Observations on the Interaction

of Ion Exchange Resins

with some Cupric Compounds

Thesis by

Thomas Edwin Ferington

In Partial Fulfillment of the Requirements

for the Degree of

Master of Science

California Institute of Technology

Pasadena, California

1951

Acknowledgement

The author wishes to express his sincere appreciation and gratitude to Dr. Norman Davidson, who suggested this work and under whose guidance it was carried out.

Abstract

The interaction of the Sulfonic Acid Resin, Nalcite HCR, with Cu^{II} halide solutions was studied in hope of obtaining dissociation constants for the complex ions CuX^+. The fact that CuX^+ is absorbed by the resin to an appreciable extent prevented the attainment of this goal. It was found in the case of CuF^+ that the complex ion is absorbed even more strongly than Cu^{++}. The presence of a $Cu^{++}-F^-$ complex was indicated by spectrophotometric observations.

The action of the carboxylic acid resin, IRC-50 was studied in a column. It was found that the volume of the resin in the Cu^{++} salt form depended on the salt with which the resin was treated. In the case of solutions of $Cu(OAc)_2$ it was found that $Cu(OAc)^+$ was taken into the resin as well as Cu^{++}.

A titration curve for IRC - 50 with NaOH in solutions of ionic strength one is given.
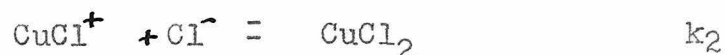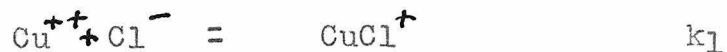
Table of Contents

Part I

Interactions of a strong acid Resin with solutions

containing ions of the type CuX^+

Introduction

McConnell and Davidson (1) have determined the constants for the reactions

$$Cu^{++} + Cl^- = CuCl^+ \qquad k_1$$

$$CuCl^+ + Cl^- = CuCl_2 \qquad k_2$$

to be: $\quad k_1 = 1.30 \pm .03 \qquad 25.2^\circ$ C

$\qquad k_2 = .23 \pm .15$

by spectrophotometric means, at $\mu = 1$. Näsänsen (2), however, gives $k_1 = .34$ under the same conditions.

Schubert (3), Schubert and Richter (4) and Schubert, Russell and Myers (5) have studied the dissociation constants of several complex ions, which are neutral or have a negative charge, by means of cation exchange resins using tracer amounts of cation in solution. It was hoped that by using a similar method we could determine the constant for $CuCl^+$ with sufficient accuracy to warrant a decision between the two values mentioned above.

Since it has been observed (6,7) that divalent ions are much more strongly taken up by an ion exchanger than monovalent ones, we made the assumption that the absorption of $CuCl^+$ by the resin would be negligible. In such a case the situation in the

solution which is in contact with the resin is as follows.

There are two equilibria competing for Cu^{++}

$$(1) \quad Cu^{++} + 2NaR = CuR_2 + 2Na^+ \quad k_R'$$

$$(2) \quad Cu^{++} + Cl^- = CuCl^+ \quad k_i$$
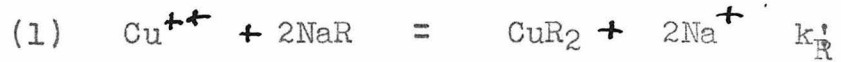
where NaR refers to the sodium salt form of the resin and CuR_2 to the copper salt form.

$$k_R' = \frac{(CuR_2)}{(Cu^{++})} \frac{(Na^+)^2}{(NaR)^2}$$

but the amounts of Cu^{++} and CuR_2 which are involved are so small that the ratio $(Na^+)^2/(NaR)^2$ is constant and we may write

$$k_R = \frac{(CuR_2)}{(Cu^{++})}$$

Let: c_O = the initial amount of Cu^{++} present in the solution in any form.

c_f = the final amount of Cu^{++} in solution in any form.

$c_O - c_f = \Delta c$ = amount of Cu^{++} taken up by the resin.

