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A Study of Some Tetraarylborate-PVC Membrane Electrodes

Boonrod Hirunmitnakon
Loyola University Chicago

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A STUDY OF SOME TETRAARYLBORATE-PVC
MEMBRANE ELECTRODES

by

Boonrod Hirunmitnakon

A Thesis Submitted to the Faculty of the Graduate
School of Loyola University in Partial
Fulfillment of the Requirements
for the Degree of Master
of Science

June

1976

LIFE

Boonrod Hironmitnakon was born in Bangkok, Thailand, September 22, 1946.

He was graduated from Triam Udom High School, Bangkok, Thailand and from Sul Ross State University, Alpine, Texas, June 1971, with the degree of Bachelor of Science.

He began work for the Master of Science degree in the Graduate School of Loyola University in September, 1973.

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. STATEMENT OF PROBLEM	4
III. PREPARATION OF CALOMEL ELECTRODE	5
IV. PREPARATION OF MEMBRANES	7
A. Preparation of the PVC membrane of cesium triphenylcyanoborate.	7
B. Preparation of the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)borate	8
C. Preparation of the PVC membrane of trimethylammonium tetrakis(metafluorophenyl) borate.	9
D. Preparation of the PVC membrane, coated on copper foil, which contained trimethyl- ammonium tetrakis (metafluorophenyl) borate.	10
E. Preparation of the PVC membrane, coated on zirconium, which contained trimethyl- ammonium tetrakis (metafluorophenyl) borate.	11
F. Preparation of the PVC membrane, coated on platinum, which contained trimethyl- ammonium tetrakis (metafluorophenyl) borate.	11
V. PREPARATION OF MONOVALENT AND DIVALENT ION SOLUTIONS	13

	Page
VI. POTENTIOMETRIC MEASUREMENTS OF MONOVALENT AND DIVALENT IONS	15
VII. POTENTIOMETRIC TITRATIONS USING MEMBRANES.....	74
A. The PVC membrane of cesium triphenylcyano- borate.	
B. The PVC membrane of cesium tetrakis-(p-tri- fluoromethylphenyl) borate.	
C. The PVC membrane of trimethylammonium tetrakis (metafluorophenyl) borate.	
D. The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis (meta- fluorophenyl) borate.	
VIII. DISCUSSION AND CONCLUSIONS	75
IX. SUMMARY	79
BIBLIOGRAPHY	81

LIST OF TABLES

Table,	Page
I. Potentiometric Measurement of Monovalent Ions Using the PVC Membrane of Cesium Triphenylcyanoborate.....	16
II. Potentiometric Measurement of Monovalent Ions Using the PVC Membrane of Cesium Tetrakis(p-trifluoromethylphenyl)borate.....	20
III. Potentiometric Measurement of Monovalent Ions Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.....	24
IV. Potentiometric Measurement of Divalent Ions Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.....	27
V. Potentiometric Measurement of Monovalent Ions Using the PVC Membrane, Coated on Copper Foil, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	31
VI. Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Copper Foil, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	34
VII. Potentiometric Measurement of Monovalent Ions Using the PVC Membrane, Coated on Zirconium, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	38
VIII. Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Zirconium, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	41

Table	Page
IX. Potentiometric Measurement of Monovalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	45
X. Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	48
XI. Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	53
XII. Potentiometric Measurement of Monovalent and Divalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)-borate Compared to Platinum Electrode.....	57
XIII. The Average Voltage Change/Decade in the Range of $10^{-1}M$ to $10^{-3}M$	60
XIV. Potentiometric Titration by Using the PVC Membrane of Cesium Triphenylcyanoborate.....	62
XV. Potentiometric Titration by Using the PVC Membrane of Cesium Tetrakis(p-trifluoromethylphenyl)borate.....	65
XVI. Potentiometric Titration by Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.....	68
XVII. Potentiometric Titration by Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	71
XVIII. The Average Voltage Change/Decade Change of Concentration in the Range of $10^{-1}M$ to $10^{-3}M$ of Monovalent Ion Halide Salts.....	76

XIX. The Average Voltage Change/Decade Change of Concentration in the Range of $10^{-1}M$ to $10^{-3}M$ of Divalent Ion Halide Salts.....	77
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LIST OF FIGURES

Figure	Page
I. Schematic Diagram of Membrane Electrodes.....	6
II. Diagram of Membrane Coated on Copper Foil.....	11
III. Diagram of Platinum Electrode.....	12
IV. Emf as Function of Monovalent Ion Halide Salt Concentration Measured Using the PVC Membrane of Cesium Triphenylcyanoborate.....	18
V. Emf as Function of Monovalent Ion Halide Salt Concentration Measured Using the PVC Membrane of Cesium Tetrakis(p-trifluoromethylphenyl)borate.....	22
VI. Emf as Function of Monovalent Ion Halide Salt Concentration Measured Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.....	26
VII. Emf as Function of Divalent Ion Halide Salt Concentration Measured Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.....	29
VIII. Emf as Function of Monovalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Copper Foil, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	33
IX. Emf as Function of Divalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Copper Foil, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	36

Figure	Page
X. Emf as Function of Monovalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Zirconium, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	40
XI. Emf as Function of Divalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Zirconium, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	43
XII. Emf as Function of Monovalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	47
XIII. Emf as Function of Divalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	50
XIV. Emf as Function of Divalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.....	55
XV. Emf as Function of Monovalent and Divalent Ion Halide Salt Concentration Measured Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate Compared to Platinum Electrode.....	59

Figure	Page
XVI. Potentiometric Titration of Boric Acid and Ammonium Chloride Solution Titrated with Sodium Hydroxide Using the PVC Membrane of Cesium Triphenylcyanoborate...	64
XVII. Potentiometric Titration of Boric Acid and Ammonium Chloride Solution Titrated with Sodium Hydroxide Using the PVC Membrane of Cesium Tetrakis(p-trifluoromethylphenyl)borate.....	67
XVIII. Potentiometric Titration of Boric Acid and Ammonium Chloride Solution Titrated with Sodium Hydroxide Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.....	70
XIX. Potentiometric Titration of Boric Acid and Ammonium Chloride Solution Titrated with Sodium Hydroxide Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)-borate.....	73

CHAPTER I

INTRODUCTION

The membrane electrode is a useful tool for the analytical chemist in determining the activity of ions by measuring the potential of two different concentrations of electrolyte separated by a membrane (1). The membrane electrode was first recognized by Haber after Nernst and Risenfeld showed the potential difference by ion exchange of two electrolyte solutions separated by the membrane. It was developed by Scotchard and Marshall (2). Scotchard then used the general equation for the electromotive force of a cell to develop the ion exchange equation and lay the basis for the ion exchange electrode.

The ion exchange electrode showed ion mobility high enough to give a useful conductivity but low enough so as not to give excessive diffusion. The ion exchange of cationic and anionic species for hydrolytic diffusion became important.

Marshall (3) has described the application of high ionic selectivity by using zeolite membranes which showed mechanical sieve action for the quantitative determination of cations. This membrane has been studied for potassium ion activities and has also been used for the determination of other monovalent cations. The quantitative determinations of potassium and sodium were improved with zeolite membranes. Marshall and Krinbill (4) also developed clay membranes which were sensitive to monovalent cations especially sodium. These membranes showed excellent reproducibility. Sollner (5) has developed a potentiometric method to determine cations and anions with collodion and protamine-collodion membrane electrodes, respectively. Collodion

membranes show high ionic selectivity in the potentiometric determinations of cations, such as K^+ , Na^+ , Li^+ , NH_4^+ and Mg^{++} . Protamine-collodion membranes have been used for potentiometric determination of Cl^- , Br^- , I^- , ClO_3^- , ClO_4^- , BrO_3^- , IO_3^- , NO_3^- and acetate $^-$. The potential difference between a known solution and unknown solution on each side of the membrane were evaluated on the basis of semi-theoretical standard curve.

Kressman (6) indicated an ion exchange process by using resin membranes and resin-impregnated filter paper. Resin membranes were prepared containing $-SO_3H^-$, $-COO^-$ or amino groups, which were stable and free from cracks. The membranes consisted of cross-linked resin polymers of identical composition to the well known granular ion exchange resins which were insoluble in all aqueous and non aqueous liquids. When resin-impregnated filter paper was developed, the ionic mobility within the resin was exploited to separate ions by passing an electrical current between electrodes clamped to the ends of the paper.

Gregor and coworkers (7) developed multilayer membrane electrodes showed selective permeability to certain cations in the presence of other ions of the same charge. These membranes were useful in measuring activities of ions in mixed electrolytes.

In the recent years, Baum and Lynn (8) developed plasticized polyvinyl chloride membranes which showed both flexibility and toughness and yet retained a high degree of semipermeability. The membranes were prepared by using either dibutylphthalate or dioctylphthalate as plasticizer; however, membranes prepared with the former plasticizer exhibited the better flexibility and toughness.

We chose to study the PVC membranes of cesium triphenylcyanoborate,

cesium tetrakis(p-trifluoromethylphenyl)borate, trimethylammonium tetrakis(metafluorophenyl)borate, the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate, the PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)borate and the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate.

CHAPTER II

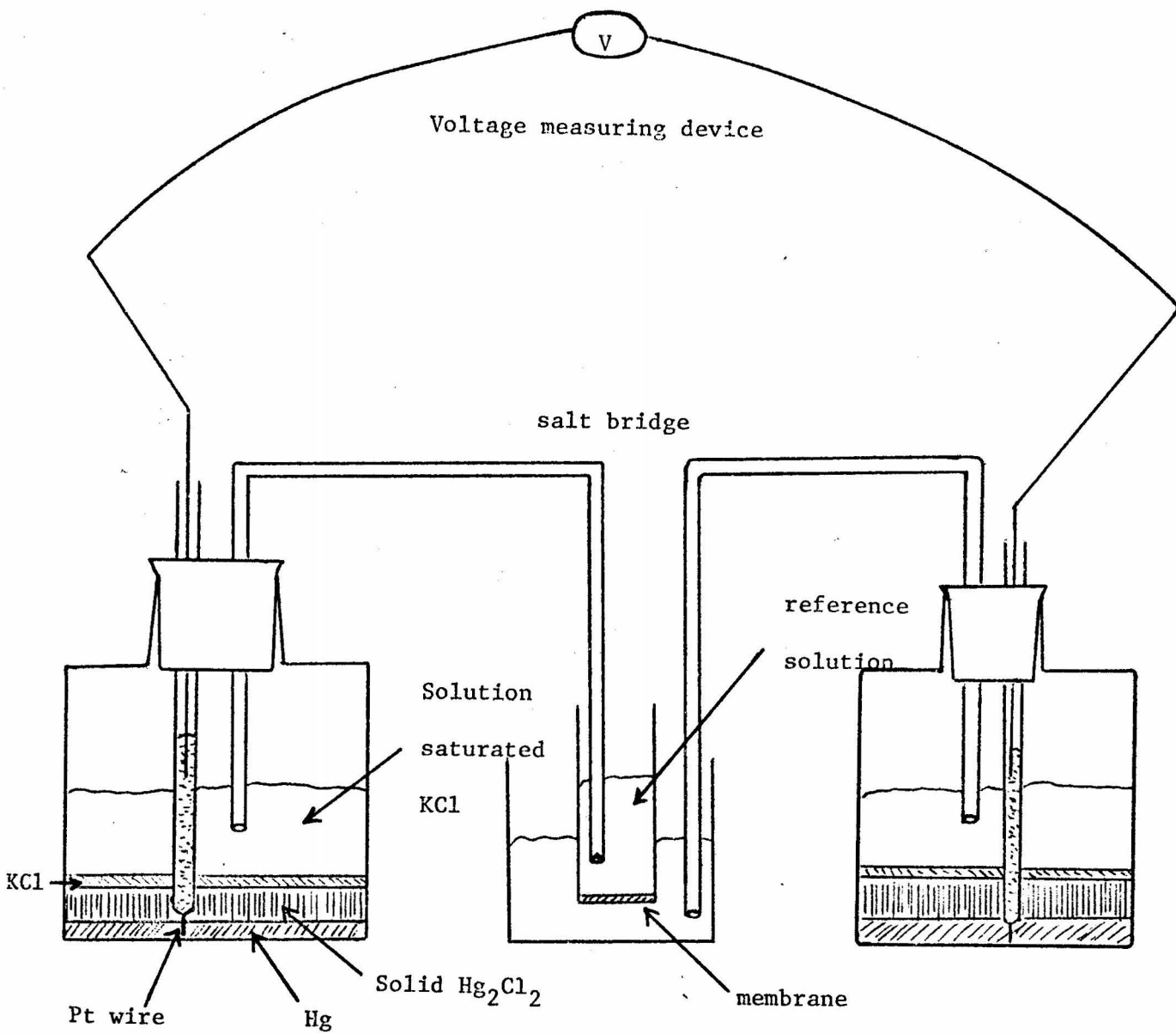
STATEMENT OF THE PROBLEM

The purpose of this study is to investigate techniques of preparing electrode membranes and to determine the type of membrane which shows the most sensitive response for monovalent and divalent ions. The aim of this study was also to obtain an electrode which exhibited reproducible Nernstian response which is important in measuring the voltage response. Dibutylphthalate was the plasticizer used for obtaining a tough flexible membrane.

CHAPTER III

PREPARATION OF CALOMEL ELECTRODE

A saturated calomel electrode was constructed by using a widemouth bottle which was 3.5 cm. diameter at the mouth and approximately 6 cm. in diameter at the bottom. The height of the bottle was approximately 14 cm. The bottle was sealed with a two-hole stopper. In one hole of the stopper was a small tube, which was sealed with a small piece of platinum wire at the end, in order to provide electrical contact between the interior and the exterior of the cell. The other hole of the stopper was a U shaped tube which was approximately 9 mm. in diameter. This U shaped tube contained the salt bridge which connected the calomel cell to the indicator portion of the cell. The salt bridge was prepared by heating agar in a saturated potassium chloride solution and pouring this into the tube. The tube was allowed to stand in ice for about 30 minutes until a conducting gel was formed. The bottom part of the cell was layered with mercury to a depth of approximately 4 mm. Upon this is layered a paste which is prepared by grinding pure mercury (I) chloride with mercury metal and saturated potassium chloride (9). The next layer added is potassium chloride. Finally, the paste is overlaid with saturated potassium chloride. Before using the cell, it was kept at room temperature for a few days in order to allow the cell to reach equilibrium and to develop a constant potential (9).



