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An Investigation of the Applicability of the New Ion Exchange Resin, Reillex™-HPQ, in ATW Separations

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Milestone IV
and
Final Report

September 7, 1993

An Investigation of the Applicability of the New Ion Exchange Resin, Reillex™-HPQ, in ATW Separations

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ABSTRACT:

The investigations with the anion exchange resin Reillex™-HPQ is continuing along several different paths. The topics of current investigations that are reported here are:

1. The sorption behavior of chromium(VI) on Reillex™-HPQ from nitric acid solutions and from sodium hydroxide/sodium nitrate solutions.
2. The sorption behavior of F^- on Reillex™-HPQ resin in acidic sodium nitrate solution.
3. The sorption behavior of Cl^- on Reillex™-HPQ resin in acidic sodium nitrate solution.
4. The sorption behavior of Br^- on Reillex™-HPQ resin in acidic sodium nitrate solution.
5. The Honors thesis by one of the students is attached as Appendix II

The most significant result for each item will now be listed.

1. The sorption behavior of chromium(VI) on Reillex™-HPQ in 0.010 to 10.0 M nitric acid solutions can be described by the equation: $K_d' = {}^{Cr(VI)}_{NO_3}K / [NO_3^-]$ with a value for ${}^{Cr(VI)}_{NO_3}K$ of 1.02 ± 0.25 mmol/g. K_d' is the experimental distribution coefficient and is defined by the relationship:

$$K_d' = \frac{\text{mmol Cr(VI) on resin}}{\text{mmol Cr(VI) in solution}} = \frac{\dfrac{\{Cr(VI)\}_{total} - \{Cr(VI)\}_{sol\ tot} x V_{sol}}{\text{mass of dry resin}}}{\dfrac{\{Cr(VI)\}_{sol\ tot} x V_{sol}}{V_{sol}}}$$

In a solution of 1.00 M $NaNO_3$ and 0.010 to 5.0 M NaOH, the sorption behavior can be described by assuming that two ion exchange sites are needed for the CrO_4^{2-}. The equation to fit this behavior is:

$$\frac{{}^{CrO_4}_{NO_3}K R_t^2}{\left({}^{OH}_{NO_3}K [OH^-] + [NO_3^-]\right)^2} = \frac{\left[(R^+)_2 CrO_4^{2-}\right]}{\left[CrO_4^{2-}\right]} = K_d'$$

The value of ${}^{CrO_4}_{NO_3}K$, the equilibrium constant for the CrO_4^{2-} and the nitrate form of the resin, is 59.1 ± 38.0 mmol/mL. The value of ${}^{OH}_{NO_3}K$, the equilibrium constant for OH^- ion and the nitrate form of the resin, is 3.22 ± 1.10 mmol/mL.

2. The fluoride anion has a K_d too small to measure below a pH of 2.0

3. The determination of the values of K_d (see 1. above) for Cl^- with Reillex™-HPQ at ionic strengths of 0.001, 0.002, 0.005, 0.05 M give values of about 300, 154, 115, and 58 mL/g, respectively.

4. The determination of the values of K_d (see 1. above) for Br^- with Reillex™-HPQ at ionic strengths of 0.020 and 0.050 M give values of about 60 and 20 mL/g, respectively. The value of K (see 1. above) is 1.9-3.2 mmol/g.

INTRODUCTION

This Milestone Report is for the period June 8, 1992 to August 31, 1993. This fourth milestone and Final Report is to report on *"The final report combining the three previous reports and the last quarter results will be submitted."* If the previous reports are combined with this final report, the length will exceed 225 pages. Because of the large number of pages, we wish to have considered the Final Report as being this Report **and** the June Milestone combined. You have already the June Milestone.

This Milestone will address the following research topics.

1. The sorption behavior of chromium(VI)) on Reillex™-HPQ in acid and in base solution.
4. The sorption behavior of F^- on Reillex™-HPQ resin in acidic sodium nitrate solution.
3. The sorption behavior of Cl^- on Reillex™-HPQ resin in acidic sodium nitrate solution.
4. The sorption behavior of Br^- on Reillex™-HPQ resin in acidic sodium nitrate solution.

Each one of the areas will be addressed in a different section. Whenever applicable, reference will be made to the work reported in the previous Milestones. They were included in the June Milestone. Some of the stated objectives have not been reached. This is not a result of any dereliction of effort on our part, but is instead a result of the unanticipated difficulties of the experimental work. Additionally, a great deal of effort was spent completing and writing for publication the results of the investigation of the sorption of TcO_4^- on Reillex™-HPQ. This paper has been accepted for publication. This digression was at the mutual agreement between Kent Abney and myself.

SECTION 1

The Sorption Behavior of F^- and Br^- on Reillex™-HPQ in Sodium Nitrate Solutions.

The Sorption Behavior of Br^- and F^- on Reillex™-HPQ in Sodium Nitrate Solutions.

Abstract

Reillex™-HPQ resin, a newly available macroporous anion exchange resin, is based on a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene. Reillex™-HPQ resin consists of 63% strong-base and 37% weak-base functional groups and carries peculiar ion exchange properties. In this report, bromide and fluoride will be used as the model ions for the measurement of the distribution coefficient (K_d') and the investigation of the sorption kinetics of the Reillex™-HPQ resin. The concentration of the bromide and flouride ions were measured with an appropriate ion-selective electrode coupled with a double-junction reference electrode. The K_d' values of bromide were found to be about 69 mL/g for μ = 0.02000 M and about 20 mL/g for μ = 0.05000 M. One trend noted was that the K_d' values of bromide were found to decrease as the ionic strength increased. Another trend noted was that the K_d' increases when the bromide concentration in the solution decreases. Therefore, the HPQ resin is more suitable for low loading separations. The fluoride K_d' values were not able to be calculated because the fluoride did not load.

Introduction

In this part of the study the isotherm measurements for bromide and the K_d measurements for fluoride using Reillex™-HPQ were investigated. The reaction of interest for bromide is given in Reaction 1 and for fluoride in Reaction 2.

$$R^+NO_3^- + Br^- \rightleftharpoons R^+Br^- + NO_3^- \quad (1)$$

$$R^+NO_3^- + F^- \rightleftharpoons R^+F^- + NO_3^- \quad (2)$$

The method used to determine the K_d' was to maintain 0.01000 M HNO_3 and vary the ionic strength by the amount of $NaNO_3$ used with a set amount of resin. In these sets of experiments, K_d' measurements were made using dry resin at each ionic strength. The concentration of the free bromide ion was measured with an ion selective electrode. Before the K_d' experiments were performed, the response of the electrode under the conditions of the experiment were established by construction of a calibration curve. For each ionic strength a calibration curve was constructed.

Experimental

Reagents and Solutions

All water used in this investigation was 18 MΩ deionized water. All reagents were analytical grade; hence, no additional purification was performed. The standard HNO_3 and HF solutions were prepared from concentrated HNO_3 and HF and

standardized against a secondary standard NaOH solution. The secondary standard NaOH solution was prepared from a 19.6 M NaOH solution, standardized against a primary standard potassium hydrogen phthalate (KHP) and stored in a plastic bottle with a tight cap. Sodium bromide (NaBr), sodium nitrate ($NaNO_3$), and sodium fluoride (NaF) were obtained from J.T. Baker, Fisher Scientific Company, and from Fluka-Chemica, respectively. The salts were dried at 110°C for at least two hours. The Relliex™-HPQ resin was obtained from Reilly Industries as a 30-60 mesh in the chloride form. It was converted to the nitrate form as described in the December Milestone. The resin was then eluted with deionized water until the pH of the eluent was between 3.0 and 3.5.

Instrumental Methods

The pH electrode was standardized using commercial buffers of pH 2.00, 4.00, and 7.00. All potentials were measured with a Orion Model EA-940 Expandable Ionanalyzer in conjunction with a bromide ion Selective Electrode (94-35 BN) coupled with a double-junction reference electrode (90-02). A water bath was maintained at 25 °C for all measurements and all solutions were stirred during potential measurements. It took about 10 seconds for the $[Br^-]>10^{-4}$ voltage readings to stabilize and about 60 seconds for $[Br^-]<10^{-4}$ readings to stabilize. It took about 30 seconds for all fluoride readings to stabilize.

Auto Titrations

Titrations were also done using an auto titrator. Calibration curves for bromide and titrations of resin with bromide were performed. With each titration a 50.00-mL plastic syringe was used and the titration rate was 0.333 mL/min which consumed forty mL in two hours and 0.059 mL/min for a twelve hour titration which consumed the same amount of bromide solution. A three-neck 200.0-mL round bottom flask was used in all titrations. In the calibration curves, 50.0-mL of 0.02000 M nitrate solution was pipeted into the round bottom flask and the mV reading was allowed to stabilize. The blank solution was then titrated with 0.0200 M bromide solution.

For the resin titration, 10 g of Reillex resin in the nitrate form was eluted with 10 bed volumes of 0.0200 M sodium nitrate solution, dried at 60°C for 48 hours, and then allowed to cool in a desicator. Into a 200.0-mL round bottom flask, 50.0-mL of 0.02000 M sodium nitrate solution was pipeted and 0.2000 g of Reillex™-HPQ resin was transferred. The resin was then ground by stirring with a stirring bar for twelve hours, then titrated with 0.02000 M bromide solution. Three titrations with resin were done.

Isotherm Measurements

In further studies of Relliex™-HPQ resin with bromide as the model ion, isotherm measurements were done at various ionic strengths. All experiments were performed under the condition of $[H^+] = 0.01000$ M. Six additional bromide % total capacities were done in addition to the ten reported in the June Milestone. The added % total capacities ranged from 460% to 42%. One set of isotherm measurements was done at $\mu = 0.0200$ M and one at $\mu = 0.0500$ M. In the experiments with $\mu = 0.0200$ M, a certain amount of bromide solution containing 0.0100 M NaBr and 0.0100 M HBr was added to a set amount of resin. Then the appropriate amount of nitrate solution needed to make the desired volume was added. The nitrate solution contained 0.0100 M HNO_3 and 0.0100 M $NaNO_3$. Blank solutions were also run at the each % total capacity. The blank solutions were of the same composition except no resin was used. Table 1 shows the composition of the resin and blank cells for $\mu = 0.0200$ M.

In the experiments with μ = 0.0500 M, a certain amount of bromide solution containing 0.0400 M NaBr and 0.0100 M HBr was added to a set amount of resin. Then the appropriate amount of nitrate solution needed to make the desired volume was added. The nitrate solution contained 0.0100 M HNO_3 and 0.0400 M $NaNO_3$. Blank solutions were also run at the each % total capacity. The blank solutions were of the same composition except no resin was used. Table 2 shows the composition of the resin and blank cells for μ = 0.0500 M.

Table 1 Composition of the reaction and blank cells for the bromide isotherm measurements in 0.0200 M ionic strength.

	% total capacity					
Reagents added	42	70	97	137	232	464
g dry resin	0.3374	0.3374	0.3374	0.3374	0.2000	0.1000
mL Br^- soln	30.0*	50.0*	70.0*	99.0*	99.0*	99.0
mL blank soln	69.0	49.0	29.0	0.0	0.0	0.0
total volume	100.0	100.0	100.0	100.0	100.0	100.0
meq resin	1.439	1.439	1.439	1.439	0.853	0.427
mmol Br^-	0.6000	1.000	1.400	2.000	2.000	2.000

*0.02 M bromide solution.

Table 2. Composition of the reaction and blank cells for the bromide isotherm measurements in 0.0500 M ionic strength.

	% total capacity					
Reagents added	42	70	97	136	143	464
g dry resin	0.8439	0.8436	0.8436	0.8436	0.8002	0.4007
mL Br- soln	30.0*	50.0*	70.0*	97.5*	97.6*	98.8*
mL blank soln	69.0	49.0	29.0	0.0	0.0	0.0
total volume	100.0	100.0	100.0	100.0	100.0	100.0
meq resin	3.5977	3.5977	3.5977	3.5977	3.4117	1.7058
mmol Br^-	1.5000	2.5000	3.5000	4.8750	4.8800	4.9400

* 0.05 M bromide solution.

The following equations were used to calculate the isotherm values. The volume of resin is calculated as shown in Eq. 3.

$$\text{resin volume} = \text{g of dry resin} \times 1.958 \text{ mL/g} \quad (3)$$

The supernatent volume can be calculated by Eq. 4.

supernatant volume = total volume - resin volume (4)

The total equivalents of bromide ion is calculated by Eq. 5.

meq Br^- = concentration (M) of bromide ion x mL of bromide used (5)

The potential difference (ΔE) can be calculated as given in Eq. 6.

ΔE = mV reading of blank cell - mV reading of resin cell (6)

The percent loading can be calculated as given in Eq. 7.

$$\% \text{ loading} = (1-10^{-\Delta E/59.16}) \times 100\% \quad (7)$$

Eq. 8 gives the equation for equivelents of bromide in the solution.

meq $(Br^-)_{sol}$ = total meq of bromide x (1- percent loading) (8)

Eq. 9 gives the equation for the milliequivalents of bromide in the resin.

meq $(Br^-)_{res}$ = total equivalents of bromide x percent loading (9)

Eq. 10 is the equation for the amount of nitrate (meq) in the resin.

meq $(NO_3^-)_{res}$ =
(ionic strength x volume supernatant) - meq bromide in solution (10)

Eq. 11 is the equation for meq of nitrate in the solution.

meq $(NO_3^-)_{sol}$ =
(g dry resin x 0.9271 g 110°/60° x 4.6 meq/g 110°) - bromide meq resin (11)

The bromide in the resin and the bromide in the solution can now be calculated. Eq. 12 is for the bromide in the resin.

$$\frac{[Br^-]_{resin}}{[Br^-]_{resin} + [NO_3^-]_{resin}} \quad (12)$$

Eq. 13 is for the bromide in the solution .

$$\frac{[Br^-]_{soln}}{[Br^-]_{soln} + [NO_3^-]_{soln}} \quad (13)$$

Fluoride Calibration Curve

In the construction of the calibration curve for fluoride, six standards were prepared ranging from 0.1000 M to $1x10^{-6}$ M F^-. Table 3 lists the composition of the calibration curve solutions.

Table 3. Composition of blank and fluoride solution for calibration curve for K_d' measurements at an ionic strength of 0.10 M.

	Fluoride Solution	Blank Solution
First fluoride solution.		
M HNO_3	0.0000	0.01000
M NaNO3	0.0000	0.09000
M HF	0.01000	0.0000
M NaF	0.09000	0.0000
Second fluoride solution.		
MHNO_3	0.01000	0.01000
M NaNO3	0.08000	0.09000
M HF	0.00100	0.0000
M NaF	0.00900	0.000
Third fluoride solution.		
M HNO_3	0.01000	0.01000
M NaNO3	0.08900	0.09000
M HF	0.00010	0.0000
M NaF	0.00090	0.000
Fourth fluoride solution.		
M HNO_3	0.01000	0.01000
M NaNO3	0.08990	0.09000
M HF	0.00001	0.0000
M NaF	0.00009	0.0000
Fifth fluoride solution.		
M HNO_3	0.01000	0.01000
M NaNO3	0.08999	0.09000
M HF	0.000001	0.0000
M NaF	0.000009	0.0000
Sixth fluoride solution.		
M HNO_3	0.01000	0.01000
M NaNO3	0.089999	0.09000
M HF	0.0000001	0.0000
M NaF	0.0000009	0.0000

Fluoride K_d Measurements

The fluoride K_d measurements were performed in the same manner as the bromide K_d' measurements. All K_d' experiments were performed under the condition of 0.01000 M [H^+] Thirteen different fluoride % total capacities were used. The % total capacities ranged from 695.0% to 0.104% at μ = 0.10 and 69.5% to 0.104% at μ = 0.01. One set of K_d' measurements were done at each ionic strength. Since the ion being used was fluoride, all experiments were carried out in plastic beakers and no pH readings were taken. In each case, a certain amount of fluoride was added to a set amount of resin, then the appropriate amount of nitrate solution needed to make the desired volume. Blanks were also run at the same % total capacity. The blanks were of the same composition except no resin was added. In all measurements resin volume was ignored. Table 4 shows the composition of the resin and blank cells for μ = 0.100 M.

Table 4. Composition of the reaction and blank cells for fluoride K_d' measurements in 0.1000 M ionic strength.

	% total capacity					
Reagents added	695	47	208	104	35	21
g dry resin	0.3373	0.3378	0.3378	0.3372	0.3375	0.3377
mL Br^- soln	100.0[a]	50.0[a]	30.0[a]	15.0[a]	5.0[a]	30.0[b]
mL blank soln	0.0	50.0	70.0	85.0	95.0	70.0
total volume	100.0	100.0	100.0	100.0	100.0	100.0
meq resin	1.4391	1.4391	1.4391	1.4391	1.4391	1.4391
mmol Br^-	10.000	5.0000	3.0000	1.5000	0.5000	0.3000
	% total capacity					
Reagents added	10	3.5	2.1	1.0	0.35	0.21
g dry resin	0.3371	0.3371	0.3377	0.3371	0.3378	0.3373
mL Br^- soln	15.0[b]	5.0[b]	30.0[c]	15.0[c]	5.0[c]	30.0[d]
mL blank soln	85.0	95.0	70.0	85.0	95.0	70.0
total volume	100.0	100.0	100.0	100.0	100.0	100.0
meq resin	1.4391	1.4391	1.4391	1.4391	1.4391	1.4391
mmol Br^-	0.1500	0.0500	0.0300	0.0150	0.0050	0.0030

	% total capacity
Reagents added	0.10
g dry resin	0.3371
mL of Br^- soln	5.0[d]
mL blank soln	85.0
total volume	100.0
meq resin	1.4391
mmol Br	0.0015

[a] First fluoride solution.
[b] Second fluoride solution.
[c]Third fluoride solution.
[d]Fourth fluoride solution.

Table 5 shows the composition of the blank and fluoride solutions for μ = 0.0100 M and Table 6 shows the composition of the resin and blank cells for μ = 0.01.

Table 5. Composition of blank and fluoride solution for isotherm measurements in an ionic strength 0.01 M .

	Fluoride Solution	Blank Solution
First fluoride solution.		
M HNO_3	0.0000	0.01000
M NaNO3	0.0000	0.0000
M HF	0.01000	0.0000
M NaF	0.01000	0.0000
Second fluoride solution.		
M NO_3	0.01000	0.01000
M NaNO3	0.0000	0.0000
M HF	0.00100	0.0000
M NaF	0.00100	0.0000
Third fluoride solution.		
M HNO_3	0.01000	0.01000
M NaNO3	0.0000	0.0000
M HF	0.00010	0.0000
M NaF	0.00010	0.0000

Table 6. Composition of the reaction and blank cells for fluoride K_d' measurements in 0.01000 M ionic strength.

	% total capacity					
Reagents added	69.8	20.8	10.4	2.08	1.04	0.69
g dry resin	0.3379	0.3372	0.3378	0.3379	0.3371	0.3378
mL Br^- soln	100.0[a]	30.0[a]	15.0[a]	30.0[b]	15.0[b]	10.0[b]
mL blank soln	0.0	70.0	85.0	70.0	85.0	0.0
total volume	00.0	100.0	100.0	100.0	100.0	100.0
meq resin	1.4391	.4391	1.4391	1.4391	1.4391	1.4391
mmol Br	1.0000	0.3000	0.1500	0.0300	0.0150	0.0100

	% total capacity			
Reagents added	0.34	0.21	0.14	0.10
g dry resin	0.3371	0.3371	0.3376	0.3377
mL of Br- soln	5.0b	30.0c	20.0c	15.0c
mL blank soln	95.0	70.0	80.0	95.0
total volume	100.0	100.0	100.0	100.0
meq resin	1.4391	1.4391	1.4391	1.4391
mmol Br-	0.0050	0.0030	0.0020	0.0015

a First fluoride solution.
b Second fluoride solution.
[c]Third fluoride solution.

Results and Discussion

The mV and pF values are given in Table 7 and the calibration curve for fluoride is shown in Figure I. The calibration curve is linear but the slope is about 65 mv instead of the 56 mV that the electrode manual stated. One possible reason for this difference is that when the pH is below 5, the fluoride ion exists as HF and H_2F^-, neither of which the fluoride ion-selective electrode can measure. The $[H^+]$ in all solutions was 0.0100 M.

The K_d values of the fluoride loadings could not be calculated because the fluoride did not load. The mV readings of the blank cell and the resin cell were nearly identical showing that the fluoride and the blank solution only mixed in both of the cells. Table 8 shows the mV readings of the blank and resin cell for $\mu = 0.10$. Table 9 shows the mV readings of the blank and resin cell for $\mu = 0.01$

Table 7 The mV and pF values for the fluoride calibration curve.

Concentration	pF	mV
$1x10^{-1}$	1.0	-110.3
$1x10^{-2}$	2.0	-19.4
$1x10^{-3}$	3.0	64.4
$1x10^{-4}$	4.0	125.8
$1x10^{-5}$	5.0	181.4
$1x10^{-6}$	6.0	214.1

Table 8 The mV readings for $\mu = 0.10$ at various % total capacities.

% Total Capacity	mV Reading Dummy Cell	mV Reading Resin Cell
694.9	-110.3	-110.0
347.4	-90.3	-89.1
208.5	-72.5	-71.2
104.2	-42.4	-41.3
34.7	12.0	11.8
20.8	30.9	29.7
10.4	52.0	51.4
3.5	85.1	81.8
2.1	95.2	94.9
1.0	114.0	112.6
0.3	142.3	139.7
0.2	154.7	156.9
0.1	170.3	169.9

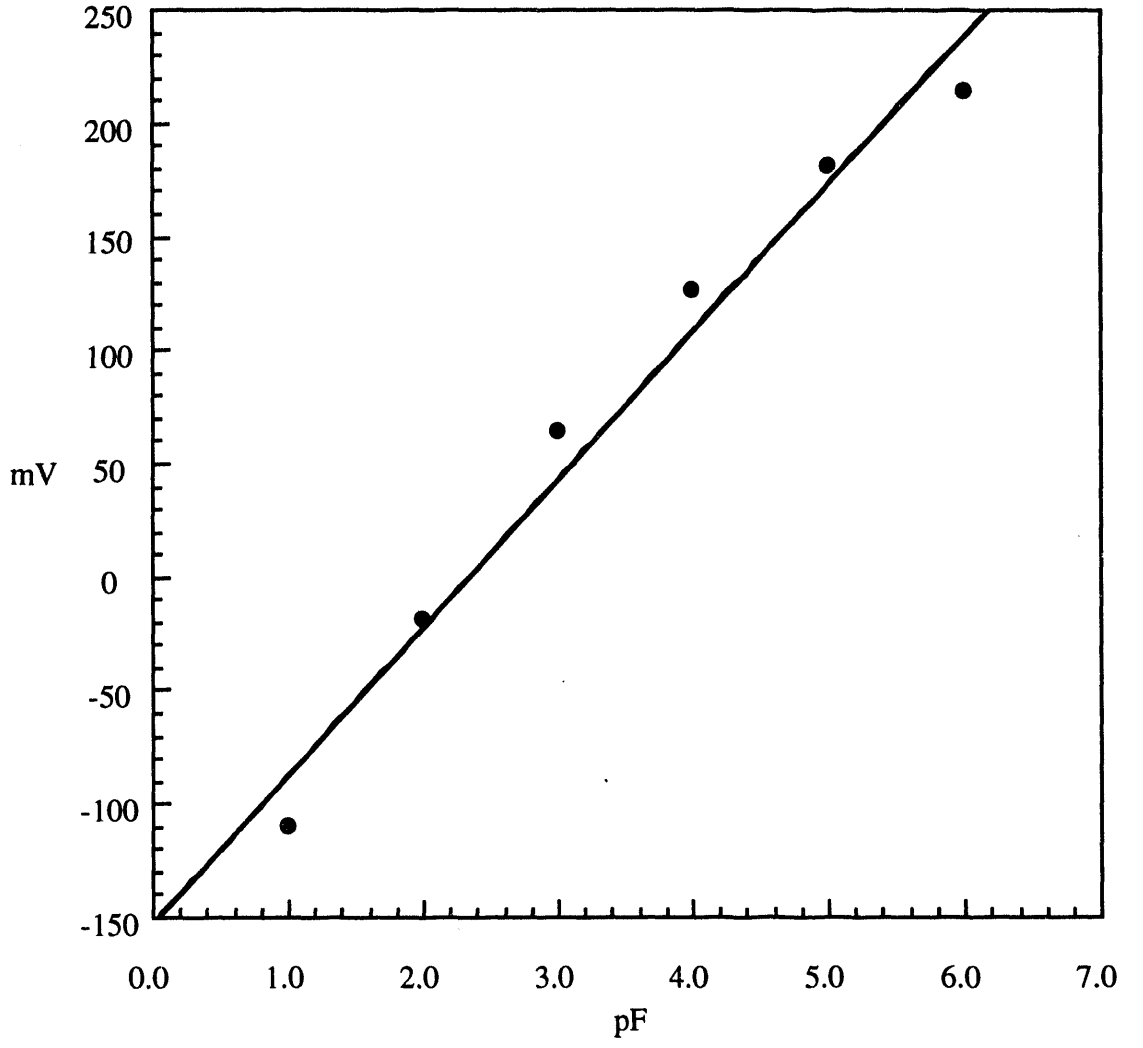

Figure I. The fluoride calibration curve for 0.0100 M $[H^+]$ and an ionic strength of 0.100 M. The line is the fit of the data to the equation mV = (-151.6 ± 20.6) + (65.3 ± 5.3)(pF).