$c_f = (Cu^{++}) + k_i(Cu^{++})(Cl^-) = (Cu^{++})(1 + k_i(Cl^-))$

then

$$k_R = \frac{(CuR_2)}{(Cu^{++})(1 + k_i(Cl^-))} = \frac{k_R^O}{1 + k_i(Cl^-)}$$

where k_R^O refers to the case in which $(Cl^-) = 0$

so

$$k_i = \frac{\frac{k_R^O}{k_R} - 1}{(Cl^-)} = \frac{\frac{c^O v^O c_f w}{c_f w^O c v} - 1}{(Cl^-)}$$

v, the volume of the solution and w, the weight of the resin were kept constant in all experiments.

Experimental

The experiments were carried out at unit ionic strength, using sodium perchlorate made by neutralizing perchloric acid with carbonate free NaOH to maintain this strength.

The sulfonic acid resin used was Nalcite HCR distributed by the National Aluminate Corporation (also available as Dowex 50 (8)). It was converted to the sodium form for use in these experiments by washing with a saturated solution of NaCl until the effluent liquid was neutral and then washing with distilled water until chloride free. The resin was dried in air at room temperature to constant weight and used in that state. The capacity of the resin for Cu^{++} was determined by saturating a small column of it with a solution of 0.5F $Cu(ClO_4)_2$. The Cu^{++} was washed out with NaCl solution and determined. As a check the column was then saturated with 0.5F $CuCl_2$ solution and the Cu^{++} again determined. The capacity of both the H^+ and Na^+ forms was 3.75 meq. of Cu^{++} per gram of air dried resin.

The method of analysis for Cu^{++} was that of Moeller (9), which uses the yellow complex formed by Cu^{++} with 8-hydroxyquinoline solutions in chloroform.

Optical density readings were taken on a Beckman Model DU Spectrophotometer.

The chemicals used were all reagent grade.

The solutions to be studied were placed in tightly stoppered test tubes with the resin and fastened to a slowly rotating shaft so that they were thoroughly mixed for 24 hours. It was found that the air in the mixing apparatus varied from 26° to 28° during this period.

It has been pointed out in a recent article (10) that the dry resin when placed in solution takes up some water in swelling and thus changes the concentration of the final solution even before any exchange takes place. This effect makes the final observed concentration larger than it would be if all of the water were still in the solution. When 2 g. of my air dried resin were placed on a watch glass in a desiccator with a beaker of $1F$ $NaClO_4$ aqueous solution (vapor pressure about 17mm at 30°) it was found that it had gained 0.653 g. in weight after 16 days when equilibrium was nearly attained. I have used this value in computing c_f(corr.) in the tables.

Results

The precision of the method may be judged from the determination of $\Delta c^{\circ}/c_f^{\circ}$ as given in Table I.

Table I

c_O^0 (F)	c_f^0 (F)	c_f^0(corr.)(F)	Δc^0(F)	$\dfrac{\Delta c^0}{c_f^0}$
5.06×10^{-5}	2.53×10^{-5}	2.49×10^{-5}	2.57×10^{-5}	1.03
2.00×10^{-4}	1.02×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.00
5.06×10^{-5}	2.50×10^{-5}	2.46×10^{-5}	2.60×10^{-5}	1.05
5.06×10^{-5}	2.64×10^{-5}	2.60×10^{-5}	2.46×10^{-5}	0.95
5.06×10^{-5}	2.61×10^{-5}	2.56×10^{-5}	2.66×10^{-5}	1.04

Average value of $\Delta c^0 / c_f^0 = 1.01 \pm .03$

The results of the study of the $Cu^{++} - Cl^{-}$ solutions are shown in Table II. In the first column of the table the first number in each group refers to the Cu^{++} concentration, ~~and~~ the second to the $NaClO_4$ concentration and the third to the chloride ion (NaCl) concentration. All other figures refer to concentration of Cu^{++}.

