

CHROM. 13,149

MEASUREMENT OF THE RELAXATION TIME OF WATER PROTONS IN ION EXCHANGER–WATER SYSTEMS

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SUMMARY

The spin–lattice relaxation time, T_1 , of the water protons inside Dowex 50 ion exchangers as a function of the type of counter ion (H^+ , Na^+ , K^+) and degree of cross-linking (2, 4, 8, 12) of the resin was studied by the method of inversion recovery. In these systems T_1 decreased with increasing concentration of the counter ions, and at a particular degree of cross-linking it increased with increasing resin selectivity. Both observations can be interpreted, at least qualitatively, if the effects of the concentration and charge density of the counter ions are taken into consideration.

INTRODUCTION

Measurement of the nuclear magnetic relaxation times has become a valuable tool in the study of solute–solvent interactions in electrolyte and non-electrolyte solutions¹. However, very little use has been made of this technique in the study of the interactions inside ion exchangers.

Creekmore and Reilley² studied the effect of cross-linking on the linewidth of the ^{23}Na resonance. The estimated relaxation times, T_1 , obtained were compared to the values for sodium *p*-toluenesulphonate solutions at various concentrations. The differences at comparable concentration levels were interpreted as a result of the strong association of Na^+ with the active group of the resin, which causes the correlation time of the ion to increase and, in turn, decreases the measured T_1 .

Blaedel *et al.*³ studied the relaxation time for both water protons and ^{23}Na counter ions. These measurements indicated that the spin–lattice and spin–spin relaxation times, T_1 and T_2 , became independent of cross-linking for water contents above 6 moles of water per ion-exchange site. More recently, Soldatov *et al.*⁴ measured T_1 for 7Li in a strongly acidic cation exchanger. They found that T_1 decreases rapidly with decreasing number of water molecules inside the exchanger phase.

We have studied the effect of cross-linking on the relaxation time of water protons in the hydration sphere of various counter ions of the Dowex 50 ion-exchange resin.

EXPERIMENTAL

From Dowex 50 (100–200 mesh) cation-exchange resin of various degrees of cross-linkings (2, 4, 8 and 12), samples in the hydrogen, lithium, sodium, potassium and caesium forms were prepared. The resins were swollen in water at room temperature and their water contents determined after drying the resins for 12 h at 105°C. Their capacities were determined by the usual method⁵ and the molality of the counter ion was calculated.

For the measurement of the relaxation time of the water protons the paramagnetic oxygen has to be removed from the samples. Thus a small portion of the suspension was transferred to the apparatus shown in Fig. 1. The suspension was frozen in liquid nitrogen and the apparatus was evacuated, usually to better than 4 Pa (0.03 Torr). The tap of the vacuum line was closed and the frozen liquid was carefully melted by hot air while the oxygen was desorbed from the sample. After three repetitions of this procedure, the suspension was transferred into a precision NMR capillary tube (2 mm I.D.), by inverting the sample container (see arrow in Fig. 1) and allowing oxygen-free nitrogen into the system. The NMR tube was then removed from the PTFE stopper and the resin bed was closed by a vortex plug. The air space of the tube was filled with nitrogen and the opening of the tube was quickly sealed.

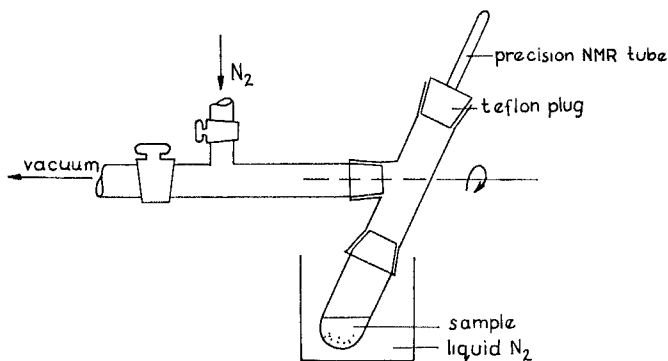


Fig. 1. Glass apparatus used for the deoxygenation of the resin–water suspension.

The ^1H NMR spectra of the samples were recorded by a Bruker WH 90 Fourier-transform instrument at ambient probe temperature. Tetramethylsilane (TMS) dissolved in $[\text{}^2\text{H}]$ chloroform served as an external standard. For the recording of partially relaxed Fourier-transform (PRFT) NMR spectra the following pulse sequence was used: $180^\circ-t_d-90^\circ-t_r$. The length of the 180° pulse was $64\ \mu\text{sec}$ and that of the 90° pulse was $32\ \mu\text{sec}$. The delay time, t_d , between the pulses was varied from 0.1 to 10 sec by 0.1-sec increments. After the application of the two pulses a 10-sec recovery time, t_r , was allowed before the release of the next train of pulses.

RESULTS AND DISCUSSION

The pioneering work of Gordon⁶ and later by Dinius *et al.*⁷, Gough *et al.*^{8,9} and Howery *et al.*¹⁰ showed that the ion exchanger–water suspension has a well defined and reproducible ¹H NMR spectrum. The resin phase and the bulk water generally provide two chemically different environments for the water protons, and there is a continuous exchange of water molecules between these. The rate of this process, k , determines the average residence time, t , of the water molecules in a particular chemical environment.

