[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOLKYN]

Characterization of Ion Exchange Resins. I. Acidity and Number of Constituent Cation Exchange Groups[1,2]

BY HARRY P. GREGOR AND J. I. BREGMAN[3]

Investigations of the resinous ion exchange process are possible only on an empirical level without a knowledge of the physio-chemical properties of the resins themselves. In order to determine the numbers and kinds of exchange groups making up a resin, two techniques were developed, the first being a direct titration of the resin with base in the presence of neutral electrolyte; the second procedure involved adding to the resin the salt of a weak acid and determining the extent of reaction by back-titration of the buffer. Resins made from known starting materials have been characterized.

Cation exchange resins are high molecular weight polyacids which are virtually insoluble in aqueous and non-aqueous media. The acid or acids which constitute the exchange groups are usually of the sulfonic, carboxylic or phenolic type, and are substituents in the resin structure (usually of the phenol-aldehyde type).[4] Their exchange properties can be ascribed as being entirely due to the exchange of various cations for the dissociable hydrogen ion. Resins of the phenol-sulfonic–phenol–formaldehyde type have been prepared and are commercially available which contain 10% sulfur, and a corresponding exchange capacity of 3.1 mmoles. per gram. Therefore, the —SO_3H group itself must comprise at least 25% of the mass of the resin in the dry state. When the resin is placed in water it swells strongly, usually doubling its weight. Thus approximately 60% of the hydrated mass of the resin is the exchange group itself and the water associated with it. Therefore, a true picture of a cation exchanger is that of a structure containing large polar exchange groups held together by a three-dimensional hydrocarbon network.

If the direct titration of a cation exchange resin in the hydrogen state is attempted, there will be no *p*H change in the external solution until the end-point of the titration is reached if the exchanger contains only strong acid groups. The reaction can be written

$$R{-}SO_3H + NaOH = R{-}SO_3Na + H_2O$$

Here the actual titration is taking place within the pores of the resin, and the *p*H changes cannot be measured directly. An exact empirical expression[5] describing the exchange reaction is

$$\frac{(Na^+)_R}{(H^+)_R}\left[\frac{(H^+)_S}{(Na^+)_S}\right]^n = K$$

where the subscripts refer to the resin and external solution phases. Since the ratio of the activity coefficients of univalent cations is nearly equal to unity, concentrations are used in place of activities. If a large excess of a neutral sodium salt is added, the ratio $(Na^+)_R/(Na^+)_S$ becomes small because n is 0.8–1.0 and K is 0.5–2.0 for most resins. The ratio $(H^+)_S/(H^+)_R$ must become very large and virtually all of the hydrogen ions are in the solution phase. Thus the addition of neutral salt displaces an ion into solution upon dissociation, and yields results comparable to those which would be obtained if the resin were soluble. This is also the case for the weak acid resins.

For the buffer titration an acid resin is added to the salt of a weak acid. An excess of neutral salt is also required, and the reaction is

$$R{-}H + Na^+ + A^- = R{-}Na + H^+ + A^-$$

where R—H represents the acid resin and HA the weak acid. The number of exchangeable hydrogen ions of the resin equals the moles of hydrogen ions which are displaced at the equilibrium *p*H. The resin is filtered and the solution back-titrated with sodium hydroxide to the initial *p*H of the buffer salt solution; the number of displaced hydrogen ions in the resin is the equivalent of base required at the equilibrium *p*H. A plot of these capacity values as a function of *p*H is the equivalent of the titration curve of the resin acid.

The terms "number of exchangeable" hydrogen ions and the conventional term "exchange capacity" do not necessarily mean the same thing, for the number of cations taken up by a hydrogen exchanger may be greater[6] than the number of hydrogen ions displaced. This may be due to complex ions, and is usually found when polyvalent ions are exchanged.

Experimental

Selection and Treatment of Resins.—The resins were either ones prepared from the patent literature or commercial resins where the procedures for the synthesis were known. Since the chemicals were usually of technical grade, the resins themselves were, as a rule, not of high purity. In addition, the curing treatment which includes heating for prolonged periods at elevated temperatures may partially decompose the resins and introduce new exchange groups. The resins used included: (A) phenol–formaldehyde, alkaline condensed[7]; (B)

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(1) Presented before the Division of Colloid Chemistry of the American Chemical Society, New York, N. Y., September 16, 1947.

(2) This work is abstracted from the Dissertation of J. I. Bregman presented in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at the Polytechnic Institute of Brooklyn, October, 1947.

(3) Present address: Fels and Company, Philadelphia, Pa.

