

**Apparatus.**—A Leeds and Northrup Type E Electro-Chemograph was used with a thermostated H-cell<sup>17</sup> ( $25 \pm 0.1^\circ$ ) containing a saturated calomel reference electrode. A Beckman Model G pH meter was used for pH measurement. All measuring apparatus were calibrated. The dropping mercury electrodes, prepared from Corning marine barometer tubing, had  $m$  and  $t$  values (open circuit, distilled water,  $25^\circ$ , 65 cm. uncorrected mercury head) for capillaries F and G of 0.966 and 0.982 mg./sec., and 5.85 and 5.78 sec., respectively. At  $0^\circ$ ,  $m$  for capillary G was calculated<sup>18</sup> to be 0.89 mg./sec. The macro-scale electro-reductions were conducted in a modified Lingane<sup>19</sup> coulometric apparatus maintained at  $25 \pm 0.1^\circ$ .

(17) J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

(18) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, New York, N. Y., 1952, pp. 91-92.

(19) J. J. Lingane, *THIS JOURNAL*, **67**, 1916 (1945).

**Polarographic Procedure.**—Stock solutions were prepared by dissolving a weighed amount of phenacyl fluoride in 95% ethanol. Test solutions were made by pipetting 5.00 ml. of stock solution into a 50-ml. volumetric flask and diluting with buffer solution. The test solution after transference to the polarographic cell was deoxygenated for 5 min. and then electrolyzed (10 min.) under a nitrogen atmosphere. The potentials reported are corrected for  $iR$  drop and are vs. S.C.E. All test solutions contained 9.5% ethanol and had an ionic strength of 0.45  $M$ ; the presence of the ethanol casts some doubt on the absolute validity of the pH measurements reported.

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## Strontium Ion Association with Partially Neutralized Polyacids

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The association of strontium ions with polymeric acid anions has been studied by means of electrical transference and diffusion methods. The experiments were carried out on polymeric acids partially neutralized with strontium hydroxide. The degree of binding of strontium to the polymeric anions was computed from the amount of strontium that appeared to move with the anion during electrical transference. The fraction of free strontium ions could also be calculated from the apparent rate of diffusion of such ions in the presence of polymeric acid. The extents of binding calculated by the two methods were in substantial agreement and could be described adequately by use of certain empirical equations of a form compatible with a simple molecular model.

### Introduction

The principal reason for the difference between the properties of polymeric ions and those of simple ions is that the charged groups of a polyelectrolyte cannot move entirely independently of each other because they are connected by the polymer chain. Thus the region which is effectively occupied by a coiling type polymer ion becomes one of much higher charge density than its surroundings. As a result, the counterions frequently penetrate into the polymer coil, and a considerable fraction of them becomes associated with the macroion because of electrostatic attraction. Previous studies<sup>1-4</sup> have demonstrated convincingly that the association of monovalent counterions with polymeric anions and cations is appreciable even for salts whose monomeric counterparts are almost completely ionized.

The purpose of this investigation was to study the association of divalent ions with partially neutralized aqueous polymeric acids as a function of the degree of neutralization, polymer concentration, temperature and degree of polymerization. Using radioactive strontium-89, the binding characteristics could be determined independently by means of transference experiments and diffusion measurements.

Divalent counterions interact with polyelectrolytes so much that flocculation results beyond low

degrees of neutralization. This effect is attributable to the fact that divalent ions can associate with two binding sites, forming "bridges" between two polyions. In high neutralization ranges, an appreciable number of "bridges" can be formed, resulting in large aggregates of polymer which show a pronounced Tyndall effect in solution and which may even precipitate out.

### Experimental

The methods employed in carrying out the Hittorf-type transference experiments have been described previously.<sup>1,2</sup> When a partially neutralized polymeric electrolyte, like polyacrylic acid, is electrolyzed, it is found that the polymeric anions move as expected toward the anode. Some of the cations migrate in the normal manner toward the cathode, but it is also observed that other cations move toward the anode. Such migration, apparently in the wrong direction, is explained by assuming that those cations are "bound" to the polymeric anion, or caught in the anionic sphere of influence, and hence constrained to move with the anion. A measure of the number of cations moving to the anode constitutes a transference determination of the extent of ion binding. The transport of counterions is most conveniently followed by radioactive counting, whereas the migration of polymer is determined gravimetrically.

