[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electrolytic Properties of Aqueous Solutions of Polymeric Electrolytes

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Electrolytic conductance and transference measurements have been made on solutions of polyacrylic acid partially neutralized with sodium hydroxide. The fraction of sodium ions bound to polymer ions, the polymer ion mobility, and the polyion transference number all decrease with increase in polymer concentration. On the other hand, the bound sodium fraction remains substantially independent of temperature from 0 to 42°. The bound cation fraction and polyion mobility are not altered if potassium ions are substituted for sodium ions. Results of special transference experiments indicate that the bound-free cation exchange rate is not greatly affected by changes in percentage neutralization, polymer concentration, univalent cation species, polyion type, or temperature of the solutions investigated.

Introduction

Electrolytic studies on aqueous solutions of polyacrylic acid partially neutralized with sodium hydroxide have shown that a substantial fraction of the sodium ions are bound to the polymer ions.[1] In carrying out these studies, it was also found that the rate of exchange between free and bound sodium ions was measurable, so a theory of ion exchange for polyelectrolytes undergoing electrolytic transference was developed[2] and applied to the experimental measurements.[3]

In developing the theory of this ion exchange, it was assumed that the free univalent ions in solution exchange with those bound to the polymer at a rate independent of the location of the bound ion within the polymer coil. If the polymer exists as a loose coil in solution, this assumption is probably not valid, for the bound ions near the center of the coiled polymer should certainly exchange less rapidly than those near the exterior of the polyion. As an alternative hypothesis, one might roughly assume that the exchanging ions fall into two groups, one consisting of ions that exchange at an infinite rate and the other of ions that exchange at zero rate; this assumption gives better quantitative agreement with the experimental results than does the assumption of only one species of exchanging ion.[3]

To provide a further test of the theory and to gain more knowledge about the behavior of polymeric electrolytes, additional electrolytic measurements have been made on polyacrylic acid–sodium hydroxide solutions over a wider range of polymer concentrations and at different temperatures. We have also investigated polyacrylic acid neutralized with potassium hydroxide, as well as the hydrolyzed maleic anhydride–styrene copolymer neutralized with sodium hydroxide. For each solution investigated we have sought to determine the transference numbers and the degree of cation binding, and for certain selected solutions the bound-free cation exchange rate.

Experimental

A discussion of the preparation of materials, the measurement of *p*H and conductance, the transference apparatus and its operation, the analytical techniques used, and the experimental procedure has already been given.[1,3,4] The experiments involved, among other things, the measurement of the net amounts of cation and polymer transferred from cathode to anode during electrolysis. To this end, radiotracers were found particularly useful for following the cations. The tracers used for this purpose were sodium 22 (obtained from Washington University, St. Louis, Missouri) and potassium 42, which was obtained from potassium carbonate subjected to irradiation at the Argonne National Laboratory, Chicago, Illinois. The activity of both tracers was sufficiently high so that only small amounts were required in the polymer solutions for tracer purposes. However, because of the short half-life of potassium 42 (12.4 hours), a decay correction was necessary when calculating potassium ion concentration changes.

A current of 4 milliamperes was used in all transference experiments except those carried out in 0.0128 normal polyacrylic acid solutions at 0°; in this case a current of 2.5 milliamperes was used.

Discussion of Results

The results of the measurements and calculations for several different polymer solutions are given in Tables I and II. These include polymeric ion transference numbers, fraction of cations in bound condition, the ratio of polymer ion charge to number of ionizable sites and the polyion mobility. By a "bound cation" we mean a cation that is caught in the sphere of influence of the large anion and which moves along with the anion. The values were calculated by methods similar to those already described.[1] The polyacrylic acid used had a weight average molecular weight of 206,000. The molecular weight of the hydrolyzed copolymer of maleic anhydride and styrene was considerably less, not exceeding 50,000.

For the polyacrylic acid–sodium hydroxide solutions the fraction of sodium ions bound to polymer ions decreases as the polymer concentration is increased, as shown in Fig. 1, while the polymer charge fraction increases with concentration, especially at higher percentages of neutralization. The polymer ion mobility decreases with increase in polymer concentration, as shown in Fig. 2, as does the polyion transference number. The polyion mobility increases with temperature, presumably because of the decrease in solvent viscosity; however, the fraction of cations bound and the polymer charge fraction for polyacrylic acid–sodium hydroxide solutions remain constant within experimental error from 0 to 42°.

