Development of Free Radicals in Sulfonated Polystyrene Ion-Exchange Resins Upon Drying

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Synopsis

On exhaustive drying of sulfonated polystyrene-based ion-exchange resins, it is shown that free-radical centers develop. These have been examined by electron-spin resonance spectroscopy. The formation of the free radicals is largely reversible with respect to desorption and sorption of water which was measured by means of a quartz spiral microbalance. The spin-concentration isotherm as a function of sorbed water concentration is obtained. The presence of free radicals, dependent on water content in the resins, interferes with proton magnetic relaxation studies of hydration of ionized resins by providing a faster electron-spin coupled nuclear magnetic relaxation mechanism.

INTRODUCTION

The state of water in ionized crosslinked ion-exchange resins is of interest in relation to the hydration of lyophilic biocolloids[1] and of natural and synthetic polyelectrolytes.[2] By gravimetric measurements,[3] the sorption isotherms for water in resins having varying degrees of crosslinkage and containing various counterions can be precisely measured, as first investigated thermodynamically by Glueckauf and Kitt.[4,5] *In situ* infrared absorption measurements on various hydrated ion-exchange resins have also been made by Zundel et al.[6,7] and give informative data on solvation and ionization at the sulfonic acid centers.

In recent years, the state of hydration around ions has been investigated by NMR spectroscopy[8,11] and, more recently and in more profitable ways, by measurements of NMR spin-lattice relaxation times.[12]

During the course of gravimetric sorption measurements[3] on sulfonate crosslinked polystyrene (Dowex) resins, we have found that the sorption isotherms and derived differential heats and entropies of sorption of water depend appreciably on the initial state of dryness of the resins, especially if the resin has been exhaustively dried *in vacuo* over P_2O_5. In attempts to

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characterize the dynamical aspects of hydration in ion-exchange resin salts by means of nuclear magnetic proton relaxation time measurements, we observed that unexpectedly short T_1 values arose in relation to those for aqueous salt solutions.[12] In other respects, an ion-exchange resin containing sorbed water should exhibit, locally, properties similar to those for a very concentrated salt solution.   On a Dowex-50-W-8%XL resin (20–50 mesh), T_1 was found to be ca. 3×10^{-2} sec, while on some other Dowex resins, T_1 was too short to be measured.   These T_1 values are comparable with those measured for water adsorbed on charcoal[13], where an additional electron-spin relaxation mechanism due to interaction between water protons and the paramagnetic centers on the charcoal shortens the measured overall relaxation times.   Besides the shortness of the relaxation times, no systematic relations between these time constants for different counterions (alkali cations) could be observed, as one would expect from analogous-measurements òn aqueous electrolyte solutions[12,14].   We have therefore examined the paramagnetic behavior of different crosslinked sulfonated polystyrene resins in their acid form under conditions of controlled dryness and in the presence of controlled quantities of sorbed water.   The isotherms for sorption and desorption of water in the resins were also measured corresponding to uptake or removal of water.

EXPERIMENTAL

ESR Spectra

The ESR spectra were obtained with a Varian E-Line spectrometer operating at a wavelength of 3 cm.   For the intensity measurements, a dual-sample cavity was used.   Each measurement was made at the same time as one on a standard reference sample of lignite having a spin concentration of 3.9×10^{17}/g.   The intensities of the signals were determined by numerical calculation of the first moments[15,16] of the digitized first derivative spectra.   The accuracy of these intensities is about 15–20% allowing for maximum uncertainties in the filling factor for the ESR tubes.

Sorption Experiments and Preparation of Samples

Resin samples were contained in thin quartz glass tubes suitable for setting in the ESR spectrometer cavity and were mounted in a thermostatted manifold connected to a high-vacuum line.   The line was also connected to a large tube containing a quartz spiral microbalance[17] on which similar samples could be weighed during the course of sorption or desorption of water in the absence of air.   The water vapor pressure could be controlled by using aqueous H_2SO_4 solutions of known water activity.[18]   Intense drying could be achieved by use of P_2O_5 and liquid-air traps in the line.