Table II

c_O(F)	c_f(F)	c_f(corr.)	Δc(F)	$\dfrac{\Delta c}{c_f}$	k_i
5.28×10^{-5} .75 .25	2.87×10^{-5}	2.82×10^{-5}	2.46×10^{-5}	.873	.65
5.66×10^{-5} .50 .50	3.39×10^{-5}	3.34×10^{-5}	2.32×10^{-5}	.695	.91
5.58×10^{-5} .25 .75	3.61×10^{-5}	3.54×10^{-5}	2.04×10^{-5}	.576	1.00
5.30×10^{-5} .06 .94	3.39×10^{-5}	3.34×10^{-5}	1.95×10^{-5}	.585	.78

Table II (cont.)

c_o(F)	c_f(F)	c_f(corr.)	Δc(F)	$\dfrac{\Delta c}{c_f}$	k_i
2.00×10^{-4} .75 .25	1.10×10^{-4}	1.08×10^{-4}	$.92 \times 10^{-4}$	.852	.74
2.02×10^{-4} .50 .50	1.20×10^{-4}	1.18×10^{-4}	$.84 \times 10^{-4}$	.712	.84
1.99×10^{-4} .25 .75	1.23×10^{-4}	1.21×10^{-4}	$.68 \times 10^{-4}$	.562	1.06
1.80×10^{-4} .06 .94	1.19×10^{-4}	1.17×10^{-4}	$.61 \times 10^{-4}$	.521	1.00

Average value of k_i .87±.12

In these experiments as in all those that follow 2 g.
of resin were used in 40 ml. of solution.

The value of k_i is fairly constant, but unfor-
tunately it is almost exactly halfway between the two
values mentioned above so it does not help to decide
between them. It seems that the absorption of $CuCl^+$
by the resin is great enough to interfere with any
quantitative result in this case.

$Cu^{++}-Br^-$ and $Cu^{++}-F^-$ solutions were also studied
in the hope of obtaining at least a series which would
give the relative complexing power of Br^-, Cl^- and F^-
for Cu^{++} in aqueous solution at unit ionic strength.
The experimental methods were the same as those used
above in the case of Cl^-. The results of the study
of Br^- are given in Table III. In the first column
the arrangement is the same as in Table II.

Table III

$c_o(F)$	$c_f(F)$	c_f(corr.)	$\Delta c(F)$	$\dfrac{\Delta c}{c_f}$	k_i
5.16×10^{-5} .75 .25	2.64×10^{-5}	2.59×10^{-5}	2.57×10^{-5}	.992	.07
5.63×10^{-5} .50 .50	2.95×10^{-5}	2.90×10^{-5}	2.73×10^{-5}	.942	.14
5.06×10^{-5} .25 .75	2.89×10^{-5}	2.84×10^{-5}	2.22×10^{-5}	.782	.39
5.19×10^{-5} .06 .94	2.84×10^{-5}	2.79×10^{-5}	2.40×10^{-5}	.825	.18
1.93×10^{-4} .75 .25	1.21×10^{-4}	1.19×10^{-4}	$.74 \times 10^{-4}$	.621	(2.5)
2.04×10^{-4} .50 .50	1.34×10^{-4}	1.32×10^{-4}	$.72 \times 10^{-4}$	.545	(1.7)
1.94×10^{-4} .25 .75	1.24×10^{-4}	1.22×10^{-4}	$.72 \times 10^{-4}$	.590	(.95)
5.05×10^{-5} .75 .25	2.61×10^{-5}	2.56×10^{-5}	2.49×10^{-5}	.973	.16
5.27×10^{-5} .50 .50	3.86×10^{-5}	3.79×10^{-5}	1.48×10^{-5}	.390	(3.18)
4.94×10^{-5} .25 .75	2.66×10^{-5}	2.62×10^{-5}	2.32×10^{-5}	.886	.19
4.98×10^{-5} .06 .94	3.00×10^{-5}	2.95×10^{-5}	2.03×10^{-5}	.689	.50
1.85×10^{-4} .75 .25	1.02×10^{-4}	1.00×10^{-4}	$.85 \times 10^{-4}$	.85	(.76)

Table III (cont.)