(4) R. J. Myers, "Advances in Colloid Science, Vol. I," Interscience Publishers, Inc., New York, N. Y., 1941.

(5) R. Griessbach, "Preparation and Applications of Ion Exchange Adsorbents," Verlag Chemie, Berlin, 1939.

(6) H. Chaya, B.S. Thesis, Polytechnic Institute of Brooklyn, May, 1947.

(7) B. A. Adams and E. L. Holmes, U. S. Patent 2,104,501, Jan. 4, 1938.

phenolsulfonic acid–phenol–formaldehyde, acid condensed[3]; (C) phenolsulfonic acid–phenol–formaldehyde, alkaline condensed[8]; (D) phenol–formaldehyde, alkaline condensed in the presence of sodium sulfite[9]; (E) phenol–formaldehyde, alkaline condensed, cured and dried, then treated with sodium sulfite[9]; (F) salicylic acid–phenol–formaldehyde, alkaline condensed[8]; (G) coal treated with 2 *M* sodium hydroxide at elevated temperatures in a bomb; (H) coal treated with hot concentrated sulfuric acid[10]; (J) polystyrene directly sulfonated with chlorosulfonic acid.[11]

The resins were wet screened to $-20 + 30$ mesh, and "conditioned," *i. e.*, treated alternately with large excesses of 1 *M* hydrochloric acid and 1 *M* sodium chloride to remove soluble components of the resin and displace any heavy metal cations present. The resins were regenerated, *i. e.*, converted to the hydrogen or acid state by passing a large excess of 1 *M* hydrochloric acid through a bed of the resin very slowly and then rinsed with carbon dioxide free distilled water to an effluent *p*H of 4. Due to resin solubility, *p*H values above 4 are usually not obtained at slow flow rates. The material was then air dried until the particles no longer adhered to one another, and its moisture content determined by drying over phosphorus pentoxide. Air dried resin was used for experiments because the desiccated form is very hygroscopic and frequently decrepitates in water. Resin ground to give particles of a smaller size was regenerated again to remove added impurities and to convert to the acid state any newly available exchange groups.

Direct Titration.—In order to obtain a resin containing different acidic groups, resin K was prepared by sulfonating phenol with an excess of fuming sulfuric acid, adding phenol and a slight excess of formaldehyde and condensing in the acid state. This resin showed an increased exchange capacity with increasing alkalinity, indicating the presence of "weak-acid" capacity.

A number of 0.5-g. portions of resin K were weighed into flasks containing 100 ml. of varying concentrations of sodium chloride made up in doubly distilled water. Different amounts of standard (0.5 *N*) sodium hydroxide were added to each flask, which was then shaken for twenty-four hours and which was sufficient for the establishment of equilibrium, as shown by tests to be described later. The equilibrium *p*H of the solution was measured with a Beckman "high *p*H" glass electrode. All values given hereafter are for 1 g. of moisture-free hydrogen resin.

Experimental values for the direct titration are shown in Fig. 1. These experimental curves, showing a displacement to lower values of *p*H as the neutral salt concentration is increased, are in qualitative agreement with curves calculated using the empirical expression given above.[5] Sodium chloride solutions more concentrated than 0.5 *N* gave the same results as the 0.5 *N* solution.

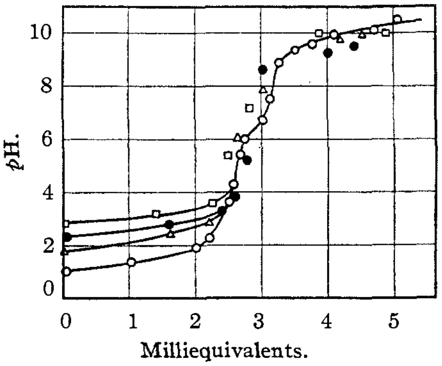

Fig. 1.—Direct titration of resin K with sodium hydroxide in sodium chloride solutions: □, 0.000 *N*; ●, 0.002 *N*; △, 0.028 *N*; ○, 0.500 *N*.

Resin K was also titrated rapidly in 0.5 *N* sodium chloride in the customary manner, and curves for $-20 + 30$ and -100 mesh material is shown in Fig. 2. The curve for 0.02 *N* hydrochloric acid is included for comparison.

