All triple points were determined in triplicate and the average value is included in Table III.

A green solvate $CuCl_2{\cdot}2H_2O{\cdot}(C_2H_4)_2O_2$ was separated from solution and attempts were made to dry it over a mixture of an excess of the solvate and some partially desolvated material in a desiccator, but all attempts failed. It was dried repeatedly between filter papers until a constant analysis was obtained. Analysis of the crystals for water and cupric chloride gave the results

	Experimental, %	Theoretical for $CuCl_2{\cdot}2H_2O{\cdot}(C_2H_4)_2O_2$, %
Cupric chloride	51.9 ± 0.2	52.00
Water	13.8 ± 0.3	13.93

This solvate was relatively unstable in air, tending to lose dioxane.

A light blue solvate $CuCl_2{\cdot}2H_2O{\cdot}2(C_2H_4)_2O_2$ was separated from solution and dried over a mixture of an excess of the solvate and some partially desolvated material in a desiccator. This was continued over a period of several months, until no further change in mass resulted. No decomposition of the crystals was indicated during the process. Analysis of the crystals for water and cupric chloride gave the results:

	Experimental, %	Theoretical for $CuCl_2{\cdot}2H_2O{\cdot}2(C_2H_4)_2O_2$, %
Cupric chloride	38.3 ± 0.2	38.79
Water	10.7 ± 0.3	10.39

This solvate was relatively unstable in air, showing a pronounced tendency to lose water.

In the extremely high dioxane concentration solutions, the stable solid phase, brown-orange in color, was dried between filter papers and analyzed for cupric chloride and water. Such analyses indicated the orange colored solid phase to be $CuCl_2{\cdot}(C_2H_4)_2O_2$ within experimental limits. The liquid above this solid was colorless and analyses for cupric chloride showed that the solid was practically insoluble in dioxane. The data for this isotherm are given in Table III and are shown graphically in Fig. 5.

Summary

1. The 25° isotherms for the systems magnesium chloride–dioxane–water cadmium chloride–dioxane–water and cupric chloride–dioxane–water have been presented.

2. The new solvates $MgCl_2{\cdot}6H_2O{\cdot}(C_2H_4)_2O_2$, $CuCl_2{\cdot}2H_2O{\cdot}(C_2H_4)_2O_2$ and $CuCl_2{\cdot}2H_2O{\cdot}2(C_2H_4)_2O_2$ have been separated and identified.

NEWARK, DELAWARE RECEIVED OCTOBER 31, 1949

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

Electrolytic Properties of Aqueous Solutions of Polyacrylic Acid and Sodium Hydroxide. I. Transference Experiments Using Radioactive Sodium[1]

BY JOHN R. HUIZENGA,[2] PHILIP F. GRIEGER AND FREDERICK T. WALL

Introduction

A considerable amount of evidence available at the present time indicates that in aqueous solutions of polyacrylic acid and sodium hydroxide, the sodium ions are associated with polyacrylate ions to an important extent. The results of Kern[3] as well as those of previous workers in this laboratory are in qualitative agreement on this point. However, they are in quantitative disagreement, so additional experimental information appears necessary to clarify the situation. This paper reports such additional information obtained by transference experiments involving the use of radioactive sodium tracer.

II. Experimental

Basis of the Experiments.—The experiments here reported involved the method employed by Brady and Salley[4] for the determination of the transference number of sodium ion in sodium long-chain electrolyte solutions using radioactive sodium tracer. Their solutions contained sodium ions, long-chain anions, and large complex ions (micelles) composed of the two simple ions. In their experiments tracer concentration was initially discontinuous (at a sintered glass frit) in an otherwise uniform solution. They took the flow of radioactive sodium across this boundary to be proportional to the total flow of sodium. Thus they implicitly assumed that the rate of exchange of sodium ions between micelles and free sodium ions is effectively infinite.

In solutions containing polyacrylic acid and sodium hydroxide, it turns out that the rate of exchange of sodium ions between polyacrylate ion and sodium ion is finite. This circumstance makes the interpretation of the experiments rather difficult unless the radioactive tracer concentration is initially uniform throughout the transference cell rather than discontinuous at an initial boundary as in Brady and Salley's experiments. Accordingly, it seems appropriate to discuss briefly the use of radioactive tracers in transference experiments from a somewhat more general point of view than that adopted by Brady and Salley.

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

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[3] Kern, *Z. physik. Chem.*, **A181**, 249 (1937–1938); **A181**, 283 (1937–1938); **A184**, 197 (1939); **A184**, 302 (1939).

[4] Brady and Salley, THIS JOURNAL, **70**, 914 (1948).

