Effect of Gamma Irradiation on the Metal Sorption and Separation of Some Divalent Metals by Some New Polymeric Bifunctional Resins

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ABSTRACT: The metal sorption and separation of some divalent metals from solutions of varying acidity by a new series of gamma-irradiated ionic polymer resins have been investigated. Three polymeric resins, viz., phosphonic acid, phosphonate monoethyl ester, and phosphonate diethyl/monoethyl ester, were used in this study. The results of metal sorption and separation were compared with those of the well-known cation exchange resin Dowex X8. The results were correlated in the usual manner of distribution coefficients (D) of three divalent metals Sr(II), Co(II) and Ni(II). The results of metal sorption by the ionic resins under investigation compared with that of sulfonic acid resin, showed that Ni showed the highest affinity for the unirradiated monoethyl ester/phosphonic acid resin, while Sr showed the highest affinity for phosphonic acid resin and Co showed the highest affinity for mono/diethyl ester phosphonic acid resin. Moreover, the three metals (Sr, Co, Ni) showed the lowest affinity toward sulfonic acid resin. The calculated separation factors for the different resins indicate that the unirradiated phosphonic acid resin has the highest capacity to separate Sr from Ni, whereas mono/diethyl ester/phosphonic acid resins have the highest capacity to separate Co from Sr and Ni. Furthermore, the affinity of the ionic polymers for the metal ions was not greatly changed after gamma irradiation. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1091–1101, 1997

INTRODUCTION

The dual-mechanism bifunctional polymers (DMBP) are a new series of ionic polymer–supported resins first synthesized and characterized by Alexandratos et al.[1–6] They are classified into three classes according to the defined mechanism by which each group of resins performs the recognition process. These resins were successfully applied in metal sorption and separation. Phosphinic acid resins, as an example of the first class, have been shown to be more selective than the well-known sulfonic acid resins (Dowex resins). The phosphinic acid resin shows better sorption capacity for Eu(III), Am(III), UO_2(II), Th(IV), and Pu(III) than the sulfonic acid resins (Dowex resins) especially in high-acid solution (4M HNO_3) due to its superior coordinating capacity of the phosphoryl oxygen. Investigations have been carried out on the metal extraction and separation by other classes of DMBP resins operating through coordination and precipitation.[6] It has been reported that the phosphonic acid resin and its derivatives displayed higher affinity and selectivity for Fe, Hg, Ag, Mn, and Zn metals than the conventional sulfonic acid resins. Moreover, the bifunctional phosphonate diester/monoester polymer shows a supported ligand synergistic interaction with Ag ions.

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Investigation dealing with the effect of high-energy radiation on the ability of ion-exchange resins to extract metal ions are scarce. Such studies are of importance whenever such resins are used in the purification and separation of radioisotopes from waste solutions, especially those containing high levels of radiation. This study aims at studying the effect of high doses of gamma radiation on the metal extraction and separation of a number of metal ions by different classes of DMBP resins. Moreover, the results of metal sorption are compared with that of a well-known cation exchange resin (Dowex X8) irradiated to the same high doses of gamma radiation.

EXPERIMENTAL

Materials

The ionic polymers used throughout this study were kindly supplied by Dr. S. D. Alexandratos, Department of Chemistry, University of Tennessee. They were synthesized among a new series of ionic resins which possess a dual mechanism of bifunctional polymers (DMBPs) with unique applications in metal ion separation. Three different cation exchange resins were investigated, viz., phosphonic acid, monoethyl ester/phosphonic acid, and mono/diethyl ester/phosphonic acid resins. All of the resins contain 2% divinyl benzene and have a total acid capacity of 4.6, 4.03, and 4.09 mEq/g, respectively.[6]

Before use, the resins were conditioned by being eluted successively with 1 L of distilled water, 1 L of 4 wt % NaOH, 1 L of distilled water, 1 L of 4 wt % HCl, and finally, 1 L of distilled water. The elution time was 1 h for each process, and at the end, the resins were dried over a Buchner funnel. Three metal salts, strontium chloride, nickel sulfate, and cobalt sulfate, were used for metal sorption studies. All the chemical reagents used were supplied by Merk Co., Germany.

Gamma Irradiation

Irradiation to the required doses was carried out in the Co-60 gamma source at the National Center for Radiation Research and Technology (Cairo, Egypt). The conditioned dry resins were irradiated in a glass bottle in the presence of air and at a dose rate range of 0.5–0.55 Mrad/h. The irradiated resins were used in dry form and without further conditioning.

Analytical Determination of the Different Metal Ions

A general procedure was used to determine the concentration of the different metal ions in solution based on measuring the light absorption of the colored solution specific for each metal. In this method, a standard curve was first constructed for each metal ion under investigation, representing a relation between known different concentrations of the metal and the corresponding light absorption. These curves were used to determine unknown concentrations of the metal ions in solution by measuring light absorption. The light absorption measurements were performed with an UV/visible spectrophotometer (Unicam 8625 series).

The Sr(II) ion solution for light absorption measurements was prepared by mixing 5 mL of 0.05% chloranilic acid solution with 5 mL of the aqueous solution of Sr(II) ions at pH 5–7.[7] The mixture was chilled in ice for 3 h and centrifuged, and the light absorption of the colored solution was measured at a constant wavelength of 530 nm.

The colored solution of nickel metal was prepared in the form of complex with ammonia.[7] The procedure involves the addition of enough ammonium hydroxide to 10 mL of a known concentration of nickel sulfate to form nickel hydroxide. An excess amount of ammonium hydroxide is then added until the complete precipitation and formation of hexamine complexes, and the solution was completed to 100 mL. The light absorption was measured at a wavelength of 580 nm.

The metal cobalt was determined by a method depending on the formation of an orange complex with 8-hydroxyquinoline and extraction in a chloroform layer.[7] The light absorption of the Co(II) solution was measured at 420 nm.