Schematic Diagram of Membrane Electrodes

FIGURE I

CHAPTER IV

PREPARATION OF MEMBRANES

Dibutylphthalate plasticizer obtained from Witco Chemical Company, Lot. No. 52 hereafter will be called DBP and polyvinyl-chloride obtained from Stauffer Chemical Company hereafter will be called PVC.

A. Preparation of the PVC membrane of cesium triphenylcyanoborate.

A stock solution was prepared by weighing 95 g. of DBP plasticizer mixing with 5 g. aluminum stearate, and heating until a gel was formed. Then 25 g. of gel was mixed with 75 g. of DBP plasticizer and 50 g. of PVC.

A 3% solution of cesium triphenylcyanoborate was prepared by mixing 0.3 g. of cesium triphenylcyanoborate with 10 ml. of stock solution.

The 3% solution of cesium triphenylcyanoborate in DBP plasticizer was mixed with a fine PVC powder (8). The solution was placed in a Petri dish and mixed vigorously by vibrating, then placed in an oven at 200°C for two minutes; under these conditions a thin film which is tough and flexible was formed. The membrane of cesium triphenylcyanoborate were tough and flexible at concentrations of 3%. At concentrations greater than 3%, the membranes were not tough and flexible.

B. Preparation of the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)borate.

A stock solution was prepared by weighing 95 g. of DBP mixing with 5 g. aluminum stearate and heating until a gel is formed. Then 25 g. of gel was mixed with 75 g. of DBP plasticizer and 50 g. of PVC.

A 2.5% solution of cesium tetrakis(p-trifluoromethylphenyl)borate was prepared by adding 0.25 g. of cesium tetrakis(p-trifluoromethylphenyl)borate to 10 ml. of stock solution.

The 2.5% solution of cesium tetrakis(p-trifluoromethylphenyl)borate in DBP plasticizer was mixed with a fine PVC. The solution was placed in a Petri dish and mixed vigorously by vibrating, then placed in the oven at 200°C for two minutes; under these conditions, a thin film which is tough and flexible was formed. The thickness of a membrane was approximately 0.3 mm.

C. Preparation of the PVC membrane of trimethylammonium tetrakis-(metafluorophenyl)borate.

A stock solution was prepared by weighing 95 g. of DBP mixing with 5 g. aluminum stearate, and heating until a gel was formed. Then 25 g. of the gel was mixed with 75 g. of DBP plasticizer and 50 g. of PVC.

A 3% solution of trimethylammonium tetrakis(metafluorophenyl)borate was prepared by adding 0.3 g. of trimethylammonium tetrakis(metafluorophenyl)borate to 10 ml. of stock solution.

The 3% solution of trimethylammonium tetrakis(metafluorophenyl)borate in DBP plasticizer was mixed with a fine PVC. The solution was placed in a Petri dish and mixed vigorously by vibrating, then placed in the oven at 200°C for one and a half minutes. Under these conditions, a thin film which is tough and flexible was formed. The thickness of the membrane is approximately 0.3 mm.

D. Preparation of the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate.

A stock solution was prepared by weighing 95 g. of DBP plasticizer mixing with 5 g. aluminum stearate, and heating until the gel was formed. Then 25 g. of the gel was mixed with 75 g. of DBP and 50 g. of PVC.

A 2% solution of trimethylammonium tetrakis(metafluorophenyl)-borate was prepared by mixing 0.2 g. of trimethylammonium tetrakis(metafluorophenyl)borate with 10 ml. of stock solution.

The 2% solution of trimethylammonium tetrakis(metafluorophenyl)borate in DBP plasticizer and 0.5 g. ammonium chloride were mixed with a finely divided PVC powder. A copper foil square 3.5 X 3.5 cm. coated on all edges with polyethylene was used to form the membrane. The square has a specific area in the center for the preparation of the membrane. The center area of the foil was coated with the solution. The foil was then placed in an oven for two minutes at 200° C. A thin film which is tough and flexible was formed on the copper foil. This will be referred to as a reference electrode.

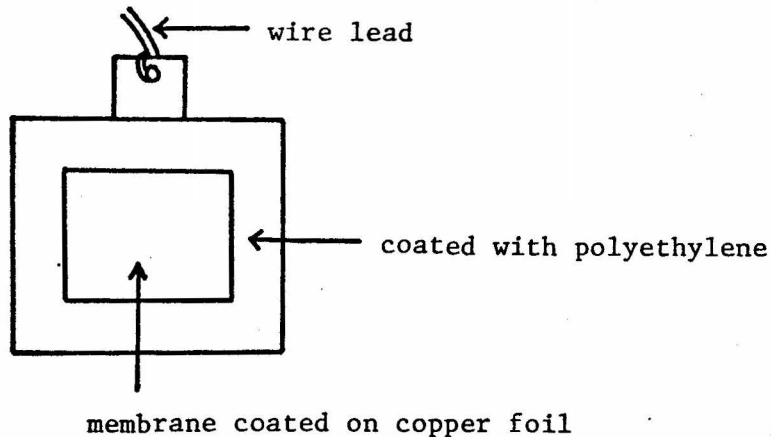


FIGURE II

DIAGRAM OF MEMBRANE COATED ON COPPER FOIL

E. Preparation of the PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)borate.

Preparation of this membrane followed the same procedure as the preparation of the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate, except that instead of using copper foil, zirconium was used.

F. Preparation of the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate.

A stock solution was prepared by weighing 95 g. of DBP plasticizer mixing with 5 g. aluminum stearate, and heating until a gel was formed. Then 25 g. of the gel was mixed with 75 g. of DBP plasticizer and 50 g. of PVC.

A 2% solution of trimethylammonium tetrakis(metafluorophenyl)borate was prepared by mixing 0.2 g. of trimethylammonium tetrakis(metafluorophenyl)borate with 10 ml. of stock solution.

The 2% solution of trimethylammonium tetrakis(metafluorophenyl)borate in DBP plasticizer and 0.5 g. ammonium chloride was mixed with

- a finely divided PVC powder. The solution was coated on a piece of platinum 7 X 8 mm., and placed in the oven for two minutes at 200°C. A thin film was formed on platinum. It has been referred as a reference electrode.

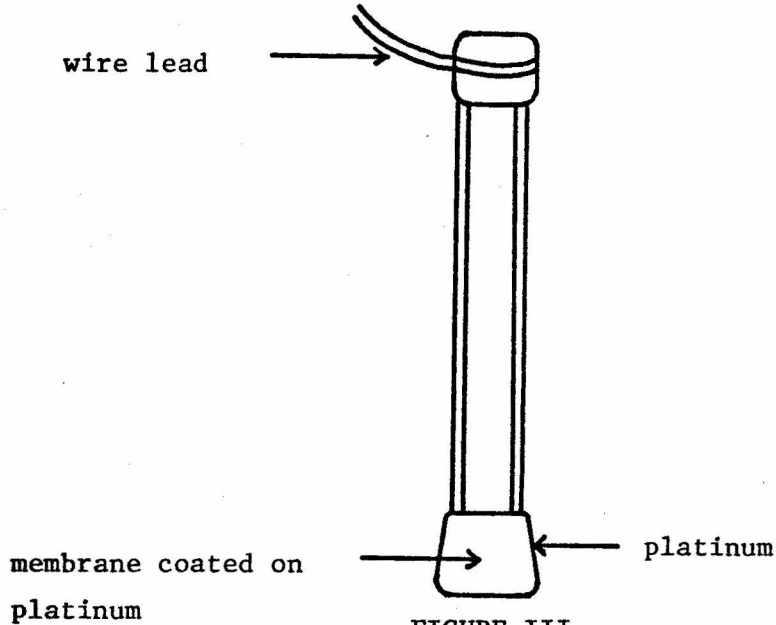


FIGURE III

DIAGRAM OF PLATINUM ELECTRODE

CHAPTER V

PREPARATION OF MONOVALENT AND DIVALENT ION SOLUTIONS

Preparation of potassium chloride solution.

Potassium chloride(1M) was prepared by weighing potassium chloride (7.455 g.) and dissolving with distilled water and making up to 100 ml.

Potassium chloride(10^{-1} M) was prepared by pipeting 10 ml. of potassium chloride(1 M) and diluting with distilled water up to 100 ml.

Potassium chloride(10^{-2} M) was prepared by pipeting 10 ml. of potassium chloride(10^{-1} M) and diluting with distilled water up to 100 ml.

Potassium chloride(10^{-3} M) was prepared by pipeting 10 ml. of potassium chloride(10^{-2} M) and diluting with distilled water up to 100 ml.

Potassium chloride(10^{-4} M) was prepared by pipeting 10 ml. of potassium chloride(10^{-3} M) and diluting with distilled water up to 100 ml.

Potassium chloride(10^{-5} M) was prepared by pipeting 10 ml. of potassium chloride(10^{-4} M) and diluting with distilled water up to 100 ml.

The preparation of sodium chloride, ammonium chloride, copper (II) chloride, magnesium chloride and calcium chloride solutions followed the same procedure as the preparation of the potassium chloride solution.

Preparation of calcium chloride solution.

Calcium chloride(1 M) was prepared by weighing calcium chloride (11.099 g.) and dissolving in distilled water, the calcium did not dissolve completely. Two drops of concentrated hydrochloric acid were added affect solution. The calcium chloride was diluted with distilled water to 100 ml.

Calcium chloride(10^{-1} M) was prepared by pipeting 10 ml. of calcium

chloride(1 M) and diluting it with distilled water up to 100 ml.

Calcium chloride(10^{-2} M) was prepared by pipeting 10 ml. of calcium chloride(10^{-1} M) and diluting with distilled water up to 100 ml.

Calcium chloride(10^{-3} M) was prepared by pipeting 10 ml. of calcium chloride(10^{-2} M) and diluting with distilled water up to 100 ml.

Calcium chloride(10^{-4} M) was prepared by pipeting 10 ml. of calcium chloride(10^{-3} M) and diluting with distilled water up to 100 ml.

Calcium chloride(10^{-5} M) was prepared by pipeting 10 ml. of calcium chloride(10^{-4} M) and diluting with distilled water up to 100 ml.

CHAPTER VI

. POTENTIOMETRIC MEASUREMENTS OF MONOVALENT AND DIVALENT IONS

The potentiometric measurements were performed at $25 \pm 0.1^\circ \text{C}$ (10). The measurements were made relative to a saturated calomel electrode connected to Orion Research Digital pH Meter, No. 801. The measurements were performed using 1 M concentration of solution as a reference and read against different concentrations.



The 1 M reference solution was contained in a tube, 2.8 X 11 cm., the membrane was fastened to the end of the tube with a screw cap.

TABLE I

Potentiometric Measurement of Monovalent Ions Using the PVC Membrane of Cesium Triphenylcyanoborate.

Voltage (mv) Conc.	NH_4^+	K^+	Na^+
10^{-1}M	-43.1	-45.8	-54.0
10^{-2}M	-92.4	-104.1	-109.2
10^{-3}M	-130.2	-140.2	-150.6
10^{-4}M	-147.8	-159.2	-142.3
10^{-5}M	-144.2	-162.1	-122.9

Emf as Function of Monovalent Ion Halide Salt Concentration
Measured Using the PVC Membrane of Cesium Triphenylcyanoborate.

A. NH_4Cl B. KCl C. NaCl

The PVC membrane of cesium
triphenylcyanoborate

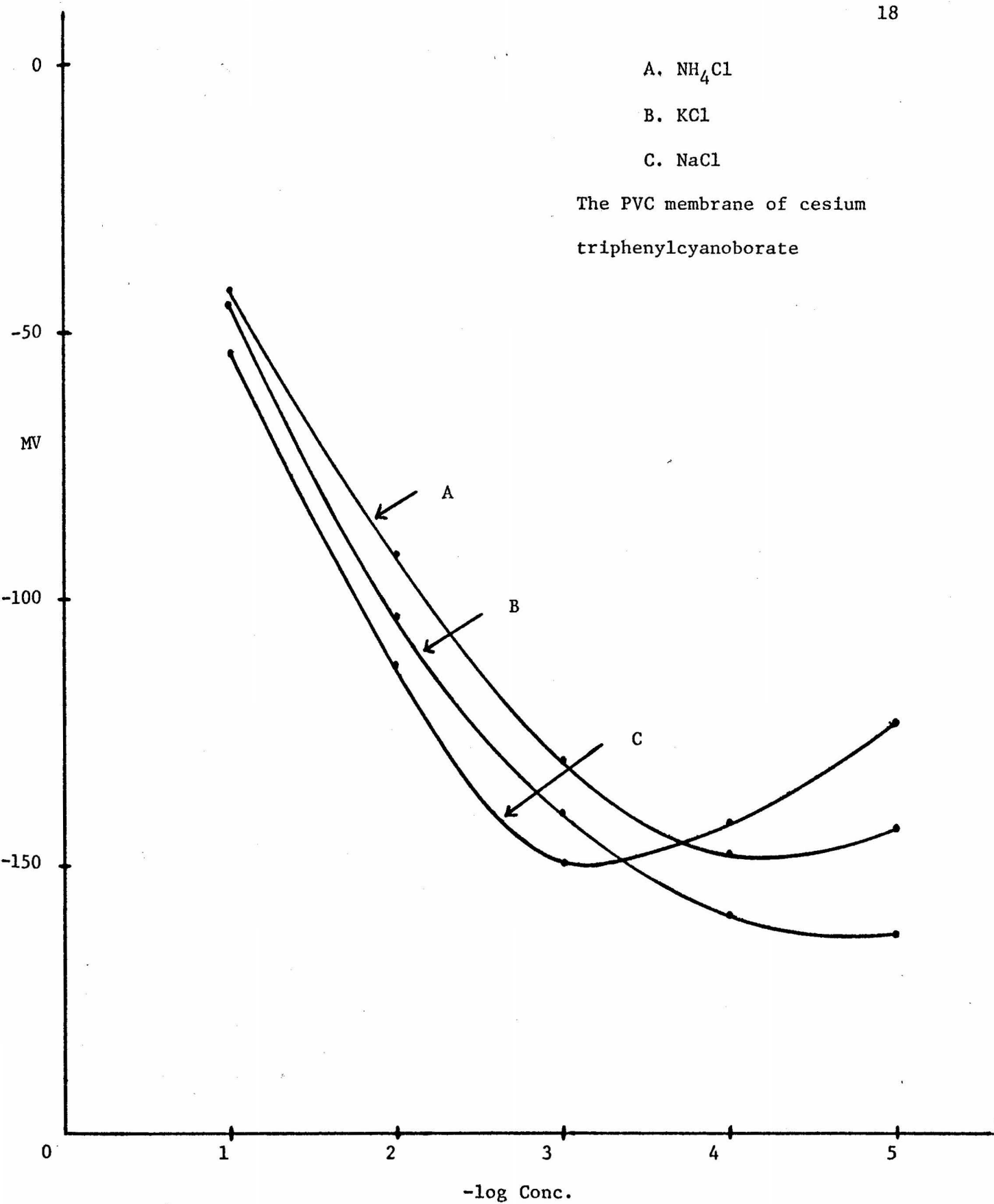


FIGURE IV

Results and Discussion:

The voltage response of monovalent ions using the PVC membrane of cesium triphenylcyanoborate was determined. The average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of ammonium ion, potassium ion and sodium ion was 43.8, 47.6 and 48.1 mv, respectively, the sodium showed slightly more voltage response than potassium. Both sodium and potassium showed more voltage response than the ammonium in the range of $10^{-1}M$ to $10^{-3}M$. The sodium had less response at concentrations below $10^{-3}M$. The voltage dropped significantly at the low concentrations $10^{-5}M$. Ammonium and potassium still showed voltage response at concentrations below $10^{-3}M$ (see Table I and Figure IV). The potassium showed the most response in the range of $10^{-1}M$ to $10^{-5}M$ to the PVC membrane of cesium triphenylcyanoborate.

