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Kinetics of Chromium Ion Absorption by Cross-Linked Polyacrylate Films

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SUMMARY

Three cross-linked ion exchange membranes were studied as to their ability to absorb chromium ion from aqueous chromium III nitrate solutions. Attention was given to the mechanism of absorption, composition of the absorbed product, and the chemical bonding. The membranes were: calcium polyacrylate, polyacrylic acid, and a copolymer of acrylic acid and vinyl alcohol.

For the calcium polyacrylate and the copolymer, parabolic kinetics were observed, indicating the formation of a chromium polyacrylate phase as a coating on the membrane. The rate of absorption is controlled by the diffusion of the chromium ion through this coating. The product formed in the copolymer involves the formation of a coordination complex of a chromium ion with 6 carboxylic acid groups from the same molecule. The absorption of the chromium ion by the polyacrylic acid membranes appears to be more complicated, involving cross-linking. This is due to the coordination of the chromium ion with carboxylic acid groups from more than one polymer molecule. The absorption rate of the chromium ion by the calcium salt membrane was found to be more rapid than that by the free polyacrylic acid membrane.

INTRODUCTION

This kinetic study is concerned with the absorption of the chromium ion by some new cation ion exchange membranes developed at Lewis Research Center. Reference 1 describes the preparation of these water insoluble membranes via electron irradiation from water soluble polymers, namely polyacrylic acid and a mixture of polyacrylic acid and polyvinyl alcohol. Membranes made by casting the aqueous polymer solution and air drying at room temperature were cross-linked by the use of 2 MeV electrons. These membranes are interesting for several reasons. The first is that they have a low equivalent weight and high ion capacity due to their high concentration of carboxylic acid (COOH) groups. Next, these membranes are easily prepared from readily obtainable raw materials. Finally, these membranes can have certain advantages over the usual granular form of ion exchange resins, e.g., ease of handling.

Various salts of these films have been prepared (ref. 1), the most useful being that of the calcium ion. Also, the diffusion rates of some of the simple ions (Li^+, Rb^+, Mg^{++}, Cl^-, and $SO_4{}^=$) through the membranes were measured (ref. 2), but no specificity for the diffusion of these ions was observed. The exchange selectivity of the cross-linked material was measured for 21 different ions as a function of pH (ref. 3); the selectivity constants for various ions ranged over five orders of magnitude. Chromium was one of the ions that exhibited a strong affinity for the cross-linked polyacrylic acid. Up to the present, the only kinetics of absorption studied for these membranes was that of the copper ion by the calcium cross-linked polyacrylate membranes (ref. 4).

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Because of our interest in the recovery of strategic materials, we turned our attention to the reaction of these films with the chromium III ion, chromium being one of the most important of these materials. Moreover, because the bonding of the chromium ion is more complex than that for the copper ion, this approach could give a good insight into the reactions and mechanisms of ions with cross-linked polyacrylic acid membranes. Three different membranes were prepared and investigated: cross-linked polyacrylic acid, PAA; cross-linked calcium polyacrylate, CaPA; and the cross-linked copolymer: polyvinyl alcohol - polyacrylic acid, COP.

The experimental part of the research involved determining the rate of pickup of the chromium ion by these membranes. The primary method used is similar to the method described in reference 4. It involves the chemical analysis of membranes for the chromium ion after immersion of the films in aqueous chromium nitrate for specified times. Dependence on the chromium nitrate concentration was also determined. In addition to determining the rate of chromium ion pickup by chemical analysis, it was measured by an optical absorption method. The absorptivity of the band peaks exhibited by a chromium-containing membrane was used as a measure of the membrane's chromium content. The same membrane is usable for all the determinations, eliminating errors due to differences in the areas and thicknesses of membranes. Such a method could have the advantanges of accuracy, speed, and convenience.

The data are compared with those for the copper ion (ref. 4). The results are discussed in terms of the mechanism of absorption, chemical bonding, and the differences between the membranes. The use of optical absorption as a method of measuring ion pickup is compared with that using chemical analysis.

The author wishes to thank Dr. Warren Philipp for the preparation of the membranes and for many valuable discussions. Thanks also goes to Mr. Warren Davis for the personal care he took in the chemical analysis of the membranes.

EXPERIMENTAL DETAILS

Preparation. - The preparation of in situ, radiation cross-linked polyacrylic acid (PAA) films is described elsewhere (ref. 1). They were made by casting 15 percent aqueous polyacrylic acid solution onto a smooth glass plate with a Gardner blade set at 100 mils (0.25 cm). After air drying, the film was swelled in moist air by placing it in a closed container with water. It was irradiated with 2 MeV electrons at 1 μA per cm^2 for 10 min which produced cross-linking. The membranes were then stored in distilled water.

The calcium form of the cross-linked polyacrylate film (CaPA) was made by immersing and storing the irradiated polyacrylic acid film in an aqueous calcium hydroxide solution (ref. 1). To achieve as close to complete neutralization as possible, about twice the stoichiometric amount of calcium hydroxide was used. The films were rinsed in distilled water immediately before using for the kinetic studies.

