compositions where we believe the K-values to be reliable. It seems reasonable to expect that alcohol of solvation would be retained in an ion pair, due to the strong local field of the HO-dipole.

Finally, we consider the limiting conductances. As shown in Table III, they increase as the amount of carbon tetrachloride in the solvent mixture increases. The viscosity simultaneously decreases, but the two changes do not compensate each other as they would if Walden's rule were valid. As shown in Fig. 3, the product $\Lambda_0\eta$ decreases as x_2 increases. The change is the largest we have observed so far among the various mixtures investigated. For comparison, our data[8] for the salt in methanol–nitrobenzene mixtures are shown in Fig. 3 (half-shaded circles). The result may be stated in terms of a sphere-in-continuum model that the equivalent ion size increases as the carbon tetrachloride content increases; alternatively, assuming constant size of the ions, the ions encounter relatively greater frictional resistance in the carbon tetrachloride-rich mixtures. The first mechanism is consistent with selective solvation by nitrobenzene, as a consequence of the polar component of the mixture concentrating near the free ions as the bulk dielectric constant decreases.

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NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Charge Reversal of Cationic Poly-4-vinylpyridine Derivatives in KBr Solutions[1]

BY ULRICH P. STRAUSS, NORMAN L. GERSHFELD AND HARRY SPIERA

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A polysoap derived from poly-4-vinylpyridine by quaternizing 13.6% of the nitrogen with n-dodecyl bromide and the remainder with ethyl bromide ("13.6%"-polysoap) was found to be completely soluble in both dilute and concentrated KBr solutions, but partly insoluble in KBr solutions of an intermediate concentration range. Electrophoresis experiments showed that the polysoap was positively charged in dilute KBr solutions and negatively charged in concentrated KBr solutions. The precipitation region surrounded the isoelectric point. A considerably wider precipitation region was found in the case of a "28.5%"-polysoap. Poly-4-vinyl-N-ethylpyridinium bromide also became negative in concentrated KBr solutions, and its electrophoretic mobility values coincided with those of the "13.6%"-polysoap. However, this polyelectrolyte was completely soluble even at the isoelectric point. The electrophoretic mobility was insensitive to additions of hydrogen or barium ions, which indicated the absence of weakly and certain strongly acidic groups. Consequently, the charge reversal of the polyions was explained by the binding of bromide ions in excess of their stoichiometric equivalent. The results show that forces other than coulombic ones between polyions and their counter ions may play a role even in the case of so-called "strong" polyelectrolytes.

In the course of an investigation concerning the influence of electrolytes on polysoap behavior it was observed that a "13.6%"-polysoap[2] derived from poly-4-vinylpyridine is completely soluble in both dilute and concentrated aqueous potassium bromide solutions, but that there is an intermediate potassium bromide concentration region where the polysoap is partially insoluble. As one goes through this region which lies approximately between the KBr molalities of 0.35 and 1.80, the amount of polysoap which is insoluble gradually increases, comes to a maximum somewhere between the KBr molalities of 0.6 and 0.9, and then decreases. To obtain an understanding of this curious phenomenon, an investigation was undertaken.

While such an effect has not been reported previously for completely cationic polyelectrolytes, precipitation regions have been observed with polyampholytes in the neighborhood of their isoelectric points.[3–7] Therefore our polysoaps were tested for the possible presence of an isolectric point by electrophoresis measurements. The question of why the polysoap was only partially insoluble in the precipitation region also was investigated. Finally in order to cast further light on these problems it was decided to perform, whenever expedient, similar experiments with a "28.5%"-polysoap, a "37.9%"-polysoap, and a typical polyelectrolyte, poly-4-vinyl-N-ethylpyridinium bromide, all derived from the same parent poly-4-vinylpyridine as the "13.6%"-polysoap.

Experimental

The preparation of the "13.6%"-, the "28.5%"- and the "37.9%"-polysoaps[2] (our samples No. G 147, No. G 146 and No. G 145, respectively) and the poly-4-vinyl-N-ethylpyridinium bromide (our sample No. G 254) from poly-4-vinylpyridine (our sample No. G 13), D.P. ≈ 6000, has been described previously.[8]

The potassium bromide and the lithium bromide were C.P. products obtained from Coleman and Bell.

