

chains are added, a point will be reached where the polysoap molecule becomes insoluble at the isoelectric point. As more dodecyl groups are added, a greater electrical charge will be needed to keep the polysoap ion in solution. Hence the precipitation region will spread on both sides of the isoelectric point. In the light of these considerations, the observation that a polysoap has a soluble and an insoluble fraction in a given KBr solution can best be interpreted as indicating polydispersity with respect to the relative dodecyl group content. The fact that despite the polydispersity the electrophoretic boundary remains sharp is a further indication that the mobility is not affected by the dodecyl group content of the polysoap ions. However, the above results suggest the possibility of solubility fractionation by the use of several KBr solutions of varying concentrations.

It is desirable to explore the nature of the charge reversal somewhat further. The fact that bromide ions are bound by the polyion even when the latter is negative indicates that factors other than coulomb forces between a bromide ion and the net charge of the polyion are responsible for the binding. Probably the hydration and possibly the polarizability of the bromide ion are involved here. Studies with other counter-ions differing in these properties from the bromide ion are under way to test this point.

The question arises as to how the polyions acquire their net negative charge. Do they bind bromide ions in excess of the stoichiometric equivalent of their pyridinium groups, or do they perhaps contain some negative groups as unintended impurities? The observed insensitivity of the electrophoretic mobility to  $pH$  excludes the presence of weakly acidic negative groups. As for strongly

acidic groups, the only ones which might be remotely possible are sulfate or sulfonate groups. The absence of these groups was shown in two ways. First, a sodium fusion test for sulfur proved negative; second, the effect of 0.05 molal barium bromide on the electrophoretic mobility of the polysoap ion in a concentrated KBr solution was shown to be negligible within the experimental uncertainty of the method (half-shaded circle in Fig. 1). If the negative charge was due to sulfate or sulfonate groups attached to the polyion, one would expect these groups to become neutralized by the barium ions,<sup>14</sup> which would have resulted in the restoration of the positive charge on the polyion. Therefore one can reach no other conclusion than that the charge reversal of the polyions is due to their binding of bromide ions in excess of the stoichiometric equivalent of pyridinium groups.<sup>15</sup>

Charge reversal effects caused by bromide and other negative ions previously have been observed in the case of certain proteins possessing both positive and negative groups.<sup>16</sup> To our knowledge this is the first time that such an effect has been definitely established for polyelectrolytes possessing only cationic groups.

**Acknowledgment.**—This investigation was supported by research grants from the Office of Naval Research and the Rutgers Research Council.

(14) M. Lerner and W. Rieman, III, *Anal. Chem.*, **26**, 610 (1954).

(15) This conclusion was previously advanced as a hypothesis to explain the observed decrease in electrical conductivity of a 0.61 *N* alcoholic lithium bromide solution upon the addition of poly-4-vinyl-*N*-*n*-butylpyridinium bromide [U. P. Strauss and R. M. Fuoss, *J. Polymer Sci.*, **4**, 457 (1949)].

(16) L. Teunissen—Van Zijp, Thesis, Leiden (1938). See also H. G. Bungenberg de Jong in "Colloid Science," Vol. II, H. R. Krut, ed., Elsevier Publishing Co., New York, N. Y., 1949, pp. 299-300.

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## Titration Studies as a Means of Characterizing Anion-exchange Resins<sup>1</sup>

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Several recently developed anion-exchange resins of the substituted quaternary ammonium type with polystyrene-divinylbenzene matrices have been titrated in the hydroxide form in aqueous solution. The usefulness and reliability of the titration method of studying resinous exchangers are discussed in some detail. Nearly all resins showed from 1-5% capacity attributable to ternary amine or other types of weak bases. Qualitative correlations have been obtained between the structure of the resin ionic groups and the "basic strength" of the resin deduced from the shape of the titration curves. The titration behavior of the weaker quaternary ammonium resins considered as polyelectrolytes was found to be described by  $pH = pK - n \log (1 - \alpha)/\alpha$  over a limited range, where  $pK$  and  $n$  are constants and  $\alpha$  is the degree of neutralization. Values of  $n$  of 1.3-1.5 were obtained in the absence of added salt.

