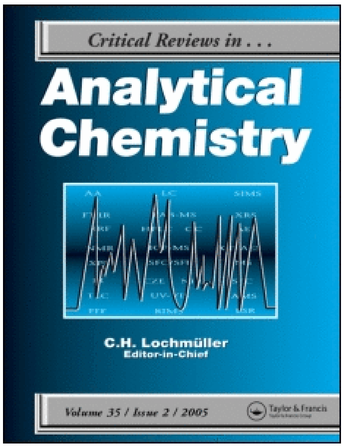

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ION EXCHANGE IN NONAQUEOUS AND MIXED MEDIA

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I. INTRODUCTION

A. History, Purpose, Scope

The study of ion exchange in solvents other than pure water started about 20 years ago. Several reviews of this field have been published since then, as will be seen in the following chapter. It is the purpose of this review to bring this information up to date, and to deal in particular with certain aspects of the field that are of interest to the analytical chemist, such as the exchange of organic ions, but that have not been covered sufficiently by these earlier reviews.

Most of the work published so far has been done with mixed solvent systems containing water. In many instances where anhydrous solvent phases were used, evidence or proof of the absence of water from the exchanger phase is lacking, which makes it difficult to distinguish between water-containing and anhydrous systems. Moreover, it seems that a certain small amount of water is often necessary to achieve optimum absorption and separation of ionic species. Therefore, this review follows the scope of the ones published earlier by dealing both with solvent mixtures containing water and with anhydrous solvent systems.

B. Clarifying Terminology

The following definitions of terms are felt to be necessary to avoid confusion. Synthetic ion exchange resins are classified in this review as either *microporous* or *macroporous*, which refers to the pore size of the dry, unswollen resins. The terms gel-type instead of microporous and macroreticular instead of macroporous are used by some authors, but seem to be less appropriate. Swelling and gel formation by solvent sorption is not an exclusive property of the conventional microporous resins, and Kun and co-workers[1] and Kun and Kunin[2] have shown by electron micrographs of macroporous exchange resins that their non-gel interstices are channels between agglomerates of minute spherical gel particles. It is also known that macroporous resins in contact with an appropriate solvent can swell even more than a microporous resin of high degree of cross-linking. As to the term macroreticular, it should be noted that according to the Oxford dictionary,[3] reticular means "resembling a net in appearance or construction; net-like," which are characteristics customarily connected with the high polymer skeleton of an exchange resin rather than with its pore size. This net-like structure of the skeleton does not have any direct causal relation to the pore size. A resin can have small pores although its polymer skeleton can be relatively little cross-linked, or it can have large pores although its polymer skeleton may be highly cross-linked. To avoid confusion, terms referring to net-like structure such as "macroreticular" should not be used to describe the porosity of the resin.

II. EARLIER REVIEWS

In 1960, Pietrzyk and Fritz[4] reviewed the first 10 years of research on ion exchange in mixed and nonaqueous media, giving 34 references. In 1966, Korkisch[5] published a rather thorough review in monographic form with 156 references. Dealing exclusively with the exchange and separations of metal cations on either cation exchange resins or in form of anionic complexes on anion exchangers, this review consists to a large extent of the important work of separations of lanthanides and actinides carried out by the author himself and his co-workers since 1959. A review on anion exchange in nitrate solutions by Faris and Buchanan,[6] also published in 1966, gives 233 references, of which an important number deal with mixed or nonaqueous solvent systems for the separation of metals. It includes over 20 references not mentioned by Korkisch. As in the latter's review, the emphasis is on separations of lanthanides and actinides. Another comprehensive review, dealing with inorganic ion exchange in organic and aqueous-organic solvents and giving 282 references, was published by Moody and Thomas[7] in 1968. These authors also reviewed, and gave certain emphasis to, the work done so far on the theoretical aspects of the field. The same authors[8] added another more concise review with 117 references in 1970, dealing with the stability and swelling behavior of exchange resins and the separations by ion exchange of both inorganic and organic ions. In 1966, Marhol[9] reviewed the preparation and properties of special ion-exchange materials, with emphasis on exchangers with functional groups containing phosphorus, arsenic, or antimony, and their application to the treatment of radioactive materials. Both organic and inorganic exchangers are discussed. The analytical chemist interested in exchangers of high specific selectivity, resistance to radioactivity or having other special properties, will find this review with 590 references a rewarding source of information. Ion exchange in molten systems is the subject of a review by Freiling and Rowell,[10] which was published in 1969 with 112 references. It deals with systems of two phases, one of which is a molten salt or glass, while the other is either a similar melt or a solid crystalline or vitreous inorganic exchanger such as zeolithes, feldspathoides, oxides, salts, or glasses. Although not of particular interest to the analytical chemist, it is worth mentioning because of the interesting theoretical aspects of this special field.

Two recently published books should also be mentioned. A monograph on methods for the separations of rarer metal ions by Korkisch[11] is a monumental compilation, containing 620 pages and over 4200 references, dealing with various separation methods including ion exchange in both aqueous and nonaqueous media, conveniently arranged by elements. It covers the literature up to the beginning of 1967. A no less thorough monograph on ion exchange and solvent extraction of metal complexes by Marcus and Kertes[12] was published the same year. Out of a total of over 2800 references, 488 are given in the chapters on ion exchange in both aqueous and nonaqueous media. Both the fundamental aspects and applications are discussed. There is also an interesting chapter with 251 references on nonaqueous electrolyte solutions, which is of interest in connection with nonaqueous ion exchange.

Much of the work published up to the beginning of 1968 and discussed in these reviews was aimed at developing new and improved methods for separating and purifying lanthanides and actinides, mostly by anion exchange in mixed solvents containing water. In certain solvents many of these elements form stable, negatively charged coordination complexes, especially with the nitrate or chloride anions. As these complexes are easily absorbed on anion exchangers, and often afford considerably increased separation factors, many improved separations have been developed. This does not mean that this new type of ion exchange is not also advantageous for other elements, and a number of improved or even new separations have been reported for elements from the other groups, including the alkali metals. However, relatively little has been published on the exchange behaviors of inorganic anions other than metal complexes or of organic ions.

A certain number of experimental studies have been undertaken to unravel and interpret the fundamental mechanisms of mixed and nonaqueous ion-exchange systems, but very few attempts have been made at developing a theory, which is lacking so far. Moody and Thomas[7] included this aspect in their review and discussed in some detail the theoretical work by Gupta,[13,14] who developed an equilibrium equation with six integrals for the simplest case, that of uni-univalent cation exchange, and succeeded in establishing a certain measure of supporting experimental evidence.

The fundamental properties of mixed water-containing and nonaqueous exchange systems discussed in the reviews mentioned can be summarized briefly as follows. Distribution coefficients and separation factors in solutions of lower dielectric constant are often greater than in aqueous solutions. In mixtures of water with a less polar solvent, the distribution coefficient is sometimes greater than in either pure solvent. The order of selectivities for a given series of ions is often the same in both water and the less polar medium, but there is a variation from species to species in the extent to which the affinities of individual ions for the exchanger increase when polarity decreases. This frequently leads to greater separation factors, and sometimes brings about a reversal of the order of selectivities. Although the polarity of the medium as expressed by its dielectric constant is an important factor, it cannot be solely responsible for the rather unpredictable effects resulting from modifications of the solvent composition. Other factors such as solvation, hydrogen bonding, or coordinating abilities of the solvent are probably not less important.

Solvent sorption and the degree of swelling of microporous exchange resins decrease with decreasing polarity of the solvent, while macroporous resins swell only slightly or not at all but do absorb considerable amounts of nonpolar solvents. When mixtures of water and less polar solvents are involved the former is sorbed preferentially. This effect increases with decreasing polarity of the other solvent, and therefore, in mixtures with a non-polar solvent such as dioxane, the solvent in the resin phase can become almost pure water. The ion exchange thus becomes combined with a distribution equilibrium between two liquid phases and column separation becomes a combination of partition and ion exchange chromatographies. This can sometimes improve separations, but certainly also contributes to the difficulties of the theoretical treatment of the subject.

Non-exchange sorption of uncharged species is far greater in less polar solvents than in water, either by adsorption through London forces or by invasion of non-dissociated electrolyte. Molecules and ion pairs become the predominant species in solvents of low polarity, and their penetration into the resin is not restricted by a Donnan equilibrium condition. This electrolyte invasion is still further favored in mixed media due to the above mentioned higher polarity of the solvent in the resin phase.

The exchange absorption of metal cations on anion exchangers is often easier from anhydrous or water-containing mixed solvents than from water. As the dielectric constant of the medium decreases, the extent of ion solvation tends to decrease, and this facilitates the formation of negatively charged complexes. Numerous separations of inorganic cations have been improved or newly developed using this phenomenon. On the other hand, certain coordinating solvents such as glycols and glycol ethers form stable positively charged complexes with transition metal cations, and thereby prevent their absorption by anion exchangers. This fact can likewise be used for efficient separations.

The rates of exchange with microporous exchangers are generally lower in nonaqueous solvents than in water, probably chiefly because the lesser swelling decreases the pore size of the resin. Other factors could be differences in the diffusion coefficients, in the degrees of solvation of the exchanging species, and in the viscosities. The few kinetic studies that have been done have showed that exchange rates can sometimes be even higher than in water, and that rates can be controlled either by "film diffusion" or by "particle diffusion," i.e., diffusion inside the resin. Macroporous resins show generally higher exchange rates, especially in media of low polarity.

Ion exchange chromatography of cations can sometimes be improved by eluting with water-containing solvent mixtures instead of the anhydrous solvent, using either a mixture of constant composition or a sequence of several mixtures of different compositions.

III. SYNTHETIC EXCHANGE RESINS

A. Microporous Resins

1. Fundamental Properties

a. Equilibrium

Gupta and co-workers[15,16] have continued their attempts to establish a general equation for the rational thermodynamic equilibrium constant of an uniunivalent ion-exchange reaction in mixed solvents based on the solid-solution approach as developed by Gaines and Thomas.[17] Their initial work,[13,14] the theoretical development of the equation, and the supporting experimental evidence obtained with water-methanol mixtures, was discussed in some detail in the review by Moody and Thomas.[7] They have since extended their experimental work to measurements on Li-H, Na-H, and K-H exchanges on Amberlite® IR-120 and Dowex® 50W-X4 in ethanol-water and acetone-water mixtures. Their equilibrium equation includes a term γ°, which corrects the activity coefficients in the mixed solvents at infinite dilution to the standard state of infinite dilution in water.[17a] These terms being known in the literature only for water-methanol mixtures, the authors applied the equation to the results obtained in ethanol-water and acetone-water, taking an empirical approach in order to circumvent the use of the γ° terms. This led them to conclude that equilibrium-constant values for a particular exchange system in water-containing mixed solvents could be predicted from the experimentally determined equilibrium constant in water provided the relevant γ° values are known. These authors[16] also studied the effect of the temperature on the exchange equilibria for the exchange Li-H on Amberlite® IR-120 in methanol-water mixtures. In pure water, H^+ is the preferred cation and therefore the equilibrium constant for the reaction Li-H is smaller than 1. The value increases with increasing temperature but does not become greater than 1, i.e., no reversal of selectivity occurs. However, in water-methanol mixtures reversal does take place: the equilibrium constants are greater than 1 and increase both with increasing temperature and with increasing methanol content. It was also found that both the enthalpy change ΔH° and the entropy change ΔS° for the exchange reaction increase markedly when methanol is added. This results in an interesting situation: contrary to the rule in aqueous systems, which is that the sorption of the preferred ion is accompanied by a liberation of heat, the sorption of Li^+, which is now the preferred ion, absorbs heat. These observations led the authors to conclude that, in contrast to aqueous solutions where ΔH° controls the selectivities, ΔS° is the governing parameter in mixed solvents. While several authors have suggested that ion-pair formation can explain the variations of selectivities in water-containing mixed solvents, Gupta and co-workers deem it unlikely that ion-pair formation could be involved in the present case of Li-H exchange.

Starobinets, Novitskaya, and Sevost'yanova[18] studied the equilibria for the exchanges of alkali metals for protons on the strongly acidic sulfonated exchange resin KU-2X6 in water-acetone mixtures and also for the Na-H exchange on Dowex® 50-X8 in water-methanol mixtures. They determined also the distribution of the two solvent components between the liquid and the resin phase in order to attain a better understanding of the exchange process by this parallel study of ion exchange and solvent distribution. To describe this process thermodynamically, the authors applied the experimental results to both the Gibbs-Donnan equilibrium equation[19] and the Gupta equation.[13] In the first case, they introduced into the Gibbs-Donnan equation the relative activity coefficients which take into account the transition from the standard state in the given binary solvent to the standard state in the aqueous solution. The maximum deviation from the experimental values of the values of K_H^M thus calculated did not exceed 30%. These deviations were thought to be probably due to insufficient accuracy of the estimate of the thermochemical work. The original Gupta equation, when applied to the results of the Na-H exchange in water-methanol, gave results for log K_H^{Na} which deviated from the experimental values by 50 to 130%. However, when the Gupta equation was slightly modified by a term that takes into account the selective sorption of water by the resin, the differences at low methanol content were only of the order of 10%. For the exchange of the alkali metals with the proton in acetone-water solutions, the agreement between the experiments and the modified Gupta equation was quite satisfactory for lithium and semiquantitative for sodium and potassium, respectively.

In 1959, Izmailov[20] proposed the following equation for the exchange equilibria in nonaqueous solvents, which should describe the equilibrium state when passing from water to a nonaqueous solvent:

$$\ln K_{s_M} - \ln K_{s_{H_2O}} = \frac{e^2N}{RT}\left[\left(\frac{Z_2}{a_2} - \frac{Z_1}{a_1}\right)\frac{1}{\epsilon_M} - \left(\frac{Z_2}{a_2} - \frac{Z_1}{a_1}\right)\frac{1}{\epsilon_{H_2O}}\right] - \frac{\Sigma\Delta Ac}{RT} + \ln\frac{K_{b_M}}{K_{b_{H_2O}}}$$

where e is the electronic charge, N is Avogadro's number, R is the gas constant, T is the absolute temperature, Z_1 and Z_2 are the valences of the exchanging ions, K_b and ϵ is the dielectric constant of the solvent and the basic dissociation constant denoted by the subscript, ΔAc is the sum of the differences between the energies of the ion-dipole interaction between the exchanging ions on one side, and the solvent in the solution and in the resin on the other side. The subscripts H_2O and M refer to the two solvents.

