

^1H NMR Studies of Ion Exchange Resins in Light and Heavy Water

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We have determined the solvent regains and proton magnetic resonance spectra of the following ion exchange resins: Dowex 50W-X8 ionic forms Na^+ , K^+ , NH_4^+ , Mg^{2+} , Zn^{2+} , and six resins Dowex 50W ionic form H^+ with different cross-linkages. At room temperature, all of the resins we studied adsorb larger mol amounts of H_2O than of D_2O . At 308 K the chemical shifts of interior water of the metal form resins as referred to the exterior water signals of the same samples are nearly equal in H_2O and D_2O . The widths of both the interior and the exterior water lines are smaller in D_2O than in H_2O , which is most readily explained with smaller dipole-dipole interactions in the former solvent. This implies that the dipolar effect is one of the main reasons for line broadening in resin suspensions, which contradicts the views of earlier investigators. In H_2O the chemical shifts of the hydrogen form resins calculated per unit mol fraction of hydronium ion are independent of the acid concentration, $s/p = 11.7 \pm 0.2$, indicating that the resin acid is completely ionized. In D_2O the absolute values of the shifts are larger and go through a maximum with decreasing acid concentration approaching the H_2O suspension value in dilute acid solutions. This behavior is believed to be connected with the large solvent uptake of the resins with low cross-linkage.

The sulfonated polystyrene cation exchangers suspended in water usually exhibit two distinct ^1H NMR peaks.¹ One peak is very similar to that of pure water, and it is caused by the exterior water outside the resin particles. The other peak caused by the interior water within the resin bead resembles the peaks yielded by solutions of strong electrolytes. This establishes the strong electrolyte model of these ion exchangers.¹ To study electrolytic solutions,

substituting the ordinary light water with heavy water, deuterium oxide, has proven to be a very fruitful research procedure.² Here it is applied to ^1H NMR studies of a number of cation exchange resins. We expected the resonance of the remaining protons in heavy water to give information of their molecular environment in the suspended resin bead.

EXPERIMENTAL

Commercial sulfonated polystyrene resins Dowex 50W, 50 to 100 mesh, manufactured by Dow Chemical Co., were used in the experiments. The resins, originally in the hydrogen form, were washed with methanol, analytical grade hydrochloric acid, and distilled water. The exchange capacities were determined by a standard titrimetric method,³ and the molecular weights of the various ionic forms were calculated from the results. (One mol of resin is defined as the amount which contains a number of sulfonic acid groups equal to Avogadro's number.) Portions of the X8 hydrogen form resin were converted to other ionic forms in column using a tenfold amount of Merck's analytical grade metal chlorides. All the resins were dried overnight at 120 °C before further use. The solvent regains of the resins were determined at room temperature by a centrifugal method described by Creekmore and Reilly.⁴ The repeated determinations were consistent within 2%. The electrolytic concentrations in the interior solvents (inner concentrations) were calculated from the solvent regains and molecular weights of the resins and were expressed in aquamolalities⁵ (mol of solute per 55.51 mol of water species L_2O). The deuterium oxide was manufactured by Norsk Hydro-elektrisk Kvaestofaktieselskab; its deuterium fraction was 0.997.

The NMR samples were prepared by suspending 450 mg of dry resin in 1.00 ml of solvent in 5 mm NMR tubes (Wilmad Glass, New Jersey). In the case of the X8 resins this procedure gave a swollen resin layer about 35 mm high with 10 mm of solvent on top of it. The samples were allowed to stand at least for a few hours, since immediately after suspending there are three proton resonance peaks.⁶ The spectra were obtained using a JEOL JNM-PMX 60 magnetic resonance spectrometer (60 MHz) with a probe temperature of 35 °C. The sweep was in the direction of increasing field, and means of at least two spectrometric runs were used. The chemical shifts were measured on calibrated chart papers with an accuracy of 0.5 Hz.

