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### Nuclear Magnetic Resonance Studies of Ion-Exchange Resins. I. Effect of Counter Ion

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# Nuclear Magnetic Resonance Studies of Ion-Exchange Resins.

## I. Effect of Counter Ion\*

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### SUMMARY

The nuclear magnetic resonance spectra of packed beds containing the cation exchanger Dowex 50W-X8 in water vary with counter ion. Chemical shifts for water protons internal to the resin bead are in the order  $H^+$  (lowest frequency)  $\ll Zn^{2+} \approx Cd^{2+} < Pb^{2+} \approx Mg^{2+} < Ag^+ < Ca^{2+} \approx Tl^+ \approx NEt_4^+ \approx Ba^{2+} \approx Li^+ \approx NMe_4^+ \approx Sr^{2+} < NH_4^+ < Rb^+ \approx K^+ \approx Na^+ \approx NBu_4^+$ . The concentrated electrolyte model of ion-exchange resins is substantiated by generally good agreement between 1) chemical shifts/g equiv./kg for cations in aqueous solutions referred to  $NH_4^+$  and 2) chemical shifts/g equiv./kg for resin forms referred to  $NH_4^+$  form resin.

### INTRODUCTION

The methods of nuclear magnetic resonance spectroscopy furnish information on the solvent structure within ion exchange resins. The work of Gordon [1] suggests many possibilities for using NMR to study ion exchanger-solvent systems. Two relatively narrow proton peaks are generally observed for packed beds containing ion exchange resins in water, implying

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that water proton exchange within the bead is quite rapid while exchange between external (interstitial) water and internal water is relatively slow [2]. Protons on the hydrocarbon polymer matrix produce a broad solid-like band which is not observable on a 60 MHz spectrometer [3]. The proton spectrum arises from two thermodynamically distinct phases: an external solution phase and an internal resin phase.

## EXPERIMENTAL

The cation exchanger used was Dowex 50W-X8, Analytical Grade, 20-50 mesh, purchased from Bio-Rad Laboratories. Samples were converted to the various ionic forms by elution for one full day or more with usually a 100-fold or more excess of the appropriate salt. All salts were Analytical Grade except  $\text{RbNO}_3$  from Alfa Inorganics, and  $\text{TlNO}_3$  and the tetra-alkylammonium halides from Fisher. Overnight elution with water ensured removal of imbibed electrolyte.

Spectra of the thoroughly tapped packed beds were obtained on a Varian A-60A spectrometer at ambient temperature (40-42°C) using a chloroform-TMS external reference. Spectra of at least two samples prepared at different times for each ionic form were obtained; five spectra which agreed to within  $\pm 0.2$  Hz were obtained for each sample. Samples which gave only one peak were further checked by carefully removing resin to see if the internal and external peaks were separable.

## RESULTS AND DISCUSSION

The results are summarized in Table 1 in which are given for each resin form the chemical shift of the internal protons,  $\tau_i$ , and the chemical shift of the external water protons,  $\tau_e$ ; the width at half height of the internal water peak,  $W_i$ , and the width at half height of the interstitial water peak,  $W_e$ ; and the ratio of the integral of the internal peak to the integral of the external peak,  $I_i/I_e$ . The uncertainties in the  $\tau$  and  $W$  are of the order  $\pm 1$  Hz; because the internal and external peaks generally overlapped considerably, the uncertainty in  $I_i/I_e$  is  $\pm 10\%$  or greater.

The effect of ions on the structure of water has been reviewed in depth by Kavanau [4], while Diamond and Whitney [5] and Reichenberg [6] have discussed in detail the interactions one would expect in the resin phase. Probably the main difference between water structure in

concentrated solutions of electrolytes and water structure in ion exchangers of comparable internal molalities is that the water in a resin, though forming a continuous phase, exists primarily in small "pockets" about the ion exchange sites.

### Interpretation of Chemical Shifts

Chemical shifts for electrolytes in water are usually explained in terms of the discussion of Shoolery and Alder [7]. The interpretation has been further refined by many including Hindman [8] and Franconi and Conti [9]. The two primary effects are 1) an upfield shift due to breaking of hydrogen bonds and 2) a downfield shift arising from polarization of the water molecules by the ions. These ideas should apply equally well to ion exchangers if the magnitude of the internal molality is taken into account [10] and if ion pairing is not enhanced within the resin phase.