The films of copolymer (COP) of polyacrylic acid and polyvinyl alcohol (Aldrich, M.W. 14 000) were made by the technique described previously for cross-linking the PAA films. The aqueous casting solution was prepared by mixing 15 percent solutions of polyacrylic acid and polyvinyl alcohol in the volume ratio of 1:1. Casting was done by setting the Gardner blade at 100 mils

(0.25 cm). After the air drying and swelling in moist air, the film was irradiated in the usual manner. We believe the radiation produced the cross-linked copolymer. These films were also stored under distilled water until used. The weight ratio of polyacrylic acid to polyvinyl alcohol in the polymer was found to be 0.96 to 1 (ref. 4).

Primary method. - The PAA and COP samples were used in the form of stamped out one inch diameter circular specimens. Because of the brittleness of the CaPA, specimens could not be stamped out. Thus, the CaPA was used as square specimens, approximately 2 by 2 cm.

Kinetic studies were performed by exposing membrane specimens to 500 ml of a stirred 0.2 or 0.02 molar aqueous solution of chromium nitrate for a specified time. A separate specimen was used for each determination. The solutions were prepared from analytical grade $Cr(NO_3)_3.H_2O$. The pH of the 0.2 molar solution was 2.2; that of the 0.02 molar solution was 2.55. After removal of a film from its solution, it was rinsed, and its dimensions in the wet condition were recorded. After air drying, its dimensions were again recorded, and the specimen was weighed. The films were digested in nitric acid and analyzed for chromium by an atomic absorption technique. Atomic absorption was also used to determine the amount of calcium in the CaPA films.

Optical method. - Special specimens of PAA (about 2.5 x 0.5 cm) were cut for this method. Each was mounted in a plastic holder which permitted a beam of light to pass through the central portion of the membrane. Each holder containing a membrane was placed in a cuvet filled with distilled water. The optical absorption spectrum of each film was measured so as to know its background curve for subsequent measurements.

Following this, the holder with the first membrane was exposed to a 0.033 molar chromium nitrate solution. After a measured time, the holder with sample was removed from the chromium nitrate solution, rinsed with distilled water, and returned to its cuvet containing water so that its optical absorption spectrum could again be determined. It was immediately returned to its chromium nitrate solution for an additional length of time. This process of measuring its optical absorption spectrum and exposure to chromium nitrate solution was repeated until the absorptivity of its spectral peaks approached a value of 2. At this point, the accuracy in the measurement of the absorptivities of the peaks is poor. At the end of the experiment, the film was analyzed chemically for chromium so that the optical absorptivity values could be converted to mg of chromium per unit surface area (both sides) of the specimen.

The pickup of chromium by two other films was determined by the optical method. One of the films was exposed to 0.066 molar chromium nitrate solution; the other was exposed to 0.016 molar chromium nitrate. For both of these films, an important change was made in the method: every time the film in a holder was placed in the cuvet containing water for optical measurements, it was kept there for several days. During this time its optical absorption spectrum was monitored.

The optical method was not applied to the CaPA and COP membranes because they were somewhat cloudy, and the optical absorption data would have been unreliable.

RESULTS

In order to give the reader a proper understanding of the kinetic data, it is first necessary to present some auxiliary findings.

Area of the specimens. - In figure 1, the wet and dry diameters of the PAA and COP specimens are plotted as a function of the exposure time to aqueous 0.2 molar chromium nitrate. At short exposure times, the diameter of a wet PAA circular disk is decreased in diameter to about 41 percent of its original value. According to figure 1, a COP membrane also shrinks in diameter in a short time, but only to 81 percent of its original value. The data for the dry disk specimens are given for comparison. For the PAA membrane, the dry diameter is only slightly less than the wet diameter, indicating a compact structure (one with a minimal amount of water) for the wet membrane after exposure to chromium nitrate. The similar behavior for exposure to 0.02 molar chromium nitrate solution is indicated in figure 1 by the triangular points. No measurable shrinking was observed for the CaPA membranes when exposed to aqueous chromium nitrate solution. All the data presented in this report are based on the absorption area (both sides of the specimen) at the end of an exposure to the chromium nitrate solution and not on its original area.

Examination of the film. - Upon exposure to the chromium ion, all films took on the blue violet color characteristic of the chromium ion. When we scraped the surfaces of some of the films (CaPA, PAA, and COP), we were unable to find an uncolored substrate characteristic of the original membrane. We reported earlier (ref. 4) that CaPA films exposed to copper ion did reveal an uncolored unreacted original film under the colored coating of copper polyacrylate.

In addition to becoming colored after exposure to chromium nitrate solutions, the PAA and COP membranes were easier to hold and manipulate than the original membranes. This is a result of the shrinking (loss of absorbed water) evident in figure 1.

Loss of calcium from CaPA. - Figure 2 illustrates the loss of calcium ion from CaPA as a function of exposure time to 0.2 and 0.02 molar aqueous chromium nitrate solutions. The rate of calcium ion removal is greater for the more concentrated chromium nitrate solution. Also, the calcium content is inversely proportional to the square root of the exposure time, at least for ninety percent removal. The time required for removal of ninety percent of the calcium ion using the 0.2 molar solution is 1.4 hr; the time for the 0.02 molar solution is 25 hr. We refer to ninety percent removal rather than one hundred percent removal because at even long time exposure to chromium nitrate, some calcium ion was always detectable in the film.