TABLE II

Potentiometric Measurement of Monovalent Ions Using the PVC Membrane of Cesium Tetrakis(p-trifluoromethylphenyl)borate.

Voltage (mv) Conc.	NH_4^+	K^+	Na^+
10^{-1}M	-29.3	-35.8	-56.3
10^{-2}M	-98.6	-91.2	-103.5
10^{-3}M	-144.5	-129.4	-154.3
10^{-4}M	-171.6	-158.7	-166.5
10^{-5}M	-174.2	-168.5	-161.4

Emf as Function of Monovalent Ion Halide Salt Concentration
Measured Using the PVC Membrane of Cesium Tetrakis(p-triflu-
oromethylphenyl)borate.

- A. KCl
- B. NaCl
- C. NH_4Cl

The PVC Membrane of Cesium
Tetrakis(p-trifluoromethylphenyl)-
borate

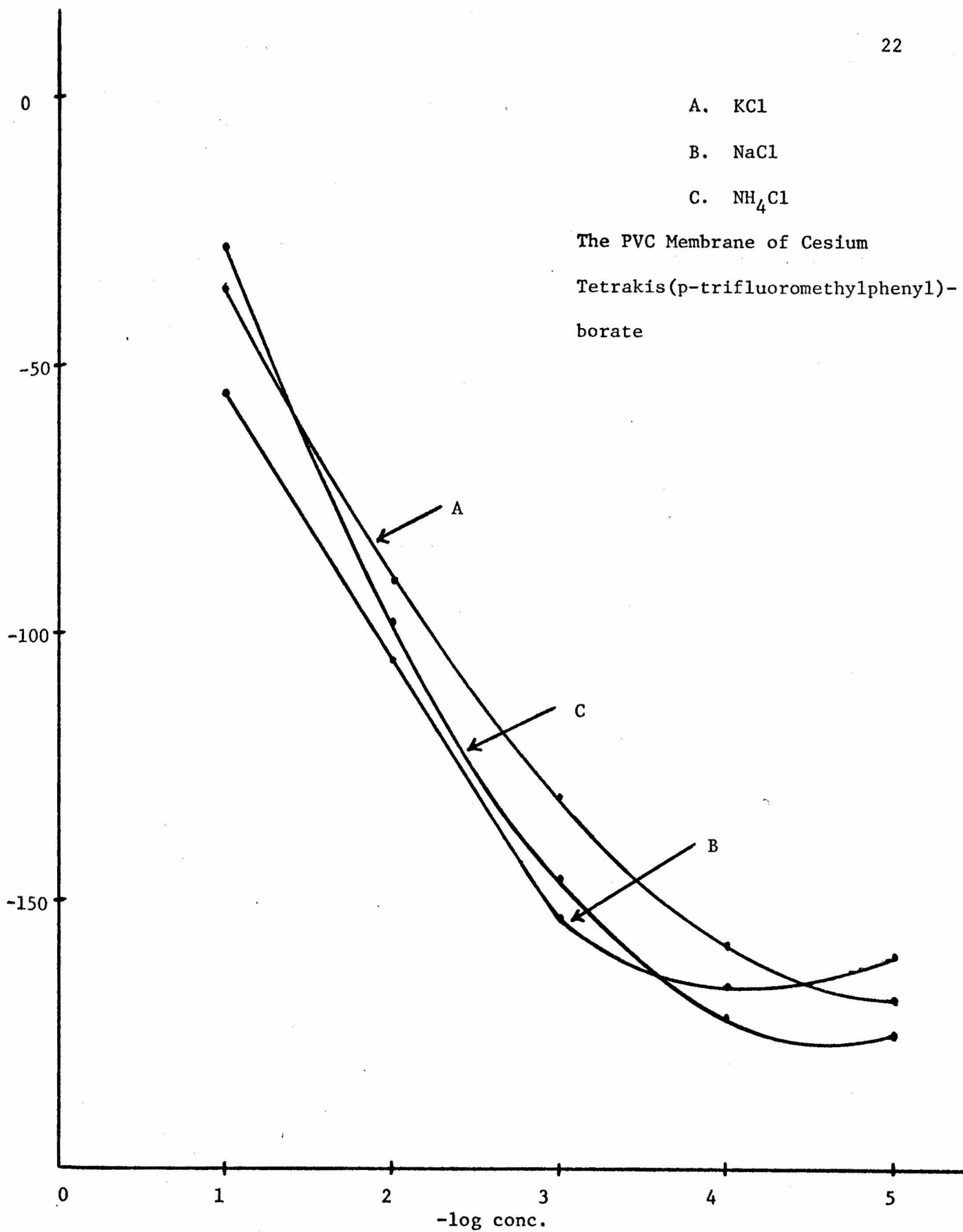


FIGURE V

Results and Discussion:

The voltage response of monovalent ions using the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)borate was determined. The average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of ammonium ion, potassium ion and sodium ion was 58.1, 47.2 and 40.0 mv, respectively. The ammonium showed more voltage response than potassium and sodium. For this membrane, the sodium had less response at concentrations below $10^{-3}M$. Ammonium showed more response than sodium and potassium in the range of $10^{-1}M$ to $10^{-5}M$ (see Table II and Figure V). The ammonium showed the most response to the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)borate and had a more sensitive response than the PVC membrane of cesium triphenylcyanoborate.

TABLE III

Potentiometric Measurement of Monovalent Ions Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.

Voltage (mv) Conc.	NH_4^+	K^+	Na^+
10^{-1}M	-60.5	-55.8	-63.8
10^{-2}M	-104.6	-114.2	-120.8
10^{-3}M	-149.2	-149.8	-165.4
10^{-4}M	-178.4	-172.0	-175.5
10^{-5}M	-186.5	-183.7	-178.2

Emf as Function of Monovalent Ion Halide Salt Concentration Measured
Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)
borate.

- A. KCl
- B. NaCl
- C. NH_4Cl

The PVC Membrane of Trimethyl-
ammonium Tetrakis(metafluorophenyl)-
borate

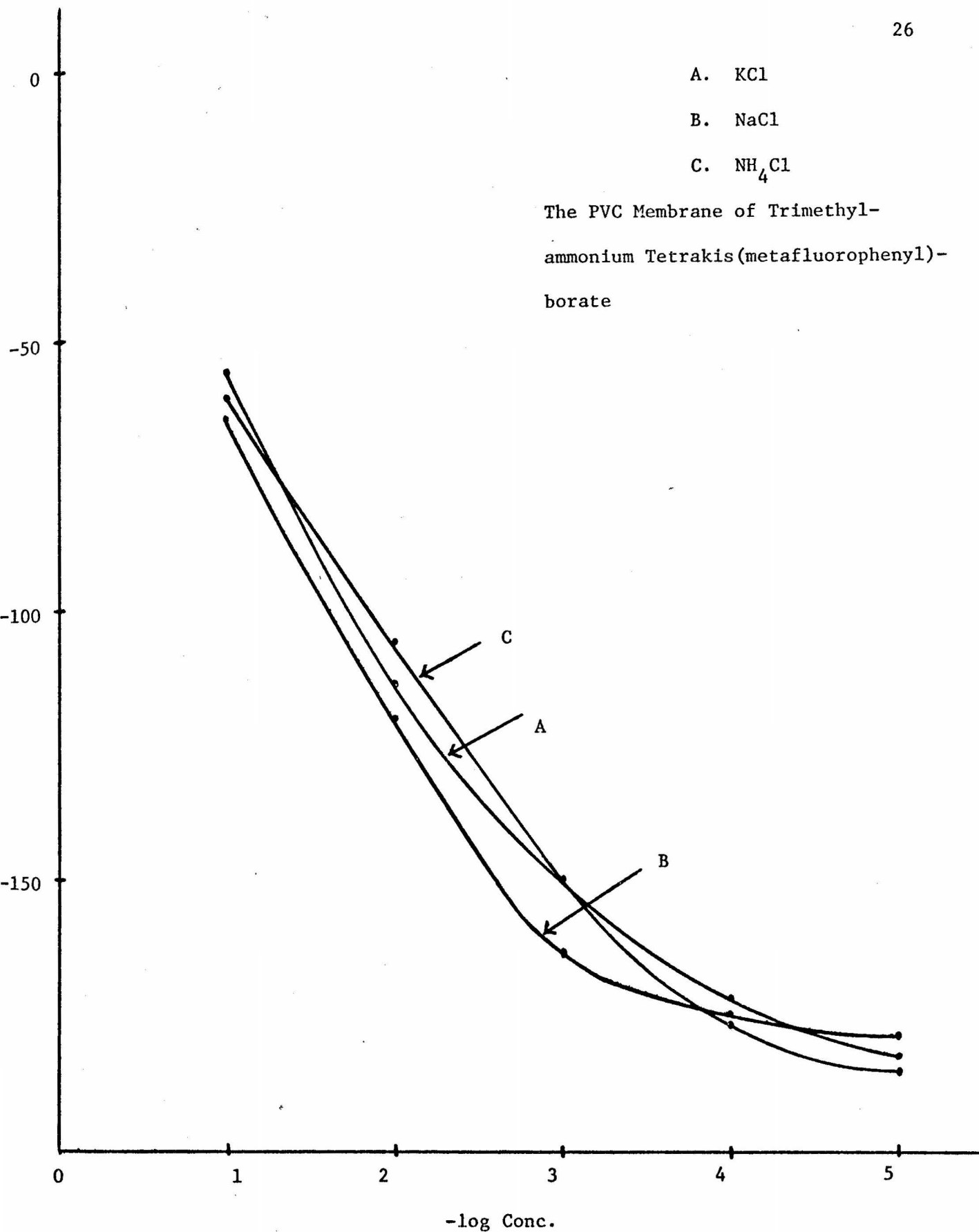


FIGURE VI

TABLE IV

Potentiometric Measurement of Divalent Ions Using the PVC Membrane of Trimethylammonium Tetrakis(metafluorophenyl)borate.

Voltage (mv) / Conc.	Cu ⁺⁺	Ca ⁺⁺	Cd ⁺⁺	Mg ⁺⁺
10 ⁻¹ M	-87.3	-79.5	-86.9	-81.7
10 ⁻² M	-115.4	-96.3	-103.6	-111.8
10 ⁻³ M	-140.5	-109.4	-119.1	-131.9
10 ⁻⁴ M	-151.2	-119.2	-128.6	-145.6
10 ⁻⁵ M	-159.8	-123.7	-133.9	-149.2

Emf as Function of Divalent Ion Halide Salt Concentration
Measured Using the PVC Membrane of Trimethylammonium Tetrakis
(metafluorophenyl)borate.

A. CuCl_2 B. CaCl_2 C. CdCl_2 D. MgCl_2

The PVC Membrane of Trimethylammonium

Tetrakis(metafluorophenyl)borate

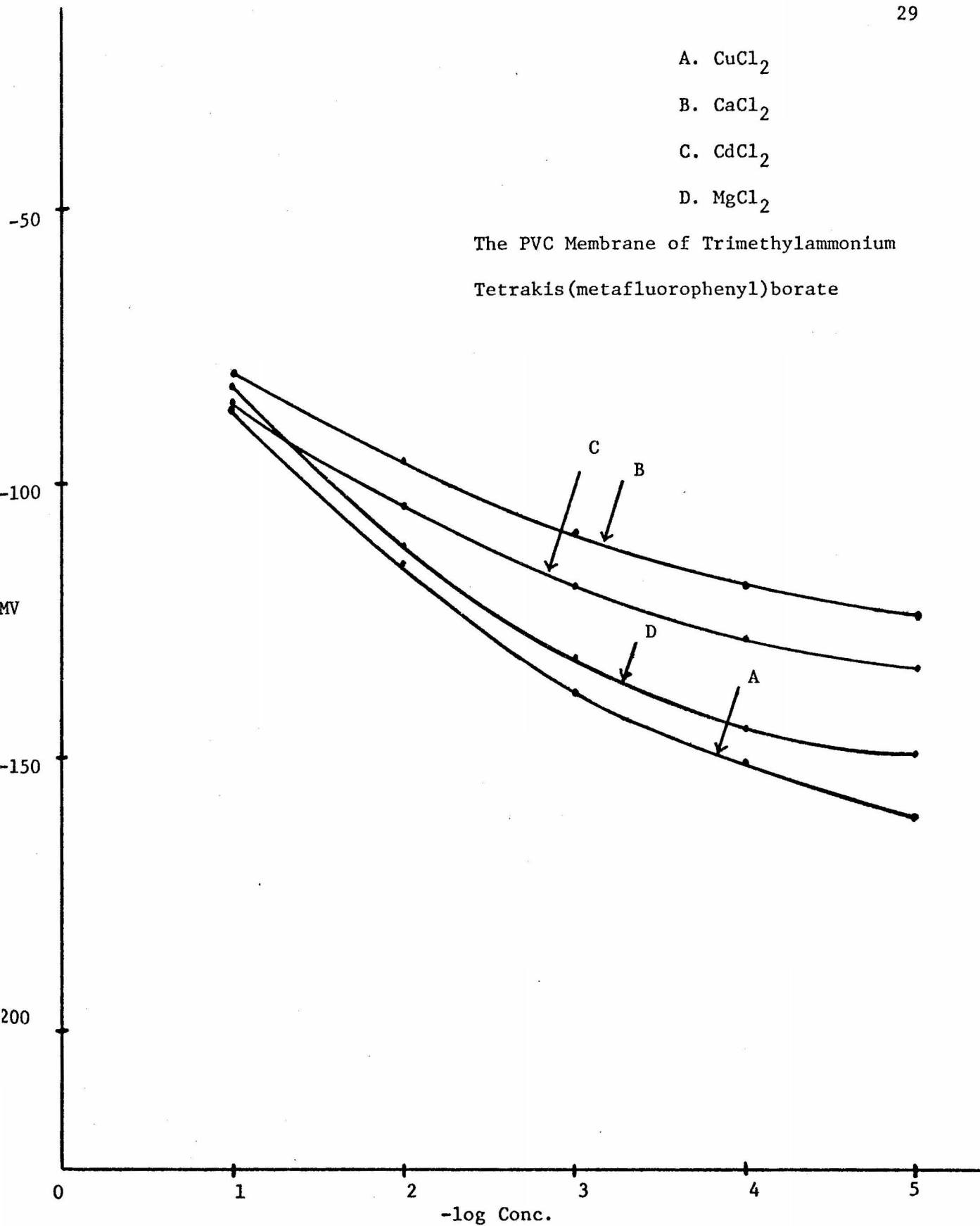


FIGURE VII

Results and Discussion:

