

Synthetic Resins and Base Exchange Phenomena

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The phenomenon of base exchange which has been known for a long time was first applied by Way (50) in 1850 to the adsorption of cations by soils. However, the discovery of the exchangeability of bases is usually credited to Eichorn (12). Half a century passed before this reaction was put to practical purposes, when in 1906 Gans (16) patented the first commercial application for the use of zeolites in water softening. Since then the development of zeolites has progressed to the point where the use of these inorganic base exchangers is world-wide in scope. Not only are zeolites applied to the softening of industrial waters for laundry, textile, boiler feed, and other purposes, but they are likewise used in domestic and other small-scale water softening plants. In 1938 200,000 zeolite softeners were in operation throughout the United States (37). Since then the number has increased markedly.

The fundamental principles of the base exchange process are based on the following reactions:

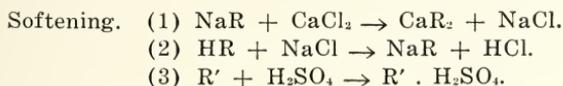
Softening. $\text{Na zeolite} + \text{Ca salts} \rightarrow \text{Ca zeolite} + \text{Na salt.}$

Regeneration. $\text{Ca zeolite} + \text{NaCl} \rightarrow \text{CaCl}_2 + \text{Na zeolite.}$

Austerweil (5a-c) gives a physico-chemical explanation for the base exchange reaction in zeolites, the principal point of which is the fact that the relationship between a cation in aqueous solution and a zeolite fully saturated with only a single different cation is an extraction process, the solid base-exchange substance playing the part of a non-miscible solvent for the cation in aqueous solution. The reaction follows the fundamental extraction law. Nernst showed that every extraction phenomenon is independent of the concentration. That base-exchange reactions are likewise independent of concentration has been shown by Austerweil (5c), thus confirming some former investigation in this direction by Ramann and Spengel (36). Besides this extraction process, there is a second phenomenon which complies with the law of mass action and the phase rule. It indicates that the extraction is accompanied by an equilibrium between the two cations in the solution, which equilibrium is itself determined by the ratio of the concentrations of the two zeolites present, the original one and the newly formed one. Austerweil based this theory on experiments of this type: The zeolite base-exchanger is first washed with water till it has a pH of 7. Then the zeolite is carefully saturated with the cation, the exchange of which is to be investigated. After washing, the exchangeable cation content of the zeolite is determined by the usual analytical methods.

The discovery of Adams and Holmes (1) that phenol-formaldehyde resins exhibited base exchange properties focused attention on the pos-

sibility of using organic exchangers. Ellis (12) suggested that all base exchange substances of organic origin be called 'organolites' to distinguish them from the inorganic zeolites. The ion exchange and adsorption reactions of synthetic resins are based on the following equations:



NaR is the sodium salt of a cation exchange resin, HR is the hydrogen form of a cation exchange resin, and R' is an anion exchange or acid adsorbent resin. As is evident, the use of organolites permits the removal not only of calcium ions, but also the removal of the alkali metal salts originally present or formed by the calcium removal. The usual regenerative technic is used.

Though various theories have been advanced to explain adsorption on synthetic resins by consideration of solubility, valency, coagulation, and other factors, no successful theory has been brought forth to explain all the facts. Bhatnagar and his co-workers (10a) showed the molecular weight of the anion to have a great effect on adsorbability. The anion apparently must be accommodated in the internal capillary structure of the adsorbent. The adsorption of acids by synthetic resins appears to be governed by at least two simultaneous processes, adsorption through surface forces, and physio-chemical interaction of hydrogen ions with basic groups in the resin. In the case of polyhydric phenol-formaldehyde resins, Burrell (12) believes base exchange to take place through the functional phenolic group. These resins are insoluble compounds possessing salt-forming hydroxyl or sulfonic acid groups, which functional groups react with cations and hold them in the insoluble adsorbent until the regenerating medium removes them. Burrell found that base exchange ceased when the phenolic group was oxidized. This theory is also confirmed by Akeroyd and Broughton (3) who studied the adsorption rates of calcium, barium, sodium, and trimethylbenzylammonium hydroxides on simple mono-, di-, and tri-hydroxy phenol-formaldehyde resins. The adsorption differences for various adsorbents were explained by pointing to the varying degrees of accessibility of the hydroxyl groups, which is controlled by the structure of the phenol in question and by the degree of polymerization of the resin.