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[1] Part of these results will be contained in a thesis to be submitted by N. L. Gershfeld to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Paper presented at the American Chemical Society Meeting, Division of Polymer Chemistry, New York, N. Y., September, 1954.

[2] In this paper, an "X%"-polysoap denotes a compound prepared from poly-4-vinylpyridine by quaternizing X% of the nitrogen with n-dodecyl bromide and nearly all of the remaining nitrogen with ethyl bromide.

[3] T. Alfrey, H. Morawetz, E. B. Fitzgerald and R. M. Fuoss, THIS JOURNAL, **72**, 1864 (1950).

[4] H. L. Wagner and F. A. Long, *J. Phys. Colloid Chem.*, **55**, 1512 (1951).

[5] T. Alfrey and H. Morawetz, THIS JOURNAL, **74**, 436 (1952).

[6] T. Alfrey, R. M. Fuoss, H. Morawetz and H. Pinner, *ibid.*, **74**, 438 (1952).

[7] A. Katchalsky and I. R. Miller, *J. Polymer Sci.*, **13**, 57 (1954).

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

Electrophoretic mobilities were measured in a Perkin-Elmer Model 38 Tiselius apparatus. Solutions containing 0.5 or 1.0 g. of polysoap per 100 ml. were dialyzed for several days against large volumes of the electrolyte solutions against which the boundaries were to be formed. These electrolyte solutions were of potassium bromide ranging in molality from 0.05 to 1.85. In a few instances the *p*H, which usually ranged from 6.4 to 6.8, was brought near 2 by the addition of hydrobromic acid. Cell currents ranged from 5 to 20 milliamp., the electric fields from 0.6 volt/cm. in the most concentrated to 9.2 volt/cm. in the most dilute KBr solutions. At least three photographs were taken of each ascending and descending boundary, and the mobility *u* was calculated from their average displacements. No change of the mobility during the period of any experiment was observed. In general, the descending boundary was somewhat more diffuse than the ascending which retained its original sharpness.

In order to determine the solubility behavior, 1% solutions of the polysoaps were prepared and brought to the desired KBr molality by the addition of weighed amounts of this salt. The separation of the insoluble gel usually took several days.[9] After centrifugation, the gel portion was found to be insoluble in a fresh KBr solution of the same molality as was used originally. The gel was then dissolved in water and its concentration determined with a model D. U. Beckman spectrophotometer. From the known volume of the solution the total amount of gel could then be calculated. As a check, the amount of polysoap which was soluble in the KBr solution was determined similarly. In order to find out whether equilibrium was reached by this method, an experiment was also done in which the dry "13.6%"-polysoap was added directly to the KBr solution. After several days of end-over-end tumbling, the value of the soluble fraction was found to be identical with that obtained by using the first method.

Results and Discussion

The results of the electrophoresis experiments are presented in Fig. 1 where the mobility *u*, in cm.^{2}/volt-sec., is shown as a function of the logarithm of the KBr molality *m*. The data obtained with 0.5% solutions of the 13.6% polysoap at *p*H's between 6.4 and 6.8 (open circles) and at *p*H's between 2.1 and 2.5 (shaded circles), as well as the data obtained with 1% solutions of this polysoap at *p*H's between 6.4 and 6.8 (open squares) can all be represented by the same straight line, indicating that the mobility is insensitive to both the *p*H and the polysoap concentration.

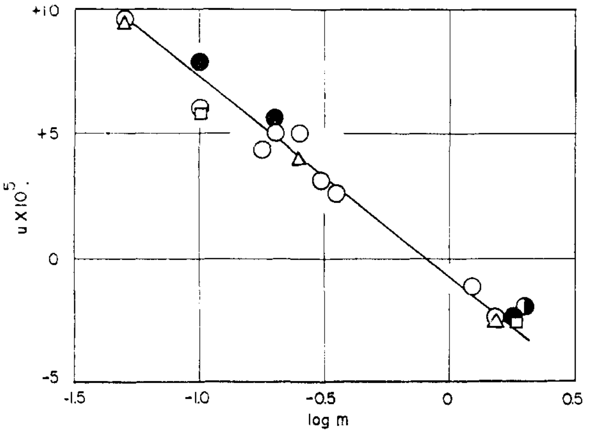

Fig. 1.—Electrophoretic mobility of cationic derivatives of poly-4-vinylpyridine as a function of potassium bromide molality: 0.5% solutions of "13.6%"-polysoap, ○, *p*H 6.4–6.8; ●, *p*H 2.1–2.5; ◑, added $BaBr_2$ ($m = 0.05$); □, 1% solutions of "13.6%"-polysoap; △, 0.5% solution of poly-4-vinyl-N-ethylpyridinium bromide. A positive mobility value indicates that the polysoap moves toward the cathode.