Chromium absorption by CaPA.- Figure 3 shows the chromium ion absorption per unit surface area of a CaPA specimen plotted as a function of the time. The initial pickup is proportional to the square root of the time. The rate of absorption due to the exposure to the 0.2 molar chromium nitrate solution is 0.38 $mg/cm^2\ hr^{1/2}$; the rate due to the exposure to the 0.02 molar solution is noticeably less, 0.045 $mg/cm^2\ hr^{1/2}$. Dependence of ion absorption on the square root of time was also observed for the copper ion into CaPA membranes (ref. 4); its rate of absorption was found to be 0.069 $mg/cm^2\ hr^{1/2}$, independent of the copper ion concentration.

Figure 3 also shows that at long times, the membranes appear to have become saturated with the chromium ion. The saturation occurs close to the time at which the calcium in the membranes is ninety percent depleted, as indicated in the figure. The degree of saturation appears to depend on the concentration of the chromium nitrate solution. For the 0.2 molar chromium nitrate solution, saturation occurs near 7.2 percent; for the 0.02 percent solution, it occurs at about 5.7 percent. Saturation was also reported to occur for the absorption of copper by a membrane composed of the calcium salt of COP (ref. 4).

Chromium absorption by PAA. - Figure 4 shows the chromium ion absorption per unit surface area of PAA films as a function of time. Two of the curves are based on the primary (chemical analytical) method, whereas the curve for the intermediate chromium nitrate concentration (dashed line) is based on the optical method, the one in which the specimen was exposed to distilled water for only short periods of time. All three curves seem to fall within a single wide scatter band. Closer observation reveals that the initial portion of each curve is parabolic, and that the initial rate varies directly with the concentration of the chromium nitrate solution. The rate for the 0.2 molar solution is 0.085 $mg/cm^2\ hr^{1/2}$; that for the 0.033 molar solution is 0.067 $mg/cm^2\ hr^{1/2}$; and that for the 0.02 molar is 0.034 $mg/cm^2\ hr^{1/2}$. The differences in these rates of pickup are believed to be within experimental error. The values themselves are less than the values found for the absorption of chromium by CaPA.

All three curves quickly deviate form his parabolic dependence: their slopes decrease. This happens most rapidly for the most concentrated solution and least rapidly for the most dilute solution. None of the curves reach saturation during the time interval used. The maximum amount of chromium content for the each specimen falls in the range of 6.7 to 8.4 percent.

Optical method. - Two strong optical absorption bands (at 415 and 570 mμ) were found for the chromium-containing PAA membrane. The positions of these bands corresponds closely to the positions of the peaks of the chromium ion in aqueous linear polyacrylic acid (appendix A). Bands at these locations are characteristic of the chromium III ion.

The intensity of these bands increased with exposure time to the chromium nitrate solution. In addition, chromium-containing specimens exhibited increased optical absorptivity at these peaks after exposure to water even though there was no increase in chromium content. The average increase upon exposure to water for periods of several days amounted to 0.03 absorptivity units; sometimes increases as high as 0.06 were observed. The position of the peak did not shift detectably by the water treatment.

Figure 5 gives the curves for the chromium ion pickup by PAA membranes as determined by the optical absorption method. This includes the curve given in figure 4 for the specimen that had minimal contact with distilled water between its exposures to the chromium nitrate solution. All the curves show an initial parabolic dependent. However, the one for the specimen with minimal contact with distilled water quickly and very noticeably shows a deviation from this behavior; the slope decreases. The treatments of the other specimens with water appear to have preserved their rapid absorption rate for the chromium ion. The initial rates for the water treated specimens are 0.17 and 0.13 $mg/cm^2\ hr^{1/2}$, respectively, for the 0.066 and 0.016 molar solutions. The initial rate for the specimen with minimal contact with distilled water is 0.067 mg/cm^2 hr$^{1/2}$. Note that the slopes for the water treated specimens are essentially independent of the chromium nitrate concentration.

The curves in figure 5, indicate that their corresponding specimens did not reach saturation during the time period used. The range of maximum chromium content for these specimens is found to be 5.6 to 6.9 percent.

COP membranes. - Figure 6 gives our results for the COP membranes. Again, the initial portions of the curves indicate parabolic dependence. The rates vary with the concentration of the chromium nitrate solution. For 0.2 molar solution, the rate is 0.052 mg/cm^2 hr$^{1/2}$; for the 0.02 molar solution, the rate is 0.010 mg/cm^2 hr$^{1/2}$. Saturation is rapidly reached for the more concentrated solution. This saturation corresponds about 6.2 percent chromium. The curve for the 0.02 molar solution indicates that a long time is required to reach saturation: about 10 000 hrs (1.2 yrs). No deviation from parabolic dependence is observable in either of the two curves.

Numerical data. - The data from the curves are summarized in table I. The calculated ratios of acrylic acid (carboxylic acid) groups to a chromium ion were found by assuming no additional species present in the polymer and must be taken as only approximate values. These values are lowest for the COP membranes.

