled with care under sterile conditions at low temperatures. Finally, since life processes are planned around water as the solvent medium, nature has finally evolved as her most important compounds substances which are water soluble but insoluble in most other liquids. This limitation is a serious barrier to a general understanding of the physical chemistry of polyelectrolytic materials, because many of their properties are determined by the interaction of electrical forces between ions, and the intensity of these forces depends on the dielectric constant of the solvent. Obviously, unless we can control this variable, we are unable to investigate its effect.

In recent years polymer chemists have shown how it is possible to synthesize compounds of high molecular weight by a variety of methods from known compounds (monomers) of low molecular weight. Familiar examples include polystyrene, synthetic rubber, and Nylon. These and other linear polymers consist essentially of long chains of atoms (usually carbon, oxygen, and nitrogen) which are held together by stable electronic bonds and to which are attached, at regular intervals, side groups of one sort or another which impart special chemical and physical properties to the polymer. If the monomer can react with only two other molecules, the resulting macromolecule is necessarily a chain, which usually assumes a curled-up configuration; if the monomer can react with three or more other molecules, networks and lattices of very high molecular weight result. Bakelite and vulcanized rubber are examples of the latter types. An additional controllable variable is at the disposal of the synthetic chemist: by polymerizing mixtures of monomers, copolymers can be made in which different chemical units follow each other in the resulting chain molecule in sequences which are approximately predictable. We thus have the techniques available for the synthesis of new compounds of high molecular weight and, within reasonable limits at least, we can

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design and make molecules with properties especially desirable for a given purpose.

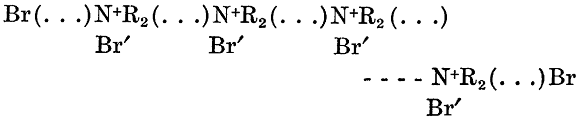
SYNTHESIS

As has been suggested by the foregoing introductory remarks, the tools of the polymer chemist can be applied to the problem of polyelectrolytes. All that is required is the synthesis of electrolytes which have high molecular weight and known structure. We may then study their properties and learn how these depend on concentration, temperature, dielectric constant, and structure, and how they are affected by the presence of other chemical compounds of low and high molecular weight. A much wider range of variables is obviously available than is offered by naturally-occurring substances, and we may hope that eventually some of the problems of the biochemist will be reduced to special problems in a broader field—that of polyelectrolytes in general. It should, of course, be emphasized that the similarity sought between the natural and the synthetic polyelectrolytes is electrical rather than chemical. We may, for instance, never learn the detailed sequence of amino acids in a protein molecule, but we may hope to synthesize a molecule which will be its electrical analogue. In other words, our goal is not the ambitious one of duplicating nature's products in detail, but the more modest one of making models whose electrochemical behavior will resemble that of the biochemical substances. We may, then, be able to extrapolate from the known to the unknown.

When possible in a research program, it is usually preferable to start with simple systems and gradually work up to more complicated ones. As our initial problem, therefore, we have been investigating strong polyelectrolytes of several kinds. Proteins owe their electrical properties to the presence of amino groups and carboxyl groups, both of which give rise to weak electrolytes. As has already been mentioned, a discussion of weak electrolytes is complicated by the fact that dissociative equilibria must be considered as well as the effects of interionic Coulomb forces, whereas with strong electrolytes only electrostatic forces need to be taken into account.

Three examples of synthetic polyelectrolytes will be described; all are based on the reaction between alkyl halides and tertiary amines. In a tertiary amine, such as trimethylamine, 3 of the 5 valence electrons of nitrogen are paired with electrons from the carbon atoms of the methyl, ethyl, or other alkyl group. We might indicate the structure by $R_3N{:}$, where R stands for a methyl group and the colon indicates the remaining two electrons of the nitrogen. If an alkyl halide—for example, methyl bromide—comes in contact with the amine, we may write the resulting reaction formally as an addition of the methyl group to the pair of electrons to give a quaternary ammonium ion, R_4N^+, a structure with a net positive charge. Simultaneously, the bromine atom of the alkyl halide becomes a negatively charged bromide ion, Br', because the bromine nucleus is now surrounded by a swarm of electrons containing one negative charge in excess of the positive nuclear charge of the bromine. In other words, two electrically neutral substances have reacted by electron rearrangement to form two charged ions. The resulting compound, tetramethylammonium bromide, is a typical strong electrolyte which resembles sodium chloride in many of its properties.

