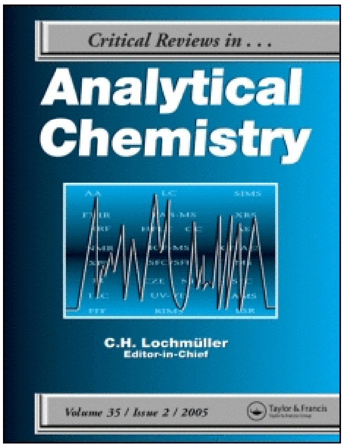

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ION EXCHANGER-SOLVENT INTERACTIONS: PROPERTIES AND METHODOLOGY

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I. INTRODUCTION

The phenomenon of ion exchange has been scientifically recognized since the middle of the 19th century.[1,2] Many of these early scientific investigations were carried out with naturally occurring clays and minerals, such as the zeolites. The zeolites which attracted most of the attention contain alumino-silicate skeletons with exchangeable alkali metal or alkaline earth cations. Artificial silicates were also prepared and successfully used.

The ion exchange properties of naturally occurring organic materials, such as cellulose and coal, were also studied. However, their applications were limited because they had low capacities and were not completely ionized. Even laboratory modifications of the celluloses, coals, and other naturally occurring organic materials were not sufficient to overcome these limitations.

In 1935 the first synthetic organic ion exchangers were prepared by Adams and Holmes.[3] The cation exchanger was synthesized via the condensation of a dihydric phenol and formaldehyde, followed by sulfonation. The anion exchanger was a condensation product of *m*-phenylenediamine and formaldehyde. Their capacities were large, and they were able to ionize to a high degree. Potential uses were realized immediately with the first major application being in water softening where a combination of cation and anion exchangers was used as a replacement for the zeolites.

Subsequently, other types of ion exchangers were synthesized. Many of these exchangers had high capacities, were readily ionized, had physical strength, and could be regenerated. The principal cation and anion exchangers contain the styrene-divinylbenzene copolymer backbone.[4,5] The copolymer is sulfonated to produce the strongly acidic cation exchanger, or it is first chloromethylated followed by conversion to the quaternary ammonium salt to produce the strongly basic anion exchanger. Ion exchangers synthesized with different types of cationic or anionic exchanger sites containing chelating groups and mixed functional groups, capable of undergoing oxidation or reduction, and possessing specialized properties as the result of improved or different polymer formulation and modification have also been prepared.

The early exchangers and their successors were designed to remove unwanted ions from solutions. However, it was soon realized that the reverse process, removal of useful ions from solution, had potential value. Subsequently, ion exchange resins were used for the concentration of electrolytes, separation of multicomponent mixtures of cations or anions into less complex mixtures or individual components, preparation of reagents, and dissolution of insoluble electrolytes. It was also realized that separations of mixtures of weak organic electrolytes and nonelectrolytes were possible on ion exchangers, and numerous practical laboratory and industrial organic-biochemical applications were developed. The fact that the exchanger will exhibit strong acidic and basic properties or can be charged in certain cationic or anionic forms has also led to wide use of the exchangers as catalysts.

Historically, as the technology of the synthesis of the ion exchangers expanded, their applications and the investigation of their physical and chemical properties broadened. Thus, experimental methods for determining capacity and investigating the underlying equilibria and kinetics were devised. Based on these and related phenomena, theoretical models of the ion exchange process were proposed. Detailed discussion and reviews of these advances are found elsewhere.[5-13]

The ideal ion exchange resin should combine high capacity, excellent equilibrium properties, and rapid kinetics and undergo minimal chemical breakdown itself in its applications. Indeed, the synthetic technological advances were in this direction. For example, capacities of the currently readily available strong acid ($-SO_3H$) cation exchanger (polystyrene-divinylbenzene copolymer) are usually as large as 5 mmol/g of exchanger (about 4 mmol/g of strong base-type exchanger). In contrast, other minerals and naturally occurring organic exchangers and their modifications have capacities of usually less than 1 to 2 mmol/g. Some zeolites have larger capacities, but often decompose in acid or base solution, which limits their usefulness in ion exchange applications.

These general ideal requirements are interrelated; frequently, an improvement in one is at the expense of another. Furthermore, other properties (such as the extent and type of cross-linking, particle size and shape, chemical nature of the functional group and its availability on the exchanger, the nature of the polymeric backbone structure, the extent to which the resin beads swell, the nature of the external solution, and potential deterioration as a result of physical or chemical breakdown) are very important and will influence or determine capacity, equilibria, kinetics, and exchanger stability. Detailed discussions of the synthesis of the many different ion exchangers are found elsewhere.[4,5,9,11-14]

With water as solvent and for a suitable solute ion-exchanger system, the conditions required for ion exchange are present. That is, the solute is soluble and partially or totally dissociated; similarly, the exchanger functional groups are partially or totally dissociated. The ions from both sources are free to move and exchange places since the exchanger backbone is either porous (as a result of a rigid open lattice) or expanded (as a result of swelling of the resin beads). If, however, a water-organic solvent mixture or an anhydrous organic solvent is used, noticeable changes in the exchange conditions, as well as the physicochemical properties of the ion exchanger, are observed.

These changes have been used advantageously in many applications. For example, aqueous HCl was used as an eluting agent in the first detailed study of the separation of complex metal ion mixtures on a strong base-type anion exchanger.[1-5,9-12,15] By a successive decrease in the HCl concentration from 12 to 0.001 F, it was possible to complete the separation of multimetal ion mixtures. If water is partially replaced by an organic solvent, the HCl concentration required for the separation is often significantly reduced.[16-22]

Using the mixed solvent increases the number of eluting conditions. Thus, (1) the water-organic solvent ratio can be fixed and the HCl concentration varied; (2) the HCl concentration can be fixed and the water-organic solvent ratio varied; or (3) either the first or the second condition can be imposed whereby different organic solvents are used. Two principal advantages are gained through this increase in the number of eluting conditions. First, the concentration of HCl required for the elution is reduced. Second, and more important, many separations that are impossible or difficult with aqueous eluting mixtures are successfully completed with eluting mixtures containing a combination of water, HCl, and organic solvent. These successful operations even include the separation of metal ions that are not even sorbed by the anion exchanger in aqueous HCl.

Utilizing mixed solvents is not restricted to the HCl-anion exchange resin system. Indeed, this modification is possible with cation exchangers and most other types of complexing agents as well, providing numerous alternate eluting conditions for metal ion separations.[5,6,9-13,16-22]

Methods for the separation of strong organic electrolytes or their exchange for hydrogen or hydroxyl ions are somewhat similar to those for inorganic analysis in which aqueous eluting mixtures are used. In contrast, the separation of weak electrolytes or nonelectrolytes on cation and anion exchangers often requires an organic solvent or a mixture of water and an organic solvent as the eluting system.[4-6,9-13,20-24] In these latter applications the ion exchangers are often participating in a retention process other than an exchange of ions, particularly in the case of the separation of nonelectrolytes.[5-13]

Several factors must be considered in the separation of organic weak and nonelectrolytes on ion exchangers. Briefly, the more significant considerations are as follows.

1. Since organic solvents are often used, there must be concern as to how the properties of the exchanger are affected by the presence of the solvent in contrast to the properties exhibited by the exchanger in water. (These effects are briefly surveyed in Section II.)
2. Recognition of the nature of the retention process, which usually does not involve ion exchange, will facilitate the selection of the optimum eluting condition. Retention, in general, is molecular and involves ion exclusion, salting in, salting out, various polar-polar interactions, differences in solute size, hydrogen bonding, or partitioning.[5-13]
3. The size of the different organic molecules being separated may cover an extensive range. In general, the organic molecules are often several orders of magnitude larger than inorganic ions. Thus, the ion exchanger must be permeable to large as well as small organic molecules if the exchangers are to be useful in the separation of organic mixtures. Resin permeability will be influenced by the exchanger's ability to swell or by the fact that the exchanger has a high degree of permanent porosity. The former is largely a function of the nature of the solvent in contact with the exchanger, while the latter is a property which is primarily brought about synthetically.

Many inorganic and organic reactions can be catalyzed by ion exchangers and include reactions in the gas phase as well as in the liquid phase. In general, catalysis in the liquid phase is analogous to homogeneous-phase catalysis by dissolved electrolytes; therefore, it can be explained in terms of the catalytic activity of the counter ions in the ion exchanger. Hence, the catalytic activity is directly related to ion exchange properties. In contrast, catalysis of gaseous reactions by ion exchangers and its relationship to ion exchange properties are not clearly understood.

The proper choice of the operating conditions and the ion exchanger to be used as the catalyst will determine the efficiency of the catalysis. Since the relationship to ion exchange is present, those exchanger variables which influence the properties of ion exchangers are, therefore, important to the overall efficiency. A major consideration is the choice of solvent; it must provide exchanger stability, substantial swelling of the exchanger, and rapid equilibrium between the exchanger and solutes. Capacity, particle size, cross-linking, and exchanger stability towards temperature are other significant properties that must be considered.

Ion exchangers are most often used as acid (hydrogen form) or base (hydroxide form) catalysts. However, they are not limited to only these type of applications and can be used in other charged forms. The catalysis procedure can be performed batchwise or continuously in a column; the former experimental technique is more commonly used. Most investigations have dealt with the applications of ion exchangers as catalysts rather than with the theory of ion exchange catalysis. Extensive reviews are available, and ion exchange catalysis will not be surveyed here.[25-31]

The purpose of this review is severalfold. The influence of mixed and anhydrous solvents on the properties of ion exchangers and the role these solvents play in influencing separation and catalysis have been the subject of considerable concern in recent years. Fortunately, other reviews,[13,18,20,21,32-34] books,[5-11,22] and certain research papers[6-19,23,35-37] provide excellent surveys of the earlier literature from a practical as well as a fundamental point of view. This review will serve as a supplement. In addition to surveying exchanger-solvent interactions and their characterization, this review will emphasize the techniques employed in determining these ion-exchanger properties and subsequent conclusions that are drawn from these measurements. Finally, the subject of exchanger stability and the techniques for this determination will be surveyed. Current practical applications of ion exchangers in column operation at gravity flow, at high pressure, or in sheet methods will not be included in this review. It is anticipated that by surveying the underlying fundamental properties, the prediction of future applications of ion exchangers in these areas will be facilitated.

II. PROPERTIES OF ION EXCHANGERS IN SOLVENTS

A. General Survey of Properties of Exchangers in Water

When an ion exchanger and an aqueous electrolyte solution are brought together, an exchange of ions will occur if certain requirements are satisfied. These are summarized briefly in the following paragraph.

If the ion exchanger is in a dry state, it must first swell. (If the exchanger is preswollen, it may actually contract rather than swell when placed in the aqueous electrolyte solution. Whether it swells or contracts will be determined by the initial state of the exchanger, the type of exchanger, and its charged form.) The swelling property of the exchanger allows the aqueous solution to penetrate to the interior of the ion exchange particle where the exchange sites are located. The amount and type of cross-linking in the exchanger are parameters which will influence the exchanger's ability to swell. This will also influence the exchanger's overall stability and solubility (if the exchanger is only lightly cross-linked). The equilibrium position for the exchange will depend on the type of functional group present (its degree of dissociation), solvation of the ionic species and sites in the system, and the swelling of the exchanger. When this position is established for a given pair of ions, at a specified level of concentration, a *selectivity order* is defined. That is, this is the order of preference that the exchanger shows for one ion over another under specified conditions. The rate at which equilibrium is reached, which is dependent on the particle size of the exchanger, is, in general, determined by interdiffusion of the counter ions in the exchanger itself or across an adherent liquid film. The capacity defines the maximum number of accessible sites that will participate in the exchange, assuming that only an ion exchange process is occurring. In aqueous solution the stability of the exchanger (bead fracture) will be a function of the abruptness and extent to which the particle expands or contracts. Cross-linking will have an important influence on this property. If temperature changes from room temperature are modest for the exchanger-aqueous system, decomposition, in most cases, is negligible, particularly for the cation exchanger.

B. General Survey of Properties of Exchangers in Mixed and Nonaqueous Solvents

These properties of ion exchangers described in the previous section will often differ when the exchangers are placed in water-organic solvent mixtures or nonaqueous solvents. Furthermore, these differences will vary depending on whether the exchanger is microporous (gel) or macroporous (macroreticular). The following is a summary of these differences based on earlier investigations.[4-7,10-13,20-24,32-41]

In general, selectivities for the exchange of a given pair of ions is greater in an organic solvent of a lower dielectric constant than water. For water-organic systems the selectivities may be intermediate, larger, or smaller when compared to selectivities in the pure solvents. Often, reversal in selectivities is observed.

Several investigators have singled out the dielectric constant of the solvents involved as the most important factor affecting the exchange efficiency. Although this is important, other factors (such as solvation of the exchange sites, hydrogen bonding between the exchange sites and solvent, coordination properties of the solvent, and interactions between the solvent and the resin backbone) are of equal if not greater importance under certain circumstances. Clearly, exchanger swelling will have a strong dependence on the nature of the solvent.

A practical consequence of the enhanced or altered selectivity is that separation factors are often improved. Thus, certain separations become possible, while others are improved or more readily completed by utilizing an organic solvent or mixed solvent in place of water in the eluting mixture.

Rates of exchange are generally slower in mixed or nonaqueous solvents; as the polarity of the solvent and the swelling of the exchanger decrease, the exchange rate will decrease. However, there are few detailed kinetic studies in this kind of media.[4-8,13,20,21,32,35,42-44] The effect of the solvent on exchange rate will also be influenced by whether the exchanger is microporous or macroporous. In general, particle diffusion is the rate-determining step for exchange of electrolytes in mixed or nonaqueous solvents. Since weak electrolytes and nonelectrolytes can be retained by exchangers by processes other than ion exchange, the kinetic phenomena and factors which influence it become more complex.

Ion exchange resins are capable of taking up anhydrous solvents as well as mixed solvents. For mixtures of water and common water-miscible organic solvents, water is often preferred. This preference generally holds up to about 80% by volume organic solvent after which the interior solvent composition approaches that of the bulk composition. The nature of the charged form of the exchanger, whether it is an anion or cation exchanger, the extent of swelling (amount of cross-linking), whether the exchanger is microporous or macroporous, the ratio of organic solvent to water, and the polarity of the organic solvent used in the solvent mixture are significant factors that influence the solvent preference. (It is possible to observe a preference of the organic solvent over water for certain combinations of these parameters.) Because of the differences in the bulk vs. interior solvent composition, the role of partitioning must be considered in ion-exchange separation applications, particularly when weak and nonelectrolytes are being separated.

Uptake of anhydrous solvents generally decreases with decrease in polarity. Also, the type of anhydrous solvents taken up and the extent of uptake are markedly different for the macroporous exchanger when compared to the microporous exchanger.

Because of this large preference of water by ion exchangers, some investigations of solvent preference and/or swelling are misleading since the ion exchanger used in the study was preswollen. That is, the exchanger contained water initially (depending on temperature, humidity, and pretreatment, ion exchangers may hold as much as 50% water by weight after air drying), and this was not accounted for in the experiments. This is particularly serious if the study involves anhydrous-type solvents.

The microporous exchangers will swell to the greatest extent in the more polar solvents. In nonpolar solvents this type of exchanger will remain collapsed, provided that the exchanger is free of water. If the exchanger is preswollen in water and then added to the nonpolar solvent, it will remain swollen because of the exchanger's preference towards water.

In general, exchanger capacities for strong electrolytes will remain the same even in mixed or nonaqueous solvents. Capacity for weak and nonelectrolytes can vary substantially since molecular retention is often involved. Furthermore, the type of solvent mixture, its polarity, and the charged form of the exchanger will have a significant effect on the capacity exhibited by the exchanger towards the weak electrolyte and nonelectrolyte.