Details of the diffusion method for determining ion binding have also been described previously.<sup>1,2</sup> In these experiments tracer ion diffusion takes place across a sintered glass frit from a well-mixed "hot" solution into a stirred, initially "cold," but chemically identical, solution. It is observed that polymeric anions tend to reduce the rate of diffusion of cations, a behavior attributed once again to ion binding. The extent of ion binding is determined by relating the reduced diffusion tendency of the ions in the presence of polymer to the rate of diffusion of the same ions in the absence of polymer. As a simplifying assumption, the diffusion rate of the bulky polymer ions is considered negligible compared to that of the smaller counterions.

Actually, the rate of exchange between bound and unbound counterions also influences the diffusion data. This

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

(2) F. T. Wall, J. J. Ondrejcin and M. Pikramenou, *ibid.*, **73**, 2821 (1951); F. T. Wall and R. H. Doremus, *ibid.*, **76**, 868 (1954); **76**, 1557 (1954).

(3) G. I. Cathers and R. M. Fuoss, *J. Polymer Sci.*, **4**, 121 (1949).

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

effect readily can be taken into account,<sup>5</sup> but in all systems considered here the exchange rate was fast in comparison with the diffusion process. Therefore, the earlier theory,<sup>1,2</sup> assuming infinite exchange rate, was applicable to the present computations.

**Materials and Analyses.**—Two samples of polyacrylic acid and copolymer of styrene and maleic anhydride were used in the present study. These polymers were prepared from their monomers using controlled amounts of benzoyl peroxide catalyst.<sup>6,7</sup> The copolymer was not water soluble in its original form, and it had to be hydrolyzed by prolonged contact with water at 70°.

The aqueous polyacid solutions were standardized by weighing solute obtained from aliquot portions after drying at 100° for two days. The equivalent weight of the copolymer was taken to be 101.10, since it had been prepared from equimolar quantities of styrene and maleic anhydride.

Strontium hydroxide was freed from carbonate by filtration of concentrated solutions. Diluted solutions were then standardized against potassium biphthalate. Care was taken, however, to avoid prolonged contact of strontium hydroxide solutions with air containing carbon dioxide. For this reason, all storage bottles and burets were equipped with carbon dioxide traps containing "Ascarite."

Radioactive ionic strontium-89 was obtained from the Oak Ridge National Laboratories. Solutions were made radioactive by addition of small amounts of tracer solution. All radioactive mixtures were then allowed to stand for about a week to allow sufficient time for complete exchange of radioions with the "cold" ions in the associated state.

### Results and Discussion

Ionic equivalent conductances at the appropriate temperatures and concentrations were obtained graphically from salt equivalent conductances and transference numbers given in the literature.<sup>8,9</sup> Additional data are reported in the Appendix to this article.

All experiments reported here were carried out with solutions of sufficiently low concentrations to

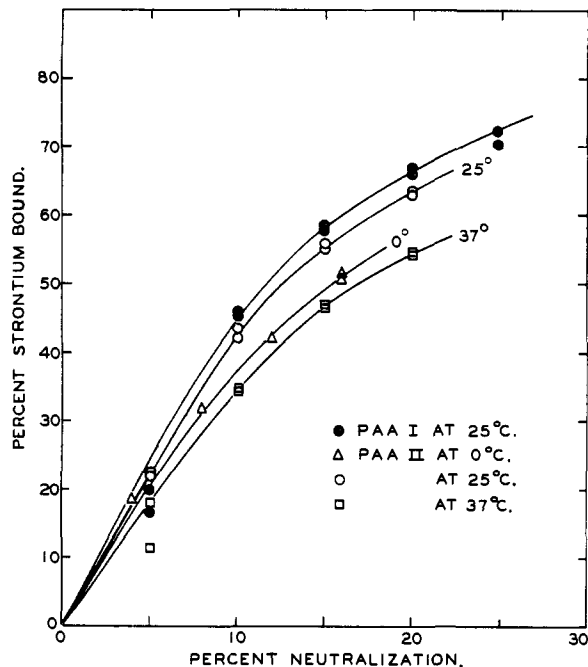


Fig. 1.—Binding data from transference experiments.

