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THE EFFECT OF GAMMA RADIATION ON ION EXCHANGE RESINS

by

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ABSTRACT

Four commercial ion exchange resins were irradiated in a high intensity gamma field to doses between 10^8 to 10^9 rad. The resulting changes in the physical and chemical properties of the resins were measured to determine the extent and nature of the radiation damage.

CONTENTS

	<u>Page</u>
Introduction	4
Summary	4
Discussion	5
General Background	5
Experimental Methods	6
Results and Conclusions	7
Bibliography	14

LIST OF TABLES AND FIGURES

Table

I	Effect of Gamma Radiation on Cation Exchange Resins	8
II	Effect of Gamma Radiation on Anion Exchange Resins	11

Figure

1	Effect of Gamma Radiation on Capacity	9
2	Effect of Gamma Radiation on Relative Moisture Content	10
3	Effect of Gamma Radiation on Equivalent Moisture Content	12

THE EFFECT OF GAMMA RADIATION ON ION EXCHANGE RESINS

INTRODUCTION

Organic ion exchange resins are of interest in processes involving highly radioactive materials. The commercial resins are known to have moderate stability toward radiation damage, but a quantitative measure of the effects of radiation on resins of specific interest was not available. In an effort to determine the extent and nature of radiation damage, the resins of interest were irradiated in a high intensity gamma field, and changes in their physical and chemical properties were measured.

SUMMARY

The cation exchange resins, "Dowex" 50W-X12 and "Duolite" C-10, and the anion exchange resins, "Dowex" 1-X4, "Dowex" 1-X8, and "Permutit" SK, were irradiated in various ionic forms. The total ion exchange capacity, "salt-splitting" capacity, moisture content, and particle size of the resins were measured after various gamma doses up to 2.7×10^8 rad. The infrared absorption spectra were also studied for confirmatory information.

"Dowex" 50W-X12 cation resin was relatively stable to radiation damage. A dose of 2.7×10^8 rad caused no significant change in the total ion exchange capacity, but the salt-splitting capacity was decreased by 8%. The main source of damage to this resin was the breaking of cross-linkages in the polymer matrix. Tests indicated that there was some replacement of sulfonic acid groups by phenolic groups in the resin matrix.

"Duolite" C-10 cation resin, a sulfonic acid type on a phenolic matrix, was less stable than "Dowex" 50W. The resin lost 8% of its total capacity and 17% of its salt-splitting capacity after irradiation to 1.5×10^8 rad.

The anion exchange resin "Dowex" 1 was severely degraded by a dose of 2.7×10^8 rad. At that dose the resin lost 58% in total capacity and 85% in salt-splitting capacity. The strong-base quaternary ammonium groups were replaced to some extent by weak-base groups.

"Permutit" SK, an anion resin containing pyridine groups, was far more resistant to radiation damage than "Dowex" 1. After exposure to 2.7×10^8 rad this resin lost only 8% in total capacity and 55% in salt-splitting capacity. The hydroxyl form of "Permutit" SK was found to be relatively unstable in storage.

DISCUSSION

GENERAL BACKGROUND

When organic ion exchange resins are exposed to intense sources of radiation, as is the case in many radiochemical applications, chemical changes may be produced by the direct absorption of energy by the resin itself and, if water is present, by the indirect action of radicals and hydrogen peroxide produced by radiolysis of the water. The physical and chemical properties of the resins may be radically altered by processes involving attack on the polymer network or by processes producing changes in the number and types of functional groups on the resin. As a result the ion exchange capacity of the resin may be reduced, gases may be liberated in the resin columns, and undesirable organic materials may be released into the system.

Several investigators⁽¹⁻⁴⁾ have studied the radiation stability of various types of synthetic organic ion exchange materials in efforts to determine the nature and extent of such damage, and to find a resin with superior resistance to radiation. The data obtained by various workers are difficult to compare and evaluate due to the use of different experimental techniques. Marinsky and Guiffrida⁽⁵⁾ tabulated the radiation stability data of other investigators and summarized the data as follows:

(a) Exposure to gamma radiation of 10^7 rad results in negligible damage to all types of ion exchange resins.

(b) The strong-acid, sulfonated polystyrene resins are stable up to radiation levels of 10^8 rad. When exposed to 1.7×10^9 rad about 25% of the total cation exchange capacity is lost. Fisher⁽⁴⁾ has shown that replacement of sulfonic acid groups by phenolic groups is responsible for maintenance of total capacity.

(c) The sulfonic-phenolic resins are more stable than the sulfonated polystyrene type at lower radiation levels. Upon exposure to 1.7×10^9 rad the amount of degradation is about the same for both types of resins.