Referring to Table 1, we see that the internal chemical shifts do follow the trend one would expect from charge density and size considerations. For example, the internal peaks of monovalent ionic forms are generally upfield to those of divalent ionic forms. The internal peak for the  $H^+$  form is furthest downfield due to the ability of the proton to promote additional structuring of the internal water. Peaks of Ag and Tl forms are downfield to water as anticipated from the relatively large polarizabilities of these ions [11]; differences in polarizability probably explain why the Zn and Cd forms resonate further downfield than the alkaline earth forms. Frank [12] reports that  $NBu_4^+$  is a strong structure maker, but such a conclusion apparently does not hold for this high molality resin. The chemical shifts of the smaller tetraalkylammonium ions,  $NMe_4^+$  and  $NEt_4^+$ , do indicate slight structure making as compared to the  $NH_4^+$  form, consistent for these ions with investigations in solutions [4].

### Reference for Resin Shifts

If we choose the  $NH_4^+$  form as our reference and take into account the internal molalities of the resin forms, we calculate the chemical shifts, in ppm/g equiv./kg of water, given in Table 2. Some values relative to the ammonium ion assigned to cations in aqueous solution are shown for comparison. The generally favorable agreement between resin and solution shifts reinforces the generally accepted description of the resin as a concentrated electrolyte. We follow Hindman [8] in choosing  $NH_4^+$  as the reference, since this ion probably least disrupts the normal structure of

Table 1. Data from NMR Spectra of Packed Beds of Ion Exchangers

[Spectra of Dowex 50W-X8, 20-50 mesh, taken at ambient temperature (40-42°C.) on Varian A-60 A spectrometer. All  $\tau$  values relative to TMS external standard.]

Resin form	$\tau_1^a$	$\tau_e^b$	$W_1^c$	$W_e^d$	$I_1/I_e^e$
H <sup>+</sup>	3.93	5.34	8	5	0.8
Li <sup>+</sup>		5.32 <sup>f</sup>			6 <sup>f</sup>
Na <sup>+</sup>	5.60	5.35	6	11	.7
K <sup>+</sup>	5.60	5.32	7	11	.6
Rb <sup>+</sup>	5.58	5.32	8	14	.6
Ag <sup>+</sup>		5.17 <sup>g</sup>			20 <sup>g</sup>
Tl <sup>+</sup>		5.25 <sup>h</sup>			15 <sup>h</sup>
NH <sub>4</sub> <sup>+</sup>	5.45	5.34	5	9	.5
NMe <sub>4</sub> <sup>+</sup>		5.33 <sup>f</sup>			10 <sup>f</sup>
NEt <sub>4</sub> <sup>+</sup>		5.30 <sup>f</sup>			10 <sup>f</sup>
NBu <sub>4</sub> <sup>+</sup>	5.63	5.34	14	8	.2

Mg <sup>2+</sup>	5.00	5.30	11	10	.9
Ca <sup>2+</sup>		5.25 <sup>f</sup>		10 <sup>f</sup>	-
Sr <sup>2+</sup>		5.33 <sup>f</sup>		11 <sup>f</sup>	-
Ba <sup>2+</sup>		5.30 <sup>f</sup>		16 <sup>f</sup>	-
Zn <sup>2+</sup>	4.90	5.30	10	13	.6
Cd <sup>2+</sup>	4.93	5.30	13	13	.9
Pb <sup>2+</sup>		5.00 <sup>i</sup>		34 <sup>i</sup>	-

<sup>a</sup>Chemical shift for internal water, ppm.

<sup>b</sup>Chemical shift for external water, ppm.

<sup>c</sup>Half height width for internal peak, Hz.

<sup>d</sup>Half height width for external peak, Hz.

<sup>e</sup>Ratio of integral of internal peak to integral of external peak.

<sup>f</sup>One symmetrical peak, unseparable.

<sup>g</sup>One peak with shoulder upfield, unseparable.

<sup>h</sup>One peak with shoulder downfield, separable into internal peak at 5.25 and external peak at 5.30, equilibration at pH 3.5.

<sup>i</sup>One peak with shoulder upfield, separable into internal peak at 4.98 and external peak at 5.30, equilibration at pH 3.0.