In addition to affecting the properties of ion exchange resins, the presence of organic solvents in the solvent system will also influence the properties of the species being separated. The combination of these two effects has led to a variety of practical separations, including separation of ionic and weakly ionic species, as well as nonionic species. In the latter case, as pointed out previously, the presence of the organic solvent influences retention through several factors. In the past few years considerable interest has been shown in the application of ion exchangers towards the separation of organic weak electrolytes and nonelectrolytes on ion exchangers by both gravity flow and high-pressure techniques. Understanding the role of the mixed or nonaqueous solvent in the eluting mixture, can only lead to improvement of the technique and the development of new procedures for these kinds of separations.

C. Macroporous Ion Exchangers

Prior to the earlier 1960's, the ion exchange resins used were structures that are essentially homogeneous cross-linked polyelectrolyte gels with the exchange sites statistically distributed throughout the entire particle. The availability of these sites, almost all of which are in the interior of the bead, and the subsequent distances between the chains and cross-links depend on the capability of the resin to swell and the environment in which it is placed. For the most part, the gel-type resin in the swollen state will have surface areas of under 0.1 m^2/g of exchanger and porous-like distances that are often less than 30Å (depending on the degree of swelling).

In the following years a development in synthetic technology led to the preparation of macroporous-type ion exchange resins.[45-47] In general, these are highly cross-linked exchanger systems with the physical appearance of a multitude of randomly packed gel-like microspheres grouped together into a larger bead. The larger bead, therefore, is composed of two distinct phases: a gel shape (as previously described) and a phase composed of large pores. Its surface area for example, > 50 m^2/g and its porosity (for example, $\gg 100$Å) are large in comparison to the microporous exchanger.

Because of the rigid permanent-like porosity of the macroporous exchanger, it has many practical advantages over the gel-type exchanger, particularly in the presence of organic solvents. For example, the former exchanger tends to be physically and chemically more stable, will function in completely nonpolar solvents even if the exchanger is not preswollen, becomes organically fouled-up in continuous column operation at a much slower rate, will take up solvent (and swell) much differently than the gel-type exchanger, and will be permeable towards large organic ions and molecules in nonaqueous as well as aqueous media. Comparison of these two types of exchangers has been reviewed previously,[13,20,21,23,32,35-37,45-54] and this review will contain more recent investigations.

III. ION EXCHANGER-SOLVENT INTERACTIONS

A. Determination of Water in Ion Exchangers

The properties of ion exchangers, particularly in anhydrous solvents, will depend on the level of water in the exchanger. For the microporous exchanger, the difference between containing some and no water is the difference between the exchanger being swollen and collapsed. Although many investigations of the properties of ion exchange resins in water-organic and anhydrous solvent systems have been reported, frequently the level of water in the exchanger is not determined, determined inaccurately, not controlled, or in some cases not even considered. If a moist exchanger is to be used, a procedure should be available for storing the exchanger so that the moisture content can be maintained at a fixed known value.

The water content of ion exchangers can be determined by measuring the weight loss upon drying of the exchanger; Karl Fischer titration; azeotropic distillation; measuring the change in an indicator or electrolyte solution after immersion of the resin in the solution; treatment with tritiated water; and a nuclear magnetic resonance (NMR), calorimetric, or isopiestic method.

The initially recommended methods were based on weight loss by drying, azeotropic distillation, and isopiestic measurements. Subsequently, the others were introduced. More recently, these methods have been compared, and from these critical evaluations it is now possible to select a method according to the level of water in the exchanger that is to be determined, the type of exchanger, and the level of accuracy desired. These investigations have also led to procedures which permit the preparation of exchanger samples that contain known water levels and permit the storing of exchangers at a fixed known water level.

The type of method chosen for determining the water level will depend on whether the exchanger sample is completely or partially preswollen (water-wetted) or if the exchanger is part of a solution system. Furthermore, the accuracy of the latter will be influenced by the technique used to remove the wetted exchanger from the solution.

Various combinations of temperature, vacuum, and/or desiccant have been employed in water determination by weight loss. Often, investigators have noted differences in weight loss as a result of the different conditions used.

Decomposition of the exchanger must also be considered in any method in which heating is involved. For example, in a study of drying conditions, Heumann and Rochon[55] reported that a slight decomposition for Dowex® 50 occurred at the optimum drying conditions of 120°C under vacuum. A slight decomposition for a cation resin at 105°C was also noted by Gregor et al.[56] In some cases drying was done at elevated temperature over P_2O_5.[56-58] It should also be noted that this slight decomposition of the cation resin will vary according to whether it is charged in the hydrogen or metal form. Decomposition of an anion exchanger (depending on charged form) can be substantial even at 60°C.

Usually, the decomposition of the cation or anion exchanger results in a loss in capacity for the exchanger. Hence, the determination of capacity can be used as a means for detecting and/or following exchanger stability during the drying process.

The Karl Fischer titration was apparently first used by Dickel and Hartmann[59] for the determination of water in ion exchangers. Subsequently, this technique was used in other investigations. Several years later comparison of this method to others and variations of the method were investigated.

Sharma et al.[60] used this method to determine the water content of two cation exchangers that had been equilibrated with aqueous solution containing salts, HCl, or methanol. Water levels were from 17 to 50%. In a more detailed study, where effects of cross-linking and type of charged form for Dowex 50 cation exchanger were considered, it was concluded that a rapid accurate water determination by a direct Karl Fischer titration is possible only if the water content is not too low.[61] A titration time of 20 to 35 min was required for an exchanger water level of 9 to 13%.

Blasius and Schmitt[62] suggest that lower water levels can be determined by having the exchanger in contact with excess Karl Fischer reagent for at least 24 hr. The excess is then back-titrated with a standard water solution.

Takeshita and Iguchi[63] also reported favorable results for the Karl Fischer titration of macro amounts of water in weak and strong acid cation exchangers that were in the H-, Na-, or Me_4N^+-form. Two different procedures were employed. In the first, a direct titration of the exchanger was done in methanol or ethylene glycol. In the second, the exchanger was heated in a stream of N_2 that subsequently passed into the organic solvent which was then titrated with the Karl Fischer titrant. Different heating temperatures were employed for the different exchangers. Good agreement was reported between the two procedures.

Determination of water by Karl Fischer titration in anion exchangers (Dowex 1 X 8, Cl-form) presents additional problems since in the course of the reaction the exchanger is converted to the iodide form which subsequently takes up additional amounts of iodine.

$$\begin{aligned} &I_2 + SO_2 + H_2O \longrightarrow 2HI + SO_3 \\ &\text{Resin–Cl} + HI \longrightarrow \text{Resin–I} + HCl \\ &\text{Resin–I} + nI_2 \longrightarrow \text{Resin–}I_{2n+1} \end{aligned}$$

Thus, no stable end point is reached. However, by equilibrating the wet anion exchanger in a water-acetic acid mixture of known composition and subsequent titration of the water-acetic acid (separated from exchanger), it is possible to determine the original water content of the exchanger.[64,65] Other parameters which must be determined are the ratio of internal to external water as a function of water content of the external solution and the solvent uptake of the exchanger at the given experimental condition. Results for two different batches of exchangers were found to be 0.80 ± 0.02% and 0.35 ± 0.04% (resin had been vacuum dried for 14 days over P_2O_5).[64,65] Apparently, an acetate-chloride exchange does not interfere. It also appears that water in cation exchangers could be determined similarly and that solvent mixtures other than H_2O-HOAc could be used. In contrast, favorable results were reported for the Karl Fischer titration of water in anion exchangers at different percent cross-linking in the ClO_4^- and I^- form. However, water levels for these exchangers were at the 17 to 25% by weight level.[66]

Heumann and Rochon[67] reported that at least 2 hr was needed to reach a stable end point for the Karl Fischer titration of Dowex 50 X 8, and they found considerable difference in water content when compared to the weight-loss method. They also noted that as the water content decreased, the titration end point was reached at a slower rate.

Pollio[68] compared the weight-loss, Karl Fischer, and distillation methods for the determination of water in a macroporous cation exchanger. Favorable results were found over a wide range of water contents. For an average value of 11.22%, the average deviation was found to be ±0.07. It was also shown that at 100°C and <1 mm Hg almost all of the water is lost in the first hour of drying.

Grieser et al.[49] compared the weight-loss and Karl Fischer methods to a calorimetric method. These data are summarized in Table 1. Macroporous- and microporous-type cation resins in the H-form were studied. As the exchanger was dried, the water content dropped rapidly. Also, the differences between the weight-loss and Karl Fischer methods increased; at very low water contents, no useful analyses were obtained by the Karl Fischer titration. In fact, when the ion exchanger samples containing very low water levels were added to the solvent for the Karl Fischer titration, the resulting titrations were often less than that found for the solvent blank. Apparently, the exchanger acts as a desiccant and dries the solvent and subsequently retains the trace water with such strength that the Karl Fischer titrant is unable to undergo a reaction with it in a reasonable time period. In the middle range of water contents, end points were obscured by the exchanger beads and contributed to an error. It was concluded that the vacuum oven-drying method is the better one. This method not only allows the determination of water contents, but also provides a means of achieving an initial "reproducibly dry" state for the cation exchanger.

It was also shown that the heat of immersion is linearly related to water content of the cation exchangers except at very low water levels.[49] In these experiments the exchangers were equilibrated with several common desiccants in an isopiestic-type experiment. The water contents (by weight loss) and their heats of immersion were determined. A calibration curve of these data will therefore provide a method for determining small amounts of water in exchangers, since the water levels in the exchanger standards were from 3 mmol H_2O/meq of exchanger to nearly 0 water (over P_2O_5).

The molality and percent water in strongly acidic and strongly basic ion exchange resins have been determined by nuclear magnetic resonance (NMR). It is also possible to investigate many other properties of ion exchange resins by the NMR technique. A more detailed discussion of these investigations and the resulting spectra are treated in a later section.

According to the procedure of deVilliers and Parrish,[69] a spectrum is first obtained for the exchanger suspended in water (internal and external peak) and then for the same tube containing only water (single peak). The three peaks are integrated, and the volume percent of water, P, is calculated by

$$P = \frac{\text{area internal } H_2O \times 100}{\text{area } H_2O \text{ only} - \text{area external } H_2O}$$

It is also possible to calculate the density for the H-form cation exchanger directly from the P values found by NMR. Typical data are summarized in Table 2.

The water content in an anion exchanger can be accurately and readily determined when it is in the iodide form.[69] If it is in the hydroxide form, it will have a larger chemical shift (external-internal water peak positions), but measurements on an exchanger in this form are more difficult because of lower exchanger stability. The chemical shift

TABLE 1

Water Content by Weight Loss and Karl Fischer Titration and Heat of Immersion in Water as a Function of Drying Time[a]

Drying time	Water content by weight loss, g water/g of dry exchanger	Water content by Karl Fischer titration, g water/g of dry exchanger	Heat of immersion, cal/dry g of exchanger
	Dowex 50 × 8		
0	0.251	0.250	-8.31
15 min	0.060	0.081	-36.8
30 min	0.004		-57.2
1 hr	0.003		-60.6
3 hr	0.0009		-61.5
24 hr	0.0006		-60.8
	Amberlyst-15		
0	0.218	0.202	-7.00
15 min	0.009	0.024	-48.4
30 min	0.003	0.010	-54.0
1 hr	0.002		-53.0
3 hr	0.002		-52.4
24 hr	0.0003		-54.8

[a] 100°C at 5 mm Hg.

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for the chloride form is less than that for the iodide form, and resolution for the two water peaks is poor. It should also be noted that the internal water peak for the iodide-form exchanger is at a lower field rather than at a higher field, as found for the fluoride- and hydroxide-form exchangers. Typical NMR spectra for several exchangers illustrating the internal and external water peaks are shown in Figure 1.

Recently, Subramanian and Sharma[66,70] compared the NMR procedure suggested by deVilliers and Parrish[69] to the Karl Fischer titration and the weighing-drying method for the determination of water in cation resin[66] and anion exchangers.[70] It should be noted that the ion exchanger samples were completely preswollen (water wetted). At lower water levels the NMR method as well as the Karl Fischer titration[49,61,67] were less accurate. Furthermore, if the exchanger does not swell appreciably, the internal water peak area is small, and the error in its estimation is large. Also, in the NMR method the charged form of the cation and anion exchanger will influence the accuracy since its form will determine the overlappage of the external and internal water peaks.[66,69,70]

The water content of ion exchangers can be determined from a calibration curve which relates the chemical shift of the internal water peak to the molality of the solution inside the exchanger.[48,69,71-76] However, chemical shifts, particularly for forms of cation exchangers, are not always linear.[74]

If the internal and external water peaks overlap, it is difficult to determine the chemical shifts accurately. Also, particle size of the exchanger will influence the overlappage. Thus, for particles below <100 μm, coalescence of the interior and exterior peaks is observed,[76] and the method of deVilliers and Parrish[69] is no longer applicable.

The moisture-holding capacity, C, of a Mg-form acrylic acid-type exchanger was determined as a function of temperature by NMR.[77] The expression used was

$$C(T) = 100/w[1 + I_t(1 - w)]$$

where T = the temperature (21.5 to 57.0°C); I_t =

TABLE 2

Data for the Determination of Water Levels and Density of Ion-exchange Resins

Resin	% water by NMR	% water by drying
AG 50 X 2	74.0	78.3
AG 50 X 4	64.6	66.5
AG 50 X 8	54.0	53.0
AG 50 X 12	44.2	45.6
AG 50 X 16	36.0	37.0
AG 1 X 2	33.0	31.4
AG 1 X 8	23.6	21.6
AG 1 X 10	22.9	22.4
IRA-400	27.1	26.2

	Density from P value[a]	Density by S.G. bottle[a]	Density by flotation[a]
AG 50 X 2	1.12	1.09	1.09
AG 50 X 4	1.16	1.15	1.15
AG 50 X 8	1.20	1.21	1.21
AG 50 X 12	1.27	1.25	1.26
AG 50 X 16	1.32	1.30	1.34

[a]Density in g/cc.

From deVilliers, J. P. and Parrish, J. R., *J. Polym. Sci. Part A*, 2, 1331 (1964). With permission.

integral ratio of the NMR peak of the water released from the exchanger to the NMR peak of the water inside the exchanger at temperature T; w = weight fraction of water inside the exchanger at 22°C. It was also shown that the water released at the higher temperatures originated from the interior bulk water rather than from the interior cation hydration water.

It is possible to determine the uptake of water by immersing a dry ion exchanger into a dilute solution of a reference solute of known concentration. After equilibrium is reached, the increase in concentration of the reference solute in the solution is determined; from these data the water uptake can be calculated. Frequently, the reference solute is a dye, and the concentration change is determined spectrophotometrically (for example, see Reference 78). For cation exchangers, an acidic dye can be used, while for anion exchangers a basic dye is used. It is important to establish that the sorption of the chromophoric solute remains negligible during the measurement since sorption will lead to a significant error. Because sorption is often encountered, this method is not recommended.

