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

Counterion Association with Partially Neutralized Polyacids in the Presence of Neutral Salt

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A study has been made of counterion association with partially neutralized polyacids in the presence of a neutral salt with a cation in common to that of the base used for neutralization. The experiments were carried out on polyacrylic acid and a copolymer of styrene and maleic acid using sodium, strontium and zinc counterions. Although the degree of cation binding is appreciable when the acid is neutralized with alkali, further addition of neutral salt produces only a slight increase in cation binding. The effect is markedly dependent on the charge of the cation for, in the case of strontium, the addition of neutral salt results in more association than in the case of sodium. The results are in agreement with qualitative electrostatic considerations.

Introduction

Previous investigations$^{1-3}$ have shown that the number of counterions associated with partially neutralized polymeric acids increases strongly with the degree of neutralization, principally because of the increased charge density inside the coiled polymer ions. The effect of charge is superimposed on that of mass action, for the concentration of counterions eligible for association is also enhanced with increasing neutralization. Hence it was of interest to study this mass action effect separately by investigating the behavior of partially neutralized polyacids in the presence of a neutral salt of the cation of the neutralizing base.

Basis of the Experiments

The present investigation was carried out by means of Hittorf-type transference experiments using radioactive counterions, similar to the method of Huizenga, Grieger and Wall.[1] Once again use was made of the fact that associated and unassociated counterions migrate in opposite directions under the action of an applied electric field, but the customary expedient of analyzing aliquot samples from each electrode compartment for solute content has been dispensed with here.

Assuming the ion migrations in dilute aqueous solutions to be mutually independent, the specific conductance K of the solution will be given by an appropriate sum of the separate ionic contributions K_l and K_m

$$K = K_{l'} + \sum_{l}{}' K_l + \sum_{m} K_m \tag{1}$$

In this equation, l′ refers to the polymeric anion, l to all other anions, and m refers to cations. Σ' has been written for summation over all ion species l, save l′.

The ionic specific conductance is now related to the ionic equivalent conductance Λ_k of each ion species k by

$$K_k = c_k \Lambda_k' \tag{2}$$

where for convenience Λ_k' has been written for $\Lambda_k/1000$, and c_k represents the effective ionic normality. c_l equals the stoichiometric anion normality, since no association is assumed for ions charged in the same sense as the polymeric ion. However, only a fraction f_m of the counterions m remains unassociated, so that

$$c_m = r_m f_m$$

where r_m is the stoichiometric concentration of counterions m. Similarly, if only i groups of s ionizable groups on the polymer carry a charge, then

$$c_{l'} = c_p (i/s)$$

where c_p is the polyion normality.

For the above described system the equation of electroneutrality is

$$c_p (i/s) = \sum_{m} r_m f_m - \sum_{l}{}' c_l \tag{3}$$

Furthermore, if j_m/s is the fractional number of bound counterions per ionizable group, then

$$c_p (j_m/s) = r_m (1 - f_m) \tag{4}$$

Denoting the partially radioactive counterion species by m′, we have the additional relation

$$\frac{Q_{m'}}{N_e} = \frac{Q_p}{N_e} (j_{m'}/s) - \frac{K_{m'}}{K} \tag{5}$$

Here the net number of equivalents of labeled ion transferred to the anode compartment by the passage of N_e equivalents of electricity has been represented by $Q_{m'}$, while Q_p stands for the equivalents of polymer transferred to the anode compartment. It will be noted that eq. 5, while written in the form of transference numbers, states that the net amount of counterion moved to the anode per faraday of electricity equals the amount transferred in the bound state less the amount moving in the free state in the opposite direction. In this connection, use was made of the fact that the transference number for unassociated ions of species m′ can be written

$$t_{m'} = K_{m'}/K \tag{6}$$

Similarly, we have for the polymer ion transference number

$$t_p = \frac{Q_p}{N_e} (i/s) = \frac{K_p}{K} \tag{6a}$$

Using equations 6a, 4 and 3 with equation 5, one can solve for $r_{m'} f_{m'}$ to obtain

