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determination of formation constants of complex species in
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AN INVESTIGATION OF SOLVENT EXTRACTION
TECHNIQUES IN THE DETERMINATION
OF FORMATION CONSTANTS OF COMPLEX
SPECIES IN AQUEOUS SILVER
CHLORIDE SOLUTION

A THESIS
SUBMITTED TO THE
DEPARTMENT OF CHEMISTRY
BRIGHAM YOUNG UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Arts

by
David M. Bodily

July, 1960

This Thesis by David M. Bodily is accepted in its present form by the Department of Chemistry as satisfying the thesis requirement for the degree of Master of Arts.

PREFACE

The work reported in this thesis is part of an investigation of molecular species in ionic equilibrium sponsored by the National Science Foundation. The first phase of the investigation consisted of solubility studies of the silver chloride system. This work is part of the second phase which is an investigation of ion exchange and solvent extraction techniques in the determination of formation constants for the complex species. Once these techniques are developed, they will be applied to various unsaturated systems to yield information concerning molecular species. This work deals specifically with solvent extraction techniques.

I wish to extend my gratitude and appreciation to Dr. Eliot A. Butler and Dr. Keith P. Anderson for their advice and direction during the course of this investigation. I also wish to thank Dr. Richard L. Snow for his assistance in the calculations.

My appreciation is extended to the National Science Foundation and the Brigham Young University for the financial assistance that I have received.

I wish to express my gratitude and love to my wife, Beth Alene, who has supported and encouraged me during this period of study.

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I INTRODUCTION

STATEMENT OF PROBLEM This investigation is part of a study of molecular (undissociated) species in ionic equilibrium. The first part of the investigation^{1,2} consisted of solubility studies of the silver chloride system. The silver chloride system was chosen because it lends itself well to solubility studies, formation constants are known for the complex species that exist in the system, and the work of Jonte and Martin³, Lieser⁴, and others shows the existence of molecular species.

The second phase of the investigation is an attempt to find methods for calculating the formation constants for the complex species in unsaturated solutions. Hecht² and Pyper⁵ have investigated ion exchange techniques and this work is an extension of the work of Tingey¹ in investigating solvent extraction techniques.

Once a satisfactory method is developed to calculate the formation constants for complex species, it will be applied to systems other than the silver chloride system to yield information concerning molecular species.

¹G. L. Tingey, Master's Thesis, Brigham Young University, 1959.

²H. G. Hecht, Master's Thesis, Brigham Young University, 1959.

³J. H. Jonte and D. S. Martin, J. Am. Chem. Soc., 74, 2052 (1952).

⁴K. H. Lieser, Z. anorg. Chem., 292 97 (1957).

⁵J. W. Pyper, Master's Thesis, Brigham Young University, 1960.

THE SILVER CHLORIDE SYSTEM The silver chloride system has long been of interest to chemists, not only because of its analytical importance, but also because of the nature of the system. The solubility of silver chloride in chloride ion solutions reaches a minimum value and then increases as the chloride ion concentration increases. The same phenomenon is observed in silver ion solutions as the silver ion concentration is increased. Early workers found that the solubility product constant varied with the method by which it was determined. The results were higher when a method was used which measured the amount of silver in the solution than when a method was used which measured only the activity of the silver ion in solution.

Drucker⁶ proposed that the unusual solubility of silver chloride was due to the formation of a colloid which crystallized so slowly that the intermediate steps were definitely defined and reproducible. The colloidal theory has been replaced and the discrepancies explained by the discovery of complex ions and molecular species.

In 1907, Noyes and Bray⁷ proposed the existence of dichloro silver (I) ion, AgCl_2^- . Forbes⁸ found evidence for the trichloro silver

⁶K. Drucker, Z. Chem. Ind. Kolloide, 4, 216 [C. A., 5, 434 (1911)].

⁷A. A. Noyes and W. C. Bray, J. Am. Chem. Soc., 29, 166 (1907).

⁸G. S. Forbes, J. Am. Chem. Soc., 33, 1937 (1911).

(I) ion, AgCl_3^- , and the tetrachloro silver (I) ion, AgCl_4^{3-} . Later, Forbes and Cole⁹ extended this investigation to solutions of lower chloride ion concentrations and found evidence for the dichloro silver (I) ion. They also had a constant in their solubility expression which they attributed either to undissociated silver chloride or to colloidal silver chloride. Pinkus and Hanrez¹⁰ found that the solubility of silver chloride was independent of particle size and thereby discredited the colloidal theory. Pinkus and coworkers^{11,12,13,14} produced further evidence for polychloro silver complex ions.

Jonte and Martin³ calculated formation constants for the molecular species and for the dichloro silver (I) ion by analysis of the solubility curve. The total concentration of all silver-containing species was plotted versus the chloride ion activity. A value for the solubility product constant which had been determined potentiometrically by Owen¹⁵ was assumed and the constants were calculated by analysis of the curve.

⁹G. S. Forbes, and H. I. Cole, J. Am. Chem. Soc., 43, 2492 (1921).

¹⁰A. Pinkus and P. Hanrez, Bull. soc. chim. Belg., 47, 532 (1938). [C. A., 33, 1572 (1939)].

¹¹A. Pinkus and N. Berkolaiko, J. chim. phys., 27, 364 (1930) [C. A., 24 5574 (1930)].

¹²A. Pinkus, S. Frederic, and R. Schepmans, Bull. soc. chim. Belg., 47, 304 (1938) [C. A., 32, 8243 (1938)].

¹³A. Pinkus, and M. Haugen, Bull. soc. chim. Belg., 45, 693 (1936) [C. A., 31, 2965 (1937)].

¹⁴A. Pinkus and A. M. Timmermans, Bull. soc. chim. Belg., 46, 46 (1937) [C. A., 31, 4874 (1937)].

¹⁵B. B. Owen, J. Am. Chem. Soc., 60, 2229 (1938).

Others^{1,2,4,16,17,18} have used methods similar to that of Jonte and Martin and have obtained values for the constants which agree quite well with those of Jonte and Martin.

The value obtained for the dissociation constant of the molecular species is of the same order as the dissociation constant for the diamminesilver (I) complex ion. Silver chloride is therefore a weak electrolyte and a saturated solution of silver chloride in water is only about 97% dissociated at 25°C. The slight solubility of silver chloride limits the maximum concentration of the molecular species to about 3.6×10^{-7} molar at 25°C.

SOLVENT EXTRACTION Nernst¹⁹ explained the behavior of a solute distributed between two immiscible solvents by the distribution law. The law states that at equilibrium, the ratio of the concentrations of the solute in the two phases is constant for a given temperature. This law is not thermodynamically valid, but it can be shown from thermodynamic

¹⁶E. Berne and I. Leden, Svensk. Kem. Tidskr., 65, 88 (1953) [C. A., 47, 10392 (1953)].

¹⁷I. Leden, Svensk. Kem. Tidskr., 64, 249 (1952) [C. A., 48, 3114 (1954)].

¹⁸V. V. Fomin, Zhur. Fiz. Khim., 29, 1728 (1955) [C.A., 50, 7546 (1956)].

¹⁹W. Nernst, Z. Physik. Chem., 8, 110 (1891) [Morrison and Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons Inc., New York, 1957 p. 8.]

considerations that the law is a good approximation²⁰. At equilibrium the chemical potential of the solute in phase one is equal to the chemical potential of the solute in phase two. This is expressed in equation (1). (The subscripts 1 and 2 refer to the phases 1 and 2.)

$$\mu_1 = \mu_2 \quad (1)$$

By substitution this becomes

$$\mu_1^{\circ} + RT \ln a_1 = \mu_2^{\circ} + RT \ln a_2, \quad (2)$$

and

$$\mu_1^{\circ} + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^{\circ} + RT \ln m_2 + RT \ln \gamma_2. \quad (3)$$

Rearrangement of equation (3) yields

$$m_2/m_1 = (\gamma_1/\gamma_2)e^{-(\mu_2^{\circ} - \mu_1^{\circ})/RT}. \quad (4)$$

At low solute concentrations the activity coefficients approach unity.