$c_O(F)$	$c_f(F)$	c_f(corr.)	$\Delta c(F)$	$\dfrac{\Delta c}{c_f}$	k_i
1.81×10^{-4} .50 .50	1.02×10^{-4}	1.00×10^{-4}	$.81 \times 10^{-4}$	.81	.50
1.75×10^{-4} .25 .75	1.01×10^{-4}	$.99 \times 10^{-4}$	$.76 \times 10^{-4}$	.769	.42

Average value of k_i $.28 \neq .15$

The values in parentheses were left out in calculating the average value because they were so far away from the others. Three of them were done at the same time and under the same experimental conditions so apparently something interfered with that batch.

Again there is some constancy indicated, but the value does not compare well with that of $2.1 \neq .25$ obtained by P. Farrington (11) by spectrophotometric means.

The case of Cu^{++} - F^- solutions which was studied last was interesting because the results were so unexpected. It was impossible to prepare 1F solutions of NaF due to the limited solubility of the salt. Table IV gives the experimental results for this case. In the first column of the table, the first number in each group refers to the Cu^{++} concentration, the second number to the NaF and the third to the $NaClO_4$. All other figures refer to the concentration of Cu^{++}.

Table IV

$c_0(F)$	$c_f(F)$	$c_f(corr.)$	$\Delta c(F)$	$\dfrac{\Delta c}{c_f}$
4.76×10^{-5} .90	$.87 \times 10^{-5}$	$.86 \times 10^{-5}$	3.90×10^{-5}	4.54
5.05×10^{-5} .18 .80	2.32×10^{-5}	2.28×10^{-5}	2.77×10^{-5}	1.21
5.50×10^{-5} .54 .40	1.94×10^{-5}	1.91×10^{-5}	3.59×10^{-5}	1.88
5.29×10^{-5} .90	1.52×10^{-5}	1.49×10^{-5}	$*3.80 \times 10^{-5}$	2.54

*This value is a little small due to difficulties in the analysis.

The expectation in each of the above cases had been that the addition of a complexing agent to the solution would decrease the amount of copper taken up by the resin. This expectation was realized in the case of Cl^- and Br^-, but when F^- was added to the solution the amount of copper which was taken up was increased (compare Table I). This effect may be due to the presence of a copper fluoride positively charged complex which is more strongly absorbed in the resin than Cu^{++}. If CuF^+ has a smaller ionic radius than hydrated Cu^{++} this explanation is probably true, since it has been found that the affinity of a resin for a cation increases as the hydrated radius of the ion decreases (6). Another possible explanation for the effect would be that the F^- ion has some sort of unusual

influence on the resin and alters the equilibrium. This does not seem too likely.

A spectrophotometric study was made of the Cu^{++} - F^- system to see if a complex was present. The result is presented on Graph I. Curve 1 is obtained from a 0.01215 F $Cu(ClO_4)_2$ solution; curve 2 from a 0.9 F NaF solution; curve 3 was obtained by adding curves 1 and 2, and curve 4 was obtained from a solution which was 0.01215 F in Cu^{++} and 0.9 F in NaF. It appears from the difference in absorption between curves 3 and 4 in the region 230 mμ to 260 mμ that a complex may be formed. This favors the idea that CuF^+ is more strongly held by the resin than Cu^{++}.

Conclusion for Part I

This procedure is not usable for the determination of dissociation constants of complex cations due to the affinity of the resin for the complex ion itself. The procedure could be used, however, to determine whether or not a complex is present if the system is such that spectrophotometric means will not detect it.