(5) M. J. Eitel, University of Illinois Thesis, 1954.

(6) F. T. Wall, J. W. Drenan, M. R. Hatfield and C. L. Painter, *J. Chem. Phys.*, **19**, 585 (1951).

(7) F. T. Wall and E. H. deButts, Jr., *ibid.*, **17**, 1330 (1949).

(8) "International Critical Tables," Vol. 6, McGraw-Hill Book Co., New York, N. Y., p. 229 ff, 309 ff.

(9) L. G. Longworth, *This Journal*, **54**, 2741 (1932).

justify the assumption of independent ion migration. In other words, the values of ionic equivalent conductance were found to be independent of the choice of reference salt in the experimental concentration ranges.

The results are compiled in Tables I and II. The binding data are also shown graphically in Figs. 1, 2 and 3. The following notation will be employed throughout the subsequent discussion.

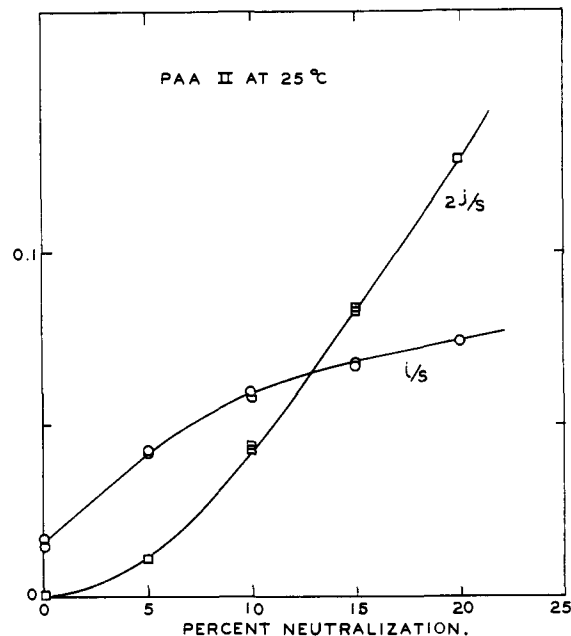


Fig. 2.—Neutralization dependence of charge fraction and strontium fraction.

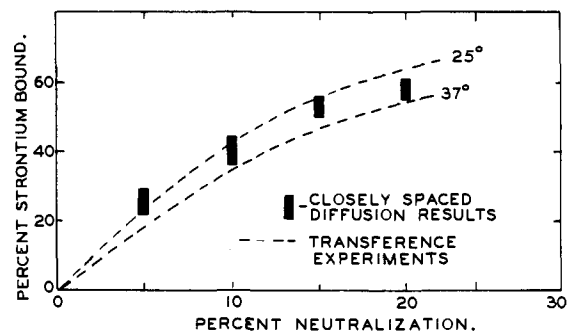


Fig. 3.—Comparison of binding data from diffusion and transference experiments.

It is interesting to note that the binding data of Fig. 1 do not show any pronounced dependence on the polyacrylic acid (PAA) concentration in the range 0.02 to 0.1 normal. The shape of the binding curves is very similar to those for sodium gegenion association.<sup>1,2</sup> However, recently reported association results which do show a concentration dependence<sup>1,2</sup> are not entirely correct, because they were obtained for solutions so concentrated that the assumption of independent ion migration is not strictly valid.

PAA I and II were polymer specimens of weight-average molecular weights of 215,000 and 107,000, respectively, as determined by light-scattering ex-

