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Nuclear Magnetic Resonance Study of Ion-exchange Resin-Solvent Systems

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The results of measurements of NMR spectral parameters (chemical shifts, line widths, and relaxation times) of water molecules, counterions, and adsorbed molecules in the ion-exchange resin phase are discussed in detail and compared and the conclusions concerning their state and motion are analysed. The scope and difficulties in the application of the NMR method to the investigation of ion-exchange equilibria and kinetics are demonstrated.
The bibliography includes 91 references.

CONTENTS

I.	Introduction	823
II.	The chemical shift of internal water protons	823
III.	The internal water ^{1}H NMR line width	827
IV.	The relaxation times T_1 and T_2	828
V.	Magnetic resonance of the counterion nuclei	829
VI.	The state of equilibrium of the ion-exchange resin - solvent system	831
VII.	Exchange processes	833

I. INTRODUCTION

Ion-exchange resins are insoluble substances which, however, swell in the solvent and are capable of absorbing from an electrolyte solution positive or negative ions in exchange for equivalent amounts of other ions of like sign[12,13]. The skeleton of synthetic ion exchangers consists of an irregular network of hydrocarbon chains, usually polystyrene chains, connected by a necessary number of cross links. In cation exchangers, fixed groups bearing negative charges ($-SO_3^-$, $-CO_2^-$, $-PO_3^{2-}$, etc.) are grafted to the resin matrix, while in anion exchangers there are similar groups bearing positive charges ($-NH_3^+$, $\rangle NH_2^+$, $\rangle S^+$, etc.).

A dry ion-exchange resin is virtually of no practical interest. All ion-exchange processes, including the dissociation of the ionogenic groups, the diffusion of counterions, and the ion exchange between the external solution and the resin phase take place only in the presence of a solvent. The selectivity of ion exchange is likewise related to the size of the water-exchangeable ion hydrate complex. The electrical conductivity of the ion-exchange resin depends on its water content. In order to optimise ion-exchange processes, it is necessary to investigate the mechanisms of the interaction of all the components in the resin phase. The state of water and of the hydrate complexes in the ion exchanger can be investigated successfully by NMR.

Nuclear magnetic resonance (NMR) yields much information in the study of substances in any state of aggregation. The essential physical features and theory of NMR and the characteristics of the relevant apparatus as well as the results of studies carried out over a period of many years by this method have been described in a number of monographs[1-6] and reviews[7-11]. In the NMR method, the directly measured parameters are the chemical shifts, widths, and integral intensities of the spectral lines and the longitudinal and transverse relaxation times.

More than 10 years have elapsed since the beginning of studies on synthetic ion-exchange resins by nuclear magnetic resonance. However, the wide physicochemical variety of ion-exchange resins, their increasing practical importance, the endeavour to optimise technical exchange processes, and the necessity to investigate the solvent structure within the resins in order to apply the latter as dielectrics or electrolytes are all factors which have now given rise to increased interest in ion-exchange resins. Extensive experimental NMR data on the solvent (usually water) structure in specific types of ion exchangers have accumulated. The parameters of the NMR spectra yield information not only about the state of the external or internal, with respect to the resin, solvent, but also about the state of inorganic or organic exchangeable ions. These parameters usually depend on the initial material of the matrix, the method of preparation of the resin, the nature of the fixed groups and counterions, the percentage content of divinylbenzene (DVB) or another cross-linking agent, the total exchange capacity of the ion exchanger, the shape and size of the resin grains and the proportion of defects they contain, the contamination of the resin, the presence, the concentration and nature of impurity or defect paramagnetic centres in the resin, the content of water or another solvent, and the temperature of the specimen.

II. THE CHEMICAL SHIFT OF INTERNAL WATER PROTONS

1. Characteristics of the Experimental Methods for the Ion-exchange Resin-Water System

The ion-exchange resin-water system consists of swollen resin grains, the space between which may be filled by the solvent. The first NMR study[14] on a suspension of Dowex-50 sulphonic acid cation-exchange resin

in water showed that the ^{1}H NMR spectrum of water consists of two lines of approximately equal intensity, belonging to the internal and external water. The chemical shift between the external and internal water may be due to various causes.

It is frequently stated that the structure of internal water is disrupted to a greater extent than that of the external water. This effect[1] must cause a displacement of the line due to the internal water relative to that due to the external water in the direction of higher fields. The displacement of the internal water line can also be caused by the influence of the benzene ring currents on the shielding constant of the nearest protons. It is known[1] that the gradual diluton of a solution with an aromatic solvent leads to an upfield displacement of the proton signal. The major proportion of the signal due to the methyl protons of the solvent in the resin has been attributed to this effect[14]. In the study of the chemical shift in an ion-exchange resin, the influence of aromatic rings on the position of the line is frequently either not considered at all or its contribution is believed to be insignificant.

Another cause of the chemical shift between the water absorbed by the ion-exchange resin and pure water is the difference between the volume magnetic susceptibilities (χ_V) of water and the ion-exchanger material. Gordon[14] estimated χ_V for spherical grains of pure cross-linked polystyrene and, having observed the influence of these grains on the chemical shifts of water, toluene, dioxan, and acetonitrile, concluded that the position of the external solvent line is determined by the effect of volume magnetic susceptibility. For the internal solvent, there is no need[14] to apply a correction for χ_V if the resin grains are ideally spherical. However, it is known[15] that the number of defective grains in the KU-2 and AV-17 resins, most widely used in the USSR, reaches 50–60%. The few available experimental data on the influence of the artificial disruption of resin grains on the ^{1}H NMR chemical shift of water are contradictory. The majority of investigators worked solely with spherical grains or with a small number of defective grains. In subsequent studies, it was shown that the difference between χ_V of water and the swollen resin increases with increase of the degree of cross-linking of the latter, its exchange capacity, and the atomic weight of the counterion. Nevertheless, all workers believe that this difference is small and neglect the correction for this effect; using the rotating tube method, Weiner and Howery[16] determined the absolute values of χ_V in a swollen Dowex-50W cation-exchange resin (with 4, 8, and 12% of divinylbenzene) in 10 ionic forms (H^+, Na^+, NH_4^+, NMe_4^+, Rb^+, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, and La^{3+}). The chemical shifts of the external and internal water relative to a standard were corrected for χ_V taking into account the results. The contribution of the χ_V correction to the chemical shift of the internal water was indeed found to be insignificant.

Since the concentration of the counterions in the resin phase is fairly high, the next factor influencing the position of the ^{1}H NMR line of the internal water is the polarising action of diamagnetic ions on the water molecules, as happens in electrolyte solutions.

The technology of the preparation of ion-exchange resins is such that the latter contain a large percentage of impurities, including paramagnetic impurities. In salt solutions containing parmagnetic ions, fairly large shifts of the ^{1}H NMR signals are observed[1] due to the contact interaction between the unpaired electrons of the paramagnetic ions and protons. The artificial introduction of a small number of Fe^{3+} or Fe^{2+} ions into the KU-2 cation-exchange resin causes[17] an appreciable shift of the ^{1}H NMR line of the water absorbed by the resin. Information about the state of the paramagnetic impurities obtained by other physical methods is therefore of definite value even when the resin is carefully purified.

The dimensions of industrial ion-exchange resin grains vary between 0.002 and 2.0 mm.[13,18] In addition, the majority of investigators have measured the chemical shift of the ^{1}H NMR line due to the water absorbed by the resin relative to the ^{1}H NMR signal of the external water as a standard. It is therefore important to know how the position of the resonance lines of the external and internal water depends on the particle size. Darickova et al.[19] suggested that all resin grains be divided into three groups in terms of their dimensions. The first group includes resins consisting of large grains for which the external water chemical shift is approximately the same as for pure water, while the chemical shift of the internal water is equal to the shift for the aqueous solution of acid at the equivalent concentration. The second and third groups comprise resins with intermediate and fine grains (for sulphonic acid cation-exchange resins, the diameter is less than ~0.1 mm), the decrease of the size of which is accompanied by the mutual approach of the ^{1}H NMR signals of the external and internal water. This phenomenon is explained by an increase of the rate of exchange of water molecules between the resin phase and the external solvent which is confirmed by the dependence of the effect on temperature and the number of cross links. We may add that the average number of hydrogen bonds per molecule in the external water decreases and the effect of volume magnetic susceptibility becomes more pronounced with decrease of the diameter of the resin grains.

It follows from the foregoing that certain causes of the displacement of the ^{1}H NMR resonance lines of an aqueous suspension of an ion exchanger are eliminated in the preparation of the specimen which involves the removal of defective grains and the elimination of paramagnetic and organic impurities from the resin. The presence of impurities in the resin is a cause of the non-reproducibility of the results. Other causes of non-reproducibility may be the non-identity of resins having the same designation but manufactured by different companies and also the different diameters of the resin grains investigated. Small discrepancies may arise in consequence of the differences between the methods used to eliminate the external water (absorption of water by filter paper, centrifugation in tubes with a porous bottom, the passage of a stream of dry air through the column, etc.).

In order to interpret the chemical shift data, it is almost always necessary to have quantitative data for the water content in the resins. It has been shown[20] that there is a satisfactory agreement between the results of the determination of the water content by the Fischer titration method, by the drying method, and from the integral intensities of the ^{1}H NMR signals. However, the titration method is free from the limitations of the drying and ^{1}H NMR methods and yields a rapid and exact estimate of the moisture content (10 wt.% and above) for the majority of resins.