It was found that a Tesla coil discharge near the resins increased the spin concentrations; hence, no part of the vacuum system was leak-tested during the preparation and mounting of the samples, in their glass tubes, on the

vacuum line. Due to the significant swelling which the resin undergoes upon sorption of water, the spin concentrations for water-containing resins must be normalized to a scale based on the filling factor $f°$ in the ESR tubes when the dry resin is used. If W is the weight per cent water, then the normalized spin concentration S^0 is given by

$$S^0 = (Sf^0/f)[(100 - W)/100]$$

where S is the apparent spin concentration calculated from the experimental data per gram of resin plus water, f is the tube filling factor (grams of resin plus sorbed water per centimeter of filling height in a standard tube) and f^0 is the corresponding filling factor for the dry resin. The significance of the corrections for swelling due to water sorption is indicated in Table I, where the values of S and S^0 are seen to differ appreciably, especially at higher extents of water sorption.

Ion-Exchange Resins

The ion-exchange resins were all of the sulfonated polystyrene type, crosslinked with divinylbenzene. The extent of crosslinking is indicated by the XL percentage number in Table I. Dowex, Amberlite and J. T. Baker Co. materials were used. The specified traces of heavy paramagnetic metals in these resins cannot account for the ESR spectra exhibited in these materials when dried, since the g factor (see below) and line width do not correspond to the spectra of the transition metal trace impurities.

RESULTS AND DISCUSSION

The ESR spectra of all resin samples clearly indicated the presence of unpaired electron spins. A typical spectrum of a dry resin is shown in Figure 1. The unpaired electron spin concentrations S^0 for several resins with various water contents are given in Table I. A small signal was also found in dry Dowex 50W-1%XL, but with increasing water content to 2.8 mole H_2O/SO_3^- group, the signal became undetectable. Clearly, the dried resins have much higher spin concentrations than the wet ones. The change in spin concentrations was found to be largely reversible, since the Dowex 50W-8%XL samples of 26 and 49% water content were measured after water was added to the exhaustively dried resins, while the other wet samples were measured before drying. Figure 2 shows the striking difference between the ESR spectrum of the ultra-dry and the wet (saturation absorption of H_2O) Dowex 50W-8%XL resin.

There is some indication that the spin concentrations are greater in the more highly crosslinked samples and that the color also depends on the spin concentration in a given resin, as in Dowex 50W-8%XL, becoming darker as the sample is dried and as the spin concentration increases. This concentration could imply that the radicals might be located on the crosslinking divinylbenzene centers, but no direct evidence is yet available to support this.

TABLE I

Apparent (S) and Corrected (S^0) Spin Concentrations for Four Crosslinked Polystyrene Sulfonate Ion-Exchange Resins (Acid Form) as a Function of Water Content W