Table 9 The mV Readings for μ = 0.10 at various % total capacities.

% Total Capacity	mV Reading Dummy Cell	mV Reading Resin Cell
69.5	10.1	9.9
20.8	39.7	38.4
10.4	56.6	56.3
2.1	97.8	96.9
1.4	107.9	107.2

1.0	114.9	113.8
0.7	125.7	124.7
0.3	144.1	143.4
0.2	156.2	155.8
0.1	173.6	172.1

Figure II shows the calibration data from the titration. Figure III shows the resin titration data. From the graphs, the curves are nearly identical. Table 10 gives the percent loading, K_d', and $[NO_3^-]$ for $\mu = 0.02$ and Table 11 gives the percent loading, K_d', and $[NO_3^-]$ for $\mu = 0.05$ M. The isotherm measurements for bromide are listed in Tables 12 and 13 for $\mu = 0.02$ and $\mu = 0.05$ M. Figure IV shows the data for $\mu = 0.02$ and Figure V the data for $\mu = 0.05$. The last six cells in the $\mu = 0.0500$ M data are currently being redone since the data is so scattered.

Table 10 The percent loading, K_d', and $[NO_3^-]$ for $\mu = 0.02000$ at various % total capacities.

% Total Capacity	Percent Loading	K_d'	$[NO_3^-]$
464	25.31	33.90	0.000×10^{1}
232	37.07	58.91	0.000×10^{1}
137	44.65	80.69	0.000×10^{1}
97.0	42.91	75.15	1.400×10^{-3}
70.0	39.71	65.68	1.000×10^{-3}
42.0	40.18	67.16	6.000×10^{-4}
20.0	39.00	63.94	4.063×10^{-4}
10.0	42.24	73.12	2.804×10^{-3}
5.00	41.33	70.44	5.203×10^{-3}
2.00	40.87	69.12	5.863×10^{-3}
3.00	39.00	63.94	9.040×10^{-3}
1.00	42.46	73.79	9.280×10^{-3}
0.50	41.33	70.44	9.520×10^{-3}
0.20	40.87	69.12	9.904×10^{-3}
0.10	44.44	79.99	9.928×10^{-3}
0.01	28.72	40.30	9.992×10^{-3}

Table 11 The percent loading, K_d', and $[NO_3^-]$ for $\mu = 0.05$ at various % total capacities.

% Total Capacity	Percent loading	K_d'	$[NO_3^-]$
464	19.90	6.21	$0.000x10^1$
143	31.18	11.24	$0.000x10^1$
136	34.32	13.06	$0.000x10^1$
97.0	30.37	10.90	$3.500x10^{-3}$
70.0	27.89	9.67	$2.500x10^{-3}$
42.0	27.61	9.53	$1.500x10^{-3}$
20.0	42.68	18.62	$1.122x10^{-2}$
10.0	44.09	20.53	$2.561x10^{-2}$
5.00	45.51	20.88	$2.561x10^{-2}$
2.00	44.82	20.34	$2.273x10^{-2}$
3.00	45.93	21.24	$3.712x10^{-2}$
1.00	45.30	20.70	$3.865x10^{-2}$
0.50	44.66	20.17	$3.856x10^{-2}$
0.20	43.79	19.47	$3.971x10^{-2}$
0.10	39.47	16.30	$3.966x10^{-2}$
0.01	32.50	12.04	$3.999x10^{-2}$

Table 12. Bromide ion isotherm measurements for $\mu = 0.02000$ bromide (1 ml of resin = 1.4391 meq).

	% total capacity			
	464	232	137	97
resin volume	0.1942	0.3922	0.6608	0.6602
supernatant vol.	99.3398	99.6078	99.3392	99.3398
total eq Br^-	2.0000	2.0000	1.9800	1.4000
eq Br- solution	1.4937	1.2586	1.0958	0.7993
eq Br- resin	0.5063	0.7414	0.8842	0.6007
eq NO3- solution	0.5063	0.7414	0.8910	1.1875
eq NO3- resin	0.0833	0.1128	0.5551	0.8374
Br^- solution	0.7468	0.6293	0.5551	0.4023
Br^- resin	1.1968	0.8680	0.6143	0.4177

	% total capacity			
	70	42	20	10
resin volume, mL	0.6604	0.6602	0.6610	0.6602
supernatant vol.	99.3396	99.3398	99.3390	99.3398
total eq Br-	1.0000	0.6000	0.2878	0.1439
eq Br- solution	0.6029	0.3589	0.1755	0.0831
eq Br- resin	0.3971	0.2411	0.1225	0.0607
eq NO3- solution	1.3839	0.6279	1.8112	1.9037
eq NO3- resin	1.0414	1.1970	1.3275	1.3773
Br- solution	0.3035	0.1807	0.0883	0.0418
Br- resin	0.2760	0.1676	0.0779	0.0423

	% total capacity			
	5	3	2	1
resin volume, mL	0.6602	0.6610	0.6604	0.6602
supernatant vol.	99.3398	99.3390	99.3396	99.3398
total eq Br^-	0.0780	0.0413	0.0288	0.0144
eq Br- solution	0.0422	0.0255	0.0176	0.0081
eq Br^- resin	0.0297	0.0176	0.0112	0.0061
eq NO_3^- solution	1.9446	1.9613	1.9692	1.9785
eq NO_3^- resin	1.4083	1.4221	1.4272	1.4319
Br^- solution	0.0212	0.0128	0.0088	0.0042
Br^- resin	0.0207	0.0123	0.0078	0.0042

	% total capacity			
	0.50	0.20	0.10	0.01
resin volume, mL	0.6602	0.6608	0.6602	0.6602
supernatant vol.	99.3398	99.3392	99.3398	99.3398
total eq Br^-	0.0072	0.0029	0.0013	0.00014
eq Br^- solution	0.0042	0.0017	0.00080	0.00010
eq Br^- resin	0.0030	0.0012	0.00064	0.000041
eq NO_3 solution	1.9826	1.9851	1.9860	1.9867
eq NO_3 resin	1.4351	1.4381	1.4374	1.4380
Br^- solution	0.0021	0.00086	0.00040	0.00005
Br^- resin	0.00021	0.00082	0.00044	0.000029

Table 13. Isotherm measurements for bromide in μ=0.05 M (2 ml of resin = 2.8781 meq).

	% total capacity			
	464	143	136	97
resin volume, mL	0.7846	1.5668	1.6518	1.6518
supernatant vol.	99.2154	98.4332	98.3482	98.3482
total eq Br^-	4.9408	4.9408	4.8750	3.5000
eq Br^- solution	3.9577	3.4003	3.2020	2.4371
eq Br^- resin	0.9830	1.5404	1.6730	1.6730
eq NO_3^- solution	1.0031	1.5213	1.7154	2.4803
eq NO_3^- resin	0.7258	1.8722	1.9246	2.5347
Br^- solution	0.7978	0.6909	0.651	0.4956
Br^- resin	0.5753	0.4514	0.4650	0.2955

	% total capacity			
	70	42	20	10
resin volume, mL	1.6518	1.6524	1.3213	1.3218
supernatant vol.	98.3482	98.3476	98.6787	98.6782
total eq Br^-	2.5000	3.5000	0.5756	0.2878
eq Br^- solution	1.8028	1.0859	0.3299	0.1581
eq Br^- resin	0.6972	0.4141	0.2457	0.1298
eq NO_3^- solution	3.1146	3.8315	4.6040	4.7759
eq NO_3^- resin	2.9005	3.1849	2.6321	12.7493
Br^- solution	0.3666	0.2208	0.0669	0.0320
Br^- resin	0.1938	0.1151	0.0854	0.0451

	% total capacity			
	5	3	2	1
resin volume, mL	1.3211	1.3211	1.3213	1.3217
supernatant vol.	98.6789	98.6789	98.6787	98.6784
total eq Br^-	0.1439	0.0863	0.0576	0.0288
eq Br^- solution	0.0784	0.0476	0.0311	0.0157
eq Br^- resin	0.0655	0.0387	0.0264	0.0130
eq NO_3 solution	4.8555	4.8863	4.9028	4.9182
eq NO_3 resin	2.8119	2.8386	2.8514	2.8656

Br^- solution	0.0159	0.0097	0.0063	0.0032
Br^- resin	0.0228	0.0135	0.0092	0.0045

	% total capacity			
	0.50	0.20	0.10	0.01
resin volume	0.6602	0.6608	0.6602	0.6602
supernatant vol.	98.6789	98.6782	98.6780	98.6785
total eq Br^-	0.0144	0.0058	0.0028	0.00028
eq Br^- solution	0.0080	0.0032	0.0017	0.00019
eq Br^- resin	0.0064	0.0025	0.0011	0.000094
eq NO_3^- solution	4.9260	4.9307	4.9322	4.9337
eq NO_3^- resin	2.8709	2.8766	2.8784	2.8781
Br^- solution	0.0016	0.00066	0.00035	0.000039
Br^- resin	0.0022	0.00088	0.00039	0.000033

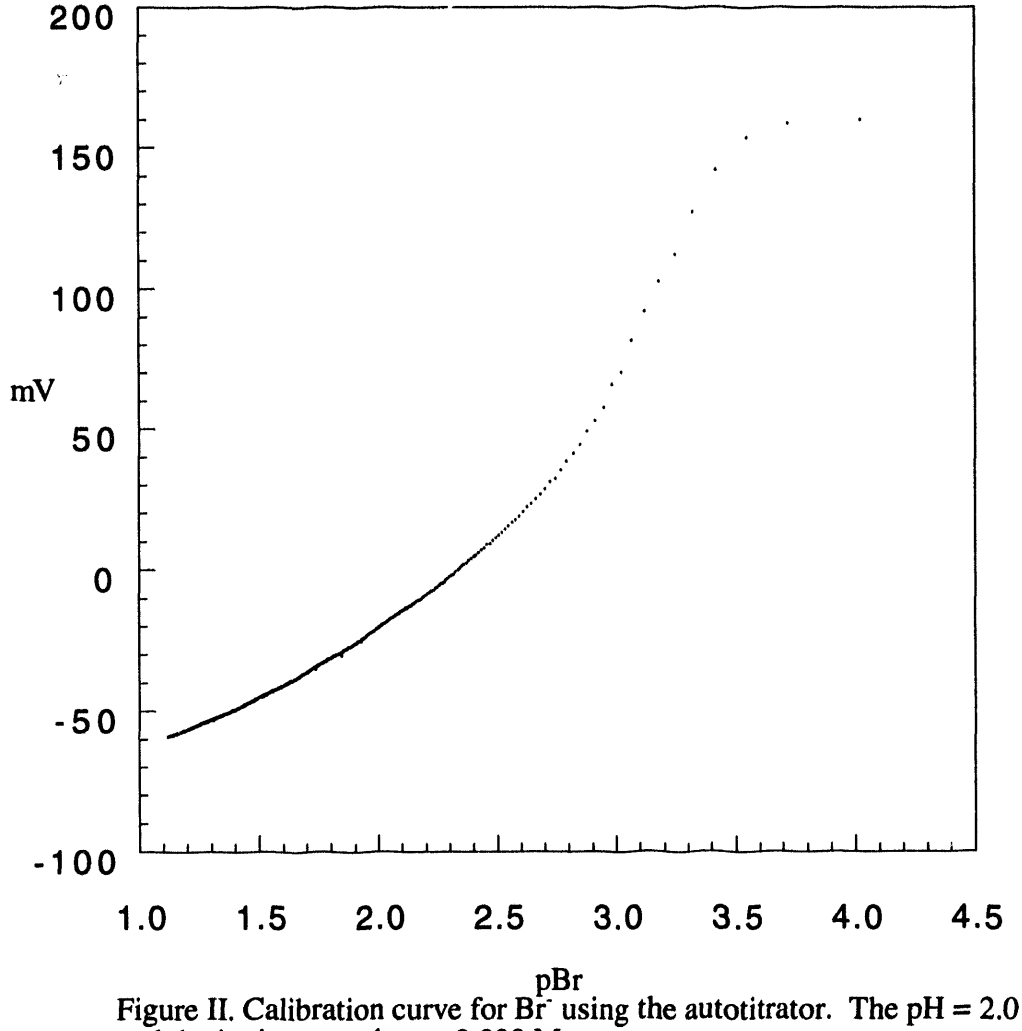

Figure II. Calibration curve for Br^- using the autotitrator. The pH = 2.0 and the ionic strength was 0.020 M.

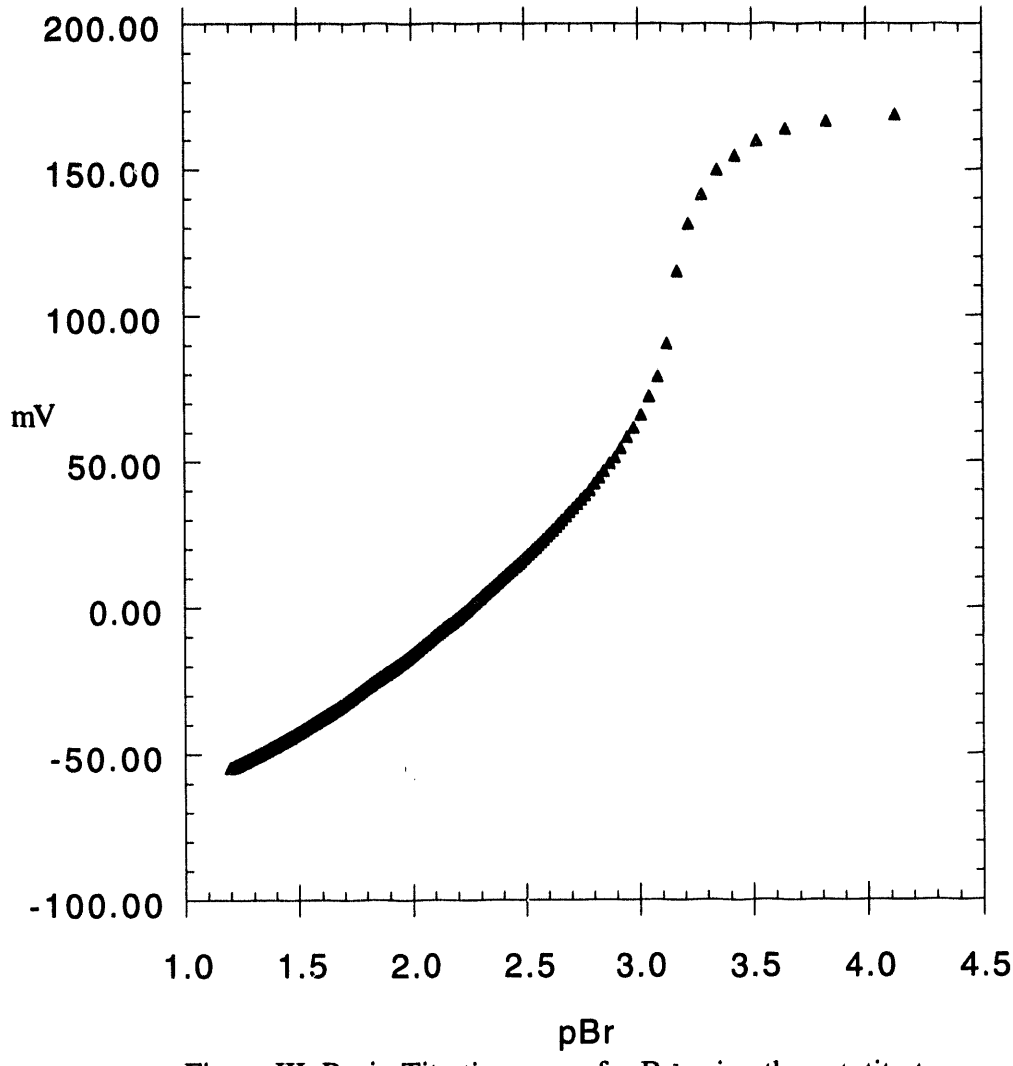

Figure III. Resin Titration curve for Br^- using the autotitrator. The pH = 2.0 and the ionic strength was 0.020 M.

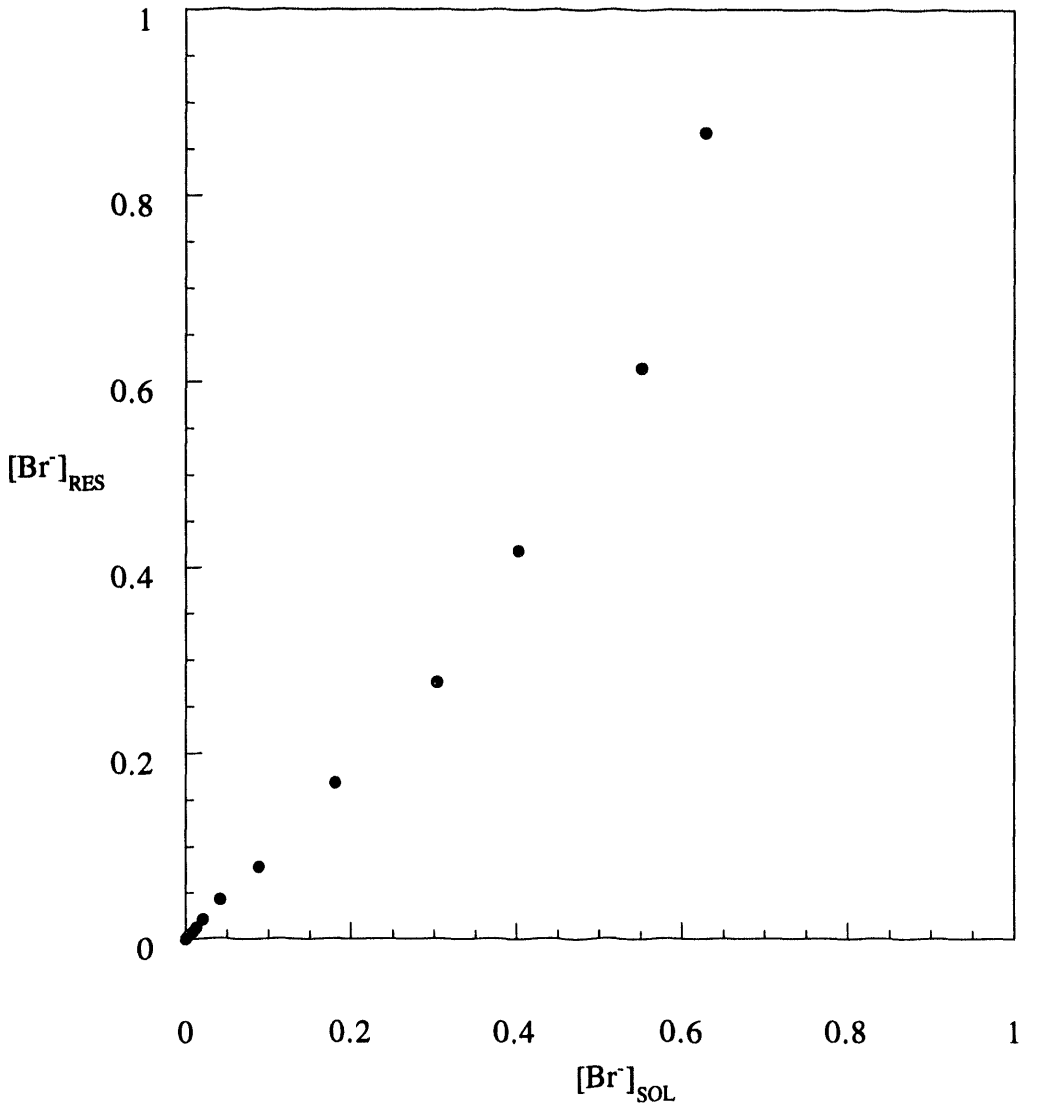

Figure IV. The sorption isotherm for bromide ion on Reillex™-HPQ in 0.0100 M H^+ and an ionic strength of 0.0200 M ($NaNO_3$).

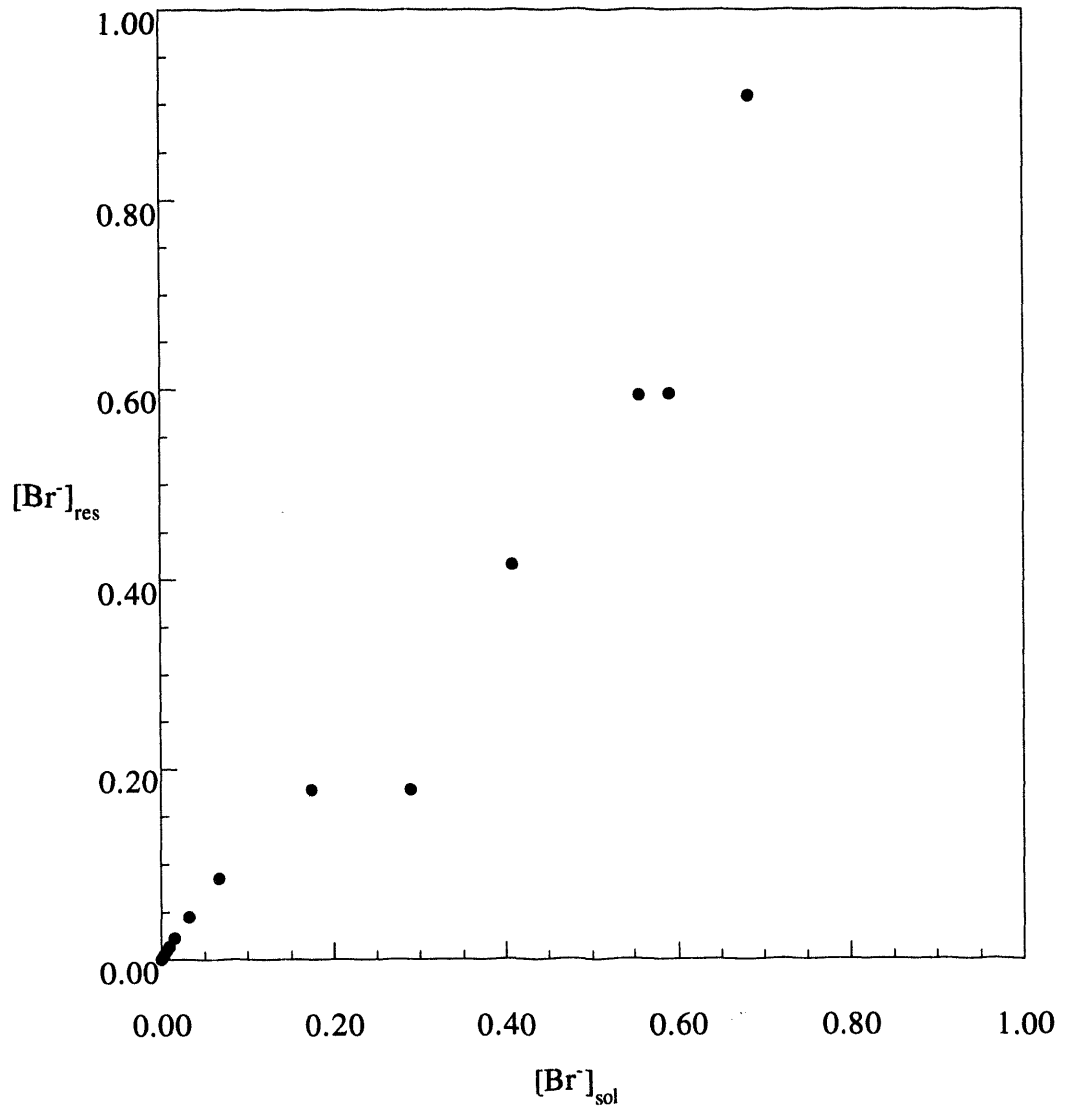

Figure V. The sorption isotherm for bromide ion on Reillex™-HPQ in 0.0100 M H^+ and an ionic strength of 0.0500 M ($NaNO_3$).

SECTION 2

The Sorption Behavior of Cl^- on Reillex™-HPQ Resin in Sodium Nitrate Solutions.

The Sorption Behavior of Cl^- on Reillex™-HPQ Resin in Sodium Nitrate Solutions.

Abstract

The values for K_d' for Cl^- with Reillex™-HPQ at 0.0020, 0.0050 and 0.050 M ionic strengths were determined. The K_d' values for ionic strength 0.0020 M and pH = 3.0 ranged from 154 to 27 mL/g. The K_d' values for ionic strength 0.0050 M and pH = 3.0 values ranged from 115 to 37 mL/g. The K_d' values for ionic strength 0.050 M and pH = 2.0 ranged from 58 to 3.0 mL/g.