$$r_{m'} f_{m'} = \frac{\Lambda_p' r_{m'} - Q_{m'} K/N_e}{\Lambda_p' + \Lambda'_{m'}} \tag{7}$$

while equation 1 yields, using equations 2 and 3

$$r_{m'} f_{m'} = \frac{K - \Lambda_p'\left(\sum_{m}{}' r_m f_m - \sum_{l}{}' c_l\right) - \sum_{l}{}' c_l \Lambda_l' - \sum_{m}{}' r_m f_m \Lambda'_m}{\Lambda_p' + \Lambda'_{m'}} \tag{8}$$

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

(2) F. T. Wall and R. H. Doremus, *ibid.*, **76**, 1557 (1954).

(3) F. T. Wall and M. J. Eitel, *ibid.*, **79**, 1550 (1957).

RESULTS OF TRANSFERENCE EXPERIMENTS AT 25°

Normality of base	Normality of salt	$Q_{m'} \times 10^3$	$Q_p \times 10^3$	$\kappa \times 10^3$	$N_e \times 10^3$	pH	Λ_p	t_p	$1 - f$	j/s	i/s	$s\omega_p \times 10^{-9}$ cm./dyne-sec.
0.07 N PAA with NaOH and NaCl												
0	0.00905	−0.0627	0.324	1.49	0.257	2.89	26.9	0.00655	0.102	0.00132	0.0052	33.4
0	.0302	− .0740	0.762	3.85	.257	2.88		0.0169	.424	.0183	0.0057	
0	.0604	− .114		7.00	.317	2.87			.454	.0392		
0.0237	0.00604	−0.110	0.407	1.84	0.324	5.29	33.1	0.255	0.319	0.135	0.203	1.05
.0237	.0121	− .112	.294	2.47	.324	5.21	32.1	.178	.280	.143	.195	1.06
.0237	.0211	− .132	.132	3.41	.310	5.13	20.7	.0913	.194	.124	.215	0.62
.0237	.0302	− .128	.102	4.34	.310	5.07	20.4	.0673	.173	.133	.205	0.64
0.0474	0.00604	−0.0300	0.363	2.43	0.336	6.57	37.5	0.319	0.500	0.382	0.295	0.82
.0474	.0151	− .0706	.235	3.34	.336	6.48	33.3	.204	.432	.385	.291	.74
.0474	.0302	− .126	.187	4.88	.439	6.34	29.8	.122	.353	.391	.286	.67
.0474	.0453	− .139	.137	6.43	.439	6.23	28.6	.0872	.299	.396	.280	.66
0.0695	0.00905	−0.0132	0.299	2.97	0.396	8.48	32.1	0.268	0.569	0.638	0.355	0.64
.0695	.0302	− .0612	.178	5.16	.396	8.38	33.1	.147	.467	.665	.328	.65
.0695	.0453	− .0954	.190	6.70	.521	8.32	34.9	.112	.418	.686	.307	.74
.0695	.0604	− .130	.138	8.19	.521	8.23	31.0	.0820	.368	.682	.310	.65
0.07 N PAA with $Sr(OH)_2$ and $Sr(NO_3)_2$												
0	0.00270	−0.0257	0.527	0.778	0.176	2.90	33.4	0.0353	0.162	0.00313	0.0117	18.4
0	.00491	− .0323	.629	1.034	.176	2.89	52.9	.0297	.145	.00505	.00829	41.3
0	.00768	− .0623	.914	1.35	.276	2.88	63.6	.0220	.111	.00610	.00666	61.8
0	.0132	− .121		1.95	.276	2.87		.0214	.946	.00895	.00143	
0.00752	0.00270	−0.129	0.512	0.612	0.297	3.88	15.1	0.0896	0.393	0.0287	0.0519	1.88
.00752	.00491	− .147	.377	0.841	.341	3.84	13.3	.0526	.349	.0310	.0475	1.81
.00752	.00768	− .142	.277	1.122	.341	3.80	13.0	.0332	.317	.0344	.0408	2.06
0.0150	0.00270	−0.0722	0.470	0.632	0.254	4.32	16.7	0.112	0.612	0.0775	0.0604	1.79