TABLE I  
RESULTS OF TRANSFERENCE EXPERIMENTS

% Neutralization	$Q_{Sr} \times 10^3$	$Q_p \times 10^3$	$K \times 10^3$	$N_o \times 10^3$	pH	$A_p$	$t_p$	$I -$	$\Sigma j/s$	$i/s$	$s\omega_p \times 10^{-9}$
0.02 N PAA I at 25°											
25	0.00277	0.213	0.1154	0.0746	4.91	16.5	0.214	0.702	0.176	0.0750	1.42
0.0736 N PAA I at 25°											
5	-0.0494	0.557	0.2665	0.224	3.72	9.01	0.110	0.167	0.00834	0.0443	1.32
10	-0.0734	.723	.3011	.224	4.06	13.2	.179	.459	.0459	.0552	1.55
15	-0.0629	.705	.3357	.224	4.27	14.4	.201	.585	.0877	.0637	1.46
20	-0.0336	.699	.3568	.224	4.44	15.1	.214	.660	.132	.0685	1.43
25	-0.00959	.475	.3659	.149	4.52	15.8	.223	.721	.180	.0701	1.46
0.1 N PAA I at 25°											
5	-0.0831	0.794	0.3341	0.298	3.65	8.88	0.113	0.198	0.00992	0.0423	1.36
10	-0.111	.887	.3917	.298	3.99	11.6	.166	.452	.0452	.0558	1.35
15	-0.0860	.933	.4383	.298	4.21	13.7	.198	.582	.0872	.0634	1.40
20	-0.0535	.928	.4582	.298	4.38	14.3	.208	.667	.133	.0670	1.38
0.07 N PAA II at 25°											
0	.....	0.452	0.4301	0.339	2.93	8.20	0.0224	...	.....	0.0168	3.16
5	-0.0179	0.548	0.2619	0.297	3.59	6.90	0.0782	0.225	0.0113	0.0424	1.05
10	-0.0414	1.07	0.3029	0.457	3.93	10.2	.140	.422	.0422	.0594	1.11
15	-0.0528	0.835	0.3337	0.311	4.16	12.8	.180	.559	.0839	.0671	1.23
20	-0.00324	0.799	0.3616	0.299	4.34	13.8	.198	.633	.127	.0740	1.21
0.1 N PAA II at 25°											
0	.....	0.424	0.5191	0.332	2.85	6.63	0.0180	...	.....	0.0141	3.04
5	-0.0344	.564	.3381	.292	3.55	6.53	.0807	0.221	0.0111	.0418	1.01
10	-0.0189	.703	.4005	.291	3.88	9.67	.139	.437	.0437	.0577	1.08
15	.0319	.657	.4472	.295	4.10	9.96	.152	.551	.0827	.0681	0.95
20	.0664	.557	.4763	.253	4.28	10.5	.163	.633	.127	.0739	0.92
0.07 N PAA II at 0°											
0	.....	0.392	0.2535	0.331	2.83	4.30	0.0250	...	.....	0.0211	1.32
8	-0.0396	1.11	.1652	.376	3.83	6.97	.154	0.374	0.0299	.0522	0.86
16	0.0332	0.842	.2193	.291	4.27	9.06	.227	0.515	0.0824	.0784	0.75
0.1 N PAA II at 0°											
0	.....	0.339	0.3456	0.287	2.83	4.09	0.0175	...	.....	0.0148	1.79
4	-0.0737	.767	.2015	.305	3.43	5.06	.0913	0.185	0.00739	.0363	0.90
8	-0.0726	.947	.2290	.328	3.83	6.62	.162	.318	.0254	.0561	.76
12	-0.0229	.945	.2703	.336	4.07	7.61	.198	.422	.0506	.0702	.70
16	.0396	.954	.3025	.334	4.25	8.66	.227	.508	.0813	.0792	.71
0.07 N PAA at 37°											
0	.....	0.510	0.4808	0.356	2.83	9.84	0.0302	...	.....	0.0211	3.02
5	-0.0786	.689	.3507	.325	3.55	10.6	.0954	0.181	0.00906	.0450	1.53
10	-0.101	.767	.4503	.275	3.93	18.0	.188	.344	.0344	.0673	1.73
15	-0.0736	.639	.5405	.209	4.15	23.6	.245	.473	.0710	.0801	1.91
20	-0.414	.511	.6137	.179	4.31	25.0	.262	.545	.109	.0917	1.77
0.1 N PAA II at 37°											
0	.....	0.513	0.6005	0.356	2.74	8.65	0.0262	...	.....	0.0182	3.08
5	-0.106	.783	.4637	.325	3.59	11.2	.113	0.115	0.00574	.0468	1.55
10	-0.121	.772	.6167	.275	3.86	17.3	.188	.345	.0345	.0669	1.68
15	-0.0773	.609	.7454	.209	4.05	21.7	.235	.468	.0703	.0806	1.74
20	-0.0617	.510	.8547	.179	4.25	24.3	.263	.542	.108	.0923	1.71
0.0284 N SMAC at 25°											
0	.....	...	0.4006	...	3.00	..	...	...	.....	0.0352	..
7.14	-0.0138	0.664	.1842	0.387	3.69	11.1	0.109	0.210	0.0150	.0636	1.13
14.3	.0525	.837	.1948	.387	4.21	14.8	.188	.404	.0577	.0872	1.10
21.4	.0564	.682	.2625	.404	4.47	15.6	.213	.417	.0892	.126	0.80
28.5	.0818	.667	.3415	.404	4.82	19.9	.266	.438	.125	.161	0.80