For the sake of brevity the discussion is restricted to solutions containing only two kinds of ions, such as sodium and polyacrylate ions, present at concentrations n_1 and n_2, expressed as ions per cm.^{3}. The extension to systems containing any number of ions presents no difficulties, so by holding the discussion to two ions no real loss in generality is involved.

It will be further assumed that a suitable isotope is present in the system as a tracer. (In this work radioactive sodium was used for the purpose.) Denote the tracer isotope by A^* and the corresponding non-tagged constituent by A. Let p_1 and p_2 equal the total number of A and A^* atoms present in each of the ions of types 1 and 2. (In the present experiments, $p_1 = 1$ for simple sodium ions, whereas p_2 is a relatively large number for the polyacrylate ions.) Let ρ_1 and ρ_2 denote the fractions of the aforementioned constituents which are of the tracer variety. The total concentration of tracer atoms will accordingly be equal to $n_1p_1\rho_1 + n_2p_2\rho_2$.

Suppose that in the absence of any kind of field the exchange rate of A^* between the two species is given by the law.

$$-n_1p_1\partial\rho_1/\partial t = +n_2p_2\partial\rho_2/\partial t = k(\rho_1 - \rho_2)$$

Then the two equations of continuity are

$$\begin{aligned} -\partial(n_1p_1\rho_1)/\partial t &= \operatorname{div} \mathbf{J}_1^* + k(\rho_1 - \rho_2) \\ -\partial(n_2p_2\rho_2)/\partial t &= \operatorname{div} \mathbf{J}_2^* - k(\rho_1 - \rho_2) \end{aligned}$$

where $\mathbf{J}_1^*$ is the flow of A^* in species 1, expressed in atoms or ions per sec. per cm^2. The flow[5] is given by

$$\mathbf{J}_1^* = \rho_1 n_1 p_1 \omega_1 e_1 \mathbf{E} - k_B T \omega_1 \operatorname{grad} \rho_1 n_1 p_1$$

where ω_1 is the mobility, e_1 is the ion charge, and $\mathbf{E}$ is the electric field intensity. Then if n_1, n_2, and $\mathbf{E}$ are uniform in space, and if the ordinary diffusion of the tracer can be neglected in comparison with that caused by the electric field, the equations for the one-dimensional case are

$$\begin{aligned} -\partial\rho_1/\partial t &= V_1\partial\rho_1/\partial x + (\rho_1 - \rho_2)k/n_1p_1 \\ -\partial\rho_2/\partial t &= V_2\partial\rho_2/\partial x - (\rho_1 - \rho_2)k/n_2p_2 \end{aligned} \tag{1}$$

where $V_1 = \omega_1 e_1 E$ and $V_2 = \omega_2 e_2 E$.

The equations (1) are particularly simple when the exchange constant is either infinite or zero. In the limit as $k \to \infty$, $\rho_1 \to \rho_2 = \rho$ and (1) becomes

$$-\partial\rho/\partial t = U\partial\rho/\partial x \tag{1'}$$

where $U = (V_1n_1p_1 + V_2n_2p_2)/(n_1p_1 + n_2p_2)$. The general solution of (1′) is

$$\rho = \rho(x - Ut)$$

For example, if ρ were initially discontinuous, the discontinuity would move in an electric field with a velocity U. In an infinite tube of uniform cross section, then, with initial conditions $\rho_1 = \rho_2 = \rho_0$ for $x < 0$, $\rho_1 = \rho_2 = 0$ for $x > 0$, the number of A^* atoms passing the point $x = 0$, per cm.^{2}, in time t, is

$$\rho_0(n_1p_1 + n_2p_2)Ut = \rho_0(V_1n_1p_1 + V_2n_2p_2)t$$

assuming $U > 0$.

For the other extreme, with $k = 0$, equations (1) become simply

$$\begin{aligned} -\partial\rho_1/\partial t &= V_1\partial\rho_1/\partial x \\ -\partial\rho_2/\partial t &= V_2\partial\rho_2/\partial x \end{aligned} \tag{1''}$$

Hence if ρ_1 and ρ_2 were initially discontinuous, the discontinuities would move independently with velocities V_1 and V_2, respectively.

If the initial conditions are $\rho_1 = \rho_2 = \rho_0$ for all x, then the flow of A^* equals ρ_0 times the flow of $(A + A^*)$ for all values of k. Therefore, in a transference experiment, if one desires to use the transfer of A^* to measure the transfer of $A + A^*$, it is necessary to make the initial concentration of tracer uniform throughout the cell unless it can be shown that the rate of exchange is practically infinite. In this instance, as indicated above, the same information can be gained from experiments in which tracer is placed on only one side of an initial boundary. Whenever possible it is advantageous to carry out the experiment in this way for then the radioactive counting accuracy is improved.