Determination of the Distribution Coefficient

The distribution coefficient (D) was determined by the general procedure in which 0.5 g of the resin in an aqueous 10-mL solution of the heavy metal salt (10^{-4} mol/L) was shaken for 3 days. The distribution coefficient of the different metal ions was determined in $HClO_4$ background solutions throughout this work according to the following equation[8]:

$$D = \frac{\text{Concentration of Metal Ion in Resin}}{\text{Concentration of Metal Ion in Filtrate}} \times \frac{\text{Volume of Filtrate}}{\text{Mass of Resin}} \text{ mL/g} \quad (1)$$

The distribution of coefficients of the different metals were measured in different concentrations of $HClO_4$ (1–4M); however, in plotting the date, the molarity of the acid background was converted to the corresponding calculated pH values (0 to −0.6).

RESULTS AND DISCUSSION

In metal uptake, the pH of the solution has been shown to play an important role on the resin extraction process. The relation between the pH of the solution and the distribution coefficient is as follows[5]:
The extraction process at equilibrium can be written as:

$$M^{+n} + nA^- + R\text{--}H \leftrightarrow R_a\text{--}M + nH^+ + nA^- \quad (2)$$

where M^{+n} is the metal ion in aqueous solution, A^- is the associated anion in aqueous solution, R--H is the resin phase in the acid form, R_n--M is the resin phase in the metal-exchanged form.

The standard equilibrium constant is given in eq. (3), which is rewritten as eq. (4) in terms of the distribution coefficient.

$$K = ([R_nM][H])/[M + n][RH] \quad (3)$$

$$D = [H^+]^{-n}K[RH]^n \quad (4)$$

The logarithmic form of the equation is its most useful form because it shows the dependence of the extraction on the pH of the aqueous solution:

$$\log D = n \log[H^+] + n \log K + n \log[RH] \quad (5)$$

Measuring log D as a function of the solution pH with low metal ion concentration (that is, $10^{-4}N$) so as to keep the rightmost term constant is expected to give a straight line with a slope n (the number of protons exchanged for each metal ion transferred into the resin phase).[5] For a pure ion exchange reaction, generally, the slope is also the valence of the metal ion. It can be less than the valence, though, due to the formation of intermediate salt complexes. The purely coordinative mechanism gives a slope of zero since no protons are exchanged into the solution and the uptake is pH independent.[5]

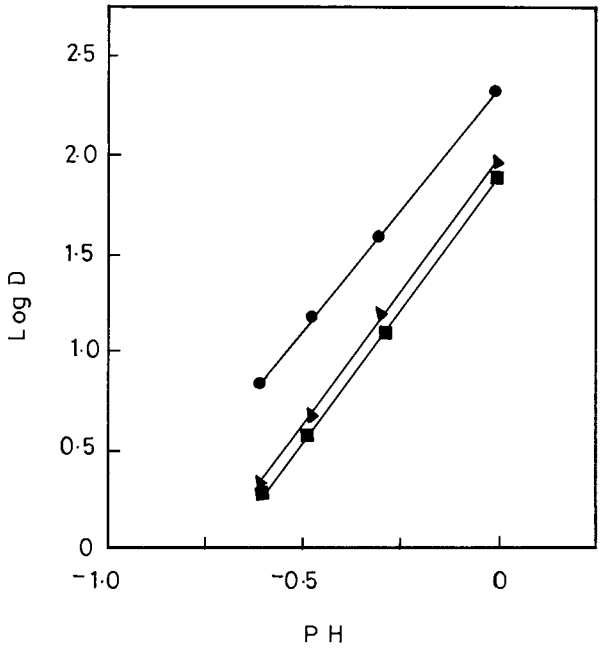
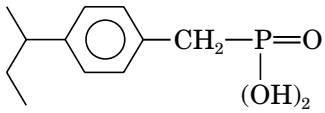


Figure 1 Log D versus pH plots for the sorption of strontium metal by phosphonic acid resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

Effect of Gamma Irradiation on the Metal Uptake by Phosphonic Acid Resins and Their Derivatives

Phosphonic acid or the ion exchange/coordination resins are examples of the class II of the (DMBP) ion exchange resin. In these resins, the phosphonic acid group is the ion exchange group while the coordination group allows tight binding of targeted ions onto the polymer support. The coordination groups are either phosphorus ester (mono- or diethyl ester) or tertiary amine. The metal sorption by gamma-irradiated phosphonic acid resin is as follows:



Figures 1–3 show the log D versus pH plots of gamma-irradiated phosphonic acid resin to different doses for the metal sorption of Sr(II), Co(II), and Ni(II) ions. The calculated slopes of these plots are presented in Table I.

It can be observed that the unirradiated phosphonic acid resin displays different complexation behavior toward the different metals. It shows a classic ion exchange behavior in solutions of vary-

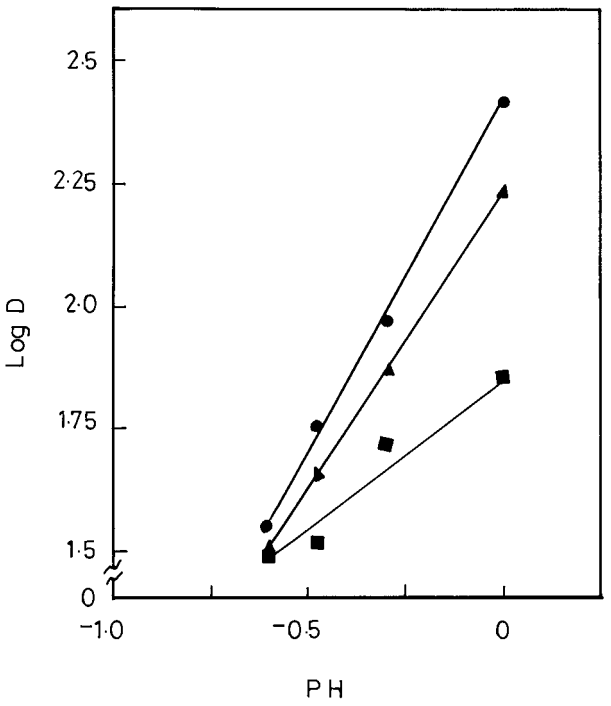


Figure 2 Log D versus pH plots for the sorption of cobalt metal by phosphonic acid resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