Titration curves have been widely used in characterizing ion exchange materials.<sup>3-6</sup> From a

(1) Presented before the Division of Physical and Inorganic Chemistry at the 122nd National Meeting of the American Chemical Society, Atlantic City, September, 1952.

(2) Based on a thesis submitted by Ralph W. Gable to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Master of Arts, June, 1953.

(3) H. P. Gregor and J. I. Bregman, *THIS JOURNAL*, **70**, 2370 (1948).

(4) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, 3299 (1949).

(5) R. Kunin and R. J. Myers, "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 26 ff.

(6) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1951).

chemical point of view these substances can be regarded as a collection of exchange groups—usually ionic—tied to an inert matrix. Much can be learned about their exchange sites from  $pH$  titrations since a cation exchanger may be readily put in the  $H^+$  ion form and an anion exchanger in the  $OH^-$  ion form. Such titrations have been used to indicate (a) exchange capacity, (b) polyfunctionality and (c) the degree of dissociation of exchange groups.

Alternatively, considering their electrical properties, ion exchange materials may be regarded primarily as polyelectrolytes. Again titration

curves offer an approach, and they have already been employed in characterizing a variety of weak linear polyelectrolytes. Admittedly molecules of that type are more tractable theoretically than the ion exchangers, which are usually strongly ionized. Katchalsky and co-workers<sup>7</sup> and Hermans and Overbeek<sup>8</sup> in particular have made use of titration data in developing theoretical descriptions of weak linear or lightly cross-linked polyelectrolytes. Their ideas may be at least qualitatively extended to systems involving resinous ion exchangers.

In the present investigation direct titrations of the suspended, finely ground resin have been made on a relatively new series of anion exchangers of the quaternary ammonium type with polystyrene-divinylbenzene matrices. These are listed in Table I.<sup>9</sup> Titrations were carried out on the resins in the OH<sup>-</sup> ion form in aqueous solution to elucidate chemical and polyelectrolyte characteristics dependent on the type resin rather than on properties of particular samples. Two different titration procedures are discussed in the literature (1) the batchwise method of adding reagent and salt to water suspensions of the resin, equilibrating, and titrating the filtered supernatant liquid<sup>8</sup> and (2) the batchwise or continuous process of directly titrating the aqueous suspension of finely ground resin with or without added salt.<sup>4,5</sup> The second procedure appeared better adapted to the goals of this research and was selected. In the experimental section there is a careful consideration of the usefulness and reliability of titration techniques as a method of studying cross-linked polyelectrolytes.

TABLE I  
RESIN CHARACTERISTICS<sup>a</sup>

Resin functional group; R represents hydrocarbon matrix <sup>c</sup>	Exchange capacity <sup>b</sup>	
	Total (meq./dry g.) Cl <sup>-</sup> form	Weak (% of total)
RNMe <sub>3</sub> <sup>+d</sup>	3.90	2.1
RNEt <sub>3</sub> <sup>+</sup>	1.74	7.5
RNBu <sub>3</sub> <sup>+</sup>	0.76	26
RNMe <sub>2</sub> EtOH <sup>+e</sup>	3.05	2.9
RNMe(EtOH) <sub>2</sub> <sup>+</sup>	2.11	3.0
RNMe <sub>2</sub> PrOH-2 <sup>+</sup>	1.99	3.8
RNMe <sub>2</sub> Benzyl <sup>+</sup>	1.87	5.2
RNMe <sub>2</sub> Phenyl <sup>+</sup>	0.59	18
RPyridinium <sup>+</sup>	1.4	100

<sup>a</sup> All resins were made with 6% DVB. <sup>b</sup> Determined by titration of the hydroxide form. <sup>c</sup> The abbreviation PrOH-2 indicates propanol-2. <sup>d</sup> Dowex-1. <sup>e</sup> Dowex-2.

