

PRECIPITATION AND SEPARATION OF SALTS
FROM AQUEOUS SOLUTIONS

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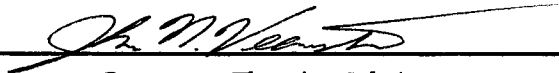
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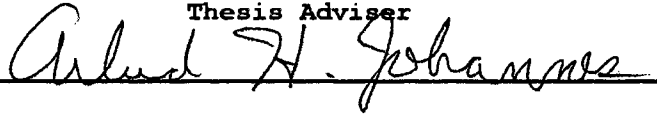
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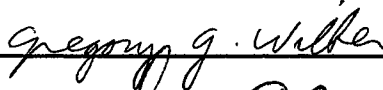
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PREFACE

The study of an organic solvent effect in the solubility phase behavior of aqueous-salt solutions is of considerable practical and theoretical value. As such, this work proceeded in two distinct phases in dealing with two elements of applied research: experimental data acquisition, and data reduction and correlations using thermodynamic principles and the tools of statistics and numerical computations.

In the first section, an experimental database for the precipitation of chloride and sulfate salts associated with six cations (sodium, potassium, magnesium, calcium, barium, and strontium) from aqueous solutions was generated using isopropylamine as the precipitation agent. The experimental precipitation database included: (1) chloride salts at 5,000 mg/L: magnesium, magnesium-sodium, magnesium-potassium, calcium, calcium-sodium, calcium-potassium, calcium-magnesium, calcium-barium, and calcium-strontium; (2) chloride salts at 10,000 mg/L: magnesium, magnesium-sodium, magnesium-potassium, calcium, and calcium-sodium; and (3) sulfate salts at 1,000 mg/L: calcium, magnesium, calcium-magnesium, calcium-sodium, and calcium-potassium. The precipitation measurements covered the most practical concentration range of these systems. The measurements were carried out to demonstrate the precipitation of a single salt and the coprecipitation of binary salts from aqueous solutions using an organic solvent. Consistency tests performed on the acquired precipitation data

indicated a high level of experimental consistency. The precipitation fractions of all chloride salts (at 5,000 and 10,000 mg/L) over the studied range of solvents volume ratio were approximately identical and their small variations were within their experimental uncertainty. In contrast, the precipitation fractions of sulfate salts (1,000 mg/L) over the studied range of solvents volume ratio were appreciably varied depending on the solubility of each salt in the organic solvent. The precipitation measurements provided by this work were useful for both practical applications and a basic understanding of the precipitation concept.

In the second section, two rigorous frameworks consisting of creditable equations derived from thermodynamics principles were developed to model the precipitation measurements. The first framework was based on the criteria of solid-liquid equilibria employing the excess Henry's constant approach. Wohl's expansion was used to express the excess Gibbs free energy function. The framework provided two flexible and general predictive equations (the 2-Suffix and 3-Suffix equations). In general, both equations were reasonably adequate for predicting the solubility phase behavior of salts in a mixed-solvents mixture as well as for estimating optimum interaction parameters. As suggested by the quantitative results, the 3-Suffix Equation is quantitatively better than the 2-Suffix Equation. The regressed interaction parameters were useful for estimating the precipitation fractions of studied salts at a higher solvents volume ratio where no experimental data was available, and solubility of the studied salts in the organic solvent.

The second framework was based on the criteria of liquid-liquid equilibria. The power series function was employed to express the activity coefficients in terms of a given salt and organic solvent mole fractions in a mixture. The framework provided two predictive equations (the 2-Power and 3-Power Equations). While both equations were adequate for predicting the solubility phase behavior of salts in a mixed-solvents mixture, the 3-Power Equation was more accurate. The resultant interaction parameters could be used to estimate the precipitation fractions of the studied salt at a higher solvents volume ratio where no experimental data was available.

This work completed another major cycle of my life; the higher I climb, the clearer the view. This dissertation complements my first dissertation in Chemical Engineering. Both encountered an uphill climb; a period of preparation, initiation, and challenges through which I came to recognize and improve my weaknesses, and to appreciate my strengths. I thank God for giving me the opportunity, motivation, and strength to achieve my goals.

In work of this nature, there are many people to thank for their contributions. To those from the School of Civil and Environmental Engineering, the School of Chemical Engineering, and others, I wish to express my heartfelt gratitude.

I am grateful to Professor J.N. Veenstra who served on two advisory committees, as a member and as a chairman, for his support, and continuous interest in my work.

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I gratefully acknowledge Professor Khaled A.M. Gasem from the School of Chemical Engineering whose knowledge and standards of excellence have significantly helped in shaping so much of my work.

I am deeply grateful to Professor M.S.E. Abdo from the Department of Chemical Engineering, University of Alexandria, Egypt, who guided my educational career during my undergraduate years, and directed my career toward graduate schools. His enthusiasms and joy to aid provided the catalyst for my progress at the time; looking back I recognize the profound scope of his guidance and encouragement.

My abiding appreciation to all members of my family, particularly my parents, whose shoulders I stand upon; to them I humbly dedicate this work. Special acknowledgment, with love and gratitude, to my father, the sage that led me by example in directing my innate drive for meaning and purpose; I respectfully bow to you Sir.

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NOMENCLATURE

a	Constant characteristic of the interaction between molecules
%AAD	Percent average absolute deviation
A_i	Area-Under-the-Curve of analyzed sample i
A_m	Mean (average) area-under-the-curve
C_F	Concentration of salt species in filtered sample
C_S	Concentration of salt species in standard sample
C_i	Model's interaction parameters
D_F	Dilution factor
dG	Change in Gibbs free energy
f_i^s	Fugacity of a pure solute (solid)
\hat{f}_i^L	Fugacity of species i in a liquid solution
f_i^o	Fugacity of the hypothetical pure liquid.
g^E	Excess Gibbs energy
H_i^E	Excess Henry's constant of species i in liquid solution
H_i	Henry's constant of species i in liquid solution
m	Slope of the calibration curve
n_i	Number of moles of species i
N	Number of sample replicates
R	Gas constant
RMSE	Root mean square error
SS	Objective function

T	Temperature
v_i	Molar volume of solvent i
V_R	Ratio of solvent molar volumes
V_i	Volume of solvent i
x_i	Mole fraction (solubility) of species i in liquid solution
$x_{i,j}$	Mole fraction (solubility) of species i in solvent j
$x_{i,m}$	Mole fraction (solubility) of species i in mixed-solvents mixture m
y	Integer power
z	Integer power

Greek Symbols

Λ_1	the salt binary-solvent interaction parameter (ternary constant)
Λ_{ij}	Wohl's interaction parameter of species i in solvent j ; or interaction parameters in the power series expansion
$\alpha_{i,j}$	Relative volatility of species i in solvent j
$\alpha_{i,m}$	Relative volatility of species i in mixed-solvents mixture m
γ_i	Symmetric activity coefficient of species i in liquid solution
$\gamma_{i,j}$	Symmetric activity coefficient of species i solvent j
$\gamma_{i,m}$	Symmetric activity coefficient of species i in mixed-solvents mixture m
μ_i^s	Chemical potential of a pure solute
μ_i^L	Chemical potential of species i in a liquid solution
θ_i	Volume fraction of solvent i
σ	Standard deviation
u_i	number of cation or anion species

Subscripts

1	Salt species
2	Water solvent
3	Organic solvent
cal	Calculated
exp	Experimental
m	Mixed-solvents mixture
p	Pure solute
s	Solute

Superscripts

E	Excess
L	Liquid phase
s	Solid phase
α	Liquid phase in the reference solvent (water)
β	Liquid phase in the mixed-solvents mixture (water and organic)

SECTION I - EXPERIMENTAL WORK

CHAPTER I

INTRODUCTION

Water is the mother solvent for a wide variety of inorganic species, simple and complex. Excessive amounts of such species can render water either unusable for general consumption or specific agricultural and industrial uses or pose a high risk to the environment. The term "excessive" depends on the acceptable daily intake or virtual safe concentration for these species. As such, effective and economically-sound separation processes to concentrate and separate inorganic species from aqueous solutions have long been sought.

Precipitation is one of the oldest separation concepts [1-3]. Although there are many kinds of separation processes, precipitation is recently receiving a new attention. The renewed interest in the precipitation concept as a viable separation technique is attributed, in part, to the continuing stringent environmental regulations, and the significant economic and environmental impacts of concentrating and separating inorganic species from aqueous solutions in many applications. Hence, a new vital basis might be delineated to the precipitation concept for development into industrial and environmental applications [4-9].

The precipitation action is usually carried out either by adding a precipitation agent to the original solution or by changing the conditions such as temperature and pH to form a new phase (solid) from the mother phase [1-3]. Selecting a suitable precipitation agent and/or controlling the conditions are key factors in the precipitation process. The impact of the precipitation method selection is evident when examining the overall efficiency in forming precipitates and the economy of the process [4].

The objective of this study was to provide experimental precipitation measurements on chloride and sulfate salts using isopropylamine as the precipitation agent. Such measurements targeted: (1) chloride salts at 5,000 mg/L: magnesium, magnesium-sodium, magnesium-potassium, calcium, calcium-sodium, calcium-potassium, calcium-magnesium, calcium-barium, and calcium-strontium; (2) chloride salts at 10,000 mg/L: magnesium, magnesium-sodium, magnesium-potassium, calcium, and calcium-sodium; and (3) sulfate salts at 1,000 mg/L: calcium, magnesium, calcium-magnesium, calcium-sodium, and calcium-potassium.

In Chapter II, the "salting-out" and "solventing-out" processes, selection of organic solvents in the precipitation process, and experimental data relevant to this work are briefly reviewed. Chapter III describes the experimental methods and procedures employed to measure the precipitation fractions of the targeted salts. The acquired experimental precipitation measurements along with the relevant error analysis and consistency tests are presented and discussed in Chapter IV.

CHAPTER II

LITERATURE REVIEW

This chapter constitutes a brief review and analysis to the: (1) "salting-out" and "solventing-out" processes; (2) selection of organic solvents in the precipitation process; and (3) experimental data relevant to this work.

"Salting-out" and Solventing-out" Processes

One of the earliest separation processes to remove an organic component from an aqueous solution was accomplished by using a salt. Lescoeur [10] reported that Raymond Lully, in the twelfth century, found that potassium carbonate would salt out most of the ethanol from aqueous solution. Since then, salts and organic solvents are frequently used to suppress the solubility of targeted components (organics or salts) from aqueous solutions.

The reduction in the solubility of an organic component in aqueous solutions upon the addition of a salt is called "salting-out" while the reduction in the solubility of a salt in the aqueous solutions upon the addition of an organic solvent is termed "solventing-out". Both processes play a significant role in advancing several analytical and industrial applications.

Non-volatile dissolved salts were employed as separating agents in separation processes such as conventional or extractive distillation to

alter the phase behavior of organics exhibiting either azeotropes or low relative volatilities or miscibility gaps with their aqueous solutions in composition region critical to the separation [see e.g., 11-18]. On the other hand, organic solvents were used to salt out inorganic salts from aqueous solutions either in methods of analysis or in industrial applications [see e.g., 19-28]. This work is devoted to studying the effect of organic solvents in precipitating targeted salts from their aqueous solutions.

Selection of Organic Solvents

Since the organic solvent has a pronounced impact on the overall precipitation efficiency, the selection of an organic solvent is probably the most significant aspect in the precipitation process. A large number of organic solvents may be appropriate for use in the precipitation process. However, the preferred organic solvents are those which have the capability to meet the following criteria.

First, the selected organic solvent must be miscible in water. Of equal importance, inorganic salts must be insoluble in the selected organic solvent. The addition of such a selected organic solvent to an inorganic salts aqueous solution leads to capture part of the water molecules and reduces the solubility of salts in water which forms insoluble precipitates. The nature of the influence of the organic solvent is on the hydration of salts [4,28]. Such an influence can be determined by studying the solubility of salts in a mixed-solvents mixture (water and soluble organic) [4,29]. Thus, solubility is the

obvious thermodynamic property of concern in forming and affecting salt precipitates.

Second, for ease of recovery and recycle, the selected organic solvent must have favorable physical properties such as a low boiling point, high vapor pressure, high relative volatility, and no azeotrope formation with water.

Third, the selected organic solvent must have low toxicity since traces of the organic solvent (e.g., at ppm or ppb levels) always remain in the discharge water. Moreover, the solvent vapors are of prime health and environmental concerns.

Finally, from a design standpoint, the selected organic solvent must be chemically stable, compatible with the process, and relatively inexpensive. These characteristics are very important because of their environmental and economic impacts on the overall process design.

All the above factors, except the solubilities of salt in the selected organic solvent, can reasonably be established from a search of the literature. The impact of salts solubilities in the organic solvent on the overall precipitation process efficiency is the most important factor and must be determined in the laboratory. The effects of the organic solvents on the solubilities of salts in water may be recognized as twofold. First, precipitation depends upon the miscibility of the organic solvent in water and its capability to form a strong hydrogen bond with water which influences the hydration of salts [4,5]. Second, the precipitation fraction of a salt from an aqueous-saline solution depends upon the solubility of such a salt in the organic solvent; the lower the solubility, the higher the precipitation [30,31].

Several organic solvents have been identified for potential use in the precipitation process development [6]. The identified organic solvents are amines selected from the group consisting of isopropylamine, diisopropylamine, propylamine, ethylamine, diethylamine, and dimethylamine [6]. These organic solvents are listed as examples, and many others may be employed. Isopropylamine is the preferred organic solvent for the precipitation process [4,23,29]. Such a preference is attributed to: (1) the high precipitating capability of isopropylamine with several inorganic species; (2) the low boiling point (32.5°C), high vapor pressure (585 mmHg) and relative volatility, and non azeotrope formation with water; and (3) minimal environmental risks (e.g., not carcinogens). Furthermore, isopropylamine has been used as a herbicide (isopropylamine salts) for agricultural purposes [4,9].

Related Experimental Data

Knowledge of the organic solvent effect in the solubility of inorganic-aqueous systems is of importance to investigators in many fields (e.g., analytical chemistry, pharmaceutical, etc.). Several researchers have compiled references for such data. These compilations include data for different classes of organic solvents (see, e.g., 1-3).

The experimental data in the literature that deals with precipitation of inorganic salts from aqueous systems using organic solvents and related to this study are gathered and presented in Tables 1 through 4. Only limited useful and reliable data are available.

Typically, the precipitation measurements were conducted using the following experimental procedure. First, standard solutions of aqueous

TABLE 1

PRECIPITATION MEASUREMENTS FOR MAGNESIUM CHLORIDE AND MAGNESIUM SULFATE
BELOW SATURATION USING ISOPROPYLAMINE AS A PRECIPITATION AGENT [4]

V_R^*	%P**	
	MgCl ₂	MgSO ₄
0.005	15.0	--
0.002	--	47.0
0.010	23.1	--
0.020	77.9	60.4
0.050	97.9	84.7
0.100	--	96.8
0.200	98.8	96.0
0.300	98.9	--
0.500	99.1	97.5

* V_R = Solvents Volume Ratio; ** %P = Precipitation Fractions

TABLE 2

PRECIPITATION MEASUREMENTS FOR POTASSIUM CHLORIDE AT SATURATION
USING ACETONE A PRECIPITATION AGENT [22]

V_R^*	$\%P^{**}$
0.200	24.4
0.500	40.7
0.700	51.8
1.000	57.8
1.500	70.7
2.000	76.5
3.000	84.7
4.000	89.4
5.000	91.1

TABLE 3

PRECIPITATION MEASUREMENTS OF SODIUM CHLORIDE AT SATURATION
USING DIFFERENT ORGANIC SOLVENTS [23]

V_R^*	$\%P^{**}$		
	Isopropylamine	Acetone	Acetonitrile
0.100	9.1	8.8	7.6
0.200	17.3	15.0	9.8
0.300	--	--	13.1
0.500	28.2	24.5	16.0
1.000	38.2	31.4	--
1.500	50.1	38.1	21.8
2.000	62.2	40.9	24.3
2.500	--	49.7	25.2
3.000	75.5	56.1	35.1
3.500	--	61.2	--
4.000	--	70.0	44.2
4.500	--	75.0	--
5.000	89.1	76.7	52.6
5.500	--	80.5	--
6.000	90.7	85.3	58.1
6.500	--	89.2	--
7.000	--	91.5	69.1
7.500	--	92.7	--
8.000	91.7	---	73.1
8.500	--	95.4	--
10.000	93.3	95.6	82.7
15.000	93.5	97.8	95.9

TABLE 4
 PRECIPITATION MEASUREMENTS FOR POTASSIUM SULFATE AT SATURATION
 USING DIFFERENT ORGANIC SOLVENT [24]

V_R^*	$\%P^{**}$		
	Isopropylamine	Propylamine	Acetone
0.040	10.8	11.9	5.2
0.060	24.4	21.6	20.2
0.080	30.5	28.8	26.4
0.100	40.6	36.3	33.1
0.150	51.2	49.4	48.2
0.250	65.6	67.7	68.1
0.400	78.8	84.0	80.7
0.500	89.5	88.0	87.0
0.700	95.0	91.9	91.5
1.000	96.1	96.0	95.2
2.000	97.6	97.8	97.7
3.000	98.2	97.9	98.7
4.000	98.8	98.1	99.0
5.000	99.2	98.2	99.0

salt systems were prepared by dissolving excessive amounts of targeted salts in hot distilled water. The standard sample of the aqueous salt solution was determined by taking a small amount (typically, 1.0 mL) of the solution to dryness at 300°C and weighing the precipitate. Different amounts of the organic solvent were then added to several 1.0 mL aqueous salt solutions. Next, the samples were filtered to remove precipitates and the decanted samples were dried at 300°C and weighed.

Several problems were associated with such measurements. First, most of the precipitation measurements were conducted at supersaturated salts concentrations [22-24] (e.g., saturation limit of NaCl: 360,000 mg/L; KCl: 340,000 mg/L; K₂SO₄: 110,000 mg/L; MgCl₂: 546,000 mg/L; and MgSO₄: 272,000 mg/L [4]). Such precipitation measurements at very high concentrations of salts in water are far from the practical concentrations ranges of the studied aqueous salt systems. Furthermore, the fact that precipitation can be accomplished for almost any saturated salt in aqueous solutions.

Second, the exact concentrations of such salts were unknown. This hindered modeling progresses [4,28] to derive a means of predicting the effect of organic solvents in suppressing salts solubilities in aqueous solutions and to draw some general quantitative conclusions regarding the controlling factors in the precipitation phenomenon.

Third, precipitation fractions were determined gravimetrically. The integrity of the gravimetric analysis is entirely questionable at such a small volume of samples (e.g., 1.0 mL). As such, a question may be raised on the usefulness of reported data and whether some of such data are truly reliable or not.

CHAPTER III

EXPERIMENTAL METHODS AND PROCEDURES

This chapter describes the experimental methods used to obtain the precipitation measurements. The methods included experimental setup and procedure, Ion Chromatograph (IC) calibration, Gas Chromatograph (GC) calibration, materials, determination of the precipitation fractions and their uncertainties, and determination of trace quantities of isopropylamine in water and their uncertainties. Although the experimental methods outlined below were relatively straightforward, the success of each experiment depended on its careful implementation.

Experimental Setup and Procedure

Aqueous-saline solutions were prepared by dissolving the required amount of the targeted salt in 300 mL of distilled water at room temperature. The concentration of the targeted anion (chloride or sulfate) in the 300 mL of the distilled water forms the stock aqueous-saline solution. In the case of studying the precipitation of the targeted anion from a single salt, the concentration of such a salt is calculated based on the equivalent weights of both the targeted anion and the mother salt, weighed, and dissolved in 300 mL of distilled water. In the case of studying the coprecipitation of the targeted anion from binary salts, both salts evenly contributed to the concentration of the targeted anion.

Eight samples, each of which consisted of 25 mL, were then drawn from the stock aqueous-saline solution and injected into 100 mL volumetric flasks. These eight samples were used to study the precipitation of the targeted anion from the stock aqueous-saline solution in the presence of different amounts (concentrations) of miscible organic solvent. Another 25 mL sample was also drawn from the stock aqueous-saline solution and injected into 25 mL microflasks to be used as a standard (reference) sample.

Isopropylamine was used as a precipitation agent. Different amounts of isopropylamine (2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 35.0, and 50.0 mL) were drawn and injected into each of the 25 mL aqueous-saline solution samples. These amounts of isopropylamine provided a reasonable range of precipitation measurements without wasting excessive amounts of isopropylamine. The injected amounts of isopropylamine formed instant salt precipitates in different percentages. However, the fraction of the salt precipitate depended upon the amount of isopropylamine added to the 25 mL sample.

A schematic diagram of the experimental setup is shown in Figure 1 [6,31]. For each of the eight 25 mL organic-aqueous saline solution samples, the salt precipitates were separated from the organic-aqueous solution by vacuum filtration using 0.5 μm glass microfiber filters (Gelman). The vacuum filtration apparatus was connected to 500 mL receiving flasks. The receiving flasks were, in turn, connected to a vacuum manifold with 1/4 inch Swagelok union tees via thick walled vacuum tubes (Tygon). One end of the manifold was connected to a Sargent-Welch air-free displacement vacuum pump via a glass cold trap.

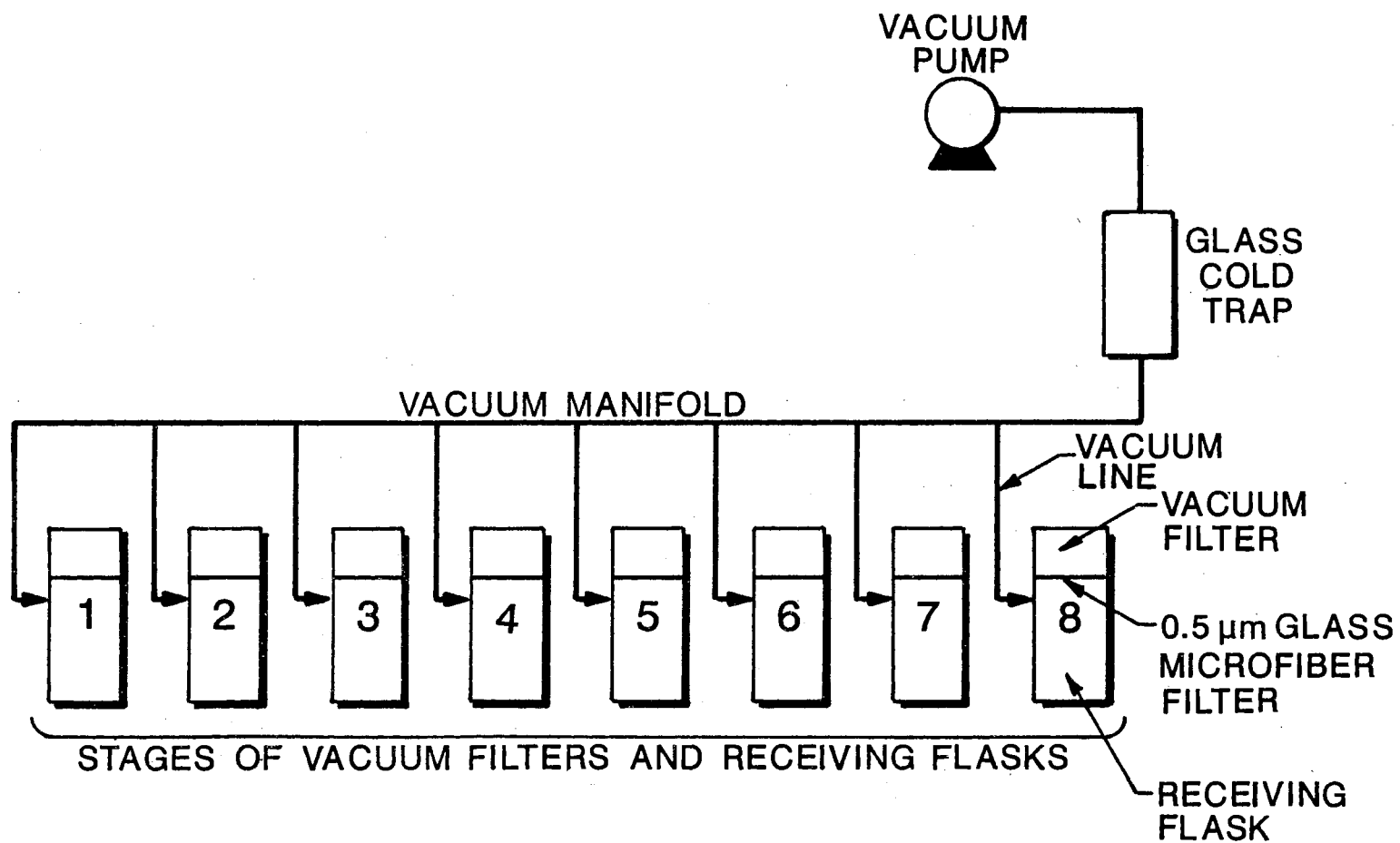


Figure 1. Schematic Diagram of the Experimental Setup [6,31]

The glass cold trap was immersed in liquid nitrogen to trap and recover the condensable isopropylamine.

Ion Chromatograph (IC) Calibration

A Dionex series 2000i/sp IC (Dionex, Co.) equipped with anion separator column (AS4A), guard column (AG4A), and suppressor (AMMS) was used for the analysis of salt concentrations. Chromatograms were reported with a Hewlett-Packard integrator (Model 3380A). The integrator is capable of directly integrating the area under the curve of the analysis peaks.

Anion salts were separated on the AS4A anion exchange separator column with a carbonate/bicarbonate buffer eluant. Sodium carbonate (0.191 gm/L) and sodium bicarbonate (0.143 gm/L) were used to generate the eluant solution which was prepared from a concentrated stock solution (19.1 g/L of sodium carbonate and 14.3 g/L of sodium bicarbonate) at a dilution ratio of 1:100. A Denver Instrument balance was used to weigh the salts (Denver Instrument Co.). The balance was tested prior to each measurement against standard weights with a certification traceable to the National Bureau of Standards. Similarly, regenerant was also prepared from a concentrated stock solution (75 mL of sulfuric acid/L) at a dilution ratio of 1:100. The purpose of preparing the eluant and regenerant stock solutions was to provide a consistent supply of these reagents during the course of this study.

Calibration curves for the chloride and sulfate salts were developed. Stock solutions consisting of 1000 mg/L for each anion salt were prepared. Sodium chloride (1.648 gm/L) and sodium sulfate

(1.479 gm/L) were used to prepare the 1000 mg/L stock solutions of the chloride and sulfate, respectively. Following is a description of the calibration curve procedure.

Several standard solutions for each of the anion salts were prepared using the stock solution. The desired amount was drawn from the stock solution (depending on the linear range of the targeted anion salt) and added into a 100 mL empty volumetric flask. One mL of the eluant solution was also added into the 100 mL flask. The addition of one mL of the eluant solution helped to stabilize the base line of the IC, and thus aided in better precision. Distilled water was then added into the 100 mL flask until the liquid filled the flask completely (100 mL). Next, the standard solution was mixed using a magnetic stirrer. Three separate 0.5 mL samples of the standard solution were drawn into a syringe and injected into the IC. Thus, the precision could be determined through replication. This procedure was repeated until the calibration data were obtained for the entire linear range of concentrations. It was found that the linear range for both anions (chloride and sulfate) could be extended to 20 mg/L. The calibration data of the chloride and sulfate salts were fitted to a straight line using a Marquardt regression routine [32]. These data, along with their linear fits, are shown in Figures A.1 and A.2, Appendix A.

Gas Chromatograph (GC) Calibration

A Hewlett Packard GC model 5890 equipped with a flame ionization detector (FID) was used for composition analysis of isopropylamine in water. Helium was used as the carrier gas and hydrogen and excess air

were used to ignite and maintain the flame in the detector.

Chromatograms were reported with a Hewlett-Packard integrator (Model 3391A). The integrator is capable of directly integrating the area under the curve of the analysis peaks. Table B.1 (Appendix B) lists specific information on the GC column and the operating conditions.

The vapor pressure of pure isopropylamine is 585 mmHg at 25 °C [33]. This indicated a significant presence of isopropylamine in the vapor phase (high volatility). Thus, to establish a reliable GC calibration for the entire range of interest, a procedure, which was previously developed [34], was adapted to minimize the volume of the vapor phase during the analysis of isopropylamine-water system. Following is a description of the adapted calibration procedure.

Microflasks (Alltech Associate, Inc.) with a 15 cc total volume were used in developing the calibration curves for the isopropylamine-water system. Microflasks are designed with an open hole screw cap and Teflon-Rubber face seals (septa). First, an empty microflask with the cap, septa, and magnetic rod were weighed using a Denver Instrument balance (Denver Instrument Co.). The balance was tested prior to each GC calibration against standard weights with a certification traceable to the National Bureau of Standards.

Second, a standard solution was prepared by adding the desired amount of distilled water into the empty microflask and weighing it. The proper amount of a pure isopropylamine was then drawn in a gas-tight syringe and injected into the microflask (which was partially loaded with distilled water) until the liquid filled the microflask completely (15 cc) without leaving space for vapor. After that, the microflask was weighed to determine the mass of isopropylamine in the standard

solution, which, in turn, was used to determine the volume of isopropylamine in the solution.

Third, the solution was mixed well using a magnetic stirrer. Then, several 1 μ L samples of the solution were drawn into a 1 μ L gas-tight syringe and injected into the GC. Thus, the precision could be determined through replication.

Subsequently, a desired amount of distilled water was injected into another empty microflask and weighed. A determined amount of the above standard solution was then drawn into a gas-tight syringe and carefully injected into the microflask. Several 1 μ L samples of this solution were then drawn and injected into the GC.

This procedure, known as a serial dilution, was repeated until the calibration data were obtained for the desired experimental range.

The basic assumption used in calculating the mole fractions of the mixture (isopropylamine and water) using the calibration curve was that the volumes of isopropylamine and water which were present in the injected 1 μ L sample are additive. This assumption stems from the inability of the FID detector to detect water. Thus, the volume of injected samples was a key element in analyzing the composition of the liquid phase of isopropylamine.

The experimental GC calibration data of an isopropylamine-water system were fitted to a straight line using a Marquardt regression routine [32]. These data, along with their linear fits, are shown in Figure B.1, Appendix B.

Materials

All chemicals used in this study were obtained from commercial suppliers. These high purity chemicals were used as received and without further purification. The Milli-Q plus system was used as a source to provide the highly purified distilled water used in this work.

Determination of the Precipitation Fractions

Since the concentrations of the targeted anions are much higher than the concentrations within the linear range, a serial dilution procedure was adapted for the analysis of the anions concentrations (standard and filtered samples). The concentrations of the targeted anions in the standard and the filtered samples determine the number of dilution steps. Two dilution steps were sufficient to carry out the analysis for chloride salts and one dilution step was sufficient for the sulfate salts.

For the chloride salts a minimal amount (1.0 mL) from the standard and filtered sample was drawn and injected into a 100 mL empty volumetric flask in the first dilution step. One mL of the eluant solution was also injected into the 100 mL flask. The 100 mL flask was then filled with distilled water. After that, the solution was mixed.

In the second dilution step, a sufficient amount (10 mL) from the first dilution solution was drawn and injected into another 100 mL empty volumetric flask. After that, one mL of the eluant solution was added. Distilled water was then added to completely fill the 100 mL volumetric flask. The solution was mixed, and three separate 0.5 mL

samples of the solution were drawn into a syringe and injected into the IC. Hence, the precision could be determined through replication.

For sulfate salts, one dilution step was sufficient to carry out the analysis in the linear range.

The serial dilution procedure served two purposes. First, anions concentrations were analyzed within their linear range of the calibration data. Second, the effect of trace quantities of isopropylamine in the filtered samples on the separator column were minimized. Thus, the serial dilution procedure was a key element in analyzing the concentrations of the targeted anions in the standard and filtered samples.

Once the anions concentrations in both the standard samples (C_s) and the filtered samples (C_F) were determined, the precipitation fraction (P) could be calculated as follows [4]:

$$P = 1 - \frac{C_F}{C_s} \quad (1)$$

Error Analysis

The uncertainty in the experimental values of the precipitation fractions due to random variations in the variables can be estimated by error propagation methods. Error propagation allows an estimate for the uncertainty interval which should be associated with the experimental results based on the observations in the raw data. The uncertainty is obtained in terms of variance (σ^2) as follows [34]:

$$\sigma_F^2 = \sum_{i=1}^N \left(\frac{\partial F}{\partial X} \right)_i^2 \sigma_{X_i}^2 \quad (2)$$

where F is an observable which depends on the measured independent variables (X).

As given by Equation (1), the random variations in the concentrations of the targeted anion in the standard sample (C_S) and filtered samples (C_F) should be estimated. Hence, the variance in the experimental precipitation fractions can be written in terms of these two variables (C_S and C_F) as follows:

$$\sigma_{P_i}^2 = \left[\frac{\partial P_i}{\partial C_{F_i}} \right]^2 \sigma_{C_{F_i}}^2 + \left[\frac{\partial P_i}{\partial C_{S_i}} \right]^2 \sigma_{C_{S_i}}^2 \quad (3)$$

Equation (3) can be written as follows:

$$\sigma_{P_i}^2 = \left[\frac{1}{C_{S_i}} \right]^2 \sigma_{C_{F_i}}^2 + \left[\frac{C_{F_i}}{C_{S_i}^2} \right]^2 \sigma_{C_{S_i}}^2 \quad (4)$$

Factoring out P_i^2 :

$$\sigma_{P_i}^2 = \left[\left[\frac{1}{C_{S_i} - C_{F_i}} \right]^2 \sigma_{C_{F_i}}^2 + \left[\frac{C_{F_i}}{C_{S_i}(C_{S_i} - C_{F_i})} \right]^2 \sigma_{C_{S_i}}^2 \right] P_i^2 \quad (5)$$

Thus, an estimate for the standard deviation (σ) of the precipitation fractions can be obtained by the following relationship:

$$\sigma_{P_i} = \left[\left[\frac{1}{C_{S_i} - C_{F_i}} \right]^2 \sigma_{C_{F_i}}^2 + \left[\frac{C_{F_i}}{C_{S_i}(C_{S_i} - C_{F_i})} \right]^2 \sigma_{C_{S_i}}^2 \right]^{1/2} P_i \quad (6)$$

The concentrations of the targeted anion (C_i) in the standard and filtered samples were calculated by converting the area-under-the-curve data of the injected sample into a concentration (mg/L) present in that sample using the calibration curve data as follows:

$$C_i = \left[\frac{A_i}{m} \right] \quad (7)$$

where A_i is the area-under-the-curve of the targeted anion, and m is the slope of the calibration curve. Determining the anion concentrations in the standard and filtered samples allows calculation of the precipitation fraction.

The variance in the concentrations of the targeted anion in the standard and filtered samples can be estimated using Equations (2) and (7) as follows:

$$\sigma_{C_i}^2 = \left(\frac{\partial C_i}{\partial A_i} \right)^2 \sigma_{A_i}^2 + \left(\frac{\partial C_i}{\partial m} \right)^2 \sigma_m^2 \quad (8)$$

where:

$$\left(\frac{\partial C_i}{\partial A_i} \right)^2 = \left(\frac{1}{m} \right)^2 \quad (9)$$

$$\left(\frac{\partial C_i}{\partial m}\right)^2 = \left(-\frac{A_i}{m^2}\right)^2 \quad (10)$$

Substituting Equations (9) and (10) into Equation (8) and factoring out C_i^2 , lead to:

$$\sigma_{C_i}^2 = \left[\left(\frac{1}{A_i}\right)^2 \sigma_{A_i}^2 + \left(\frac{1}{m}\right)^2 \sigma_m^2 \right] C_i^2 \quad (11)$$

Hence, an estimate for the standard deviation in the concentrations of the targeted anion in the standard and filtered samples can be obtained as follows:

$$\sigma_{C_i} = \left[\left(\frac{1}{A_i}\right)^2 \sigma_{A_i}^2 + \left(\frac{1}{m}\right)^2 \sigma_m^2 \right]^{1/2} C_i \quad (12)$$

The mean of three sample values of the area-under-the-curve was taken. Thus, the deviation from the mean could be used to account for the uncertainty in the solute area-under-the-curve as follows:

$$\sigma_{A_i}^2 = \frac{\sum_{i=1}^N (A_i - A_m)^2}{N - 1} \quad (13)$$

where A_m is the mean (average) area-under-the-curves of the solute and N is the number of sample replicates. The uncertainty in the slope of the calibration curve was estimated by fitting the calibration data to a straight line equation.

Determination of Trace Isopropylamine in Water

The liquid mole fraction of isopropylamine was calculated by converting the area-under-the-curve data of the 1 μ L injected sample into the volume of isopropylamine present in the sample using the calibration curve data as follows:

$$V_i = \frac{A_i}{m} \quad (14)$$

where A_i is the area-under-the-curve of isopropylamine, and m is the slope of the calibration curve. Determining the volume of isopropylamine in the injected 1 μ L sample to the GC allows to calculate the number of moles of isopropylamine and water in that sample through a material balance as follows:

$$n_i = \frac{V_i \rho_i}{MW_i} \quad (15)$$

$$n_w = \frac{(1 - V_i) \rho_w}{MW_w} \quad (16)$$

where n_i , n_w , ρ_i , ρ_w , MW_i and MW_w are respectively the number of moles of isopropylamine, number of moles of water, density of isopropylamine, density of water, molecular weight of isopropylamine, and molecular weight of water. Thus, the liquid mole fraction of isopropylamine can be calculated as follows:

$$x_i = \frac{n_i}{n_i + n_w} \quad (17)$$

Error Analysis

The variance in the liquid mole fraction of isopropylamine can be written as follows:

$$\sigma_{x_i}^2 = \left(\frac{\partial x_i}{\partial n_i} \right)^2 \sigma_{n_i}^2 + \left(\frac{\partial x_i}{\partial n_w} \right)^2 \sigma_{n_w}^2 \quad (18)$$

where:

$$\left(\frac{\partial x_i}{\partial n_i} \right)^2 = \left[\frac{n_w}{(n_i + n_w)^2} \right]^2 \quad (19)$$

$$\left(\frac{\partial x_i}{\partial n_w} \right)^2 = \left[-\frac{n_i}{(n_i + n_w)^2} \right]^2 \quad (20)$$

$$\sigma_{n_i}^2 = \left(\frac{\partial n_i}{\partial v_i} \right)^2 \sigma_{v_i}^2 + \left(\frac{\partial n_i}{\partial \rho_i} \right)^2 \sigma_{\rho_i}^2 \quad (21)$$

$$\sigma_{n_w}^2 = \left(\frac{\partial n_w}{\partial v_i} \right)^2 \sigma_{v_i}^2 + \left(\frac{\partial n_w}{\partial \rho_w} \right)^2 \sigma_{\rho_w}^2 \quad (22)$$

and

$$\left(\frac{\partial n_i}{\partial v_i} \right)^2 = \left(\frac{\rho_i}{MW_i} \right)^2 \quad (23)$$

$$\left(\frac{\partial n_i}{\partial \rho_i} \right)^2 = \left(\frac{V_i}{MW_i} \right)^2 \quad (24)$$

$$\left(\frac{\partial n_w}{\partial V_i} \right)^2 = \left(\frac{\rho_w}{MW_w} \right)^2 \quad (25)$$

$$\left(\frac{\partial n_w}{\partial \rho_w} \right)^2 = \left(\frac{1 - V_i}{MW_w} \right)^2 \quad (26)$$

The variance in the volume of isopropylamine can be estimated using Equation (14) as follows:

$$\sigma_{V_i}^2 = \left(\frac{\partial V_i}{\partial A_i} \right)^2 \sigma_{A_i}^2 + \left(\frac{\partial V_i}{\partial m} \right)^2 \sigma_m^2 \quad (27)$$

where:

$$\left(\frac{\partial V_i}{\partial A_i} \right)^2 = \left(\frac{1}{m} \right)^2 \quad (28)$$

$$\left(\frac{\partial V_i}{\partial m} \right)^2 = \left(-\frac{A_i}{m^2} \right)^2 \quad (29)$$

The mean of three sample values of the area-under-the-curve was taken. Thus, the deviation from the mean can be used to account for the uncertainty in the solute area-under-the-curve as follows:

$$\sigma_{A_i}^2 = \frac{\sum_{i=1}^N (A_i - A_m)^2}{N - 1} \quad (30)$$

where A_m is the mean (average) area-under-the-curves of isopropylamine and N is the number of sample replicates. The uncertainties in the slope of the GC calibration curve were estimated by fitting the calibration data to a straight line equation while the uncertainties in the densities of isopropylamine and water could be obtained as follows [35]:

$$\sigma_{\rho_i}^2 = (0.003\rho_i)^2 \quad (31)$$

$$\sigma_{\rho_w}^2 = (0.003\rho_w)^2 \quad (32)$$

CHAPTER IV

PRESENTATION AND ANALYSIS OF EXPERIMENTAL DATA

To evaluate the viability of the experimental methods and the acquired experimental data, error analysis and instrumental consistency test are essential elements in the overall experimental effort. Although there is no unquestionably correct data, these tests are usually indicative of the overall quality and provide a means of detecting inconsistency of the reported data. Presentation of the experimental data along with error analysis, followed by assessments for the consistency of the reported values, discussion of the experimental data, and the recovery of the organic solvent are discussed below.

Presentation of Experimental Data

Precipitation measurements for chloride and sulfate salts involving six cations (sodium, potassium, magnesium, calcium, barium, and strontium) using isopropylamine as the precipitation agent were obtained. The precipitation data for chloride and sulfate salts along with their error analysis are presented in Tables 5 to 23. The precipitation data includes: (1) chloride salts at 5,000 mg/L: magnesium, magnesium-sodium, magnesium-potassium, calcium, calcium-sodium, calcium-potassium, calcium-magnesium, calcium-barium, and calcium-strontium; (2) chloride salts at 10,000 mg/L: magnesium, magnesium-sodium, magnesium-potassium, calcium, and calcium-sodium; and

TABLE 5

PRECIPITATION MEASUREMENTS FOR MAGNESIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4152.1 68.4	18.2 1.9	20.1 16.3
5.0	0.2	3988.1 66.6	21.4 1.8	23.2 19.6
10.0	0.4	3546.1 62.4	30.1 1.7	31.8 28.5
15.0	0.6	3367.8 60.3	33.6 1.6	35.2 32.1
20.0	0.8	3025.5 56.3	40.4 1.5	41.9 38.9
25.0	1.0	2890.9 55.3	43.0 1.4	44.4 41.6
35.0	1.4	2592.3 50.7	48.9 1.3	50.2 47.6
50.0	2.0	2125.8 43.5	58.1 1.1	59.2 57.0

C_s (mg/L) /:	5075.8/			
σ_{C_s} :	80.4			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 6

PRECIPITATION MEASUREMENTS FOR MAGNESIUM-SODIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4094.9 67.6	19.3 1.9	21.2 17.4
5.0	0.2	3985.6 65.9	21.5 1.8	23.3 19.6
10.0	0.4	3634.8 60.3	28.4 1.7	30.1 26.7
15.0	0.6	3432.6 57.2	32.4 1.6	34.0 30.8
20.0	0.8	3075.4 50.5	39.4 1.4	40.8 38.0
25.0	1.0	2892.9 48.3	43.0 1.3	44.3 41.7
35.0	1.4	2534.2 42.6	50.1 1.2	51.3 48.9
50.0	2.0	2063.6 39.1	59.3 1.0	60.4 58.3

C_g (mg/L) / : 5074.8/
 σ_{C_g} : 84.4

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 7
PRECIPITATION MEASUREMENTS FOR MAGNESIUM-POTASSIUM CHLORIDE
AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4183.2 65.8	17.7 1.8	19.5 15.8
5.0	0.2	4018.0 65.0	20.1 1.8	21.9 18.2
10.0	0.4	3552.6 58.2	29.3 1.6	30.9 27.7
15.0	0.6	3406.6 55.9	32.2 1.5	33.8 30.7
20.0	0.8	3172.1 53.6	36.9 1.5	38.4 35.4
25.0	1.0	2798.1 47.9	44.3 1.3	45.6 43.0
35.0	1.4	2495.2 47.4	50.4 1.2	51.6 49.1
50.0	2.0	2073.4 40.3	58.4 1.0	59.8 57.7

C_S (mg/L) / : 5026.2/
 σ_{C_S} : 79.8

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 8
PRECIPITATION MEASUREMENTS FOR CALCIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4142.8 68.3	17.6 1.9	19.5 15.7
5.0	0.2	3922.1 64.8	22.0 1.8	23.8 20.2
10.0	0.4	3520.0 58.4	30.0 1.6	31.6 28.4
15.0	0.6	3364.5 56.1	33.1 1.6	34.7 31.5
20.0	0.8	3044.8 51.1	39.4 1.4	40.8 38.0
25.0	1.0	2887.2 48.8	42.6 1.3	43.9 41.3
35.0	1.4	2530.3 43.5	49.7 1.2	50.9 48.5
50.0	2.0	2074.6 40.5	58.7 1.0	59.7 57.7
<hr/>				
C_s (mg/L) /:	5026.5/			
σ_{C_s} :	81.8			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 9

PRECIPITATION MEASUREMENTS FOR CALCIUM-SODIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4092.8 65.8	18.4 1.8	20.2 16.6
5.0	0.2	3853.5 62.2	23.2 1.7	24.9 21.5
10.0	0.4	3498.8 57.7	30.3 1.6	31.9 28.7
15.0	0.6	3374.5 57.0	32.8 1.6	34.4 31.2
20.0	0.8	3063.7 52.1	39.0 1.4	40.4 37.6
25.0	1.0	2814.2 49.9	43.9 1.3	45.2 42.6
35.0	1.4	2499.4 45.1	50.2 1.2	51.4 49.0
50.0	2.0	2101.3 42.3	58.1 1.1	59.2 57.0
<hr/>				
C_s (mg/L) /:	5018.2/			
σ_{C_s} :	79.9			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 10

PRECIPITATION MEASUREMENTS FOR CALCIUM-POTASSIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4110.2 65.3	18.1 1.8	19.9 16.3
5.0	0.2	3844.6 61.4	23.4 1.7	25.1 21.7
10.0	0.4	3524.2 57.6	29.7 1.6	31.3 28.1
15.0	0.6	3386.0 58.0	32.5 1.6	34.1 30.9
20.0	0.8	3012.4 52.6	39.9 1.4	41.3 38.5
25.0	1.0	2830.1 50.0	43.6 1.3	44.9 42.3
35.0	1.4	2531.6 46.9	49.5 1.2	50.7 48.3
50.0	2.0	2099.1 44.7	58.2 1.1	59.3 57.1
<hr/>				
C_s (mg/L) /:	5015.9/			
σ_{C_s} :	80.1			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 11

PRECIPITATION MEASUREMENTS FOR CALCIUM-MAGNESIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4087.5 65.3	18.6 1.9	20.5 16.7
5.0	0.2	3895.9 63.6	22.4 1.8	24.2 20.6
10.0	0.4	3515.2 62.4	30.0 1.6	31.6 28.4
15.0	0.6	3372.0 56.7	32.9 1.6	34.5 31.3
20.0	0.8	3074.3 53.6	38.8 1.5	40.3 37.3
25.0	1.0	2788.8 49.9	44.5 1.3	45.8 43.2
35.0	1.4	2510.8 49.6	50.0 1.3	51.3 48.7
50.0	2.0	2053.4 43.4	59.1 1.1	60.2 58.0
<hr/>				
C_S (mg/L) /:	5075.8/			
σ_{C_S} :	80.4			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 12

PRECIPITATION MEASUREMENTS FOR CALCIUM-BARIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4109.4 67.0	18.1 1.9	20.0 16.2
5.0	0.2	3896.1 64.3	22.3 1.8	24.1 20.5
10.0	0.4	3544.6 59.4	29.4 1.6	30.0 27.8
15.0	0.6	3389.1 58.0	32.5 1.6	34.1 30.9
20.0	0.8	3113.7 54.8	37.9 1.5	39.4 36.4
25.0	1.0	2813.5 50.3	43.9 1.3	45.2 42.6
35.0	1.4	2486.4 49.1	50.4 1.3	51.7 49.1
50.0	2.0	2100.0 44.1	58.1 1.1	59.2 57.0
<hr/>				
C_s (mg/L) /:	5017.4/			
σ_{C_s} :	79.9			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 13

PRECIPITATION MEASUREMENTS FOR CALCIUM-STRONTIUM CHLORIDE AT 5,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	4153.4 66.2	17.2 1.9	19.1 15.3
5.0	0.2	3895.8 63.3	22.4 1.8	24.2 20.6
10.0	0.4	3519.7 57.9	29.9 1.6	31.5 28.3
15.0	0.6	3370.5 60.0	32.8 1.5	34.4 31.3
20.0	0.8	3097.4 54.4	38.3 1.5	39.8 36.8
25.0	1.0	2897.3 53.0	42.3 1.4	43.7 40.9
35.0	1.4	2514.5 47.0	49.9 1.2	51.1 48.7
50.0	2.0	2111.0 43.8	58.0 1.1	59.0 56.8
<hr/>				
C_s (mg/L) /:	5018.7/			
σ_{C_s} :	79.9			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 14

PRECIPITATION MEASUREMENTS FOR MAGNESIUM CHLORIDE AT 10,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	8316.2 132.7	16.8 1.9	18.7 15.0
5.0	0.2	7958.6 127.9	20.4 1.8	22.2 18.6
10.0	0.4	7113.4 114.8	28.8 1.6	30.5 27.2
15.0	0.6	6641.3 108.9	33.6 1.5	35.1 32.1
20.0	0.8	6270.3 104.1	37.3 1.4	38.7 35.8
25.0	1.0	5810.8 100.9	41.9 1.4	43.2 40.5
35.0	1.4	4955.0 87.6	50.4 1.2	51.6 49.2
50.0	2.0	4151.0 82.6	58.5 1.1	59.5 57.4
<hr/>				
C_s (mg/L) /:	9997.7/			
σ_{C_s} :	158.7			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 15