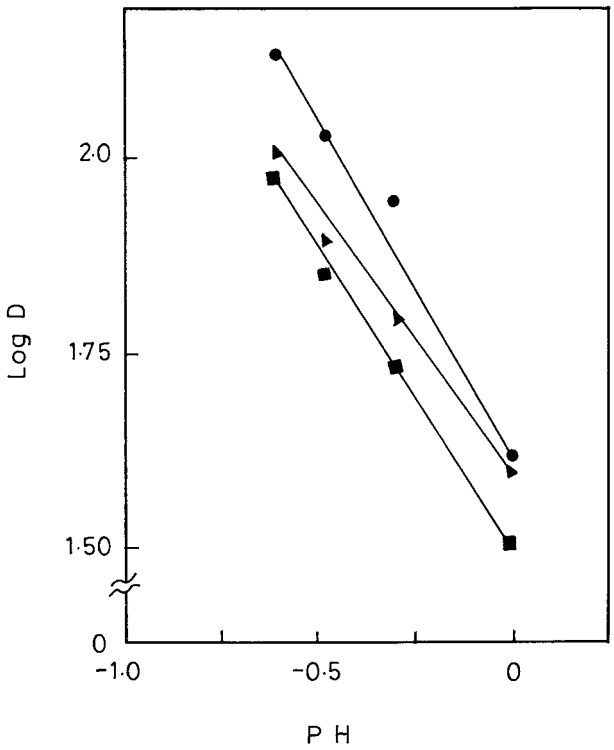


Figure 3 Log D versus pH plots for the sorption of nickel metal by phosphonic acid resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

ing acidity toward Sr(II) metal, given that the log D/pH plots yield a slope of 2.5. The greater value of the given slopes than 2 may be attributed to the presence of traces of trivalent metals or impurities in the metal salts used. The behavior is different in the case of Ni(II) and Co(II) under the same conditions; the resin displays a coordination mechanism given a slope less than 2. Exposure to gamma irradiation affects the exchange capacity of phosphonic acid resin for the Co(II) metals to a great extent. Moreover, irradiation seems to have no effect on the resin capacity to uptake Sr(II).

The logarithmic value of the distribution coefficient ($\log D$) of the metal is an important parameter and can be used to illustrate the affinity and selectivity of the metals for the resin matrix. The ratio between the distribution coefficients of the different metals (separation factor) is another important factor in separation science. The greater the deviation of this factor from unity, the easier will be the separation. In the work presented here the separation factors for different pairs of metals with unirradiated and phosphonic acid resin irradiated to different doses have been determined.

Comparing the $\log D$ values of the unirradiated resin in high-acid solutions, it can be noticed that the resin selectivity for the investigated metals was in the order Ni > Co > Sr. However, in low-acid solutions, the resin shows a selectivity series in the order Co > Sr > Ni. It is clear that the phosphonic resin tends to prefer Sr(II) over Ni(II) ions (SF = 5.3) in low-acid solutions rather than in high-acid solutions (SF = 0.052). Moreover, the resin shows a higher preference for

Table I The Slopes of log D/pH Plots of the Metal Sorption of Sr(II), Co(II) and Ni(II) by Gamma-Irradiated Phosphonic Acid Resin for Different Doses

Irradiation Dose (Mrad)	Slopes of log D Versus pH		
	Ni(II)	Sr(II)	Co(II)
Unirradiated	0.8	2.5	1.4
400	0.7	2.7	1.2
600	0.8	2.7	0.6

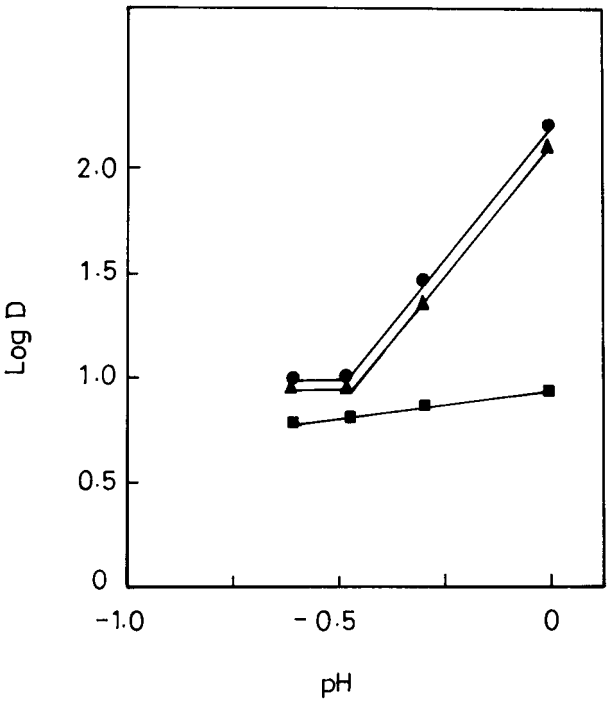
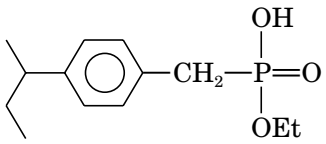


Figure 4 Log D versus pH plots for the sorption of strontium metal by phosphonic monoethyl ester resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

Co(II) over Ni(II) in low-acid solutions than in the high-acid ones, with SF values of 6.25 and 0.25, respectively. Furthermore, the unirradiated resin shows a high selectivity behavior for Co(II) over Sr(II) in high-acid solution with SF for Co/Sr of 12.58, while the value of SF in low-acid solutions is 1.18.

