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An Investigation of the Mechanism of Water Molecules Interaction with Hydrophilic Disperse Substances by the NMR Method

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The paper presents the results of an investigation of the line-widths and chemical shifts of, the NMR of protons of water molecules and some magnetic nuclei of counterions (Li^+ , F^- , NH_4^+ , H^+) in aqueous dispersions of a number of ion-exchange resins and aluminosilicates in solutions of high-molecular compounds. The spectra have been recorded by the high-resolution NMR type INM-4H-100 spectrometer with a 100 MHz work frequency for protons and 40 MHz for ^7Li in a wide temperature range from 173 K to 373 K.

The phenomenon that the shift of water signal *versus* temperature variation is smaller for electrolyte solutions than for pure water, is proposed to be utilized for the evaluation of the hydration numbers of ions in electrolyte solutions. The activation energy of molecular motion at low temperatures, calculated, from temperature dependence of the linewidth is 8–16 kcal mol⁻¹ and it is in good agreement with the results obtained by other techniques. A model of interaction of water molecules between each other and with the active centres of hydrophilic disperse systems has been proposed. The peculiarities of the interaction of water molecules with ions of various electron structure have been elucidated. The hydration numbers of counterions have been determined and compared with those for aqueous solutions of corresponding salts. The special features of water molecules on the interface at low temperatures have been discussed. The role of hydrogen bonds in the determination of the freezing temperature of water has been elucidated.

The problem of interaction of water molecules and other liquids with the interface of different hydrophilic dispersions plays an important role in the determination of their physicochemical characteristics. It is also a major issue in the electrochemistry of concentrated solutions, *i. e.*, in the interpretation of ion-exchange selectivity, structure formation processes, the mechanism of selective filtration of solutions, *etc.*

Recently the mechanism of intermolecular interactions in the condensed state has been extensively studied thanks to the development and improvement of new physicochemical techniques permitting an insight into processes on the molecular level. Methods of investigation affecting the system only by external perturbations are the most valuable. Such are vibrational and electronic spectroscopy, radiospectroscopy (NMR, NQR, EPR) γ -spectroscopy and dielectrometry. Each of these methods has some advantages and shortcomings and enables

the solution of a part of the problem. The advantages of radiospectroscopic methods are their high sensitivity, selectivity and the unambiguity of the information obtained. By means of these methods valuable data can be obtained on the character of hydrogen bonds, the orientation and mobility of molecules on the interface, and on phase transitions. They also enable estimation of the surface effect on the degree of ordering in various layers of the adsorbed liquid.

This paper presents the results of an investigation of the linewidths and chemical shifts of the NMR of protons of water molecules and some magnetic nuclei of counterions (Li^+ , F^- , NH_4^+ , H^+) in aqueous dispersions of a number of ion-exchange resins and aluminosilicates in solutions of high-molecular compounds. The spectra have been recorded by the high-resolution NMR type INM-4H-100 spectrometer with a 100 MHz work frequency for protons and 40 MHz for ^7Li in a wide temperature range from -100 to 100°C .

Figure 1. shows the typical NMR spectra of the water suspension of cationite KY-2 and anionite AB-17 in different diamagnetic salt forms. In the spectrum the bands of water absorbed by ionite and those outside the resin grains are distinctly seen. After the removal of water from the suspension the intensity of one of the signals decreases, whereas the other one remains practically unchangeable. One may, therefore, ascribe the peaks of absorption bands to the internal and external water of ionite. Their separate observation in the spectrum is explained by the small exchange rate between the molecules in ionite gels and those outside the resin grains. Their exchange rate constant, measured by the double homonucleus resonance method¹ is $K = 0.73 \text{ sec}^{-1}$. The molecular exchange rate determination in the given case is, probably, inappropriate because it is different on the interface and in the depth of the resin grain.

The difference in the signal positions of the external and internal liquids in ionite suspensions is typical only for molecules or atom groups which take part in bond formations. Separate signals are observed, for instance, for water protons and the hydroxyl groups of alcohols (Figure 2.). On the other hand, the signal bands of the methyl and methylene groups of alcohol inside and outside the ionite are practically not separated in the NMR spectra. The same applies to the dioxan molecules during the absorption of water-dioxan mixtures by ionite². In the NMR spectrum of cations in the ammonium form the band of protons of the NH_4^+ ion (Figure 1) is also present. At room temperature is split into a triplet due to an interaction with the nitrogen nucleus ^{14}N , the spin of which is 1. Thus, at bond formation the displacement of absorption bands in the NMR spectra is observed. This phenomenon may be utilized for the quantitative evaluation of intermolecular interactions in ionites and other disperse systems.

Figure 1 shows, that the position of the water signal absorbed by ionite strongly depends on the type of the counterion. The greater the polarizing ability of ions the greater the NMR signal shift towards the weak magnetic field. In addition we assume that at a given temperature the external water signal remains in the same position for various diamagnetic salt forms.