Water uptake can be established by determining exchanger capacity for the wet exchanger and comparing this value to that found for the dry exchanger.[79] Changes in electrolyte concentration for dry vs. wet exchanger have also been used.[58,80,81]

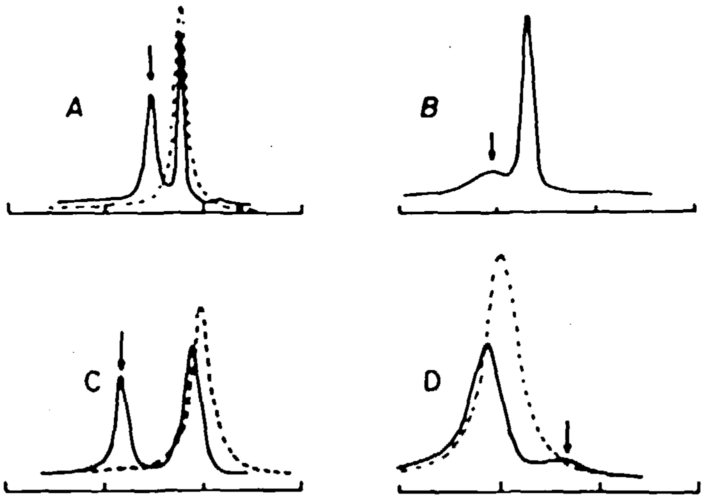

FIGURE 1. NMR spectra for several ion exchangers in water: (A) Amberlite 200, H-form; (B) phenolsulfonic acid-formaldehyde copolymer, H-form; (C) Dowex 2 X 8, OH-form; (D) Dowex 2 X 8, I-form. (–) Exchanger in water. (-) Water only. (↓) Marks the internal water peak. (From deVilliers, J. P. and Parrish, J. R., *J. Polym. Sci. Part A*, 2, 1331 (1964). With permission.)

These methods were found to be particularly useful when determining water contents for cation resins that are immersed in concentrated electrolyte solutions.

Numerous investigators have used the isopiestic technique to establish the moisture sorption isotherms for cation and anion exchangers.[49,82-86] In these experiments exchangers of known water levels are prepared from a dry exchanger rather than determining water directly in the moist exchanger. However, it is possible to use ion exchangers of known water levels as standards for preparation of calibration curves, whereby a property of the exchanger that is affected by water content is plotted vs. the water content in the exchanger. Thus, water levels for other samples of the ion exchanger can be determined by comparison to the calibration curve. Although this is a useful and accurate method for determining macro and micro levels of water in ion exchangers, the isopiestic procedure is used more often for preparing exchangers of known water content so that they can be used in the investigation of other properties of the exchanger (for example, thermodynamic properties). Additional investigations employing the isopiestic technique are cited in Section III.B.

In general, the procedure involves a careful placement of the weighed dried exchanger into a closed chamber which also contains a known solution that will provide a fixed vapor pressure. The temperature is fixed, the system may or may not be placed under a vacuum (known), and equilibrium is allowed to be reached. Subsequently, the exchanger is reweighed. A variation is to directly determine the increase in weight of the exchanger as it rests on a balance arrangement within the closed system while in contact with a known vapor pressure. Aqueous salt or H_2SO_4 solutions and desiccants are usually used as the sources of known vapor pressure.

The determination of water in ion exchangers and the drying of the exchangers have been accomplished through azeotropic distillation. Xylene, toluene, trichloroethylene, perchloroethylene, tetrachloroethane, and carbon tetrachloride have frequently been used.[67,68,70,87,88] It is also possible to dry ion exchangers in a stream of a gas, such as N_2[63] or H_2,[89] collect the water vapor from the gas stream, and determine it by other means, usually Karl Fischer titration. Procedures of this type are suitable for macro water levels, but also tend to be time consuming.

Tritium-labeled water as a tracer has been used to determine very low concentrations of water in cation exchangers.[62] The limit of detection was suggested to be 10^{-10}mg of water, and this method was shown to be much more sensitive than the Karl Fischer titration.

If the ion exchanger is in a solution system or if the "wet" state of the exchanger is to be established by first inserting it into water, it is necessary to remove the exchanger before its water content can be determined. This can be done by centrifugation.[37,56,78,90-96] The wet exchanger is weighed after centrifugation, dried (by using a combination of heat, desiccant, and vacuum), and then reweighed.

In the early development of the centrifugation method, centrifugation rate[56,58,78,92,93] and the presence of anionic[95] and cationic[96] detergents were studied in detail, and procedures for the correction for interstitial water were evaluated. Kraus and Moore,[96] and subsequently Scatchard and Anderson,[92] demonstrated that glass beads could be used to obtain a correction for interstitial water. The procedure used by Scatchard and Anderson[92] employed centrifugation at four different centrifugal fields. The weight of the wet exchanger was found from a plot of these data which included a glass bead correction.

In 1965 Parrish[90] further developed the centrifugation procedure outlined by Scatchard and Anderson. Contact angles centrifugation rate and time, irregular particle size, exchanger bead compression, and equilibrium rate were factors used in estimating interstitial water. It was concluded that by using a nonionic detergent of high molecular weight, errors due to these factors can be eliminated.

Fricke et al.[91] examined the centrifugation method for determining the wet weight of ion exchange beads (cation exchangers). The procedure involved the determination of the volume of water remaining on the exchanger following centrifugation to a constant weight. They found that when centrifugal force and volume of liquid on the surface of the exchanger bead are plotted, a plateau exists. The water on the beads at this plateau is a constant volume for a series of solutions differing in density, viscosity, and surface tension. The effect of size distribution was also considered.

It should be noted that errors in the centrifugation method due to interstitial water are generally small, provided that the depth of the exchanger bed in the centrifugation step is shallow and a proper centrifugal field and time are used. Often, the level is less than 5 mg/g of exchanger and hence can be neglected, except for those situations requiring a high degree of accuracy. The interstitial error in the presence of organic solvents is even less for solvents that are viscous, such as *n*-butanol.[37]

Moisture in ion exchangers has been determined by treating the exchanger with dimethylformamide. After equilibration the refractive index of the solution is determined, and the water content is calculated from the change in refractive index.[97] Several factors which influence high-frequency measurements of moist ion exchangers have been evaluated, and this method can be used to determine water levels.[98] A gravitational settling procedure employing a Reynolds number has been used to determine water contents of cation exchangers in different charged forms. These data were used to establish the water sorption isotherms as a function of the charged ion valence.[99]

B. Exchanger-water Interactions

The main factors which will influence exchanger-water interactions are the type of counterion that is present, the amount of cross-linking agent, the nature of the resin matrix and cross-linking component, and the structure of the polymeric system (micro- or macroporous). Several different experimental techniques can be used to investigate these variables. In addition to those techniques cited in this section, the reader should also consult the sections on NMR and IR. Both of these are invaluable in the examination of exchanger-water interactions, particularly the NMR technique.

A quantitative characteristic of the interaction between an ion exchanger and water is provided by the isotherms (isopiestic lines) derived from the determination of the adsorption of water from a vapor phase or solution (isopiestic technique). As indicated in Section III.A, this procedure can be used to determine water levels in ion exchangers.[49,82-86] However, it is perhaps a more valuable technique for the examination of water-exchanger interactions. For example, if the isopiestic lines are measured under vapor pressures ranging from negligibly low values to pure solvent at several temperatures, it is possible to calculate the thermodynamic functions characterizing the exchanger-water interaction. In general, the thermodynamic approach has been developed largely by analogy with the thermodynamics of the hydration of natural macromolecular compounds. Theoretical development and discussion of the experimental techniques have been described in detail before,[5,34,82-86,100-105] and for this reason investigations since 1969 will be emphasized here.

Cation exchangers in H- and metal-ion forms have been investigated. As Dowex 50 was equilibrated at increasing humidities, the water content and volume of the exchanger particles increased in a sigmoidal direction.[106] The effect of cross-linking was considered, and a hydrated and free-water region was identified in the curves. From these data the hydration number for the cation exchanger was suggested to be 4. The water content of the cation exchanger KU-2 was found to be 25 to 30% more for the exchanger in the H-form as compared to the Na-form.[107] An experimental exchanger which included the $-CONH_2$ group in addition to the $-SO_3H$ group had the opposite effect. Hydrogen bonding between H and the $-CONH_2$ was suggested to be responsible for this reversal. Osmotic phenomena, diffusion, and pressure of swelling were factors that were evaluated in another study.[108]

Dowex 50 in the H-, K-, Ca-, and Ag-form and at 1 and 12% cross-linking was investigated at six different equilibrium vapor pressures.[109] Swelling, density of the exchangers, and the time required to reach equilibrium were determined. The differences in these data and in the isopiestic lines were suggested to be due to changes in the water structure within the exchanger. These investigators also reported that water sorption from solution experiments was greater than from vapor pressure experiments.[110] Similar studies were done with the KU-5 exchanger in the Li-, Na-, K-, Mg-, Ca-, and Al-form.[111] It was concluded that the H_2O molecules are taken up initially by the sulfonic acid groups. After this, the differing cations make their effects visible until they are saturated with water molecules. Subsequently, the response of the different charged forms to additional uptake of water is very similar. Isopiestic lines were determined for a Cu-form of a strong acid ion exchanger (KU-2) and compared to the H-form.[112] It was concluded that 2 water molecules per Cu are taken up, with the second being held more weakly than the first. As the percent cross-linking increases, the sorption of water decreases. It was also found that the diffusion coefficient decreased sharply at cross-linkings above 8%.

Isopiestic data were collected for the anion exchanger Dowex 1 X 4 in F-, Cl-, Br-, and I-form.[113,114] Integral sorption enthalpies, free energies, and entropies were calculated for the four forms of the exchanger. Sorption of water by the exchanger was found to decrease for the charged ion exchanger in the order $F \gg Cl > Br > I$. The thermodynamic data were used to explain sorption of the initial water molecules in order to better understand the state of the water within the anion exchanger. The anion exchanger AV-17 was investigated in a similar fashion.[115] Eleven different anionic forms were used, and from the isopiestic and integral-free energy data it was suggested that the major factors influencing water sorption were the nature of the charged form and the interaction with the fixed group. For example, for singly charged counterions the number of millimoles of H_2O in the monolayer decreased with increasing ionic radius. For ions of approximately equal radii, water content increased with an increase in charge.

Water sorption at different humidities was determined for a series of exchangers that differed by the length of the cross-linking agent used in the polymer backbone.[116] At high humidities these exchangers had a larger quantity of retained water than that found for the KU-2 exchanger. At lower humidities the shorter cross-linked exchanger had more water. Also, a difference in water content was found when Na- and H-form KU-2 were compared, but not for the exchangers with variable lengths in the cross-link. These differences in hydration were attributed to the fact that the modified exchangers possessed larger interstitial spaces.

Conductivity measurements were used to evaluate the mobility of water molecules in cation exchangers charged in different metal forms.[117] Hydration numbers could also be determined. Hydration of an acrylic acid-type exchanger in the H- and Na-form[118] and of a carboxylic acid-type exchanger[119] was also studied by conductivity.

It was shown that when a cation exchanger exchanges an organic counterion, an appreciable amount of dehydration occurs within the resin.[120] However, as this occurs the volume of the exchanger phase as a whole changes very little.

Different states of hydration in ion exchangers have been determined experimentally through dielectric constant measurements of exchangers containing known water levels that were prepared isopiestically.[121] Cation exchangers with phosphonic or sulfonic acid exchange sites and strong base anion exchangers were examined. The level of hydration was shown to be dependent on the charge form and type of exchanger, which results in differences in polarization at the exchange site.

Bucher et al.[122] have suggested that by choosing the pure salt resinate as the standard state, exchanger selectivity is then primarily determined by the external solution phase. This is in contrast to past models and derivations describing selectivity in which the process is suggested to be mainly a function of exchanger properties. These researchers further state that the properties and characteristics of one phase may dominate the exchange; hence, exchanger selectivity results from the differences of the two ions in the two different phases. This was established in a series of experiments in which selectivity coefficients were determined for the series ReO_4^-, CrO_4^{-2}, and WO_4^{-2} vs. Cl^- and $Cr(CN)^{-3}$, $Co(CN)_6^{-3}$, and $Fe(CN)_6^{-3}$ vs. CN^- on Dowex 1 X 8. From these data it was concluded that the direction of the exchange is determined by the hydration of the ions in the dilute aqueous phase over that in the exchanger phase and not by ion pairing in the latter phase.

An expression was derived which related the ion exchange selectivity to the differences between free energies of swelling for the two monoionic forms of the exchanger.[123] In this model the dehydrated forms of the resin are chosen as the standard state. Selectivities in aqueous solution have been determined on macroporous exchangers and highly cross-linked exchangers.[13,20,21,32,33,124]

C. Exchanger-organic Solvent Interactions

1. Water-organic Solvent Mixtures

Several excellent reviews are available which describe the numerous investigations of ion exchange selectivity.[5-14,20,21,32,33,125] Therefore, this important property of ion exchangers will not be surveyed in detail in this review. However, more recent investigations will be cited here. Furthermore, the emphasis in this review will be on the role of the solvent in influencing ion exchanger selectivity.

Correlation of exchange phenomena to dielectric properties of the solvent mixture, as pointed out earlier,[4-7,10-13,20-24,32-40] continues to be developed. Sorption of cations on anion exchangers in mixtures of water with methanol, ethanol, propanol, and acetone were correlated to dielectric constant for the solvent mixtures.[126] Dielectric constant and solvent basicity were considered to be the dominant solvent properties which influenced the Na-H selectivity coefficient on Dowex 50 X 8.[127] Water mixed with HCOOH, $HC_2H_3O_2$, and dioxane and $HCOOH\text{-}HC_2H_3O_2$ mixtures were considered. A relationship between log distribution coefficients for Mg, Co, and Mn on a cation exchanger and dielectric constant $\frac{1}{\epsilon}$ was reported for aqueous solutions of MeOH, EtOH, or $HC_2H_3O_2$ that were 0.1 to 2 M in $HClO_4$, H_2SO_4, or HCl.[128] The relationship was linear in the acid range of 0.1 to 1 M. Also, Mg sorption was shown to be related to activity coefficients for the acids at 0.1 to 2 M. Selectivity measurements for these same systems were also reported.[129] The exchange between a series of alkylammonium ions (RNH_3^+) and H or Li on the cation exchangers Dowex 50 X 2 and Dowex 50 X 8 was determined in different H_2O-MeOH mixtures. As the length of the alkyl group R was increased, the selectivity of the exchanger towards RNH_3^+ was found to reach a maximum when R was equal to a propyl group.

The selectivity coefficients for the exchange of alkali metal ions and ammonium ion with H-form ZeoKarb 225 (8% cross-linked) were determined as a function of alcohol- or acetone-water mixtures.[40] As the system passes from an aqueous to a nonaqueous one, the selectivity, K_H^M, was found to increase; large differences and reversals were also apparent. The effects of dielectric constant and solvation were noted. Smits et al.[41] also noted the importance of solvation in establishing the selectivity for the exchange of Rb or Mg with H-form Dowex 50 X 8 in DMSO-water mixtures. They concluded that solvation determined selectivity in solvents that consisted mainly of water, but not in a solvent that consists mainly of DMSO.

The selectivity of Dowex 1 X 4 and Dowex 2 X 4 towards halides, thiocyanate, and hydroxide ions was determined in H_2O-MeOH mixtures.[131] The sorption of H_2O and MeOH by the exchanger decreased in the order Cl > Br > I at all H_2O:MeOH ratios that were examined.

The normal aqueous-phase selectivity order for halides on Dowex 1 X 4 is reversed in dioxane-water mixtures.[132] This reversal, according to the authors, is explained by the fact that ion exchange selectivity occurs as the result of a competition of exchanging ions for that phase which provides the best solvation. Thus, the ion most readily solvated is one which has the highest charge density, the most acidic cation, or the most basic anion. In general, in water the external aqueous phase provides the better solvating condition. As dioxane is introduced, the mixed external phase becomes a poorer solvating agent relative to the interior phase since the exchanger preferentially takes up water. Hence, the ion most in need of solvation enters the interior phase. Similar experiments were carried out with water-isopropanol mixtures.[133] These experiments and related observations supported the earlier findings.