Introduction

In this part of the study the K_d' for Chloride and the Reillex™-HPQ is determined. The reaction of interest is represented in Eq. 1. The general approach in measuring

$$R^+NO_3^- + Cl^- \rightleftharpoons R^+Cl^- + NO_3^- \qquad (1)$$

the K_d' is to measure the potential of a chloride specific electrode immersed in a solution containing all of the desired reagents **except** the Reillex™-HPQ resin. This potential is then compared to an identical solution with the resin in it. The value of the K_d' can then be calculated from Eq. 2. The value ΔE is defined by Eq 3.

$$K_{d'} = \frac{10^{\Delta E/59.16} \text{ X volume of solution}}{1-10^{\Delta E/59.16} \text{ X mass or volume of resin}} \qquad (2)$$

$$\Delta E = E_{\text{reference solution}} - E_{\text{sample solution}} \qquad (3)$$

Experimental

Reagents and Solutions

All water used in the investigation was 18 mΩ deionized water. All reagents were analytical grade; hence no additional purification was performed. The standard HNO_3 and HCl solutions were prepared from concentrated solutions and standardized against a secondary standard NaOH solution. The secondary standard NaOH solution was prepared from a 19.6 M NaOH solution, standardized against a primary standard potassium hydrogen phthalate (KHP), and stored in a plastic bottle. The NaCl was obtained from Fisher Scientific Company and $NaNO_3$ from the Fluka-Chemica. The Reillex-HPQ™ resin was obtained from Reilly Industries as a 30-60 mesh in the chloride form. The resin was converted to the nitrate form as described in the December Milestone and then eluted with 1.0 M HNO_3 until free of chloride ion. It was then eluted

with water until a pH of 3.2-3.5 was reached and finally eluted with 20 bed volumes of blank solution.

The concentration of HNO_3 was maintained at 0.00100 M or 0.01000 M in all solutions prepared. The standard chloride solutions and blank solution for μ = 0.002 M μ = 0.005 M and μ = 0.05 M were prepared as described in Tables 1-6

Table 1. Details for Series I experiments.

	% Nominal Loading			
Reagents added	20	10	2	0.2
mL of wet Resin	5.0	5.0	5.0	5.0
mL Cl- soln	10.00[1]	5.00[1]	10.00[2]	10.00[3]
mL of eluent[5]	2.5	2.5	2.5	2.5
mL 0.01000 M HNO_3	12.5	17.5	12.5	12.5
total volume in mL	30.0	30.0	30.0	30.0
meq resin[4]	7.2	7.2	7.2	7.2
mmol of Cl^-	0.0560	0.0280	0.00560	0.000560
mmol of NO_3^-	0.0150	0.0200	0.00150	0.0150
M of NO_3^-	0.000600	0.0000800	0.000600	0.000600

[1] 0.140 M NaCl solution used. [2]0.0140M NaCl solution used. [3]0.00140 M NaCl solution used. [4]1.439 meq/1 mL packed resin. [5]This is from the volume of eluent (0.01000 M HNO_3) and volume of 0.01000 M HNO_3.

Table 2. Details for Series II experiments.

	% Nominal Loading			
Reagents added	20	10	2	0.2
mL of wet Resin	5.0	5.0	5.0	5.0
mL Cl^- soln	10.00[1]	5.00[1]	10.00[2]	10.00[3]
mL of eluent[5]	2.5	2.5	2.5	2.5
mL 0.00100 M HNO_3	12.5	17.5	12.5	12.5
total volume in mL	30.0	30.0	30.0	30.0
meq resin[4]	7.2	7.2	7.2	7.2
mmol of Cl^-	0.0560	0.0280	0.00560	0.000560
mmol of NO_3^-	0.0150	0.0200	0.00150	0.0150
M of NO_3^-	0.000600	0.0000800	0.000600	0.000600

[1] 0.140 M NaCl solution used. [2]0.0140M NaCl solution used. [3]0.00140 M NaCl solution used. [4]1.439 meq/1 mL packed resin. [5]This is from the volume of eluent (0.00100 M HNO_3) and volume of 0.001000 M HNO_3.

Ion Specific Electrode Calibration

The pH electrode was standardized using commercial buffers of pH 2.00, 4.00 and 7.00. Chloride calibration standards for each ionic strength were prepared using standard HCl and HNO_3 solutions. Ten mL of each calibration standard solution was pipetted into a clean 30-mL beaker. A potential reading and pH reading of each solution were recorded. The temperature was 25 °C and solutions stirred during all potential measurements.

TABLE 3. The details for Series III experiments. Wet resin was used at 0.002 M ionic strength in the solutions. The hydrogen ion concentration is 0.0010 M.

	% Nominal Loading				
Reagents added	14	10	5	3	2
mL of wet Resin	1.0	1.0	1.0	1.0	1.0
mL Cl^- soln	100.0[1]	100.0[2]	50.0[2]	40.0[3]	30.0[3]
mL of eluent[6]	4.00	4.00	4.00	4.00	4.00
mL of NO_3^- soln[6]	0	0	45.0	55.0	65.0
total vol.	105	105	100	100	100
meq resin[7]	1.4	1.4	1.4	1.4	1.4
mmol of Cl^-	0.200	0.150	0.0750	0.040	0.0300
mM of Cl^-	1.91	1.43	0.750	0.400	0.300

	% Nominal Loading			
Reagents added	1	0.5	0.2	0.1
mL of wet Resin	1.00	1.00	1.00	1.00
mL Cl^- soln	15.00[3]	15.00[4]	30.00[5]	15.00[5]
mL of eluent[6]	4.00	4.00	4.00	4.00
mL of NO_3^- soln[6]	80.00	80.00	65.00	80.00
total volume in mL	100	100	100	100
meq resin[7]	1.4	1.4	1.4	1.4
mmol of Cl^-	0.0150	0.00750	0.00300	0.00150
mM of Cl^-	0.150	0.0750	0.0300	0.0150

[1]0.002 M Cl^- solution used. [2]0.0015 M Cl^- solution used. [3]0.001 M Cl^- solution used. [4]0.0005 M Cl^- solution used. [5]0.0001 M Cl^- solution used. [6]The nitrate solution and the eluent is the same solution, 0.001 M HNO_3 and 0.001 M $NaNO_3$. [7]1.439meq/1 mL packed resin.

K_d' and Isotherm Determinations

Six different Series of experiments were performed. The general approach was to add together the desired amounts and volumes of reagents. It was discovered that very small amounts of chloride ion diffused out of the resin over long periods of time. In order to help account for this chloride concentration, an amount of eluent solution from a Reillex™-HPQ column was added to the reference and sample solution of all wet loadings. Wet loadings is a K_d measurement that uses wet resin, measured in a graduated cylinder, not resin that has been dried at 60 °C and massed. The amount of eluent added was estimated to be the amount contained in the resin added. The experiments within a series are denoted by the chloride ion added in percent of nominal loading. That is, if 1.4 mmol of chloride is added to 7.2 meq of resin, this would be 20% loading.

The potentials of the wet loading samples were measured every 15 seconds for 10 minutes, at 30 minutes, and then the next morning to insure that equilibrium had been attained. The potential of the samples with dry resin were measured after one week, two weeks, and three weeks. The potentials of the reference solutions were measured at the same % total capacity. The reference solutions were of the same composition except that the resin was replaced with 1.00 mL of eluent.

Table 4. The details for Series IV experiments. Dry resin was used at 0.0020 M ionic strength in the solutions. The hydrogen ion concentration is 0.0010 M.

	% Nominal Loading				
Reagents added	14	10	5	3	2
g of dry Resin	0.3372	0.3371	0.3372	0.3376	0.03375
mL Cl^- soln	100.00[1]	100.00[2]	50.00[2]	40.00[3]	30.00[3]
mL of eluent[6]	0.00	0.00	5.00	5.00	5.00
mL of NO_3^- soln[6]	0.00	0.00	45.00	55.00	65.00
total vol.	100.0	100.0	100.0	100.0	100.0
meq resin[7]	1.55	1.55	1.55	1.55	1.55
mmol of Cl^-	0.200	0.150	0.0750	0.040	0.0300
mM of Cl^-	1.91	1.43	0.714	0.381	0.286

	% Nominal Loading			
Reagents added	1	0.5	0.2	0.1
mL of wet Resin	0.3375	0.3372	0.3375	0.3373
mL Cl^- soln	15.00[3]	15.00[4]	30.00[5]	15.00[5]
mL of eluent[6]	5.00	5.00	5.00	5.00
mL of NO_3^- soln[6]	80.00	80.00	65.00	80.00
total volume in mL	100.0	100.0	00.0	100.0
meq resin[7]	1.55	1.55	1.55	1.55
mmol of Cl^-	0.0150	0.143	0.0714	0.0286
mM of Cl-	0.0143	0.714	0.0286	0.0143

[1]0.002 M Cl^- solution used. [2]0.0015 M Cl^- solution used. [3]0.001 M Cl^- solution used. [4]0.0005 M Cl^- solution used. [5]0.0001 M Cl^- solution used. [6]The nitrate solution and the eluent is the same solution, 0.001 M HNO_3 and 0.001 M $NaNO_3$. [7]4.6/1 g dry resin.

Instrumental Methods

All potentials were measured with an Orion Model EA-940 Expandable Ionanalyzer in conjunction with a chloride ion Selective Electrode(94-17 BN) coupled with a double-junction reference electrode(90.02). A water bath was maintained at 25 °C for all measurements. It took about 10 seconds for the $[Cl^-]>10^{-4}$ M voltage readings to stabilize and longer than 60 seconds for $[Cl-]<10^{-4}$ readings to stabilize.

In this section of the study an initial inquiry of the differences of K_d' for uncontrolled loading at pH = 2.00 (Series I) and pH = 3.00 (Series II) was investigated. The ionic strength was not controlled with $NaNO_3$. Also, solutions with μ = 0.0020 M and pH = 3.0, μ = 0.0050 M and pH = 3.0, and μ = 0.050 M and pH = 2.0 (ionic strength controlled will $NaNO_3$) will be examined. All chemicals were dried at 110 °C and stored in a desiccator.

Table 5. The details for Series V experiments. Dry resin was used at 0.005 M ionic strength in the mL of solutions. The hydrogen ion concentration is 0.0010 M.

	% Nominal Loading				
Reagents added	30	20	10	5	3
g of dry resin	0.3375	0.3374	0.3375	0.3374	0.3376
mL Cl^- soln	85.00[1]	70.00[2]	50.0[3]	25.00[3]	15.00[3]
mL of eluent[9]	5.00	5.00	5.00	5.00	5.00
mL of NO_3^- soln[9]	10.00	25.00	45.00	7.00	80.00
total vol.	100.0	100.0	100.0	100.0	100.0
meq resin[10]	1.55	1.55	1.55	1.55	1.55
mmol of Cl^-	0.425	0.28	0.15	0.075	0.045
mM of Cl^-	4.25	2.80	1.50	0.75	0.45
	% Nominal Loading				
Reagents added	2	1	0.5	0.2	0.1
g of dry resin	0.3375	0.3373	0.3373	0.3377	0.3373
mL Cl^- soln	15.00[4]	15.00[5]	25.00[6]	15.00[7]	15.00[8]
mL of eluent[9]	5.00	5.00	5.00	5.00	5.00
mL of NO_3^- soln[9]	80.00	80.00	70.00	80.00	80.00
total vol.	100.0	100.0	100.0	100.0	100.0
meq resin[10]	1.55	1.55	1.55	1.55	1.55
mmol of Cl^-	0.03	0.015	0.0075	0.003	0.0015
mM of Cl^-	0.3	0.15	0.075	0.03	0.015

[1]0.005 M Cl solution used. [2]0.004 M Cl solution used. [3]0.003 M Cl solution used. [4]0.002 M Cl solution used. [5]0.001 M Cl solution used. [6]0.0003 M Cl solution used. [7]0.0002 M Cl solution used. [8]0.0001 M Cl solution used. [9]0.001 M HNO_3 and 0.004 M $NaNO_3$. [10]4.6/1 g dry resin.

Table 6. The details for Series VI experiments. Dry resin was used at 0.050 M ionic strength in the solutions. The hydrogen ion concentration is 0.0100 M.

	% Nominal Loading				
Reagents added	300	200	100	50	30
g of dry resin	0.3375	0.3372	0.3375	0.33760	3375
mL Cl^- soln	85.00[1]	60.00[1]	0.0[1]	20.00[2]	15.00[3]
mL of eluent[9]	5.00	5.00	5.00	5.00	5.00
mL of NO_3^- soln[9]	10.00	35.00	65.00	75.00	80.00
total vol.	100.0	100.0	100.0	100.0	100.0
meq resin[10]	1.55	1.55	1.55	1.55	1.55
mmol of Cl^-	4.25	3.0	1.50	0.8	0.45
mM of Cl^-	43	30	15	8.0	4.5

	% Nominal Loading				
Reagents added	20	10	5	2	1
g of dry resin	0.3375	0.3376	0.3376	0.3377	0.3376
mL Cl^- soln	10.00[3]	5.00[3]	5.00[4]	5.00[5]	30.00[6]
mL of eluent[9]	5.00	5.00	5.00	5.00	5.00
mL NO_3^- soln[9]	85.00	90.00	90.00	90.00	65.00
total vol.	100.0	100.0	100.0	100.0	100.0
meq resin[10]	1.55	1.55	1.55	1.55	1.55
mmol of Cl^-	0.30	0.15	0.075	0.025	0.015
mM of Cl^-	3.0	1.5	0.75	0.25	0.15

	% Nominal Loading		
Reagents added	0.5	0.2	01
g of dry resin	0.3376	0.3373	0.3372
mL Cl^- soln	5.00[7]	5.00[6]	30.00[8]
mL of eluent[9]	5.00	5.00	5.00
mL NO3- soln[9]	80.00	80.00	70.00
total volume in mL	100.0	100.0	100.0
meq resin[10]	1.55	1.55	1.55
mmol of Cl^-	0.0075	0.0025	0.0015
mM of Cl^-	0.075	0.025	0.015

[1]0.05 M Cl solution used. [2]0.04 M Cl solution used. [3]0.03 M Cl solution used. [4]0.015 M Cl solution used. [5]0.005 M Cl solution used. [6]0.0005 M Cl solution used. [7]0.0015 M Cl solution used. [8]0.00005 M Cl solution used. [9]0.001 M HNO_3 and 0.004 M $NaNO_3$. [10]4.6/1 g dry resin.

Results and Discussion

The hydrogen ion concentration was adjusted to either 1.0×10^{-3} (pH = 3.0) or 1.0×10^{-2} (pH = 2.0) in the solutions. At pH = 3.0 the weak base site on the resin is 21% deprotonated. If the pH were to increase, there would be additional deprotonation with a loss of exchange capacity. The pH of the solutions are tabulated in Table 7. The pH of the solutions for the most part remain the same.

Table 7 The pH of the sample and the reference solutions.

Series I Sample	pH Reference Solution	Sample solution
20%	1.624	1.859
10%	1.627	1.845
2.0%	1.620	1.806
0.2%	1.625	1.741

Series II Sample	pH Reference Solution	Sample solution
20%	2.678	4.329
10%	2.746	3.659
2.0%	2.772	3.762
0.2%	2.811	3.419

Series III Sample	pH Reference Solution	Sample solution
14%	2.974	1.754
10%	2.988	2.031
5%	2.979	3.227
3%	2.969	3.220
2%	2.962	3.267
1%	2.948	3.260
0.5%	2.939	3.197
0.2%	2.917	3.173
0.1%	2.901	3.151

Series IV Sample	pH Reference Solution	Sample solution
14%	2.974	3.143
10%	2.988	2.862
5%	2.979	3.163
3%	2.969	3.173
2%	2.962	3.142
1%	2.948	3.091
0.5%	2.939	3.216
0.2%	2.917	3.061
0.1%	2.901	3.035

Series V Sample	pH Reference Solution	Sample solution
30%	2.983	3.156
20	2.952	3.126
10%	2.994	2.650
5%	2.978	2.943
3%	2.856	3.370
2%	2.854	3.196
1%	2.854	3.212
0.5%	2.842	3.159
0.2%	2.853	3.151
0.1%	2.846	3.166

Series VI Sample	pH Reference Solution	Sample solution
300%	1.942	1.982
200%	1.790	2.035
100%	1.752	2.035
50%	1.855	2.021
30%	1.850	2.003
20%	1.900	1.963
10%	1.728	2.070
5%	1.740	2.047
2%	1.714	2.026
1%	1.811	2.111
0.5%	1.710	2.096

0.2%	1.843	2.061
0.1%	1.726	2.033

The calculations of the values of K_d' for Series I through VI are based on Eq. 2 and tabulated in Table 8. Series I is for the resin measured by wet volume at an uncontrolled ionic strength, with a pH = 2.0. Series II is for the resin measured by wet volume at an uncontrolled ionic strength, with a pH = 3.0. Series III is for the resin measured by wet volume at an ionic strength of 0.0020 M. Series IV is for the resin measured by dry mass at an ionic strength of 0.0020 M. Series V is for the resin measured by dry mass at an ionic strength of 0.0050 M. Series VI is for the resin measured by dry mass at an ionic strength of 0.050 M.

Table 8 The K_d' and % loadings of Series I, II, III, IV, V, VI.

	Series I			*Series II*		
Sample	mmol NO_3^-	% Loading	K_d'	mmol NO_3^-	% Loading	K_d'
20	6.0 x 10-4	61.31	166.4	6.0 x 10-4	46.59	103.3
10	8.0 x 10-4	64.21	179.4	8.0 x 10-4	63.65	175.1
2	6.0 x 10-4	81.96	454.3	6.0 x 10-4	85.88	608.3
0.2	6.0 x 10-4	85.03	568.2	6.0 x 10-4	92.97	1321
	Series III			*Series IV*		
Sample	mmol NO_3^-	% Loading	K_d'	mmol NO_3^-	% Loading	K_d'
14	0.0381	39.24	67.80	0.0400	60.55	153.5
10	0.0381	39.71	69.15	0.0400	43.57	77.21
5	0.0990	39.24	67.80	0.940	59.62	147.7
3	1.18	49.98	99.93	1.14	58.02	138.2
2	1.37	53.55	115.3	1.34	56.18	128.2
1	1.66	50.18	100.7	1.64	53.91	117.0
0.5	1.66	35.08	54.04	1.64	47.18	89.33
0.2	1.37	22.44	48.74	1.34	32.77	48.74
0.01	1.66	4.37	27.29	1.64	21.44	27.29
	Series V			*Series VI*		
Sample	$[NO_3^-]$	% Loading	K_d'	$[NO_3^-]$	% Loading	K_d'
300	-	-	-	0.0075	36.83	58.2
200	-	-	-	0.020	14.75	17.30
100	-	-	-	0.035	23.85	31.32
50	-	-	-	0.042	25.90	34.95
30	7.5 x 10^{-4}	53.55	115.3	0.044	10.33	11.51

20	0.0022	41.56	71.11	0.046	22.95	29.79
10	0.0035	51.70	107.1	0.048	13.41	15.49
5	0.0043	34.57	52.84	0.049	6.77	7.26
3	0.0046	40.41	67.81	-	-	-
2	0.0047	33.55	50.48	0.050	3.44	3.56
1	0.0049	39.47	65.22	0.050	8.21	8.92
0.5	0.0049	28.17	39.21	0.050	3.07	3.16
0.2	0.0050	44.22	79.29	0.050	2.69	2.76
0.1	0.0050	27.04	37.06	0.050	3.07	3.16

Tables 9 and 10 contain the mV reference cell, mV sample cell, % Loading, and K_d' for Series I and II respectively. Series I is for the resin measured by wet volume at an uncontrolled ionic strength, with a pH = 2.0. Series II is for the resin measured by wet volume at an uncontrolled ionic strength, with a pH = 3.0. The K_d' values for Series I range from 568 to 166 mL/g. The K_d' values for Series II range from 1321 to 103 mL/g.

Table 9. Series I chloride K_d' calculations for uncontrolled ionic strength pH = 2.0.

	% Nominal Loading			
	20	10	2	0.2
mV reference cell	59.8	74.1	109.8	64.2
mV sample cell	84.2	100.5	153.8	213.0
% Loading	61.31	64.21	81.96	85.03
K_d'	166.4	179.4	454.3	568.2

Table 10. Series II chloride K_d calculations for uncontrolled ionic strength pH = 3.0.

	% Nominal Loading			
	20	10	2	0.2
mV reference cell	61.7	75.6	108.8	161.6
mV sample cell	79.3	101.5	159.1	229.8
% Loading	46.59	63.65	85.88	92.97
K_d'	103.3	175.1	608.3	1321

Table 11, 12, 13, and 14 describe the results for Series III, IV, V and VI, respectively. Series III is for the resin measured by wet volume at an ionic strength of 0.0020 M. Series IV is for the resin measured by dry mass at an ionic strength of 0.0020 M. Series V is for the resin measured by dry mass at an ionic strength of 0.0050 M. Series VI is for the resin measured by dry mass at an ionic strength of 0.050 M. The K_d'

values for Series III ranged from 115 to 27 mL/g. The K_d' values for Series IV ranged from 154 to 27 mL/g. The K_d' values for Series V ranged from 115 to 37 mL/g. The K_d' values Series VI ranged from 58 to 3.0 mL/g

Table 11. Series III chloride ion isotherm measurements and K_d' calculations for μ = 0.0020 ionic strength.

	% Nominal Loading			
	14	10	5	3
resin volume	1.0	1.0	1.0	1.0
supernatant vol, mL	104.0	104.0	99.0	99.0
total eq Cl^-	0.2000	0.1500	0.0750	0.0400
eq Cl^- soln	12.15	9.04	4.55	2.00
eq Cl^- resin	0.0785	0.0596	0.0294	0.0200
Cl^- soln	58.426	43.480	23.016	10.105
Cl^- resin	0.055	0.041	0.020	0.014
% Loading	39.237	39.708	39.237	49.98
K_d'	67.803	69.154	67.803	99.93

	% Nominal Loading		
	2	1.0	0.5
resin volume, mL	1.0	1.0	1.0
supernatant vol, mL	99.0	99.0	99.0
total eq Cl^-	0.0300	0.0150	0.0075
eq Cl^- soln	1.39	0.747	0.487
eq Cl^- resin	0.0161	0.0075	0.0026
Cl^- soln	7.038	3.774	2.459
Cl^- resin	0.011	0.005	0.002
% Loading	53.548	50.177	35.081
K_d'	115.28	100.7	54.04

	% Nominal Loading	
	0.2	0.1
resin volume, mL	1.0	1.0
supernatant vol, mL	99.0	99.0
total eq Cl^-	0.0300	0.0015
eq Cl^- soln	2.45	0.144
eq Cl^- resin	0.0055	6.3×10^{-5}
eq NO_3^- soln	0.1785	0.1975

eq NO_3^- resin	1.4294	1.4348
Cl^- soln	12.38	0.726
Cl^- resin	0.004	4.3×10^{-5}
% Loading	22.44	4.374
K_d'	48.735	27.292

Table 12. Series IV chloride ion isotherm measurements and K_d' calculations for μ = 0.0020 ionic strength.

	% Nominal Loading			
	14	10	5	3
resin volume	0.6602	0.6600	0.6602	0.6610
supernatant vol, mL	99.3398	99.3400	99.3398	99.3390
total eq Cl^-	0.1986	0.1490	0.0750	0.0400
eq Cl^- soln	0.0783	0.0840	0.0302	0.0167
eq Cl^- resin	0.1203	0.0649	0.0447	0.0232
eq NO_3^- soln	0.1203	0.1145	0.1684	0.1818
eq NO_3^- resin	1.3177	1.3726	1.3933	1.4165
Cl^- soln	0.3944	0.4232	0.1524	0.0845
Cl^- resin	0.0836	0.0451	0.0310	0.1611
% Loading	60.553	43.569	59.621	58.02
K_d'	153.5065	77.2061	147.655	138.2

	% Nominal Loading		
	2	1	0.5
resin volume, mL	0.6608	0.6608	0.6602
supernatant vol, mL	99.3392	99.3392	99.3398
total eq Cl^-	0.0300	0.0150	0.0075
eq Cl^- soln	0.0131	0.0069	0.0039
eq Cl^- resin	0.0168	0.0080	0.0035
eq NO_3^- soln	0.1855	0.1917	0.1947
eq NO_3^- resin	1.4224	1.4312	1.4345
Cl^- soln	0.0661	0.0347	0.0199
Cl^- resin	0.0117	0.0056	0.0024
% Loading	56.182	53.908	47.182
K_d'	128.22	116.96	89.327

	% Nominal Loading	
	0.2	0.1
resin volume, mL	0.6608	0.6604
supernatant vol, mL	99.3392	99.3396
total eq Cl^-	0.0300	0.0015
eq Cl^- soln	0.0201	0.0011
eq Cl^- resin	0.0098	0.0003
eq NO_3^- soln	0.1785	0.1975
eq NO_3^- resin	1.4294	1.4348
Cl^- sol n	0.1015	0.0059
Cl^- resin	0.0068	0.0002
% Loading	32.766	21.440
K_d'	48.735	27.292

Table13. Series V chloride ion isotherm measurements and K_d' calculations for μ = 0.0050 ionic strength.