It is known that the chemical shifts of water are very sensitive to temperature variation as it elicits breakage or restoration of a part of the hydrogen bonds in water structure. For instance, when the temperature rises, breakage of a part of the hydrogen bonds occurs resulting in water signal displacement

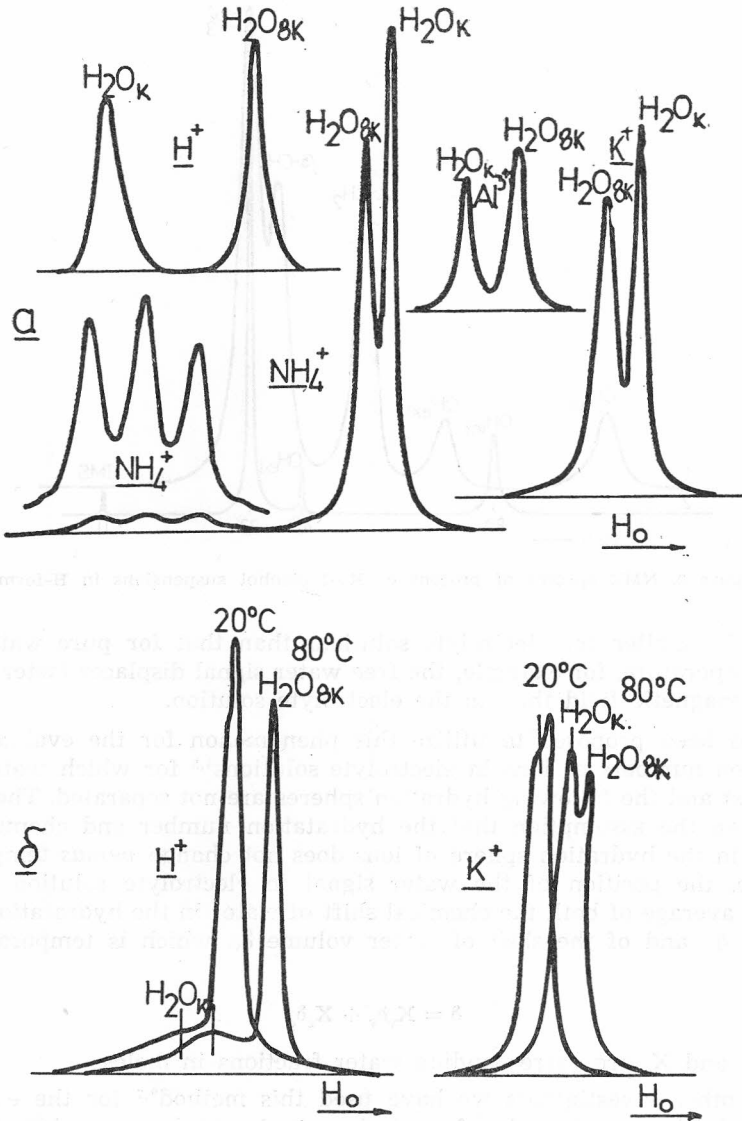


Figure 1. NMR spectra of protons of aqueous suspensions of $K\gamma$ -2 cationite, AB-17 (a) anionite and KB-4 (b) cationite.

towards the highest magnetic field. The dilution by the solvent, causing hydrogen bonds dissociation gives an effect equivalent to the increase in temperature. For pure water the signal displacement *versus* temperature is described by a linear function and its derivative $d\delta/dt$ is $0.95-0.98 \cdot 10^{-2}$ ppm/degree^{3,4}.

As the incorporation of ions of dissolved salts leads to the breakage of a part of hydrogen bonds in water, the shift of water signal *versus* temperature

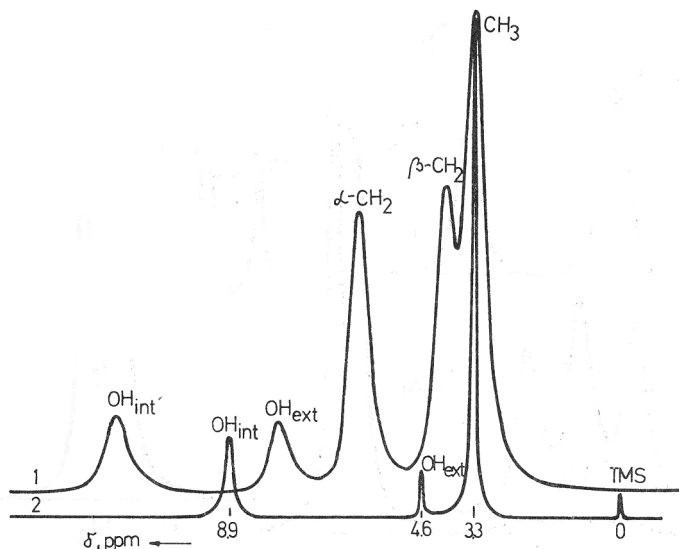


Figure 2. NMR spectra of protons of KY-2 alcohol suspensions in H-form.

variation is smaller for electrolyte solutions than that for pure water. At a rise in temperature, for example, the free water signal displaces faster towards the high magnetic field than in the electrolyte solution.

It has been proposed to utilize this phenomenon for the evaluation the hydration numbers of ions in electrolyte solutions^{4,5} for which water bands in the first and the following hydration spheres are not separated. The method is based on the assumption that the hydration number and chemical shift of water in the hydration sphere of ions does not change *versus* temperature. Therefore, the position of the water signal in electrolyte solution δ is the weighted average of both the chemical shift of water in the hydration sphere of cation δ_c , and of the shift of water volume δ_v , which is temperature dependent

$$\delta = X_v \delta_v + X_c \delta_c \quad (1)$$

where X_v and X_c are corresponding water fractions in moles.