Knowing the water content and capacity of the resin, it is possible to calculate its molality. Reichenberg and Laurenson[21] established that the chemical shift between the lines of the external and internal water is an unambiguous function of the number of water molecules per sulphogroup. Since the chemical shift of the internal water line is proportional[21,22] solely to the molality of the ions in the resin phase, such molality can be determined directly

from the chemical shift. However, in a later study[19] it was shown that the concentration of fixed ions can be determined by the ^{1}H NMR method only for large-grained ion-exchange resins and that the minimum permissible grain size depends on the chemical shift between the internal and external water, i.e. on the degree of cross-linking and molality in the resin phase. According to Darickova et al.[19], the independence of the difference between the chemical shifts of the external and internal water of the resin grain size should serve as a criterion of the possibility of measuring the internal molality in the resin by NMR.

2. Dependence of the Chemical Shift of the Concentration of Counterions

There exist several model representations of ion-exchange resins. The ion exchanger is sometimes[23] compared with a concentrated electrolyte solution, subject to allowance for the characteristics introduced by the resin matrix. ^{1}H NMR studies on the internal water confirmed[14,24-30] the validity of such comparison. In this case one can use in the interpretation of the chemical shifts in the resin phase certain assumptions and empirical formulae which have been employed previously[9] in the study of aqueous electrolyte solutions by high-resolution NMR. The shift of the ^{1}H NMR line of the internal water must be mainly determined by the interaction of the water dipoles with the counterions and fixed groups. The molal chemical shifts should reveal positive or negative hydration of the counterion. Here it is necessary to bear in mind that the internal molality in the resin depends on the degree of cross-linking of the latter and the nature of the counterion.

The electrostatic nature of the interaction between water molecules and counterions is expressed by the linear relation between the ^{1}H NMR signal shift and the square of the reciprocal of the radius of the cation[26] (K^+, Na^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Li^+, and Mg^{2+}) in the KU-2 resin or the corresponding quantity for the anion[29] (F^-, Cl^-, Br^-, and I^-) in the AV-17 resin, the molal chemical shifts in cation exchangers ($\delta^0_{M^+}$) and anion exchangers ($\delta^0_{M^-}$) saturated by univalent and polyvalent counterions are identical as regards sign and order of magnitude[24,25,28,30] with the corresponding values in aqueous solutions of diamagnetic salts. The maximum discrepancy between the resin and solution is observed for H^+ and F^- ions and has been explained by the high capacity of these ions for the formation of ion pairs with the fixed groups.

The consistently lower values of $|\delta^0_\pm|$ in resins for univalent cations[25] and anions[28] compared with the values of $|\delta^0_\pm|$ in the corresponding electrolyte solutions are regarded by the authors as evidence for intensifying ion–ion interactions in the resin. It is emphasised[25,27,28] that the counterions in the resin exhibit their "structure forming" or "structure breaking" properties almost to the same extent as in pure water. The dependences of the ^{1}H NMR chemical shifts δ of the internal water on the internal molality m† in ion-exchange resins resemble the corresponding plots for aqueous electrolyte solutions and have similar deviations from linearity at high concentrations of the ions in the resin. An exception is the hydrogen-form of the resin, where the linearity persists up to $m = 7$. The values of δ for all the counterions extrapolate to zero when $m \to 0$; thus, the external and internal water have the same chemical shifts at $m = 0$. Since δ tends to zero when $m \to 0$ and does not depend on the grain size, the authors explain the shift of the internal water signal relative to the external water as a result of ion–dipole interactions between the counterions and the solvent.

The deviation from linearity towards decreasing values of $|\delta|$ for the Mg^{2+}-, Be^{2+}-, and Al^{3+}-forms of the cation-exchange resin is more marked than for univalent counterions and begins at lower concentrations. Whereas $|\delta|$ for Be^{2+} and Al^{3+} increases up to 16% DVB under these conditions, albeit at a reduced rate, the plot of $\delta = f(m)$ for Mg^{2+} passes through a maximum and $\delta = 0$ at $m = 3.52$ (which corresponds to 16% DVB). Sharma and Subramanian[27] explain the shape of the $\delta = f(m)$ curve for the Mg^{2+}-form of the cation exchanger by the conversion of the $SO_3^- - H_2O - Mg^{2+}$ ion pair into the $SO_3^-Mg^{2+}$ contact ion pair (i.e. the fixed group substitutes one water molecule in the first coordination sphere of the counterion). The authors explain the decrease of the overall effect of this cation on the water structure (or on δ for the internal water) by an increase of the number of water molecules outside the first hydration shell. Owing to their high charge density, the Be^{2+} and Al^{3+} counterions retain their first hydration shells in the cation exchanger with 16% DVB. Thus associated species of the type fixed group–solvent–counterion continue to exist and there is only a decrease in the number of molecules outside the first hydration shell. We may add that an increase of the negative shift of the internal water for the Be^{2+}- and Al^{3+}-forms of a sulphonic acid cation-exchange resin with increase of the internal molality is correlated with the capacity of these ions for the protolytic cleavage of the molecules of the water of hydration, as has been pointed out by Zundel[31].

3. Temperature Dependence of the Chemical Shift

(a) The range of positive temperatures. Hydration numbers. Malinowski et al.[32] developed a method for the determination of the total effective hydration numbers of ions h in an electrolyte solution from the temperature dependence of the ^{1}H NMR chemical shift. Here h is defined as the number of moles of water of hydration per unit molality of the salt. It was assumed that the chemical shift of the water of hydration is independent of concentration and temperature. Since the states of the external and internal water are different in aqueous suspension of an ion-exchange resin, Greekmore and Reilly[33] applied Malinowski's method to the calculation of h in the resin phase using the difference between the temperature dependences of δ_{int} and δ_{ext}. The formula for the calculation of h is

$$h = \frac{55.55}{m}\left[\frac{d\Delta/dt}{d\delta_{H_2O}/dt}\right], \qquad (1)$$

where m is the molality in the resin, $\Delta = \delta_{ext} - \delta_{int}$, and δ_{H_2O}, δ_{ext}, δ_{int} are the chemical shifts of pure water and the external and internal water in an aqueous ion-exchange resin suspension respectively. The Table lists the total effective hydration numbers for different ionic forms of Dowex-AG-50W and KU-2 cation-exchange resins and of Dowex-AG-1 and AV-17 anion-exchange resins taken from a number of communications[27,28,33,34].

A qualitative correlation between the values obtained in the resins and in the corresponding electrolyte solutions

† The molality was altered by changing the degree of cross-linking of the resins.

is evident. The hydration numbers of the counterions in the cation-exchanger phase are systematically lower than the values of h for the analogous cations in salt solutions. This fact can be explained by the stronger interaction between the counterion and the fixed group than between the anion and the cation in solution, and also by the more pronounced hydration of anions in solution compared with the fixed groups. It is suggested that one coordination site of a univalent counterion may be occupied by a sulpho-group. The high hydration numbers of bivalent counterions can be explained by the fact that their influence extends to the second hydration shell.

The total effective hydration numbers in different ionic forms of resins.

DVB, wt.%	2	4	8	10	12	16	8–10
	AG-50W[27, 28(33)]						KU-2[34]
NH_4^+	—	2.2	1.7	—	—	1.4	3.5
H^+	0.6	—	2.0 (2.9)	—	—	—	2.7
Li^+	—	—	—	—	—	—	3.7
Na^+	(3.5)	4.8 (3.0)	3.6 (2.9)	—	(2.8)	2.2	3.1
K^+	—	4.4	3.0 (2.7)	—	—	—	3.0
Rb^+	—	3.0	2.6 (2.6)	—	—	1.9	2.6
Cs^+	—	2.7	2.4 (3.2)	—	—	2.1	2.0
Ca^{2+}	—	—	—	—	—	—	4.9
Mg^{2+}	6.4	—	6.4 (6.7)	—	—	7.0	8.0
Zn^{2+}	—	—	—	—	—	—	6.4
Al^{3+}	11.9	—	15.1	—	—	—	
	AG-1[28(33)]						AV-17[34]
OH^-	—	—	—	—	—	—	3.0
ClO_4^-	0.6	0.6	—	0.5	—	—	—
F^-	0.0	1.1	—	1.8	—	—	2.4
Br^-	—	—	(1.3)	—	—	—	1.7
I^-	—	1.6	(1.2)	0.7	—	—	1.4
NO_3^-	—	1.3	—	—	—	—	
Cl^-	—	—	—	—	—	—	1.7

Mank et al.[35] investigated the KB-4P2 carboxylic acid cation-exchange resin in the H^+- and K^+-forms. They obtained $h(H^+) = 2$ and $h(K^+) = 2.9$. They concluded that the water molecules form strong hydrogen bonds with the carboxy-group of the type $C\begin{matrix}O\ldots H_2O\\ OH\ldots OH_2\end{matrix}$. In the resin containing the K^+ counterion, only some of the COOK groups are dissociated.

The results of measurements of the temperature dependence ($t > 0°C$) of the ^1H NMR chemical shifts of aqueous suspensions of resins with different degrees of cross-linking and in different ionic forms have also been reported in other communications[36–41].