Several investigators have reported results from experiments in which anion exchangers are equilibrated with aqueous-organic solvent mixtures of strong acids.[134-137] A significant difference between bulk and internal solvent mixtures was reported for Dowex 2 X 8 in water-alcohol and water-acetone mixtures up to 7 M HCl.[134] For strong acid (HNO_3 or H_2SO_4)-$HC_2H_3O_2$-H_2O mixtures, a mutual influence of the individual components effects the uptake by an anion exchanger and results in a simultaneous sorption of the strong and weak electrolyte.[135,136] Also, the composition of the interior phase differed from the exterior phase, and this composition was dependent on the ratio of the ternary mixture. HCl-electrolyte invasion and resin-swelling data were used to calculate mean activities of HCl in the resin phase for the system Dowex 1 X 8 and aqueous MeOH, EtOH, and n-PrOH mixtures.[137] The invasion of HCl was reported to be higher in mixed solvent and increased as the mole fraction of alcohol increased. As HCl increases, the uptake of water from the mixed solvent decreases. Uptake of the alcohol solvents at different concentrations of HCl and H_2O was also reported.

The cation exchanger KU-2 X 8 was equilibrated with aqueous MeOH and Me_2CO solutions containing 0.5 to 2.0 M $HClO_4$.[138] Asymmetric isotherms were found over the entire concentration of $HClO_4$; the isotherms in Me_2CO solutions were more asymmetric. Also, retention of $HClO_4$ was lower from the Me_2CO solution.

Selectivities were reported for alkali metals on macroporous cation exchangers in H_2O-MeOH[139] and H_2O-Me_2CO mixtures.[140] The differences in exchange selectivities at different solvent ratios were attributed to the porous character of the exchanger and subsequent distribution of the solvent components between the interior and exterior phases. The effect of mixed solvents on the properties of macroporous exchangers and their application in the separation of inorganic and organic compounds have been noted before.[9-13, 20-24,26,33-42]

Several other studies were devoted to or included an investigation of mixed solvent uptake. The total solvent uptake was determined for the cation exchanger KB-4PZ (a phosphorus-containing exchange site) in the H-form in dioxane-H_2O mixtures.[141] As the dioxane concentration increases, the total solvent uptake increases and reaches a maximum at 80% by volume dioxane. Water was shown to be preferentially retained from H_2O-MeOH mixtures on Dowex 50 X 2 and Dowex 50 X 8 for the exchangers charged in the H-, Li-, $MeNH_3^+$-, $BuNH_3^+$-, and octyl NH_3^+-form.[142] However, as the chain length of amine increased, water preference decreased.

Water sorption by anionic and cationic exchangers in alcohols containing small amounts of water increased in the order MeOH > EtOH > n-PrOH > BuOH > iso-BuOH.[143] Similar trends were noted for alkyl carboxylic acids and aldehydes as solvent. For the anion exchanger, the water sorption followed the order $NO_3 < I < Br < Cl < F$ when the exchanger was charged in these forms. The effect of the counterion on solvent uptake of AV 17 anion exchanger in aqueous acetone was reported.[144] The swelling of Dowex anion exchanger of different cross-linkings in the Cl- and ClO_4-form was determined for a series of aqueous-organic solvent mixtures by centrifugation[145] and calorimetry.[146] The alcohol-water mixtures were studied in detail. In the water-rich region, the alcohol was found to be preferred over water; this preference was also more pronounced for the ClO_4-form of the exchanger than for the Cl form. In the intermediate region water is preferred; as the water is decreased (alcohol-rich region), the selectivity of water over alcohol becomes extreme. In general, the preferred sorption decreases in the order from PrOH to MeOH. These observations were explained by considering the effect of the organic solvent on the structure of water outside the resin and by preferential ion solvation effects.

Solvent uptake for the cation exchanger KU-2 was determined by centrifugation in water-alcohol mixtures under saturated conditions.[147] In this study two solvent systems were used, water saturated with n-BuOH or larger chain alcohols and n-BuOH or larger chain alcohols saturated with water. The exchangers were in the H-, Li-, Na-, K-, Mg-, and Fe^{+3}-form. For the water-saturated condition, the total amount of solvent uptake was about the same for all the water-saturated alcohol systems. For the reverse of alcohol-saturated water system, the uptake was significantly reduced and appeared to be less as the alkyl straight-chain increased. Branching in the chain resulted in less uptake than that found for the corresponding straight-chain alcohol of the same number of carbons.

In H_2O-EtOH mixtures the selectivity of H_2O by Li-, Na-, and K-form macroporous cation exchangers and Cl-, Br-, and I-form macroporous anion exchangers is reported to be lower than that found for corresponding microporous exchangers as the water content of the solvent mixture increases.[148]

Solvent uptake by macro- and microporous cation exchangers in the H-form was determined for alcohol-water mixtures by a centrifugation-Karl Fischer titration procedure.[48] Furthermore, these researchers were able to determine the exchanger's internal and external solvent composition by NMR measurements. In these experiments the macroporous cation exchangers, like the microporous exchangers, preferentially take up water. However, measurements were not made at the extreme end of low water or low alcohol concentration.

2. *Nonaqueous Solvents*

The uptake of nonaqueous solvents by cation and anion exchangers has been reviewed extensively,[5,13,20,21] particularly in two recent reviews.[32,34] Therefore, this section will serve as a supplement to these latter two reviews.

Solvent uptake for the two strong acid cation exchangers SDV-3 and KU-2 was determined, and the uptake decreased in the order EtOH > isoamyl alcohol > MeCOEt > $CHCl_3$.[149] Dowex 50 X 8, Dowex 50 X 4, and Dowex 1 X 8 were used in another study.[150] For the H-form exchanger the uptake decreased in the order H_2O > MeOH > EtOH > $HC_2H_3O_2$ > Py=dioxane=DMF. Water was reported to be higher in the Na-form exchanger than in the H-form, and EtOH uptake was reported to be very low relative to MeOH. (Results that are partially different than these have also been reported; see Table 3 and a discussion in a later part of this section.[37]) The anion exchanger was studied in the OH- and Cl-form; the uptake for the latter resin decreased in the order H_2O > MeOH > CH_2OHCH_2OH > $HC_2H_3O_2$ > EtOH > DMF=dioxane=py. A similar study was done with several different macroporous cation (H- and Na-form) and anion exchangers (Cl- and OH-form) in the same solvents.[151]

Calorimetric measurements[50] and changes in the amplitude of an NMR signal[152] have been correlated to the rates at which solvents are taken up by cation exchangers. In the latter study the cation exchanger KU-2 containing different levels of cross-linking was used. EtOH, BuOH, and octyl alcohol were the solvents. A procedure was devised which permitted the determination of the percent divinyl benzene in the cation exchanger.

Figure 2 illustrates the results found in the calorimetric studies.[50] Experimentally, the heat loss was determined as a function of time after immersion of the cation exchanger (dry state) into the solvent. The rate for heat evolution for the cation exchanger in DMF and DMSO was very slow (over 30 min). In contrast, the heat evolution for the macroporous cation exchanger Amberlyst 15, H-form, corresponded to Curve a in Figure 2 for all the systems except butanol. However, even for butanol the heat evolution, and consequently solvent uptake, occurred at a faster rate for the macroporous exchanger. It would appear that this technique[50] would be a useful one for following solvent uptake in a more detailed kinetic examination.

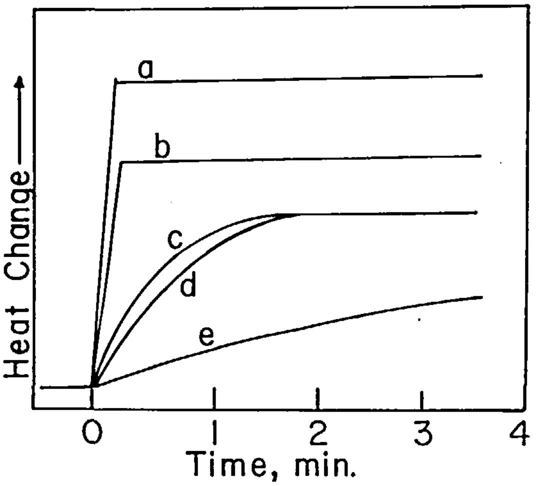

FIGURE 2. Heat loss for Dowex 50 X 8, H-form in several solvents as a function of time: (a) water; (b) methanol; (c) ethanol; (d) n-propanol; (e) n-butanol. (Reproduced with permission from Wilks, A. D. and Pietrzyk, D. J., *Anal. Chem.*, 44, 676 (1972). Copyright by the American Chemical Society.)

The more rapid uptake by the macroporous cation exchanger was also demonstrated in experiments designed to establish the optimum contact time between dry solvent and the cation exchanger solvent uptake experiments.[37] Centrifugation was used in this procedure. Table 3 lists the solvent uptake data determined for the macroporous and microporous cation exchangers.

Several broad generalizations are evident.[37,50] The cation exchangers prefer water over any other solvent examined. In all cases the macroporous exchanger takes up more solvent than the microporous exchanger. The largest difference was observed for the nonpolar nonoxygenated-type solvents where the microporous exchanger hardly takes up any of the solvent. This difference is attributed to the permanent porosity exhibited by the macro-

TABLE 3

Solvent Uptake (g Solvent/g of Dry Exchanger) for Macroporous and Microporous Cation Exchangers

	Ion exchanger[a]		
Solvent	A-15	A-15 Na	D-50
Water	1.21	0.95	1.16
Methanol	0.82	0.59	0.70
Ethanol	0.85	0.59	0.68
n-Propanol	0.91	0.53	0.72
Isopropanol	0.89	0.46	0.60
n-Butanol	0.91	0.40	0.69
Dimethylformamide	0.83	0.61	0.60
Acetonitrile	0.55	0.49	0.29
Nitromethane	0.74		0.32
Tetrahydrofuran	0.83	0.39	0.59
Dioxan	0.85	0.47	0.04
Ethyl acetate	0.72	0.45	0.43
Acetic acid	0.91	0.81	0.57
Chloroform	0.84	0.62	0.39
Carbon tetrachloride	0.50	0.43	0.03
Benzene	0.33	0.32	0.014
Hexane	0.20	0.21	0.013
Cyclohexane	0.26	0.27	0.009

[a]Capacity for macroporous A-15 is 4.81 meq/dry g and for microporous D-50 it is 4.85 meq/dry g of exchanger.

From Pietrzyk, D. J., *Talanta,* 16, 169 (1969). With permission.

porous exchanger. For the nonpolar hydrocarbon solvents, the uptake is independent of the ionic form. However, for the oxygenated solvents, the H-form exchanger has a much higher solvent uptake than that found for the Na-form exchanger. This was attributed to a greater solvation for the H-form exchanger.

Isopiestic-type measurements have been utilized to investigate the properties of cation exchangers (macro- and microporous, weak and strong acid-type) in the presence of alcohol vapor.[153-155] The shapes of the isopiestic lines are, in general, similar to that found for water. As the cross-linking in the exchanger increased, the middle range of the isopiestic line was found to rise more sharply.

Solvent effects were considered in a study of the retention of aromatic compounds on a series of anion exchangers.[156] The adsorption mechanism was suggested to involve either hydrogen-bond formation of π-bond attraction between an aromatic compound and the exchanger counterion. Hydrogen bonding ability of the solvent was found to be more influential than Van der Waal's forces in determining the solvent's ability as an eluting agent.

IV. METHODS FOR THE DETERMINATION OF EXCHANGER PROPERTIES

A. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has been found to be very useful in the investigation of cation and anion exchangers when suspended in water, mixed solvents, and nonaqueous solvents. The NMR proton spectra will generally show resonances which originate from the fluid or solvent protons in the interior of the resin (interior peak) and resonances from the void region about the ion exchange bead (exterior peak). Identification of the two is usually made by comparing the spectrum to one obtained for water only. In some cases the interior peak is sharper than the exterior peak. However, as will be brought out in the following discussion, several exchanger parameters will influence the actual shape of the NMR spectrum. Hence, in some cases the two peaks are so close that they appear as a single broad, unsymmetrical band. If water is the solvent and the ion exchange beads are allowed to settle, a sharp internal water resonance peak and a broader external water resonance peak are observed. When the spectrum is recorded prior to settling of the beads, a third resonance is suggested to appear as a shoulder on the external water peak which is attributed to bulk water being removed from the ion exchange bead as it settles.[74] However, not all investigators have reported the presence of this shoulder, and perhaps this is due to the fact that most spectra are usually taken long after the exchanger beads have settled. Typical NMR spectra for cation and anion exchangers were shown in Figure 1.

In 1962 Dinius and Choppin[157] reported the NMR spectra for *p*-toluenesulfonic acid, 2-naphthalenesulfonic acid, and 2,7-naphthalenedisulfonic acid as a function of concentration. These data were used to calculate the dissociation constants for the strong sulfonic acids, since these acids, as well as polystyrene sulfonic acid,[158] are often used as model compounds for cation exchangers. NMR data were also collected for Dowex 50 X 4 and Dowex 50 X 16 H-form. A subsequent comparison between the chemical shifts for the model compounds and the Dowex 50 cation exchanger was used to suggest that the cation exchangers are stronger acids and that the 4% cross-linked resin is a stronger acid than the 16% cross-linked Dowex 50. Furthermore, in subsequent and more detailed investigations, it was suggested that the Dowex 50 X 4 is a stronger acid than HCl and probably similar in strength to $HClO_4$, Dowex 50 X 16 is slightly weaker than HNO_3, and Dowex 50 X 8 is intermediate in acid strength compared to the 4 and 16% cross-linked exchangers.[71,159]

Also in 1962, Gordon[72,160] reported NMR proton spectra for ion exchangers in water, water-*t*-butanol mixtures, and nonpolar solvents. Cation resins in the H-, NH_4^+-, and Me_4N^+-form and anion resins in the Cl-, HCO_2-, HO-, anisate-, and *p*-nitrobenzoate-form were studied. Dowex, Amberlite®, and Permutit® cation exchangers at different particle size and cross-linking were used. General features of the spectra which have been observed include the following.

1. Rather narrow lines which are well defined are usually found.
2. Separate signals were observed for interior and exterior solvent, and the sign and magnitude of the shift of the interior peak relative to the exterior peak depends on the nature of the

proton under observation and the nature of the resinate salt.

3. Suspension of the exchanger in the solvent broadens the exterior solvent resonance and causes a shift in its position.

4. The resonance lines resulting from the interior solvent and proton-containing counterions are broadened.

As a result of these initial investigations, the NMR technique was established as a tool for the direct observation of many properties of ion exchangers. These include the effects of cross-linking, homogeneity within the exchanger, internal concentration of counterions, rate of exchange of water, internal-external solvent composition for an exchanger in a mixed solvent, hydration of counterions in the exchanger phase, solvation, and similarities between concentrated homogeneous solutions of electrolytes and the heterogeneous water-exchanger system. As indicated previously in this review, the NMR technique can also be used to determine the molality and percent water in strongly acidic and basic ion exchangers.[48,61,66,69-76]

Several investigators[69,71-76,161-163] have correlated chemical shifts for Dowex 50 and Dowex 1 in water to cross-linking within the resin. (Correlations have also been reported for other industrial ion exchangers; see the following NMR references in this section.) Capacities and water-uptake values for the different cross-linked ion exchangers must first be determined, and subsequently these data are used to calculate molalities for the internal water. When the differences in chemical shift between internal and external water are plotted vs. the molalities, a straight-line relationship is obtained up to about 8*M*. This correlation has been reported in water for H-form cation exchangers, for cation exchangers in different metal ion forms, and for anion exchangers in different anionic forms in water as the solvent. For example, with Dowex 50 the water content decreases in the order $H > Li > Na > K > Rb > Cs$ at cross-linkings of 1 to 16%.