| Resin			W, wt-%	n H$_2$O molecules per SO$_3^-$	Filling factor, g/cm height		Spin concentration/g	
Type	Mesh	Color			f Wet resin	f^0 Dry resin	S	S^0
Dowex 50W-1%XL	50–100	Yellow-brown	0.0	0		0.070	8×10^{16}	8×10^{16}
		White-yellow	2.2	2.2	0.02346		8.4×10^{14}	3.0×10^{15}
			25.0	2.8	0.024		No signal	No signal
Dowex 50W-2%XL	60–100	Amber	0.0	0		0.030	2.2×10^{17}	2.2×10^{17}
Dowex 50W-8%XL	20–50	Amber	0.0	0		0.027	1.9×10^{17}	1.9×10^{17}
		Amber	4.34	0.5	0.024		1.7×10^{17}	2.0×10^{17}
		Amber	4.7	0.8	0.024		9.8×10^{16}	10.9×10^{16}
		Amber	9.0	1.1	0.024		7.7×10^{16}	9.5×10^{16}
		Amber	15.0	1.9	0.024		8.4×10^{15}	11.1×10^{15}
		Dark yellow	19.7	2.7	0.028		2.0×10^{15}	2.5×10^{15}
		Yellow	26.0	4.0	0.026		6.6×10^{14}	9.3×10^{14}
		Light yellow	49.0	10.0	0.024		4.1×10^{14}	9.2×10^{14}
Amberlite IR 120 8%XL	20–50	Brown	34.5		0.028		7.0×10^{15}	ca. 10^{16}
AGC-242 10%XL (J. T. Baker)	16–50	Dark brown-black	0.0	0		0.027	3.0×10^{17}	3.0×10^{17}
		Dark brown-black	44.7		0.0215		2.4×10^{15}	5.5×10^{15}
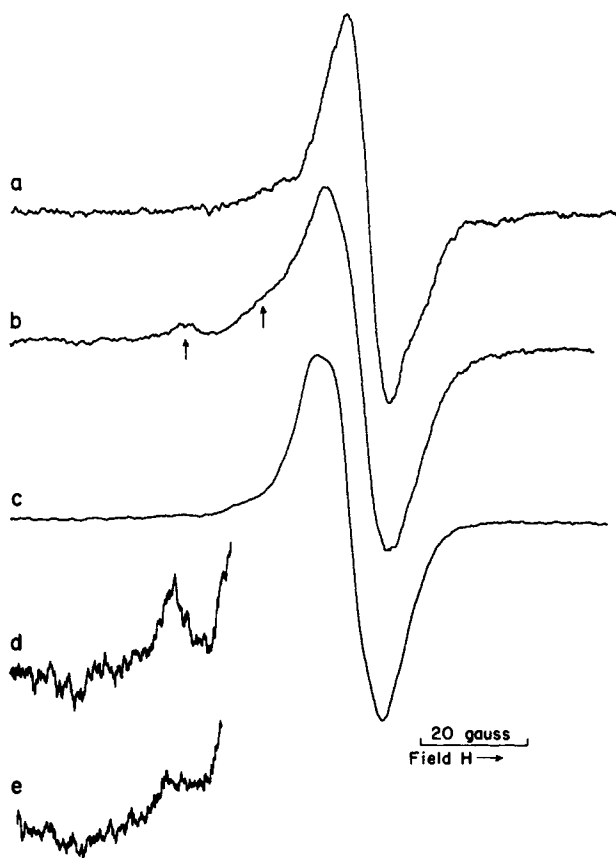
Fig. 1. ESR spectra at 25°C for Dowex 50W-8%XL ion exchange resin (acid form): (a) dry resin, 0.2 mW power level; (b) same sample, 10 mW power level (arrows indicate low-field resonance lines); (c) dried resin after treatment with TCNE, 20 mW power level; (d) Same as (b), 5 × greater gain, showing low-field region; (e) Same as (c), 12.5× greater gain, showing low-field region.

For the acid form of the Dowex 50W-8%XL resin, the spin concentrations S were measured systematically for seven levels of water sorption and for the ultra-dry material. The water concentrations were determined gravimetrically by means of the quartz spiral balance and the sorption isotherm for the resin on which the spin measurements were made is shown in Figure 3 for 25°C together with that for 55°C for comparison (these data together with other measurements at various temperatures give[4,5] the differential entropies and heats of water sorption, to be reported elsewhere). The spin density and water concentration data for this resin are shown in Table I. A clear dependence of S^0, the spin density corrected for swelling of the resin, on degree of hydration of the resin is demonstrated by the spin isotherm shown in Figure 4. For water contents greater than ca. 4 molecules H_2O per $SO_3{}^-$ group, the corrected spin density S^0 reaches an almost
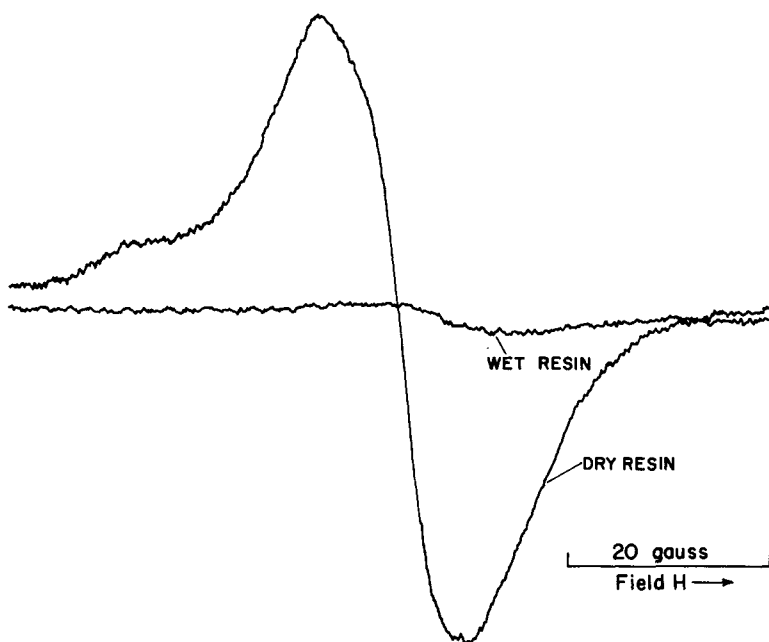
Fig. 2. ESR spectra at 25°C for Dowex 50W-8%XL ion exchange resin in the ultra-dry
state and under the saturation absorption conditions.