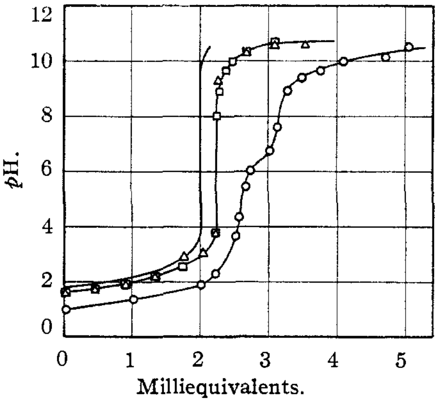

Fig. 2.—Rapid direct titration in 0.5 *N* sodium chloride of resin K: △, $-20 + 30$ mesh; □, -100 mesh; ○, $-20 + 30$ equilibrium value; —, 0.02 *N* hydrochloric acid.

Buffer Titrations.—These determinations were carried out by adding 0.5-g. samples of resin K to 100 ml. of 0.02 *M* solutions of sodium salts of weak acids in 0.5 *N* sodium chloride, shaking for twenty-four hours, filtering off resin and back titrating to the original *p*H of the solution with sodium hydroxide. Buffer salts were selected which covered the *p*H range from 3 to 10, and which gave a sharp back titration end-point. These included sodium tartrate, acetate, citrate, monohydrogen phosphate, carbonate and phosphate. The buffer titration curve for resin K is shown in Fig. 3, together with the direct titration curve for the same resin.

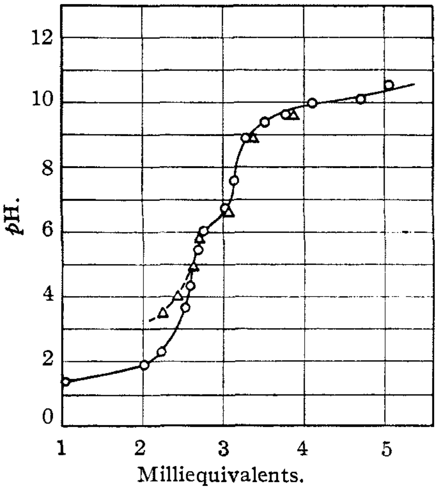

Fig. 3.—Direct (○) and buffer (△) titration curves for resin K.

Several variations of the above procedure were investigated. When sodium salts were replaced with those of lithium and potassium, identical titration curves were found. When the concentration of the buffer salt was varied from 0.01 to 0.1 *M*, the curves were unchanged when corrected to an ionic strength of 0.5. When the

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[8] H. Wassenegger and K. Jaeger, U. S. Patent 2,204,539, June 11, 1940.

[9] H. Wassenegger, R. Griessbach and W. Sutterlein, U. S. Patent 2,228,159, Jan. 7, 1941.

[10] P. Smit, U. S. Patent 2,191,063, Feb. 20, 1940.

[11] G. F. D'Alelio, U. S. Patent 2,366,007, Dec. 26, 1944.

sodium chloride concentration was made lower than 0.2 *N* the titration curves became altered, presumably because insufficient neutral salt was present to displace all of the dissociated hydrogen ions.

When the −20 + 30 mesh resin was ground to −100 mesh, regenerated and titrated, the titration curve was found to be unchanged. However, when a lot of commercial resin was screened and each fraction tested, wide variations in the results frequently appeared.

The rate of exchange was determined by treating hydrogen resin with 0.5 *N* sodium chloride with rapid stirring, using a glass electrode to measure the rate. After a constant *p*H was reached, the resin was filtered and placed in a 0.02 *M* solution of disodium hydrogen phosphate in 0.5 *M* sodium chloride, and the rate measured as before. At equilibrium the process was repeated with trisodium phosphate. The milliequivalents of hydrogen ion displaced were calculated from the experimental *p*H values, using as a calibration curve the titration of that same buffer salt solution with hydrochloric acid.

While the rate was measured at a variable *p*H value, well defined results were obtained, as shown in Fig. 4 with resin C.

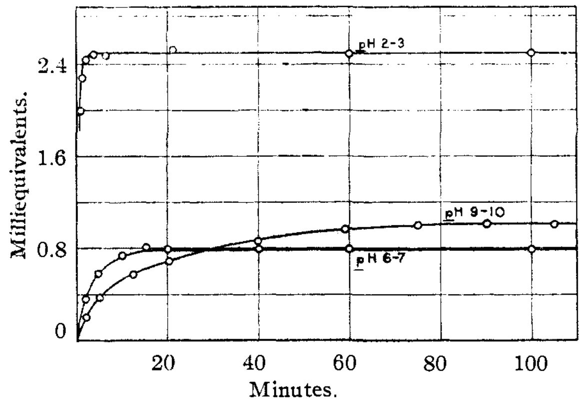

Fig. 4.—Rate of exchange at different *p*H levels for resin C.