	% Nominal Loading			
	30	20	10	5
resin volume	0.6608	0.6606	0.6608	0.6606
supernatant vol, mL	99.3392	99.3394	99.3392	99.3394
total eq Cl^-	0.250	0.2800	0.1500	0.7570
eq Cl^- soln	0.1974	0.1636	0.0742	0.0490
eq Cl^- resin	0.2275	0.1163	0.0775	0.0259
eq NO_3^- soln	0.2992	0.3330	0.4242	0.4476
eq NO_3^- resin	1.2117	1.3225	1.3617	1.4129
Cl^- soln	0.3974	0.3294	0.1458	0.0987
Cl^- resin	0.1581	0.808	0.0538	0.0180
% Loading	53.55	41.56	51.70	34.57
K_d'	115.28	71.11	107.06	52.84
	% Nominal Loading			
	3	2	1	0.5
resin volume, mL	0.6610	0.6608	0.6604	0.6604
supernatant vol, mL	99.3390	99.3392	99.3396	99.3396
total eq Cl^-	0.0450	0.0300	0.0150	0.0075
eq Cl^- soln	0.0268	0.0199	0.0090	0.0053
eq Cl^- resin	0.0181	0.0100	0.0059	0.0021

eq NO_3^- soln	0.4698	.4767	0.4876	0.4913
eq NO_3^- resin	1.4215	1.4292	1.4325	1.4363
Cl^- soln	0.0539	0.0401	0.0182	0.0108
Cl^- resin	0.0126	0.0069	0.0041	0.0014
% Loading	40.41	33.55	39.47	28.17
K_d'	67.81	50.48	65.22	39.21

	% Nominal Loading	
0.2	0.1	
resin volume, mL	0.6612	0.6604
supernatant vol, mL	99.3388	99.3396
total eq Cl^-	0.0030	0.0015
eq Cl^- soln	0.0016	0.0010
eq Cl^- resin	0.0013	0.0041
eq NO_3^- soln	0.4950	0.4956
eq NO_3^- resin	1.4388	1.4381
Cl^- soln	0.0033	0.0022
Cl^- resin	0.0009	0.0002
% Loading	44.22	27.04
K_d'	79.29	37.06

Table 14. Series VI chloride ion isotherm measurements and K_d' calculations for μ = 0.050 ionic strength.

	% Nominal Loading			
	300	200	100	50
resin volume	0.6608	0.6602	0.6608	0.6610
supernatant vol, mL	99.34	99.34	99.34	99.34
total eq Cl^-	4.3	3.0	1.5	1.6
eq Cl^- soln	2.68	2.56	1.14	1.19
eq Cl^- resin	1.5650	0.4424	0.3577	0.4143
eq NO_3^- soln	2.2820	2.4094	3.824	3.7812
eq NO_3^- resin	0.1257	0.9955	1.0815	1.0254
Cl^- soln	0.5405	0.5149	0.2299	0.2387
Cl^- resin	1.0873	0.3077	0.2485	0.2877
% Loading	36.83	14.75	23.85	25.896
K_d'	58.29	17.30	31.32	34.95

	% Nominal Loading			
	30	20	10	5
resin volume, mL	0.660Ɛ	0.6608	0.6610	0.6608
supernatant vol, mL	9.34	99.34	99.34	99.34
total eq Cl^-	0.45	0.30	0.15	7.5×10^{-2}
eq Cl^- soln	0.40	0.23	0.13	0.07
eq Cl^- resin	4.6×10^{-2}	6.9×10^{-2}	2.0×10^{-2}	5.0×10^{-3}
eq NO_3^- soln	4.56	4.74	4.84	4.90
eq NO_3^- resin	1.39	1.37	1.42	1.43
Cl^- soln	8.1×10^{-2}	4.7×10^{-2}	2.6×10^{-2}	1.4×10^{-2}
Cl^- resin	3.2×10^{-2}	4.8×10^{-2}	1.4×10^{-2}	3.5×10^{-3}
% Loading	10.33	22.95	13.41	6.77
K_d'	11.51	29.79	15.49	7.26

	% Nominal Loading		
	2	1	0.5
resin volume, mL	0.6612	0.6610	0.661
supernatant vol, mL	99.34	99.34	99.34
total eq Cl^-	2.5×10^{-2}	1.5×10^{-2}	7.5×10^{-3}
eq Cl^- soln	2.4×10^{-2}	1.4×10^{-2}	7.2×10^{-3}
eq Cl^- resin	8.0×10^{-4}	1.2×10^{-3}	2.0×10^{-4}
eq NO_3^- soln	4.94	4.95	4.96
eq NO_3^- resin	1.44	1.44	1.44
Cl- soln	4.8×10^{-3}	2.7×10^{-3}	1.4×10^{-3}
Cl- resin	5.0×10^{-4}	8.0×10^{-4}	1.0×10^{-4}
% Loading	3.44	8.21	3.07
K_d'	3.56	8.94	3.16

	% Nominal Loading	
	0.2	0.1
resin volume, mL	0.6604	0.6602
supernatant vol, mL	99.34	99.34
total eq Cl^-	2.5×10^{-3}	1.5×10^{-3}
eq Cl^- soln	2.4×10^{-3}	1.4 x 10-3
eq Cl^- resin	6.7×10^{-5}	5.0×10^{-5}
eq NO_3^- soln	4.97	4.97
eq NO_3^- resin	1.44	1.44
Cl^- soln	4.0×10^{-4}	2.0 x 10-4

Cl^- resin	4.7×10^{-5}	3.2×10^{-5}
% Loading	2.69	3.07
K_d'	2.76	3.16

SECTION 3

The Sorption Behavior of Chromium(VI) on Reillex™-HPQ from Nitric Acid Solutions and from Sodium Hydroxide Solutions

The Sorption Behavior of Chromium(VI) on Reillex™-HPQ from Nitric Acid Solutions and from Sodium Hydroxide Solutions

ABSTRACT

The investigations into the sorption behavior of chromium(VI) on Reillex™-HPQ resin are continuing. The experiment of the sorption of chromium (VI) onto the Reillex™-HPQ resin while varying nitric acid concentrations from 0.010 - 10 M has been repeated to check the questionable validity of the results reported in the June Milestone. This system can be described by the equation: $K_d' = {}^{Cr}_{NO3}K / [NO_3]$ with a K of (1.02 ± 0.25) mmol/g. K_d' is the experimental distribution coefficient and is defined by the relationship:

$$K_d' = \frac{\text{mmol Cr(VI) on resin}}{\text{mmol Cr(VI) in solution}} = \frac{\dfrac{\{Cr(VI)\}_{total} - \{Cr(VI)\}_{sol\ tot} x V_{sol}}{\text{mass of dry resin}}}{\dfrac{\{Cr(VI)\}_{sol\ tot} x V_{sol}}{V_{sol}}}$$

The sorption characteristics of the resin in 1.00 M sodium hydroxide and sodium nitrate concentration varying from 0.0100 to 5.00 M was studied. Due to the presence of both NO_3- and OH^- anions and depending upon the assumptions made, the system can be described by two equations:

$$K_d' = \frac{{}^{CrO4}_{NO3}K\, R_t}{[NO_3^-] + {}^{OH}_{NO3}K[OH^-]} \quad \text{or} \quad K_d' = \frac{{}^{CrO4}_{NO3}K\, R_t^2}{[NO_3^- + \left({}^{OH}_{NO3}K[OH^-]\right)^2}$$

For the first equation ${}^{CrO4}_{NO3}K = 59.05 \text{mmol/g}$ and ${}^{OH}_{NO3}K = 3.22$. For the second equation ${}^{CrO4}_{NO3}K = 59.05 \text{mmol/g}$ and ${}^{OH}_{NO3}K = 3.22 \text{mmol/g}$.

EXPERIMENTAL

Assay Techniques

The analytical grade potassium dichromate in the following assays were acquired from Merck & Co., Inc. (Lot # 73021). The other reagents used in the assay were the same as previous milestones. The chromium assays performed on the AA followed the same general procedure as the rhenium analyses. However, instead of a NO-acetylene flame, a reducing air-acetylene flame was used.

Resin Preparation

The Reillex™-HPQ resin (Lot # 90928AC) was acquired from Reilly Industries as a 30-60 mesh resin in the chloride form.[1] It was washed with at least 20 volumes of 18 MΩ deionized water (all water used in this study was of this type) by decantation in order to remove the beads that floated. It was converted to the nitrate form by passing 20 bed volumes of 0.10 M HNO_3 through the resin. This also had the effect of protonating the weak base sites of the unmethylated pyridine. The resin was washed with 20 bed volumes of water and stored in water until used. The resin was dried at 60°C for 24 hours and then stored in a desiccator over silica gel.

Ion-Exchange Studies

The K_d determinations were performed in the following manner. Each sample was prepared by accurately massing 3.0 g of the dried resin in an Oak Ridge centrifuge tube. Then 37 mL of 9.00 mM $Cr_2O_7^{2-}$ and the desired HNO_3, $NaNO_3$, or NaOH concentration was added to the tube. The solution and resin were then shaken for at least 60 hours. The resin was then removed from the solution by gravity filtration using Whatman #4 filter paper. The filtrate was analyzed for chromium by AA methods.

RESULTS AND DISCUSSION

The reaction studied is represented by Eq 1. R^+ represents the exchange site on

$$q R^+NO_3^- + Cr_xO_yH_z^{q-} \rightleftharpoons R_q^{+q}Cr(VI)^{-q} + q\,NO_3^- \qquad (1)$$

the Reillex™-HPQ resin, $R^+NO_3^-$ represents the exchange site with nitrate ion as the counter ion, and $R_q^{+q}Cr(VI)^{q-}$ represents the exchange site with an unidentified oxochromium anion species as the counter ion, and $Cr_xO_yH_z^{q-}$ represents the unidentified Cr(VI) species. It is explicitly understood that R^+ represents both the weak and strong base exchange sites.

The reasons for writing Eq. 1 as an ambiguous equation is evident when it is realized that Reactions 2, 3 and 4 can be written and are applicable in the aqueous solutions.[2] Figure I is a plot of the distribution of the chromium species as a function of -log[H^+].

$$H_2O + Cr_2O_7^{2-} \rightleftharpoons 2\,HCrO_4^- \qquad K = 6.31 \times 10^{-3} \qquad (2)$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K = 4.1 \qquad (3)$$

$$HCrO_4^- \rightleftharpoons CrO_4^{-2} + H^+$$

$$K = 1.26 \times 10^{-6} \qquad (4)$$

This uncertainty in which species are being sorbed onto the resin, the complications due to the changing concentrations of the hydrogen ion (the independent variable), and the changing concentrations of the chromium(VI) monomers and dimers in solutions as a result of sorption make this a difficult system to model. At this time, the data is not of the necessary precision (vide infra) to warrant this effort.

The maximum amount of dichromate added to the resin was 0.333 meq/13.8 meq resin (0.024 meq/meq resin). The exchange capacity of the resin is about 4.6 meq/g dry resin.[1]. The loading of the resin varied from an average of 0.35% at 10.0 M HNO_3, 1.07% at 0.1 M HNO_3, and 1.48% at 0.01 M. The loading in base was less than 1 %.

The composite equilibrium constant represented by Reaction. 1 is defined by Eq. 5.

$$K' = \frac{\left(R_q^{+q}Cr(VI)^{-q}\right)\left[NO_3^-\right]^q}{\left(R^+NO_3^-\right)^q\left[Cr_xO_yH_z^{-q}\right]} \qquad (5)$$

Under the loading conditions of these experiments, the concentration of $R^+NO_3^-$ can be regarded as constant and Eq. 6 can be written.

$$K = \frac{\left(R_q^{+q}Cr(VI)^{-q}\right)[NO_3^-]^q}{\left[Cr_xO_yH_z^{-q}\right]} = K'(R^+NO_3^-)^q \qquad (6)$$

The experimental distribution coefficient is defined by Eq. 7. The quantity

$$K_d' = \frac{\text{mmol Cr(VI) on resin}}{\text{mmol Cr(VI) in solution}} = \frac{\dfrac{\{Cr(VI)\}_{total} - \{Cr(VI)\}_{sol\ tot} x V_{sol}}{\text{mass of dry resin}}}{\dfrac{\{Cr(VI)\}_{sol\ tot} x V_{sol}}{V_{sol}}} \qquad (7)$$

$\{Cr(VI)\}_{total}$ represents the total amount of chromium (VI) in mmoles in contact with the resin. $\{Cr(VI)\}_{sol\ tot}$ indicates all of the chromium (VI) in contact with the resin solution of volume V_{sol}.

The values of the experimental K_d' are tabulated in Table 1 and Table 2. The plot of K_d' versus $[HNO_3]$ is depicted in Figures II. The plot of K_d' versus $[NO_3^-]$ is depicted in Figures III.

The line in Figure II is the least-squares fit of the data to Eq. 9. Eq. 8 is derived from Eqs. 6 and 7. Eq. 9 is written assuming that q = 1.

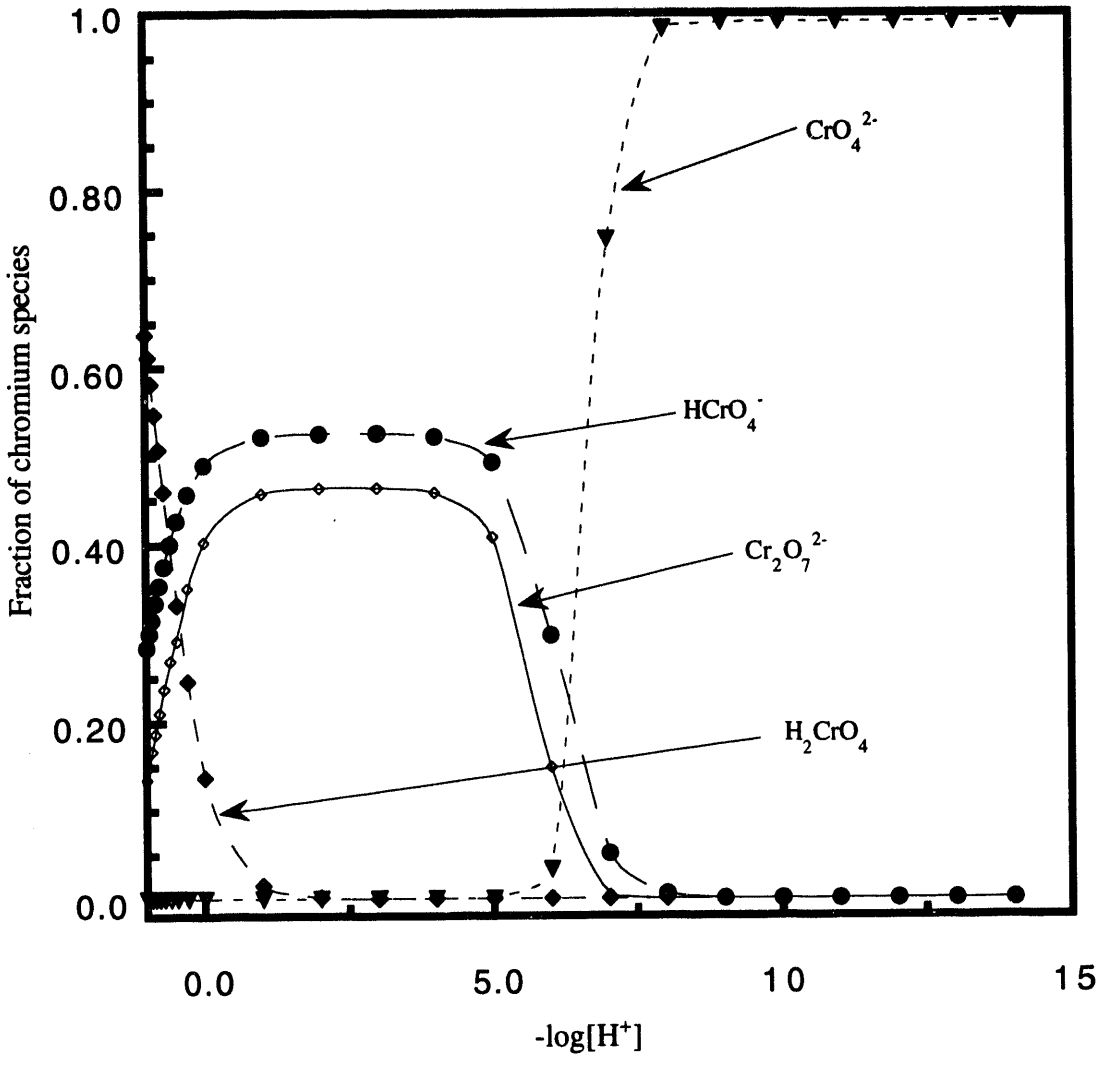

Figure I. The distribution data for the chromium species using the constants in the text.

TABLE 1. Values of K_d' for chromium(VI) on Reillex™-HPQ in varying nitric acid concentration.

[HNO3], M	K_d', mL/g	[HNO3], M	K_d', mL/g
10.0	1.24	0.5	4.23
9.0	1.24	0.4	4.82
8.0	1.32	0.3	7.34
7.0	1.64	0.2	7.02
6.0	1.09	0.1	9.47
5.0	0.94	0.09	9.47
4.0	1.02	0.08	9.4
73.0	1.64	0.07	20.89
2.0	1.80	0.06	23.88

1.0	1.80	0.05	27.48
0.9	1.88	0.04	31.85
0.8	1.97	0.03	44.32
0.7	2.97	0.02	50.20
0.6	3.26	0.01	41.78

TABLE 2. Values of K_d' for chromium(VI) on Reillex™-HPQ in 1.00 M[NaOH] and varying sodium nitrate concentration.

[$NaNO_3$], M	K_d', mL/g	[$NaNO_3$], M	K_d', mL/g
5.0	0.63	0.2	5.33
4.0	1.71	0.1	7.94
3.0	2.67	0.09	5.92
2.0	2.67	0.08	6.55
1.0	3.09	0.07	7.95
0.9	3.31	0.06	2.27
0.8	3.09	0.05	5.19
0.7	3.89	0.04	4.91
0.6	2.37	0.03	5.05
0.5	3.89	0.02	6.55
0.4	4.14	0.01	4.26
0.3	4.78		

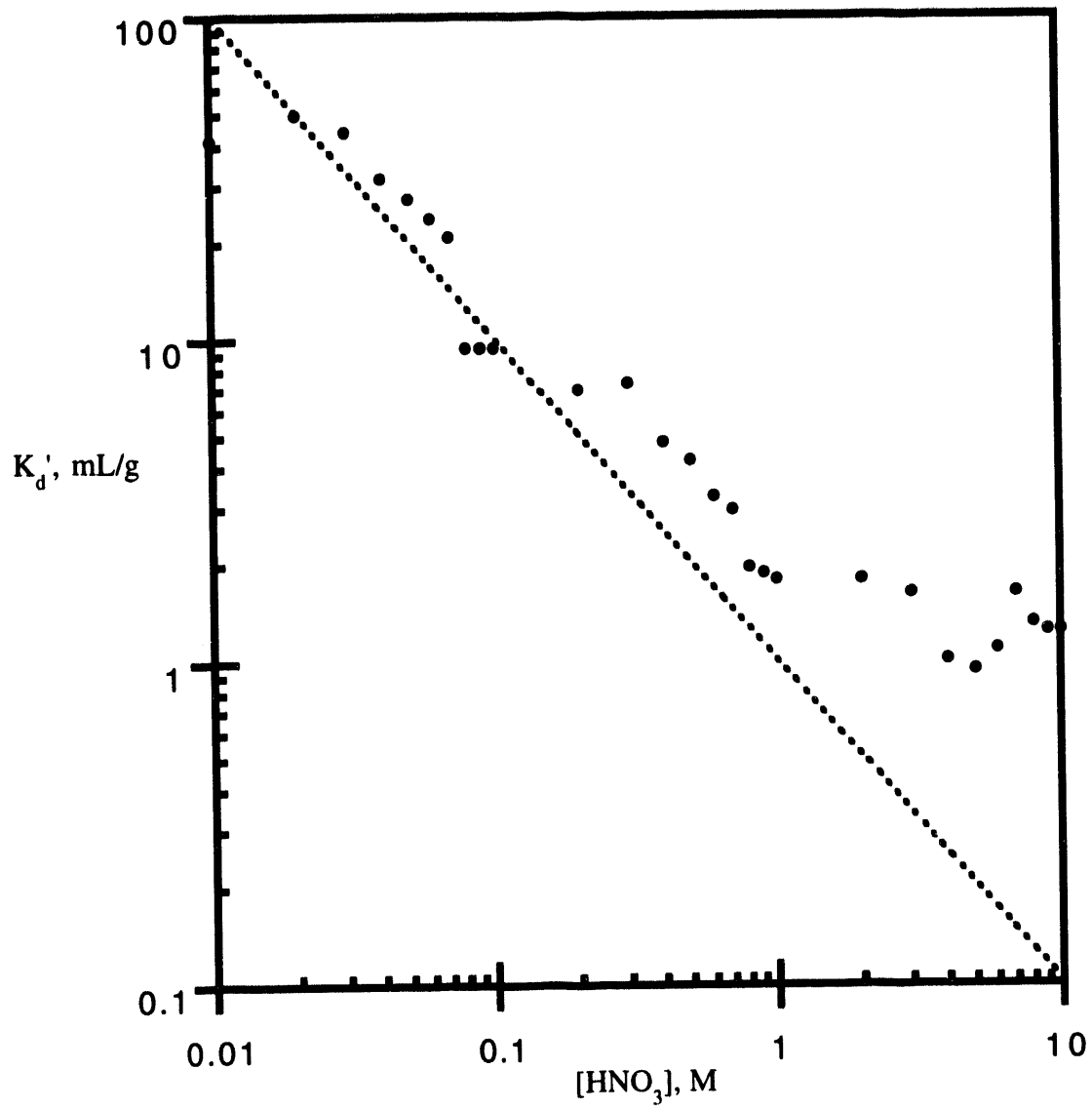

Figure II. The variation of the value of K_d' as a functionof $[HNO_3]$.
The line is the fit of the data to the equation $K_d' = (1.02 \pm 0.25)/[HNO_3]$

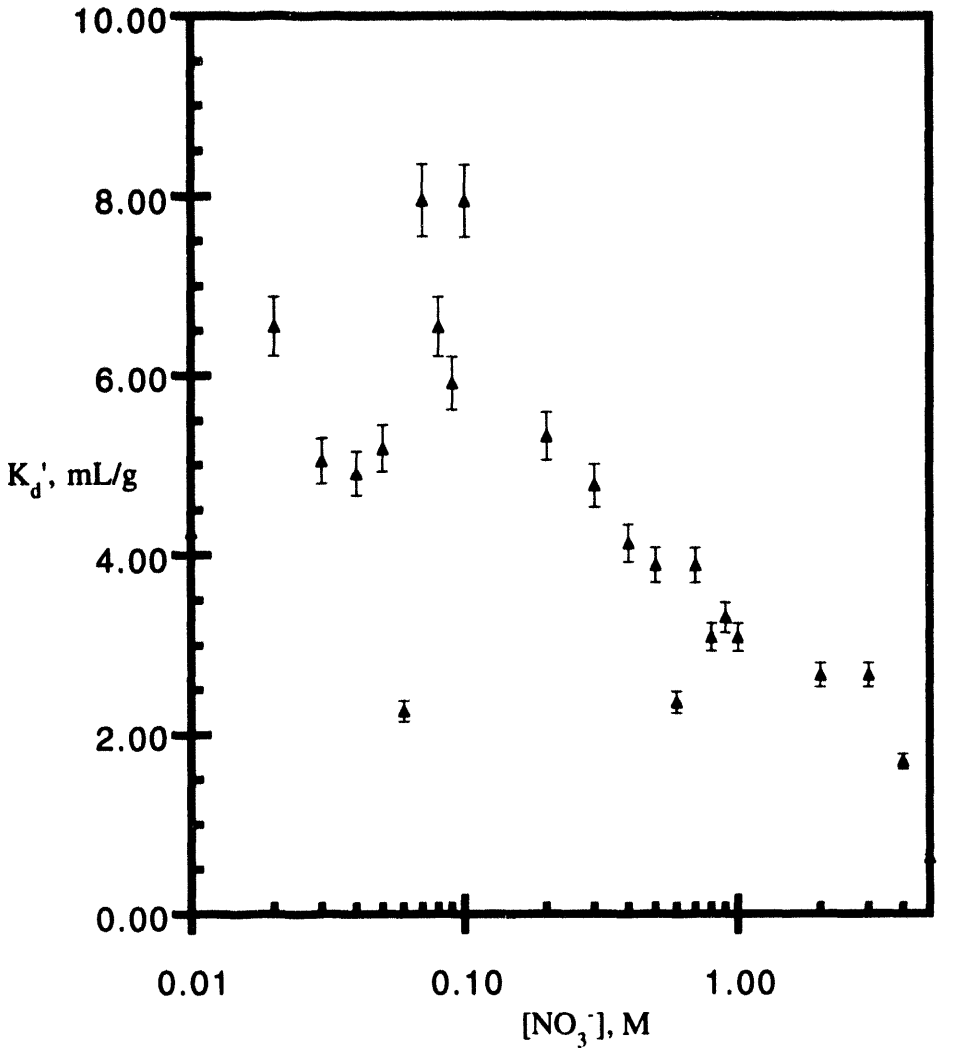

Figure III. The variation of the values of K_d' as a function of $[NO_3^-]$ in 1.00 M NaOH. The error bars are ± 5 %.

$$K = K_d'[NO_3^-]^q \tag{8}$$

$$K_d' = \frac{K}{[NO_3^-]} \tag{9}$$

At this point , there is no detailed interpretation placed on this fit. It is intended to be only a phenomenological descriptor. However, it is important to realize that the value of 1.02 ± 0.25 mL/g (K) is composite value for K_d for chromium (VI). Also, we want to point out that the values that we reported in the June Milestone are not as reliable as these numbers reported here.

The values of K_d' in Table 1 indicate that the sorption of chromium(VI) is not going to be very great above an acidity of 1.0 M. This will probably be an advantage in the separation of pertechnetate from the various streams.

