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Ion Exchange Selectivity for Cross-Linked Polyacrylic Acid

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SUMMARY

The ion separation factors for 21 common metal ions with cross-linked polyacrylic acid were determined as a function of pH and the percent of the cross-linked polyacrylic acid neutralized. The calcium ion was used as a reference. At a pH of 5 the decreasing order of affinity of the ions for the cross-linked polyacrylic acid was found to be: Hg^{++}, Fe^{+++}, Pb^{++}, Cr^{+++}, Cu^{++}, Cd^{++}, Al^{+++}, Ag^{+}, Zn^{++}, Ni^{++}, Mn^{++}, Co^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Mg^{++}, K^{+}, Rb^{+}, Cs^{+}, Na^{+}, and Li^{+}. Members of a chemical family exhibited similar selectivities. The Hg^{++} ion appeared to be about a million times more strongly bound than the alkali metal ions. The relative binding of most of the metal ions varied with pH; the very tightly and very weakly bound ions showed the largest variations with pH. The calcium ion - hydrogen ion equilibrium was perturbed very little by the presence of the other ions. The separation factors and selectivity coefficients are discussed in terms of equilibrium and thermodynamic significance.

INTRODUCTION

Recently Philipp et al. (refs. 1 to 3) have reported on the preparation and some properties of new ion exchange membranes. The newness lies in their homogeneity, thinness, low equivalent weight, and manner of preparation. The method of preparation involves the radiation cross-linking of a film cast from water solution. One of the membranes is cross-linked polyacrylic acid (CLPAA). The calcium salt of the CLPAA membrane requires no support mesh and is capable of removing some ions from solution to less than a ppm. To achieve the maximum usefulness of a membrane in ion exchange applications, one must know its selectivity for various ions as a function of pH and the fraction of active carboxylic groups used.

In this work we have determined the separation factors (ref. 4) for 21 common cations with CLPAA. The calcium ion was used as the reference ion. The measurements were made as a function of pH and percent of the CLPAA neutralized. Powdered samples of CLPAA were used; because the rate of ion exchange is at least partially controlled by solid state diffusion, the finely powered samples should allow more complete ion exchange in a given time than a membrane. A large range of selectivities was found. The range is compared with the ranges found for other types of ion exchange materials. The results are discussed in terms of attainment of equilibrium, formation of additional phases, and the significance of separation factors.

EXPERIMENTAL DETAILS

Materials. - The CLPAA powder used in this investigation was prepared as follows: A 15 percent aqueous acrylic acid solution was linearly polymerized

by heating to 90° C under a nitrogen purge and then adding a small amount of potassium peroxysulfate (less than 0.1 percent) while keeping it at temperature for an hour. The solution was diluted to 10 percent and irradiated with 2 MeV electrons at a beam current of 1 μA/cm^2 for 10 minutes to affect cross-linking. The precipitate which formed was CLPAA; it was filtered off, washed with hot water, and air dried. The resultant product was ball milled. The material had a crystalline appearance under a microscope. The average particle size was about 3 μm.

Each metal ion investigated was used in the form of an aqueous solution of one of its reagent grade salts. The metals used as their acetates were calcium, cobalt, copper II, mercury II, lead, nickel, potassium, sodium, and zinc. Those used as their nitrates were aluminum, barium, cadmium, chromium III, iron III, lithium, magnesium, silver, and strontium. Cesium and rubidium were used as their chlorides while manganese II was used as its sulfate.

Method. - This investigation was intended only as a survey of the relative binding of the metal ions with CLPAA so that more detailed work on specifically selected ions could follow. For this reason, we designed a method of determining separation factors that required relatively little time and a minimum of chemical analyses.

The experimental procedure that we used follows: A weighed quantity (0.076 g, a little more than a milliequivalent) of CLPAA was placed into a 250 ml centrifuge tube containing a Teflon coated magnetic stirring bar. Ninety ml of water was added. Into this solution was pipetted 10 ml of a solution 0.05 normal in calcium acetate and 0.05 normal in the salt of the metal ion being studied. The tube was covered and the contents were stirred for at least 6 hours, after which time it was centrifuged with the magnetic stirrer still in the tube. Two ml of the supernatant liquid was pipetted out and quantitatively analyzed for the two metal ions present. The pH of the remaining 98 ml was determined with a pH meter which changed neither the volume nor the composition of the solution.