This equation, which can be regarded as a further development of the equation proposed by Pauley[21] for aqueous exchange systems, is based on a model that takes into account the differences in the energies of electrostatic interaction between the exchanging ions and the fixed resin ions, and also the differences in the energies of solvation of the ions in solution and in the resin. The final term of Izmailov's equation accounts for differences between the basic strengths of the two solvents. Although this equation appears to be worth testing experimentally, rather little notice has been taken of it in the literature so far. Izmailov[22] showed that for the exchange on the hydrogen forms of cation-exchange resins, the parameters of the last term of his equation are largely responsible for the differences between the exchange equilibria in solvents of different chemical character. Izmailov and Ignatov[23] also showed that for the case of salt exchange the displacement of anion-exchange equilibrium, when water is replaced by another solvent, takes place in accordance with the Izmailov equation. Ignatov and Shostenko[24] tested the equation for the exchange Cs-H on cation exchangers of different acid strengths in solvents of the same character, namely water, methanol, ethanol, butanol, and 3-methylbutanol. The ion exchangers were the strongly acidic sulfonic resins KU-1 and KU-2, the weakly acidic phosphonic resin RF, and the carboxylic resins KB-4P2 and KFU. With strongly acidic resins, the equilibria varied only slightly when passing from water to the alcohols, and it was found that for these water-like solvents the logarithm of the equilibrium constant was inversely proportional to the dielectric constant of the solvent. However, in acetone or methylethyl ketone, two solvents whose chemical character differs from that of water and the alcohols, the sorption of cesium differed significantly from its sorption in water. On the weakly acid exchangers, the sorption of cesium decreased considerably when passing from water to alcoholic solutions; according to the authors, this is due to a change in the degree of dissociation of the weakly acidic exchange groups of the resin. In this case the last term of the Izmailov equation becomes important. On the other hand, the strongly acidic sulfonic groups are not affected by the slight change in basicity when passing from water to the alcohols, and the last term of the equation has, therefore, little significance for the strongly acidic resins. The Cs-H exchange thus resembles a salt exchange, for which, according to Izmailov and Ignatov,[25] log K in solvents of the same character varies linearly with the reciprocal of the dielectric constant of the solvent, and the equilibrium constant depends only on the first two terms of the Izmailov equation. This was confirmed by Ignatov and Shostenko[24] by plotting log K against $1/\epsilon$ for water and the alcohols, which yielded a straight line only for the strongly acidic resins.

Gorshkov and Vovk[26] determined the equilibrium constants for the exchanges Ba^{2+}-Cs^+ and Ba^{2+}-Rb^+ in water and water-methanol solutions containing up to 60% methanol, on the strongly acid exchange resins KU-1 and KU-2. Determinations were made for various ratios of the exchangeable cations in the solution phase. It was found that in aqueous solutions $K_{Cs}^{Ba} < K_{Rb}^{Ba}$. With increasing methanol content K_{Rb}^{Ba} decreases whereas K_{Cs}^{Ba} increases, so that the order of selectivities is reversed. Over the range of solution compositions measured $(5 \geqslant C_{BaCl_2}/C_{MCl} \geqslant 0.1)$, the separation factor K_{Rb}^{Ba}/K_{Cs}^{Ba} in water varied between 1.32 and 1.6, whereas in 60% methanol it varied between 0.32 and 0.15. The authors tried to explain these results by a model similar to that used by Izmailov[20] for uni-univalent exchange, but applied to the divalent-univalent exchange

$$\frac{1}{2}M^{2+} + M^+R = M^+ + \frac{1}{2}M^{2+}R \quad ,$$

which leads to the following equilibrium equation:

$$RT \ln K_{M^+}^{M^{2+}} = \frac{Ne^2}{\epsilon}\left(\frac{1}{r_{M^{2+}}} - \frac{1}{r_{M^+}}\right) + \frac{1}{2}\left(\bar{Q}_{M^{2+},r} - \bar{Q}_{M^{2+},s}\right) + \bar{Q}_{M^+,s} - \bar{Q}_{M^+,r}$$

where r are the distances between the centers of the counterions and the fixed resin ions, $\bar{Q}_s$ the solvation energies, and $\bar{Q}_r$ the interaction energies between the counterions in the resin and the solvent in the resin. While Izmailov's equation uses the ionic valences and the radii of the solvated ions, the present equation uses instead the distances of closest approach of the counterions to the exchange site, because the authors suppose that the equation should be based on a model with elementary cells which at equilibrium must necessarily contain equivalent amounts of fixed ions and counterions, so that ionic valences become irrelevant. However, as these distances of closest approach as well as the dielectric constants of the solvent in the resin phases are not known, the authors were unable to compare their equation with the experimental results.

b. Solvent Uptake

Pauley and co-workers[27] determined the swelling of the Li, Na, K, and Cs forms of the sulfonic cation exchange resin Bio-Rad AG50W, X-1 in water and in mixtures of water with methanol, ethanol, dioxane, and acetic acid at 25°C. At low organic solvent content, the order of swelling for the various ionic forms was found to be the same as in water, i.e., Li > Na > K > Cs. However, with decreasing water content the order of swelling for K and Cs was reversed in water-methanol and water-ethanol. The authors explained this by changes in the relative hydration of the two ionic forms of the resin. However, it appears possible that instead of a simple change in degree of hydration the more complicated mechanism of transsolvation could well be the cause of the reversal. No such reversal occurs in water-dioxane, where in general swelling is less and differences between the ionic forms are rather small. This appears understandable since dioxane is a very poor solvating agent and does not interact or compete with water. This behavior of the water-dioxane system is also in keeping with the finding that little or no selective sorption of solvent was found in any of the systems studied. Although this is contrary to practically all other reports in the literature, the authors found the explanation in the rather high degree of swelling of this little cross-linked resin (1% DVB). In other terms, the water structure in such a resin is closer to that in the liquid phase than in the case of the more cross-linked resins.

Grigorovich, Skorokhod, and Zinevich[28] studied the sorption of water, acetone, and their mixtures by the sulfonic resin KU-2. The counterion was either Cd^{2+} or its coordination complexes with the following nitrogen-containing ligands: phenanthroline (phen), pyridine (py), ammonia (NH_3), and ethylenediamine (en). All these forms of the exchanger sorbed water preferentially from the acetone-water mixtures, even at very low mole fractions of water. This the authors explained by the presence of the polar hydrophilic sulfonic groups in the resin, which prefer the more polar component of the solvent mixture. The order of decreasing swelling for the various counterions over the whole composition range from pure water to acetone was the following: Cd – resin > $Cd(phen)_2$ – resin > Cd(py) – resin > $Cd(NH_3)_4$ – resin > Cd(en) – resin > $Cd(en)_2$ – resin. From this sequence the authors draw the conclusion that steric effects are probably less responsible for the decrease of swelling than polar interactions. The screening effect of the ligands on the charge of the central ion decreases the polarity of the resin, which leads to a decreased absorption of the more polar component of the solvent mixture. However, the sorption of acetone decreases likewise when Cd^{2+} is replaced by its complexes. The authors ascribe this phenomenon to an increased salting-out effect due to increased electrolyte concentration in the resin phase in its complex forms.

Marcus and Naveh[29] investigated the swelling of the chloride and perchlorate forms of the strongly basic anion exchanger Dowex®-1 of various degrees of cross-linking in several solvents and their mixtures with water. As the authors point out, only very little has been published before on the swelling behavior of anion exchangers in solvents other than pure water. They found that the swelling of the chloride forms in the pure solvents decreased in the order water > formamide > methanol > ethanol > acetonitrile > propanol > isopropanol > acetone > dioxane. The perchlorate forms showed markedly less swelling, but relatively high swelling with formamide and dimethylformamide. In mixed aqueous-organic solvents, the alcohols are sorbed preferentially at low mole fractions up to about 0.2. At intermediate compositions the preferences are reversed to become most pronounced in favor of water sorption at low water mole fractions. This behavior is most pronounced over the whole composition range for propanol and least pronounced for methanol. Both amides behave similarly, but like methanol with little emphasis. The preferential sorption of the alcohols at low mole fractions tends to be markedly more pronounced with the perchlorate forms than with the chlorides.

The authors explain these observations in terms of changing solvent structure, solvation, and steric hindrances. In the water-rich media, the explanation is thought to be the effect of low concentrations of alcohol on the structure of the water, which can be supposed to be much less structured in the tight, swollen perchlorate resin than in the more swollen chloride resin. There are consequently fewer water-water bonds to be broken, and alcohol-water bonds form more easily, with an overall decrease in enthalpy in the less structured resin phase. To this is added the increasing possibility of hydrophobic interaction with the resin skeleton and increasing loss of entropy in the highly structured solution with increasing molecular weight of the alcohols. This means that the entropy increases with alcohol transfer into the resin. In the region of intermediate solvent composition, the water has become much less structured and can more easily compete for ion solvation in the resin phase, while hydrophobic alcohol bonding with the resin skeleton becomes less important. Water has become the preferred solvent in the resin phase and the extent of the preference increases as alcohol molecules become larger. With higher alcohol fractions in the solutions, the swelling decreases and steric hindrance in the resin becomes more important. This can explain why the swelling with isopropanol is less than with *n*-propanol. The two amide solvents formamide and dimethylformamide showed a rather interesting behavior. Their mixtures with water, like those of methanol and water, showed only slight deviations from nonselective sorption by the resin. The perchlorate resin swelled significantly more with dimethylformamide than with the alcohols, while the opposite was the case with the chloride forms. This phenomenon is explained in terms of solvation and hydrogen bonding.

Having thus studied the swelling behavior of 2 resin salts with 13 solvents, the authors conclude that no quantitative theory for predicting the swelling behavior can yet be proposed. From this work, as well as from all the other work published so far, it appears to be evident that the mechanisms of swelling and ion exchange in solvents other than pure water are much more complicated than some of the earlier authors seemed to believe when they tried to explain their results in terms of a single parameter such as the dielectric constant of the medium.

c. Distribution Coefficients, Selectivities

Pauley and co-workers[27] studied the exchanges of alkali metal ions on the sulfonic resin Bio-Rad AGW50, X-1 in water and in binary mixtures of water with methanol, ethanol, and dioxane. Alkali metal-barium exchanges in acetic acid-water mixtures were also investigated. The exchange resins were first dried in vacuo at 120°C. According to Heumann and Rochon,[30] who studied the efficiencies of several drying methods, the alkali metal forms of sulfonic resins of the type Dowex®50 can be dehydrated completely by drying in vacuo at 120°C within several hours. It can, therefore, be assumed that the present work is one of the few where truly anhydrous exchangers were used. The selectivity data generally show the same trend for the various solvent systems. The selectivity coefficients for the exchange of lithium with another ion decrease in almost linear fashion with decreasing water content of all solvent systems studied. The other exchanges, however, do not follow such a simple pattern. The general tendency of the selectivity coefficients to increase with decreasing water content for the K-Na and Cs-Na exchanges, whereas it decreases for the Li-Cs, Li-Na, K-Ba, Na-Ba, and Li-Ba exchanges, can be explained by the decrease in dielectric constant. However, the maxima or minima observed for some of the exchanges when the water content decreases, and the change in the relative selectivity between exchange pairs cannot be explained by means of any single parameter. The authors used the electrostatic model previously proposed by Pauley and co-workers.[31] According to this model, selectivity coefficients are determined by the dielectric constant and the solvated radii of the competing ions. The authors point out that the observed anomalies would be accounted for by this model, but they conclude that quantitative predictions of solvent effects are quite complex, and that although dielectric constant effects are significant, it is also necessary to consider ionic solvation, solvent-solvent interactions, solvent-resin interactions, solvent-structure changes, and the degree of cross-linking, at least for more highly cross-linked resins.

Strelow, Van Zyl, and Bothma[32] determined the distribution coefficients and investigated the cation exchange of 45 elements in water-ethanol-hydrochloric acid media on the sulfonated resin Bio Rad AG50W-X8 (H^+ form). The ethanol content varied from 0 to 95%, and the hydrochloric acid concentration between 0.1 and 3.0 *M*. Although several similar studies have been reported in the past,[5] none covered so many elements, nor did they deal with acid concentrations above 1.2 *M*. Over 900 distribution coefficients presented in tables show a generally decreasing tendency with increasing acid concentration. When ethanol is added to the water, the coefficients increase at first with increasing alcohol content until a point is reached where a sudden decrease occurs. This is explained by a gradual weakening of the hydration field around the cation until the water dipoles in the coordination shell can be replaced by chloride anions. With cations having a fairly strong tendency to form chloride complexes, the coefficients increase only slightly or not at all even at low ethanol content, and the decrease occurs at a lower alcohol content. It was also found that at acid concentrations below 0.5 *M*, exchange rates are fast and of the order of those in water. However, exchange rates seem to be lower when the alcohol content and acid concentration are high. The usefulness of this kind of thorough investigation is demonstrated by three examples of chromatographic separations of mixtures containing five to six elements, which are eluted with a sequence of water-ethanol mixtures containing various concentrations of both alcohol and acid. The chromatograms show throughout well-defined narrow peaks with rather little tailing. In a more recent study, Strelow and co-workers[33] investigated the cation-exchange behaviors of 54 elements under the same conditions as in the preceding work (sulfonated resin Bio Rad AG50W-X8, solvent content 0 to 95%, hydrochloric acid concentrations 0.1 to 3.0 M), but using acetone instead of ethanol in the solvent mixture. From over 1200 tabulated distribution coefficients it can be seen that, as with the water-ethanol-HCl system, the coefficients generally decrease with increasing acid concentration, and increase with increasing acetone content until a certain solvent content is reached, where a sudden decrease begins. As contrasted with the ethanol-containing system, this reversal occurs here at considerably lower concentrations of both acetone and HCl. This is apparently due to the fact that chloride complexes form much more easily in acetone than in ethanol. For the same reason several separations could be carried out at lower acid concentrations than in water-ethanol, and several others, which had been found to be difficult or even impossible in water-ethanol, succeeded in water-acetone. As the authors pointed out, the HCl-acetone systems offers many possibilities beyond those that can be achieved in ethanol or methanol systems. Because of the low viscosity of acetone, flow rates are faster and elutions sharper. These points were well illustrated by several examples of column separations of mixtures containing up to 6 elements, all giving again rather well-defined and spaced peaks almost without any tailing.