The experiments in base are somewhat easier to interpret. Figure I shows that the only chromium(VI) species in basic solution is CrO_4^{2-}. Reactions 10, 11, and 12 represent the interaction of the resin and the various ions in basic solution.

$$R^+NO_3^- + OH^- \rightleftharpoons R^+OH^- + NO_3^- \quad (10)$$

$$2R^+NO_3^- + CrO_4^{2-} \rightleftharpoons (R^+)_2CrO_4^{2-} + 2NO_3^- \quad (11)$$

$$2R^+OH^- + CrO_4^{2-} \rightleftharpoons (R^+)_2CrO_4^{2-} + 2OH^- \quad (12)$$

The associated equilibrium constants for the reactions are , respectively, Eqs. 13, 14, and 15.

$$^{OH}_{NO_3}K = \frac{[R^+OH^-][NO_3^-]}{[R^+NO_3^-][OH^-]} \quad (13)$$

$$^{CrO_4}_{NO_3}K = \frac{[(R^+)_2CrO_4^{2-}][NO_3^-]^2}{[R^+NO_3^-]^2[CrO_4^{2-}]} \quad (14)$$

$$^{CrO_4}_{OH}K = \frac{[(R^+)_2CrO_4^{2-}][OH^-]^2}{[R^+OH^-]^2[CrO_4^{2-}]} \quad (15)$$

In the solutions of 1.00 M NaOH and variable sodium nitrate, the total concentration of resin (R_t) must be considered. This is given by Eq. 16. This can be written in terms of only $[R^+NO_3^-]$ by combining Eqs. 16 and 13. Substituting Eq. 17 into Eq. 14 and rearranging gives Eq 18. K_d' is the experimentally determined quantity.

$$R_t = [R^+OH^-] + [R^+NO_3^-] \quad (16)$$

$$R_t = \left(\frac{^{OH}_{NO_3}K\,[OH^-] + [NO_3^-]}{[NO_3^-]} \right) [RNO_3^-] \quad (17)$$

$$\frac{^{CrO_4}_{NO_3}KR_t^2}{\left(^{OH}_{NO_3}K\,[OH^-] + [NO_3^-] \right)^2} = \frac{[(R^+)_2CrO_4^{2-}]}{[CrO_4^{2-}]} = K_d' \quad (18)$$

Assuming that Eq. 14 involves only a first power dependence upon $[R^+NO_3^-]$, Eq. 19 can be derived.

$$\frac{{}^{CrO_4}_{NO_3}KR_t}{\left({}^{OH}_{NO_3}K\,[OH^-] + [NO_3^-]\right)} = \frac{\left[(R^+)_2CrO_4^{2-}\right]}{\left[CrO_4^{2-}\right]} = K_d' \qquad (19)$$

Figure IV is the plot of Eq. 18 and Figure V is the plot of the data to Eq 19. One can see that the data can be fit to both equations. This is not at all surprising since the precision of the data is not that good.

The fit to Eq. 18 gives:

$$K_d' = (59.1 \pm 38.0) / \{[NO_3^-] + (3.22 \pm 1.10)\}^2$$

The fit to Eq. 19 gives:

$$K_d' = (7.24 \pm 2.42) / \{[NO_3^-] + (1.25 \pm 0.47)\}$$

Just from the associated uncertainties, the fit to Eq. 19 is better. Interestingly, in both models, the OH^- anion is preferred over NO_3^- for the Reillex™-HPQ. This is not what was observed in the studies this past summer with TcO_4^-.

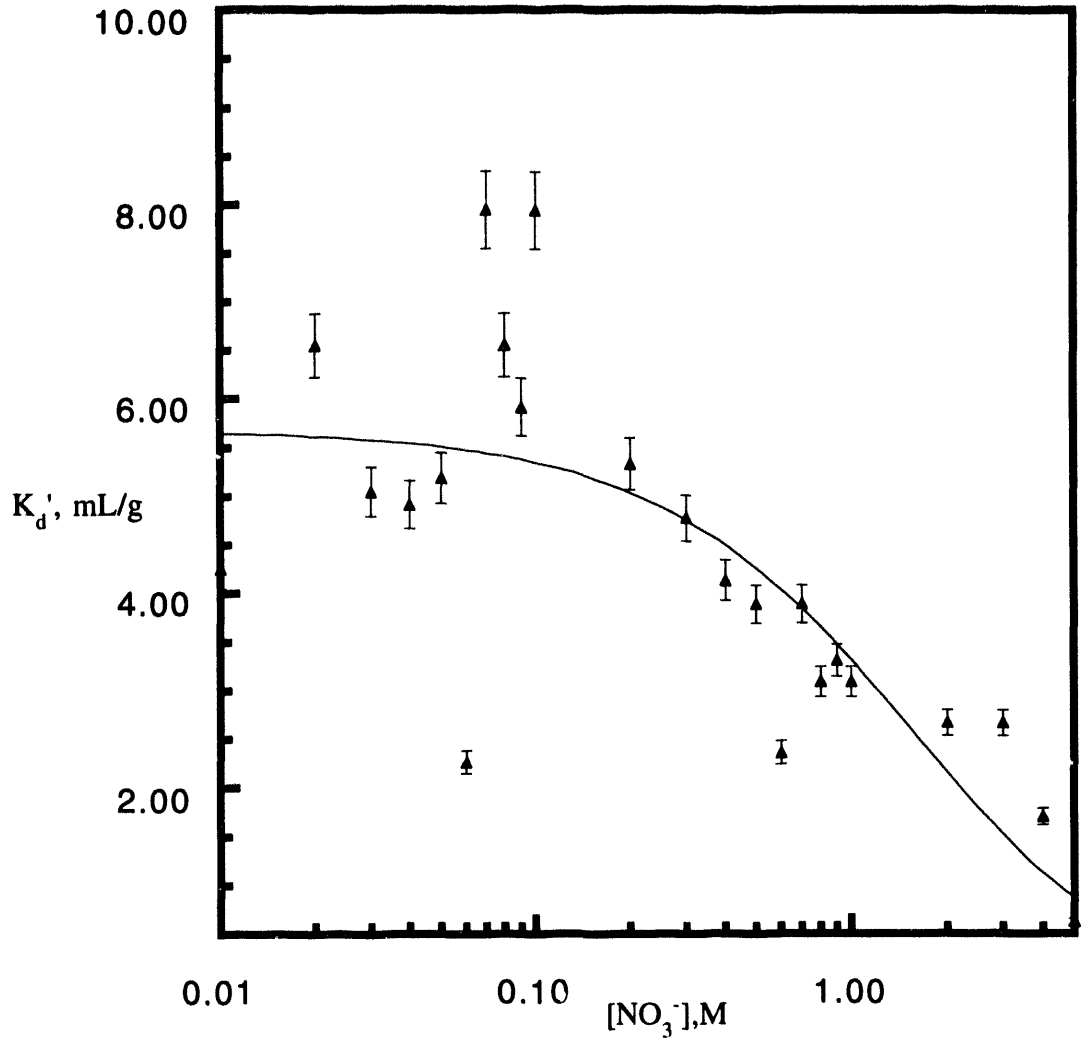

Figure IV. The variation of the values of K_d' as a function of $[NO_3^-]$. The line is the fit of the data to the equation

$$K_d' = (59.1 \pm 38.0)/(3.22 \pm 1.10 + [NO_3^-])^2$$

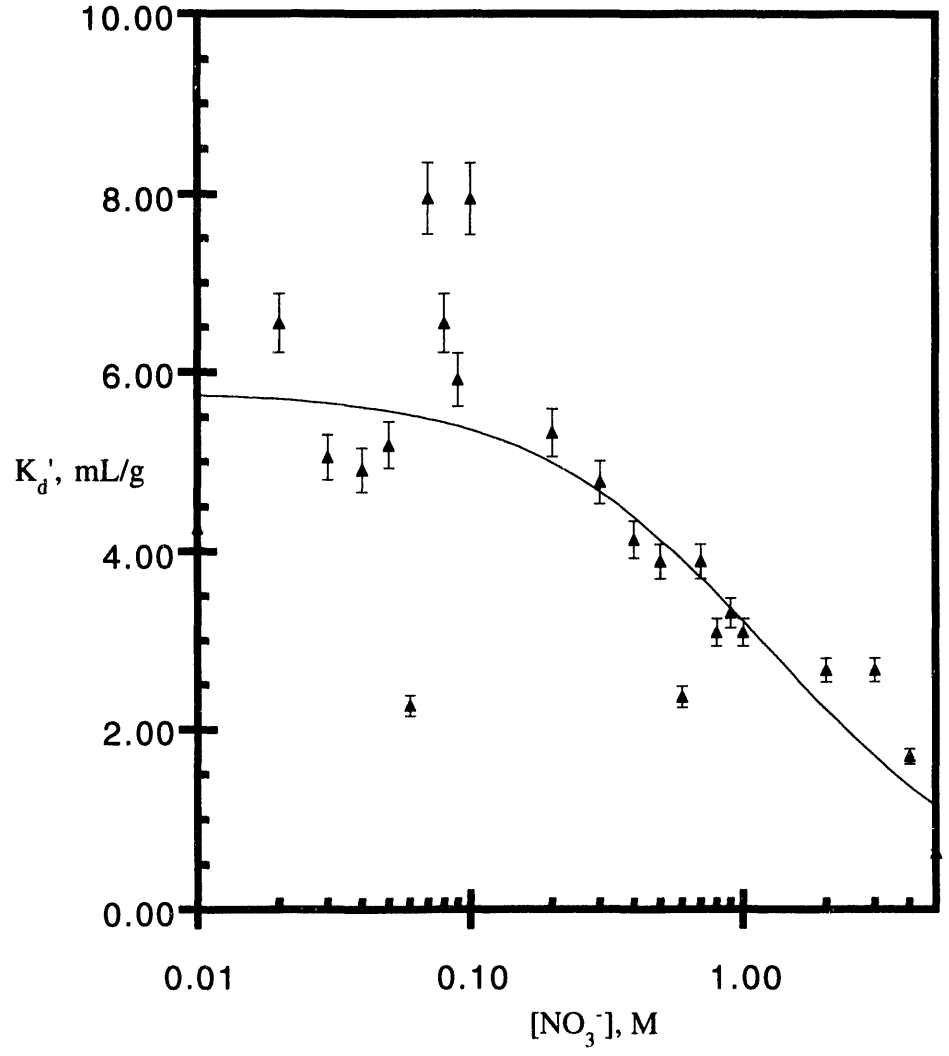

Figure V. The variation of the values of K_d' as a function of $[NO_3^-]$. The line is the fit of the data to the equation

$$K_d' = (7.24 \pm 2.42)/(1.25 \pm 0.48 + [NO_3^-])$$

REFERENCES

1 Reilly Industries Inc., 1510 Market Square Center, 151 N. Delaware St. , Indianapolis, IN 46204.

2. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed. Wiley-Interscience, 1980, p733.

Appendix I

Statement of Work

An Investigation of the Applicability of the New Ion Exchange Resin, Reillex™-HPQ, in ATW Separations

Introduction

The separation and isolation of pertechnetate ion in various waste streams is an important technology that still has not attained the level necessary to be universally applicable.[1] This is very evident with regard to the problems associated with the Accelerated Transmutation of Waste (ATW). The use of ion exchange resins to separate various ions from solutions is well documented.[2-5] In fact, the resin Dowex-1 has proven to be very useful for the isolation of pertechnetate ion.[2]

Recently a new ion exchange resin made from polystyrene and vinylpyridine to give a strong base resin with $RC_5H_4NCH_3^+$ as the exchange site has been introduced.[6] This resin is called Reillex™ and has been found to be very resistant to radiation damage.[4] The behavior of plutonium(IV) on the Reillex™ has been reported to be very favorable for the isolation of the ion.[3] However, no general data with other ions were reported.

Because of the very good radiolytic stability, there is a need to explore the utility of this resin for the isolation of TcO_4^-. As a beginning in this investigation the characterization of the resin with all types of ions must also be established. This is the subject of the requested investigation.

Requested Research

The Chemistry Department at East Texas State University will investigate the behavior of perrhenate ion ($ReO4^-$) on the anion exchange resin Reillex™-HPQ. Also, the behavior of OH^-, NO_2^-, HCO_3^-, F^-, Cl^-, Br^-, I^-, I_3^-, and I_2 with the nitrate form of the Reillex™-HPQ resin will be studied. These will be investigated as the apparent necessity warrants and the time permits. The quantitative data of interest are the values of the distribution coefficient, K_d, (mL of solution/grams of resin). The needed characterization data will include, but will not necessarily be limited to, the following items:

1. The adsorption of ReO_4^- onto the Reillex-HPQ resin (NO_3^- form) as a function of:
   i. The time in contact with the resin.
   ii. The $[H^+]$ concentration.
   iii. The nitrate ion concentration.
   iv. The hydroxide ion concentration.
   v. The nitrite ion concentration.
   vi. The bicarbonate ion concentration.

2. The elution of ReO_4^- from the Reillex-HPQ resin (NO_3^- form) as a function of:
   i. The time the ReO_4^- ion is on the resin.
   ii. The eluent flow rate.
   iii. The $[H^+]$ concentration.
   iv. The nitrate ion concentration.
   v. The hydroxide ion concentration.
   vi. The nitrite ion concentration.
   vii.. The bicarbonate ion concentration.

3. The determination of the values of K_d for ReO_4^- under the conditions outlined in 1. above.

4. The determination of the values of K_d for OH^-, NO_2^-, HCO_3^-, F^-, Cl^-, Br^-, I^-, I_3^-, and I_2. These will be investigated as the apparent necessity warrants and the time permits.

The above outline of proposed experiments is very ambitious. The outline is given as an indication of the direction that the research is to take. It is anticipated that some of the activities will not be able to be explored. Also, as the endeavors unfold, some of the proposed experiments might lose their urgency. However, the characterization of the Reillex™-HPQ resin with the ions of interest associated with ATW is the overriding direction of the requested research.

References

1. Bostick, W. D., Shoemaker, J. L., Osborne, P. E., and Evans-Brown, B. in *Emerging Technologies in Hazardous Waste Management*; Tedder, D. W. and Pohland, F. G., Ed.; American Chemical Society: Washington, D. C., 1990.
2. Roberts, F. P., Smith, F. M. and Wheelwright, E. J. HW-SA-2581 (1962).
3. March, S. F. *Solvent Extraction and Ion Exchange* **1989**,*7*, 889.
4. March, S. F. *LA-11912 UC-704* **1990**.
5. March, S. F. *LA-12055 UC-731* **1991**.

Results

Expectations

The requested research can be considered directed basic research. There will be tangible results. However, the exact nature of these results cannot be anticipated. Hence, the expectations will be nothing more than the results of the experiments. The abilities and judgments of the investigators will be depended upon to pursue the most fruitful lines of development in the research. It should be explicitly noted that the investigators and Kent Abney and other LANL staff will be in weekly communication. This will insure that the evolving interest of the ATW project will be communicated to the investigators and that the investigations will drift in the direction of program needs.

Deliverables

The expected deliverable is a final report. This report is to contain a detailed description of all experimental work performed, the results of those experiments, and the interpretation of those results. Three interim reports and a final report will be expected. These will constitute the Milestones.

Milestones

There will be three quarterly reports and a final report submitted. The dates for these quarterly reports to be received by Kent Abney are December 7, 1992, March 7, and June 7, 1993. The final report will be due by September 7, 1993. The expected progress is outlined below.

December 7, 1992

The general analytical techniques and the specific analysis for ReO_4^{-1} will be developed. Preliminary results of the adsorption of ReO_4^{-1} on Reillex™-HPQ will be obtained.

March 7, 1992

The behavior of ReO_4^{-1} on Reillex™-HPQ as a function of the conditions stated in Items 1 and 2 in the Requested Research section will be reported. The determination of the values of K_d for ReO_4^{-1} on Reillex™-HPQ under these conditions will be reported. This is Item 3 in the Requested Research section.

June 7, 1993

The results of the experiments suggested in Item 4 will be reported.

September 7, 1993

The final report combining the three previous reports and the last quarter results will be submitted.

Appendix II

The Ion Exchange Properties of a New Macroporous Resin Using Bromide as the Model Ion in Aqueous Nitrate Solutions

An Honor's Thesis

THE ION EXCHANGE PROPERTIES OF A NEW MACROPOROUS RESIN USING BROMIDE AS THE MODEL ION IN AQUEOUS NITRATE SOLUTIONS

AN HONORS THESIS

by

MELISSA RACHELLE GRISSOM

Submitted to the University Honors Committee
East Texas State University
in Partial Fulfillment of the Requirements
for Graduation with Honors with a
Bachelor of Science
August of 1993

ABSTRACT

THE ION EXCHANGE PROPERTIES OF A NEW MACROPOROUS RESIN USING BROMIDE AS THE MODEL ION IN AQUEOUS NITRATE SOLUTIONS

Melissa R. Grissom, B.S.
East Texas State University, 1993

Adviser: Professor Yen-Yuan James Wu

Reillex-HPQ™ resin, a newly available macroporous anion exchange resin, is based on a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene. Reillex-HPQ™ resin consists of 63% strong-base and 37% weak-base functional groups and carries peculiar ion exchange properties. In this thesis bromide will be used as the model ion for the measurement of the distribution coefficient (K_d) and the investigation of the sorption kinetics of the Reillex-HPQ™ resin. The concentration of the bromide ion was measured with an ion-selective electrode coupled with a double-junction reference electrode. In addition, this thesis will discuss various ways of massing the resin and the development of practical experimental techniques. The K_d values were found to decrease as the ionic strength increased. Another

trend noted was that the K_d increases when the bromide concentration in the solution decreases. Therefore, the HPQ resin is more suitable for low loading separations.

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considered reliable, the resin must be reasonably durable under the ionizing radiation emitted by the radiolytic species from the nuclear waste (*22*). If the resin degrades too soon it must be replaced more frequently, which results in higher operating costs. The quaternary-amine based resins often show a decreasing exchange capacity when exposed to high-level ionizing radiation, making the use of them more expensive and the ion exchange process less reliable (*22, 26, 27*).

In order to improve the anion exchange process Permutit™ SK, a pyridine-based resin formed by the copolymerization of 2-methyl-5-vinylpyrdine and divinylbenzene, was examined under the same chemical conditions as other quaternary-amine based resins have encountered (*22*). The testing results were satisfactory. The stability of the Permutit™ SK was attributed to its chemical structure. In the quaternary-amine based resin, the ring is susceptible to electrophillic aromatic substitution and hence less resistant to acid attack. In contrast, the pyridine-based resin has an electron deficiency in the aromatic ring, hence a much higher resistance to such substitutions. According to Goldstein, Gangwer, and Pillary, "Resins with pyridine exchange groups are more stable than all other types of synthetic organic ion-exchangers that have been examined for radiation-induced chemical changes." (*21*)

In order to take advantage of this special property of pyridine, the Los Alamos National Laboratory and the Reilly

Industries Inc. worked together for the development of a new macroporous polyvinylpyridine resin which is also more resistant to radiolytic degradation (*22*). After about two years of collaboration, a new resin, Relliex-HQP^{TM}, emerged. The new resin is a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene. The basic structure of the Relliex-HQP^{TM} resin is shown in Figure 2 (*20*).

A peculiar property of the HPQ resin, which was specified by the researchers in the Los Alamos National Laboratory, is that only 63% of the nitrogen atoms, in the pyridine ring, are quaternized. Consequently, the HPQ resin is a mixture of 63% strong-base and 37% weak-base resin (*22*). The structure of the HPQ resin is shown in Figure 3.

The average pK_a of the resin is 3.575 (*28, 29*) and it has a mesh size of 30-60 U. S. standard mesh, or 250-595 microns. The Relliex-HPQ^{TM} resin has a dry exchange capacity of 4.6 meq/g and a wet exchange capacity of 1.4 meq/mL (*29, 30*). This new resin is insoluble in water, acids, bases, and organic solvents (*31*). Relliex-HPQ^{TM} resin has proven to be more resistant to gamma and alpha radiations. Experimental results indicated that after the acidic and radiolytic treatments the exchange capacity of the HPQ resin remained the same and the weight loss of the resin was much less than those of the quaternary-amine based resins (*20, 22, 26*). In addition, the HPQ resin has a better thermal stability with faster sorption kinetics. Studies published by S. Fredric Marsh (*20, 22, 26*) have compared HPQ with other quaternary-

Figure 2

Structure of Relliex-HPQ™ a new polyvinylpyridine resin.

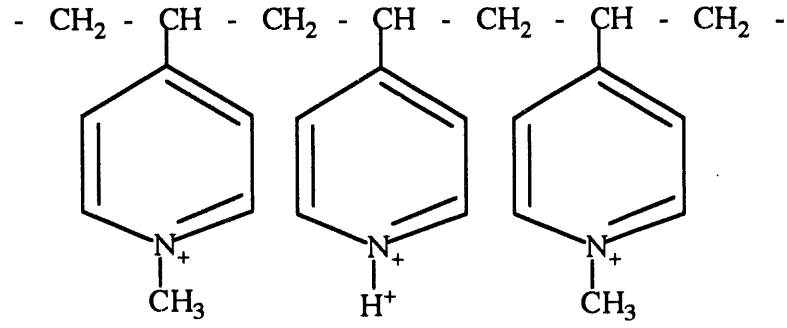
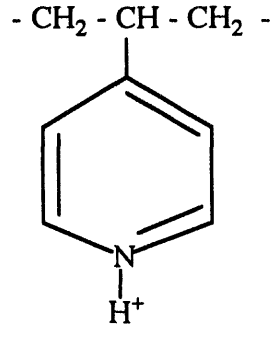


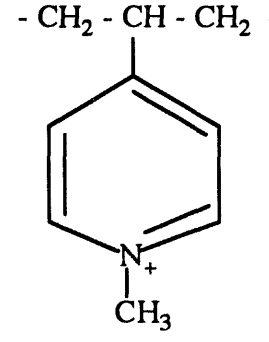
Figure 3

The strong and weak sites of the Relliex-HPQ™ resin.

Strong Base Sites 63%



Weak Base Sites 37%



amine based resins and concluded that the HPQ is indeed superior to all other resins used before in nearly every perspective. However, since the resin is relatively new, very little research on its applications has been performed, and most of its basic chemical properties remain unknown at this stage. In this thesis, the thermodynamic and the kinetic properties of the HPQ resin will be investigated.

THEORETICAL

In this section, the theoretical perspective of the measurements of the **distribution coefficient, K_d,** (*30, 32*) of the Relliex-HPQ^{TM} resin in aqueous nitrate solutions will be described. Throughout this research, the bromide ion will be used as the model ion.

The reaction of interest is given below.

$$R^+NO_3^- + Br^- \rightleftharpoons R^+Br^- + NO_3^- \qquad (1)$$

From the reaction given above the **selectivity coefficient,** (*2*) **K'**, can be expressed as follows.

$$K' = \frac{[R^+Br^-][NO_3^-]}{[R^+NO_3^-][Br^-]} \qquad (2)$$

Equation 2 defines the selectivity of Br^- over NO_3^- in the resin. If Br^- is preferred, $K'>1$; otherwise, $K'\leq 1$. From K', the **formal distribution coefficient, K,** can be expressed as follows.

LIST OF FIGURES

Chapter I

INTRODUCTION

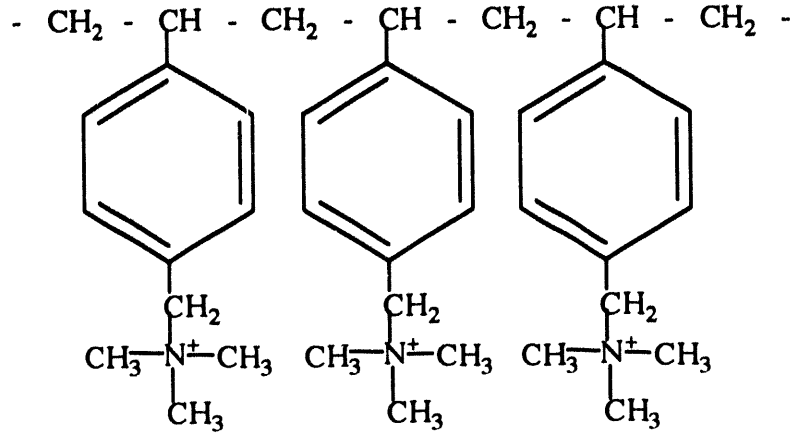
BACKGROUND

The treatment of nuclear waste has been a serious problem since the beginning of the Manhattan Project in 1942, yet it lingers into a crisis after 50 years of tinkering and procrastination. Anion exchange (*1-19*) was employed for the plutonium recovery (*20*) in the early stage; currently, it becomes one of the major techniques for the pre-treatment of the nuclear waste (*16, 20-22*). In the past, most of the resins used were quaternary-amine based synthetic resins formed by the copolymers of polystyrene and divinylbenzene (*6-18, 20, 23, 24*). Please refer to Figure 1 for the general structure. These resins were proven to be neither safe nor cost effective. Almost all of them have a tendency to react violently when they come in contact with radiolytic species in concentrated nitric acid (*22*). Under critical conditions, even explosions may occur. Because of the explosive nature of the quaternary-amine based resins, strict safety rules have been imposed in the nuclear industry (*22*).

Another concern facing the industry is the lifetime of the resin (*22, 25*). For an ion exchange process to be

Figure 1

Structure of conventional quaternary amine based resins.



$$K = K'[R^+NO_3^-] = \frac{(R^+Br^-)[NO_3^-]}{(R^+Br^-)} = K_d[NO_3^-] \qquad (3)$$

The $K'[R^+NO_3^-]$ term in equation 3 correlates the K_d with the nitrate concentration in the solution phase. From the formal distribution coefficient, the **distribution coefficient, K_d,** is hence defined by the following equation.

$$K_d = \frac{[R^+Br^-]}{[Br^-]} = \frac{[Br^-]_{resin}}{[Br^-]_{soln}} = \frac{\dfrac{\text{mmol } Br^- \text{ in resin}}{\text{mL of resin}}}{\dfrac{\text{mmol } Br^- \text{ in solution}}{\text{mL of solution}}} \qquad (4)$$

The K_d can be calculated from experimental data according to the following derivations.