The following classification of exchange adsorbents was suggested by Myers, Eastes, and Myers (32):

I. *Cation-Exchange adsorbents*

A. Inorganic:

1. Natural origin, unmodified and modified (greensands)
2. Synthetic (synthetic gel zeolite)

B. Organic:

1. Natural origin, unmodified (peat) and modified (sulfonated coal)
2. Synthetic (tannin and phenol formaldehyde resins)

II. *Anion-Exchange adsorbents*

A. Inorganic:

1. Natural origin (dolomite)
2. Synthetic (heavy-metal silicates)

B. Organic:

1. Natural origin, unmodified (horn, wool) and modified (alkali-treated asphalt)
2. Synthetic (amine-formaldehyde resin)

The types of resins used to date for cation removal are (a) phenol-formaldehyde (acid- or ammonia-condensed), (b) resorcinol-formaldehyde (acid- or ammonia-condensed), (c) m-phenylenediamine-formaldehyde, and (d) protein-formaldehyde.

Three types of resins can be used for anion adsorption. (a) aromatic bases, (b) amides including sulfonamides, and (c) proteins. Much of the work on anion removal has been done with aromatic bases. Resins formed from amides are yet to be systematically examined for ion-exchange ability. The use of amino-resins opens up the possibility of removing fluorides, silicates, sulfates, chlorides, and other anions from solution.

There is very little in the literature on anion exchange with the exception of patents, although a few fundamental papers on this subject have been published (5b, 5d, 10b, 10c, 13, 18, 32, 40). The same is true of the literature with respect to synthetic resins as cation exchange materials. While there are a few general articles on the subject (3, 5a-b, 12, 32), most of the available literature is confined to patents. The results obtained with the various types of resins are systematically summarized in the following discussion.

Despite the fact that Sato and Sekine (39) had drawn attention to the amphoteric nature of phenol-formaldehyde resins and Shone (41) had recorded the behavior of some forty metallic salts which reacted with the latter, it remained for Adams and Holmes (1) to make the first systematic study of the adsorptive properties of these substances. Prior to this work, resins were rated solely on their physical properties, but these authors called attention to a consideration of the chemical as well as of the physical properties; since then there has been a rapid expansion in the application of synthetic resins to both cation and anion exchange.

Adams and Holmes tested the exchange capacity of their adsorbents in a simple manner. Solutions of each salt were prepared containing 0.0035 moles per liter and possessing pH values characteristic of the salt used. The solution of the cation being tested was passed through 10 grams of the washed, dried, and sieved resin at a rate of about 200 ml. per hour. The presence of the cation was tested in 50 to 100 ml. of the filtrate by the usual analytical procedures. When cations were detected in the filtrate, denoting exhaustion of the resin bed, the material was treated with 5 per cent hydrochloric acid to remove the adsorbed cation and regenerate the resin. The resins examined

were catechin, phloroglucinol, pyrocatechol, pyrogallol, quebracho-tannin, resorcinol (ammonia-condensed), and resorcinol (acid-condensed). Although difficulties due to channelling made the results more or less qualitative, polyhydric phenol-resins were found to exhibit strong and selective adsorptive properties for a large number of cations, and amino-resins were found to be quite efficacious for the removal of anions from solution. The consecutive use of phenolic and amino-resins was suggested to effect complete removal of dissolved salts from solution.

An examination of Adams and Holmes' data reveals several interesting points, which can be summarized as follows: (1) number of cases where adsorption did not occur; (2) decided general adsorption by phloroglucinol and quebracho-tannin resins; (3) decided selective adsorption by catechol, resorcinol, quinol, pyrogallol, and catechin resins; and (4) considerable removal of certain heavy metals with one or more of the adsorbents, e.g., mercury, silver, tin, vanadium, and uranyl ions.

Other significant facts were that adsorption occurred under relatively acidic conditions, i.e. pH as low as 1 or 2; that arsenic could be separated from antimony by selective adsorption; and that lead acetate and lead nitrate were adsorbed in different degree. The quebracho-tannin resin showed an adsorption for cations, the amount of which was inversely proportional to the valency of the cation.