For polyacrylic acid–sodium hydroxide mixtures the exchange rate of sodium ion between polyacrylate ion and free sodium ion is not effectively infinite. Thus in a number of preliminary experiments tracer was added to the cathode side of the transference cell only. After the passage of current, some tracer was found on the anode side. Conversely, tracer was also found to move from the anode to the cathode side. But if the rate of exchange were infinite, tracer would appear to move in only one direction, according to equation (1′).

On the other hand the rate of exchange is certainly not zero. As far as the experiments just mentioned are concerned, zero exchange rate is a possibility, for equations (1″) show that tracer could appear to move in both directions. To test this possibility the following pair of experiments was performed. In both experiments, tracer was placed initially in the cathode side and its movement to the anode side determined. In one experiment, tracer was added to the sodium hydroxide used to neutralize the polyacrylic acid, whereas in the other, tracer was added to the cathode solution just before starting the current. The electrolysis was allowed to take place for a relatively short time (ten minutes), but little difference in the quantity of radioactive sodium transported to the anode side was found between the two experiments. Accordingly it is concluded that the exchange is rapid but not infinite.[5a]

For all of the experiments here reported, radioactive sodium concentrations, as well as the stoichiometric concentrations of polyacrylic acid and sodium hydroxide, were initially made uniform throughout the cell. The total flow of sodium

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(5) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(5a) Subsequent experiments of this type on Aerosol-O. T. solutions showed that virtually no radioactive sodium was moved toward the anode when tracer was initially added only to the cathode side. On the basis of this test, there is no reason to suppose that the results of Brady and Salley (ref. 4) are in error.

was established by radioactive count. The total flow of solute was determined gravimetrically, and hence, by difference, the flow of polymer was computed. The radioactive counting technique simply served as a convenient and rapid analytical method for total sodium transported.

By simple stoichiometry, we see that if

N_e = total equivalents of electricity
g = increase in weight of solute in anode compartment (in grams)
q_2 = increase in equivalents of polymeric anion in anode compartment
q_1 = increase in equivalents of sodium in anode compartment
c = stoichiometric concentration of polyacrylic acid in equivalents per liter
= (1/72.1) (grams of polyacrylic acid per liter)
r = stoichiometric concentration of sodium hydroxide in equivalents per liter

then

$$g = 71.1q_2 + 23q_1 + q_2(1 - r/c) + X$$

where X represents the change in weight due to flow of hydrogen and hydroxyl ions, as well as that due to the electrode reaction (formation of hydrogen ions). In all of the present experiments X is negligible. Thus to an extremely good approximation q_2 is related to the observables by

$$q_2 = (g - 23.0q_1)/(72.1 - r/c) \qquad (2)$$

Apparatus and Procedure. Transference Experiments.—The transference cell simply consisted of a horizontal straight glass tube, 20 cm. long, 20 mm. in diameter with a sintered glass frit (Pyrex, coarse) sealed to the tube near its center. The electrodes, both of bright platinum, were sealed into the tube near its ends. Above the electrodes were filling tubes, which permitted the escape of gas during electrolysis. Thus the solution was divided into only two parts; no attempt was made to work with one or more "middle portions."

The current was regulated by means of a variable resistance in series with the cell. The total quantity of electricity passed through the cell was computed from current-time observations and was checked by means of a silver coulometer. In no experiment was more than one-tenth of the polyacrylic acid originally present in one compartment transported to the other.

The change in weight of total solutes was determined by evaporating to dryness two 20-ml. aliquots from each compartment. The four observations were always in good agreement.

The experiments were carried out at room temperature, in the neighborhood of 25°, without thermostating.

It appears unlikely that significant errors were caused by endosmosis or by the establishment of thermal gradients. Thus when identical solutions of 0.04 N polyacrylic acid 80% neutralized with sodium hydroxide were electrolyzed at two different currents (4×10^{-3} and 1×10^{-3} amp.) the quantity q_1/N_e was found to be nearly constant. All the experiments reported below (Section III) were carried out with currents in the range 2×10^{-3} to 4×10^{-3} amp. The field strength was between 1 and 4 volts/cm. As direct evidence that endomosis was negligible, it was observed that there was never any appreciable difference in height of solutions in the filling tubes during electrolysis.

Conductance Measurements.—A Jones type bridge, designed and built by Cooke[6] was used. The cell electrodes were black platinized. Resistance measurements were made at only one frequency, 1000 cycles/sec. The cell was thermostated at 25 ± 0.1°.

***p*H Measurements.**.—A Beckman glass electrode *p*H meter (model G) was used. Precise values of the hydrogen ion concentration are not required for any of the calculations made below.

Radioactive Counting Measurements.—The radioactivity of the solutions was determined in a glass jacketed Geiger counter tube with a conventional amplifying and scaling circuit. Sufficient counts were taken to make the probable counting error less than ±1%.