RESULTS AND DISCUSSION

The results of the measurements with various ionic forms of the Dowex 50W-X8 resins are presented in Table 1. Preliminary experiments were carried out on lithium, cesium and barium forms, too, but because the two proton peaks were not resolved these forms were omitted. It appears that all of the resinates adsorb larger mol amounts of H₂O than of D₂O implying that the inner electrolytic solutions are more concentrated in the latter case. This agrees with the results of adsorption experiments from vapor phase.⁷ The chemical shifts of interior water were measured with respect to the exterior water signal of the same samples, since this reference is the most distinct in this case. The usual

reference ion NH₄⁺ is now unsuitable because of its poor spectral resolution in D₂O and the theoretical difficulties caused by hydrogen exchange reactions. No susceptibility corrections were applied, since they are believed to be small with spherical resin particles.^{4,8} Measurements of the hydrogen form resin in various heavy water solutions revealed that the chemical shift is a nearly linear function of the deuterium fraction (with a small negative deviation from ideal). Thus, the result of the H⁺ resin originally obtained in 97.7% D₂O was corrected to pure D₂O by a short extrapolation. The results are best interpreted in terms of the chemical shifts in unit concentration, δ/m , the accuracy of which is here believed to be better than 5%. The δ/m values measured in H₂O agree moderately well with the earlier results of Gordon,⁹ Gough and co-workers,^{6,8} and Howery and co-workers.¹⁰ The small variance arises mainly from the differences in water regain measurements and partly from the different probe temperatures. We found no reference values in the literature for the D₂O samples. Excluding the H⁺ form resin, the chemical shifts in H₂O and D₂O are almost equal. Thus, there are no great differences between the environments of the L₂O protons in the isotopically different waters. Except for the Na⁺ resin, the interior water resonance in D₂O occurs, however, at a little lower field relative to the exterior water than in H₂O. This can be explained in two ways: (i) In the D₂O samples the HDO protons are actually less shielded

Table 1. Results of the NMR measurements with the Dowex 50W X8 resins suspended in H₂O and D₂O. The chemical shifts are referred to the exterior water peaks of the same resins.

Ionic form	Solvent	Inner aqua-molality m	Chemical shift of interior water		Line widths at half height	
			δ	δ/m	interior W _i /Hz	exterior W _e /Hz
H ⁺	H ₂ O	4.53	-84.0	-18.5	9.0	9.5
H ⁺	D ₂ O	4.63	-108.3	-23.4	8.0	6.5
Na ⁺	H ₂ O	5.32	15.9	3.0	14.0	20.0
Na ⁺	D ₂ O	5.34	16.8	3.1	6.5	14.0
K ⁺	H ₂ O	6.05	17.3	2.9	6.0	13.0
K ⁺	D ₂ O	6.17	17.2	2.8	4.5	12.0
NH ₄ ⁺	H ₂ O	5.23	5.2	1.0	(8.5)	(11)
NH ₄ ⁺	D ₂ O	5.37	(4.5)	(0.8)	(5.5)	(10)
Mg ²⁺	H ₂ O	5.43	-15.2	-2.8	13.5	14.5
Mg ²⁺	D ₂ O	5.61	-16.7	-3.0	6.5	10.5
Zn ²⁺	H ₂ O	5.09	-24.0	-4.7	8.0	15.0
Zn ²⁺	D ₂ O	5.21	-24.9	-4.8	7.0	14.0

or (ii) the reference peak is shifted upfield. Which of the explanations is correct, cannot be deduced from the present data.

It is hard to explain the line widths of the water protons in resin suspensions. In the case of the acid form Dowex 50W-8X resin the longitudinal relaxation times T_1 are 2.9 and 0.45 s for the exterior and the interior water protons, respectively.¹¹ This implies much narrower lines than those actually observed. Neither is the exchange of water between bound and free forms believed to cause the broadening.^{9,11,12} Gordon⁹ concluded that the difference in volume magnetic susceptibilities between the bulky solvent and the resin matrix is responsible for the broadening of the exterior water line; the broadening of the interior water line he ascribed to the heterogeneity of the resin particles. In Frankel's opinion¹² the broadening in both cases is caused by susceptibility effects. The lines in H₂O suspensions observed in this study are of the same widths as reported earlier.^{9,10,12} As a new feature we found a clear narrowing of all lines when H₂O was replaced with D₂O. This cannot be explained by any differences in the physical structure of the resin particles, such as heterogeneity, because in both cases the samples were prepared identically from the same resin. It is also hard to believe that the small differences between the susceptibilities¹³ of various water species could give rise to the observed changes in line widths. It seems that they are most readily explained with a dipolar effect. The magnetic dipoles

of H and D are 2.79 and 0.86 Bohr magnetons,¹⁴ respectively. When H₂O is replaced with D₂O the dipole-dipole interactions observed by the remaining protons are decreased. This results in larger homogeneity in the local magnetic field and, consequently, in narrower lines. This explanation implies that the dipolar effect is one of the main reasons for line broadening, which contradicts the views of the earlier investigators.^{9,12}