Bhatnagar, Kapur and Puri (9) found that the adsorption of a homologous series of organic acids on an acid-condensed phenolic resin increased strongly with increase in molecular weight. However, Tsuruta (43) studied the adsorption of these acids on an ammonia-condensed phenolic resin and found the reverse to hold, i.e. adsorption decreased with increasing molecular weight. Bhatnagar (10a), who confirmed Tsuruta's work for ammonia-condensed resins, substantiated his previous results for acid-condensed resins and found that ammonia-condensed invariably gave much greater adsorption than acid-condensed resins.

The adsorption experiments of Bhatnagar and his co-workers were conducted in a simple manner. One gram of the powdered resin was placed in a glass-stoppered bottle containing 100 ml. of the solution to be examined. The bottle was shaken for five minutes and allowed to settle for 36 hours. The supernatant liquid was then decanted and the amount of solute determined by the usual analytical methods. A blank experiment carried out simultaneously gave the original concentration. The difference gave the amount adsorbed from 100 ml. of the aqueous solution.

Considerable emphasis has been laid on cation removal by phenol-formaldehyde resins as is seen by the many patents on this subject (2a, 22, 24d, 24j, 25c, 25j).

The adsorption of potassium chloride, potassium bromide, and potassium iodide by a *m*-phenylenediamine-formaldehyde resin was studied by Bhatnagar (10a) and the results showed clearly that with increasing weight of anion, a marked decrease in the quantity adsorbed is obtained. This order is exactly the reverse of that obtained for the adsorption of the potassium salts on charcoal by Oden and Langelius (34) and others.

This is to be expected, for Bhatnagar found that in basic resins the normal Traube's rule¹ is reversed for an homologous series of fatty acids, the order of adsorption being formic>acetic>butyric and oxalic>malonic>succinic>adipic, showing that the adsorption decreases with the increase in molecular weight. It is also interesting to note that the order of adsorption of the potassium salts is exactly the reverse of the order of the solubilities of the salts in water. This result is confirmed by the observations of Beckley and Taylor (7), and Mukhrjee and Ray (31) who also found that the less soluble salts are adsorbed more than the soluble ones.

An examination of the univalent complex anions showed that the inverse solubility-adsorption relationship does not hold in an exact manner. While there is a general relationship between the solubility and the adsorbability of a solute, there are many exceptions. Low solubility alone is insufficient to determine adsorbability; it is necessary to consider whether or not the anion can be accommodated in the internal capillary structure of the adsorbent. For example, Bhatnagar (10a) found that in the case of chlorate, bromate, and iodate, though bromate is less soluble than the chlorate and should have been expected to be adsorbed more strongly, it is adsorbed less owing to its greater molecular weight. Thus, the order of adsorption is chlorate>bromate>iodate. He also pointed out that the order of adsorption for bivalent anions was dichromate>chromate>thiosulfate, which is exactly the reverse of the solubility. Bhatnagar claims that there is no relation between valency and adsorbability.

Bhatnagar (10b-c) studied the adsorption of formic, acetic, and butyric acids on resorcinol-formaldehyde (both acid- and ammonia-condensed), m-phenylenediamine-formaldehyde, and protein-formaldehyde resins in different solvents. The results in benzene solution, carbon tetrachloride, and chloroform showed the adsorption order: formic>acetic>butyric. In water solution the order of adsorption was the same for all the materials except for the acid-condensed resorcinol resin, which had the adsorption order: butyric>acetic>formic. Thus, in nonpolar solvents Traube's rule is reversed even in the case of acid-phenolic resins. As the dipole moment of the solvent decreased, the percent adsorption increased, the adsorption being at a maximum in carbon tetrachloride which has a zero dipole moment.

The work on the adsorption of different homologous series of organic acids on resorcinol-formaldehyde, protein-formaldehyde and m-phenylenediamine-formaldehyde resins reveals several points of interest:

(1) For an homologous series of acids the adsorption increases with an increase of molecular weight on an acid-condensed resin, while there is a decrease of adsorption with increasing molecular weight on an ammonia-condensed resin.

¹Traube's rule states that for the members of an homologous series, there is an increase of adsorption with increasing molecular weight. The increase of adsorption is due to the decreased effect of the members of a series on the surface tension of a given solvent as one ascends the series.

(2) The extent of adsorption apparently increases with increase in ionization constant. For example, the chloroacetic acids are more adsorbed the greater their ionization, i.e., trichloroacetic > dichloroacetic > chloroacetic.

(3) The adsorption by ammonia-condensed amino and protein resins increases with the introduction of carboxyl, hydroxyl, chloride, or bromide. However, such groups as NH_2 or alkyl cause a decrease in adsorption.