The voltage response of monovalent and divalent ions using the PVC membrane of trimethylammonium tetrakis(metafluorophenyl)borate was determined. For monovalent ions, the average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of ammonium, potassium and sodium ions was 44.2, 46.3 and 51.2 mv, respectively. The sodium showed more voltage response than potassium and ammonium in the range of $10^{-1}M$ to $10^{-3}M$, but at low concentrations below $10^{-3}M$, the sodium had less response than ammonium and potassium. For this membrane, ammonium showed a linear response in the range of $10^{-1}M$ to $10^{-3}M$, which followed Nernstian response. Sodium and potassium did not show quite a linear response as was the case with ammonium. In the range of $10^{-1}M$ to $10^{-5}M$, ammonium showed the most response for the PVC membrane of trimethylammonium tetrakis(metafluorophenyl)borate (see Table III and Figure VI). For divalent ions, the average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of copper(II), calcium, cadmium and magnesium was 26.3, 16.1, 18.2 and 24.9 mv, respectively. Copper(II) had more voltage response than calcium, cadmium and magnesium. Monovalent ions had significantly more voltage response than divalent ions(11).

For the PVC membrane of trimethylammonium tetrakis(metafluorophenyl)borate, the sodium had the most response in the range of $10^{-1}M$ to $10^{-3}M$. Ammonium had the most voltage response in the range of $10^{-1}M$ to $10^{-5}M$ and followed Nernstian response. Copper(II) had the most response for the divalent ions (see Table IV and Figure VII). This membrane showed Nernstian response and had more response than the PVC membrane of cesium triphenylcyanoborate and the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)borate.

TABLE V

Potentiometric Measurement of Monovalent Ions Using the PVC Membrane, Coated on Copper Foil, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate.

Voltage (mv) Conc.	NH_4^+	Na^+	K^+
10^{-1}M	-110.2	-127.2	-105.2
10^{-2}M	-160.3	-177.3	-164.9
10^{-3}M	-206.3	-226.5	-217.5
10^{-4}M	-231.7	-240.1	-245.3
10^{-5}M	-243.2	-235.3	-259.4

Emf as Function of Monovalent Ion Halide Salt Concentration
Measured Using the PVC Membrane, Coated on Copper Foil, which
Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.

- A. NH_4Cl
- B. KCl
- C. NaCl

The PVC Membrane, Coated on Copper Foil, which Contained Trimethyl-ammonium Tetrakis(metafluorophenyl)-borate

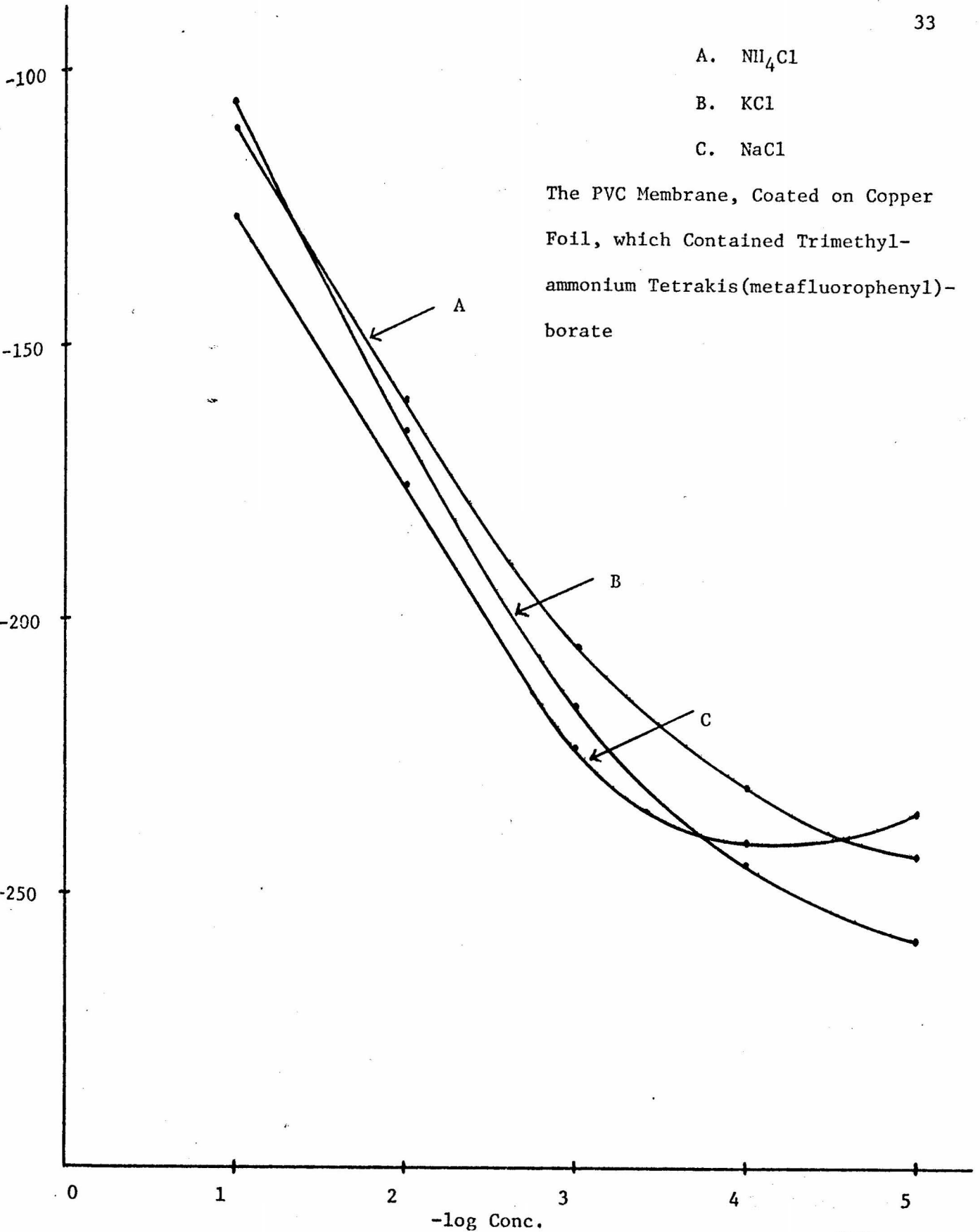


FIGURE VIII

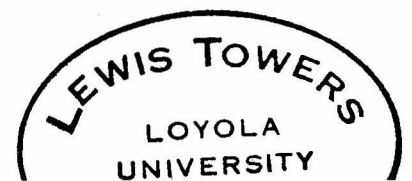


TABLE VI

Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Copper Foil, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate.

Voltage (mv) Conc.	Cu ⁺⁺	Ca ⁺⁺	Cd ⁺⁺	Mg ⁺⁺
10 ⁻¹ M	-68.2	-128.1	-133.4	-154.9
10 ⁻² M	-80.4	-149.3	-153.2	-170.2
10 ⁻³ M	-86.3	-162.6	-168.6	-190.1
10 ⁻⁴ M	-92.7	-174.7	-180.9	-190.1
10 ⁻⁵ M	-96.5	-181.4	-187.1	-194.3

Emf as Function of Divalent Ion Halide Salt Concentration Measured
Using the PVC Membrane, Coated on Copper Foil, which Contained
Trimethylammonium Tetrakis(metafluorophenyl)borate.

The PVC Membrane, Coated on Copper
Foil, which Contained Trimethylammon-
ium Tetrakis(metafluorophenyl)borate

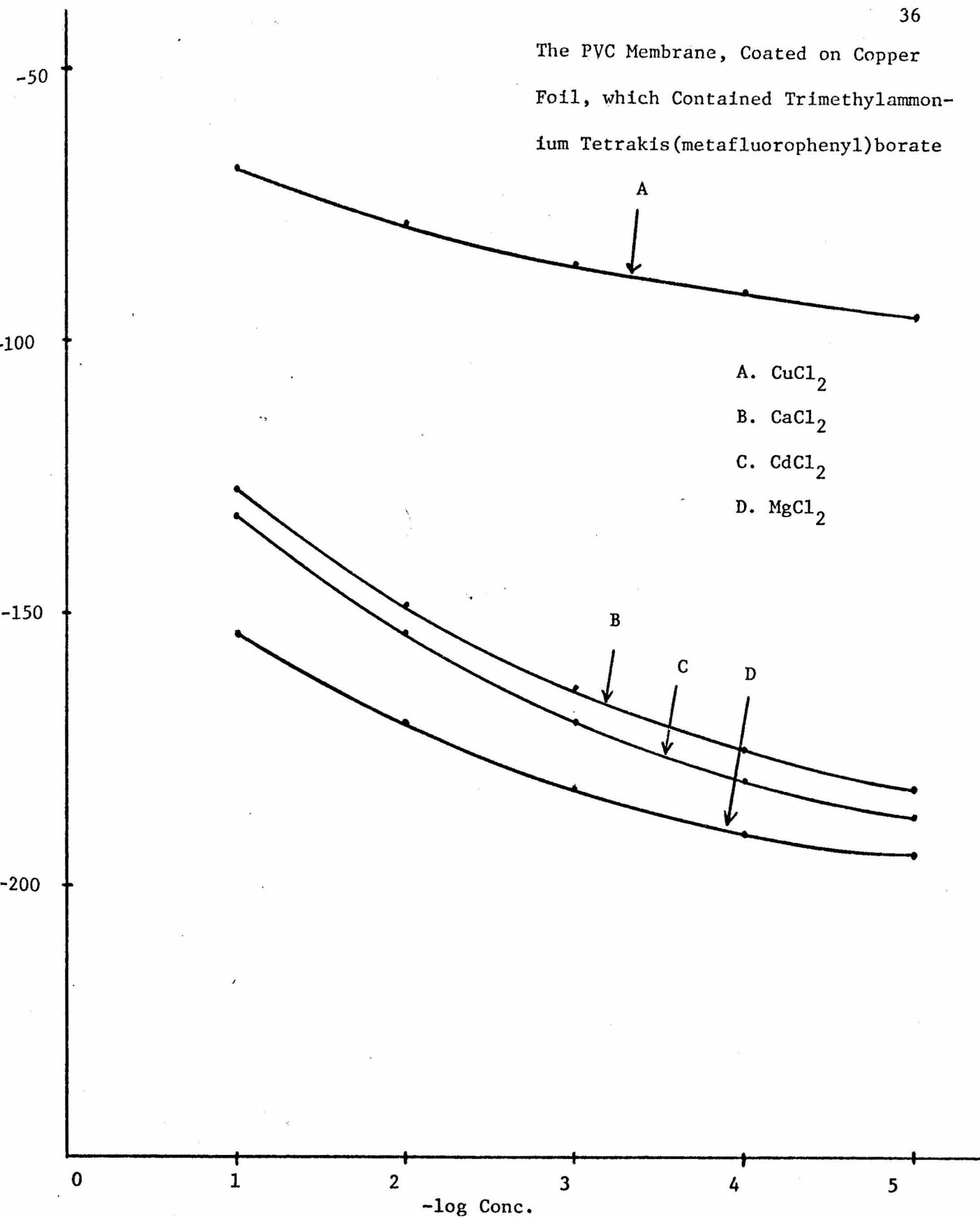


FIGURE IX

Results and Discussion:

The voltage response of monovalent ions using the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate was determined. Potassium showed the most response and had a linear response in the range of $10^{-1}M$ to $10^{-3}M$. Potassium and ammonium still showed a response at low concentrations, but sodium had less response at concentrations below $10^{-3}M$. The average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of ammonium, potassium and sodium ions was 45.6, 56.9 and 50.7 mv, respectively (see Table V and Figure VIII). For the divalent ions, the cadmium showed the most voltage response for this membrane. The voltage responses of divalent ions showed no significant difference from each other. The average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of copper(II), calcium, cadmium and magnesium was 9.2, 17.6, 18.2 and 14.1 mv, respectively. Copper ion showed weaker response to the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate (see Table VI and Figure IX). The voltage response in the range of $10^{-1}M$ to $10^{-5}M$ was significantly lower compared to other ions. It has been thought that copper(II) chloride may react with copper foil to form a copper chloride complex and thus show a different response from the other divalent ions.

TABLE VII

Potentiometric Measurement of Monovalent Ions Using the PVC Membrane, Coated on Zirconium, which Contained Trimethylammonium Tetrakis(meta-fluorophenyl)borate.

Voltage (mv) Conc.	NH_4^+	K^+	Na^+
10^{-1}M	-62.8	-57.8	-92.3
10^{-2}M	-107.2	-100.6	-137.9
10^{-3}M	-147.3	-140.7	-173.2
10^{-4}M	-181.4	-175.4	-188.6
10^{-5}M	-207.9	-202.1	-196.7

Emf as Function of Monovalent Ion Halide Salt Concentration
Measured Using the PVC Membrane, Coated on Zirconium, which
Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.

A. NH_4Cl

B. KCl

C. NaCl

The PVC Membrane, Coated on Zirconium,
which Contained Trimethylammonium
Tetrakis(metafluorophenyl)borate.

