

Retention of Gallium Ions from Acidic Solutions by Pyridine Strong-Base Anion Exchangers

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ABSTRACT: Using the batch method, the retention of Ga(III) from HCl solutions by two gel-type pyridine strong-base anion exchangers containing 1-methyl- or 1-butyl-4-vinylpyridinium chloride structural units, called S₁ and S₂ resins, respectively, was studied. The influence of the HCl and Ga(III) concentrations as well as of the contact time between the resin and the liquid phase was investigated. The parameters, which characterize the retention process, were estimated using Langmuir and Freundlich isotherms. Both resins exhibited a higher affinity for gallium ions from a 6M HCl solution. According to Langmuir isotherms, max-

imum retention capacities of 44.44 and 60 mg Ga(III)/g dry resin for the S₁ and S₂ resins, respectively, were obtained. Freundlich isotherms provide additional proof for a higher affinity of the S₂ resin for Ga(III) from HCl solutions. It is clear that the substituent length increase on N⁺ atoms led to an increasing affinity of the pyridine strong base anion exchangers toward Ga(III). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3440–3444, 2002

Key words: adsorption; ion exchangers; metal-polymer complexes; resins

INTRODUCTION

The increasing need for gallium in the electronics industry led to the synthesis of different ion-exchange resins used for the removal, recovery, and determination of trace gallium.^{1–4} It is well known that the recovery, purification, and preconcentration of some metals as noble metals and plutonium occur from acid solutions. In this condition, the metal cations exist as complex anions and the strong-base ion exchangers are used for their retention. As an example, for more than 30 years, the anion-exchange process has been used to recover and purify plutonium from nitric acid solutions.

Recently, styrene strong-base anion exchangers with alkyl substituents of different length on N⁺ atoms were studied and their Pu(IV) retention capacities from nitric acid solutions were compared. The alkyl length effect from N⁺ atoms was observed.⁵ Also, the sorption of platinum group metals and gold chloro-complexes by styrene anion exchangers was reported.⁶

An alternative to the styrene strong-base anion exchangers for retention processes of some complex anions can be those based on quaternized 4-vinylpyridine–divinylbenzene copolymers. Thus, the anion-exchangers with 1-alkyl-4-vinylpyridinium chloride structural units were suggested in the recovery and purification of plutonium from nitric acid solutions of scrap materials.⁷

Our previous studies showed the retention of the Fe(III) cation as an aquasulfocomplex as well as of Hg(II), Zn(II), and Pb(II) cations as chlorocomplexes by pyridine strong-base anions with different substituents on N⁺ atoms. These exchangers exhibited higher retention capacities compared to those of two styrene commercially available strong-base anion exchangers, namely, Amberlite IRA-400 and Amberlite IRA-410. The influence of the chemical nature of the substituents on N⁺ atoms from pyridine rings was observed.^{8,9}

The present study evaluated the Ga(III) retention possibility from HCl aqueous solutions and water by two pyridine strong-base anion exchangers with methyl and butyl substituents on N⁺ atoms. The results are compared to those obtained with the commercially available strong-base anion exchanger Amberlite IRA-400. The influence of the following factors, resin type, HCl solution concentration, and contact time between the resin and the liquid phases as well as the Ga(III) concentration were investigated. The parameters, which characterize the retention process, were estimated using Langmuir and Freundlich isotherms.

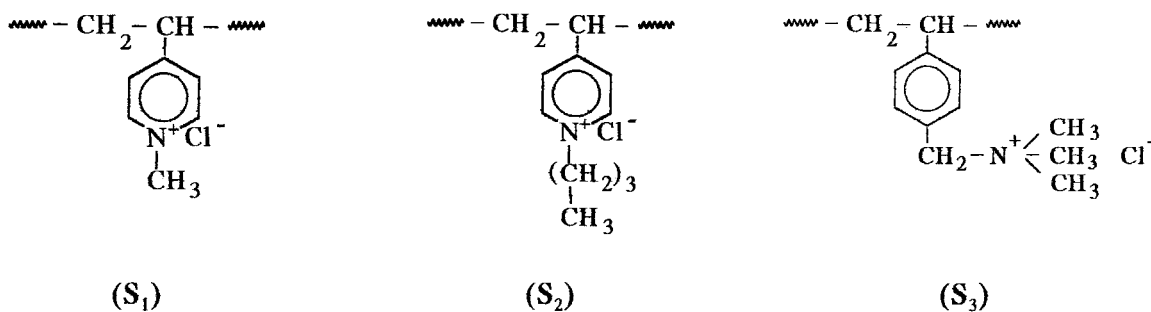
EXPERIMENTAL

Materials

Ion-exchanger resins

Two pyridine strong-base anion-exchanger and Amberlite IRA-400, so-called S₁, S₂, and S₃, respectively, samples were used, which have the following active structural units:

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All the resins were of a gel type and 8% crosslinked with divinylbenzene. Their ion-exchange capacity values were 5.07; 3.77, and 4.98 meq/g dry resin, respectively, of the Cl⁻ form as well as 2.03; 1.58, and 1.47 meq/mL wet resin, respectively, of the same form.

The synthesis and the main characteristics of these resins were shown elsewhere.^{10,11} The resins were sieved at a particle size of 0.4–0.8 mm. Before the retention process, S₁–S₃ samples were left in 1M HCl, then washed with deionized water until the absence of Cl⁻ ions in the washing water.

Reagents

An aqueous Ga(III) stock solution of 1000 μg/mL was prepared from Ga(NO₃)₃ · 8H₂O. Working solutions were prepared by dilution of the stock solution to the wanted concentrations: a Rhodamine B solution of a 0.5% concentration in 6M HCl, an aqueous hydroxylamine hydrochloride solution of 1.0% concentration, and aqueous HCl solutions of different concentrations.

Methods: measurement of retention capacity for Ga(III) cations

The retention process was performed by the batch method as follows: Each anion-exchanger sample of 0.2 g with known humidity was contacted at room temperature (about 25°C) with volumes of different liquid phases, as will be shown in the next section. The different contact times with permanent shake were used. The retained Ga(III) amount was determined from the difference between the ion concentration in the solution before and after the retention process.

Gallium was spectrophotometrically determined by the Rhodamine B method.¹² From a 6M HCl medium, the ionic association between [GaCl₄⁻] and the dye was extracted with benzene and determined at λ 565 nm respecting the conditions of the Lambert–Beer law. A Specord UV-VIS was used. Reproducibility was verified by duplication.

RESULTS AND DISCUSSION

Individual solutions of 100 μg Ga(III)/mL in 2, 3, 4, 5, and 6M HCl were studied. A resin, 0.2 g, with a

known humidity was contacted for 24 h with 15 mL of each of the five HCl solutions. A comparison of the Ga(III) retention as a function of the HCl concentration is presented in Figure 1. From the results plotted in Figure 1, the following aspects can be noted:

- The retention feature of the S₁ resin differs markedly from those of the other two resins. For this resin, an abrupt decrease of the retention capacity in the 3–4M HCl range and a fast increase from 4 to 5M HCl occurs. This situation can be explained by the fact that the metal cations in aqueous solutions with an excess of anions (here Cl⁻ from HCl) form different species which can have various retention properties. S₁ resin, with the lowest hydrophobicity, probably excludes from the retention process the species which exist in the 3–4M HCl range. At higher HCl concentrations, such as 5M and especially 6M HCl, the [GaCl₄⁻] complex anion is prevalent and the retention by means of ion exchange is favorable.
- For all the three resins, the highest retention capacity values of the Ga(III) cations [mg Ga(III)/g

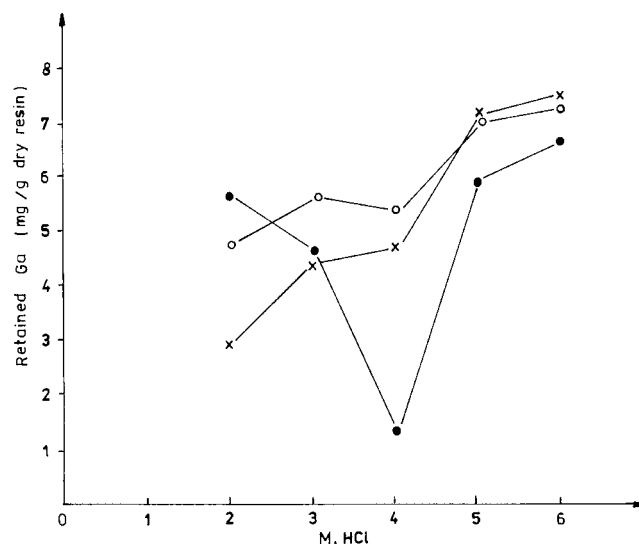


Figure 1 Retention of Ga(III) from HCl aqueous solutions versus acid concentration: (●) S₁ resin; (×) S₂ resin; (○) S₃ resin.