Next, 2 ml of 0.1 normal aqueous potassium hydroxide, KOH, was added to the 98 ml in the centrifuge tube. The mixture was again stirred for at least 6 hours and then recentrifuged. After this, another 2 ml was removed by pipetting and was also analyzed quantitatively for the metal ions. The pH was again determined. This procedure of adding KOH, stirring, centrifuging, removing an aliquot, and measuring pH was repeated about 6 times, that is, until the solution was distinctly basic (pH > 7). All of the manipulations were performed at 23±1° C. When the potassium ion was being investigated, sodium hydroxide, NaOH, was used in place of KOH to make the solution basic. In the determination of the separation factor for mercury II, we used a larger proportion of mercury to calcium so that the amount of mercury II in the aliquot would be above the detection limit.

Chemical analyses were generally accomplished via atomic absorption spectroscopy; for aluminum, plasma absorption spectroscopy had to be used to obtain sufficient sensitivity. The original solutions were also quantitatively analyzed for the metals in a similar fashion; these analyses were needed for the calculation of the selectivity coefficients and separation factors described in Appendix A.

RESULTS AND DISCUSSION

The results are summarized in figure 1. Here, the separation factor, S, for each metal ion is plotted as function of pH. The calcium ion was used as

the reference; this means that the S for the calcium ion was unity. The curves near the top (large values of S) indicate that the respective ions have high affinity for the CLPAA and consequently these ions are the easiest ones to remove from aqueous solution by the CLPAA. The curves near the bottom (small values of S) imply that the respective ions have little affinity for CLPAA and as a result are the most difficult to remove from aqueous solution by the CLPAA. For a specific pH, one can set up a series for the metal ions in their decreasing order of affinity for CLPAA, i.e., their decreasing value of S. For example at a pH of 5 (arbitrary value), the order would be: mercury II, iron III, lead, chromium III, copper II, cadmium, aluminum, silver, zinc, nickel, manganese II, cobalt, calcium, strontium, barium, magnesium, potassium, rubidium, cesium, sodium, and lithium. At the pH of 5 the value of S for mercury II is about a million times greater than that for the lithium ion. A qualitative evaluation of the reliability of the data is given in Appendix B.

Calmon (ref. 5; pp 10-11) lists the relative selectivities (equivalent to S) for two ion exchange materials: a chelating carboxylic acid type and a sulfonic acid type. In figure 2, our CLPAA values of S for 12 bivalent ions (pH = 5) are compared with the S values for the chelating carboxylic acid type (a styrene-divinylbenzene copolymer matrix with iminodiacetic acid groups: ref. 5, p 37). In general, an ion with high affinity for CLPAA also shows a high affinity for the chelating exchanger. However, in specific cases (e.g., Ni^{++} and Cd^{++}) the relative affinities are reserved. The range of S values for both polymers extend over five orders of magnitude. In contrast, the range of S for the sulfonic acid ion type resins (ref. 5; p 10) is only one order of magnitude. The similar behavior found for our CLPAA and the carboxylic acid chelating resin is probably attributable to the weak acid nature of the functional group present on both exchangers. Such exchangers exhibit a high specificity for divalent ions (ref. 5, p 30) and presumably trivalent ones.

As seen in figure 1, the metal ions with values of S relatively close to unity exhibit but little variation of S with pH. But the dependence on pH of the value of S for the more tightly or loosely bound ions is more pronounced. A tightly bound ion often shows a maximum while a loosely bound one tends to show a minimum. Also of interest is the crossing of some of the curves (fig. 1); for example, at a pH of 5, the manganese (II) ion appears to be less tightly bound than the nickel ion while at a pH of 6 the opposite appears to be true. This kind of phenomenon suggests that adjustment of pH may allow the CLPAA membrane to be used in the separation of one ion from another. The phenomenon is generally referred to as selectivity reversal (ref. 4) and is more common when a resin contains two different functional groups.

As expected, the Group I alkali metals (lithium, sodium, potassium, rubidium, and cesium) exhibit similar values for S; the S for the lithium ion shows the greatest deviation from the S's of the rest of the group. Also, the lithium ion has the lowest S value of all the ions tested. The values of S for the Group II divalent alkaline earth metal ions, calcium, strontium, and barium, are also close together. There is, however, considerable variability in S for the other divalent ions.