Materials.—The polyacrylic acid was prepared from pure acrylic acid furnished by the Minnesota Mining and Manufacturing Company. The polymerization was carried out by a method similar to that of Condo, Krister and Lundquist.[7] Concentration of polyacrylic acid solutions was determined by evaporation of aliquot portions to dryness. The polyacrylic acid–sodium hydroxide mixtures were prepared using sodium hydroxide solutions containing Na^{22} as tracer.[7a]

Sodium hydroxide was freed from sodium carbonate by the method of Pierce and Haenisch.[8] The concentration of the base was determined by titration against potassium acid phthalate.

The specific conductance of the water used in making solutions was in the neighborhood of 1×10^{-6} ohm.$^{-1}$ cm.$^{-1}$.

III. Results

In Table I the experimental results are given for three stoichiometric acid concentrations, c, as a function of per cent. neutralization, 100 r/c. The symbols g, q_1, q_2, r and N_e are defined in section II, with q_2 calculated from equation (2). Each g and q_1 value is the average of four and two separate determinations, respectively. The specific conductance of the solvent has been subtracted from the total conductance of the solutions to yield the κ values given in Table I.

TABLE I

TRANSFERENCE, CONDUCTANCE AND *p*H MEASUREMENTS ON AQUEOUS MIXTURES OF POLYACRYLIC ACID AND SODIUM HYDROXIDE

% Neutral, 100 r/c	*p*H	$10^4 \times$ κ in ohm.$^{-1}$ cm.$^{-1}$	$10^2 \times$ g in g.	$10^5 \times$ q_1 in equiv.	$10^4 \times$ q_2 in equiv.	$10^4 \times$ N_e in equiv.
		Series 1.	$c = 0.0151\ N$			
0	3.39	1.472	0.77	....	1.07	0.62
9.60	4.45	1.176	0.78	−1.37	1.13	.28
24.0	5.41	2.381	1.67	−3.29	2.42	.93
41.3	6.21	3.457	1.35	−1.59	1.94	.93
61.7	6.96	4.179	1.27	+1.60	1.72	.93
81.6	7.80	4.573	1.17	+3.53	1.53	.93
97.9	8.96	5.344	1.00	+4.35	1.27	.93
		Series 2.	$c = 0.0378\ N$			
9.60	4.25	2.449	3.85	−7.32	5.59	1.54
24.0	5.11	5.419	3.60	−8.87	5.30	2.24
41.3	5.88	8.062	3.91	−4.33	5.61	2.98
61.7	6.68	9.829	3.74	+3.31	5.13	2.98
81.6	7.44	11.01	3.36	+6.82	4.50	2.98
97.9	8.78	11.40	2.66	+9.70	3.43	3.00
		Series 3.	$c = 0.1189\ N$			
61.7	6.20	30.70	3.28	−1.00	4.62	2.98

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(6) Cooke, University of Illinois Thesis, 1936.

(7) Condo, Krister and Lundquist, U. S. Patent 2,286,062, June 9, 1941.

(7a) The tracer was obtained from Prof. A. L. Hughes of Washington University, St. Louis, Missouri.

(8) Pierce and Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1943.

Of the various quantities measured, q_1 (which is essentially the difference between two approximately equal quantities), has the greatest percentage uncertainty. Accordingly it has been used (*cf.* Section IV) only as a relatively minor correction factor in the final calculations.

It is notable that q_1 is small compared to q_2 and hence that the polymer anion carries roughly half the sodium over most of the range. Below above 50% neutralization the flow of sodium as sodium ions is greater than that in polymer, above 50% neutralization the converse is true. The interesting curve obtained by plotting q_2/N_e against per cent. neutralization is shown in Fig. 1.

IV. Discussion

Calculation of the Fraction of Sodium Associated, Polymer Ion Transference Number, Equivalent Conductance, etc.—Throughout this discussion it is assumed that there exists in each polyacrylic acid–sodium hydroxide solution only one species of polymeric anion and that the solvent velocity is zero.

Let c, c_{Na}, c_H and c_{OH} be, respectively, the stoichiometric polyacrylic acid, free sodium ion, hydrogen ion and hydroxide ion concentrations, all expressed in equivalents per liter

Also let κ, κ_p, κ_{Na}, κ_H and κ_{OH} be, respectively, the total specific conductance minus the solvent conductance, the contribution to the specific conductance due to polymer ion, sodium ion, hydrogen ion and hydroxide ion, expressed as usual in ohm.$^{-1}$ cm.$^{-1}$. q_2, N_e, and r are the same as in section II

And finally, i = number of charges on polymer ion; j = number of sodium ions associated with each polymer ion; s = degree of polymerization = number of monomer units per polymer unit; f = fraction of sodium ions not associated with polymer