### Experimental

**Materials.**—All resins were furnished as beads in the chloride form and contained considerable amounts of polar organic impurities. Repeated alcohol and 1 N HCl washings to remove impurities were followed by deionized water rinsings until free of acid. After air drying the resin beads were finely ground. Particles of 200–325 mesh were separated

(7) (a) A. Katchalsky and P. Spitnik, *J. Polymer Sci.*, **2**, 432 (1947); (b) A. Katchalsky and J. Gillis, *Rec. trav. chim.*, **68**, 879 (1949); (c) A. Katchalsky, N. Shavit and H. Eisenberg, *J. Polymer Sci.*, **13**, 69 (1954); (d) A. Katchalsky and I. Michaeli, *Bull. Research Council Israel*, **2**, No. 3 (1952).

(8) J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).

(9) Kindly made available through G. E. Boyd, Oak Ridge National Laboratory, who obtained them from the Physical Research Laboratory, Dow Chemical Company.

by dry screening and stored in the stable chloride form in a controlled humidity atmosphere.

The water content of resin samples was ascertained by vacuum drying for 20–24 hours at 50° with a Dry Ice trap in the line. For some samples there was evidence of very slight decomposition. Longer drying at 50° produced an insignificant further loss of weight in three representative resins.

For titration weighed samples of chloride-form resin were converted to the hydroxide form without admitting carbon dioxide and washed with deionized water until the effluent gave no phenolphthalein test. The conversion was readily accomplished with all except a quinolinium type, which was not titrated. Two attempts to put that resin in other ionic forms were unsuccessful; treatment with large amounts of 1.5 N NaOH or with K<sub>2</sub>SO<sub>4</sub> solution failed to produce any significant exchange.

The titrations were made with 1 N HCl solution. Reagent grade acid (12 M) was diluted 1:1 and distilled in an all glass system. The central portion was collected and made up with deionized water to the required concentration.

Deionized water was obtained by passing distilled water through a monobed column of mixed purified Amberlite IR-120 and IRA-400 resin in hydrogen and hydroxyl form, respectively. The specific conductance of effluent water proved of the order of 10<sup>-7</sup> ohm<sup>-1</sup> cm.<sup>-1</sup>.

**Capacities.**—Capacities in milliequivalents of hydroxide ion (converted resin) per gram of dry chloride-form resin were calculated from the titration curves. Both strongly and weakly basic groups appeared to be present, and the total capacity was accordingly subdivided. The curves showed a steep end-point for the former about pH 7; for the weak base the end-points appeared to be at pH 4.5–6.

**Titration Procedure.**—About one gram of resin was prepared for each titration. Immediately following conversion to the hydroxide from the sample was quantitatively transferred with about 50 ml. of deionized water into a Polythene titration vessel which was then tightly stoppered. Magnetic stirring kept the resin suspended. The pH of the suspension was determined by a model G Beckman pH meter with a Beckman external glass electrode (No. 1190) and an external calomel electrode, which was connected to the system by a special KCl bridge described below. Periodically, the system was standardized against pH 4.0, 7.0 and 10.0 buffers. The temperature was kept at 29–31° for the runs. During the titration the standard HCl solution was admitted from a microburet.

Before acid was added, the resin was stirred in the deionized water for 12–60 hours. The measured pH ordinarily increased by one or two units during this period and then remained constant. When steady readings were obtained, the titration of the resin was carried out in conventional fashion except for the manipulation of the salt bridge described.

Efforts were made to keep the amount of "external" electrolyte to a minimum so that the pH curve would be characteristic of all "ionic" groups on the chain. The solution path from the calomel electrode for that reason was established through a 1 M KCl bridge immobilized by agar. In many of the determinations the bridge was also fitted with a coarse glass frit (water flowed rapidly through it under a small gravity head) at the titration vessel end. The end of the bridge was also inserted only at the time of making a measurement.

The diffusion of KCl into the suspension from the bridge appeared mainly responsible for the initial pH rise. In a few of the titrations the initial equilibration was hastened by admitting a very small amount of KCl. Potassium analyses, made by flame photometer, after titrations had reached the point of neutralization of the quaternary base indicated that the total KCl was no more than 0.002 N.

