The EPR Spectra of Manganese(II) on Sulfonated Polystyrene Resins Cross-linked with Pure Divinylbenzene Isomers

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SUMMARY

The EPR spectra of manganese(II) ions on sulfonated polystyrene cross-linked with either pure meta or pure para divinylbenzene show distinctions indicative of ionic environments of different symmetry.

INTRODUCTION

We have recently reported the rates of sulfonation [1] and mass spectral characteristics [2] of bead copolymers of styrene cross-linked with m- and p-divinylbenzenes, and the rates of peroxide-induced degradation [3] of the sulfonated bead copolymers. It has been pointed out that these data show differences which can be related to differences in the cross-linked structures produced by differences in the copolymerization characteristics [4] of m- and p-divinylbenzenes.

Since electron paramagnetic characteristics depend on the electrostatic field about the paramagnetic species, the spectra of paramagnetic ions, such as those of manganese(II) exchanged with the cations of various ion exchange resins, should also give some information about possible structural differences in the resin environment. We have, therefore, studied the EPR spectra of manganese(II) exchanged with the cations—

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either hydrogen or sodium—of sulfonated polystyrene beads cross-linked with 8 mole % of pure para, pure meta, and commerical divinylbenzene, and of a commercial resin.

EXPERIMENTAL

The sulfonated copolymer beads used for this experiment were the ones prepared for a previous study [3]. The total capacity for the polystyrene cross-linked with 8 mole % pure p-divinylbenzene was 5.16 meq/g; for the resins cross-linked with 8 mole % pure m-divinylbenzene and 8 mole % commerical divinylbenzene, these values were 4.97 and 5.14 meq/g, respectively. The commerical resin (Dowex 50W-X8) was obtained from Baker Chemical Co. with specified total exchange capacity of 5.09 meq/g.

Approximately 3 g samples were weighed in flasks, a 10^{-3} M solution of manganese(II) sulfate was added, and the flasks were stoppered. Three series of runs were made: series 1, with the acid form of the resin and excess of manganese(II) ion; series 2, with the sodium form of the resin and excess of the manganese(II) ion; and series 3, with the sodium form of the resin and ca. one-half the equivalent amount of manganese(II) ion needed to replace all of the sodium ion.

The manganese(II) solutions were allowed to stand 10-12 hr to equilibrate with the resins at room temperature with occasional shakings of the flasks. The resins were then washed several times with distilled water until the washings did not show the EPR signal of the manganese(II) ion. The data for manganese(II) sulfate in aqueous media run under comparable conditions are in Table 1.

After being dried in a vacuum oven at 40°C for 3 hr, the resins were placed in quartz sample tubes (3 mm o.d.; 14 cm length), packed to a length of approximately 5 cm. The EPR spectra of these samples were obtained at room temperature using a Varian Model V-4502-15 spectrometer with 12 in. magnet; V-4560, 100 kc field modulation unit; V-4532 dual sample cavity. The first derivative spectra were recorded for all the samples and are shown in Figures 1 to 3.

The values of the magnetic field were assigned from the field dial readings. The hyperfine structure intervals (peak separations) and line widths (peak widths) were measured from these spectra. The five or six values for each of the readings are given in Table 1 and the average values are summarized in Tables 2 and 3.