DISCUSSION

Some of our discussion is highly speculative because this is the first time these systems have been investigated.

Parabolic kinetics. - Our most obvious finding is that the amount of absorption (pickup) of chromium by all three membrane types is initially proportional to the square root of the exposure time. In our work on the absorption of the copper ion by such membranes (ref. 4), we found similar results and attributed them to the diffusion of the ions though an ever increasing thickness of a copper polyacrylate coating which was building up on the original membrane. An actual blue coating of copper polyacrylate could be detected visually on the membrane. The buildup of a coating on the surface of a membrane is very similar to the buildup of oxide coatings on some metals during oxidation (ref. 5). All such processes exhibit parabolic dependence, and their rates depend upon the concentration of the diffusing species.

Visually, we have been unable to detect a chromium polyacrylate coating on our chromium-containing membranes. Moreover, dependence of absorption on the square root of time can also occur for diffusion through a single phase (ref. 6). For single phase diffusion, there is deviation from the square root dependence similar to that seen for our PAA data in figures 3 and 4. Such processes are not explicitly dependent upon the concentration of the diffusing species, just as we have found for the pickup of chromium ion by our PAA membranes. If the pickup by PAA (or COP) membranes involved diffusion through a coating phase, the pickup rate would have to depend on the chromium ion concentration (ref. 4) because the diffusion of the hydrogen (counter) ion is rapid. (Pickup by the CaPA membranes involving diffusion through a coating phase would not have to be dependent on the chromium concentration because the rate could depend on the diffusion rate of the calcium outward.) Thus, we believe that the chromium ion pickup by PAA does not involve the formation of a chromium polyacrylate coating and follows the kinetics for single phase diffusion.

In figures 3 and 6, we see that the chromium pickup by the CaPA and COP membranes is dependent on the chromium ion concentration. Moreover, there is no pronounced deviation from parabolic behavior. As a consequence, we believe that for the CaPA and COP membranes, the mechanism of absorption involves the formation of a chromium polyacrylate coating, and that the kinetics is controlled by the diffusion of the chromium ion through this coating. The rates for the CaPA and COP membranes (slopes of the curves) should be proportional to the square root of the chromium ion concentration (ref. 4). Thus, we would have predicted that the rate of absorption from a 0.2 molar chromium nitrate solution would be 3.14 times the rate for a 0.02 molar solution. From table I, one can calculate this ratio to be about 8 for the CaPA membrane and about 5 for the COP membrane. These larger than expected values indicate that the dependence of the diffusion on concentration is greater than first power. Such a dependence could result if some of the diffusion occurs via an aggregate chromium ion.

The copper ion exhibited a more rapid pickup by the calcium salt of COP than by the calcium salt of PAA (ref. 4). We might therefore reason that the pickup of chromium by COP should be more rapid than by PAA; but the opposite is true. One can, of course, attribute this to the difference in mechanism that we are postulating for the PAA with respect to the COP. If our mechanisms are correct, the data imply that pickup by the single phase diffusion mechanism is more rapid than by the diffusion through a coating phase.

Compound formed. - The next questions to answer involve the nature of the chromium compound formed. How many acrylate groups combine with one chromium ion? What kind of coordination exists? In the case of copper ion absorption, the copper concentration in saturated membranes indicates that a normal copper polyacrylate forms at low pH and the basic salt forms at higher pH. Due to the ability of the chromium ion to coordinate with carboxylic acid groups, one would expect 6 polyacrylate groups around each chromium III ion. This is the approximate value found for the COP membranes (table I). Our present data do not define the structure of the coordinate complex. The complex could consist of three ionized carboxylate groups and three nonionized carboxylate acid groups. Or it could contain three nitrate ions and six carboxylic acid groups. These are only two of the many structures that could be postulated for the complex. The experimental ratio is not precise enough to make a distinction between the many possibilities. A mixture may even exist.

In these COP membranes, the carboxylic acid groups are diluted with relatively nonreactive alcohol groups from the polyvinyl alcohol, so that coordination is more likely to take place within a single polyacrylic acid chain or molecule of the polymer. We think that this it more likely to result in the formation of a second phase than if the chromium connected two different molecular chains of the polymer together. The latter corresponds to cross-linking. Intramolecular coordination resulting in the formation of a second phase is in accord with our proposed mechanism for the absorption of chromium ion by the COP membranes.

PAA. - The PAA membranes did not become saturated with chromium during the running of the tests. The curves in figures 4 and 5 indicate that if saturation were achieved, the ratio of carboxylic acid groups to a chromium ion would approach 6 to 1. However for PAA, each coordination group might involve carboxylic acids groups from different molecules because several different molecules might be in close proximity; they could not be as separated as in the case of the COP membranes. This coordination between different molecules would correspond to cross-linking which could likely inhibit the formation of a second distinct phase of chromium polyacrylate. The existence of cross-linking is also indicated by the extreme contraction of these PAA films (fig. 1) when exposed to chromium nitrate solutions. The cross-linking in the PAA membranes is probably similar to that occurring during the gelatinizing of the water soluble linear chromium polyacrylate (appendix A).