Then

$$\kappa = \kappa_p + \kappa_{Na} + \kappa_H + \kappa_{OH}{}^{9} \qquad (3)$$

where

$$\kappa_p = c\Lambda'_p i/s$$
$$\kappa_{Na} = rf\Lambda'_{Na}$$
$$\kappa_H = c_H \Lambda'_H$$

where for convenience Λ' has been written for $10^{-3}\ \Lambda$. The fraction of the current carried by polymer ion, t_p, is given by

$$t_p = q_2 i/sN_e = \kappa_p/\kappa$$

The equation of electroneutrality is

$$ci/s = c_H + rf - c_{OH}$$

On combining these relations, there is obtained

$$\kappa - c_H(\Lambda'_H + \kappa q_2/cN_e) - c_{OH}(\Lambda'_{OH} - \kappa q_2/cN_e) = fr(\Lambda'_{Na} + \kappa q_2/cN_e)$$

from which f can be computed. Also, from the sodium balance equation we see that

$$j/s = r(1 - f)/c$$

Furthermore, from the flow equation and (3)

$$s\omega_p = (6.508 \times 10^6\ \Lambda_p/(i/s))\ \text{cm./sec. dyne}$$

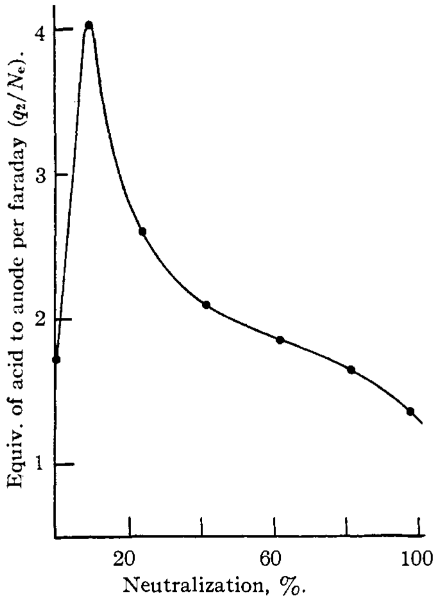

Fig. 1.—Equivalents of acid moving to the anode per faraday *vs.* % neutralization: ●, 0.0151 *N* polyacrylic acid.

Thus without knowing the degree of polymerization we can obtain f, t_p, Λ_p, i/s (the polymer charge fraction), j/s (the polymer sodium fraction), and $s\omega_p$.

In the above-described method for calculating f, more data and equations are used than are absolutely necessary. Thus it is possible to dispense with *p*H measurements by using the equation

$$(q_2/N_e)(j/s) - rf\Lambda'_{Na}/\kappa = q_1/N_e$$

which states that the fraction of the current carried by sodium ions bound to polymer plus the fraction of the current carried by free sodium ions equals the fraction of the current carried by the species sodium ion without reference to its condition. However the value of f so calculated is subject to greater error by reason of the more direct dependence on q_1, which is the most uncertain of the measured quantities. In the recommended procedure, involving an additional measurement, f is only weakly dependent on q_1, and hence is not subject to the same degree of uncertainty. Surprisingly, the two methods of calculation give substantially the same values for f, but we consider this fortuitous, and attach greater significance to the results calculated by the recommended method.

Estimate of the Sodium Ion Mobility.—The various quantities listed above are given in Table II. In making the calculations, Λ_H and Λ_{OH} were taken as constant and equal to 350 and 198, respectively. No significant error is caused by these approximations since κ_H and κ_{OH} are always small compared to κ. The choice of Λ_{Na} values is more important, of course, but fortunately several of the quantities are slightly dependent on Λ_{Na}. The values of Λ_{Na} used in the

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[9] There is an inappreciable error here which comes from including the conductance of the hydrogen ions of the solvent approximately twice.

computation were chosen as follows. In the first approximation f was calculated using $\Lambda_{Na} = 50$, from which an estimate of the sodium ion concentration $= rf$, was made. From a plot of Λ_{Na} in sodium chloride[10] against square root of salt concentration, Λ_{Na} values were taken corresponding to the rf values. Values of Λ_{Na} obtained in this way were used in Table II.

To give some idea of the variation of $1 - f$, t_p, etc., with Λ_{Na}, the calculations have been made for the solution $c = 0.0378\ N$, per cent. neutralization = 61.7 using three values of Λ_{Na}. Entry (b), $\Lambda_{Na} = 46.4$, was obtained by the method just described. Entry (a), $\Lambda_{Na} = 50.1$, equals Λ_{Na}^0, while entry (c), $\Lambda_{Na} = 37.0$, corresponds to Λ_{Na} in sodium chloride at concentration equal to $(^1/_2)\ (rf + ci^2/s)$ where s has been chosen as 250. The per cent. variation in all the calculated quantities is less than one-half the per cent. variation in Λ_{Na}, and Λ_p is nearly independent of the assumed value for Λ_{Na} in this range.