The entire water in the resin can be conveniently divided[12] into free and bound, i.e. the water of hydration. Sharma and Subramanian[28] determined the relative contents of the free and bound water using for this purpose the effective hydration numbers and concluded that the amount of free water for a given content of divinylbenzene is almost constant in resins saturated by alkali metals.

A distinctive feature of a swollen resin compared with an electrolyte solution is that the space between the hydration shells in the resin is "filled" by the hydrophobic matrix. For this reason, h can characterise correctly the number of molecules hydrating the fixed group and the counterion, but may not agree with the value of h for the corresponding salt solution. An attempt has already been made[28] to relate the hydration numbers to the selectivity of the ion exchanger.

(b) The negative temperature range. Systematic studies by microwave spectroscopy of the state of water in ion-exchange resins in the region of negative temperatures were begun by Nikolaev and coworkers[37,40–42] and then by Mank and coworkers[34,38,39]. As the temperature of an aqueous resin suspension is reduced to zero, the external water crystallises and the intensity of its spectral line becomes negligible owing to its marked broadening as a result of the increasing dipole–dipole interaction of the water protons. The crystallisation of an equivalent Na_2SO_4 solution (1.45 M) or a solution of toluenesulphonic acid takes place[41] at $-7°$ or $-30°C$ respectively. With decrease of temperature below zero, the NMR signals of the internal water protons shift downfield to a greater extent the lower the degree of cross-linking of the resin. This is explained[37,40] by an increase of concentration in the internal solution, which occurs as a result of the freezing out of the "free" water from the resin phase. An interesting experimental result has been obtained[37,40]: for a given ionic form of the resin, there is a definite temperature at which the ^1H NMR chemical shift of the internal water is independent of the amount of cross-linking agent and tends to a limiting value. The latter may be determined by the nature of the counterion. At any rate, the chemical shifts of the internal water in ion exchangers at temperatures below $-70°C$ will be useful for the investigation of stable hydration structures or counterion–water–fixed group complexes.

Mank and coworkers[34,39] noted the possibility of determining the ion hydration numbers from the number of water molecules whose translational motion does not cease below 0°C. By comparing the areas under the experimental ^1H NMR spectral curves at temperatures of aqueous suspensions above and below 0°C, they were able to reach the conclusion that the water which is not bound to the cations crystallises in the resin phase. They found that $h(Ba^{2+}) = 6$ and $h(NH_4^+) = 5$.

The amount of "free" water (not influenced by the counterions and the fixed groups) can be increased sharply by creating artificially large pores within the resin. The states of water in the gel component of the resin and within its pores should differ significantly. However, owing to the rapid proton exchange above 0°C, a single resonance line is observed for the internal water in macroporous cation-exchange resins[41,45]. At $-2°C$ the proton exchange is retarded[37] so much that the line of the internal water in the KU-23 resin splits to give a doublet. A separate ^1H NMR line of the water in the pores is observed down to $-15°C$ and then vanishes owing to its marked broadening, while the signal due to the water in the gel component of the KU-23 resin continues to be recorded down to $-70°C$. Both lines shift downfield with decrease of temperature.

The study of the state of water in synthetic ion-exchange resins at negative temperatures yields important practical results[37]. The absence of the crystallisation of the internal water gives rise to the hope that ion exchangers with a gel structure are fairly resistant to the action of low temperatures (down to approximately $-70°C$). On the other hand, the presence of defects and cracks within the resin grains (with a size exceeding 100 Å), in which the phase transition to a crystalline state takes place, leads to the disruption and cracking of resins on cooling. The results obtained for the state of water in the resins on

cooling are of interest for the analysis of the changes in the state of water when the temperature is reduced below 0°C in ion-exchange membranes and living cells.

III. THE INTERNAL WATER ^{1}H NMR LINE WIDTH

The width of the ^{1}H NMR spectral lines due to the internal water in synthetic ion-exchange resins depends on a number of factors and is usually appreciably greater than the line width for pure water. In order to interpret the results, it is very important to isolate the dominant cause of the broadening of the line and to exclude the broadening due to preventable effects.

The presence of inorganic paramagnetic impurities in commercial resins leads[14,17] to a significant broadening of the spectral line due to the internal water. Spectrographic studies of the ash of resins, even those which have been carefully washed, reveal[22,43] small amounts of iron and manganese. The paramagnetic centres arising on formation of different defects in the matrix structure, or in the spontaneous scission of sulpho-groups, or as a result of the oxidation of phenolic groups[44] can also be a cause of line broadening.

The line broadening due to the difference between the volume magnetic susceptibilities of water and the resin in spherical grains should not occur[14]. The creation of defects in the grains of the IR-120 sulphonic cation-exchange resin in the H^+-form by a sharp change of temperature[36] or mechanical grinding[22] hardly alters the resonance line width. The opposite result has been obtained[21] for the grinding of a specially prepared sulphonic acid cation-exchange resin to a grain size less than 0.076 mm, the increase in the ^{1}H NMR line width of water following the disruption of the grains depending on the ionic form of the resin. In all the studies where the shape of the grains was stated, spherical resin particles were investigated. However, the effect of volume magnetic susceptibility can be expressed[14] by the influence of the grain size on the line width and can be accounted for by the creation within the grain of inhomogeneous local magnetic fields due to the nearest neighbours. A change in the sulphonic acid cation exchanger grain size (8–15% DVB) by a factor of 2–3 does not alter[21,36] the internal water ^{1}H NMR line width.

Howery and coworkers[16,30] and then Frankel[36] showed by means of various experiments that the main cause of the broadening of the line is the effect of volume magnetic susceptibility.

The internal inhomogeneity of the resin grain (a non-uniform distribution of the cross-links and fixed groups) also leads to an increase of the width of the internal water ^{1}H NMR line, provided that the proton exchange between the chemically non-equivalent equilibrium positions of the water molecules is fairly slow. Otherwise the line width is not a measure of the homogeneity of the resin. This was emphasised by Gordon[14], when he characterised the internal resin grain phase as homogeneous. The fact that resins with very different physical structures (gel and macroporous resins) give comparable line widths[36,37] confirms the occurrence of rapid proton exchange between the inhomogeneous sections of the resin. The existence of a single internal water resonance line, the low rate of proton exchange between the resin grains, and the marked dependence of the position of the internal water line on the counterion molality demonstrate, according to Gordon[14], the narrow limits of the inhomogeneous region between the grains as regards the number of cross-links, the degree of sulphonation, etc. The rate of exchange can be reduced by lowering the temperature of the specimen. Thus the resolution of the ^{1}H NMR signals for water within the macropores and in the gel component of the resin was achieved in the macroporous KU-23 sulphonic acid cation-exchange resin at −2°C.[37] In the range of negative temperature, an appreciable broadening of the internal water resonance line was also observed in gel-type resins[40,42,45].

In certain cases the difference between the line widths for pure water and the water absorbed by the resin may be a result of an incomplete averaging of the dipole–dipole interactions following a decrease of the mobility of the water molecules within the resin grains. The independence of the line width of the degree of cross-linking of the resin[14,36] (the DVB content was varied from 2 to 12%) and of its ionic form[41] ($\Delta\nu \simeq 10$ G for the Cs^+-, K^+-, Na^+-, and Li^+-forms of the KU-2 × 8 cation-exchange resin) shows that, for univalent counterions at temperatures above 0°C, the above cause of the broadening is not dominant. The conversion of the resin into the ionic form saturated by polyvalent counterions leads to a broadening of the internal water line even in highly acidic cation-exchange resins. For example[27], the line widths in the spectra of the Dowex-AG-50W × 16 resin in the Be^{2+}- and Al^{3+}-forms are 72 and 90 G respectively, the line becoming broader with increase of the degree of cross-linking of the resin or with decrease of temperature. This effect has been observed for the Zn^{2+}- and La^{3+}-forms[27] and for the Mg^{2+}-form.[27,33] The dependence of $\Delta\nu$ on the DVB content and temperature has been explained[27,33] by the presence of "free" water and the water of hydration, the large difference between the relaxation times of the two types of water, and the low rate of exchange between their molecules. The narrowing of the line in the spectrum of Dowex-AG-50W × 16 resin in the Mg^{2+}-form may be[27] a result of the formation of a contact ion pair comprising a fixed group and a counterion, i.e. the capture by the SO_3^- group of one coordination site in the first hydration shell of the counterion.

The line widths of the adsorbed water in the spectra of weakly acid and weakly basic resins usually amount to several tens of G, i.e. are much higher than in the spectra of highly acid and highly basic resins[14,22,35,36] and on conversion of the resins into a salt-form the resonance lines are significantly narrowed. The high value $\Delta\nu = 130$ G in the spectrum of the KB-4P2 resin in the H^+-form has been explained[35] by the binding of two water molecules by each COOH group via strong hydrogen bonds. The activation energy for molecular motion $E_a = 4.9$ kcal mole^{-1}, comparable to the dissociation energy of a single hydrogen bond, has been determined[36] from a plot of $\ln(\Delta\nu)^{-1}$ against $1/T$, $\Delta\nu$ being the line width in G and T the absolute temperature. The broadening of the line to $\Delta\nu =$ 30 G in the spectrum of the KU-1 sulphophenol cation-exchange resin is attributed[41] to the influence of the phenoxy-radicals recorded[44] by ESR.