(4) Adsorption increases with the polarity of the molecule in ammonia-condensed and amino-resins, while it decreases for an acid-condensed resin. In the former cases the percentage adsorption increases with increasing dipole moment.

(5) For the ketonic acids, pyruvic and levulinic, the percentage of adsorption was greater for the acid of higher molecular weight in the case of acid-condensed resins, while the reverse was true for ammonia-condensed and amino-resins.

(6) Maleic and citraconic acids are adsorbed more than fumaric, leading one to believe that the adsorption of the cis-form is greater than the trans-form in ammonia-condensed and amino-resins. The order of adsorption is again reversed in the case of the acid-condensed resin.

The reversal of Traube's rule in the case of ammonia-condensed, amino, and protein resins is explained (10c) on the basis of the orientation of molecules at the adsorbent-solvent surface according to the theories of Langmuir (29) and Harkins (20). The results obtained in the case of acid-condensed phenolic resins are opposed to those obtained with basic materials. This may be due to the fact that an acid resin is less polar than water. Bhatnagar (10c) found that in non-polar solvents the results with acid-condensed resins are in line with those obtained using basic resins. From his studies Bhatnagar concluded that the ammonia-condensed and amino-resins behave as strongly polar substances while the acid-condensed behave as non-polar or weakly polar substances.

The results of Schwartz, Edwards, and Boudreau (40) in removing chlorides and sulfates by a m-phenylenediamine-formaldehyde resin showed that the solutes were removed as whole molecules and ion exchange played a minor role in the reaction. They failed to obtain anion adsorption on such substances as m-phenylenediamine-furfural-ammonia and furfuryl alcohol-hydrochloric acid resins. This work was confirmed by Myers, Eastes and Urquhart (33) who showed that acids were removed as whole molecules and that the adsorption data of Schwartz gave isotherms of the Freundlich type. They pointed out that there might be a relation between the adsorption isotherms and exchange capacity of synthetic resins. If such would be the case, then a rapid method would be available to evaluate new resins. They were able to calculate the exchange capacity from the adsorption isotherm and arrived at results which came close to the actual figures. The work of Bhatnagar and his associates (10a-c) also gave typical isotherms.

No cation exchange was noted (1) in resins of the glyptal, hydrocarbon-formaldehyde, urea-formaldehyde and vinyl types. Burrell (12)

found no sodium-calcium base exchange in the rosin-maleic anhydride type. Furfural-condensed resins with resorcinol or aniline were likewise incapable of ion adsorption.

'Mixed' resins (25h), formed from the condensation of formaldehyde with amino-hydroxy or amino-hydroxy-carboxylic acids, are effective in cation and anion removal. Organolites derived from the formaldehyde condensation of aromatic amines such as aniline, m-toluidine, and sym-m-xylidine can be used as anion adsorbents (2b, 19, 23, 24c). A sugar-m-phenylenediamine condensed resin can likewise be used for anion exchange (35a). Other patents on anion exchange have been issued covering the use of aromatic amines condensed with aldehydes (25d, 26, 30a-b, 35b-c, 44).

Patents on base exchange materials cover the use of resins formed from such substances as cyclic organic compounds having an imino group in the ring (45a), or by the aldehyde condensation of naphthalene or anthracene (25f, 49), and by the sulfonation of plastic reaction products as those derived from benzene and ethylene chloride (51). Resins produced from amides, e.g., urea or guanidine, and a cyanuric acid-condensed resin can be used for cation exchange (24g). Compounds formed by dehydration of coal, starch or wood meal with zinc chloride were found capable of base exchange (42a-b).

Other patents on base exchange cover a variety of types such as sulfonated resins and resins of varying aromatic amines condensed with polyhydric compounds and carboxylic acids (6b, 15, 17, 24e, 25a-b, 25i, 45b, 52).

Applications. The application of synthetic resins to the purification of industrial waters has already been put on a small scale operation by Resinous Products and Chemical Company and awaits large scale development. Water purification for high-pressure steam generation, textile processing, beverage manufacturing, and other uses where water of very low solid content is a necessity has been accomplished with synthetic exchange adsorbents.