The exchanges of methyl- and ethyl-substituted ammonium ions for K^+ on the sulfonic resin Dowex® 50W of various degrees of cross-linking in water-methanol media was investigated by Athavale, Krishnan, and Venkateswarlu.[34] The exchange coefficients in pure water were found to increase with increasing size of the ammonium ions on low cross-linked exchangers, but to decrease on highly cross-linked ones. In water-methanol media, the exchange coefficients decrease on exchangers of all degrees of cross-linking and also with increasing methanol content of the solution. The order of selectivities in water on low cross-linked resins is reversed by the addition of sufficient methanol. The authors explain these results in terms of ion-pairing. In the slightly cross-linked resins, which are highly swollen in water, the latter can be supposed to be structured. Under this condition, the large anion RSO_3^- and the equally large substituted ammonium cations will tend to form so-called "water-structure-enforced ion-pairs," which means pairs of hydrated ions as contrasted with Bjerrum type (direct-contact) ion-pairs. For the former type, selectivity increases with ionic size. On the resins of cross-linking degrees greater than 4, the molality of the resin phase is rather high and the water content comparatively low. These conditions can be assumed to be more favorable for the formation of contact-type ion-pairs, which should explain the reversal of the order of selectivity. The same approach is used to explain the decrease in selectivity with increasing methanol content. The addition of methanol causes the water structure to break down and also decreases the water content of the resin phase of all degrees of cross-linking.

Some work has also been done on the exchange of inorganic anions. Jensen and Diamond[35] studied the sorption and distribution of the anions F^- Cl^-, Br^-, I^-, and ReO_4^- as lithium salts on the strongly basic resin Dowex® 1-X4 and on the weakly basic Dowex® 3-X4 from water-dioxane mixtures of various compositions. It was found that with increasing mole fraction of dioxane in the solvent the distribution coefficients decreased and so did the selectivities. Around a mole fraction of 0.5 of dioxane all of the distribution coefficients became almost equal, only that for fluoride remaining slightly smaller. The nonexchange electrolyte invasion of the resin increased considerably as the mole fraction of dioxane increased. For example, for an aqueous 0.0104 *M* solution of lithium chloride the concentration of nonexchange electrolyte in the resin phase was found to be about 10^{-3} meq/g of resin, whereas for a solution with 0.9 mole fraction of dioxane it was about 5 meq/g. The authors' explanation of these results is based on solvation as the main parameter. In dilute pure aqueous solution the liquid phase provides the better solvation medium and is therefore preferred by the ions most in need of solvation. This is usually the ion with the highest charge density, or the most acidic cation or the most basic anion. Therefore, in the case of the five anions investigated, the order of selectivities is $F^- < Cl^- < Br^- < I^- < ReO_4^-$. However, as the mole fraction of dioxane in the solvent increases, the liquid phase becomes an increasingly poor solvation medium whereas the solvation capacity of the resin phase improves, as in this phase the mole fraction of water is higher than in the liquid phase. The latter becomes thus less attractive for the smaller anions most in need of solvation, which now will tend to enter the resin phase where solvation has become comparatively easier. Therefore, both the distribution coefficients and the selectivities among the anions should decrease and become less different. Thus the ratio of the distribution coefficient for perrhenate to that for iodide is over 1000 in water, whereas if the mole fraction of dioxane is 0.2 this ratio decreases to about 15, and with a mole fraction of 0.5 it is only about 3. Solvation thus appears to be the important parameter, although others such as nonexchange electrolyte invasion of the resin, and the change in dielectric constant, contribute also. The decrease of the dielectric constant favors the formation of electrostatic Bjerrum-type ion-pairs in both phases. Such ion-pairing should be easier between the small lithium cation and the anions than between the large alkylammonium cations of the resin and the anions. As this ion-pairing will take place in the liquid phase, it will tend to compensate partially for the effect of dioxane as mentioned above. Replacing lithium by a large cation such as $(CH_3)_4N^+$ should then compensate less, and the overall effect of dioxane should become more pronounced. It was found indeed, that with the tetramethylammonium halides the decrease of the distribution coefficient values and the selectivities went even further than with lithium halides, and at about 0.6 mole fraction of dioxane the order of selectivities started to reverse. Many investigations mentioned in earlier reviews have shown that distribution coefficients and separation factors in mixed water-containing solvents tend to be greater than in water. This is especially the case with solvents which are themselves more or less polar and capable of solvation such as the lower aliphatic alcohols. The conclusion to be drawn from these seeming contradictions is that solvation is an important parameter, often more important than the polarity of the medium, and that it remains rather difficult to make predictions for any particular system.

The distribution coefficients of 10 anions for their exchange with the OH^- form of the strongly basic exchanger Wofatit SBW-X4 in mixtures of 20% water with methanol, ethanol, isopropanol, or glycol respectively, were determined by Gürtler, Fürtig, and Holzapfel.[36] All anions were used in form of their sodium salts, of which 5 meq (50 ml of an 0.1 *M* solution) were always equilibrated with 5 meq of resin (7.5 ml). It was found that in all solvent mixtures the sequence of selectivities is the same as in water, i.e., $OAc^- < CN^- < Cl^- < NO_2^- < ClO_3 < Br^- < NO_3 < I^- < SNC^-$, with the exception of a small deviation for CN^-. However, the numerical values of these coefficients range only from 1.75 to 32.1, whereas the corresponding values in water are 1.0 and 91.0. This means that the separation factors are considerably smaller in the solvent mixtures than in water. According to the authors, the main cause of this phenomenon is the destruction of both the water structure and the hydration shell of the fixed resin cations and the counter anions, while other parameters such as the dielectic constant and the dipole moments of the alcohols, and their ability to form hydrogen bonds, are considered to be contributing factors. Other authors have tried to explain changes of selectivities in similar solvent mixtures (water-alcohols) mainly in terms of dielectric constants, ascribing only secondary contributions to the other parameters. This difference in approach is probably defensible, as most authors investigated changes of selectivities over wide ranges of solvent compositions, while the present work deals only with 1 mixture for each alcohol, i.e., 20% water and 80% alcohol. At this high alcohol content, the water structure can be supposed to be destroyed completely, while the other solvent, here always an alcohol, has solvated the ions to a large extent. Under these conditions, the change of the water structure and solvation could well be the dominant factors. The fact that the alcohol-solvated ions in the solution phase must be larger than the hydrated ions in water should explain the decrease of the selectivities. This alcoholic solvation, being due to the protolytic nature of the alcohols and their ability to form strong hydrogen bonds, is greater with anions than with cations, and will be easiest with the smallest and most electronegative anions. That means, that the order of the degrees of solvation should be the reverse of the above given order of selectivities. Transsolvation could thus account for the order of selectivities being the same in both water and its mixtures with the alcohols.

To the work just discussed, which concerned only water-miscible protonizing solvents, Gürtler and Fürtig[37] added a report on identical experiments with the water-miscible polar aprotic solvents acetone, dimethylsulfoxide (DMSO), and acetonitrile, again in mixtures containing 20% of water. The distribution coefficients, which as mentioned above, range 1.0 to 91.0 in water and from 1.75 to 32.1 in the alcohol-water media, were narrowed down here to values between 1.55 and 8.1, while the order of selectivities was different from that in water and varied somewhat from solvent to solvent. The authors once again took the solvation approach by explaining that although the hydration shell is destroyed by these solvents as well as by the alcohols, solvation by the nonaqueous component can take place only to a much smaller extent than with the alcohols because there is no possibility of hydrogen bonding. Therefore, the small anions such as Cl^- remain unsolvated or "naked," which makes them more reactive than in the strongly solvating solvents. On the other hand, large and more easily polarizable anions such as I^- or SCN^- can now become solvated somewhat more easily and therefore, the mentioned reversals of selectivities will take place.

Tolmacheva, Davydov, and Drobnitskaya[38] studied the exchange of NO_3^--Cl^- and CNS^--Cl^- on the strongly basic anion exchanger AV-17 (chloride form) in water-ethanol media containing up to 90% ethanol. Both the degree of swelling and the exchange capacity changed little when alcohol was added to the water. However, the exchange constant for both anions increased markedly with increasing ethanol content of the solvent. When passing from pure water to 90% ethanol the K-value for NO_3^--Cl^- increased from 0.18 to 0.62, and that for CNS^- from 0.06 to 0.41. These data were found by this reviewer in the English translation of the Russian original, but not without coming upon some startling inconsistencies in the text. Plots of log K against $1/\epsilon$ in the Russian paper show that the curves for both anions have positive slope, which is in keeping with the mentioned change of K-values. However, the accompanying text reads as follows: "As [these] plots. . . show, the value of K increases as the dielectric constant increases. Thus, the sorbability of nitrate and thiocyanate ions in solution is lowered by adding alcohol to the solution. . . ." On the other hand, the pertinent part of the abstract at the beginning of the paper reads as follows: "The sorbability of the nitrate and thiocyanate anions increases with alcohol content." Not having seen the original paper, one cannot be sure who is at fault, but undoubtedly somebody along the line of communication goofed in a rather unscientific manner. It is also worth mentioning that there are some contradictions between the work of these authors and that by Gürtler, Fürtig, and Holzapfel.[36] The latter authors found that the K-values decrease when ethanol is added and that the affinity of the thiocyanate ion for the exchanger is greater than that of the nitrate ion, while the present authors report the contrary. Even though there are some differences in the experimental conditions, these seem not to be great enough to explain the rather significant differences between the results.

d. Kinetics

Relatively little work has been published so far concerning the kinetics of nonaqueous ion exchange. A study of bivalent-univalent cation exchange in benzene was undertaken by Kotova, Tokareva, and Valisheva,[39] who investigated the $Cu^{2+} - H^+$ and $Ni^{2+} - H^+$ exchanges on the strongly acid resins KU-1 and SBS-1 from benzene solutions of the respective metal naphthenates. One gram portions of resin (total exchange capacity 3.6 meq for KU-1 and 2.8 for SBS-1) were equilibrated with 50/ml of benzene containing various amounts of naphthenates, and the sorption determined at certain time intervals. From a solution containing 0.25 meq of copper, sorption was quantitative within 3 min on KU-1, while 1.4 meq required 1 hr on KU-1 and 2 hr on SBS-1. The rates for nickel were of the same order. No metal remained in the solutions, which now contained an amount of free acid equivalent to the absorbed metal. Dynamic experiments with a column of 5 g resin swollen in benzene were also carried out. The breakthrough capacities were found to be 2.6 to 2.7 meq/g resin for nickel on both resins, and 1.05 and 1.7 meq/g for copper on KU-1 and SBS-1 respectively. No explanation for these differences between the two metals was attempted. When KU-1 was used in the Na^+ form, the breakthrough capacity for nickel was only 0.3 meq/g. This the authors attribute to probable differences in diffusion rates of hydrogen and sodium ions in the organic solvent and to differences in swelling of the resin.

There are several points in this work which need clarification. It seems to be evident that these reactions involve true ion exchange without any nonexchange adsorption. This should be in itself rather surprising in a strictly anhydrous benzene medium, where ionic dissociation, which is believed to be necessary for an ion-exchange reaction, is extremely low. Kraus and coworkers[40,41] determined the dissociation constants of several strong electrolytes in benzene, which ranged from 10^{-17} to 10^{-20}. The present authors do not state whether the exchangers were really anhydrous, but even if some water remained in the resin phase distribution of the metal naphthenates between the benzene and water with ionic dissociation in the water to any significant amount is unlikely, as these naphthenates are insoluble in water or almost so. Even if such a system were operative, the ion transfer should be rather slow, whereas the experiments showed relatively high rates of sorption. The considerable difference between the breakthrough capacities for nickel on the hydrogen and sodium forms of KU-1 is explained by differences between the diffusion rates of the hydrogen and sodium ions in benzene, although one may question the importance of this factor in view of the extremely low concentrations of ions that are present in benzene. The high rates of sorption in benzene are also most interesting, as sulfonated resins are known to swell very little or even not at all in this solvent. Both exchange rates and capacities should, therefore, be rather low. According to Davydov and Lisovina,[42] exchange equilibria on the sulfonic cation exchanger KU-2 in anhydrous methanol, ethanol, and formic acid, all relatively polar solvents giving higher degrees of swelling, were attained only after 30 to 32 days. Little work has been done so far on ion exchange in *non-polar and truly anhydrous media*, and results tend to be inconsistent and to lack accuracy. Some careful investigations are needed to establish whether ion exchange is really possible in such medium.

The dependence of the kinetics of exchange resin swelling on temperature, degree of cross-linking, grain size, and the nature of the solvent was studied by Marchevskaya and Kurilenko.[43] The swelling of the strongly acid resins KU-2, X4 and X16, and Ku-1 (H, Li, Na, Ca and Fe forms) and of the carboxylic resin KB-4P-2 (H, Li, Na, K and Ca forms) was investigated according to cation type, temperature (20 to 100°C), solvent type (water, methanol, ethanol, propanol, butanol, acetone), and grain size. The degree of swelling was practically independent of the temperature, whereas the swelling velocity and the activation energy of swelling increased rapidly with temperature. As could be expected from what is known of aqueous systems, swelling of KU-2 decreased with increasing cross-linking. The heat of swelling of KU-2 decreased when water was replaced by the other solvents, and was very small with benzene. Both the swelling velocity and the degree of swelling increased with decreasing grain size. The most interesting result of this work is perhaps the slight, but measurable heat of wetting found with benzene, which proves that even a sulfonic resin, or at least its polymer matrix, is not completely indifferent to this non-polar solvent.

2. Ion Separations

a. Cation Separations in Acid Media

With the thoroughness which characterizes their earlier work, Korkisch and co-workers[44-47] studied the cation exchange on Dowex® 50W-X8 of up to 25 elements including uranium, thorium, and many transition elements, in mixtures of water with methanol, ethanol, *n*-propanol, isopropanol, glycol monomethyl ether, acetic acid, tetrahydrofuran, and acetone, containing either hydrochloric,[44] nitric,[45] hydrofluoric,[46] or hydrobromic acid.[47] The solvent contents ranged from 0 to 90% and the acid concentrations from 0.15 to 1.2 *M*. All determinations of distribution coefficients were made under identical conditions for easy comparison, and as a total of over 4000 coefficients were tabulated, this work represents a wealth of information for those wanting to resolve separation problems.