One can see in figure 4 that the rate of deviation from parabolic behavior varies directly with the chromium nitrate concentration. This tends to indicate that the rate of cross-linking varies with either the chromium concentration or the acidity of the solution. In contrast with the curves in figure 4, those in figure 5 for the water treated specimens do not show this pronounced deviation from the parabolic behavior. At the same time, the optical spectrum of these specimens change during their exposure to distilled water. Thus, we realize that some sort of molecular rearrangement is occurring. We postulate that the water by virtue of its higher pH, allows a more stable system to form via rearrangement of the coordination bonds. The coordination bonds connecting different molecules could rearrange to connect carboxylic acid groups within the same molecular chain instead of two different chains. Thus, the cross-linking would be broken, and a two phase system could form, giving rise to curves which appear to be more parabolic in nature. However the actual absorption which occurs when the membrane is reexposed to the chromium nitrate solution could still involve cross-linking. Thus in our experimental procedure, we have a repeating system of cross-linking and uncross-linking.

CaPA. - Although saturation is apparently reached for the CaPA membranes, the carboxylic acid group to chromium ion ratio is still considerably above the 6 to 1 value that we would expect for the proper coordination. Apparently something is blocking the reaction from going to completion and the membrane from reaching true saturation. The pickup rate by the CaPA membrane appears to be faster than by any other of the membranes. This is due to the fact that the chromium ions replace the calcium ions rather than hydrogen ions. (The chromium ions pickup and the calcium ion removal versus time both show parabolic dependence. Also, the chromium concentration reaches a maximum at about the same time that nearly all the calcium ion is removed.) We postulate that this rapid pickup causes unreacted carboxylic acid groups to be trapped between coordinated ones so that the ratio of carboxylic acid groups to a chromium ion would indeed by greater than 6 to 1. Rapid reaction would also mean that a chromium ion would be coordinating with carboxylic acid groups that are relatively close together, ones on the same molecular chain. In turn, this would permit the formation of a distinct chromium polyacrylate phase.

Optical method. - We have seen that the optical method we used did not work as well as we had expected. The difficulty arises from the possible reaction of a membrane with water during the measurement of the optical absorption. In many cases, reaction will not occur, but our optical method must always be confirmed by a chemical method where the pickup of an ion is not continually interrupted by a concentration measurement. However another type of optical method might be successful; it would have to involve the measurement of the optical absorption while still in the solution under investigation.

Even though our optical method did not serve the purpose for which it was intended, it gave us additional information as to the absorption mechanism. It might serve a similar purpose in the study of the pickup of other ions by membranes.

Practical considerations. - Although the primary intention of the present work was not for its application to immediately practical problems, our data do show that the chromium ion can effectively be absorbed at least partially by the membranes tested. One should note that free polyacrylic acid membranes do not absorb chromium ion as quickly a calcium polyacrylate membranes, although the total pickup is more. Generally, the pickup rate is more important than the total content.

The total chromium ion pickup is not as great as with copper ion because of the large coordination number of chromium with respect to the valence of copper. However, the absorption rate by CaPA for the chromium ion is more rapid than that for the copper ion. The most rapid pickup of the copper ion was via a COP membrane containing the calcium ion. One would expect that such a membrane would also show the greatest rate of pickup for the chromium ion; however, this type of membrane was not tested with chromium.

When the polyacrylic acid membranes were first developed, we were somewhat concerned about their extreme hydrophilic nature; this made them lack toughness, and so they were difficult to handle. Because of this, we prepared the calcium polyacrylate membrane which is tougher and therefore easier to handle. The present work indicates that a polyacrylate membrane with only a small amount of chromium ion absorbed (2.5 percent) contains little water (see fig. 1), is sufficiently tough, and is at least as easy to handle as the CaPA membrane.

CONCLUDING REMARKS

As we have just commented, the membranes we have tested will indeed absorb the chromium ion. The pickup rate is the greatest with the calcium salt of PAA.

The mechanism for the absorption of chromium by CaPA and COP is very simple, like that of the copper ion by CaPA. It involves the formation of a chromium ion polyacrylate coating containing one chromium ion for about 6 carboxylic acid groups. The kinetics are controlled by the diffusion of the chromium ion through this coating, resulting in parabolic dependence. The rate varies with the chromium ion concentration as would be predicted.

The mechanism is more complex when the chromium ion is absorbed by an undiluted PAA membrane. Cross-linking occurs due to the coordination of a chromium ion with the carboxylic acid groups from different molecules. This cross-linking prevents the formation of a second phase, and so the kinetics deviate from parabolic. The initial rate of pickup for these undiluted PAA membranes is greater than that for COP.

APPENDIX A

LINEAR POLYACRYLIC ACID

In auxiliary experiments, we discovered that the chromium III ion reacted with the soluble (linear) polyacrylic acid. Within a two week period a gel would form. The time required for gel formation decreased with temperature, being about 10 minutes near 100° C. At room temperature, we determined the optical spectrum of mixtures of chromium nitrate with linear polyacrylic acid as a function of time. Two optical absorption bands were observed. They were originally at 407 and 574 mμ. The one at 407 mμ appeared to shift somewhat in wavelength (to 410 mμ) with time. More noticeable was the increase in absorptivity with time; a total increase of about 20 percent was observed over the period of several months. These results indicate that the chromium III ion cross-links linear polyacrylic acid. The data are interpretable as first-order kinetics.