Metal Sorption by Gamma-Irradiated Phosphonate Monoethyl Ester Resin



Mono- and diethyl ester derivatives are considered the coordinating groups on the phosphonic acid resin. Figures 4–6 show the log D/pH plots of irradiated monoethyl ester/phosphonic resin for the extraction behavior of the different metals. The corresponding calculated slopes of these plots are shown in Table II. Considering the log D values of the different metals at the representative acid concentration, a few points may be drawn:

1. In general, within the studied range of pH, the resin is highly selective for the different metals since log D values are greater than 1.
2. When the metal extraction was performed at a low-acid concentration, the unirradiated monethyl ester/phosphonic resin shows some selectivity for the different metal ions in the order Co(II) > Sr(II) > Ni(II). At a high-acid concentration, the selectivity series is in the order Ni(II) > Co(II) > Sr(II).
3. Considering the ratio between the distribution coefficient values of the different metal ions, it is shown that the SF values for Sr/Ni at low- and high-acid concentrations are 1.6 and 0.03, respectively. These values suggest the preference of Sr over Ni at low-acid concentrations rather than at high-

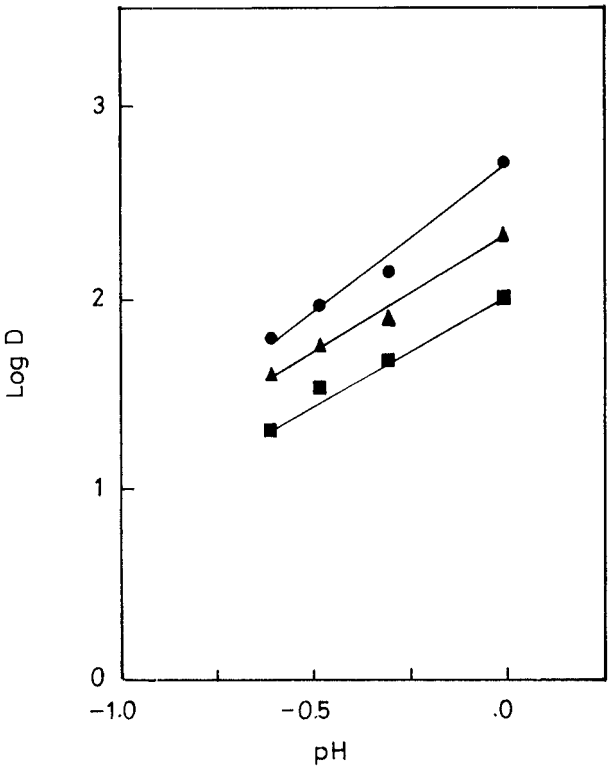


Figure 5 Log D versus pH plots for the sorption of cobalt metal by phosphonic monoethyl ester resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

acid concentrations. The SF values for Co/Ni at the same acid concentrations are 5.4 and 0.2, respectively, suggesting that the resin is more selective for Co over Ni at low-acid concentrations than at high-acid concentrations. In the case of Co/Sr, the SF values were 3.3 and 6.4 under the same acid concentration, respectively, which shows that the resin's capacity to separate Co mixed with Sr at high-acid concentrations is almost double that at low-acid concentrations.

Table II Slopes of log *D*/pH Plots of Unirradiated and Irradiated Monoethyl Ester/Phosphonic Acid Resin for Different Metals

Irradiation Dose (Mrad)	Calculated Slopes		
	Ni(II)	Sr(II)	Co(II)
Unirradiated	0 (4–3*M*)	0 (4–3*M*)	1.54
	1.2 (4–1*M*)	2.5 (3–1*M*)	
400	0 (4–3*M*)	0 (4–3*M*)	1.21
	2.8 (3–1*M*)	2.5 (3–1*M*)	
600	0.6	0.3	1.15

It is clear that the introduction of a monoethyl ester group on the polymer support of phosphonic acid resin has a pronounced effect on its capacity to sorb the different metals under investigation. The unirradiated and irradiated resins (400 Mrad) display no ion exchange behavior toward Ni(II), giving a slope of zero within the high-acid range (4–3*M*). In the range of the acid concentration 3–1*M,* these resins show a sorption behavior via a coordination mechanism in the case of the unirradiated resin, while the irradiated resin (400 Mrad) exhibits a normal ion exchange behavior. On the other hand, at higher irradiation doses (600 Mrad), the resins showed a pure coordination sorption mechanism over the range studied of 4*M* $HClO_4$ to 1*M* $HClO_4$. Similar trends are observed in the case of the sorption of Sr(II) metal by monoethyl ester/phosphonic acid resin on irradiation. It is to be noted that the slopes of log *D* versus pH in the case of the sorption of Ni(II) showed a reverse direction (negative slopes) rather than those observed with Sr(II). This behavior indicates that the sorption of Ni(II) by monoethyl ester resin is much higher at a high-acid concentration than at a low-acid concentration. These findings are in accordance with the work of Alexandratos et al. on the sorption of Ag(I) by diethyl and dimethyl ester resin.[6]

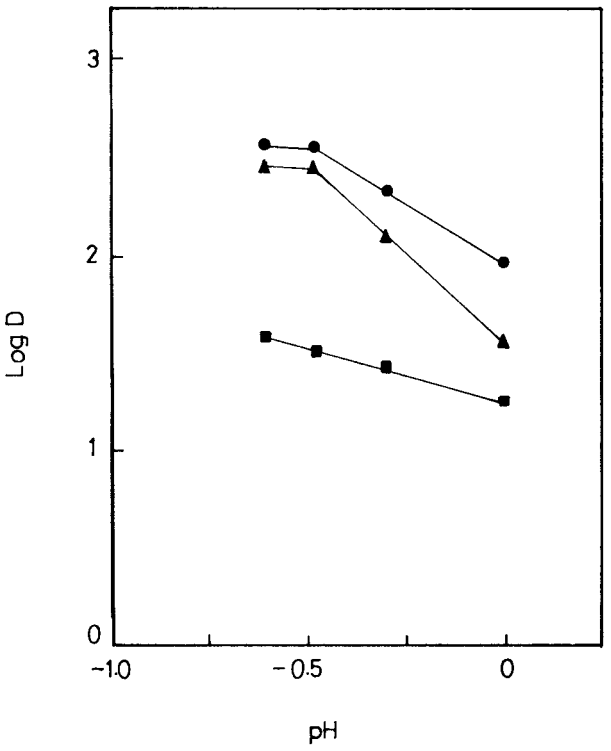


Figure 6 Log *D* versus pH plots for the sorption of nickel metal by phosphonic monoethyl ester resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