Bhatnagar, Trivedi, and Bala[48] drew attention to nitrous acid as a novel acid medium for separations in aqueous ethanol. They determined about 350 distribution coefficients K_D of Ag, Hg, Pb, Cu, Co, Cd, Ni, and Zn in water and aqueous ethanol containing 30, 40, or 50% alcohol, on both the cation exchanger Amberlite® IR-120 (Na^+ form), and the anion exchanger Dowex® 1-X8 (NO_3^- form). As could be expected, increasing nitrite concentration and alcohol content caused the K_D-values on the cation exchanger to decrease for those metal cations which form negatively charged nitrite complexes more easily, whereas the reverse trend could be observed with the anion exchanger. On the cation exchanger with 50% ethanol, efficient separations of copper from cobalt, nickel, lead, or cadmium are possible, as only copper is absorbed strongly while the other ions are not absorbed at all at various nitrite concentrations. Similar possibilities are demonstrated with the anion exchanger.

For the purpose of neutron activation analysis, Van den Winkel and co-workers[49] proposed glacial acetic acid for the separation of various elements in trace amounts from large amounts of sodium and potassium. They studied mixtures of Cs, K, and Na with 10 other metals and bromide and found that the anion exchanger Dowex® 1-X8 did not absorb the alkali metals, whereas the distribution coefficients of the other ions increased with increasing acid content and reached values ranging from 100 to 10^6 in glacial acetic acid. The only similar work done so far was reported by Hazan and Korkisch,[50] who proposed the use of glacial acetic acid for separating milligram amounts of uranium from comparable amounts of rare earth elements on Dowex® 1-X8 in the acetate form.

b. Elution with Extractants

The work on cation separation on columns by selective elution with solvents containing complexing agents started more than 10 years ago. For a number of years it remained limited mostly to the use of strong acids such as hydrochloric and nitric acids as complexing agents. It was reviewed and discussed by Korkisch,[6] and Moody and Thomas.[7] During the last few years, however, Korkisch and co-workers[51-55] have initiated the use of extractants used currently in liquid-liquid extractions of metal ions, as complexing eluants in mixed water-containing solvents for selective elutions on the cation exchanger Dowex® 50W-X8 (H^+ form). Orlandini and Korkisch[51] found that from a mixture of tetrahydrofuran and aqueous 1 *M* nitric acid (95:5) Ag, Cu, Bi, the alkali metals and alkaline earth metals, Pb, the rare earths, U, Th, Fe, Co, Zn, and Cd were easily absorbed, while Hg and Sb were not retained at all. From this absorbed mixture Ag, Cu, and Bi were selectively eluted by a 0.01 *M* solution of dithizone in tetrahydrofuran 1 *M* aqueous-HNO_3 (95:5). Korkisch and Orlandini[52] separated thorium from many other elements in a mixture of methanol and 12 *M* aqueous nitric acid (95:5) containing 0.01 *M* trioctylphosphine oxide (TOPO). As contrasted with strongly acidic aqueous solutions, from which thorium is strongly absorbed, it is only weakly sorbed from the present medium, whereas many other elements are sorbed rather strongly. It is interesting to note that this separation of thorium, in tracer amounts as well as in macro amounts, can be achieved in two ways: namely, either by preventing its absorption by introducing into the resin column the mixture of metals in a solution already containing the extractant TOPO, or by eluting it selectively with a solution containing TOPO from the mixture of elements previously absorbed on the column. Thorium cannot be separated by this method from uranium, hafnium or zirconium, which have distribution coefficients of the same order (about 1) as has thorium. Korkisch and Orlandini[53] used this fact to develop a method for the separation of hafnium and zirconium from other metals when thorium and uranium are absent, using the same medium of TOPO-methanol-HNO_3. In another study, Korkisch and Orlandini[54] used 2-thenoyltrifluoroacetone (TTA) in pyridine to separate radioactive alkali metals from other metals. From a 0.1 *M* solution of TTA in pyridine the alkali metals are strongly absorbed. With the exception of thallium, antimony, and bismuth, which show a limited affinity for the exchanger, no other metal is absorbed from this medium. This fact was used to develop a method for the removal of tracer amounts of cesium-137 or sodium-22 from radioactive materials with better than 99.9% recovery and with radiochemical purity near 100%. The whole operation requires less than 3 to 4 hours, which is an important point in this case, as the exchange resins are subject to decomposition upon prolonged exposure to irradiation. It is for this reason that the separation of radioactive alkali metals could not be achieved properly with exchange resins before. The authors explain the high selectivity for the alkali metals by their inability to form stable TTA chelates in pyridine, while the other metals obviously form stable pyridine-soluble TTA complexes. The solvent acts thus as an extractant for these latter metals, which is a good example for the combined ion exchange-solvent extraction (CIESE) principle. Another application of the same principle with a high degree of selectivity was described by Wahlgren, Orlandini, and Korkisch[55] for the separation of nickel from a large number of other elements. In a mixture of acetone and 6 *M* aqueous HCl (90:10), nickel has a distribution coefficient of 227 and is absorbed by the cation exchanger together with most other elements, which have distribution coefficients of up to above 10^3. Only metals that easily form anionic chloride complexes are not absorbed. Nickel can then be eluted selectively with an 0.25 *M* solution of dimethylglyoxime in acetone 6 *M* aqueous-HCl (90:10). Nickel can thus be separated in both tracer and macro amounts from many elements.

c. Dimethylsulfoxide Systems

During the last five years, dimethylsulfoxide (DMSO) has been explored as a promising novel solvent for ion exchange separations. It is an excellent solvent for many metal salts and other electrolytes, it mixes freely with water and most organic solvents, and it associates strongly with water. It is a rather strong ligand for many cations, but solvates anions very weakly. In water-DMSO mixtures, there should be selective competition between the two solvents for cation solvation, while this would be much less the case with anions. It could, therefore, be expected that anions or anionic complexes may be more reactive in DMSO-containing systems. On the other hand, the behavior of cations may vary according to their respective tendencies to be solvated preferentially with either DMSO or water. This solvent could, therefore, become a very interesting addition to the list of useful solvents in ion exchange.

Janauer[56] undertook a distribution study of Mg, Ca, Sr, Ba, Ga, In, Sn, and Pb between the cation exchanger Dowex® 50W-X8 and water-DMSO-HCl media with concentrations of DMSO and HCl ranging from 20 to 95% and from 0.10 to 1.20 *M* respectively. It was found that at high DMSO and HCl concentrations, the values of the distribution coefficient D were similar to those in corresponding water systems. However, at intermediate and lower concentrations, these values differed considerably from those in water, especially with 20 to 50 mol % of DMSO. With the exception of Pb and Sn, the plots of log D against mol % of DMSO, at constant acid concentration, showed maxima between 30 and 40 mol %. This appears interesting, as according to earlier studies,[57] DMSO associates with water probably as a 1:2 complex, which corresponds to 33.3 mol % of DMSO. This opinion is also supported by Janauer's observation that the volume contraction resulting from mixing water with DMSO and HCl is greatest around 30 mol % of DMSO. In another study Janauer and coworkers[58] investigated the exchange behaviors of Be, Co, Ni, Pd(II), Al, and Bi with respect to Dowex® 50W-X8(H^+ form) in water-DMSO-HCl media with concentrations of up to 90% of DMSO and up to 1.20 *M* of HCl. They measured also the solvent uptakes of the exchanger in the hydrogen and Co(II) forms. Rather small but opposite trends towards selective solvent uptake were found for the two ionic forms. Water-DMSO mixtures are probably the first among the mixtures studied so far to show so little selective solvent sorption. This fact, together with these authors' observation that the swelling with DMSO-containing mixtures is greater than with water alone, seems to indicate that DMSO has a considerable solvating power. The exchange behavior of Ni and Co(II) is about the same as found for most metals by Janauer[56] in his preceding study, i.e., at high DMSO content and high acid concentration, the distribution coefficients are similar to those in water, whereas at intermediate DMSO content they are higher and pass through a maximum around 30 mol % of DMSO. For palladium (II), however, the distribution coefficient goes through a minimum of about zero in this region. This the authors explain by the fact that, except for Pt(II), Pd(II) is the only cation known to coordinate DMSO via the latter's sulfur atom to form an uncharged complex $[PdCl_2(DMSO)_2]^0$; this is of unusual strength and can be expected not to be very strongly absorbed by the exchanger. This behavior of Pd(II) is another example of solvent interference by complex formation similar to that of Fe(III) in glycol-containing media, from which it cannot be absorbed.[59] In the case of beryllium, the distribution coefficient increases with increasing DMSO content without passing through a maximum, whereas with bismuth a maximum occurs at low acid concentration only, and aluminum behaves somewhat irregularly. In all these three cases, however, the coefficient decreases with increasing acid concentration. It thus appears that maximum values of D at intermediate DMSO contents occur only with the elements which do not form chlorocomplexes easily or not at all. Of the various factors determining ion exchange in mixed solvents, the authors exclude the bulk dielectric constant from consideration as this constant is still about 56 for the present system, even at a DMSO content as high as 90% v/v. Nor can selective solvent uptake be significant, as even the hydrogen form of the exchanger shows very little selective sorption. It is the authors' opinion that the metal-hydrogen exchange in DMSO-water media is probably controlled by a strong medium effect on the proton in combination with differences in solvation behavior of the various metals in the solution phase. Using the experimental results, a chromatographic separation of nickel from palladium(II) was developed, which the authors believe to be superior to other ion-exchange methods.

Birze, Marple, and Diehl[60] carried out a study quite similar to those by Janauer and coworkers.[56,58] Using the same strongly acid cation exchanger and mixtures of water and DMSO containing up to 90% of the latter together with hydrochloric acid at concentrations ranging from 0.1 to 1.0 *M*, they investigated the distribution of Bi, Cd, Cu, Pb, Sn, Zn, and Ag. Although the distribution coefficients D were determined in almost exactly the same way as by Janauer's group, the only difference being that the total salt concentration of the solutions was 4 x 10^{-3} *M* as compared with 3 x 10^{-2} *M* in Janauer's work, the plots of log D against DMSO content at constant acid concentration did not show the maxima observed by Janauer. All plots were more or less linear, as were those for the exceptions in Janauer's reports, i.e., Pb, Sn, and Bi. It should, however, be pointed out that the elements showing these maxima belong to quite different groups of the periodic system than those without maxima, and that the latter group, as contrasted with the former, includes elements which tend to form easily chlorocomplexes. Using the D-values found, Birze and co-workers describe successful simple column separations for eight samples containing two metals each, and for three others containing three metals each. Separations were achieved by elutions with sequences of changing DMSO and HCl concentrations of samples containing 0.4 to 0.7 m/mol of each metal. With a few exceptions, recoveries were 99.6 to 100.1%.

An anion exchange study in DMSO under essentially anhydrous conditions was undertaken by Phipps,[61] who determined the degree of swelling of the strongly basic exchanger Dowex® 1-X8 in various anionic forms, and the selectivity coefficients K for the exchanges of Cl^-, Br^-, SCN^-, and ClO_4^- with the NO_3^- form of the resin. The rates of swelling of the various ionic forms were found to be much slower than in water, but the final degrees of swelling were higher than those with water. While the ratio swollen volume/dry volume with water is of the order of 1.3, it is 1.49 to 1.68 for the various ionic forms with DMSO. The selectivity coefficients were quite different from those in water and the order of selectivities $Br^- > Cl^- > I^- > SCN^- > ClO_4^-$ is radically different from, and indeed almost the reverse of, that in water $ClO_4^- > SCN^- > I^- > Br^- > Cl^-$. Moreover, the values for K in DMSO cover a much narrower range than in water, namely 0.48 to 2.81 as compared with 0.31 to 19. Considering the numerous factors and models which have been proposed to explain ion exchange, the authors point out, that the theory of ion-exchange selectivity by Reichenberg[62] appears to fit best the observed behavior of the studied anions. According to Reichenberg, anion selectivity is governed by the energy of solvation, which leads to a correlation between selectivity and hydration enthalpy. If there is no ion-solvent interaction, selectivity should be determined only by electrostatic forces. Using crystallographic data, Reichenberg established the electrostatically controlled sequence $Cl^- > Br^- > I^- > ClO_4^-$, which is more or less the order found by the authors in DMSO. This would mean that solvation is insignificant or almost so, which is in keeping with the fact that DMSO solvates anions only weakly.

d. Strongly Basic Anhydrous Solvents

The first attempt at cation exchange in a strongly basic anhydrous medium was made in 1953 by Keenan and McDowell,[63] who showed in a brief communication, that the exchange $K^+ - NH_4^+$ on the exchanger Dowex® 50 takes place in liquid ammonia at -33°C, and that the counter-ion K^+ is as difficult to elute by NH_4Cl in ammonia as by HCl, or rather H_3OCl in water. A more thorough study in the same medium was undertaken by Phipps and Hume,[64] who investigated the exchange behaviors of the alkali metals, the alkaline earths, and Ag^+, Tl^+, Cu^{2+}, and Ni^{2+} with Dowex® 50W (NH_4^+form) of various degrees of cross-linking and those of Cl^-, Br^-, I^-, NO_3^-, SCN^-, and ClO_4^- on Dowex® 1-X8 (OH^- form), all at -74°C. The swelling characteristics of the various cationic and anionic forms are similar to those found in water. Although the rates and the degrees of swelling are somewhat smaller than in water, they are considerably higher than in many other anhydrous solvents. This is also true for methanol, which has about the same dielectric constant as ammonia at the temperature of the experiments, i.e. 29 and 32 respectively. With the exception of Ag^+, all cations had significantly higher values of the selectivity coefficient K_s than in water, and this was particularly true for the divalent species. According to the authors, the only explanation is essentially undissociated ion binding between the metal ions and the fixed anionic groups. Large K_s-values due to this type of association cause proportional reductions in exchange rates, which were indeed found to be much slower than in water for univalent ions and rather critically small for divalent ions. For the exchange Ni^{2+}-NH_4^+ they were so slow that the selectivity coefficient could not be determined. On the other hand, the authors were able to show that the exchange rates for the alkali metals are still high enough to permit the separation of sodium and potassium on a small column by elution with an ammoniacal solution of NH_4NO_3 much more efficiently than in water. As to the anions studied, the range of selectivity coefficients is much narrower than that of the cations, the order of selectivities for the NO_3^- form of the resin is different from that of the Br^- form, and the tendency of the K_s-values to increase when going from water to ammonia is less general than with the cations. It therefore appears difficult to establish any simple correlation between this behavior and any of the parameters involved.