As the chemical shifts of the hydrogen form resin were interesting, the experiments were extended to resins of other cross-linkages. The results given in Table 2 show that the adsorption of H₂O is larger than of D₂O. In absolute value the chemical shifts are larger in D₂O than in H₂O. To get a more detailed view of the behavior of the resin acid the experimental results were subjected to the customary treatment.¹⁵⁻¹⁸ In the solutions of strong monobasic acids the mol fraction p of protons in hydronium ions is given by Gutowsky's variable¹⁵ $p = 3x/(2-x)$, where x is the stoichiometric mol fraction of the acid. When the chemical shifts $|s|$ obtained from the acid solutions are divided by p , the chemical shift $\delta_{\text{H}_3\text{O}^+}$ of proton in unit mol fraction is obtained. This parameter should, of course, be constant at a constant temperature for all strong acids, but the experimental values for different acids in H₂O vary between 9.1 and 14.5 ppm.¹⁸ The variance is usually explained by anion hydration effects.¹⁸⁻²⁰ According to the present data the chemical shift $\delta_{\text{H}_3\text{O}^+}$ for the resin acid is essentially constant, 11.7 ± 0.2 (standard error),

Table 2. The dependence of the chemical shifts of the hydrogen form Dowex 50W resins on the cross-linkage. The shifts are referred to the exterior water peak of the same resins and corrected to pure D₂O. The parameter p is Gutowsky's variable.

Cross-linkage	Solvent	Inner aquamolality m	Mol fraction of the acid x	Chemical shift		$\delta_{\text{H}_3\text{O}^+} = s /p$
				$-\delta/\text{Hz}$	$-s/\text{ppm}$	
1X	H ₂ O	0.965	0.0171	16.8	0.280	10.8
1X	D ₂ O	0.977	0.0173	17.8	0.297	11.3
2X	H ₂ O	1.75	0.0306	33.2	0.553	11.9
2X	D ₂ O	1.78	0.0310	35.9	0.598	12.7
4X	H ₂ O	2.68	0.0461	49.6	0.827	11.7
4X	D ₂ O	2.72	0.0466	57.6	0.960	13.4
8X	H ₂ O	4.53	0.0754	84.0	1.400	11.9
8X	D ₂ O	4.63	0.0770	108.3	1.805	15.0
12X	H ₂ O	6.08	0.0986	108.3	1.805	11.6
12X	D ₂ O	6.16	0.0999	144.4	2.407	15.3
16X	H ₂ O	7.49	0.1189	138.0	2.300	12.1
16X	D ₂ O	7.56	0.1199	170.8	2.847	14.9

indicating that the acid is completely ionized. A little lower value, 11.2 ± 0.2 , can be calculated from the measurements of Gough and co-workers.⁶ These values may be compared with the chemical shift $\delta_{\text{H}_3\text{O}^+} = 11.5 \pm 0.3$ obtained for polystyrene sulfonic acid by Kotin and Nagasawa.²¹

Adding deuterium oxide to hydrogen form resin samples increases the absolute value of the chemical shift $\delta_{\text{H}_3\text{O}^+}$, as was observed also in the cases of nitric and perchloric acids by Duerst and co-workers.^{16,17} They explained the effect by the preference of H to reside on hydronium ion, and the same explanation is, in principle, valid also in the case of resin acid. The situation here is, however, a little more complicated: With the said acids the *s/p* value increases or remains constant with decreasing mol fraction *x*; here it goes through a maximum approaching the value of H₂O suspension in dilute acid solutions. Apparently the resin matrix adsorbs H₂O and HDO molecules more readily than D₂O molecules, and therefore the hydronium ions L₃O⁺ are not as preferred by protons as in the case of homogenous solutions of nitric and perchloric acids.

Acknowledgement. The English language of the manuscript was checked by Ms. Kyllikki Kauppinen-Walin, translator.

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Received April 2, 1979.