Like other investigators we have used this method^{6,7} for the evaluation of the hydration numbers h , of counterions in ion-exchange resins. A simple expression⁸ has been derived:

$$h = \frac{58,1}{m} \frac{d\Delta}{dt}$$

where m is the effective molarity of the electrolyte solution resin in mol/l $d\Delta/dt$ -is, the temperature derivative of the difference between the signal positions of external water and water absorbed by ionite expressed in Hz/degree for a 100 MHz type spectrometer. It should be noted that for ion-exchange resins KY-2, AB-17, KB-4 the difference Δ is linearly dependent on temperature.

Table I presents the calculated hydration numbers in ionites obtained by the NMR technique and by water adsorption heat measurements as well as relevant data for electrolyte solutions obtained by other techniques.

The table shows that the hydration numbers of ion in aqueous electrolyte solutions and in ion-exchange resins are practically identical. Therefore, the mechanism of counterions hydration in ionites does not sufficiently differ from that in electrolyte solutions. The hydration numbers of univalent cations determined by different experimental methods do not exceed 3—4 and decrease with the increase in ion radius. For divalent cations the hydration numbers exceed coordination number 6. The great polarizing ability of these ions seems to lead to a perturbation of water structure not only in the first but also in the higher coordination spheres of ions.

All the experimental techniques give small hydration numbers for anions in solutions and in ion-exchange resins. This is usually explained by the poor solubility of anions. However, the results of the investigations suggest that the anion-water molecule interaction should not be neglected.

An analysis of the chemical shift values of water absorbed by ionites gives an insight into the mechanism of intermolecular interactions in the gel phase of resin. The magnitude of the chemical shift of water molecules in electrolyte solutions is determined by factors such as disturbance of hydrogen bond due to the reorientation of molecules under the actions of ions, changes in the water structure itself in the ion environment, the polarization effect bound to the effect of the electric field of the ion on the electronic distribution around the water hydrogen atoms and effects of nonelectrostatic nature⁹. In ion-exchange resins and on other adsorbents surfaces the formation of a developed lattice of hydrogen bonds between water molecules can hardly be expected. Thus, the main contributions to the chemical shift value is due to the polarization effect and to the disturbance of hydrogen bonds. For a resin in different salt forms one may take into account only the variations of the polarization contribution. Therefore, assuming the electrostatic mechanisms, the chemical shift will be determined by the electric field created by the ion at the place of water molecules. The error in the electrostatic calculation of the ion hydration energy caused by neglecting the covalence of bonds decreases with increasing ion radius, moreover, this error is small for the ions of alkali and alkaline earth elements having an electron shell like that of inert gases.

As it is known²⁴, the change of the nuclear magnetic screening constant in the presence of an electric field is determined by the ratio

$$\Delta\sigma = -AE_z - BE_z^2 \quad (2)$$

where A and B are constants depending on the chemical environment of the nucleus, E_z is the electric field directed along the axis of the bond containing the nucleus studied. For protons the greatest contribution to the screening change is due to the term linear in field whereas the quadratic term is negligible. The electric field created by the ion is proportional to its charge Ze and inversely proportional to ion radius τ^{-2} . The literature data on this problem are not uniform. In the given case the model of point charges does not adequately describe the electric ion-water molecule interaction. More precise calculations show that the comparison of ion hydration energies and their

chemical shifts should be based on the magnitude of τ^{-1} . The literature data on this problem are not uniform.

Figure 3 shows the dependences of chemical shifts of water on the magnitude of Ze/τ^2 for a number of ion-exchange forms of cationite KY-2 and anionite AB-17. One can see that the experimental values of chemical shifts for a number of alkali and alkaline earth elements fit well on the lines representing electrostatic interaction. The more polarizing the force of ions the greater the NMR signal shift towards the low magnetic field region.

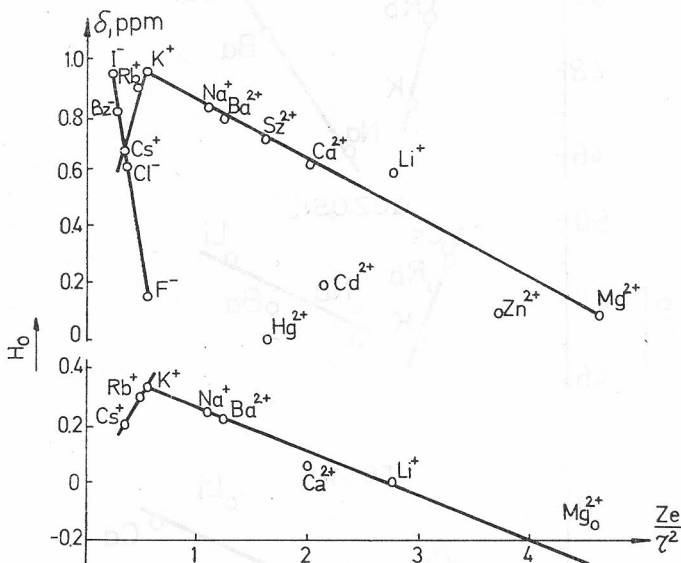


Figure 3. Dependence of the chemical shift of water protons on the value of ze/r^2 for ion-exchange forms of KY-2 cationite and AB-17 anionite.