First, the difference of the bromide potentials (ΔE) measured from the reaction cell and the dummy cell must be calculated.

$$\Delta E = E_{rxn} - E_{dummy} \qquad (5)$$

The definitions of the reaction cell and dummy cell will be described in chapter 2.

Next, the **percent loading (%L)** of the bromide in the reaction cell at 25°C is calculated as shown in equations 6 and 7.

$$\frac{100 - \%L}{100} = \frac{[Br^-]_{rxn}}{[Br^-]_{dummy}} = 10^{-\Delta E/59.16} \quad (6)$$

$$\%L = (1-10^{-\Delta E/59.16})*100\% \quad (7)$$

The %L calculation in equation 7 is then used for the calculation of K_d.

$$K_d = \frac{\frac{\%L}{mL\ resin}}{\frac{100 - \%L}{mL\ of\ solution}} \quad (8)$$

Equation 8 is consistent with the definition of the distribution coefficient, K_d, as shown in equation 9.

$$K_d = \frac{[Br^-]_{resin}}{[Br^-]_{solution}} \quad (9)$$

It should be noted that Equation 9 is identical to equation 4.

THESIS PROPOSAL

In this thesis, bromide will be used as the model ion for the measurement of the distribution coefficient, K_d, (7,

8, 17, 18) and the investigation of the sorption kinetics (*20, 24, 33*) of the Reillex-HPQ™ resin. The concentration of the bromide ion is measured with a bromide ion-selective electrode coupled with a double-junction reference electrode. In addition, in this research a reproducible way of drying the resin and some practical experimental techniques will be developed.

Chapter II

Experimental

In this chapter, the experimental procedures for glassware cleaning, resin treatment, resin drying, calibration of electrodes, instrumental methods, and K_d determinations will be described in detail.

GLASSWARE CLEANING

All volumetric glassware used was cleaned with the peroxydisulfate cleaning solution, which was prepared by dissolving 16.4 grams of $(NH_4)_2S_2O_8$ (ammonium peroxydisulfate) in 1.0 liter of 98% (w/w) H_2SO_4,(sulfuric acid). For most experiments, the glassware was also soaked in 1.0 M HNO_3 (nitric acid) solution overnight, then rinsed thoroughly with deionized water (18 MΩ) before use. The elution columns were cleaned with 1.0 M HNO_3 only.

REAGENTS

All reagents were of the analytical grade, hence no additional purification was performed. The standard HNO_3 solutions were prepared from concentrated HNO_3 solution (15.9 M) and standardized against a secondary-standard NaOH (sodium hydroxide) solution. The secondary-standard NaOH solution was

prepared from a 50% (w/w) NaOH solution, then standardized against primary standard KHP (potassium hydrogen phthalate), $C_6H_4(COOH)(COOK)$, before being preserved in a plastic bottle with a tight cap to prevent any carbonate contamination. The solid NaBr (sodium bromide) was obtained from J. T. Baker and $NaNO_3$ (sodium nitrate) from Fluka-Chemica. The Relliex-HPQ™ resin was obtained from the Reilly Industries. The size of the resin particles in its chloride form is about 30-60 mesh.

RESIN TREATMENT

The Relliex-HPQ™ resin was first washed with deionized water to remove all the organic impurities including incompletely polymerized material that leaches out slowly from the resin when in use. The floating resin beads were also removed at the same time. The resin was converted to its nitrate form by passing 20 bed volumes of 0.10 M HNO_3 through the column. Additional 1.0 M HNO_3 was eluted through the resin when necessary, while the eluent was monitored by a chloride ion-selective electrode to ensure a complete removal of the chloride ion. This step also ensured that the unquaternized ionogenic groups were fully protonated.

RESIN DRYING

An experiment was designed to establish a drying procedure for the resin since the mass of the resin is essential for the determination of K_d. In order to establish the length of time required to dry the resin to a constant weight, ten batches of 10.0-mL wet resin, measured with a 10.0-mL graduated cylinder,

were first aspirated in a sintered glass funnel to remove the excess water. The resin samples were then transferred to a 125-mL beaker, covered with a watch glass, and dried in an oven at 60°C for 2 hours. They were then placed in a desiccator containing silica gel and allowed to cool. The cooled resin samples were weighed before being returned to the oven for further drying. This procedure was repeated 14 times before the resin samples reached a constant weight. At the end of the 28 hour total heating time, the resin samples were heated for another 20 hours to ensure that they had indeed reached a constant weight.

The weight ratio of the resin dried at 60°C and 110°C (in a vacuum oven) was determined next. With this ratio, it will be possible to convert data between experiments where the resin may be dried at either of the two different temperatures. For instance, researchers at the Los Alamos National Laboratory dry the resin at 110°C instead of 60°C. To determine the weight ratio, ten batches of 20.0-mL wet resin, measured with a 25.0-mL graduated cylinder, were each aspirated in a sintered glass funnel to remove the excess water. Each batch of aspirated resin was placed in a 50.00-mL volumetric flask since the resin is very electrostatic. The long neck of the volumetric flask prevents the resin from popping out. The resin samples were then dried in an oven at 60°C for 48 hours, then an additional 24 hours, for a total of 72 hours. After each drying period, the resin was allowed to cool in a desiccator containing silica gel before being weighed on an analytical balance. The flasks containing the resin were then placed in a vacuum oven at 110°C and further dried for

98 hours, then two additional 24-hour periods, for a total of 146 hours. After each drying period, the flasks were allowed to cool in the oven. They were then capped, placed in a desiccator, and weighed immediately since the resin is extremely hygroscopic after being dried at 110°C.

CALIBRATION OF ELECTRODE

During the construction of the calibration curve, the ionic strength was maintained at 1.0000 M and the concentration of HNO_3 at 0.01000 M. The bromide stock solution was prepared by dissolving 2.5723 g NaBr, 19.1058 g NaNO3, and an appropriate amount of HNO_3 in a 250.0-mL volumetric flask. The blank solution was prepared by dissolving 170.02 g $NaNO_3$ in 20.000 mmol of HNO_3 in a 2.000-L volumetric flask. Table I shows the composition of these two solutions. All bromide standard solutions were prepared by successive dilution. The blank solution was used for all dilutions in order to maintain the pH and the ionic strength. The range of bromide concentrations was from 0.1000 M to 2.000×10^{-7} M. Table II shows the preparation of the bromide standard solutions.

In order to accommodate all K_d measurements, three additional calibration curves were constructed under various ionic strengths and acidities. The acidities of the first two calibration curves were controlled with 4.000 M and 1.000 M HNO_3, respectively. No additional $NaNO_3$ was added to control the ionic strength. The acidity of the third calibration curve was controlled with 0.1000 M HNO_3 and solid $NaNO_3$ was added to maintain the ionic strength at 1.000 M. For each of these three calibration curves, two bromide

Table I

Composition of the Bromide Stock Solution and the Blank Solution for the Bromide Calibration Curve at 0.01000 M Ionic Strength

Solutions	$[Br^-]$ (M)	$[HNO_3]$ (M)	$[NaNO_3]$ (M)	μ^* (M)
Bromide Solution	0.10000	0.01000	0.89000	1.0000
Blank Solution	0	0.01000	0.99000	1.0000

* The ionic strength of the solution.

Table II

Composition of the Bromide Standard Solutions for the Bromide Calibration Curve at 0.01000 M Ionic Strength

$[Br^-]$(M)	pBr	[HNO3]	[NaNO3]	μ*	pH	mV†
1.000×10^{-1}	1.000	0.01000 M	0.8900 M	1.000 M	1.579	-102.5
5.000×10^{-2}	1.301	0.01000 M	0.9400 M	1.000 M	1.612	-84.1
2.000×10^{-2}	1.699	0.01000 M	0.9700 M	1.000 M	1.646	-59.6
1.000×10^{-2}	2.000	0.01000 M	0.9800 M	1.000 M	1.653	-43.0
5.000×10^{-3}	2.301	0.01000 M	0.9850 M	1.000 M	1.632	-25.0
2.000×10^{-3}	2.699	0.01000 M	0.9880 M	1.000 M	1.628	-1.0
1.000×10^{-3}	3.000	0.01000 M	0.9890 M	1.000 M	1.635	16.7
5.000×10^{-4}	3.301	0.01000 M	0.9895 M	1.000 M	1.626	34.4
2.000×10^{-4}	3.699	0.01000 M	0.9898 M	1.000 M	1.620	58.6
1.000×10^{-4}	4.000	0.01000 M	0.9899 M	1.000 M	1.666	75.8
5.000×10^{-5}	4.301	0.01000 M	0.9900 M	1.000 M	1.671	93.3
2.000×10^{-5}	4.699	0.01000 M	0.9900 M	1.000 M	1.680	116.4
1.000×10^{-5}	5.000	0.01000 M	0.9900 M	1.000 M	1.664	131.0
5.000×10^{-6}	5.301	0.01000 M	0.9900 M	1.000 M	1.669	145.4
2.000×10^{-6}	5.699	0.01000 M	0.9900 M	1.000 M	1.639	161.1
1.000×10^{-6}	6.000	0.01000 M	0.9900 M	1.000 M	1.632	164.0
5.000×10^{-7}	6.301	0.01000 M	0.9900 M	1.000 M	1.667	170.6
2.000×10^{-7}	6.699	0.01000 M	0.9900 M	1.000 M	1.619	173.4

* Ionic strength of the solution.
† Measured by a bromide ion-selective electrode coupled with a double-junction reference electrode.

standard solutions were prepared with bromide concentrations of $1.0x10^{-2}$ M and $1.0x10^{-3}$ M, respectively. The composition of the stock solutions are listed in Table III and that of the bromide standard solutions are given in Table IV.

INSTRUMENTAL METHODS

All potentials (mV) were measured with an ORION Model EA-940 Expandable Ionalyzer in conjunction with a bromide ion-selective electrode (94-35 BN) coupled with a double-junction reference electrode (90.02). The thermal bath was maintained 25°C for all measurements. Usually, it took about 10 seconds for the voltage readings to stabilize when $[Br^-] > 10^{-4}$ M and about 60 seconds when $[Br^-] < 10^{-4}$ M.

K_d DETERMINATION

In this research, Br^- was used as the model ion for the measurement of K_d in aqueous nitrate solutions. Eight sets of experiments were performed during which the ionic strength was varied from 1.000 M to about 0.01000 M. Except for the eighth set of measurements, solid $NaNO_3$ was used to control the ionic strength. The concentration of HNO_3 was maintained at 0.01000 M through all measurements. The temperature of the thermal bath was maintained at 25°C at all times. The pre-treated resin were eluted with deionized water until the pH increased to about 3.5. In each of the nine sets of measurements, a different amount of bromide was added with a pipet. The bromide potential, which corresponds to the concentration of bromide ions in the solution

Table III

Composition of the Bromide Stock Solutions and the Blank Solutions for the Bromide Calibration Curves under 4.000 M, 1.000 M, and 0.1000 M HNO_3

ACIDITY	SOLUTION	$[Br^-]$(M)	$[HNO_3]$(M)	$[NaNO_3]$(M)	μ^*(M)
4.0 M HNO_3	Bromide	0.01000 M	4.000	0	4.00
	Blank	0	4.000	0	4.00
1.0 M HNO_3	Bromide	0.01000 M	1.000	0	1.00
	Blank	0	1.000	0	1.00
0.1 M HNO_3	Bromide	0.01000 M	0.1000	0.8900	1.00
	Blank	0	0.1000	0.9000	1.00

* Ionic strength of the solution.

Table IV

Composition of the Bromide Standard Solutions for the Bromide Calibration Curves under 4.000 M, 1.000 M, and 0.1000 M HNO_3

$[Br^-]$(M)	pBr	[HNO3](M)	[NaNO3](M)	μ*(M)	pH	mV**
1.000×10^{-2} †	2.000	4.0000	0	4.000	-1.077	-112.3
5.000×10^{-3} †	2.301	4.0000	0	4.000	-0.984	-85.7
2.000×10^{-3} †	2.699	4.0000	0	4.000	-0.952	-59.6
1.000×10^{-3} †	3.000	4.0000	0	4.000	-0.527	-45.5
5.000×10^{-4} †	3.301	4.0000	0	4.000	-0.599	-24.1
2.000×10^{-4} †	3.699	4.0000	0	4.000	-0.910	-5.0
1.000×10^{-2} ·	2.000	1.0000	0	1.000	-0.129	-72.5
5.000×10^{-3} ·	2.301	1.0000	0	1.000	-0.149	-56.9
2.000×10^{-3} ·	2.699	1.0000	0	1.000	-0.178	-32.7
1.000×10^{-3} ·	3.000	1.0000	0	1.000	-0.004	-15.0
5.000×10^{-4} ·	3.301	1.0000	0	1.000	-0.033	-3.7
2.000×10^{-4} ·	3.699	1.0000	0	1.000	------§	27.6
1.000×10^{-2} ‡	2.000	0.1000	0.8900	1.000	0.588	-44.6
5.000×10^{-3} ‡	2.301	0.1000	0.8950	1.000	0.563	-36.1
2.000×10^{-3} ‡	2.699	0.1000	0.8980	1.000	0.561	-11.4
1.000×10^{-3} ‡	3.000	0.1000	0.8990	1.000	0.655	5.0
5.000×10^{-4} ‡	3.301	0.1000	0.9995	1.000	0.625	12.7
2.000×10^{-4} ‡	3.699	0.1000	0.9998	1.000	0.614	19.5

* Ionic strength of the solution. ** Measured by a bromide ion-selective electrode with a double-junction reference electrode and a pH meter. † 4.000 M HNO_3. · 1.000 M HNO_3. ‡ 0.1000 M HNO_3. § Not measured.

phase, was then measured. The amount of bromide added to the resin was calculated in terms of the "**percent total capacity (%TC)**" of the resin in the reaction cell. The definition of %TC is given by equation 10.

$$\%TC = \frac{\text{mL } Br^- \times \underline{M}\ Br^-}{\text{mL wet resin} \times 1.4 \text{ meq/mL}} \qquad (10)$$

Note that the exchange capacity of the wet resin is about 1.4 meq per mL. For example, the reaction cell designated as 20% total capacity was prepared by mixing 20.00 mL of 0.1400 $\underline{M}$ bromide solution, 10.00 mL of wet resin, 5.0 mL of eluent, and 44.8 mL of blank solution.

The bromide potentials were taken with bromide ion-selective electrode previously calibrated according to the procedure prescribed in the electrode manual (*34*). The potential of the reaction cell which contained resin and blank solution was taken before the bromide was added. After bromide was added with a pipet, bromide potential readings were taken every 15 seconds for 30 minutes. For each measurement, a corresponding dummy cell was also prepared. Each dummy cell had the same composition as the reaction cell except no resin was used; however, an extra amount of eluent was used in order to compensate for the volume of resin. Figures 5, 6, and 7 show the composition of the reaction cells for each of the 8 sets of measurements. In order to establish the validity of the measurements, additional bromide potential readings were performed by adding ISA (ionic-strength adjustor) to

Figure 5

Cell Chart of the First Set of K_d Measurements

RESIN
ELUENT
BROMIDE
BLANK

Reaction Cells

20.0%	10.0%	2.00%	0.20%
10.0 mL	10.0 mL	10.0 mL	10.0 mL
5.0 mL	5.0 mL	5.0 mL	5.0 mL
20.0 mL	10.0 mL	2.0 mL	0.2 mL
44.8 mL	35.0 mL	43.0 mL	25.0 mL

Dummy Cells

20.0%	10.0%	2.00%	0.20%
0.0 mL	0.0 mL	0.0 mL	0.0 mL
15.0 mL	15.0 mL	15.0 mL	15.0 mL
20.0 mL	10.0 mL	2.0 mL	0.2 mL
44.8 mL	35.0 mL	43.0 mL	25.0 mL

Figure 6

Cell Chart of the Second Set of K_d Measurements

2 of 2

Reaction Cells

20.0%	10.0%	2.00%	0.20%
10.0 mL	10.0 mL	10.0 mL	10.0 mL
5.0 mL	5.0 mL	5.0 mL	5.0 mL
20.0 mL	10.0 mL	2.0 mL	0.2 mL
25.0 mL	35.0 mL	43.0 mL	44.8 mL

Dummy Cells

20.0%	10.0%	2.00%	0.20%
0.0 mL	0.0 mL	0.0 mL	0.0 mL
15.0 mL	15.0 mL	15.0 mL	15.0 mL
20.0 mL	10.0 mL	10.0 mL	10.0 mL
25.0 mL	35.0 mL	43.0 mL	44.8 mL

Figure 7

Cell Chart of the Third to Eighth Set of K_d Measurements

Reaction Cells

20.0%	10.0%	2.00%	0.20%
5.0 mL	5.0 mL	5.0 mL	5.0 mL
2.5 mL	2.5 mL	2.5 mL	2.5 mL
10.0 mL	5.0 mL	10.0 mL	10.0 mL
12.5 mL	17.5 mL	12.5 mL	12.5 mL

Dummy Cells

20.0%	10.0%	2.00%	0.20%
0.0 mL	0.0 mL	0.0 mL	0.0 mL
7.5 mL	7.5 mL	7.5 mL	7.5 mL
10.0 mL	5.0 mL	10.0 mL	10.0 mL
12.5 mL	17.5 mL	12.5 mL	12.5 mL

each solution measured before. The solutions for the ISA measurements were prepared by pipeting 5.000 mL of ISA ([HNO_3]=0.01000 M, ionic strength 2.000 M) and 5.000 mL of the solution from the reaction cells. The ISA measurement of the dummy cells was performed in the same way.

For the measurement of the first set of K_ds (distribution coefficients), the ionic strength of all solutions was controlled at 1.000 M. Also, all solutions contained 0.01000 M of HNO_3. The resin was first eluted with 10 bed volumes of the blank solution at a rate not exceeding 0.5 mL a minute. The blank solution was prepared by dissolving 170.01 g $NaNO_3$ and 10.00 mmol of HNO_3 with deionized water in a 1.000-L volumetric flask. The last part of the eluent was collected for later use. The bromide stock solution was prepared by dissolving 2.8808 g NaBr, 14.5977 g $NaNO_3$, and 2.000 mmol HNO_3 in a 200.0-mL volumetric flask. Throughout the entire research, the wet resin and the eluent were measured together with a 25.0-mL graduated cylinder, the bromide stock solution was delivered with pipets, and the blank solution was delivered with a 50.00-mL Class-A buret. All reactions were performed in 100-mL beakers with watch glasses on top. The dummy cells were prepared in a similar fashion except the eluent was delivered with pipets. Table V shows the composition of the stock solutions and Table VI shows how the reaction cells and the dummy cells were prepared.

The second set of K_d measurements was almost exactly the same as the first set except the resin was first eluted with deionized water until the acidity of the eluent was about 3.5 pH. Table VII

Table V

Composition of Stock Solutions For First Set of K_d Measurements

STOCK SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
Bromide Solution	0.1400 M	0.01000 M	0.8500 M	1.0000 M
Blank Solution	0	0.01000 M	0.9900 M	1.0000 M

* Ionic strength of the solution.

Table VI

Composition of the Reaction and Dummy cells in the First Set of K_d Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	Resin (mL)	Eluent†† (mL)	Total Volume(mL)
20.0	20.00	44.80	10.0 (0.0)*	5.0 (15.00)*	79.8
10.0	10.00	35.00	10.0 (0.0)*	5.0 (15.00)*	60.0
2.00	2.00	43.00	10.0 (0.0)*	5.0 (15.00)*	60.0
0.20	0.20	25.00	10.0 (0.0)*	5.0 (15.00)*	40.2

† Refer to Table V.
†† The blank solution was used as the eluent.
* The volume embraced by the parentheses is for the preparation of the dummy cell.

Table VII

Composition of Stock Solutions for the Second Set of K_d Measurements

STOCK SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
Bromide Solution	0.1400 M	0.01000 M	0.8500 M	1.0000 M
Blank Solution	0	0.01000 M	0.9900 M	1.0000 M

* Ionic strength of the solution.

shows the composition of the stock solutions and Table VIII shows how the reaction cells and the dummy cells were prepared.

For the measurement of the third set of K_ds, the ionic strength of all the solutions was controlled at 0.5000 M. Also, all solutions contained 0.01000 M of HNO_3. Starting from this set of measurements, all resin used was first elueted with deionized water until the acidity of the eluent was about 3.5 pH, then 10 bed volumes of the appropriate blank solution at a rate not exceeding 0.5 mL a minute. In this set, the blank solution was prepared by dissolving 21.0378 g $NaNO_3$ and 10.00 mmol of HNO_3 with deionized water in a 1.000-L volumetric flask. In order to maintain better precision of the solution concentrations three bromide stock solutions were prepared. The first bromide stock solution was prepared by dissolving 2.5208 g NaBr and 2.500 mmol HNO_3 in a 250.0-mL volumetric flask. The second and the third bromide stock solutions were prepared by successive dilutions with the blank solution. Table IX shows the composition of the stock solutions and Table X shows how the reaction cells and the dummy cells were prepared.

For the measurement of the fourth set of K_ds , the ionic strength of all the solutions was controlled at 0.2000 M. Also, all solutions contained 0.01000 M of HNO_3. The blank solution was prepared by dissolving 8.1577 g $NaNO_3$ and 10.00 mmol of HNO_3 with deionized water in a 1.000-L volumetric flask. The first bromide stock solution was prepared by dissolving 0.9777 g NaBr and 2.500 mmol HNO_3 in a 250.0-mL volumetric flask and the rest of the bromide stock solutions were prepared by successive dilutions.

Table VIII

Composition of the Reaction and Dummy Cells for the Second Set of K_d Measurements

% Total Capacity	Bromide Solution(mL)	Blank† Solution(mL)	resin (mL)	eluent†† (mL)	Total Volume(mL)
20.0	20.00	25.00	10.0 (0.0)*	5.0 (15.00)*	60.0
10.0	10.00	35.00	10.0 (0.0)*	5.0 (15.00)*	60.0
2.00	2.00	43.00	10.0 (0.0)*	5.0 (15.00)*	60.0
0.20	0.20	44.80	10.0 (0.0)*	5.0 (15.00)*	60.0

† Refer to Table VII.
†† The blank solution was used as the eluent.
* The volume embraced by the parentheses is for the preparation of the dummy cell.

Table IX

Composition of Stock Solutions For the Third Set of K_d Measurements

STOCK SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
1st Bromide Solution	0.49000 M	0.01000 M	0	0.5000 M
2nd Bromide Solution	0.04900 M	0.01000 M	0.4410 M	0.5000 M
3rd Bromide Solution	0.00490 M	0.01000 M	0.4851 M	0.5000 M
Blank Solution	0	0.01000 M	0.4900 M	0.5000 M

* Ionic strength of the solution.

Table X

Composition of Reaction and Dummy Cells for the Third Set of Kd Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	resin (mL)	eluent†† (mL)	Total Volume(mL)
20.0	10.00*	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0
10.0	5.00*	17.50	5.0 (0.0)*	2.5 (7.5)*	30.0
2.00	10.00**	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0
0.20	10.00***	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0

† Refer to Table IX.
†† The blank solution was used as the eluent.
* 1st bromide stock solution.
** 2nd bromide stock solution.
*** 3rd bromide stock solution.

Table XI shows the composition of the stock solutions and Table XII shows how the reaction cells and the dummy cells were prepared.

For the measurement of the fifth set of K_ds, the ionic strength of all the solutions was controlled at 0.1000 M. Also, all solutions contained 0.01000 M of HNO_3. The blank solution was prepared by dissolving 3.8641 g $NaNO_3$ and 10.00 mmol of HNO_3 with deionized water in a 1.000-L volumetric flask. The first bromide stock solution was prepared by dissolving 0.4630 g NaBr and 2.500 mmol HNO_3 in a 250.0-mL volumetric flask and the rest were prepared by successive dilution. Table XIII shows the composition of the stock solutions and Table XVI shows how the reaction cells and the dummy cells were prepared.

For the measurement of the sixth set of K_ds, the ionic strength of the solutions was controlled at 0.05000 M. Also, all solutions contained 0.01000 M of HNO_3. The blank solution was prepared by dissolving 1.7174 g $NaNO_3$ and 10.00 mmol of HNO_3 with deionized water in a 1.000-L volumetric flask. The first bromide stock solution was prepared by dissolving 0.2059 g NaBr, and 2.500 mmol HNO_3 in a 250.0-mL volumetric flask and the rest were prepared by successive dilutions. Table XV shows the composition of the stock solutions and Table XVI shows how the reaction cells and the dummy cells were prepared.

For the measurement of the seventh set of K_ds,the ionic strength of the solutions was controlled at 0.02000 M. Also, all solutions were 0.01000 M in HNO_3. The blank solution was prepared by dissolving 0.4293 g $NaNO_3$ and 10.00 mmol of HNO_3 in deionized

Table XI

Composition of Stock Solutions for the Fourth Set of K_d Measurements

SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
Bromide Stock Solution	0.19000 M	0.01000 M	0	0.2000 M
2nd Bromide Solution	0.01900 M	0.01000 M	0.1710 M	0.2000 M
3rd Bromide Solution	0.00190 M	0.01000 M	0.2119 M	0.2000 M
Blank Solution	0	0.01000 M	0.1900 M	0.2000 M

* Ionic strength of the solution.