The cation exchange in anhydrous ethylenediamine was studied by Heumann, Dionne, and Tremblay[65] on the exchanger Dowex® 50W of cross-linkings between X1 and X8. The swelling of the Li^+ and $(C_4H_9)_4N^+$ forms was determined and found to be only slightly smaller than in water. This is analogous to the swelling behavior in anhydrous ammonia.[64] The rates of swelling are rather low, maximum swelling requiring up to two days. As contrasted with aqueous systems, the swelling of the pure resin increases upon contact with a solution of non-exchange electrolyte. This was interpreted as being caused by considerable invasion of non-exchange electrolyte, as even the so-called strong electrolytes are only slightly dissociated in this weakly polar solvent[66] and therefore behave like rather weak electrolytes. This explanation was confirmed by the observation that in water the same exchange resin which deswelled in solutions of LiBr or $(C_4H_9)_4NBr$, increased its volume somewhat in solutions of acetic acid, and still more in solutions of phenol. Since it was found that the exchange capacity of the more cross-linked resins for larger ions in ethylenediamine is limited, several exchange reactions were carried out with Dowex® 50-X2. The alkali metal ions and $(C_4H_9)_4N^+$ exchanged easily in both directions and pure solutions of tetrabutylammonium ethoxide, and of the 2-aminoethoxides of tetrabutylammonium and potassium respectively, were prepared. None of these solutions or solutes, although of interest as possible potential strong bases for non-aqueous acid-base titrations, had been prepared before.

Arnold, Macintosh, and Reichenberg[67] studied the influence of the basicity of the medium on the behaviors of the weakly acidic carboxylic cation exchanger Amberlite® IRC-50 and the strongly acidic sulfonic resin Amberlite® IR-120 by following the exchanges between the hydrogen ion and the alkali metals in ethanolamine. It was found that all ion-exchange processes are slow both on the sulfonic and the carboxylic resin, and for a given pair of ions there is no significant difference in exchange rates on the two resin types. Although the hydrogen forms of both resins exchange slowly, the sodium and potassium forms exchange so much more slowly that equilibrium could be attained only at 100°C. These low rates are partly due to the high viscosity of the solvent. The fact that the hydrogen form of the carboxylic resin exchanges as fast as that of the sulfonic resin and much faster than the alkali metal forms seems understable, although in water its exchange rate is much slower than those of the other forms and of the sulfonic resin. The low exchange rate of the carboxylic hydrogen form in water is due to its low degree of dissociation, which obviously increases with increasing basic strength of the solvent in analogy with, for example, the increase of acid strength of acetic acid when going from water to anhydrous ethylenediamine or ammonia.

e. Organic Ions

Relatively little attention has been paid to the ion-exchange separation of acidic or basic organic compounds. In a recent review, Moody and Thomas[8] discussed this field briefly, giving 22 references (including several dealing with applications in petroleum chemistry) that cover pretty well the work done up to 1969. Apart from the fact that many organic compounds are little soluble in water, it was found that separations of basic compounds on cation exchangers or of acidic compounds on anion exchangers can be much simpler and more efficient in methanolic or ethanolic media than in aqueous solutions. Such separations have been carried out even in nonpolar solvents especially with petroleum products, and it seems rather surprising that these promising possibilities have not been followed up more extensively.

An interesting analytical application of this kind is the analysis of waxes, metal soaps, lubricants, and similar fatty solids, proposed by Presting and Jänicke[68,69] already in 1960.

According to this method, a benzene solution of the sample is percolated first through a column of a strongly acid cation exchanger in its hydrogen form, which has been conditioned by washing with ethanol and benzene. All cations are retained, and the effluent is then passed through a strongly basic anion exchanger in its hydroxyl form, where all free acids are absorbed. Evaporation of the effluent yields the neutral part, from which, after saponification, a further separation of saponifiables can be obtained by a similar treatment. The authors demonstrated by several examples that the values obtained coincided very well with those obtained by accepted but more tedious conventional methods.

Kil Sang Lee and co-workers[70] attempted the separation of several aromatic acids, such as salicylic and substituted salicylic acids or oxine, by selective elution from Dowex® 1-X8 (Cl^- form) with ferric chloride as complexing agent dissolved in mixtures in various proportions of water with methanol, ethanol, propanol, or acetone respectively. Several separations of 2 or 3 acids with 0.05 *M* $FeCl_3$ in either methanol-water containing 50 to 90% methanol, or 50% ethanol-water were carried out successfully. The separation of metal cations on cation exchangers by selective elution with organic solvents containing complexing agents has become quite common, but it seems that the present work is the first in which the reverse principle is used for the separation of anions, namely, the selective elution of anions having ligand properties by an organic solvent containing a metal cation able to form complexes.

Churáček and Jandera[71] developed a cation-exchange method for the separation of alcohols, glycols, or amines on Dowex® 50W-X2(H^+ form) in methanol-water or ethanol-water media. These compounds easily form N,N-dimethyl-*p*-aminobenzeneazobenzoyl esters or amides, which have been used for their separations and identifications by paper or thin-layer chromatography. The authors attempted to apply this method to cation-exchange chromatography and found that the protonated forms of these compounds are sorbed from 80% methanol or ethanol by the exchange resin in the hydrogen form, and that the distribution between the two phases is determined by the basicities of the non-ionized forms and can be modified by altering the acidity of the solvent phase by means of hydrochloric acid. Elutions were therefore carried out with 0.9 *M* HCl in 80 to 90% ethanol and the compounds eluted in the order of increasing basicities. Separations of microgram amounts are demonstrated, but the separations as shown in the chromatograms do not appear to be good enough for quantitative determinations.

f. Separation of Metal Complexes

In a series of investigations King and co-workers[72-75] studied the solvent coordination complexes of chromium(III) in water-methanol,[72] water-ethanol,[73] water-pyridine-N-oxide,[74] and water-dimethylsulfoxide[75] mixtures over the whole range of solvent composition. In order to identify the solvated species present in a given medium and to determine the various equilibria, the individual complexes were separated by cation-exchange chromatography on Dowex® 50W resins in their hydrogen forms, having cross-linking degrees X2 for pyridine *N*-oxide, X4 for dimethylsulfoxide, and X12 for both methanol and ethanol. At operating temperatures of 0 to 5°C, the rate of transsolvation by water of the Cr(III)-solvent complexes is so slow that the columns containing the absorbed complex mixtures could be washed free of excess solvent by water without danger. The complexes were then eluted with aqueous solutions of either sulfuric, hydrochloric, or perchloric acid of gradually increasing concentrations ranging from 0.1 to 6.0 *M*. The effluent fractions were then analyzed for chromium and solvent ligand. Up to eight complexes, some of them isomers, could thus be separated from samples containing a total of a few m/mol of chromium.

3. Other Applications

a. Purification of Liquids, Solvents, and Reagents

The following are a few examples of removal of ionic trace impurities from non-aqueous liquids, solvents, or solutions of reagents. Traces of formic acid, dimethylamine, and salts can be removed from N,N-dimethylformamide by passing the solvent first through a bed of a sulfonic cation exchanger, and then through one of a weakly basic anion exchanger.[76] Acids and esters, but not aldehydes, can be removed from rectified ethanol by passing it through a weakly basic anion exchanger such as Amberlite® IRA-401, whereby the amount of these impurities is easily reduced by 80%.[77] Traces of amines were removed from methanol by the sulfonic resin Amberlite®

IR-120, although the sorption is slow.[78] A weakly basic impurity was removed from nitromethane by a similar procedure.[79] Acetonitrile was purified by passing it either through a mixed bed of Amberlite® IR-120 and Amberlite® IRA-400[80] or through a bed of the weakly acid carboxylic resin Amberlite® IRC-50.[81] Peroxides can be removed from diethyl ether by passing it through the strongly basic resin Dowex® 1 (OH^- form) previously washed with ether.[82] By storing it in contact with the resin the ether can be kept almost free of peroxides. Traces of iron can be removed from methanol, diethyl ether, or hexanetriol by a sulfonated resin in the hydrogen or sodium form.[83] Heavy metals such as iron, copper, or lead are removed from a solution of SO_3 in SO_2 or in a mixture of SO_2 and chlorinated aliphatic hydrocarbons by passage through a bed of an alkali salt of a cation exchanger.[84] To obtain spectrophotometrically pure crystal violet for testing of trace acidity in textile fibers, its pseudobase has first to be prepared free of anionic impurities, which is usually done by repeated recrystallization from organic solvents protected from atmospheric carbon dioxide. This is a tedious procedure with rather poor yields, but it can be circumvented by passing a benzene solution of the pseudobase through a weakly basic anion-exchange resin. From the colorless effluent the pure base crystallizes in white crystals upon addition of petroleum ether.[85] Fatty acids and other trace impurities can be removed from glyceride oils by means of a strongly basic anion-exchange resin.[86] With viscous oils, the operation can be carried out at a higher temperature or with the oil dissolved in a non-polar solvent such as hexane.

b. Deionization of Nonaqueous Polar Liquids

Bright and Makin,[87] in an article on methods for the purification of polar liquids published in 1967, reviewed two purification methods using ion-exchange resins, namely mixed-bed deionization and electrodialysis. Both methods were initiated by Felici and co-workers in France, who demonstrated for the first time in 1959[88] that polar liquids such as ethanol can be deionized in the same way as water by mixed-bed ion exchange, i.e., by passing them through a column containing a mixture of a strongly acid cation exchange resin (hydrogen form) and a strongly basic anion exchange resin (hydroxyl form). Since then these workers have prepared from commercial "absolute" ethanol a product having a specific electrical resistance of 4.4 x 10^{10} ohm/cm at 25°C, which is rather close to the probable theoretical value of about 5 x 10^{10} ohm/cm. They also prepared nitrobenzene having a specific resistance of 5 x 10^8 ohm/cm, which was 1000 times greater than the best value published previously. Using an electrodialysis cell with stainless steel electrodes and membranes of either sheets of cation and anion exchange resins or layers of resin beads between plates of porous glass, they obtained nitrobenzene with a specific resistance of 3 x 10^{10} ohm/cm. Both methods appear to be promising and suitable for continuous procedures.

4. Special Systems

a. Oleophilic Resins

A novel type of exchange resins for anhydrous ion-exchange was conceived by Gregor and co-workers[89] and given the name oleophilic resins. To increase swelling in non-polar anhydrous solvents, they introduced non-polar, oleophilic elements such as long aliphatic chains into the resin matrix. The polymer skeleton becomes thus less polar and able to sorb non-polar liquids. This resin characteristic can be achieved in two ways: either by incorporating long-chain building elements into the polymer molecule or by forming "snake-in-cage" type polymers which are really two polymers, one a long-chain aliphatic hydrocarbon, the other a conventional polystyrene-divinylbenzene type copolymer which forms a cage around the former. Thus, for example, carboxylic acid resins were prepared by copolymerization of methacrylic acid and dodecyl methacrylate with divinylbenzene for cross-linking, while sulfonated resins were prepared by copolymerization of styrene, divinylbenzene and isobutylene. Sulfonic acid cage polymers were obtained by forming styrene-divinylbenzene cages around polyisobutylene, which is oil-soluble. A number of other similar syntheses were described, and swelling behavior and other data of numerous experimental cation- and anion-exchange resins were tabulated. By properly balancing the respective proportions of oleophilic elements and ionic groups, resins were obtained which swell in both non-polar and polar solvents, and which have exchange capacities of the same order as those of the conventional resins.

Tsuk and Gregor[90] developed a theory of swelling for a cross-linked polymer network with a large number of side-chains, along the lines of the statistical-mechanical approach by Flory. This theory, which was supposed to fit the behavior of the oleophilic resins, enabled the authors to predict the swelling behavior of several resin types and to confirm it experimentally. Tsuk and Gregor[91] also investigated the reactions between organic bases and sulfonic oleophilic resins in polar and non-polar media. The hydrogen form of the resins easily absorbed bases such as diethylamine, pyridine, aniline, *n*-butylamine, and benzylamine from various solvents including water, methanol, acetone, cyclohexane, and toluene. At equilibrium, the uptake was equal to or slightly higher than the exchange capacity of the resins, which ranged from 0.8 to 3.1 meq/g of dry resins. The uptake of diphenylamine, a very weak base, was only partial and stronger bases exchanged it easily on the resin. The sorption rates depended mainly on the degree of swelling, while base concentration and temperature were only minor factors. This sorption of the bases is explained as being an acid-base reaction of the type

$$RSO_3H + B \rightleftharpoons RSO_3^- \cdot \, {}^+HB$$

where R is the resin matrix and B a base. For this reaction to take place, ionic dissociation in the solution is not required, and therefore the reaction is possible in non-polar solvents. Besides, this is an example of sorption by a chemical reaction without ion exchange, which can also be used for separations of ionic species. The exchanger being a very strong acid, the equilibrium of this reaction will generally be far to the right, and only with extremely weak bases such as diphenylamine will the base uptake at equilibrium be significantly below the resin's capacity. It was also found that generally the stronger bases are held more strongly by the exchanger, and that for bases of low molecular weight, when the pK-values in water of two bases differ by at least 2 to 3 units, the stronger base replaced the weaker one quantatively. Based on these findings, the authors carried out several successful chromatographic separations such as that of pyridine from aniline in heptane by elution with *n*-butylamine, or that of 100 mg of each of four alkaloids of the reserpine family in dichloroethane by elution with pyridine. In the latter case, the differences in basic strength are small and not sufficient to explain the separations. With such large and complex molecules structural differences certainly play an important role.

Shida and Gregor[92] investigated the swelling of a strongly basic oleophilic anion exchanger in anhydrous mixed solvents and compared it with a conventional microporous resin. The oleophilic resin was prepared by amination of a chloromethylated polystyrene-divinylbenzene copolymer with N,N-dimethyldodecylamine, while the conventional resin was quite similar to Dowex® 1-X1. The solvent mixtures used were methanol-benzene and ethanol-chloroform. In both media the oleophilic resins showed large shifts of swelling maxima towards less polar solvent compositions as compared with the conventional resin. While the latter sorbed the more polar solvent component preferentially over the whole composition range, the oleophilic resin preferred the less polar solvent over the larger part of the composition range. A thermodynamic discussion of the swelling data on the oleophilic resin in ethanol-chloroform, in which the work of Newman and Krigbaum[93] on mixed solvents was used, led the authors to the conclusion that there seems to be a strong similarity of the liquid-liquid interaction terms in the resin phase and those in the solution phase.