The results with Co(II) are strikingly different, as shown in Figure 5. Overall, the varying acid concentration range, the log *D* versus pH plots of the unirradiated and irradiated resin give slopes more than 1 and less than 2. This is probably due to the extraction of the neutral species [Co $(CLO_4)2]^o$ and the free divalent cation in the proportion, which gives the observed slope.[5] However, the calculated slopes are shown to decrease with increasing irradiation dose from 400 to 600 Mrad.

It is to be noted that the uptake of Ni(II) ions by phosphonic and monoethyl/ester derivatives in terms of log *D* versus pH displays a different trend from that obtained in the case of the uptake of Co(II) and Sr(II) ions by these types of resins. The resins sorb Ni(II) to a higher level than Co(II) or Sr(II), especially from the high-acid solutions.

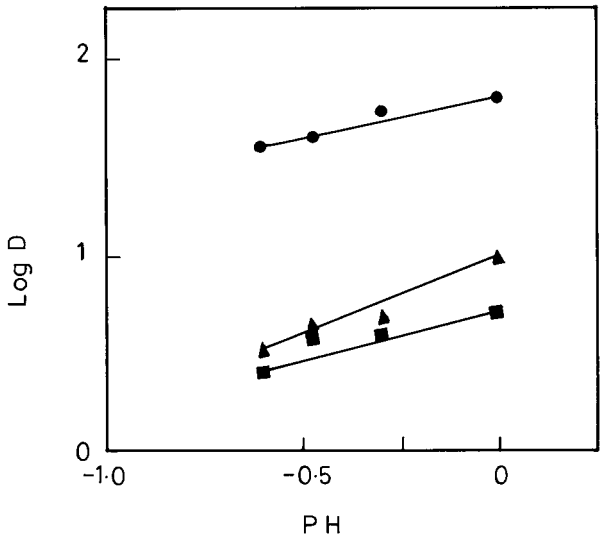
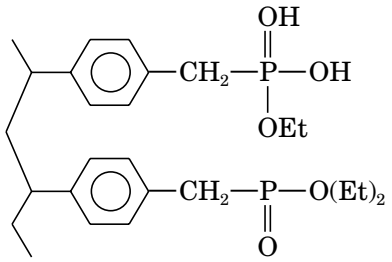


Figure 7 Log D versus pH plots for the sorption of strontium metal by phosphonic mono/diethyl ester resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

Metal Sorption by Gamma-Irradiated Phosphonate Mono/diethyl Ester Resin



Figures 7–9 show the capacity of irradiated mono/diethyl ester/phosphonic acid resin to complex Ni(II), Sr(II) and Co(II) as log D/pH plots. The corresponding calculated slopes of the log D/pH plots are shown in Table III.

It is evident that neither the unirradiated nor the irradiated resin at the pH range studied is selective for the different metals under investigation. Irrespective of the irradiation dose, the slopes for the different metals are less than 1, suggesting that the sorption process is performed through an ion exchange and coordination mechanism.

If the values of the log D of the different metals obtained in the case of the unirradiated resin are compared with those of the irradiated resin, a few important conclusions can reached.

1. At low- and high-concentrated acid solutions, the unirradiated resin shows a selectivity series in the order of Co > Ni > Sr. This order of selectivity does not change on exposure to gamma irradiation at low-acid concentration. However, at high-acid concentration ($4M$), this order was found to change to be Ni > Co > Sr.
2. The calculation of the SF for different metal pairs indicates that the unirradiated resin shows a high capacity to separate Ni(II) from Sr at high-acid concentrations rather than at low-acid concentrations: the SF values are 4.6 and 1.3, respectively. Also, the resin prefers Co over Ni at low-acid concentrations (SF = 14.4), while the value of SF at high-acid concentrations is 1.6. Moreover, the values of SF for Co/Sr at low-acid concentrations is 19.0, while the SF for Co/Sr at high-acid concentrations is 7.1.

Metal Sorption by Gamma-Irradiated Dowex X8 Resin (A Comparative Investigation)

The capacity of sulfonic acid resin (Dowex X8) to exchange Sr(II), Co(II), and Ni(II) in terms of

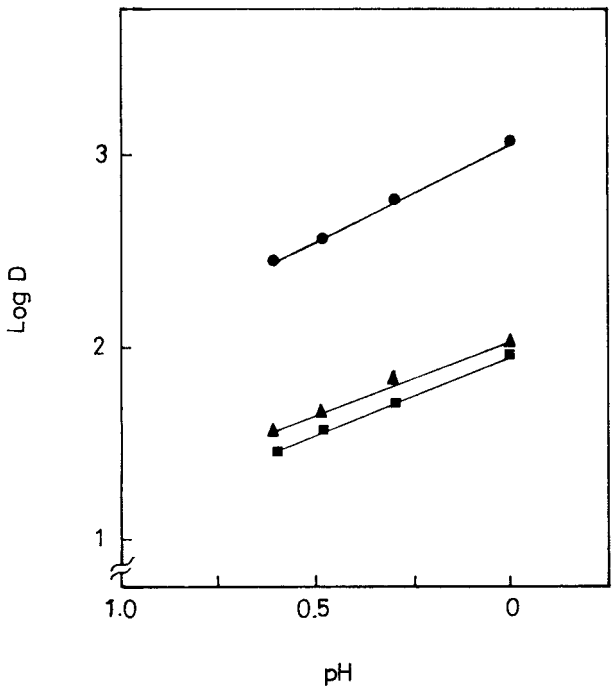


Figure 8 Log D versus pH plots for the sorption of cobalt metal by phosphonic mono/diethyl ester resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