If the solute does not have a distorting effect on the mutual solubilities of the two solvents, the equation becomes a statement of the Nernst Distribution Law.

$$K_d = m_2/m_1 \quad (5)$$

The requirements for a solvent extraction system are quite rigid²¹.

²⁰G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons Inc., New York, 1957 pp. 8-9.

²¹L. C. Craig, Anal. Chem., 23, 41 (1951).

One must have immiscible solvents, (solvents which are slightly soluble may each alter the nature of the other solvent to such an extent that the extraction process may not be practical), the rate of exchange of the solute between the two solvents must be rapid enough to be practical, and the solute must be stable in both phases.

For quantitative work, the distribution coefficient must be constant over the concentration range involved and some means must be available to determine the amount of solute present in a given phase.

For selective extraction processes, it is necessary to find solvents which will extract the desired species without extracting interfering species.

Surface activity, tendency to form emulsions, density differences, and distorting effects of solute on phase volumes can also cause difficulties.

Liquid-liquid extraction falls into three general classes²² organic, organometallic, and inorganic. This work is concerned with inorganic extractions.

The distribution ratio is of particular importance in inorganic extractions of metals from aqueous solutions. It is defined as the ratio of the total concentration of all metal containing species in the organic phase to the total concentration of all metal-containing species in the aqueous phase. When only one species is present in both phases, the distribution ratio reduces to the distribution coefficient constant.

²²G. H. Morrison, Anal. Chem., 22, 1388 (1950).

Several metals have been extracted as complexes from hydrochloric acid solutions. Chalkey and Williams²³ list many of the references concerned with the extraction of ferric ion from hydrochloric acid solution. The extracted species is reported to be $\text{HFeCl}_4 \cdot n\text{H}_2\text{O}$ and optimum extraction is obtained from solutions about 7F. in hydrochloric acid. A variety of solvents has been used, including mixed solvents, and ketones gave the best extractions.

Gallium^{24,25,26}, molybdenum^{27,28}, gold²⁹, antimony³⁰, indium³¹, and arsenic³² have all been extracted from hydrochloric acid solution with organic solvents. Rossotti³¹ reported that InCl_3 was extracted at low hydrogen ion concentrations, but in all other cases the extracted

²³D. E. Chalkley and R. J. P. Williams, J. Chem. Soc., 1955, 1920.

²⁴N. H. Nachtrieb and R. E. Fryxell, J. Am. Chem. Soc., 71, 4035, (1949).

²⁵E. H. Swift, J. Am. Chem. Soc., 46, 2375 (1924).

²⁶D. C. Grahame and G. T. Seaborg, J. Am. Chem. Soc., 60, 2524 (1938).

²⁷S. Yamamoto, Bull. Shimane Univ., No. 1, 14 (1951).

²⁸I. Nelidow and R. M. Diamond, J. Phys. Chem., 59, 710 (1955).

²⁹W. A. E. McBryde and J. H. Yoe, Anal. Chem., 20, 1094 (1948).

³⁰F. C. Edwards and A. F. Voigt, Anal. Chem., 21, 1204 (1949).

³¹F. J. C. Rossotti, Rec. trav. chim., 75, 743 (1956).

³²M. G. Arcand, J. Am. Chem. Soc., 79, 1865 (1957).

species was a chloro-metallic acid. The pH for optimum extraction was below 1 in all cases.

Nelidow and Diamond²⁸ explain the extraction of metals from hydrohalic acid solutions as due to four main factors: (1) association or polymerization of the metallic species in either phase, (2) possible acid ionization in the organic phase, (3) complex formation of the metal and the halide ions, and (4) solvation and hydration in the two phases. The distribution coefficient would therefore depend upon the metal ion, hydrogen ion, and halide ion concentrations and upon the nature of the solvent.

Since molecular silver chloride has been shown to exist in aqueous silver chloride solution, it should be possible to extract it with an organic solvent. Krathohvil and Tezak³³ determined the solubility of silver chloride in miscible mixtures of water and organic solvents. They found that the solubility of the silver chloride increased with increasing concentration of organic solvent. This indicates that molecular silver chloride might be extracted with a solvent of lower dielectric constant than water.

³³J. Krathohvil and B. Tezak, Rec. trav. chim., 75, 774 (1956).

II. EXPERIMENTAL

All chemicals used in the preparation of solutions were of reagent grade purity. The water used to prepare solutions was redistilled from alkaline permanganate solution. All volumetric glassware was calibrated.

A standard silver perchlorate solution was prepared from radioactive silver and carrier silver. Seven millicuries of $\text{Ag}^{110\text{m}}$ were obtained from the Oak Ridge National Laboratory in the form of silver nitrate in nitric acid solution. The specific activity of the solution was 263 millicuries per gram of silver. ($\text{Ag}^{110\text{m}}$ decays to Cd^{110} by the emission of beta and gamma rays and has a half life of 270 days.) The silver was deposited on a platinum electrode from a solution approximately 0.04 F. in potassium cyanide. Electrolysis was continued for 45 minutes at 4.0 volts, during which time the current varied from 1.0 to 0.2 amp. The electrode was rinsed in ethanol, dried, and weighed. The silver was then dissolved from the electrode in 5 F. nitric acid and the electrode was again rinsed with ethanol, dried, and weighed. Two milliliters of 71% perchloric acid were added to the acid solution of the silver and the solution was heated on a steam plate. The addition of perchloric acid and the heating process were repeated three times to ensure the removal of the nitric acid. The volume of the solution was about 6 ml. after the heating was completed. The resulting solution of silver perchlorate in perchloric acid was diluted to a known volume and the formality of the silver perchlorate was calculated from the weight of the silver and the final volume of the solution.

A standard 1 F. sodium chloride solution was prepared directly from dried sodium chloride. This solution was diluted to prepare solutions of lower concentrations. The concentration of the chloride ion was checked by a Mohr titration.

Sodium perchlorate solutions were prepared from reagent grade sodium perchlorate monohydrate, obtained from the G. Fredrick Smith Chemical Company. A weighed portion was dissolved in water and diluted to a known volume.

Equilibration solutions were prepared in 125 ml. glass-stoppered Erlenmeyer flasks from the standard silver perchlorate and sodium chloride solutions, the sodium perchlorate solution, and redistilled water. The silver ion concentration varied from 5×10^{-7} to 2×10^{-5} F. while the chloride ion concentration varied from 2×10^{-5} to 0.1 F. The sodium perchlorate solution was used to adjust the ionic strength to a constant value of 0.0973. The aqueous phase was diluted to 20.0 ml. and equilibrated with 20 ml. of organic solvent.

The reagent grade nitrobenzene used in these experiments was found to contain impurities which precipitated with silver ion. Therefore it was necessary to wash the nitrobenzene 5 times with equal volumes of redistilled water to remove water-soluble impurities.

The solutions were allowed to come to equilibrium in a 27 liter water bath which was thermostatically controlled to 25.00 ± 0.02 C. Unsaturated solutions were equilibrated for at least 36 hours and

saturated solutions were equilibrated for one week. The temperature of the bath was controlled by a mercury expansion thermoregulator and a Supersensitive relay manufactured by the American Scientific Company. The relay regulated a 200 watt heating coil which provided heat for the bath. A continuous stream of cold water flowed through a copper coil to cool the bath. A 1/30 horsepower pump provided continuous mixing of the water, thereby assuring temperature equilibrium throughout the bath.