Buffer titration curves for a number of different resins are shown in Figs. 5 and 6, the letters adjacent to each curve referring to the resins described earlier.

Discussion

The direct or buffer titration of a resin, when carried out in an excess of neutral salt, gives results comparable to those that would be obtained if the resin were in true solution. Since the process is one of displacement of the hydrogen ion, the nature of the cation used does not appreciably affect the results when only alkali metal cations are used.

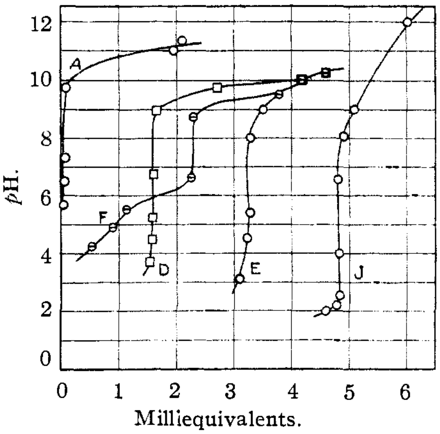

Fig. 5.

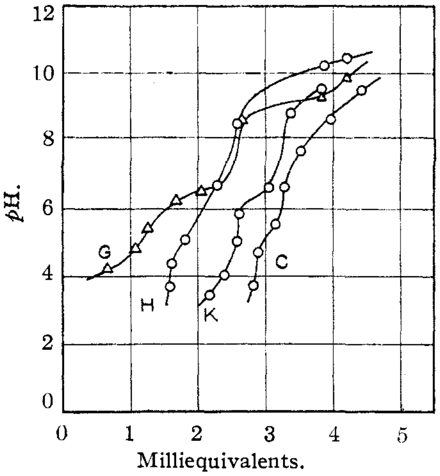

Fig. 6.

The apparent anomalies in the rate studies can be explained by considering that the strong acid groups, by virtue of their high degree of hydration and large hydrated volume, are surrounded by a more open resin matrix than the smaller, weakly dissociated groups. Therefore the rate of diffusion of the exchanging ion to a strong acid group is greater than for a weak acid group. This is shown by the rate studies in Fig. 4. When the particle is reduced in size by grinding, the fractures probably occur at the wider pores, and the time for reaction of a weak acid group is reduced only by the time required for diffusion into the wider pores. Thus a rapid titration of even a resin of small particle size does not show the presence of weak acid groups. Further studies are in progress to test the validity of this postulate.

The electro-chemical nature of the acidic groups does not seem to be strongly affected by their being a part of the resin structure. The phenolic group has a *pKa* value of approximately 10, and the carboxyl group has a *pKa* value of 5.5. Resins prepared using sodium sulfite do not show the diverse groups which appear in the sulfonated resins, presumably as a result of the oxidizing sulfonating procedure. The two cation exchangers not of resinous nature show titration curves compatible with their preparative procedures. The gradual slopes of their curves indicate the complex nature of these natural products.

A true cation exchange resin can now be defined as a solid phase containing dissociable cations which will exchange for any other cation independently of the nature of the anion of the exchanging cation in solution. A base absorbent is a solid phase containing dissociable cations which will exchange for any other cation only when weak acid anions or hydroxyl ions are the anions of the exchanging cation in solution. A comparable definition would restrict true cation exchange resins to those which contain only completely dissociated acidic groups, *i. e.*, strong acid resins.

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[CONTRIBUTION NO. 75 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Transfer in the Polymerization of Styrene. II. The Reaction of Styrene with Carbon Tetrachloride[1]

BY R. A. GREGG AND FRANK R. MAYO

Using literature data on the uncatalyzed polymerization of styrene, a previous paper[2] from this Laboratory showed that the effects of solvents in reducing the molecular weight of polymerizing styrene could be correlated on the basis that the growing polymer radical captures an atom from the solvent molecule, resulting in a radical which starts a new chain[3] and in the incorporation of solvent in the polymer. Since these relations promised to be useful in making quantitative comparisons of the reactivities of solvents toward free radicals, a thorough test of the equations and concepts on the styrene–carbon tetrachloride system was begun. The present paper considers both the uncatalyzed and peroxide-catalyzed polymerization of styrene at 60–132° to give products averaging more than thirty styrene units per polymer molecule, or per incorporated carbon tetrachloride molecule. A succeeding paper[4] will consider formation of products averaging as low as two styrene units per carbon tetrachloride residue.