TABLE I
Ga(III) Retention from 6M HCl Solution
Compared to Those from Water

| Resin | Retained Ga(III) (mg/g dry resin) | Retained Ga(III) (%) | K_d | Retention medium |
|----------------|--------------------------------------|----------------------------|---------|---------------------|
| S ₁ | 6.69 | 89.92 | 669.35 | 6M HCl |
| | 4.87 | 66.75 | 147.68 | Water |
| S ₂ | 7.34 | 99.04 | 7339.14 | 6M HCl |
| | 5.07 | 68.26 | 160.90 | Water |
| S ₃ | 7.26 | 98.03 | 3634.03 | 6M HCl |
| | 4.96 | 66.75 | 150.26 | Water |

dry resin] were obtained in 6M HCl. At this HCl concentration, the retention-capacity value of the S₂ resin slightly exceeded that of the S₃ resin, but in the case of the two pyridine exchangers, the S₂ sample has a higher retention than that of the S₁ sample. This aspect suggests that, in the pyridine resins replacing the methyl substituent from N⁺ atoms with the butyl substituent, a more efficient resin for Ga(III) was obtained.

- The ion-exchange capacity values do not have a role in the retention process. The S₁ resin, with greater ion-exchange capacities, has a lower retention than that of the S₂ resin, which has smaller ion-exchange capacities.

In the same experimental conditions, the retention capacities of Ga(III) both from the 6M HCl solution and water by all the three resins were determined. In addition, the distribution coefficients (K_d) were calcu-

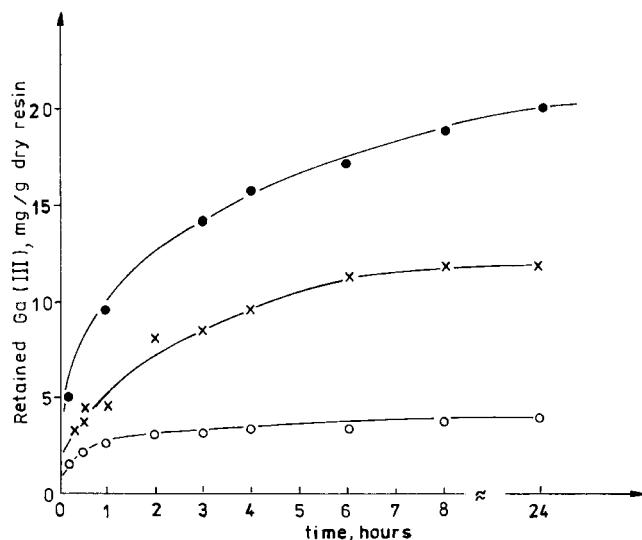


Figure 2 Retention of Ga(III) from 6M HCl solutions with different metal ion concentrations by S₁ sample versus contact time between liquid phase and resin: (○) 18 µg Ga(III)/mL; (×) 54 µg Ga(III)/mL; (●) 90 µg Ga(III)/mL.

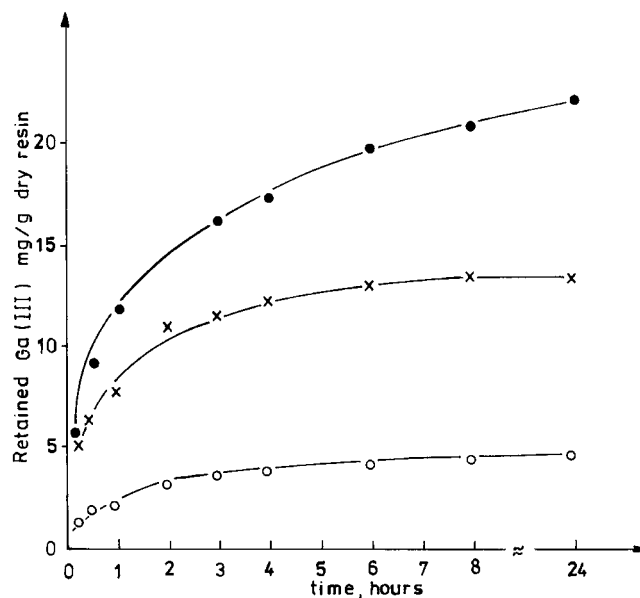
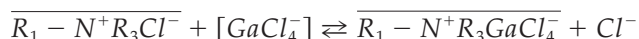