The R_b — and C_s — forms of resin are an exception. For these cations an inverse dependence is observed: the shift of the NMR signal towards the low field increases with the increase of the cation radius. The anomalous behaviour of the cations charged by the R_b^+ and C_s^+ ions has also been discovered by other experimental techniques^{25,26}. It is ascribed to the peculiarities of the hydration of these ions. When the cation radius increases above a critical value the effect of its polarizing energy becomes smaller than that required for the reorientation of water molecules. The energy of interaction of water molecules with each other and with the adsorbed centres of resin exceed that of their interaction with cations. With the increase of the cation radius from R_b^+ to C_s^+ the competitive effect of hydrogen bonds also increases.

By extrapolating the line in Figure 3 up to the value of infinity for the ion radius, one may evaluate the interaction of water molecules with the fixed ion, since in this case water signal displacement is mainly determined by the formation of hydrogen bonds with the oxygen atoms of the SO_3^- ionite group. The displacement is about 1 ppm towards the higher field, in comparison with free water. For comparison we shall note that the signal of water vapour which has practically lost its hydrogen bonds is displaced 4.6 ppm

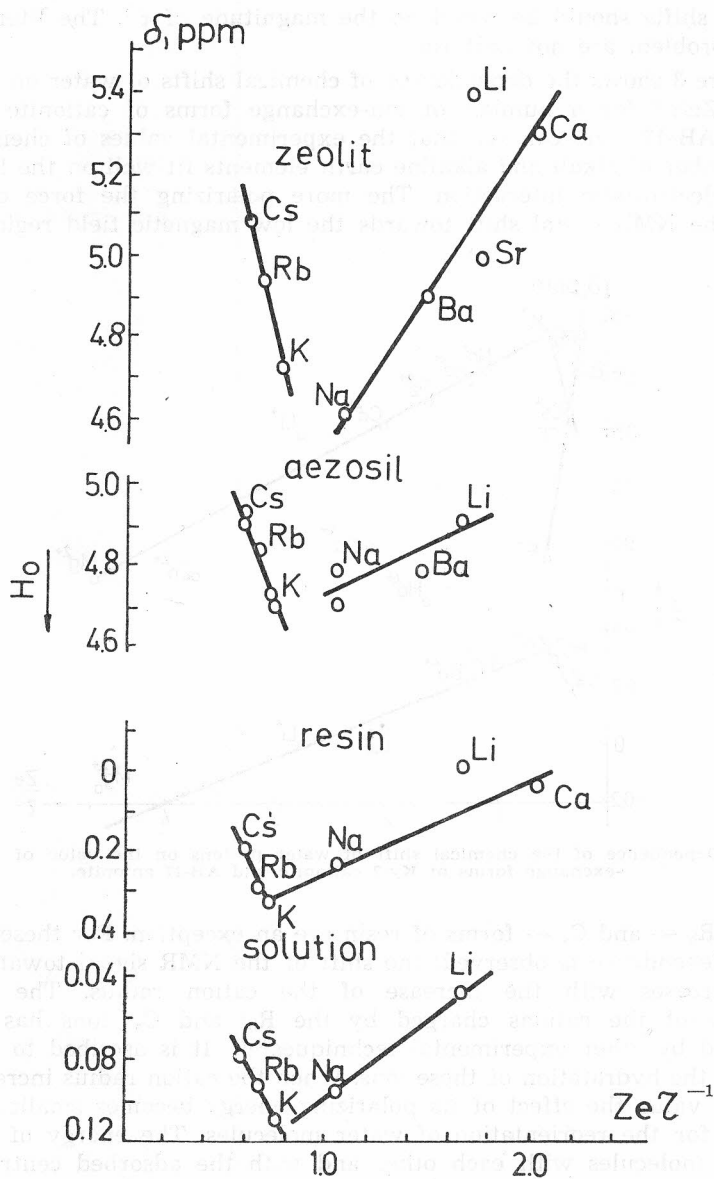


Figure 4. Dependence of the chemical shift of water protons adsorbed by zeolites, aerosil, ion-exchange resin and in aqueous solutions of corresponding salts on the value of ze/r^{-1} .

towards the higher field. Therefore, the water molecules in ionite form sufficiently strong hydrogen bonds with the oxygen ions of the sulphonic-acid groups.

As Figure 3 indicates the interaction of ions which have filled external d-electron orbitals (Hg^{2+} , Cd^{2+} , Zn^{2+}) with the water molecules, is not outlined by the electrostatic mechanism. It is known that these ions are capable of

forming complexes with environmental water due to the contact interaction of the d-electron orbitals of ions with the lone electron pairs of water molecules. In addition, with redistribution of the electronic density of water molecules on the orbitals of hydrated ions a decrease in electronic density round the hydrogen atoms of water molecules occurs. This causes additional signal displacement towards the low magnetic field (Figure 3).