There may be some question as to whether or not these values of Λ_{Na} are in further doubt because of the high *solution* viscosities. Thus at $c = 0.0378\ N$ the viscosities of the pure acid solution and the 100% neutralized solution are about three and five times that of water, respectively. In spite of this, the Λ_{Na} values in aqueous sodium chloride are doubtless appropriate.

Thus other measurements made in this Laboratory[11] on the self-diffusion of sodium ion in polyacrylic acid–sodium hydroxide solutions using radioactive sodium tracer indicate that the mobility of sodium ion is not appreciably altered by the presence of polyacrylic acid.

State of the Polymer Ion.—It is interesting to note from Table II that the polymer ion conducts nearly one half the current in the range 25 to 100% neutralization. In pure acid solutions,[8,11] hydrogen ion carries virtually all the current, by reason of the large size and low charge of the polymer ion. It is clear, however, that in partially neutralized solutions the polymer ion has a large enough charge to make it a relatively good conductor. Therefore it is readily apparent why an attempt[12] to estimate the fraction of sodium ions associated with polymer, based on conductance measurements alone together with the assumption that the polymer ion conducts no current, leads to very low values.

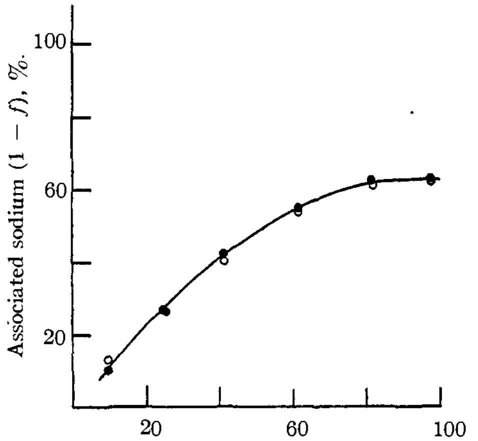

Fig. 2.—% Associated sodium *vs.* % neutralization: ●, 0.0151 N polyacrylic acid; ○, 0.0378 N polyacrylic acid.

Added hydroxide ions react almost quantitatively with the hydrogens of polyacrylic acid (only about 0.5% fail to do so) whereas sodium ions react to a lesser extent. As can be seen on inspection of Table II and Fig. 2, the fraction of sodium ions associated with polymeric anion increase monotonically. However, the quantity $1 - \Delta(rf)/\Delta r$, as shown in Table II, goes through a maximum in the neighborhood of 80% neutralization.

It will be seen from the values of i/s given in Table II and shown graphically in Fig. 3 that the charge of the polyacrylate ion increases with increase in neutralization. Moreover the charge is so great over most of the range that polyacrylate ion is a relatively good conductor despite its large size. This is readily apparent upon inspection of the Λ_p values listed in Table II and shown in Fig. 4. Λ_p reaches a maximum value at about 60% neutral, although the charge on the polymer increases monotonically. This is an interesting but not necessarily surprising result, for as the charge on the polymer ion increases, the effective volume of the ion is expected to increase

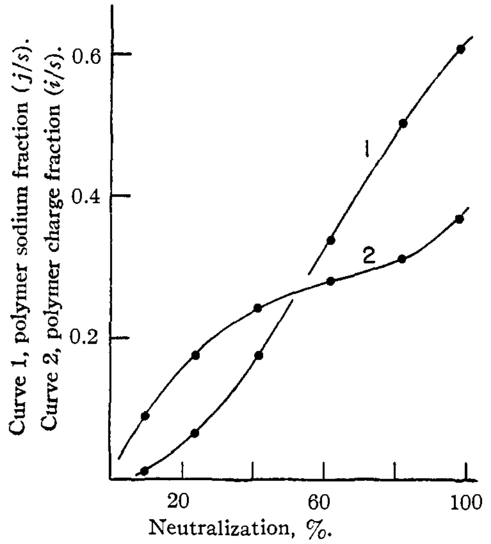

Fig. 3.—Curve 1, j/s *vs.* % neutralization; Curve 2, i/s *vs.* % neutralization: ●, 0.0151 N polyacrylic acid.

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(10) Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934); Longsworth, THIS JOURNAL, **54**, 2741 (1932).

(11) Huizenga, University of Illinois Thesis, 1949.

(12) See, for example, Kern, *Z. physik. Chem.*, **A181**, 268 (1937–1938).