In part the initial equilibration process is believed traceable to fragmentation of the resin particles and the release of low molecular weight fragments. Microscopic examination after titration showed that an appreciable percentage of the particles were no longer 45–70 μ (250–325 mesh) in dimensions but about 1–3 μ. The increase in the total surface area should increase the number of "external" hydroxyl ions and raise the measured pH.

The time needed to establish equilibrium within the suspension after addition of a portion of HCl varied from several minutes to many hours, depending on the type of resin and the pH. The more strongly basic resins equilibrated

more quickly. In the pH region from 4–8, however, obtaining a constant pH value required from three to upwards of ten hours for many of the resins. The steady value was the one recorded. In extreme cases obtaining a value which did not vary within a period of two hours by more than 0.02 pH unit was considered to indicate equilibrium.

Measurements of the pH of a resin suspension were found to vary in reliability with the amount of added simple electrolyte. In 0.01 *N* KCl the reproducibility of the data between duplicate titrations was about  $\pm 0.02$  pH unit. When only the KCl diffusing from the salt bridge was present, however, the reproducibility fell to about  $\pm 0.12$  unit. The varying diffusion and the greater difficulty of measurements in solutions of very low conductivity are believed responsible. The differences between the curves for different resins were appreciably greater than the uncertainty in the curves, and qualitative interpretations were not affected.

**Suspension Effects.**—The difficulties of interpreting measurements on pH suspensions of polyelectrolytes such as clays and ion exchangers have been extensively discussed in recent years.<sup>6,10–13</sup> Both batch and continuous titration procedures are subject to uncertainties. These pH measurements involve typically the cell

Ag/AgCl/0.1 *N* HCl/glass membrane/

suspension: KCl:KCl Hg<sub>2</sub>Cl<sub>2</sub>/Hg  
: *c* : sat.

I II

It is the presence of the suspension which has forced a consideration of the character of the electrode response at I and the magnitude of the junction potential at II.

**Glass Electrode Response.**—The pH of an aqueous solution as measured by a glass electrode is a quantity which is quite directly related to the hydrogen ion and hydroxide ion activity of the solution. The pH of a suspension such as that of an hydroxide resin is much less easily interpreted; the principle of electrical neutrality demands that most of the hydroxyl ions remain within or near the highly charged particles rather than be evenly distributed through the medium in contact with the electrode. Exchanger particles in the size range of 1–50  $\mu$  (300 mesh and smaller) contain from 10<sup>9</sup> to 10<sup>14</sup> ionic sites, assuming a capacity of two meq./cc. In an aqueous suspension, though the resin exchange groups are ionized, the concentration of the hydroxyl ions in the solution will be small and decrease rapidly with distance from the particles.

To characterize resin behavior it is believed unnecessary that all the hydroxyl ions be free; it is required rather that the number in contact with the electrode must be representative of the ionic character, ease of diffusion, etc., for the resin. Whether this criterion is met depends on particle size and to some extent on external electrolytes. Wheaton and Bauman<sup>6</sup> found reproducibility and significance in their measurements using –200 + 400 mesh beads. The same initial size range was found suitable in this work. Smaller particles proved difficult to handle in a column in preparatory stages, and larger ones did not behave as reproducibly on titration. Collision-induced fragmentation further diminished the average size before and during the titration and improved electrode-resin contact.

The effect of added simple electrolyte must also be discussed. In titrating resin suspensions it has often been the practice to do some titrations after adding known amounts of electrolyte.<sup>5</sup> The influence of adding KCl on the pH at the start of a titration shows clearly in Table II. Essentially an exchange effect, hydroxide ions were replaced by chloride ions and the measured pH rose as the concentration of KCl was increased.

Though the displacement of hydroxyl ions into a region where they may equilibrate with the glass electrode simplifies the experimental interpretation, it modifies the true resin behavior. Actually, the added electrolyte generates a solution of KOH, and some of the weak electrolyte character of the resin tends to be "swamped out."<sup>15</sup> In the present work the added salt concentration has been minimized.