(d) The strong-base quaternary amine anion resins are severely damaged by high-intensity radiation. An exposure of 3.8×10^8 rad results in a capacity loss of 40-50%, while a dose of 1.7×10^9 rad almost completely degrades the resin.

(e) The weak-base anion resins are more stable than the quaternary amine type. Some have been found to approach the stability of the strong-acid cation resins.

(f) The data on the carboxylic acid resins are contradictory and inconclusive.

To obtain more systematic information on the radiation stability of resins used in radiochemical separations processes, a number of resin samples were irradiated to dose levels of 10^8 - 10^9 rad. The resins selected for this study were:

(a) "Dowex" 50W, a strongly acidic cation exchange resin containing sulfonic acid groups on a polystyrene-divinylbenzene matrix.

(b) "Duolite" C-10, a cation resin containing methylene sulfonic acid groups on a phenolic matrix.

(c) "Dowex" 1, a strongly basic anion exchange resin containing quaternary ammonium groups on a polystyrene-divinylbenzene matrix.

(d) "Permutit" SK, an anion resin containing both strong and weak base groups, and containing some pyridine groups.

EXPERIMENTAL METHODS

The effects of radiation on the properties of the resin were measured by the following procedures.

Moisture Content - The resin was soaked in water, filtered, dried with filter paper, and weighed. A sample of the resin was then dried to constant weight in a vacuum oven. The cation exchange resins were dried at 110°C ; the anion resins at 60°C .

Total Ion Exchange Capacity - The total capacity of the cation resins was determined by introducing a weighed sample of resin in the hydrogen form into a flask containing an excess of sodium chloride and a known amount of standardized 1M sodium hydroxide. The excess base was back-titrated with standard hydrochloric acid. The total capacity is expressed as milliequivalents per gram of dry resin.

The total capacity of the anion resins was determined in a similar manner. The resin sample in the hydroxyl form was introduced into a known amount of 1M HCl containing an excess of NaCl; the excess hydrogen ion was then back-titrated with standard base.

Salt-splitting Capacity - This quantity is a measure of the strong acid or strong base functional groups in the resin. For cation resins the salt-splitting capacity was determined by adding a weighed quantity of resin in the hydrogen form to a solution of NaCl. The solution was then titrated with 0.1N NaOH to a phenolphthalein end point. For anion resins, the sample in the hydroxide form was added to a solution of NaCl, and the solution was titrated with 0.1N HCl. In some cases the color of the resin obscured the end point, and it was necessary to separate the resin from the solution before the titration. The results are expressed as milliequivalents per gram of dry resin.

Wet Resin Volume - This quantity was determined by weighing a sample of resin into a 5-ml graduated cylinder, adding water and noting the volume of the resin after it was completely settled. The results are expressed as milliliters per gram of dry resin.

Infrared Absorption Spectra - The infrared spectra were examined for information concerning changes in the functional groups of the resins and for changes in the structure of the polymer network. This method was useful for interpreting results from capacity and moisture data.

Particle Size and Appearance - Comparative photomicrographs of the resins were examined to determine the extent of fissuring or fragmentation of the particles.

Aqueous Leach from Irradiated Samples - After irradiation the resins were leached with distilled water to recover aqueous-soluble fragments. A portion of the leach solution from the irradiated cation resins was used for a sulfate determination. The other portion received the following treatment to obtain a measure of the soluble organic degradation products. The solution was heated and then neutralized with $\text{Ba}(\text{OH})_2$ to precipitate the sulfate. After filtration the solution was evaporated to dryness, the residue was washed with hot ethanol, and the infrared spectrum of this residue was examined for sulfonic acid and phenol groups. The leach solutions from the irradiated anion exchange resins were examined by the infrared technique; complex mixtures of compounds were observed and a detailed analysis of this material was not attempted.

The cation resins were irradiated in the hydrogen form either immersed in water or as air-dried samples. The anion resins were irradiated in the chloride, hydroxide, and nitrate forms, immersed in water or air-dried. Irradiations were at room temperature.

Samples were irradiated in a gamma field produced by mixed fission products contained in spent reactor fuel. The average gamma energy was about 0.75 mev; the average intensity was 3×10^5 rad/hr. Dose rates were measured with the ferrous sulfate dosimeter.

RESULTS AND CONCLUSIONS

The results are listed in Tables I and II and are shown graphically in Figures 1, 2, and 3. The data on capacities show that "Dowex" 50-X12 was only slightly affected by a dose of 10^8 rad. As the radiation dose was increased to 2.67×10^8 rad, the total capacity increased slightly and the salt-splitting capacity decreased. This indicates that sulfonic acid groups were lost, and were replaced by weak acid groups, presumably phenols, so that the total capacity was maintained. It is recognized that in the experimental determination of the salt-splitting capacities of "Dowex" 50W a possible source of error was the use of phenolphthalein

as an indicator. Because of the pH response of phenolphthalein, some of the weak-acid groups in irradiated "Dowex" 50W may have been titrated along with the strong-acid groups. However, if a few such groups were titrated, the values given in Table I for the salt-splitting capacities would be too high, and the actual difference between total capacity and salt-splitting capacity would be even greater.