Well-separated signals from the internal and from the external water protons can only be recorded if:

$$|\nu_i - \nu_e| > 1/t = k \quad (1)$$

In this case two peaks are observed in the spectra at the frequencies ν_i and ν_e due to the internal and to the external water protons respectively.

The position of the resonance of the external water is slightly dependent on the type of counter ion due to the change of the diamagnetic susceptibility of the sample, but this effect does not concern us here. The resonance frequency of the internal water protons, however, may be upfield or downfield in comparison to the ν_e signal, depending on the structure-breaking or -making property of the counter ion⁸. For a given type of ion, the magnitude of the difference $\nu_i - \nu_e$ depends strongly on the internal concentration of the resin phase¹¹. When eqn. 1 does not hold for a system then only one peak can be observed at a frequency corresponding to the average of the chemical environments. In Table I the positive sign indicates systems where the two peaks were clearly separated, while the negative sign indicates those systems where the exchange was so fast that only one, more or less broadened, peak could be detected.

TABLE I

DOWEX 50 RESINS WHOSE ¹H NMR SPECTRA WERE STUDIED IN AQUEOUS SUSPENSION

A positive sign indicates spectra with two peaks, a negative sign spectra with one peak.

Ionic form	Divinylbenzene molecules			
	2	4	8	12
H ⁺	+	+	+	+
Li ⁺	–	–	–	–
Na ⁺	–	+	+	+
K ⁺	–	+	+	+
Cs ⁺	–	–	–	–

The T_1 experiments were run only for those systems where the two peaks were clearly separated. A typical series of PRFT NMR spectra is shown in Fig. 2.

The quantitative relationship between the relaxation time T_1 and the magnetization, M (M is proportional to signal intensity) is given by the well-known Bloch equation, which after integration yields¹²:

$$\log(M_0 - M_t) = \log 2M_0 - (0.43/T_1)t_d \quad (2)$$

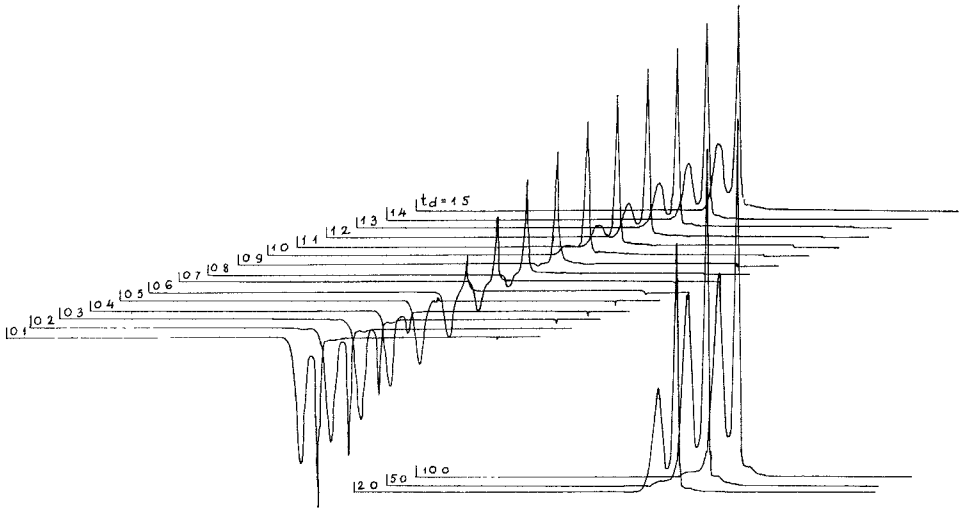


Fig. 2. Series of PRFT NMR spectra of Dowex 50-X12 (K^+). Peaks: upfield resonance due to internal water; downfield is the external water.

Here M_0 is the equilibrium value of the magnetization and M_t its value at a given time, t_d , following the perturbation effect of the 180° pulse. If $\log(M_0 - M_t)$ is plotted as a function of t_d then according to eqn. 2 a straight line should be obtained, from the slope of which the spin-lattice relaxation time, T_1 , can be calculated. In Fig. 3 this plot is shown for the internal water protons of Dowex 50-X12 resin (K^+).

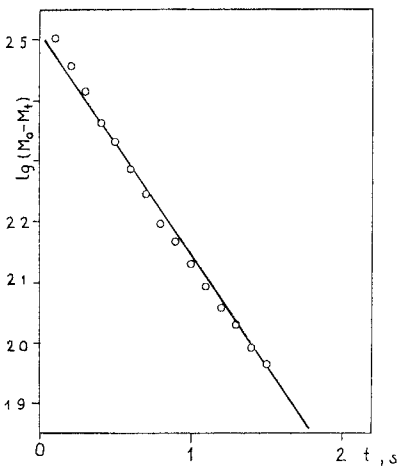


Fig. 3. Plot of $\log(M_0 - M_t)$ vs. t used for the calculation of T_1 of the water protons inside a Dowex 50-X12 (K^+) resin. $T_1 = 1.19$ sec.