A similar anion exchanger was used by Walden[94] to investigate the sorption of acetic, capric, myristic, and stearic acids from toluene and hexane solutions. Sorption was found to be quite rapid, and when the hydroxyl form of the resin was used neutralization reactions were quantitative. When an excess of acid was used, amounts in excess of the equivalent were absorbed, obviously as a result of adsorption by the polymer matrix. In the case of capric acid, the resin was able to absorb twice the equivalent amount of the acid, which is quite remarkable taking into account the size of the latter's molecule [$CH_3(CH_2)_8$ COOH]. On the other hand, it is obviously just the size of its aliphatic chain, which makes its adsorption by the oleophilic polymer easy.

b. Exchange Papers

This chapter deals with papers impregnated with ion exchange resins. Nonimpregnated cellulose exchange papers are discussed in Chapter IV. A.

A group of Italian workers started studying chromatographic separations on ion exchange papers almost 11 years ago. Lederer, Moscatelli, and Padiglione[95] investigated the absorption of 18 metal cations and several anions from methanol,

ethanol, isopropanol, and acetone containing acids such as hydrochloric, nitric, and sulfuric acids, on cellulose paper or on paper impregnated with zirconium phosphate, sulfonic resin, or quaternary ammonium resin. The authors suggested the following mechanisms as contributing to the ionic absorption: ion exchange, complex formation with sulfonic or phosphoric acid groups of the exchangers, complex formation by solvation, partition between the solution and the water retained on a polar support, and adsorption on the polymer network of either the paper or the impregnating resin. Due to this multitude of possible factors, the changes of absorption of a given ionic species when going from one type of paper to another were rather difficult to predict.

Ossicini and Lederer[96] extended the earlier investigations to other metal ions and hydrochloric acid solutions, using solvents such as benzene or mixtures of water with acetic acid, phenol, and ethyl acetate, with the sulfonic resin paper Amberlite® SA, the quaternary ammonium resin paper Amberlite® SB-2, and the quaternary ammonium cellulose paper Macherey-Nagel. They determined and tabulated about 370 R_F-values for 13 cations (alkali metals, alkali earths, transition and rare earth metals), and several complex anions, coming to the conclusion that the results do not seem to have analytical applications. This is probably a good example of a useful collection of negative results.

Sinibaldi and Lederer[97] studied the sorption behavior of gold as $AuCl_4^-$ on several cellulose papers and on the four resin-impregnated papers Amberlite® WA-2 (weak acid), Amberlite® SA-2 (strong acid), Amberlite® WB-2 (weak base), and Amberlite® SB-2 (strong base). The solvents used were mixtures of varying proportions of water with methanol, ethanol, isopropanol, and acetone, and they contained hydrochloric acid at various concentrations. This work was undertaken to clarify the question under what form, anionic or neutral protonated, the chlorocomplex of gold is absorbed. By comparison and discussion of the numerous data gathered, the authors came to the conclusion that $AuCl_4^-$ seems to be the preferred species in water, whereas the ion-pair $[H^+.AuCl_4^-]$ seems to predominate in inorganic solids and solutions.

c. Non-exchange Separations

Separations without exchange of ions on columns of ion-exchange resins can be based on a chemical reaction such as an acid-base reaction (sorption of amines by the hydrogen form of a cation exchanger) or a complex formation between the fixed resin ion and a solute or between the metal counterion and a ligand solute (ligand-exchange chromatography). It can also be based on a physical principle such as in partition chromatography, where the exchange resin, by preferential sorption of the more polar component of a mixed solvent, functions as support for the stationary phase.

Tsuk and Gregor[91] described the chromatographic separation of amines on a sulfonate resin in the hydrogen form. This method, which is based on a non-exchange acid-base reaction, was discussed in more detail in Chapter III.A.4.a. on oleophilic resins. Another application of the same principle is the removal of pyridine bases from crude benzole by means of a sulfonic resin in the hydrogen form as described by Banerjee, Roy, and Lahiri.[98] The benzole was percolated through columns of either Dowex® 50 or Amberlite® IR-120, whereby 98% of the bases was absorbed. The bases were then eluted with aqueous or alcoholic solutions of mineral acids.

A method based on complex formation is the separation of aliphatic sulfoxides from other sulfur-containing compounds such as sulfides and sulfones, which was described by Horák and Pecka.[99] The sulfonic resin Dowex® 50 (in the hydrogen form) absorbed the sulfoxides selectively from benzene containing a mixture of sulfur compounds, and the pure sulfoxide was easily desorbed into ethanol, from which it could then be removed by distillation. Several aliphatic sulfoxides could thus be isolated in purities between 99.1 and 100%. Aromatic sulfoxides are not absorbed. The authors explain this specific sorption of the aliphatic sulfoxides as being due to interaction of their sulfinyl groups with the sulfonic group of the exchanger, probably by hydrogen bonding.

Samuelson[100] published in 1969 a review with 32 references entitled *Partition Chromatography of Sugars, Sugar Alcohols, and Sugar Derivatives*, which deals with the use of ion-exchange resins as support for the stationary phase in partition chromatography in mixed aqueous-ethanolic media. The author himself and his co-workers initiated this principle almost 20 years ago and they have contributed most of the work done so far. Due to the preferential sorption of water from a water-ethanol mixture by strongly acidic or strongly basic exchange resins on one hand, and to the greater solubility of sugars in water on the other hand, these compounds are absorbed by the resin phase from aqueous ethanolic solutions and can then be separated by elution with a water-ethanol mixture containing a large proportion of ethanol. It was found that in many instances columns of strongly basic anion-exchange resins in the sulfate form are the most efficient, but certain separations can be realized more easily with sulfonated cation exchangers in their lithium forms. In one example given by the author, 13 different monosaccharides, each in amounts of 100 to 600 μg, were separated on a column of 6 x 600 mm of Dowex® 1-X8 in about 160 min by elution with a total of about 350 ml of 86% ethanol. In another experiment, a sample of 5 μl of sulfite spent liquor from a spruce pulping process was chromatographed on a resin bed of 3 x 610 mm of the anion exchanger Technicon® by elution with about 130 ml of 86% ethanol to separate ligninsulfonic acid, furfural, and six monosaccharides.

More recently, Martinson and Samuelson[101] undertook a study of the chromatographic behavior with both the cation exchanger Dowex® 50W-X8 (in the lithium form) and the strongly basic anion exchanger T5C (sulfate form) of 22 monosaccharides and 15 di- and oligosaccharides, most of which had not been investigated before. As found in earlier work, a few monosaccharides which did not separate with the anion exchanger, did so when eluted from the lithium form of the cation exchanger. It was further confirmed that in general the distribution coefficients increase with the polarity of the compounds (increase of the number of hydroxyl groups) and decrease with the number of non-polar groups such as $-CH_2-$ or $-CH_3$, and finally, that compounds of smaller molecular weight are eluted before those of greater weight.

B. Macroporous Resins

1. Introduction

Microporous resins in the dry state have an essentially homogeneous structure with negligibly small pores of not more than a few Å in diameter. Their polymer matrix is flexible, which enables the resin to swell while absorbing a solvent and to become thus a porous gel. The pore size of resins of medium to low degree of cross-linking, when swollen in water, is of the order of 10 to 30 Å. Dry macroporous resins, however, have large pores of 100 to 1200 Å in diameter, but a more or less rigid polymer matrix consisting of randomly packed microspheres able to swell by absorbing solvent. These resins swell only little or not at all when absorbing a solvent. These significant structural differences have been established by electron micrography by Kunin and co-workers.[1,2]

As the uptake of a solvent by a microporous resin is due mainly to solvation of the ionic groups of the resin and of the counterions, the degree of swelling and with it the final pore size decrease with decreasing polarity or solvating ability of the solvent. The sorption of non-polar solvents is therefore practically nil. In the macroporous resin, only a minor part of the sorbed solvent may be used for solvation, while large pore spaces can be simply filled by free solvent and therefore, the uptake of non-polar solvents such as hydrocarbons can be almost as great as that of water. This also explains why Millar and co-workers[102] found that the water uptakes of the H^+, Li^+, Na^+, and K^+ forms of macroporous sulfonic resins are practically the same, whereas in microporous resins the water uptake decreases in the order $H^+ > Li^+ > Na^+ > K^+$, which is the order of decreasing hydration of the ions.

Table 1 lists the macroporous exchange resins commercially available at present from several sources.

2. *General Properties and Comparison with Microporous Resins*

A comprehensive and careful study of ion-exchange resins in non-aqueous solvents with a comparison of micro- and macroporous resins was carried out by Pietrzyk.[103-105] The first part[103] deals with sorption rates of *p*-nitroaniline under anhydrous conditions on the strongly acid cation exchangers Dowex® 50, Amberlite® IR-120, and Amberlyst® 15, from solutions in the lower alcohols, acetonitrile, acetic acid, dioxane, and benzene. The resins, being used in the hydrogen form, reacted as strong acids and therefore the sorption of the amine was obviously not an ion-exchange reaction, but an acid-base reaction with ion-pair formation as follows:

$$R\text{-}SO_3^-.H^+ + R'NH_2 = R\text{-}SO_3^-.{}^+H_3NR'$$

The *p*-nitroaniline was chosen because, being a very weak base, it should allow the observation of

TABLE 1

Macroporous Ion Exchange Resins

Name	Manufacturer	Type of Function		Approximate Pore Size, A
Amberlyst® 15	Rohm and Haas Co.	$R\text{-}SO_3^-$	strong base	290
Amberlyst® A-21	Rohm and Haas Co.	R_3N	weak base	700 to 1200
Amberlyst® A-26[a]	Rohm and Haas Co.	R_4N^+	strong base	400 to 700
Amberlyst® A-27	Rohm and Haas Co.		strong base	400 to 800
Amberlyst® A-29[b]	Rohm and Haas Co.	R_4N^+	strong base	200 to 600
Deacidite® K	Permutit Company, Ltd. London		strong base	
Imac C8P	Imacti, Amsterdam	$R\text{-}SO_3^-$	strong acid	
Imac C16P	Imacti, Amsterdam	$R\text{-}SO_3^-$	strong acid	
Imac A20	Imacti, Amsterdam	RNH_2, -NH, -N	weak base	
Imac A21	Imacti, Amsterdam	R_3N	weak base	
Imac S5-40	Imacti, Amsterdam	$R(CH_3)_3N^+$	strong base	
Imac S5-50	Imacti, Amsterdam	$R(CH_3)_3N^+$	strong base	
Imac S5-42	Imacti, Amsterdam	$R[N(CH_3)_2C_2H_4OH]^+$	strong base	
Lewatit® SP 120	Farbenfabriken Bayer	$R\text{-}SO_3^-$	strong acid	
Lewatit® CNP	Farbenfabriken Bayer	$R\text{-}COO^-$	weak acid	
Lewatit® MP 62	Farbenfabriken Bayer	R_3N	weak base	
Lewatit® MP 64	Farbenfabriken Bayer		medium strong base	
Lewatit® MP 600	Farbenfabriken Bayer	R_4N^+	strong base	
Lewatit® MP 500	Farbenfabriken Bayer	R_4N^+	very strong base	

[a] formerly Amberlyst® XN-1006
[b] formerly Amberlyst® XN-1002

solvent effects more easily than a strong base which would be retained too strongly by the exchanger. The sorption rates for the amine, expressed in time required for reaching equilibrium, were faster on the microporous Dowex® 50 than on the macroporous Amberlyst® 15 in the lower alcohols methanol, ethanol, and *n*-propanol, but the reverse was found in isopropanol and butanol. In the less polar solvents butanol, acetic acid, and dioxane, sorption by the macroporous resin was markedly faster, while in benzene it was fast with the macroporous and nil with the microporous resins. The distribution coefficients D for both types of resins increased in general with decreasing dielectric constant of the solvent and tended to be somewhat higher with the macroporous resin. The latter showed high D-values in dioxane and benzene, whereas the microporous Dowex® 50 showed its lowest value with dioxane and nil with benzene. The last two values are obviously the result of insufficient swelling. A notable exception was acetonitrile, which showed a high D-value although it was the solvent with the highest dielectric constant. The explanation can probably be found in its rather weak solvating power, whereas the lower alcohols, although less polar than acetonitrile, are much stronger solvating agents. This factor is important for both the swelling of the microporous resins and the steric hindrance around the sulfonic group to which the amine molecule must become attached. The latter point should also explain why in the macroporous resin, where swelling is unimportant, the D-values in the non-polar solvents and in acetonitrile are much higher than in the polar alcohols. Similar observations were reported by Cassidy and Streuli[107] for the sorption of anilides from methanol and acetonitrile.

The effect of small amounts of water on the distribution equilibria was shown to be remarkable. Even amounts as small as those corresponding to residual water from incomplete drying of the resin or to traces of water in commercial "pure" solvents were sufficient to cause considerable changes of D-values, especially in low-polar solvents. The D-values with Dowex®

50 increased with traces of water in dioxane, while in benzene some water in the resin was necessary to obtain any sorption at all. This is easily explained by the increase of swelling by the water, which leads to an increase of the number of accessible exchange sites in the resin. On the other hand, the D-values decrease with water in the macroporous resin. Here the sulfonic groups are not solvated in the pure non-polar solvents and are therefore easily accessible, while small amounts of water will cluster around the sulfonic groups, which thus are not directly accessible any more. Besides, the water gives rise to a liquid-liquid partition equilibrium which will influence the D-values. As the author pointed out correctly, small amounts of water can thus lead to unreliable and ambiguous D-values, and as the distribution coefficient is one of the most important parameters for separations, its value should be determined with reasonable accuracy. Unfortunately this is not always done, as sometimes not enough attention is paid to the presence or absence of water.