PRECIPITATION MEASUREMENTS FOR MAGNESIUM-SODIUM CHLORIDE AT 10,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	8309.5 135.6	16.9 1.9	18.8 15.0
5.0	0.2	8075.6 132.9	19.2 1.9	21.1 17.4
10.0	0.4	7155.2 119.1	28.5 1.6	30.1 26.9
15.0	0.6	6543.1 110.0	34.6 1.5	36.1 33.1
20.0	0.8	6346.4 108.0	36.5 1.5	38.0 35.0
25.0	1.0	5727.8 99.3	42.7 1.3	44.0 41.4
35.0	1.4	5075.7 92.4	49.2 1.2	50.4 48.0
50.0	2.0	4267.9 82.8	57.3 1.1	58.4 56.2
<hr/>				
C_S (mg/L) /:	10000.6/			
σ_{C_S} :	158.9			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 16
PRECIPITATION MEASUREMENTS FOR MAGNESIUM-POTASSIUM CHLORIDE
AT 10,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	8280.2 133.3	17.3 1.9	19.2 15.4
5.0	0.2	7989.5 129.0	20.2 1.8	22.0 18.4
10.0	0.4	6976.6 113.4	30.3 1.6	31.9 28.7
15.0	0.6	6594.6 109.2	34.1 1.5	35.6 32.6
20.0	0.8	6183.0 103.4	38.2 1.4	39.6 36.8
25.0	1.0	5707.4 97.1	43.0 1.3	44.3 41.7
35.0	1.4	4997.9 89.0	50.1 1.2	51.3 48.9
50.0	2.0	4211.4 78.5	57.9 1.0	59.0 56.9

C_s (mg/L) / : 10011.1/
 σ_{C_s} : 158.6

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 17

PRECIPITATION MEASUREMENTS FOR CALCIUM CHLORIDE AT 10,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	8302.4 132.1	16.8 1.9	18.7 14.9
5.0	0.2	7966.6 127.3	20.2 1.8	22.0 18.4
10.0	0.4	7125.6 114.2	28.6 1.6	30.2 27.0
15.0	0.6	6621.0 108.8	33.7 1.5	35.2 32.2
20.0	0.8	6257.4 103.4	37.3 1.4	38.7 35.9
25.0	1.0	5762.5 96.4	42.3 1.3	43.6 41.0
35.0	1.4	5056.3 88.1	49.3 1.2	50.5 48.1
50.0	2.0	4194.9 78.3	58.0 1.0	59.0 57.0
<hr/>				
C_S (mg/L) /:	9982.3/			
σ_{C_S} :	160.8			

 $*V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 18

PRECIPITATION MEASUREMENTS FOR CALCIUM-SODIUM CHLORIDE AT 10,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P / σ_P	%P \pm σ_P
2.5	0.1	8281.3 131.2	17.3 1.9	19.2 15.4
5.0	0.2	7981.3 129.1	20.3 1.8	22.1 18.5
10.0	0.4	6964.7 114.0	30.4 1.6	32.0 28.8
15.0	0.6	6608.9 110.3	34.0 1.5	35.5 32.5
20.0	0.8	6148.5 104.4	38.6 1.4	40.0 37.2
25.0	1.0	5728.1 99.3	42.8 1.3	44.1 42.5
35.0	1.4	4877.1 93.5	51.3 1.2	52.5 50.1
50.0	2.0	4250.9 85.3	57.5 1.1	58.6 56.4
<hr/>				
C_s (mg/L) /:	10010.4/			
σ_{C_s} :	158.7			

 $V_R^* = V_3/V_2$; and $V_2 = 25$ mL

TABLE 19
PRECIPITATION MEASUREMENTS FOR CALCIUM SULFATE AT 1,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	893.36 9.77E00	9.39 1.40E00	10.79 7.98
5.0	0.2	478.91 5.27E00	51.42 7.55E-1	52.17 50.67
10.0	0.4	234.47 3.01E00	76.22 4.02E-1	76.62 75.82
15.0	0.6	169.18 2.27E00	82.84 2.98E-1	83.14 82.54
20.0	0.8	112.80 1.79E00	88.56 2.21E-1	88.78 88.34
25.0	1.0	83.80 1.54E00	91.50 1.82E-1	91.68 91.32
35.0	1.4	41.55 1.01E00	95.79 1.12E-1	95.90 95.68
50.0	2.0	17.65 4.78E-1	98.21 5.23E-2	98.26 98.16
<hr/>				
C_s (mg/L) /:	991.9/			
σ_{C_s} :	10.8			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 20

PRECIPITATION MEASUREMENTS FOR MAGNESIUM SULFATE AT 1,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	835.72 9.70E00	15.28 1.41E00	16.69 13.87
5.0	0.2	807.98 9.64E00	18.09 1.38E00	19.47 16.71
10.0	0.4	733.28 8.85E00	25.67 1.26E00	26.93 24.41
15.0	0.6	667.23 8.26E00	32.36 1.16E00	33.52 31.20
20.0	0.8	593.06 7.46E00	39.88 1.04E00	40.92 38.84
25.0	1.0	523.06 6.78E00	46.98 9.34E-1	47.91 46.04
35.0	1.4	460.98 6.12E00	53.27 8.34E-1	54.10 52.44
50.0	2.0	399.46 5.79E00	59.51 7.60E-1	60.27 58.75
<hr/>				
C_s (mg/L) /:	992.5/			
σ_{C_s} :	10.8			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 21

PRECIPITATION MEASUREMENTS FOR CALCIUM-MAGNESIUM SULFATE AT 1,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	793.14 9.01E00	19.81 1.32E00	21.13 18.49
5.0	0.2	708.36 8.18E00	28.38 1.18E00	29.56 27.20
10.0	0.4	500.16 6.07E00	49.43 8.57E-1	50.29 48.57
15.0	0.6	418.60 5.29E00	57.68 7.33E-1	58.41 56.95
20.0	0.8	383.43 4.94E00	61.24 6.78E-1	61.92 60.56
25.0	1.0	321.29 4.63E00	67.52 6.05E-1	68.13 66.92
35.0	1.4	284.63 4.43E00	71.22 5.62E-1	71.78 70.66
50.0	2.0	231.08 4.23E00	76.64 5.09E-1	77.15 76.13

C_S (mg/L) /:	989.1/			
σ_{C_S} :	11.7			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 22

PRECIPITATION MEASUREMENTS FOR CALCIUM-SODIUM SULFATE AT 1,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P / σ_P	%P \pm σ_P
2.5	0.1	824.50 9.51E00	17.23 1.31E00	18.54 15.92
10.0	0.4	454.10 5.41E00	54.41 7.36E-1	55.15 53.67
15.0	0.6	399.54 5.26E00	59.89 6.86E-1	60.58 59.20
20.0	0.8	351.74 5.29E00	64.69 6.56E-1	65.35 64.03
25.0	1.0	304.90 5.02E00	69.39 6.05E-1	70.00 68.79
35.0	1.4	258.32 4.64E00	74.07 5.45E-1	74.62 73.53
50.0	2.0	186.30 3.87E00	81.30 4.39E-1	81.74 80.86

C_S (mg/L) /:	996.1/			
σ_{C_S} :	10.9			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

TABLE 23

PRECIPITATION MEASUREMENTS FOR CALCIUM-POTASSIUM SULFATE AT 1,000 mg/L

V_3 (mL)	V_R^*	C_F (mg/L) / σ_{C_F}	%P/ σ_P	%P \pm σ_P
2.5	0.1	865.18 10.50E00	12.97 1.44E00	14.41 11.53
5.0	0.2	766.49 9.54E00	22.89 1.30E00	24.19 21.59
15.0	0.6	434.68 6.10E00	56.27 7.88E-1	57.06 55.48
20.0	0.8	453.97 5.53E00	64.29 6.88E-1	64.98 63.61
25.0	1.0	244.64 3.84E00	75.39 4.76E-1	75.87 74.91
35.0	1.4	100.89 1.73E00	89.85 2.08E-1	90.06 89.64
50.0	2.0	49.37 1.11E00	95.03 1.25E-2	95.16 94.91
<hr/>				
C_g (mg/L) /:	994.1/			
σ_{C_g} :	11.2			

* $V_R = V_3/V_2$; and $V_2 = 25$ mL

(3) sulfate salts at 1,000 mg/L: calcium, magnesium, calcium-magnesium, calcium-sodium, and calcium-potassium. The tabulated precipitation data (Tables 5 to 23) include the volume of isopropylamine (V_3), the solvents volume ratio (V_R), the filtered sample concentrations (C_F) and their standard deviations (σ_{C_F}), the percent precipitation fractions (%P) and their standard deviations (σ_P), the upper and lower limit of the percent precipitation fractions ($P \pm \sigma_P$), and the standard concentrations (C_S) and its standard deviation (σ_{C_S}). The precipitation measurements have covered the most practical concentrations range of the studied systems. Graphical representations of the precipitation fractions at different solvents volume ratio (V_R) along with their error analysis are given in Figures 2 to 20.

Instrumental Consistency

Instrumental consistency for the Ion Chromatograph was established by frequent calibration. In addition, the Ion Chromatograph was tested by determining the known concentration of the targeted salts (C_S) prior to and after each set of measurements to ensure proper analysis. The measured (weighed) and the determined (analyzed by Ion Chromatograph) concentrations of the targeted anions (salts) in distilled water are given in Tables 24 to 26. Comparisons of these data indicate excellent agreement. The observed differences are within the uncertainty of the Ion Chromatograph. The instrumental consistency tests were taken as a confirmation of reasonable analysis of the precipitation measurements as well as the employed experimental procedures (e.g., calibration curves, dilution steps, and dilution analysis).

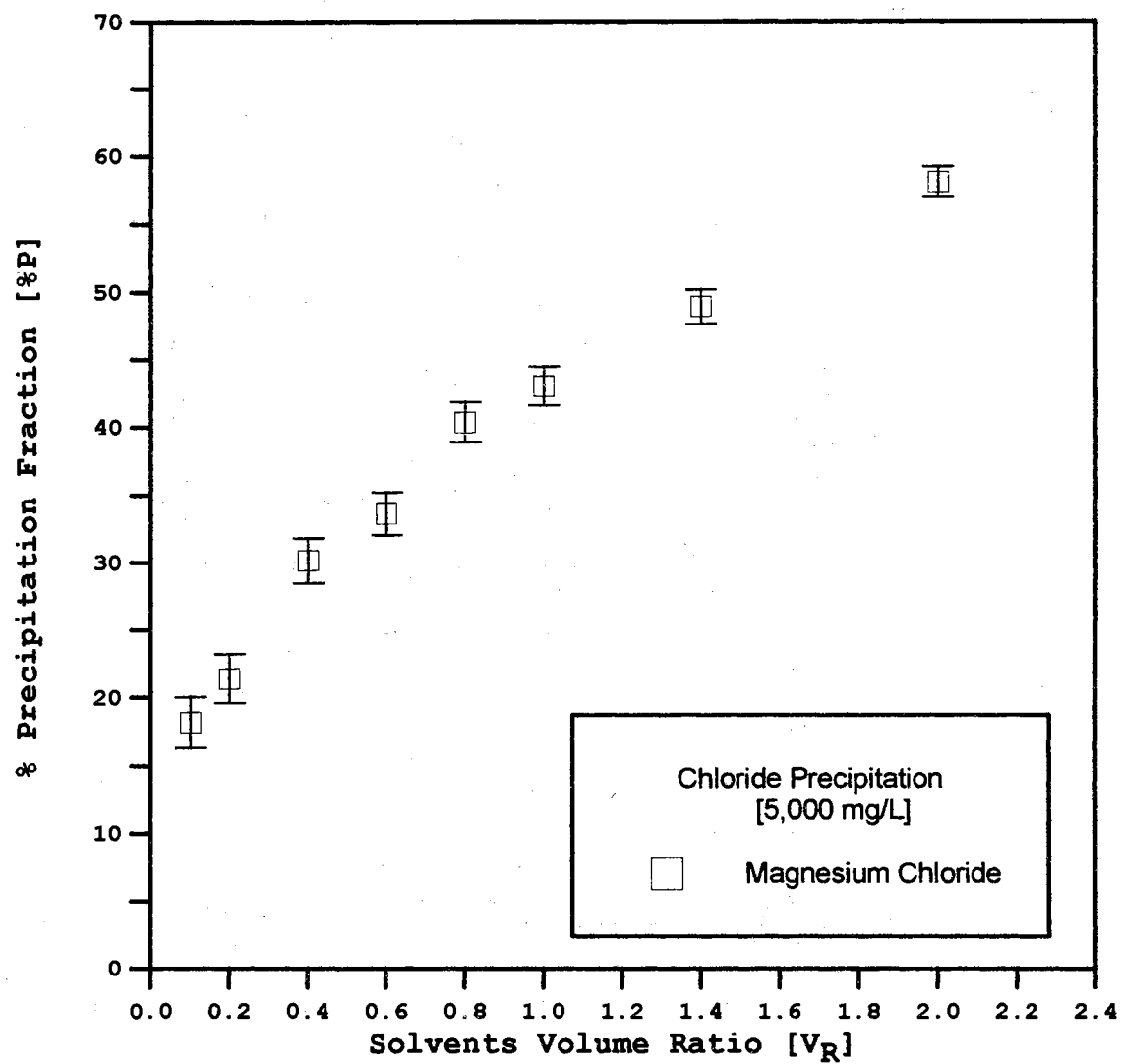


Figure 2. Precipitation Fraction for Magnesium Chloride at 5,000 mg/L

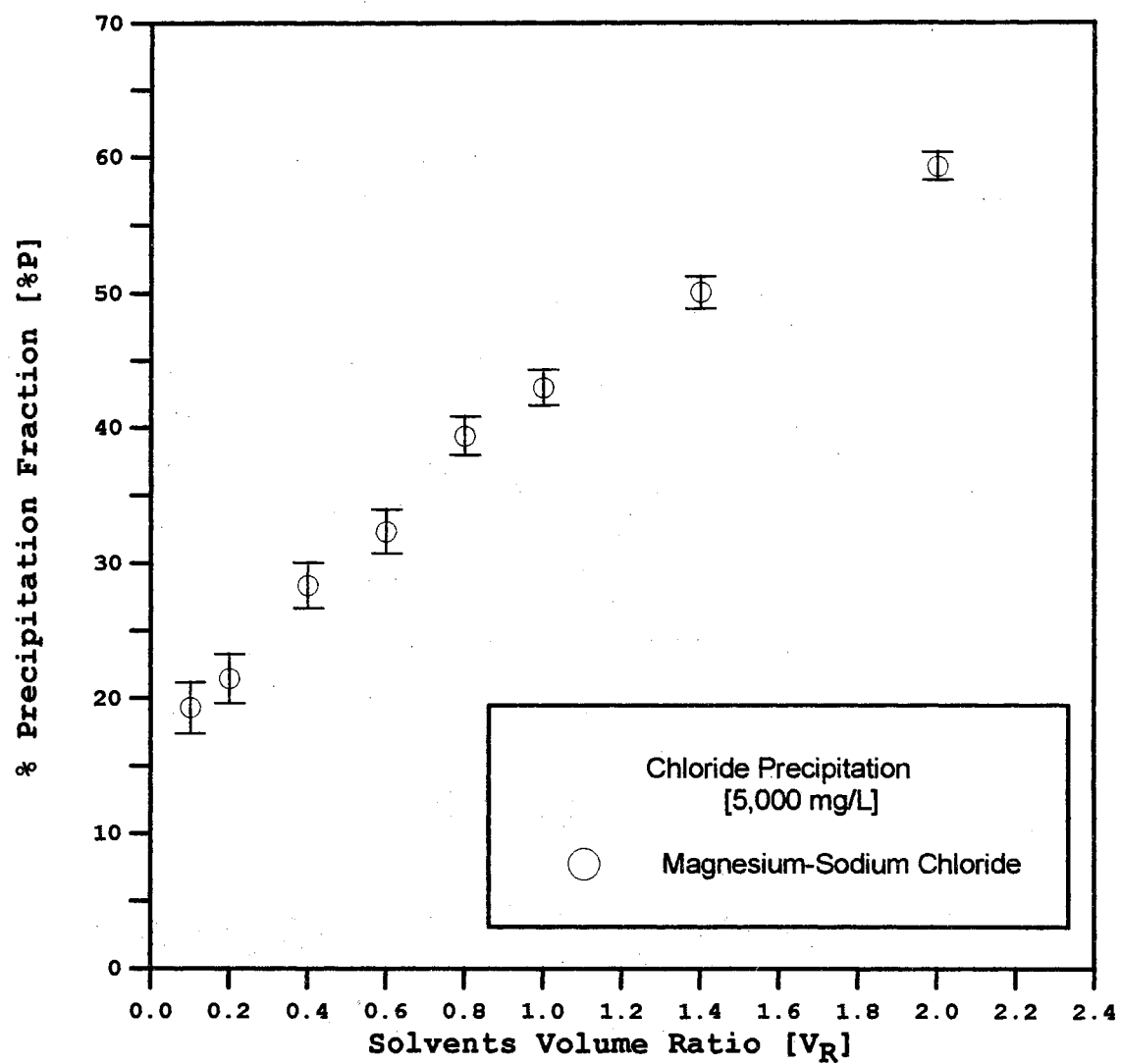


Figure 3. Precipitation Fraction for Magnesium-Sodium Chloride at 5,000 mg/L

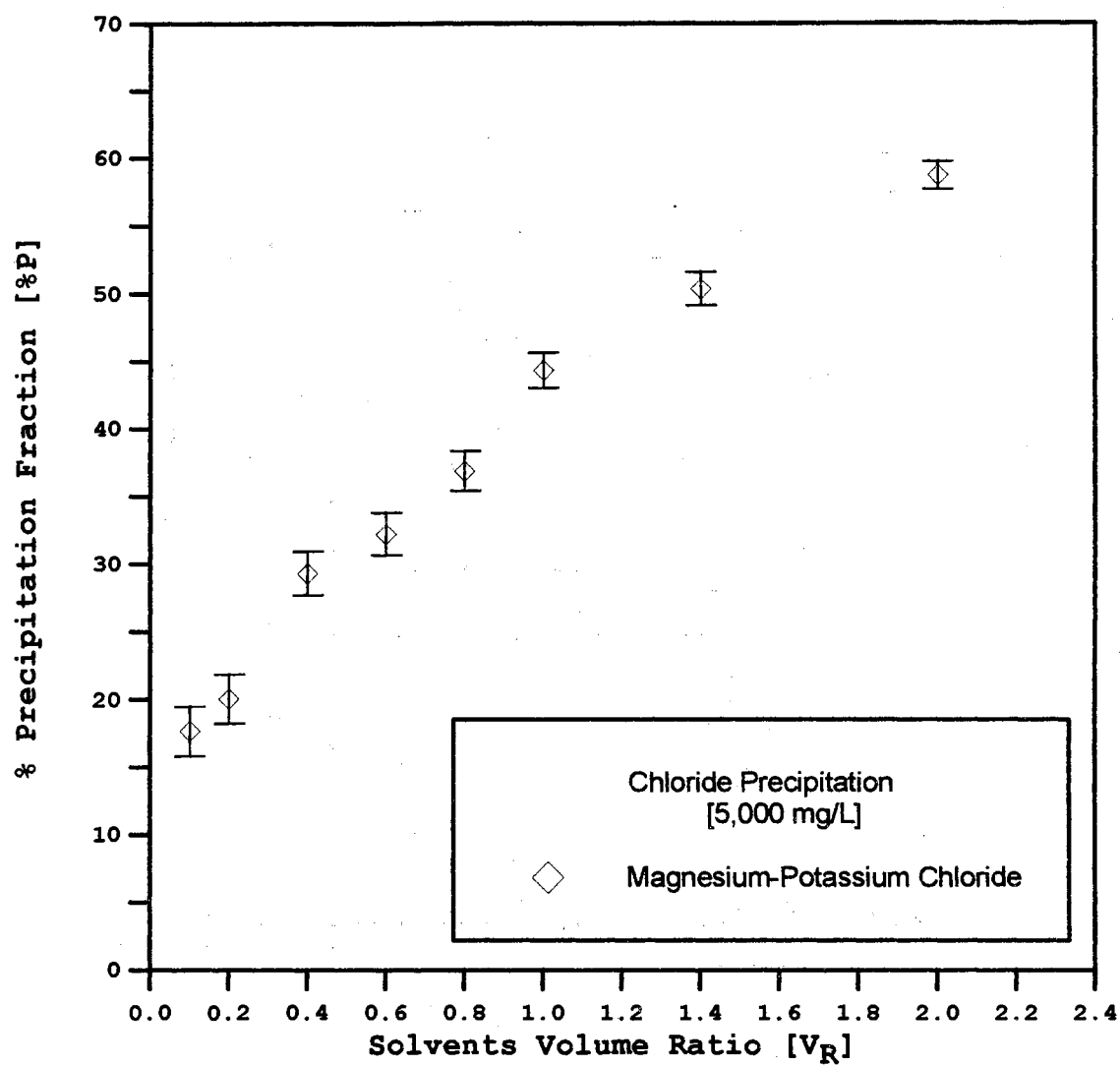


Figure 4. Precipitation Fraction for Magnesium-Potassium Chloride at 5,000 mg/L

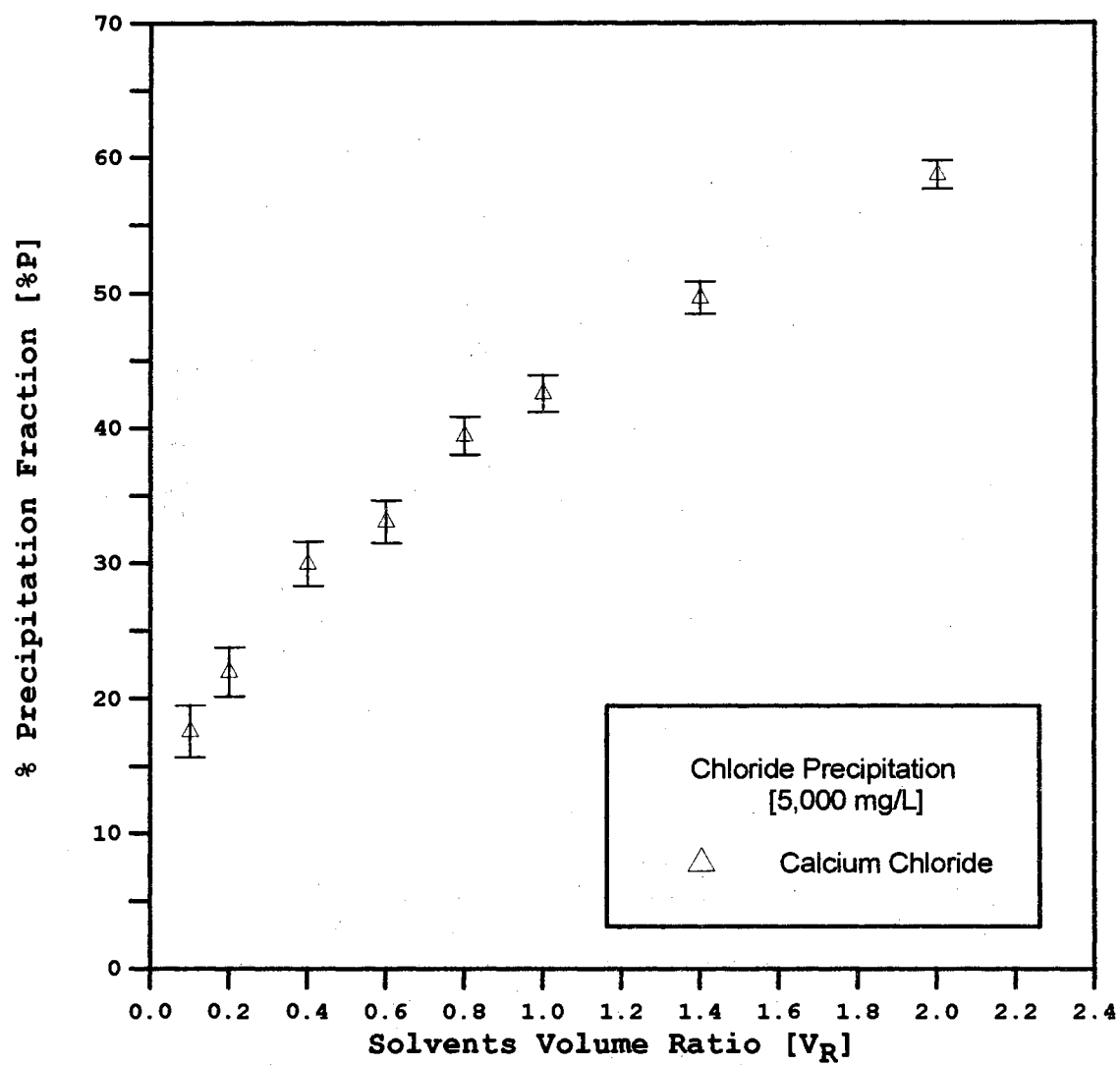


Figure 5. Precipitation Fraction for Calcium Chloride at 5,000 mg/L

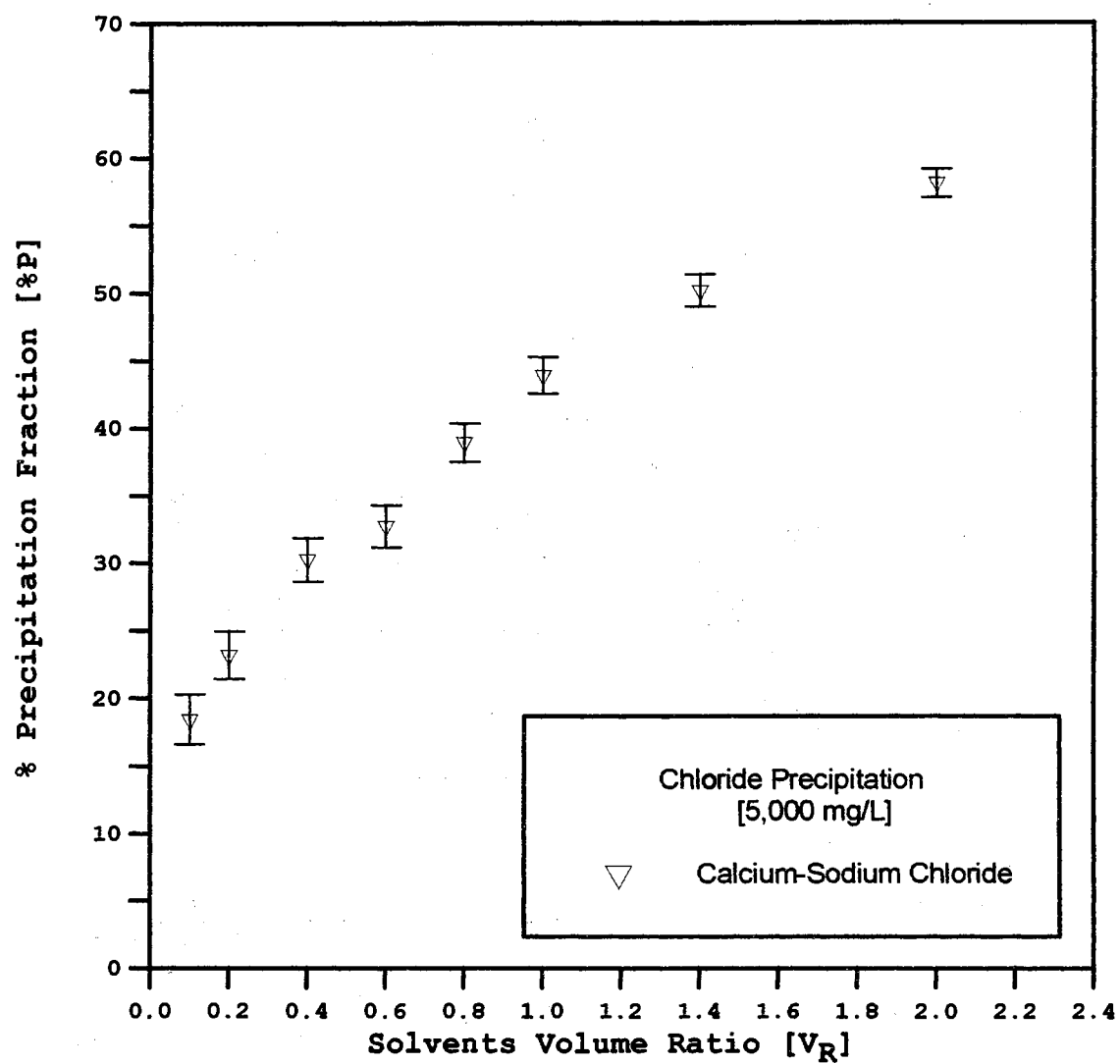


Figure 6. Precipitation Fraction for Calcium-Sodium Chloride at 5,000 mg/L

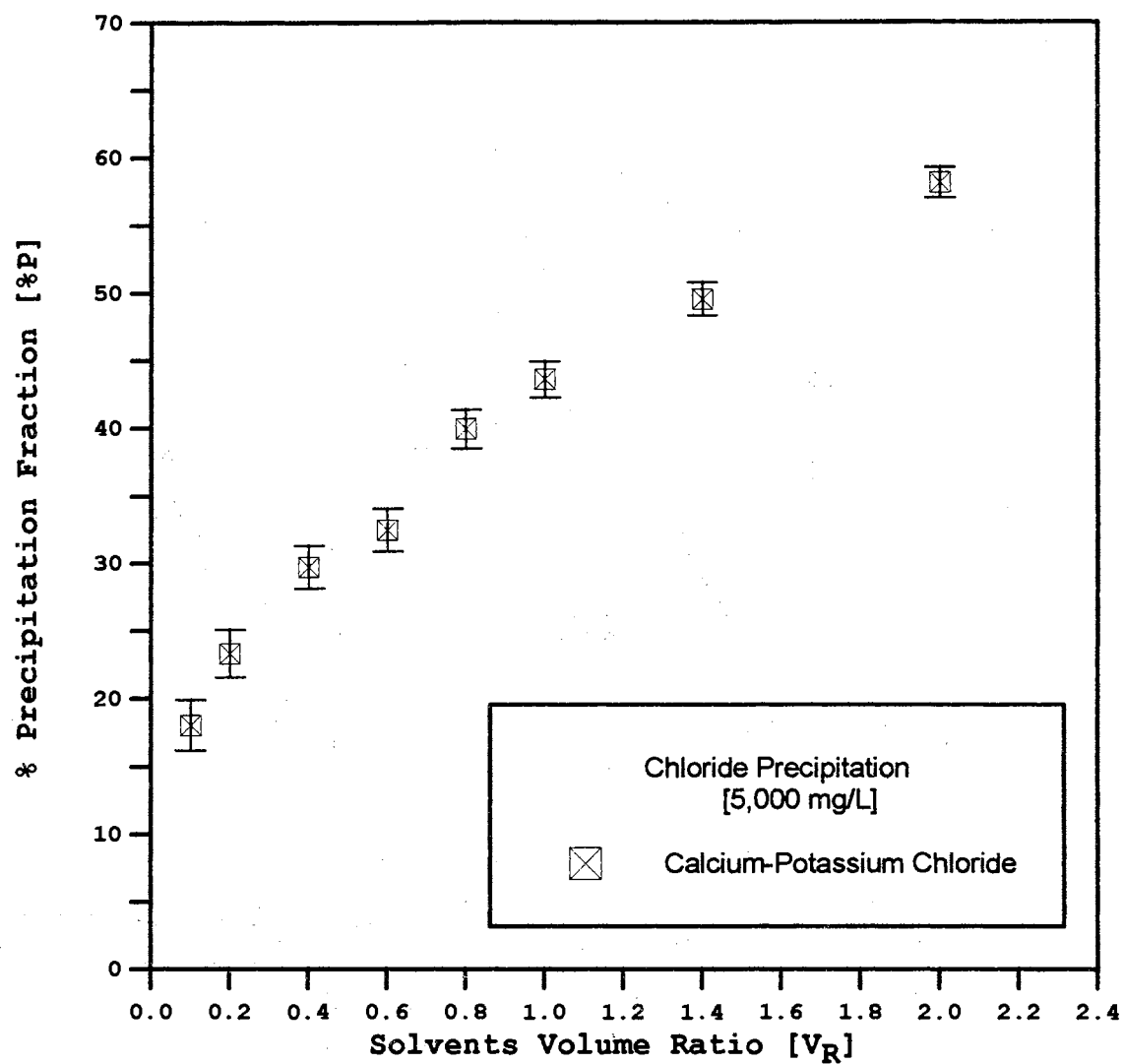


Figure 7. Precipitation Fraction for Calcium-Potassium Chloride at 5,000 mg/L

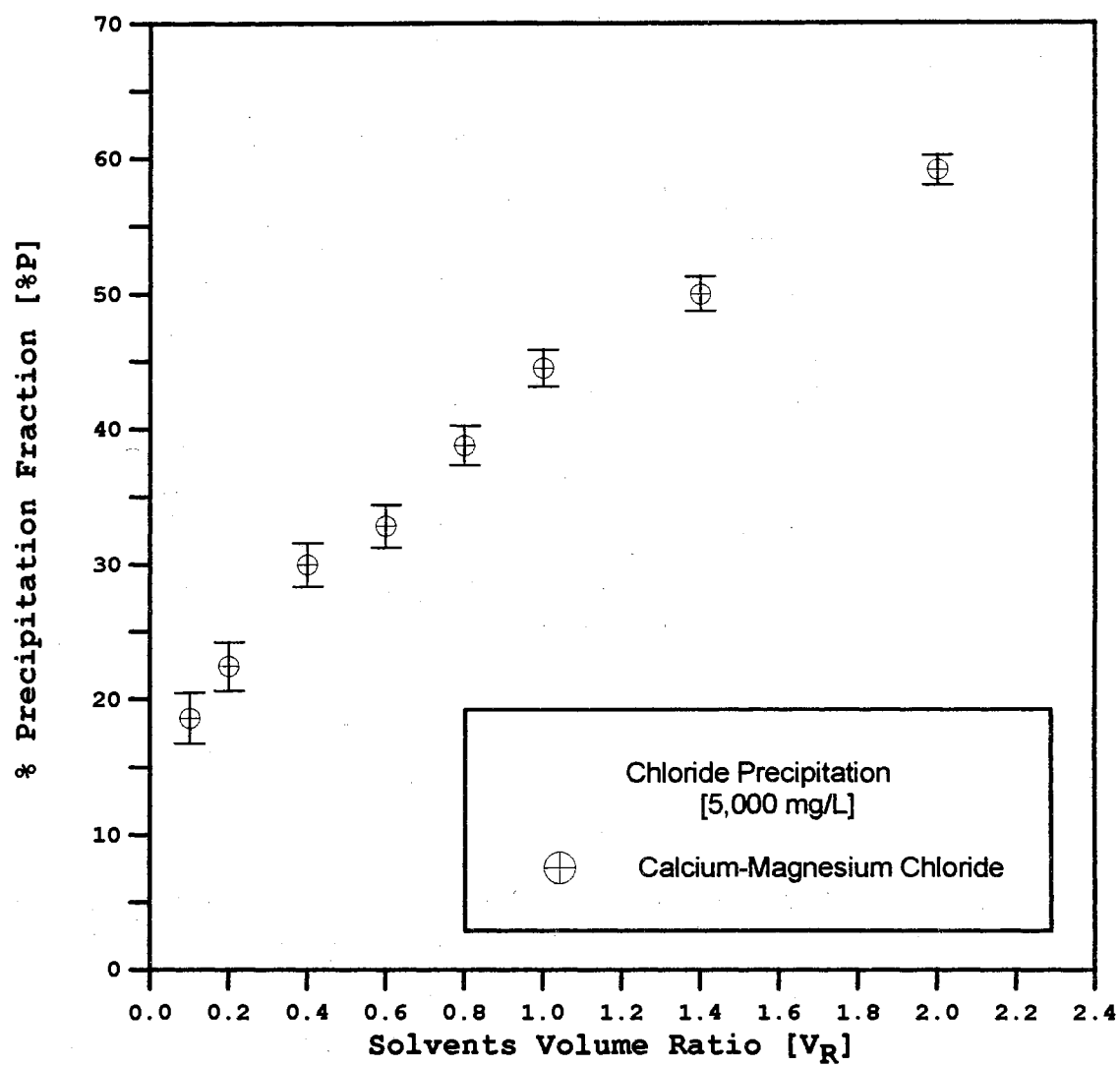


Figure 8. Precipitation Fraction for Calcium-Magnesium Chloride at 5,000 mg/L

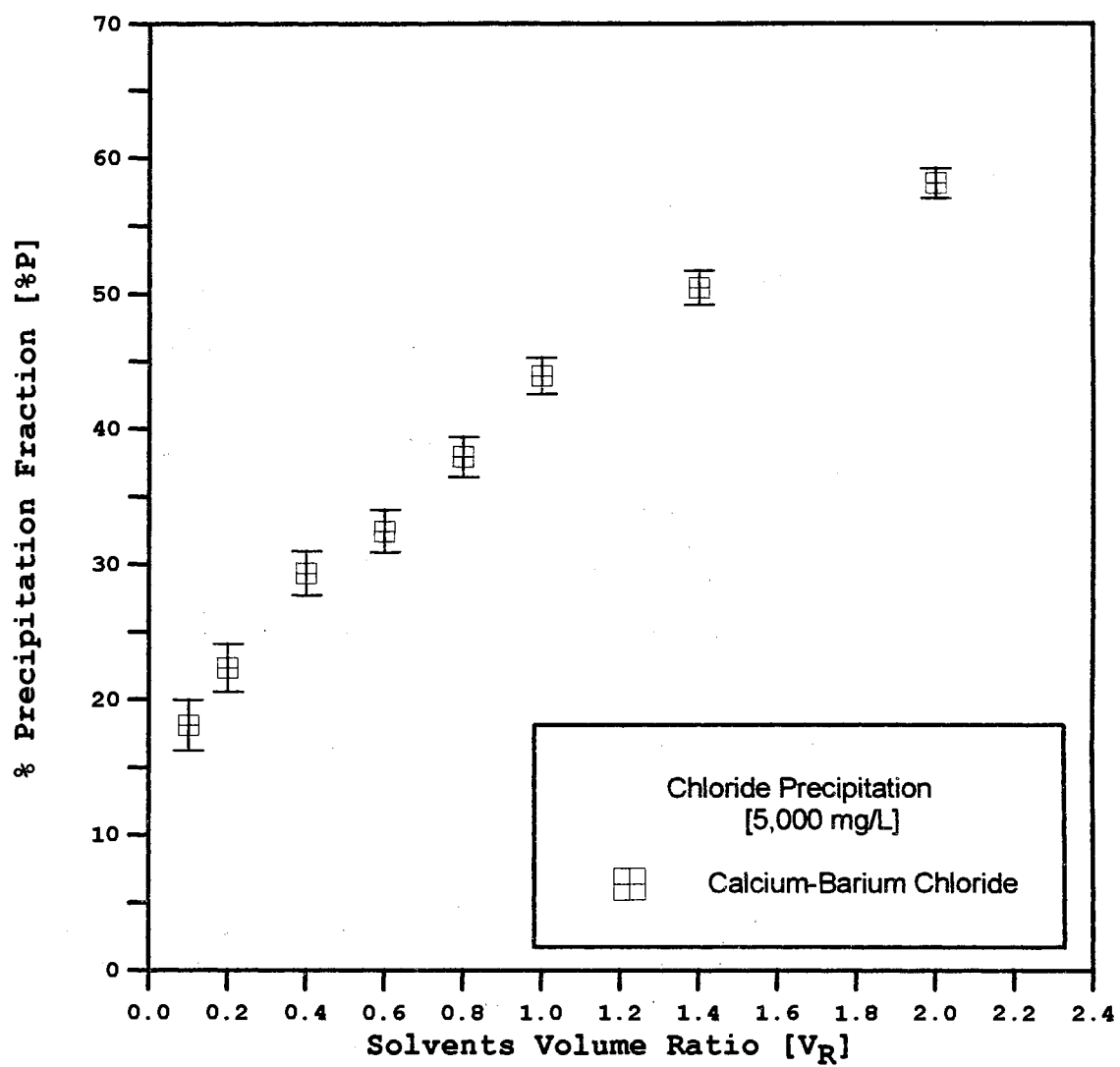


Figure 9. Precipitation Fraction for Calcium-Barium Chloride at 5,000 mg/L

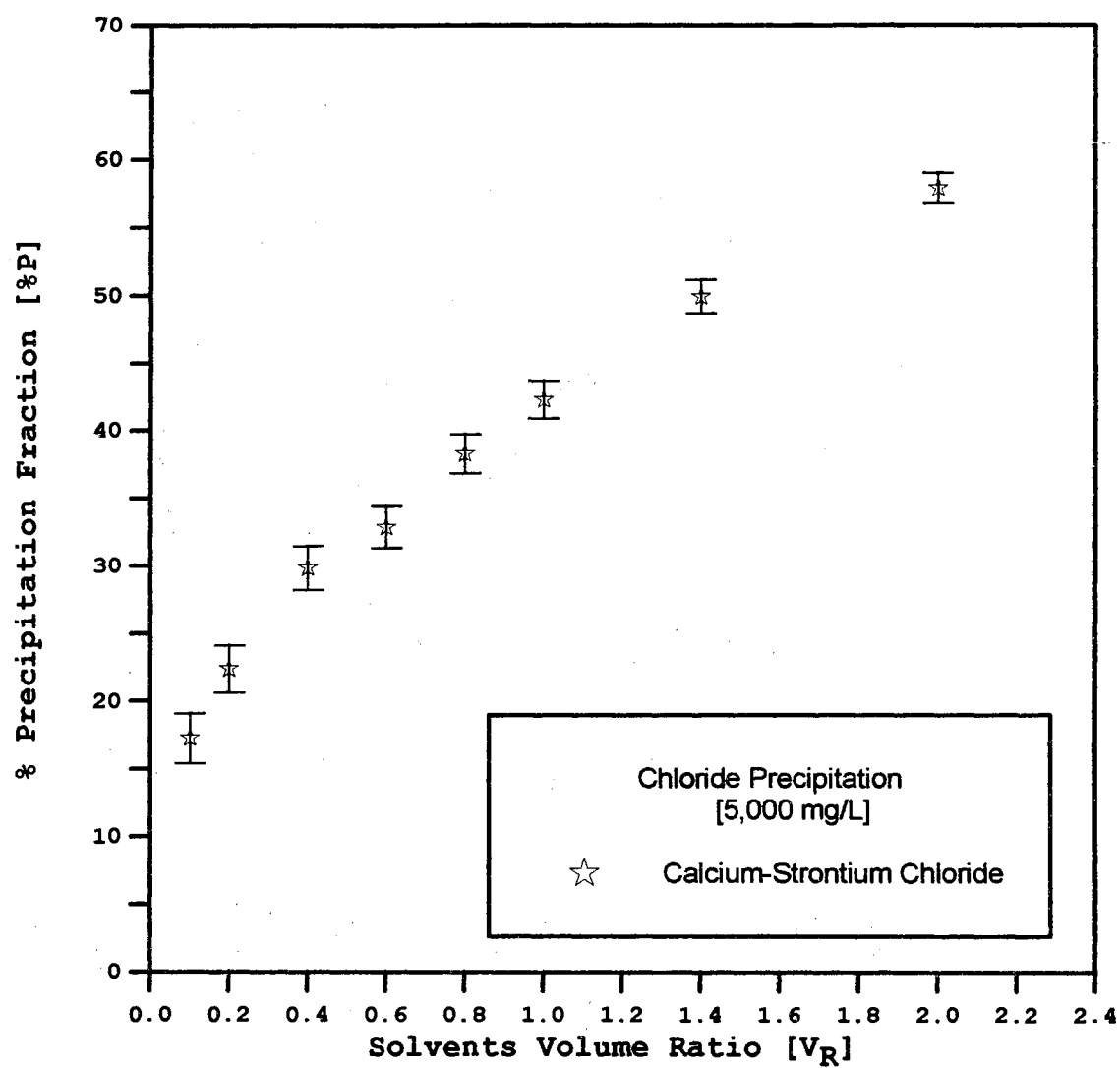


Figure 10. Precipitation Fraction for Calcium-Strontium Chloride at 5,000 mg/L

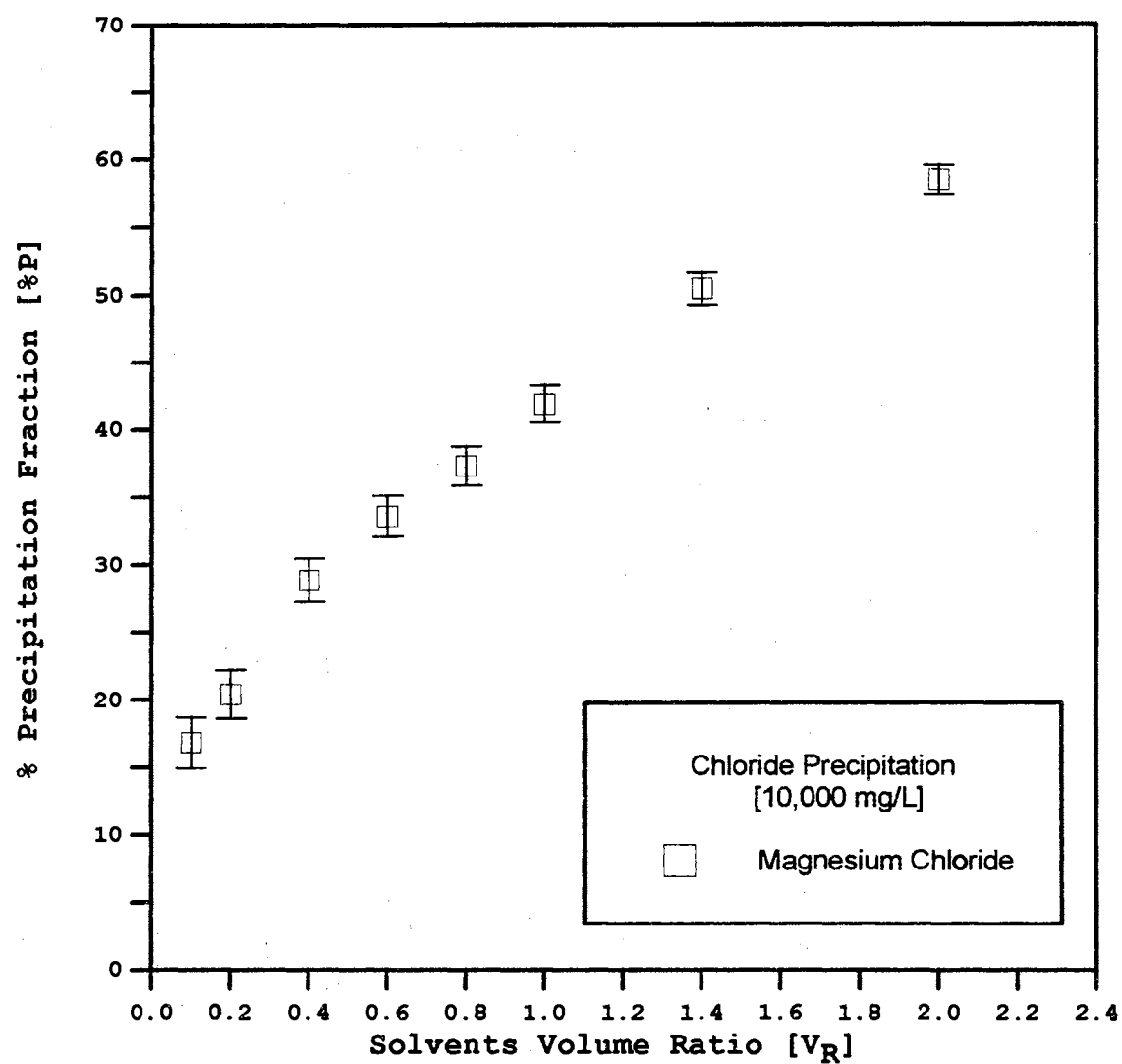


Figure 11. Precipitation Fraction for Magnesium Chloride at 10,000 mg/L

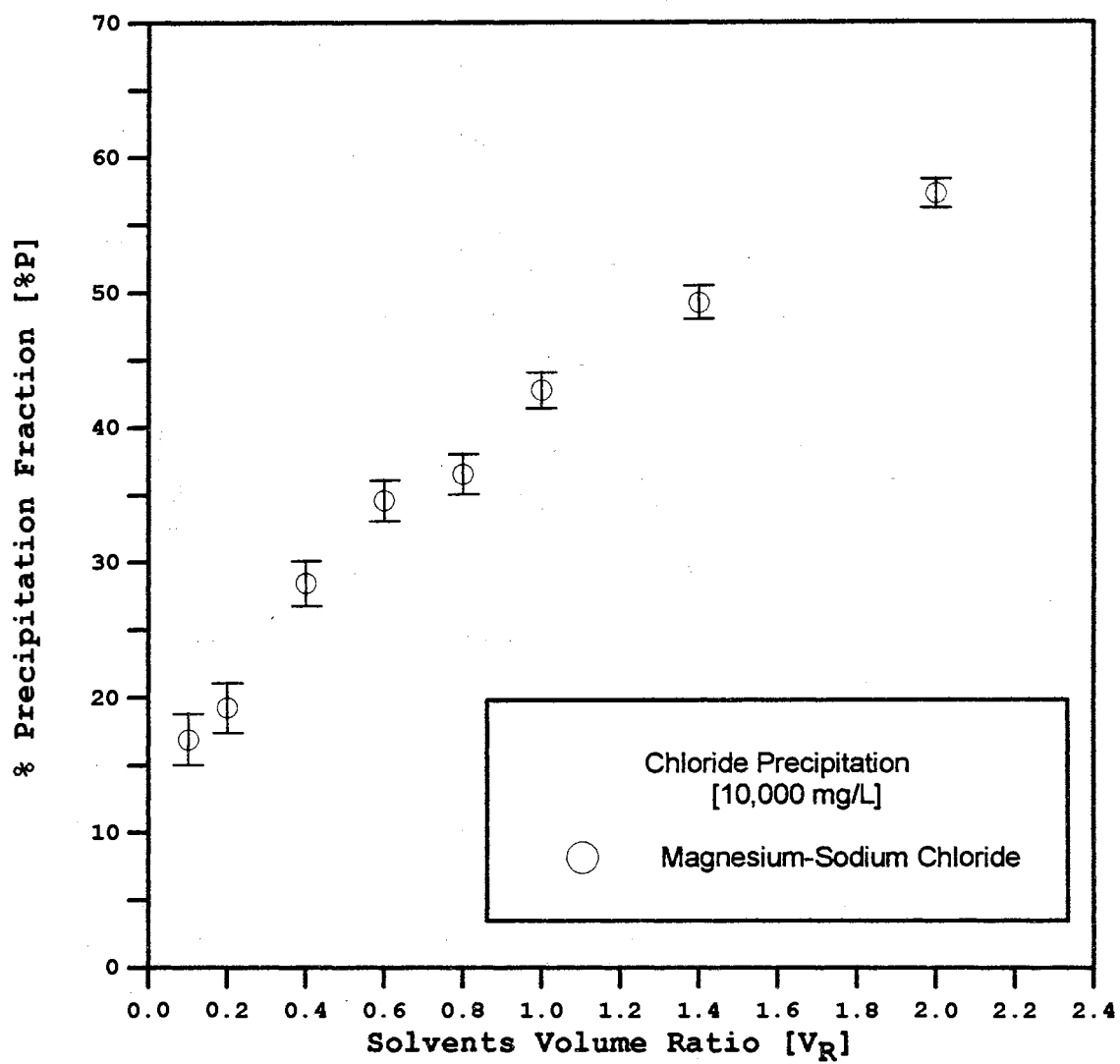


Figure 12. Precipitation Fraction for Magnesium-Sodium Chloride at 10,000 mg/L

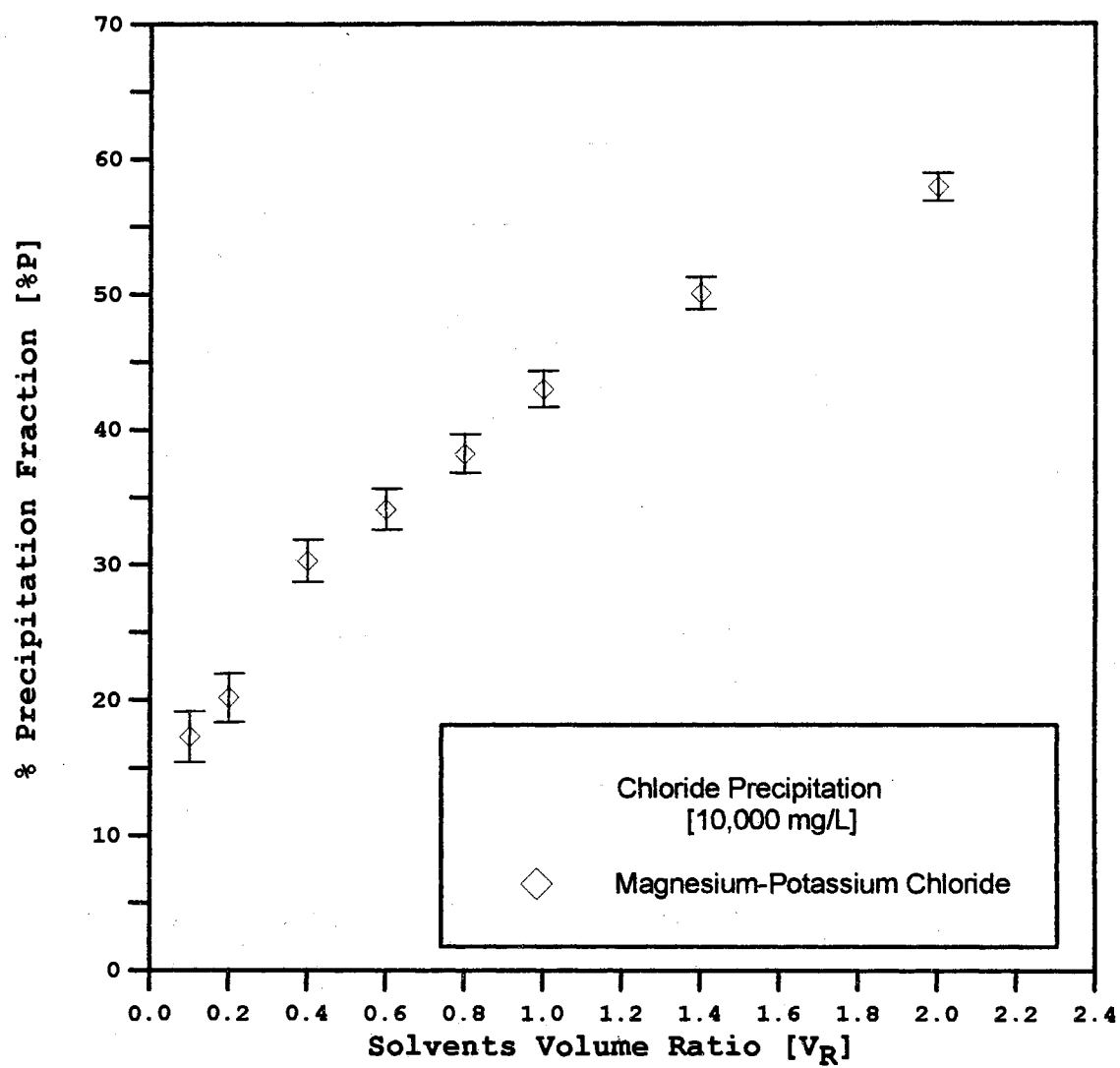


Figure 13. Precipitation Fraction for Magnesium-Potassium Chloride at 10,000 mg/L