GRAPH I

- 11 -
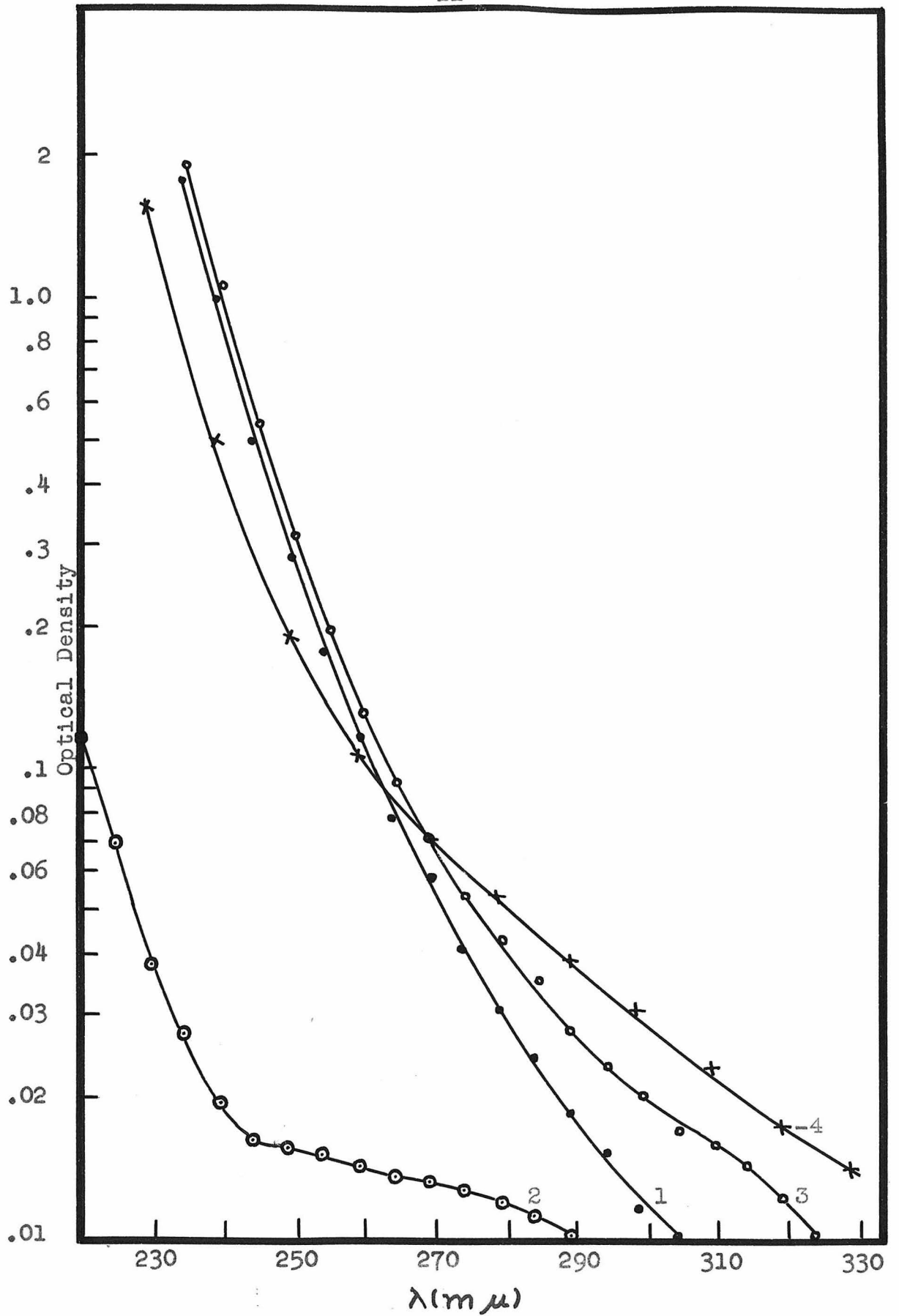
Part II

The Interaction of Various Cu^{++} Solutions

with Columns of Resin

Experimental

The carboxylic acid resin IRC - 50 (12,13) man-
ufactured by the Rohm and Haas Company was studied in
a small column containing 3.54 g. of the air dried H^+
form of the resin. In preliminary experiments it was
found that no detectable exchange took place between
the H^+ form of the resin and Cu^{++} solutions so the
resin in the column was changed to the Na^+ form before
each new experiment by washing it thoroughly with 1 N
sodium hydroxide solution. The resin was rinsed with
NaCl solution to remove the excess base, while pre-
venting hydrolysis of the salt of the weakly acidic
resin. Most of the chloride ion was then washed away
with small portions of distilled water. A solution of
the salt to be tested was then allowed to flow slowly
through the column from the top until the blue color
of the resin indicated that it was completely saturated
with Cu^{++}. After an excess of the solution was passed
through the column it was washed free of Cu^{++} solution
with five 10 ml. portions of water and then slowly with
1 F $HClO_4$ until the Cu^{++} had been entirely removed. The
resulting solution was diluted until it was less than
0.1 F in Cu^{++} to prevent loss of iodine from the solu-

tion during titration and an aliquot analyzed for Cu^{++}
by adding 3 g. KI and titrating with 0.1 N $Na_2S_2O_3$
in an atmosphere of CO_2 to a starch iodine end point (14).
Since it was also desired to obtain a rough measure of
the degree of swelling which the resin underwent in the
various solutions, the column was washed upward with
water before each experiment so that the resin was
loosened and was then allowed to settle before the
liquid was drawn off and the experiment started.. At
the end of the experiment the column was tapped sharply
to help the resin to settle together and the height of
the column was measured. The results were reproducible
to 0.3 cm.

Results

The results of treating the resin with various
solutions are shown in Table V.

Table V

Solution passed through column	Height of column	meq absorbed in resin
1 F NaOH	16.8 cm.	32.2
1 F HCl	10.3 cm.	29.5*
1 F $CuSO_4$	14.2 cm.	31.8
.5 F $Cu(OAc)_2$	13.5 cm.	36.4
.5 F $Cu(ClO_4)_2$	14.0 cm.	31.5

*The meq of HCl used up were determined by evaporating
the solution and weighing the residue of NaCl. Some of