Since the NMR technique allows examination of the internal and external solvent in suspended ion exchange beads, it should be possible to examine the "internal electrolyte solution." This has been the subject of several studies in which water was the solvent.

Chemical shifts for internal water protons will vary as a function of the charged form.[73] For example, chemical shifts were found to be in the order $H \ll Zn \approx Cd < Pb \approx Mg < Ag < Ca \approx Tl \approx NET_4^+ < Ba \approx Li \approx NMe_4^+ \approx Sr < NH_4^+ < Rb \approx K \approx Na \approx NBu_4^+$ where H is at lowest frequency.[161,164] A similar order for the mono- and divalent cations was also reported.[74,162] The chemical shift for the internal water relative to the standard (usually NH_4^+) occurs more upfield as cross-linking increases.[74,162,164] If the shift is calculated per counterion concentration in the exchanger, the upfield shift in most cases is small, although it still tends to increase with increasing cross-linking. The observed shifts are similar to those found in aqueous solution and are an indication that the ion-solvent interactions within the ion exchanger are similar to that found in water.[72-74,161-164] Figure 3 compares the NMR shift found for cation exchangers charged in monovalent cation form to the shift found for the corresponding electrolyte in aqueous solution.

Chemical shift data for the different metal-ion forms of the cation exchanger can be used to calculate the hydration number for the system, provided that the data are collected as a function of temperature. (Figure 4 illustrates, in general, how temperature affects the interior and exterior water peak.[73]) Table 4 summarizes the hydration numbers determined in different independent NMR studies.

Similar hydration phenomena and correlation to aqueous solutions of corresponding salts have been found for KU-2 (sulfonated polystyrene-

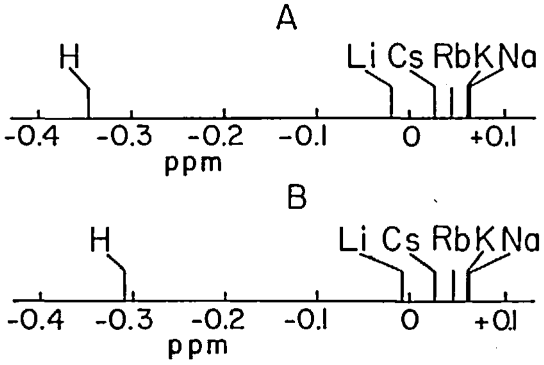

FIGURE 3. Comparison of the effect of cations on the proton shift of water for homogeneous electrolyte (A) and Dowex 50 X 8 (B). (Reproduced with permission from Creekmore, R. W. and Reilley, C. N., *Anal. Chem.*, 42, 570 (1970). Copyright by the American Chemical Society.)

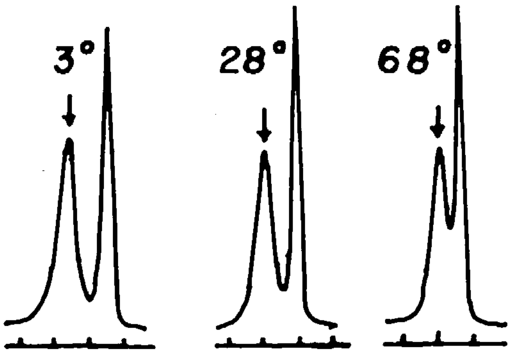

FIGURE 4. Effect of temperature (°C) on the NMR spectra for Dowex 50 × 8, Na-form in water. (↓) Marks the internal water peak. (Reproduced with permission from Creekmore, R. W. and Reilley, C. N., *Anal. Chem.,* 42, 570 (1970). Copyright by the American Chemical Society.)

TABLE 4

Hydration Numbers for Dowex 50 × 8

Counterion	Hydration number
H^+	2.9
Na^+	2.9
K^+	2.7
Rb^+	2.6
Cs^+	3.2
Mg^{+2}	6.7

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divinylbenzene copolymer) cation exchanger charged in different forms.[165-171] The effects of cross-linking, exchanger matrix, nature and concentration of ions and temperature (−80 to 80°C) were investigated.

The differences in the measured hydration numbers are partly the result of assumptions made in relating the total effective hydration number and molality; hence, the original articles should be consulted. Regardless of this difference, it is clear that the NMR technique is useful for investigating solvent-ion interactions within the ion exchanger. Furthermore, when these results are compared to hydration numbers of homogeneous solutions of simple electrolytes, the numbers within the exchanger are, in general, lower. It has been concluded that this is an indication of a low level of association between the anion and cation within the ion exchanger.[73,74,162,163]

The rate of free exchange of water protons between the interior and exterior region in an ion exchanger in an aqueous system was measured by an NMR double-resonance technique.[172] The rate was found to be $7.3 \times 10^{-1}\,\text{sec}^{-1}$ for Dowex 50 X8, 50 to 100 mesh, H-form resin. In addition, it was possible to evaluate the longitudinal relaxation times for the exterior bulk water protons (2.9 sec) and interior exchanger water protons (0.45 sec). The rate constant is in good agreement with the value reported earlier by Gordon.[74] It should be noted that changes in particle size, cross-linking, counterion, and heterogeneity will have an effect on these values.

A pulsed NMR technique was used by Blaedel et al.[173] to measure longitudinal and transverse relaxation times for water protons (Dowex 50). Cross-linking and moisture content were major variables considered in this study. From the data it was concluded that cross-linking effects on the relaxation times were slight and that at above 6 mol of water per exchange site, the water protons were in a water-like environment; below 6 mol of water per site, the water is suggested to be structured.

It was concluded from NMR data that as the temperature of the cation exchanger (KU-2) aqueous system is decreased, the mobility of the internal water decreases gradually down to about −30°C, at which point a sharper decrease in mobility occurs.[118,166-171,174-176] The nature of the hydration state at these lower temperatures was also discussed. Effects of cross-linking and charge form and the determination of relaxation times were major considerations in these experiments. It has also been shown by NMR measurements using an acrylic-type ion exchanger that as temperature is increased, interior bulk water and not interior cation hydrated water is lost first.[77]

deVilliers and Parrish[69] reported NMR data for weakly acidic-type ion exchangers. Very broad bands were observed for both internal and external water for polystyrene exchangers with phosphonous and phosphonic acid groups (Bio-Rex 62 and 63). No separate signal was found for the weak acid exchanger Amerlite IRC-50 (cross-linked polymethacrylic acid) in the hydrogen form. In the Na- and K-form, an unresolved broadening was found and was suggested to be due to hydrolysis of the salts. When the exchanger was charged in the $(CH_3)_4N^+$-form, a separate internal peak was observed. A similar spectrum was obtained for the ion retardation exchanger AG-11A8 in the zwitterion form which contains the carboxyl- and benzyltrimethylammonium-type groups.

More recently, interior and exterior water NMR peaks were observed for the weak carboxyl-type exchanger IRC-84 (cross-linked polyacrylic acid), and these data were compared to the strong sulfonic acid-type exchanger IR-120.[177] In general, the chemical shift is independent of temperature for the former exchanger, unlike that found for the IR-120. The exterior water-line width is similar to that found for IR-120, while the interior water-line width leads to an activation energy which is much larger than that for IR-120. Last, the high-temperature line widths for the two exchangers are nearly the same. Even though the weak acid exchanger in the H-form is poorly dissociated ($<1\%$), the major cause of the chemical shift and line width is probably the result of the interaction between the carboxylic acid group and water. Spectra for weak acid carboxyl-type exchangers have also been observed by others.[66,163]

Proton magnetic relaxation times were measured for water adsorbed on a cross-linked poly(methacrylic acid)-type exchanger in the H-, Na-, and Cs-form.[178] The concentration of water, degree of swelling, and effect of the charge form were noted. Signals were also reported for the weak carboxylic acid-type exchanger KB-4P2 in the H- and K-form,[171,179] for phosphonated cation exchangers,[176] phosphoralated cellulose,[180] and carboxymethyl-type celluloses.[180,181] Three distinct types of line widths were noted for the phosphoralated and carboxymethyl celluloses in the H-, Na-, and Ca-form as a function of water level.[180,181] At low water concentrations, line widths were about the same. As water concentration is increased, the binding of the water decreases. This change is accompanied by a linear decrease in the line width. At very large water concentrations the widths become nearly equal again. Throughout all the regions the line width depends on the charge form and has the greatest effect at higher water levels. NMR shifts for Na-, Cd-, and Cu-forms of a polystyrene-aminoacetic-acid-type exchanger have been reported.[182] The observed shifts were stated to be the result of coordinated water.

The chemical shifts for the anion exchanger Dowex 1 at cross-linkings of 1 to 10% have been measured for different charged forms and are in the order $F < Cl < Br \approx NO_3 < I < ClO_4$.[162] The shifts are slightly lower than those found for the corresponding electrolytes in aqueous solution, but the data still suggest that the ion-solvent interactions in the exchanger are similar to those observed in aqueous solution.[73,162] Table 5 summarizes the hydration numbers determined for the anion exchanger in independent studies. Similar results have been reported for the anion exchanger AV-17.[167,171,175]

deVilliers and Parrish[69] were unable to detect an internal water peak for weakly basic exchangers either in their neutral or charged form. Subsequently, NMR shifts have been found for weakly basic exchangers in aqueous solutions.[163,177] However, in some cases the chemical shifts are small and not readily measured. Exchangers that have been studied in the neutral form are polystyrene-divinylbenzene matrix-type exchangers containing polyamine and t-amine groups and a polyacrylic matrix-type exchanger containing a t-amine group[177] and a pyridinium group on a polystyrene lattice.[163]

Lithium-7 NMR studies of cation exchangers have been carried out.[183-187] Proton and ^{7}Li NMR line widths using a KU-2 cation exchanger have been compared; the proton line width is generally larger. It has been suggested that these measurements can be used to determine exchanger cavity dimensions.[181]

TABLE 5.

Hydration Numbers for Dowex 1 X 4

Counterion	Hydration number
ClO_4^-	0.6
F^-	1.1
Br^-	1.3[a]
I^-	1.6
NO_3^-	1.3

[a] For Dowex 1 X 8.

From Sharma, H. D. and Subramanian, N., *Can. J. Chem.*, 49, 457 (1971). Reproduced by permission of the National Research Council of Canada. 49, 457 (1971). (See also References 73, 162, 167, 171, and 175.)

Relaxation times by ^{7}Li NMR have been determined for KU-2 cation exchanger using a −80 to 50°C temperature range.[186] It was found that the relaxation times were very dependent on the moisture level. Relaxation times for the exchangers KRS-2 and KRS-4 in the Li-form were compared to those for LiCl solutions; the exchangers were found to have the higher values.[184] These types of relaxation values were also compared to those found in frog muscle cells, which were also less than those found for aqueous LiCl solutions. The difference was suggested to be due to an interaction between lithium ion and the charge site in the case of the exchanger and to an interaction between lithium ion and cellular macromolecules for the frog cell. Similarity between these two interactions was also discussed.[184]

Sodium-23 NMR data have been reported for the Na-form cation exchanger (Dowex 50 2 to 12% cross-linked).[73,173,187,188] In the early experiments 8% cross-linked resin was used, which resulted in a broad undefined band;[188] however, as cross-linking is decreased, the band becomes sharper.[73] The increase in ^{23}Na line width with increasing cross-linking is probably the result of an increase in the interaction between the fixed ion ($-SO_3^-$) and mobile ion (Na^+). Pulse NMR techniques were also used to measure the longitudinal and transverse relaxation times for ^{23}Na in the Na-form exchanger (Dowex 50 2 to 12% cross-linked).[173] The ^{23}Na relaxation is not as clearly defined as that found for the proton system. However, ^{7}Li and ^{23}Na NMR data have been used to determine the amount of Li and Na in the exchanger.[187]

The ^{19}F chemical shifts for an anion exchanger (Dowex 1) in F-form have been measured as a function of cross-linking.[73] As the cross-linking increases, the downfield shift increases (increased interior electrolyte concentration). This shift is suggested to be due to a deshielding of the fluoride ion by electrostatic association with the fixed ion.

If a cation exchanger (Dowex 50 X 8) is equilibrated with solutions of two counterions, H^+ and Na^+, it can be shown that the chemical shift for the internal water proton is linearly proportional to the equivalent fraction composition of the mixed-form exchanger.[161] Hence, it should be possible to determine exchanger composition (mixed-charge form) through a calibration curve rather than by elution and analysis of the eluate.

As a mixture of a cation exchanger (Amberlite IR-120, 200, and 252) in two different ionic forms (Na and H) is brought into contact, ion exchange will occur. This exchange process was followed with time by observing the variation in chemical shift as the exchange process is completed.[189] Initially, two separate interior water peaks, one for each exchanger, are observed. As the exchange process is completed, the two peaks coalesce into a single peak because the solvent environment is identical in each exchanger bead. This method of studying ion exchange kinetics is not influenced by ion selectivity and co-ion effects. Ion form (H, Na, Li, NH_4) and cross-linking were major variables that were considered, and the rate-determining step was shown to be particle diffusion through the cross-linked matrix.

It was suggested that interior line widths would reflect ion exchanger homogeneity.[72] In fact, many different investigators in earlier NMR studies utilized this measurement as an indicator of exchanger homogeneity.[72-76,162,163] In general, it was assumed that a single narrow interior line will imply a high degree of homogeneity, both intra- and interparticulate, in the exchanger. Factors (such as internal molality, cross-linking, number of functional sites, and internal uniformity) were recognized as influencing these measurements. Thus, Gordon[72] used line widths to divide a series of commercially available cation exchangers which differed in particle size, cross-linking, porosity, and probably in synthetic route, according to order of homogeneity. One group gave evidence of containing two or more distinct fractions. A second group included ion exchangers which had unusually broad interior water lines when they were used as received. When two of the exchangers were recycled, the line was sharpened, which is possibly an indication that the broadening was due to the presence of paramagnetic counterions. A third group provided normal line widths and the fourth consisted of ion exchangers which did not show an interior water line. (This latter group contained weak acid and weak base sites in the free acid and base form and has since been shown by others to provide evidence of interior water lines.[66,163,171,177-181])

Particle size (specially prepared sulfonated polystyrene divinylbenzene) was shown to have a significant effect on line width and resolution of the interior and exterior water peaks.[76] Increased percent of divinylbenzene and/or higher temperature will also affect the shift, resolution, and width. For large particles (>100 μm), spacing of the external and internal water peaks is independent of particle size. In the intermediate range (approximately 50 to 100 μm) kinetic phenomena became appreciable, and coalescence of the two peaks occurs to a variable extent. At smallest range (approximately <50 μm) a single peak is found which is independent of the particle size. In the intermediate range the internal molality cannot be determined from the NMR data. The same is true for the smallest particles. However, in this range it is possible to use the data to determine the volume capacity of the exchanger. The original article should be consulted for a discussion of the limitations of these size generalizations.[76]

Particle size will also influence the NMR spectra for macroporous ion exchangers. If the particles are large (micron size), the internal water line may be broadened. If they are small (about 100 Å), it is suggested that line widths become more a function of the exchanger's structure and can, therefore, be utilized to characterize the kinetic processes within the exchanger.[190]

Homogeneity is an important property of ion exchangers and is very difficult to evaluate directly. In a more recent study several different macroporous-type cation exchangers (strong and weak acid type) were investigated,[177] and these data were compared to data reported by Gordon[72] which were for microporous-type cation exchangers. The macroporous cation exchangers have only one interior water peak, just as was observed for the microporous ion exchanger. No separate pore- and gel-phase water resonances are observed for the macroporous-type exchanger.[177] Therefore, the water in the pore and gel phase of the macroporous exchanger undergoes rapid solvent exchange; this is estimated to be about 2×10^3 sec^{-1} at 25°C. The solvent exchange rate between exterior water and interior water is also greater for the macroporous exchanger in comparison to the microporous exchanger. The former,[177] depending on the exchanger and its charged form, will range from 20 to 100 sec^{-1}, while for the latter[72] (Dowex 50 X 8), a value of 7.3×10^{-1} sec^{-1} was reported.