Twelve other ions (including iron III) exposed to the soluble polyacrylic acid did not exhibit gel formation under similar conditions.

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TABLE I. - MEMBRANE RESULTS

Membrane	$Cr(NO_3)_3$ concentration, molar	Method	Initial slope,[a] $mg/cm^2-hr^{1/2}$	Maximum chromium pickup, percent	Is saturation reached?	COOH/Cr ratio
CaPA	0.2	Chemical	0.38	7.2	yes	9.3
CaPA	.02	Chemical	.066	5.7	yes	11.9
PAA	.2	Chemical	.085	7.9	no	8.4
PAA	.02	Chemical	.034	8.4	no	7.7
PAA	.033	Optical	.067	6.7	no	10.0
PAA[b]	.066	Optical	.173	6.9	no	9.7
PAA[b]	.016	Optical	.133	5.6	no	12.1
COP	.2	Chemical	.051	6.2	yes	5.5
COP	.02	Chemical	.010	4.5	no	7.7

[a] Slope for copper ion absorbed into the calcium salt of COP is 0.069 $mg/cm^2-hr^{1/2}$.

[b] Specimens were exposed for a long time to distilled water between chromium pickups.

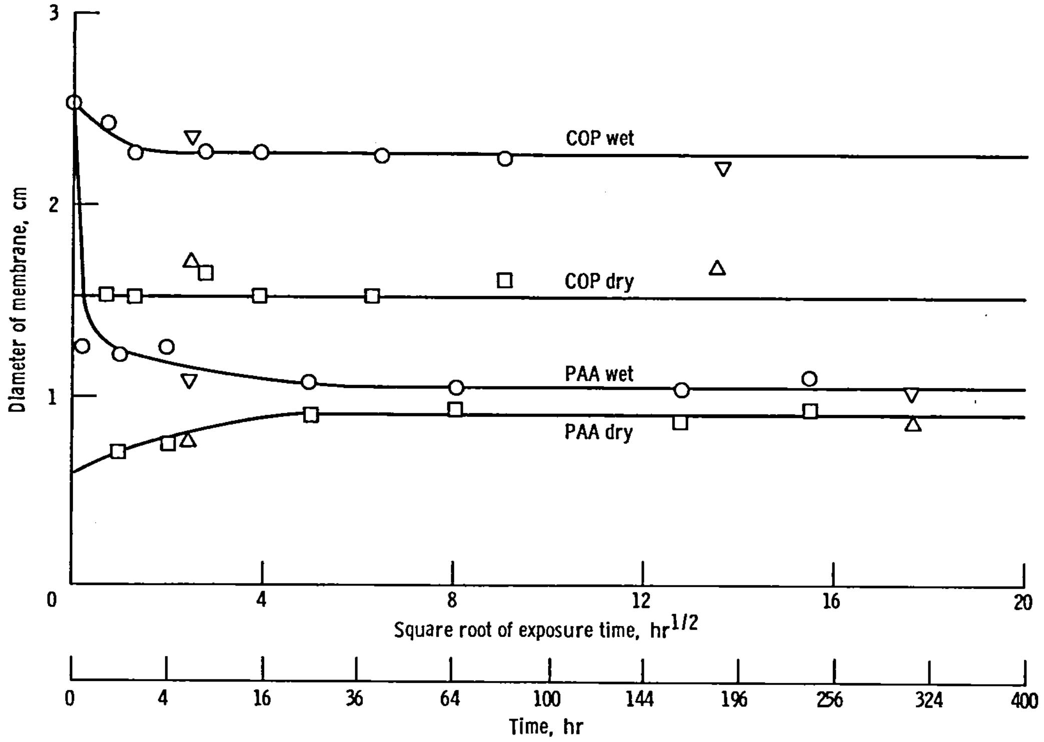

Figure 1. - Dependence of specimen size on exposure time (crosslinked PAA and COP in 0.2 M Cr $(NO_3)_3$ solution).