$\kappa$	= specific conductance of the soln., mho/cm.
$N_e$	= equiv. of electricity passed through the transference cell
$Q_p$	= equiv. of polymer ions transferred to the anode compartment during the expt.
$Q_{Sr}$	= equiv. of strontium ions transferred to the anode compartment
$\Lambda_p, \Lambda_{Sr}$	= ionic equiv. conductances
$t_p$	= polymer transference no.
$f$	= fraction of strontium ions remaining unassociated
$s$	= basicity of the polymeric acid
$i$	= net charge no. carried by the polymeric ion
$j$	= av. no. of gegenions associated with each polyion
$\omega_p$	= polyion mobility, cm./dyne-sec.
$D_p, D_{Sr}$	= ionic diffusion coefficients, cm. <sup>2</sup> /hr.
$R$	= ratio of radioactive counts obtained from equal vol. of soln. taken from the initially "cold" diffusion compartment after completion of the expt., to those obtained on the soln. used for filling the "hot" compartment initially

periments, using the procedure of Wall, *et al.*<sup>6</sup> Figure 1 shows clearly that stronger binding results with the higher molecular weight polymer, but the effect is only small in the molecular weight range under observation.

TABLE II  
RESULTS OF DIFFUSION EXPERIMENTS

% Neutralization	Run time, hr.	R	$D_{Sr} \times 10^3$ used	1 -
0.07 N PAA II at 25°				
5	48	0.0848	27.0	0.273
10		.0749	25.9	.375
15		.0488	25.6	.508
20		.0430	25.0	.566
0.1 N PAA II at 25°				
5	48	0.0817	26.4	0.286
10		.0691	25.4	.414
15		.0459	24.9	.526
20		.0408	24.6	.579
0.07 N PAA II at 37°				
5	48.5	0.115	35.5	0.238
5		.116	35.4	.223
10		.101	34.6	.389
10		.0993	34.7	.400
15		.0655	34.5	.528
15		.0649	34.5	.534
20		.0589	34.2	.590
20		.0597	34.1	.584
0.1 N PAA II at 37°				
5	48.25	0.108	35.0	0.272
5		.107	35.0	.284
10		.0928	34.1	.432
10		.0930	34.1	.431
15		.0621	33.7	.542
15		.0641	33.6	.526
20		.0562	33.4	.599
20		.0591	33.2	.576

The plot of  $j/s$  versus degree of neutralization of Fig. 2 is interesting, because conclusions can be drawn from it as to the nature of the counterion association phenomenon. It will be seen that  $j/s$ , the fractional number of associated counterions per carboxyl group, increases slowly at low degrees of neutralization and then rises sharply and steadily at higher neutralization. This shows that binding

is weak when the charged groups are still widely separated, but strong association sets in as soon as an appreciable charge density has been acquired by the polymer coil.

Neutralization with base was found to increase the charge  $i$  of the macroion appreciably; and although the number of free counterions is increased also, the polyion transference number was found to increase with the degree of neutralization.

While the polymer ion mobility is very sensitive to experimental error, a decrease of  $s\omega_p$  with neutralization should be generally observed. Since neutralization enhances the polyion charge, an expansion of the polymer coil can be assumed to result because of mutual repulsion of the charged groups attached to the polymer chain. Thus the polymer coil will offer increased resistance to motion through the viscous medium.