The second paper[104] reports on the extension of the preceding work to the sorption of *p*-nitroaniline and several other weak bases on the same sulfonic resins in 14 different water-miscible solvents in mixtures of varying composition with water. The rates of sorption of *p*-nitroaniline by both types of resins from 80% ethanol were several times faster than those determined previously with anhydrous ethanol. This was attributed to the increased polarity of the medium. The distribution coefficients of *p*-nitroaniline on Amberlyst® 15 (hydrogen form) in the 14 water-organic solvent mixtures over the composition range 100 to 20% solvent were determined. The D-values decreased considerably upon addition of water to the alcohol, reaching a minimum around 70 to 80% organic solvent, and then increased again on further increasing the water content. The author explains these changes of D by a change of the sorption mechanism as follows: first, the water added in small amounts causes a decrease of the acidic and basic strengths of the sulfonic acid and amino groups, respectively, which results in a shift of the acid-base equilibrium towards the side of the reactants. This would be analogous to the effect that small amounts of water have on acid-base titrations in non-aqueous solvents. Upon further increase of the water content, the increase of D-values is brought about by a form of non-electrolyte sorption similar to that known in "solubilization chromatography."[106]

Studying the sorption of other weak bases such as *m*- and *o*-nitroaniline and caffeine, it was found that the D-values increased with increasing basic strength of the sorbed species. It was also found that, in solvents exhibiting basic properties, sorption of amines at high organic solvent content was negligible and D-values remained small even at higher water content. From pyridine, the most basic solvent investigated, no sorption of *p*-nitroaniline occurred even at 80% water content. These facts seem to prove that the sorption of amines is based mainly on an acid-base reaction. A special case was acetic acid as solvent. The D-values were rather high, for *p*-nitroaniline by far the highest for all solvents at higher solvent content. Undoubtedly the amine is largely protonated in this strongly acid solvent, and therefore the sorption must be due to an ion-exchange reaction. Besides, solvation of the sulfonic acid groups must be rather poor in the anhydrous or slightly aqueous solvent, which probably makes the exchange reaction easier.

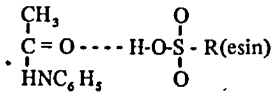
The third part of the study was undertaken by Pietrzyk[105] in order to gain more insight into the possible uses of ion-exchange resins in nonaqueous solvents as catalysts, in syntheses, and for chromatographic separations. He determined the uptake of 19 currently used solvents by the hydrogen and sodium forms of the microporous resins Amberlite® IR-120 and Dowex® 50-X8 and the macroporous Amberlyst® 15, using a carefully developed centrifugation method, and dehydrating the resins equally carefully by drying in vacuo at 95 to 105°C for 24 to 36 hr. For the purpose of comparison, the uptake by several non-exchange adsorbents used in chromatography was determined likewise. As the solvents did not contain more than 0.01 to 0.1% of water and 1.5 g of resin was always equilibriated with 25 ml of solvent, the amount of water in the system was insignificant. This is one of the few investigations where the medium was well defined and practically anhydrous. The rates of solvent sorption were also measured with several solvents. Ethanol was sorbed faster and in larger amounts by the macroporous Amberlyst® 15 than by the microporous Dowex® 50 and equilibrium was reached within a few minutes. Butanol, being more viscous and less polar than ethanol, shows a similar but less pronounced difference between the two resins.

As to benzene, the uptake by the microporous exchanger, though it was only 0.014 g/g of resin, is very slow and probably takes several days, whereas the macroporous resin is equilibriated in less than 1 hr after having absorbed 0.33 g/g of resin.

As could be expected, both types of resin prefer water, the most polar solvent studied, over any other solvent. For any of the nineteen solvents, uptake is larger by the macroporous than by the microporous resin. This difference is greatest with non-polar, non-oxygenated solvents, of which the microporous resins sorb only traces, whereas the macroporous one takes up considerable amounts such as 0.20 g of hexane or 0.50 g of carbon tetrachloride/g of resin. The macroporous resin was also investigated in its sodium form. The uptake of non-polar solvents was found to be independent of the ionic form, but large differences appeared with the oxygenated solvents, where the hydrogen form absorbed up to twice the amount sorbed by the sodium form. This phenomenon, which has also been observed by other investigators, was explained by the hydrogen-bonding properties of these solvents. No correlation could be found between the sorption data and the dielectric constants or the acid-base properties of the solvents, as the solvent uptake varied quite irregularly with both of these properties.

Some interesting conclusion as to the role of the resin matrix in ion-exchange reactions could be drawn from the comparison of the solvent uptake by the sulfonated resins with the uptake by the corresponding unsulfonated hydrocarbon polymers. As could be expected, both types of hydrocarbon resins are virtually free of water uptake. While both the microporous and the macroporous resins easily sorb benzene, only the macroporous one absorbs hexane or cyclohexane, and this to a much larger extent than the corresponding sulfonated resin does. The uptake of aliphatic alcohols by the microporous resin is rather limited as compared with the corresponding sulfonated resin, but the macroporous resin takes up alcohols freely, though still less than does the corresponding sulfonated resin. These results suggest that solvent interaction with either the ionic resin group or with the polymer matrix is of much greater importance for the solvent uptake by the microporous than for the macroporous exchange resins. In this respect the macroporous exchange resins seem to resemble the true adsorbents, which was confirmed by measuring the uptake of 14 solvents by several typical adsorbents such as activated carbon, silica gel, molecular sieves and alumina. Their solvent sorption behavior appeared indeed to be similar to that of Amberlyst® 15.

Cassidy and Streuli[107] studied the sorption and separation of acetanilides and several other amides in anhydrous solvents on the microporous Dowex® 50W and the macroporous Amberlyst® 15. The resins were probably sufficiently dehydrated as they were dried in vacuo at 60°C until their vapor pressure remained at 0.5 mm. The acetanilides, which are very weakly basic, were sorbed much more strongly from acetonitrile than from methanol although these two solvents are of comparable polarity. This the authors explained by the fact that methanol solvates the sulfonic groups of the resins easily by a strong hydrogen bridge through its hydroxyl group, whereas acetonitrile cannot form such bridges and is a weak solvating agent. Therefore, only methanol can compete with the anilides successfully for the bonding to the sulfonic group. The anilides are believed to form a hydrogen bridge between their carbonyl groups and the hydrogen of the sulfonic acid group as follows:



$$\overset{\displaystyle CH_3}{\underset{\displaystyle HNC_6H_5}{C}}{=}O\cdots\cdots H\text{-}O\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\text{-}R(\text{resin})$$

The sorption of these bases would thus be neither an ion-exchange nor an acid-base reaction, but a form of selective solvation.

Although the distribution coefficients of the acetanilides in methanol were found to be of the same order for both types of resins, namely about 5, in acetonitrile they were greater than 1000 with Dowex® 50W and far larger still with Amberlyst® 15. Thus *N*-propylacetanilide was absorbed by the latter resin completely, and acetanilide had a distribution coefficient of 6000, although this value decreased dramatically upon addition of small amounts of methanol; with only 1% of methanol the value decreased to 99, to reach 4 with 80% methanol. This illustrates very well the competition between the anilide and the alcohol for the bonding to the sulfonic acid group. In accordance with the differences in sorption behavior between the two types of resins, acetanilide and *N*-propylacetanilide could not be separated in a methanol-acetonitrile medium on Dowex® 50W because of excessive tailing, whereas the macroporous column afforded almost quantitative separation.

The authors suggest that the important parameters in this type of sorption and separation are the solvation of the sulfonic group by hydrogen bonding and similar interactions between solvent molecules, while some weaker attraction between the resin matrix and the anilides can be another, less important parameter.

The inferior role of solvent-resin interaction in the macroporous resins is also apparent in a study by Blasius and Schmitt,[108] who compared the solvent uptake from water-dioxane and water-dimethylsulfoxide mixtures by Dowex® 50W with that by Amberlyst® 15. Both resins were used in several counter-ion forms. Although both exchangers showed preferential sorption of water, this was markedly less pronounced with the macroporous resin. The authors suggest that in the microporous resins, once the sorbate layers have been formed by water-resin interaction, little room is left for "free solvent," while in the macroporous resin the sorbate layers occupy only a minor part of the pore space, which remains available for "free solvent," i.e., for nonselective sorption of the solvent mixture.

Fritz and Waki[109] compared the macroporous anion exchanger Amberlyst® XN-1002 with the microporous Dowex® 1-X8 for the separation of magnesium and calcium in 0.5 *M* solutions of nitric acid in 90% alcohols. Batch experiments showed that sorption rates with Amberlyst® were always higher than with Dowex® 1. Magnesium in tert-butanol, a rather viscous medium, attained sorption equilibrium with the macroporous resin in less than 30 min, while more than 2 hr were required with the microporous exchanger. The authors concluded, therefore, that the macroporous resin is to be preferred for chromatographic separations in nonaqueous media. Based on these results, Fritz and Greene[110] proposed a method for the separation of rare earth metals from other metals on Amberlyst® XN-1002 in a medium of 1.5 *M* nitric acid in 85% isopropanol. Here again, comparing this resin with Dowex® 1 X-8 showed that sorption rates were faster and column separations sharper with less tailing when the macroporous resin was used.

Inczédy and co-workers[111,112] studied the swelling behavior of both micro- and macroporous exchangers in several solvents. Inczédy and Pásztler[111] investigated the swelling of the strongly acidic resins Dowex® 50-X4 and X8, and of the strongly basic Dowex® 1-X4 in water and in seven water-miscible solvents. The cation exchangers were used in their hydrogen and sodium forms and the anion exchanger in its hydroxide and chloride forms. Their results confirm earlier reports that swelling is at its maximum with water and that the alcohols and glycols produce also significant swelling, but they also found a surprisingly great difference between the solvent sorption by the hydrogen and sodium forms of the cation exchangers in ethanol, while the corresponding difference was much less in methanol. The authors assume that increased ion-pair formation of the resin in sodium form is the cause of the very low swelling of the sodium form in ethanol, where the solvent uptake in moles of solvent/gram-equivalent of dry resin was found to be 2.5 and 0.3 for Dowex® 50-X8 in the hydrogen and sodium forms respectively. This approach fails, however, to explain why this effect should be so much less in methanol, where the corresponding figures are 3.75 and 2.2 mol/gram-equivalent.

These swelling data were obtained with resins containing according to the authors about 0.6 mol water/gram-equivalent of resin, and with solvents containing 0.05 to 1.4% of water. Taking into account the small equivalent weight of water, this amounts to up to 5 mol % or 0.05 mol fraction of water in the solvents, which can hardly be called a nonaqueous or anhydrous system. Knowing from other work[103,107] the considerable effect that small amounts of a solvent of higher solvating power such as water can have on the sorption behavior of exchange resins, one can assume that under truly anhydrous conditions the present swelling data could be quite different.

In another study Inczédy and Högye[112] investigated the uptake of water or ethanol by the following macroporous exchange resins: the strongly acidic Imac C8P, Imac C16P and Lewatit® SP100 (H^+ and Na^+ forms), the weakly basic Imac A20 and Lewatit® MP60, and the strongly basic Lewatit® MP500 and MP600 (in the hydroxide and chloride forms). The experimental conditions were the same as with the microporous resins in the preceding work,[111] i.e., the media were not quite anhydrous. No significant differences from the microporous resins were found. The same considerable differences in ethanol uptake between the hydrogen and sodium forms of the strongly acid microporous resins were found with the corresponding macroporous resins. Thus the uptake in moles of ethanol per equivalent of resin for Imac C8P was 2.6 and 0.2 for the hydrogen and sodium forms respectively. The corresponding values in water were 11.7 and 12.5. The comparison of these data led the authors to the conclusion that the macroporous structure is not enough to ensure higher solvent uptake. This statement certainly needs to be qualified. It may apply to certain solvents such as the water-like alcohols, but certainly not to non-polar or non-solvating solvents.

Fritz and Tateda[113] studied the uptake of organic acids and phenols by Amberlyst® A-26 from water-methanol and water-acetone mixtures. The distribution coefficients of acetic, propionic, butyric, and valeric acids in aqueous methanol containing sodium chloride were found to increase with increasing chloride concentration and to decrease with increasing methanol content. The acids were believed to be in their molecular form, and the effect of the chloride was believed one of salting-out. It was further found that the distribution coefficients in methanol- or acetone-water mixtures were generally larger in alkaline than in acidic solution, and that the zone of pH-values where the change started seemed to coincide with the pK of the acid. It was concluded that the sorption in alkaline solution is an ion-exchange reaction of the anion formed on dissociation of the acid, whereas in acidic solution molecular sorption of the undissociated acid takes place, probably by interaction with the resin matrix. The latter type of sorption seemed also to occur partially in alkaline solution, as capacity studies showed some extra uptake of benzoate and nitrophenol that could not be accounted for by ion exchange. These uptake mechanisms are opposed by solvation of the acid in the solution phase, which increases for organic acids with increasing methanol or acetone content. Other anions in the solution will compete with the organic anions for the fixed resin sites, but inorganic anions may enhance the sorption of the organic acid by a salting-out effect.

Ishibashi and co-workers[114] studied the sorption of mercaptans and dialkyl sulfides on Amberlyst® 15 in various metal forms from toluene, hexane, and methanol. The exchanger's counterions were Cu(II), Co(II), Ni(II), Zn(II), and Ag(I). The copper form absorbed 2 to 3 mol of *n*-propylmercaptan per equivalent of resin, depending on the solvent, while the other metal forms sorbed only minor amounts. This corresponds to the known fact that copper generally coordinates more strongly with sulfur than do the other metals. The sorption could, therefore, be due to a non-exchange complex-forming reaction with the mercaptans. This explanation is supported by the observation that the sodium form of the resin did not absorb mercaptans at all. On the other hand, only copper could reduce the mercaptans to disulfides which, being more basic, coordinate more easily than mercaptans. That could mean that only the disulfides are able to react with the exchanger. This could also explain why the silver form did not absorb mercaptans at all, but sorbed as easily as did the copper form the lower dialkyl sulfides, which should also coordinate more easily than the mercaptans.

3. Separations and Other Applications

Fritz, Waki, and Garralda[115] separated magnesium, calcium, and strontium by chromatography on the anion exchanger Amberlyst® XN-1002 (now Amberlyst® A-29, in the nitrate form) in a methanol- (or ethanol)- water-nitric acid medium.. After elution of magnesium with ethanol-0.25*M* nitric acid (95:5), calcium was eluted with methanol-0.25*M* nitric acid (95:5), followed by water to elute strontium. Attempts to separate calcium from strontium by elution with isopropanol-nitric acid were unsuccessful. In this connection it is interesting to note that Kurokawa Kazuo,[116] in a separation method for beryllium, magnesium, calcium, and strontium on a column of the same exchanger, separated calcium from strontium by eluting the former with methanol-isopropanol-water-1 *M* potassium nitrate-7 *M* nitric acid (80:10:3:2:5). The separation that was impossible in one medium was thus achieved in another medium of similar chemical character but of somewhat different chemical composition, a possibility which probably exists in many instances.