**Junction Potential.**—It is conventional to define the pH in terms of the e.m.f. of the cell pictured, which includes

TABLE II  
CONCENTRATION OF HYDROXIDE IONS IN SUSPENSIONS WITH  
KCl ADDED<sup>a</sup>

KCl concn., <i>N</i>	Measured pH	$\frac{(\text{OH}^-) \text{ exptl.}^b}{(\text{OH}^-) \text{ max.}}$
0.002	11.0	0.02
.01	11.6	.09
.1	12.0	.2
1.0	12.2	.3

<sup>a</sup> The resin was RNMe (EtOH)<sub>2</sub><sup>+</sup> OH<sup>–</sup>. <sup>b</sup> The "maximum concentration" of OH<sup>–</sup> ions was 0.05  $\pm$  0.01 *M*. It was calculated by assuming the total equivalents of hydroxide ion were dissolved as a simple electrolyte.

a liquid junction potential at II. When dealing with simple electrolyte systems, this potential is commonly minimized by utilizing an electrolyte with ions of nearly equal transference numbers as the principal current carrier at the junction. This device may not be effective in the case of insoluble polyelectrolytes where the salt gradient is formed within the membrane or suspension.<sup>10,12</sup> The difficulty arises from the high concentration of fixed charges in the polyelectrolyte material, which greatly reduces the mobilities of ions having the same sign as that of the polyion.<sup>14</sup> Ions of the opposite charge should be relatively unaffected.

Marshall's comments seem to represent the consensus of thinking on the problem.<sup>12</sup> He concludes that the junction potential will be small when formed in the presence of a suspension if the bridge electrolyte (KCl) is concentrated with respect to that of the colloid. It is also important that the bridge contacts a representative cross-section of the polyelectrolyte system. Estimating the potential requires a knowledge of transference numbers and a consideration of the Donnan effect. An overly detailed analysis of the magnitude of various potentials seems meaningless. Overbeek<sup>13</sup> has pointed out that the separation of the potential into contributions from the junction and from the Donnan effect always involves arbitrariness so that even if attempted it is not susceptible to experimental verification.

In the present study it is believed that Marshall's conditions have been met and that any potential which may have been set up was small. The salt bridges used were filled with either 1 *N* or saturated KCl in agar and the concentration of ionic sites in the suspension was 0.05 *N* or less. The suspension was well stirred and made good contact with the 8-mm. frit of the bridge, satisfying the second condition to the extent it applies to this work.

## Results

**Polyfunctional Character.**—The total exchange capacities of the resins as determined by pH titration may be compared with those measured by potentiometric analysis by Soldano and Boyd<sup>15</sup> for other samples of the same resins in the bromide form. Even when their data are recalculated on the basis of the chloride form, they are found to differ appreciably from those in Table I in most cases. Different degrees of decomposition of the resins are believed responsible.

To some extent all of the resins studied were polyfunctional; *i.e.*, they contained attached weakly basic groups in addition to the quaternary sites. Others have also reported a small degree of polyfunctional character in the strongly basic resins.<sup>6,16</sup> The titration curves showed inflection points in the pH range 4.5 to 6, a reasonable range for the end-points of binary or ternary amines. The amounts as determined from the titration curves are listed

(14) H. De Bruyn and J. Th. G. Overbeek, *Kolloid-Z.*, **84**, 186 (1938).

(15) B. A. Soldano and G. E. Boyd, *THIS JOURNAL*, **75**, 6099 (1953). By private communication from the authors, it has been learned all data in their Table II is based on the bromide form.

(16) H. P. Gregor, J. Belle and R. A. Marcus, *THIS JOURNAL*, **76**, 1984 (1954).

(10) H. Jenny, *et al.*, *Science*, **112**, 169 (1950).

(11) K. J. Mysels, *ibid.*, **114**, 424 (1951).

(12) C. E. Marshall, *ibid.*, **115**, 361 (1952).