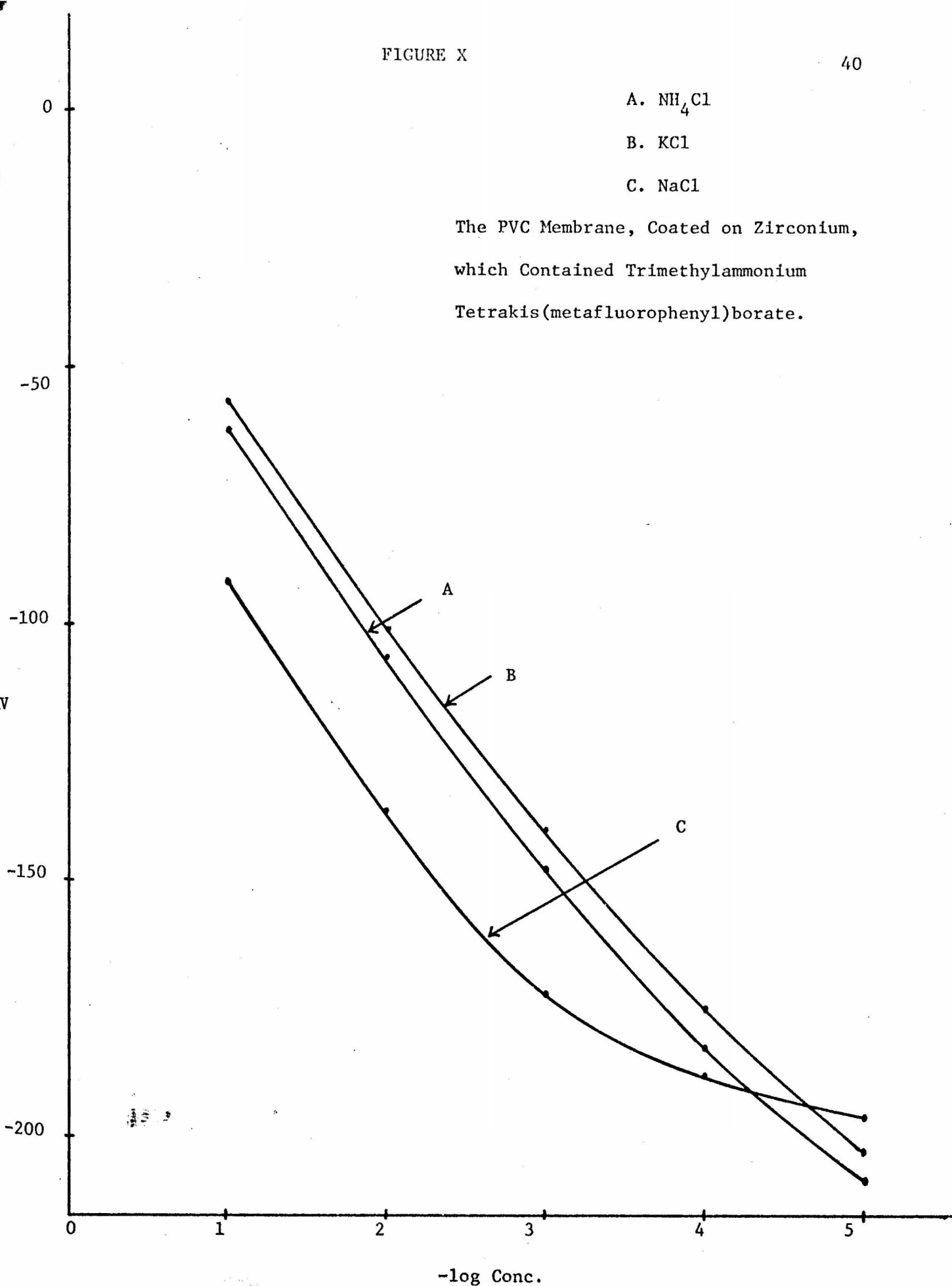


TABLE VIII

Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Zirconium, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate.

Voltage (mv) Conc.	Cu ⁺⁺	Ca ⁺⁺	Cd ⁺⁺	Mg ⁺⁺
10 ⁻¹ M	-15.2	-8.5	+5.2	+8.4
10 ⁻² M	-40.9	-37.2	-22.6	-19.3
10 ⁻³ M	-55.9	-60.8	-42.3	-38.2
10 ⁻⁴ M	-66.4	-75.9	-55.9	-47.6
10 ⁻⁵ M	-71.8	-84.2	-65.8	-51.9

Emf as Function of Divalent Ion Halide Salt Concentration Measured
by Using the PVC Membrane, Coated on Zirconium, which Contained
Trimethylammonium Tetrakis(metafluorophenyl)borate.

A. CuCl_2 B. CaCl_2 C. CdCl_2 D. MgCl_2

The PVC Membrane, Coated on Zirconium, which
Contained Trimethylammonium Tetrakis(metafluoro-
phenyl)borate.

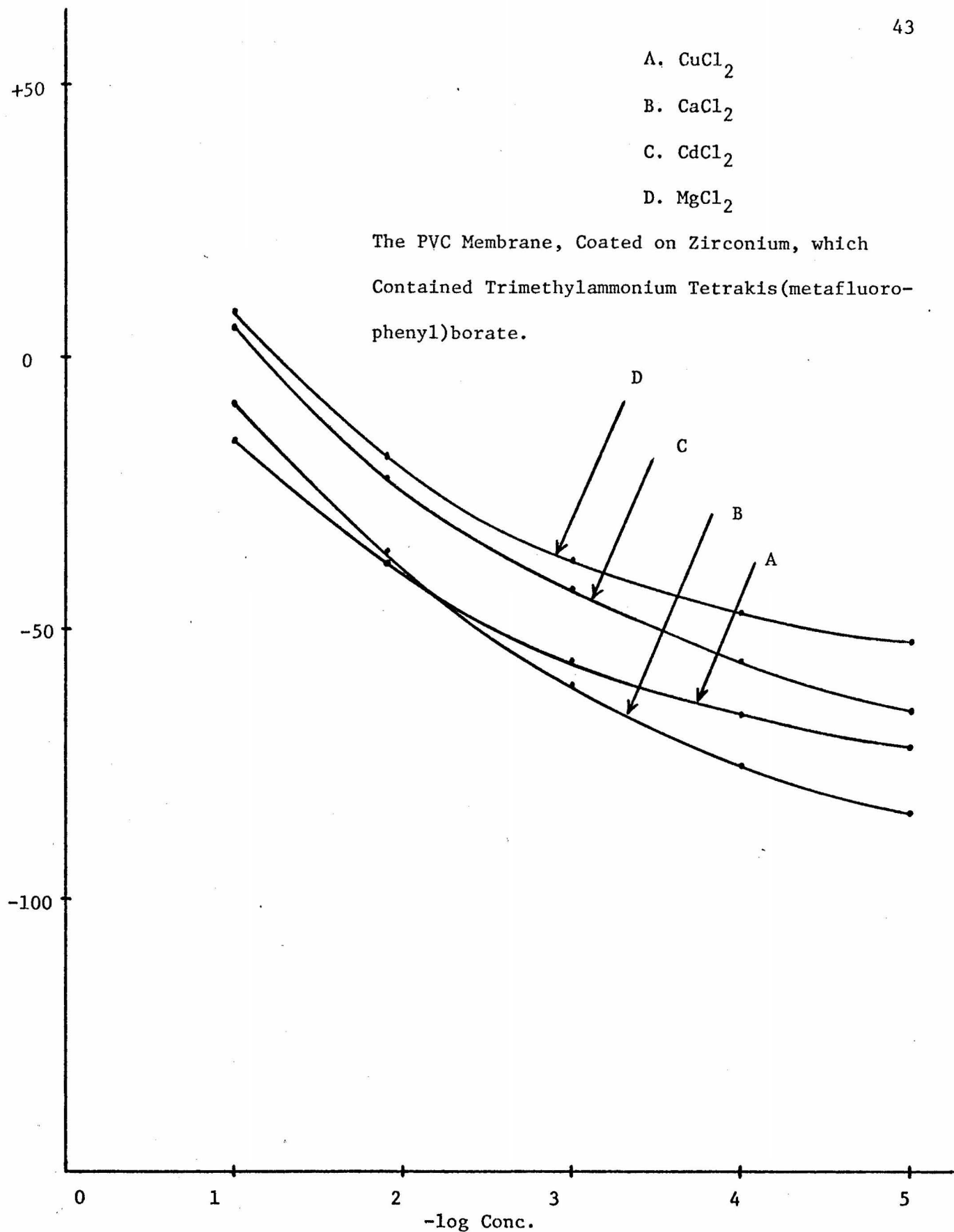


FIGURE XI

Results and Discussion:

The voltage response of monovalent ions using the PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate was determined. Ammonium ion showed the most voltage response in the range of $10^{-1}M$ to $10^{-3}M$. Potassium and ammonium had a linear response in the range of $10^{-1}M$ to $10^{-3}M$ which followed Nernstian response. Sodium had less response at concentrations below $10^{-3}M$. In the range of $10^{-1}M$ to $10^{-5}M$ ammonium and potassium showed voltage response almost the same. The membrane prepared by using the PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)borate showed a linear response for ammonium and potassium and showed a voltage response quite sensitive at concentrations below $10^{-3}M$. This response was better than the PVC membrane of cesium triphenylcyanoborate and the PVC membrane of cesium tetrakis-(p-trifluoromethylphenyl)borate. The average change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of ammonium, potassium and sodium was 42.1, 41.9 and 40.7 mv, respectively (see Table VII and Figure X). For divalent ions, the average change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of copper(II), calcium, cadmium and magnesium was 20.6, 26.3, 23.2 and 22.2 mv, respectively. Calcium showed the most response for this membrane. The PVC membrane showed more response than other polymeric membrane electrodes(13). Most divalent ions had voltage response almost the same (see Table VIII and Figure XI). Monovalent ions showed significantly more voltage response than divalent ions.

The PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)borate showed a quite sensitive response, especially, for ammonium and potassium ion.

TABLE IX

Potentiometric Measurement of Monovalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate.

Voltage (mv) Conc.	NH ₄ ⁺	K ⁺	Na ⁺
10 ⁻¹ M	-93.1	-124.6	-120.1
10 ⁻² M	-42.5	-77.8	-70.3
10 ⁻³ M	+4.5	-30.5	-24.3
10 ⁻⁴ M	+22.8	+9.2	-5.7
10 ⁻⁵ M	+30.9	+24.1	+4.6

Emf as Function of Monovalent Ion Halide Salt Concentration
Measured Using the PVC Membrane, Coated on Platinum, which
Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.