The above mentioned mechanism of interaction of water molecules with cations of alkali and alkali-earth elements in ion-exchange resins is also typical for other systems (Figure 4). In aqueous electrolyte solutions, for example, the cation dependent water signal is displaced in the same way as in ionites²⁷. Similar chemical shift dependences have been observed for water adsorbed by the diamagnetic salt forms of zeolites and aerosils. Therefore, in hydration character on interface and in volume, *i. e.*, the quantity of water molecules interacting with ions and the nature of this interaction is identical.

There is a basic difference between the interaction of water molecules with cations and anions. Around a cation water is mostly oriented by its lone pairs of electrons, and formation of covalent bonds is possible. The interaction of an anion with near-by water molecules with their protons oriented towards the anion is similar to that of hydrogen bonds in pure water. As shown in Figure 3 the dependence of the position of the water signal on the square of the inverse radius of the exchange anion in AB-17 is also linear. The greater the size of the anion the greater the signal displacement toward the higher magnetic field, and the weaker the bonds. This displacement is also much greater than that for cations. Thus, the interaction of anions with water molecules may also be interpreted on the basis of the electrostatic mechanism. It is, however, more reasonable to compare chemical shifts with the electron — donor capacity of anions.

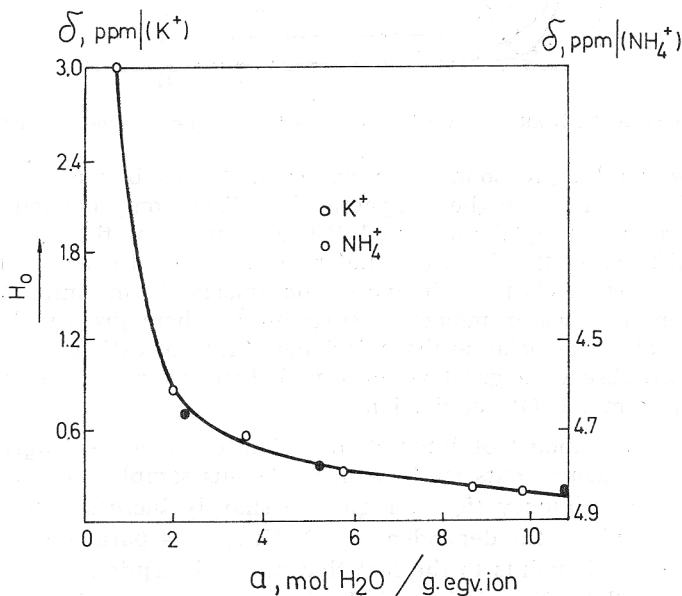


Figure 5. Chemical shifts of water in Ky-2 cationite in K- and NH₄-forms as a function of humidity.

Figure 5 shows the dependence of the chemical shift of water absorbed by K⁺ and the NH₄⁺ forms of KY-2 ionite on their humidity. During the removal of water from ionite a small signal displacement occurs towards the higher field, up to humidities of 2–3 mol H₂O/g equiv. ion. At lower humidities the signal displacement rapidly increases. The linewidth (Figure 6) changes in an analogous manner which indicates that the mobility of water molecules decreases at ionite dehydration. The water adsorption heat measurements indicated the same changes in molecular mobility. These dependences could be explained in the following way. At the beginning of the ionite dehydration process the removal of osmotically bound water, forming perfectly developed hydrogen bonds takes place. The slight signal displacement towards the higher field is explained by the increase in the relative contribution to the common signal of the water molecules bound with counterions and fixed

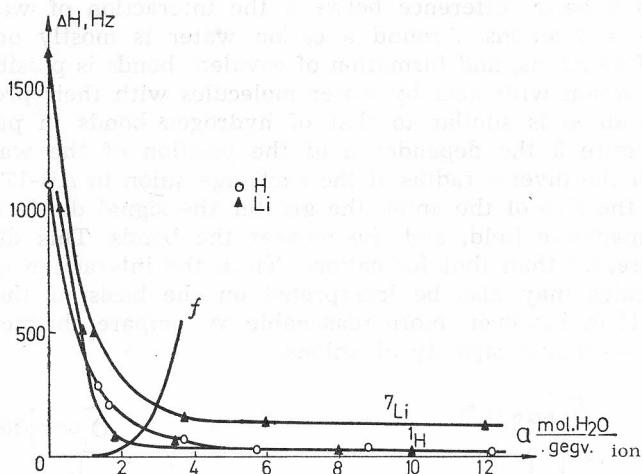


Figure 6. Change in the NMR bandwidth of protons in cationites depending on their humidity.

groups. The band corresponding to water molecules bound to fixed groups is displaced towards the higher magnetic field. When only bonded water molecules remain in ionite (about 3 mol H₂O/g equiv. ion) the character of the chemical shift and of the linewidth undergoes significant changes. The removal of these molecules leads to an increased ion association in ionite. The mobility of counterions and water molecules surrounding them greatly decreases and as the result of ion association the polarizing ability of cations sharply reduces. Therefore, we observe a great water signal displacement when humidity decreases below 3 mol H₂O/g equiv. ion

The described model of interaction in ionites is in good agreement with the dielectric measurements made with analogous samples. The critical dielectric relaxation frequency (f_{kp} in Figure 6) sharply increases in the range of resin humidity where the dependence of NMR spectra parameters on humidity becomes weak. This points to the fact that at an absorption of 2–3 mol H₂O/g equiv. ion complete dissociation of the ionogenic group of resin occurs and that a joint mobility of counterions and of surrounding water molecules

begins. These conclusions are also in good agreement with the results of the ir-spectroscopic investigations made by Zundel²⁸.