Figure 3 Retention of Ga(III) from 6M HCl solutions with different metal ion concentrations by S₂ sample versus contact time between liquid phase and resin: (○) 18 µg Ga(III)/mL; (×) 54 µg Ga(III)/mL; (●) 90 µg Ga(III)/mL.

lated. All the data are shown in Table I. The results described in Table I suggest that the 6M HCl solution is more suitable than is water for the retention of Ga(III). In the 6M HCl solution, Ga(III) cations exist as $[GaCl_4^-]$ complex anions and the prevalent retention mechanism occurs by an ion-exchange process as follows:



In water, probably, the sorption phenomenon of the Ga(NO₃)₃ electrolyte takes place. The influence of different parameters such as the Ga(III) concentration in the 6M HCl solution and contact time between the

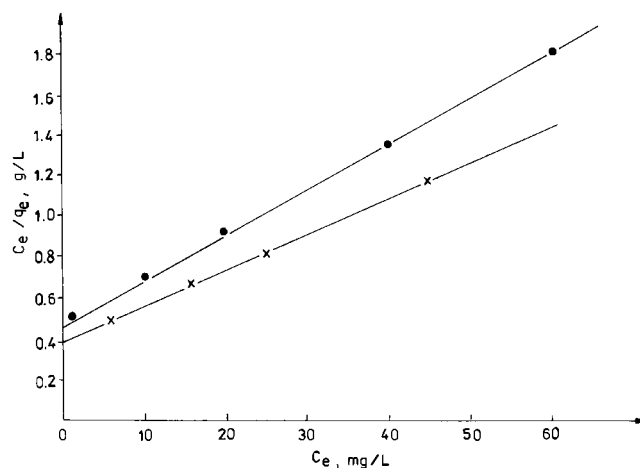


Figure 4 Langmuir plots for retention of Ga(III) by resins: (●) S₁; (×) S₂.

TABLE II
Analysis of Langmuir Isotherms

| Anion exchangers | Q^0 (mg g ⁻¹) | b (mg ⁻¹ L) | K_L (L g ⁻¹) | C_0 (mg L) | R_L |
|------------------|--------------------------------|-----------------------------|-------------------------------|-----------------|-------|
| S ₁ | 44.44 | 0.0468 | 2.083 | 18 | 0.540 |
| | | | | 54 | 0.283 |
| | | | | 90 | 0.191 |
| | | | | 180 | 0.106 |
| S ₂ | 60.00 | 0.0066 | 0.400 | 18 | 0.894 |
| | | | | 54 | 0.735 |
| | | | | 90 | 0.627 |
| | | | | 180 | 0.457 |

resin and the liquid phase were investigated. For this situation, individual solutions of 18, 54, 90, and 180 μg Ga(III)/mL in 6M HCl were studied. Then, 0.1 g of the resin with known humidity was contacted with 25 mL of each of the four solutions for different times. The results are plotted in Figures 2 and 3 for the S₁ and S₂ samples. The three curves in each figure represent the results measured in the solutions of 18, 54, and 90 μg Ga(III)/mL.

The two figures give the following results:

- The rate of retention in the initial stage proceeds quickly in every solution;
- The retention in the solution of 18 μg Ga(III)/mL needs less time to come to an end than does that in the other two solutions;
- As expected, the retention capacities increase with increasing concentrations.

By analogy with the adsorption process, the ion-exchange process was described using Langmuir and Freundlich isotherms.