In figure 3 we have plotted the values of S as a function of the percent of the CLPAA neutralized. The method of calculating the percent neutralized is given in Appendix A, Part I. Figure 3 merely gives another way of presenting the data. As expected, the data for the more tightly bound ions correspond to the higher percentage regions; the data for the loosely bound ions correspond to the lower percentage regions. While looking at figure 3, we

call attention to a possible reason for the variation of S with pH. As a polybasic acid such as CLPAA is neutralized, its ionization constant decreases (ref. 6), so that one could say that the actual nature of the acid is being changed. As a result, one should not be surprised that the binding power of CLPAA changes with the degree of neutralization. From this point of view, figure 3 is a more meaningful way of plotting the data than figure 1; however, figure 1 is more convenient to use because the pH is the more easily determined quantity.

The quantity S is a practical number which is used to determine the ease with which an ion exchange material will pick up a particular ion. In some cases, S may be only a figure of merit because equilibrium may not always be attained due to a slow diffusion process (App. B; ref. 2). However, if equilibrium is established, and if the metal ion has the same valence as the reference ion, then S is directly relatable to K (App. A, Part II; ref. 4), the selectivity coefficient, which is an equilibrium quantity. When calcium is the reference ion, K is equal to S squared. Thus, one could easily add to figure 1 as well as figure 3, a vertical axis which gives the K for the $+2$ ions. The K values for ions that exhibit $+1$ or $+3$ valances cannot be calculated directly from their S values.

<u>Hydrogen ion</u>. – When the present project was begun, we sought to use the hydrogen ion as the reference for simplicity. Because the experimental results of this preliminary work did not seem to be readily interpretable, we converted to the present method. However, from the experimental data used in this report, one can calculate quasi-constants for the hydrogen ion with CLPAA (App. A, Part III). Figure 4 incorporates essentially all of our experimental data; it gives the quasi-selectivity coefficient, K', for hydrogen with CLPAA as a function of pH; again, calcium is the reference ion. The data points for all the metals fall roughly on the same curve showing that the selectivity coefficient of hydrogen ion with respect to the calcium ion is not perturbed significantly by the presence of other metal ions. The value of K' increases with pH. This is expected because K' increases with the degree of neutralization (eq. (7)) which, of course, increases with pH.

CONCLUSIONS

The decreasing order of affinity of ions for CLPAA at a pH of 5 is: mercury II, iron II, lead, chromium III, copper II, cadmium, aluminum, silver, zinc, nickel, manganese II, cobalt, calcium, strontium, barium, magnesium, potassium, rubidium, cesium, sodium, and lithium. Members of a chemical family generally exhibit similar affinities. The values of the separation factors range over six orders of magnitude. In this respect, CLPAA seems to be a typical carboxylic acid exchanger. The affinity is a function of pH or, more correctly, a function of the percentage of CLPAA neutralized. The calcium ion – hydrogen ion equilibrium is not significantly perturbed by the presence of other cations.

APPENDIX A – CALCULATIONS

Part I: Separation Factors. – For an ion exchange material, the separation factor, S, of one ion, m, with respect to a reference ion, r, is defined as follows (ref. 4):

$$S(m:r) = \frac{C(m,p)\ C(r,w)}{C(m,w)\ C(r,p)} \tag{1}$$

where the C's are the concentrations of the m and r ions, the p refers to the polymer phase and the w refers to the aqueous phase. Equation (1) treats an ion exchange system as the distribution of two ions between two phases and is useful in describing which ions will be more easily removed from an aqueous solution. Because the concentrations of the two different ions in the polymer are based on the same volumes of water and polymer, the amount, A, of an ion may be substituted for its concentrations in equation (1). The amount of each ion in the CLPAA was found by subtracting the amount of a metal ion found through the analysis of each aliquot from the total amount of that metal added. The total amount of an ion was always corrected for the amount removed by all the previous aliquots.