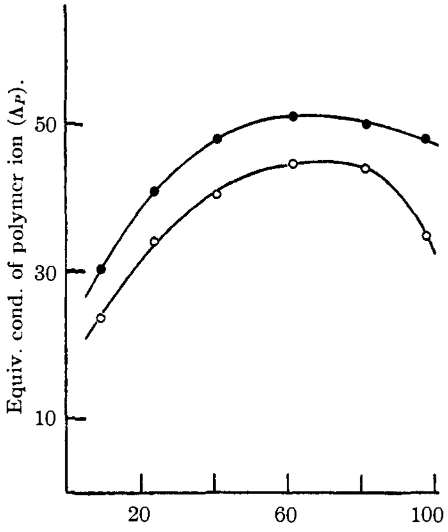

Fig. 4.—Equivalent conductance of polymer ion *vs.* % neutralization: ●, 0.0151 *N* polyacrylic acid; ○, 0.0378 *N* polyacrylic acid.

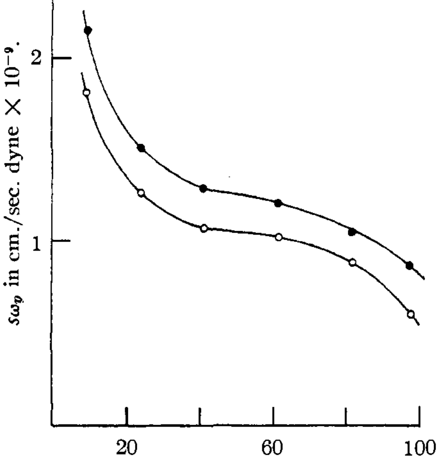

Fig. 5.—$s\omega_p$ in cm./sec. dyne × 10^{-9} *vs.* % neutralization: ●, 0.0151 *N* polyacrylic acid; ○, 0.0378 *N* polyacrylic acid.

due to the increase in intraionic electrical repulsion. As can be seen from the values of $s\omega_p$ given in Table II and Fig. 5, ω_p decreases monotonically as ion charge increases. Hence the increase in Λ_p is less than proportional to the polymer charge over the entire range of neutralization, and finally over the range 60 to 100% neutral the volume effect becomes large enough to cause a decrease in Λ_p.

According to the results of Table II, only Λ_p and $s\omega_p$ show a significant variation with acid concentration at constant neutralization, over the range investigated. The fraction of sodium associated with the anions decreases very slightly with increase in c in most instances, while the charge appears to increase by a small amount. On the other hand, Λ_p and $s\omega_p$ decrease appreciably with increase in acid concentration. A decrease in ω_p is to be expected with increase in ionic strength because of the interionic attraction effect. The decrease of ω_p with increase in neutralization at constant c can be ascribed partially

TABLE II

FRACTION OF SODIUM ASSOCIATED, POLYMER TRANSFERENCE NUMBER, EQUIVALENT CONDUCTANCE AND RELATED QUANTITIES

% Neutral, 100 r/c	Λ_{Na} used	Fraction sodium associated $1 - f$	10^2 × free sodium ion concn., c_{Na}	$1 - \Delta rf/\Delta r$	t_p	Λ_p	Polymer charge fraction i/s	Polymer sodium fraction j/s	10^{-9} × $s\omega_p$ in cm./sec. dyne
				Series 1. $c = 0.0151$ *N*					
0	...	....	....	...	0.047	....	....	....	....
9.6	48.7	0.102	0.130	0.102	.358	30.2	0.092	0.0098	2.15
24.0	48.1	.267	.265	.378	.459	41.1	.176	.064	1.51
41.3	47.8	.421	.361	.634	.500	47.9	.239	.174	1.29
61.7	47.7	.547	.422	.707	.518	51.2	.280	.337	1.21
81.6	47.5	.619	.469	.843	.513	49.9	.311	.505	1.03
97.9	47.3	.623	.558	.638	.503	48.2	.369	.610	.86
				Series 2. $c = 0.0378$ *N*					
9.6	48.0	0.135	0.313	0.135	0.307	23.5	0.085	0.013	1.81
24.0	47.1	.267	.664	.355	.417	34.0	.176	.064	1.26
41.3	46.6	.405	.928	.596	.464	40.2	.246	.167	1.07
61.7	50.1[a]	(.555)	(1.04)	...	.(470)	(44.4)	(.275)	(.342)	(1.05)
	46.4[b]	.537	1.08	.790	.490	44.6	.286	.331	1.02
	37.0[c]	(.480)	(1.21)	...	(.544)	(44.1)	(.320)	(.296)	(.89)
81.6	46.1	.603	1.22	.881	.490	44.0	.324	.492	.88
97.9	45.9	.617	1.42	.676	.427	34.4	.375	.604	.60
				Series 3. $c = 0.1189$ *N*					
61.7	44.0	.503	3.65	...	.476	40.0	.307	.310	.85

to this effect, although it seems likely in view of Table II that increase in size of the polymer ion with increase in charge is the principal factor involved.