.0150	.00436	− .0551	.226	0.820	.167	4.28	15.9	.0823	.559	.0775	.0608	1.69
.0150	.00602	− .0257	.140	1.002	.0957	4.24	21.0	.0811	.533	.0800	.0554	2.45
0.0284 N SMAC with $Sr(OH)_2$ and $Sr(NO_3)_2$												
0	0.00491	−0.0282	0.284	1.09	0.156	2.87	69.9	0.0514	0.112	0.0097	0.0282	16.1
0	.00768	− .0273	.285	1.42	.156	2.82	91.7	.0290	.140	.0189	.0158	37.5
0	.0132	− .0483	.275	2.02	.208	2.79	94.2	.0121	.104	.0241	.0092	66.6
0.00376	0.00270	−0.0553	0.296	0.491	0.208	3.65	24.6	0.0586	0.436	0.0496	0.0412	3.87
.00376	.00436	− .0748	.253	.679	.251	3.60	24.1	.0362	.368	.0525	.0360	4.34
.00376	.00602	− .0463	.450	.884	.251	3.55	55.9	.0508	.331	.0570	.0283	12.8
0.00752	0.00214	−0.0583	0.375	0.415	0.265	4.24	20.7	0.0891	0.599	0.102	0.0629	2.13
.00752	.00325	− .0620	.274	.554	.240	4.19	22.2	.0741	.532	.101	.0651	2.21
.00752	.00445	− .0023	.487	.688	.240	4.15	49.1	.0927	.525	.110	.0457	6.94
0.07 N PAA with $Zn(OH)_2$ and $ZnCl_2$												
0.00488	0.00386	−0.108	0.682	0.875	0.309	3.48	27.6	0.125	0.155	0.0096	0.0565	3.16
.00973	.00386	− .103	.719	1.056	.309	3.70	35.1	.221	.244	.0237	.0952	2.38
.0137	.00386	− .157	.708	1.164	.417	3.87	28.3	.222	.267	.0335	.131	1.40
.0195	.00386	− .144	.633	1.394	.417	3.96	30.3	.268	.312	.0520	.176	1.11
0.0284 N SMAC with $Zn(OH)_2$ and $ZnCl_2$												
0.00168	0.00386	−0.0573	0.432	0.833	0.280	3.22	45.3	0.0789	0.184	0.0179	0.0512	5.72
.00335	.00386	− .0719	.366	.763	.280	3.48	35.1	.0939	.246	.0312	.0719	3.16
.00503	.00386	− .0761	.314	.746	.267	3.70	30.8	.110	.297	.0466	.0939	2.13
.00670	.00386	− .0797	.309	.794	.267	3.89	32.4	.149	.306	.0570	.129	1.63

Solving equations 7 and 8 for Λ'_p, we have

$$\Lambda'_p = \frac{\kappa + Q_{m'}\kappa/N_e - \sum_{l}' c_l\Lambda'_l - \sum_{m}' r_m f_m \Lambda'_m}{r_{m'} + \sum_{m}' r_m f_m + \sum_{l}' c_l} \qquad (9)$$

Using literature values of equivalent conductances and transport numbers of reference electrolytes,[4-7] $r_{m'}$, $f_{m'}$ and $\Lambda_{m'}$ were then adjusted simultaneously by trial and error calculations using equation 8, as described previously.[1]

Experimental

A discussion of the transference apparatus and materials used and the experimental procedures has been given previously.[1,3]

Radioactive zinc-65 was furnished by the Oak Ridge National Laboratories in form of metal turnings. Weighed amounts of zinc were dissolved in excess hydrochloric acid and dried at 150° to leave the chloride only, before standard solutions were made up.