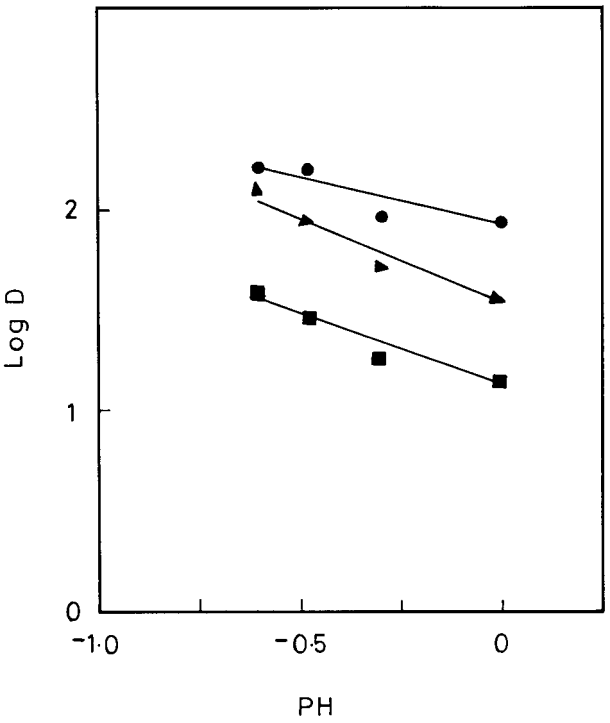


Figure 9 Log D versus pH plots for the sorption of nickel metal by phosphonic mono/diethyl ester resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

log D versus pH before and after being exposed to different radiation doses is shown in Figures 10–12.

It is clear that the resin displays a similar exchange capacity for Sr(II) and Co(II) and a different capacity for Ni (II) metal. For the complexation of Sr (II) metal, the unirradiated resin shows ion exchange behavior in solutions of varying acidity with log D versus pH plots yielding a slope of 2.8, as shown in Table IV. The ion exchange sorption behavior for Sr (II) is totally

Table III The Slopes of log D/pH Plots of Unirradiated and Irradiated Mono/Diethyl Ester/Phosphonic Acid Resin for Different Metal Ions

Irradiation Dose (Mrad)	Slopes of log D Versus pH Plots		
	Ni(II)	Sr(II)	Co(II)
Unirradiated	0.5	0.44	1
400	1	0.8	0.74
600	0.7	0.5	0.82

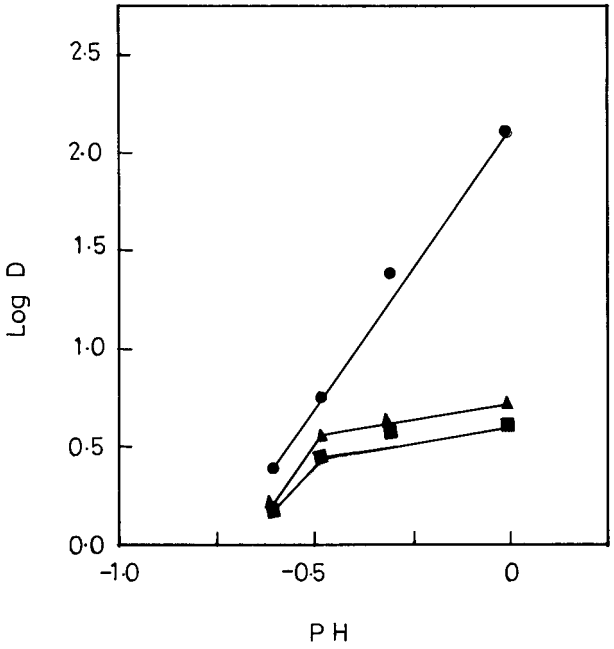


Figure 10 Log D versus pH plots for the sorption of strontium metal by Dowex resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

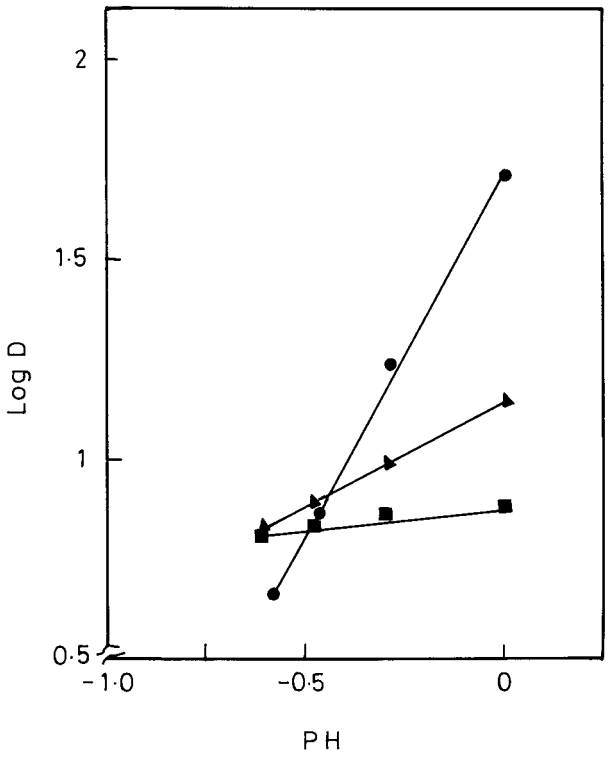


Figure 11 Log D versus pH plots for the sorption of cobalt metal by Dowex resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