(13) J. Th. G. Overbeek, *J. Colloid Sci.*, **8**, 593 (1953).

in Table I as percentages of the total capacity. It is known that at least some of these groups resulted from Hoffman degradation and other reactions of the quaternary ammonium groups. *E.g.*, a sample of a dimethylisopropyl alcohol resin which stood in the relatively unstable hydroxide form for five weeks showed 14% weak base rather than the 4% usually found. Both that type of decomposition and possible side reactions with primary and secondary amine impurities present during the initial quaternization are believed responsible for the polyfunctional character.

The increase in the percentage of weak base in the series of alkyl-substituted resins is surprising. Increasing thermal instability may account for this trend. Also, as Soldano and Boyd<sup>15</sup> have noted, the amount of total ionic capacity falls in the series. Thus the total capacity trend is probably a result not only of the slowness or steric hindrance of the quaternizing reaction as larger amines are used, but may also result from accelerated decomposition of the exchangers containing the larger ionic groups at the time of manufacture and subsequently.

**Alkyl- and Alkanol-substituted Resins.**—Titration curves for the highly ionized alkyl-substituted resins are similar to those of conventional strong bases. The alkanol resin curves, on the other hand, exhibit progressively larger slopes in the range of *pH* 8–10 in going from  $\text{RMe}_3\text{NOH}$  to  $\text{RMe}_2(\text{EtOH})\text{NOH}$  to  $\text{RMe}(\text{EtOH})_2\text{NOH}$  indicating the weakness of these hydroxides relative to the alkyl-substituted ones. The introduction of hydroxyl groups on the beta carbons has the expected inductive or hydrogen-bonding effect of making it more difficult to remove the quaternary ammonium hydroxide ion. Wheaton and Bauman's titration curves for Dowex 1 and 2 show the same relative trends. Recent results of Gregor and co-workers,<sup>16</sup> however, for titrations of these materials in the presence of  $\text{KCl}$  (1 *M*) show Dowex 2 to be more basic than Dowex 1.

Where ionic selectivity data are known, the titration results are borne out. The trimethyl- and dimethylethanol resins have selectivities of 0.09 and 0.65 for  $\text{OH}^-$  ions, respectively, relative to  $\text{Cl}^-$  ions<sup>6</sup> also indicating the greater basic strength of the trimethyl resin. For the other resins, the *pH* at the start of the titration can be used as an approximate selectivity index. (The initial resin *pH* must be attributed largely to the displacement of  $\text{OH}^-$  ions by  $\text{Cl}^-$  diffusing in from the salt bridge.) Such data are listed in Table III for the alkanol resins; though they show the relative weakness of the bases, they fail to distinguish variations among the members of the group.

TABLE III  
INITIAL *pH* DATA FROM TITRATIONS

Resin functional group	Measured <i>pH</i>	$\frac{(\text{OH}^-) \text{ exptl.}^a}{(\text{OH}^-) \text{ max.}}$
$\text{RNMe}_3^+$	12.3	0.40
$\text{RNMe}_2\text{EtOH}^+$	11.0	.02
$\text{RN}(\text{EtOH})_2\text{Me}^+$	11.1	.03
$\text{RN}(\text{PrOH}-2)\text{Me}_2^+$	11.2	.05

<sup>a</sup> The "maximum concentration" of  $\text{OH}^-$  ions is calculated to be  $0.04 \pm 0.01$  *M* by assuming the total equivalents of hydroxide ion in the resin are free in the solution.

**Aryl Resins.**—A set of "aryl" ammonium hydroxide resins was also titrated. The dimethylbenzyl and pyridinium resins in particular appeared weaker than the alkyl ammonium resins. Too few points were obtained for the phenyl-dimethyl resin to justify comments. In the case of the pyridinium resin, there was no evidence of strongly basic behavior; the curve showed initial buffering and appeared to have an end-point about *pH* 5.5.

**Degree of Cross-linking.**—So that the influence of cross-linking on ionization might be ascertained, the dimethylethanol resin was procured in several degrees of cross linking ranging from 1 to 16% D.V.B. Samples of each were titrated in the hydroxide form and gave curves which were almost identical when adjusted for capacity differences.<sup>15</sup> While increasing cross-linking seemed to have little influence on the degree of dissociation of the exchange groups, it did produce a slight trend toward higher slopes in plots of *pH* vs.  $\log(1 - \alpha)/\alpha$  (see below).