The most important aspect of these data is the change in sign of the mobility. At low KBr concentrations the polysoap ions are positive and move toward the cathode, but at high KBr concentrations they move toward the anode, which indicates that they are now negatively charged. The isoelectric point is located at $m = 0.83 \pm 0.08$ where the straight line crosses the *m*-axis.

It is of interest that the mobility data of the poly-4-vinyl-N-ethylpyridinium bromide (triangles) also fall on the line. In view of the fact that the reduced viscosity of this typical polyelectrolyte is more than an order of magnitude larger than the reduced viscosity of the "13.6%"-polysoap,[10] it appears that the mobility is independent of the compactness of the polymer coil. The mobility seems to be governed only by the KBr concentration and by the pyridinium groups attached to the polymer chain.

It should be noted that the isoelectric point of the "13.6%"-polysoap lies near the center of the precipitation region (on the log *m* scale). In line with this result, the precipitation region of the "28.5%"-polysoap overlaps that of the "13.6%"-polysoap, but is much wider. It starts at $m \approx 0.14$ and is not quite finished even at $m = 5.75$ which corresponds to KBr saturation.[11] However, in solutions of the more soluble LiBr, the precipitation region was found to be between the LiBr molalities of 0.1 and 5.[12] With the "37.9%"-polysoap the precipitation region started at $m \approx 0.02$, but the end could not be reached even with LiBr. On the other hand, the polyvinyl-N-ethylpyridinium bromide was completely soluble at all KBr concentrations. As the precipitation region becomes wider with increasing dodecyl group content, there is a corresponding decrease of the polysoap fraction which is soluble near the isoelectric point. Thus while 80% of the "13.6%"-polysoap was soluble in 0.73 *m* KBr, only 28% of the "28.5%"-polysoap and none of the "37.9%"-polysoap was soluble in this solvent.

All these results indicate that the KBr influences the solubility of the polysoaps through its effect on their electrical potential. An increase in the absolute value of this potential increases the solubility. It already has been mentioned that the polyelectrolyte without dodecyl side chains is completely soluble even at the isoelectric point where it is uncharged.[13] As hydrophobic side

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[9] For the "13.6%"-polysoap the following phenomenon occurred which was unique for this polysoap. Upon the dissolution of the KBr, the solution became perceptibly turbid and after several minutes turned into a suspension of needle-like particles. These needles grew to an estimated average length of 3 mm. over a period of several hours. At the same time the turbidity of the solution increased. Eventually gel separated on the wall of the flask until the solution had become clear at the end of two days. Since precipitates of synthetic high polymers do not usually show such a directional bias, this phenomenon is of special interest and is therefore under further investigation.

[10] U. P. Strauss and N. L. Gershfeld, unpublished results.

[11] H. Hering, *Ann. chim.*, [11] **5**, 483 (1936).

[12] In comparing the LiBr with the KBr results it should be remembered that because of the high hydration of the lithium ion which lowers the amount of water available as solvent, the effective bromide ion concentration in a concentrated LiBr solution is much higher than that in a KBr solution of the same molality.

[13] However, it will be of interest to find out by light scattering or by osmotic pressure measurements whether a minimum in solvent-polyelectrolyte affinity exists at the isoelectric point.

chains are added, a point will be reached where the polysoap molecule becomes insoluble at the isoelectric point. As more dodecyl groups are added, a greater electrical charge will be needed to keep the polysoap ion in solution. Hence the precipitation region will spread on both sides of the isoelectric point. In the light of these considerations, the observation that a polysoap has a soluble and an insoluble fraction in a given KBr solution can best be interpreted as indicating polydispersity with respect to the relative dodecyl group content. The fact that despite the polydispersity the electrophoretic boundary remains sharp is a further indication that the mobility is not affected by the dodecyl group content of the polysoap ions. However, the above results suggest the possibility of solubility fractionation by the use of several KBr solutions of varying concentrations.