Continuous mixing of the two phases was accomplished by means of a shaking rack powered by a 6 volt automobile windshield wiper motor.

Samples of each phase were taken while the flasks were kept at constant temperature. The flasks were tilted to decrease the area of contact of the two phases and 1 ml. portions of the aqueous phases were pipeted into planchets. Care was taken to be sure that none of the organic phase was removed with the aqueous phase.

Sampling of the organic phase was much more difficult since a slight contamination from the aqueous phase would change the count rate of the organic phase considerably. A 10 mm. glass tube with an opening of about 1 mm. diameter was inserted into the flask while a slow stream of air was being forced through the tube. The stream of air prevented the aqueous phase from entering the tube. When the tip of the tube was below the surface of the organic phase, the pressure was released and the organic phase was allowed to flow into the tube. A pipet was inserted into the tube and about 8 ml. of the organic phase were

removed. This portion of the organic phase was then centrifuged for 10 minutes at constant temperature and the upper portion discarded. One milliliter portions of the remaining solution were pipeted into planchets.

It was necessary to centrifuge the aqueous phase of saturated solutions to ensure the settling of any finely divided silver chloride present in the solutions.

A constant temperature air bath was used to control the temperature during the centrifuging and pipeting operations. A liquid expansion thermoregulator was used to control a blackened light bulb to furnish heat. Cooling was accomplished by circulating cold water through a copper coil. A small fan was used to provide air circulation. The temperature of the bath was controlled at 25.0°C . with a variation of $\pm 0.2^{\circ}\text{C}$.

The pH of the aqueous phase was measured with a Leeds and Northrup pH meter. It was necessary to place the calomel electrode in 1 F. ammonium nitrate solution to prevent a reaction between the silver ion and the chloride ion of the electrode. The ammonium nitrate solution was connected to the silver chloride solution by a salt bridge of ammonium nitrate set in a glass tube with agar gel. The pH values of the solutions were in the range of 5-6.

Three one milliliter samples were taken of each phase. The planchets containing the samples were placed under a heat lamp and the liquid portion was evaporated. The dried samples were counted

with a Tracerlab SC-51 Autoscaler with Tracerlab SC-6D Automatic Sample Changer and SC-5F Printing Interval Timer attachments. Each sample was counted three times for a total counting time of about 10 minutes. Count rates were adjusted to give the counts per minute per milliliter of solution. Coincidence losses were calculated with a Nuclearule slide rule. Corrections were made for background radiation and for coincidence and self-absorption losses.

Planchets were cleaned with chromic acid cleaning solution and were reused when the count rate did not exceed background by more than 5 counts per minute.

Caution was used in the handling of radioactive materials. All radioactive solutions were kept in lead chambers. Wastes and residues were disposed of in waste water after appropriate dilution. One tenth of the maximum permissible concentration of $\text{Ag}^{110\text{m}}$ in drinking water ³⁴ was used as the upper limit for the concentration of radioactive material disposed of in the waste water.

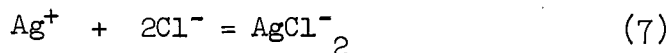
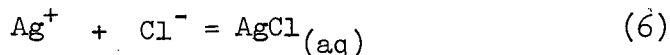
Glassware which came in contact with the radioactive solutions was soaked in a sink of water until it was decontaminated sufficiently to be used again. The sink had water flowing through it continuously.

³⁴ National Bureau of Standards, "Maximum Permissible Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure, "Handbook 69, Government Printing Office, Washington, D. C., 1959 p. 47.

Landsverk model L-24 dosimeters were worn by everyone working in the radiation area. Periodic surveys of the area were made with a Nuclear Chicago model 1613-A Monitor and a Tracerlab model Su5A Survey Meter. These instruments were also used during the preparation of solutions of high activities.

III RESULTS AND CALCULATIONS

CALCULATION OF CONSTANTS In the chloride ion activity range of 2×10^{-5} to 0.1, the silver containing-species present in appreciable concentrations in unsaturated aqueous solutions of silver chloride are silver ion, molecular silver chloride, and the dichloro silver (I) ion. The equilibria involved are as follows:



$$K_1 = a_{\text{AgCl}_{(\text{aq})}} / a_{\text{Ag}^+} a_{\text{Cl}^-} \quad (8)$$

$$K_2 = a_{\text{AgCl}_2^-} / a_{\text{Ag}^+} a_{\text{Cl}^-}^2 \quad (9)$$

(The subscript (aq) refers to the aqueous phase.)

When a silver chloride solution is equilibrated with an immiscible organic solvent, the species may be distributed between the two phases. One would not expect the silver ion to be extracted to an appreciable extent by a solvent of lower dielectric constant than water, and the dichloro silver (I) ion should not be extracted if the hydrogen ion concentration is low. Experiments conducted in this laboratory indicate that nitrobenzene does not extract dichloro silver (I) ion from solutions with pH values in the range 5-6. The extraction of silver ion from aqueous solution by an equal volume of nitrobenzene is less than 0.4%. Therefore, molecular silver chloride is the only species distributed between the phases and the equilibrium may be expressed as follows:

$$\text{AgCl}_{(\text{aq})} = \text{AgCl}_{(\text{org})} \quad (10)$$

$$K_d = [\text{AgCl}_{(\text{org})}] / [\text{AgCl}_{(\text{aq})}] \quad (11)$$

(The subscript (org) refers to the organic phase and the [] refer to molar concentrations.

One may express the total silver concentration as the sum of the concentrations of the silver-containing species.

$$[\text{Ag}_{(\text{total})}] = [\text{Ag}^+] + [\text{AgCl}_{(\text{aq})}] + [\text{AgCl}_2^-] \quad (12)$$

By appropriate substitution of the equilibrium relationships, one obtains

$$[\text{Ag}_{(\text{total})}] = \frac{[\text{AgCl}_{(\text{org})}]\gamma_o}{K_d K_1 \gamma_1 a_{\text{Cl}^-}} + \frac{[\text{AgCl}_{(\text{org})}]}{K_d} + \frac{[\text{AgCl}_{(\text{org})}] K_2 a_{\text{Cl}^-}}{K_d K_1 \gamma_1} \quad (13)$$

and

$$\frac{[\text{AgCl}_{(\text{total})}]}{[\text{AgCl}_{(\text{org})}]} = \frac{\gamma_o}{K_d K_1 \gamma_1 a_{\text{Cl}^-}} + \frac{1}{K_d} + \frac{K_2 a_{\text{Cl}^-}}{K_d K_1 \gamma_1} \quad (14)$$

(γ_o and γ_1 refer to the activity coefficients of the uncharged and singly charged species respectively.) $[\text{Ag}_{(\text{total})}] / [\text{AgCl}_{(\text{org})}]$ is the reciprocal of the distribution ratio, D , and is constant for a given chloride ion activity. This can be shown by appropriate substitutions into equations (12) and (11) to obtain

$$[\text{Ag}_{(\text{total})}] = [\text{Ag}^+] (1 + K_1 \gamma_1 a_{\text{Cl}^-} / \gamma_o + K_2 a_{\text{Cl}^-}^2) \quad (15)$$

and

$$[\text{AgCl}_{(\text{org})}] = [\text{Ag}^+] K_d K_1 \gamma_1 a_{\text{Cl}^-} / \gamma_o \quad (16)$$

Upon dividing equation (15) by equation (16) one obtains

$$\frac{[\text{Ag}_{(\text{total})}]}{[\text{Ag}_{(\text{org})}]} = \frac{1 + K_1 \gamma_1 a_{\text{Cl}^-} / \gamma_0 + K_2 a_{\text{Cl}^-}^2}{K_d K_1 \gamma_1 a_{\text{Cl}^-} / \gamma_0} \quad (17)$$