constant level of 9.2 × 10^{14} spins/g. The spin isotherm is reversible, as
shown by the two sets of points in Figure 4.

   At low microwave power levels (<1 mW), the ESR signal displays a
fairly symmetric resonance curve, having a peak-to-peak width of 5 to 10
gauss, depending on the sample.   The g values of signals from various resins
lie in the range 2.0035 ± 0.0005.   These features suggest that the spins are
most probably located at C on hydrocarbon structures, probably with some
interaction with bonded oxygens or involving a weaker interaction with
sulfur.   The increase of spin concentration for the dried materials appears
to be due to some cracking process in the carbon chains in the polymer.
This is probably related to the appearance of macroscopic fractures of the
resin beads which can be observed for resins in which the water content is
progressively lowered.[19]   The radicals do not originate from peroxides
which might be formed from molecular O_2, because such peroxides have
greater g values.

   ESR signals are also known[20] to develop in so-called proliferous poly-
merization of styrene–divinylbenzene mixtures over certain concentration
ranges and remain in the solid glasslike product.   These radical centers
arise when the polymerization involves a large concentration of growing
chains, so they are also presumably located at C centers.

   If the microwave power level is raised to the range 2–10 mW, two addi-
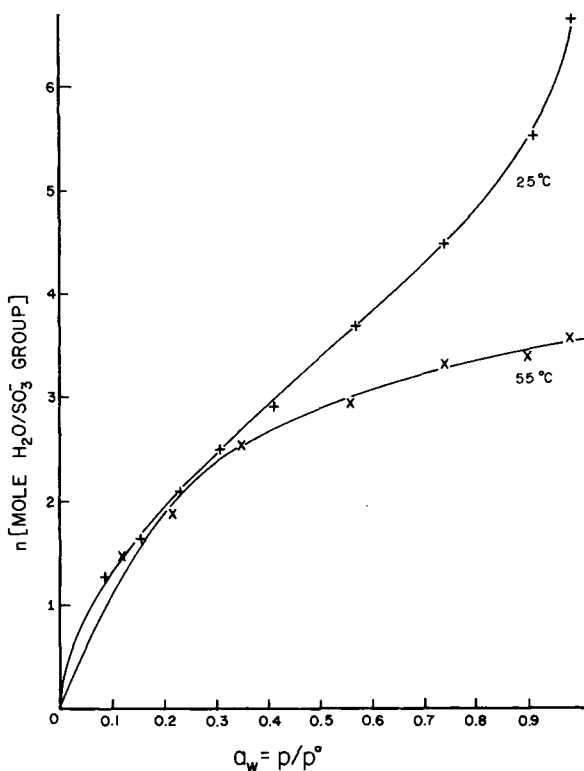tional weak components appear in the spectrum as shown in Figure 1b.

Fig. 3. Sorption isotherms for water uptake in Dowex 50W-8%XL resin (acid form) at 25 and 55°C, expressed in terms of water activity $a(= p/p°)$.

These arise at about 17 and 30 gauss on the low-field side of the main line. There is also a slight change in the shape of the main line suggesting the presence of a third component at the low field peak of the main line. These lines have not been thoroughly investigated but may be tentatively ascribed to sulfur-bearing radicals. These would have a somewhat higher g value than the hydrocarbon radicals and hence would give resonance at lower fields. They would also have a greater spin-lattice relaxation than the hydrocarbon species. Thus, their resonance, being less easily saturated than that of the hydrocarbon centers, would become relatively stronger at higher power levels. If the temperature is lowered to $-176°C$ or the microwave power level is increased further, the spectra show marked changes in shape which appear to result from the different degrees of saturation which then arise in the different lines.