the NaCl, however, was lost in the process on two attempts.

In view of the agreement of the other results I did
not feel that it was worth while to repeat this deter-
mination.

A solution which was 0.5 F in $CuCl_2$ was also tried,
but a precipitate formed in the column so it could not
be used. The precipitate may have been a basic cupric
chloride formed by the hydrolysis of the sodium salt
of the weakly acidic resin. It was not possible to
prevent the formation of this precipitate even by the
addition of a 0.1F acetate buffer mixture to the solu-
tion.

The height of the column, which is a measure of
the degree of swelling of the resin, varies from a
large value for the Na^+ form of the resin to a much
smaller one for the resin in the H^+ form. The degree
of swelling of the resin is determined by the osmotic
pressure inside the resin particles. In the Na^+ form
of the resin the active groups are completely ionized
like a salt and consequently there are a large number
of Na^+ ions to contribute to raising the osmotic pressure.
In the case of the Cu^{++} salt form of the resin the
number of ions is about half of that in the first case
so the osmotic pressure is lower and the swelling less.
Finally, the H^+ form of the resin has few ions because
the weakly acidic groups are only slightly ionized.
The above explains the results with $CuSO_4$ and $Cu(ClO_4)_2$,

but $Cu(OAc)_2$ is out of line in both columns of the
table. The resin in contact with its solution does
not swell as much as it does in the case of other
Cu^{++} solutions and more meq of copper are absorbed
from it than from the others. This effect may be due
to the fact that Cu^{++} forms complexes with carboxylic
acids (15) and the active groups in the resin are
carboxylic acid groups. The $CuOAc^{+}$ group which is
present in the solution may migrate into the resin
as a unit and there unite with an acid group to form
a complex such as $Cu(OAc)(RCOO)$ which would be fairly
stable. The effect of such action would be to reduce
the number of ions or particles in solution inside the
resin and thus reduce the osmotic pressure and swelling.
The number of milliequivalents of copper which could
be taken up would be greater due to the fact that in
some cases one acidic group would suffice to hold one
Cu^{++} inside the resin, whereas ordinarily it requires
two such groups. The results of the experiments are
accounted for by the above.