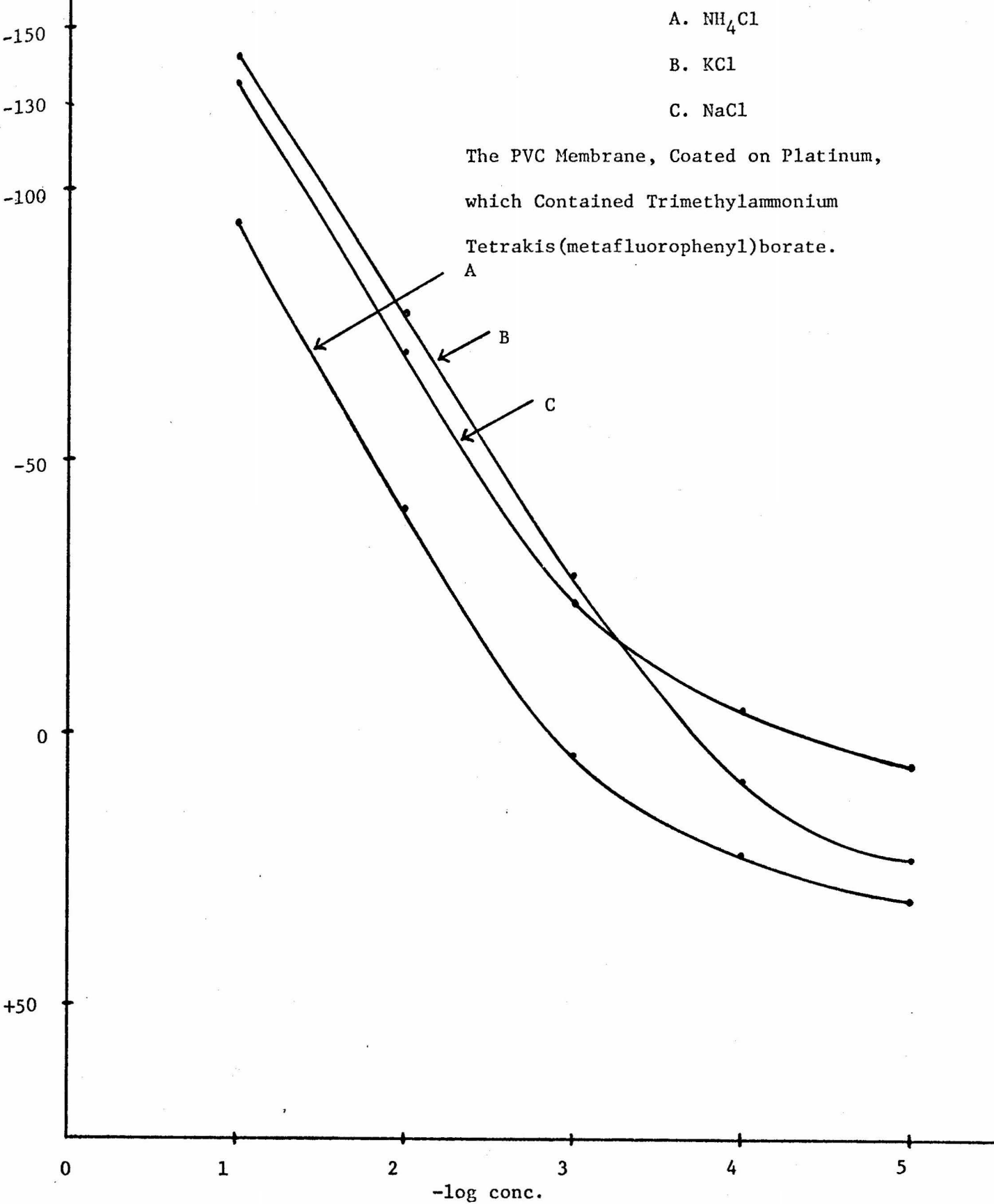


FIGURE XII

TABLE X

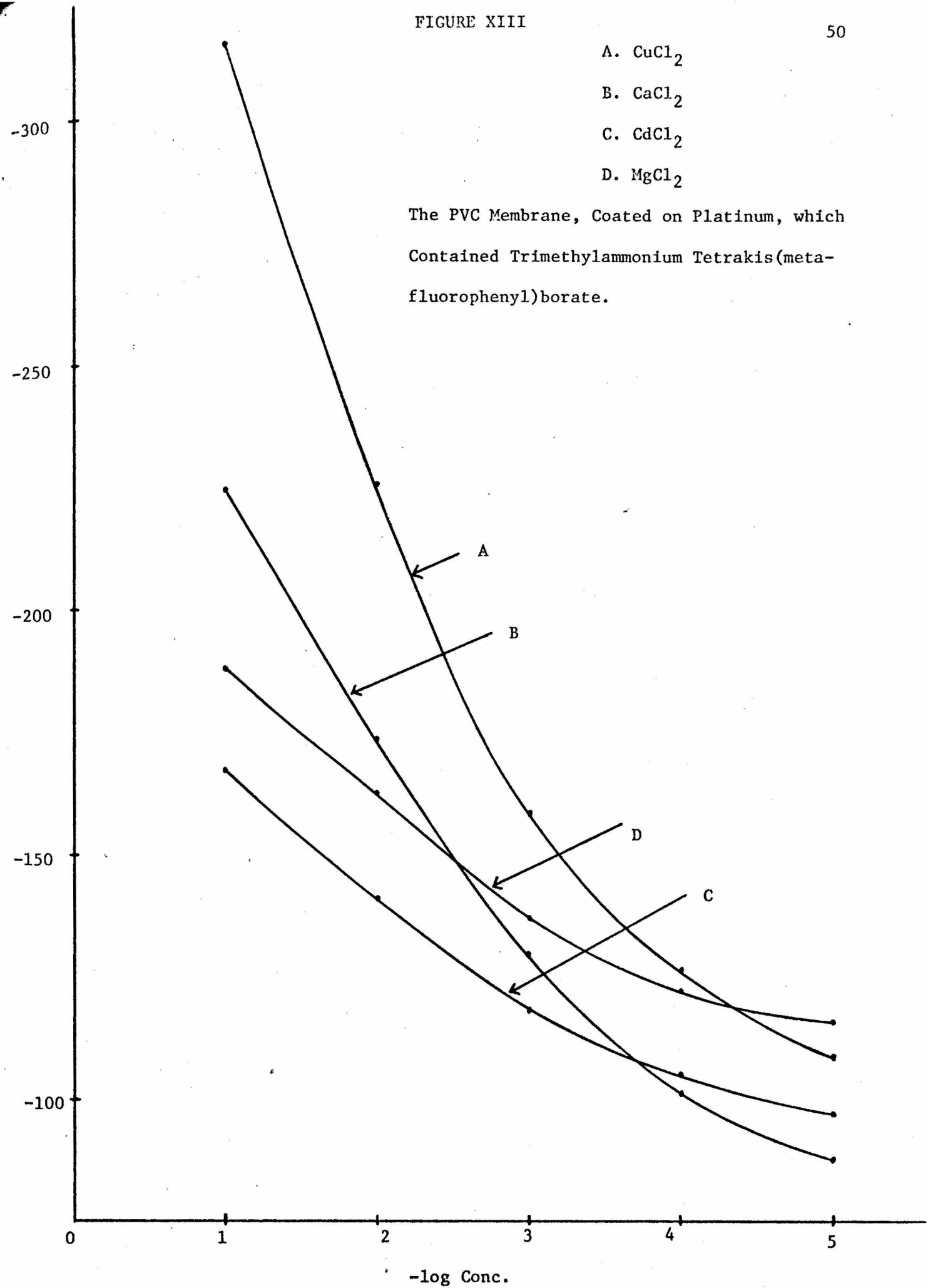
Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate.

Voltage (mv) Conc.	Cu ⁺⁺	Ca ⁺⁺	Cd ⁺⁺	Mg ⁺⁺
10 ⁻¹ M	-315.6	-222.4	-168.4	-187.8
10 ⁻² M	-226.8	-174.2	-141.6	-163.6
10 ⁻³ M	-158.4	-132.7	-117.6	-137.4
10 ⁻⁴ M	-126.7	-101.9	-103.9	-122.9
10 ⁻⁵ M	-109.3	-88.5	-97.2	-116.1

Emf as Function of Divalent Ion Halide Salt Concentration
Measured Using the PVC Membrane, Coated on Platinum, which
Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.

- A. CuCl_2
- B. CaCl_2
- C. CdCl_2
- D. MgCl_2

The PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(meta-fluorophenyl)borate.



Results and Discussion:

The voltage response of monovalent and divalent ions using the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis-(metafluorophenyl)borate was determined. The average voltage change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of ammonium, potassium and sodium was 49.2, 47.1 and 48.0 mv, respectively. The average change was almost the same for monovalent ions in the range of $10^{-1}M$ to $10^{-3}M$. The response times are generally more rapid than proceeding from dilute to concentrated system(14). Ammonium and sodium showed less response at concentrations below $10^{-3}M$. Potassium still showed a significant response at low concentrations such as $10^{-5}M$ and the voltage deviation are smaller if the solution prepared fresh(15). This membrane gave quite linear response for monovalent ions in the range of $10^{-1}M$ to $10^{-3}M$ which follow Nernstian response (see Table IX and Figure XII). This membrane also gave a more sensitive response than the PVC membranes of cesium triphenylcyanoborate, cesium tetrakis(p-trifluoromethylphenyl)-borate. Potassium showed the most response in the range of $10^{-1}M$ to $10^{-5}M$ for this membrane. The electrodes have been successfully employed for potentiometric titrations or direct potentiometric measurements under suitable conditions, even if interfering ions were present at low concentrations(16). The average voltage change per decade of divalent ions in the range of $10^{-1}M$ to $10^{-3}M$ of copper(II), calcium, cadmium and magnesium was 78.1, 47.5, 26.3 and 26.2 mv, respectively. Copper(II) ion showed the most significantly sensitive response for this membrane. It has been believed that copper(II) showed a voltage response as a monovalent ion by passing each ion through the membrane coated on platinum as monovalent ion. This is the reason that copper(II) ion showed

the most sensitive response for the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate and copper(II) which is more response than monovalent ions for this membrane (see Table X and Figure XIII).

For divalent ions, the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate showed a more sensitive response than other membranes, especially, copper(II) ion.

TABLE XI

Potentiometric Measurement of Divalent Ions Using the PVC Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate.

Voltage (mv) Conc.	Copper (II) chloride	Copper nitrate	Copper sulfate	Cadmium Chloride	Cadmium sulfate
$10^{-1}M$	-315.6	-190.5	-171.4	-168.4	-186.2
$10^{-2}M$	-226.8	-169.3	-159.6	-141.6	-173.3
$10^{-3}M$	-158.4	-150.2	-147.9	-117.6	-161.8
$10^{-4}M$	-126.7	-139.7	-140.1	-103.9	-152.5
$10^{-5}M$	-109.3	-133.2	-139.1	-197.2	-145.4

Emf as Function of Divalent Ion Salt Concentration Measured
Using the PVC Membrane, Coated on Platinum, which Contained
Trimethylammonium tetrakis(metafluorophenyl)borate.

FIGURE XIV

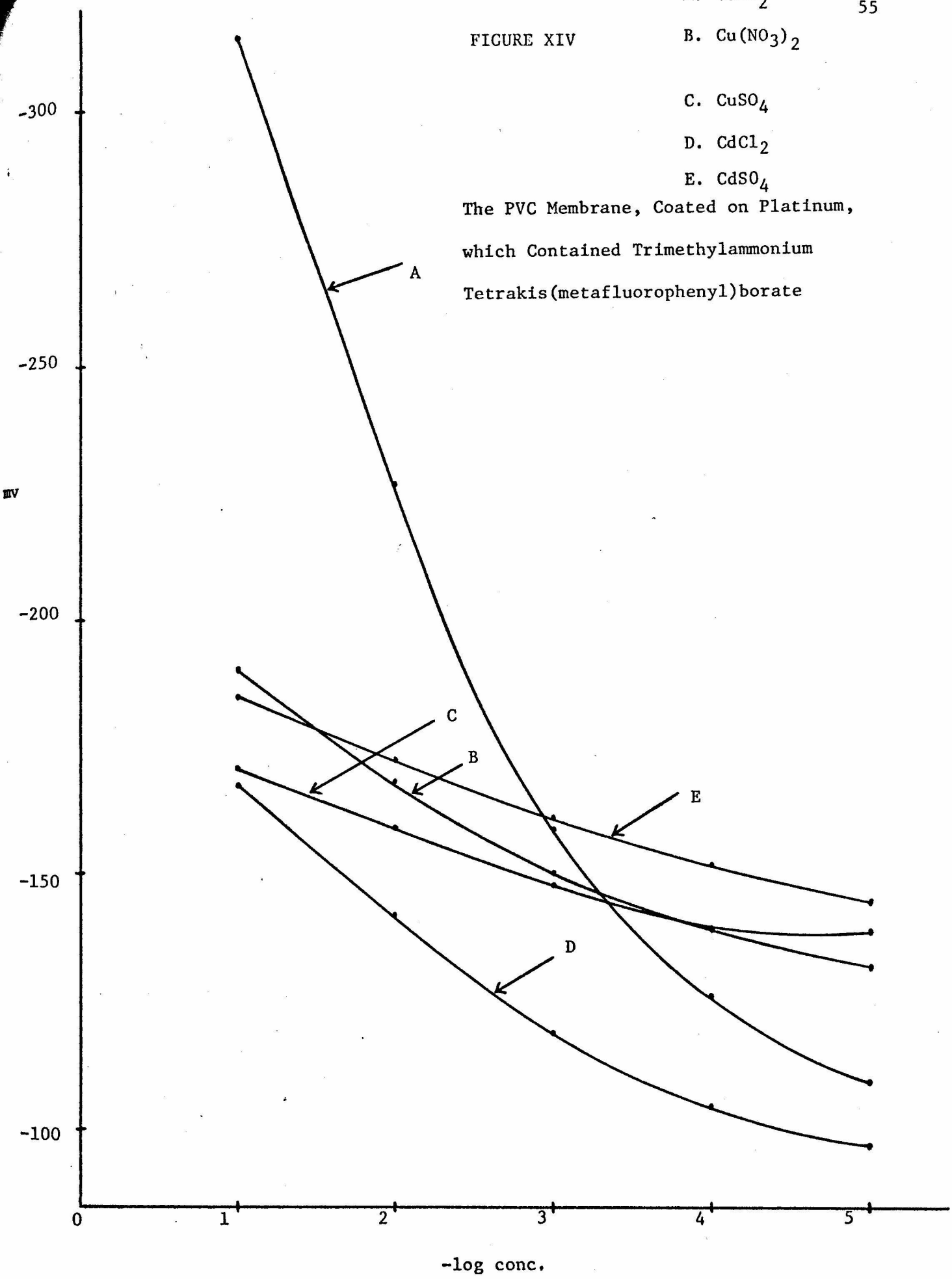
B. $\text{Cu}(\text{NO}_3)_2$

C. CuSO_4

D. CdCl_2

E. CdSO_4

The PVC Membrane, Coated on Platinum,
which Contained Trimethylammonium
Tetrakis(metafluorophenyl)borate



Results and Discussion:

The voltage response of divalent compounds using the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate was determined. The average change per decade in the range of 10^{-1}M to 10^{-3}M of CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, CdCl_2 and CdSO_4 from Table XIII was 78.1, 20.5, 12.0, 18.5 and 12.0 mv, respectively.

Copper(II) chloride exhibited more significantly sensitive response than other compounds. It was believed that copper(II) ion passed through the membrane coated on platinum by acting the same as a monovalent ion.

Copper sulfate and cadmium sulfate had the same average change in the range of 10^{-1}M to 10^{-3}M (see Table XI and Figure XIV). These two sulfate compounds showed less response than other compounds. It is believed that sulfate group had tendency to form a π bond interaction between one of the phenyl rings of the tetraphenylborate and the metal(17).

Therefore, it appears that the membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate exhibits the most sensitive response for copper(II) chloride and exhibits the least response for sulfate compounds: i.e. copper sulfate and cadmium sulfate.

TABLE XII

Potentiometric Measurements of Monovalent and Divalent Ions Using the Membrane Coated on Platinum, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate Compared to Platinum Electrode.

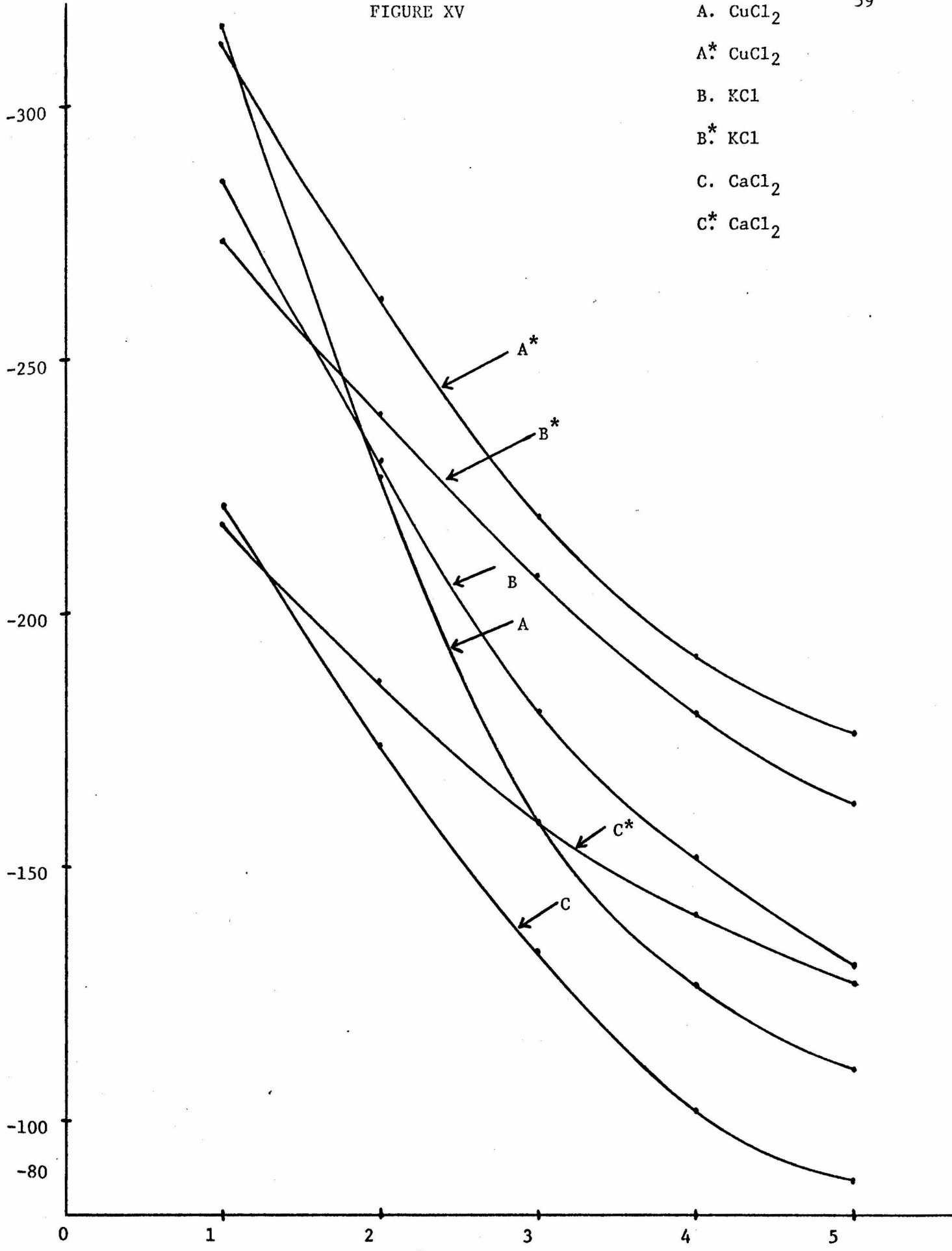
The Membrane Coated on Platinum, which Contained Trimethylammonium Tetrakis-(metafluorophenyl)borate

Platinum Electrode

Voltage (mv) Conc.	Copper(II) chloride	Potassium chloride	Calcium chloride	Copper(II) chloride	Potassium chloride	Calcium chloride
$10^{-1}M$	-315.6	-286.3	-222.4	-313.2	-274.8	-218.2
$10^{-2}M$	-226.8	-230.4	-174.2	-262.1	-241.6	-187.3
$10^{-3}M$	-158.4	-179.9	-132.7	-219.5	-207.8	-139.5
$10^{-4}M$	-126.7	-151.5	-101.9	-191.8	-179.7	-139.5
$10^{-5}M$	-109.3	-134.8	-88.5	-176.5	-162.8	-127.8

Emf as Function of Monovalent and Divalent Ion Halide Salt
Concentrations Measured Using the PVC Membrane, Coated on Platinum
which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate
Compared to Platinum Electrode.