The effect of dimethyl sulfoxide (DMSO) on the anionic distribution coefficients and the separations of 26 elements on Amberlyst® A-26 in methanol-0.6*M* hydrochloric acid was investigated by Fritz and Gillette.[117] Some interesting and useful ion exchange effects were observed. Lead-and silver-chloride complexes which are only slightly soluble in water or in the alcohols were sufficiently soluble in methanol-DMSO to make separations of macro amounts possible. Certain elements such as Au(III), Fe(III), and U(VI) have high distribution coefficients in methanol, but very small coefficients in methanol-DMSO mixtures having a significant DMSO content. For many elements which require rather high concentrations of hydrochloric acid in water to have higher distribution coefficients, similar values are found in methanol-DMSO solvents with much lower acid concentrations. The authors interpret these effects of DMSO as follows. The chloride complexes of the metals form more easily in the organic medium because coordinated water is displaced more easily in this medium than in water. The metal-chloride complex can then be taken up by the resin. If there is a sufficiently strong solvating agent in the outside solution such as DMSO, solvation of the chloride complexes in the solution phase may compete successfully with the sorption by the resin. This is probably the case with those metals which have lower distribution coefficients when DMSO is present. The usefulness of the system studied was demonstrated by 27 column separations of mixtures of 2 to 4 elements. Even for 4 elements, columns of 10 cm length were sufficient for obtaining clean elution peaks without tailing at flow rates of 1 ml/min.

What can be achieved by the application of what has been found so far on ion exchange in mixed or nonaqueous solvents was shown by a separation scheme for 27 elements described by Fritz and Latwesen.[118] Combining the microporous Dowex® 50W-X8 with the macroporous Amberlyst® A-26 and the macroporous non-ionic polymer Amberlyst® XAD-2 (identical with the resin matrix of Amberlyst® A-26) in a sequence of five columns, separations were obtained by eluting with either water or mixtures of water with methanol, ethanol, or acetone containing various concentrations of one of five mineral acids. Amberlyst® XAD-2 was used as the support for organic solvents for partition chromatography. Dowex® 50W was used for some cations which were found to separate better on this microporous resin than on the macroporous one. The efficiency of the scheme was demonstrated by analyzing six U.S. National Bureau of Standards reference samples (5 alloys and 1 limestone), containing up to 7 metals with contents ranging from about 0.1 to 88%. Average recovery was 99.7% for contents greater than 2%, and 101.0% for contents below 2%; the respective relative standard deviations being 0.4 and 3.5%. These excellent results are the more convincing as the sizes of the columns were not more than 4 to 11 ml, the flow rates 1 to 2 ml/min, and most samples were not larger than 40 to 50 mg each.

To demonstrate the many interesting possibilities anhydrous ion exchange with macroporous resins offers to the analytical chemist in the petroleum industry, Webster, Wilson, and Franks[119] described methods for the separation of naphthenic acids, alkylphenols, pyrrolic compounds, and nitrogen bases from toluene, kerosene, or heavy gas oil. The two anion exchangers Amberlyst® A-29 and Deacidite® K and the cation exchanger Amberlyst® 15 were used. The latter was used either in the hydrogen form to sorb selectively the nitrogen bases by an acid-base reaction, or in the Ni(II), Cu(II), or Fe(III) forms for ligand-chromatography separation of complex-forming compounds. The authors pointed out that these techniques are applied regularly in the British Petroleum Company's Research Centre with the result that certain tedious separation processes have been eliminated and that in some cases analytical problems were solved which otherwise would have to be left unresolved.

Macroporous exchange resins are undoubtedly well suited for the removal of trace impurities from nonaqueous liquids. Applebaum[120] described an industrial installation for the removal of ionic impurities, mostly calcium compounds, from mixtures of methanol, acetone, and methyl ethyl ketone, whereby the solvent passes successively through columns of Amberlite® 200, a macroporous strongly acid cation exchanger, then through Amberlyst® 15, and finally through Amberlite® IRA-93, a macroporous weakly basic anion exchanger. Vioque, Albi, and Albi[121] treated olive oil for 16 hr with Amberlyst® 15 (in the hydrogen form), removing practically all traces of iron and most of the traces of manganese, copper, and zinc. They thus obtained a product of lighter color without any change of the analytical constants. Other exchangers such as Dowex® 50, Amberlites, and zeolites were found to be ineffective. According to a French patent,[122] oxazole impurities can be removed from acrylonitrile by passing it through a column of

Amberlyst® 15. This is most probably a non-exchange acid-base reaction. Dorfner[123] described the removal of traces of mercaptans from aliphatic hydrocarbons by passing the latter through a bed of Amberlyst® XN-1002 (now Amberlyst® A-29), in the hydroxide form, which had been washed with ethanol. This is again a non-exchange sorption which could perhaps be due to adsorption by the polymer matrix or to one of the following reaction mechanisms:

1. Complex formation through hydrogen bonding with the hydroxyl group

$$R_4N^+\cdot O\cdots H\cdots SR', \text{ or}$$

2. Acid-base reaction with the ion-pair formation

$$R_4N^+\cdot OH^- + HSR' \rightleftharpoons R_4N^+\cdot SR' + H_2O.$$

The first alternative seems to be less probable, as even after washing with ethanol the resin probably retains enough water to maintain a hydration shell around the ionic sites to make this reaction more difficult. The author describes an example, where a 25 ml column removed 500 ppm of octylmercaptan quantitatively from almost 4 l. of isooctane at a flow rate of 2.5 ml/min before breakthrough at the rate of 5 ppm occurred.

IV. OTHER EXCHANGERS

Among the various materials capable of ion exchange, only celluloses have so far been used for ion-exchange separations in media other than water. According to Sookne and Harris[124] pure natural cellulose always contains a small amount of carboxylic groups capable of being neutralized by cations. The carboxyl content ranges from about 0.002 up to about 0.06 meq/g of cellulose, which corresponds to densities of ionic sites roughly 100 to 1000 times smaller than those in synthetic cation-exchange resins. Pure cellulose should, therefore, be suitable for ion-exchange chromatography with small amounts of ionic materials, and within these limits it can be considered to be a true ion exchanger. The term "modified cellulose" as used in this review refers to celluloses which have been chemically altered to contain ionic groups such as sulfonic, phosphoric, or carboxylic groups for cation exchange or amino or quaternary ammonium groups for anion exchange. In cellulose papers impregnated with ion exchange resins the cellulose itself is not chemically altered and the main exchange materials are synthetic resins. These papers are discussed in Chapter II. A.4.b.

A group of Hungarian workers[125-127] started about 10 years ago to study the ion-exchange behaviors of modified celluloses in organic solvents and their use for the sorption of traces of metals. More recently Lásztity and co-workers from this group[128] investigated the sorption of copper(II) and cobalt(II) on carboxycellulose, carboxymethylcellulose, cellulose phosphate, and sulfoethyl cellulose in methanol, ethanol, propanol, butanol, acetone, and formamide. The exchange capacities of these exchangers, which were used in the hydrogen form, ranged from 0.14 to 0.7 meq/g. Sorptions of metal ions were determined by equilibrating 0.1 g of cellulose with 20 ml of solvent containing 100 μg of metal ion. It was found that the most efficient exchangers were cellulose phosphate, sulfoethyl cellulose, and carboxycellulose, and that both the rate of sorption and the total amount absorbed tended to decrease with decreasing dielectric constant of the solvent. Thus, for the most efficient celluloses the sorption of cobalt(II) from water or methanol attained 70 to 80%, whereas from butanol it was less than 10%. Methanol, ethanol, acetone, and formamide were found to be most suitable.

Lásztity and Ösy[129] investigated in more detail the sorption of cobalt (II) on carboxycellulose (hydrogen form) from water-solvent and formamide-solvent mixtures of various compositions. The solvents were the lower alcohols methanol through butanol, acetone, and dioxane. The results show that both the rate of exchange and the amount of ion absorbed increase markedly when a basic solvent of high dielectric constant (water or formamide) is added to a less basic and less polar solvent. No linear relationship between the dielectric constant and the absorbed amount could be found, and the authors conclude that selective swelling of the exchanger, the basicity of the solvent, and complex formation are much more important parameters than the dielectric constant. This influence of the basic strength on the exchange equilibrium is in keeping with the Izmailov equation[20] and its discussion and verification by Ignatov and Shostenko,[24] which were discussed in Chapter III. A.1.a.

A practical application of these investigations of cellulose exchangers was proposed by Schulek and co-workers,[130] who used carboxycellulose to remove traces of metal ions from extremely dilute solutions for the purposes of either trace enrichment or purification. The carboxycellulose used had a pK-value of 3.46 at 20°C in 1*M* sodium chloride solution and a capacity of 0.22 meq/g. On columns of 1 to 5 g of exchanger, metals at the 0.001 to 0.1 ppm level could be collected from 100 to 1000 ml of solution. The collection of 24 metals was studied and it was found that the usual metallic trace impurities in water, reagent solutions, or various anhydrous solvents could be reduced from $10^{-4}\%$ to $10^{-7}\%$.

Muzzarelli, Martelli, and Tubertini[131] investigated the possibility of using both natural and modified celluloses for ligand-exchange chromatography. Natural cellulose powder was found to absorb antimony, cobalt, and silver ions from diethyl ether solutions in amounts of 0.1 to 0.6 μmol/g of cellulose, while diethylaminoethyl and *p*-aminobenzoyl celluloses and cellulose phosphate absorbed somewhat larger amounts, i.e., 0.5 to 2.5 μmol/g. These metal-loaded celluloses sorbed aliphatic amines such as dimethylamine, trimethylamine, and ethylenediamine in larger amounts than the non-loaded materials. Thus 1 g of natural cellulose absorbed 29 μmol of dimethylamine, whereas the same cellulose loaded with antimony or cobalt absorbed 63 or 55 μmol, respectively. Aniline was sorbed much less than the aliphatic amines by the unloaded celluloses, and still less or even not at all by the metal-loaded materials. Using 15 x 1 cm columns in ether, sharp chromatographic separations of aniline from trimethylamine and dimethylamine, or of these 2 amines from ethylenediamine on antimony-pretreated diethylaminoethyl cellulose were achieved. The chromatograms obtained with metal-loaded celluloses showed, in general, sharper peaks than those from unloaded materials. The x-ray diffraction data for the metal-loaded celluloses showed that there is strong interaction with the celluloses even at very low metal concentrations. This fact and the absorption results are evidence for the formation of coordination complexes between the metal counterions of the cellulose and the amines. From this point of view, the poor sorption of aniline is understandable, as this amine is a rather weak ligand. The mentioned separations of amines are apparently a clear example of ligand-exchange chromatography, and the authors consider the celluloses to be very promising materials for this type of chromatography in columns as well as on paper or in thin layers.

Fritz and Peters[132] used the microcrystalline cellulose Avicel® of American Viscose, FMC Corporation, to carry out separations in microamounts of magnesium, earth alkali metals and radium in a methanol-hydrochloric acid medium. Successive elutions of magnesium, calcium, and strontium were made with methanol-hydrochloric acid (70:30), while barium could be eluted with methanol-water-HCl (80:15:5) or even with water alone. The latter also eluted radium. On columns 10 mm in diameter and 190 to 490 mm long, amounts of individual cations between 10 and 100 μmol were easily separated with recoveries mostly close to 100%. In a 10 mg sample of reagent grade strontium chloride with a stated barium content of 0.002%, the latter could be separated and determined with 96.8% recovery.

V. SUMMARY AND CONCLUSION

Enough experimental data on nonaqueous ion-exchange separations have been gathered to show that one is dealing with a field whose theoretical aspects are infinitely complicated. The separations can be based on several different types of chemical reactions. Apart from true ion exchange, sorption can take place by non-exchange reactions such as acid-base reactions or complex-formation, either by hydrogen bonding or by metal-ligand coordination. All these reactions can be influenced by a multitude of parameters such as solvent polarity, solvent-solute interaction by solvation or complex formation, solvent structure changes, solvent-resin matrix interaction, solvent-solvent interaction, acid-base properties of the solvent, non-exchange electrolyte invasion, and so on. Any one or several of these parameters may or may not be operative in a given case, and a given parameter can be of primary importance in one case and be only a minor contributing factor in another. In view of such complexity, one should not be surprised that the few attempts so far made to develop a theory of nonaqueous ion exchange were not too successful and could be applied only to a few rather simple cases. Even considering only one type of chemical reaction, the true ion exchange, the chances of ever arriving at a comprehensive theory appear to be pretty slim.

An intriguing subject from a fundamental point of view is ion exchange in non-polar anhydrous solvents such as benzene, in which the degrees of ionic dissociation, even of strong electrolytes, are extremely low. Little fundamental work on this subject has been done so far, and still less has been done under well-defined experimental conditions. This is particularly the case with respect to the strict absence of water, which even in quite small amounts can have disproportionately great effects on ion-exchange systems in less polar solvents. A careful investigation of ion exchange in benzene or similar solvents under strictly anhydrous conditions would be an interesting subject, which could perhaps reveal the answer to the intriguing question whether ion exchange is possible only between free (dissociated) ions, or whether it can take place also between ion-pairs! This would be undoubtedly a valuable contribution to our limited knowledge on electrolytes in nonaqueous solutions.

From the point of view of chemical analysis, nonaqueous ion exchange has already developed into a valuable enrichment of the analytical chemist's arsenal of separation methods. The best chances for further useful developments seem to involve separation methods based on complex-forming reactions. Many complexes form more easily in solvents less polar than water, and their ion-exchange behaviors can be influenced by modifying the solvent composition, which provides more versatility than can be expected in water. The separation of metals by anion exchange of their anionic complexes has already been well developed during the last 10 years, mostly by the use of water-containing mixed solvents. Nonexchange separations by complex formation, either by hydrogen bonding or by acid-base reaction or by ligand-exchange chromatography on resins having coordinating metal counterions, are methods particularly suitable for the use of nonpolar solvents or solvents of low polarity. The macroporous resins absorb easily considerable amounts of these solvents and therefore should afford an impetus to the development of these unique possibilities of separation methods for various organic compounds.

The most important and useful numerical factor for the separation of a given species is its distribution coefficient. There are many thousands of numerical values dispersed in the literature, some determined under well-defined conditions but others of only limited value because the experimental conditions were ill-defined. Quite often, indeed, one can hardly compare values from different sources because of differences in defining the coefficients. It would be most helpful for the practicing analytical chemist if reliable values were available in tables, as is the case for R_F-values in chromatography or for absorption peak frequencies in spectroscopy. The following steps could help to attain this goal:

1. Establish by convention a definition of the distribution coefficient and perhaps determine the conditions for its determination.
2. Collect published data and catalogue those judged to be well-defined and of reasonable accuracy.

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