It is desirable to explore the nature of the charge reversal somewhat further. The fact that bromide ions are bound by the polyion even when the latter is negative indicates that factors other than coulomb forces between a bromide ion and the net charge of the polyion are responsible for the binding. Probably the hydration and possibly the polarizability of the bromide ion are involved here. Studies with other counter-ions differing in these properties from the bromide ion are under way to test this point.

The question arises as to how the polyions acquire their net negative charge. Do they bind bromide ions in excess of the stoichiometric equivalent of their pyridinium groups, or do they perhaps contain some negative groups as unintended impurities? The observed insensitivity of the electrophoretic mobility to *p*H excludes the presence of weakly acidic negative groups. As for strongly acidic groups, the only ones which might be remotely possible are sulfate or sulfonate groups. The absence of these groups was shown in two ways. First, a sodium fusion test for sulfur proved negative; second, the effect of 0.05 molal barium bromide on the electrophoretic mobility of the polysoap ion in a concentrated KBr solution was shown to be negligible within the experimental uncertainty of the method (half-shaded circle in Fig. 1). If the negative charge was due to sulfate or sulfonate groups attached to the polyion, one would expect these groups to become neutralized by the barium ions,[14] which would have resulted in the restoration of the positive charge on the polyion. Therefore one can reach no other conclusion than that the charge reversal of the polyions is due to their binding of bromide ions in excess of the stoichiometric equivalent of pyridinium groups.[15]

Charge reversal effects caused by bromide and other negative ions previously have been observed in the case of certain proteins possessing both positive and negative groups.[16] To our knowledge this is the first time that such an effect has been definitely established for polyelectrolytes possessing only cationic groups.

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(15) This conclusion was previously advanced as a hypothesis to explain the observed decrease in electrical conductivity of a 0.61 *N* alcoholic lithium bromide solution upon the addition of poly-4-vinyl-N-*n*-butylpyridinium bromide [U. P. Strauss and R. M. Fuoss, *J. Polymer Sci.*, **4**, 457 (1949)].

(16) L. Teunissen—Van Zijp, Thesis, Leiden (1938). See also H. G. Bungenberg de Jong in "Colloid Science," Vol. II, H. R. Kruyt, ed., Elsevier Publishing Co., New York, N. Y., 1949, pp. 299–300.

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[Contribution from the Department of Chemistry, Duke University]

Titration Studies as a Means of Characterizing Anion-exchange Resins[1]

By H. A. Strobel and R. W. Gable[2]

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Several recently developed anion-exchange resins of the substituted quaternary ammonium type with polystyrene–divinylbenzene matrices have been titrated in the hydroxide form in aqueous solution. The usefulness and reliability of the titration method of studying resinous exchangers are discussed in some detail. Nearly all resins showed from 1–5% capacity attributable to ternary amine or other types of weak bases. Qualitative correlations have been obtained between the structure of the resin ionic groups and the "basic strength" of the resin deduced from the shape of the titration curves. The titration behavior of the weaker quaternary ammonium resins considered as polyelectrolytes was found to be described by $pH = pK - n \log (1 - \alpha)/\alpha$ over a limited range, where pK and n are constants and α is the degree of neutralization. Values of n of 1.3–1.5 were obtained in the absence of added salt.

Titration curves have been widely used in characterizing ion exchange materals.[3-6] From a chemical point of view these substances can be regarded as a collection of exchange groups—usually ionic—tied to an inert matrix. Much can be learned about their exchange sites from *p*H titrations since a cation exchanger may be readily put in the H$^+$ ion form and an anion exchanger in the OH$^-$ ion form. Such titrations have been used to indicate (a) exchange capacity, (b) polyfunctionality and (c) the degree of dissociation of exchange groups.

Alternatively, considering their electrical properties, ion exchange materials may be regarded primarily as polyelectrolytes. Again titration

(1) Presented before the Division of Physical and Inorganic Chemistry at the 122nd National Meeting of the American Chemical Society, Atlantic City, September, 1952.

(2) Based on a thesis submitted by Ralph W. Gable to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Master of Arts, June, 1953.

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(4) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, 3299 (1949).

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(6) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1951).