The plotting of figure 3 requires that one knows the percent of CLPAA neutralized, P. This was calculated as follows:

$$P = 100\ (A(t,p) - A(r,p) - A(m,p) - A(K^+,p))/A(t,p) \tag{2}$$

where the A's are expressed in equivalents. The A(t,p) is the total amount of polymer used. The method of calculating A(r,p) and A(m,p) has already been described. The A(K⁺,p) is the amount of potassium ion in the polymer due to KOH additions and can be calculated from the amount added, the selectivity coefficient for the potassium ion (about 10 with calcium as a reference; App. A, Part II), and the amount of the reference ion present. The value of A(K⁺,p) was found to be insignificant in the actual calculations.

Part II: Selectivity Coefficients. – Instead of using the separation factor, one can define a selectivity coefficient, K, as follows (ref. 4):

$$K(m:r) = \left(\frac{C(m,p)}{C(m,w)}\right)^{V(r)} \left(\frac{C(r,w)}{C(r,p)}\right)^{V(m)} \tag{3}$$

where V refers to the valence of the respective ion. Equation (3) is written in terms of V(r) x V(m) equivalents of polyacrylate ions. It treats the system in a thermodynamic manner and is based on the existance of equilibrium in the chemical reaction between the CLPAA salt of the metal ion and the CLPAA salt of the reference ion. If the concentrations in equation (3) are expressed in terms of amounts, it can take the following form.

$$K(m:r) = \left(\frac{A(m,p)}{A(m,w)}\right)^{V(r)} \left(\frac{A(r,w)}{A(r,p)}\right)^{V(m)} R^{V(r)-V(m)} \tag{4}$$

where R is the ratio of the volume of water to the volume of the polymer. The actual numerical value of K depends upon the standard states that are used. If the standard states are based on a concentration per liter for both the water and the polymer and if the density of the polymer is assumed to be about one, then the value of R is about 1000. When the metal ion exhibits the same valence as the reference ion, the value of R drops out from equation (4). With calcium as the reference ion, K (as written) is equal to S squared for +2 ions. The K for a metal exhibiting a +1 or +3 valence cannot be simply related to S when the calcium ion is the reference.

Part III: The hydrogen ion. - Equations (1), (3), and (4) are just as valid for the hydrogen ion as for metal ions. However, $A(H^+,p)$ which is needed to compute K is difficult to calculate because some of the ionizable hydrogen in the CLPAA is nonionized. To bypass this difficulty, we define K', a quasi-selectivity coefficient for hydrogen.

$$ K' = \left(\frac{C(m,p)}{C(m,w)}\right) \left(\frac{C(n,p)}{C(H^+,w)}\right)^2 = \left(\frac{A(m,p)}{A(m,w)}\right) \left(\frac{A(n,p)}{A(H^+,w)}\right)^2 R \qquad (5) $$

where "n" refers to nonionized hydrogen. The value of $A(n,p)$ is easily obtained by subtracting the total amount of metal ions and ionized hydrogen present in the CLPAA (in equivalents) from the total amount of CLPAA (in equivalents). The amount of ionized hydrogen can be ignored in the calculation because it is small with respect to the amount of metal ions. The value of $A(H^+,w)$ is obtainable by multiplying 10^{-pH} by the volume of the water solution.

To relate K' to K, one must define another equilibrium constant, K", which involves the ionization of the hydrogen within the polymer itself.

$$ K'' = C(i,p) \ C(H^+,p)/C(n,p) = C(i,p) \ A(H^+,p)/A(n,p) \qquad (6) $$

where "i" refers to all the ionized groups within the polymer. $A(i,p)$ is equal to the sum of the amounts of metal ions and the ionized hydrogen; again, one can ignore the small contribution of the ionized hydrogen. From equations (5) and (6), it follows that

$$ K' = C(i,p) \ K \ / \ K'' \qquad (7) $$

As one goes to higher pH, more of the CLPAA becomes neutralized and consequently ionized. Thus $C(i,p)$ increases with pH. Because K and K" should be constants, it follows from equation (7) that K' should increase with increasing pH. A quasi-separation factor, S', for the hydrogen ion could be calculated in a similar fashion, but it would not have the potential equilibrium significance that K' might have.

Thus far in the calculation, we have assumed that the CLPAA consisted of a single phase. If two phases exist as in the case of copper II (ref. 2), the $A(n,p)$ in equation (5) would again be calculated in the same manner: the amount of metal ion in the second phase would still have to be subtracted from the total amount of the CLPAA. However, the value of R (volume ratio of water to CLPAA) would be increased somewhat because only the volume of one polymer phase should be included in the calculation. It is unlikely, that R would

increase by more than a factor of 2, so that equation (5) should be approximately correct. Finally, plotting K' against pH is preferable to plotting it against the fraction of CLPAA neutralized because there would be confusion as to meaning of the latter term.