Now suppose we have a molecule which contains two tertiary amino groups, one at each end, such as $R_2N(\ldots)NR_2$, and allow it to react with a dihalide, $\mathrm{Br}(\ldots)\mathrm{Br}$, with, say, bromine atoms at each end. By repetition of the simple reaction described above we obtain a chain electrolyte:



$$\begin{array}{l}\mathrm{Br}(\ldots)\underset{\mathrm{Br}'}{\mathrm{N^+R_2}}(\ldots)\underset{\mathrm{Br}'}{\mathrm{N^+R_2}}(\ldots)\underset{\mathrm{Br}'}{\mathrm{N^+R_2}}(\ldots)\\ \qquad\qquad\qquad\qquad ----\underset{\mathrm{Br}'}{\mathrm{N^+R_2}}(\ldots)\mathrm{Br}\end{array}$$

In this compound all of the nitrogen atoms have become centers of positive charge, which are tied together by the carbon atoms symbolically indicated by $(\ldots)$. The bromide ions are small, negatively charged units which, in a solvent medium, are free to swim around within the coil of the polymeric chain or in the solvent medium between individual polymeric ions. A similar compound is often obtained if one attempts to prepare a molecule with a halogen atom at one end and an amino-nitrogen at the other. Meisenheimer and Marvel have both described examples of this sort.

We may also make polyelectrolytes by first synthesizing a chain molecule which contains tertiary nitrogen and then adding alkyl halide to the resulting compound. For example, condensation of succinic anhydride and methyl-diethanol amine gives a polyester, in which tertiary nitrogens are simultaneously chain atoms. Subsequent addition of methyl bromide gives the desired polyelectrolyte. By varying the number of neutral atoms between the nitrogen atoms in both this and the preceding compound, it is possible to make chain electrolytes in which the charges appear at different but known spacings along the chain.

Vinylpyridine offers the possibility of the synthesis of polyelectrolytes of somewhat different type. Vinylpyridine is superficially similar to the familiar styrene in that a vinyl group is attached to a ring of 6 atoms, and, just as in styrene, the vinyl groups will polymerize to form long chains, the rings being appended to every other carbon atom of the chain. But there is a significant difference between the benzene ring in polystyrene and the pyridine ring in polyvinylpyridine: the latter contains a nitrogen atom which will again add alkyl halide to form a strong electrolyte. The positive pyridonium ions are in this case not part of the polymer chain but are attached to it by carbon-carbon bonds. Here we may vary the spacing of the charges by copolymerizing a mixture of vinylpyridine and styrene; on treatment with alkyl halide, addition will naturally occur only at the pyridine groups. And we can make chains which have, on an average, 1 ion to 10 chain atoms, 1 ion to 100 chain atoms, or whatever ratio we choose.

CONTRAST WITH SIMPLE ELECTROLYTES AND NEUTRAL POLYMERS

All of these strong polyelectrolytes possess one fundamental difference when contrasted with ordinary strong electrolytes like salt and hydrochloric acid. In the latter, both positive and negative ions are free, in the sense that they are capable of independent relative motion. In solution, we have (almost) a uniform distribution of positive and negative ions; by this, we mean that any microscopic exploratory element of volume would encounter, on an average, equal numbers of cations and anions as we move it through the solution. As we dilute such a solution, the average relative distances between all charges will increase. Not so, however, in the case of the polyelectrolytes. In the examples described above the positive ions are bound to the polymer chain. If we imagined an extremely dilute solution, the negative ions could diffuse away from the positive polyion, but the individual positive charges could, under the influence of their mutual repulsion, move apart only until the chain reached its maximum extension, after which further separation would become impossible. Consequently, the ionic distribution in a solution of polyelectrolyte is markedly different from that in one of ordinary electrolyte: instead of a uniform distribution of positive and negative ions, we will find positive charges in clusters, separated by solvent which contains only negative ions (except for possible impurities). The distribution of negative ions in the space between the polycations will not be spatially uniform. Due to the high concentration of charge in the region of the polymeric ions, bromide ions will be drawn into their vicinity by electrostatic attraction and will not act at all like the relatively free bromide ions in a solution of sodium bromide.

The geometrical configuration of the polyion will also be quite different from that of a neutral polymer molecule such as polystyrene, as a consequence of electrostatic forces. In very dilute solutions we would expect a rather extended configuration, as has already been mentioned. As concentration increases and bromide ions are drawn into the sphere of the polyion, internal repulsions will be compensated, and the normal tendency of the chain to curl up will appear, possibly enhanced by interionic attraction of the sort which stabilizes a salt crystal.

Let us now turn to a consideration of the observed properties of the synthetic polyelectrolytes in solution.