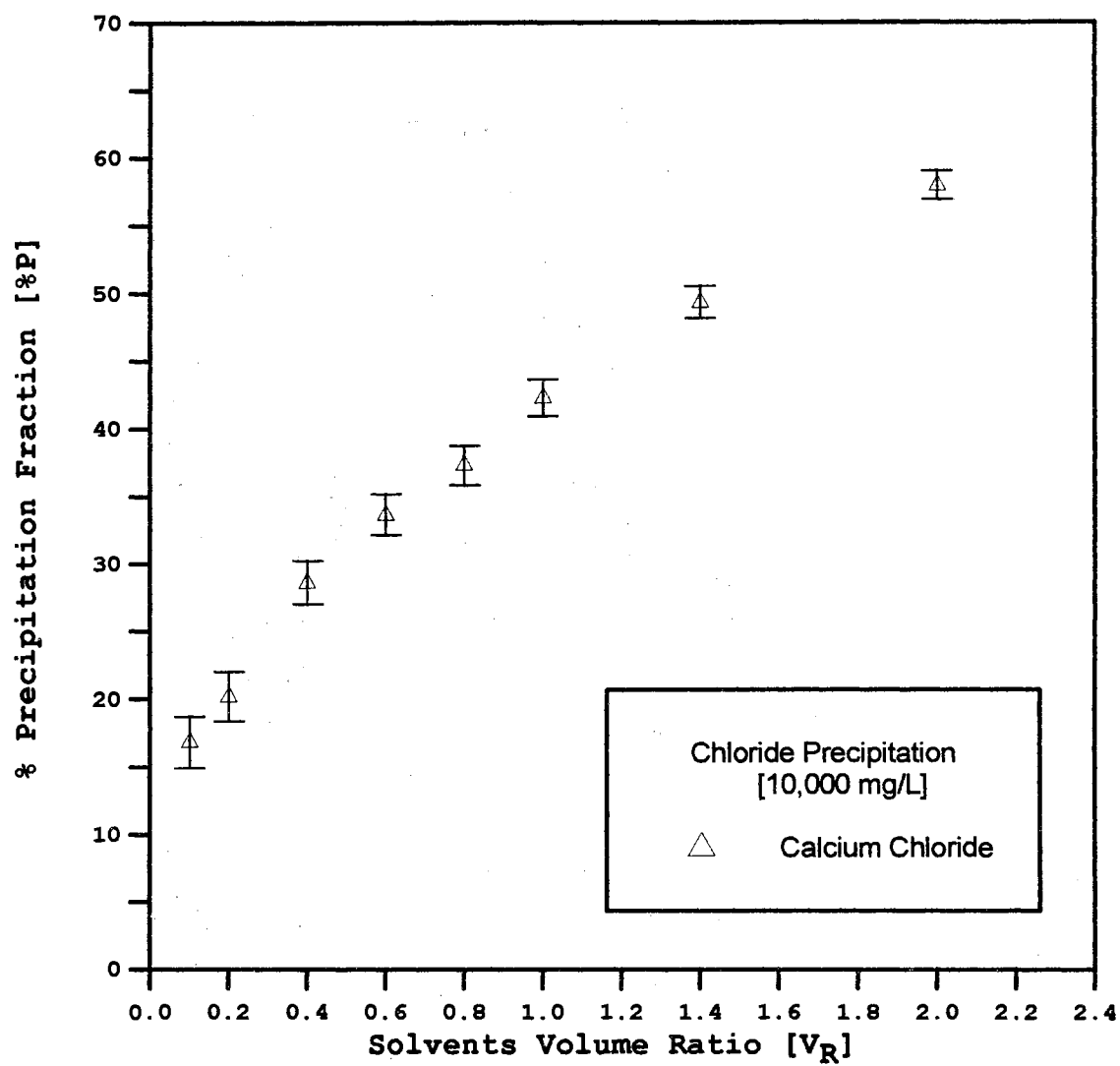


Figure 14. Precipitation Fraction for Calcium Chloride at 10,000 mg/L

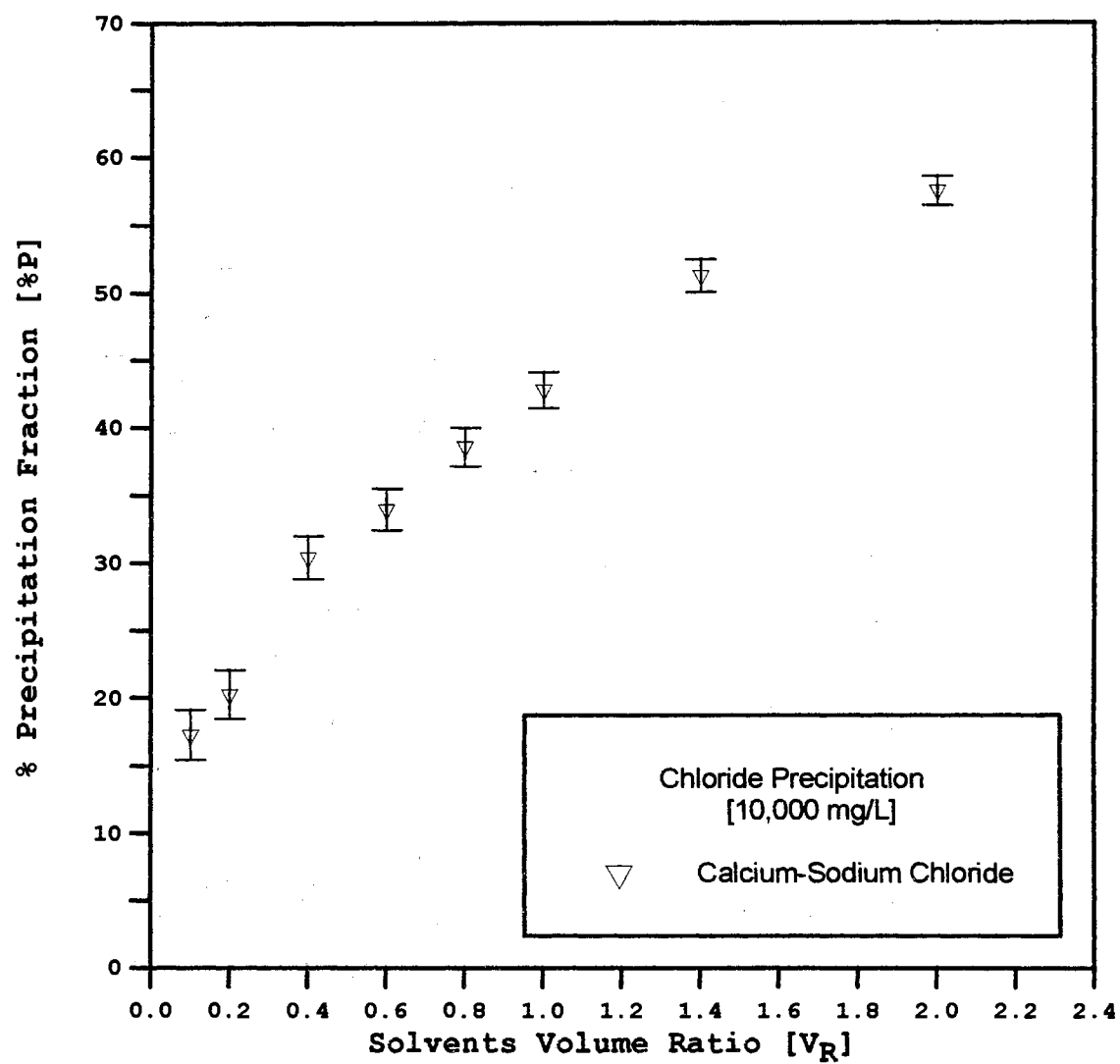


Figure 15. Precipitation Fraction for Calcium-Sodium Chloride at 10,000 mg/L

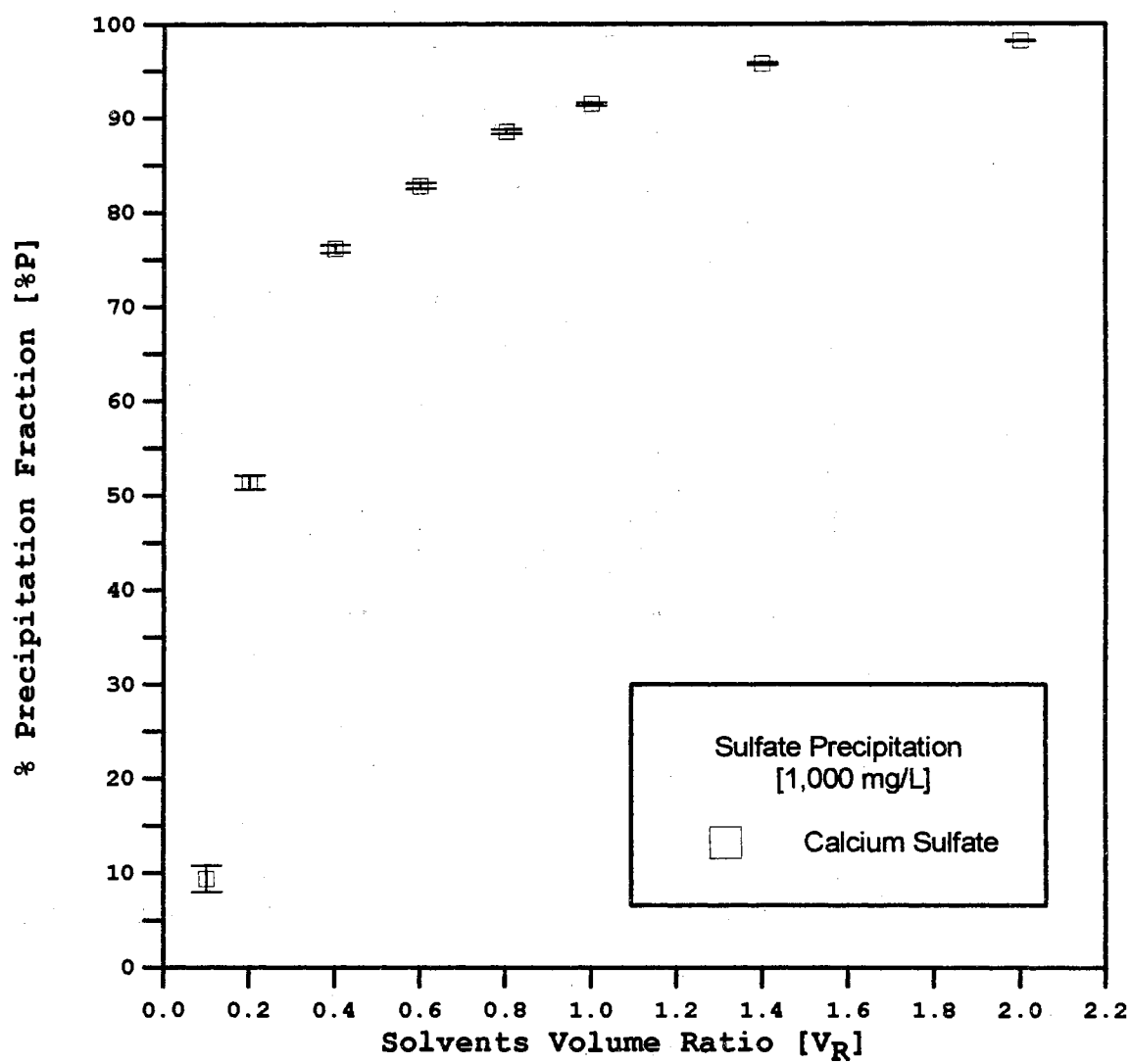


Figure 16. Precipitation Fraction for Calcium Sulfate at 1,000 mg/L

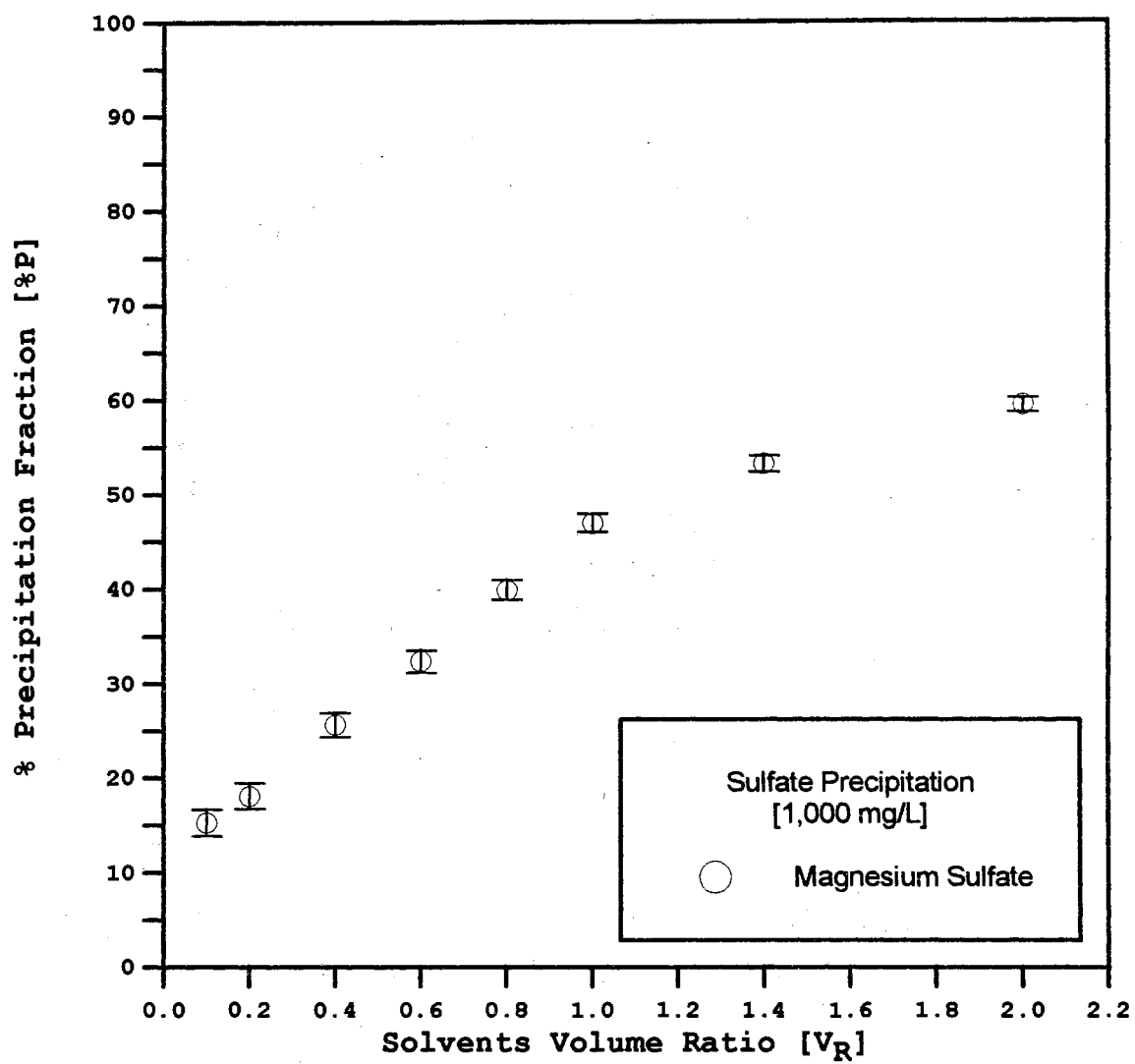


Figure 17. Precipitation Fraction for Magnesium Sulfate at 1,000 mg/L

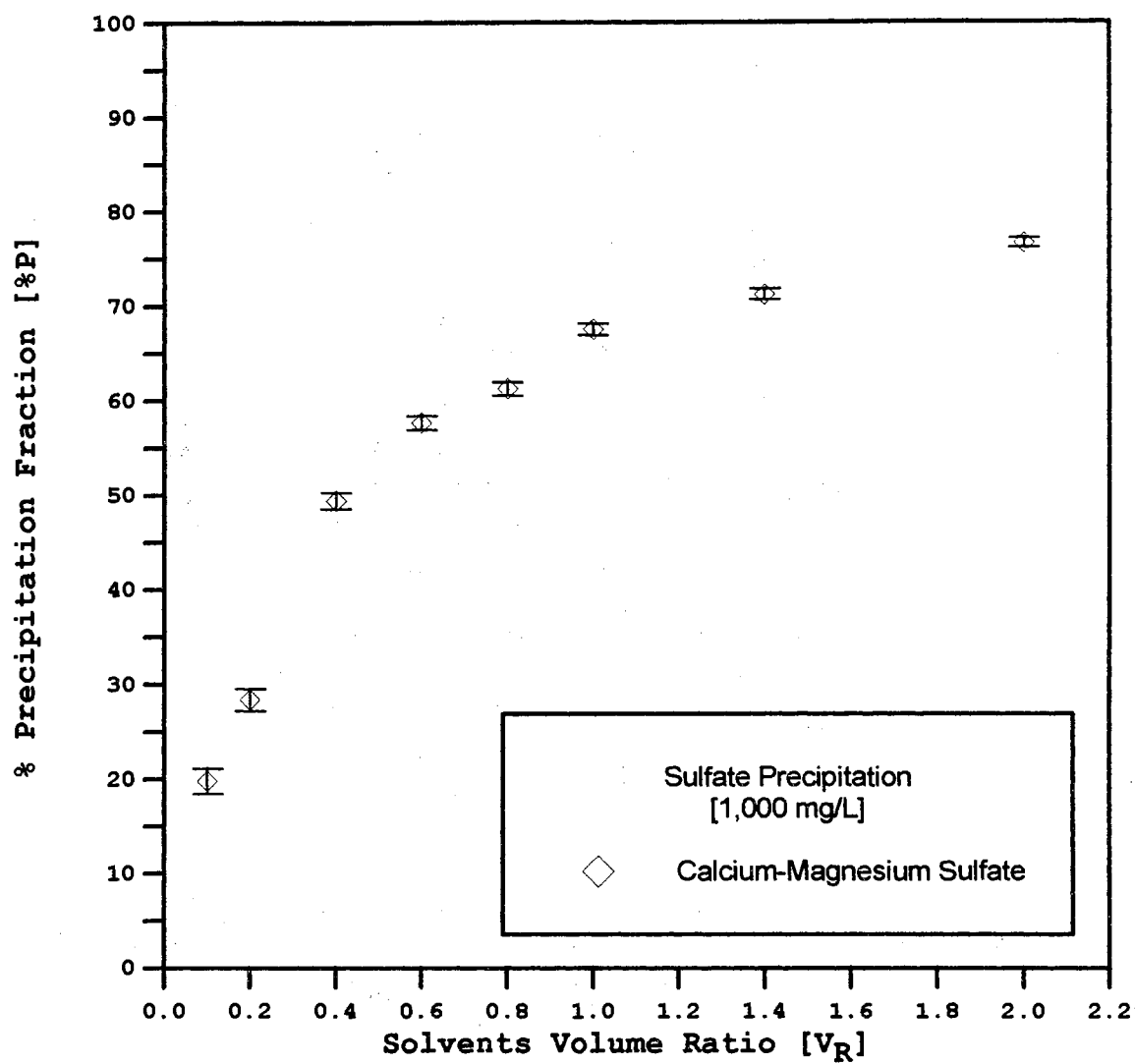


Figure 18. Precipitation Fraction for Calcium-Magnesium Sulfate at 1,000 mg/L

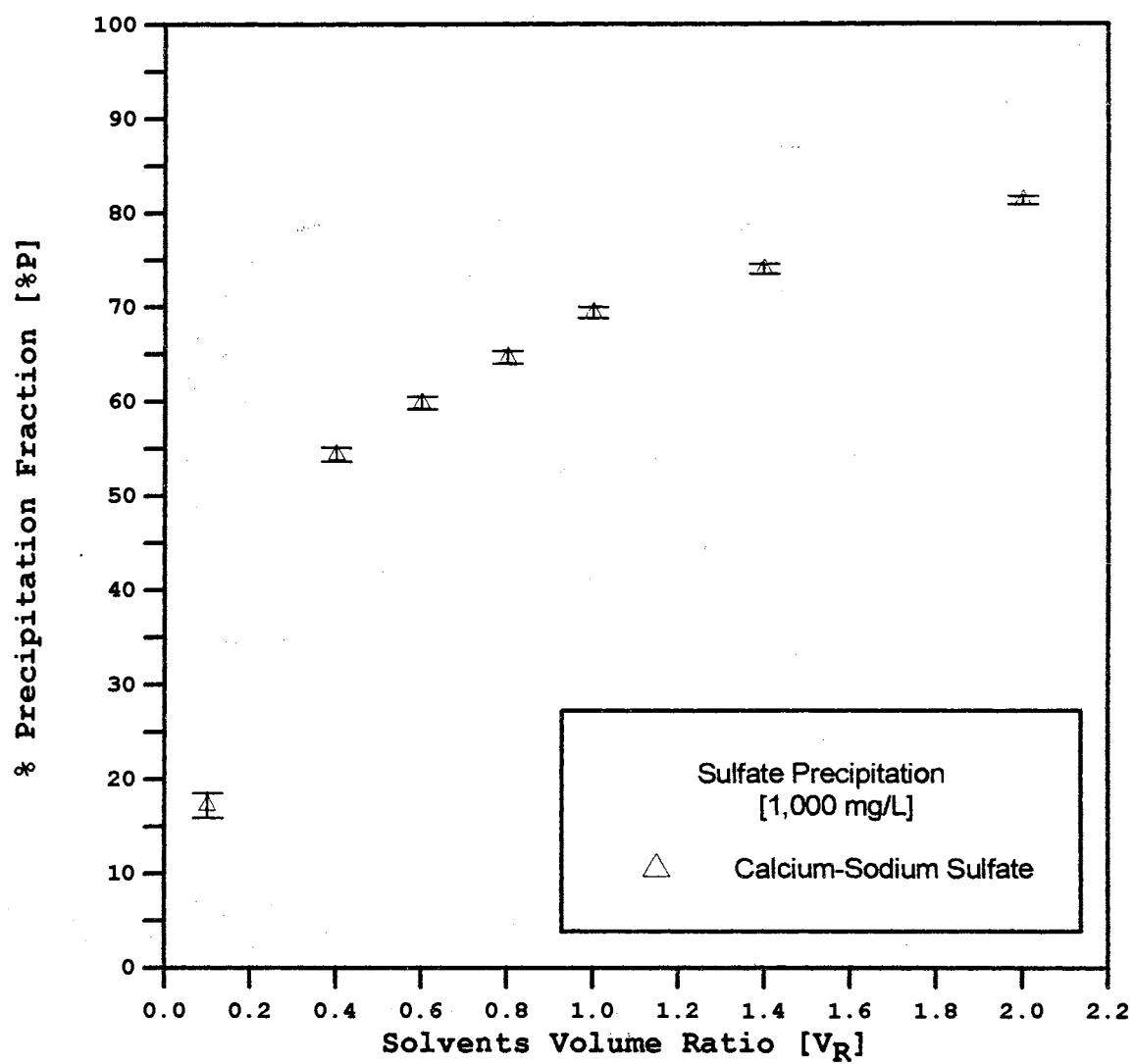


Figure 19. Precipitation Fraction for Calcium-Sodium Sulfate at 1,000 mg/L

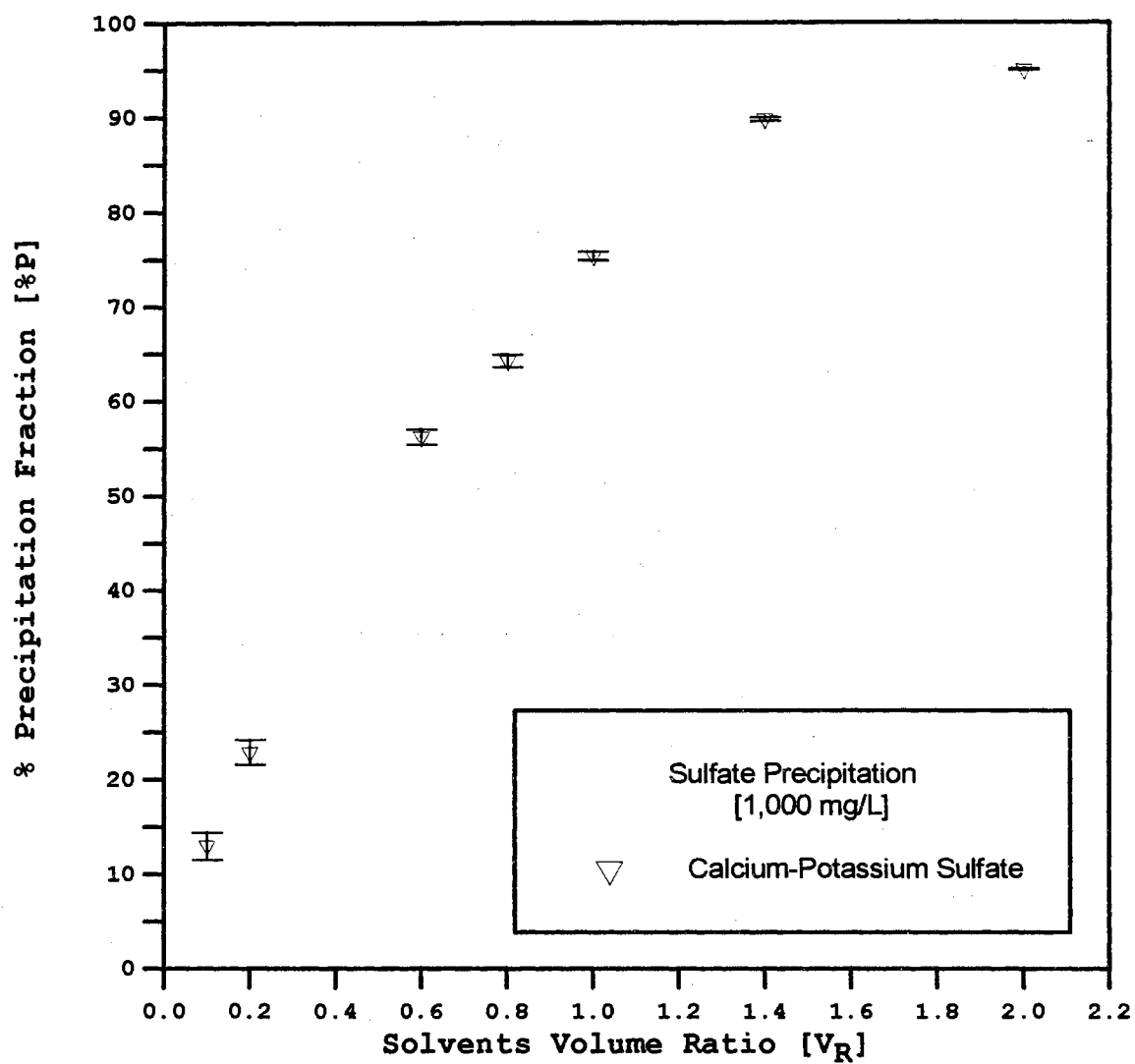


Figure 20. Precipitation Fraction for Calcium-Potassium Sulfate at 1,000 mg/L

TABLE 24
COMPARISONS OF THE WEIGHED AND DETERMINED CHLORIDE
CONCENTRATIONS AT 5,000 mg/L IN WATER

System	Concentration (mg/L)	
	C_s^*	C_s^{**}/σ_{C_s}
Magnesium	5000.3	5075.8/80.4
MgCl ₂ -6H ₂ O	5003.3	
Magnesium-Sodium	4999.7	5074.8/84.4
MgCl ₂ -6H ₂ O/	2499.3	
NaCl	2500.4	
Magnesium-Potassium	4993.9	5026.2/79.8
MgCl ₂ -6H ₂ O/	2499.3	
KCl	2494.6	
Calcium	4998.8	5026.5/81.8
CaCl ₂ -2H ₂ O	4998.8	
Calcium-Sodium	5001.4	5018.2/79.9
CaCl ₂ -2H ₂ O/	2500.3	
NaCl	2501.1	
Calcium-Potassium	5006.1	5015.9/80.1
CaCl ₂ -2H ₂ O/	2499.4	
KCl	2506.7	
Calcium-Magnesium	5000.0	5075.8/80.4
CaCl ₂ -2H ₂ O/	2500.2	
MgCl ₂ -6H ₂ O	2499.8	
Calcium-Barium	5000.9	5017.4/79.9
CaCl ₂ -2H ₂ O/	2499.8	
BaCl ₂ -2H ₂ O	2501.1	
Calcium-Strontium	5003.0	5018.7/79.9
CaCl ₂ -2H ₂ O/	2500.7	
SrCl ₂ -6H ₂ O	2502.3	

* Weighed Concentration;

** Determined Concentration by the Ion Chromatograph.

TABLE 25
COMPARISONS OF THE WEIGHED AND DETERMINED CHLORIDE
CONCENTRATIONS AT 10,000 mg/L IN WATER

System	Concentration (mg/L)	
	C_s^*	C_s^{**}/σ_{C_s}
Magnesium	10007.5	9997.7/158.7
MgCl ₂ -6H ₂ O	10007.5	
Magnesium-Sodium	10000.7	10000.6/158.9
MgCl ₂ -6H ₂ O/	5000.4	
NaCl	5000.3	
Magnesium-Potassium	9999.8	10011.1/158.6
MgCl ₂ -6H ₂ O/	5000.6	
KCl	4999.2	
Calcium	10002.5	9982.3/160.8
CaCl ₂ -2H ₂ O	10002.5	
Calcium-Sodium	10001.7	10010.4/158.7
CaCl ₂ -2H ₂ O/	5000.7	
NaCl	5001.0	

* Weighed Concentration;

** Determined Concentration by the Ion Chromatograph.

TABLE 26
COMPARISONS OF THE WEIGHED AND DETERMINED SULFATE
CONCENTRATIONS AT 1,000 mg/L IN WATER

System	Concentration (mg/L)	
	C_s^*	C_s^{**}/σ_{C_s}
Calcium	996.3	991.9/10.8
CaSO ₄	996.3	
Magnesium	996.6	992.5/10.8
MgSO ₄ -7H ₂ O	996.6	
Calcium-Magnesium	1001.8	993.1/11.7
CaSO ₄ /	501.7	
MgSO ₄ -7H ₂ O	500.1	
Calcium-Sodium	1005.0	996.1/10.9
CaSO ₄ /	499.3	
Na ₂ SO ₄	505.7	
Calcium-Potassium	995.9	994.1/11.2
CaSO ₄ /	497.2	
K ₂ SO ₄	498.7	

* Weighed Concentration;

** Determined Concentration by the Ion Chromatograph.

Discussion of Experimental Data

The targeted salts are divided in this work into alkali metals (monovalent) and alkaline earth metals (divalent). The alkaline earth metals (e.g., magnesium, calcium, barium, and strontium) in chloride or sulfate forms can be precipitated when their concentrations in aqueous solutions are below saturation. However, the coarseness of the precipitates (ease of separation) increases as the molecular weight of the alkaline earth metals decreases [3]. In contrast, the alkali metals (e.g., sodium and potassium) in the form of chloride or sulfate can not be precipitated when their concentrations in aqueous solutions far below saturation. Hence, studies in this work were conducted to coprecipitate the alkali metals in forms of chloride or sulfate with the alkaline earth metals in forms of chloride or sulfate.

Chloride salts, single and binary, were studied at 5,000 mg/L and 10,000 mg/L to point out the precipitation and coprecipitation of such salts as well as the precipitation capability of isopropylamine. As given in Tables 5 to 18 and shown in Figures 2 to 15, the precipitation fractions of the chloride salts at 5,000 mg/L and 10,000 mg/L, single and binary, over the studied range of the solvents volume ratio are nearly identical (typically e.g., $P = 18\%$ at $V_R = 0.1$ to $P = 59\%$ at $V_R = 2.0$). The small variations in the precipitation fractions of these systems are within the experimental uncertainty. Figures 21 and 22 combine the precipitation fractions of studied chloride salts at 5,000 mg/L and 10,000 mg/L, respectively.

The discussion above implies two observations. First, monovalent chloride salts can be coprecipitated with other divalent chloride salt

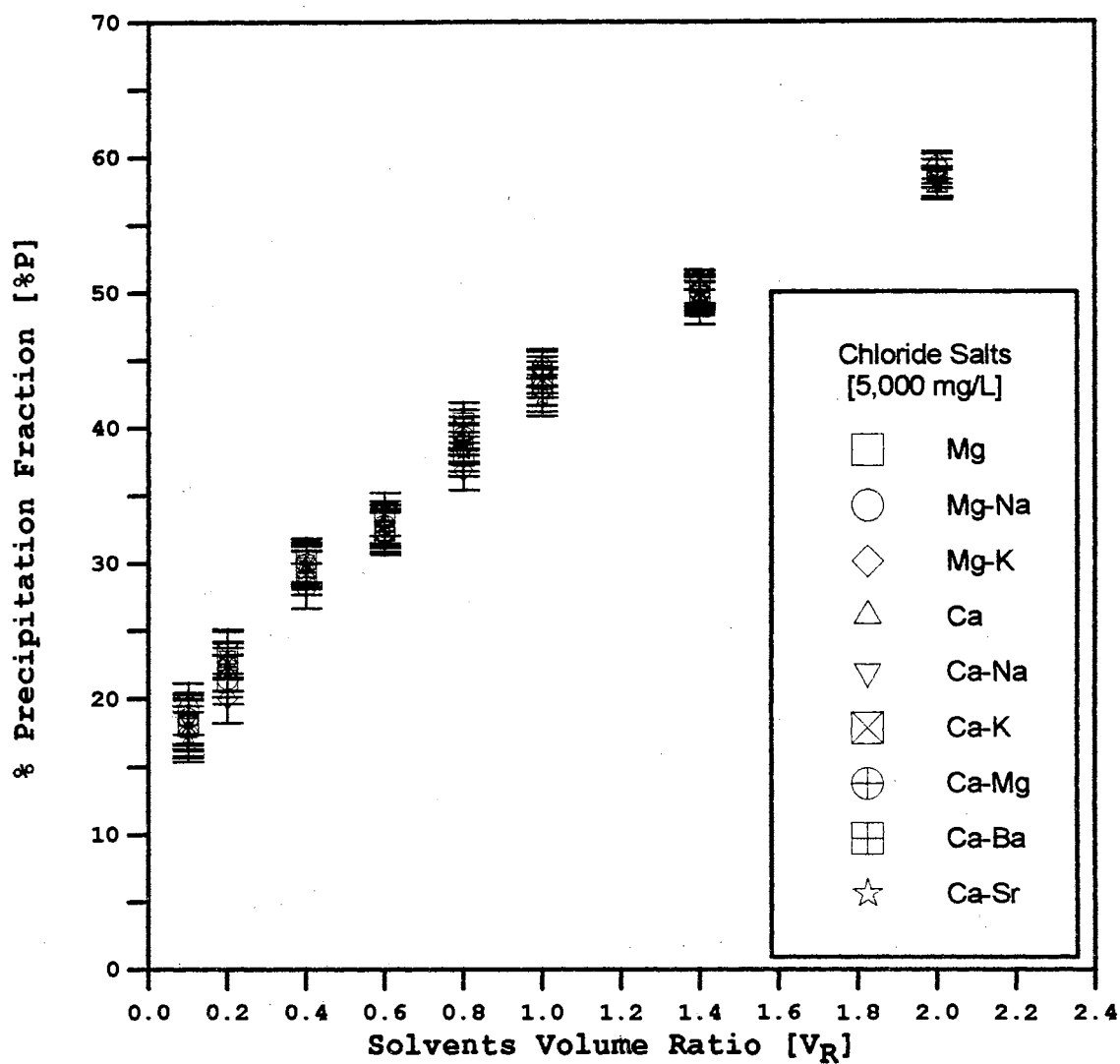


Figure 21. Precipitation Fraction for Chloride Salts at 5,000 mg/L

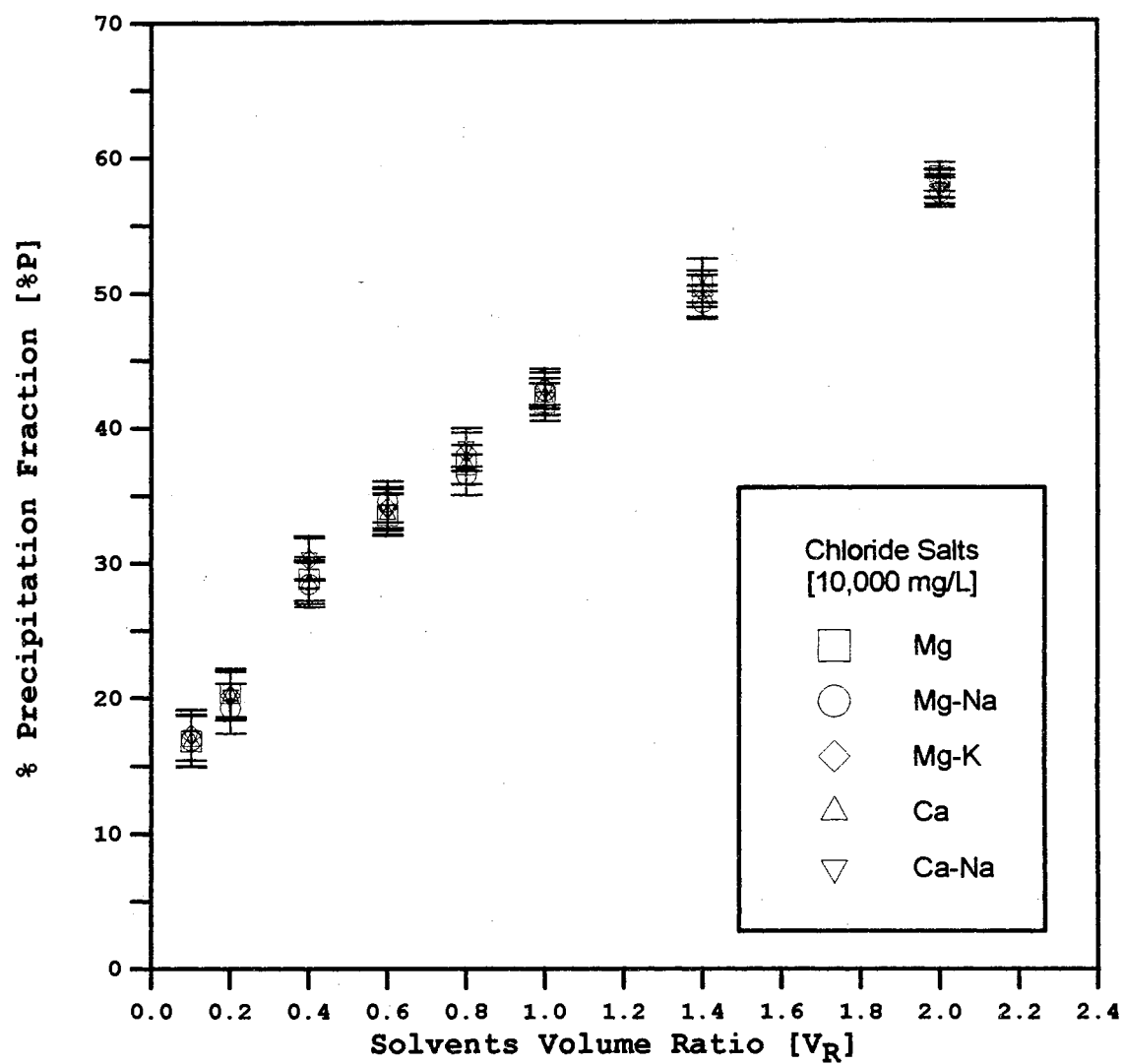


Figure 22. Precipitation Fraction for Chloride Salts at 10,000 mg/L

when their concentrations in aqueous solutions are below saturation. Such a coprecipitation would result in similar overall precipitation fractions. Second, for the studied chloride systems, it seems that the precipitation fractions of chloride salts are strongly dependent on the solubilities of these salts in isopropylamine.

The precipitation of sulfate salts, single and binary, were also studied at 1,000 mg/L to demonstrate the extent of the precipitation and coprecipitation of the targeted salts as well as the precipitation capability of isopropylamine. Figures 16 to 20 illustrate the trends of the precipitation fractions for the studied system. The precipitation fraction of the sulfate ion from calcium sulfate system drastically increases at a solvents volume ratio of 0.2 ($P = 51.4\%$) and reaches asymptotic value ($P = 98.2\%$) at a solvents volume ratio of 2.0. The 1,000 mg/L of sulfate is equivalent to 2,000 mg/L of calcium sulfate (near saturation). Thus, the high values of the precipitation fractions of the sulfate ion from the calcium sulfate system may be attributed to the high concentration of calcium sulfate. Table 19 and Figure 16 reveal the precipitation measurements of the sulfate ion from the calcium sulfate system.

The precipitation fractions of the sulfate ion from the magnesium sulfate system are gradually increased with the increase of the solvents volume ratio. However, such precipitation fractions are significantly lower than the precipitation fractions of calcium sulfate system. The 1,000 mg/L of sulfate ion is equivalent to 6,582 mg/L of magnesium sulfate, which is substantially lower than the solubility limit (272,000 mg/L) of the magnesium sulfate in water [36]. Table 20 and Figure 17 illustrate the precipitation fractions of sulfate ion from the

magnesium sulfate system.

The precipitation fractions of the sulfate ion from the calcium-magnesium sulfate system are lower than the precipitation fractions of the calcium sulfate system, but they are higher than the precipitation fractions of magnesium-calcium sulfate system (P: 19.8-76.6%). This suggests that the low precipitation of magnesium may exhibit a negative effect on the precipitation fractions of sulfate ion from the calcium-magnesium sulfate system. The precipitation fractions of such a system are presented in Table 21 and depicted in Figure 18.

Sodium sulfate and potassium sulfate do not precipitate. However, they can be coprecipitated with divalent sulfate salts. The precipitation fractions of the sulfate ion from the calcium-sodium sulfate and calcium-potassium sulfate systems are higher than the ones that resulted from the calcium-magnesium sulfate or magnesium sulfate systems. This may suggest that the ionic charge has some influence on solubility of the salts in the organic solvent, and thus it affects the precipitation capability. It should be pointed out that the precipitation fractions of the sulfate ion from the calcium-potassium sulfate system sharply increased at high solvents volume ratio (1.0, 1.4, and 2.0). Tables 22 and 23 along with Figures 19 and 20 illustrate the precipitation fractions of the sulfate ion from the calcium-sodium and calcium-potassium sulfate systems.

Although it seems that the complexity of intermolecular forces and interactions such as inter-ionic forces, ion-molecules forces, hydration effect, polarity of the organic solvent, dielectric constants of the solvents (water and organic solvent) as well as other factors play some

role in determining the effect of the organic solvent in suppressing the salt solubility, it is highly likely that the salt concentration in the aqueous solution is the primary factor in causing precipitation, whereas the salt solubility in the organic solvent is the controlling factor in determining the magnitude of the precipitation fractions [4].

Recovery of Organic Solvents

The practicality of the precipitation process depends on the capability of recovering the precipitation agent. The physical properties of isopropylamine suggests the ease of recovery. During the course of this study, approximately 73% of the used isopropylamine was recovered while 27% of the isopropylamine was vented to atmosphere during the filtration process in each experimental run.

The trace concentration of isopropylamine in the filtered water was about 942 mg/L. The evaporation of isopropylamine from the filtered water was accomplished by mechanical agitation combined with proper ventilation. After 24 hours of evaporation, the concentration of isopropylamine in the filtered water was about 115 mg/L. The large interfacial area between the filtered water and air, mechanical agitation, and high relative volatility resulted in a significant amount of isopropylamine being desorbed.