Therefore, $1/D$ is constant for constant chloride ion activity and does not depend on the degree of saturation of the solution. Table 1 contains calculations from data obtained from extraction experiments using nitrobenzene as the extracting solvent. The hydrogen ion concentrations of the solutions were in the range of 10^{-5} - 10^{-6} F. and the ionic strengths of the solutions were held constant. The value of $1/D$ was calculated from the count rates of the two phases. The activity of the chloride ion was calculated from the original molar concentrations of the chloride ion, since there was always a large excess of chloride ion over silver ion. The values of $1/D$, a_{Cl^-} , and $\frac{a_{\text{Cl}^-}}{D}$ are tabulated in Table 1. The value of γ_0 was assumed to be unity from the Debye-Huckel limiting law. The value of γ_1 was determined from the activity coefficients for hydrochloric acid calculated by Crouthamel and Martin³⁵ from the experimental results of Harned and Ehlers³⁶. These values are within 1% of the values calculated by Randall and Young³⁷.

An attempt was made to calculate values for the equilibrium constants by the method of least squares. Equation (14) may be written in the form

$$1/D = A/a_{\text{Cl}^-} + B + C a_{\text{Cl}^-} \quad (18)$$

³⁵C. E. Crouthamel and D.S. Martin, J. Am. Chem. Soc., **73**, 570 (1951).

³⁶H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc., **55**, 2179 (1933).

³⁷M. Randall and L. E. Young, J. Am. Chem. Soc., **50**, 989 (1928).

TABLE I

DATA FROM SOLVENT EXTRACTION MEASUREMENTS

a_{Cl^-}	$1/D$	a_{Cl^-}/D	$\log a_{Cl^-}$	$\log 1/D$	$\log a_{Cl^-}/D$
7.80×10^{-2}	51.00	3.978	-1.11	1.71	0.60
7.80×10^{-2}	61.39	4.788	-1.11	1.79	0.68
6.95×10^{-2}	73.51	5.109	-1.16	1.87	0.71
6.17×10^{-2}	14.68	0.9058	-1.21	1.17	-0.04
6.17×10^{-2}	51.87	3.200	-1.21	1.72	0.51
5.41×10^{-2}	40.38	2.185	-1.27	1.61	0.34
5.41×10^{-2}	33.48	1.811	-1.27	1.53	0.26
3.85×10^{-2}	9.53	0.3669	-1.41	0.98	-0.44
3.85×10^{-2}	37.61	1.448	-1.41	1.58	0.16
2.71×10^{-2}	21.47	0.5818	-1.57	1.33	-0.24
2.32×10^{-2}	22.08	0.5123	-1.63	1.34	-0.29
1.94×10^{-2}	8.34	0.1618	-1.71	0.92	-0.79
1.93×10^{-2}	19.51	0.3765	-1.71	1.29	-0.42
1.56×10^{-2}	11.84	0.1847	-1.81	1.07	-0.73
1.56×10^{-2}	13.09	0.2042	-1.81	1.12	-0.69
1.25×10^{-2}	9.38	0.1173	-1.90	0.97	-0.93
4.62×10^{-3}	7.69	0.03553	-2.34	0.89	-1.45
1.55×10^{-3}	9.72	0.01507	-2.81	0.99	-1.82
1.16×10^{-3}	4.91	0.005696	-2.94	0.69	-2.24
7.78×10^{-4}	3.57	0.002777	-3.11	0.55	-2.56

TABLE I Cont.

a_{cl^-}	$1/D$	a_{cl^-}/D	$\log a_{cl^-}$	$\log 1/D$	$\log a_{cl^-}/D$
7.78×10^{-4}	3.57	0.002777	-3.11	0.55	-2.56
2.64×10^{-4}	12.69	0.003350	-3.58	1.10	-2.47
1.91×10^{-4}	5.70	0.001089	-3.72	0.76	-2.96
1.90×10^{-4}	17.73	0.003369	-3.72	1.25	-2.47
1.90×10^{-4}	12.69	0.002411	-3.72	1.10	-2.62
1.52×10^{-4}	20.60	0.003131	-3.82	1.31	-2.50
1.51×10^{-4}	13.94	0.002105	-3.82	1.14	-2.68
1.13×10^{-4}	19.03	0.002150	-3.95	1.28	-2.63
1.13×10^{-4}	18.34	0.002072	-3.95	1.26	-2.68

Where

$$A = r_o / K_d K_1 r_1,$$

$$B = 1/K_d,$$

and

$$C = K_2 / K_d K_1 r_1.$$

The expression for the residual is

$$d_i = 1/D_i - A/a_{Cl_i} - B - C a_{Cl_i}. \quad (19)$$

Upon differentiating the sum of the squares of the residuals of the experimental points and equating the derivatives to zero, one obtains the following equations.

$$\begin{aligned} \sum_{i=1}^i 1/D_i a_{Cl_i} &= A \sum_{i=1}^i 1/a_{Cl_i}^2 + B \sum_{i=1}^i 1/a_{Cl_i} + nC \\ \sum_{i=1}^i 1/D_i &= A \sum_{i=1}^i 1/a_{Cl_i} + nB + C \sum_{i=1}^i a_{Cl_i} \\ \sum_{i=1}^i a_{Cl_i} / D_i &= nA + B \sum_{i=1}^i a_{Cl_i} + C \sum_{i=1}^i a_{Cl_i}^2 \end{aligned}$$

Simultaneous solution of the equations gives the following values for the constants.

$$A = 5.03 \times 10^{-3}$$

$$B = -5.55$$

$$C = 8.48 \times 10^2$$

A plot of $1/D$ versus the activity of the chloride ion using the above values of A , B , and C does not fit the experimental points. This is due to the fact that a few values in the high chloride ion activity range have a much greater effect on the shape of the curve than any of the other points. The method of least squares minimizes

the absolute deviation of the points from the curve. A small relative deviation in the high chloride ion activity range may have a greater absolute deviation than a large relative deviation in the low chloride ion activity range. A reliable value for C is obtained since it is most important in the high chloride ion activity range, but the values of A and B are not accurate.

Equation (18) may be rearranged to yield

$$a_{\text{Cl}^-}/D = A + Ba_{\text{Cl}^-} + Ca_{\text{Cl}^-}^2. \quad (20)$$

Equation (20) was solved by the method of least squares to calculate the values of the constants. The equations obtained by differentiating the sum of the squares of the residuals are as follows.

$$\begin{aligned} \sum_{i=1}^i a_{\text{Cl}_i^-}/D_i &= nA + B \sum_{i=1}^i a_{\text{Cl}_i^-} + C \sum_{i=1}^i a_{\text{Cl}_i^-}^2 \\ \sum_{i=1}^i a_{\text{Cl}_i^-}^2/D_i &= A \sum_{i=1}^i a_{\text{Cl}_i^-} + B \sum_{i=1}^i a_{\text{Cl}_i^-}^2 + C \sum_{i=1}^i a_{\text{Cl}_i^-}^3 \\ \sum_{i=1}^i a_{\text{Cl}_i^-}^3/D_i &= A \sum_{i=1}^i a_{\text{Cl}_i^-}^2 + B \sum_{i=1}^i a_{\text{Cl}_i^-}^3 + C \sum_{i=1}^i a_{\text{Cl}_i^-}^4 \end{aligned}$$

Simultaneous solution of these equations yields

$$A = 0.113,$$

$$B = -12.5,$$

and

$$C = 8.91 \times 10^2.$$

These values of A and B are also in error since the curve does not fit the experimental points. Again this is caused by the influence

of the points in the high chloride ion activity range.