**Polyelectrolyte Character.**—In the last few years several theoretical studies of the solution behavior of linear polyelectrolytes have appeared. Both Katchalsky and co-workers<sup>7</sup> and Hermans and Overbeek<sup>8</sup> have developed expressions which relate the degree of ionization of a dilute solution of a weak polyacid to the activity of the hydrogen ion. These expressions take the form

$$pH = pK_0 - \log \frac{(1 - \alpha)}{\alpha} + \frac{0.4343}{kT} \frac{\partial F_e}{\partial \nu} \quad (1)$$

for a linear polyelectrolyte, where  $K_0$  is the intrinsic ionization constant of an ionizable acid group in a monofunctional polyelectrolyte,  $\partial F_e/\partial \nu$  is the differential of the electrostatic energy with respect to the stage of ionization, and  $\alpha$  is the degree of neutralization or ionization. Katchalsky<sup>7c,d</sup> has recently emphasized the  $\partial F_e/\partial \nu$  is to be taken at constant radius of the ionic atmosphere as determined by small mobile ions and that equation 1 may be modified to fit cases of weak cross-linking.

Two new approaches have sought to overcome the limitations of dilute solutions and weak electric fields. One treatment has been based on the Donnan approximation that the local charge density is zero,<sup>17</sup> and the other on a new solution of the Poisson-Boltzmann equation.<sup>18</sup> Both appear much more satisfactory at high electrolyte concentration; neither has been extended to cover titrations.

The usefulness of equation 1 in handling comparatively highly ionized resins appeared questionable. It seemed of interest, however, to apply a related equation suggested first on an empirical basis by Kern<sup>19</sup> and later independently by Katchalsky and Spitnik<sup>7a</sup>

$$pH = pK - n \log(1 - \alpha)/\alpha \quad (2)$$

Though the constants  $pK$  and  $n$  are not simply related to polyelectrolyte parameters, they may be put in terms of  $pK_0$  and  $\partial F_e/\partial \nu$  of equation 1 as

(17) G. Kimball, M. Cutler and H. Samuelson, *J. Phys. Chem.*, **56**, 57 (1952).

(18) F. Osawa, N. Imio and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1954).

(19) W. Kern, *Biochem. Z.*, **301**, 338 (1939).

shown by Katchalsky, providing one has information about the flexibility of the polymer. A practical difficulty with equation 2 is the concentration dependence of the constants; both tend to decrease as simple electrolyte is added to the system. Activity corrections have been proposed to allow for this.<sup>7a,20</sup> When  $n = 1$ , equation 2 is seen to reduce to the familiar Henderson-Hasselbach formula.

Rewritten for a polybase, equation 2 becomes

$$pH = pK' + n \log(1 - \alpha)/\alpha \quad (3)$$

where  $pK'$  is the constant for the conjugate acid form. The less highly dissociated cross-linked polyelectrolytes such as the alkanol-substituted quaternary ammonium exchange resins do seem to satisfy equation 3 over a range of values of  $\alpha$ . This is the more interesting since  $\alpha$  for these ion exchangers represents only the degree of neutralization and no longer measures the real ionization. In Fig. 1 are plotted  $pH$  vs.  $\log(1 - \alpha)/\alpha$  for several titrations of the methyldiethanol resin in varying concentrations of added KCl. No attempt was made to fit the region where the very weakly basic groups became important; for the graphing, the resin was considered neutralized when the quaternary base had reacted. Attention should be called to the correlation between the slope and the external electrolyte concentration for the series. Values of the slope are listed together with results for some other resins in Table IV. As KCl was added, the polyelectrolyte character of the material was lost and the slope fell to one, a value which is more characteristic of the monomer.