The possibility of appreciable recovery in the amount isopropylamine, and thus appreciable reduction in the trace of isopropylamine in the filtered (product) water can be achieved by employing a closed vacuum filtration system or a distillation system.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

Conclusions

A database for the precipitation of chloride and sulfate salts in several cation forms from aqueous solutions was generated using isopropylamine as the miscible organic solvent. The precipitation database consists of: (1) chloride salts at 5,000 mg/L (magnesium, magnesium-sodium, magnesium-potassium, calcium, calcium-sodium, calcium-potassium, calcium-magnesium, calcium-barium, and calcium-strontium); (2) chloride salts at 10,000 mg/L (magnesium, magnesium-sodium, magnesium-potassium, calcium, and calcium-sodium); and (3) sulfate salts at 1,000 mg/L (calcium, magnesium, calcium-magnesium, calcium-sodium, and calcium-potassium). Highly consistent experimental precipitation data were obtained. The precipitation fractions of all chloride salts (at 5,000 and 10,000 mg/L) over the studied range of solvents volume ratio are approximately identical while the precipitation fractions of sulfate salts (1,000 mg/L) are appreciably varied. The precipitation measurements provided by this work are new and a valuable addition to the literature.

Recommendations

Based on this work, specific recommendations for further

precipitation measurements are given as follows. First, the existing Ion Chromatograph should be upgraded and modified to: (1) prevent frequent leaks; (2) replace the existing anion separator column, if needed; (3) include a cation separator column to handle both monovalent and divalent cations; and (4) include an automated sampling systems. The suggested upgrade and modification to the Ion Chromatograph is strongly recommended to effectively and fully analyze samples within a short period of time.

Second, pH values should be reported for future precipitation measurements. A reliable pH meter is strongly recommended.

Third, additional precipitation measurements on chloride salts at 20,000 and 50,000 mg/L and sulfate salts at 500 mg/L should be made.

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APPENDIX A

ION CHROMATOGRAPH (IC) OPERATING CONDITIONS AND CALIBRATION

This appendix contains specific information on the IC operating conditions and IC calibration data (the fitted lines and uncertainties) for the chloride and sulfate ions.

TABLE A.1
THE OPERATING CONDITIONS OF THE IC

Anion Column	AS4A
Guard Column	AG4A
Supressor	AMMS
Eluant Pressure	5.0 psi
Regenerant Pressure	10.0 psi
Conductivity	16.2 μ s
Retention Time	
Chloride Ion	1.8 min
Sulfate Ion	7.9 min

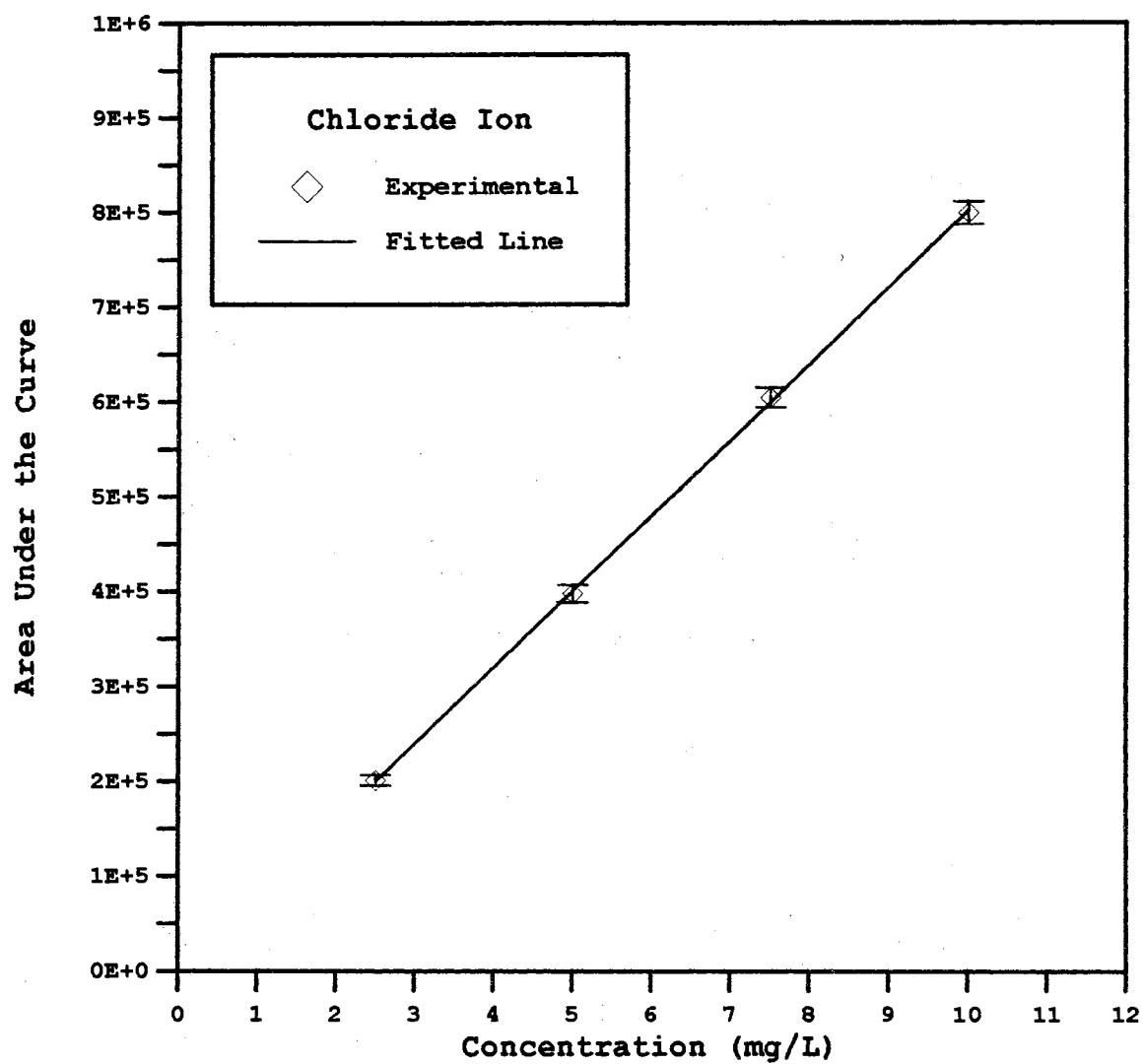


Figure A.1. Calibration Curve of Chloride Ion

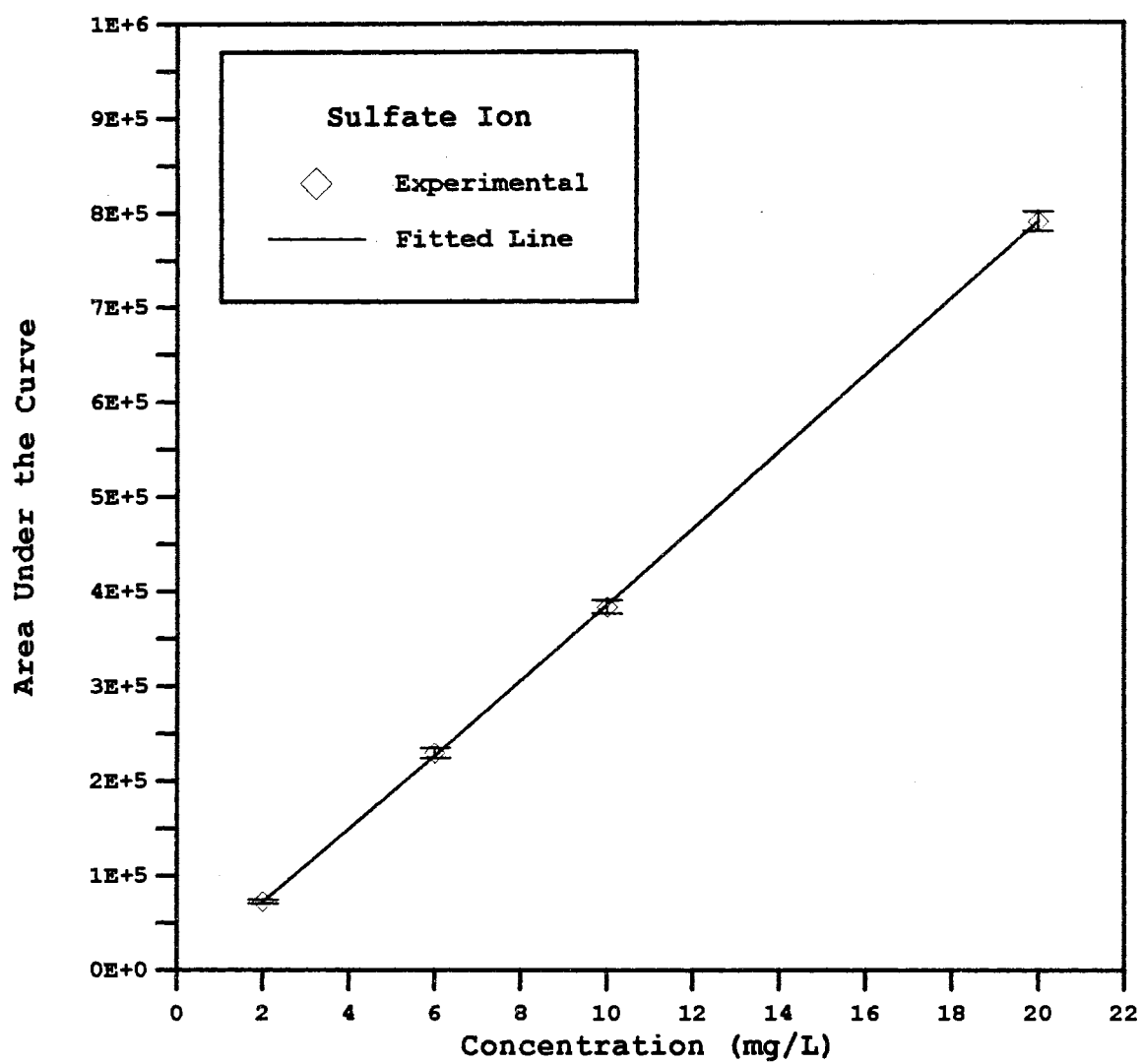


Figure A.2. Calibration Curve of Sulfate Ion

APPENDIX B

GAS CHROMATOGRAPH OPERATING CONDITIONS AND CALIBRATION

This appendix contains specific information on the GC operating conditions, GC calibration data, uncertainties and the fitted lines for the isopropylamine-water system.

TABLE B.1
THE OPERATING CONDITIONS OF THE GC

Column	
Material	Glass
Length	2 m
Inside Diameter	2 mm
Support	Carbograph 1 NKA
Mesh	60/80
Column Temperature	120 °C
Injector Temperature	200 °C
Detector Temperature	250 °C
Helium (Carrier Gas)	
Inlet Pressure	30 psig
Flow Rate	21 cc/min
Hydrogen	
Inlet Pressure	30 psig
Flow Rate	34 cc/min
Air	
Inlet Pressure	40 psig
Flow Rate	355 cc/min
Retention Time	
Isopropylamine	2.3 min

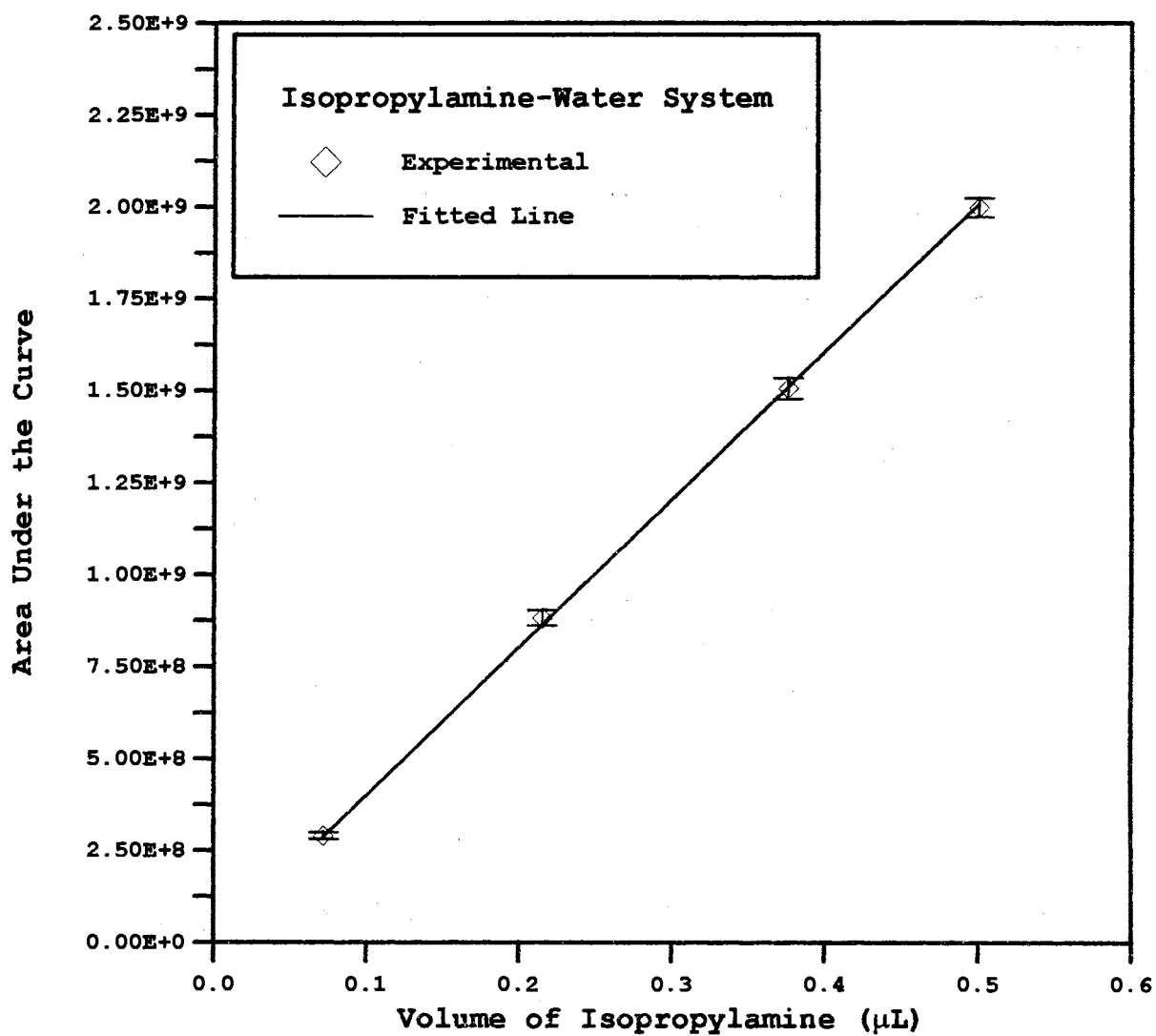


Figure B.1. Calibration Curve of Isopropylamine-Water System

SECTION II - THEORETICAL WORK

CHAPTER I

INTRODUCTION

One goal of solution thermodynamics is to formulate models to describe quantitatively the phase behavior of pure fluids and mixtures. Most of these models are semi-empirical and their development and evaluation require phase equilibrium data and proper mathematical and statistical tools. Therefore, in engineering applications, one of the main advantages of thermodynamic models is the reduction of experimental efforts [Bader, 1993c].

An important area of solution thermodynamics is the study of inorganics (electrolytes) phase equilibria. Knowledge of inorganics phase equilibria in pure and mixed solvents plays an important role in advancing chemical technologies (e.g., azeotropic and extractive distillations, saline water desalination, brine associated with oil production and geothermal energy production, precipitation and crystallization processes, partitioning processes in biochemical systems, etc.). A remarkably less amount of work in the field of inorganics thermodynamics, however, has been undertaken compared to organics thermodynamics [Prausnitz, 1989]. This situation is attributed to the lack of: (1) understanding of inorganics thermodynamics and aqueous chemistry (e.g., chemical and ionic identities), and thus the

lack of developing rigorous theories; and (2) extensive and reliable data with which to formulate, test, and evaluate thermodynamic frameworks. Hence, the need for inorganic thermodynamics theories and frameworks often justifies the efforts dedicated to the development of accurate correlation and prediction models.

Correlation and prediction of solubility phase behavior of inorganic species in organic-aqueous mixtures are of prime fundamental and practical importance in the precipitation process. This section is concerned with the formulation of thermodynamics frameworks as a means to predict phase behavior of the precipitation process. The impetus of the modeling efforts in this work is guided, in part, by three facts. First, the precipitation phenomena is a novel concept that does not appear in classical thermodynamics textbooks and requires attention. Second, predicting and understanding the thermodynamic phase behavior of salt solubilities in mixed-solvents mixtures provide an insight into the controlling factors influencing and characterizing the precipitation phenomena. Third, precipitation measurements are costly and time consuming; thus, it is important to have a model with a reliable prediction capability.

Efforts were extended to utilize creditable model equations which would have some theoretical basis by providing a set of model parameters to describe the precipitation measurements without a significant loss of accuracy. Specifically, the objective of this section was to develop and apply rigorous thermodynamics frameworks to model the solubility phase behavior of a given salt in a mixed-solvents mixture. The modeling effort was directed toward establishing semi-empirical expressions with a theoretical foundation for the precipitation

measurements which would fulfill practical needs. A preference was given to model expressions which predicted mixture equilibrium properties by using pure component properties. Thus, the acquired precipitation database in the experimental section was employed to test and evaluate the viability of the developed framework equations to describe the phase behavior of the precipitation measurements, and to provide optimum interaction parameters for such measurements.

In Chapter II, related thermodynamic frameworks and previous attempts to model the precipitation measurements are briefly reviewed. Model developments are presented in Chapter III. The model testing and evaluations are presented and discussed in Chapter IV.

CHAPTER II

LITERATURE REVIEW

In this chapter previous modeling attempts used to correlate mixtures consisting of a salt and two liquid components and related to this work are briefly reviewed. A preference is given to thermodynamic principles which underlie the solubility phase behavior of a salt in a mixed-solvents mixture. As such, this chapter is served: (1) to explore the relationships between existing models by which correlations of precipitation measurements might be sought; (2) to highlight the merits of solution thermodynamics theories for liquid mixtures containing salts; and thus (3) to provide the foundation for the model development efforts presented in Chapter III.

Precipitation Concept and Methods of Modeling

Precipitation is the process by which rapid formation of solid precipitates from a solution occurs. In contrast, fractional precipitation or crystallization denotes the formation of crystalline materials from a solution, melt, or vapor by any crystallization technique. The principle difference between precipitation and crystallization is that solid precipitates which resulted from the precipitation process did not need to be crystalline [Gordon, et al., 1959].

The literature revealed that most modeling efforts, particularly in the crystallization process, were directed toward the microscopic level; the kinetics of crystalline growth from aqueous, organic, or organic-aqueous solutions. The need for highly purified materials and crystallographic perfection in several industrial applications (e.g., electronic materials, ceramics, glass technology, synthetic diamonds, etc.) rendered kinetics as a tool for studying rates and mechanisms of crystalline reactions.

The characterization of the molecular structure of solid precipitates which resulted from the precipitation process addressed in this work is not the central focus. However, the ability to selectively precipitate a salt or salts from aqueous-saline solutions by adding a miscible organic solvent is the major thrust of this work. The macroscopic approach in terms of measurable properties such as temperature (T), pressure (p), and composition (x_1) would be appropriate to prevail the state of equilibrium of the existing phases in the solution. Hence, a preference was given to review thermodynamics principles, which had the ability to relate measured properties (T , p , and x_1) into a unified framework of quantitative relationships.

Solutions containing inorganic species are common in living organisms, environment, and many industrial applications. Therefore, thermodynamic properties of such solutions are of prime interest in a wide variety of applications (e.g., chemical, environmental, biological biochemical, and pharmaceutical industries). Considerable modeling works were developed and directed to correlate and predict the salt effect on the phase behavior of organic-aqueous or organic-organic systems (e.g., the "salting-out" and "salting-in" processes). Such

modeling efforts could be directed and applied with some modifications to the precipitation process. Thus, a presentation for the existing theories and models employed to correlate the "salting-out" and "solventing-out" processes is given below.

"Salting-out" and "Salting-in" Concepts

Separation processes such as extractive distillation employs non-volatile dissolved salts as separating agents to alter the phase behavior of organic-aqueous systems exhibiting either azeotropes or low relative volatility in the composition region critical to the separation. The influence of salts on thermodynamic properties (e.g., activity coefficient and solubility) of organics in aqueous solutions is of a prime interest. The increase in the activity coefficient (decrease in solubility) of the organic component in aqueous solutions upon the addition of a salt is termed "salting-out". The reverse effect, however, is called "salting-in".

Various theories and models have been proposed for predicting the salt effect in the phase equilibria of a system containing two-liquid components. These theories and models can be classified into four categories: (1) prediction models based on inorganics theories and pure component properties; (2) models based on empirical and semi-empirical relations; (3) models based on the Gibbs-Duhem relation; and (4) models based on the group contribution methods. The prediction and correlation models of how salt affects organic-aqueous and organic-organic systems can be extended to the reverse phenomenon; the effect of miscible

organic solvents in the solubility of salt-aqueous systems. Following is a presentation of prediction and correlation models.

Prediction Models Based on Pure-Component Properties

Several theoretical explanations based on physical and chemical phenomena exist to interpret the salt effect. The most notable ones are the internal pressure [Tammann, 1893], the hydration [Philip, 1907], the electrostatic interaction [Debye and McAuley, 1925], and the van der Waals forces [Linderstrom-Lang, 1923; Kortum, 1936; Long and McDevit, 1952; Bockris, et al., 1951]. Pure component properties such as salt solubility, partial molar volume, vapor pressure lowering, degree of dissociation, ionic properties, polarity, structural geometry, and others were sought to predict the salt effect.

The internal pressure concept was based on the general observation that the addition of a dissolved salt to an aqueous system lead to contraction in the system volume. A fundamental relation was proposed by referring salt effects to the changes in both the molar volume and compressibility of the solvent (water) [Long and McDevit, 1952].

The hydration theory assumed that "salting out" was due to a preferential attraction between ions and water molecules. This suggested that each salt ion ties up its share of water molecules and minimizes the solvent role of water molecules, and salt ions have no effect on the non-aqueous (organic) component in the mixture. The second factor is the main objection to the hydration theory pronounces the inherent failure of this theory in explaining the "salting-in" process.

The electrostatic phenomenon explained the "salting-out" concept by relating the salt effect to the influence of the organic component on the dielectric constant of an aqueous system. Accordingly, if a given organic component decreases the dielectric constant of its aqueous system such a component would be salted-out, and vice versa. Debye and McAuley [1925] expressed the dielectric constant as a linear function in terms of salt and organic concentrations.

Since the electrostatic attractions between ions and a neutral molecule were to a large extent short-range forces, the electrostatic theory was extended by the van der Waals theory to include such forces. Other short-range forces such the dispersion forces, which may play an appreciable role in certain ions effect, were also included.

None of the above theories has the capability to quantitatively predict the salt effect using pure-component properties except for very limited cases [Long and McDevit, 1952; Prausnitz and Targovnik, 1958; Johnson and Furter, 1960]. This is attributed to the physical chemistry of inorganic systems which is complex due to phenomenon interactions such as long-range electrostatic interactions between ions, solvation of ions, and the association between cations and anions. These interactions become more complicated for systems containing inorganic species in mixed-solvent mixtures. Hence, it is not surprising that rigorous theories are not yet available. However, these theories are somewhat useful in rationally interpreting the qualitative aspects of given experimental data since they are aimed at understanding the effect of various types of forces on structural and thermodynamic properties.

Models Based on Semi-Empirical and Empirical Relations

Since solution thermodynamics of the salt effect in vapor-liquid equilibrium are complex and not fully understood, empirical or semi-empirical models with some fundamental justification have been sought to correlate the phase equilibrium behavior of a complex mixture containing a non-volatile salt dissolved in a binary organic-aqueous mixture.

One of the most popular approaches to correlating the salting-out process is based on relating empirically the activity coefficient of the organic species as a power series in the compositions of both salt and organic species at constant temperature and pressure [Cohn and Edsall, 1943]. Water is assumed to be a structureless dielectric continuum and all deviations from ideality are due to electrostatic interaction [Debye and McAulay, 1925]. The general semi-empirical relation is given as follows [Cohn and Edsall, 1943]:

$$\ln \gamma_{i,m} = \sum_{y,z} C_{yz} x_i^z x_j^y \quad (1)$$

where $\gamma_{i,m}$ is the activity coefficient of the organic species in the mixture, y and z are integer powers, C_{yz} is an interaction parameter, x_j is the salt mole fraction, and x_i is the salt-free organic mole fraction. A further assumption is that the concentrations of salt and organic species should be low enough (dilute range) to retain the linearity. Thus, if the salt is labeled as species 1, the water as species 2, and the organic as species 3, Equation (1) can be written in linear form as follows:

$$\ln \gamma_{3,m} = C_{13}x_1 + C_{33}x_{3,2} \quad (2)$$

where C_{13} is the salt-organic interaction parameter and C_{33} is the organic self-interaction parameter.

Most existing salt effect correlations were concerned with the determination of the salt-organic interaction parameter (C_{13}) and not with the organic self-interaction parameter (C_{33}). Hence, several relationships which stemmed from Equation (2) were proposed to model the salt effect on a mixture of two-liquid components (organic-water). One of the most popular equations used to evaluate salt effect on vapor-liquid equilibrium of organic-aqueous system was proposed by Furter [1958]. Furter expressed the difference in salt effects on the chemical potentials of two liquid components in terms of relative volatilities as a function of salt composition using the linear form of Equation (1) as follows:

$$\ln \frac{\alpha_{3,m}}{\alpha_{3,2}} = C_{13}x_1 \quad (3)$$

where $\alpha_{3,m}$ is the relative volatility of the organic in the mixture, $\alpha_{3,2}$ is the relative volatility of the organic in pure water, C_{13} is an empirical constant representing the overall specific effect of a given salt on the vapor-liquid equilibrium, and x_1 is the salt mole fraction. At constant temperature, pressure, and composition of the organic and water species, Equation (3) relates the salt effect on the vapor phase of the organic-aqueous system to the salt composition in the liquid

phase of the system. Relative volatility is the most important factor for indicating the ease of separation of components by distillation methods. The ratio of relative volatility is a very convenient parameter for use in distillation column design calculations (e.g., tray-to-tray calculations).

Sada and coworkers [Sada, et al., 1974] derived a relation similar to Equation (3), but with no empirical constant. The derived relation is based on reducing a ternary mixture to a binary mixture which consists of a salt-free component and a component containing salt. The proposed relation is given as follows:

$$\ln \frac{\alpha_{3,m}}{\alpha_{3,2}} = x_1^* \quad (4)$$

and

$$x_1^* = \left[\frac{(v_c + v_a)n_1}{(v_c + v_a)n_1 + n_3} \right] \quad (5)$$

where x_1^* is the salt mole fraction, v_c and v_a are the numbers of cation and anion produced by dissociation of one molecule of salt, n_1 is the number of moles of the salt, and n_3 is the number of moles of the volatile component.

Equation (4) is independent of the nature of the added salt as well as the compositions of volatile components in the liquid phase. The equation is restricted to systems in which the salt is soluble in only one of the mixture's component. The equation was satisfactorily tested with very limited data including salt-organic-organic systems.

Equations (3) and (4) share several theoretical limitations.

First, the derivation relates the salt effect on the vapor composition of a given system at constant liquid composition (salt-free basis) of the more volatile component present in the mixture. Hence, both Equations are only valid when the ratio of volatile components present in the liquid phase remain constant.

Second, Equations (3) and (4) are only applicable to dilute solutions of both organic and salt species. This fundamental limitation is attributed to the linear form of these equations (only valid for dilute solutions), and the derivation of these equations neglects the effect of boiling point elevation on relative volatilities and the effect of salt presence on the non-ideality of the vapor phase.

Third, the salting-out process is a complex phenomenon of interactions and self-interactions between all components present in the mixture. Each of system's components is most likely to be a function of composition, salt dissociation, and other interaction factors. It would not be reasonable to assume that the linear form of Equation (3) with a single constant or Equation (4) with no regressed constant are capable of characterizing and describing a complex phenomenon such as the salting-out process.

Therefore, empirical and semi-empirical relations with more than one constant have been sought. Hashitani and Hirata [1969] proposed a purely empirical equation with two constants to account for the interaction of concentrations of the salt as well as the volatile component. The relation is given as follows:

$$\ln \frac{\alpha_{3,m}}{\alpha_{3,2}} = C_1 C_2^{x_2} x_1 \quad (6)$$

where C_1 and C_2 are empirical constants representing the salt effect and x_2 is the salt-free mole fraction of the volatile component in the mixture. Equation (6) is a curve fitting two-constant relations with no theoretical foundation.

Jaques and Furter [1972a] proposed a relation with six regressed constants based on the expansion of Equation (1) and the Redlich-Kister equation [Redlich and Kister, 1948]. This relation is given as follows:

$$\ln \frac{\alpha_{3,m}}{\alpha_{3,2}} = C_1 x_1 + (C_3 + C_5 x_1) x_1^2 + (C_2 + C_4 x_{3,2}) x_{3,2} x_1 + C_6 x_{3,2} x_1^2 \quad (7)$$

The proposed relation was tested with several systems with excellent fit.

Jaques [1975] proposed a relation which did not require the linear assumption with the salt concentration. The derivation of the proposed relation was based on reducing the ternary mixture to a binary one consisted of each solvent with salt. The relation could be expressed in a form similar to Equation (3) as follows:

$$\frac{\alpha_{3,m}}{\alpha_{3,2}} = \frac{C_{13}}{1 - x_1} \quad (8)$$

Equation (8) was tested with two cases. These cases were the salt was only soluble in one liquid component and the salt was soluble in both components. It was concluded that Equation (8) was applicable to

systems where the salt was soluble in both components; however, Equation (8) is not valid over the entire liquid composition range (deviation from the linear range).

Schuberth [1974] used the expansion function of Equation (1) (polynomial series) to overcome the nonlinear deviation with the increase of liquid composition. The relation is given as follows:

$$\ln \frac{\alpha_{3,m}}{\alpha_{3,2}} = C_1 x_1 + C_2 x_1^2 \quad (9)$$

Bedrossian and Cheh [1974] suggested two empirical relations without theoretical justifications. These relations were used to correlate systems which included soluble salt (e.g., potassium acetate) in both liquid components (e.g., ethanol-water system) where Equation (3) failed to correlate such systems.

Models Based on the Gibbs-Duhem Relation

The Gibbs-Duhem relation is the most useful relation in solution thermodynamics. It provides the foundation for the most fundamentally-sound approaches [Prausnitz, et al., 1986]. Partial molar properties of components in a mixture are related to each other by the Gibbs-Duhem relation. While the Gibbs-Duhem relation is applicable to all partial excess properties, it is most useful for the partial molar excess Gibbs energy. The partial molar excess Gibbs energy is related directly to the activity coefficient. Hence, most rigorous thermodynamic frameworks are built around the molar excess Gibbs energy relation [Van Ness and Abbott, 1982; Prausnitz, et al., 1986].

A mixture consisting of a salt and two liquid components could be treated either as a pseudo-binary mixture or as a complete ternary mixture. In the pseudo-binary approach the ternary system can be treated as a binary in which compositions of non-electrolyte species are expressed on a salt-free basis. Therefore, the knowledge of the degree of salt dissociation can be avoided. In contrast, knowledge of the degree of salt dissociation is needed for the ternary mixture approach. This approach would require additional phase equilibrium data which is not readily available. As such, the pseudo-binary mixture approach is conceptually inferior compared to the ternary mixture approach.

A considerable amount of work has been reported in the literature to correlate the salt effect using the Gibbs-Duhem relation [see e.g., Carlson and Colburn, 1942; Trusi and Thompson, 1951; Hala, 1969; Larson and Tassios, 1972; Rousseau, et al., 1972; Jaques and Furter, 1972b; Sada and Morisue, 1973; Boone, et al., 1976; Bekerman and Tassios, 1976, Hala, 1983; Mock, et al. 1986]. Both the pseudo-binary mixture and ternary mixture approaches were applied and tested with selected salt-organic-aqueous systems to study the effect of salt on the vapor-liquid equilibrium. The Gibbs-Duhem models such as Margules [1895], van Laar [1910], Wohl [1946], Redlich-Kister [Redlich and Kister, 1948], Wilson [1964], NRTL [Renon and Prausnitz, 1968], and UNIQUAC [Abrams and Prausnitz, 1975] were extensively employed with some modifications to estimate the thermodynamic properties (e.g., γ_1) of components (salt-organic-water) present in a given mixture. The success of these approaches hinged on the complexity of the treated systems and the versatility of the applied Gibbs-Duhem model [Bader, 1992; Bader, 1993c].

Models Based on the Group Contribution Concept

Group contribution methods such as ASOG (Analytical Solution of Groups) [Derr and Deal, 1969], and UNIFAC (UNIQUAC Functional-group Activity Coefficients) [Fredenslund, et al., 1977] models are used to estimate activity coefficients and other excess thermodynamic properties of non-electrolyte liquid mixtures when no experimental data are available. In the ASOG model the molecular activity coefficient is separated into two parts. One part provides the contribution due to molecular interactions (functional groups), estimated by the Wilson model. The other part counts for the contribution due to molecular size, estimated by the Flory-Huggins relation. In concept, the UNIFAC model is similar to the ASOG model except that the UNIFAC model combines the solution of functional groups with a model of activity coefficients based on extension of the UNIQUAC (universal quasi-chemical) equation of liquid mixtures [Abrams and Prausnitz, 1975].

Kawaguchi and coworkers [Kawaguchi, et al., 1981, 1982] extended the ASOG model to single and multiple inorganics in aqueous systems by accounting for the hydration effect. Hence, the structural activity coefficients expression in the modified ASOG model was extended to include the hydration model. Such an extension was employed to determine the water activity coefficient when ion-ion interactions existed in the aqueous system. The modified ASOG model was never tested to predict the phase behavior of mixed-solvent-salt mixtures.

The UNIFAC model was also extended to predict the salt effect on the phase behavior of mixed-solvent mixtures [Kikic, et al. 1991; Achard, et al., 1994]. Kikic and coworkers [1991] extended the original

structural activity coefficients expression in the UNIFAC model to include the Debye-Huckel expression as described by Cardoso and O'Connell [1987]. The Debye-Huckel expression accounts for interactions between ions and solvent groups while interactions between solvent groups were estimated using the interaction parameters of Gmehling and coworkers [Gmehling, et al., 1982].

On the other hand, Achard and coworkers [1994] employed the Debye-Huckel expression as given by Pitzer [1973, 1980] along with the solvation model to account for the hydration effect. The interactions of solvent groups were estimated using the modified version of the UNIFAC model as given by Larsen and coworkers [Larsen, et al. 1987]. The advantage of the Achard and coworkers modification over the work of Kikic and coworkers [1991] was in considering the hydration phenomenon between water molecules and ion species using the solvation model. Due to a reliable data shortage, both models have very limited functional groups. Hence, the models were tested with very limited systems such as salt alcohol-aqueous systems. This precludes drawing a firm conclusion regarding the reliability of the salt-related UNIFAC versions.

The practical value of the group contribution methods stems from their prediction capabilities when no experimental data is available. Several problems are frequently encountered when using the group contribution methods concept such as the UNIFAC model [Bader, 1993c].

First, is the inherent inability of the group contribution method to represent the intrinsic molecular structure of the system components. the method is unable to distinguish the details in the molecular structure (neighboring effect). For strong interacting molecules such as organic-aqueous-salt systems, charged ions superimpose many

complications on the already complex organic-aqueous interactions. Thus, the choice of neighbors in molecules structure are heavily influenced by a complexity of intermolecular forces and interactions (e.g., long range electrostatic forces, short-range physical interactions, hydration effect, etc.).

Second, the accuracy and reliability of the predictions capability are severely limited, particularly in the dilute region. This problem is attributed to the lack of reliable experimental data in the dilute region to estimate the interaction parameters and the inability of the UNIFAC model to predict the large change in thermodynamic properties in the dilute region (e.g., γ_i^∞), especially for systems containing components with appreciable complexity of forces and sizes.

"Solventing-out" and "Solventing-in" Concepts

One of the precipitation methods is to employ a miscible organic solvent to reduce the solubility of a salt in an aqueous solution. The influence of the miscible organic solvent on thermodynamic properties such as the solubility (activity coefficient) of salt in the aqueous solution is a major fundamental concern. The decrease in the solubility of salt in the aqueous solution upon the addition of the miscible organic solvent is termed "solventing-out". "Solventing-in" refers to the reverse phenomenon.

Various experimental data of miscible organic solvents effect in reducing the solubility of inorganic species from their aqueous solutions have been reported. No concerted efforts have been made to fit such data into fundamentally-sound correlating frameworks. Limited

modeling attempts on the precipitation aspects exist. Such attempts are uncertain in nature and tend to lack the fundamental foundation.

Following is a brief discussion of the existing modeling attempts by which the precipitation data can be correlated.

Setschenow Equation

One of the oldest relations which can be derived from basic principles of thermodynamics is the Setschenow equation [Setschenow, 1889]. The Setschenow equation has often been employed to correlate the salt effect in the vapor-liquid equilibrium of two liquid components as well as the gas solubility in aqueous salt solutions. This equation is also applicable to the "solventing-out" process. In the case of the "solventing-out" process, the Setschenow equation can be written as follows:

$$\ln \left[\frac{x_{1,2}}{x_{1,m}} \right] = C_1 x_3 \quad (10)$$

or

$$-\ln \left[\frac{x_{1,m}}{x_{1,2}} \right] = C_1 x_3 \quad (11)$$

where C_1 is the precipitation constant. Equation (10) can also be expressed in terms of the salt-free volume fraction of the miscible organic solvent (θ_3) instead of the mole fraction of the miscible organic solvent (x_3) as follows:

$$-\ln \left[\frac{x_{1,m}}{x_{1,2}} \right] = C_1 \theta_3 \quad (12)$$

Although Equation (10) is a fundamentally-based relation, such an equation with a single-constant would provide inadequate representation to the precipitation measurements over a wide composition range of miscible organic solvent (e.g., beyond the linear range of the data).

Jentoft and Robinson Graphical Method

An incentive for adding a miscible organic solvent to a mixture containing a given salt in water is to precipitate the salt and then to recover the valuable miscible organic solvent from the mixed-solvent mixture (e.g., industrial processes) or to remove the miscible organic solvent from precipitates (e.g., analytical methods). Fundamentally, the precipitation fraction would be expected to reach an asymptotic increase with an increase in the amount of added miscible organic solvent to a salt-water mixture. Determining the optimum amount of the miscible organic solvent is of prime importance.

Jentoft and Robinson [1954] proposed a graphical method based on an empirical relation to determine optimum compositions of miscible organic solvents in the precipitation process. The method was based on the following empirical relation:

$$\left[x_{1,m} D_F \right]_{\min} = \frac{x_{1,m}}{1 - \theta_3} \quad (13)$$

where D_F is the dilution factor and given as follows:

$$D_F = \frac{1}{1 - \theta_3} \quad (14)$$

Equation (13) can be implemented by plotting the volume fraction of the miscible organic solvent (θ_3), as the x-axis, versus the salt solubility in the mixed-solvent mixture ($x_{1,m}$), as the y-axis. The tangent of the solubility should pass through the points of the θ_3 -axis at $\theta_3 = 1$ and $x_{1,m} = 0$, and intersect the $x_{1,m}$ at the minimum value of $[x_{1,m} D_F]$. The tangent can be expressed by the straight line equation as follows:

$$x_{1,m} = C_1 \theta_3 + C_2 \quad (15)$$

where the values of $x_{1,m}$ and θ_3 are equivalent to those of the solubility curve at the point of tangency, C_1 is the slope, and C_2 is the intercept which is equivalent to the minimum value of $[x_{1,m} D_F]$.

Although the method provides a systematically-sound evaluation of existing precipitation (solubility) measurements, a visual evaluation can be easily achieved to determine the optimum composition of the added miscible organic solvent. This method is of little modeling value.

Mosseri and Alfassi Relation

Mosseri and Alfassi [1983] suggested an empirical relation to fit the precipitation data. The precipitation fraction of a given salt was fitted by the following relation:

$$P = C_1 \ln \left[\frac{V_R}{C_2} \right] \quad (16)$$

where P is the precipitation fraction, V_R is the solvents volume ratio (miscible organic solvent to water), and C_1 - C_2 are empirical constants.

Equation (16) is a two-constant empirical relation in linear form. Several inherent deficiencies are associated with Equation (16). First, the equation depicts a linear relationship between the precipitation fraction and the volume of miscible organic solvent and therefore breaks down as the volume of miscible organic solvent increases (deviates from the linear range). Second, the equation is physically meaningless when V_R is smaller than C_2 since the negative value of P has no physical meaning. Third, Equation (16) predicts an unlimited increase of P , whereas there is no physical meaning for P greater than one (100%). Fundamentally, the precipitation fraction (P) will never reach unity since any given salt has a certain solubility in pure organic solvent. For a large volume of a given miscible organic solvent, precipitation fractions (P) decreases due to solvent dissolution [Jentoft and Robinson, 1954; Bader, 1993a].

Telotte Model

A more fundamental scheme to describe the excess solubility of salt in a mixed-solvents mixture was suggested by Telotte [1989]. The ternary mixture was reduced to pseudo-binary, and treated as a mixture of a solute and a solvent. The solvent could have a variable composition, but reference was given for much of the solvent composition effect on the salt solubility. Reference solubility varies with the organic solvent composition. The precipitation data was correlated as follows [Telotte, 1989]:

$$\ln \left[\frac{x_{1,m}}{x_{1,2}} \right] = C_1 \theta_3 + C_2 \theta_3^2 + C_3 \theta_3^3 + \dots \quad (17)$$

where C_1 - C_3 are empirical constants. Equation (17) is equivalent to Equation (12) with the exception that the expansion terms (θ_3^2 and θ_3^3) in Equation (17) were added to improve the fitting as the volume of miscible organic solvent increased (deviated from the linear range). These expansion terms are empirical in nature with little physical meaning.

Using this approach was based on the assumption that the volume of the organic solvent required for high precipitation of a given salt was at least four times the volume of the original solution (salt-water). Hence, Telotte concluded that there was no need to model the solubility phase behavior of a given salt in mixed-solvents mixtures that are almost pure organic. This assumption is open to question since it was based on limited data [Mosseri and Alfassi, 1983]. This is not always the case for a large number of precipitation systems [Bader, 1993a; Bader 1995].

Solution Thermodynamics Frameworks

The precipitation mechanism is centered on the difference in the solubilities of the components in the mother solution. To reduce the aqueous solubility of a given salt, the precipitation process requires the addition of a miscible organic solvent to the aqueous solution. A more rigorous thermodynamic description of a salt in a mixed-solvents mixture would consider the relation between the salt solubility in the

mixed-solvents mixture and the salt solubility in each of the pure solvents or in the reference solvent (water). This can be expressed in terms of dilute activity coefficients. An adequate molar excess Gibbs free energy model could then be employed to predict the properties of the multi-component mixture based on information from the interactions formed by the mixture's components.

The fundamental sensitivity of the suggested approaches lies in (1) the validity and the performance ability of the applied molar excess Gibbs free energy model in the dilute region for a given system; (2) the versatility in modeling the salt interactions in the mixture; and (3) the utilization of pure component properties rather than mixture properties to predict interactions phase behavior of the system's components. No existing molar excess Gibbs free energy model completely fulfills the above requirements. Various proposed models provide adequate approximations in targeted applications and certain systems [Bader, 1992; Bader, 1993c].

In the next chapter two frameworks to correlate and predict the solubility phase behavior of a salt in a mixed-solvents mixture using thermodynamic principles are presented. Both frameworks have a common foundation, but emphasize different approaches to the precipitation phenomenon.

CHAPTER III

MODEL DEVELOPMENT

In this chapter, the developed frameworks equations, which are based on the basic fundamentals of solution thermodynamics, are presented. Thermodynamics principles of solid-liquid and liquid-liquid equilibria are used to express the salt solubility in a mixed-solvents mixture. An excess Gibbs free energy model or a power series function is employed to express the activity coefficient expressions. The relationship between the precipitation measurements and the models equations is presented. Following is a presentation of the developed frameworks equations [Bader, 1993a; Bader, 1993b; Bader, 1994; Bader, 1995].

Framework Based on Solid-Liquid Equilibrium

Salt Solubility in a Mixed-Solvents Mixture

Phase behavior is generally controlled by the change in Gibbs free energy of mixing. For solid-liquid mixtures, the change in Gibbs free energy (dG) is given as follows [Prausnitz, et al., 1986]:

$$dG = \mu_i^s - \mu_i^L = RT \left[\ln \frac{f_i^s}{\hat{f}_i^L} \right] = 0 \quad (18)$$

or

$$f_i^s = \hat{f}_i^L \quad (19)$$

where μ_i^s is the chemical potential of a pure solute, μ_i^L is the chemical potential of a solute in a liquid solution, R is the gas constant, T is the temperature, f_i^s is the fugacity of a pure solute (solid), and \hat{f}_i^L is the fugacity of a solute in a liquid solution. Equation (19) reveals that the fugacity of a pure solute is equal to the fugacity of a solute in a solution at equilibrium with its solid phase. However, the fugacity of a solute in a liquid solution can be expressed as follows [Prausnitz, et al., 1986]:

$$\hat{f}_i^L = x_i \gamma_i f_i^\circ \quad (20)$$

where x_i is the mole fraction of a solute, γ_i is the symmetric activity coefficient of a solute, and f_i° is the fugacity of the hypothetical pure liquid. Thus, the solubility as expressed in a mole fraction can be written as follows:

$$\ln x_i = \ln \left[\frac{f_i^s}{f_i^\circ} \right] - \ln \gamma_i \quad (21)$$

The activity coefficient is either defined by Raoult's law with reference to an ideal solution (symmetric activity coefficient), or by Henry's law with reference to an ideal dilute solution (unsymmetric activity coefficient). For a solute in a solution, the symmetric activity coefficient is related to the unsymmetric activity coefficient

as follows [Prausnitz, et al., 1986]:

$$\lim_{x_i \rightarrow 0} \ln \gamma_i = \ln \gamma_i \quad (22)$$

Thus, the activity coefficient can be expressed based on Henry's law for a dilute solution as follows [Prausnitz, et al., 1986]:

$$\ln \gamma_i = \ln \left[\frac{H_i}{f_i^\circ} \right] \quad (23)$$

where H_i is Henry's constant of a solute in a given solvent.

In this work, the precipitation of a salt from an aqueous-saline solution requires the addition of a miscible organic solvent. If the salt is labeled as species 1, water as species 2, and miscible organic solvent as species 3, expressions for the solubility of the salt in the water solvent ($x_{1,2}$), in the miscible organic solvent ($x_{1,3}$), and in the mixed-solvent mixture ($x_{1,m}$) can be derived as follows:

$$\ln x_{1,2} = \ln \left[\frac{f_1^s}{H_{1,2}} \right] \quad (24)$$

$$\ln x_{1,3} = \ln \left[\frac{f_1^s}{H_{1,3}} \right] \quad (25)$$

$$\ln x_{1,m} = \ln \left[\frac{f_1^s}{H_{1,m}} \right] \quad (26)$$

The solvent compositions are typically described by the volume

fraction [O'Connell and Prausnitz, 1964; Prausnitz, et al., 1986]. The volume fraction is given as follows:

$$\theta_i = \left[\frac{x_i v_i}{\sum_{i=2}^3 x_i v_i} \right] \quad (27)$$

where v_i is the pure solvent molar volume. As the solubility of a salt (x_1) in the solvent mixtures approaches zero (high precipitation), the volume fraction of such a salt (θ_1) also approaches zero. Thus, the volume fractions of water (θ_2) and miscible organic solvent (θ_3) become salt-free ($\theta_2 + \theta_3 = 1$). As such, the fugacity of the precipitated salt can be expressed in terms of the solvent salt-free volume fractions as follows:

$$\ln f_1^s = \theta_2 [\ln x_{1,2} + \ln H_{1,2}] + \theta_3 [\ln x_{1,3} + \ln H_{1,3}] \quad (28)$$

Consequently, the solubility of a salt in a mixed-solvents mixture can be expressed as follows:

$$\ln x_{1,m} = \theta_2 \ln x_{1,2} + \theta_3 \ln x_{1,3} - \ln H_1^E \quad (29)$$

where H_1^E is the excess Henry's constant and given as [Prausnitz, et al., 1986]:

$$\ln H_1^E = \ln H_{1,m} - \theta_2 \ln H_{1,2} - \theta_3 \ln H_{1,3} \quad (30)$$

The Excess Gibbs Free Energy Model

The excess Henry's constant is related to the unsymmetric activity coefficient. Hence, expressions for the activity coefficient from the excess Gibbs free energy are needed to use Equation (29). Models such as the one-term Margules [1895], van Laar [1910], Wohl expansion [1946], Kirkwood-Buff [1951], Wilson [1964], T-K Wilson [1975], and others can be employed to express the excess free energy function [Bader, 1992; Bader, 1993c]. These models involve semi-empirical correlations for activity coefficient with the exception of the Kirkwood-Buff model which is based on statistical mechanical theory [O'Connell, 1971]. The Wohl expansion model and its special cases (e.g., the one-term Margules and the van Laar models) do not require a knowledge of the solute-solvents interactions. In contrast, knowledge of these interactions is needed for models such as the Wilson or the T-K-Wilson to characterize the non-ideality of the system. The flexibility of the Wohl's expansion model compared to other models makes it more appropriate as a general form to model the excess Henry's constant of a salt in a mixed-solvents mixture [Bader 1994; Bader, 1995].