The manufacture of drugs, C.P. chemicals, enzymes, dyestuffs, sugars, and vitamins can be aided by the removal of electrolytes and foreign substances from solution. A patent (6a) has been granted on the use of synthetic materials prepared from lignite, anthracite, and vegetable substances as water softeners. These can be used in the manufacture of salts by the base-exchange process, the purification of sugar juice, and the adsorption of bases from smoke, vapors and gases, e.g. the removal of nicotine from smoke. Sugar solutions can be purified by passage through a hydrogen exchanger and then through an anion exchanger, leaving the conductivity of the effluent equal to that of distilled water.

The use of ion-exchange resins for the recovery of valuable electrolytes present in very dilute solutions has immense possibility. The recovery of copper from industrial effluents or from mine wastes has been patented (21). Specifically, the recovery of copper from the waste liquor of a copper rayon factory has been effected by the use of sulfon-

ated *m*-phenylenediamine-formaldehyde (24b) or ethyleneimine-methylene chloride resins (24a). Ellis (14) was able to remove metallic elements such as lead and gold from water by the use of an organolite. Patents have been issued for ion-exchange materials used in the removal of all salts or of specific ions from solutions (6a, 11, 25e, 25g, 26). The removal of valuable materials from sea water might be attempted, using basic exchange resins.

The anion-exchange resins have been successfully employed in combination with a hydrogen exchanger in the production of a high-quality 'chemically distilled' water in the laboratory. Myers (32) used two 50 mm. tubes filled to a depth of 900 mm. each with the organolite to remove all the dissolved salts from tap water. The effluent showed no chlorides or sulfates, maintained a pH greater than 5.0 (due to carbon dioxide only) and was often equal to distilled water in other qualities. Silica was not removed by this method.

The use of base exchange materials in analytical chemistry was studied by Samuelson (38a-c). With the aid of a sulfonic acid organolite, it was possible to remove all aluminum ions from a solution containing a little more than two milliequivalents of aluminum sulfate; hydrogen ions replaced aluminum ions in the solution. The hydrogen ion equivalent of the aluminum could then be titrated with sodium hydroxide to a methyl red-end point. While most of the values were excellent, there was as much as one per cent error in a few cases. With 5 g. of organolite, saturated with ammonium ions, one could completely remove 2 milliequivalents of potassium, forming the ammonium salts of the anions in the filtrate. Then, by washing with hydrochloric acid all the adsorbed alkali cations can be removed and, after evaporation to dryness and careful ignition, the chloride equivalent to the potassium could be titrated with silver nitrate. Such a method is particularly advantageous when a non-volatile anion such as vanadate is present. Much less time is required than when the vanadate is removed by means of the insoluble lead salt, and the results are more accurate. Analogous technics involving ion replacement were applied to the determination of sulfate (38b) and the separation of ferric and aluminum ions from secondary calcium phosphate (38c). Complex anion formation does not interfere with the latter. This method has distinct possibilities in analytical chemistry particularly for determining total milliequivalents of cations and anions present in a solution.

The fact that ion-exchange resins behave as exchange adsorbents suggests that they might be suitable in chromatographic separations. While the black color of many resins obscures this phenomenon, it has been noticed (32) that certain light-colored anion-exchange materials showed marked banding when a mixture of anions was passed through the column. These bands were proven to be pure derivatives of the components of the solution when subjected to chemical analysis. This phenomenon merits further investigation.

Advantages of Resins Compared to Zeolites. The outstanding advantages offered by synthetic resins when compared to zeolites are

evident. Resins surpass their inorganic counterparts not only in the width of applicability but likewise in specific cases, as in water softening, where zeolites predominate.

An important advantage of organolites over zeolites lies in the ability of a resin to be regenerated by an acid whose anion forms a soluble salt with the cation exchanged for hydrogen ion. Zeolites are attacked by acids, lowering their exchange capacity (8, 37). Moreover, resins are fairly stable to change of pH while zeolites deteriorate when subjected to waters of low pH (27). If the pH of water is high, or the silica content is very low, silica from siliceous zeolites will be dissolved. The silica pick-up is greater from the synthetic, precipitated type of zeolite than from glauconite (4).

Synthetic resins are lighter than zeolites in weight and suffer in loss of physical strength. Nevertheless, disruption of the silicate lattice easily occurs when a heavily hydrated ion is exchanged for a lighter ion producing a strain on the lattice. The synthetic resins have a flexible structure and can withstand strain to a remarkable degree.

The advantages and uses for synthetic resins indicate a promising future for resin chemistry in the field of base exchange.

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