Table 1. Manganese(II) Spectra on Various Ion Exchange Resins

| Series | Sample | Spectrum | | | | | | | | | | | | |
		Line width (gauss)							Peak separation (gauss)					
		1	2	3	4	5	6	Average	1-2	2-3	3-4	4-5	5-6	Average
1	Dowex	45.3	37.5	40.3	40.1	48.8	40.0	42.0	89.8	87.4	114.2	77.1	94.4	92.6
	Commercial	51.6	40.0	40.6	40.0	44.4	48.1	44.1	83.6	89.1	91.5	96.0	99.4	91.9
	m-DVB	71.9	37.5	42.2	41.9	45.9	50.0	48.2	101.5	88.3	88.8	93.7	97.9	94.0
	p-DVB	57.5	41.9	42.5	45.3	42.0	46.9	46.0	89.0	89.2	90.8	93.9	97.5	92.1
2	Dowex	53.1	43.1	48.1	45.0	46.3	57.2	48.8	87.2	89.7	92.1	95.7	98.2	92.6
	Commercial	53.5	53.1	44.1	49.7	49.4	74.1	54.0	90.5	89.2	87.8	94.8	108.3	94.1
	m-DVB	44.0	49.4	57.5	56.2	58.1	65.6	55.1	72.0	84.1	94.0	105.7	116.2	94.4
	p-DVB	56.3	43.8	48.7	47.5	51.9	58.8	51.2	79.3	85.7	92.5	95.9	105.3	91.7
3	Dowex	53.0	42.2	43.7	40.5	43.4	55.9	46.5	87.9	85.2	91.8	95.8	102.9	92.7
	Commercial	54.7	34.4	44.4	45.0	44.4	55.7	46.5	83.6	85.6	97.8	90.0	100.7	91.6
	m-DVB	53.1	46.9	51.2	45.6	48.7	51.9	49.6	82.8	93.1	84.7	101.0	98.4	92.0
	p-DVB	48.8	44.7	41.2	44.1	41.3	53.4	45.6	84.6	88.5	92.1	96.1	102.3	92.7
	Manganese(II) aq. soln.	27.0	27.0	31.7	25.0	26.5	30.7	28.0	98.0	91.7	96.3	89.8	85.9	92.3
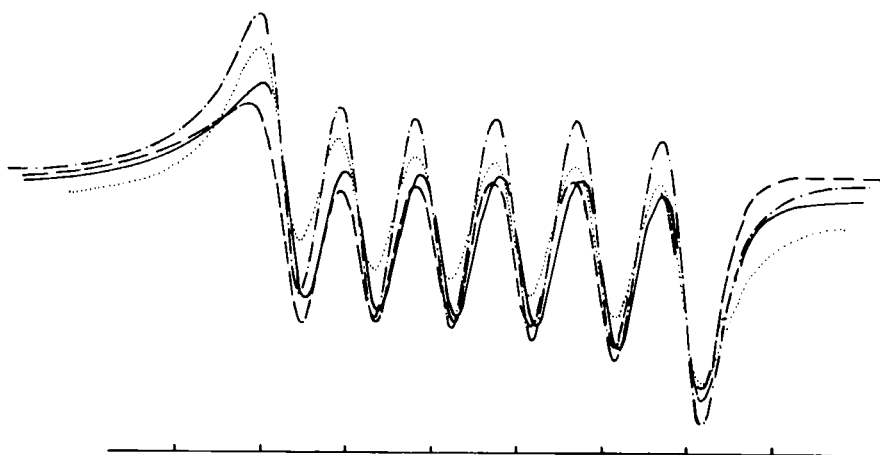
Fig. 1. EPR spectra of Mn(II) on various ion exchange resins: sulfonated polystyrene cross-linked with 8% m-divinylbenzene (– –); with 8% p-divinylbenzene (——); and with 8% commercial (55%) divinylbenzene (– ·); and for a commercial resin (Dowex 50W-8X) (···). Scale division, 100 gauss. Readings of line widths and peak separations are given in the Tables. The samples were prepared by exchange of excess Mn(II) sulfate with the acid form of the resins (series 1).
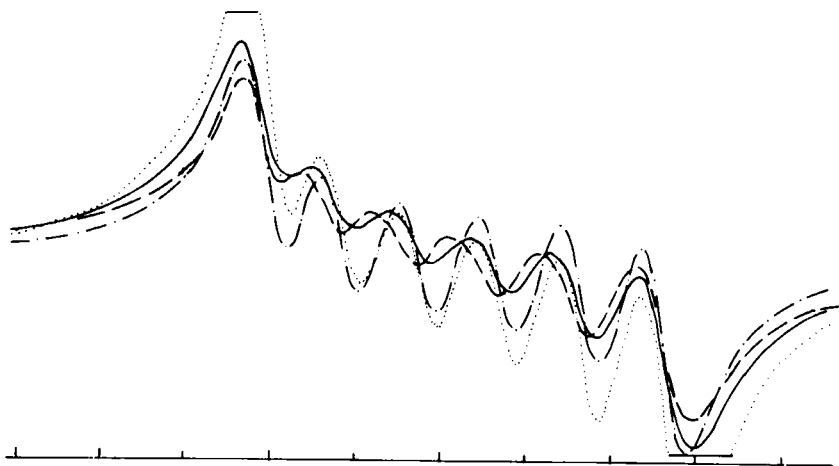

Fig. 2. EPR spectra of Mn(II) on various ion exchange resins: The legend is the same as for Fig. 1. The samples were prepared by exchange of excess Mn(II) sulfate with the sodium form of the resins. (series 2).
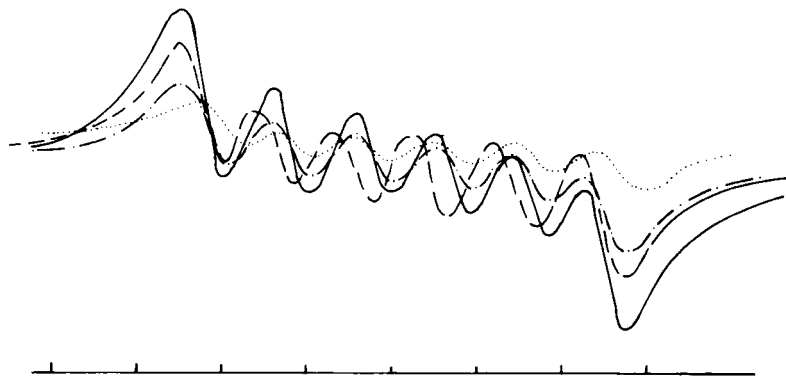
Fig. 3. EPR spectra of Mn(II) on various ion exchange resins: The legend is the same as for Fig. 1. The samples were prepared by exchange of ca. one-half the equivalent amount of Mn(II) sulfate with the sodium form of the resin (series 3).