Frankel[177] carefully considered other factors that might influence interior line widths, which previously had been considered to be a major reflection of ion exchanger homogeneity. Using macroporous and microporous exchangers, he concluded that interior water line broadening was predominantly due to the difference in diamagnetic susceptibility between the exchanger interior phase and the exchanger exterior phase for the strong acid cation exchanger and to the interaction between the carboxylic acid group and water in the weak acid cation exchanger.

Line broadening for cation exchangers was shown to be minimized by using a sample angle of 54.7° with respect to the applied magnetic field.[191-193] It was suggested that by using this procedure, line widths become a better indication of the kinetic processes that are present in large exchanger particles (> 1 μm range). In small particles (~100Å) interparticle heterogeneity is better characterized.[193]

One of the most important physical properties of a macroporous exchanger is the fraction of the total volume of the exchanger occupied by the pores. This porosity can be determined via a mercury porosimeter or a helium densitometer.[51] However, an exchanger in the dry state is required. Frankel[194] has shown that the porosity of a hydrated macroporous exchanger can be determined from the NMR spectra and the moisture-holding capacity of the ion exchanger. The basis for the measurement is the fact that the macroporous exchanger does not show separate water resonances for pore- and gel-phase water; therefore, the interior water peaks account for all the interior water.[113]

In 1962 Gordon[72] considered the effect of solvent on line broadening for the exterior solvent peak. Solvents examined in addition to water were toluene, dioxane, and CH_3CN. In 1970 Howery et al.[195] used the NMR technique to examine solvent selectivity for the system: Dowex 50 X 8, H-form, water-organic solvent mixtures. As the organic solvent mole fraction is increased, the internal water peak shifts downfield to a greater extent relative to the water-exchanger system. Seven different organic solvent-water systems were investigated. One suggested model to explain this behavior has the counterions surrounded predominantly by water, while the polymer backbone is surrounded to a major extent by the organic solvent. Hence, as the mole fraction of water in the initial mixture is decreased, a greater fraction of the internal water should come under the polarizing influence of the proton counterions. A similar downfield molal chemical shift pattern is observed for aqueous solutions of acids. The solvent selectivity for anion exchangers (strong

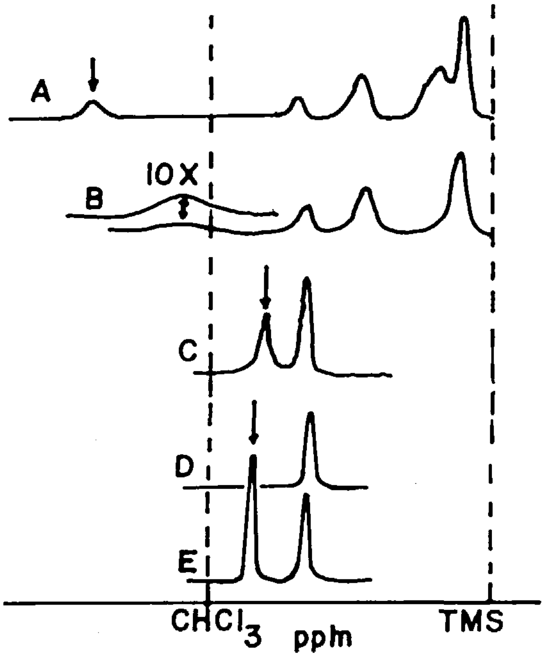
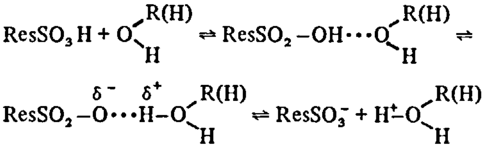


FIGURE 5. NMR spectra for several ion exchangers in water and alcohol: (A) Dowex 50 × 8 in n-propanol; (B) Amberlyst-15 in ethanol; (C) Amberlyst-15 in water; (D) Amberlite XAD-2 in water; (E) Dowex 50 × 8 in water. (↓) Marks the internal water peak. (Reproduced with permission from Casey, W. J. and Pietrzyk, D. J., *Anal. Chem.*, 45, 1404 (1973). Copyright by the American Chemical Society.)

base exchanger Amberlite IRA-400 and weak base exchanger Amberlite IR-15 in F-, Cl-, Br-, and I-form) in aqueous DMSO and aqueous CH_3CN had been investigated by NMR.[196]

The NMR technique has been used to learn more about solvation phenomena, dissociation of the sulfonic acid site, and solvent mobility in mixed and nonaqueous solvents containing strong acid-type ($-SO_3H$) ion exchangers.[48,152,197-199]

Figure 5 compares several NMR spectra for a macroporous cation exchanger (Amberlyst) and a microporous exchanger (Dowex) in water-organic solvents. Both exchangers are in the H-form, while XAD is a porous polystyrene-divinylbenzene copolymer without any exchange sites. If the shift for the interior water peak is plotted vs. the molality of solution inside the exchanger for Dowex 50, H-form at different cross-linkings, a linear relationship between shift and molality is observed. A similar relationship is found for the Dowex exchanger in MeOH, EtOH, n-PrOH, and n-BuOH, where the downfield shift increases in the order n-BuOH > n-PrOH > EtOH > MeOH > H_2O.[48] These experiments suggest that the alcohol molecules solvate the sulfonic acid group in a manner similar to the water molecules. Hence, the solvation can be represented by



$$\mathrm{ResSO_3H} + \mathrm{O}^{\mathrm{R(H)}}_{\mathrm{H}} \rightleftharpoons \mathrm{ResSO_2{-}OH\cdots O}^{\mathrm{R(H)}}_{\mathrm{H}} \rightleftharpoons$$

$$\mathrm{ResSO_2{-}}\overset{\delta^-}{\mathrm{O}}\cdots\overset{\delta^+}{\mathrm{H}}\mathrm{{-}O}^{\mathrm{R(H)}}_{\mathrm{H}} \rightleftharpoons \mathrm{ResSO_3^-} + \mathrm{H^+{-}O}^{\mathrm{R(H)}}_{\mathrm{H}}$$

The internal peak represents a summation of the species $-SO_3H$, ROH, R(or H)OH_2^+, since exchange occurs. If it is assumed that the $-SO_3H$ and ROH contributions are nearly the same for all the systems, the observed trend is consistent with the acidity that would be exhibited by the solvated proton; that is, $BuOH_2^+$ is the most acidic and H_3O^+ is the least acidic.[48]

If a water-alcohol mixture is used, the internal and external resonance peaks in the presence of the cation exchanger are still observed.[48,197-199] However, five species will now contribute to the system: $-SO_3H$, ROH, ROH_2^+, H_2O, and H_3O^+. Figure 6 lists the NMR shift for *p*-toluene-sulfonic acid (a model compound) and two exchangers (macro- and microporous) as a function of mixed solvent composition. (The original article should be consulted for additional data and for a discussion of the experimental conditions and conclusions.[48,198]) The linear downfield shift in the model system results because of the increased acid molality and because of the larger contribution from the more acidic alcohol-solvated proton species ($MeOH_2^+$). A similar trend, although not linear, was found for the system containing the ion exchanger, water, and alcohol (see Figure 6). It appears that these latter systems can be divided into four stages (I to IV in Figure 6) and that the stages represent a transition from dependence on the H_3^+O species (stage I) to dependence on the ROH_2^+ species (stage IV).[48,197] This observed trend is consistent with the interior solvent composition.[48]

It should be noted that the NMR data on the macroporous exchanger suggest that the exchanger shows a preference for water over the alcohol solvent at higher water concentrations, just as in the case of the microporous exchanger. This was confirmed by determining the interior composition of the exchanger.[129] Effects of particle size, comparison of macroporous and microporous ex-

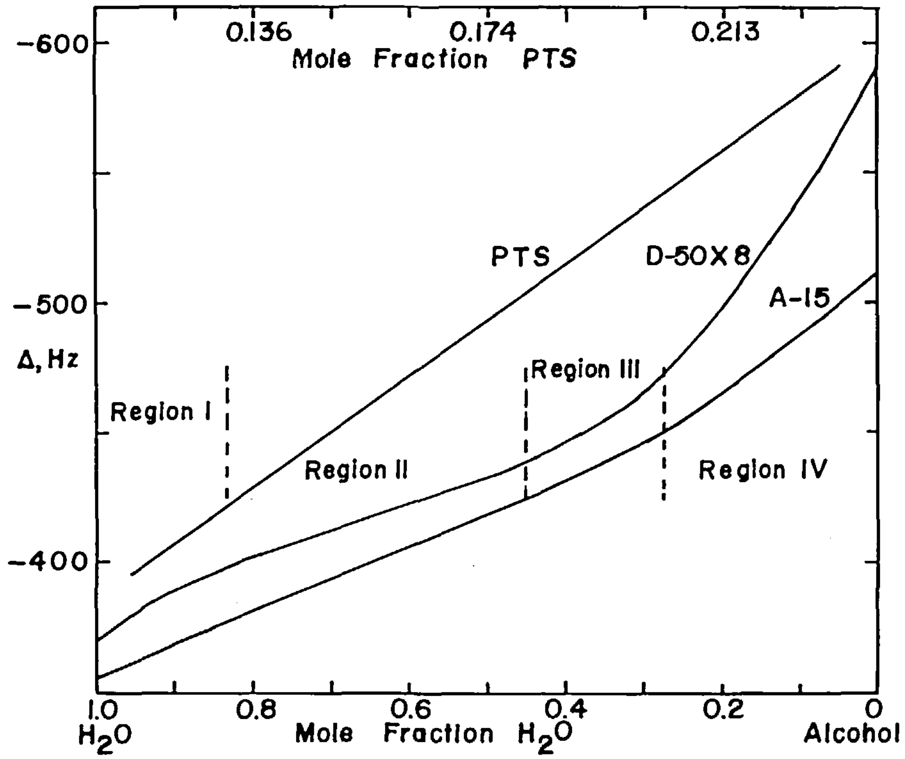


FIGURE 6. Shift of the interior solvent peak relative to TMS as a function of bulk solvent composition for *p*-toluenesulfonic acid (PTS) in methanol-water, microporous Dowex 50 X 8 in ethanol-water, and macroporous Amberlyst-15 in ethanol-water. (Reproduced with permission from Casey, W. J. and Pietrzyk, D. J., *Anal. Chem.*, 45, 1404 (1973). Copyright by the American Chemical Society.)

changers, and band broadening were considered in these studies.[48,197-199] The influence of association of the sulfonic acid site was also cited.[48,197-199]

It is possible to obtain ^{13}C NMR signals for groups bound to cation exchangers.[200] For example, several amino acids bound to Dowex 50 cation exchangers have been studied this way using pulsed Fourier transform techniques. (The original article should be consulted for a detailed discussion of the spectra and experimental direction required for obtaining suitable spectra.)

B. Electron Spin Resonance

Electron spin resonance (ESR) methods have not been widely used in the investigation of the properties of ion exchangers because of the specificity of the measurement. However, signals have been observed with exchanger samples. In some cases these signals arose after heating (decomposition) of the exchanger. For example, sufonated ion exchangers containing a polymer backbone derived from a condensation reaction between formaldehyde and several different aromatic compounds have been shown to have paramagnetic centers.[201,202] When Dowex 50 was exposed to ionizing radiation, an increase in the presence of free radicals was observed.[203] This increase was attributed to breaking of the C-S bonds. Also, the results were dependent on handling of the sample.

An ESR procedure was proposed[204,205] for investigating the mobility of water molecules in a bifunctional cation exchanger containing phenolic groups and sulfonic groups in the H-form. The basis of the method is that as the temperature is changed, molecular motion changes; hence, the magnitude of the relaxation parameters is affected. These physical effects can then be used to obtain information on the mobility about fixed paramagnetic centers of molecules having nonzero nuclear spin. Mobility in the weak acid exchanger DB-2 ($-CO_2H$) in the Na- and H-form was investigated at several cross-linkings by using a nitroso derivative as a radical probe.[206] An ESR study of Dowex 1 X 4 containing 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid was done in the presence and absence of hydration.[207] No radicals were observed below pH 9 or in organic solvents.

The spin label 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-ol was used as a probe with Dowex 50 at several different cross-linkings and charged in the Li-, Na-, and K-form.[208] The various ionic forms yielded little difference. However, a significant dependence on cross-linking was observed. Rotational correlation times increased up to 10% cross-linking and then decreased. It was suggested that this trend was a property of the heterogeneous nature of the interior of the exchanger.

Ion exchange kinetics on a cation resin (KU-2) in Mn^{+2}-form was studied by ESR.[209] ESR was also used to investigate Dowex 50 in the Mn^{+2}-form as a function of temperature and different degrees of hydration.[210] Relaxation and line-shape data were collected, and it was possible to use these data to determine the mean lifetime for association between Mn^{+2} and the exchange site.

ESR measurements can be used to study the exchange kinetics for other metal ions,[211] such as exchangers in Cu^{+2}-form[212-215] and Fe^{+3}-form[216] Exchangers containing sulfonic, phosphonic, carboxylic, and iminodiacetic acid groups in the Cu-form have been examined.[213] Water mobility, hydration, and coordination data were obtained from these experiments. Four types of signals were found for KU-2 X 8 exchanger in the Cu-form.[214,215] The exchanger containing a low concentration of Cu^{+2} exhibits an asymmetric spectrum of isolated Cu^{+2} ions in a tetragonal crystal field. As the Cu^{+2} concentration is increased, an additional maxima is observed. Fully hydrated samples yield a spectrum of $Cu(H_2O)_6{}^{+2}$. Air-dried samples containing low Cu^{+2} concentration at 77 and 300°K yield a spectra showing the Cu^{+2} coordinated to four water molecules and one sulfonate group. Hydration studies on KU-2 exchanger in Fe^{+3}-form have also been reported.[216]

C. Electron Microscopy, X-Ray Techniques, and Optical Microscopy

One of the techniques which directly distinguishes the macroporous ion exchanger from the microporous exchanger is electron microscopy.[46,47,217,218] With this technique the shape, location, and character of the pore-like properties of ion exchangers can be determined. It has also been demonstrated that the porosity results obtained by electron microscopy, are comparable to the results obtained by other indirect methods for determining porosity.[218]

With this technique the macroporous exchanger was shown to have a significant amount of nongel porosity in addition to the normal gel porosity. The nongel interstices, as shown by electron micrographs, are channels between agglomerates of minute spherical particles. Furthermore, these spaces have characteristic pore dimensions. In contrast, the microporous exchanger, as shown by electron micrographs, has a continuous polymeric phase.[46,47] Electron microscopy has also been used to compare pore structure of several different anion exchangers having pore diameters of 1,000 to 10,000Å.[219]

The effects of percent cross-linking in a series of cation exchangers were studied by electron microscopy.[220,221] These data were used to determine average pore sizes and to describe the heterogeneous nature of the resin structure.

Macropore properties of cation exchangers were determined by electron microscopy and electrolyte uptake.[222] If the exchanger had pores greater than 2,000Å, the two different methods were in poor agreement. At a lower pore size, the two methods were found to be in good agreement.

Depositing magnetite in the anion exchanger AV-17 by a ferritization process was used to study pore structure by electron spectroscopy within the exchanger.[223] It was suggested that this procedure could be used for studies of other types of exchangers.