In order to investigate the effect that complexing
agents might have on the absorption of Cu^{++} by a strong
acid resin a small column of Dowex 50 containing 6.87 g
of the air dried sodium form of the resin was prepared
and treated with solutions of cupric salts as follows

Table VI

Form of resin	Solution	meq Cu^{++} absorbed
H^+	$.5F\ Cu(ClO_4)_2$	25.6
Na^+	$.5F\ Cu(ClO_4)_2$	25.4
Na^+	$.5F\ CuCl_2$	25.4

As was expected the resin has the same capacity for copper in both the sodium and hydrogen forms. The same amount of Cu^{++} was absorbed by the resin from the $Cu(ClO_4)_2$ solution in which it is presumably un-complexed and from the $CuCl_2$ solution in which about 50% of the Cu^{++} is present as $CuCl^+$. The strongly ionized sulfonic acid groups do not exert any complexing effect on the $CuCl^+$.

Part III

Batch Study of IRC - 50

A titration curve of IRC - 50 resin was run by placing .2 g samples of the H^+ form of the resin in test tubes and equilibrating for several days with solutions containing various amounts of NaOH in 1 F $NaClO_4$. The pH of the resulting solutions was read on a Beckman Model G pH Meter. The results are shown on Graph II. The curve is similar to those published for neutralization with KOH (13), but displaced some-what since the reaction is not simply the neutraliz-ation of an acid by a base, but rather:

$$RCOOH + Na^+ = RCOO^- Na^+ + H^+$$

$$H^+ + OH^- = HOH$$

The ability of the cation to replace H^+ in the resin is the important factor in determining the nature of the titration curve.

The titration curve was used to prepare some of the resin which was buffered at pH = 5.2 by equili-brating the H^+ form with the correct amount of NaOH in 1 F $NaClO_4$. Tests were run on the copper absorbing power of this buffered resin and it was found that .1 g of the resin would remove 90% of the Cu^{++} from 50 ml of .001 F Cu^{++} solution. Since .1 g of resin represents about 1 meq, the resin was 5% saturated. For the exp-

TITRATION OF IRC-50 RESIN

Base NaOH
Vol - 30 ml
$\mu = 1$ (NaClO4)