TABLE I
Effect of Gamma Radiation on Cation Exchange Resins

Resin	Irradiation Conditions	Dose, rad	Moisture Content,		Wet Resin Volume, ml/g dry resin	Total Capacity, meq/g dry resin	Salt-splitting Capacity, meq/g dry resin
			% H ₂ O	g H ₂ O/eq resin			
"Dowex" 50W-X12 50-100 mesh	H-form	None	42.8	145	2.29	5.17	5.17
"Dowex" 50W-X12 50-100 mesh	H-form immersed in H ₂ O	0.88x10 ⁸	44.4	157	2.37	5.09	5.04
"Dowex" 50W-X12 50-100 mesh	H-form dry	0.76x10 ⁸	44.6	161	2.36	5.00	4.98
"Dowex" 50W-X12 50-100 mesh	H-form dry	1.10x10 ⁸	48.0	178	2.44	5.19	5.00
"Dowex" 50W-X12 50-100 mesh	H-form dry	2.67x10 ⁸	55.9	244	2.99	5.19	4.78
"Duolite" C-10 16-40 mesh	-	None	-	-	-	6.80	3.68
"Duolite" C-10 16-40 mesh	H-form dry	1.5x10 ⁸	-	-	-	6.24	3.06

The moisture content (see Figure 2) of "Dowex" 50W increased with increasing radiation dose, indicating a decrease in cross-linking. A comparison of the infrared spectra of the irradiated and unirradiated resins confirmed the conclusions from the capacity and moisture data. The spectrum of the resin receiving the lowest dose showed no significant change, while the spectra of the resins receiving the higher doses showed evidence of phenol groups and also a slight degree of depolymerization. A determination of the sulfate content of the aqueous leach indicated that H₂SO₄ was the main decomposition product. The infrared spectra of the residues obtained from the aqueous leaches showed a mixture of sulfonic acid fragments, with phenol groups appearing at the two highest levels of irradiation. Comparative photomicrographs of the irradiated and unirradiated resins indicated that the amount of fissuring or fragmentation was negligible and that the resin beads remained essentially intact.

FIG. 1 EFFECT OF GAMMA RADIATION ON CAPACITY

FIG. 2 THE EFFECT OF GAMMA RADIATION ON RELATIVE MOISTURE CONTENT

"Duolite" C-10 was slightly less stable than "Dowex" 50W. The "Duolite" resin showed about an 8% loss in total capacity and a 17% loss in salt-splitting capacity at a dose of 1.5×10^8 rad. The loss of sulfonic acid groups was not accompanied by the formation of weak acid groups as occurred with "Dowex" 50W resin. There was no significant damage to the polymer network.

The data in Table II show that "Dowex" 1-X8 suffered considerable damage at a dose of 10^8 rad; at a dose of 2.67×10^8 rad degradation was severe with a loss of 58% in total capacity and 85% in salt-splitting capacity. The difference between total and salt-splitting capacities of irradiated resin indicates that the strong-base groups, $-\text{CH}_2-\text{N}(\text{CH}_3)_3^+$, were replaced to some extent by weak-base groups, probably secondary and tertiary amines. The losses in capacity were about the same for the resin in the Cl form as in the OH form.

"Dowex" 1-X4 irradiated in the NO_3 form was more stable than "Dowex" 1-X8 irradiated in the OH form. At approximately equivalent doses the loss in total capacity for the NO_3 form was only about 14% compared with 35% for the OH form and the loss in salt-splitting capacity was about 20% for the NO_3 form compared with 50% for the OH form. It should be pointed out, however, that the degree of cross-linkage as well as the ionic form of the resin may affect the results, since it has been reported that quaternary amine polystyrene resins

have maximum stability at 5% cross-linkage⁽³⁾. "Dowex"-1 irradiated in the Cl form showed approximately the same losses in capacity as when irradiated in the OH form. Some investigators⁽³⁾ reported that the OH form was the more stable; others found the Cl form more stable⁽⁷⁾.