APPENDIX B – RELIABILITY

In our method when the amount of a metal ion bound in a polymer is small compared with the amount in the aqueous solution, the precision of the amount in the polymer is expected to be lower because the quantity is based on the difference between two very close numbers. This can lead to low precision and low reproducibility in the values of S and K. Such lower precision is more likely to be found at low pH when the binding of metal ions with the polymer should be low. Lower precision can also be expected to result when the value of S is far from unity. An extremely high value for S means that the amount of the reference ion bound in the polymer is small; an extremely low value for S means that the amount of the metal ion bound in the polymer is small.

Another factor that we expected to affect the precision of our measurements was failure to achieve equilibrium, either due to slow diffusion or due to the fact that the type of equilibrium required by equation (3) cannot exist. Here, we call attention to some earlier work (ref. 2) involving the pickup of the copper II ion by CLPAA. Parabolic kinetics was observed indicating that a distinct copper polyacrylate phase builds up on the surface of a cross-linked calcium polyacrylate membrane. The existance of this second phase indicated that equations (1) and (2) should not be obeyed in the case of the copper ion. Current work indicates a similar situation for the chromium III ion. However, even if equations (1) and (2) do not logically apply, the value S may still be used as a figure of merit for those ions.

There is still another finding in this previous work (ref. 2) that could have a bearing on some of the present results. At low pH the copper ion was found to form a normal salt with CLPAA while at higher pH, it formed a basic salt. Thus, depending on pH, the copper ion could effectively exhibit either a +1 or +2 valence with respect to the CLPAA. Such behavior could also be expected for other transition metal ions, for example, iron III and chromium III. It is this effective valence that should be used in the calculation of K in equations (3) and (4). Even if the dependence of the effective valence with pH were known for the ions under investigation, introduction of this dependence into equations (3) and (4) would be a difficult matter. By treating our data in this report in terms of S, we have avoided all such questions.

Because of all these possible difficulties, we were cautious in selecting an ion for the evaluation of our method. Because barium is very similar to our reference ion, calcium, we decided to use the barium ion. In figure 5 is shown the value of S for barium / calcium / CLPAA system as a function of pH. Two distinct experiments were run. The reproducibility between the data shows that the scatter in the value of S for a well behaved ion is less than about 20 percent. Notice that in figure 5, the value of S is relatively constant in the higher pH region; this constancy enhances our confidence in the value of S in this region.