V. Summary

1. An investigation of the system polyacrylic acid–sodium hydroxide, with water as solvent, has been made by transference experiments using radioactive sodium tracer to determine the total flow of sodium. Measurements were made over the range 0 to 100% neutralization at two stoichiometric acid concentrations, namely, 0.0151 and 0.0378 N, and at 61.7% neutralization for an acid concentration of 0.1189 N.

2. A considerable fraction of the sodium ions are associated with polymer over most of the range; about one fourth of them at 25% neutralization, about two thirds of them at 100% neutralization.

3. The fraction of sodium ions associated increases monotonically with increase in neutralization at constant acid concentration. However, at constant neutralization, this quantity appears to decrease slightly with increase in acid concentration over the six-fold range investigated.

4. Over the range 25 to 100% neutralization the fraction of the current carried by polyacrylate ion is surprisingly high and roughly constant (0.4 to 0.5).

5. With increase in neutralization, the charge and size of the polymer ion increase and the equivalent conductance of the polymer ion goes through a maximum in the neighborhood of 60% neutralization.

6. With increase in acid concentration over the range 0.015 to 0.12 N, the charge and number of sodium ions on the polymer ion remain practically constant, but the polymer ion mobility decreases appreciably.

7. The effect of finite ion exchange on transference experiments is briefly considered.

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

Separation of Organic Acids[1]

BY C. S. MARVEL AND R. D. RANDS, JR.

In connection with the problem of the structure of diene polymers we have encountered the need for a rapid and efficient method for the separation of organic acids which have some degree of water solubility. Such a method has now been developed using partition chromatography. The apparatus is simple and the procedure has been standardized so that it may be used in qualitative examinations of acid mixtures by reference to a table of threshold volumes determined with known acids. Quantitative data are obtained at the same time for acids that are separated well and the standard procedure can be easily modified or extended to allow better separation of overlapping bands. Only 5–80 mg. of an acid mixture is required.

Several methods have been used for the separation of mixtures of organic acids. They include fractional distillation of methyl esters,[2] fractional crystallization,[3] and fractional extraction.[4] Separation by distillation of esters is limited to those acids having sufficiently volatile esters. Fractional crystallization usually fails with compounds of similar solubility properties. Extraction technics have been more successful in recent years but still are not always easy to apply to complex mixtures. Partition chromatography[5] has recently been used with considerable success to separate amino acids,[6] fatty acids,[7] and some polybasic acids.[8]

In the present investigation we have tried to develop a system which would separate as many of the water-soluble acids as possible. The system reported here is similar to those described by Isherwood[8a] and by Claborn and Patterson[8b] except we have systematically increased the polarity of the developing solvent. This scheme makes it possible to separate mixtures containing from two to seven water-soluble acids and also of separating these acids from less-polar acids or other less-polar compounds. As little as 0.5 mg. of an acid can be detected in an 80-mg. mixture under proper conditions. With a larger column than the one described here, several grams of acid mixtures have been separated into their component parts.

Water adsorbed on silicic acid acts as the immobile phase. The developing liquid or eluant is made progressively more polar in order to develop the more water-soluble acids. This is

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(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) (a) Desparmet, French Patent 663,425, Feb. 17, 1928; *C. A.*, **24**, 628 (1930); (b) Rabjohn, Bryan, Inskeep, Johnson, and Lawson, THIS JOURNAL, **69**, 314 (1947).

(3) Lehman and Schroter, U. S. Patent 2,323,061, June 29, 1944.

(4) (a) Cassidy, THIS JOURNAL, **63**, 2735 (1941); (b) Ney, Crouch, Rannefeld and Lochte, *ibid.*, **65**, 770 (1943); (c) Craig, *J. Biol. Chem.*, **155**, 519 (1944); (d) Martin and Synge, *Biochem. J.*, **35**, 91 (1941); (e) Sato, Barry and Craig, *J. Biol. Chem.*, **170**, 501 (1947).

(5) Martin and Synge, *Biochem. J.*, **35**, 1358 (1941).

(6) (a) Consden, Gordon and Martin, *ibid.*, **38**, 224 (1944); (b) Stein and Moore, *J. Biol. Chem.*, **176**, 337 (1948).

(7) (a) Ramsey and Patterson, *J. Assoc. Official Agr. Chem.*, **28**, 644 (1945); (b) Ramsey and Patterson, *ibid.*, **31**, 139 (1948); (c) Ramsey and Patterson, *ibid.*, **31**, 441 (1948); (d) Elsden, *Biochem. J.*, **40**, 252 (1946).

(8) (a) Isherwood, *ibid.*, **40**, 688 (1946); (b) Claborn and Patterson, *J. Assoc. Official Agr. Chem.*, **31**, 134 (1948).