According to the Wohl's expansion model [Wohl, 1946], the excess Gibbs energy of a ternary mixture (3-suffix) is expressed in terms of increasing powers of the volume fractions (θ) of the species as follows:

$$\begin{aligned}
\frac{g^E}{RT[x_1v_1 + x_2v_2 + x_3v_3]} = & 2a_{12}\theta_1\theta_2 + 2a_{13}\theta_1\theta_3 + 2a_{23}\theta_2\theta_3 \\
& + 3a_{112}\theta_1^2\theta_2 + 3a_{122}\theta_1\theta_2^2 + 3a_{113}\theta_1^2\theta_3 \\
& + 3a_{133}\theta_1\theta_3^2 + 3a_{223}\theta_2^2\theta_3 + 3a_{233}\theta_2\theta_3^2 \\
& + 6a_{123}\theta_1\theta_2\theta_3
\end{aligned} \tag{31}$$

where the v 's are the effective volume or cross section of the molecules and the a 's are the interaction parameters. The ratio of the v 's is assumed to be the same as the ratio of the pure component liquid molar volumes [Prausnitz, et al., 1986]. The physical significance of the a 's is in a rough way similar to that of the virial coefficients, but they do not have the exact theoretical basis [Prausnitz, et al., 1986]. The following abbreviations can be introduced [Wohl, 1946]:

$$v_1[2a_{12} + 3a_{122}] = \Lambda_{12} \tag{32}$$

$$v_2[2a_{12} + 3a_{112}] = \Lambda_{21} \tag{33}$$

$$v_1[2a_{13} + 3a_{133}] = \Lambda_{13} \tag{34}$$

$$v_3[2a_{13} + 3a_{113}] = \Lambda_{31} \tag{35}$$

$$v_2[2a_{23} + 3a_{233}] = \Lambda_{23} \tag{36}$$

$$v_3[2a_{23} + 3a_{223}] = \Lambda_{32} \tag{37}$$

$$\Lambda_1 \left[\frac{v_2}{v_1} \right] = \Lambda_2 \quad (38)$$

The activity coefficient is related to the excess Gibbs free energy by the following relation [Prausnitz, et al., 1986]:

$$RT \ln \gamma_i = \left[\frac{\partial g^E}{\partial x_i} \right]_{T,P,x_j} \quad (39)$$

Wohl's definition of excess free energy is based on the symmetric convention for the activity coefficients, and thus in this case, the unsymmetric convention activity coefficients are already related to those of the symmetric ones. Therefore, the activity coefficient of a salt (γ_1) in the mixed-solvents can be obtained by differentiating Equation (31) with respect to x_1 (θ_1) using the abbreviations given by Equations (32) to (38):

$$\begin{aligned} \ln \gamma_1 = & \theta_2^2 \left\{ \Lambda_{12} + 2\theta_1 \left[\Lambda_{21} \left(\frac{v_1}{v_2} \right) - \Lambda_{12} \right] \right\} \\ & + \theta_3^2 \left\{ \Lambda_{13} + 2\theta_1 \left[\Lambda_{31} \left(\frac{v_1}{v_3} \right) - \Lambda_{13} \right] \right\} \\ & + \theta_2 \theta_3 \left\{ \Lambda_{21} \left(\frac{v_1}{v_2} \right) + \Lambda_{13} - \Lambda_{32} \left(\frac{v_1}{v_3} \right) + 2\theta_1 \left[\Lambda_{31} \left(\frac{v_1}{v_3} \right) - \Lambda_{13} \right] \right. \\ & \left. + 2\theta_3 \left[\Lambda_{32} \left(\frac{v_1}{v_3} \right) - \Lambda_{23} \left(\frac{v_1}{v_2} \right) \right] - \Lambda_1 (1 - 2\theta_1) \right\} \end{aligned} \quad (40)$$

The number of adjustable parameters can be reduced by neglecting third body interactions between the solute and each of the solvents

[Wohl, 1946]:

$$a_{122} = a_{112} \quad (41)$$

$$a_{113} = a_{133} \quad (42)$$

It should be pointed out that the van Laar equation can be obtained if the same justification applied to the solvent-solvent interaction parameters (Λ_{23} and Λ_{32}) by setting [Wohl, 1946]:

$$a_{223} = a_{233} \quad (43)$$

The approximations given by Equations (41) and (42) lead to

$$\frac{\Lambda_{21}}{\Lambda_{12}} = \frac{v_2}{v_1} \quad (44)$$

$$\frac{\Lambda_{31}}{\Lambda_{13}} = \frac{v_3}{v_1} \quad (45)$$

As x_1 (θ_1) approaches zero and by introducing Equations (44) and (45) into Equation (40), expressions for the activity coefficients of the salt in the water solvent ($\gamma_{1,2}$), in the miscible organic solvent ($\gamma_{1,3}$), and in the mixed-solvents mixture ($\gamma_{1,m}$) can be expressed as follows:

$$\lim_{x_1 \rightarrow 0} \ln \gamma_{1,2} = \Lambda_{12} \quad (46)$$

$$\lim_{x_1 \rightarrow 0} \ln \gamma_{1,3} = \Lambda_{13} \quad (47)$$

$$\lim_{x_1 \rightarrow 0} \ln \gamma_{1,m} = \Lambda_{12}\theta_2 + \Lambda_{13}\theta_3 + \Lambda_{32}\theta_2\theta_3 \frac{v_1}{v_3} [2\theta_3 - 1] - \Lambda_{23}2\theta_2\theta_3^2 \frac{v_1}{v_2} - \Lambda_1\theta_2\theta_3 \quad (48)$$

where Λ_{12} and Λ_{13} are interaction parameters between the salt and the solvents, Λ_{23} and Λ_{32} are interaction parameters between the solvents, and Λ_1 is the salt binary-solvent interaction parameter (ternary constant). Equation (48) reveals that the salt-solvents interaction parameters (Λ_{21} and Λ_{31}) are canceled out. This demonstrates the simplicity of Wohl's expansion model over, for instance, the Wilson or T-K-Wilson models, to account for the non-ideality of the system.

Substituting Equations (46) to (48) into Equation (30) through the use of Equation (23), leads to

$$\ln H_1^E = \theta_2\theta_3[2\theta_3 - 1]\Lambda_{32} \frac{v_1}{v_3} - 2\theta_2\theta_3^2\Lambda_{23} \frac{v_1}{v_2} - \theta_2\theta_3\Lambda_1 \quad (49)$$

In Equation (49), the fugacity of the hypothetical pure liquid (f_1^0) is canceled out in the final expression of the excess Henry's constant. Thus, the 3-suffix equation for the solubility of salt in a mixed-solvents mixture can be expressed as follows:

$$\ln x_{1,m} = \theta_2 \ln x_{1,2} + \theta_3 \ln x_{1,3} - \theta_2\theta_3[2\theta_3 - 1]\Lambda_{32} \frac{v_1}{v_3} + 2\theta_2\theta_3^2\Lambda_{23} \frac{v_1}{v_2} + \theta_2\theta_3\Lambda_1 \quad (50)$$

Equation (50) can be rearranged to yield

$$\ln \left[\frac{x_{1,m}}{x_{1,2}} \right] = \theta_3 \ln \left[\frac{x_{1,3}}{x_{1,2}} \right] - \theta_2 \theta_3 [2\theta_3 - 1] \Lambda_{32} \frac{v_1}{v_3} + 2\theta_2 \theta_3^2 \Lambda_{23} \frac{v_1}{v_2} + \theta_2 \theta_3 \Lambda_1 \quad (51)$$

The Precipitation Measurements

Such an overall picture of the ternary mixture provides a reasonable approximation for the precipitation measurements. However, precipitation measurements are presented in terms of the salts precipitation fractions (P) upon the addition of a miscible organic solvent. Therefore, the left-hand side of Equation (51) can be related to the salt precipitation fraction as follows [Bader, 1993a; Bader, 1995]:

$$\ln \left[\frac{x_{1,m}}{x_{1,2}} \right] = \ln[1 - P] \quad (52)$$

Thus, the final expression of the ternary 3-Suffix equation for the precipitation measurements is given as follows:

$$\ln[1 - P] = \theta_3 \ln \left[\frac{x_{1,3}}{x_{1,2}} \right] - \theta_2 \theta_3 [2\theta_3 - 1] \Lambda_{32} \frac{v_1}{v_3} + 2\theta_2 \theta_3^2 \Lambda_{23} \frac{v_1}{v_2} + \Lambda_1 \theta_2 \theta_3 \quad (53)$$

The ternary 2-Suffix equation can also be obtained by ignoring the third body interactions (Equation (31)) as follows:

$$\ln[1 - P] = \theta_3 \ln \left[\frac{x_{1,3}}{x_{1,2}} \right] + \theta_2 \theta_3 \Lambda_{32} \frac{v_1}{v_3} \quad (54)$$

Solvent-Solvent Interaction Parameters

If the solubility of the targeted salt in the miscible organic solvent is available ($x_{1,3}$), the solvent-solvent interaction parameters (Λ_{23} and Λ_{32}) can be obtained from the vapor-liquid equilibrium data. The vapor-liquid equilibrium data can be used to fit the excess free energy to any suffix equation. The excess Gibbs free energy for the ternary 3-Suffix equation is given as follows:

$$\frac{g^E}{RT} = \theta_2 \theta_3^2 \Lambda_{23} \left[\frac{x_2 v_2 + x_3 v_3}{v_2} \right] + \theta_2^2 \theta_3 \Lambda_{32} \left[\frac{x_2 v_2 + x_3 v_3}{v_3} \right] \quad (55)$$

and the ternary 2-Suffix equation is given as follows:

$$\frac{g^E}{RT} = \theta_2 \theta_3 \Lambda_{23} \left[\frac{x_2 v_2 + x_3 v_3}{v_3} \right] \quad (56)$$

where

$$\frac{g^E}{RT} = \sum_{i=2}^3 x_i \ln \gamma_i = x_2 \ln \gamma_2 + x_3 \ln \gamma_3 \quad (57)$$

As shown by Equation (57), the activity coefficients of the salt-free solvents (water-organic) are needed. The UNIFAC model, which is a group contribution method, can be used to estimate the activity coefficients of the water-isopropylamine systems [Fredenslund, et al.,

1977; Larsen, et al., 1987]. The UNIFAC model should provide reasonable estimates for the activity coefficients of the mixed-solvents since the water-isopropylamine system is a relatively simple system [Bader, 1993b; Bader and Gasem, 1996b]. The solvent-solvent activity coefficients, mole fractions, and molar volumes can then be used to estimate Λ_{23} and Λ_{32} by combining either Equation (55) or (56) with Equation (57).

Framework Based on Liquid-Liquid Equilibrium

Salt Solubility in a Mixed-Solvents Mixture

In the liquid-liquid equilibrium approach, the precipitation measurements is modeled in terms of salt solubility in the reference solvent (water) whereby, total volume does not change during the precipitation process and the salt solubility in both solvent (water and miscible organic solvent). The change in Gibbs free energy for the transformation of a dissolved salt in a liquid solution containing pure water (α) to a solution with less salt solubility containing both water and miscible organic solvent (β) can expressed as follows [Prausnitz, et al., 1986]:

$$dG = \mu_1^{L\alpha} - \mu_1^{L\beta} = RT \left[\ln \frac{\hat{f}_1^{L\alpha}}{\hat{f}_1^{L\beta}} \right] \quad (58)$$

or

$$\hat{f}_1^{L\alpha} = \hat{f}_1^{L\beta} \quad (59)$$

where $\mu_1^{L\alpha}$ is the chemical potential of a dissolved salt in pure water,

μ_i^{LB} is the chemical potential of a dissolved salt in a liquid mixture (water and organic), R is the gas constant, T is the temperature, \hat{f}_i^{La} is the fugacity of a dissolved salt in pure water, and \hat{f}_i^{LB} is the fugacity of a dissolved salt in a liquid mixture (water and organic). Equation (58) indicates that the fugacity of a dissolved salt in pure water is equal to its fugacity in a liquid mixture containing both water and miscible organic solvent. The fugacity of a given solute in a liquid mixture can be expressed by Equation (20). As such, Equation (59) can be rewritten as follows:

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \quad (60)$$

If the salt is labeled as species 1, water as species 2, and miscible organic solvent as species 3, Equation (60) can be expressed as follows:

$$\gamma_{1,2} x_{1,2} = \gamma_{1,m} x_{1,m} \quad (61)$$

or

$$\ln \left[\frac{\gamma_{1,m}}{\gamma_{1,2}} \right] = \ln \left[\frac{x_{1,2}}{x_{1,m}} \right] \quad (62)$$

where $\gamma_{1,m}$ is the activity coefficient of a given salt in the mixture (water and organic), $\gamma_{1,2}$ is the activity coefficient of a given salt in pure water, $x_{1,2}$ is the solubility of a salt in pure water, and $x_{1,m}$ is the solubility of salt in the mixture.

Activity Coefficients Expression Based on The Power Series Function

Equation (1) can be used to express the activity coefficients of a given salt in pure water and in a mixture containing both water and miscible organic solvent as follows:

$$\ln \gamma_{1,m} = \sum_{y,z}^{\infty} \Lambda_{yz} x_{1,2}^z x_3^y \quad (63)$$

where y and z are integer powers and Λ_{yz} represents interaction parameters. Expanding Equation (63) for $y + z \leq 3$, leads to the following expression for the activity coefficient of a given salt in a mixture of water and miscible organic solvent:

$$\begin{aligned} \ln \gamma_{1,m} = & \Lambda_{00} + \Lambda_{01} x_{1,2} + \Lambda_{10} x_3 + \Lambda_{11} x_{1,2} x_3 + \Lambda_{02} x_{1,2}^2 + \Lambda_{20} x_3^2 \\ & + \Lambda_{03} x_{1,2}^3 + \Lambda_{12} x_{1,2}^2 x_3 + \Lambda_{21} x_{1,2} x_3^2 + \Lambda_{30} x_3^3 \end{aligned} \quad (64)$$

Similarly, an expression for the activity coefficient of a given salt in pure water ($x_3 = 0$) can be generated as follows:

$$\ln \gamma_{1,2} = \Lambda_{00} + \Lambda_{01} x_{1,2} + \Lambda_{02} x_{1,2}^2 + \Lambda_{03} x_{1,2}^3 \quad (65)$$

Therefore, Equation (62) can be expressed as follows:

$$\ln \left[\frac{\gamma_{1,m}}{\gamma_{1,2}} \right] = \ln \left[\frac{x_{1,2}}{x_{1,m}} \right] = \Lambda_{10} x_3 + \Lambda_{11} x_{1,2} x_3 + \Lambda_{20} x_3^2 + \Lambda_{12} x_{1,2}^2 x_3 + \Lambda_{21} x_{1,2} x_3^2 + \Lambda_{30} x_3^3 \quad (66)$$

If Equation (63) expanded with respect to $y + z \leq 2$, Equation (66) would be reduced to the following form:

$$\ln \left[\frac{\gamma_{1,m}}{\gamma_{1,2}} \right] = \ln \left[\frac{x_{1,2}}{x_{1,m}} \right] = \Lambda_{10}x_3 + \Lambda_{11}x_{1,2}x_3 + \Lambda_{20}x_3^2 \quad (67)$$

If $y + z \leq 1$ is used in expanding Equation (63), Equation (66) would be collapsed to the following form:

$$\ln \left[\frac{\gamma_{1,m}}{\gamma_{1,2}} \right] = \ln \left[\frac{x_{1,2}}{x_{1,m}} \right] = \Lambda_{10}x_3 \quad (68)$$

The form Equation (68) is similar to the well-known Setschenow equation [Setschenow, 1889].

As the precipitation of a given salt increases with the increase in the amount of miscible organic solvent, the solubility of such a salt decreases ($x_{12} \rightarrow 0$). For high precipitation fractions of a given salt, Equation (66) can be reduced to the following form:

$$\ln \left[\frac{x_{1,2}}{x_{1,m}} \right] = \Lambda_{10}x_3 + \Lambda_{20}x_3^2 + \Lambda_{30}x_3^3 \quad (69)$$

Similarly, Equation (67) can be reduced as follows:

$$\ln \left[\frac{x_{1,2}}{x_{1,m}} \right] = \Lambda_{10}x_3 + \Lambda_{20}x_3^2 \quad (70)$$

The Precipitation Measurements

Experimentally, precipitation measurements are given in terms of the salts precipitation fractions (P) upon the addition of a miscible organic solvent. Therefore, the left-hand side of Equations (62) and (69) can be related to the salt precipitation fraction as follows [Bader, 1993a; Bader, 1995]:

$$\ln \left[\frac{x_{1,m}}{x_{1,2}} \right] = -\ln[1 - P] \quad (71)$$

Water and organic mole fractions (x_2 and x_3) can be expressed in terms of their salt-free volume fractions ($\theta_2 + \theta_3 = 1$) as given in Equation (27). It should be pointed out that the right-hand side of Equation (71) is always negative, therefore Equations (67) and (69) can be rewritten as follows:

$$\ln[1 - P] = \Lambda_{10}\theta_3 + \Lambda_{20}\theta_3^2 + \Lambda_{30}\theta_3^3 \quad (72)$$

and

$$\ln[1 - P] = \Lambda_{10}\theta_3 + \Lambda_{20}\theta_3^2 \quad (73)$$

CHAPTER IV

RESULTS AND DISCUSSION

Database Used

Precipitation data for systems including sodium, potassium, magnesium, calcium, barium and strontium in forms of chloride, and sulfate salts using isopropylamine as a precipitation agent acquired in the experimental section were employed in this study. Detailed information for each system containing the volume of isopropylamine (V_3), the volume ratio of isopropylamine to water (V_R), the salt concentration in water (C_S), the salt concentrations in the mixed-solvents mixture (C_F), and the precipitation fractions (P) along with their uncertainties are presented in Tables 1 through 19, Section I.

Data Reduction Procedure

Regressions of the precipitation measurements were performed using the weighted least squares objective function (SS). A Marquardt nonlinear regression procedure was employed in the precipitation calculations [Marquardt, 1963]. The objective function, SS, used for the evaluation of the models equations is given as follows:

$$SS = \sum_{i=1}^{NP} \left[\frac{Y_{Cal} - Y_{exp}}{Y_{exp}} \right] \quad (74)$$

where Y_{cal} is the calculated variable, and Y_{exp} is the experimental variable, and given as follows:

$$Y = \ln[1 - P] \quad (75)$$

According to Equation (74), the root-mean-square-error (RMSE) provides an appropriate measure for overall performance of the model for a given data set more so than %AAD.

Model Evaluations

The 2-Suffix and 3-Suffix Equations (Solid-Liquid Equilibrium)

The acquired precipitation database was used to test and evaluate Equations (53) and (54). Tables 1 and 2 present a summary of the results of the tested Equations (53 and 54) for the studied systems. These tables include interaction parameters of the model equations and complete statistics.

Due to the lack of knowledge of salts solubilities in isopropylamine ($X_{1,3}$), Equations (55) to (57) reported in the model development chapter were not used to estimate the solvent-solvent interaction parameters. The solvent-solvent interaction parameters (Λ_{23} and Λ_{32}) were obtained using the objective function of Equation (74) through the precipitation calculations. However, $X_{1,3}$ can be reasonably estimated from the regressed parameters of Equations (53) or (54).

Figures 1 through 19 reveal the experimental precipitation measurements along with the predictions of Equations (53) and (54).

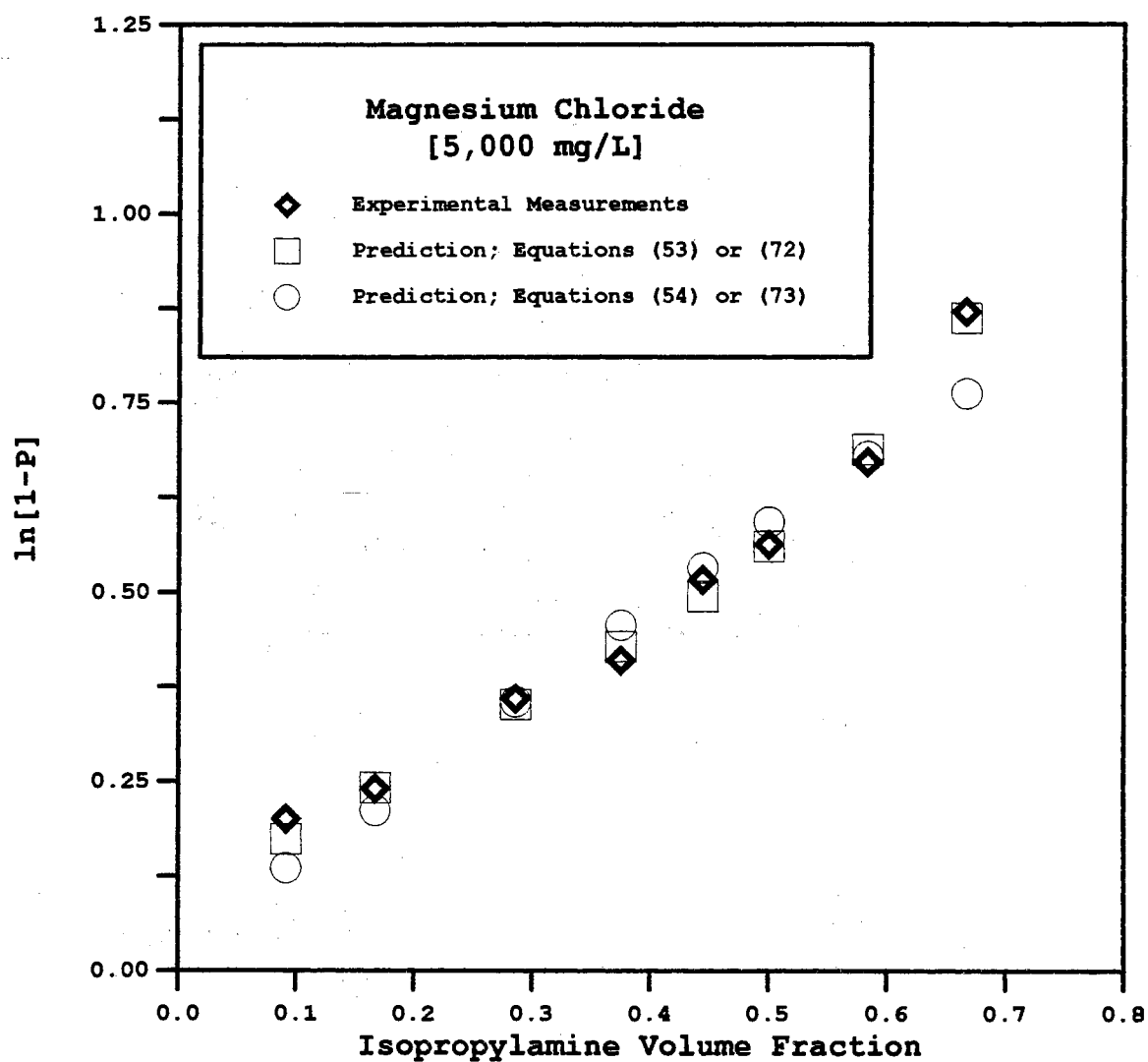


Figure 1. Precipitation of 5,000 mg/L Chloride Ion from Magnesium Chloride System

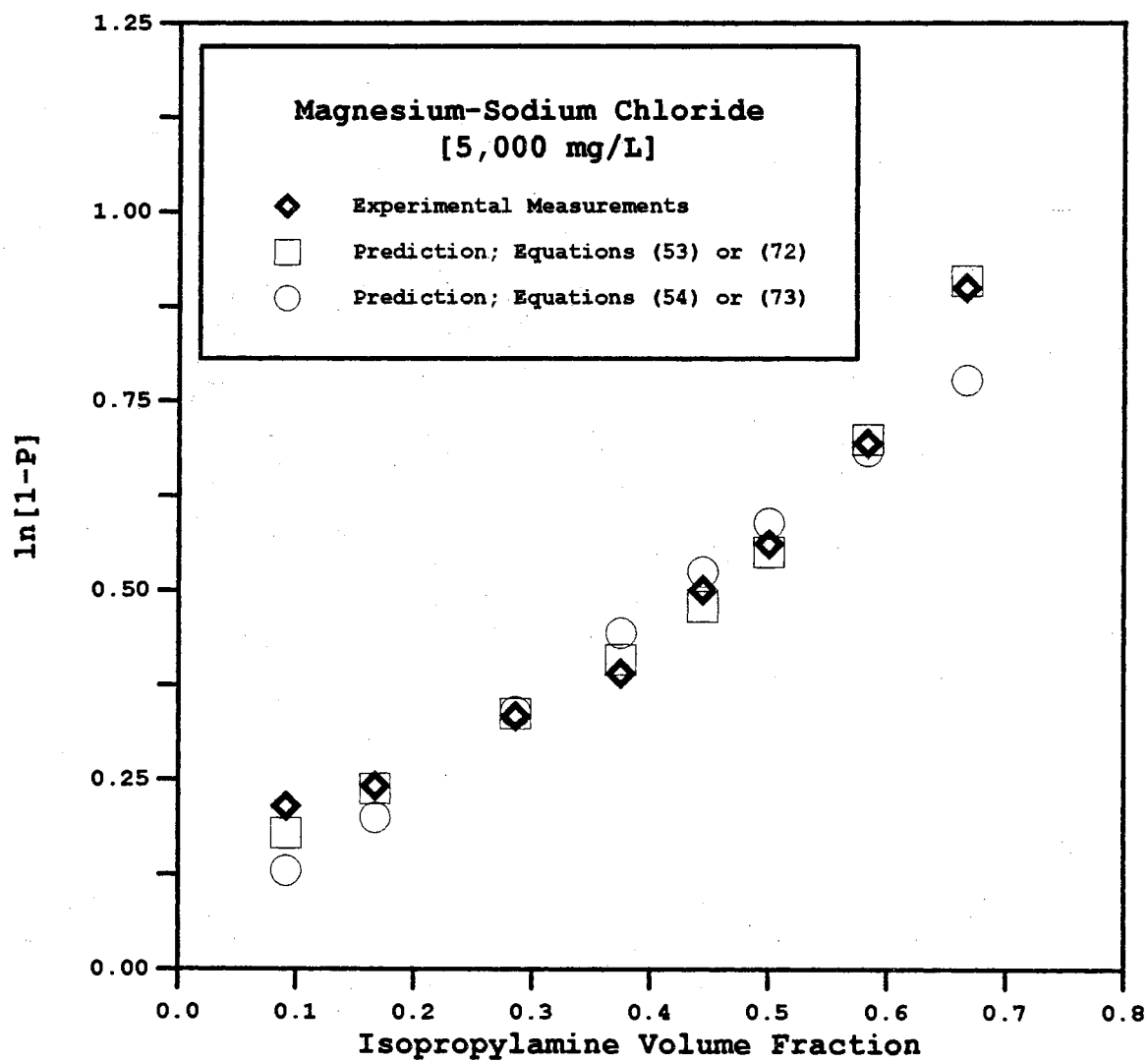


Figure 2. Precipitation of 5,000 mg/L Chloride Ion from Magnesium-Sodium Chloride System

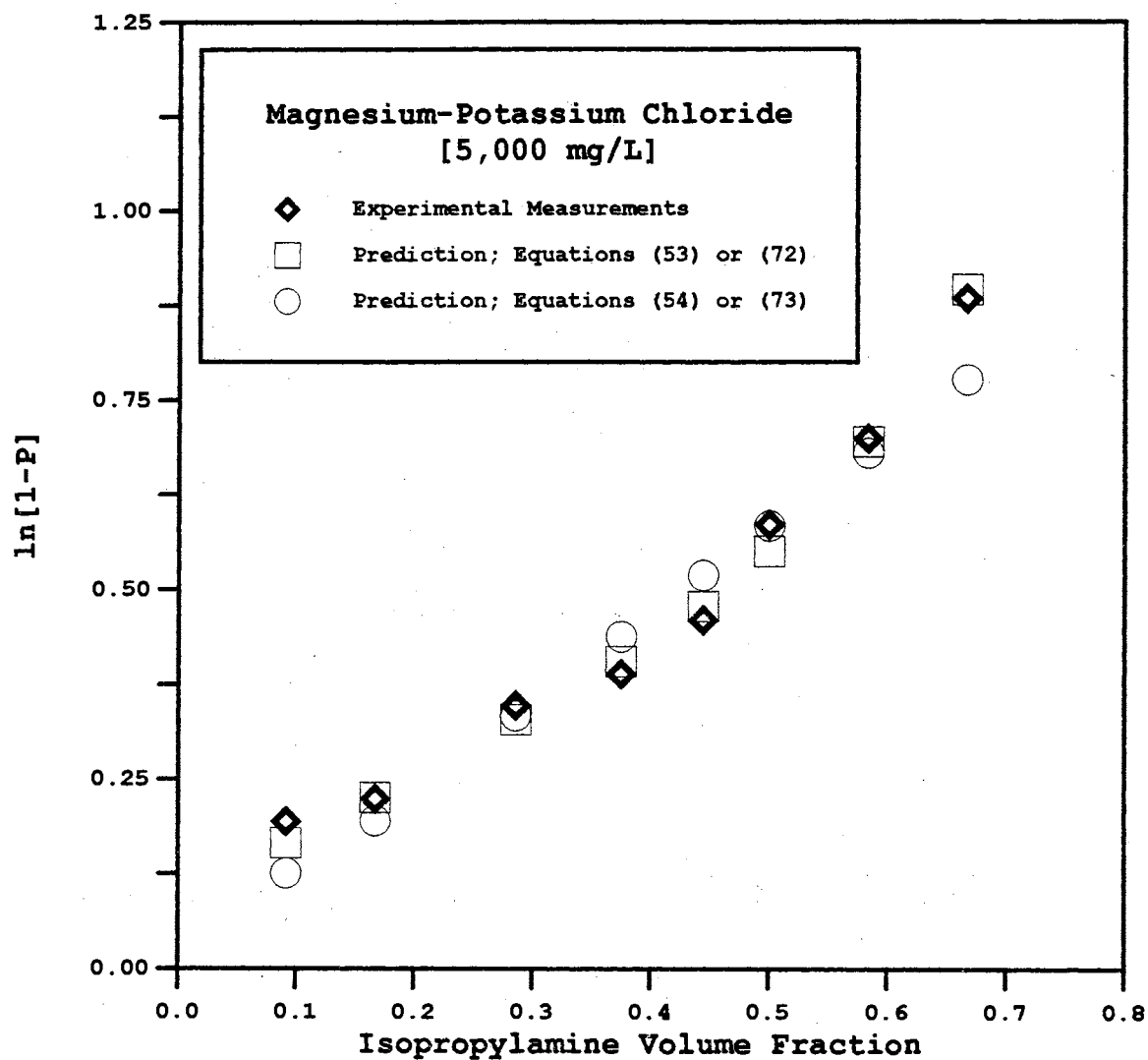


Figure 3. Precipitation of 5,000 mg/L Chloride Ion from Magnesium-Potassium Chloride System

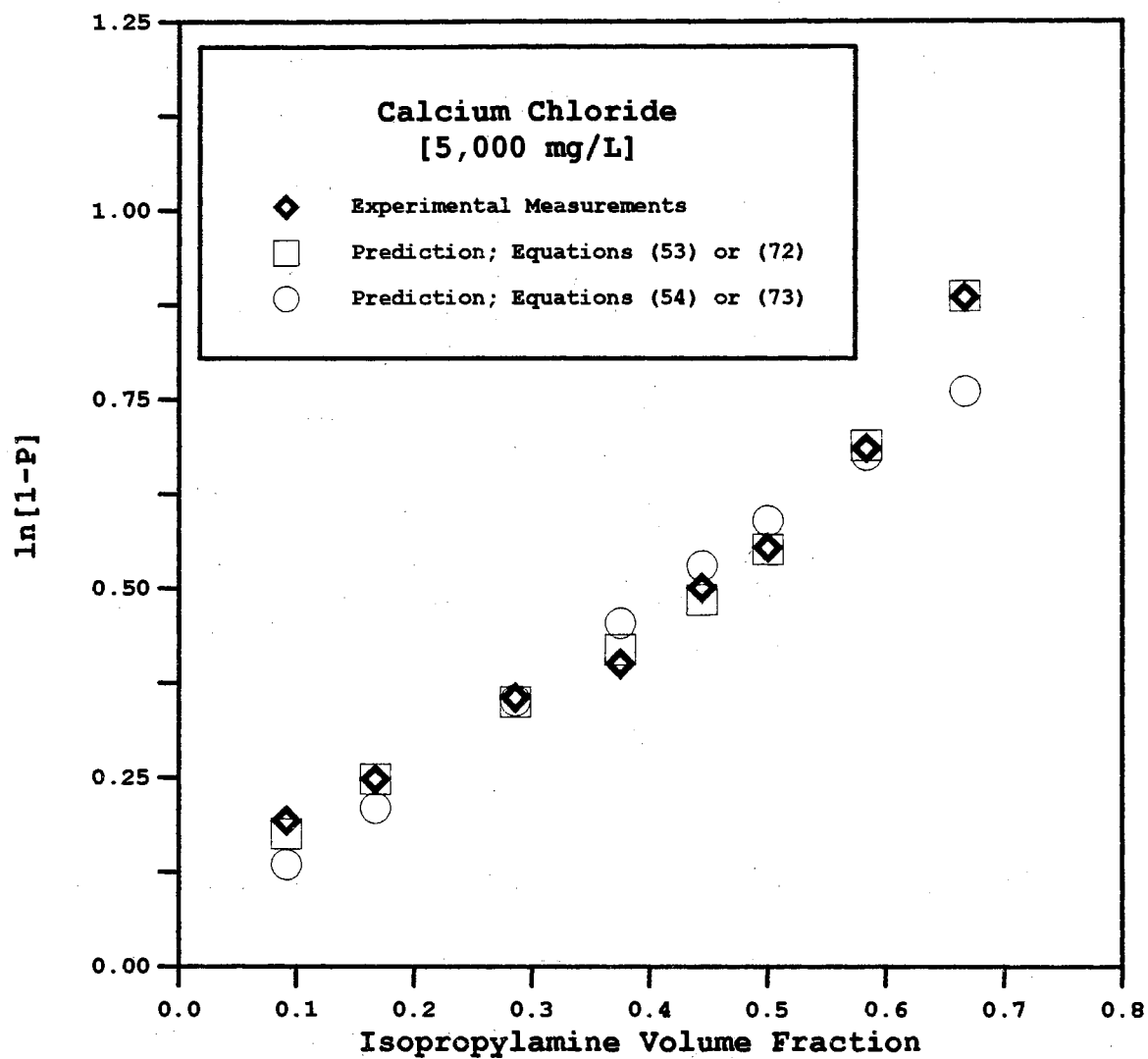


Figure 4. Precipitation of 5,000 mg/L Chloride Ion from Calcium Chloride System

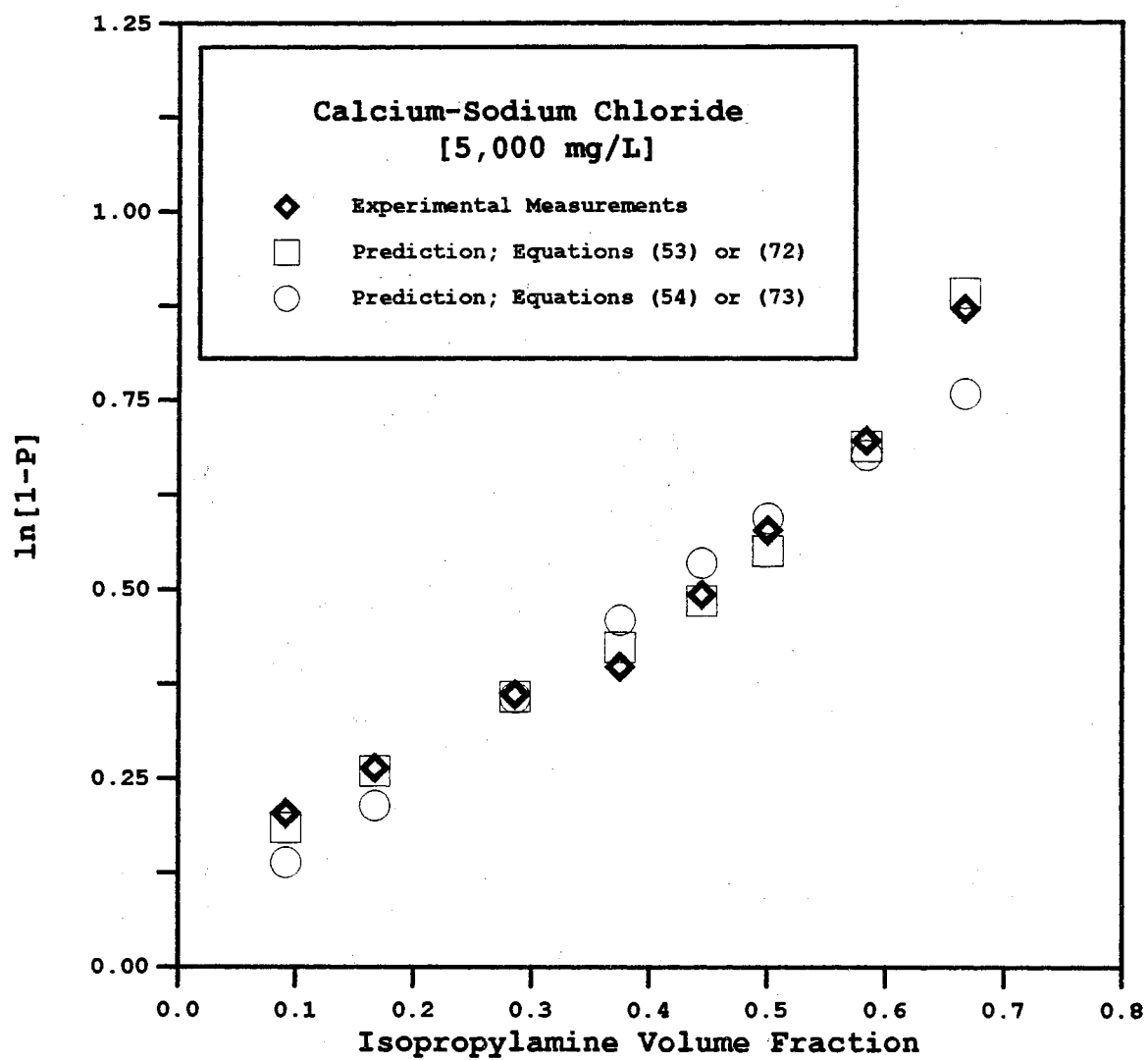


Figure 5. Precipitation of 5,000 mg/L Chloride Ion from Calcium-Sodium Chloride System

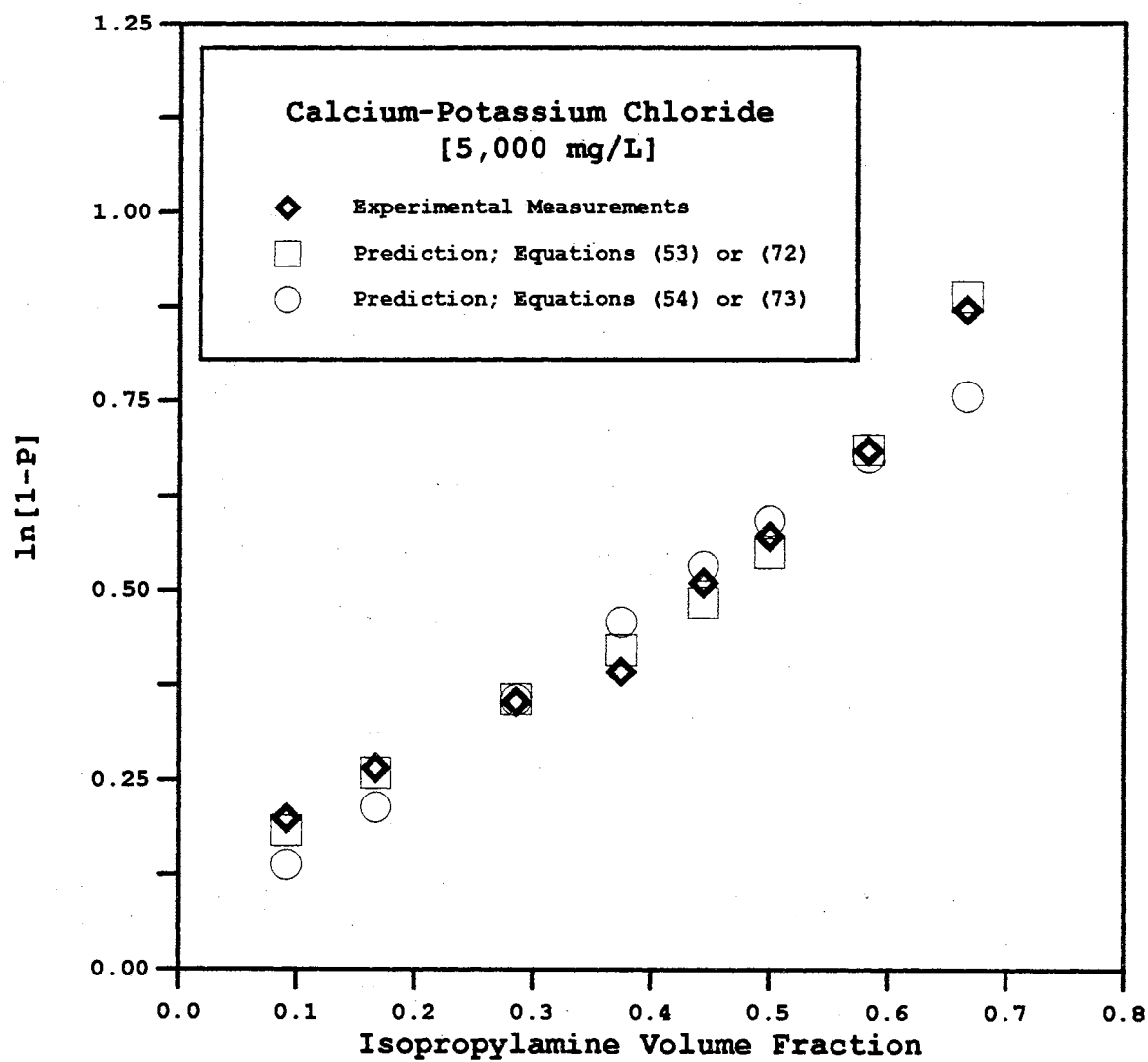


Figure 6. Precipitation of 5,000 mg/L Chloride Ion from Calcium-Potassium Chloride System

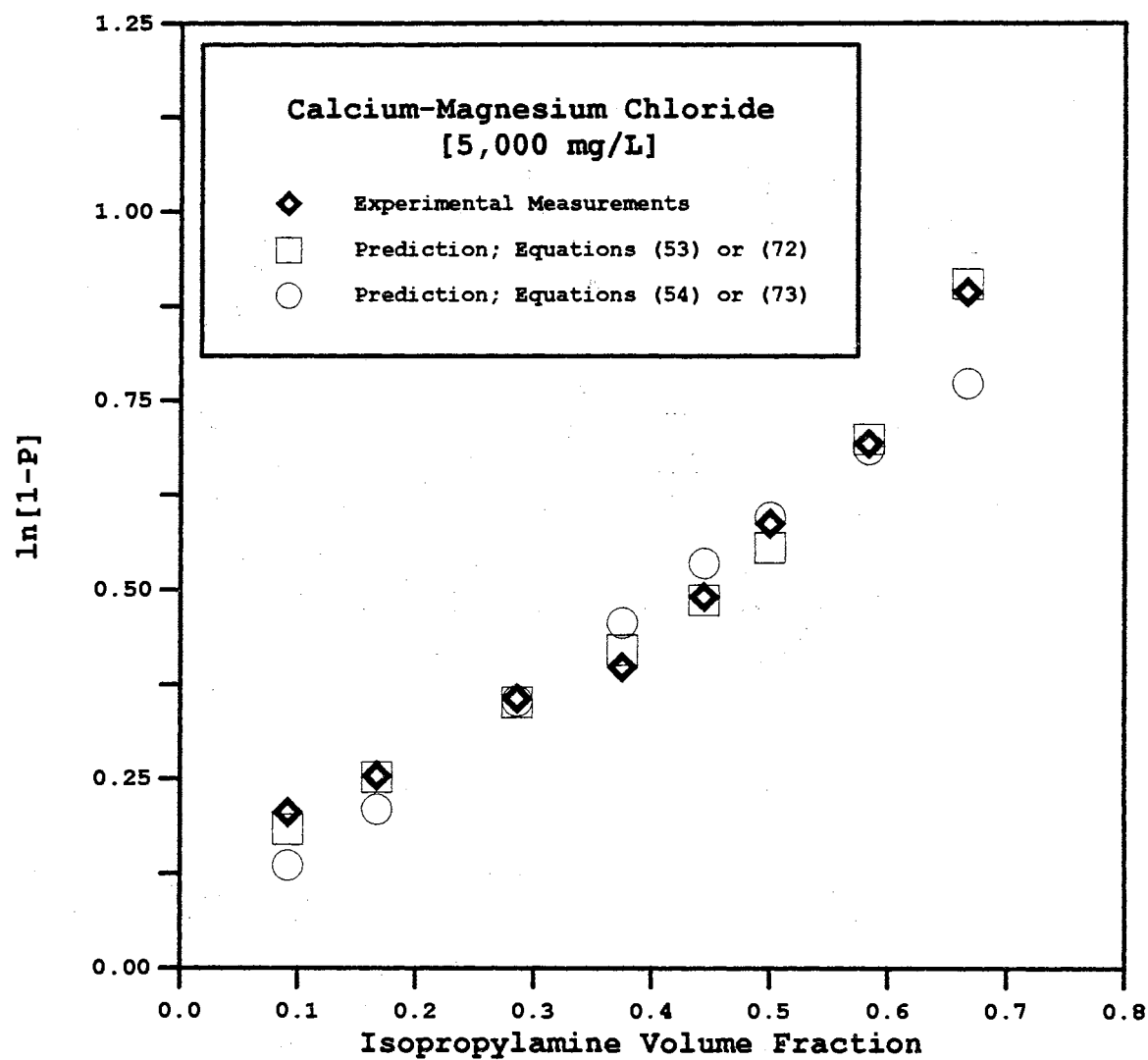


Figure 7. Precipitation of 5,000 mg/L Chloride Ion from Calcium-Magnesium Chloride System

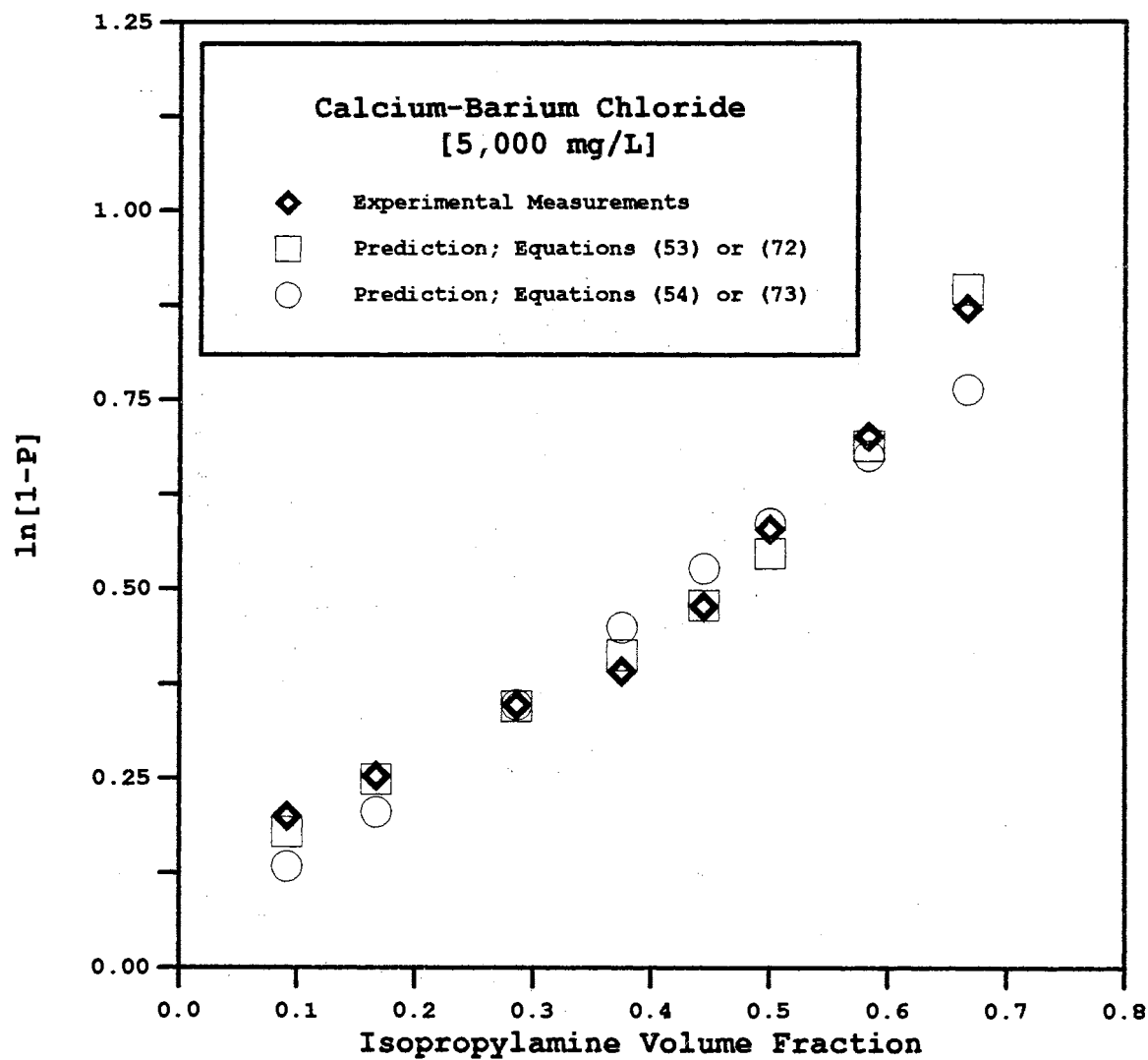


Figure 8. Precipitation of 5,000 mg/L Chloride Ion from Calcium-Barium Chloride System