VISCOSITY

Perhaps the most striking property of these compounds is the high viscosity which they impart to a liquid. For example, an alcoholic solution containing only 7% of the butyl bromide addition product of polyvinylpyridine is 10 times as viscous as alcohol, and a 1% solution of a similar compound of lower molecular weight in water has over three times the viscosity of water at the same temperature. Polymers in general are known to increase the viscosity of solvents, and valuable information concerning the shape and size of polymer molecules may be deduced from the viscosity curves. The polyelectrolytes differ from the neutral polymers in that the magnitude of the viscosity increment is enormously larger and the shape of the curves is markedly different. The shape of a curve is the visual representation of the underlying mathematical function which connects two variables—here, viscosity and concentration. When we say, therefore, that the shapes of the viscosity-concentration curves are different for polyelectrolytes and neutral polymers, we are in effect saying that viscosity depends on concentration in two quite different ways in the two cases. This is best illustrated if we plot the ratio of viscosity increment over concentration along the vertical axis against concentration. For neutral polymers, the data lie on a straight line, which climbs with *in*creasing concentration. For our polyelectrolytes, the data give a curve which climbs very sharply with *de*creasing concentration.

Heidelberger observed in 1932 exactly this sort of viscosity curve for the sodium salt of the polysaccharide isolated from *Pneumococcus III*. Chemically, the two compounds are completely different: the synthetic material is a polypyridonium salt with a positively charged chain, whereas the polysaccharide is a polycarboxylate with a negatively charged chain. It thus appears that, just as in the theory of ordinary electrolytes, the number and distribution of charges, rather than their chemical derivation, is the fundamental variable in controlling physical properties of polyelectrolytes. As a matter of fact, if we plot both Heidelberger's data and our own on the same graph, using a function which was empirically derived from the data on the polypyridonium compound, both sets of points fall on the same straight line. This necessarily indicates an underlying similarity despite the superficial difference in the two compounds.

It becomes necessary at this point to introduce a few mathematical symbols to facilitate further discussion. Suppose we denote concentration, our independent variable, by c. Let z stand for the measured dependent variable, the ratio of specific viscosity increment to concentration. Then the function which was found to represent the data within the limit of experimental error is written

$$z = A/(1 + B\sqrt{c}) + D,$$

where A, B, and D are numerical constants which can be obtained from the data by simple arithmetic.

For various reasons we suspected that the constant A would depend primarily on the size of the polyelectrolyte, while B would be a measure of the electrostatic interaction. By working with polymers of different molecular weights, we could show that A did indeed vary in a systematic way with polymer size. But if we had been limited to working in aqueous solutions, we would have had to stop there. Fortunately, our polymers are soluble in a variety of organic solvents such as alcohol, nitromethane, and dioxane; by measuring viscosities in different solvents, we could investigate the effect of media of different dielectric constant on the viscosity. We found that B increased with decreasing dielectric constant, which is what would be expected on the basis of Coulomb's law if B were a measure of the intensity of electrostatic interaction. Consequently, it becomes possible to predict from measurements in one solvent the behavior of a polyelectrolyte in a different medium.

We are thus led to the assumption that the high viscosity of polyelectrolytic solutions and its concentration dependence are due to the presence of the high charge density at the polyions. We may now test this hypothesis by an experiment which it suggests. At a given concentration we imagine the polycations to be surrounded by a space charge of negative ions, and, furthermore, we assume that some negative ions are held within the polymer coil by electrostatic attraction. The aggregate acts like a droplet of concentration solution with a net positive charge. The solvent between these clusters contains free-swimming anions. Suppose we add a simple one-one electrolyte like potassium bromide, which will put singly charged positive potassium ions and an excess of negatively charged bromide ions in the solution. By a simple mass-action effect, under the influence of Coulomb attraction, we would expect the polycations to attract more negative ions (which would be repelled from the negative ionic atmosphere) and thus reduce their own net charge. If this happens, however, the long-range electrostatic effect on viscosity would decrease and, in the presence of a large enough excess of added electrolyte, should vanish. This is just what one observes experimentally. Even as dilute a solution as 0.001 N potassium bromide as solvent eliminates the sharp rise in the z-c curves near zero concentration and at somewhat higher concentrations produces linear z-c plots which closely resemble those of uncharged neutral polymers.