An attempt was made to obtain better values for the constants by analysing portions of the curve separately. In the high chloride ion activity range, C is most important. Therefore, equation (20) was solved by the method of least squares using only the experimental points for which the chloride ion activity was greater than 2.5×10^{-3} .

The values obtained are

$$A = 0.970,$$

$$B = -58.0,$$

and

$$C = 1.37 \times 10^3.$$

The values of all three of the constants are in error because of the influence of points in the higher part of the chloride ion activity range, and the curve does not fit the data.

Since the curve approaches a straight line as the chloride ion activity increases, an equation for a straight line was next used to solve for the values of the constants. This should give a good value for C even though the value of B will be in error. All points with chloride ion activities higher than 2.5×10^{-3} were used in the calculations. The equation used was

$$1/D = B + C a_{Cl^-}, \quad (21)$$

and the equations used for solving by the method of least squares are

$$\sum_{i=1}^n 1/D_i = nB + C \sum_{i=1}^n a_{Cl_i^-}$$

and

$$\sum_{i=1}^n a_{Cl_i^-} / D_i = B \sum_{i=1}^n a_{Cl_i^-} + C \sum_{i=1}^n a_{Cl_i^-}^2.$$

The values obtained for the constants are

$$B = -3.15$$

and

$$C = 8.05 \times 10^2.$$

This value of C is reasonable, but the value for B is unreasonable it is negative and this would require a negative distribution coefficient.

Equation (20) was again solved using all points below a chloride ion activity of 2.5×10^{-3} . Values obtained for the constants are

$$A = 2.86 \times 10^{-3},$$

$$B = -4.83,$$

and

$$C = 7.46 \times 10^3.$$

The values of B and C are in error since the curve does not fit the experimental points in the range where they are important.

The value of A is slightly high due to the negative value of B.

The curve should approach a minimum value of A, but since B is negative A is slightly higher than the minimum of the curve. The curve approaches a straight line with a slope of zero in the low chloride ion activity range, but it is impossible to use an equation for a straight line to determine the constants since many of the experimental points are on the sloping portion of the curve.

The value of A which yielded the best curve in the region controlled by A was selected from the several attempts to fit the data. The same procedure was followed to select a value for C. The value of B was then calculated from the following equation.

$$a_{\text{Cl}^-}/D - A - Ca_{\text{Cl}^-}^2 = Ba_{\text{Cl}^-} \quad (22)$$

The values used for A and C are

$$A = 2.86 \times 10^{-3}$$

and

$$C = 8.05 \times 10^2,$$

and the expression for the least squares solution is

$$B = \frac{\sum_{i=1}^n (a_{\text{Cl}^-}_i/D_i - A - Ca_{\text{Cl}^-}^2_i) / \sum_{i=1}^n a_{\text{Cl}^-}_i}{\sum_{i=1}^n a_{\text{Cl}^-}_i}$$

Using the experimental points in the chloride ion activity range of 1×10^{-3} to 9×10^{-3} , one obtains 4.11 for the value of B.

The best values of A, B, and C. determined from the several attempts to fit the data and the values of the constants determined from these constants are as follows.

$$A = 2.86 \times 10^{-3}$$

$$B = 4.11$$

$$C = 8.05 \times 10^2$$

$$K_d = 0.243$$

$$K_1 = 1.96 \times 10^3$$

$$K_2 = 3.00 \times 10^5$$

Fig. 1 is a plot of $\log 1/D$ versus $\log a_{\text{Cl}^-}$. The curve is drawn from the calculated values of A, B, and C. The shape of the curve is of interest since it is the same as the solubility curve determined by Tingey¹ (Fig. 2). The curve approaches a slope of a positive one in the high chloride ion activity range and a negative one in the low chloride ion activity range. Tangents to the slopes intercept the $\log a_{\text{Cl}^-}$ axis at