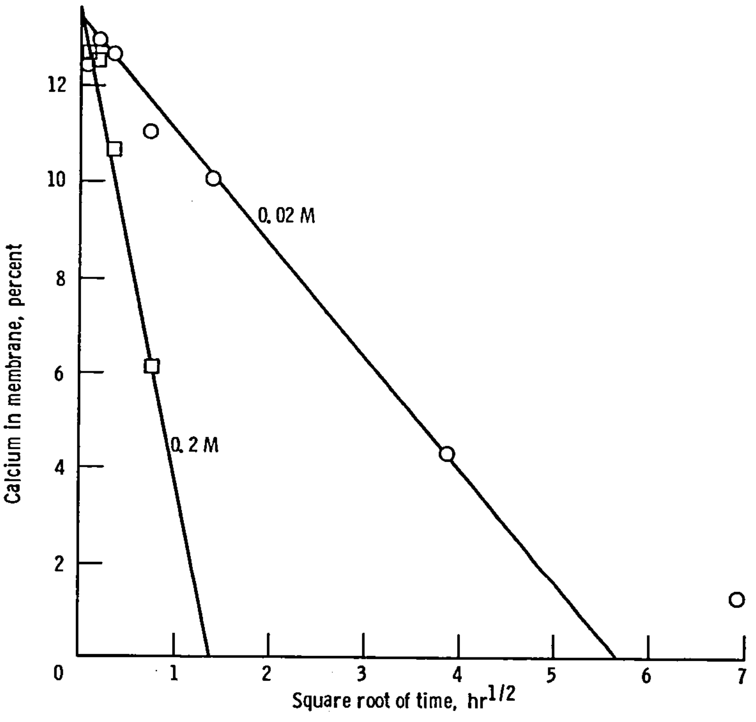

Figure 2. - Variation of calcium content of Ca PA membrane with exposure time to aqueous chromium nitrate.

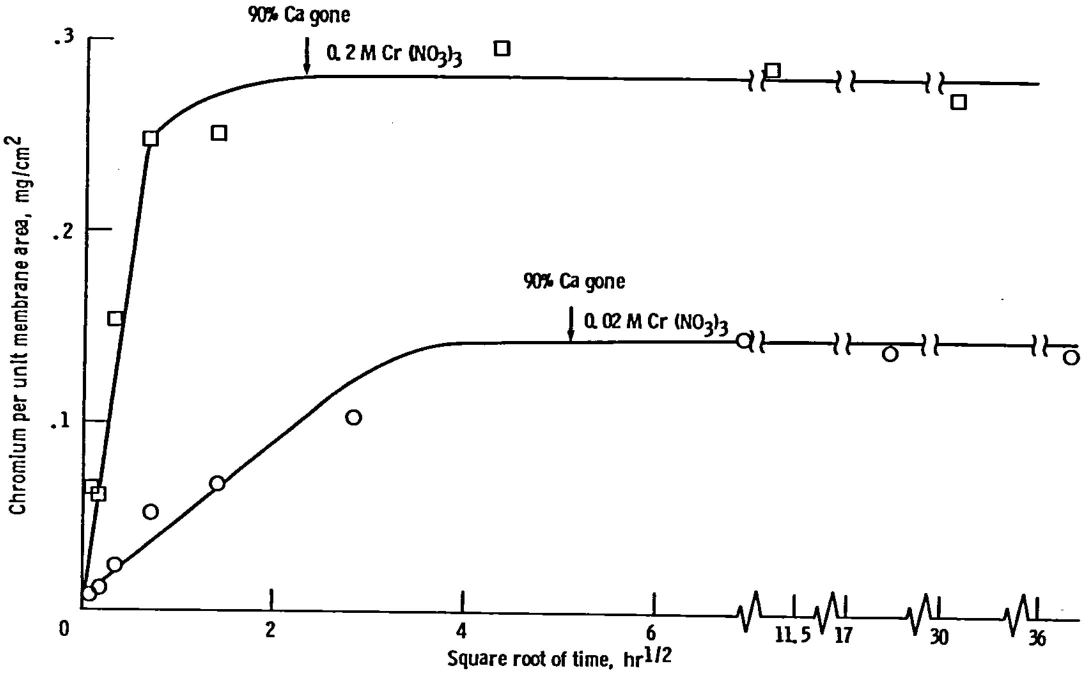

Figure 3. - Absorption of Cr III by CaPA membranes.

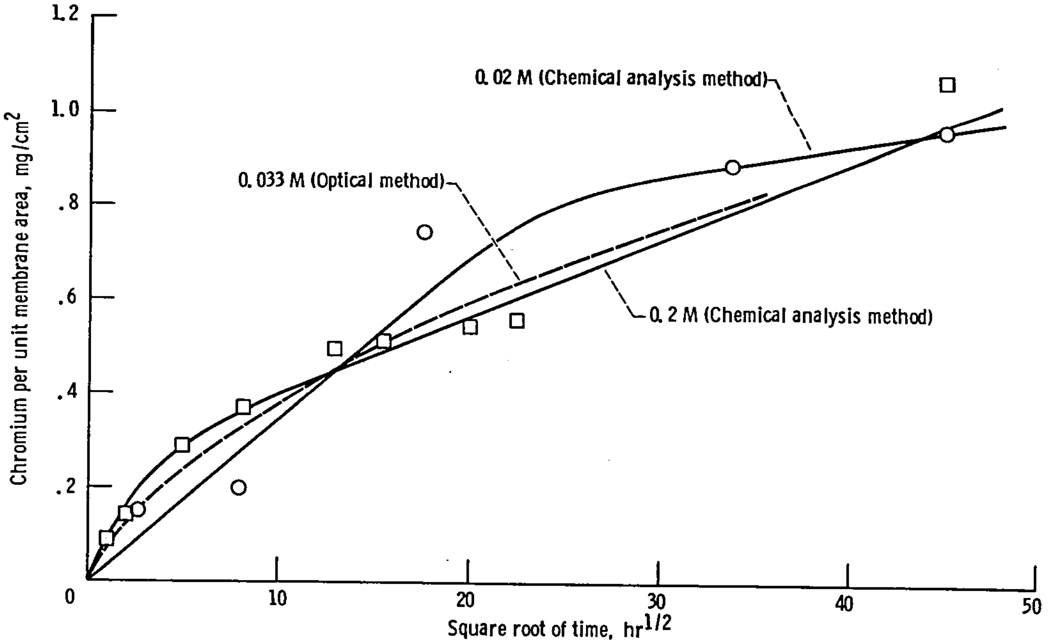

Figure 4. - Absorption of Cr III by PAA membranes (limited or no exposure to distilled H_2O during absorption experiment).