A further test of this model can be made if we add other kinds of simple electrolytes—for example, magnesium bromide also gives bromide ions and a doubly charged *positive* ion. Since the polycation would strongly repel ions of like charge, we expect—and find—that at the same bromide ion strength, magnesium and potassium bromides have identical effects on the behavior of the polysalt. On the other hand, if we add potassium sulfate, where the *negative* ion now has the double charge, we expect—and find—a different result as compared with potassium bromide. Similar effects have been found on the addition of neutral salts to naturally-occurring polyelectrolytes.

ELECTRICAL PROPERTIES

Conductance is a characteristic property of all electrolytes, and a study of its dependence on the pertinent variables results in a better understanding of molecular behavior and structure. Past research has established certain general principles which may be applied to any conducting system. For a given charge, a small ion moves faster, *i.e.* has a higher conductance, than a larger one. The higher the charge on an ion of given size, the more current it carries and hence the higher the conductance. At a given concentration, a given electrolyte has a lower conductance in a solvent of lower dielectric constant, because increased association of oppositely charged ions under the influence of electrostatic attraction decreases the relative number of ions free to carry current in the latter case. With dilution, conductance increases, due to decreasing intensity of long- and short-range ionic interaction. The conductance of the polyelectrolytes was therefore studied in various solvents in order to see what might be learned by applying these principles to the observed experimental facts.

The very first measurements of conductance showed that the polyelectrolytes were strikingly different from ordinary electrolytes. One conventionally plots the equivalent conductance against square root of concentration; on this scale, where familiar electrolytes approximate linearity, the polyelectrolytes give curves which are convex to the concentration axis. This may be interpreted as due to a change in the relative number of conducting particles, to a change of mobility with concentration, or to a simultaneous change of both variables. Our results show that the latter description best fits the facts. At a given concentration a certain fraction of bromide ions are located in the solvent between polycations and are free to migrate under the influence of external electrical fields. The large polymeric ions have a certain average number of anions associated with them, but still have a net positive charge and hence also contribute to the current. Now suppose we decrease the total concentration by adding more solvent: since more space is available, some of the bromide ions previously bound to or in the polyions will move away from them as a consequence of normal Brownian motion. Two consequences appear, both of which increase conductance: the newly released anions increase the negative current, whereas the contribution of the positive ions is now greater because of their increased net charge. The latter effect will, to some extent, be compensated by a dilation of the polyion under the influence of its increased internal field.

The most direct experimental proof of the existence of ionic association in the case of the polyelectrolytes is obtained if we compare the conductance in different solvents. In a series of nitromethane-dioxane mixtures, for example, the conductance at a fixed concentration steadily decreases as the dioxane content of the solvent increases. Since dioxane has a dielectric constant of only 2.2 while that of nitromethane is nearly 40, this result is what would be expected on the basis of our model. Finally, by studying the conductance of salts of copolymers of styrene and vinylpyridine, it was possible to estimate the fraction of current carried by the two species of ions present, the small bromide ions and the large polyions, Again, the variation with structure was in agreement with predictions based on the model.

One other electrical property requires mention. Cole has shown that a variety of naturally-occurring membranes have a striking similarity in their behavior in alternating electrical fields. A plot of the power absorbed per cycle in the membrane against its dielectric constant gave a circular arc, regardless of the origin of the membrane. Copolymer salts of the type mentioned in the last paragraph are insoluble in water when the styrene content is high. Membranes were made from them, and their a-c properties were measured. The impedance locus turned out to be a circular arc also. This observation suggests that some of the properties of biological membranes are due to the presence of ions which are immobilized in the structure of the membrane, similar to the pyridonium ions in the synthetic membranes.

OSMOTIC PRESSURE

The last property of polyelectrolytes which we shall discuss is osmotic pressure. For over a century the osmometer has been a useful tool in research, both on natural and synthetic compounds, because, in effect, it permits us to count the number of molecules which are contained in a given weight of sample. Van't Hoff's theoretical treatment of the problem was largely based on the data obtained by the botanist, Pfeffer. Very briefly stated, measurement of osmotic pressure permits determination of the molecular weight of molecules in solution and—still more important—gives information bearing on molecular interaction. Solutions of macromolecules gave osmotic pressures which were quite puzzling, until Flory and Huggins formulated a theory which showed that the deviations from behavior predicted on the basis of classical theory were due to entropy terms arising from the many configurations which, because of its flexibility, a chain molecule could assume in solution. Similarly, early work on osmotic pressures of protein solutions gave results which could not be correctly interpreted until the significance of the isoelectric point was emphasized by Loeb and until the effects of Donnan equilibria were considered. Except at the isoelectric point, the osmotic pressure of a protein solution is higher than corresponds to its moleculer weight, due to the presence of accompanying counter ions.