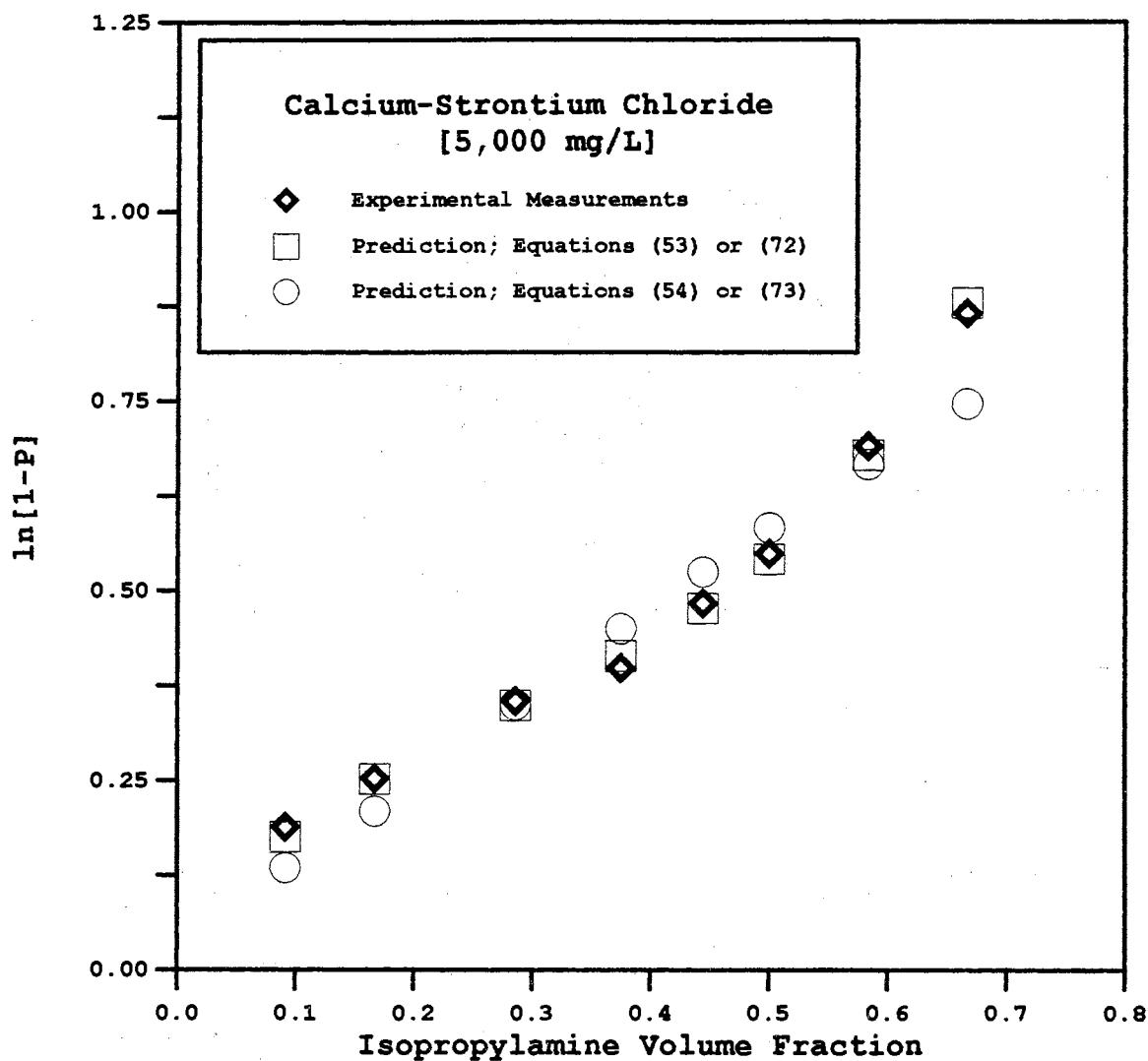


Figure 9. Precipitation of 5,000 mg/L Chloride Ion from Calcium-Strontium Chloride System

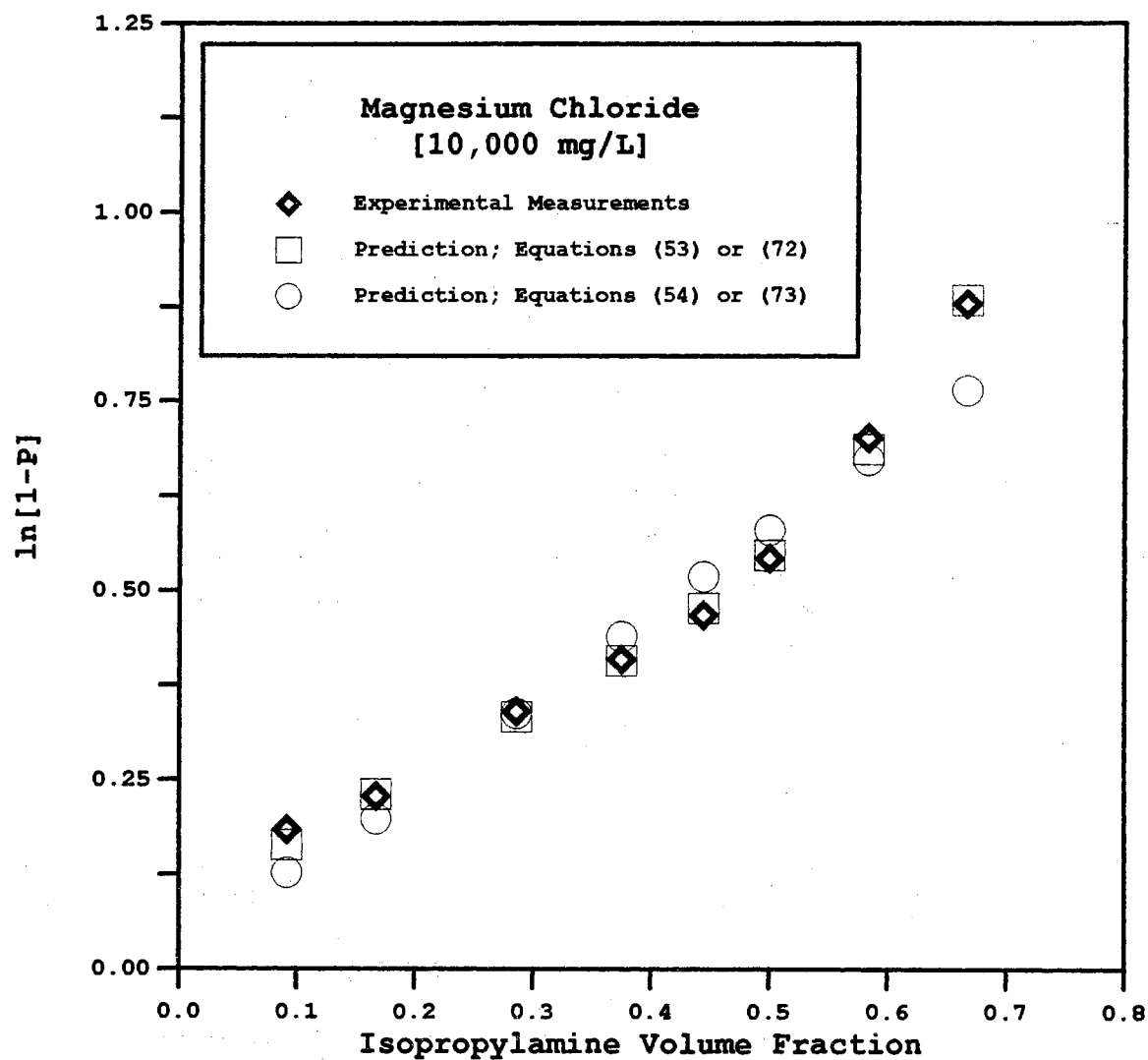


Figure 10. Precipitation of 10,000 mg/L Chloride Ion from Magnesium Chloride System

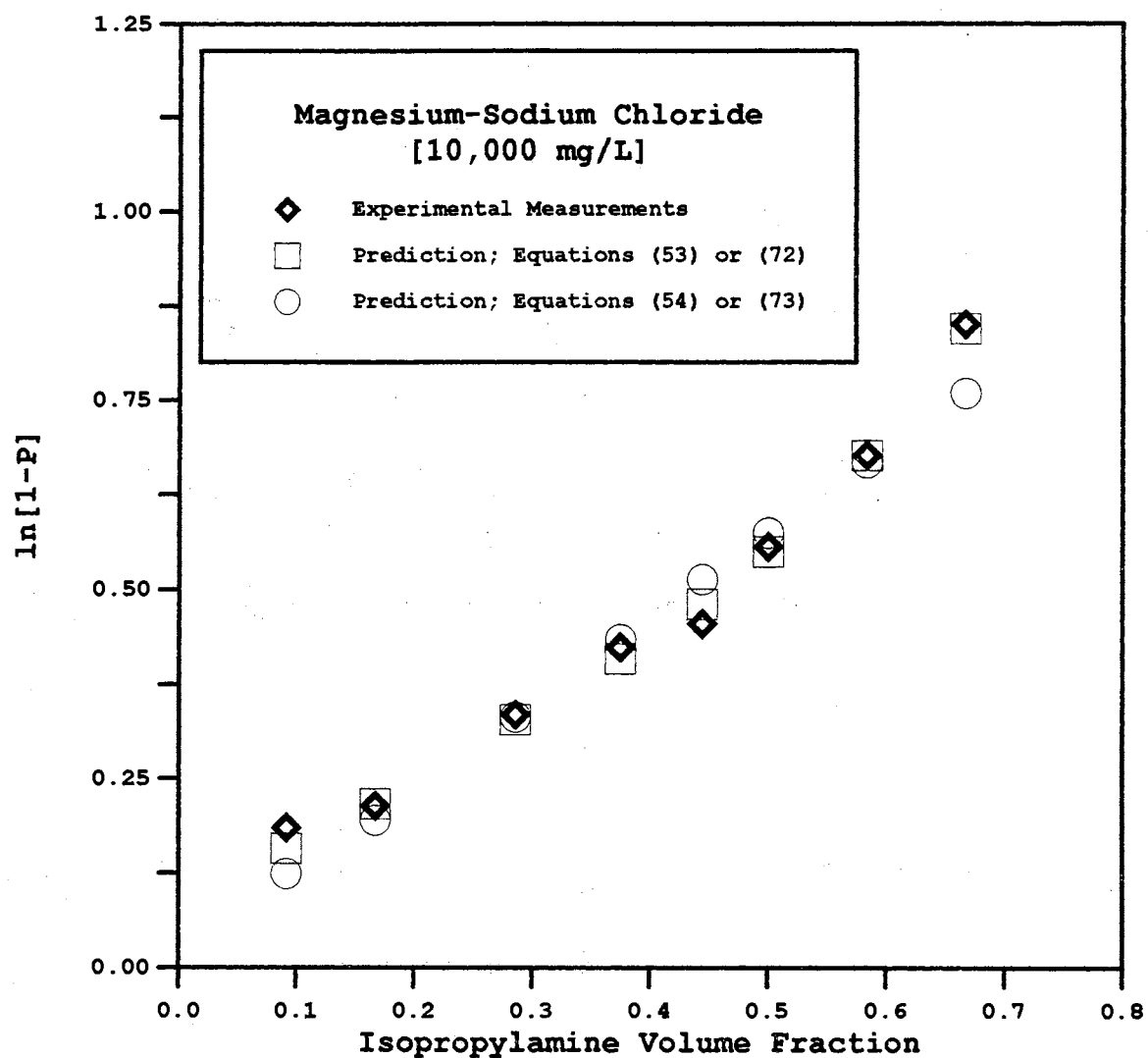


Figure 11. Precipitation of 10,000 mg/L Chloride Ion from Magnesium-Sodium Chloride System

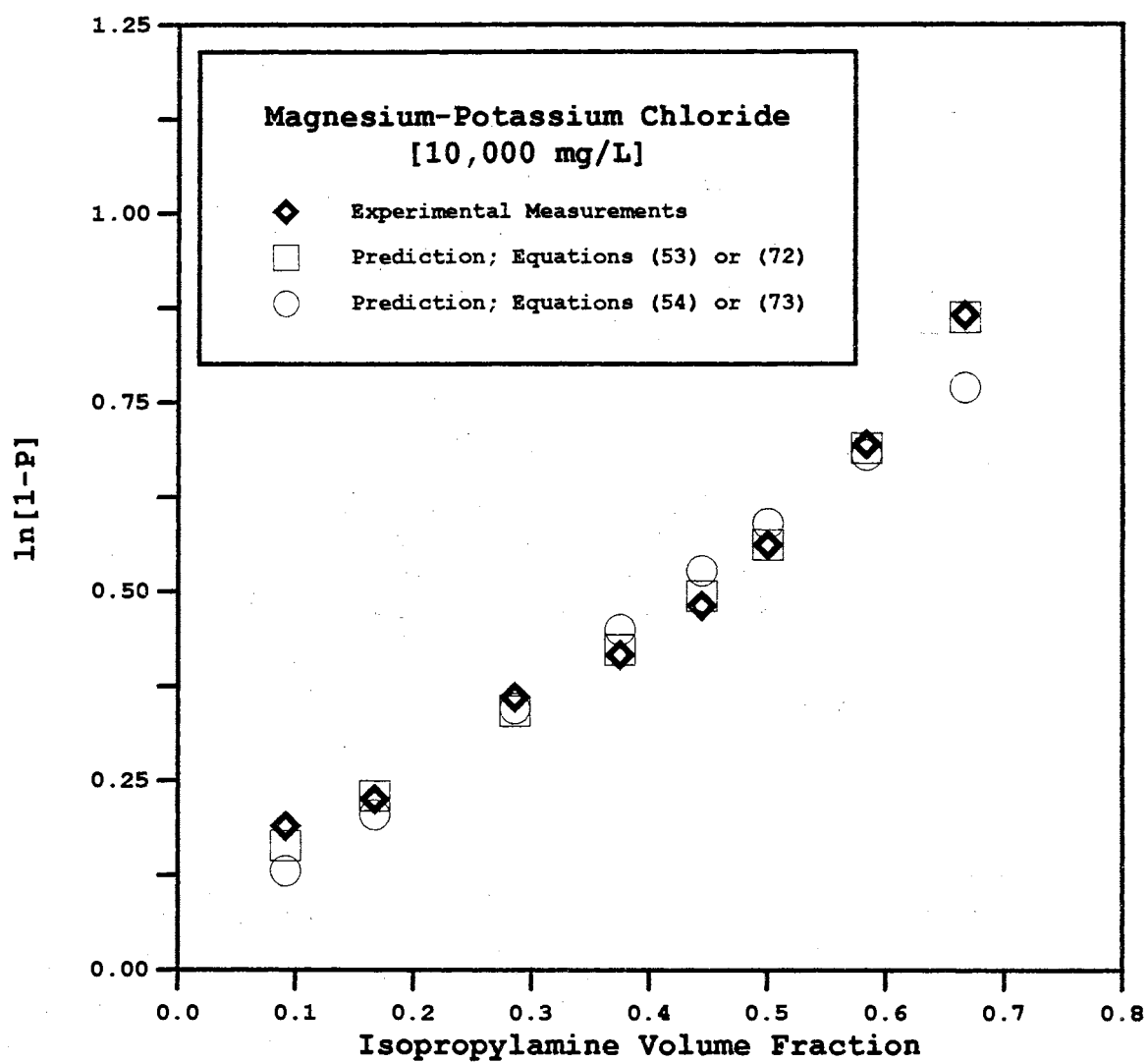


Figure 12. Precipitation of 10,000 mg/L Chloride Ion from Magnesium-Potassium Chloride System

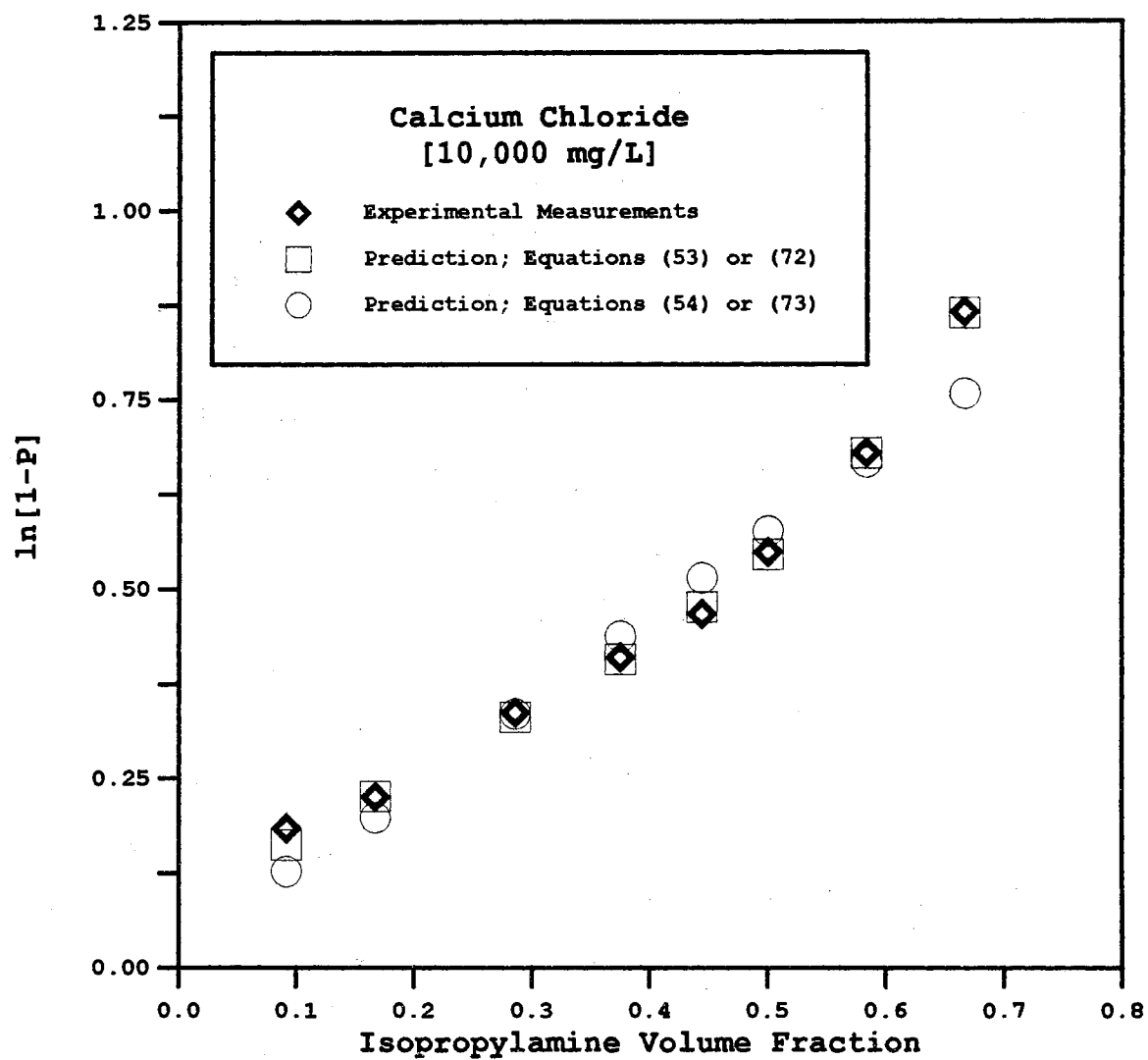


Figure 13. Precipitation of 10,000 mg/L Chloride Ion from Calcium Chloride System

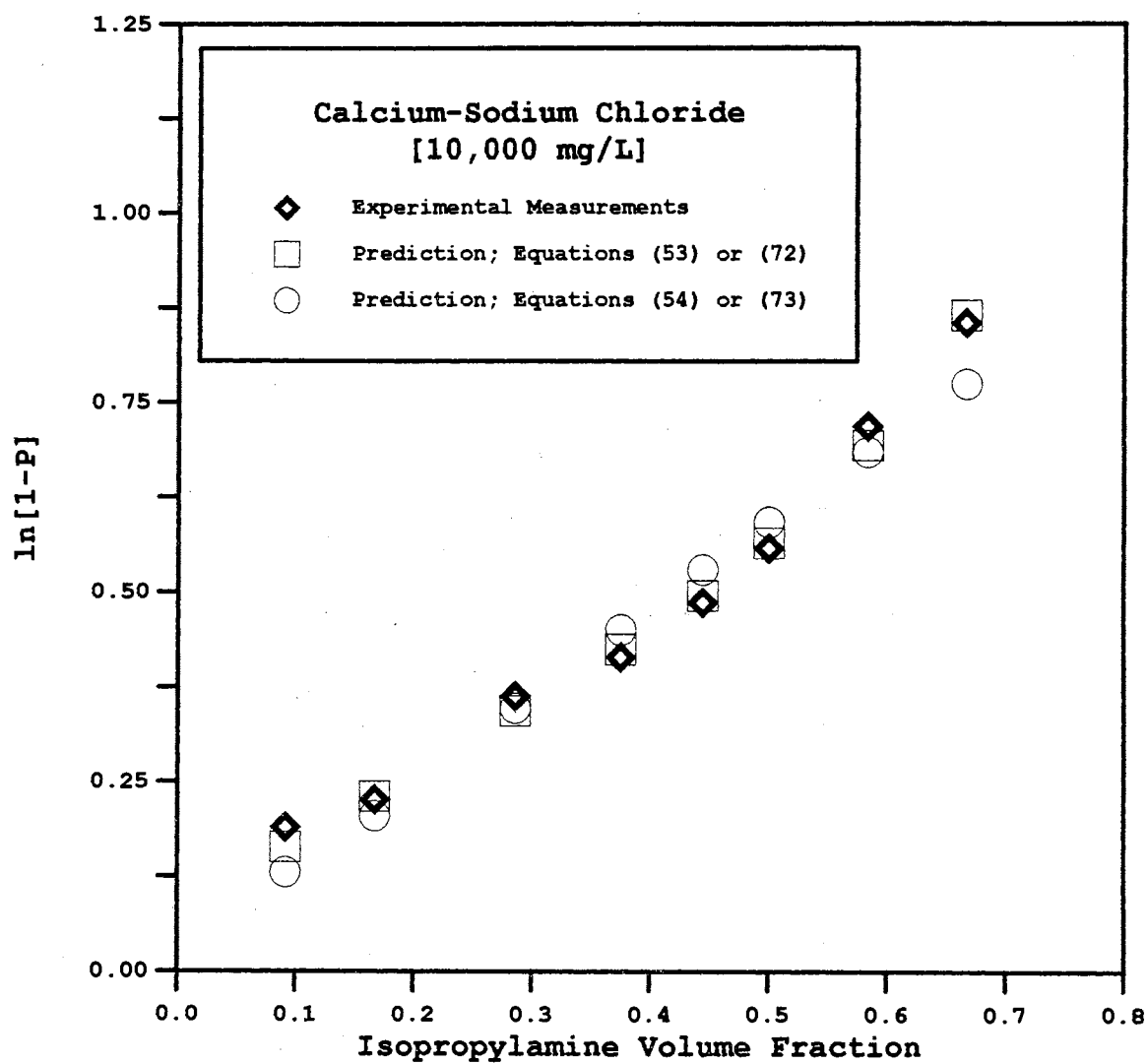


Figure 14. Precipitation of 10,000 mg/L Chloride Ion from Calcium-Sodium Chloride System

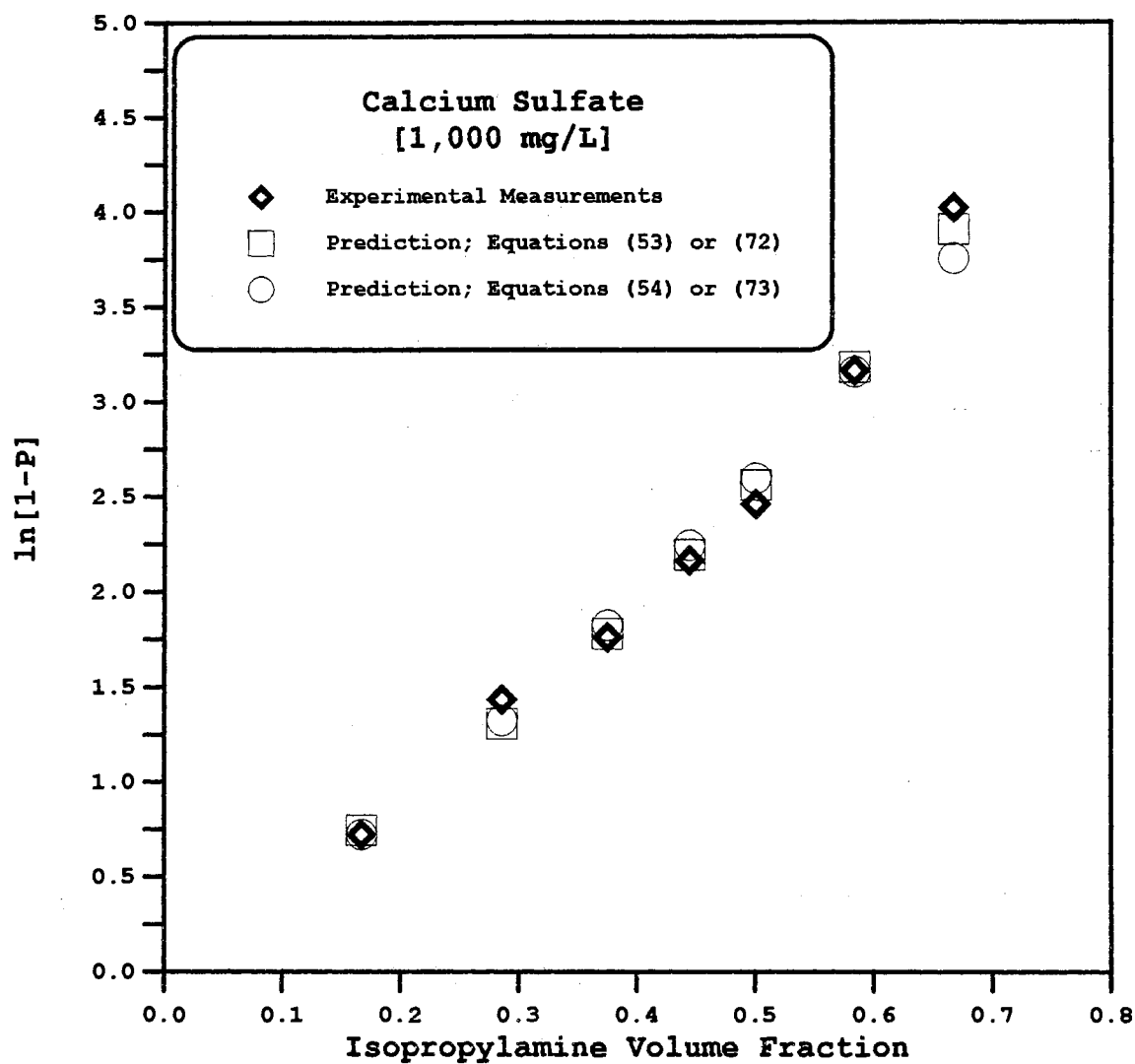


Figure 15. Precipitation of 1,000 mg/L Sulfate Ion from Calcium Sulfate System

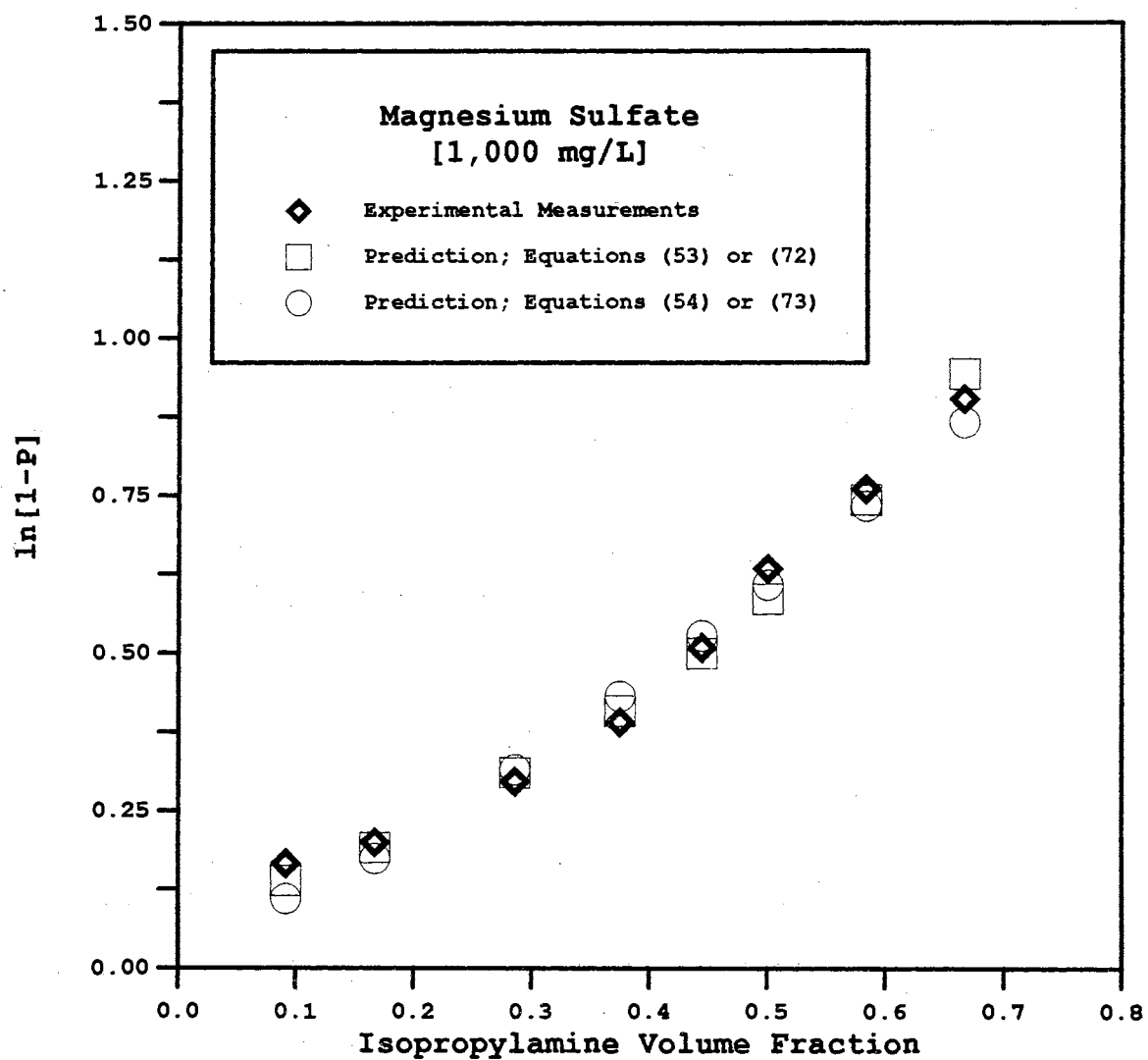


Figure 16. Precipitation of 1,000 mg/L Sulfate Ion from Magnesium Sulfate System

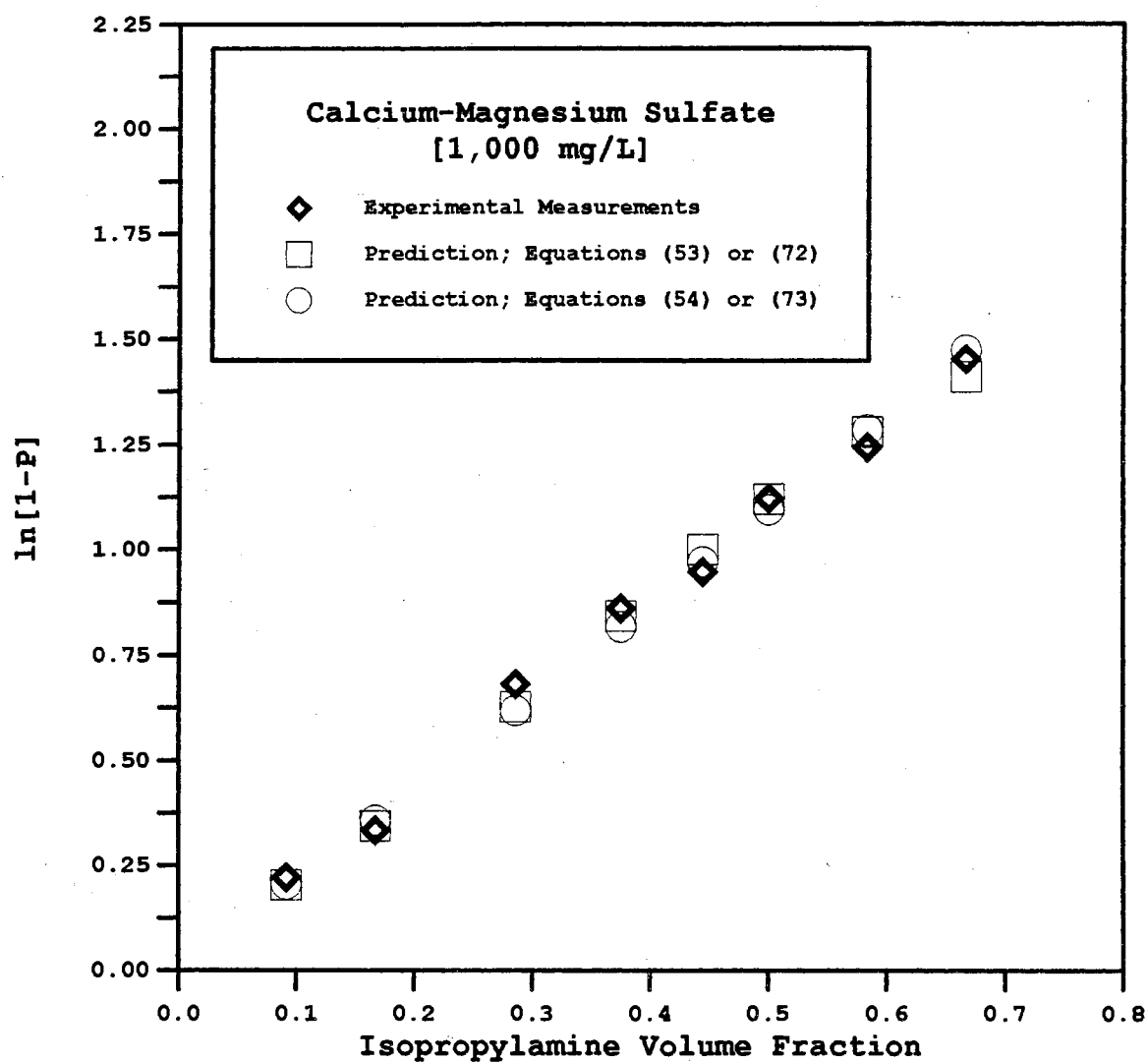


Figure 17. Precipitation of 1,000 mg/L Sulfate Ion from Calcium-Magnesium Sulfate System

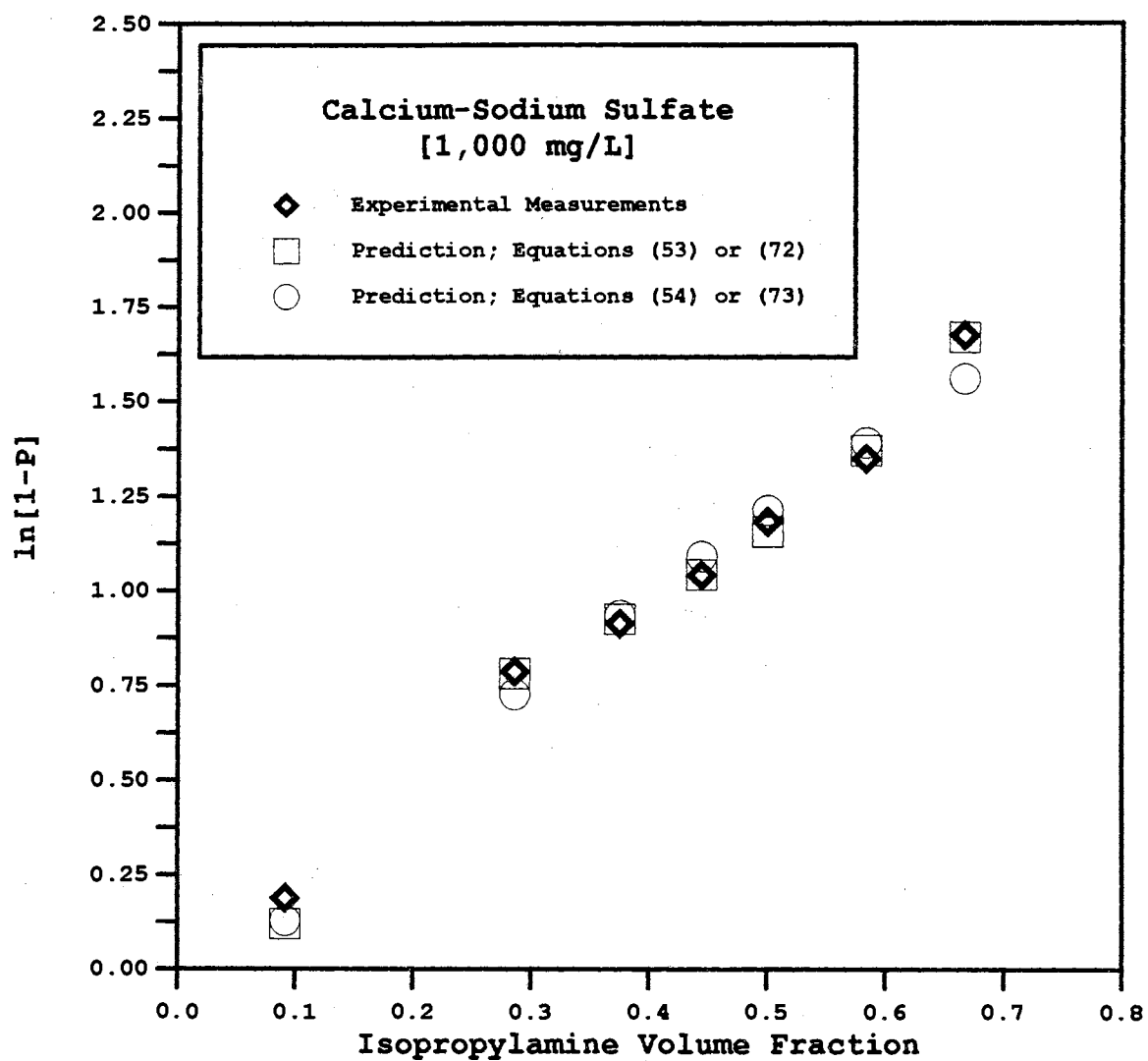


Figure 18. Precipitation of 1,000 mg/L Sulfate Ion from Calcium-Sodium Sulfate System

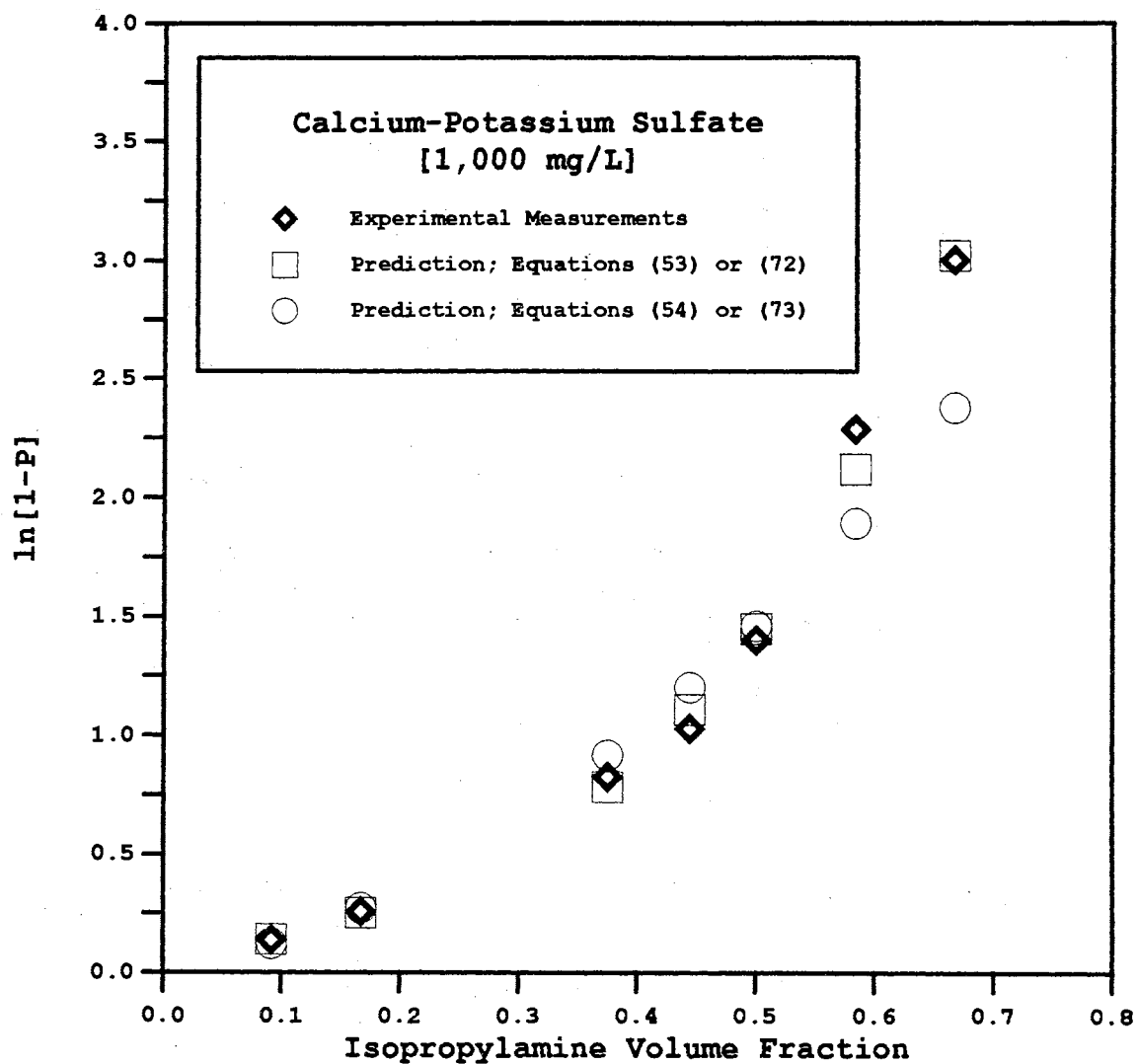


Figure 19. Precipitation of 1,000 mg/L Sulfate Ion from Calcium-Potassium Sulfate System

These figures exhibit plots of the left-hand side of these equations versus the isopropylamine salt-free volume fraction (θ_3). Without the addition of isopropylamine, the left-hand side of these equations is zero since there is no precipitation ($P = 0$). However, without the use of the solvent-solvent interaction parameters (Λ_{32} and/or Λ_{23}), the precipitation measurements can be fit with a straight line. This situation is equivalent to the ideal mixture solubility based on Henry's law. To extend the model fitting to the maximum value of θ_3 , the solvent-solvent interaction parameters are needed.

The 3-Suffix equation, Equation (53), with four interaction parameters (including Λ_1) represents the ultimate correlative ability. Such a level of complexity may be excessive since the RMSE for the precipitation measurements using Equation (53) without Λ_1 are mostly within the expected experimental uncertainty in the combined precipitation data sets used. The salt binary-solvent interaction parameter (Λ_1) in Equation (53) is neglected.

As shown in Table 1, Equation (54), the 2-Suffix Equation, with one solvent-solvent interaction parameter (Λ_{32}) provides acceptable predictions over the entire range of θ_3 . As given in Table 2, however, substantial improvements in the predictive ability were achieved when the two solvent-solvent interaction parameters were employed by Equation (53), the 3-Suffix Equation (e.g., for magnesium chloride system at 5,000 mg/L; Equation (54): RMSE = 0.0479, %AAD = 6.65; Equation (53): RMSE = 0.0129, %AAD = 2.07). Such improvements were attributed to the unsymmetric solvent-solvent interaction parameters with respect to θ_3 . The combination of these two solvent-solvent interaction parameters (Λ_{32} and Λ_{23}) in Equation (53) provides good predictions of the

TABLE 1

THE 2-SUFFIX EQUATION (EQUATION 54) REPRESENTATION OF THE TESTED SYSTEMS

System	Model's Parameters		RMSE	%AAD	NP
	C ₁	C ₂			
-----Chloride Salts at 5,000 mg/L-----					
Magnesium	-1.0561	-1.8747	0.0479	6.65	8
Magnesium-Sodium	-1.1476	-0.4333	0.0545	8.22	8
Magnesium-Potassium	-1.1674	-0.0054	0.0517	8.19	8
Calcium	-1.0619	-1.7106	0.0559	8.20	8
Calcium-Sodium	-1.0386	-2.1482	0.0551	8.87	8
Calcium-Potassium	-1.0357	-2.1331	0.0549	8.48	8
Calcium-Magnesium	-1.0911	-1.4655	0.0564	8.29	8
Calcium-Barium	-1.0834	-1.3221	0.0539	8.74	8
Calcium-Strontium	-1.0279	-1.9949	0.0566	9.12	8
-----Chloride Salts at 10,000 mg/L-----					
Magnesium	-1.1179	-0.6211	0.0533	8.10	8
Magnesium-Sodium	-1.1211	-0.4171	0.0423	5.72	8
Magnesium-Potassium	-1.1033	-1.1037	0.0448	6.93	8
Calcium	-1.1015	-0.7582	0.0488	6.97	8
Calcium-Sodium	-1.1148	-1.0236	0.0429	7.36	8
-----Sulfate Salts at 1,000 mg/L-----					
Calcium	-6.5038	5.8016	0.1264	3.90	8
Magnesium	-1.4701	1.1334	0.0289	6.47	8
Calcium-Magnesium	-2.2507	0.2566	0.0372	4.47	8
Calcium-Sodium	-2.1647	-1.1747	0.0616	4.58	7
Calcium-Potassium	-4.5601	7.8052	0.3085	10.02	7

$$c_1 = \ln \left[\frac{x_{1,3}}{x_{1,2}} \right]; c_2 = \Lambda_{32}$$

TABLE 2

THE 3-SUFFIX EQUATION (EQUATION 53) REPRESENTATION OF THE TESTED SYSTEMS

System	Model's Parameters			RMSE	%AAD	NP
	C ₁	C ₂	C ₃			
-----Chloride Salts at 5,000 mg/L-----						
Magnesium	-2.3042	2.5413	3.5875	0.0129	2.07	8
Magnesium-Sodium	-2.7322	5.2114	4.9460	0.0123	2.19	8
Magnesium-Potassium	-2.5727	5.1708	4.4624	0.0180	3.18	8
Calcium	-2.6175	3.7341	4.5919	0.0096	1.53	8
Calcium-Sodium	-2.7405	3.5254	4.9728	0.0172	2.17	8
Calcium-Potassium	-2.7263	3.4764	4.9418	0.0186	3.23	8
Calcium-Magnesium	-2.7404	4.2334	4.9415	0.0158	2.30	8
Calcium-Barium	-2.7466	4.3612	5.0166	0.0180	2.55	8
Calcium-Strontium	-2.6893	3.6870	4.8689	0.0100	1.67	8
-----Chloride Salts at 10,000 mg/L-----						
Magnesium	-2.5388	4.5891	4.3836	0.0078	1.34	8
Magnesium-Sodium	-2.1536	3.4519	3.1999	0.0124	2.17	8
Magnesium-Potassium	-2.2357	3.0572	3.3753	0.0090	1.72	8
Calcium	-2.3912	3.9640	3.9432	0.0048	0.87	8
Calcium-Sodium	-2.2308	3.0538	3.3416	0.0138	2.44	8
-----Sulfate Salts at 1,000 mg/L-----						
Calcium	-8.1855	8.0337	2.8621	0.0758	3.15	8
Magnesium	-2.3699	2.2162	1.1202	0.0264	4.18	8
Calcium-Magnesium	-1.4346	-7.4918	-0.7563	0.0368	3.61	8
Calcium-Sodium	-4.2572	-0.7614	1.8197	0.0156	1.08	7
Calcium-Potassium	-9.1327	16.4653	5.8814	0.0507	3.35	7

$$c_1 = \ln \left[\frac{x_{1,3}}{x_{1,2}} \right]; c_2 = \Lambda_{32}; c_3 = \Lambda_{23}$$

precipitation measurements. While both the 2-Suffix and 3-Suffix equations are capable of predicting the solubility phase behavior of salts in mixed-solvents mixtures, the 3-Suffix equation is statistically deemed superior.

Graphical representations of the experimental precipitation fractions at different solvents volume ratio (V_R) along with their error intervals and the predicted precipitation fractions by the optimum predictive equation, Equation (53), are given in Figures A.1 through A.19, Appendix A. These figures demonstrate the ability of Equation (53), the 3-Suffix equation, to accurately predict the precipitation fractions of the studied systems. Detailed tables for each studied system containing the volume fraction of isopropylamine (θ_3), solvents volume ratio (V_R), experimental precipitation fractions along with their uncertainties, and predicted precipitation fractions by both the 2-Suffix and 3-Suffix Equations are presented in Tables B.1 through B.19, Appendix B.

The produced optimum interaction parameters can be used to estimate the precipitation fractions of the studied systems at a higher solvents volume ratio where no experimental data are available (e.g., $V_R = 3.0$ or 4.0 , etc.). This would provide economy of experimental effort, and cost savings (not to waste the organic solvent). A further benefit of the model's interaction parameters is to provide a reasonable estimate for the solubility of the targeted salts in the organic solvent. The estimate of the salt solubility in the organic solvent would facilitate further interpretation to the controlling factors in precipitation phenomenon. Moreover, the solubility of salts in organic solvents is a valuable thermodynamic

property, which is lacking in the literature, and is highly needed in several industrial and engineering applications (e.g., azeotropic distillation, pharmaceutical, etc.).

Since the precipitation fractions of all chloride salts (at 5,000 and 10,000 mg/L) are almost identical, general interaction parameters are regressed using all the chloride systems (14 systems). The general regressed parameters for all chloride using the 3-Suffix equation, the optimum predictive case, along with the statistics are given as follows: $C_1 = -2.0509$; $C_2 = 5.4493$; $C_3 = 3.0554$; $RMSE = 0.0510$; $\%AAD = 12.42$; and $NP = 112$. Such general interaction parameters can be used to estimate: (1) the precipitation fractions of the tested chloride salts by isopropylamine at different concentrations; and (2) the solubilities of the tested chloride salts in isopropylamine.