The distinction between the water bound to the active groups of ionite and the water bound osmotically becomes more evident at low temperatures. The latter freezes at a temperature of about 0 °C whereas bound water remains mobile below 0 °C. This is deduced from the temperature dependence of the intensity of the water signal in ionite. At 0 °C the signal of »external« water and that of a part of »internal« water in the ionite suspension (as the result of its freezing) becomes so broad that it is inconvenient to observe it by a high-resolution spectrometer. The band of ice protons is 4 orders wider than that of water in ionite. Therefore, in the NMR spectrum of water suspensions of ionite the band of »external« water disappears and the band of »internal« water decreases in intensity. Figure 7. shows variations of the area below

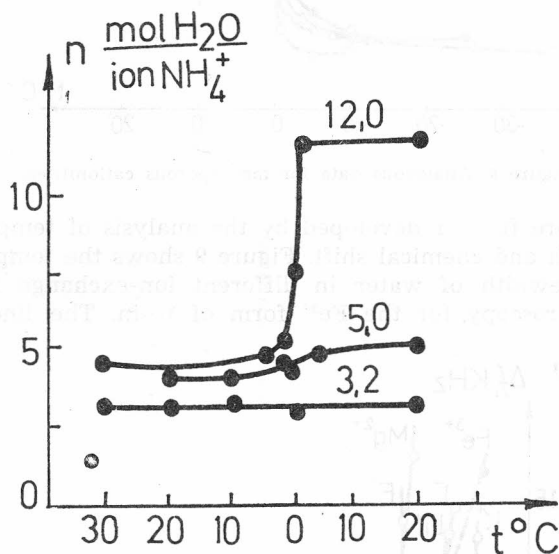


Figure 7. Temperature changes of the absorption curve areas of water protons in cationites for different quantities of unfrozen water.

the absorption curve of the NMR signal of water *versus* temperature. It is obvious that in spite of the initial humidity of resin, equal quantities of water remain unfrozen below 0 °C. If resin humidity is less than that this limiting value, no change in signal intensity occurs at temperatures below 0 °C. It should also be noted that this limiting value of unfrozen water calculated in g equiv. ion coincides with the hydration numbers determined above. Hence, one may assume that below 0 °C, the water which is directly bound to counterions and fixed ions remains mobile in ionite. The results of investigations on macroreticular cationites have led to an analogous conclusion (Figure 8). They have shown that irrespective of the initial humidity the quantities of unfrozen water below 0 °C are equal.

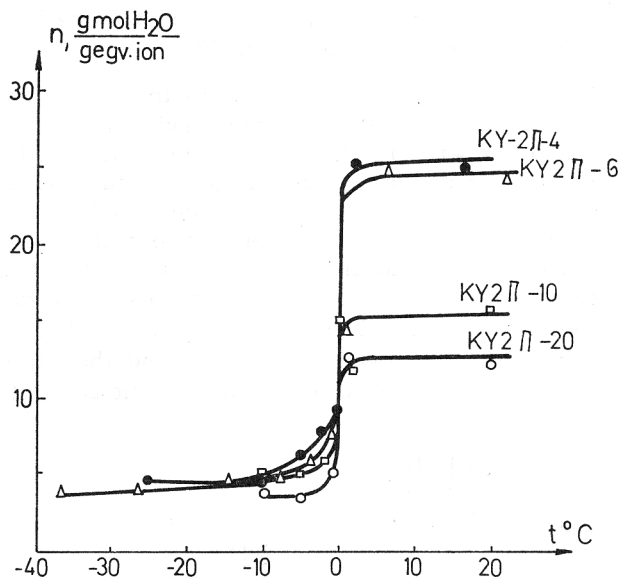


Figure 8. Analogous data for macroporous cationites.

These ideas are further developed by the analysis of temperature dependence of linewidth and chemical shift. Figure 9 shows the temperature dependence of the linewidth of water in different ion-exchange forms and the results of γ -spectroscopy for the Fe^{3+} form of resin. The linewidth slightly

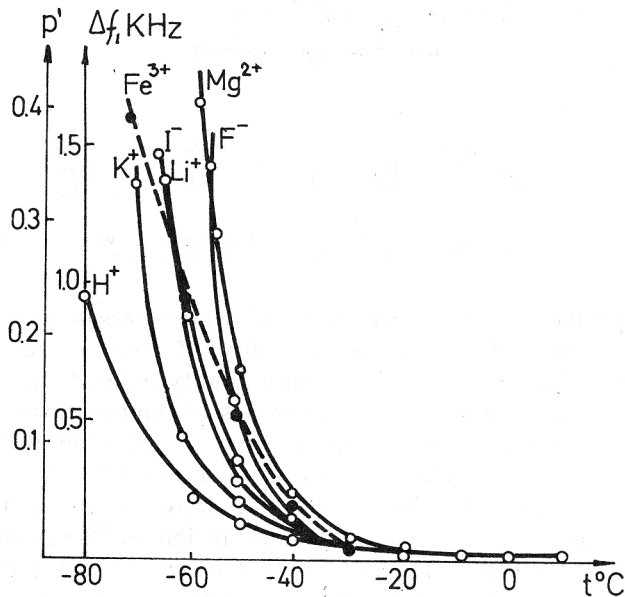


Figure 9. Temperature dependence of the bandwidth of water protons in Ky-2 cationite and the possibilities of the Mössbauer effect.