Table XII

Composition of the Reaction and Dummy Cells of the Fourth Set of K_d Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	resin (mL)	eluent†† (mL)	Total Volume(mL)
20.0	10.00*	12.50	5.0 (0.0)*	2.5 (7.50)*	30.0
10.0	5.00*	17.50	5.0 (0.0)*	2.5 (7.50)*	30.0
2.00	10.00**	12.50	5.0 (0.0)*	2.5 (7.50)*	30.0
0.20	10.00***	12.50	5.0 (0.0)*	2.5 (7.50)*	30.0

† Refer to Table XI.
†† The blank solution was used as the eluent.
* 1st bromide stock solution.
** 2nd bromide stock solution.
*** 3rd bromide stock solution.

Table XIII

Composition of Stock Solutions For the Fifth Set of K_d Measurements

STOCK SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
1st Bromide Solution	0.09200 M	0.01000 M	0	0.1000 M
2nd Bromide Solution	0.00920 M	0.01000 M	0.0808 M	0.1000 M
3rd Bromide Solution	0.00092 M	0.01000 M	0.0891 M	0.1000 M
Blank Solution	0	0.01000 M	0.0900 M	0.1000 M

* Ionic strength of the solution.

Table XIV

Composition of the Reaction and Dummy Cells of the Fifth Set of Kd Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	resin (mL)	eluent†† (mL)	Total Volume(mL)
20.0	10.00*	12.50	5.00 (0.00)*	2.50 (7.50)*	30.0
10.0	5.00*	17.50	5.00 (0.00)*	2.50 (7.50)*	30.0
2.00	10.00**	12.50	5.00 (0.00)*	2.50 (7.50)*	30.0
0.20	10.00***	12.50	5.00 (0.00)*	2.50 (7.50)*	30.0

† Refer to Table XIII.
†† The blank solution was used as the eluent.
* The volume embraced by the parentheses is for the preparation of the dummy cell.

Table XV

Composition of Stock Solutions for the Sixth Set of Kd Measurements

STOCK SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
1st Bromide Solution	0.04000 M	0.01000 M	0	0.05000 M
2nd Bromide Solution	0.00400 M	0.01000 M	0.0360 M	0.05000 M
3rd Bromide Solution	0.00040 M	0.01000 M	0.0396 M	0.05000 M
Blank Solution	0	0.01000 M	0.0400 M	0.05000 M

* Ionic strength of the solution.

Table XVI

Composition of the Reaction and Dummy Cells for the Sixth Set of K_d Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	resin (mL)	eluent†† (mL)	Total Volume(mL)
20.0	10.00*	12.50	5.0 (0.0)	2.5 (7.5)	30.0
10.0	5.00*	17.50	5.0 (0.0)	2.5 (7.5)	30.0
2.00	10.00**	12.50	5.0 (0.0)	2.5 (7.5)	30.0
0.20	10.00***	12.50	5.0 (0.0)	2.5 (7.5)	30.0

† Refer to Table XV.
†† The blank solution was used as the eluent.
* The volume embraced by the parentheses is for the preparation of the dummy cell.

water in a 1.000-L volumetric flask. The first bromide stock solution was prepared by dissolving 0.0518 g NaBr and 2.500 mmol HNO_3 in a 250.0-mL volumetric flask and the rest were prepared by successive dilution with the blank solution. Table XVII shows the composition of the stock solutions and Table XVIII shows how the reaction cells and the dummy cells were prepared.

For the measurement of the eighth set of K_ds, the ionic strength of the solutions was not controlled. In other words, no $NaNO_3$ was added to the solutions. However, all solutions still contained 0.01000 M of HNO_3. The resin was only eluted with deionized water until the acidity of the eluent was about 3.5 pH. The blank solution was 1.000-L of 0.01000 HNO_3. The bromide stock solution was prepared by dissolving 3.6012 g NaBr and 2.500 mmol HNO_3 in a 250.0-mL volumetric flask. Table XIX shows the composition of the stock solutions and Table XX shows how the reaction cells and the dummy cells were prepared.

Table XVII

Composition of Stock Solutions For the Seventh Set of K_d Measurements

STOCK SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
1st Bromide Solution	0.01000 M	0.01000 M	0	0.02000 M
2nd Bromide Solution	0.00100 M	0.01000 M	0.0090 M	0.02000 M
3rd Bromide Solution	0.00010 M	0.01000 M	0.0099 M	0.02000 M
Blank Solution	0	0.01000 M	0.01000 M	0.02000 M

* Ionic strength of the solution.

Table XVIII

Composition of the Reaction and Dummy Cells of the Seventh Set of K_d Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	Resin (mL)	Eluent†† (mL)	Total Volume(mL)
20.0	10.00*	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0
10.0	5.00*	17.50	5.0 (0.0)*	2.5 (7.5)*	30.0
2.00	10.00**	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0
0.20	10.00***	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0

† Refer to Table XVII.
†† The blank solution was used as the eluent.
* The volume embraced by the parentheses is for the preparation of the dummy cell.

Table XIX

Composition of Stock Solutions For the Eighth Set of K_d Measurements

SOLUTION	$[Br^-]$	$[HNO_3]$	$[NaNO_3]$	μ^*
1st Bromide Solution	0.14000 M	0.01000 M	0	----------
2nd Bromide Solution	0.01400 M	0.01000 M	0	----------
3rd Bromide Solution	0.00140 M	0.01000 M	0	----------
Blank Solution	0	0.01000 M	0	----------

* Ionic strength was not controlled in this set of measurements.

Table XX

Composition of the Reaction and Dummy Cells of the Eighth Set of K_d Measurements

% Total Capacity	Bromide† Solution(mL)	Blank† Solution(mL)	resin (mL)	eluent†† (mL)	Total Volume(mL)
20.0	10.00*	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0
10.0	5.00*	17.50	5.0 (0.0)*	2.5 (7.5)*	30.0
2.00	10.00**	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0
0.20	10.00***	12.50	5.0 (0.0)*	2.5 (7.5)*	30.0

† Refer to Table XIX.
†† The blank solution was used as the eluent.
* The volume embraced by the parentheses is for the preparation of the dummy cell.

CHAPTER III

RESULTS AND DISCUSSION

In this chapter, the experimental results of the resin drying, the calibration of the bromide ion-selective electrode, the investigation of the sorption kinetics, and the measurements of the distribution coefficients will be described in detail. The implications of the experimental results will also be discussed.

RESIN DRYING

In Table XXI, the weights of the seven batches of HPQ resin dried at 60°C are listed as a function of time. Also, the mean weight and the standard deviation are listed in Table XXII. The mean weight as a function of time is plotted in Figure 7.

The plot indicates that the resin has reached a constant weight after about 24 to 26 hours of drying. The exceptionally low weight of every batch of the resin after 22 hours of drying might be due to an unexpected high temperature in the oven at that time. The standard deviation of the resin weights might be attributed to the measuring techniques of the volume of the wet resin. The standard deviation becoming greater in the later stages was due to the

Table XXI

Resin Weights as a Function of Time When Dried at 60°C*

Time	Beakers						
	1	2	3	4	5	6	7
2 hours	6.6273	6.1737	5.5463	5.8363	6.2734	5.7344	6.1694
4 hours	5.7243	5.2299	4.4109	4.7381	5.4840	4.2488	5.0757
6 hours	5.0569	4.3356	3.3398	3.7969	4.3725	3.2365	4.1004
8 hours	4.5165	3.7497	3.1683	3.2969	3.7033	3.1918	3.3769
10 hours	3.9086	3.3636	3.1368	3.1813	3.2554	3.1823	3.2136
12 hours	3.5611	3.2470	3.1153	3.1461	3.0729	3.1716	3.1404
14 hours	3.3610	3.2024	3.0991	3.1203	3.0161	3.1581	3.1064
16 hours	3.3293	3.1915	3.1010	3.1158	3.0045	3.1583	3.1013
18 hours	3.3136	3.1865	3.0904	3.1169	2.9984	3.1609	3.1008
20 hours	3.3010	3.1736	3.0862	3.1116	2.9864	3.1523	3.0877
22 hours	2.8111	2.7339	3.5596	3.0439	2.7711	2.9888	2.8160
24 hours	3.7943	2.7454	3.5716	3.0565	2.7757	3.0010	2.8234
26 hours	3.7895	2.7388	3.5604	3.0518	2.7686	2.9947	2.8172
28 hours	3.7895	2.7405	3.5646	3.0529	2.7699	2.9960	2.8167
48 hours	3.7689	2.7199	3.5454	3.0343	2.7548	2.9759	2.8010

* All numbers are in units of gram.

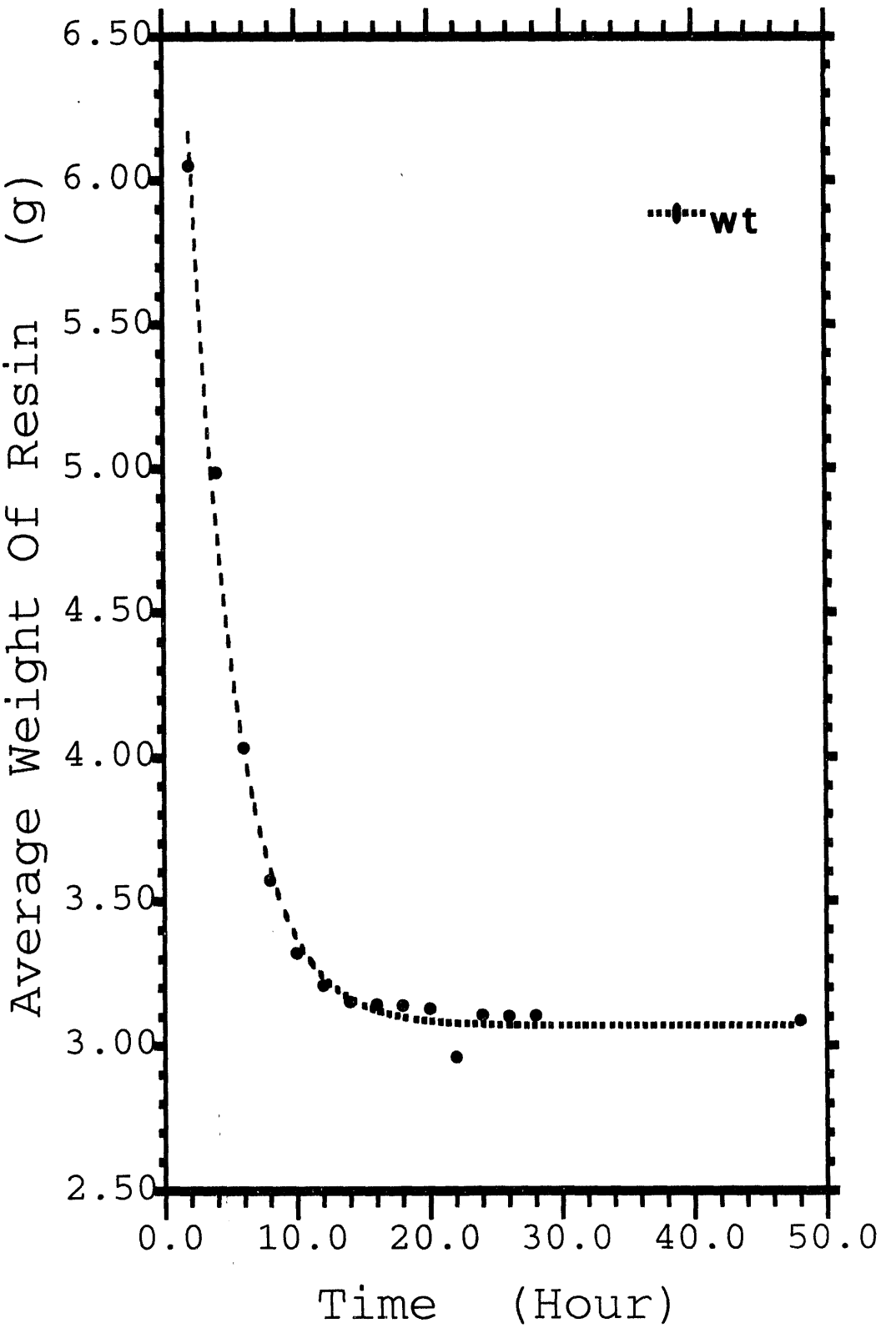
Table XXII

Mean and Standard Deviation of Resin Weights Dried at 60°C

Time	Mean	Standard deviation
2 hours	6.0515 g	0.2290 g
4 hours	4.9874 g	0.3243 g
6 hours	4.0341 g	0.4783 g
8 hours	3.5719 g	0.5698 g
10 hours	3.3204 g	0.3475 g
12 hours	3.2078 g	0.2104 g
14 hours	3.1519 g	0.1273 g
16 hours	3.1431 g	0.1140 g
18 hours	3.1387 g	0.1064 g
20 hours	3.1281 g	0.1067 g
22 hours	2.9606 g	0.0025 g
24 hours	3.1097 g	0.4854 g
26 hours	3.1030 g	0.4862 g
28 hours	3.1043 g	0.4864 g
48 hours	3.0857 g	0.4840 g

Figure 7

The drying curve of the Relliex-HPQ™ resin at 60°C as a Function of Time. The dashed curve came from an arbitrary polynomial fitting.


6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
Average Weight Of Resin (g)
wt
0.0
10.0
20.0
30.0
40.0
50.0
Time (Hour)

slow drying mechanism of the resin since the resin layer at the bottom of the small beaker appeared to be too thick.

From the data reported above, a minimum of 28 hours will be required to dry the resin to a constant weight. However, a 36 to 48-hour drying period is recommended to ensure reproducibility.

Data for the resin dried at 60°C and at 110°C (in a vacuum oven) is reported in Table XXIII. The raw data shows that the resin dried at 60°C reaches a constant weight after 48 hours and the resin dried at 110°C (in a vacuum oven) reaches a constant weight after 96 hours. Further experiments show that the relationship between the volume of the wet resin after aspiration and the weight of the resin dried at 60°C is (1.958 ± 0.094) mL/g (*35*). For the resin dried at 110°C, the volume-weight ratio is (2.112 ± 0.101) mL/g. When the resin already dried at 60°C was dried again at 110°C, the percent weight loss is (7.5844 ± 0.4304)% (*29*). The **weight ratio (WR)** between the resin dried at these two different temperatures is (0.9271 ± 0.0053) (*29*), which was calculated according to the following equation.

$$WR = \frac{\text{weight } 110^{\circ}C \text{ resin}}{\text{weight } 60^{\circ}C \text{ resin}} \qquad (11)$$

CALIBRATION OF ELECTRODE

The calibration procedure of the bromide ion-selective electrode was repeated several times until reproducible data

Table XXIII

Weight Ratio Conversion Data

Sample Number	Resin Weight (g) 60°C	Resin Weight (g) 110°C	Weight* Difference (g)	Percent** Difference
1	4.3277	3.9887	0.3390	7.8333
2	4.5709	4.2207	0.3502	7.6616
3	4.7378	4.4091	0.3288	6.9389
4	4.7225	4.3439	0.3786	8.0170
5	4.4397	4.1021	0.3376	7.6042
6	4.2590	3.9511	0.3097	7.2295
7	4.5605	4.2458	0.3147	6.9006
8	4.8604	4.4629	0.3975	8.1783
9	4.5961	4.2409	0.3552	7.7283
10	4.7803	4.4097	0.3706	7.5844
Average	**4.5855**	**4.2375**	**0.3480**	**7.5844**
Standard Deviation	**0.1873**	**0.1776**	**0.0283**	**0.4304**

* Weight difference calculated by : (60°C "weight") - (110°C "weight").
** Percent calculated by : ("weight" difference)/(110°C "weight").

extreme care in order to avoid any possible bromide contamination.

The first calibration curve matched the standard calibration curve reported in the electrode manual very closely and is shown in Figure 8. The correlation coefficient of the calibration curve was 0.9999 and the slope of the calibration curve was 58.792 mV per tenth-fold of the bromide concentration.

The effect of the ionic strength and the acidity on the calibration curves was established by running calibration curves at three different acidities. Figure 9 shows the bromide calibration curves under 4.000 M HNO_3, 1.000 M HNO_3, and 0.1000 M HNO_3. The ionic strengths of the solutions used for these three calibration curves were 4.000 M, 1.000 M, and 1.000 M, respectively. The slopes of the three calibration curves were all in a very narrow range between 58.057 to 59.028, which indicate that the acidity and the ionic strength have very little effect on the sensitivity of the bromide ion-selective electrode.

The performance of the bromide ion-selective electrode in diluted acidic solutions was also investigated. Figure 10 shows the calibration curves under 4.000 M, 1.000 M, 0.1000 M and 0.01000 M HNO_3. In the 0.1000-M HNO_3 and 0.01000-M HNO_3 calibration curves, the ionic strength of the standard solutions was controlled at 1.000 M. The bromide potential readings of the first two calibration curves, where the ionic strength was dictated by its acidity, shifted dramatically.

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Figure 8

Bromide calibration curve for [HNO_3] = .01000 M and an ionic strength of 1.000 M.

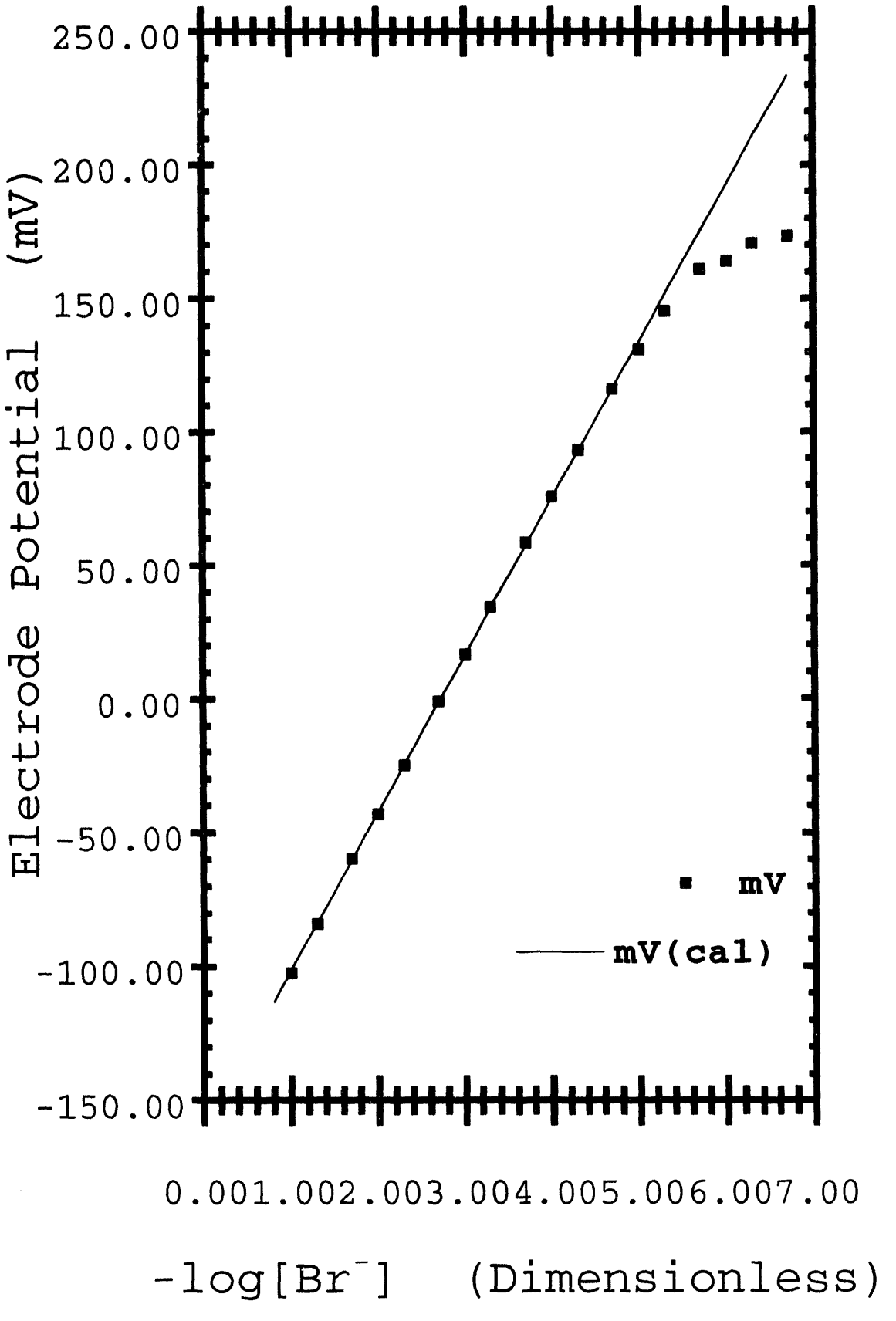

250.00
200.00
150.00
100.00
50.00
0.00
-50.00
-100.00
-150.00
Electrode Potential (mV)
mV
mV(cal)
0.001.002.003.004.005.006.007.00
-log[Br⁻] (Dimensionless)

Figure 9

Bromide calibration curves under 4.000 M, 1.000 M, and 0.1000M HNO_3, where I. S. stands for ionic strength. (Δ - I. S. = 1.0 M, $[HNO_3]$ = 0.1000 M, $[NaNO_3]$ = 0.90 M; o - I. S. = 1.0 M, $[HNO_3]$ = 1.000 M,; • - I. S. = 4.0 M, $[HNO_3]$ = 0.4000 M)