Neutralizing the polyacrylic acid with potassium hydroxide instead of sodium hydroxide does not result in an appreciable change in the fraction of cations that are bound to polymer ions or in the polyion mobility, as shown in Figs. 1 and 2. The polymer charge fraction is also the same in both

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[1] J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636, 4228 (1950).

[2] F. T. Wall and P. F. Grieger, *J. Chem. Phys.*, **20**, 1200 (1952).

[3] F. T. Wall, P. F. Grieger, J. R. Huizenga and R. H. Doremus, *ibid.*, **20**, 1206 (1952).

[4] F. T. Wall and E. H. deButts, *J. Chem. Phys.*, **17**, 1330 (1949).

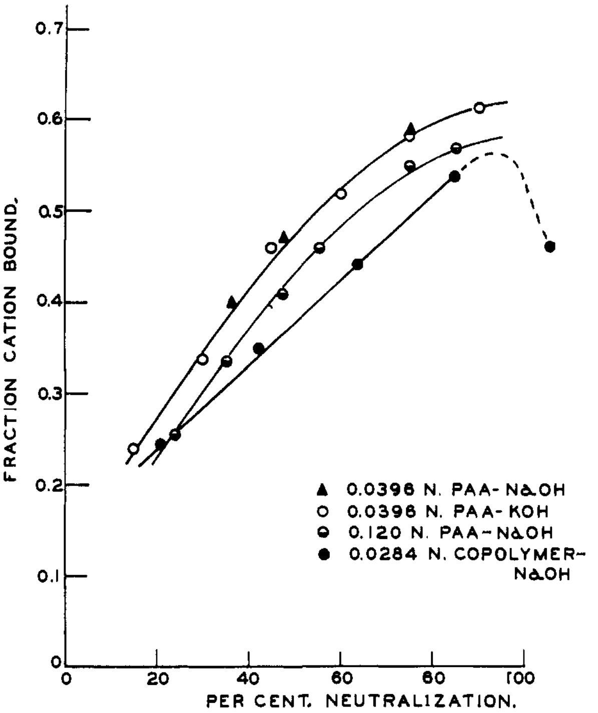

Fig. 1.—Fraction cation bound for various polyelectrolyte solutions plotted *vs.* percentage neutralization.

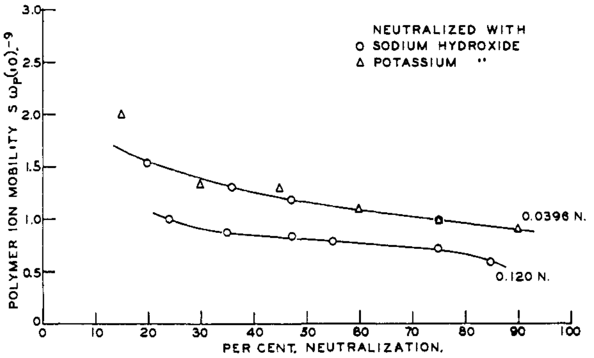

Fig. 2.—Polyacrylate ion mobility plotted *vs.* percentage neutralization for different concentrations and different bases.

cases. These results indicate that substituting potassium ions for sodium ions does not alter the polyion configuration. However, the polymeric anion transference number of the potassium salts is lower because of the higher mobility of potassium ions in aqueous solution.

Solutions of hydrolyzed maleic anhydride–styrene copolymer partially neutralized with sodium hydroxide have somewhat different properties. The fraction of cations bound to polymer is less than that found for polyacrylic acid–sodium hydroxide, as shown in Fig. 1, and the polymer charge fraction is greater than for sodium polyacrylate. The rational ion mobility, $s\omega_p$, is lower, because of the extension of the polyion coil with the increased charge, and because of the lower molecular weight (s equals the basicity of the acid).