Zinc hydroxide was freshly prepared by precipitation from zinc chloride solution with sodium hydroxide. The precipitate was washed carefully to remove all sodium and chloride ions and was then allowed to react with the polymeric

[4] "International Critical Tables," Vol. 6, McGraw-Hill Book Co., New York, N. Y., pp. 229 ff, 309 ff.

[5] L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932).

[6] D. M. Egan and J. R. Partington, *J. Chem. Soc.*, 191 (1945).

[7] A. C. Harris and H. N. Parton, *Trans. Farad. Soc.*, **36**, 1139 (1940).

acids for several days under vigorous agitation. Subsequently, the reaction mixture was filtered and diluted with polymeric acid solution until all cloudiness had disappeared. The resulting solution was standardized by drying aliquot portions and weighing the total amount of solute. These samples were also ignited in a muffle furnace and weighed again. From the weight of zinc oxide obtained in this manner and from the initial weighing, the normality of polymer and its degree of neutralization could be determined.

Results and Discussion

In Figs. 1 and 2 some binding data are shown graphically in terms of the average fractional number of counterions associated with each carboxyl group, $j_{\mathrm{m}'}/s$. The steep curves are given for partially neutralized polyacrylic acid only, while the branches of the plots were obtained by further addition of neutral salt. In addition to the experimental points, the points at which the branches meet were utilized in these graphical representations.

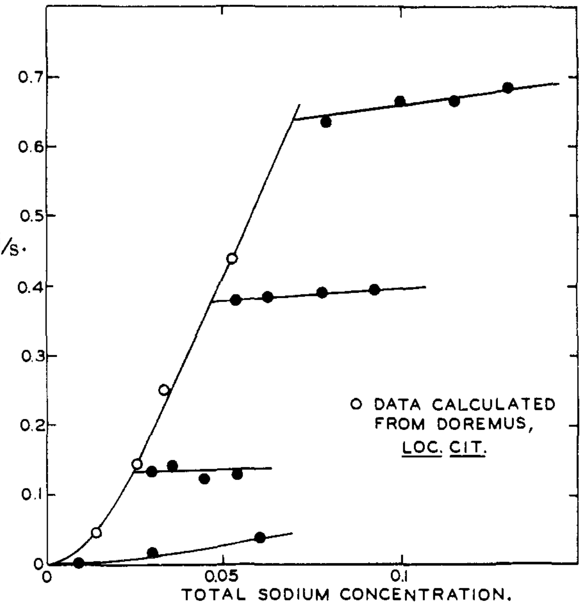

Fig. 1.—Sodium ion association in aqueous mixtures of 0.07 N PAA, NaOH and NaCl.

It was found that the addition of sodium chloride to partially neutralized polyacrylic acid does not affect the total sodium association appreciably. The small increase of (j/s) with salt concentration indicates that the chloride ions tend to stay away from the polymeric ion with its large negative charge, thereby keeping an almost equivalent number of sodium ions outside of the region of binding.

With divalent strontium ions, however, quite a pronounced increase of (j/s) with strontium nitrate concentration was observed. This was to be expected, since the nitrate ions are less effective in keeping the doubly charged strontium ions away from the highly charged polyions.

It will be seen readily that the branches of Figs. 1 and 2 become steeper with increasing degree of neutralization. Since the polyion charge increases also with the degree of neutralization, it appears plausible that the small anions become less effective in holding counterions away from more strongly charged macroions.