increases when cooling the samples from -20 to -30 °C, whereafter a strong increase is observed. It is worth noting that below 0 °C the observed signal is due to unfrozen water only, whereas above 0 °C is due to the entire water absorbed by ionite. The sharp broadening of water signal depends on the kind of counterion. The greater the hydration ability of the ion the higher the temperature when the broadening of the signal appears. Thus, a correlation is observed between the broadening of signals and the hydration ability of counterions. However, the freezing temperature of the aqueous solutions of corresponding salts decreases.

Therefore, the phenomenon of water thawing in the pores of ionites and other disperse systems which we mentioned is mainly associated with the disturbance of hydrogen intermolecular bond typical for free water. It is known that the freezing temperature of water with no hydrogen bonds (by analogy with hydrides of oxygen group) would be 120 °C lower.

The probability of the Mössbauer effect (Figure 9) also increases sharply in the temperature range where a strong broadening of the NMR lines occurs. Therefore, there is a sharp decrease in the progressive mobility of counterions and water molecules at the same temperature. This also shows that below 0 °C water molecules bound to counterions with which they perform combined movement remain mobile.

Parallel investigations of the NMR linewidth of water protons and ${}^7\text{Li}$ nuclei of counterions in the Li-form of KY-2 resin (Figure 10) and of the

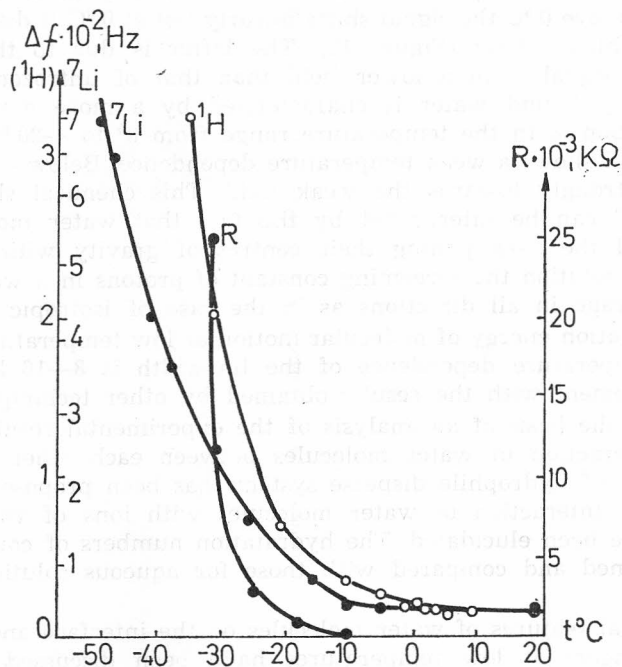


Figure 10. Bandwidth of water protons and Li nuclei in the Li-form of K-2 resin as a function of temperature.

electric conductivity of ionite (Figure 11) also corroborates the model of intermolecular interaction in ionites which we have proposed.

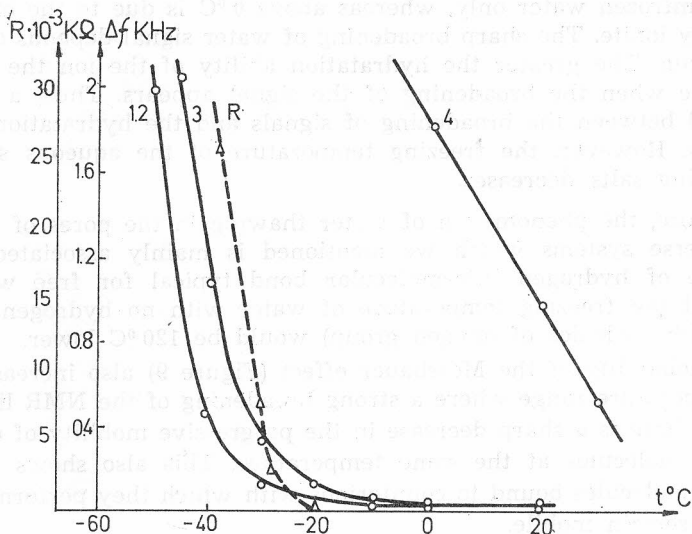


Figure 11. Temperature dependence of the NMR bandwidth and of the electric resistance (R) in $K\gamma$ -2 cationite.

The temperature dependence of chemical shifts is more complex. At a temperature above 0°C the signal shifts linearly but at 0°C it displaces sharply towards the higher field (Figure 12). The latter is due to the freezing of water whose signal is in a lower field than that of unfrozen water, since the osmotically bound water is characterized by a more developed lattice of hydrogen bonds. In the temperature range from 0° to -20°C the position of water signal shows a weak temperature dependence. Below -20°C it starts to displace strongly towards the weak field. This chemical shift behaviour below -20°C can be interpreted by the fact that water molecules rotate mainly round the axes joining their centres of gravity with ions. As the result of this rotation the screening constant of protons in a water molecules does not average in all directions as in the case of isotropic rotation.