Table 2. Comparison of Chemical Shifts

Cation	$\tau_i^{\text{O}^a}$	$\tau_a^{\text{O}^b}$
H <sup>+</sup>	-0.30 <sub>4</sub>	-0.34 <sub>6</sub>
Li <sup>+</sup>	-0.02 <sub>8</sub>	-0.01 <sub>6</sub>
Na <sup>+</sup>	0.02 <sub>7</sub>	0.05 <sub>0</sub>
K <sup>+</sup>	0.02 <sub>5</sub>	0.04 <sub>7</sub>
Rb <sup>+</sup>	0.02 <sub>1</sub>	0.03 <sub>7</sub>
Ag <sup>+</sup>	-0.05	-0.05 <sub>2</sub>
Tl <sup>+</sup>	-0.02	-
NH <sub>4</sub> <sup>+</sup>	0.000	0.000
NMe <sub>4</sub> <sup>+</sup>	-0.02	-
NEt <sub>4</sub> <sup>+</sup>	-0.02	-
NBu <sub>4</sub> <sup>+</sup>	0.01	-
Mg <sup>2+</sup>	-0.04 <sub>0</sub>	-0.09
Ca <sup>2+</sup>	-0.02	-0.02
Sr <sup>2+</sup>	-0.01	-0.01
Ba <sup>2+</sup>	-0.01	0.01
Zn <sup>2+</sup>	-0.05 <sub>0</sub>	-
Cd <sup>2+</sup>	-0.04 <sub>3</sub>	-
Pb <sup>2+</sup>	-0.03 <sub>0</sub>	-

<sup>a</sup>Chemical shift of cation in resin, referred to NH<sub>4</sub><sup>+</sup> form resin, ppm/g equiv./kg.

<sup>b</sup>Chemical shift of cation in aqueous solution, referred to NH<sub>4</sub><sup>+</sup> (aq.), ppm/g equiv./kg.

water [4]. Internal molalities were calculated from the data of Bonner and Smith [13] and Gregor et al. [14]. The internal molality of the NBu<sub>4</sub><sup>+</sup> form was determined by us using the method of Pepper et al. [15]. From the observed resonance and the molality of the NH<sub>4</sub><sup>+</sup> form, it is inferred that the sulfonate exchange sites produce a shift of 0.02 ppm/g equiv./kg upfield relative to water.

Aqueous molal shifts for the Group I cations were taken from the work of Hindman [8]. Average molal shifts for several anions were calculated from Hindman's data for 1:1 salts (which had been corrected for bulk susceptibility differences between the solutions and water) [8]. Then, assuming additivity of chemical shifts, average molal shifts for the Group II cations were calculated from the data of Franconi and Conti [9] for

2:1 electrolytes. Since the resin and aqueous shifts agree so well, it may be that the bulk susceptibilities of the resins and of water are nearly identical, as suggested by Gordon [1]. We cannot explain why the  $Mg^{2+}$  form shift is out of line with the aqueous solution value.

Not shown in Table 1 is the fact that  $Be^{2+}$  and  $Al^{3+}$  forms of Dowex 50 show downfield shifts almost as great as that of the  $H^+$  form. The width at half-height for both forms is in excess of 25 Hz, possibly indicating slow exchange between internal water protons and the various hydrolyzed species of the counter ion. These resin forms were prepared by elution with 1N salt solutions at pH's of 2.0 and 2.1, respectively. Since  $Be^{2+}$  and  $Al^{3+}$  uptakes were not determined, the observed shifts have only a qualitative significance.

Our results clearly substantiate the findings of Reichenberg and Lawrenson [10] that resin chemical shifts are uniquely related to the internal molality of a given form of resin. The resin matrix does not appear to play any major role in determining the internal water proton resonance. Since resin beads are near perfect spheres, one does not have to correct internal water shifts for the difference between the diamagnetic susceptibility of water and resin [1]. Our results confirm those of Gordon in that the external peaks are shifted by the beads an average of only 1 Hz downfield (see Table 1). Line broadening of the internal water is generally of the same order as the broadening of the external water. The only trend noted in the half-height widths of the internal peaks is that the divalent forms have peaks usually slightly broader than those of the monovalent forms. When the ratio of the integral of the internal peak to the integral of the external peak could be measured, the values obtained are in fair agreement with known water contents of resins [13, 14].

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