Cu and Creti[224] employed small angle scattering of X-rays to study the macroporous cation resin Amberlyst-15. Their scattering data showed that the matrix has a random distribution of inhomogeneities or pores, with most of these pores being accessible. A deviation away from a random distribution of the pores was observed whenever the bulk swelling ratio became large.

X-ray powder data were collected for a series of cation exchangers (KU-2).[225] The effect of charge form and cross-linkings on distances was determined.

X-ray diffraction and X-ray spectroscopy were utilized to study a series of anion exchangers (AV-17 and EDE-100) in Cl^--, $TeCl_6{}^{-2}$-, and $CuCl_4{}^{-2}$-forms.[226] It was possible to examine structural order within the pores of the exchanger.

X-ray diffraction was also used to study the structure of Dowex 50 X 8 in alkali and alkaline earth form.[227] Homogeneity of KU 2-8 and KU 2-12P was studied by X-ray techniques.[228]

Exchanger swelling can be determined by techniques involving centrifugation, dye dilution, electrolyte dilution, or microscopy. Of these, the first method has been used the most. In general, the accuracy that is obtained by centrifugation will be determined by the uncertainty associated with where the resin phase ends and where the solution phase begins. The two dilution procedures, on the other hand, suffer from adsorption effects and errors that result from effects that occur when exchanger beads are in contact with each other.

In contrast, microscopy offers an approach to determine swollen exchange volume at a fairly high degree of accuracy. The major reasons for this are the following.

1. Image diameter can be measured with a high precision since optical devices are available to resolve images of ion exchange particles.
2. Calibration techniques are possible which compensate for magnification and criterion errors.
3. The system is not disturbed in the course of the measurement.
4. An accurate relationship that relates measured average particle diameter and particle volume is available since, in general, most ion exchangers possess a high degree of particle sphericity.

An excellent review describing the required conditions for an accurate measurement, techniques for the calibration of the microscope, and techniques for working with single particles is available;[229] hence, these points will not be discussed here. References cited in this review will not be included.

In general,[229,230] the procedure for the determination of the swelling ratio (wet-to-dry volume ratio) in water requires the measurement of the diameter of the ion exchanger in the swelling solvent (H_2O) and in a nonswelling solvent (such as n-octane). The best and most reproducible measurements for exchanger swelling in water require the presence of an electrolyte and that the measurement be made rapid enough so that surface contamination by fungi growth is minimal. As expected, exchanger cross-linking will have a significant effect on the swelling of the exchanger. Differences in swelling between cation and anion exchangers (same polymeric matrix) have been encountered and are the result of differences in hydration. Other properties examined by the microscopic swelling technique include detection of the nonhomogeneous nature of commercial ion exchangers and using an anisotropic effect as the result of a swelling gradient to test for equilibrium. It has also been shown that swelling results obtained by microscopic techniques (for commercially available strong acid and base exchangers of reproducible quality) are in good agreement with the results obtained by other procedures used for the determination of exchanger swelling.

A microscopic technique was used to study the macropore-micropore properties of a wide variety of cation and anion exchangers.[231] From these and microhardness data, the authors suggested models which describe the internal structure of ion exchange particles. These are (1) hetereoporous (nonuniform cross-linking); (2) macroporous (large pores); and (3) isoporous (uniform structure, similar pores, absence of close bonds). Additional conclusions are as follows. All the heteroporous, highly porous, and isoporous exchangers studied contain macropores. Macropores in the size range from 0.001 to 0.014 mm are distributed more uniformly in the exchangers than in activated carbons. Spherical and elipsoidal macropores predominate in most exchangers; in some cases, macropores were slit-like. A microhardness scale was derived, and the level of microhardness exhibited by an exchanger was found to be dependent on the structure, composition, salt form, and synthetic conditions for the exchanger.

Microscopic techniques were used to measure the swelling of H-form microporous (Dowex 50 X 8) and macroporous (Amberlyst 15) ion exchange particles in water, DMSO, MeOH, EtOH, and CH_3CN.[50] In water the D-50 exchanger increased by 116%, while the A-15 exchanger increased by 71%. In alcohols the D-50 swells more than the A-15 (20 to 30% more and is greatest for EtOH). The opposite was found for DMSO and CH_3CN where the percent swelling for the A-15 exchanger was much greater than for the D-50. The original article should be consulted for a discussion of the experimental problems encountered and their effect on the overall error in the measurement.[50]

D. Infrared Spectroscopy

Infrared (IR) absorption of ion exchangers has been largely used in three ways. First, molecular structure of the exchanger can be examined, which also includes the investigation of solvation at the exchange site. In general, the spectra tend to be simple, and absorption bands due to the exchange centers, cross-linking groups, and the repeating units can often be identified. Usually, confirmation of assignments is completed by an IR examination of ion exchanger films and model compounds. Second, decomposition of ion exchangers can be followed by IR by measuring the appearance of exchanger fragments. Third, species retained by the exchanger site can often be examined.

If the exchanger is not initially prepared in a thin film, mull or alkali halide disc-sampling procedures are usually employed. Since ion exchangers will, in general, have refractive indices in the range 1.5 to 1.6, KBr discs of the exchangers are preferred over the mull technique. Drying (done usually by heating) of the exchanger must be controlled since excessive drying can lead to decomposition, while inefficient drying leaves traces of water in the exchanger. This water (depending on amount) is bound to the exchange site and will influence the absorption of that group (for example, hydrated sulfonic acid rather than free sulfonic acid group in a cation exchanger). The ion exchange particles should be small in size, and consequently a grinding procedure is usually required. Sample sizes in the KBr disc range from 2% (for moderate absorption which is usually found for strong acid and base polystyrene-type exchangers) to 0.2% by weight (for stronger absorption which is usually found for weak acid-type resins containing carboxylic- and phosphorous-type exchange sites).

Initially, the use of ion exchange films as samples for IR examination was extensive.[232-239] This was due to the fact that the IR method was a very useful one for characterizing polymers; furthermore, when they contain exchange sites, they become suitable models of polyelectrolytes. Hydration of the exchange sites could also be readily examined. It should also be pointed out that many of these studies with ion exchanger films served as models for IR assignments that were subsequently made when using ion exchange particles as the sample. (References 232 to 239 and those cited within these should be consulted for details on film assignments.)

Sulfonated, carboxylated, and phosphorous-type exchange sites in films were examined.[232-239] In one early study the results were compared to IR data for a cation exchanger (Dowex 50) and an anion exchanger (IRA-400).[233] In several cases different charged forms were used. Hydration effects for a wide variety of charged forms were determined.[234] The hydration level of an H-form ion exchange film was extensively studied, and it was possible to correlate effects in the IR spectra to water levels within the thin film ion exchanger.[235] Assignments for anion exchange films[233,240,241] and studies of hydration effects in these films[241] were also reported.

The most extensive IR study of ion exchangers was reported by Whittington and Millar.[242] Some 50 commercial cation and anion exchangers containing sulfonic, phosphonic, carboxylic, quaternary, tertiary, and mixed amine and several corresponding low molecular weight model compounds were examined by IR using a KBr-pellet technique. In general, they have concluded that the characteristic frequencies for the functional groups in the exchangers are not too different from those found for the corresponding low molecular weight model compounds. Furthermore, in most cases, only the stronger bands are detected for the exchangers; the moderate and weaker bands, particularly the latter, tend to be overshadowed by background absorption due to scattering. A detailed investigation of IR absorption for cation exchangers has also been reported by Slovokhotova et al.,[243] Gordon,[72] and Freeman.[244] References 72, 232, and 242 to 244 should be consulted for a detailed discussion of IR assignments.

Gordon[72] collected IR data for dry and hydrated H-form, dry Na-form, and dry NH_4^+-form Dowex 50 X 8 to distinguish between the hydrated form of the sulfonic acid site and its anhydrous form. He extended these studies to dry Dowex 50 that was exposed to acetonitrile and dioxane. From the spectra he concluded that acetonitrile was not solvating the sulfonic acid site, while for dioxane an appreciable amount of solvation occurred. However, Whittington and Millar[242] have suggested that one of the absorption peaks used by Gordon[72] to indicate solvation may in fact be due to aromatic substitution.

Correlations between IR absorption and aromatic substitution or cross-linking were established and have been studied extensively.[72,242-247] Quantitative relationships are possible, particularly as a function of cross-linking.[242-247] However, caution should be exercised in choosing the correct bands since some misassignments have apparently been made.[242]

As previously stated, hydration in cation and anion exchangers can be examined by IR. Recently, this phenomenon was studied for exchangers in a variety of charged forms at various water levels using the band at 1.9 μm.[248] The data were compared to IR data for solutions of corresponding ions, and hydration numbers for the exchangers were calculated.

IR spectra for carboxylic acid exchangers obtained from several different manufacturers were reported.[249-251] Assignments were made for the observed absorption bands. In one report the position for the bands assigned to the carboxyl group was suggested to be an indication of the presence of dimer formation between carboxylic acid groups.[250] The concentration of the carboxylic acid groups within the weak acid exchanger could be determined by IR.[251] However, this method tends to be less accurate in comparison to conventional methods. The carboxyl bands have been used to demonstrate the presence of the carboxyl groups in other cation exchangers; presumably they are there as a result of oxidation of the resin.[242]

IR data have been reported for Dowex 1 X 8 in SO_4^{-2}-, NO_3^{-}-, CrO_4^{-2}-, and ClO_4^{-}-form.[252] The influence of selectivity and hydration on these data was discussed. Assignments have also been made for a cross-linked vinylpyridine copolymer which can be used as a weak base-type exchanger.[252]

Preparation, hydrolysis, chemical reactions, radiation effects, and decomposition of ion exchangers can often be conveniently followed by IR. Chloromethylation of styrene-divinylbenzene[254,255] and polymer formation or hydrolysis of acrylic acid-styrene-divinylbenzene[256] and acrylonitrile-styrene-divinylbenzene[257] copolymers have been studied this way. Intermediates in the reaction of anion exchangers with alkaline hypochlorite were identified by IR.[258] Phosphorous-containing cation exchangers (microporous KF-1 and macroporous KFP-8) were exposed to hot solutions of HNO_3 and $KBrO_3$.[259] The thermooxidative processes were followed by IR and were shown to be associated with dephosphorylation, formation of carboxyl groups, and nitration of the polymer (in HNO_3). The microporous exchanger was shown to be less reactive than the macroporous exchanger.

The thermal dehydration of 19 different M^{+}-, M^{+2}-, and M^{+3}-forms of a strong acid sulfonate-type exchanger was followed by IR.[260] The changes in the exchanger increased as the charge of the counterion increased. It was suggested that distortion occurred in the various OH- and SO-assigned bands as the last traces of water were removed from the exchanger. The thermal stability of an anion exchanger derived from a vinylpyridine-divinylbenzene copolymer in water was established by IR.[261] Oxidation to aldehyde and carboxyl groups was shown to take place. The effects of ionizing radiation on this polymer and anion exchangers derived from quinoline and isoquinoline were determined by IR.[262]

The anion exchanger AV-17 in the NO_3^{-}-form was subjected to heating under vacuum, in air, and in water.[263] The decomposition, which was followed by IR, led to the formation of tertiary amine (which was subsequently oxidized by nitrate ion to the amine oxide) and aldehyde, carboxyl, and hydroxyl groups on the polymer framework. Decomposition by heat was also compared to decomposition by ionizing radiation.

The IR technique has been used to study the nature of the species retained by cation and anion exchangers. For example, hydration and coordination phenomena associated with transition metals for exchangers charged in the transition metal form have been investigated.[264-268] A comparison of spectra for these kinds of systems to corresponding aqueous solutions of the transition metals has been described.[269]

E. Thermal Methods-Ion Exchanger Stability

In many practical applications ion exchangers are often subjected individually or in combination to thermal, chemical, and radiation conditions. The result can be an irreversible chemical change in the molecular structure of the exchanger owing to rupture of carbon-carbon bonds or of the less stable C-hetero atom bonds. These latter groups are usually part of the exchange site within the exchanger. Even mechanical wear and tear of the exchangers will result in abrasion, fissuring, and cracking in the particle and/or its surface structure. For example, this latter problem can lead to severe hygienic problems, if the exchanger is being used for water treatment, since these abrasions, etc. provide regions for retaining organic matter from the water. Furthermore, these areas will often show an increase in bacteria level as the organic matter accumulates.

Because of the wide industrial and laboratory application of ion exchangers, it is vital to be aware of the stability of the exchangers under varied conditions. Thermogravimetry and related techniques are very useful for the evaluation of exchangers as a function of temperature. In addition, this section will include a brief discussion of capacity changes as a result of thermal decomposition and the use of calorimetric techniques to correlate heat changes owing to exchanger-solute interactions.

1. Thermogravimetry-Exchanger Stability

Thermogravimetry and related methods, such as differential thermal analysis and differential thermogravimetric analysis, will yield considerable information about the stability of ion exchangers. In addition to a direct comparison of exchangers with respect to heat resistance, it is possible to gather information about phase transformations, fine chemical changes in the structure of the polymer, and (in some instances) the type and position of substituents in the polymer backbone. Additional experiments involve analysis of the volatile products and the solid residue that remain.

For sulfonated (H-form) cation exchangers of the polystyrene-divinylbenzene type, differential thermal gravimetry revealed three endothermic changes.[270–274] These occurred at 100 to 210°, 270 to 310° and above 430°C and were attributed to dehydration, desulfonation, and oxidative degradation, respectively, of the matrix. The loss of water that occurs continuously over the large temperature range was suggested to be an indication of a strong interaction between the sulfonated exchange site and water.

Evidence suggests that at the higher temperatures the sulfonic acid groups have been converted to sulfones and additional cross-links have formed. Further rise in temperature causes a breakdown in the sulfone to SO_2 and extensive degradation of the polymer backbone.[270,274]

It is necessary to use ion exchangers with the same initial state of hydration if different exchangers are to be compared by thermal techniques. Furthermore, it is absolutely necessary to characterize the material lost and the residue that remains during all stages of heating. In general, slow heating rates are recommended. Since ion exchangers are composed of a three-dimensional polymer network, long time intervals are necessary to allow for breakdown of the spatial network throughout the exchanger and for diffusion of the reaction products through the system. Lack of concern in these areas has led to misinterpretation in some cases.

Thermal analysis data have been reported for poly(arlenesulfonate) polymers,[275] α-methyl styrene-divinylbenzene sulfonated copolymers,[276] polymethacrylic-divinylbenzene and phenol-formaldehyde sulfonated copolymers,[277] carboxylic acid-type exchangers (Amberlite IRC-50),[278] and micro- and macroporous strong acid exchangers.[278,279] In general, all show dehydration over a broad temperature range, desulfonation (loss of CO_2 for carboxyl-type exchangers), and oxidative degradation of the matrix. The ranges at which these occur will vary for the different types and cross-linked exchangers.

If the cation exchangers are in the salt form, dehydration is still observed in the thermal analysis. However, desulfonation does not readily occur. A much higher temperature is needed for the M-form exchanger in comparison to the H-form exchanger.[270,273,274,280]

As pointed out previously, decomposition within the exchanger generally involves the exchange site at first, since bonds in these groups are usually weaker than those in the polymer chains. Thus, the determination of capacity, being a direct measure of the number of exchange groups present, is often used to follow exchanger decomposition as a function of the factors affecting decomposition. (Care must be exercised in choosing the method for determining capacity since in some cases the original exchange site can be replaced partly or entirely by a second exchange site which results in little or no net change.) All sorts of chemical and instrumental procedures are potentially useful for capacity measurements, and these will not be reviewed here.[5,6,9–13,19–22] Changes of the exchange site within the molecular structure can often be detected and characterized by IR.[240,259–263] Loss of groups from the exchanger can be trapped, detected, and characterized by conventional techniques.