In studying the exchange of free and bound cations, the quantity determined was the specific

TABLE I

CONDUCTANCE AND TRANSFERENCE PROPERTIES OF POLYMER–CATION SOLUTIONS

Neutral, %	Temp., °C.	Fraction cations bound	Polymer transference number	Polymer charge fraction	Polymer ion mobility × 10^{-9}
Polyacrylic acid partially neutralized with sodium hydroxide					
0.0128 normal					
34.7	25	0.385	0.51	0.214	1.52
47.2	0	.475	.51	.248	0.69
47.2	25	.472	.51	.249	1.32
47.2	42	.461	.50	.254	1.72
64	0	.546	.51	.285	0.60
64	25	.552	.52	.287	1.16
64	42	.544	.51	.287	1.56
0.0396 normal					
20	25	0.238	0.43	0.156	1.53
36.5	25	.400	.49	.219	1.31
47.2	0	.458	.49	.256	0.58
47.2	25	.470	.50	.250	1.19
47.2	42	.475	.49	.248	1.66
74.9	25	.590	.50	.306	0.98
0.120 normal					
24	25	0.255	0.38	0.178	1.00
35	25	.336	.41	.232	0.87
47.2	25	.420	.45	.274	.85
55	25	.461	.45	.296	.79
74.9	25	.550	.46	.337	.72
85	25	.568	.43	.367	.59
0.292 normal					
47.2	25	0.361	0.38	0.301	0.57

TABLE II

CONDUCTANCE AND TRANSFERENCE PROPERTIES OF POLYMER–CATION SOLUTIONS; TEMPERATURE, 25°

Neutral, %	Fraction cations bound	Polymer transference number	Polymer charge fraction	Polymer ion mobility × 10^{-9}
Polyacrylic acid partially neutralized with potassium hydroxide				
0.0158 normal				
15	0.172	0.32	0.124	1.82
30	.340	.40	.198	1.53
45	.445	.41	.250	1.27
60	.531	.43	.281	1.22
75	.597	.43	.302	1.16
90	.628	.43	.334	1.05
0.0396 normal				
15	0.240	0.33	0.114	1.99
30	.338	.37	.198	1.34
45	.461	.41	.242	1.29
60	.519	.42	.289	1.10
75	.578	.41	.317	0.99
90	.614	.41	.348	0.90
Copolymer partially neutralized with sodium hydroxide				
0.0284 normal				
21.1	0.245	0.44	0.158	1.62
42.3	.350	.47	.274	1.03
63.4	.443	.53	.352	0.97
84.5	.539	.44	.376	.76
105.6	.460	.42	.515	.69

reaction rate constant k. The definition and calculation of k from special transference measurements using radioactive tracers have already been discussed.[2,3] The rate of exchange of cations between the free and bound species in equivalents per liter-minute is $kr^2f(1-f)$, where r is the total cation concentration in equivalents per liter, f is the fraction of cations free in solution, and $1-f$ is the fraction of cations bound. Thus X, the fraction of all the cations which undergo exchange in unit time, is given by

$$X = 2krf(1-f) \qquad (1)$$

The factor 2 appears in equation 1 because there are two species of cations exchanging, those bound and those free in solution.

A two-compartment transference cell was used in the experiments to study the exchange process. Two types of experiments were carried out to obtain data for determining the cation exchange rate. In the first type, denoted by A, the anode compartment of the transference cell was initially filled with partially neutralized polymer solution to which radioactive tracer had been added, while the cathode compartment was filled with identical polymer solution without added tracer. In case B the cathode compartment was initially filled with polymer solution with tracer, and the anode compartment was filled with non-tracer solution.

TABLE IV

BOUND–FREE CATION EXCHANGE RATES FOR VARIOUS POLYMER SOLUTIONS; TEMPERATURE, 25°

Time of electrolysis, minutes					2	30	40	60	80	90	120
Series	Polymer	Polymer concn.	Cation	Neutral, %	Fraction of cations exchanging per minute (X)						
8	Polyacrylic acid	0.120	Na	47.2			0.14	0.09	0.09		0.07
9	Polyacrylic acid	.120	Na	74.9	0.86		0.22	.22	0.13		.07
10	Polyacrylic acid	.0396	K	45		0.15		.06		0.06	.08
11	Polyacrylic acid	.0396	K	75		0.51		.29		0.20	.10
12	Copolymer	.0284	Na	56	0.07		0.04	.05	0.05		.04
13	Copolymer	.0284	Na	63.4		0.09		.09		0.06	.06

If q_A and q_B are defined as the amounts of tracer which pass the boundary between the two compartments in case A and B, respectively, the theory predicts[2] that $q_A - q_B$ should be related to the time of electrolysis, t, as

$$q_A - q_B = Q't \qquad (2)$$

where Q' is the net rate of flow of tracer across the boundary for a transference experiment with uniform initial tracer concentration. Q' is constant for a given solution and can be determined from simple transference experiments.[2] The results for nearly all of the solutions discussed here fit equation 2; however, in three instances $q_A - q_B$ was not linear with time. These solutions include acrylic acid 45% neutralized with potassium hydroxide and those of the copolymer. In these cases, the q_A *vs.* time curves are similar to those found for the other solutions, but q_B is unexpectedly low for short times of electrolysis and increases to excessively high values at longer times of electrolysis. The reason for these deviations is not known.