The study of the state of water in synthetic ion exchangers at negative temperatures[38,40–42,45] is of particular interest. In contrast to pure water, the transition to the region of negative temperatures is accompanied by a small increase of the line width, reaching several hundred G at −70°C. The ^{1}H NMR line width for pure ice at −70°C is[41] 65 000 G. If the mechanism of the broadening of the ^{1}H NMR lines of pure water molecules, pure ice, and the water in the resin phase is the same and is associated solely with the mobility of the molecules, then the line width in such systems can be proportional to the correlation time τ_c for the dipole–dipole interaction. Knowing[2]

that $\tau_c = 10^{-12}$ s for water, it is possible to estimate the correlation time for ice ($\tau_c \simeq 10^{-7}$ s) and the resin ($\tau_c \simeq 10^{-9}$ s). Thus at −70°C the mobility of the water molecules in the resin is higher by at least two orders of magnitude than in ice, since in reality the ^{1}H NMR line width for the water in the resin can undergo additional broadening owing to the effects discussed above. Mank et al.[45] suggested that the correlation time in an ion exchanger at negative temperatures be determined from the formula

$$\tau_c = A\Delta\nu, \qquad (2)$$

where $\Delta\nu$ is the line width in G and the constant $A = 1.7 \times 10^{-10}$ G^{-2}. At negative temperature, there is an effect of the degree of cross-linking of the cation-exchange resin[41] and the nature of the counterion[40,45]. The greater the capacity of the cation for hydration the wider the resonance line at a given temperature[45]. Unfortunately the very important experimental data concerning the change in the integral intensity of the ^{1}H NMR signals due to the internal water with decrease of temperature virtually do not exist. Only Mank et al.[39] showed that, on passing from positive to negative temperatures, the number of mobile H_2C molecules per NH_4^+ counterion in the KU-2 cation-exchange resin decreases sharply, from ~12 to ~5, and remains almost unchanged in the range between 0° and −30°C. This effect has been explained[39] by the crystallisation of the free water in the resin.

The dependence of the ^{1}H NMR line width on the internal water content has been investigated in the Dowex-AG-50 (H^+-form; 4, 8, and 16% DVB)[43] and KU-2 (Li^+-form)[46] cation-exchange resins. The marked broadening of the spectral line in the course of the removal of water has been attributed[43] to several causes, the main one of which is the inhomogeneity of the magnetic field in the resin phase. The decrease of the mobility of the water molecules[46] and the structural inhomogeneity of the resin itself[43] can also cause the broadening of the internal water line during the dehydration of the ion exchanger. When the water content corresponds to less than approximately two molecules per counterion, the line width increases without limit[43]. We may recall that, according to Zundel[31], the fixed groups and the hydrogen counterions are associated for this degree of hydration of the sulphonic acid cation exchanger. The sharp increase[46] of the water ^{1}H NMR line in the spectrum of the Li^+-form of the cation exchanger with a moisture content corresponding to approximately 4 H_2O molecules per Li^+ ion has been explained by the stronger sorption of water for low moisture contents in the resin and is also consistent with Zundel's ideas[31]. The diameter of the cavities occupied by water molecules has been estimated[46] from the line width in the spectrum of the fully swollen cation exchanger; it amounts to approximately 8 Å.

A study has been made[45] of the temperature dependence of the line width in the spectrum of the KU-2 cation-exchange resin with different water contents. The decrease of the water content in the Li^+-form of the cation exchanger down to approximately 4 moles of water per equivalent of the resin has little influence on the nature of the $\Delta\nu = f(T)$ curve. This finding confirms yet again that, on passing to negative temperature, only the fraction of the water in the resin which does not form part of the hydration shell of the cations crystallises. The activation energies for molecular motion in the KU-2 resin in the Ca^{2+}-form have been estimated from the slopes of the linear plots of $\ln(\Delta\nu)$ against $1/T$. The values of E_a vary from 16 kcal mole^{-1} for the swollen resin to 8 kcal mole^{-1} for the resin with a water content of approximately one water molecule per Ca^{2+} ion.

Frankel[47] pointed out that additional mechanisms of the broadening of the spectral lines, associated with the existence of concentration profiles in the grains and with a non-uniform distribution of the grains containing different counterions, have been observed in studies on ion-exchange kinetics by ^{1}H NMR.

IV. THE RELAXATION TIMES T_1 and T_2

The system of magnetic nuclei is not isolated, since each nucleus in the molecules is involved in thermal motion and gives rise to a local variable or constant magnetic field at the site of a neighbouring nucleus. The time T_2 is called the spin–spin relaxation time (or the phase memory time) if it yields the average lifetime of a definite spin state due exclusively to a spin–spin interaction. It is frequently called the transverse relaxation time in order to characterise the average lifetime of the spin state, independently of the nature of the interactions bounding it. The time T_1 is called the spin–lattice relaxation time; it represents a measure of the time during which the energy passes from the spin system to other degrees of freedom. In weakly viscous liquids, $T_1 = T_2$, while in solids $T_1 > T_2$.

In an aqueous suspension of Dowex-50W × 8 cation-exchange resin at 31°C,[48] $T_1 = 2.9$ s for the external water and $T_1 = 0.45$ s for the internal water were obtained. The decrease of the internal water relaxation time can be explained by the increase of the correlation time τ_c as a result of the restriction of the mobility of the water molecules by the resin matrix and by the rapid exchange of the excess proton between the water molecules.

Using the nuclear spin echo method, Bleadel et al.[49] investigated the dependence of T_1 and T_2 on the number of water molecules per exchange group (r) in the Dowex-50W cation-exchange resin phase (Na^+-form; 2, 4, 8, and 12% DVB). They observed that, for the same water content in the resin, the times T_1 and T_2 were independent of the degree of cross-linking of the resin with the exception of a small difference in the presence of a high moisture content. This behaviour of the relaxation times may be expected if the internal water molecules are located mainly around the fixed groups and the counterions. In the region where $r > 6$, T_2 hardly varies, while T_1 increases slightly. In the region where $r < 6$, the transverse relaxation time decreases by three orders of magnitude, while the longitudinal relaxation time passes through a minimum near $r = 1.8$ and then increases again. This type of variation of T_1 and T_2 indicates a marked decrease of the mobility of the water molecules in the sulphonic acid cation-exchanger phase following a decrease of the moisture content from six water molecules per Na^+ counterion. The correlation time for the magnetic dipole–dipole interaction for $r = 1.8$ can be estimated from the data of Bleadel et al.[49]: $\tau_c = 4.1 \times 10^{-8}$ s.

T_1 and T_2 for the water protons in the sulphophenol KU-1 cation-exchanger and the sulphonic acid KU-2 cation-exchanger phases (2, 4, 8, and 12% DVB) in the ionic form produced by saturation with alkali metals have also been investigated[50,51] by a pulse method at negative temperatures. The variation of the form of the bifunctional KU-1 cation-exchange resin alters the relaxation parameters of water. An anomalously high ratio T_1/T_2 is observed, which can be explained either by the presence of paramagnetic centres in the KU-1 resin[44] or by the

existence of several correlation times. At −25°C, the rate of proton relaxation of water in the KU-2 × 8 resin exceeds by more than an order of magnitude the rate of relaxation of the water protons in a frozen LiCl solution. This finding indicates a larger number of water molecules surrounding the cation–anion pair in the frozen electrolyte solution than is present around the counterion–sulpho-group pair in the resin phase. The increase of the rate of proton relaxation of the internal water with increase of the number of cross-links in a sulphonic acid cation exchanger at −10°C has also been explained by the difference between the water contents. The influence of the type of counterion on the mobility of water molecules in the KU-2 × 8 resin is greatly reduced or masked by other interactions. The increase of the ratio T_1/T_2 with decrease of temperature might be due to the approach of T_1 to its minimum value at the point where $\omega_0\tau_C = 0.6158$. In this case, the correlation time is of a smaller order of magnitude than 10^{-8} s and the activation energy for molecular motion should be estimated from the temperature variation of T_2. The average activation energy for all the forms of the cation exchanger is approximately 9 kcal mole^{-1}. The mobility of water molecules in the swollen cation-exchange resin at −50°C is higher than at 25°C in the same cation exchanger, which, however, contains two water molecules less per exchange group, and is much higher than in ice.

Thus the relaxation parameters of the water absorbed by the cation-exchange resin indicate a similarity between the resin phase and the frozen electrolyte solution. The hydrated regions in the resin are surrounded by a virtually immobile matrix while in solutions they are surrounded by ice.

V. MAGNETIC RESONANCE OF THE COUNTERION NUCLEI

Direct information about the state of the hydration shells of the counterions, the intensity of the ion–ion interaction, and the mobility of the counterions can be obtained by studying the NMR parameters of the counterion nuclei in combination with the ^{1}H NMR parameters of the solvent.