One sample of the dry 8%XL resin was treated with an electron acceptor tetracyanoethylene (TCNE) in benzene. The main line of the resin ESR spectrum did not change significantly (Fig. 1) as a result of this treatment. No great change would be expected, however, if only a small fraction of the unpaired electrons were accepted by the TCNE since the spectrum of the
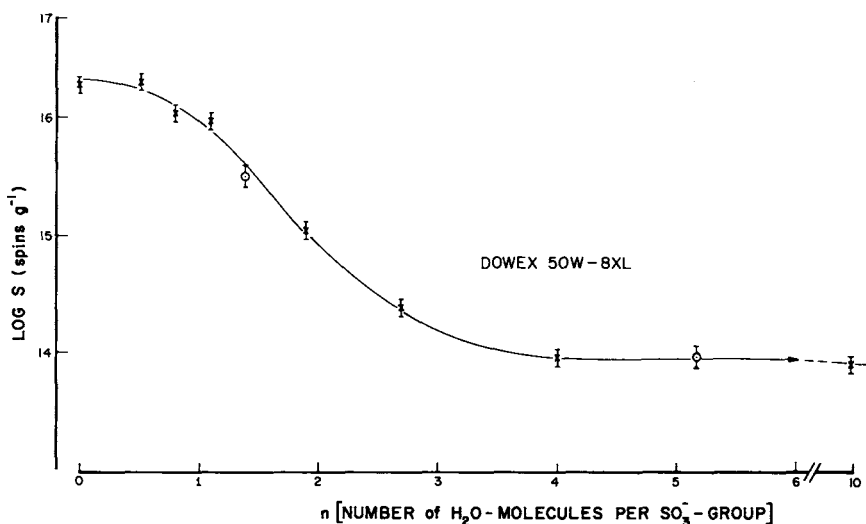
Fig. 4. Spin isotherm for corrected spin concentrations S^0 in Dowex 50W-8%XL resin (acid form) as a function of number of water molecules per SO_3^- group (25°C): (×) for increasing degrees of sorption into initially dry resin; (⊙) for decreasing degrees of sorption from an initially H_2O-saturated resin.

resulting anion radicals would be similar to that of the resin species. However, the component at lowest field at moderate microwave power disappeared almost completely (Fig. 1c). Hence, the radicals causing this component appear to have donated their spins to the TCNE. The apparent lack of reaction of TCNE with the major portion of the radicals might also be attributed to the inability of the oxidant to penetrate the resin matrix at sites where the radicals are located. Thus, the reversibility of

TABLE II
Apparent Proton Spin-Lattice Relaxation Times T_1
in Sulfonated Polystyrene Ion-Exchange Resins

Resin salt	n, molecules H_2O per SO_3^- group	T_1, sec
H^+	6.8	No signal[a]
Li^+	6.0	No signal
Na^+	4.6	No signal
K^+	4.3	28.9×10^{-3}
Rb^+	4.3	63.5×10^{-3}
Cs^+	4.3	30.3×10^{-3}
NH_4^+	3.8	Probably two values for T_1
$(CH_3)_4N^+$	4.5	36.8×10^{-3}
Mg^{++}	6.6	No signal
Ca^{++}	5.4	No signal

[a] These entries arise on account of the free-radical character of some of the resin samples which give a spin relaxation time too short to be measured. Other T_1 data may be too low due to electron-spin coupling.

the appearance of the ESR signal upon drying and wetting must imply that the spins are localized at relatively inflexible sites so that recombination can occur almost quantitatively on resorption of water. The role of water in this reversible effect suggests that the radicals may be located near the ionic sites where maximum stresses and local changes of dimensions must arise as hydration of $-SO_3H$ functions[6,7] occurs. These sorption effects are opposite to those which occur on swelling of nonionic polymers, where sorption of a solvent or plasticiser often causes chain rupture.[21-23]

The presence of these paramagnetic centers, demonstrated above, explains the shortness of our measured nuclear magnetic proton relaxation times (some apparent values are given in Table II), and it also may explain the very different results reported for the water proton magnetic resonance line widths in similar polymers.[24-26] The presence of free radicals in the polymer structure itself also may be responsible for the anomalies in the relation between rotational correlation times of added organic spin labels in the interior of these polymers and degree of cross-linkage in more highly crosslinked systems (10%XL to 12%XL), as observed by Chesnut and Hower.[27]

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