The calculated relaxation times and the internal molality of the counter ions are summarized in Table II. These data indicate that T_1 decreases with increasing concentration of the counter ions in the resin phase. A similar tendency was also found for the water protons in electrolyte solutions¹³, but a direct comparison would

TABLE II

RELAXATION TIMES (T_1 , sec) OF THE WATER PROTONS AND THE MOLALITY OF THE COUNTER IONS (\bar{m}) INSIDE DOWEX 50 RESINS

Dowex 50	H^+		Na^+		K^+	
	T_1	\bar{m}	T_1	\bar{m}	T_1	\bar{m}
2	1.87	1.04	—	—	—	—
4	1.22	2.88	1.57	3.08	1.98	3.54
8	1.16	4.89	1.23	5.29	1.40	6.88
12	0.53	5.64	0.84	6.90	1.19	7.67

be possible only if the T_1 values were available for various salts of the benzenesulphonic acid solutions. Table II also shows that at a particular degree of cross-linking the relaxation times increase in the order of increasing selectivity: $H^+ < Na^+ < K^+$.

These observations can be understood if the molecular theory of relaxation is taken into consideration. The relaxation of excited nuclei is caused and maintained by the fluctuating magnetic field generated by the random molecular motions. An important statistical parameter of this molecular motion is the so-called correlation time, τ_c , which is the average time a magnetic particle spends in a given orientation. Beside the correlation time, the efficiency of the relaxation process (the magnitude of T_1) is also dependent upon the type of interaction existing between the magnetic particles. In the present systems this interaction is of the dipole-dipole type.

When the relaxation is governed by the above mechanism, the following relationship exists¹²:

$$\frac{1}{T_1} = \frac{2\gamma^4\hbar^2 I(I+1)}{5r^6} \left[\frac{\tau_c}{1 + \omega^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2\tau_c^2} \right] \quad (3)$$

Here γ is the gyromagnetic ratio of the proton, \hbar is Planck's constant divided by 2π , I is the nuclear spin quantum number, r is the internuclear distance and ω is the Larmor angular frequency.

Under the conditions of the so-called extreme narrowing when $\omega^2\tau_c^2 \ll 1$, the relaxation time becomes independent of ω and is proportional to the correlation time, τ_c :

$$\frac{1}{T_1} = \frac{2\gamma^4\hbar^2 I(I+1)}{r^6} \tau_c \quad (4)$$

With increasing concentration of the counter ions the correlation time also increases, which in view of eqn. 4 results in a decrease in the relaxation time T_1 . The dependence of the T_1 values of the protons on the type of counter ion can be interpreted in terms of the charge density around the counter ions. The high charge density around the hydrogen ion, for example, decreases the motional freedom of the water molecules and hence its correlation time is increased. According to eqn. 4, however, an increase of the correlation time results in a decrease in the spin-lattice relaxation time T_1 . This provides an explanation for the observed increase of the relaxation times in the order $H^+ < Na^+ < K^+$.

ACKNOWLEDGEMENT

The authors thank Mr. Jim Bloxsidge for his help in the NMR experiments. Thanks are also due to Professor G. Guiochon of the École Polytechnique in Paris for providing A. M. with a grant from the Scientific Exchange Agreement in support of this work.

REFERENCES

- 1 R. G. Bryant, *Annu. Rev. Phys. Chem.*, 29 (1978) 167.
- 2 R. W. Creekmore and C. N. Reilley, *Anal. Chem.*, 42 (1970) 570.
- 3 W. J. Blaedel, L. E. Brower, T. L. James and J. H. Noggle, *Anal. Chem.*, 44 (1972) 982.
- 4 V. Soldatov, L. Ödberg and E. Högfeldt, *Ion Exchange and Membranes*, 2 (1975) 83.
- 5 J. Inczédy, *Analytical Applications of Ion Exchangers*, Pergamon, New York, 1966.
- 6 J. E. Gordon, *J. Phys. Chem.*, 66 (1962) 1150.
- 7 R. H. Dinius, M. T. Emerson and G. R. Choppin, *J. Phys. Chem.*, 67 (1963) 1178.
- 8 T. E. Gough, H. D. Sharma and N. Subramanin, *Can. J. Chem.*, 48 (1970) 917.
- 9 T. E. Gough, H. D. Sharma and N. Subramanin, *Can. J. Chem.*, 49 (1971) 457.
- 10 D. G. Howery, L. Shore and B. H. Kohn, *J. Phys. Chem.*, 76 (1972) 578.
- 11 D. Reichenberg and I. J. Lawrenson, *Trans. Faraday Soc.*, 59 (1963) 141.
- 12 T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR*, Academic Press, New York, 1971, pp. 20, 52.
- 13 C. Deverell, in J. W. Emsley, J. Feeney and L. H. Sutcliffe (Editors), *Progress in Nuclear Magnetic Resonance Spectroscopy*, Vol. 4, Pergamon, Oxford, 1969, Ch. 4, p. 235.