Langmuir isotherms

The results of the equilibrium obtained for various concentrations were analyzed on the base of the Langmuir eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{Q^0 \times b} + \frac{C_e}{Q^0} \quad (1)$$

where C_e is the equilibrium concentration of gallium in solution (mg/L); q_e , the amount of the retained gallium (mg/L); Q^0 , the maximum adsorption capacity (mg/g); and b , a constant. The values of Q^0 and b were calculated from the slope and intercept of the straight-line plots of C_e/q_e versus C_e (Fig. 4) and are given in Table II.

The essential characteristics of Langmuir isotherms can be expressed by a dimensionless constant named the parameter of equilibrium R_L (relation 2) and by the Langmuir constant k_L (relation 3):

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

$$k_L = Q^0 \times b \quad (3)$$

The value of R_L between 0 and 1 shows a favorable retention of gallium ions by the resins. The maximum retention capacities for this ion are 44.44 and 60 mg/g for the S₁ and S₂ resins, respectively.

Freundlich isotherms

The Freundlich isotherm is represented by eq. (4):

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \quad (4)$$

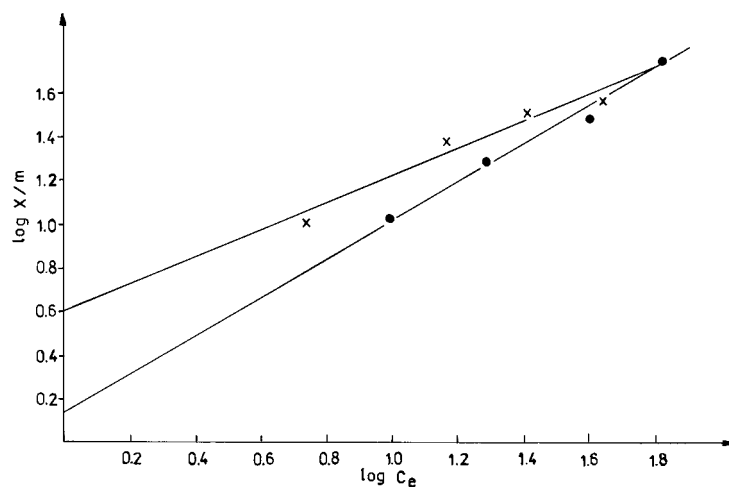


Figure 5 Freundlich plots for retention of Ga(III) by resins: (●) S₁; (×) S₂.

where x is the amount of the retained gallium (mg/L); m , the amount of the resin (g/L); C_e , the concentration at equilibrium of the gallium in solution (mg/L); and k and n , Freundlich constants.

The retention capacity of gallium increases with increase of the resin amount from 0.05 to 0.5 g. k and n values were calculated from the intercept with the ordinate and the slope of the linear plots for $\log(x/m)$ versus $\log C_e$ (Fig. 5). The values of n between 1 and 10 show a preference of the resins for the studied ion. The values of k and n of 1.38 and 1.16, respectively, for the S_1 resin and 3.98 and 1.66, respectively, for the S_2 resin were obtained. These values show a higher affinity of the S_2 resin for the Ga(III) species which exist in 6M HCl. In fact, Freundlich isotherms gave additional proof of the preference of the two pyridine strong-base anion exchangers for Ga(III) from HCl solutions, the S_2 resin having the highest affinity.

CONCLUSIONS

The retention of the Ga(III) ions by two pyridine strong-base anion exchangers containing 1-methyl- or 1-butyl-4-vinylpyridinium chloride structural units, called the S_1 and the S_2 resins, respectively, was studied. The influence of the HCl and Ga(III) concentrations as well as of the contact time between the resin and the liquid phase were investigated.

The retention-capacity values show that the 6M HCl solution is the most suitable for the retention of Ga(III), where this cation exists as a $[\text{GaCl}_4^-]$ complex anion. Both resins have an affinity for Ga(III) from 6M HCl solutions, but the resin with 1-butyl-4-vinylpyridinium chloride structural units has a much higher retention capacity than that of the other resin.

From the Langmuir isotherms, the maximum retention capacities are 44.44 and 60 mg/g for the S_1 and the S_2 resins, respectively. Therefore, the alkyl substituent increase on the N^+ atom leads to an increasing affinity of the pyridine strong-base anion exchanger for the Ga(III) cation, which is a $[\text{GaCl}_4^-]$ complex anion.

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