- A. CuCl_2
- A* CuCl_2
- B. KCl
- B* KCl
- C. CaCl_2
- C* CaCl_2



*Potentiometric measurements using platinum electrode

TABLE XIII

The Average Voltage Change/Decade in the Range of $10^{-1}M$ to $10^{-3}M$.

Type of membranes	mv/decade				
	Copper (II) chloride	Copper nitrate	Copper sulfate	Cadmium chloride	Cadmium sulfate
The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl) borate	78.1	20.5	12.0	18.5	12.0

Types of membranes	Copper (II) chloride	Potassium chloride	Calcium chloride
The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis-(metafluorophenyl)borate.	78.1	62.9	47.5
Platinum electrode	49.4	34.3	28.3

The voltage response of monovalent and divalent ions using the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate compared to platinum electrode was determined. The average change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of copper(II) chloride, potassium chloride and calcium chloride using the membrane coated on platinum containing trimethylammonium tetrakis(metafluorophenyl)borate from Table XIII was 78.1, 62.9 and 47.5 mv, respectively. The average change per decade in the range of $10^{-1}M$ to $10^{-3}M$ of copper(II) chloride, potassium chloride and calcium chloride using platinum electrode from Table XIII was 49.4, 34.3 and 28.3 mv, respectively.

Potentiometric measurements using the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate exhibited significantly greater responses than the platinum electrode. Especially, copper(II) chloride showed significantly sensitive response (Figure XV).

Therefore, it appears that the potentiometric measurements using the membrane prepared from DBP plasticizer obtained from Witco Chemical Company, Lot. No. 52 mixed with PVC obtained from Stauffer Chemical Company and trimethylammonium tetrakis(metafluorophenyl)borate coated on platinum exhibits high ion activity and was the best membrane for potentiometric measurement (Figure XV).

TABLE XIV

Potentiometric Titration by Using the PVC Membrane of Cesium Triphenylcyanoborate.

A. 25 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-66.4	-87.6	-107.8	-117.5	-105.8	-84.8	-61.4

B. 20 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-79.6	-113.5	-132.4	-147.1	-133.6	-122.3	-96.9	-72.4

C. 15 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
Voltage (mv)	-82.4	-103.5	-124.6	-145.3	-132.8	-109.6	-83.2	-58.8

Potentiometric Titration of Boric Acid and Ammonium Chloride
Solution Titrated with Sodium Hydroxide Using the PVC Membrane
of Cesium Triphenylcyanoborate.

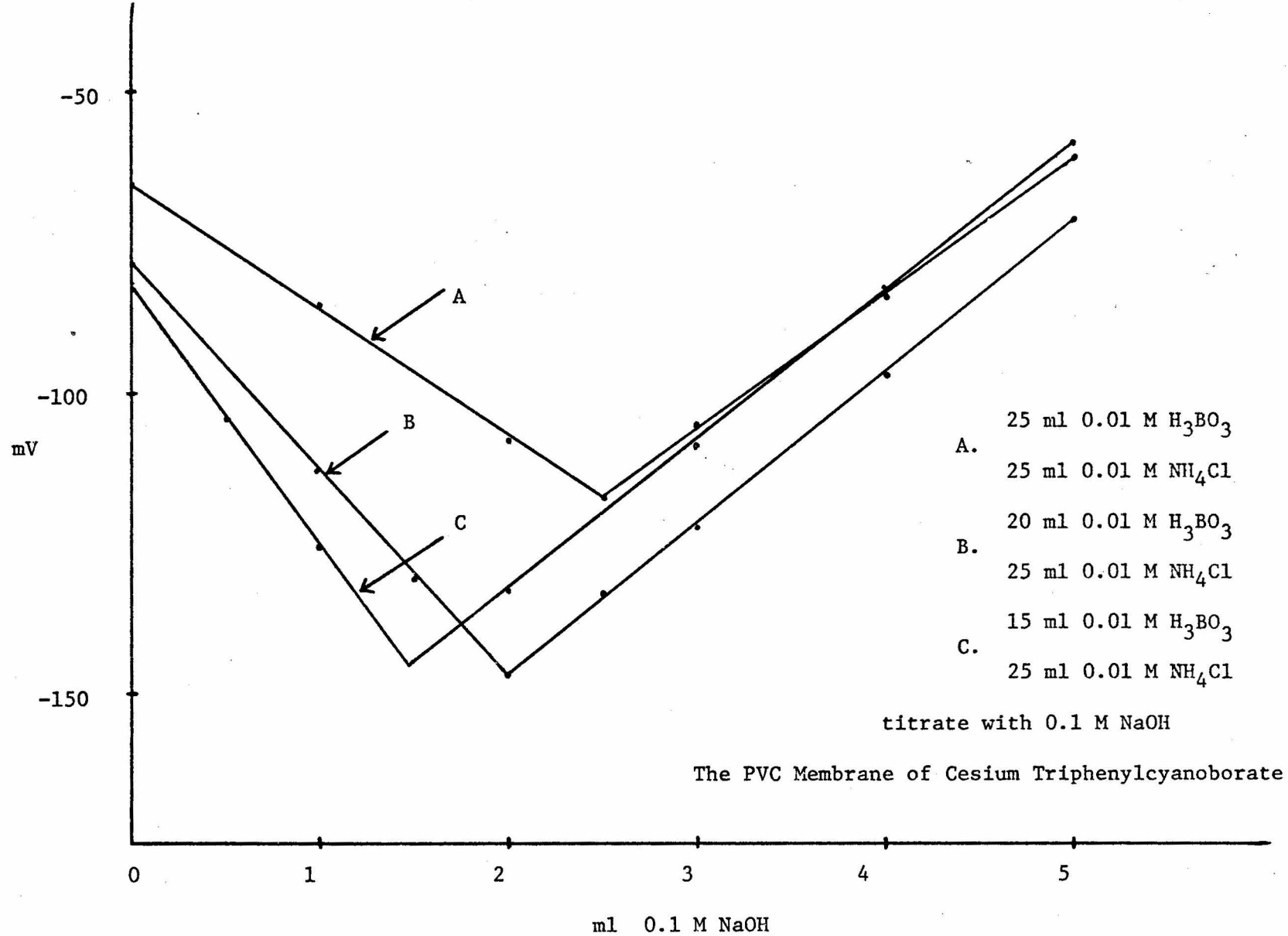


FIGURE XVI

Potentiometric Titration by Using the PVC Membrane of cesium Tetrakis-(p-trifluoromethylphenyl)borate.

A. 25 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-116.2	-103.4	-91.6	-85.1	-83.4	-79.8	-75.7

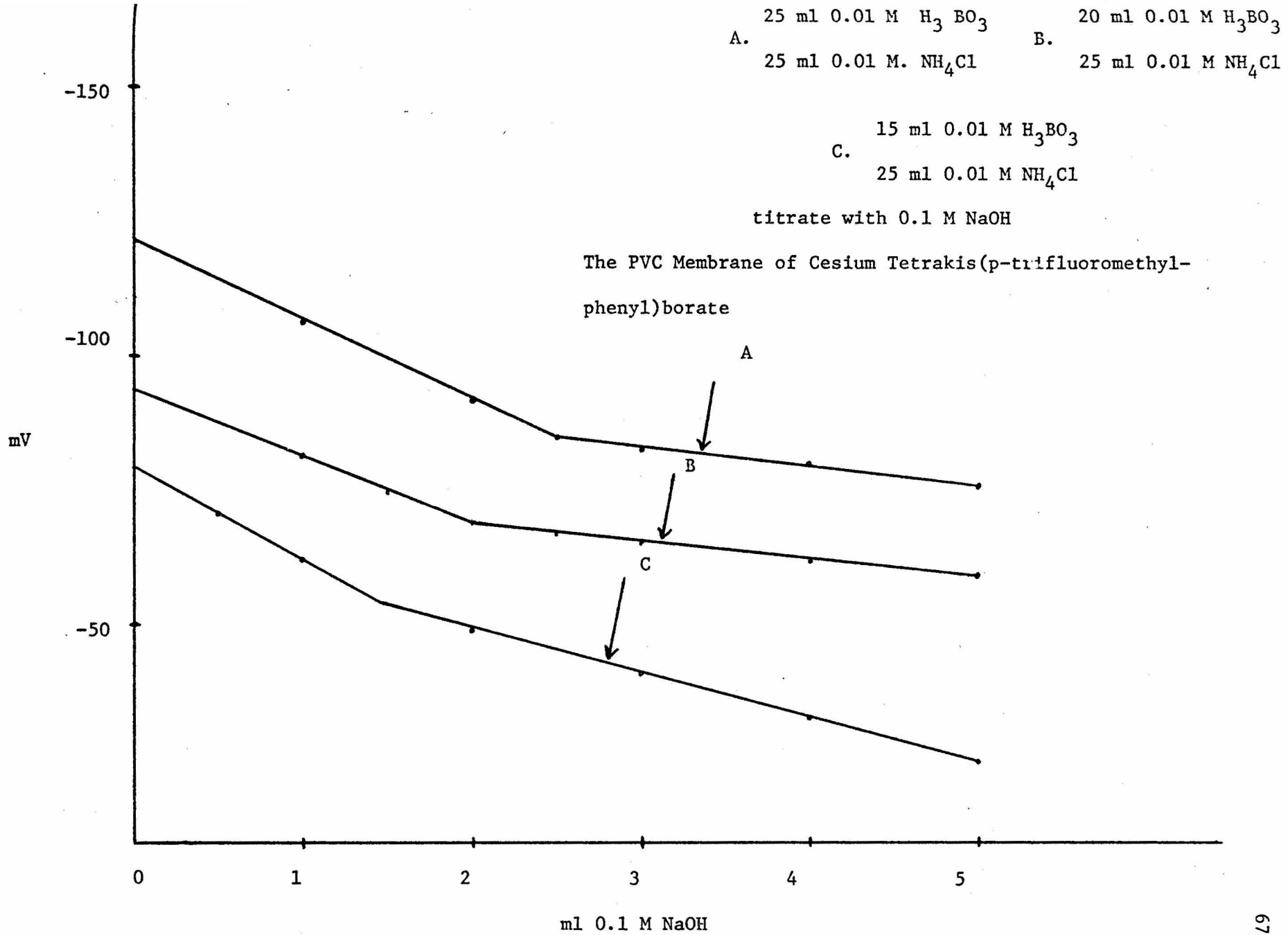
B. 20 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-96.4	-82.6	-75.3	-69.7	-67.3	-65.6	-61.9	-58.8

C. 15 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
Voltage (mv)	-80.4	-70.7	-62.2	-53.5	-49.1	-41.4	-33.6	-24.8

Potentiometric Titration of Boric Acid and Ammonium Chloride
Solution Titrated with Sodium Hydroxide Using the PVC Membrane
Cesium Tetrakis(p-trifluoromethylphenyl)borate.



ml 0.1 M NaOH

FIGURE XVII

TABLE XVI

Potentiometric Titration by Using the Membrane of Trimethylammonium
Tetrakis(metafluorophenyl)borate

A. 25 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-126.9	-110.2	-95.6	-87.3	-84.4	-79.1	-73.2

B. 20 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-100.2	-82.6	-74.4	-65.8	-62.1	-57.8	-50.2	-42.8

C. 15 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
Voltage (mv)	-73.6	-63.3	-53.5	-44.1	-40.2	-29.9	-19.6	-9.8

Potentiometric Titration of Boric Acid and Ammonium Chloride
Solution Titrated with Sodium Hydroxide Using the PVC Membrane
of Trimethylammonium Tetrakis(metafluorophenyl)borate.