Table 3 presents the estimated solubilities of chloride salts in isopropylamine. Typically, the solubility of a salt in a simple organic solvent is orders of magnitude less than the salt solubility in water [Thompson and Molstad, 1945]. As shown in Table 3, the solubilities of the chloride salts in isopropylamine are about two orders of magnitude lower than their aqueous solubilities. No experimental data are available to draw a firm conclusion regarding the reliability of the estimated values. However, it seems the model equations are capable of predicting the expected trend and providing acceptable estimates.

Since the precipitation fractions of sulfate salts are appreciably varied over the studied range of solvents volume ratio, the regressed interaction parameters for each sulfate salt (Table 2) are used to estimate its solubility in isopropylamine. Table 4 presents the estimated solubilities of sulfate salts in isopropylamine. Again, no

TABLE 3

ESTIMATION OF THE SOLUBILITY OF THE TESTED CHLORIDE SALTS IN THE
ORGANIC SOLVENT USING THE GENERALIZED INTERACTION PARAMETERS
OF THE 3-SUFFIX EQUATION (EQUATION (53))**

System	In Water		In Isopropylamine
	$x_{1,2}$	C_{12}^*	$x_{1,3}$
Chloride Salts	1.2697E-3	2500	1.6331E-5
	2.5393E-3	5000	3.2661E-4
	5.0786E-3	10000	6.5321E-4

* mg/L

** [$C_1=-2.0509$; $C_2=5.4494$; $C_3=3.0554$; RMSE=0.0510; %AAD=12.42; NP=112]

TABLE 4

ESTIMATION OF THE SOLUBILITY OF THE SULFATE SALTS IN THE
ORGANIC SOLVENT USING THE INTERACTION PARAMETERS OF
THE 3-SUFFIX EQUATION (EQUATION (53))

System	In Water		In Isopropylamine
	$x_{1,2}$	C_{12}^*	$x_{1,3}$
Calcium	1.3208E-4	996.3	3.6806E-8
Magnesium	7.2981E-5	996.6	6.8230E-6
Calcium-Magnesium	9.4507E-5	1001.7	2.2513E-5
Calcium-Sodium	1.3041E-4	1005.0	1.8469E-6
Calcium-Potassium	1.1581E-4	995.9	1.2516E-8

* mg/L

experimental data are available to draw a conclusion regarding the reliability of the estimated values, but it appears that the model equations are able to provide acceptable estimates.

The selection of organic solvent is probably the most important aspect in the precipitation process. As discussed in the Experimental Section, several factors would determine the suitability of the selected solvent. However, the most important one is the solubility of the targeted salt in the selected solvent; the lower the solubility, the higher the precipitation. As shown in Tables 3 and 4, chloride salts are more soluble in isopropylamine than the sulfate salts. This would explain: (1) the relatively low precipitation fractions of the tested chloride salts compared to the sulfate salts; and (2) the precipitation orders of the sulfate salts (except the magnesium sulfate system).

The Power Series Equations (Liquid-Liquid Equilibrium)

A summary of the evaluation results of Equations (72) and (73), applied to the acquired precipitation data is presented in Tables 5 and 6. These Tables include interaction parameters of the model equations, and complete statistics.

The 3-Suffix equation, Equation (53) and the 3-Power equation, Equation (72), contain three interaction parameters, while the 2-Suffix equation, Equation (54), and the 2-Power equation, Equation (73), contain two interaction parameters. From a statistical stand point, the prediction abilities of Equations (53) and (72), and Equations (54) and (73) are equivalent, but with different interaction parameters.

Equation (73), with two interaction parameters, provides an adequate representation to the precipitation measurements. Significant

TABLE 5

THE 2-POWER EQUATION (EQUATION 73) REPRESENTATION OF THE TESTED SYSTEMS

System	Model's Parameters		RMSE	%AAD	NP
	C ₁	C ₂			
-----Chloride Salts at 5,000 mg/L-----					
Magnesium	1.3157	-0.2596	0.0479	6.65	8
Magnesium-Sodium	1.2076	-0.0600	0.0545	8.22	8
Magnesium-Potassium	1.1682	-0.0008	0.0517	8.19	8
Calcium	1.2987	-0.2369	0.0559	8.20	8
Calcium-Sodium	1.3360	-0.2975	0.0551	8.87	8
Calcium-Potassium	1.3311	-0.2954	0.0549	8.48	8
Calcium-Magnesium	1.2940	-0.2029	0.0564	8.29	8
Calcium-Barium	1.2664	-0.1831	0.0539	8.74	8
Calcium-Strontium	1.3041	-0.2762	0.0566	9.12	8
-----Chloride Salts at 10,000 mg/L-----					
Magnesium	1.2039	-0.0860	0.0533	8.10	8
Magnesium-Sodium	1.1788	-0.0578	0.0423	5.72	8
Magnesium-Potassium	1.2561	-0.1528	0.0448	6.93	8
Calcium	1.2064	-0.1050	0.0488	6.97	8
Calcium-Sodium	1.2566	-0.1417	0.0429	7.36	8
-----Sulfate Salts at 1,000 mg/L-----					
Calcium	3.8979	2.6060	0.1264	3.90	8
Magnesium	0.9610	0.5091	0.0289	6.47	8
Calcium-Magnesium	2.1355	0.1153	0.0372	4.47	8
Calcium-Sodium	2.6923	-0.5276	0.0616	4.58	7
Calcium-Potassium	1.0542	3.5060	0.3085	10.02	7

$$C_1 = \Lambda_{10}; C_2 = \Lambda_{20}$$

TABLE 6

THE 3-POWER EQUATION (EQUATION 72) REPRESENTATION OF THE TESTED SYSTEMS

System	Model's Parameters			RMSE	%AAD	NP
	C ₁	C ₂	C ₃			
-----Chloride Salts at 5,000 mg/L-----						
Magnesium	1.9523	-3.6732	4.0251	0.0129	2.07	8
Magnesium-Sodium	2.0106	-4.3547	5.0763	0.0123	2.19	8
Magnesium-Potassium	1.8567	-3.7341	4.4500	0.0180	3.18	8
Calcium	2.1005	-4.5016	5.0187	0.0096	1.53	8
Calcium-Sodium	2.2524	-5.0903	5.5785	0.0172	2.17	8
Calcium-Potassium	2.2449	-5.0699	5.5512	0.0186	3.23	8
Calcium-Magnesium	2.1543	-4.7550	5.3411	0.0158	2.30	8
Calcium-Barium	2.1427	-4.8009	5.4048	0.0180	2.55	8
Calcium-Strontium	2.1788	-4.8864	5.3969	0.0100	1.67	8
-----Chloride Salts at 10,000 mg/L-----						
Magnesium	1.9034	-3.8719	4.5074	0.0078	1.34	8
Magnesium-Sodium	1.6756	-2.7841	3.2621	0.0124	2.17	8
Magnesium-Potassium	1.8123	-3.1792	3.6025	0.0090	1.72	8
Calcium	1.8423	-3.5510	4.0999	0.0048	0.87	8
Calcium-Sodium	1.8079	-3.1361	3.5589	0.0138	2.44	8
-----Sulfate Salts at 1,000 mg/L-----						
Calcium	4.5769	-1.4125	5.0211	0.0758	3.15	8
Magnesium	1.3745	-1.8036	2.7991	0.0264	4.18	8
Calcium-Magnesium	1.7711	2.2245	-2.5610	0.0368	3.61	8
Calcium-Sodium	4.4711	-8.4226	8.2088	0.0156	1.08	7
Calcium-Potassium	1.7368	-2.9610	10.3569	0.0507	3.35	7

$$C_1 = \Lambda_{10}; C_2 = \Lambda_{20}; C_3 = \Lambda_{30}$$

improvements were achieved when Equation (72), with three interaction parameters, was used (e.g., for magnesium chloride system at 5,000 mg/L; Equation (73): RMSE = 0.0479, %AAD = 6.65; Equation (72): RMSE = 0.0129, %AAD = 2.07). Such improvements were attributed to the unsymmetric form of Equation (72) with respect to θ_3 . Figures 1 through 19 illustrate the prediction abilities of Equations (72) and (73) in representing the precipitation measurements. These figures show plots of the left-hand side of Equations (72) and (73), $\ln[1-P]$, versus θ_3 .

Comparisons of the experimental precipitation fractions at different solvents volume ratio (V_R) along with their uncertainties and the predicted precipitation fractions by the optimum predictive equation, Equation (72), are given in Figures A.1 through A.19, Appendix A. Such comparisons indicate that the precipitation fractions are predicted accurately by Equation (72), the optimum predictive equation. Detailed tables for each studied system containing the volume fraction of isopropylamine (θ_3), the solvents volume ratio (V_R), the experimental precipitation fractions along with their uncertainties, and the predicted precipitation fractions by both Equations (72) and (73) are presented in Tables B.1 through B.19, Appendix B.

The resultant interaction parameters can be employed to estimate the precipitation fractions of the studied systems at different isopropylamine volumes when no experimental data are available. In the case of chloride salts, where the precipitation fractions are almost the same, general interaction parameters are regressed using all the chloride systems (14 systems). The general regressed parameters for all chloride systems using the optimum predictive equation, Equation (72), along with the statistics are given as follows: $C_1 = 1.2963$;

$C_2 = -1.7638$; $C_3 = 2.5183$; $RMSE = 0.0510$; $\%AAD = 12.42$; and $NP = 112$.

Such generalized interaction parameters can be employed to estimate the precipitation fractions of the tested chloride salts by isopropylamine at different concentrations.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

Conclusions

Two rigorous frameworks derived from thermodynamic principles of solid-liquid and liquid-liquid equilibrium criteria were developed to correlate and predict the precipitation measurements. In the solid-liquid equilibrium framework, the Henry's constant (dilute activity coefficient) of a given salt in a mixed-solvents mixture was related to the Henry's constants of such a salt in each of the pure solvents (miscible organic and water) using the excess Henry's constant approach. The Wohl's expansion was then employed to model the excess Gibbs free energy function. The framework provided two creditable model equations; the 2-Suffix equation with two interaction parameters (Equation (54)), and the 3-Suffix equation with three interaction parameters (Equation (53)).

In the liquid-liquid equilibrium framework, the activity coefficient of a given salt in a mixed-solvent mixture was related to the activity coefficient of such a salt in the reference solvent (water). The power series function was employed to express the activity coefficients. Two model equations were provided by the framework; the 2-Power equation with two interaction parameters (Equation (72)), and the 3-Power equation with three interaction parameters (Equation (73)).

The acquired precipitation database in the experimental section was used to evaluate the predictive capability of the frameworks equations. The precipitation measurements were adequately predicted by the two interaction parameters equations; Equation (54) and Equation (73). However, Equation (53) and Equation (72), with three interaction parameters, were more accurate in representing the precipitation measurements than Equations (54) or (73).

Optimum interaction parameters were provided by the frameworks equations. For both frameworks equations, the interaction parameters can be used predictive tools to estimate the precipitation fractions for the tested systems for which no experimental data are available. The distinct feature of the model equations based on the solid-liquid equilibrium is the abilities of Equations (53) and (54) to estimate the solubilities of the tested salts in the organic solvent (isopropylamine). As such, Equations (53) and (54) are conceptually superior compared to Equations (72) and (73). Such a superiority is attributed, in part, to the theoretical significance of the interaction parameters.

Recommendations

Based on this study, the following recommendations may be made. First, although the four model equations developed in this section are sufficient for most, if not all correlation purposes of the precipitation measurements, a more fundamental work is needed. Future fundamental work should take into account the complexity of the presence of inorganic species in organic-aqueous systems. This would include

phenomenon interactions such as solvent-solvent interactions, inorganic-inorganic interactions (e.g., long-range electrostatic interactions between ions, and the association between cations and anions), and inorganic-solvent interactions (e.g., solvation or hydration of ions).

Second, to study these complex interactions and provide a more fundamentally-sound theory or framework, advanced phase equilibrium precipitation measurements are needed. This would require a new design of equilibrium precipitation apparatus. Such an apparatus should meet the following requirements: (1) a visual equilibrium precipitation cell should be used to permit observation of the equilibrating solution; (2) properties such as a system's pH, temperature, pressure, and composition of coexisting phases (solid-vapor-liquid) should be measured simultaneously and on line to determine the required thermodynamic properties (e.g., Henry's constants, dilute activity coefficients, and solubilities); (3) samples transfer from the precipitation equilibrium cell into the Ion and Gas Chromatographs must be simple and reproducible; (4) accurate composition measurements should be carried quantitatively in the dilute region; and (5) phase equilibrium should be attained within a reasonable time. The proven dilute vapor-liquid equilibrium apparatus developed and evaluated by Bader [1993c; 1996a], with some modification, should deem effective in serving these requirements.

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APPENDIX A

GRAPHICAL REPRESENTATION OF THE EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS

This appendix contains graphical representations of the experimental precipitation fractions at different solvents volume ratio (V_R) along with their error intervals and the predicted precipitation fractions by the optimum predictive cases, the 3-Suffix equation, Equation (53), and the 3-Power equation, Equation (72).

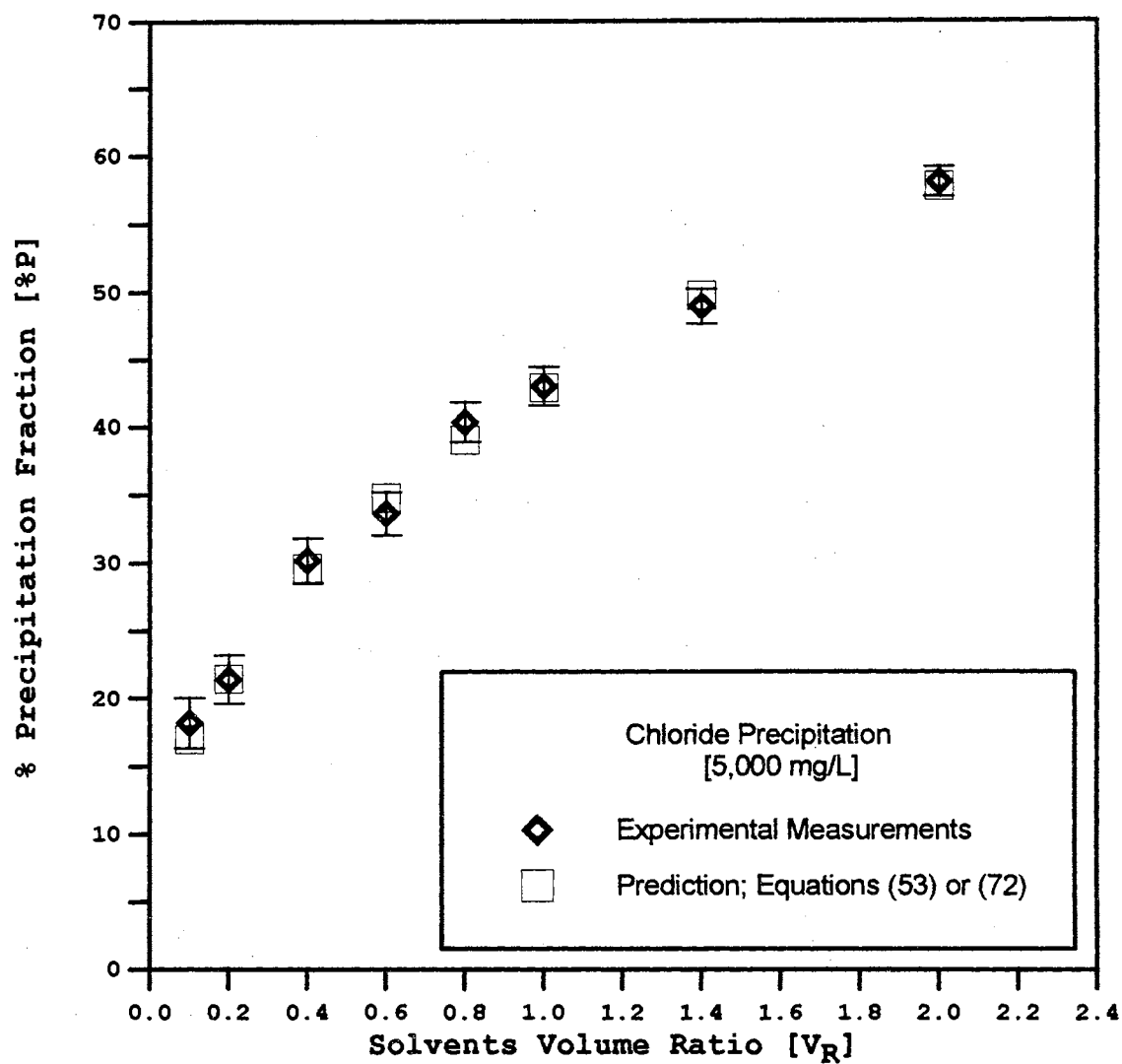


Figure A.1. Precipitation Fraction for Magnesium Chloride System at 5,000 mg/L

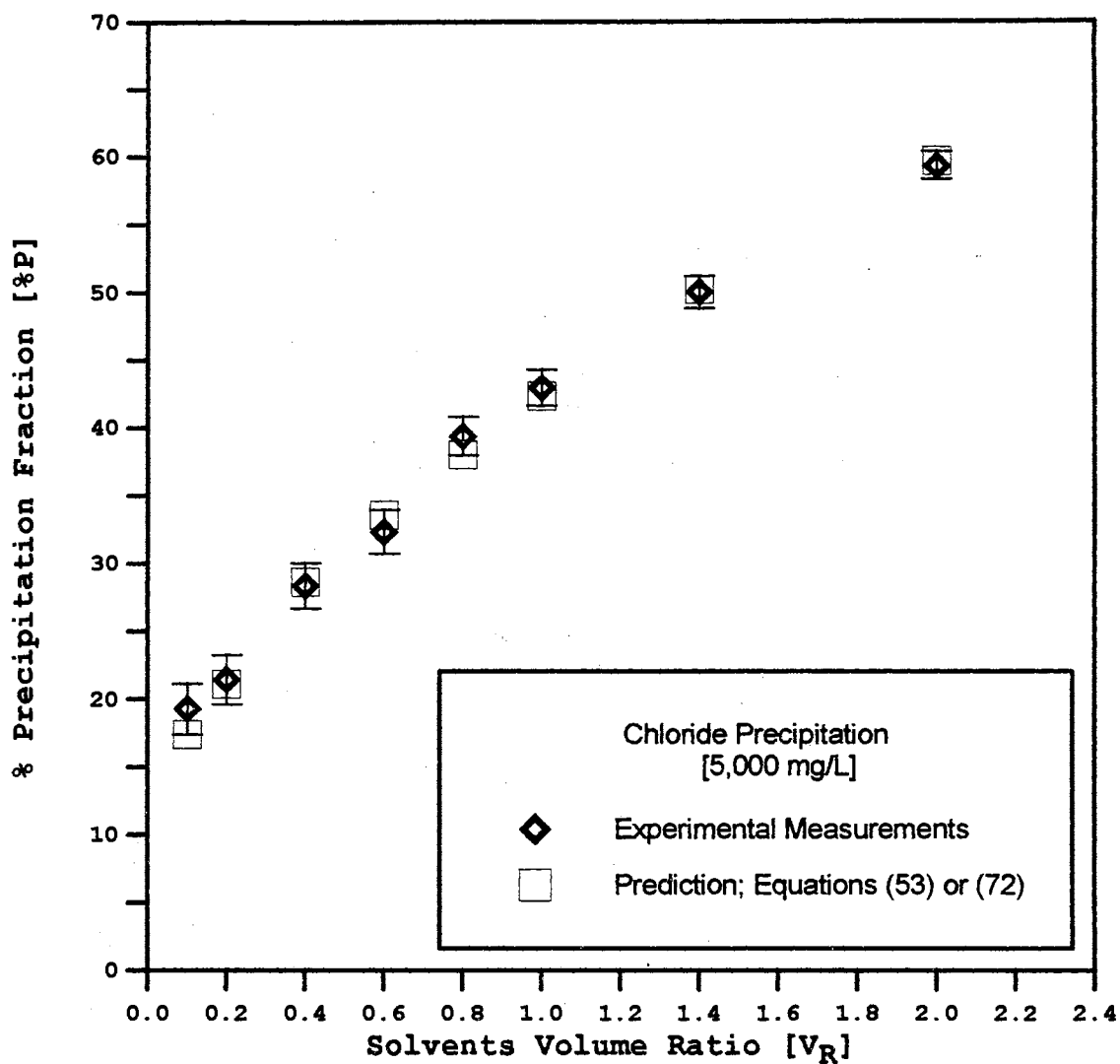


Figure A.2. Precipitation Fraction for Magnesium-Sodium Chloride System at 5,000 mg/L

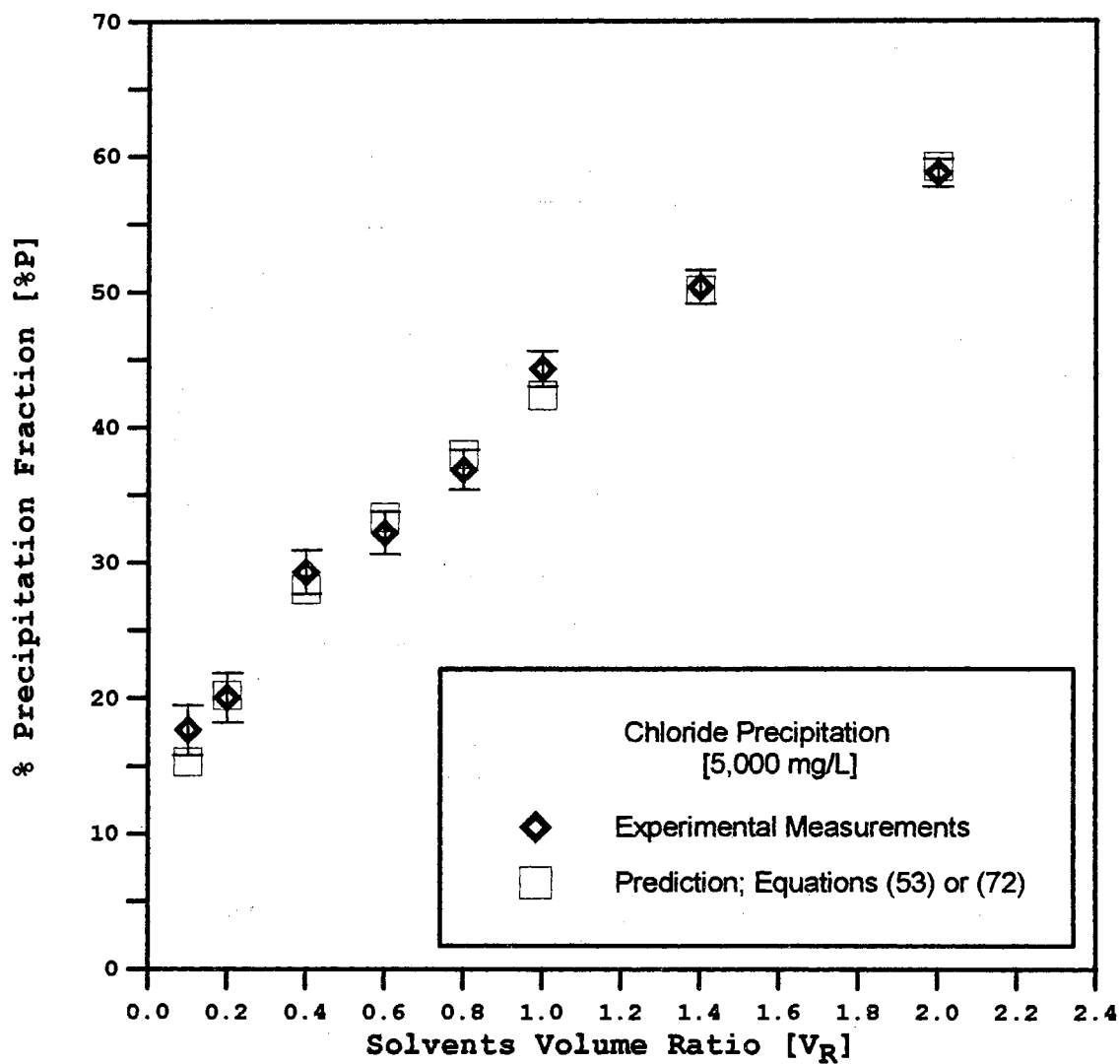


Figure A.3. Precipitation Fraction for Magnesium-Potassium Chloride System at 5,000 mg/L

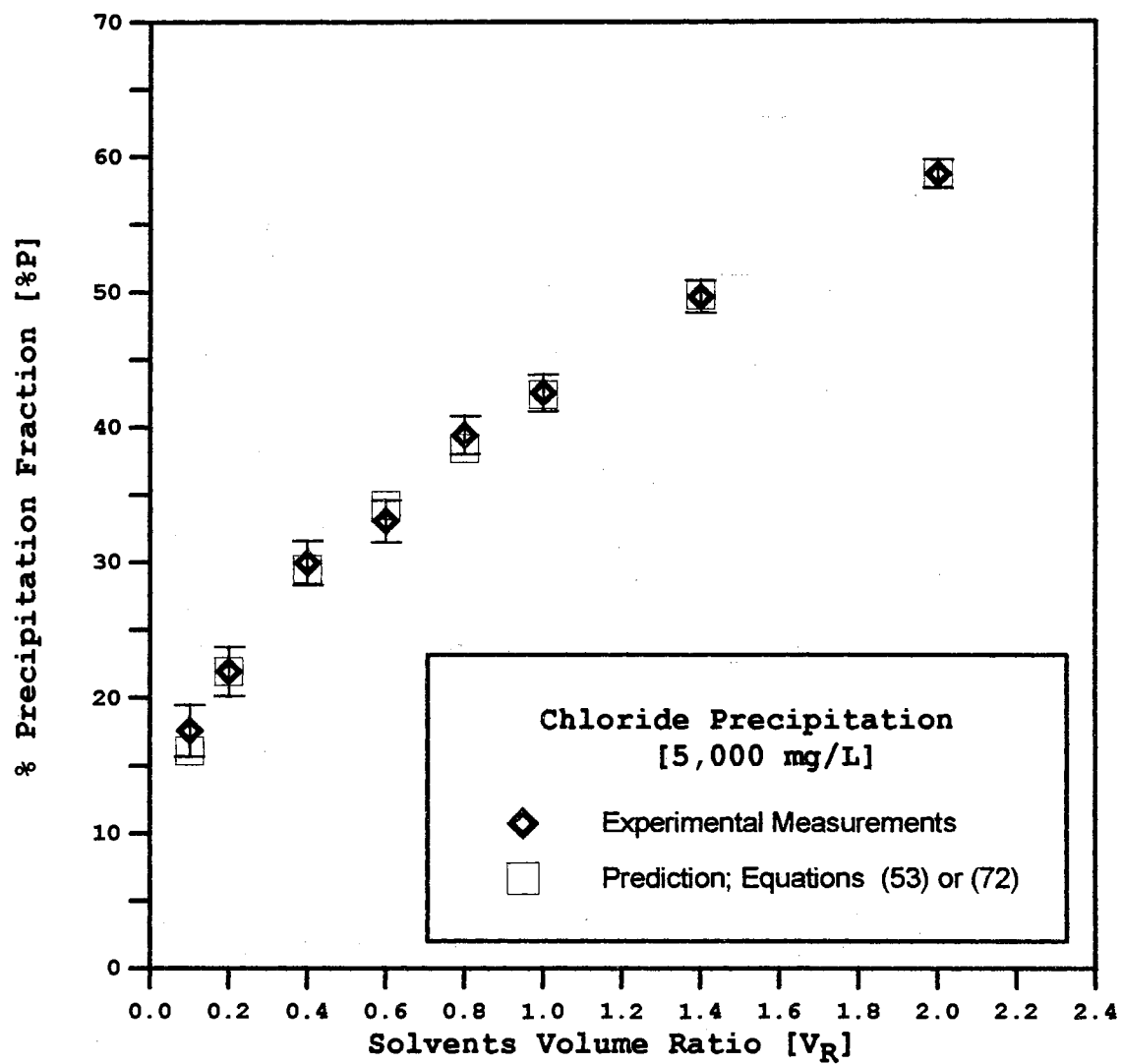


Figure A.4. Precipitation Fraction for Calcium Chloride System at 5,000 mg/L

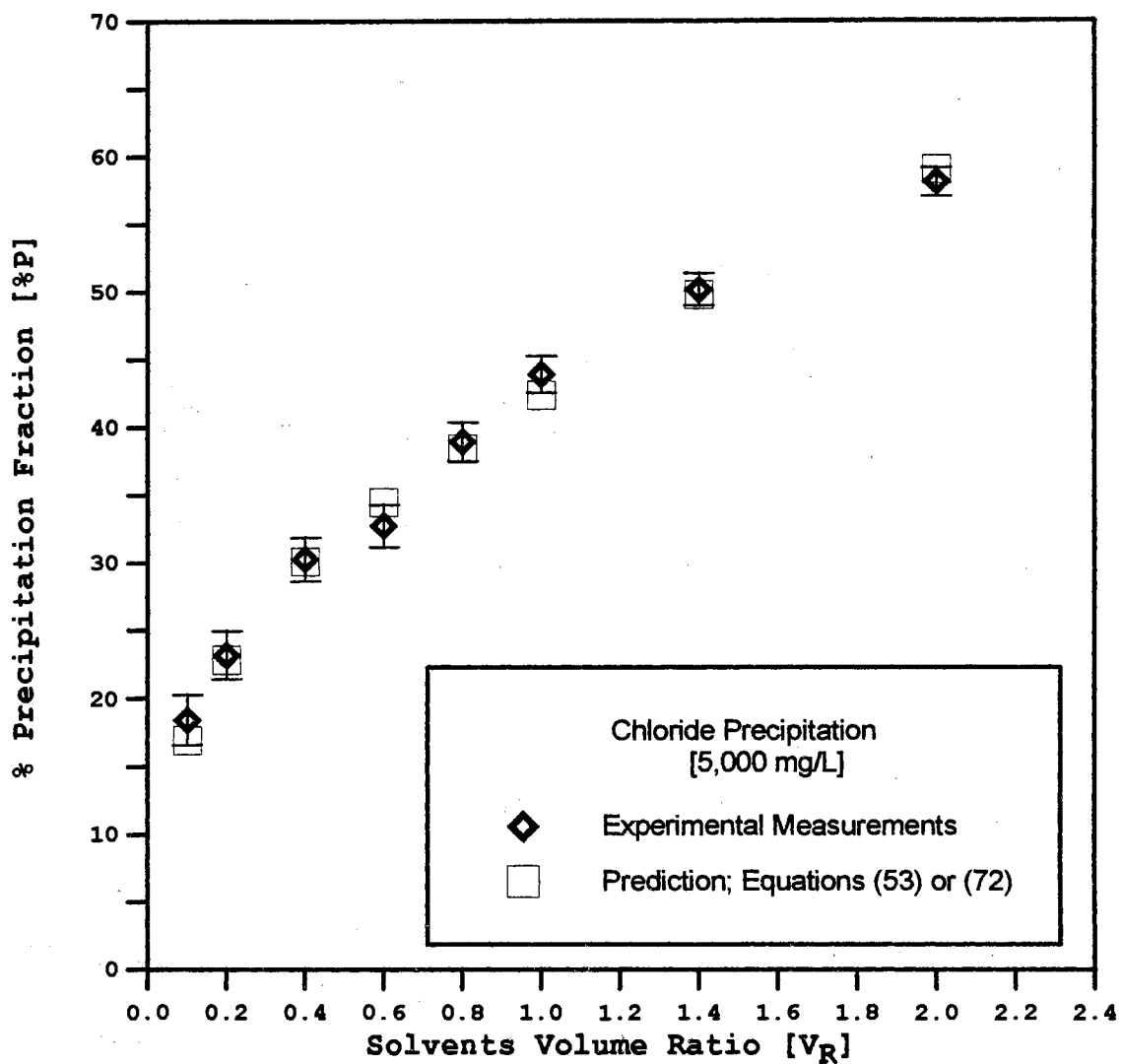


Figure A.5. Precipitation Fraction for Calcium-Sodium Chloride System at 5,000 mg/L

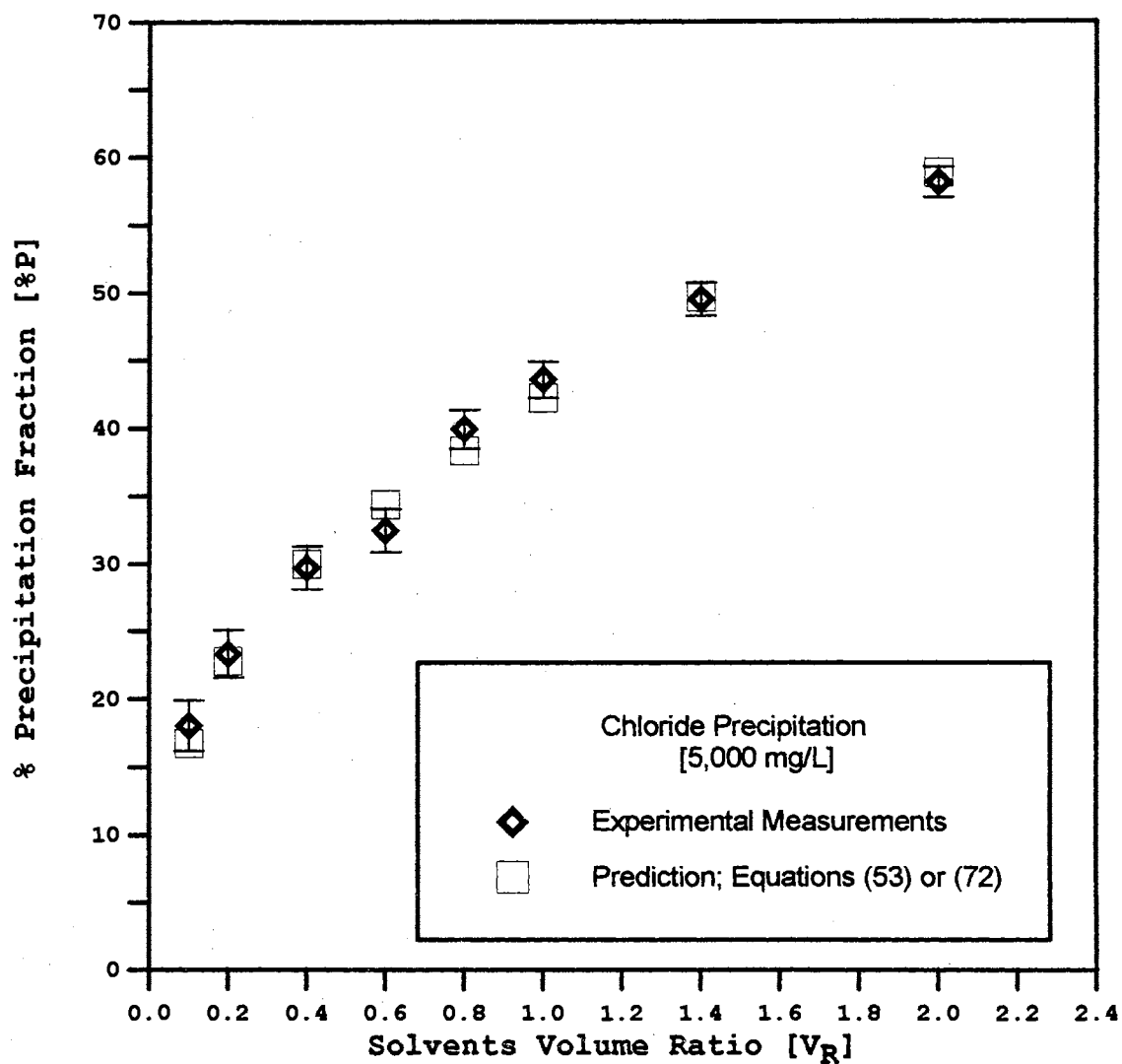


Figure A.6. Precipitation Fraction for Calcium-Potassium Chloride System at 5,000 mg/L

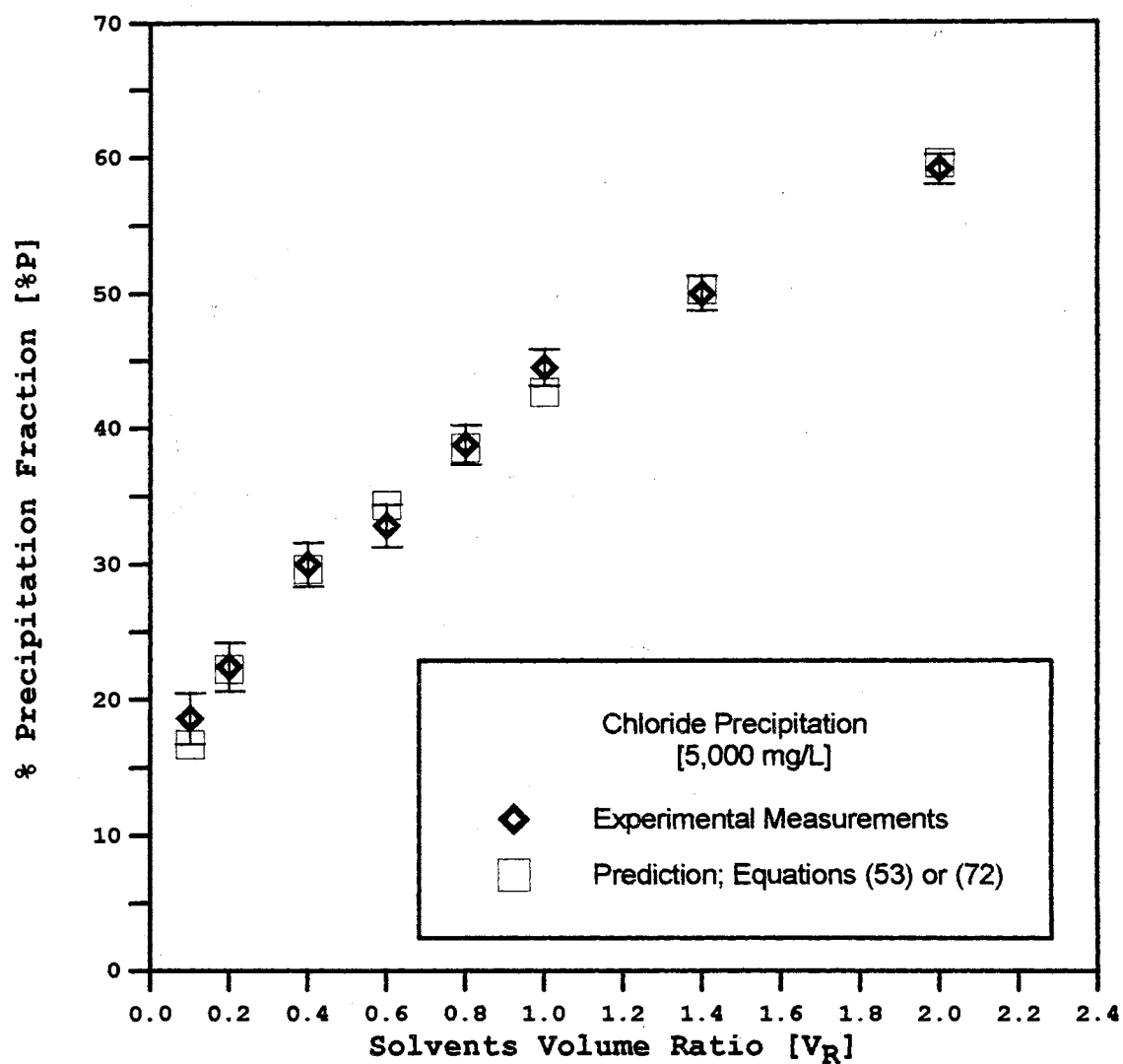


Figure A.7. Precipitation Fraction for Calcium-Magnesium Chloride System at 5,000 mg/L

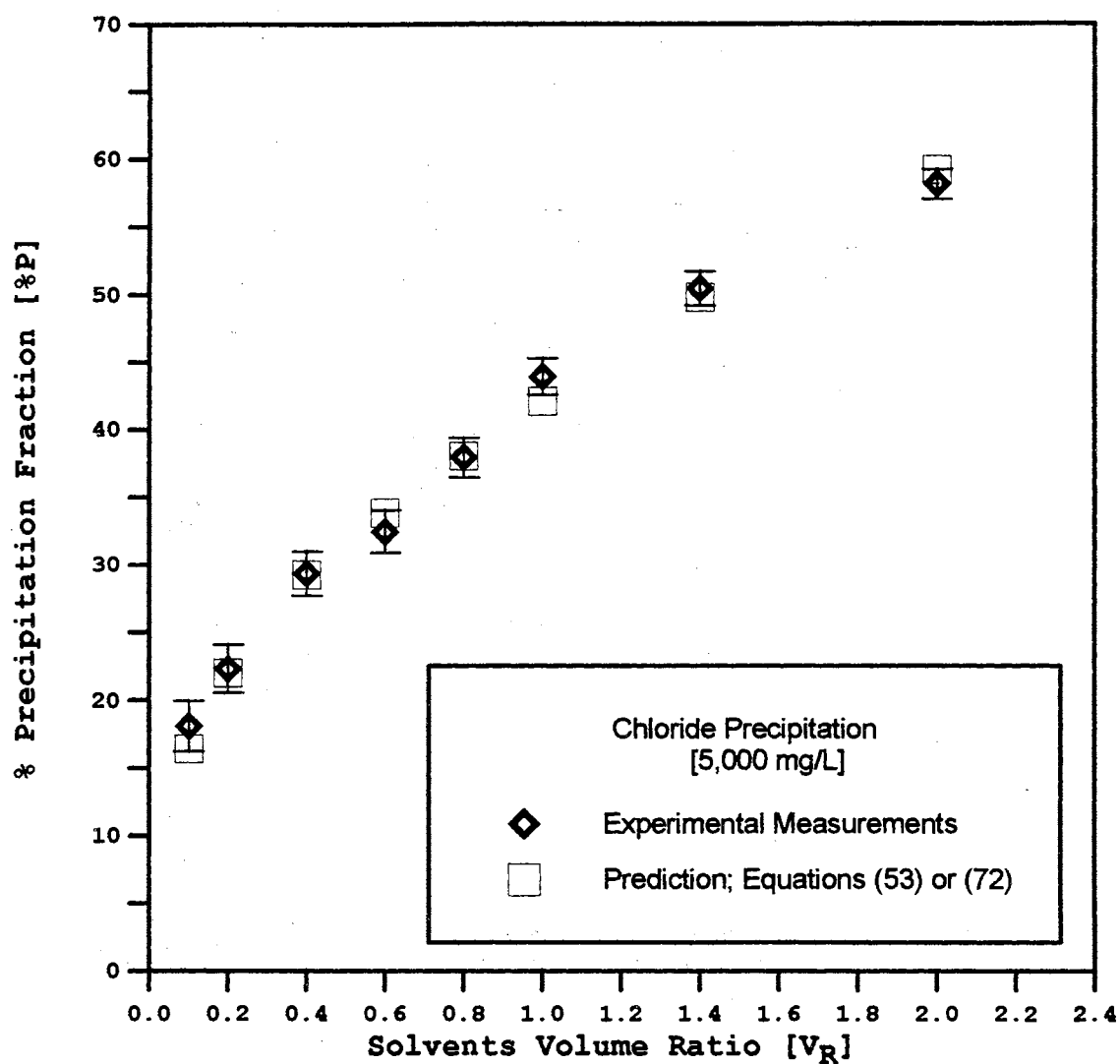


Figure A.8. Precipitation Fraction for Calcium-Barium Chloride System at 5,000 mg/L

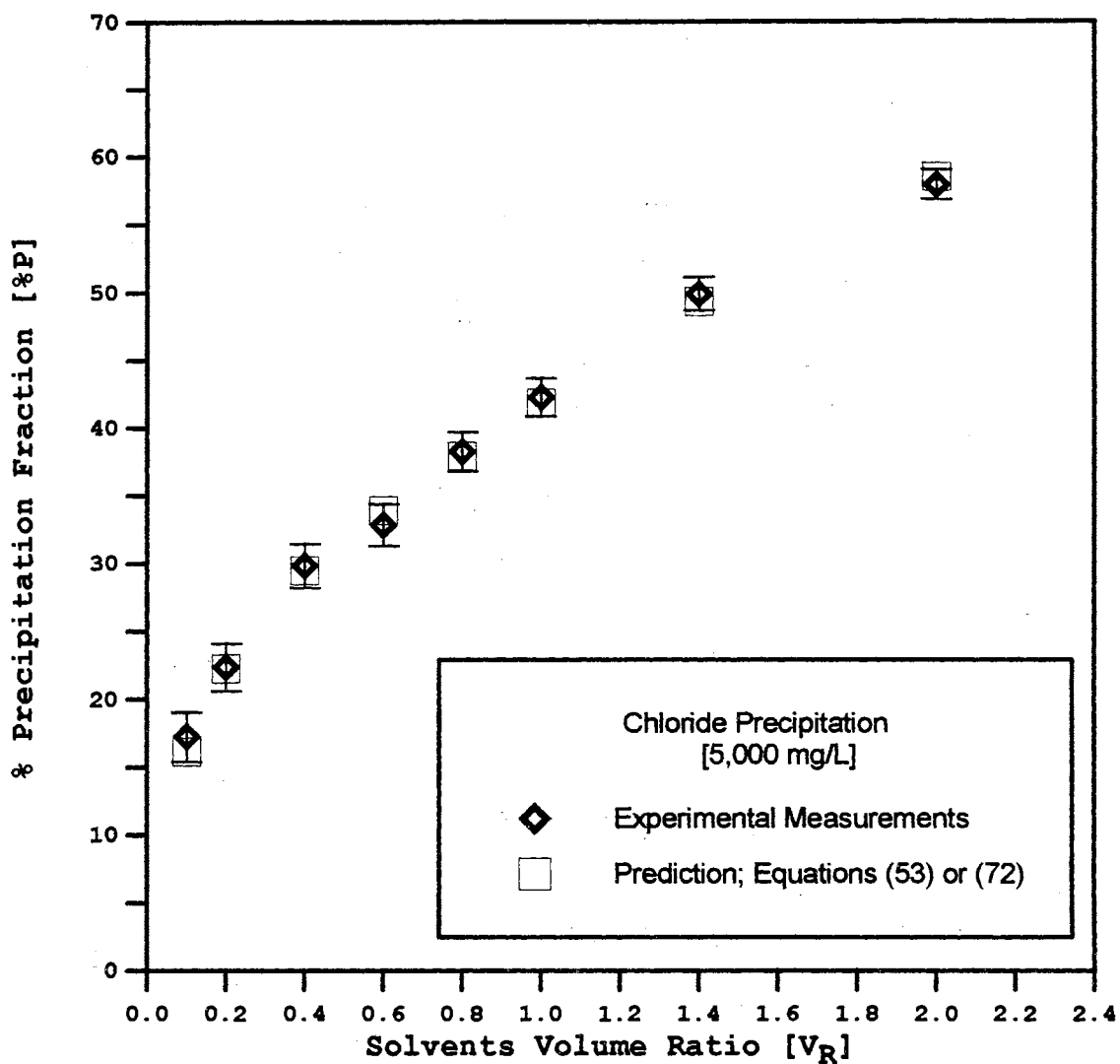


Figure A.9. Precipitation Fraction for Calcium-Strontium Chloride System at 5,000 mg/L

