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Ion Binding by Polymeric Electrolytes[1]

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RECEIVED APRIL 15, 1960

Hittorf-type transference experiments have been carried out on aqueous solutions of polyacrylic acid partially neutralized to different extents with sodium hydroxide. The results so obtained were used to calculate the fraction of sodium ions bound to the polyacrylate ions. The effect of the extent of electrolysis on the apparent fraction bound was investigated by carrying out experiments for different lengths of time at constant current. It was found that the values obtained for the ion binding decreased monotonically with increased electrolysis. By plotting an appropriate function, related to the degree of sodium ion fixation, against the total amount of electricity passed through the solution, straight lines were obtained which could be extrapolated back to zero electrolysis, thereby characterizing the original unelectrolyzed solution. It also was found that the effect of temperature on ion binding in sodium polyacrylate solutions is small.

Introduction

Numerous investigations have shown that, when an aqueous solution of a polymeric acid, such as polyacrylic acid, is partially neutralized with sodium hydroxide, a substantial fraction of the sodium ions are electrostatically or otherwise bound to the negatively charged polyacrylate ions.[2-7] This means that when such a solution is electrolyzed, the free sodium ions will migrate in normal fashion toward the cathode, while the sodium ions that are bound to the polymer will move in the opposite direction toward the anode. Thus, the net flow of sodium will depend on the relative magnitudes of the two opposing flows. It was found by Huizenga, Grieger and Wall[2] that in certain cases the net transfer of sodium was actually toward the positive electrode. Their findings, based on a combination of transference and conductance measurements, indicated that as much as 65% of the sodium ions in such a solution could be bound to polyions. The actual percentage bound was found, as would be expected, to depend on the degree of neutralization.

The method of Huizenga, Grieger and Wall involves use of a Hittorf-type transference experiment. Let us consider the changes that occur in the two electrode compartments of a transference cell as electrolysis of an aqueous solution of sodium polyacrylate progresses. The arrival of sodium ions at the cathode results in the evolution of hydrogen gas and the formation of hydroxide ions. The hydroxide ions immediately react with the (partially neutralized) polyacrylic acid, thereby further neutralizing the polyacrylate ions. Thus, as the electrolysis continues, the polymer solution in the cathode compartment becomes more and more neutralized. Simultaneously, the arrival of polyacrylate ions at the anode is accompanied by the evolution of oxygen gas and the formation of hydrogen ions. The hydrogen ions immediately attach themselves to the polyacrylate ions, making them less neutralized. Thus the polymer in the anode compartment becomes more concentrated and less neutralized and the polymer in the cathode compartment becomes less concentrated and more highly neutralized. Since the fraction of sodium bound to the polyion is a function of the degree of neutralization, the changes in the two compartments during electrolysis should have an effect on the calculated values of the fraction bound. As the electrolysis proceeds, the value calculated for the fraction bound should deviate further and further from that of the original solution.

When the first experiments using the transference method were made, it was believed that these deviations were not great. Nevertheless, several years later Wall, Terayama and Techakumpuch[8] considered this problem in a study of the effect of field intensity and quantity of electricity upon counter ion fixation by polyelectrolytes. The fraction (f) of free sodium ions in the solution was calculated as a function of total equivalents of electricity passed (N_e) for various neutralization percentages of the same polyacrylic acid solution. In evaluating the results of their experiments, these authors dwelt mainly on the effect of field intensity upon ion fixation. Concerning the effect of quantity of electricity passed, they concluded that, as N_e was increased, the pH's of the anode and cathode solutions deviated from their original values and the calculated values of f tended to increase. However, the observed dependence of f upon N_e was not large except in the case of highly neutralized polyacrylates.

It was the purpose of the present research to obtain higher reproducibility in the values of f as determined by the transference method and to reinvestigate the effect of N_e on f. It has been found that through an appropriate analysis of the data, involving an extrapolation back to zero N_e, an error inherent in the transference method can be eliminated. In this way accurate values of f can be calculated for a variety of solutions at different field strengths.

Another portion of the research was devoted to the investigation of the temperature dependence of ion association. A theoretical analysis of ion binding by Wall[9] has indicated that the effect of temperature on ion binding should be slight. To test this theory, experiments were carried out over a limited temperature range on several polyacrylic acid solutions.

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[1] Supported in part by a grant from the National Science Foundation.

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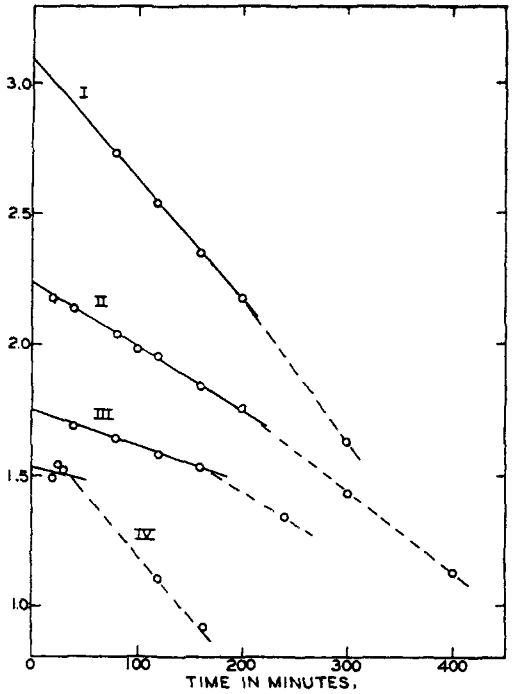

Fig. 1.—Graphs of q/N_e *vs.* time for four polyelectrolyte solutions: I, II, III and IV denote solutions described in Table I.