1. ^{1}H NMR (nuclear spin $I = 1/2$). ^{1}H NMR can be observed for counterions containing slowly exchanged protons. The ^{1}H NMR spectrum of a suspension of the Dowex-AG-50W × 2 resin in an aqueous $N(CH_3)_4Cl$ solution ($m = 2.5$) contained[14] two lines due to the methyl protons in the counterions present in the resin phase and the cations in the external solution. The ^{1}H NMR line width for the counterions increases with increase of the degree of cross-linking of the resin and approaches smoothly the value corresponding to an aqueous solution of $N(CH_3)_4Cl$. This behaviour of $\Delta\nu$ indicates a decrease of the mobility of the counterions with increase of the degree of cross-linking of the cation exchanger.

The temperature variation of the ^{1}H NMR spectrum of the NH_4^+ counterions in the KU-2 cation-exchange resin has been observed[39]. In the range 20–0°C, the spectrum consists of a triplet due to the spin–spin interaction of the protons with the ^{14}N nucleus. The constant for this interaction is 48 ± 1 G. Above 20°C and below 0°C, the triplet structure signal is converted into a singlet structure.

The ^{1}H NMR spectra of a number of aminoacids absorbed by the Dowex-AG-50W × 4 sulphonic acid cation-exchange resin have been published[52].

2. ^{7}Li NMR ($I = 3/2$). The structural changes near ions whose nuclei have a spin $I > 1/2$ can be studied because these nuclei have an electrical quadrupole moment Q. The nuclei do not possess an electric dipole moment and the energy of the nucleus is therefore independent of its orientation in a homogeneous electric field. However, as a result of the Brownian motion of the species surrounding the resonating nuclei, fluctuations of the electric field gradient arise at the nuclei. In consequence of the presence of Q, an inhomogeneous electric field can induce transitions between the magnetic energy levels, i.e. can create an additional effective magnetic relaxation mechanism. The results of the high-resolution NMR,[53] broad line[54], and spin echo[55] studies published in the first communications demonstrated the likely usefulness of ^{7}Li magnetic resonance in studies on cation-exchange resins.

Mank et al.[46] investigated the dependence of the ^{7}Li NMR chemical shift and line width on the degree of hydration of the sulphonic acid KU-2 cation-exchange resin. The chemical shift of the line due to the counterion nuclei relative to the ^{7}Li NMR signal in an aqueous solution of LiCl is within the limits of the experimental accuracy of the measurement of this quantity when the water content varies from twelve (fully swollen resin) to approximately two water molecules per counterion, i.e. the electron density at the lithium ion remains unchanged. The authors correctly explained the sharp upfield shift of the signal by approximately 16 p.p.m. after the complete dehydration of the resin by the formation of a chemical bond between the counterion and the fixed group, as a result of which the electron density around the lithium nucleus increases.

The breakdown of the structure of the hydration shell of the counterion and the enhancement of the electrostatic ion–ion interaction during the dehydration of the resin must be reflected in the broadening of the ^{7}Li NMR line. A decrease of the degree of dehydration of the resin from the fully hydrated state to approximately four water molecules per counterion is accompanied[46] by a slow increase in the width of the ^{1}H NMR line of the internal water and the NMR line of the lithium counterions. On further dehydration of the resin, the ^{7}Li and ^{1}H NMR line widths increase sharply. Presumably, when the hydration shell of the counterion is strongly deformed after the elimination of even one water molecule from the first coordination sphere, a sulpho-group tends to take its place. This results in an intensification of the ion–ion interaction.

Bystrov and Nikolaev[56,57] showed that the rate of longitudinal relaxation of the lithium counterion nuclei in the KU-2 (or KRS) sulphonic acid cation-exchange resin increases with increase of the molality (i.e. with increase of the number of cross-links in the resin). The activation energies for the relaxation processes E_a were calculated from the temperature variation of T_1 for the lithium counterion nuclei[54]. They decrease in succession with increase of the degree of cross-linking of the resin and are listed below:

DVB, %	soln. LiCl	2	4	8	12
E_a, kcal mole^{-1}	4.1	4.2	3.6	3.2	2.3

According to Hertz[58], the activation energy for the reorientation of water molecules in the hydration shell of the Li^+ ion is 4.3 kcal mole^{-1}. One may conclude that the modulation of the magnetic and quadrupolar interactions in weakly cross-linked sulphonic acid cation-exchange resins is achieved via the reorientation or jumps of the water molecules in the first hydration shell.

The rate of relaxation of ^7Li in an electrolyte solution can be expressed by the sum of several terms:

$$\left(\frac{1}{T_1}\right)_{exp} = \left(\frac{1}{T_1}\right)_{m.d.d.} + \left(\frac{1}{T_1}\right)'_{el.qu.} + \left(\frac{1}{T_1}\right)''_{el.qu.}. \quad (3)$$

Here the first term characterises the magnetic dipole–dipole relaxation mechanism, which cannot be neglected for the ^7Li nucleus [59]. It is proportional to the lifetime of the water molecules in the first hydration shell τ_h^+. The term $(1/T_1)'_{el.qu}$ is determined by the electric field gradient which has arisen as a result of the Brownian motion of the water molecules in the hydration shell of the ion and is characterised either by the reorientation time of the water molecules near the ion τ_r^+ or by τ_h^+. The third term of Eqn. (3) reflects the extent of the direct ion–ion interaction and is proportional to the correlation time τ_{ci}, which characterises the translational diffusion of the ions relative to one another. In the sulphonic acid cation-exchanger phase, the relative values of the terms of the equation may be different from those in solution.

Experiments with light and heavy water showed [57] that at 25°C the ratio of the contributions of the magnetic dipole–dipole and electric quadrupolar relaxation mechanisms to the overall rate of relaxation remain the same as in an electrolyte solution [59]. Thus the times τ_R^+ and τ_r^+ (characterising related motions) increase with the degree of cross-linking of the resin, while the structure of the hydration shell of the lithium counterion (at any rate in cation exchangers with 8% of DVB and less) is deformed insignificantly compared with the hydration shell of the ion in pure water. The changes in τ_r^+ and τ_h^+ during isotope substitution may be neglected [60], while the decrease of the degree of swelling of the cation-exchange resin [61] and the accumulation of residual H_2O in the hydration shells of the counterions [62] on passing from H_2O to D_2O only increase the rate of relaxation of the lithium counterions in D_2O.

The diffusion coefficients of the counterions are known [12,14] to change to a greater extent as the ion-exchange resin structure is altered than those of water molecules. One can therefore expect an increase of the time τ_{ci} with increase of the number of cross links. In order to explain the decrease of E_a on passing from weakly cross-linked to more cross-linked resins, one must suppose that the correlation time τ_{ci} varies with temperature less than do τ_r^+ or τ_h^+. Thus the activation energy characterises different types of motion in each specific case: the Brownian motion of water molecules in the vicinity of the counterion in the KU-2 × 2 cation-exchange resin; the oscillation of the hydrated counterion about the equilibrium position in the KU-2 × 12 resin, where the electric field gradient at the counterion nucleus is a maximum.

In the region of 0°C, the temperature dependence of T_1 undergo [56,57] an abrupt change simultaneously and show a break. This is associated with the displacement of part of the water from the resin on crystallisation of the external water. The sensitivity of the longitudinal relaxation time to structural differences between resins is indicated yet again by the experimental finding that the rate of relaxation of ^7Li in a sulphonic acid cation-exchange resin of type KRS (4% DVB) is greater than in the KU-2 sulphonic acid cation exchanger (4% DVB). This apparently reflects the more effective cross-linking in the KRS resin (purified DVB was used) than in KU-2 (industrial DVB was used).

^{13}C NMR ($I = 1/2$). The low abundance of the ^{13}C isotope (approximately 1.1%) and the low relative intensity of the resonance signals (smaller by a factor of approximately 60 than for protons in identical fields) is the main cause of the small number of ^{13}C NMR studies. There has been only one study, by Sternlicht et al. [52], in which a substance (aminoacid) sorbed on the resin (Dowex-AG-50W containing 4 and 8 wt.% DVB) was investigated by ^{13}C NMR. A common feature of the majority of aminoacids is that the ^{13}C line widths for the protonated specimens proved to be only 3–4 times greater than for the deuterated analogues, contrary to the expected increase by a factor of 10–15. Furthermore, $T_1 \gg T_2$ for all measurements and T_2 depends on the degree of cross-linking much more strongly than does T_1. These results can be explained by anisotropic rotations, which persist after the absorption of aminoacid molecules by cation-exchange resins, which leads to a non-zero time-average interaction. It is suggested that internal rotations about one or more intermolecular bonds, for example about the $D_3H^+ \ldots O_2S-R$ linkage, may occur in aminoacids. This rotation determines the rate of the spin–lattice relaxation T_1^{-1}. The slow vibrations of the resin matrix determine the rate of the spin–spin relaxation T_2^{-1}. For internal rotation at room temperature, the correlation times are approximately 10^{-9} s, while the vibrations of the ion-exchange resin lattice are described by longer correlation times.