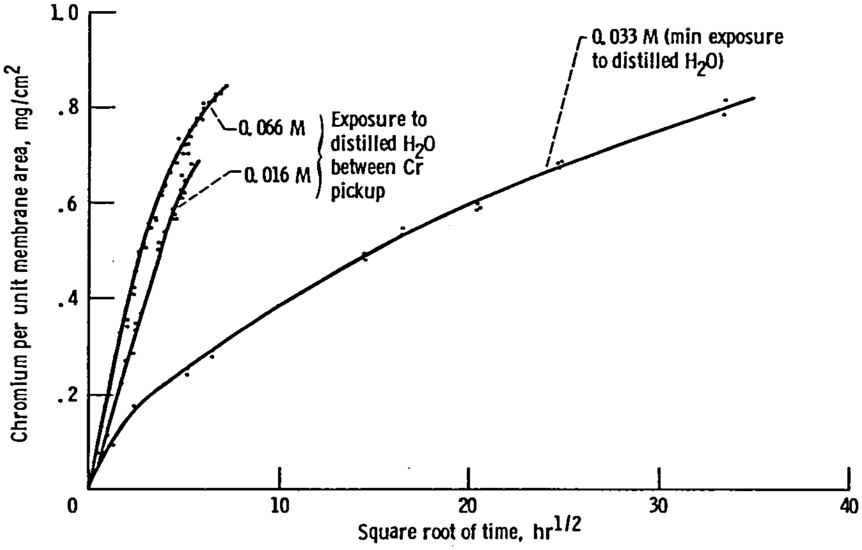

Figure 5. - Absorption of Cr III by PAA membranes (via optical method).

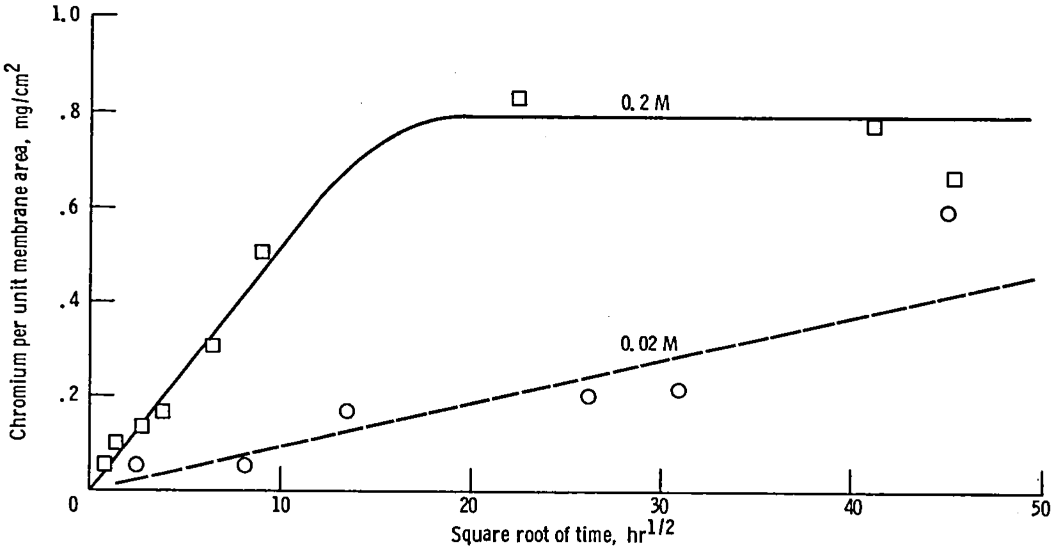

Figure 6. - Absorption of Cr III by COP membranes.

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15. Supplementary Notes

16. Abstract

Three cross-linked ion exchange membranes were studied as to their ability to absorb chromium ion from aqueous chromium III nitrate solutions. Attention was given to the mechanism of absorption, composition of the absorbed product, and the chemical bonding. The membranes were: calcium polyacrylate, polyacrylic acid, and a copolymer of acrylic acid and vinyl alcohol. For the calcium polyacrylate and the copolymer, parabolic kinetics were observed, indicating the formation of a chromium polyacrylate phase as a coating on the membrane. The rate of absorption is controlled by the diffusion of the chromium ion through this coating. The product formed in the copolymer involves the formation of a coordination complex of a chromium ion with 6 carboxylic acid groups from the same molecule. The absorption of the chromium ion by the polyacrylic acid membranes appears to be more complicated, involving cross-linking. This is due to the coordination of the chromium ion with carboxylic acid groups from more than one polymer molecule. The absorption rate of the chromium ion by the calcium salt membrane was found to be more rapid than that by the free polyacrylic acid membrane.

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