TABLE IV  
CONSTANTS OF  $pH$  vs.  $\log(1 - \alpha)/\alpha$  PLOTS FOR SEVERAL RESINS

Resin ion	$n$	$pK'$	KCl concn. ( $M$ at $\alpha = 1$ )
RNMe <sub>2</sub> EtOH <sup>+</sup>	1.32 <sup>a</sup>	11.1	0.002
	1.53 <sup>b</sup>	10.7	.002
RNMe(EtOH) <sub>2</sub> <sup>+</sup>	1.48	10.8	.002
	1.24	11.1	.01
	1.05	11.6	.1
	1.00	11.9	1.0
RNMe <sub>2</sub> (PrOH-2) <sup>+</sup>	(1.5) <sup>c</sup>		(0.003) <sup>c</sup>
RCOO <sup>-d</sup>	1.4	8.4	0.0

<sup>a</sup> 6% D.V.B. <sup>b</sup> 16% D.V.B. <sup>c</sup> Estimated. <sup>d</sup> Amberlite IRC-50 titration with KOH, R. Kunin and R. E. Barry, *Ind. Eng. Chem.*, 41, 1269 (1949).

It was hoped that the pyridinium resin might also be treated in this fashion. Two straight lines intersecting at about  $\alpha = 1/2$  were obtained in the  $\log(1 - \alpha)/\alpha$  plot, however, for which no interpretation is suggested. Data on at least one weak cation exchanger, amberlite IRC-50, a carboxylic-type resin, also appear to fit equation 3 as is noted in Table IV.

The values of  $n$  from these plots may be compared with those obtained by others for linear polyelectrolytes. Many of Katchalsky's slopes

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

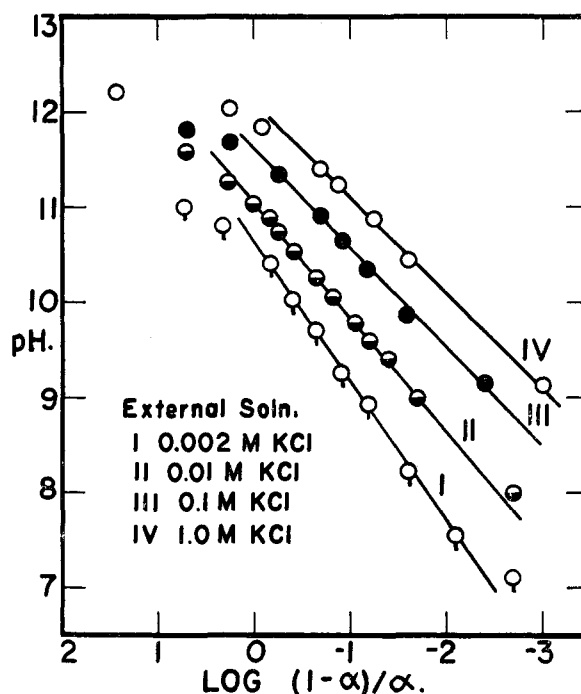


Fig. 1.—Plots of  $pH$  vs.  $\log(1 - \alpha)/\alpha$  for the Me(EtOH)<sub>2</sub>NR-OH resin titrated in the presence of added salt.

are in the neighborhood of two, but with added simple electrolyte, he found  $n$ 's as low as 1.5.<sup>7</sup>

Whether much significance can be attached to the magnitude of the  $pK'$  values given in Table IV is uncertain. The constants 11.1 and 10.8 calculated for the mono- and diethanol substituted resins in 0.002  $N$  KCl are qualitatively reasonable since the latter is expected to be a somewhat weaker base. But the  $pK$  of 8.4 for the carboxylic acid resin indicates serious difficulties in the indiscriminate application of equation 2 and 3.

**Conclusions.**—The continuous titration method proved usable for qualitatively characterizing differences among anion-exchange resins structurally rather similar.

More exact descriptions, based on titration studies, of the degree of ionization of the chemical groups or of the energetics of ionization and exchange appear to await theoretical developments and the better handling of experimental problems such as the junction potential, the response of the glass electrode to the system, and the improvement of the reproducibility when little added electrolyte is present.

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