Experimental

The theoretical basis for this research and the derivation of the equations necessary for the calculation of f, the fraction of free ions, already have been outlined in a previous paper.[2] Therefore, we shall here indicate only the final form of this equation

$$f = \frac{\mathrm{K} - \mathrm{K}_{\mathrm{H}} - \mathrm{K}_{\mathrm{OH}} - \frac{q\mathrm{K}(C_{\mathrm{H}} - C_{\mathrm{OH}})}{N_e C_p}}{\frac{qr\mathrm{K}}{N_e C_p} + \frac{r\Delta_{\mathrm{Na}}}{1000}} \qquad (1)$$

K, K_{H} and K_{OH}	are, respectively, the initial specific conductances of the solution, of hydrogen ions, and of hydroxyl ions
C_p, C_{H} and C_{OH}	are, respectively, the initial concentrations of the polymer, of hydrogen ions, and of hydroxyl ions
r	is the total concentration of sodium in the solution
Δ_{Na}	is the equivalent conductance of the free sodium ions
q	is the total equivalents of polymer transferred from the cathode compartment to the anode compartment during an electrolysis
N_e	is the total equivalents of electricity transferred during an electrolysis

When the solution is neither strongly basic nor acidic, the terms K_{H}, K_{OH}, and $(C_{\mathrm{H}} - C_{\mathrm{OH}})$ become negligible. Under these conditions, then, the equation reduces to

$$f = \frac{\mathrm{K}}{\frac{qr\mathrm{K}}{N_e C_p} + \frac{r\Delta_{\mathrm{Na}}}{1000}} \qquad (2)$$

Of the remaining quantities, K, r, C_p and Δ_{Na} are constant for a particular solution; q and N_e must, however, be measured each time an experiment is carried out. Thus, for a series of runs on the same solution, the apparent values of f will be given by

$$f = \frac{A}{q/N_e + B} \qquad (3)$$

where A and B are constants. Since, for a particular solution, the apparent variations in f depend **only** on q/N_e, we decided to plot q/N_e against N_e rather than f against N_e. From the value of q/N_e, extrapolated to zero N_e, one can then calculate an extrapolated value for f.

The apparatus and procedures for the experiments were described previously except for the following changes and additions. The platinum electrodes of the transference cell were 23 cm. apart. The anode compartment had a volume of 48.85 ml. and the cathode compartment held 50.44 ml. In all runs a current of 4.00 milliamperes was maintained and the total electricity, N_e, was calculated from current–time observations. All experiments were carried out with the transference cell in a thermostated bath regulated to ±0.1°. The value of N_e was reproducible within 0.25%.

The equation used for calculating q is

$$q = \frac{g - 22p}{72.06} \qquad (4)$$

where g is the weight of solute transferred to the anode compartment and p is the number of equivalents of sodium transferred to the anode compartment.

Results and Discussion

A. Effect of N_e on q/N_e.—Four solutions of polyacrylic acid were used for investigating the effect of N_e on q/N_e. The concentration of the polymer in each solution was kept the same but the degree of neutralization was changed. At least five runs were made on each solution, the results of which are reproduced in Fig. 1. It appears from the figure that as N_e is increased, q/N_e decreases linearly until a certain point is reached, after which the points no longer appear on a straight line. The graph for the 15% neutralized solution remains straight for the longest period of time, while that for the 90% neutralized solution begins to fall off almost immediately.

The aforementioned behavior can be explained in the following manner. As noted in the introduction, oxygen gas and hydrogen ions are produced at the anode and hydrogen gas and hydroxide ions at the cathode. The net result is that the polymer in the anode compartment becomes more concentrated and less neutralized, while the polymer in the cathode compartment becomes less concentrated and more neutralized. A study of the detailed concentration changes discloses that as long as the polyacrylic acid in the cathode compartment is less than 100% neutralized, the points appeared to lie on straight lines. However, when the concentration of the sodium ions exceeds that of the polymer, the points fall below the extrapolated straight line. Hence, the transition point in the curve is marked by the complete neutralization of the acid in the cathode compartment.

The decrease of q/N_e on the straight line portion of the curve can be attributed to the increased neutralization of the polymer in the cathode compartment. As the neutralization increases, the average charge on each polyion increases. Therefore, less acid is required to furnish a given number of equivalents of electricity. However, when the acid in the cathode compartment becomes completely neutralized, the hydroxide ions produced therein have nothing to react with, so they remain chemically unchanged in the solution. However, they immediately begin to carry a considerable portion of the current, which further decreases the equivalents of acid transferred to the anode per equivalent of total electricity passed.