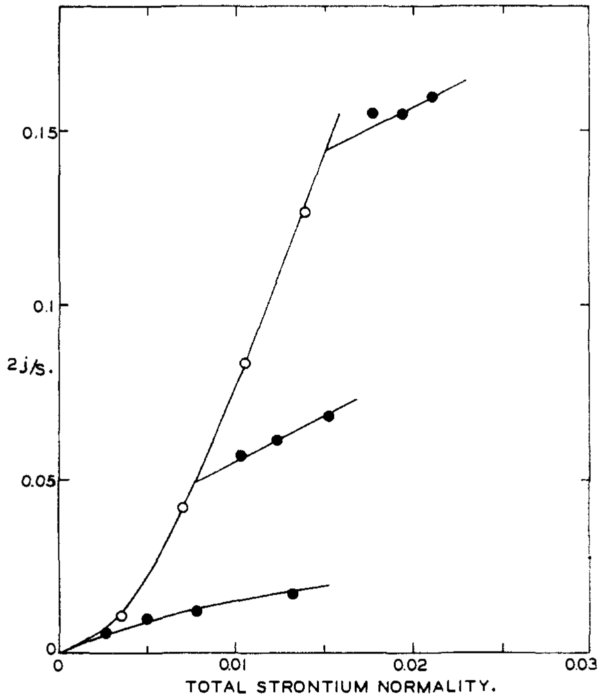

Fig. 2.—Strontium ion association in aqueous mixtures of 0.07 N PAA, $Sr(OH)_2$ and $Sr(NO_3)_2$.

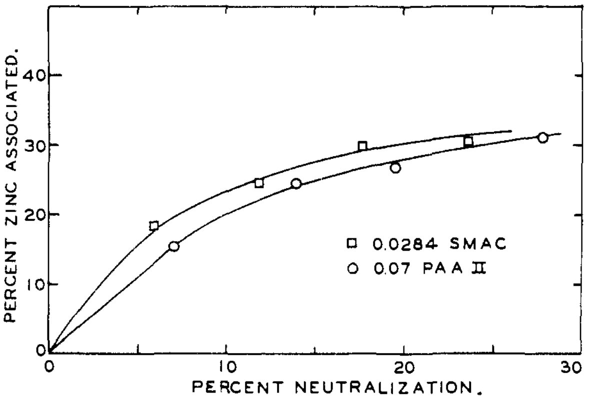

Fig. 3.—Zinc ion association with partially neutralized polymeric acids.

The dissociation of the unneutralized carboxyl groups was not entirely independent of the addition of neutral salt. Thus it was found that the pH decreased measurably with increased neutral salt concentration. Although this behavior for polymer electrolytes is at variance with the usual behavior for small electrolytes, a reasonable explanation is readily forthcoming. When the concentration of neutral electrolyte is increased, partial substitution of hydrogen ions by sodium or strontium ions will take place within the polymeric coil. Thus the polymeric electrolyte acts like a microscopic ion exchange resin, since it can provide hydrogen ions to replace metal ions in the surrounding solution.

Upon addition of salt to partially ionized polyelectrolytes, the number of small unbound ions in solution is increased sharply, and the polyion transference number decreases accordingly. Of course, increased counterion binding also reduces the polyion charge, and hence promotes further diminution of the polyion transport number. On the other hand, the polyion mobility increases markedly with salt concentration. This effect is attributed to the shrinkage of the polymer coil in solutions of high ionic strength.

Although the presence of neutral salt increases the extent of counterion binding, the association of zinc ions with partially neutralized polyacids remains small, although gelation takes place in medium concentration ranges. The experimental data are shown in Fig. 3, indicating association comparable with that shown by sodium ions.[2] This surprisingly small interaction may be due to ion hydration, which could prevent a close approach of zinc ions to any carboxylate group. If the ions have to be dehydrated before association can take place, energetic considerations may explain the observed behavior. In spite of this weak interaction, precipitation took place whenever the low neutralization range was exceeded, presumably because zinc ions can attach themselves to several carboxylate groups, resulting in the formation of polymer clusters. A similar effect was observed with strontium ions, especially in the presence of neutral salt.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Thermodynamic Properties of Technetium and Rhenium Compounds. VI. The Potential of the ReO_3/ReO_4^- Electrode and the Thermodynamics of Rhenium Trioxide[1,2]