Measurements of the osmotic pressure of synthetic polyelectrolytes have given similar results. In alcohol the osmotic pressure is over an order of magnitude greater at a given concentration than that of a neutral polymer of the same molecular weight. On the other hand, the pressure is, by far, less than would correspond to each bromide ion and each polycation contributing to the total pressure; we therefore find confirmation of our previous conclusion that polyelectrolytes are highly associated in solution.

With the pyridonium salts there is, of course, no analogue of the isoelectric point, because they are strong electrolytes and not ampholytes. The situation at the isoelectric point may, however, be simulated by the addition of an excess of simple electrolyte to the strong polyelectrolyte. When, for example, lithium bromide is added to alcoholic solutions of the polypyridonium salts, the osmotic pressure is very much reduced and is not greatly different from that which a neutral polymer of the same molecular weight would give. This result, of course, parallels our experiment with excess added electrolyte in the case of viscosity and leads to the same conclusions concerning association.

CONCLUSION

The purpose of this presentation has been to summarize some recent work on the physical chemistry of synthetic polyelectrolytes. In three fields—hydrodynamics, electrodynamics, and thermodynamics—we have seen that the properties of these compounds could be described, at least qualitatively, in terms of the chain model of neutral macromolecules combined with the effects of electrostatic forces. Similarities between the behavior of proteins and polysaccharides and that of the synthetic polyelectrolytes suggest that a better understanding of the biological materials may be attained through a study of the synthetics, thanks to the controllable variability which the latter offer to the experimenter.

University of California African Expedition—Southern Section

Charles L. Camp

THE UNIVERSITY OF CALIFORNIA at Berkeley, through the Museum of Paleontology, has, during the past 15 months, sponsored a program of scientific work in southern Africa. The primary purpose has been to search for further fossil evidence of the anatomical form, habits, environment, and geological age of the remarkable australopithecine man-apes first described by Prof. Raymond Dart and elaborated by Dr. Robert Broom.

Another important objective was a coordinated series of anthropological studies on the primitive tribes of northern South-West Africa, where conditions have been favorable for the preservation of ancient customs and tribal life. Attention was directed to ethnology, linguistics, physical and cultural anthropology, psychology, ethnobotany, ethnozoology, and musicology among the Ovambo. Some work was also done among the Kung Bushmen and the few surviving Hottentots who retain traces of their original culture.

A program having to do with recent and fossil plants has been carried out successfully. Extensive collecting of recent amphibians, reptiles, mammals, and insects, including protozoan parasites of termites and studies in ethnoentomology, are being conducted by two members still in the field.

Work began in August 1947 with a survey of Cretaceous localities near Port Elizabeth. Early in September the two paleontologists, Frank Peabody and the writer, accompanied a geological excursion arranged by Dean George B. Barbour, of the University of Cincinnati. Quaternary cave and travertine sites were visited from the Makapaans valley and Thaba Zimbi, 200 miles north of Pretoria, south to Taungs, 100 miles north of Kimberley. Members of the party included Profs. Alexander du Toit, Raymond Dart, C. J. VanderHorst, C. van Riet Lowe, and Dr. S. H. Haughton, the head of the Geological Survey.

Under their counsel it was decided to commence operations at the works of the Northern Lime Company, near Taungs, and as close as possible to the old type-site of *Australopithecus.* During the next 6 months some 30 sites were investigated in the vicinity, along the eastern edge of the Kaap Plateau from Boetsap to the quarries north of Norlim.

The earliest breccias—gray, water-washed, gravel conglomerates at the base of the Norlim lime biscuit—contain antelope and horse remains and no crushed baboon skulls such as are found in the supervening pink sandstone breccias in the *Australopithecus* zone. Above the pink breccias the travertine spring deposits are honeycombed with later, filled caves and vertical pipes containing dark brown earths and secondary lime. Many of these contain late Pleistocene artifacts and ash deposits. Still younger caves, along the outer margins of the lime bodies, remain as open cavities in which may be found brown and yellow earth, dust, ash, and bat and hyrax guano. Artifacts of pre-Bushman and Bushman types occur in these more recent deposits.

Middle Stone Age artifacts sealed in place in solidified cave floors occur with human teeth and mammal bones, south of Norlim, and the same type of artifacts were found in yellow sandy travertine at Mooiplats, 60 miles north of Zeerust.

It is therefore believed that a number of sequential stages of Quaternary history will become recognizable when the faunas and artifacts are studied. None of the man-ape sites contains evidence of fire or artifacts. They must antedate the abundant caves in which artifacts occur.