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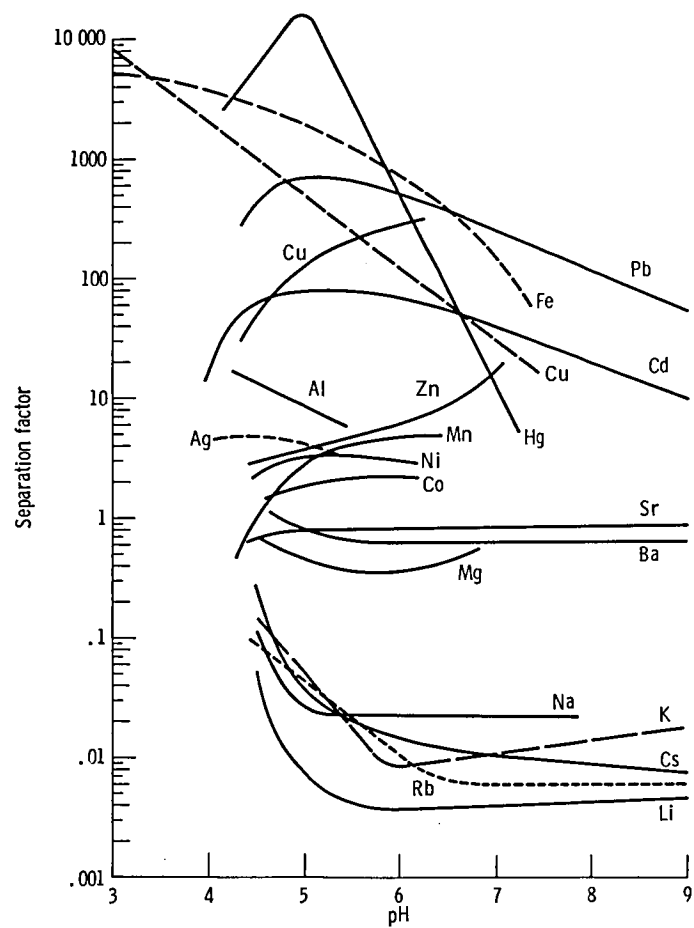
Figure 1. - Separation factors of ions with CLPAA as a function of pH
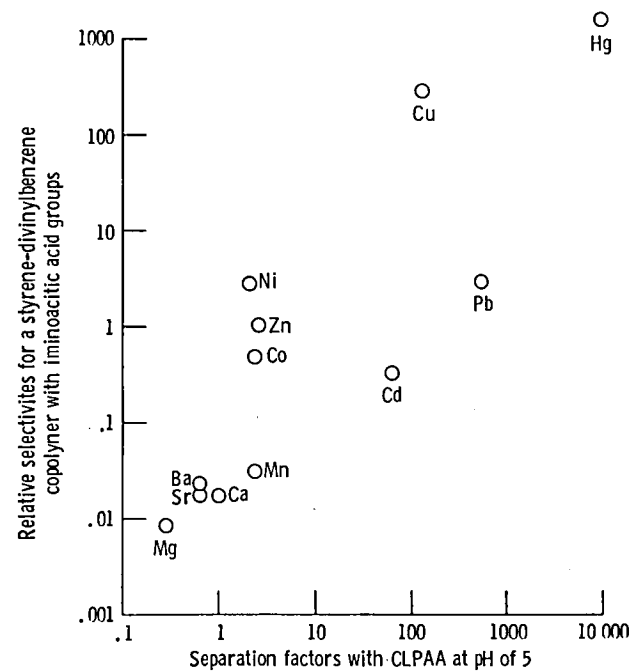[calcium ion as reference].

Figure 2. - Comparison of CLPAA with a carboxylic acid
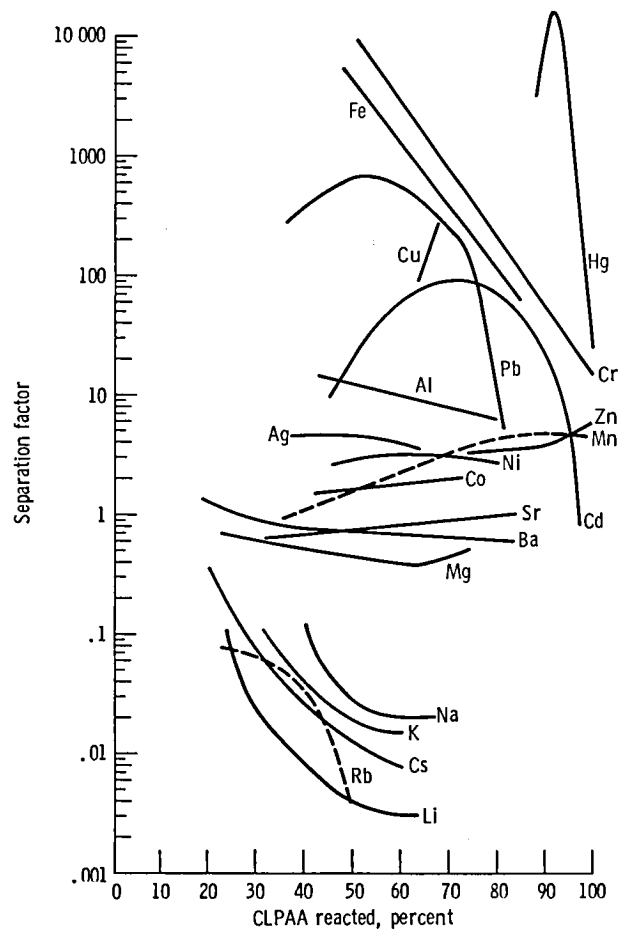chelating exchanger for divalent ions.