Experimental

Purification of Materials.—Dow styrene was freed from inhibitor by vacuum distillation and the middle fractions were partially crystallized by stirring in a Dry Ice-bath. The process was repeated from six to eight times until the freezing point became constant. The recrystallized material was distilled under nitrogen: b. p. 44.9–50° at 18 mm.; $n^{20}\mathrm{D}$ 1.5465; f. p. $-30.7° \pm 0.1°$. The styrene was stored in sealed, evacuated tubes in Dry Ice.

Reagent grade carbon tetrachloride was stirred with concentrated sulfuric acid and then with potassium hydroxide solution, washed with water, and dried over calcium chloride. It was distilled from paraffin wax[5] through a 1-meter helices-packed column: b. p. 76.8° at 760 mm.; $n^{20}\mathrm{D}$ 1.4605.

Benzoyl peroxide was twice dissolved in cold chloroform and precipitated by pouring into cold methanol, collected on a sintered glass filter, and dried under vacuum at room temperature. It liberated 100.0–100.4% of the theoretical quantity of iodine from potassium iodide in glacial acetic acid.[6]

Preparation of Polystyrene Samples.—Weighed amounts of carbon tetrachloride and styrene (and benzoyl peroxide, when used) were placed in a flamed Pyrex tube equipped with a standard taper joint. The tube was attached to the vacuum line and the sample was frozen in liquid nitrogen. The tube was then evacuated and the sample was degassed twice by thawing and refreezing. The tube was then sealed at a pressure of 10^{-5} mm. Check experiments in which both the solvent and the styrene were distilled under high vacuum into the reaction tube showed no difference, even with large volumes of other solvents. The polymerizations were carried out in thermostats at 60 ± 0.05°, 100 ± 0.1°, and 132 ± 1°, and held to about ten per cent. conversion.

The polymer was precipitated with methanol and redissolved in twenty-five to fifty times its weight of benzene. This solution was then treated with three to five times its volume of methanol. An additional solution and precipitation was used for many of the samples whose molecular weights were determined osmometrically. The decanted precipitating medium was usually centrifuged to obtain any suspended polymer. The polymer was dissolved in benzene; the solution was frozen in Dry Ice, and the benzene was removed by sublimation.[7]

The above procedure results in loss of some of the very low molecular weight polystyrene; where the average molecular weight of the polymer was low, some of the precipitating solutions were rapidly concentrated by distillation *in vacuo* and the residue was dissolved in benzene and added to the main portion of the polymer. This procedure permits distillation of monomer from a *small* amount of *low* molecular weight polymer instead of from the whole polymer and gave products, marked in Table I, with appreciably lower average degrees of polymerization.

Determination of Number Average Molecular Weights from Osmotic Pressure.—These determinations were made by Drs. R. H. Ewart, H. C. Tingey and M. Wales.[8] The osmotic pressures were measured either in glass[9] or metal osmometers[10] with cellophane membranes and at three or more concentrations. Either butanone or benzene was used as the solvent, with identical end results.

Viscosity Determinations.—Solution viscosities were determined in benzene at 30°, using Fenske viscometers with 80–120 second flow times and neglecting kinetic energy corrections. Such corrections would give an increase of about 5% in intrinsic viscosities but would not affect the present molecular weight estimates from viscosity data. Where the molecular weight was determined independently, the intrinsic viscosity,[11] $[\eta]$, was obtained from specific viscosities at three or more polymer concentrations. Otherwise, the intrinsic viscosity was obtained from the specific viscosity of a single solution, measured in two

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[1] This paper was presented before the Polymer Forum at the Atlantic City Meeting of the American Chemical Society, April 10, 1946.

[2] Mayo, THIS JOURNAL, **65**, 2324 (1943).

[3] Essentially the same development has been made independently by Hulburt, Harman, Tobolsky, and Eyring, *Ann. N. Y., Acad. Sci.*, **44**, 371 (1943), and by Medvedev, Koritskaya and Alekseeva, *J. Phys. Chem. U. S. S. R.*, **17**, 391 (1943).

[4] Mayo, paper submitted to THIS JOURNAL.

[5] Weissberger and Proskauer, "Organic Solvents," Oxford University Press, 1935, p. 156.

[6] Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940).

[7] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1943).

[8] Ewart and Tingey, *Abstracts of Papers*, 111th Meeting American Chemical Society, April, 1947, p. 4Q.

[9] French and Ewart, *Ind. Eng. Chem., Anal. Ed.*, **19**, 165 (1947).

[10] Flory, THIS JOURNAL, **65**, 372 (1943).

[11] Kraemer and Lansing, *J. Phys. Chem.*, **39**, 153 (1935).