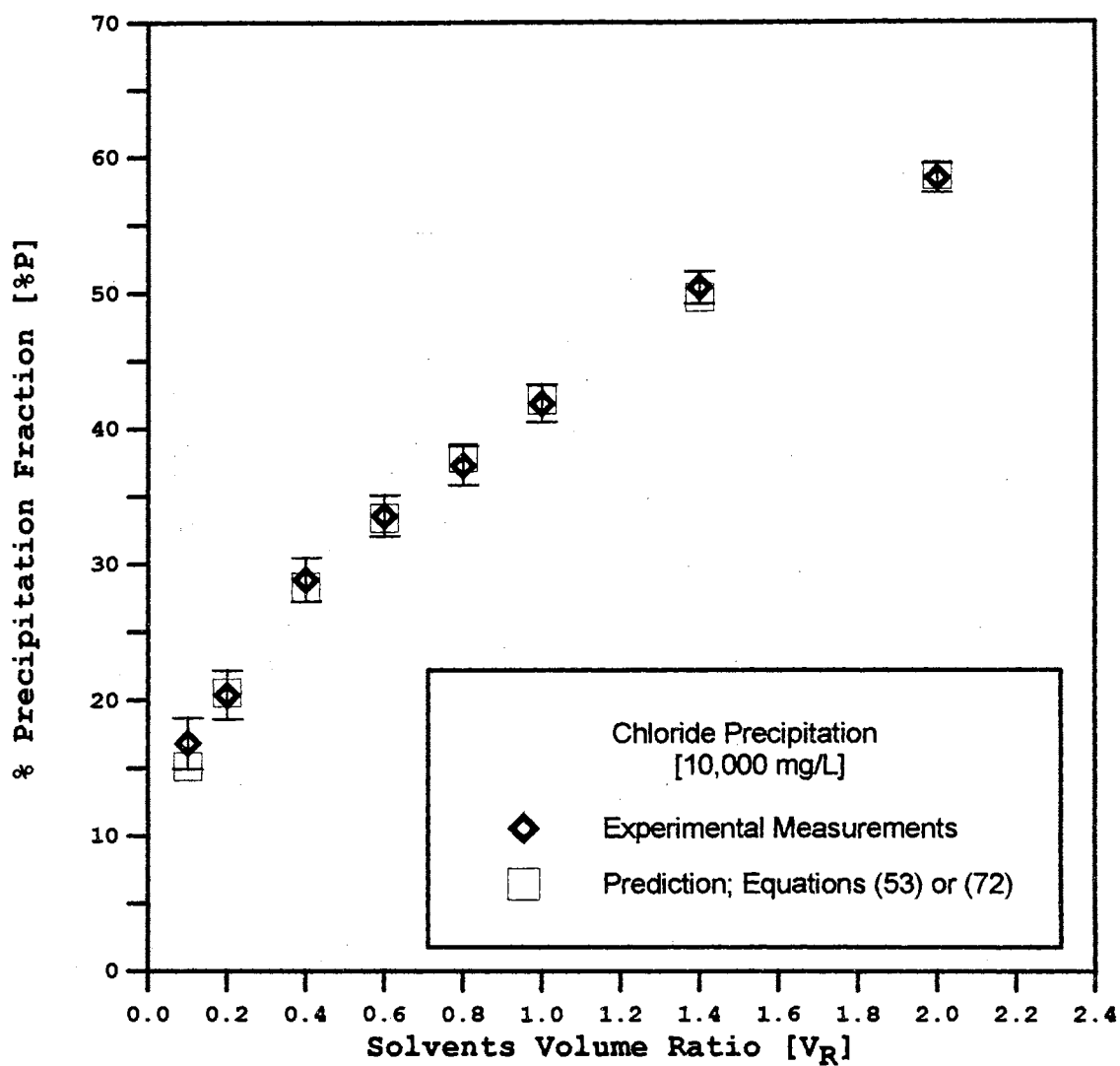


Figure A.10. Precipitation Fraction for Magnesium Chloride System at 10,000 mg/L

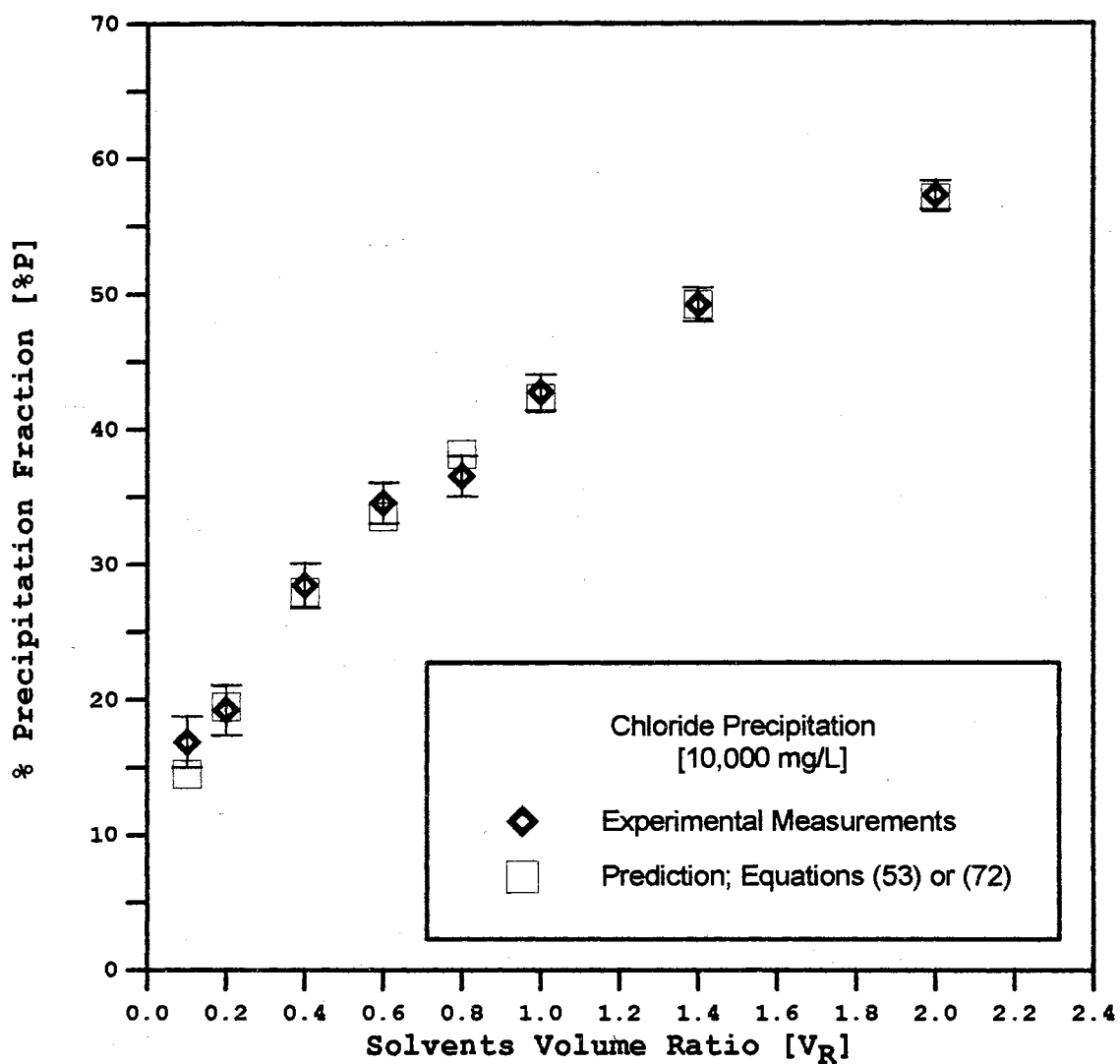


Figure A.11. Precipitation Fraction for Magnesium-Sodium Chloride System at 10,000 mg/L

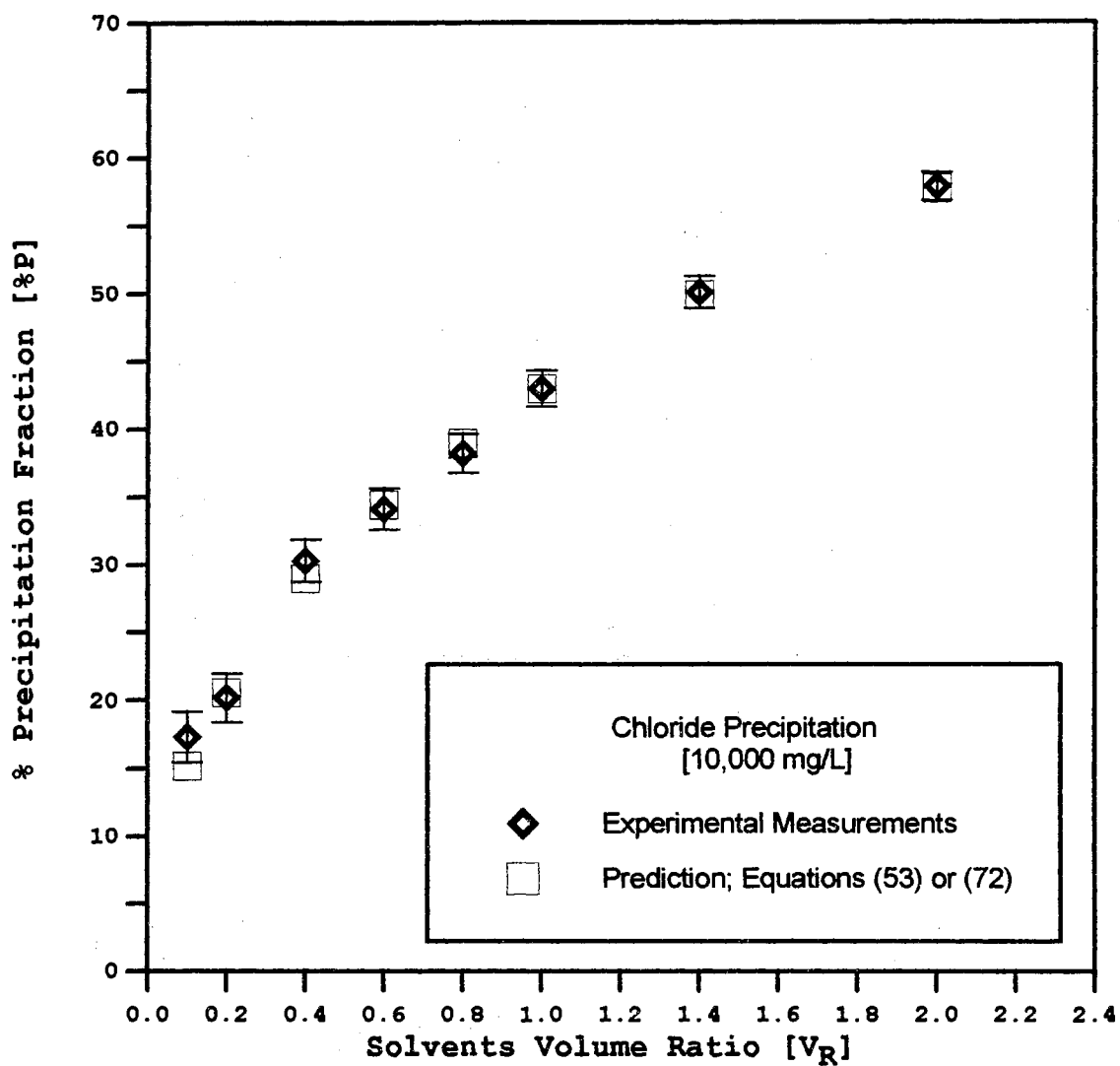


Figure A.12. Precipitation Fraction for Magnesium-Potassium Chloride System at 10,000 mg/L

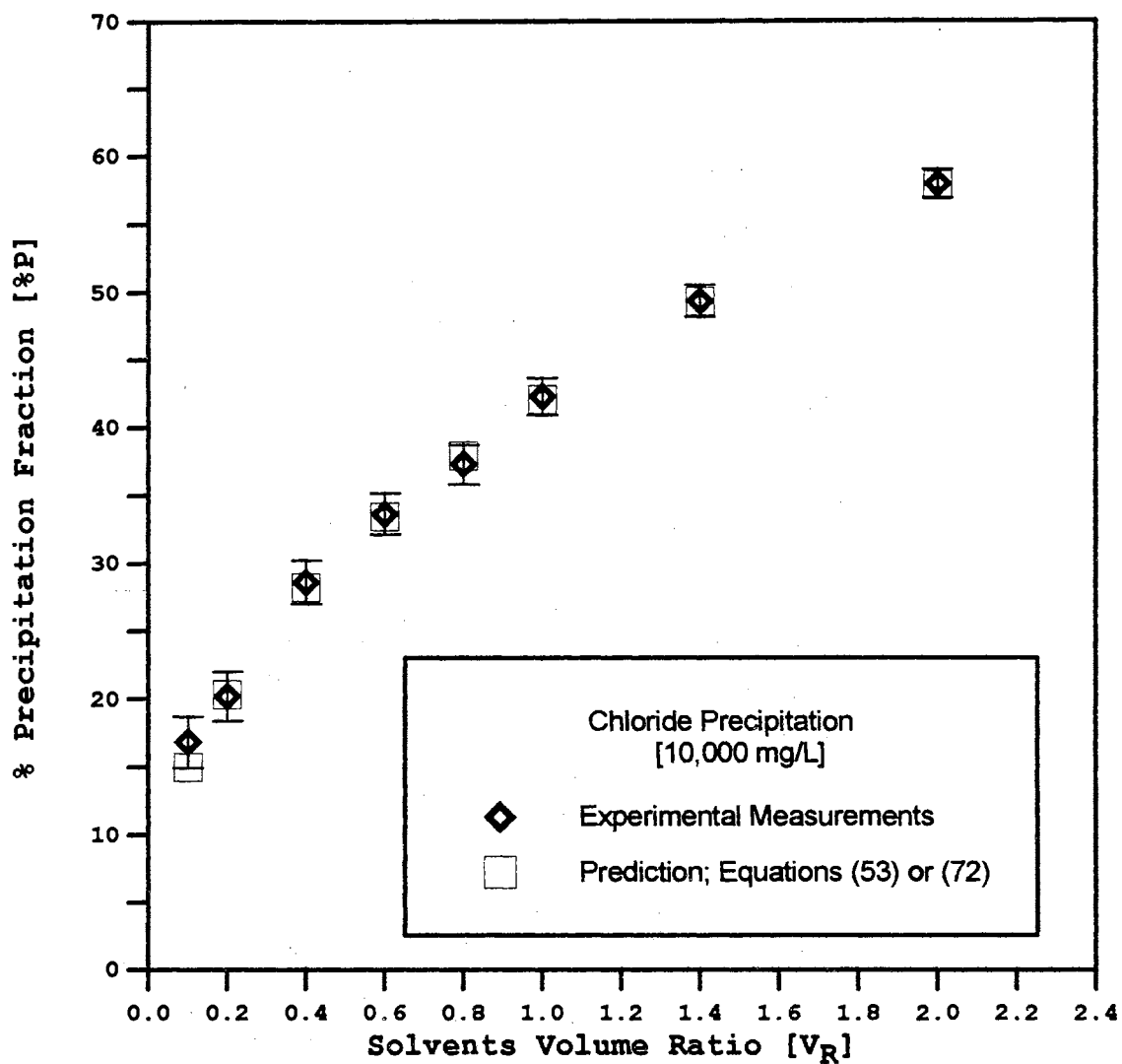


Figure A.13. Precipitation Fraction for Calcium Chloride System at 10,000 mg/L

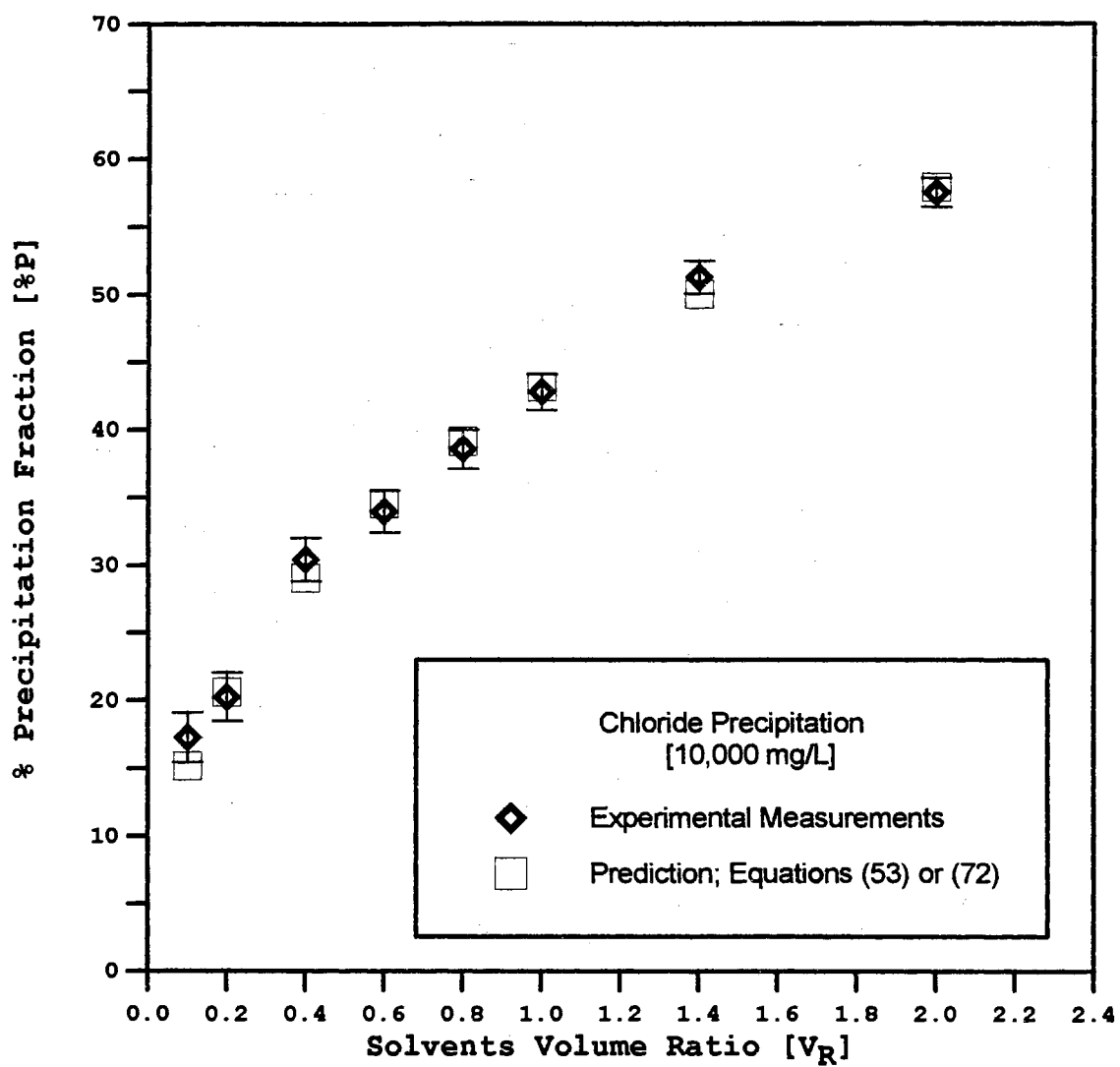


Figure A.14. Precipitation Fraction for Calcium-Sodium Chloride System at 10,000 mg/L

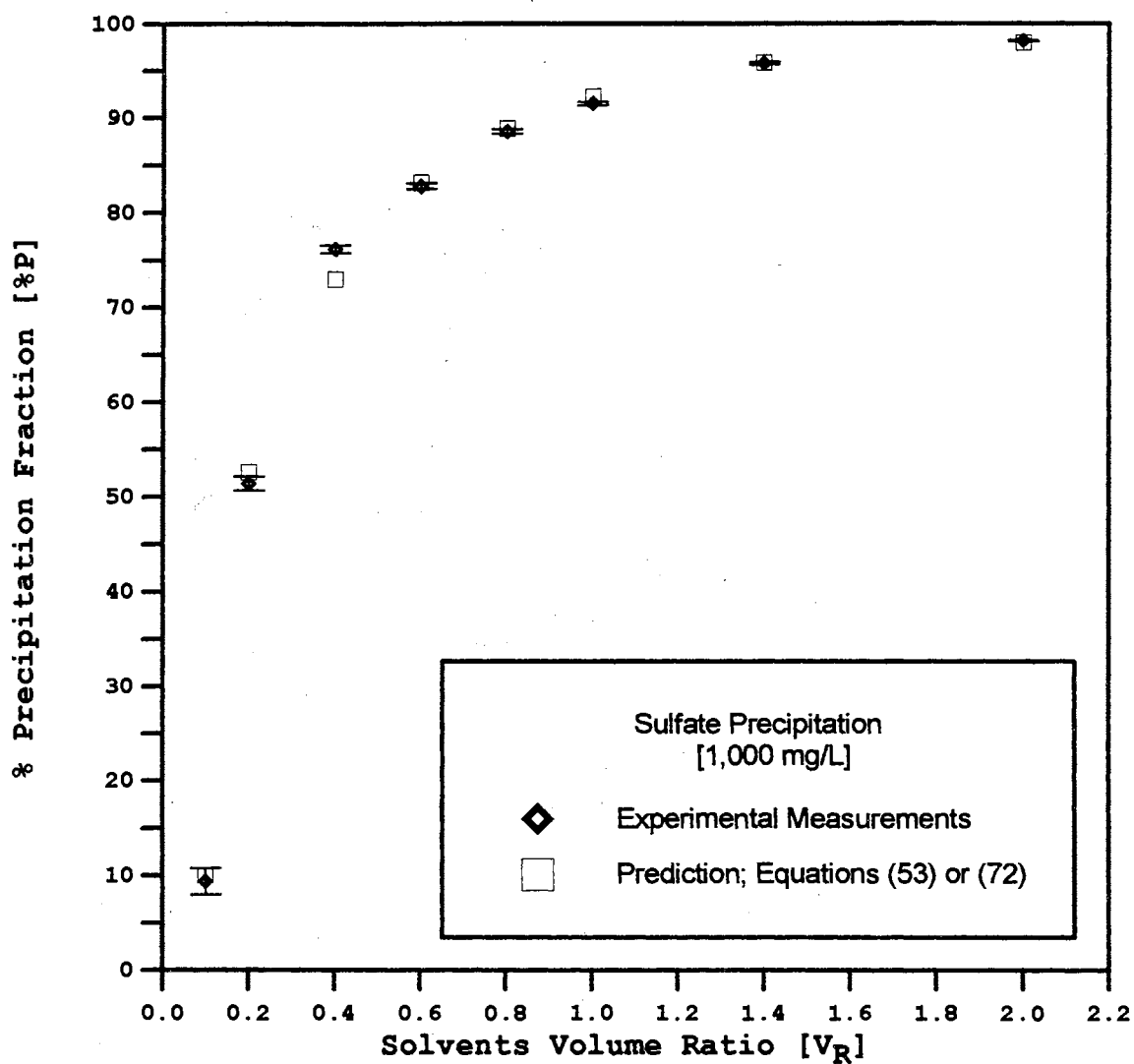


Figure A.15. Precipitation Fraction for Calcium Sulfate System at 1,000 mg/L

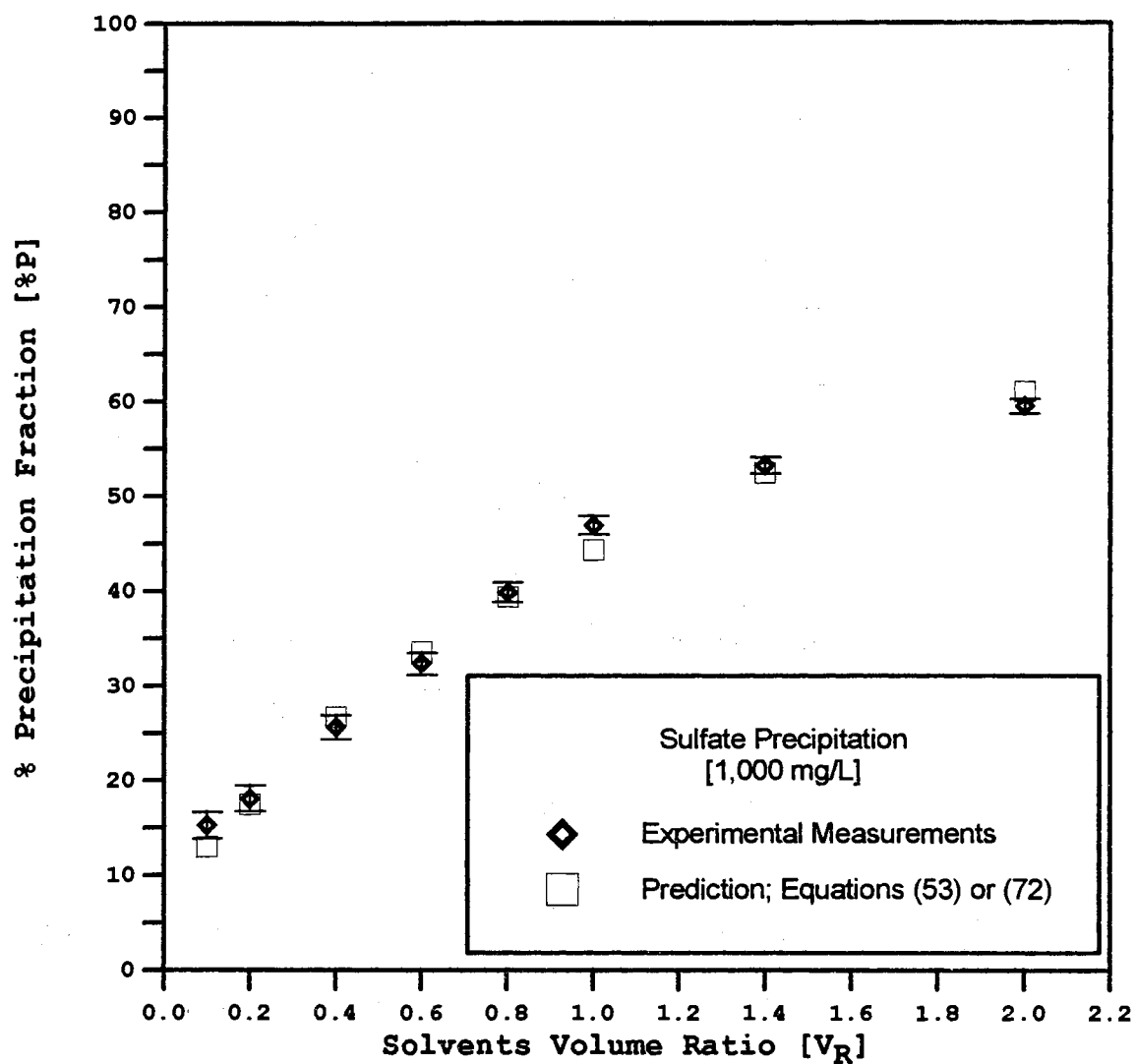


Figure A.16. Precipitation Fraction for Magnesium Sulfate System at 1,000 mg/L

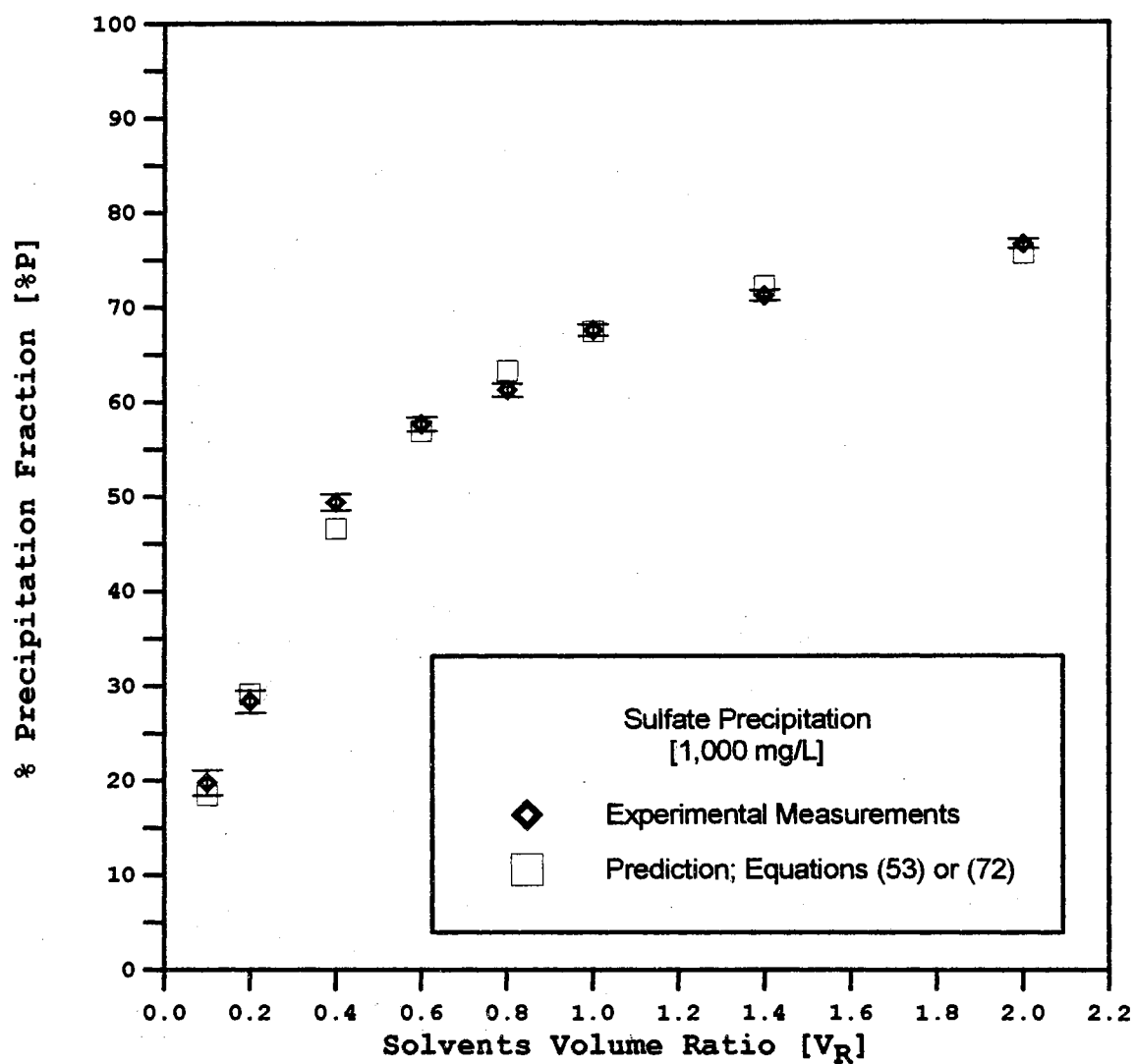


Figure A.17. Precipitation Fraction for Calcium-Magnesium Sulfate System at 1,000 mg/L

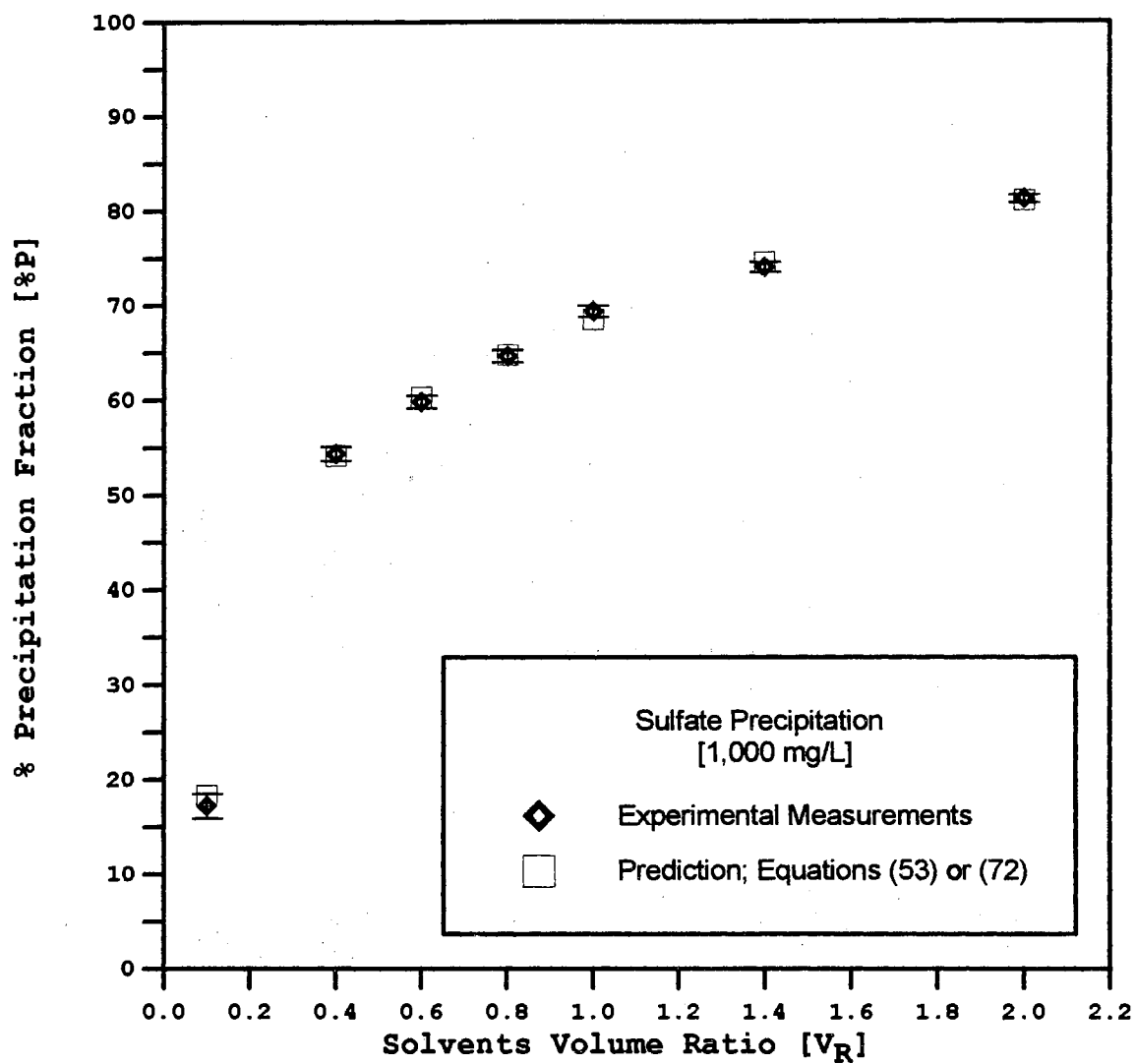


Figure A.18. Precipitation Fraction for Calcium-Sodium Sulfate System at 1,000 mg/L

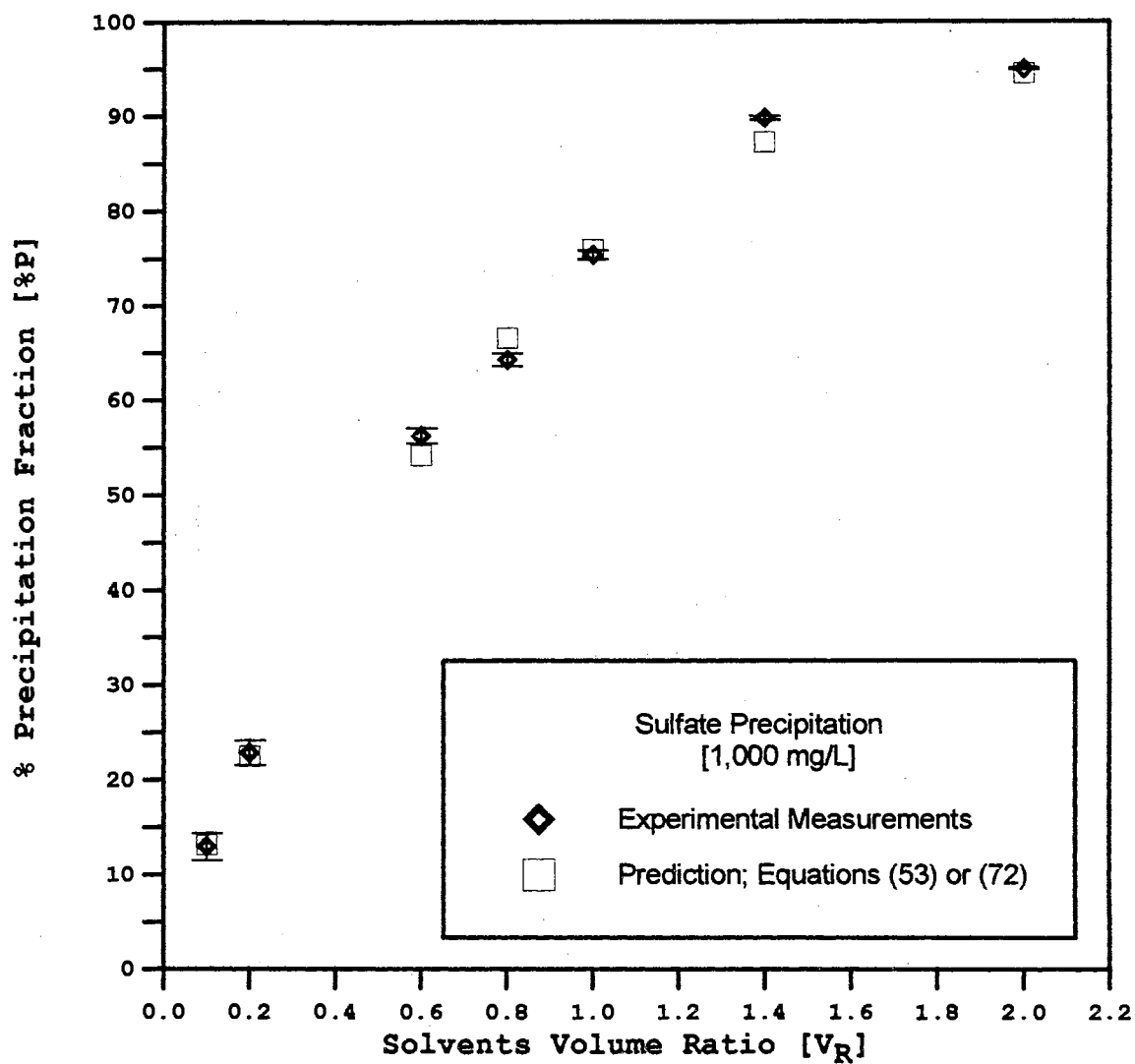


Figure A.19. Precipitation Fraction for Calcium-Potassium Sulfate System at 1,000 mg/L

APPENDIX B

REPRESENTATION OF THE EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS

This appendix contains detailed tables for each studied salt system including the volume fraction of isopropylamine (θ_3), the solvents volume ratio (V_R), the experimental precipitation fractions along with their uncertainties, and the predicted precipitation fractions by the 2-Suffix and the 2-Power equations, Equations (54) and (73), and the 3-Suffix and the 3-Power equations, Equations (53) and (72).

TABLE B.1
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	18.2	20.1	12.7	17.0
		1.9	16.3		
0.167	0.2	21.4	23.2	19.1	21.5
		1.8	19.6		
0.286	0.4	30.1	31.8	29.9	29.7
		1.7	28.5		
0.375	0.6	33.6	35.2	36.7	34.8
		1.6	32.1		
0.444	0.8	40.4	41.9	41.3	39.1
		1.5	38.9		
0.500	1.0	43.0	44.4	44.7	42.9
		1.4	41.6		
0.583	1.4	48.9	50.2	49.3	49.7
		1.3	47.6		
0.667	2.0	58.1	59.2	53.3	57.8
		1.1	57.0		

TABLE B.2
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM-SODIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	19.3 1.9	21.2 17.4	12.2	17.4
0.167	0.2	21.5 1.8	23.3 19.6	18.1	21.2
0.286	0.4	28.4 1.7	30.1 26.7	28.8	28.6
0.375	0.6	32.4 1.6	34.0 30.8	35.9	33.6
0.444	0.8	39.4 1.4	40.8 38.0	40.8	38.1
0.500	1.0	43.0 1.3	44.3 41.7	44.5	42.4
0.583	1.4	50.1 1.2	51.3 48.9	49.5	50.3
0.667	2.0	59.3 1.0	60.4 58.3	54.1	59.7

TABLE B.3

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM-POTASSIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	17.7 1.8	19.5 15.8	11.8	16.3
0.167	0.2	20.1 1.8	21.9 18.2	18.5	20.3
0.286	0.4	29.3 1.6	30.9 27.7	29.5	28.1
0.375	0.6	32.2 1.5	33.8 30.7	36.6	33.4
0.444	0.8	36.9 1.5	38.4 35.4	41.6	38.0
0.500	1.0	44.3 1.3	45.6 43.0	45.3	42.4
0.583	1.4	50.4 1.2	51.6 49.1	50.3	50.1
0.667	2.0	58.4 1.0	59.8 57.7	54.8	59.2

TABLE B.4
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	17.6	19.5	12.6	16.1
		1.9	15.7		
0.167	0.2	22.0	23.8	18.9	22.0
		1.8	20.2		
0.286	0.4	30.0	31.6	29.6	29.5
		1.6	28.4		
0.375	0.6	33.1	34.7	36.5	34.2
		1.6	31.5		
0.444	0.8	39.4	40.8	41.1	38.4
		1.4	38.0		
0.500	1.0	42.6	43.9	44.6	42.4
		1.3	41.3		
0.583	1.4	49.7	50.9	49.2	49.8
		1.2	48.5		
0.667	2.0	58.7	59.7	53.2	58.8
		1.0	57.7		

TABLE B.5
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-SODIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	18.4	20.2	12.9	16.9
		1.8	16.6		
0.167	0.2	23.2	24.9	19.3	22.9
		1.7	21.5		
0.286	0.4	30.3	31.9	30.1	30.1
		1.6	28.7		
0.375	0.6	32.8	34.4	36.8	34.5
		1.6	31.2		
0.444	0.8	39.0	40.4	41.4	38.4
		1.4	37.6		
0.500	1.0	43.9	45.2	44.8	42.4
		1.3	42.6		
0.583	1.4	50.2	51.4	49.2	49.8
		1.2	49.0		
0.667	2.0	58.1	59.2	53.2	59.0
		1.1	57.0		

TABLE B.6

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-POTASSIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	18.1 1.8	19.9 16.3	12.9	16.8
0.167	0.2	23.4 1.7	25.1 21.7	19.2	22.8
0.286	0.4	29.7 1.6	31.3 28.1	30.0	30.0
0.375	0.6	32.5 1.6	34.1 30.9	36.7	34.4
0.444	0.8	39.9 1.4	41.3 38.5	41.3	38.3
0.500	1.0	43.6 1.3	44.9 42.3	44.7	42.2
0.583	1.4	49.5 1.2	50.7 48.3	49.1	49.7
0.667	2.0	58.2 1.1	59.3 57.1	53.1	58.9

TABLE B.7

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-MAGNESIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	18.6 1.9	20.5 16.7	12.7	16.7
0.167	0.2	22.4 1.8	24.2 20.6	18.9	22.3
0.286	0.4	30.0 1.6	31.6 28.4	29.8	29.7
0.375	0.6	32.9 1.6	34.5 31.3	36.7	34.3
0.444	0.8	38.8 1.5	40.3 37.3	41.4	38.6
0.500	1.0	44.5 1.3	45.8 43.2	44.9	42.7
0.583	1.4	50.0 1.3	51.3 48.7	49.6	50.3
0.667	2.0	59.1 1.1	60.2 58.0	53.8	59.6

TABLE B.8
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-BARIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	18.1	20.0	12.5	16.4
		1.9	16.2		
0.167	0.2	22.3	24.1	18.6	22.0
		1.8	20.5		
0.286	0.4	29.4	30.0	29.3	29.3
		1.6	27.8		
0.375	0.6	32.5	34.1	36.2	33.9
		1.6	30.9		
0.444	0.8	37.9	39.4	40.9	38.0
		1.5	36.4		
0.500	1.0	43.9	45.2	44.4	42.1
		1.3	42.6		
0.583	1.4	50.4	51.7	49.2	49.8
		1.3	49.1		
0.667	2.0	58.1	59.2	53.4	59.2
		1.1	57.0		

TABLE B.9

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-STRONTIUM CHLORIDE AT 5,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	17.2 1.9	19.1 15.3	12.6	16.1
0.167	0.2	22.4 1.8	24.2 20.6	18.9	22.3
0.286	0.4	29.9 1.6	31.5 28.3	29.5	29.5
0.375	0.6	32.8 1.5	34.4 31.3	36.3	33.9
0.444	0.8	38.3 1.5	39.8 36.8	40.8	37.9
0.500	1.0	42.3 1.4	43.7 40.9	44.2	41.9
0.583	1.4	49.9 1.2	51.1 48.7	48.7	49.3
0.667	2.0	58.0 1.1	59.0 56.8	52.6	58.5

TABLE B.10

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM CHLORIDE AT 10,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	16.8 1.9	18.7 15.0	11.9	15.1
0.167	0.2	20.4 1.8	22.2 18.6	18.0	20.6
0.286	0.4	28.8 1.6	30.5 27.2	28.6	28.3
0.375	0.6	33.6 1.5	35.1 32.1	35.6	33.4
0.444	0.8	37.3 1.4	38.7 35.8	40.4	37.9
0.500	1.0	41.9 1.4	43.2 40.5	44.0	42.1
0.583	1.4	50.4 1.2	51.6 49.2	49.0	49.7
0.667	2.0	58.5 1.1	59.5 57.4	53.4	58.7

TABLE B.11
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM-SODIUM CHLORIDE AT 10,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	16.9	18.8	11.7	15.5
		1.9	15.0		
0.167	0.2	19.2	21.1	17.7	19.5
		1.9	17.4		
0.286	0.4	28.5	30.1	28.3	27.9
		1.6	26.9		
0.375	0.6	34.6	36.1	35.2	33.6
		1.5	33.1		
0.444	0.8	36.5	38.0	40.1	38.2
		1.5	35.0		
0.500	1.0	42.7	44.0	43.7	42.3
		1.3	41.4		
0.583	1.4	49.2	50.4	48.7	49.2
		1.2	48.0		
0.667	2.0	57.3	58.4	53.2	57.1
		1.1	56.2		

TABLE B.12

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM-POTASSIUM CHLORIDE AT 10,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	17.3 1.9	19.2 15.4	12.3	15.6
0.167	0.2	20.2 1.8	22.0 18.4	18.5	20.6
0.286	0.4	30.3 1.6	31.9 28.7	29.3	29.0
0.375	0.6	34.1 1.5	35.6 32.6	36.2	34.5
0.444	0.8	38.2 1.4	39.6 36.8	41.0	39.0
0.500	1.0	43.0 1.3	44.3 41.7	44.6	43.0
0.583	1.4	50.1 1.2	51.3 48.9	49.4	49.9
0.667	2.0	57.9 1.0	59.0 56.9	53.7	57.8

TABLE B.13

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM CHLORIDE AT 10,000 mg/L

θ_s	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	16.8 1.9	18.7 14.9	11.9	15.0
0.167	0.2	20.2 1.8	22.0 18.4	18.0	20.3
0.286	0.4	28.6 1.6	30.2 27.0	28.5	28.3
0.375	0.6	33.7 1.5	35.2 32.2	35.4	33.5
0.444	0.8	37.3 1.4	38.7 35.9	40.3	38.0
0.500	1.0	42.3 1.3	43.6 41.0	43.8	42.1
0.583	1.4	49.3 1.2	50.5 48.1	48.7	49.3
0.667	2.0	58.0 1.0	59.0 57.0	53.1	57.9

TABLE B.14
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-SODIUM CHLORIDE AT 10,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	17.3 1.9	19.2 15.4	12.3	15.8
0.167	0.2	20.3 1.8	22.1 18.5	18.6	20.6
0.286	0.4	30.4 1.6	32.0 28.8	29.4	29.1
0.375	0.6	34.0 1.5	35.5 32.5	36.3	34.6
0.444	0.8	38.6 1.4	40.0 37.2	41.2	39.1
0.500	1.0	42.8 1.3	44.1 42.5	44.7	43.2
0.583	1.4	51.3 1.2	52.5 50.1	49.6	50.0
0.667	2.0	57.5 1.1	58.6 56.4	53.9	57.9

TABLE B.15
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM SULFATE AT 1,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	9.4 1.4E00	10.8 8.0	11.0	10.1
0.167	0.2	51.4 7.6E-1	52.2 50.7	51.4	52.6
0.286	0.4	76.2 4.0E-1	76.6 75.8	73.5	73.0
0.375	0.6	82.8 3.0E-1	83.1 82.5	83.9	83.2
0.444	0.8	88.6 2.2E-1	88.8 88.3	89.4	88.9
0.500	1.0	91.5 1.8E-1	91.7 91.3	92.6	92.3
0.583	1.4	95.8 1.1E-1	95.9 95.7	95.8	95.9
0.667	2.0	98.2 5.2E-2	98.3 98.2	97.7	98.0

TABLE B.16
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
MAGNESIUM SULFATE AT 1,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	15.3 1.4E00	16.7 13.9	10.4	14.0
0.167	0.2	18.1 1.4E00	19.5 16.7	16.0	17.5
0.286	0.4	25.7 1.3E00	26.9 24.4	27.1	26.7
0.375	0.6	32.4 1.2E00	33.5 31.2	35.1	33.6
0.444	0.8	39.9 1.0E00	40.9 38.8	41.0	39.4
0.500	1.0	47.0 9.3E-1	47.9 46.0	45.5	44.4
0.583	1.4	53.3 8.3E-1	54.1 52.4	52.0	52.5
0.667	2.0	59.5 7.6E-1	60.3 58.8	58.0	61.1

TABLE B.17

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-MAGNESIUM SULFATE AT 1,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	19.8 1.3E00	21.1 18.5	18.5	18.5
0.167	0.2	28.4 1.2E00	29.6 27.2	30.2	29.2
0.286	0.4	49.4 8.6E-1	50.3 48.6	46.2	46.6
0.375	0.6	57.7 7.3E-1	58.4 57.0	55.8	56.9
0.444	0.8	61.2 6.8E-1	61.9 60.6	62.2	63.3
0.500	1.0	67.5 6.1E-1	68.3 66.9	66.6	67.4
0.583	1.4	71.2 5.6E-1	71.8 70.7	72.3	72.2
0.667	2.0	76.6 5.1E-1	77.2 76.1	77.1	75.6

TABLE B.18
EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-SODIUM SULFATE AT 1,000 mg/L

θ_3	V_R	%P/ σ_P	%P \pm σ_P	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	17.2 1.3E00	18.5 15.9	21.4	18.4
0.286	0.4	54.4 7.4E-1	55.2 53.7	51.6	54.2
0.375	0.6	59.9 6.9E-1	60.6 59.2	60.8	60.4
0.444	0.8	64.7 6.6E-1	65.4 64.0	66.5	64.8
0.500	1.0	69.4 6.1E-1	70.0 68.8	70.3	68.5
0.583	1.4	74.1 5.5E-1	74.6 73.5	75.1	74.6
0.667	2.0	81.3 4.4E-1	81.7 80.9	79.0	81.2

TABLE B.19

EXPERIMENTAL AND PREDICTED PRECIPITATION FRACTIONS FOR
CALCIUM-POTASSIUM SULFATE AT 1,000 mg/L

θ_3	V_R	%P/ σ_p	%P \pm σ_p	Predicted %P	
				Eqs. (54) or (73)	Eqs. (53) or (72)
0.091	0.1	13.0 1.4E00	14.4 11.5	11.5	13.2
0.167	0.2	22.9 1.3E00	24.2 21.6	23.9	22.5
0.375	0.6	56.3 7.9E-1	57.1 55.5	59.9	54.2
0.444	0.8	64.3 6.9E-1	65.0 63.6	69.9	66.6
0.500	1.0	75.4 4.8E-1	75.9 74.9	76.8	75.9
0.583	1.4	89.9 2.1E-1	90.1 89.6	84.9	87.3
0.667	2.0	95.0 1.3E-2	95.2 94.9	90.7	94.6

VITA

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