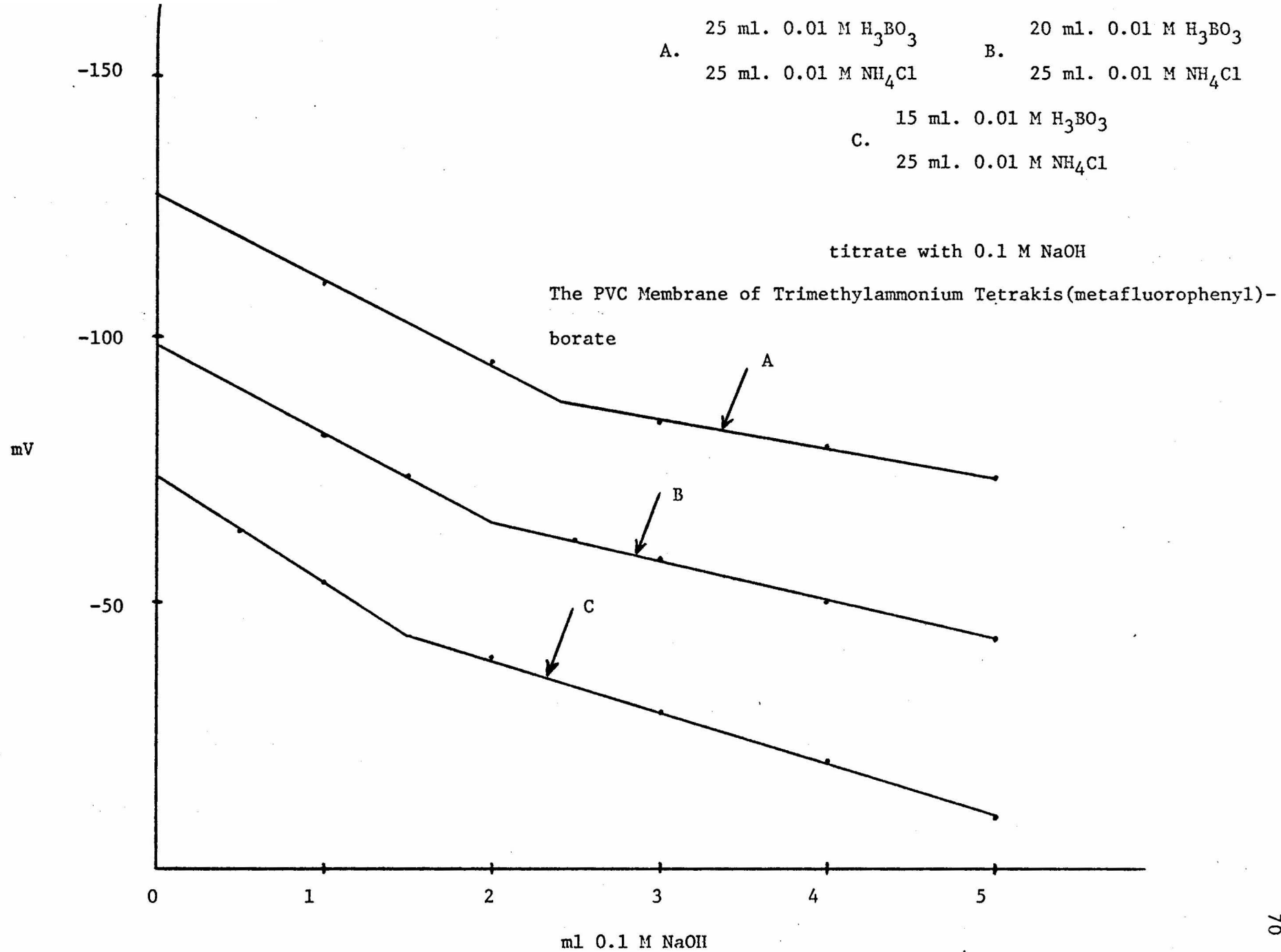


FIGURE XVIII

Potentiometric Titration by Using the Membrane, Coated on Platinum, which Contained Trimethylammonium Tetrakis(metafluorophenyl)borate.

A. 25 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-90.4	-78.1	-65.8	-60.3	-53.5	-48.5	-43.4

B. 20 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Voltage (mv)	-35.3	-26.2	-21.8	-16.0	-14.6	-12.7	-8.2	-4.3

C. 15 ml. 0.01 M H_3BO_3 titrate with 0.1 M NaOH
25 ml. 0.01 M NH_4Cl

ml. NaOH	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
Voltage (mv)	+5.6	+11.2	+14.3	+17.8	+19.0	+21.3	+23.6	+26.2

Potentiometric Titration of Boric Acid and Ammonium Chloride
Solution Titrated with Sodium Hydroxide Using the PVC Membrane,
Coated on Platinum, which Contained Trimethylammonium Tetrakis-
(metafluorophenyl)borate.

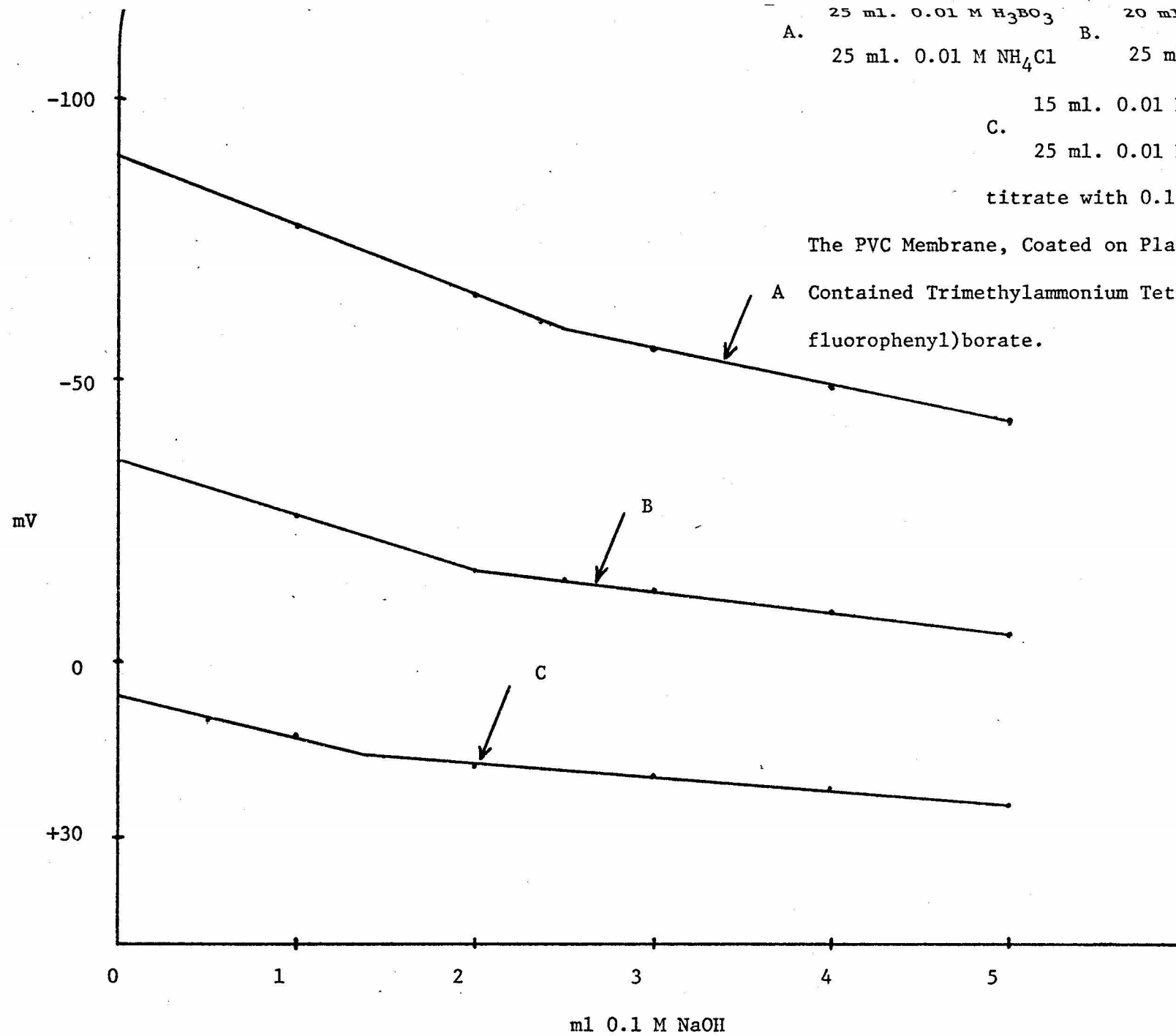


FIGURE XIX

CHAPTER VII

POTENTIOMETRIC TITRATIONS USING DIFFERENT KINDS OF MEMBRANES

The potentiometric titrations using different kinds of membranes has been divided into 3 parts. Part A using a mixed solution of 25 ml. of 0.01 M H_3BO_3 and 25 ml. of 0.01 M NH_4Cl titrated with 0.1 M NaOH. Part B using a mixed solution of 20 ml. of 0.01 M H_3BO_3 and 25 ml. of 0.01 M NH_4Cl titrated with 0.1 M NaOH. Part C using a mixed solution of 15 ml. of 0.01 M H_3BO_3 and 25 ml. of 0.01 M NH_4Cl titrated with 0.1 M NaOH. For the PVC membrane of cesium triphenylcyanoborate, the end point for parts A, B and C (Figure XVI) were 2.5, 1.9 and 1.5 ml. of 0.1 M NaOH, respectively which exhibited the expected results. The titration curve using this membrane gave sharper curve than other membranes such as the PVC membranes of cesium tetrakis(p-trifluoromethylphenyl)borate, trimethylammonium tetrakis(metafluorophenyl)borate and the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate. All of the membranes for potentiometric titrations showed the end point close to the expected result.

This fact shows that there were no interferences in the titrations because of the ammonium ion activity. The membranes of cesium tetrakis(p-trifluoromethylphenyl)borate, trimethylammonium tetrakis(metafluorophenyl)borate and the membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate exhibited the sharpness of titration curves which were almost the same.

Therefore, it appears that the membrane of cesium triphenylcyanoborate shows the best end point and the best titration curve (Figure XVI).

CHAPTER VIII

DISCUSSION AND CONCLUSIONS

The membrane electrodes were invented by chemists and they studied the development of new kinds of membranes from glass electrode and only number of years later membrane electrodes were developed for different ions. In our preparation of the membrane, the temperature and the time were important in preparation of the membranes. When the temperature exceeded 200°C , the membranes showed less activity than the membrane prepared at 200°C . At the temperature below 200°C , the membrane either did not form or they lacked toughness and flexibility. Thus the temperature was controlled at $200 \pm 5^{\circ}\text{C}$. The solutions containing substitute borates in PVC and DBP plasticizer was placed in the oven for 2 minutes. The membrane prepared by mixing DBP plasticizer with PVC showed Nernstian response. DBP plasticizer was the best plasticizer in order to obtain the membrane which was tough and flexible. In referring to Table XVIII, the membrane of cesium tetrakis(p-trifluoromethylphenyl)borate showed the greatest response to ammonium ion in the range of 10^{-1}M to 10^{-3}M . The membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate exhibited the greatest response for potassium ion in the range of 10^{-1}M to 10^{-3}M . The PVC membrane of trimethylammonium tetrakis(metafluorophenyl)borate exhibited the greatest response for Na^+ ion in the range of 10^{-1}M to 10^{-3}M . The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate followed the Nernstian behavior and exhibited the greatest response in the range of 10^{-1}M to 10^{-5}M for monovalent ions.

TABLE XVIII

The Average Voltage Change/Decade of Concentration in the Range of 10^{-1}M to 10^{-3}M of Monovalent Ion Halide Salts.

Types of membranes	mv/decade		
	NH_4^+	K^+	Na^+
The PVC membrane of cesium triphenylcyano-borate.	43.8	47.6	48.1
The PVC membrane of cesium tetrakis(p-tri-fluoromethylphenyl)borate.	58.1	47.2	49.0
The PVC membrane of trimethylammonium tetrakis(metafluorophenyl)borate.	44.2	46.3	51.2
The PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate.	45.6	56.9	50.7
The PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate.	42.1	41.9	40.7
The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate.	49.2	47.1	48.0

TABLE XIX

The Average Voltage Change/Decade of Concentration in the range of $10^{-1}M$ to $10^{-3}M$ of Divalent Ion Halide Salts.

Types of membranes	mv/decade			
	Cu^{++}	Ca^{++}	Cd^{++}	Mg^{++}
The PVC membrane of trimethylammonium tetrakis(metafluorophenyl)borate	26.3	16.1	18.2	24.9
The PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis-(metafluorophenyl)borate.	9.2	17.6	18.2	14.1
The PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)borate.	20.6	26.3	23.2	22.2
The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate.	78.1	47.5	26.3	26.2

The voltage deviations were small for freshly prepared solutions at a concentration of 10^{-5} M.

The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate (Table XIX) exhibited significantly greater response than the PVC membrane of cesium triphenylcyanoborate, the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)borate, the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate and the PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)borate. This membrane exhibited a significantly greater response in the range of 10^{-1} M to 10^{-5} M for divalent ions Cu^{++} , Ca^{++} , Cd^{++} and Mg^{++} than did the other membranes tested. Of the divalent cations tested, the greatest sensitivity was observed for Cu^{++} ion.

Therefore, it appears that the PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(metafluorophenyl)borate should be useful in determining voltage responses of different kinds of monovalent and divalent cations. Monovalent cations follow closer to Nernstian response than divalent.

SUMMARY

The measurements of membrane potentials has been an area of increasing interest in the recent years, especially for constructing potentiometric membrane electrode useful in measuring ionic activities in the solution of monovalent and divalent ions.

The field is expanding rapidly and one of the objectives of this research is the development of an electrode that is sensitive and selective. The response times are generally more rapid when proceeding from dilute to concentrated solution. The membrane prepared by mixing DBP plasticizer obtained from Witco Chemical Company, Lot. No. 52 and a finely divided PVC powder obtained from Stauffer Chemical Company exhibited toughness and flexibility. It was found that it was necessary to add plasticizer with PVC to obtain Nernstian behavior. PVC membrane electrodes exhibited the response times within a minute.

The initial aim of this study was to investigate the method of preparation different kinds of membranes which showed toughness and flexibility and studied the potentiometric measurements of membrane electrodes which exhibited high sensitive response. The PVC membrane, coated on platinum, which contained trimethylammonium tetrakis(meta-fluorophenyl)borate exhibited significantly greater response for monovalent and divalent ions than the PVC membrane of cesium triphenylcyano-borate, the PVC membrane of cesium tetrakis(p-trifluoromethylphenyl)-borate, the PVC membrane, coated on copper foil, which contained trimethylammonium tetrakis(metafluorophenyl)borate, the PVC membrane, coated on zirconium, which contained trimethylammonium tetrakis(metafluorophenyl)-borate. This membrane showed significantly very high sensitive response

for Cu^{++} ion.

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APPROVAL SHEET

The thesis submitted by Boonrod Hirunmitnakon has been read and approved by three members of the Department of Chemistry.

The final copies have been examined by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated and that the thesis is now given final approval with reference to content, form and mechanical accuracy.

This thesis is therefore accepted in partial fulfillment of the requirements for the Degree of Master of Science.

April 13, 1976

Date

Carl E. Moore

Signature of Advisor