TABLE I

RESULTS OF TRANSFERENCE, CONDUCTANCE AND pH MEASUREMENTS 0.02942 N POLYACRYLIC ACID, 20°

Soln.	% Neut.	pH	$10^4 K$	$(q/N_e)_{t=0}$	$r \times 10^3$	Λ_{Na}	f
I	15.0	4.60	2.98	3.10	4.404	47.76	0.830
II	30.3	5.44	5.32	2.24	8.911	47.16	.680
III	59.5	6.64	7.59	1.75	17.62	46.73	.469
IV	89.8	8.20	8.39	1.53	26.42	46.56	.352

TABLE II

QUANTITIES CALCULATED FROM VALUES OF f

Soln.	% Neut.	j/s	i/s	$10^4 K_P$	Λ_P	t_P
I	15.0	0.0255	0.125	1.15	31.4	0.386
II	30.3	.0969	.206	2.45	40.5	.461
III	59.5	.318	.281	3.73	45.2	.491
IV	89.8	.582	.316	4.05	43.5	.483

TABLE III

EFFECT OF TEMPERATURE ON ION BINDING

Temp., °C.	0.0309 N PAA 59.6% neut., % bound	0.0240 N PAA 30.0% neut., % bound
20.0	50.8	30.8
25.0	50.8	31.6
30.0	50.8	31.2
35.0	51.4	31.6

For solution IV, with an initial per cent. neutralization of 89.8, the acid in the cathode compartment was completely neutralized after 40 minutes. Therefore, departures from the expected straight line portion of the appropriate curve occurred after small amounts of acid were transferred. Actually the first three points for solution IV exhibit larger probable errors than do corresponding points for the other solutions. Without a knowledge of the slopes of the other curves, it would have been quite impossible to pick a "straight line" for solution IV.

No attempt has been made to account for the straight line behavior theoretically, since the exchanges taking place between three species of ions undergoing transference are quite complex. To further complicate matters, one of the species of ions continuously changes its composition during the electrolysis. The polyacrylate ions in the anode compartment gradually lose some of their charge and some of the bound sodium, while the polyacrylate ions in the cathode compartment acquire a higher charge and more bound sodium.

B. Effect of N_e on Net Transfer of Sodium Ions.—In Fig. 2 we have plotted p, the net number of equivalents of sodium ions transferred from the cathode compartment to that of the anode, *vs.* time. The curves show further that the increase in neutralization of the acid in the cathode compartment is the real cause of the effects described above.

Upon examining the curves in Fig. 2, it is seen that for solutions I and II there was initially more free sodium leaving the anode compartment than there was bound sodium being carried back in. However, as the per cent. neutralization increased in the cathode compartment, more and more sodium became bound until finally the flow in each direction was exactly the same. Such balances correspond to the minima of curves I and II. After this, the net flow reversed itself and the bound sodium moving into the anode compartment outweighed the free sodium leaving it. For solution II the total sodium transferred eventually changed sign, giving rise to a net increase in the anode compartment. Solution III initially appeared to be near neutralization balance, while solution IV was well past it at the start.

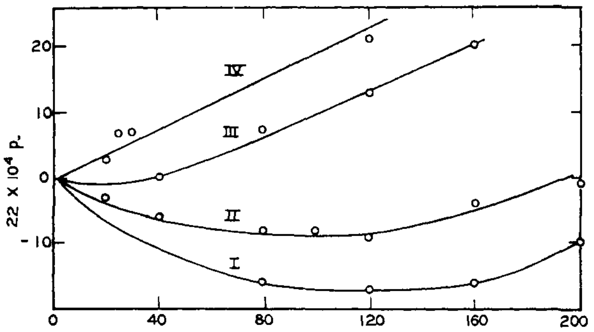

Fig. 2.—Graphs of p *vs.* time for four polyelectrolyte solutions: I, II, III and IV denote solutions described in Table I.

C. Effect of Per Cent. Neutralization on f and Other Related Quantities.—By using the values of q/N_e obtained by extrapolating the straight lines of Fig. 1 back to zero time, values of f for each of the four solutions were calculated. These in turn were used to evaluate other related quantities such as t_P, the transference number of the polyacrylate ion; j/s, the total number of bound sodium ions per monomer unit; i/s, the number of charges per monomer unit; $s\omega_P$, the "rational" mobility; and Λ_P, the equivalent conductance of the polyion. A summary of the significant quantities appears in Tables I and II.

D. Effect of Temperature on Ion Binding.—A theoretical treatment of ion binding has indicated that the effect of temperature change on the binding of counter ions should be slight.[9,10] To test this experimentally, runs were made on two polyacrylic acid solutions at temperatures of 20, 25, 30 and 35°. The results are given in Table III. It is seen that the per cent. of ions bound changed very little over this temperature range. Some of the variance that does occur certainly can be ascribed to random error, but as far as we can tell the theoretical predictions are upheld.

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