Further confirmation of this concept is offered by the observation that the product  $i\omega_p$  increases with the polymer molecular weight (see Table III). This observation shows that the charge  $i$  of the polymer increases with the degree of polymerization faster than the hydrodynamic resistance offered by polymer of increased chain length, in spite of the increased counterion binding noted above. Thus we have proof that uncoiling of the polymer chain is still incomplete, for if we had a completely uncoiled polymer chain,  $i\omega_p$  should remain essentially constant. This effect may well be due to the ability of divalent strontium ions to attach themselves to two carboxyl groups of the same molecule, forming internal strontium "bridges."

TABLE III  
POLYMER CHARGE-MOBILITY PRODUCTS OF STRONTIUM POLYACRYLATES AT 25°

% Neutralization	$i\omega_p \times 10^{-8}$ PAA I	$i\omega_p \times 10^{-8}$ PAA II
0.0736 N		
5	0.583	0.446
10	.855	.657
15	.929	.827
20	.989	.894
0.1 N		
5	0.575	0.423
10	.753	.625
15	.887	.644
20	.922	.678

In general, the inobility may be broken up into a shape factor  $C$  and the viscosity of the medium

$$\omega_p = 1/C\eta$$

Using the viscosity of water, the product  $s\omega_p\eta_w$  should then be independent of temperature, if ionic conditions rather than thermal effects determine the shape of the polymer coil. This was indeed found to be the case, as shown in Table IV.

The polymer equivalent conductance was found to increase with the degree of neutralization. This effect had been observed previously at low degrees of neutralization with polyacrylic acid partially neutralized with sodium hydroxide.<sup>1,2</sup> However, with more completely neutralized polyacrylate,  $\Lambda_p$  was found to go through a maximum. This phenomenon was not observed in the present work

TABLE IV  
QUANTITIES COMPUTED FROM THE POLYION MOBILITY

% Neutralization	Temp., °C.	$s_{app} \times 10^{-2}$
0	0	0.024
0	25	.028
0	37	.021
10	0	.015
10	25	.010
10	37	.012
20	0	.013
20	25	.011
20	37	.012

since gel formation prohibited the investigation of medium and high neutralization ranges.

Polyion diffusion constants, calculated using the relation  $D_p = kT\omega_p$ , appear to be about 1/100 as large as those for the strontium ions given in Table II. Naturally strontium ions would be expected to diffuse much faster than the bulky polyacrylate ions.

The results of our diffusion experiments were in approximate agreement with our transference runs. But whereas the diffusion experiments showed no noticeable temperature dependence, transference measurements indicated higher strontium ion association at 25° than at either 0 or 37°. This peculiar behavior was duplicated by the dissociation tendency of the carboxyl groups to yield hydrogen ions, as will be seen by inspection of the *pH* data. Since the counterion binding should depend on such properties as the extent of hydration, ionic size, etc., no simple temperature dependence can be expected for the complex systems we are working with.

The diffusion experiments should not be expected to give precise agreement with the results of electrolysis runs because of our arbitrary definition of ionic binding. The techniques can only give approximate results, since it is assumed that an ion is either associated and moving with the polymer ion, or completely free to move independently. Inter-

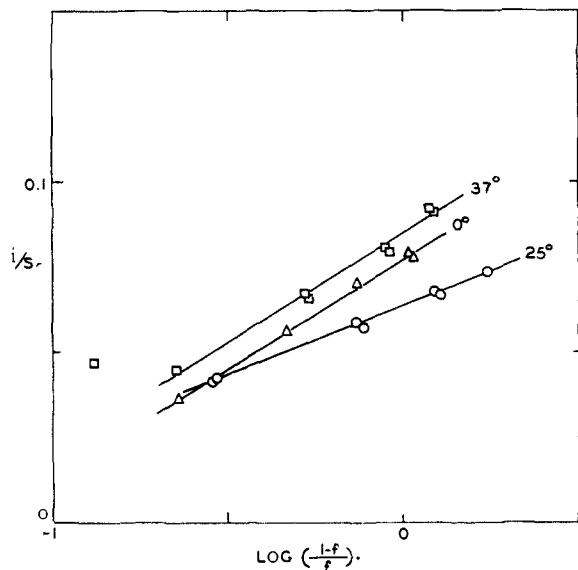


Fig. 4.—Empirical representation of strontium binding with PAA II.