Four excellent reviews on the thermal stability of ion exchangers in air, water, aqueous solutions, and organic media are available and, in general, survey the literature up to the early 1970s.[281-283] Particularly significant are the detailed critical reviews on the thermal stability of cation[281] and anion exchangers.[282]

For cation exchangers, it has been found that, in general, the thermal decomposition in the presence of solvent and subsequent loss of exchange capacity will involve, at some point, a hydrolysis step.

$$\text{Resin-SO}_3\text{H} + \text{H}_2\text{O} \longrightarrow \text{Resin-H} + \text{H}_2\text{SO}_4$$

Thus, knowledge about the hydration level of exchangers, its influence on their properties, and the manner in which it is lost becomes invaluable in unraveling the set of multiple steps that occur in thermal decomposition of exchangers. Because of the nature of the decomposition, the analysis should not only be performed on the residue (capacity determination), but also on the washings of the residue and/or trapping of the evolved acidic products (H_2SO_4). This accounts for a complete acidic material balance.

The major factors which influence the loss of capacity through thermal hydrolysis are the conditions under which the exchanger is heated (air, solvent, and temperature), the structure of the polymeric backbone of the exchanger, and the nature of the counterion. For example,[281] for the cation exchanger KU-1 ($-SO_3H$), a capacity loss of about 33% is found after heating in air at 185°C for 6 hr. Heating in water for 6 hr leads to a 9% decrease, while heating in steam at 175°C for 6 hr results in a 92% decrease. A 4-hr heating period (125°C) in isopentane reduces the capacity by 42%, while 24-hr heating (at fixed temperature of 125°C) in ethanol, n-pentanol, and n-decanol leads to 55, 62, and 27% loss, respectively. As anticipated, capacity loss increases under any condition as the temperature increases. Results for other sulfonated exchangers[280] and more recent investigations[284-289] are consistent with the trends suggested by these data.

In general, sulfonated phenolformaldehyde-type cation exchangers will lose capacity (undergo hydrolysis) more easily than the sulfonated polystyrene-divinylbenzene-type exchangers. The percent cross-linking, temperature, and whether the heating process is carried out in air (N_2) or a solvent will also influence the extent of the difference.[279,281,284,285] In one investigation the thermal stability was correlated to the position of the sulfonic acid group on the polymer matrix, the position in turn being determined by the percent cross-linking.[286] Other experimental data illustrated a better thermal stability for macroporous-type exchangers in comparison to microporous-type exchangers.[279,281,284] Also, variations of the aromatic portion of the polymeric matrix will influence the thermal stability.[281,290]

For exchangers with the same polymer backbone, it appears that the sulfonated-type cation exchangers are more readily hydrolyzed than the phosphonate- or carboxylate-type exchanger.[281,291,292] However, it should be pointed out that these latter types of cation exchangers have not received as extensive investigation as the sulfonated exchanger.

The nature of the counterion and its influence on the hydrolysis and further decomposition of the exchanger are not clearly understood. However, it does appear that the H-form exchangers are generally less stable than many M-forms.[260,281,285,293] In addition, many different counterions can act as catalysts in the hydrolysis and/or other deterioration steps. Recently, the rates of desulfonation for a series of alkali metal-forms of KU-1 and KU-2 cation exchangers were described as a function of temperature.[293] The initial water contents were controlled at a level of 2.5 ml H_2O/meq of exchanger. The KU-1 exchanger was less stable, and the rate of decomposition was found to increase in the series $Cs < Rb < K < Na < Li$.

Decreases in capacities of cation exchangers can occur as a result of heating the exchangers in solvents other than water.[281] For example, the solvent may undergo a reaction with the exchange site, form relatively unstable addition products, or catalyze reactions between the solvent molecules to yield larger molecular weight products which are subsequently attracted to the exchange site or deposited within the microporous structure of the exchanger.

Thermogravimetric methods have been used to investigate the thermal stability of anion exchangers in air. In comparison to strong acid cation exchangers, strong base exchangers are generally much less stable. For the strong base OH-form exchanger, loss of water was observed to occur at 120 to 150°C and was accompanied by decomposition and elimination of the exchange sites.[273,282] In the range 190 to 280°C, degradation of the polymer matrix occurred. It is surprising that capacity loss is not found at lower temperatures than reported in these studies.[273,282] Whether or not a complete material balance of nitrogen compounds was part of the capacity measurement is difficult to ascertain. In general, most investigators have tried strong base anion exchangers, particularly the OH-form, very cautiously. Often, they have noted considerable discoloration and other apparent decomposition at much lower heating temperatures.

In general, stronger base-type exchangers are less stable than weak base-type exchangers.[282,294,295] Furthermore, the decomposition of the site with the former type of exchanger often leads initially to formation of a weak base site. Also, the salt forms are more stable than the OH-form.[282]

The major direction in the thermal study of anion exchangers has been to examine their thermal stability in the presence of water, nonaqueous solvents, or their mixtures.[282,285] Following the change in capacity for the exchanger is an excellent indicator of their decomposition. Because of the nature of the decomposition, it is particularly important to carry out carefully established material balances that account for retained as well as lost portions of the exchange site.

Most thermal studies in solution have been with the strong base-type anion exchanger in the OH-form, probably because of the anticipation that the decomposition would follow the mechanistic route typical of the Hofmann degradation (for the type $RCH_2N(CH_3)_3{}^+OH^-$). The net change brought about thermally is deamination and degradation of the quaternary exchange site. More rigorous heating leads to degradation of the polymer matrix.

A detailed critical evaluation of the mechanistic decomposition route has been cited in a recent review[282] and will not be repeated here. In general, a Hofmann-type degradation is suggested. However, this mechanism is further complicated by the role the solvents play as potential sources of nucleophiles and by the appearance of decomposition products which can act as catalysts and participants in further reactions. Also included in this review[282] is a detailed discussion of the stability of anion exchangers in hot solutions of strong acids and bases and reducing and oxidizing agents.[263,296]

When cation exchangers are heated in concentrated solutions of strong acids and bases, hydrolysis still takes place, and in most cases the hydrolysis rates are faster than those found in water.[281,296,297] In addition, C-C bond breaking takes place, and deterioration of the polymer backbone occurs. The rate of this type of decomposition will depend on the type of polymer backbone in the exchanger.

Heating in solutions of oxidizing or reducing agents produces simultaneous desulfonation and redox processes at a rapid rate.[259,281,296,297] For example, heating in HNO_3 solutions introduces nitro and carboxyl groups into the polymer matrix along with hydrolysis.[281] Depending on the polymer backbone in the exchanger, redox processes can take place even in oxidizing or reducing solutions at ambient temperatures. For example, in large-scale industrial applications, dissolved oxygen is often removed from aqueous solutions since this has been shown to attack cross-links in the exchanger. The oxidizing conditions are often metal-ion catalyzed, and decomposition rates in oxidizing media have been shown to be faster for certain M-forms.[281,297]

A mass spectrometric study of aging effects on cross-linked polystyrene- and polyacrylic-type ion exchangers has been made.[298] Major fragments in the m/e range of 10 to 70 were attributed to OH^+, H_2O^+, CO^+, $CO_2{}^+$, supplemented by SO^+ and $SO_2{}^+$ from sulfonic-type exchangers. Storage in amber bottles for up to 2 years did not produce any major changes in the mass spectra. Evidence is presented which suggests that carboxyl groups are present in both the strong acid and strong base cross-linked polystyrene-type exchanger. It was also shown that ion intensities were independent of the state of the ion exchanger.

Cation and anion exchangers have been examined by pyrolysis gas chromatography.[299-302] This technique appears to be useful for characterizing ion exchangers and warrants further investigation even though the pyrolysis chromatograms are very complex. For example, a large number of pyrolysis products (>50) have been identified in the pyrolysis of Dowex 50 X 12.[300] The composition of pyrolysis product mixture was shown to be dependent on the particle size and charge form of the exchanger. Major products found were benzene and alkyl-substituted benzenes. A nearlinear relationship between the originally used amounts of divinylbenzene in the synthesis of the exchanger and the amounts of divinylbenzene and ethylvinylbenzene in the pyrolysis products was found for a series of cation exchangers.[301] This type of calibration was suggested as a possible procedure for determining percent cross-linking in an exchanger.

2. Calorimetry

Heats of exchange have been determined calorimetrically for systems of the type

$$\text{Resin–M}^+(\text{X}^-) + \text{M}_1^+(\text{X}_1^-) \rightleftharpoons \text{Resin–M}_1^+(\text{X}_1^-) + \text{M}^+(\text{X}^-)$$

where the ion exchanger can be a cation or anion exchanger, M and M_1 are different metal ions or organic cations (or M is H^+), and X and X_1 are different anions. Water, water-organic solvent mixtures, and organic solvents have been used. In general, the observed enthalpy change is dependent on the selectivity and charge of the ions, their electronic and/or molecular structures, the nature of the charged site, and the cross-linking of the exchanger.

The calorimetric data combined with other experimental data permit the calculation of the thermodynamic properties of the exchange system. Consequently, it is possible to fundamentally evaluate the characteristics of the ion exchange system. These studies (that is, calorimetry of strong electrolyte-ion exchangers) will not be surveyed here, and discussions can be found elsewhere (also see references cited in these articles).[5,13,303-305] Only nonelectrolyte (solvent)-exchanger interactions will be considered here.

When dry ion exchangers are immersed into a suitable solvent, an exothermic reaction will take place and can be measured calorimetrically. Heat measurements of this kind have been made with water as solvent with cation exchangers[49,50,101-103,306-310] and anion exchangers.[146,306,308] Only recently have these measurements been made with mixed or nonaqueous solvents.[50,146] Also, very few measurements have been made with weak acid and base exchangers.

The heat changes that have been measured have been referred to as heats of swelling, heats of wetting, and heats of immersion. The actual heat change that is measured is a net heat change that represents several different exothermic and endothermic processes. The first two terms represent specific processes; that is, swelling represents contraction or expansion of the particle bead, whereas wetting specifically refers to a solvation process. In contrast, heat of immersion implies the observed net change or that which is calorimetrically determined. For this reason the experimentally determined heat changes will be referred to as heats of immersion (or heat change) in this review.

When an ion exchanger is immersed into water the major energetic processes will be the hydration of the exchange site and counterion, dissociation, dilution, and stretching of the resin network. In a series of experiments with different cross-linked exchangers, two independent laboratories calorimetrically determined heat changes for the immersion into water of cation exchangers in the H-form and M-form that were of known water levels (prepared isopiestically).[101-103] When functions of these data were plotted against water levels of the exchanger which ranged from 0 to over 12 mol of water per equivalent of exchanger, a direct dependence of the thermodynamic functions on cross-linking was shown. As the water level of the exchangers increases, the exothermic heat of immersion decreases rapidly; also, a decrease in the heat of immersion is found as the percent cross-linking decreases. The heat loss decreased in the order H > Li > Na > Rb > Cs > K for strong acid exchangers charged in these forms.[102] A similar order was also reported by other investigators.[307,309]

The heat of immersion-water level graphs reported by Dickel et al.[102] appear to indicate a stepwise uptake of individual water molecules. This was not observed by others.[101,103,306] However, the calorimetric instrumentation used in the one study would not be sensitive enough for detection of this close of a difference.[306] When Dickel et al.[102] used a phenol-naphthalenesulfonic acid-type exchanger, the stepwise uptake was less distinct. This difference was attributed to the influence of an H-bond between the phenolic OH and the sulfonic acid group on the hydration process.

The heat change for the aqueous reaction between an acid and base, although larger, is similar to that found for the immersion of a strong acid H-form exchanger into water (for example −11.0 and −12.6 Kcal/equiv for Amberlyst-15 and Dowex 50 X 8, respectively). Thus, it can be qualitatively concluded that the exothermic process involves solvation of the proton and can be represented as a simple heterogeneous acid-base reaction

$$RSO_3^-H^+ + nB \rightleftharpoons RSO_3^-HB_n^+$$

where

$RSO_3^-H^+$ = the H-form resin;
B = the solvent;
HB_n^+ = the solvated proton;
n = the solvation number.

When different solvents (ten organic solvents and water) were used, the results were consistent with this expectation when using the strong acid H-form macroporous Amberlyst-15 exchanger.[50] For example, DMSO and DMF as solvents yielded heats of immersion close to that of water. The heats were also high in the simple alcohols, but less than in DMSO and DMF. In contrast, solvents unlikely to participate this way (such as CH_3CN, benzene, and heptane, particularly the latter two) yielded low exothermic heats of immersion. These results were also found for the microporous H-form Dowex 50 X 8 and Amberlite IR-120 exchanger.[50] However, in several solvents (DMF, DMSO, and n-butanol) the rate of heat loss was not only very slow, but also not very exothermic which is attributed to the microporous property of these exchangers.[50] Also, solvation in the alcohol solvents has been independently established by NMR.[48,197-199]

When an exchanger is immersed into a solvent, the heat can be represented by:

$$\Delta H_{im} = \Delta H_{sol} + \Delta H_{surf} + \Delta H_{swell}$$

ΔH_{im} = the heat of immersion;
ΔH_{sol} = the solvation of exchanger site;
ΔH_{surf} = the heat for the interaction of the solvent with the polymer matrix;
ΔH_{swell} = the energy required for swelling.[50]

In an attempt to evaluate the ΔH_{swell} for macroporous and microporous cation exchangers, heats of immersion were measured for model systems.[50] For example, the heat of immersion for ethylbenzenesulfonic acid was used for ΔH_{sol}, and microporous and macroporous styrene-divinylbenzene copolymers were used for ΔH_{surf}. When substitutions were made, the ΔH_{swell} for the macroporous resin Amberlyst-15 was found to be +1.2, +2.5, and +3.1 Kcal/equiv for H_2O, EtOH, and DMSO, respectively. The corresponding values for the microporous Dowex 50 X 8 were +0.2, −0.1, and undefined, respectively. These data should be used in a qualitative fashion for two reasons: first, the models are not exact; second, ΔH_{im} and ΔH_{surf} are integral heats while ΔH_{sol} is a differential heat.

The data, although qualitative, are consistent with the microporous and macroporous property exhibited by the two exchangers. For example, the A-15 exchanger requires more energy for swelling than the D-50 exchanger. An additional important result is the fact that the macroporous exchanger does in fact undergo physical swelling.[50]

Heats of immersion for anion exchangers (Dowex 1) in Cl- and ClO_4-form in water and five common organic solvents and their aqueous mixtures were determined as a function of cross-linking and solvent composition.[146] The exothermic heats were in the range of −4 to −8 Kcal/equiv for the Cl-form in water, methanol, ethanol, and formamide or their aqueous mixtures. The heats for the ClO_4-form and the Cl-form in solvents rich in acetone and n-propanol were considerably smaller. Heats of immersion for polystyrene-divinylbenzene copolymers under similar conditions were very small (similar to those reported before[50]), while those for the monomer analog benzyltrimethylammonium chloride were endothermic.

Marcus and Naveh[146] calculated the heats of swelling for the anion exchanger in water and for the 5 organic solvents. Unlike Casey and Pietrzyk,[50] they also included an estimated correction for the heat of fusion. The water, alcohols, and formamide yield an endothermic heat, while for acetone an exothermic value is obtained. The difference is attributed to a considerable heat gain through solvation of acetone.

Marcus and Naveh[146] also calculated excess heats of swelling for the mixed aqueous-organic solvent systems which included estimations of the heats of mixing. A strong dependence on the composition of the mixture and the solvent was apparent. Qualitatively, it was suggested that the excess heats reflect the solvent structure modifications in the narrow spaces in the poorly swollen exchanger.

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