Figure 3. – Separation factors of ions with CLPAA as function of percent CLPAA combined (calcium ion as reference).
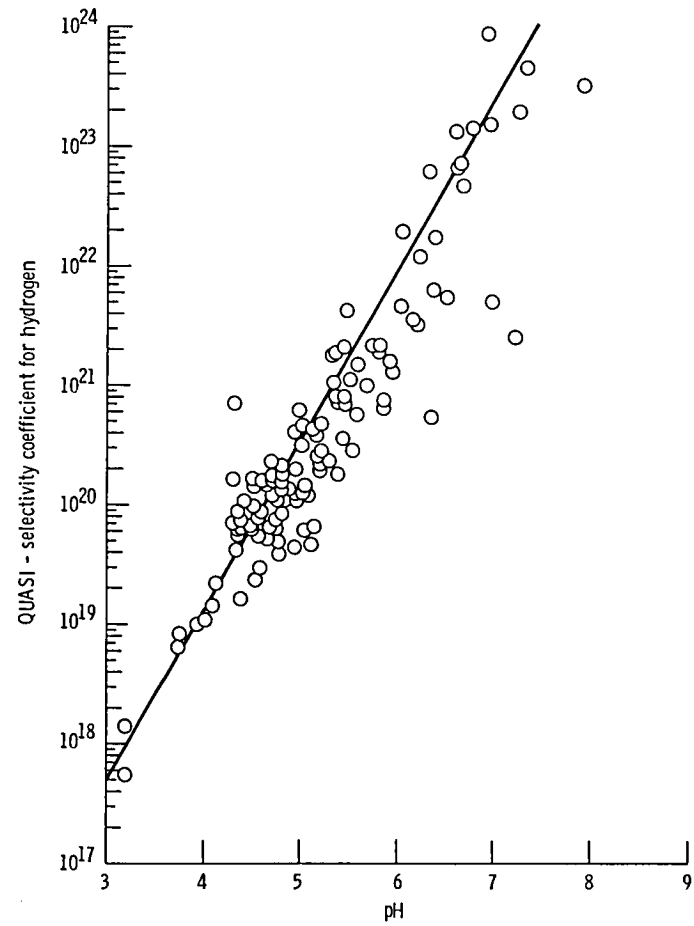

Figure 4. – Equilibrium between the hydrogen ion and calcium ion in the water – CLPAA system.
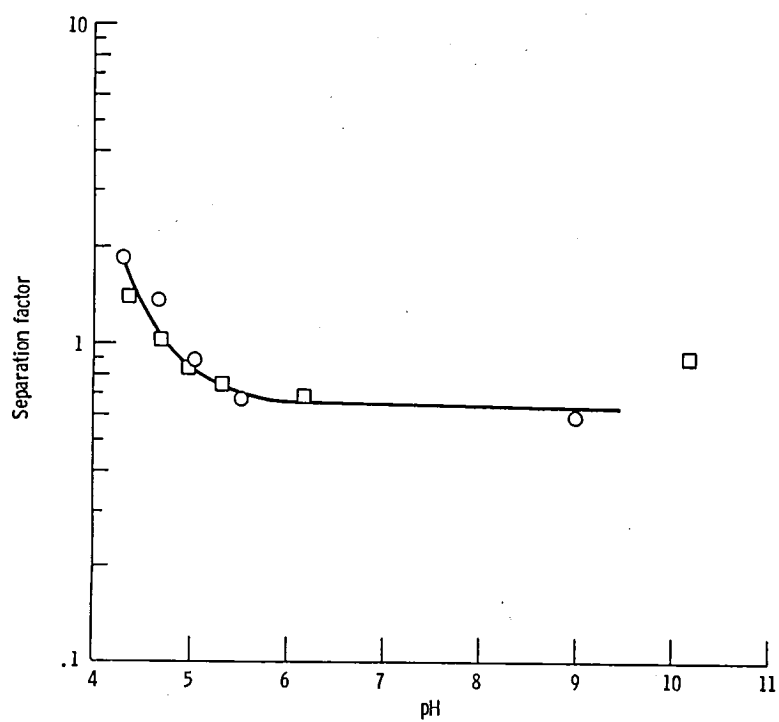
Figure 5. - Separation factor for the barium ion with CLPAA [calcium ion ref. ; different symbols refer to two different CLPAA samples].

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15. Supplementary Notes

16. Abstract

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