^{19}F NMR ($I = 1/2$). The ^{19}F chemical shifts in the AV-17 anion-exchange resin and KU-2 cation-exchange resin phases have been measured [63] as a function of concentration in the aqueous solutions in which the resins were treated. The amount of adsorbed electrolyte in the resin depends greatly on the concentration in the external solution c_{HF}. In a cation or anion exchanger, there is a possibility that the fluorine may exist in the same forms as in aqueous hydrofluoric acid solution, i.e. as cations or the F^- and HF_2^- counterions, as well as HF molecules and associated species $(HF)_n$. However, single ^{19}F resonance lines have been observed in all the systems, which indicates a rapid exchange of fluorine atoms between all the possible states. It has been found that (1) the $\delta = f(c_{HF})$ curve for the KU-2 resin exhibits a positive shift and that for the AV-17 resin a negative shift relative to an aqueous HF solution, (2) in the region where $c_{HF} < 5$ M, the ^{19}F NMR line for the anion exchanger undergoes a sharp upfield shift, and, in addition, (3) up to the concentration $c_{HF} = 18$ M the experimental $\delta = f(c_{HF})$ curve for the anion-exchange resin has undergone a downfield displacement relative to the calculated curve. The authors explain the first result by structural differences between anion- and cation-exchange resins, the second result by the existence of several forms of fluorine in the anion-exchange resin, and the third result by the effects of the solvation of the fixed groups by HF molecules. All the results can probably be accounted for by the different proportions of the fluorine species in the anion- and cation-exchange resins.

The chemical shift of the fluoride counterions in the Dowex-1 anion-exchange resin undergoes a downfield displacement [33] with increase of the number of cross links: −0.49 p.p.m. (1% DVB), −0.83 p.p.m. (2% DVB), and −2.24 p.p.m. (8% DVB). The negative ^{19}F NMR shift in anion-exchange resins relative to KF solution can be accounted for by the deshielding of the nucleus of the F^- ion as a result of the formation of an electrostatic linkage between the counterion and the fixed group.

Frankel [47] reported a study of the kinetics of the exchange of F^- and Cl^- counterions in an anion-exchange resin by ^{19}F NMR, but no quantitative interpretation is given.

^{23}Na NMR ($I = 3/2$). It is known that the dominant mechanism of the energy exchange between the spin system and the lattice in electrolyte solutions involves the interaction of the electrical quadrupole moment with the electric field gradient at the site of the nucleus, generated by the neighbouring species. The first term in Eqn.(3) is neglected [T_1(p.p.m.) > 20 s]. The mechanism of the quadrupolar relaxation of the ^{23}Na nuclei in solutions is determined in this case either by the collisions of the hydrate complexes during Brownian motion[64], or by the translational motion of water molecules from the first hydration shell of the ion and back again[64,65], or by a reorientation of the water molecules in the first hydration shell of the ion[58]. Under certain conditions, one of these types of thermal motion may become dominant.

The marked broadening of the resonance line due to the nuclei of the sodium counterions in Dowex-AG-50W × 8 compared with electrolyte solutions was pointed out for the first time by Jardetsky and Wertz[66]; it has been explained by the formation of a strong linkage between the Na^+ ion and the fixed group. The dehydration of the KU-2 cation-exchange resin is also accompanied[54] by a broadening of the resonance line due to the nuclei of the sodium counterions. The line broadening begins when the water content is below approximately 40 wt.%. A molecule of free water is probably removed initially and is followed by molecules from the hydration shell of the counterion. According to Smirnov[54], the dehydration of the cation-exchange resin is manifested much sooner in ^{23}Na NMR than in ^{7}Li NMR. Possibly this reflects the postulated[67] six-molecule hydration shell of the Na^+ ion and the four-molecule shell of the Li^+ ion. In this case one might claim that the individual hydration properties of the Na^+ and Li^+ ions persist also in the cation-exchanger phase. This conclusion was in fact reached by Bystrov and Nikolaev[56], who measured the longitudinal relaxation times T_1 of the sodium and lithium counterions in swollen KRS sulphonic acid cation-exchange resins containing 2 and 4 wt.% DVB and found that at 28°C the ratios of the rates of relaxation of ^{23}Na and ^{7}Li in an aqueous electrolyte solution and in the KRS-2 and KRS-4 cation-exchange resins are respectively 277, 265, and 254, i.e. are virtually constant. If the conclusion[57] concerning the structure of the hydration shell of the lithium counterion is correct, then the hydration shell of the sodium counterion should also not be distorted by, for example, the incorporation of a sulpho-group in the latter.

The hypothesis that one of the four coordination regions around the Na^+ counterion in Dowex-50W is occupied by a sulpho-group was put forward by Greekmore and Reilly[33] on the grounds that the hydration number $h(Na^+) < 4$ (see Table) and that there is broadening of the ^{23}Na NMR line with increase of the degree of cross-linking of the cation-exchange resin. It was concluded that the electrostatic interaction of the counterion with a fixed group is intensified and that the correlation time for the quadrupolar interaction increases with increase of the number of cross links.

However, according to other data[49], obtained in a study of the Dowex-50W cation-exchange resin in the Na^+-form containing 2, 4, 8, and 12% DVB, the relaxation times T_1 and T_2 for ^{23}Na with the same number of water molecules per Na^+ counterion depend strongly on the degree of cross-linking. On the other hand, T_1 and T_2 for the water protons are virtually independent of the number of cross links. When the mechanism of the relaxation of ^{23}Na is considered, the charge density and distribution per unit volume are apparently of considerable importance. During the dehydration of the resin, T_1 and T_2 for the Na^+ counterion nuclei diminish sooner and to a greater extent the lower the degree of cross-linking of the resin. When the water content is less than six water molecules per counterion ($r < 6$), the relaxation times in such resins become comparable and, when $r = 3$, they are virtually equal. This can be explained by the breakdown of the hydration shell as a result of the ion–ion interaction when $r < 6$ and by the formation of a contact ion pair when $r = 3$. The types of variation of the correlation time and of the quadrupolar coupling constant when water is removed from a cation-exchange resin cannot be determined separately.

^{133}Cs NMR ($I = 7/2$). There exist only two preliminary reports of ^{133}Cs NMR studies on cation-exchange resins. The line width for the nuclei of the Cs^+ counterions in the Dowex-AG-50W × 12 sulphonic acid cation-exchange resin has been measured[28] and found to be $\Delta\nu \simeq 500$ Hz. For comparison, we may quote the ^{7}Li NMR line width for the KU-2 sulphonic acid cation-exchange resin (8–10% DVB):[46] $\Delta\nu \simeq 165$ Hz. The longitudinal relaxation times T_1 for the nuclei of the Li^+ and Cs^+ counterions in the bifunctional KU-1 cation-exchange resin are approximately the same[55]: $T_1(^7\text{Li}) \geqslant 10^{-1}$ s and $T_1(^{133}\text{Cs}) \simeq 2 \times 10^{-2}$ s. A rough comparison of $\Delta\nu$ and T_1 shows that, on passing from electrolyte solutions to cation-exchange resins, the rate of relaxation of ^{133}Cs increases more than the rate of relaxation of ^{7}Li. This demonstrates a greater probability of the formation of contact ion pairs of the type $R-SO_3^- - Cs^+$.

In conclusion of the section on the magnetic resonance of counterion nuclei, we may mention that the experimental studies described are so far in many respects non-systematic, which greatly hinders comparison of the results. The conclusions reached in the course of the discussion in this Section must therefore be regarded as preliminary. The magnetic resonance of nuclei such as ^{14}N, ^{27}Al, ^{31}P (studies have been made on extraction by organophosphorus compounds; see, for example, Rozen et al.[68]), ^{35}Cl, ^{79}Br or ^{81}Br, ^{85}Rb or ^{87}Rb, ^{127}I, etc. has not been considered at all.

VI. THE STATE OF EQUILIBRIUM OF THE ION-EXCHANGE RESIN–SOLVENT SYSTEM

If the ion-exchange resin remains in contact with the solution for a sufficiently long time, an equilibrium, characterised by a constant ratio of the concentrations of the solute in the resin and in the solution, is established.

1. Determination of the Dissociation Constant

^{1}H NMR studies have been made[69,70] on aqueous solutions of a number of acids (HCl, $HClO_4$, HNO_3, and toluene-*p*-sulphonic acid) over a wide range of concentrations, the chemical shift being used to determine the acid dissociation constant. The observed chemical shift relative to pure water is determined[1] by the fraction of protons present in the hydronium ions (P):

$$\delta_{obs} = P\delta_{H_3O^+},$$
$$P = 3\chi/(2-\chi),$$

where χ is the stoichiometric mole fraction of the acid. Dinius et al.[43] investigated Dowex-50 resins with 4, 8, and 12% DVB hydrated to different extents. They postulated that $\delta_{H_3O^+}$ remains approximately constant and compared the relative acid strengths of resins cross-linked to

different extents and aqueous acid solutions on the basis of the slopes of the plots of δ_{obs} against P. According to their data, Dowex-50 with 4% DVB, for example, is a stronger acid than HCl or toluene-*p*-sulphonic acid and is comparable in strength to $HClO_4$. The authors point out that the increase of acid strength with decrease of the degree of cross-linking of the resins may be only apparent and may be the result of the different degrees of formation of ion pairs in the resins due to the difference between electrical constants [differing local dielectric constants (Ed. of Translation)]. The method described suffers from a disadvantage—the determination of the position of the line and of P is inaccurate.