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The potential of the ReO_3/ReO_4^- electrode has been measured over a wide range of concentration and *p*H and the standard electrode potential for the half reaction $ReO_3 + H_2O = ReO_4^- + 2H^+ + e^-$ has been found to be -0.768 ± 0.005 volt. The cell was demonstrated to be satisfactorily reversible by the close agreement of the standard potential calculated from measurements in both acidic and basic solutions, as well as from the reasonable entropy values obtained from a determination of the temperature coefficient. The thermodynamic functions for $ReO_3(c)$ were found to be -146.1 ± 0.8 kcal. mole^{-1}, -128.1 ± 0.8 kcal. mole^{-1} and 19.3 ± 2.5 cal. mole^{-1} deg.$^{-1}$ for the heat of formation, free energy of formation and the entropy, respectively. The revised potential diagram for rhenium in acid solutions becomes

$$\begin{tikzcd}
Re \arrow[r, dash, "-0.260"] \arrow[rrr, dash, bend right, "-0.367"'] & ReO_2 \arrow[r, dash, "-0.385"] \arrow[rr, dash, bend left, "-0.510"] & ReO_3 \arrow[r, dash, "-0.768"] & ReO_4^-
\end{tikzcd}$$

Introduction

In continuation of our general program to characterize the compounds of technetium and rhenium the potential of the rhenium trioxide–perrhenate half-cell has been determined. These data are of importance because of the discordant results previously obtained for the heat of formation of $ReO_3(c)$[3,4] by combustion calorimetry. Further, direct potential measurements establish more accurately the trend toward disproportionation of ReO_3. Finally, collection of data on reversible oxide electrodes is in itself of interest because of the obviously more complicated nature of the electrode process. Thus reversible potentials have been reported for the MnO_2/MnO_4^-,[5] TcO_2/TcO_4^-[6] ReO_2/ReO_4^-,[7] Hg/HgO,[8] Bi_2O_3/Bi_2O_4,[9] Sb/Sb_2O_3[10] and As/As_2O_3[11] electrode systems. Elucidation of some of the factors which influence reversible electrodes will be the subject of a further communication.

Experimental

Chemicals.—Rhenium heptoxide, used as a starting material in the preparation of rhenium trioxide, was obtained from the University of Tennessee. Purification and dehydration were carried out by vacuum sublimation. This sublimate was dissolved in distilled water to prepare perrhenic acid solutions or transferred by resublimation into various reaction vessels.

Rhenium trioxide was prepared by two reportedly dependable methods involving reduction of rhenium heptoxide by carbon monoxide[12] and dioxane[12,13] at moderate temperatures. It has been our experience that the material produced by the heating of the Re_2O_7–dioxane complex is frequently much darker in color than the normally bright red trioxide obtained from the direct reduction of Re_2O_7 by carbon monoxide. Supposedly the darker color indicates the

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1525.

[2] For the preceding paper of this sequence see J. W. Cobble, G. D. Oliver and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5786 (1953).

[3] W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 27 (1932); see also "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1948.

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[7] Z. Z. Hugus as reported by W. M. Latimer, "Oxidation-Potentials," Prentice-Hall, New York, N. Y., 1952, p. 243.

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[9] E. Baur and W. Lattmann, *Z. Elektrochem.*, **40**, 582 (1934).

[10] R. Schuhmann, THIS JOURNAL, **46**, 52 (1924).

[11] Ref. 7, p. 1444.

[12] L. F. Audrieth, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., New York, N. Y., 1950, pp. 186, 187.

[13] H. Nechamkin, A. N. Kurtz and C. F. Hiskey, THIS JOURNAL, **73**, 2828 (1951).