$$\log a_{\text{Cl}^-} = -\log C$$

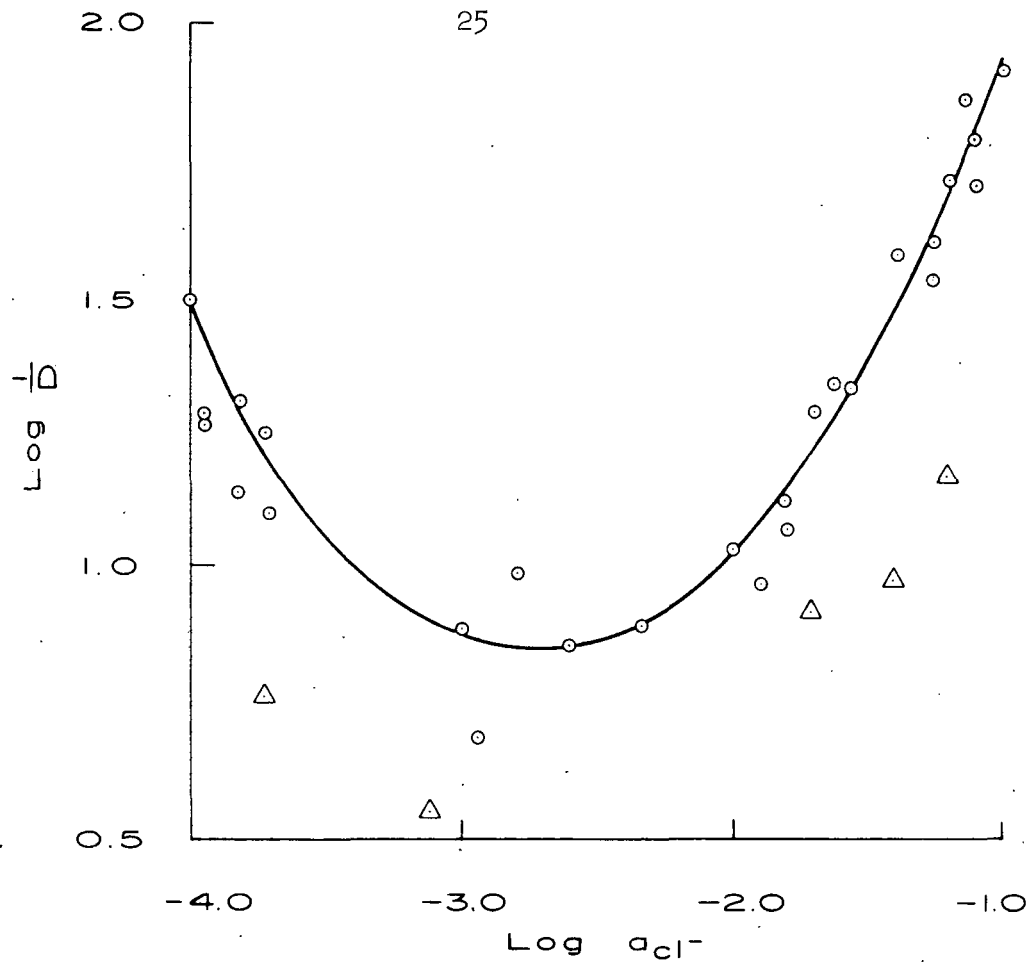
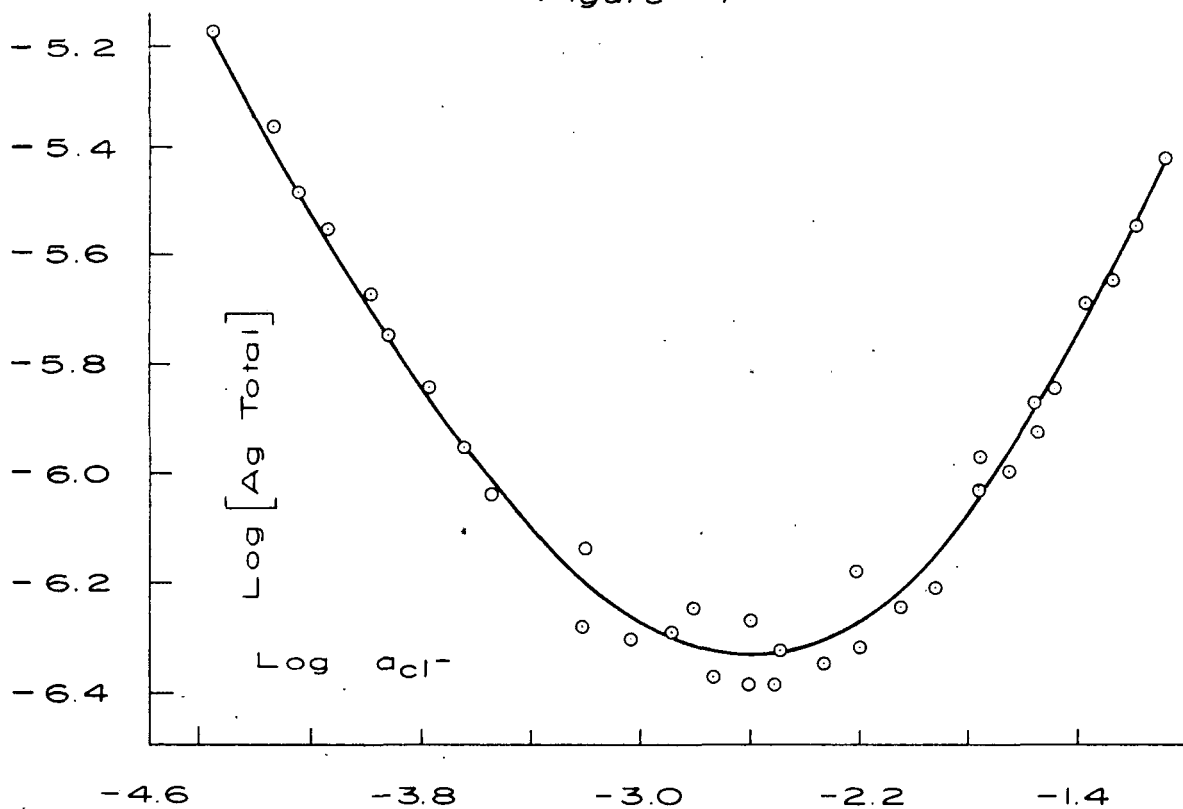
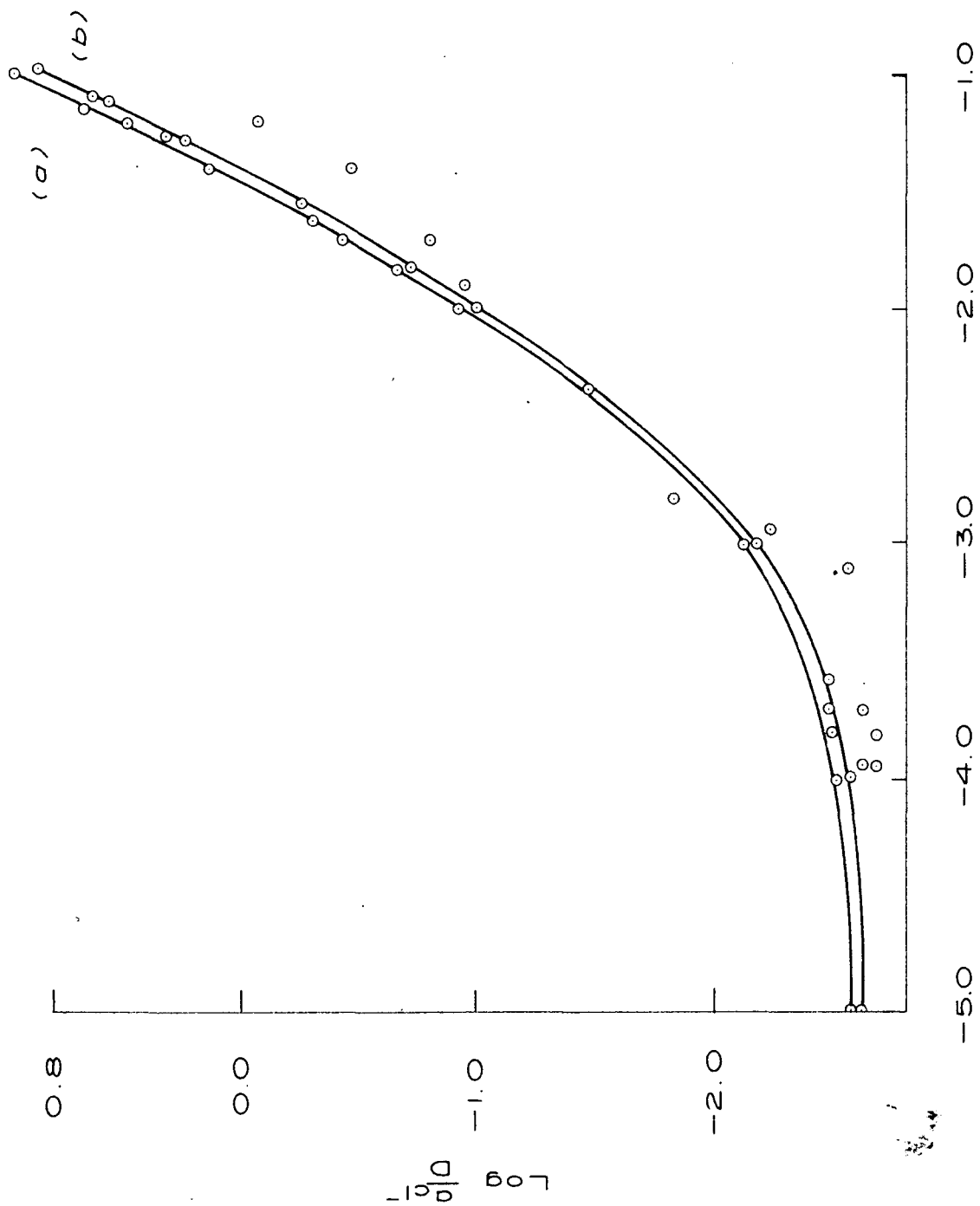


Figure 1



Solubility of Silver Chloride at 25°C.

Figure 2



Log a_c -
Figure 3

and

$$\log a_{\text{Cl}^-} = \log A$$

respectively.

Fig. 3 is a plot of $\log \frac{a_{\text{Cl}^-}}{D}$ versus $\log a_{\text{Cl}^-}$. It is readily seen from the equation that the slope of the curve in the low chloride ion activity range approaches zero, and the abscissa approaches a value of $\log A$ as the ordinate approaches negative infinity. The slope of the curve in the high chloride ion activity range must approach a value of a positive two and a tangent to the slope must intercept the $\log a_{\text{Cl}^-}$ axis at

$$\log a_{\text{Cl}^-} = -1/2 \log C.$$

Curve (a) is obtained from the values calculated for A, B, and C.

Curve (b) is a visual fit of the points. Using curve (b), one obtains the following values for the constants.

$$A = 2.40 \times 10^{-3}$$

$$B = 3.65$$

$$C = 6.92 \times 10^2$$

$$K_d = 0.308$$

$$K_1 = 1.95 \times 10^3$$

$$K_2 = 2.88 \times 10^5$$

These results indicate that the least squares method can not be used to solve equations (18) and (20) over the entire chloride ion activity range since it does not give equal importance to all experimental points. This difficulty can be overcome by

taking the logarithm of each side of the equation and solving this new equation by the method of least squares³⁸. This will give approximately equal importance to all experimental points, but the equation must be written in a different form before the method of least squares can be applied to it.