Ochiai and Seto [71] used a procedure free from the disadvantage. They investigated a resin fully swollen in water and converted into a mixed form (saturated with hydrogen and metal ions). The resin was kept in solution with specified concentrations of the necessary components and was then separated from it. The concentrations of the components in the resin were inferred from the analysis of the electrolyte composition. The authors [71] obtained the dissociation constant $K = 0.7$. Naturally, the degree of dissociation of the SO_3H group depends on the nature of the second counterion. It was concluded that toluene-*p*-sulphonic acid and the ion-exchange resin are dissociated to approximately the same extent and that the ion exchanger belongs to the category of strong acids.

2. The Adsorption of Solutes

The distribution of the solute between the liquid in the pores and the external solution is frequently referred to as the adsorption of the solute [12].

The adsorption of non-electrolytes. The concentration of the solute in the resin is usually not equal to its concentration in the solution with which the resin is in equilibrium and is characterised by the partition coefficient. The important factors which must be taken into account in the study of non-electrolyte adsorption processes are the sieve effect, the salting-out effects, different kinds of interaction forces, and complex formation processes. The adsorption is also influenced by properties of the resins such as the degree of cross-linking, the matrix structure, and the nature of the ion saturating the resin. The adsorption depends on the properties of the solute—the structure and size of its molecules and its tendency towards complex formation. In addition, the adsorption is influenced by the concentration of the solution and temperature.

Gordon [14] obtained the ^1H NMR spectra of suspensions of anion- or cation-exchange resins in a 5% solution of t-butyl alcohol or an 80% solution of dioxan in water. In the former case, the spectrum of the hydrogen-form of the resin consisted of four lines: two lines due to hydroxyl protons in the resin phase and in solution and two analogous lines due to the methyl protons of the alcohol. The positive shift of the methyl protons of the internal liquid relative to the external solution can be explained mainly by the large diamagnetic anisotropy of the aromatic portions of the matrix due to the circulation of the mobile π-electrons under the influence of the external magnetic field. The effects due to the solvation of the fixed groups and counterions are neglected. In the second case the resonance line of the dioxan protons in the resin phase coincides with the line due to the external dioxan. Gordon concluded from his results that the partition coefficients of the components of the binary solution between the resin phase and the solution can be measured.

Howery et al. [72] investigated the ^1H NMR spectra of suspensions of Dowex-50W × 8 resin (H^+-form) in aqueous solutions of acetone, dioxan, ethyl, isopropyl, and t-butyl alcohols, and dimethyl sulphoxide. The lines due to the internal water were displaced downfield for all the binary mixtures relative to the line of the internal water when the resin was swollen in pure water; the chemical shift of the internal water protons increases with increase of the mole fraction of water in the system. In some cases, selective absorption of the organic solvent by the resin was observed in the presence of a relatively large mole fraction of water. The increase of the chemical shift of the external water with increase of the mole fraction of the organic component in the binary mixture is attributed to the increasing proportion of ruptured hydrogen bonds between water molecules. The opposite effect for the internal water is explained by the polarising action of the cations. Under these conditions, the physical structure of the resin phase consists of hydrated counterions surrounded by molecules of the organic solvent. Apart from preferential hydration, the possibility of a more favourable interaction of the organic molecules with the resin matrix is considered.

The selective absorption of the solvent by weakly basic (Amberlite IR-45) and strongly basic (Amberlite IRA-400) anion-exchange resins in contact with aqueous dimethyl sulphoxide and acetonitrile solutions was investigated by Frankel [73]. Howery et al. [72] analysed the composition of the mixture in contact with the resin, while Frankel [73] removed the external solvent by centrifugation after the attainment of equilibrium in the system and determined by integration of the areas under the spectral lines for the internal liquid. The selectivity coefficient is defined by the expression $K = x_i\bar{x}_w/\bar{x}_i x_w$, where x_w and x_i are the mole fractions of water and the organic component in the binary solvent and $\bar{x}_w$ and $\bar{x}_i$ are the analogous mole fractions in the resin. It proved to be 3.12 for the fluoride-form of the resin, 1.6 for the chloride-form, 1.4 for the bromide-form, 1.01 for the iodide-form, and 0.7 for the free base. The values of K greater than unity correspond to the preferential adsorption of water. It was concluded that the dominant effects are caused by preferential solvation and the structure of the added solvent and not by the solvation of the fixed groups or steric factors.

Grigor'eva [41] measured the temperature variation of the chemical shifts of the protons of the water and acetone present in the KU-2 × 8 cation-exchange resin in the Rb^+-form. They noted a very interesting experimental fact: the presence of the organic solvent in the external phase leads merely to a decrease of the crystallisation temperature of the external water to −20°C, as happens in mixed solutions [74], while in the resin phase the crystallisation of water is not observed even at −100°C.

Ion-exchange resins in organic solutions. In order to understand the processes involving the selective absorption of one of the components of the binary solution, it is important to know the mechanisms of the interaction of ion-exchange resins with organic solvents of different types.

^1H NMR data for suspensions of the Dowex-AG-50W × 8 cation-exchange resin in dioxan and acetonitrile as well as additional infrared spectroscopic data enabled Gordon [14] to conclude that the equilibrium

$$RSO_3H \cdots X \rightleftarrows RSO_3^- \cdots HX^-$$

in the hydrogen-form of the sulphonic acid cation-exchange resin is displaced to the right when X is dioxan and to the left when X is acetonitrile.

It has been shown[27,75] that the position of the lines due to the hydroxyl and methyl protons of methanol in the ion-exchanger phase is independent of grain size (between 0.297–0.149 and 0.074–0.037 mm), the degree of cross-linking of the resin (between 1 and 8% DVB), and its form (Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Al^{3+} for cation-exchange resins and F^-, Cl^-, Br^-, and I^- for anion-exchange resins). The results can be explained by the formation of contact ion pairs within the resin phase. The maximum chemical shift between the methyl and hydroxyl protons when the cation-exchange resin is in the H^+-form is caused[75] by the displacement of the hydroxyl proton lines towards lower fields due to the proton exchange between the counterions and the OH groups of methanol.

Adsorption of strong electrolytes. When the ion-exchange resin is brought into contact with an electrolyte solution containing ions of the same type as the counterions, there is a possibility of the simultaneous sorption from solutions of ions of both charge types. The amount of adsorbed substance depends on the nature of the solutes, the degree of cross-linking of the resin, the nature and degree of ionisation of the functional groups of the resin, the electrolyte concentration, and a number of other factors.

Dinius and Choppin[76] investigated the distribution of an acid (HCl or $HClO_4$) between an aqueous solution of the acid and the Dowex-50 (4% DVB) sulphonic acid cation-exchange resin and established that the amount of sorbed HCl is smaller than that of $HClO_4$. The difference between the distributions of hydrochloric and perchloric acids is attributed by the authors to the different effects of HCl and $HClO_4$ on the water structure. It has been established by NMR[69] and infrared spectroscopy[77] that the dissolution of $HClO_4$ in water leads to a greater breakdown of the water structure than the dissolution of HCl. In their communication[43], Dinius et al. point out that the water structure in the resin phase is disrupted to a greater extent than in pure water. They therefore suggest that the ions derived from $HClO_4$ are sorbed more readily by the resin than those derived from HCl.

Reichenberg and Laurenson[21] found that the chemical shift of the signal due to hydronium ions from the position of the line for pure water is 11.5 p.p.m., and that the experimental relation $\delta = f(P)$ deviates from linearity with increase of P. Dinius and Choppin[76] also showed that the behaviour of the chemical shift for the internal liquid is very similar to that observed in acid solutions. At moderate acid concentrations, the slope of the $\delta = f(P)$ curves decreases in the sequence (HCl + HR) > ($HClO_4$ + HR) > HR, which is attributed to the decrease of the structure-forming effect in the same sequence. The deviation of the curves from linearity begins much sooner for HCl and only slightly sooner, but much more markedly, for $HClO_4$ than in the corresponding acid solutions. The results have been explained by the earlier association of the HCl ions than the association of the $HClO_4$ ions, and in the latter case there is a possibility that the association of RSO_3H begins sooner, in conformity with the qualitative determination[43] of the acid strengths: $HClO_4 > HSO_3R >$ HCl.

The ion-exchange equilibrium. The NMR spectrum of water in the Dowex-AG-50W sulphonic acid cation-exchange resin–water system, in which the resin exists in the mixed ($H^+ + NH_4^+$)-form, consists[14] of two lines (corresponding to the external and internal liquids). This indicates a rapid proton exchange between the hydration shells of the H^+ and NH_4^+ ions. Howery and coworkers[30,78] investigated by NMR the Dowex-50W (4, 8, and 12% DVB) cation-exchange resin in equilibrium with an aqueous HCl and NaCl solution (the overall molar concentration of cations was 0.02, the ratio of the cations in solution being varied). The proton chemical shift of binary electrolyte mixtures is known[1,79] to be an additive quantity, and to depend on the nature and concentration of each ion separately. It has been found that the position of the line due to the internal water in the cation exchanger in the mixed ($H^+ + Na^+$)-form depends analogously on the ratio of the concentrations of the counterions. The experimental results and the theoretical values calculated assuming additivity of the proton chemical shifts proved to be very similar. Since the moisture content in the resin changes on passing from one form of the latter to another, it has been suggested that the expected chemical shift be calculated, taking this effect into account, by the formula[30]

$$\delta = \frac{\delta_H \bar{x}_H w_H + \delta_{Na} \bar{x}_{Na} w_{Na}}{\bar{x}_H w_H + \bar{x}_{Na} w_{Na}},$$

where δ_H and δ_{Na} are the shifts for the internal water in the cation exchanger in the H^+- and Na^+-forms, $\bar{x}_H$ and $\bar{x}_{Na}$ the equivalent fraction of the H^+ and Na^+ ions in the resin, and w_H and w_{Na} the water contents in the corresponding forms of the resin. Thus each counterion influences the chemical shift of the nearest protons independently of other counterions. This very important conclusion enabled Howery and coworkers[30,78] to regard an ion-exchange resin as a concentrated electrolyte solution. Furthermore, they suggest that the ^1H NMR method be used to determined the equivalent fraction of a specific counterion when the chemical shifts of water in each ionic form of the resin differ by not less than 20 Hz.