RESULTS AND DISCUSSION

The results of these experiments show that all of the electron paramagnetic resonance signals from various cation exchange resins have six-line spectra, characteristic of the manganese(II) ion. The signals occur at 3550 to 3550 G. The spectra of the manganese(II) ions on different resins show different over-all features. These are seen in the different average hyperfine structure intervals and line widths in each spectrum and the irregularity of the derivations from average (Table 1) as well as in the figures in which the spectra are superimposed. These observed differences are not instrumental artifacts, since a blank run for aqueous manganese sulfate (10^{-3} M solution) was taken under identical conditions and the spectrum thus obtained showed regular features; i.e., six $(2I + 1)$ lines unequally spaced, due to the quadrupole moments of the metal nuclei. Our observed HFS constant [for the aqueous manganese(II)] varies from 86 to 98 G with an average of 92.3 G and our observed peak width varies from 25 to 31 G with an average of 28.0 G. These values are in good agreement with recorded values [5-9].

The average values of the measured HFS splitting between the six peaks of manganese(II) ion on various resins are listed in Table 2. These splittings (over-all average, 93 ± 1 G) are in reasonable agreement with the hyperfine splittings reported (ca. 90 G) [5-9] for manganese(II) ion either in solution or solid.

Table 2. Average Hyperfine Structure Interval[a]

Resin	Series		
	1	2	3
Dowex	92.6	92.6	92.7
Commercial	91.9	94.1	92.7
m-DVB	94.0	94.4	92.0
p-DVB	92.1	91.7	92.7

[a]Values are given in gauss for the intervals shown in Figs. 1, 2, and 3 which correspond to series 1, 2, and 3. The values are the averages of the five for each of the twelve spectra separations. Complete data in Table 1.

Table 3. Average Separation Between the Positive and Negative Extremes (Line Width)[a]

Resin	Series		
	1	2	3
Dowex	42.0	48.8	46.5
Commercial	44.1	54.0	46.5
m-DVB	48.2	55.7	49.6
p-DVB	46.0	51.2	45.6

[a]Values are given in gauss and are the average of six peaks for each of the twelve spectra.

The deviations on the various resins are considerable (77 to 116 G), are irregular in the various spectra, and are greater than those observed for the aqueous solutions of manganese(II) sulfate. The average HFS is apparently greater (94 G) for the meta-cross-linked resin than in other cases [92 G, when the resin is saturated with manganese(II)]. If the resin is less than completely exchanged (series 3) with manganese(II) ion, there is little difference.

The average measured values of the separation between the positive and negative extremes, i.e., peak width, of the spectra are listed in Table 3. As in the previous case (Table 2), the values listed here indicate maximum peak widths for manganese(II) ion on resins cross-linked with m-divinylbenzene. The value is 48 G as compared to 42-46 G in series 1.

Previously, differences in the line width broadening effects have been attributed to counter-ion effects [5], to concentration effects [9], and to ionic environment effects [9]. Changes in such factors often cause broadenings considerably greater than those we have now observed in the differences for the resin types. The counter-ion effects and concentration effects are presumably comparable for the different resin types, but there are possible structural differences in the meta- and para-cross-linked resins which can create ionic environments of different symmetry. Thus, it has been shown in previous reports that the cross-linkages are probably more uniformly distributed in the meta-cross-linked structures than they are in the para-cross-linked structures.

This can lead to two different types of environmental differences. The long linear portion of the para-cross-linked resin may provide more random orientation and thus less site differentiation with resultant greater ionic symmetry around the manganese(II) ion and accordingly less broadening. The other possibility is that the large hydrated manganese(II) ion cannot uniformly penetrate the matrix of the meta-cross-linked structure, thus also resulting in greater asymmetry. We have previously observed that, in sulfonation, the sulfonating species penetrates the meta matrix much less rapidly than it penetrates the para matrix. Either of these possibilities seem great enough to account for the small, but nevertheless real, differences in broadening effects observed in the EPR spectra.

ACKNOWLEDGMENT

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