Figure 1 has the shape of one half of a hyperbola. The general equation for a hyperbola is

$$\frac{(x - h)^2}{a^2} - \frac{(y - k)^2}{b^2} = \pm 1 \quad (23)$$

Since the asymptotes must have slopes of positive one and negative one, a and b must be equal and the equation for a hyperbola which would fit the experimental points would be

$$(x - h)^2 - (y - k)^2 = -a^2, \quad (24)$$

where

$$x = \log a_{c1} \quad (25)$$

$$\text{and} \quad y = \log 1/D. \quad (26)$$

Equation (24) may be rearranged to

$$y^2 - x^2 = 2yk - 2hx + (h^2 + a^2 - k^2) \quad (27)$$

³⁸H. Margēnau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand, Inc., New York, 1947 pp. 500-501.

Using the abbreviations

$$f = y^2 - x^2, \quad (28)$$

$$P = 2k, \quad (29)$$

$$Q = -2h, \quad (30)$$

and

$$R = h^2 + a^2 - k^2 \quad (31)$$

equation (27) becomes

$$f = Py + Qx + R \quad (32)$$

Approximate values for h, k, and a were determined from Figure 1 and equation (24). These values were

$$h = -2.6,$$

$$k = 0,$$

and

$$a = 0.849.$$

Substituting these values into equation (29), (30), and (31), approximate values for P, Q, and R. are obtained.

$$P_0 = 0$$

$$Q_0 = 5.2$$

$$R_0 = 7.56$$

The approximate values differ from the actual values by small correction terms p, q, and r as shown by the following equations.

$$P - P_0 = p \quad (33)$$

$$Q - Q_0 = q \quad (34)$$

$$R - R_0 = r \quad (35)$$

Equation (32) may be written

$$g_i(P, Q, R) = f_i - d_i \quad (36)$$

where d_i is the residual. Equation (36) may be written in terms of P_o , Q_o , and R_o to yield

$$g_i(P_o, Q_o, R_o) + p \frac{\partial g_i}{\partial P_o} + q \frac{\partial g_i}{\partial Q_o} + r \frac{\partial g_i}{\partial R_o} = f_i - d_i \quad (37)$$

Using the abbreviations

$$\frac{\partial g_i}{\partial P_o} = u_i, \quad (38)$$

$$\frac{\partial g_i}{\partial Q_o} = v_i, \quad (39)$$

$$\frac{\partial g_i}{\partial R_o} = w_i, \quad (40)$$

and

$$f_i - g_i(P_o, Q_o, R_o) = F_i, \quad (41)$$

equation (37) becomes

$$u_i p + v_i q + w_i r - F_i + d_i = 0 \quad (42)$$

Upon differentiating the sum of the square of the residual with respect to \underline{p} , \underline{q} , and \underline{r} and equating the partial differentials to zero, one obtains

$$\sum_{i=1}^i F_i u_i = p \sum_{i=1}^i u_i^2 + q \sum_{i=1}^i u_i v_i + r \sum_{i=1}^i u_i w_i, \quad (43)$$

$$\sum_{i=1}^i F_i v_i = p \sum_{i=1}^i u_i v_i + q \sum_{i=1}^i v_i^2 + r \sum_{i=1}^i v_i w_i, \quad (44)$$

and

$$\sum_{i=1}^i F_i = p \sum_{i=1}^i u_i w_i + q \sum_{i=1}^i v_i w_i + r \sum_{i=1}^i w_i^2. \quad (45)$$

From equations (32), (38), (39), and (40) one obtains

$$u_i = y_i,$$

$$v_i = x_i,$$

and

$$w_i = 1.$$

Equations (43), (44) and (45) then become

$$\sum_{i=1}^i F_i y_i = p \sum_{i=1}^i y_i^2 + q \sum_{i=1}^i x_i y_i + r \sum_{i=1}^i y_i,$$

$$\sum_{i=1}^i F_i x_i = p \sum_{i=1}^i x_i y_i + q \sum_{i=1}^i x_i^2 + r \sum_{i=1}^i x_i,$$

and

$$\sum_{i=1}^i F_i = p \sum_{i=1}^i y_i + q \sum_{i=1}^i x_i + nr.$$

These equations were solved simultaneously using all experimental

points except the six which are marked with triangles in Figure 1.

These six points were in doubt since a slight contamination of the

organic phase with the aqueous phase would cause the value of $1/D$ to

be low. Solution of the equations yielded

$$p = -0.333,$$

$$q = 0.245,$$

and

$$r = 0.780.$$

Therefore,

$$P = -0.333,$$

$$Q = 5.445,$$

$$R = 8.34,$$

$$k = -0.166,$$

and

$$h = -2.723.$$

The equations for the asymptotes of the hyperbola are

$$y - k = x - h \quad (46)$$

and

$$y - k = -x + h \quad (47)$$

and their values at the y intercept are $-\log C$ and $\log A$ respectively. From equations (46) and (47) one obtains

$$A = 2.77 \times 10^{-3}$$

and

$$C = 7.75 \times 10^2.$$

Using these values of A and C and the value of $1/D$ calculated when

$$\log a_{Cl} = -2.723,$$

one obtains

$$B = 3.51$$

from equation (18).

These values give the following values for the equilibrium constants.

$$K_d = 0.285$$

$$K_1 = 1.62 \times 10^3$$

$$K_2 = 2.80 \times 10^5$$

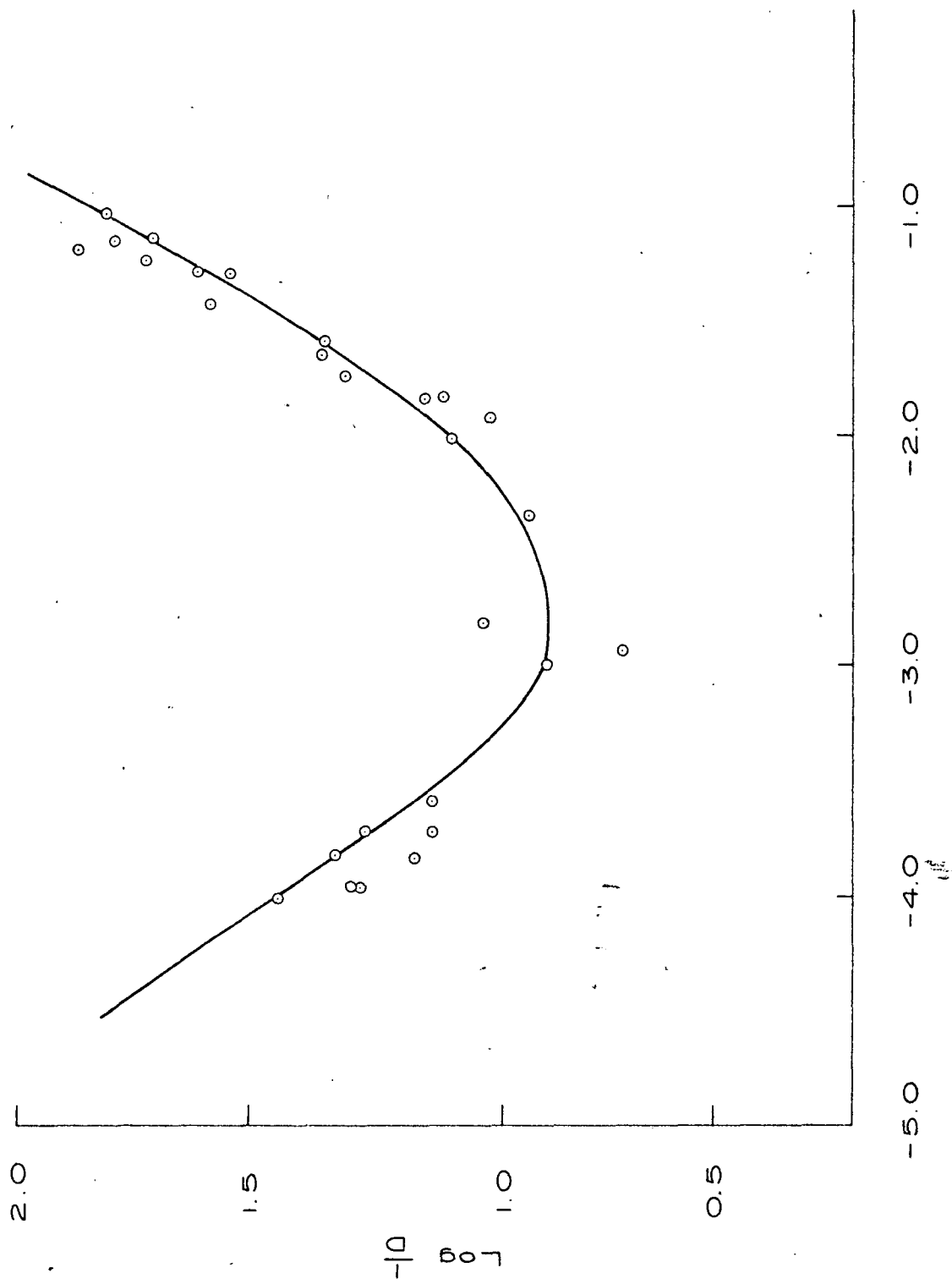
Figure 4 is a plot of $\log 1/D$ versus $\log a_{Cl^-}$ - using the values for A, B, and C calculated by this method. A good fit of the experimental points is obtained.