VII. EXCHANGE PROCESSES

1. Proton Exchange Between the Resin Phase and the Solution

As already mentioned, the spectrum of a suspension of resin grains in water consists of two lines. For simplicity, we shall assume that all the water protons in the ion-exchange resin phase exist in a single state A and have a resonance frequency ω_A, their lifetime in this state is τ_A, and the population of the state is P_A. The protons of the water filling the space between the grains are in a state B and have the corresponding values of ω_B, τ_B, and P_B, and $P_A + P_B = 1$. If the lifetimes τ_A and τ_B are long compared with $(\omega_A - \omega_B)^{-1}$, then the spectrum consists of two separate signals located in the vicinities of the frequencies ω_A and ω_B (slow exchange). In the other limiting case (rapid exchange), τ_A and τ_B are smaller than $(\omega_A - \omega_B)^{-1}$; the spectrum then consists of a single line centred on $\omega_{av} = P_A\omega_A + P_B\omega_B$. The intermediate cases, frequently encountered in practice, have been discussed in detail in the book by Pople et al.[1] On the basis of the distance between the signals, Gordon[14] established the lower limits (0.004–0.1 s) to the average lifetime of water in any phase. Frankel made a similar estimate for the macroporous Amberlite-200 cation-exchange

resin [36]. The rate of exchange of the solvent between the external and internal water is less than 100 s^{-1} for the hydrogen-form and 20 s^{-1} for the sodium-form of the resin. Since individual lines for the water in the pores and in the gel fraction of the resin were not obtained, the rate of proton exchange between these components of the resin must be more than 2×10^3 s^{-1} (at 25°C). Such high rates of exchange in the macroporous cation-exchange resins can be explained by a high surface area.

Dinius et al. [43] used heavy water to determine the lifetime of the protons in a particular phase. The resin grains swollen in H_2O were placed in D_2O (the reverse experiment was also performed). The rate of diffusion was determined from the time variation of the shape of the spectrum, i.e. from the increase of the signal due to the water protons which have diffused from the ion-exchange grain and from the decrease of the signal due to the internal water. For the Dowex-50 × 4 resin (grain size approximately 0.15 mm), the duration of the exchange was 13 s, which corresponded to a diffusion coefficient of 8×10^{-6} cm^2 s^{-1}. Using a similar method, Greekmore and Reilly [48] also found that the exchange was almost completed in 10 s. Using the double resonance method, the authors then found the rate constant for the free exchange of the water protons between the internal and external phases in a suspension of Dowex-50W × 8 resin, the result being $k = 7.3 \times 10^{-1}$ s^{-1}. However, they emphasise that the observed constant characterises only the type of ion exchanger investigated, since it depends on the degree of cross-linking, the grain size, the nature of the counter-ion, etc.

The possibility that the observed rates of proton exchange characterises the exchange of water molecules between the external and internal phases, since the rate of proton exchange is close to the rate of exchange of ^{18}O and the self-diffusion coefficients of water measured by the tracer atom method (^{18}O) and the proton magnetic resonance method are the same, is pointed out in both investigations [43,48].

2. Kinetics of Ion Exchange

Since the chemical shift of the protons of the water in the resin phase depends significantly on the ionic form of the resin, it is natural to employ the ^1H NMR method to follow the transition of the resin from one form to another, i.e. to investigate the kinetics of ion exchange. Attention was already drawn to this factor in an early study by Gordon [14].

Frankel [47] carried out a thorough investigation of the kinetics of the exchange between a mixture of granular resins in two different ionic forms (the exchange of H^+ for Na^+ and NH_4^+). In some of the experiments, the space between the grains was filled with cyclohexane, which facilitated the interpretation of the ^1H NMR spectra, since the signal due to the external water was eliminated. Analysis of the ^1H NMR spectra obtained and the kinetic curves permitted a number of important conclusions: the dependence of the rate of exchange on the square of the grain radius confirmed the internal-diffusion mechanism of exchange. A correlation was noted between the results obtained by the radioisotope method and the NMR method for ion-exchange resins of different types and different degrees of cross-linking: For the successful employment of the NMR method, it is necessary to achieve an effective resolution of the lines of the internal and external water or the lines corresponding to different forms of the resin. In particular, Frankel was unable to follow the kinetics of the exchange between the resins in the F^-- and Cl^--forms owing to the inadequate resolution of their ^1H NMR spectra. The application of the NMR method to the investigation of the kinetics of ion exchange has not been brought to a sufficient level of perfection—the fundamental methodological problem concerning the identity of the observed chemical shifts of the protons and the degree of exchange undergone by resins under dynamic conditions. At the same time, a number of new fundamental possibilities have arisen, for example the possibility of studying diffusion processes in the absence of a Donnan electrolyte in the resin phase or the exchange between the grains in a mixture of resins.

A series of studies undertaken to investigate further ion-exchange resin–solvent systems by the NMR method were published in 1974–1976. [80-90] Kurilenko and coworkers [80,82] have published a general discussion based on their earlier investigations. The nature of the bonds and the mobility of the exchangeable ions H^+, NH_4^+, Li^+, Na^+, Al^{3+}, and F^- in ion-exchange resins with different water contents have been studied by Zubenko and Mank using the NMR method [83]. They concluded that the exchangeable ions and their water of hydration move together both below and above 0°C. According to the results, the rate of the joint migration diminishes below temperatures between −20° and −30°C. They calculated the activation energy for the migration of the exchangeable ions and attempted to determine the type of bonds formed by the counterions with the fixed ionogenic groups and the surrounding water. The authors noted a high mobility of H^+ ions in the dehydrated KU-2 resin.

Studies on water in the KU-2 × 8 resin carried out by Kvlividze and coworkers [84-86] are of undoubted interest. Almost all the studies discussed above were performed on specimens saturated with water to the maximum extent. Measurements have been made [84,85] of the longitudinal (T_1) and transverse (T_2) relaxation times for water in the resin phase at the start of the saturation of the resin with water. The specimens were carefully washed free of paramagnetic impurities [85,86], since the relaxation times of the water protons in the resin phase depend significantly on the content of such impurities (the relaxation times decrease by up to two orders of magnitude in the presence of Mn^{2+} ions in the specimen at a concentration of 1.3×10^{-2} wt.% [86]).

Bukin and Kvlividze [84] showed that water does not crystallise down to 240 K in a specimen of the KU-2 × 8 resin with 23% of water; at 220 K, the signal due to the water protons is much narrower than the matrix signals and, at approximately 200 K, the spectra of the water contain broad and narrow components; only below 160 K do the NMR spectra consist of broad doublets, indicating a rigid fixation of the water molecules and a weak intermolecular interaction. The experimental data on the variation of the relaxation times T_1 and T_2 with the water content have been presented within the framework of the theory of relaxation in a two-phase system [85]. The transverse relaxation in the two phases is due to identical processes. The average correlation time for the rotation of H_2O molecules ($\tau_c \simeq 10^{-8}$ s) and the translational diffusion time ($\tau_d \simeq 10^{-7}$ s) have been determined. These data agree well with the results of Seredin and Nikolaev [91], who obtained $\tau_d = 0.8 \times 10^{-7}$ s in connection with the estimation of the coefficient of self-diffusion of water by measuring the degree of dynamic adsorption in the KU-2 resin in the Cu^{2+}-form. In the range of water contents compared, the NMR line width for the resin is determined mainly by the motion of the sorbed water protons [85].

The magnetic relaxation time of the water protons in a carboxylic acid resin (cross-linked polymethacrylic acid and its sodium and caesium salts) has been investigated by Narebska and Erdmann [81].

There has been a recent growth of interest in NMR studies on ion-exchange resin–non-aqueous solvent systems. Preliminary data have been obtained [89] from NMR studies of the sorption of ammonia by the KU-2 × 8 cation-exchange resins at reduced temperatures. Mank et al. [87] investigated the NMR spectra of the methanol protons in the KU-2 sulphonic acid cation-exchange resins with degrees of cross-linking corresponding to between 4 and 20% DVB. They established that $CH_3OH_2^+$ ions are formed when the adsorbed alcohol molecules interact with the cation exchanger and that their fraction increases with the degree of cross-linking.

The hydration of the KU-2 sulphonic acid cation-exchange resin in equilibrium with sulphuric acid solutions has been investigated [88,90].

Analysis of the results of studies on ion-exchange resin–solvent system by NMR has led to many possibilities in securing valuable and frequently unique information, although many of the research results refer to some extent to specific instances only. Evidently further systematic investigation of ion-exchange resins by NMR is required.

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