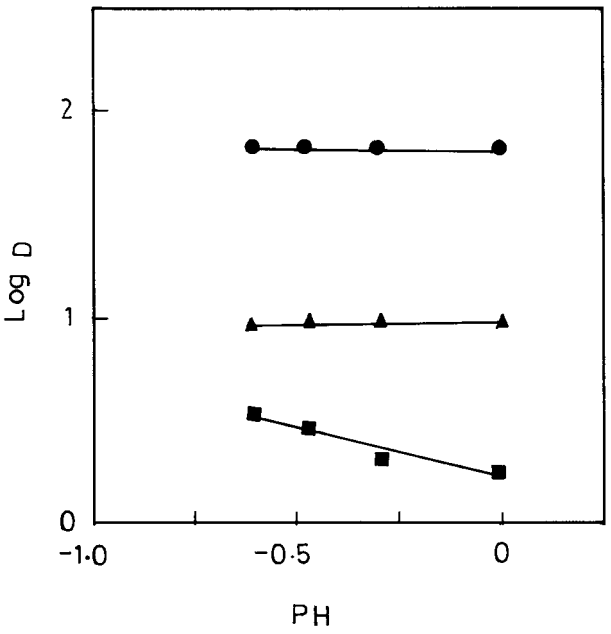


Figure 12 Log *D* versus pH plots for the sorption of nickel metal by Dowex resin irradiated to different doses: (●) unirradiated, (▲) 400 Mrad, and (■) 600 Mrad.

changed on irradiation with varying acid concentrations of solution. Irradiated Dowex X8 to 400 Mrad gives a slope of 2.4 in the limited high-acid concentration range of 3–4*M,* while the slope decreased to 0.3 within the acid range of 3–1*M*. The performance of the resin irradiated to 600 Mrad is seen to change within the studied acid concentration. The log *D* versus pH plot indicates a slope of 1.3 within the acid concentration between 4 and 3*M*. At a lower acid concentration within the acid range of 1–3*M,* the slope is 0.1.

Results of the complexation of Co(II) metal by Dowex X8 resin, shown in Figure 11, show a strikingly different exchange behavior with the metal ions. The log *D* versus pH plots of the unirradiated resin give a slope of 1.7, while the obtained slope for the irradiated resin to 400 Mrad is 0.5 within the overall acid concentration. For the irradiated resin to 600 Mrad, the plot gives a slope of 0.1. The unirradiated resin shows nearly constant uptake values for Ni (II) over all of the varying acid concentrations with a slope of zero, as shown in Figure 12. Irradiation of the resin to 400 Mrad seems to have no effect on the slope of the log *D* versus pH plots; however, the distribution coefficient is shown to decrease significantly. A higher irradiation dose of 600 Mrad is shown to decrease this ability with decreasing acid concentration. In general, the uptake of the metal ions by the resin in terms of log *D* is shown to decrease with increasing irradiation dose.

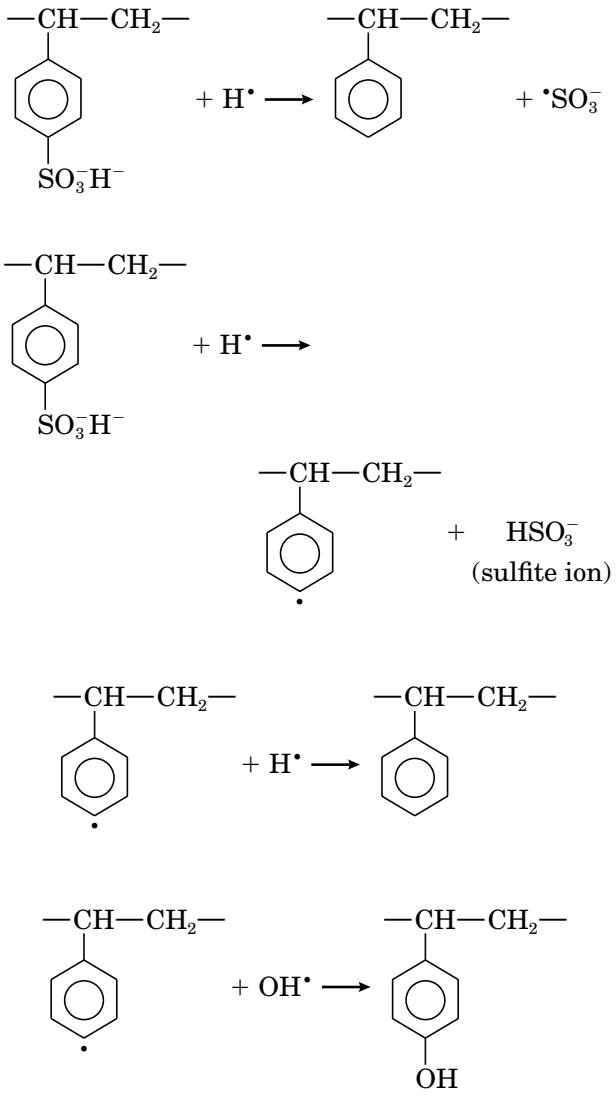
On the basis of the results of the complexation of the different metals, several points may be indicated. First, the capacity of sulfonic acid resin (Dowex X8) for the uptake of Ni (II) metal does not change within the acid concentrations studied. Moreover, gamma irradiation has no effect on the uptake behavior of the metal ions. However, the distribution coefficient of Ni (II) is shown to decrease with increasing irradiation dose. The unirradiated sulfonic resin displays an equal capacity for extracting Sr(II) and Co(II) metals within the studied acid range. Second, on irradiation, Sr(II) and Co(II) show affinity to the Dowex X8 resin dependent on the acid concentration range. The slope of log *D* versus the acid concentration plot, for Sr(II) metal in the high-acid concentration range studied, indicates that the extraction process is performed by an ion exchange mechanism. At a low-acid concentration, the sorption process seems to go by a coordination mechanism since the slope is decreased to 0.3. The irradiation results of the resin at relatively higher irradiation doses indicate higher coordinating capacity. Similar trends are observed in the case of the sorption process of Co (II) metal in both high- and low-acid concentrations. Also, the distribution coefficients of both metals are found to decrease with increasing irradiation dose. Finally, the observed decrease in distribution coefficient of the studied metals may be attributed to the damage of the resin caused by degradation. It is believed that H atoms formed by the radiolysis of the water molecule present in the solution of the resin itself induce degradation. The H atoms will react with