TABLE II
Effect of Gamma Radiation on Anion Exchange Resins

Resin	Irradiation Conditions	Dose, rad	Moisture Content,		Wet Resin Volume, ml/g dry resin	Total Capacity, meq/g dry resin	Salt-splitting Capacity, meq/g dry resin
			% H ₂ O	g H ₂ O/eq resin			
"Dowex" 1-X8 50-100 mesh	OH-form	None	59.0	383	3.68	3.80	3.80
"Dowex" 1-X8 50-100 mesh	OH-form moist	1.06x10 ⁸	52.4	465	3.48	2.47	1.88
"Dowex" 1-X8 50-100 mesh	OH-form moist	1.69x10 ⁸	46.9	411	2.92	2.15	1.64
"Dowex" 1-X8 50-100 mesh	OH-form moist	2.67x10 ⁸	31.7	294	2.18	1.58	0.57
"Dowex" 1-X8 50-100 mesh	Cl-form	None	37.9	162	2.31	3.81	3.81
"Dowex" 1-X8 50-100 mesh	Cl-form air dried	0.76x10 ⁸	41.3	238	2.54	2.96	2.77
"Dowex" 1-X8 50-100 mesh	Cl-form immersed in H ₂ O	0.87x10 ⁸	43.7	285	2.64	2.76	2.55
"Dowex" 1-X4 20-50 mesh	NO ₃ -form	None	46.6	181	2.79	4.81	4.78
"Dowex" 1-X4 20-50 mesh	NO ₃ -form moist	1.10x10 ⁸	49.4	235	2.96	4.15	3.69
"Permutit" SK 20-50 mesh	OH-form	None	69.1	501	5.02	4.47	2.87
"Permutit" SK 20-50 mesh	OH-form moist	1.69x10 ⁸	63.3	405	4.20	4.25	1.80
"Permutit" SK 20-50 mesh	OH-form moist	2.67x10 ⁸	61.4	386	3.89	4.12	1.29
"Permutit" SK 20-50 mesh	Cl-form	None	59.4	327	3.62	4.47	2.87
"Permutit" SK 20-50 mesh	Cl-form dry	1.06x10 ⁸	62.8	395	3.98	4.28	1.95
"Permutit" SK 20-50 mesh	Cl-form moist	1.08x10 ⁸	59.3	356	3.64	4.13	2.25

The moisture content (Figure 2) of "Dowex"-1, expressed as weight per cent, decreased with increasing dose for the OH form and increased for the Cl and NO₃ forms of the resin. This is explained by the fact that the moisture content is a complex function of the degree of cross-linkage, of the number and type of functional groups, and of the attached ions. Breaking of cross-linkages in the polymer network results in an increase in the moisture content, while the loss of functional groups usually leads to a decrease in the quantity of water associated with the resin. The amount of water lost is dependent on the nature of the ion attached to the functional group. The moisture content is thus a measure of the net effect of these opposing factors. The complexity of the function is illustrated in Figure 3 where the moisture content of "Dowex" 1-X8 in the OH form, expressed as g H₂O/eq resin, is shown to go through a maximum at about 10⁸ rad.

FIG. 3 THE EFFECT OF GAMMA RADIATION ON EQUIVALENT MOISTURE CONTENT

The infrared spectra of the irradiated anion resins indicated extensive depolymerization at the higher levels of irradiation. The aqueous leach had a strong amine odor, and the leach from "Dowex"-1 irradiated in the OH form contained NH₃. A detailed analysis of the decomposition products was not attempted.

"Permutit" SK was much more stable than "Dowex"-1, in agreement with the results of other investigators⁽⁶⁾. After exposure in the OH form to a dose of 2.67×10^8 rad, the "Permutit" resin retained 92% of its total capacity and 45% of its salt-splitting capacity. The moisture content decreased by only 11%. Infrared spectra showed no appreciable differences in the structure of the irradiated and unirradiated sample. The exact structure of this resin is not known but it is thought to be a polystyrene-divinylbenzene copolymer containing pyridine groups. The greater radiation stability of the resin is consistent with the trend found among organic compounds toward higher radiation resistance with increasing aromaticity. The incorporation of an exchange site, presumably pyridinium ion, directly into an aromatic nucleus would be expected to impart a protective effect against radiation.

Chemically, "Permutit" SK is much less stable in the hydroxyl form than is "Dowex"-1. The total and salt-splitting capacities reported in Table II represent values determined on a sample of the resin in the OH form that was stored for some time in a tightly stoppered bottle under a nitrogen atmosphere. Resin that was converted to the hydroxyl form and used immediately for determination of total and salt-splitting capacities gave considerably higher values.

These investigations showed that the main source of radiation damage to monofunctional cation exchange resins of the sulfonated polystyrene type is in breaking of the cross-linkages, while quaternary amine anion resins suffer more extensive damage through degradation of functional groups. The extent of damage to the anion resins is dependent on the nature of the functional group and the attached ion.

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