The activation energy of molecular motion at low temperatures, calculated from the temperature dependence of the linewidth is 8–16 kcal/mol. It is in good agreement with the results obtained by other techniques.

Thus, on the basis of an analysis of the experimental results obtained, a model of interaction of water molecules between each other and with the active centres of hydrophile disperse systems has been proposed. The peculiarities of the interaction of water molecules with ions of various electron structure have been elucidated. The hydration numbers of counterions have been determined and compared with those for aqueous solutions of corresponding salts.

The special features of water molecules on the interface and in the pores of ion-exchangers at low temperatures have been discussed. The role of hydrogen bonds in the determination of the freezing temperature of water has been elucidated.

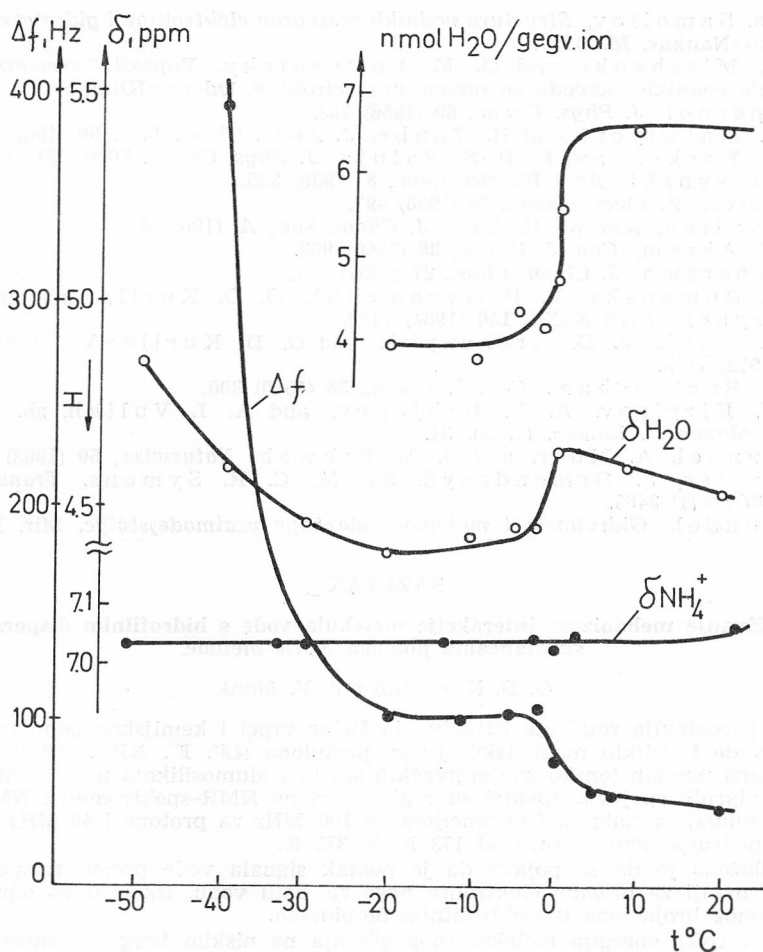


Figure 12. Temperature dependence of chemical shifts, quantities of unfrozen water and NMR bandwidths in NH_4 -form K_Y -2 cationite.

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SAŽETAK

Istraživanje mehanizma interakcije molekula vode s hidrofilnim disperznim supstancama pomoću NMR metode

O. D. Kurilenko i V. V. Mank

Rad predstavlja rezultate istraživanja širine vrpce i kemijskog pomaka NMR-a protona vode i velikih magnetskih jezgri protuiona (Li^+ , F^- , NH_4^+ , H^+) u vodenim disperzijama mnogih ionsko-izmjenjivačkih smola i alumosilikata u otopinama visoko-molekularnih spojeva. Spektri su registrirani na NMR-spektrometru NM-4H-100 visoke rezolucije s radnom frekvencijom od 100 MHz za protone i 40 MHz za ^7Li u širokom području temperatura od 173 K do 373 K.

Predloženo je da se pojava da je pomak signala vode prema temperaturnoj promjeni manji za otopine elektrolita nego za čistu vodu, iskoristi za određivanje hidratacionog broja iona u elektrolitnim otopinama.

Aktivacijska energija molekularnog gibanja na niskim temperaturama, izračunata iz temperaturne ovisnosti širine vrpce, je 8–16 kcal mol⁻¹, što se dobro slaže s rezultatima dobivenim drugim tehnikama.

Predložen je model interakcije molekula vode međusobno i s aktivnim centrima hidrofilnih disperznih sistema. Osvijetljene su specifičnosti interakcije molekula vode s ionima različitih elektronskih struktura. Hidratacijski brojevi protuiona su određeni i uspoređeni s onima za vodene otopine različitih soli. Diskutirana su posebna svojstva vodenih molekula na međupovršini i u porama ionskih izmjenjivača pri niskim temperaturama. Objasnjena je uloga vodikovih veza kod određivanja ledišta vode.

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