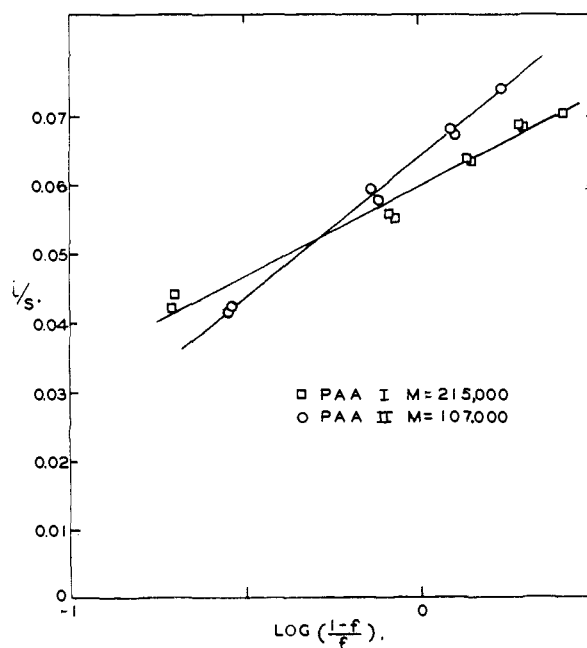


Fig. 5.—Empirical description of strontium binding with polyacrylates of different DP.

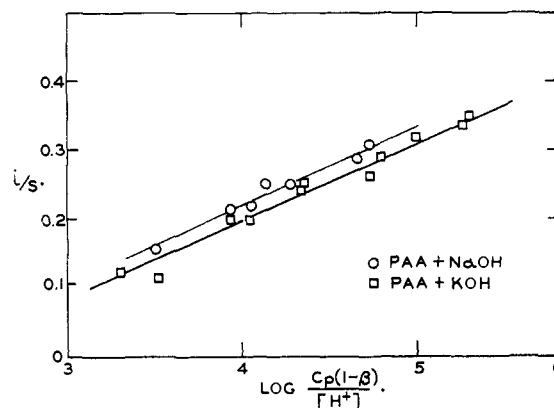


Fig. 6.—Empirical description of hydrogen ion dissociation in partially neutralized PAA; data from ref. 1, 2.

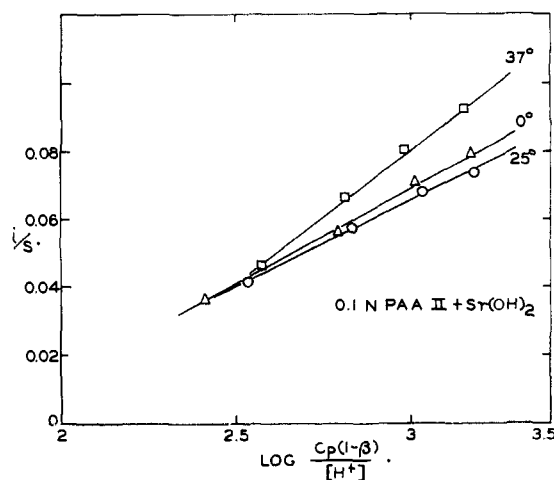


Fig. 7.—Carboxyl group dissociation in partially neutralized PAA at various temperatures.

mediate states (*i.e.*, conditions in which the polymer influences the movement of counterions without actual association) can be imagined easily, and the possibility of their actual existence cannot be denied. As a matter of fact, other work reported from this Laboratory has shown<sup>10</sup> that the binding forces are quite variable.

### Empirical Representation of the Results

Since simple equilibrium constants failed to account for the observed binding phenomena, an empirical description of the association data was devised. Thus it was found graphically that equation of the form

$$\log [(1 - f)/f] = A(i/s) + B \quad (1)$$

fit the polyacrylate association of sodium, strontium, potassium and hydrogen ions quite well. For hydrogen ions, equation 1 takes the form

$$pH + \log [c_p(1 - \beta)] = A'(i/s) + B' \quad (2)$$

where  $\beta$  denotes the degree of neutralization, and  $c_p$  is the polyion normality. While straight-line plots of  $i/s$  versus  $\log \{c_p(1 - \beta)/[H^+]\}$  were ordinarily independent of  $c_p$ , the equilibria were more complex with strontium ions present, and the dependence on  $c_p$  was not completely removed in these plots.