Table 2 compares the values of the formation constants for complex species in silver chloride solution and the distribution coefficient for the molecular species distributed between aqueous silver chloride solution and nitrobenzene. The investigator and the method are indicated in each case.

These experiments have demonstrated that solvent extraction techniques can be used to determine formation constants for complex species in solutions in which molecular species are present.

ADSORPTION Experiments indicated that a silver containing species is adsorbed on the surface of the glass containers. The adsorption was decreased by the use of new flasks which were not scratched. Therefore, the adsorption is probably taking place on scratched surfaces. An attempt was made to prevent adsorption by coating a flask with an organo-silicon compound³⁹, but the adsorption was greatly

³⁹Desicote manufactured by Beckman Instruments Inc. South Pasadena, California.



$\text{Log } a_{\text{Cl}^-}$
Figure 4

TABLE 2

EXPERIMENTAL CONSTANTS

Investigator	K_1	K_2	K_d	Temp.	Method of analysis
Tingey ¹	1.81×10^3	1.64×10^5	0.32	25°C	Analysis of solubility curve
Hecht ²	1.99×10^3	2.98×10^4		25°C.	Analysis of solubility curve
Jonte and Martin ³	2.04×10^3	1.76×10^5		25°C.	Analysis of solubility curve
Lieser ⁴	2.56×10^3	1.96×10^5		18°C	Analysis of solubility curve
Bodily	1.96×10^3	3.00×10^5	0.243	25°C	Solvent Extraction $1/D = A/a_{Cl^-} + B + Ca_{Cl^-}$
Bodily	1.62×10^3	2.80×10^5	0.285	25°C	Solvent Extraction $f = Py + Qx + R$

increased by the presence of the compound. The adsorbed species is thought to be mainly silver chloride, since the adsorption was appreciably lower in silver perchlorate solutions.

SOLVENTS Examination of the solvents used by Tingey¹ indicates that the extracting ability of several of the solvents increases in the order; benzene, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, and nitrobenzene. This is also the order of increasing electron attracting ability of the functional groups.⁴⁰

Experiments were conducted using 2,4-dinitrotoluene, *m*-dinitrobenzene, and 2,4-dinitrochlorobenzene dissolved in nitrobenzene. The extracting ability of the solvents was found to increase in the order listed, but it was found that silver ion was also being extracted to an appreciable extent and the solvents were not practical for these extraction experiments.

Cyclohexanone, ethyl acetate, benzaldehyde, 3-pentanone, and isobutyraldehyde were also investigated, but in all cases, the extraction was less than with nitrobenzene.

⁴⁰L. F. Fieser and M. Fieser, "Introduction to Organic Chemistry," D. C. Heath and Company, Boston, 1957 p. 343.

IV SUMMARY AND CONCLUSIONS

It has been demonstrated that solvent extraction techniques can be used to calculate formation constants for complex species in solutions in which molecular species are present. Nitrobenzene has been used to extract molecular silver chloride from aqueous silver chloride solution and the formation constants for the molecular species and the dichloro silver (I) ion have been calculated. The distribution coefficient for the distribution of the molecular silver chloride between aqueous silver chloride solution and nitrobenzene has also been calculated. Two methods have been used to analyze the results. The first method consisted of a least squares analysis of a curve obtained by plotting the reciprocal of the distribution ratio times the activity of the chloride ion versus the activity of the chloride ion. It was necessary to analyze portions of this curve separately to obtain reasonable values for the constants involved. The results obtained by this method are

$$K_1 = 1.96 \times 10^3,$$

$$K_2 = 3.00 \times 10^5,$$

and

$$K_d = 0.243.$$

The second method of analysis consisted of least squares analysis of a curve obtained by plotting the logarithm of the reciprocal of the distribution ratio versus the logarithm of the activity of the chloride ion. The following results were obtained.

$$K_1 = 1.62 \times 10^3$$

$$K_2 = 2.80 \times 10^5$$

$$K_d = 0.285$$

These results indicate that the techniques developed in this investigation could be applied to other systems. The accuracy of the results was limited by the low concentration of the molecular species, the low distribution coefficient, and the difficulty in obtaining complete phase separation. If these difficulties are overcome, solvent extraction could be a very useful tool in determining formation constants for complex species.

Various solvents have been tested, but in all cases the distribution of the molecular silver chloride favored the aqueous phase. Nitrobenzene has been found to be the most effective extracting solvent of the solvents tested.

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AN INVESTIGATION OF SOLVENT EXTRACTION
TECHNIQUES IN THE DETERMINATION
OF FORMATION CONSTANTS OF COMPLEX
SPECIES IN AQUEOUS SILVER
CHLORIDE SOLUTION

ABSTRACT OF THESIS
SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
BRIGHAM YOUNG UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Arts

by
David M. Bodily
July, 1960

ABSTRACT

Solvent extraction techniques have been used to determine formation constants for molecular silver chloride and dichloro silver (I) ion in unsaturated aqueous solutions. Nitrobenzene was used to extract the molecular silver chloride from the aqueous silver chloride solution. The total concentration of silver in each phase was determined by radioassay techniques and related by an expression involving the equilibrium constants. The reciprocal of the distribution ratio times the activity of the chloride ion was plotted versus the activity of the chloride ion and portions of the curve were analyzed by the method of least squares to obtain values for the constants involved. The values obtained for K_1 , K_2 and K_d were 1.96×10^3 , 3.00×10^5 , and 0.243 respectively. A second analysis of the experimental data was made by a least squares analysis of a plot of the logarithm of the reciprocal of the distribution ratio versus the logarithm of the activity of the chloride ion. The analysis was performed over the entire range of experimental points and the values obtained for K_1 , K_2 , and K_d were 1.62×10^3 , 2.80×10^5 , and 0.285 respectively.