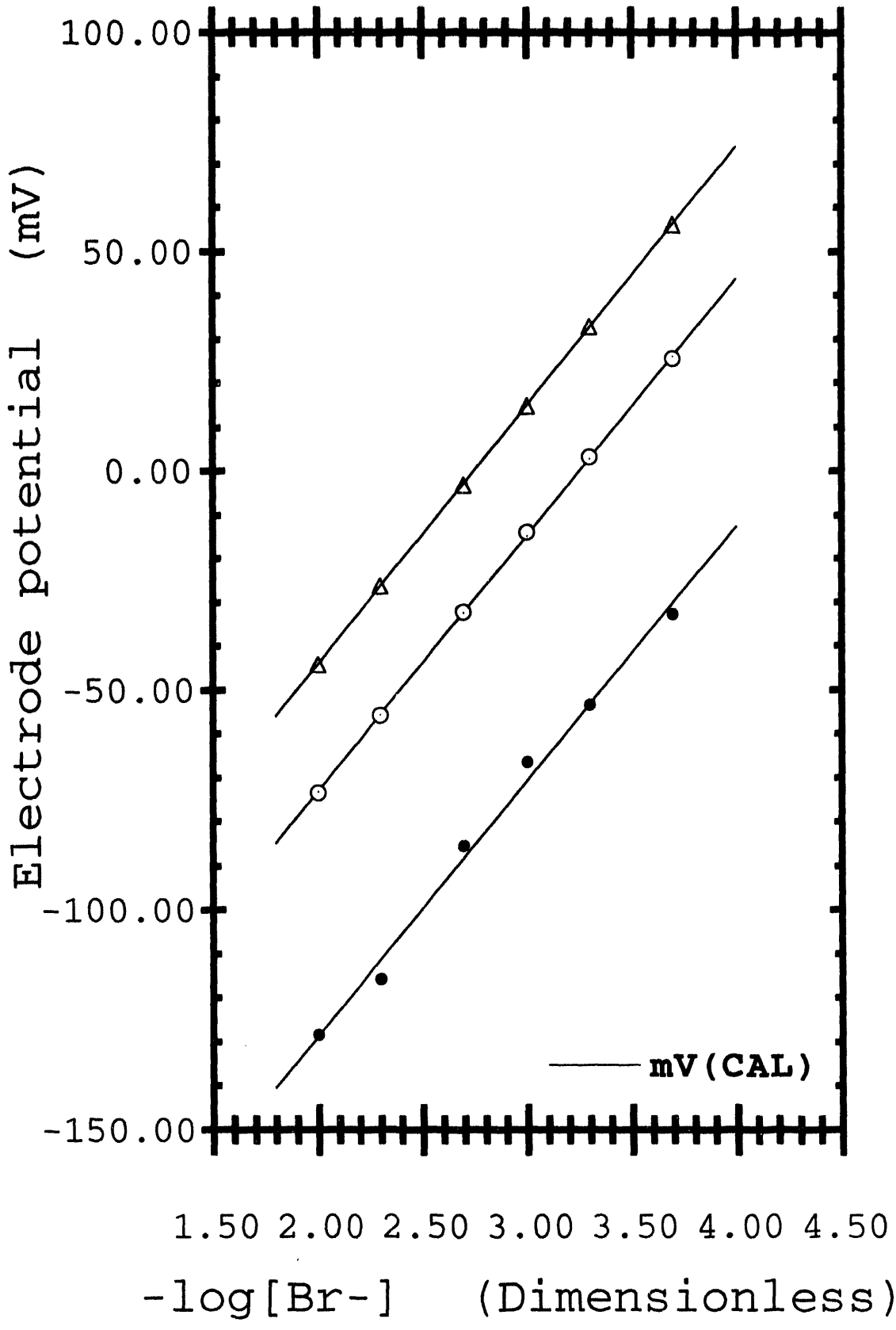
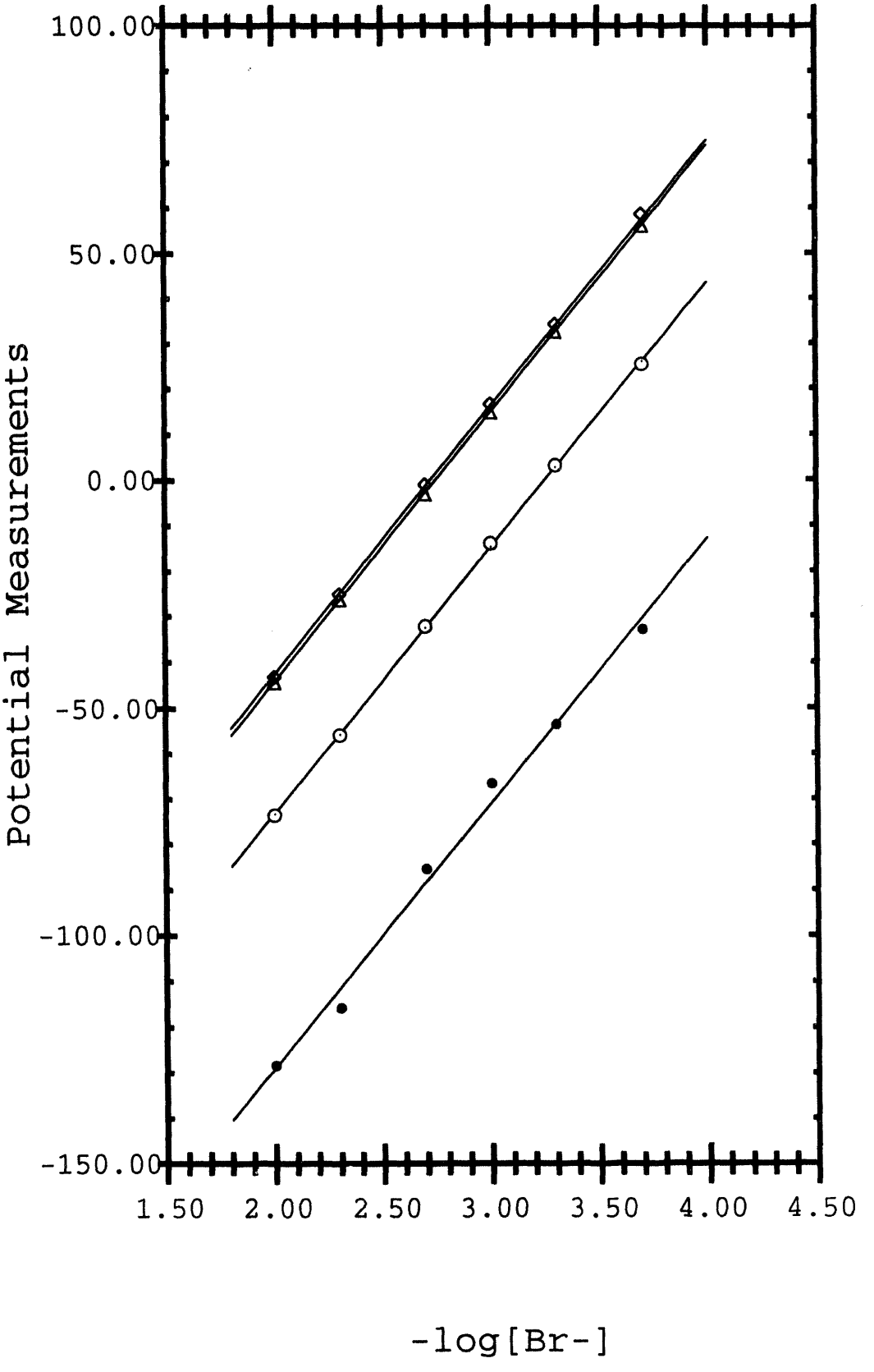

100.00
50.00
0.00
-50.00
-100.00
-150.00
Electrode potential (mV)
mV(CAL)
1.50 2.00 2.50 3.00 3.50 4.00 4.50
-log[Br-] (Dimensionless)

Figure 10

Bromide calibration curves under 4.000 M, 1.000 M, 0.1000 M, and 0.01000 M HNO_3, and 0.1000 M HNO_3, where I. S. stands for ionic strength. (◊ - I.S. = 1.000 M, [HNO_3] = 0.01000 M, [$NaNO_3$] = 0.99 M; Δ - I.S. = 1.000 M, [HNO_3] = 0.1000 M, [$NaNO_3$] = 0.90 M; o - I. S. = 1.000 M, [HNO_3] = 1.0000 M,; • - I. S. = 4.000 M, [HNO_3] = 4.000 M)


100.00
50.00
0.00
-50.00
-100.00
-150.00
Potential Measurements
1.50
2.00
2.50
3.00
3.50
4.00
4.50
-log[Br-]

However, the last two curves where the ionic strength was controlled by the addition of $NaNO_3$ were nearly identical. This experiment indicates that the concentration of the hydronium ion may change the bromide potential readings but not affect the sensitivity of the ion-selective electrode.

SORPTION KINETICS

The sorption kinetics of the Relliex™-HPQ resin in aqueous nitrate medium was investigated using bromide as the model ion. In each K_d measurement, after the bromide was loaded into the reaction cell, the bromide potential readings were taken every 15 seconds for 30 minutes. Table XXIV shows the data of a typical bromide loading process. The data is also plotted in Figure 11.

The plot shows that the concentration of the bromide ion decreases at the beginning and reaches the minimum within about 10 minutes. The bromide concentration then drifts upward but not very significantly. In fact, the potential readings changed less than 2 millivolts toward the end of the sorption reaction.

All of the sorption kinetics experiments showed that the half-life of the bromide sorption in aqueous nitrate medium was less than a minute. The sorption reaction generally finished in about 30 minutes. This fast kinetics might be due to the similar sizes of the bromide and the nitrate ions.

Table XXIV

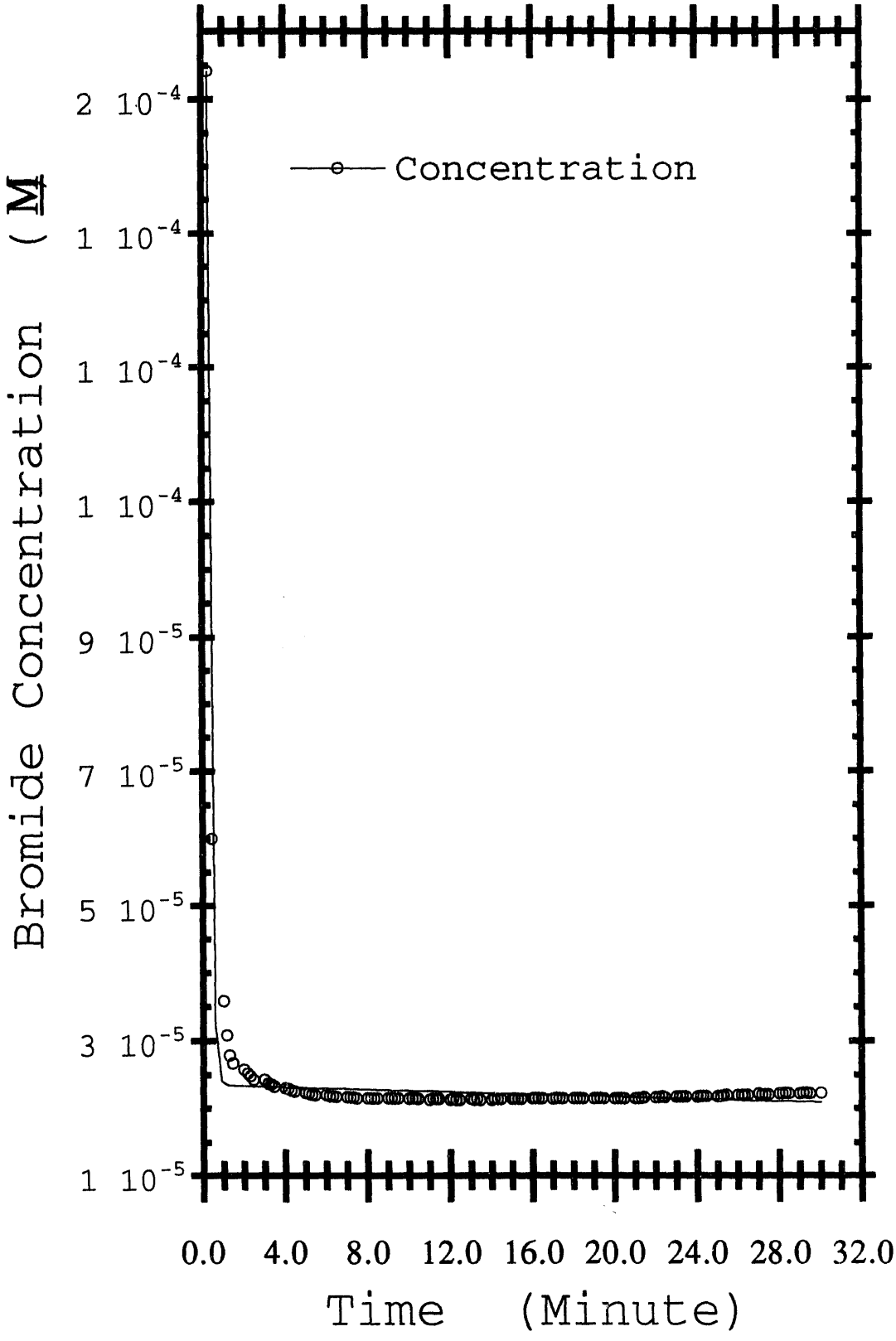
Bromide Potential Readings as a Function of Time

Time*	mV§	Time*	mV§	Time*	mV§
0.15	166.2	10.15	113.9	20.15	113.8
0.30	60.5	10.30	113.9	20.30	113.8
0.45	87.8	10.45	114.0	20.45	113.8
1.00	100.9	11.00	114.1	21.00	113.9
1.15	104.7	11.15	114.0	21.15	113.8
1.30	107.3	11.30	114.0	21.30	113.8
1.45	108.4	11.45	114.0	21.45	113.7
2.00	109.3	12.00	114.1	22.00	113.7
2.15	109.9	12.15	114.0	22.15	113.7
2.30	110.3	12.30	144.1	22.30	113.6
2.45	110.8	12.45	114.1	22.45	113.7
3.00	110.8	13.00	114.0	23.00	113.6
3.15	111.4	13.15	114.1	23.15	113.6
3.30	111.6	13.30	114.0	23.30	113.6
3.45	111.9	13.45	114.1	23.45	113.6
4.00	112.1	14.00	114.1	24.00	113.6
4.15	112.3	14.15	114.0	24.15	113.5
4.30	112.5	14.30	114.0	24.30	113.5
4.45	112.7	14.45	114.0	24.45	113.5
5.00	112.9	15.00	114.0	25.00	113.5
5.15	113.0	15.15	114.0	25.15	113.5
5.30	113.2	15.30	114.0	25.30	113.4
5.45	113.3	15.45	114.0	25.45	113.3
6.00	113.3	16.00	113.9	26.00	113.3
6.15	113.5	16.15	113.9	26.15	113.3
6.30	113.5	16.30	113.9	26.30	113.4
6.45	113.6	16.45	113.9	26.45	113.3
7.00	113.7	17.00	114.0	27.00	113.1
7.15	113.7	17.15	113.9	27.15	113.2
7.30	113.7	17.30	113.8	27.30	113.2
7.45	113.8	17.45	113.8	27.45	113.2
8.00	113.8	18.00	113.8	28.00	113.1
8.15	113.9	18.15	113.8	28.15	113.0
8.30	113.9	18.30	113.9	28.30	112.9
8.45	113.9	18.45	113.8	28.45	113.0
9.00	113.9	19.00	113.8	29.00	113.0
9.15	113.9	19.15	113.9	29.15	112.9
9.30	113.9	19.30	113.9	29.30	112.9
9.45	113.9	19.45	113.8	29.45	113.0
10.00	114.0	20.00	113.8	30.00	112.9

* The time was measured in units of minute.
§ The bromide potential readings are in units of mV.

Figure 11

Sorption kinetics plot. The solid line came from an arbitrary double exponential fitting.


Concentration
Bromide Concentration (M
2 10-4
1 10-4
1 10-4
1 10-4
9 10-5
7 10-5
5 10-5
3 10-5
1 10-5
0.0 4.0 8.0 12.0 16.0 20.0 24.0 28.0 32.0
Time (Minute)

K_d MEASUREMENTS

The pH values and the bromide potential readings of the first set of K_d measurements are listed in Table XXV. The data from the reaction cells are listed according to the percent total capacity (%TC) of the resin in the cells. The readings taken before and after the bromide ions were loaded are listed side by side. The pH and the bromide potential readings of the dummy cells are included in parentheses and the data from the ISA measurements are listed on the lower half of the Table with the same format. Dashed lines indicate that such measurements were not made. Table XXVI to Table XXXII listed the readings for the rest of the seven sets of K_d measurements.

The percent loading (%L) of the bromide ions for all the experiments are given in Table XXXIII and the corresponding K_d values are given in Table XXXIV. All values are listed according to the percent total capacity of the resin and the ionic strength of the solutions prepared. Again the data from the ISA measurements is listed on the bottom half of the tables.

Table XXXIII shows that the percent loading of the bromide ions generally increases when the percent total capacity (i.e., the amount of the bromide ions added) decreases. This indicates that the HPQ resin is more applicable at low loadings. It is worth noting that, in Table XXXIV, the K_d values stay roughly the same. This may be attributed to the similar sizes of the bromide and the

Table XXV

Bromide Potential and pH Readings of the First Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell[§]	20.0	----- (-----)*	115.9 (174.0)*	----- (-----)*	-68.4 (-79.0)*
	10.0	----- (-----)*	100.3 (174.6)*	----- (-----)*	-57.7 (-60.7)*
	2.00	----- (-----)*	97.3 (169.6)*	----- (-----)*	-15.9 (-18.7)*
	0.20	----- (-----)*	87.0 (175.6)*	----- (-----)*	33.4 (37.6)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*

§ Resin was eluted with blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXVI

Bromide Potential and pH Readings of the Second Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell§	20.0	5.228 (1.786)*	94.3 (174.8)*	4.812 (1.838)*	-77.2 (-81.5)*
	10.0	5.364 (1.778)*	75.4 (176.8)*	5.173 (1.758)*	-59.3 (-63.3)*
	2.00	----- (1.739)*	129.1 (174.6)*	5.174 (1.741)*	-15.9 (-21.2)*
	0.20	----- (1.754)*	118.8 (173.8)*	4.465 (1.751)*	38.0 (36.2)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	----- (-----)*

§ Resin was eluted with deionized water and blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXVII

Bromide Potential and pH Readings of the Third Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell§	20.0	3.892 (1.842)*	137.4 (109.5)*	3.761 (1.751)*	-107.3 (-115.0)*
	10.0	3.589 (1.840)*	163.1 (149.2)*	3.716 (1.746)*	-89.9 (-96.5)*
	2.00	3.387 (1.851)*	162.4 (160.7)*	3.792 (1.773)*	33.5 (-5.4)*
	0.20	3.792 (1.884)*	156.6 (166.2)*	3.792 (1.809)*	10.7 (2.6)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	-89.6 (-94.3)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	-69.9 (-76.7)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	-29.0 (-35.4)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	29.8 (12.1)*

§ Resin was eluted with deionized water and blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXVIII

Bromide Potential and pH Readings of the Fourth Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell§	20.0	3.603 (1.958)*	172.2 (171.8)*	3.623 (1.878)*	-84.1 (-95.4)*
	10.0	3.226 (1.904)*	174.8 (176.5)*	3.679 (1.898)*	-62.6 (-77.0)*
	2.00	3.320 (1.966)*	175.4 (165.1)*	3.748 (1.880)*	-21.1 (-34.4)*
	0.20	2.987 (1.956)*	174.8 (162.8)*	3.660 (1.886)*	38.7 (25.1)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	-57.4 (-71.9)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	-36.8 (-55.3)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	3.8 (-7.8)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	52.4 (46.0)*

§ Resin was eluted with deionized water and blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXIX

Bromide Potential and pH Readings of the Fifth Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell[$]	20.0	----- (1.944)*	121.7 (121.2)*	3.461 (1.885)*	-59.0 (-83.2)*
	10.0	3.326 (-----)*	131.4 (130.3)*	3.783 (1.916)*	-42.3 (-64.6)*
	2.00	3.703 (-----)*	111.7 (129.7)*	3.731 (1.923)*	0.3 (-21.5)*
	0.20	----- (-----)*	132.2 (128.8)*	3.628 (1.852)*	59.0 (37.4)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	-29.1 (-54.8)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	-12.8 (-37.4)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	28.4 (3.4)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	85.7 (50.1)*

$ Resin was eluted with deionized water and blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXX

Bromide Potential and pH Readings of the Sixth Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell§	20.0	3.465 (2.125)*	158.3 (163.6)*	3.338 (2.049)*	-24.9 (-63.8)*
	10.0	3.201 (2.072)*	165.0 (168.5)*	3.206 (2.187)*	-7.3 (-45.2)*
	2.00	3.159 (2.114)*	173.5 (159.6)*	3.130 (2.016)*	-48.7 (-55.0)*
	0.20	2.874 (2.178)*	174.8 (162.8)*	3.148 (2.023)*	90.6 (54.3)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	10.0 (-29.5)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	27.0 (-11.9)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	39.9 (28.5)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	118.3 (83.1)*

§ Resin was eluted with deionized water and blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXXI

Bromide Potential and pH Readings of the Seventh Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell[§]	20.0	2.727 (2.105)*	172.2 (171.8)*	2.731 (2.023)*	30.4 (-33.5)*
	10.0	2.611 (2.076)*	174.9 (162.9)*	2.764 (2.013)*	48.3 (-14.7)*
	2.00	2.716 (2.136)*	157.7 (94.2)*	2.736 (2.063)*	86.5 (24.7)*
	0.20	2.686 (2.132)*	169.0 (150.8)*	2.658 (2.065)*	138.8 (82.9)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	68.6 (4.0)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	87.9 (22.1)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	115.1 (62.6)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	129.8 (120.0)*

§ Resin was eluted with deionized water and blank solution.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXXII

Bromide Potential and pH Readings of the Eighth Set of K_d Measurements

	Percent Total Capacity	Before Bromide Added		After Bromide Added	
		pH	mV	pH	mV
Reaction Cell[§]	20.0	------ (------)*	167.7 (63.2)*	----- (-----)*	-64.3 (-96.8)*
	10.0	------ (------)*	165.0 (69.7)*	----- (-----)*	-36.6 (-82.3)*
	2.00	------ (------)*	136.1 (95.3)*	----- (-----)*	30.8 (-43.8)*
	0.20	------ (------)*	166.2 (98.8)*	----- (-----)*	112.8 (13.9)*
ISA Measurement	20.0	----- (-----)*	----- (-----)*	----- (-----)*	-30.3 (-62.4)*
	10.0	----- (-----)*	----- (-----)*	----- (-----)*	1.4 (-43.8)*
	2.00	----- (-----)*	----- (-----)*	----- (-----)*	43.8 (2.9)*
	0.20	----- (-----)*	----- (-----)*	----- (-----)*	145.5 (55.8)*

§ Resin was eluted with deionized water.
* The number in parentheses is for the dummy cell.
--- Value not measured.

Table XXXIII

The Percent Loading of Reaction and ISA cells at Various Ionic Strengths

Ionic* Strength	% Total Capcity			
	20.0	10.0	2.00	0.20
Reaction Cell				
0.50	25.8955	22.6540	21.7455	27.0402
0.20	35.5842	42.9057	40.1759	41.1000
0.10	66.0112	58.0187	57.3599	56.8592
0.05	77.9981	77.1248	77.9981	75.6550
0.02	91.6847	91.3883	90.9765	88.6472
uncontrolled†	77.7745	83.1143	94.5171	97.8706
ISA Cell				
0.50	25.0252	22.9544	22.0495	49.7876
0.20	43.1275	51.3269	36.3319	22.0495
0.10	62.3533	61.6135	62.2065	74.9826
0.05	78.5060	77.9981	35.8344	74.5901
0.02	91.9082	92.2774	87.0108	31.7115
uncontrolled†	71.3316	82.7825	95.1403	96.9537

* The ionic strength of the solution.
† In the uncontrolled loadings, the ionic strength was not controlled by $NaNO_3$.

Table XXXIV

K_d of Reaction and ISA cells at Various Ionic Strengths

Ionic* Strength	% Total Capacity			
	20.0	10.0	2.00	0.20
Reaction Cell				
0.50*	1.7472	1.4645	1.3894	1.8531
0.10*	7.8242	6.9101	6.7261	6.5900
0.05*	17.7253	16.8578	17.7253	15.5381
0.02*	55.1301	53.0602	50.4108	39.0481
uncontrolled†	12.7145	24.6109	86.1921	229.8052
ISA Cell				
0.50*	1.6689	1.4897	1.4143	4.9577
0.20*	3.7916	5.2726	2.8532	1.4143
0.10*	8.2814	8.0254	8.2298	14.9861
0.05*	18.2622	17.7253	2.7923	14.6774
0.02*	56.7908	59.7453	33.5828	2.3219
uncontrolled†	12.4407	24.0402	97.8863	159.1335

* The ionic strength of the solution.
† In the umcontrolled loadings, the ionic strength was not controlled by $NaNO_3$.

nitrate ions since the nitrate concentrations are roughly the same in each set of the measurements.

Table XXXIII shows that the percent loading of the bromide ions increases as the ionic strength decreases. This can be explained by the fact that when the ionic strength decreases, the concentration of the nitrate ions in the solution also decreases, hence there is less competition from the nitrate ions to the ionogenic groups in the resin. Accordingly, the K_d value also increases as the ionic strength of the solution decreases.

The pH change of the reaction cells before and after the addition of the bromide ions was insignificant. This may be, again, due to the similar sizes of the bromide and the nitrate ions. However, there is a general trend that, before the bromide was added, the pH values of the reaction cells decrease as the ionic strength of the solutions increases. This is a well-known phenomenon as generally the pK_a of the weak ionogenic groups decreases when the ionic strength increases (*2*).

The data obtained from the ISA measurements were practically the same as those from the reaction cells. However, it appears that the ISA measurements are more susceptible to bromide contamination. Nonetheless, these measurements have confirmed the observations and explanations made above. In fact, the consistency also indicates that the bromide potential readings can be taken without adding the ionic strength adjuster. This may imply that the amount of

work needed for future K_d measurements can be dramatically reduced.

A close examination of Table XXXIV also reveals that the K_d values are generally very small. This indicates that the HPQ resin does not select the bromide ions very much over the nitrate ions, compared with the difference in selectivities to the two ions.

Since the quaternary-amine based anion exchange resins usually show much higher preference to the bromide ion, this may imply that the HPQ resin is more applicable when bromide-metal complexes are involved in the separation.

CHAPTER VI

CONCLUSION AND FUTURE PROSPECTIVES

CONCLUSION

In this research, new experimental techniques for the determination of the distribution coefficient, K_d, of the Rellex™-HPQ resin in aqueous nitrate solutions were developed. Bromide was employed as the model ion and its concentration was measured by a bromide ion-selective electrode coupled with a double-junction reference electrode. In addition, the sorption kinetics of the HPQ resin was investigated with the same techniques.

For the pre-treatment of the HPQ resin in its nitrate form, a few conclusions were reached. First, a minimum of 24-26 hours is required to dry the resin to a constant weight at 60°C. However, a 36 to 48-hour drying period is recommended to ensure reproducibility in the determination of the resin weight. Second, the HPQ resin can be dried to a constant weight at 110°C in 96 hours. Third, when the resin already dried at 60°C was dried again at 110°C, the percent weight loss is $(7.5844 \pm 0.4304)\%$.

For a more reproducible K_d determination, it is found that the HPQ resin should be eluted with deionized water to about 3.5 pH before it was eluted with 10 bed volumes of the

blank solution at the desired acidity and ionic strength. This elution sequence ensured a consistent pH in the reaction cells. Also, to avoid bromide contamination, all glassware must be soaked in 1.0 M HNO_3 overnight.

The applicability of the bromide ion-selective electrode at different acidity and ionic strengths also have been examined. It is found that neither the acidity nor the ionic strength has any impact on the sensitivity of the electrode. However, the acidity of the solution may affect the bromide potential readings dramatically.

From the sorption kinetics experiments, it is clear that the half-life of the bromide sorption in aqueous nitrate medium was less than a minute. The sorption reaction generally finished in about 30 minutes.

All K_d values were reported in the previous chapter. This shows that the HPQ resin does not select the bromide ions very much over the nitrate ions. The percent loading of the bromide ions generally increases when the percent total capacity (i.e., the amount of the bromide ions added) decreases. However, it decreases as the ionic strength of the solution increases. The pH change of the reaction cells before and after the addition of the bromide ions was insignificant. The data obtained from the ISA measurements were practically the same as those from the reaction cells. This consistency indicates that the bromide potential readings can be taken without adding the ionic strength adjuster.

FUTURE PROSPECTIVES

In the future, the K_d values will be modeled as a function of pH and the bromide isotherms at various ionic strength will be constructed. Also, the sorption capacity of the HPQ resin under various pH will be measured. In addition, more investigations will be performed with other ions such as fluoride and carbonate.

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