Equations of the type

$$\log f = C(i/s) + D \quad (3)$$

were also found to be quite successful in describing association phenomena. This relation leads to equation 2 for hydrogen ions as well.

The validity of these empirical relationships is examined graphically in Figs. 4 to 7.

**A Crude Model.**—Various models have been proposed to account for the titration curves of coiling polymeric acids.<sup>11-13</sup> In analogy with one of the simplest of these, the "conducting sphere" model, we shall now consider a model which assigns counterions to only two energy states, the bound state and the unassociated state. Ion association will be assumed to occur within the region occupied by the polymer, whose shape will be roughly spherical.

This model enables us to analyze association data from the observed quantities since the foregoing treatment distinguishes only between these extremes of association states. However, the representation of the energies of the two states by their averages does involve a simplifying assumption.

The populations of the two sorption states of the model can be calculated from Maxwell-Boltzmann expressions

$$\begin{aligned} n_b &= C_b e^{-e_b/kT} \\ n_f &= C_f e^{-e_f/kT} \end{aligned} \quad (4)$$

(10) F. T. Wall, H. Terayama and S. Techakumpuch, *J. Poly. Sci.*, **20**, 477 (1956).

(11) A. Katchalsky, O. Kuenzle and W. Kuhn, *J. Polymer Sci.*, **5**, 283 (1950).

(12) J. J. Hermans and J. T. G. Overbeek, *Bull. soc. chim. belg.*, **57**, 252 (1948).

(13) W. Kuhn, O. Kuenzle and A. Katchalsky, *Helv. Chim. Acta*, **31**, 1994 (1948).

Here the  $e$ 's and the  $C$ 's are constants for the bound state (b) and the free state (f).

If  $a$  is the work necessary to remove a counterion from a singly charged polymer ion, then  $e_f$  and  $e_b$  are related by

$$e_f = ai + e_b \quad (5)$$

and one obtains

$$n_f/n_b = (C_f/C_b) \exp(-ai/kT) \quad (6)$$

Equation 6 can be rewritten readily in the forms of the empirical relations 1 and 2. It also predicts the experimentally observed independence of binding on dilution.

Furthermore, the dependence of binding data on polymer chain length is roughly predicted by equation 6. The slopes of the lines of Fig. 5 are in the ratio of 1:1.7, although light scattering results indicated a molecular weight ratio of 1:2 for PAA I and PAA II. To the extent that these ratios are roughly equal, the crude theory is confirmed.

Further confirmation of this model is offered by the fact that the plots of Fig. 6 give *parallel* straight lines for carboxyl group dissociation, using NaOH and KOH as neutralizing bases. The constant slope of these lines corresponds to the same value of  $a/skT$ , as was to be expected. However, much smaller slope values were obtained with systems containing strontium ions due to non-independent association of hydrogen and strontium counterions. The higher complexity of these systems will be appreciated also from the complex temperature dependence of the association data shown in Figs. 1, 4 and 7.

### Appendix

**Some Conductance Properties of Strontium Salts.**—Strontium ion transport numbers were determined by the moving boundary method in a Tiselius electrophoresis apparatus, using lithium salts of common anion as indicators.<sup>14</sup>

#### STRONTIUM ION TRANSFERENCE NUMBERS

Strontium ion, $N$	$t_{Sr}$	Strontium ion, $N$	$t_{Sr}$	Strontium ion, $N$	$t_{Sr}$
SrCl <sub>2</sub> at 0.25°		SrCl <sub>2</sub> at 37.0°		Sr(NO <sub>3</sub> ) <sub>2</sub> at 24.3°	
0.0102	0.412	0.0145	0.432	0.0111	0.443
.0145	.406	.0290	.427	.0166	.444
.0290	.395	.0435	.432	.0277	.442
.0435	.398			.0416	.442

Equivalent conductance data were obtained with the conductivity apparatus described elsewhere.<sup>1,2</sup>

#### EQUIVALENT CONDUCTANCE OF STRONTIUM CHLORIDE AT 37°

Normality	$\Lambda$
0.00200	167.3
.00600	157.9
.0116	151.0
.0140	147.3

#### URBANA, ILL.

(14) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 79.