The results of the exchange rate calculations which were carried out as described earlier,[2,3] appear in Tables III and IV. The data are given in terms of X rather than k because X has no explicit dependence upon the cation concentration. The calculated value of X is highly dependent upon α, the ratio of bound cation flow to free cation flow, which cannot be determined with high accuracy. Moreover, the experimental q_A and q_B values are also subject to many errors, so the final X values are not too reliable, especially when α is near unity. Nevertheless, the results for different times of electrolysis for the same solution can be utilized to study the mechanism of exchange, and certain rough trends in X with different solutions can be observed.

TABLE III

BOUND–FREE CATION EXCHANGE RATES FOR 0.0128 *N* POLYACRYLIC ACID PARTIALLY NEUTRALIZED WITH SODIUM HYDROXIDE

Time of electrolysis, min.			20	30	40	50	60
Series	Neutral, %	Temp., °C.	Fraction of cations exchanging per minute (X)				
1	47.2	0	0.65	0.28	0.18	0.11	
2	47.2	25	.23	.17	.11		0.08
3	47.2	42	.59	.43	.36	.29	
4	64	0	.45	.22	.16	.12	
5	64	25	.19	.17	.18	.21	0.23
6	64	42	.31	.34	.17	.20	0.19
7	34	25	.52	.37	.31	.26	

For most of the solutions investigated the value of X is high for short times of electrolysis and decreases for longer run periods, as was previously observed.[3] This decrease seems to be of an exponential nature. As mentioned in the introduction, the original development assumed that the exchange rate is independent of the location of the exchanging ion on the polymer chain. The assumption that the exchanging ions fall into two groups, one with infinite and the other with zero exchange rate, leads to somewhat different expressions for q_A and q_B.[3] These expressions require that q_A and q_B increase linearly with time of electrolysis; for many of the solutions investigated this was found to be the case.

To facilitate treating the data according to the second model, let us define a quantity α' as

$$\alpha' = -J_{22}/(J_1 + J_{21}) \qquad (3)$$

where J_1, J_{21} and J_{22} are the flows of free cations, fast exchanging bound cations, and slow exchanging bound cations, respectively. α' can thus be calculated from the experimental values of q_A and q_B.[3] Values of α' calculated from two independent equations involving q_A and q_B, respectively, are presented in Table V. The good agreement of α' found from the two methods of calculation together with the linearity of the q_A and q_B against time plots indicates that the assumption of two different types of exchanging cations is a better one than that involving one type. Values of p'/p'', the ratio of fast to slow exchanging cations, are also shown in Table V. These values were calculated from the equation[3]

$$p'/p'' = \alpha/\alpha' - 1/(1 - \alpha) \qquad (4)$$

Just as for X, the values of p'/p'' are highly dependent upon α, especially when α is close to unity. The correlation between p'/p'' and X is not especially good; that is, a solution with a high exchange rate does not necessarily have a high fast-to-slow cation ratio.

TABLE V

COMPARISON OF α' VALUES AND FAST-TO-SLOW EXCHANGING CATION RATIOS

Series	α' From q_A	α' From q_B	p'/p''
1	0.78	0.78	2.7
2	.69	.74	6.4
3	.48	.49	5.5
7	.14	.14	10.7
8	.09	.12	10.5
9	1.19	1.19	2.8
11	0.89	0.87	2.5
12	0.25	0.20	4.3

One solution investigated, series 5, was found to have a cation exchange rate that was constant with electrolysis time, and in this case the assumption of one type of exchanging cation appears to be a good one. The half-time of exchange was found to be 1.8 minutes for this solution.

From the results available no definite conclusions can be drawn as to the effect of concentration or percentage neutralization upon the exchange rates; apparently these variables do not seem to be of major importance in affecting the exchange rates over the range investigated.

The X values found for the polyacrylic acid–potassium hydroxide and copolymer–sodium hydroxide solutions are similar to those found for polyacrylic acid–sodium hydroxide. The fact that the X values for series 11 are high may be due to a slight inaccuracy in α, since α is quite close to unity for this solution.