Table IV Slopes of log *D*/pH Plots of the Metal Sorption of Sr(II), Co(II), and Ni(II) by Gamma-Irradiated Dowex X8 Resin

Irradiation Dose (Mrad)	Slopes of log *D* Versus pH Plots		
	Ni(II)	Sr(II)	Co(II)
Unirradiated	0	2.8	1.73
400	0	2.4, 0.3 (4–3*M*), (3–1*M*)[a]	0.5
600	0.7	1.3, 0.1 (4–3*M*), (3–1*M*)	0.1

[a] The values in parentheses are the molarities of the corresponding acid concentrations.

the resin and cause degradation according to the following possible reactions[9]:



The sulfite ions must have been converted to sulfate by reacting with oxygen in the atmosphere, with OH radicals, or with hydrogen peroxide (decomposition product of water). The formed SO_3^- radicals may in turn react with water molecules near the exchange group to form H atoms[9]: $SO_3^- + H_2O \rightarrow HSO_4^- + H$. The resulting H atoms can in turn induce further degradation of the resin. In addition, the possibility that degradation could occur in the main chain to give lower molecular weight fragments still exists. Similar mechanisms may be suggested for the degradation of phosphonic acid resin and its derivatives caused by gamma irradiation.

CONCLUSIONS

The obtained results for metal sorption with the investigated DMBP resins as compared with the known sulfonic acid (Dowex X8) resin for the different metals are summarized in Table V. On the basis of these data, several points may be concluded.

Affinity of the Different Metal Ions to the Unirradiated Resins

The affinity of Ni(II) metal ion for the different resins can be arranged in the following order: monoethyl ester > mono/diethyl ester > Dowex ≥ phosphonic. For Sr(II) metal ion, the order is phosophonic > monoethyl ester > dowex > mono/diethyl ester. For Co(II) metal ion, the order is mono/diethyl ester > monoethyl ester > phosphonic > Dowex.

Also, it can be observed that the highest D value was observed with mono/diothyl ester and phosphonic acid resins for Co(II). At a high-acid concentration, the affinity of Ni(II) metal ion for the different resins shows the following respective order: monoethyl ester > mono/diethyl ester > phosphonic > Dowex. For Sr(II) the order is mono/diethyl ester > monoethyl ester > phosphonic > Dowex. For Co(II), the order is mono/diethyl ester > monoethyl ester > phosphonic > Dowex. The highest D value was observed with the mono/diethyl ester resin for Co(II).

Selectivity and Preference of Unirradiated Resins for the Different Metal Ions

It is clear that all of the investigated resins displayed high affinity for the different metals at low-acid concentrations since log D values were greater than 1. However, this selectivity differs from one resin to the other and from one metal to the other. The separation factors were calculated for different pairs of metals for the different studied resins at low-acid concentration. According to the values of SF for Sr/Ni metals pairs, the resins can be arranged in the following order: phosphonic > Dowex > monoethyl ester > mono/diethyl ester. For Co/Ni metal pairs, the order is mono/diethyl ester ≫ phosphonic > monoethyl ester > sulfonic. For Co/Sr, the order is mono/diethyl ester > monoethyl ester > phosphonic > Dowex.

Table V *D* Values for the Dowex X8 and DMBP Resins Before (Upper Row) and After (Lower Row) Being Irradiated to 400 Mrad; *D* Values from Extremely Low- and High-Acid Solutions

Metal Ions	Distribution Coefficient							
	Dowex Resin SO_3H		Phosphonic Resin $PO(OH)_2$		Monoethyl Ester/ Phosphonic Resin		Mono/Diethyl Ester Phosphonic Resin	
	1*M*	4*M*	1*M*	4*M*	1*M*	4*M*	1*M*	4*M*
Ni(II)	50.1	100	41.1	135.5	93.3	355.6	77.6	162.2
	65.6	64.9	40.0	102.6	35.5	309.7	63.3	125.9
Sr(II)	126	2.4	218.3	8.68	150	9.44	59.0	35.5
	5.3	1.7	97.3	2.10	125.9	9.14	10.0	3.2
Co(II)	50.1	1.7	257.0	34.67	473.1	59.56	1122	266
	10.7	7.6	169.8	31.6	211.3	40.7	97.7	35.7

Affinity of the Different Metal Ions for Different Irradiated Resins

At low-acid concentration, gamma irradiation seems to have no effect on the affinity of Dowex resin for Ni(II). However, a remarkable effect on the affinity of Sr(II) and Co(II) metals to the resins can be seen after exposure to gamma irradiation. On the other hand, the affinity of different metals to the DMBP resins was not greatly changed after irradiation to the same dosage. The affinity order of the different metals to the irradiated resins, in terms of the percent loss in the *D* values are as follows. For Ni(II), the order is Dowex > phosphonic > mono/diethyl ester > monoethyl ester. For Sr(II), the order is monoethyl ester > phosphonic > mono/diethyl ester > Dowex. For Co(II), the order is mono/diethyl ester > monoethyl ester > phosphonic > Dowex.

In summary, it may be concluded that the new series of DMBP resins show higher capacity and better selectivity for the divalent metal ions used than the known cation exchange resin Dowex X8. Moreover, the phosphonic acid resin shows higher capacity at low-acid concentrations than the ester derivatives of phosphonic acid resins; the opposite is true at high-acid concentrations. The observed high capacity of mono/diethyl ester at high-acid concentrations may be due to the electron-donating character of the mono/diethyl ester at such acid concentration, leading to more complexation of metals rather than at low-acid concentrations. Moreover, it is shown that two ligands on a bifunctional polymer cooperate to complex more of the target species than either one could alone. The phenomenon is then termed supported ligand synergistic interaction.

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