ml 0.1N NaOH added per 0.2 g dry Resin
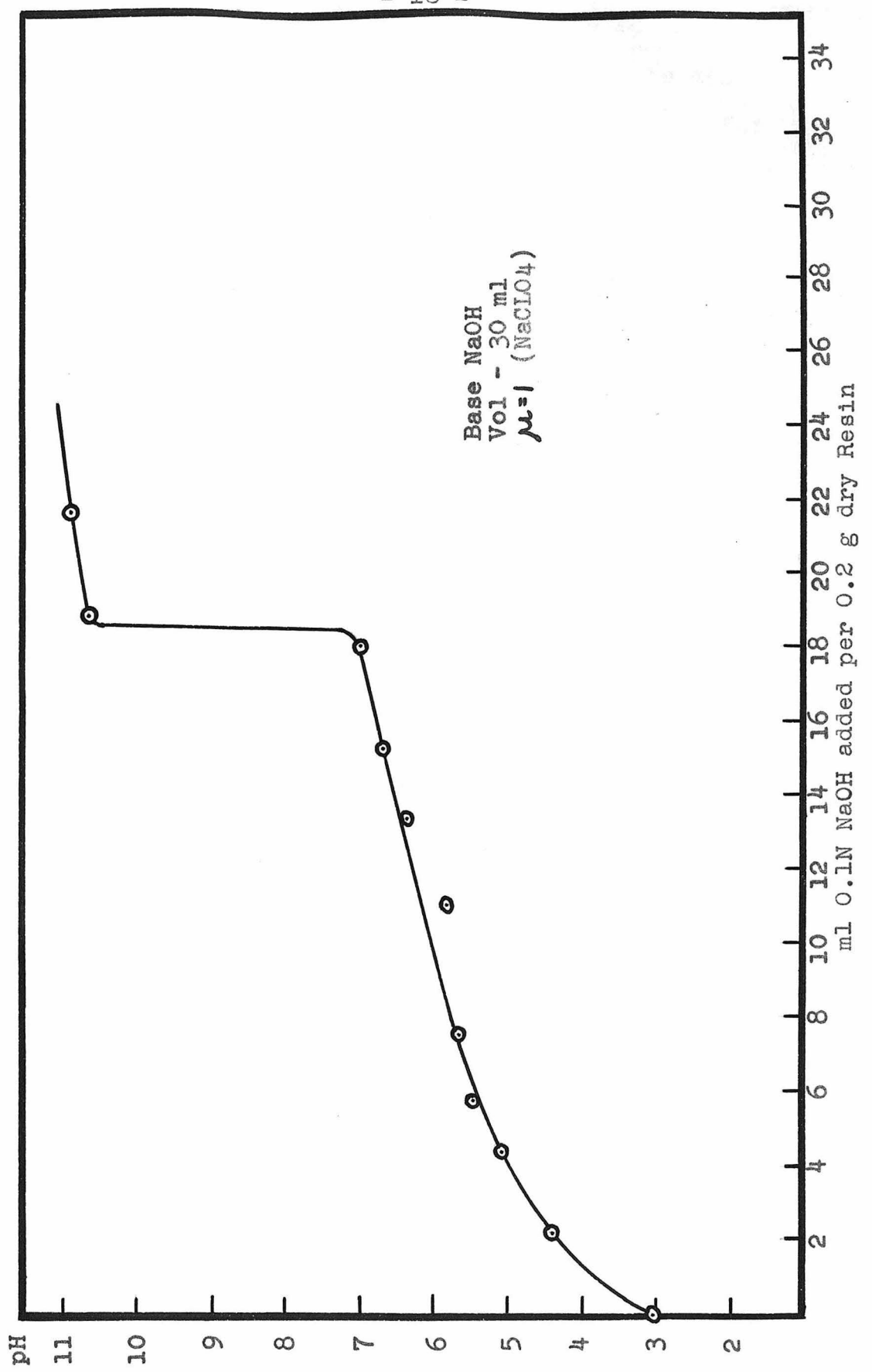
eriments with copper halides we desired a system in
which the amount of exchange would normally be about
50% and the resin would be very dilute in Cu^{++}. For
this reason the use of IRC -50 in this connection was
not pursued further.

References

1. McConnell and Davidson, J. Am. Chem. Soc., (1950)
   $\underline{72}$, 3164

2. Näsänsen, Acta Chem. Scand., (1950) $\underline{4}$, 140

3. Schubert, J. Phys. & Colloid Chem., (1948)
   $\underline{52}$, 340

4. Schubert & Richter, J. Am. Chem. Soc., (1948)
   $\underline{70}$, 4295

5. Schubert, Russell & Myers, J. Biol. Chem., (1950)
   $\underline{185}$, 387

6. Boyd, Schubert & Adamson, J. Am. Chem. Soc., (1947)
   $\underline{69}$, 2818

7. Walton, J. Phys. Chem., (1943) $\underline{47}$, 371
   Walton,   ibid   , (1945) $\underline{49}$, 479

8. Bauman & Eichorn, J. Am. Chem. Soc., (1947)
   $\underline{69}$, 2830

9. Moeller, Ind. Eng. Chem., Anal. Ed., (1943)
   $\underline{15}$, 346

10. Lowen, Stoenner, Argersinger, Davidson, & Hume,
    J. Am. Chem. Soc., (1951) $\underline{73}$, 2838

11. Farrington, Ph. D. Thesis, California Institute
    of Technology, (1950)

12. Kunin & Barry, Ind. Eng. Chem., (1949) $\underline{41}$, 1269

13. Kunin, Anal. Chem., (1949) $\underline{21}$, 87

14. Swift, "A System of Chemical Analysis", (1946)
    Prentice-Hall, New York

15. Sidgwick, "The Chemical Elements and Their Compounds",
    (1950) Oxford.