Changing the temperature over the range 0 to 42° does not seem to produce a systematic effect upon the cation exchange rate. Taking into account the experimental errors, it appears that the energy of activation for exchange is low. For low times of electrolysis, the X values are less at 25° than at either 0° or 42°, an unexpected behavior for which no reasonable explanation is readily forthcoming. With increasing temperature, the X values tend to become less dependent on time of electrolysis. These appear to be the only generalizations that can be drawn from the data of Table III.

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[CONTRIBUTION FROM THE RESEARCH DIVISION, ARMOUR AND COMPANY]

Light Scattering in Solutions of a Linear Polyelectrolyte

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Solutions of arabic acid have been investigated by the light scattering technique. The molecular weight for a standard preparation was found to be $1.00 \pm 0.05 \times 10^6$ in contrast to the 300,000 value determined by earlier osmotic pressure measurements. The molecule appears to be a stiff coil due to side branching, varying in extension from 1050 Å. at zero charge to 2400 Å. at maximum charge. Viscosity measurements are in essential agreement with the scattering data. The scattering function, Kc/R_{90}, increases with increasing polyion charge at a given value of the concentration, c. It decreases with increasing ionic strength to a limiting value of that in un-ionized systems. The scattering function is third order at high values of the charge. The dissymmetry, z, exhibits a distinct minimum at $c = 0.75 \times 10^{-3}$ g./cc. for all values of μ for the ionized acid and rises at higher c to a maximum value. The maximum is lower as μ increases and occurs at lower values of c. Some models are described which may explain the free energy relationships giving rise to the above-mentioned Kc/R_{90} *vs.* c and z *vs.* c data.

The behavior of random-coil type, high molecular weight polyelectrolytes in solution has been discussed frequently. In spite of gratifying agreement on some points, several discrepancies still exist between the theoretical behavior of model systems and the observed experimental facts. Investigations of such systems[1–3] by light scattering techniques have yielded much interesting information. The work reported here extends this type of information to a higher molecular weight system. Several details of the behavior of these systems have not been observed in lower weight systems; other details are more pronounced and more accurately measured.

The polyelectrolyte investigated was arabic acid, the acidic carbohydrate structure of gum arabic. It has been studied extensively in several ways: osmotic pressure[4–6]; dissociation constants[6–9,12,13]; conductance[7,9,10,14]; and viscosity.[11,15–17,18] Its

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[1] A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

[2] F. T. Wall, J. W. Drennan, M. R. Hatfield and C. L. Painter, *J. Chem. Phys.*, **19**, 585 (1951).

[3] R. M. Fuoss and D. Edelson, *J. Polymer Sci.*, **6**, 767 (1951).

[4] D. R. Briggs, *J. Phys. Chem.*, **38**, 1145 (1934).

[5] H. B. Oakley, *Trans. Faraday Soc.*, **31**, 136 (1935).

[6] A. W. Thomas and H. A. Murray, *J. Phys. Chem.*, **32**, 676 (1928).

[7] D. R. Briggs, *ibid.*, **38**, 867 (1934); **38**, 1145 (1934).

[8] J. Th. G. Overbeek, *Bull. soc. chim. Belg.*, **57**, 252 (1948).

[9] A. Veis, *J. Phys. Chem.*, **57**, 189 (1953).

[10] S. N. Mukherjee and K. B. Ghosh, *J. Indian Chem. Soc.*, **26**, 81 (1949); **26**, 277 (1949).

[11] S. N. Mukherjee and A. C. Bhowmik, *ibid.*, **26**, 151 (1949); **26**, 313 (1949).

[12] S. P. Saric and P. K. Schofield, *Proc. Roy. Soc. (London)*, **A185**, 431 (1946).

[13] R. Speiser, C. H. Hills and C. R. Eddy, *J. Phys. Chem.*, **49**, 328 (1945).

[14] W. Pauli, W. Koll and A. Linsker, *Kolloid Z.*, **79**, 273 (1937).

[15] L. W. J. Holleman and H. G. Bungenberg de Jong, *Kolloid-Beihefte*, **46**, 113 (1927).

[16] L. Amy, *Ann. Chem.*, 11, 2, 287 (1934).

[17] R. H. Schleif, J. Higuchi and L. W. Busse, *J. Am. Pharm. Assoc.*, **40**, 98 (1951); **40**, 221 (1951).

[18] S. Basu, P. Ch. Dasgupta and A. K. Sircar, *J. Colloid Sci.*, **6** 539 (1951).