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Separation of chloride and sulfate ions in univalent and divalent cation forms from aqueous streams

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Abstract

The precipitation and separation of chloride and sulfate in several cation forms (sodium, potassium, magnesium, calcium, strontium, and barium) from aqueous streams were studied using isopropylamine (IPA) and ethylamine (EA) as precipitation solvents. The precipitation fractions (P) of the tested chloride salts at 5000 and 10,000 ppm by both IPA and EA over the studied range of solvents volume ratio (V_R) were relatively identical (18–60%) and their small variations were within their experimental uncertainty. The P of combined sulfate at 1000 ppm (56–99.5%) and chloride at 5000 ppm (28–62%) in the form of calcium by IPA over the studied range of V_R were appreciably higher than the P of sulfate (10–98.5%) from calcium sulfate in the absence of calcium chloride, or the P of chloride (18–58%) from calcium chloride in the absence of calcium sulfate. The P of chloride from oil-field-produced waters at 106,654 ppm (20–88%) by both IPA and EA were higher than the P of chloride from diluted produced water at 20,000 (17–68%) and 10,000 ppm (16–65%) over the studied range of V_R . The small amounts of sulfate present in the produced waters (e.g., 435 ppm) were completely removed at V_R of 0.1 (the first stage of precipitation). Consistency tests performed on the acquired data indicated a good level of experimental consistency. Two model equations (2-Suffix and 3-Suffix) derived from thermodynamic principles of solid–liquid equilibrium (SLE) criteria were employed to correlate the acquired data. While both equations were adequate for correlating the precipitation data, the 3-Suffix equation was more accurate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Precipitation; Anions; Univalent and divalent cations; Organic solvents

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1. Introduction

Innovative processes for selective separation of alkaline earth cations (magnesium, calcium, strontium, barium, and radium) and alkali cations (sodium, potassium, rubidium, and cesium) in the form of chloride and/or sulfate from aqueous streams are of vital interest to provide viable solutions for several environmental and industrial problems. Environmental problems, for example, include the removal of (1) radioactive materials (e.g., rubidium, cesium, strontium, and barium) and/or sulfate from the Department of Energy (DOE) liquid waste streams, (2) naturally occurring radioactive materials (NORM) from oil-field-produced waters and other subsurface waters, and (3) chloride salts from contaminated groundwater with road de-icing salts. Industrial problems, for instance, include the removal of sulfate salts (1) from seawater to be used as a pressure support in offshore oil and gas production, (2) cooling towers blowdown streams, and (3) streams (feed and/or concentrate) in pressure-driven membrane processes (reverse osmosis, nanofiltration, ultrafiltration, and microfiltration).

A novel process was proposed [1–3] for selective separation of sulfate and chloride in several cation forms. The proposed process consists of three steps: precipitation, filtration–clarification, and reuse of the precipitation agent. Precipitation is the first step in which a suitable organic solvent is added to a targeted aqueous stream to form selective precipitates. In the second step, the formed precipitates are filtered from the aqueous stream. The solvent is then recovered and recycled in the third step.

The objective of this work, which is part of our ongoing efforts to validate the concept, is to assess the fundamental feasibility of the proposed process by (1) providing basic experimental performance data and (2) using thermodynamic principles of solid–liquid equilibrium (SLE) to correlate the acquired data. As such, experimental precipitation measurements on chloride and sulfate salts using isopropylamine (IPA) and ethylamine (EA) as precipitation solvents were studied. The measurements targeted: (1) chloride salts at 5000 ppm using EA: calcium, barium, calcium–sodium, calcium–potassium, calcium–magnesium, calcium–strontium, and calcium–barium; (2) chloride salts at 5000 and 10,000 ppm using IPA: strontium and barium; (3) combination of sulfate (1000 ppm) and chloride (5000 ppm) in the form of calcium using IPA; and (4) chloride-rich oil-field-produced waters (106,654, 20,000, and 10,000 ppm) using IPA and EA. Previously derived thermodynamic framework equations from basic principles of SLE criteria [4] were used to correlate the acquired data.

2. Experimental method and procedure

The experimental setup, method, procedure, and error analysis employed in this work were outlined in details elsewhere [5]. However, an Ion Chromatograph (IC) model DX-300 (Dionex) was used in this work for the analysis of chloride and sulfate concentrations. The experimental precipitation fraction (P) was calculated as follows [5]:

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

where $C_{1,2}$ is the anion concentration in the reference (aqueous) sample, and $C_{1,m}$ is anion concentration in the filtered (organic-aqueous) samples. The standard deviation, σ_p , in the experimental values of P due to random variations in the variables was estimated by error propagation methods [5].

3. Results and discussions

3.1. Presentation and discussion of experimental data

Instrumental consistency for the IC was established by frequent calibration. In addition, the IC was tested by determining the known concentration of the targeted anions ($C_{1,2}$) prior to and after each set of measurements to ensure proper analysis. The measured (weighed) and the determined (analyzed by IC) concentrations of the targeted anions in distilled water are reported in Table 1. Comparisons of these data indicate

Table 1
Comparisons of the weighed and determined anion concentrations in pure water

System	$C_{1,2}^a$	$C_{1,2}^b / \sigma_{c_{1,2}}$
Calcium chloride	4999.5	4988.2/88.3
CaCl ₂ -2H ₂ O	4999.5	
Barium chloride	5000.6	5005.0/81.7
BaCl ₂ -2H ₂ O	5000.6	
Calcium-sodium chloride	5002.3	5018.2/79.9
CaCl ₂ -2H ₂ O/ NaCl	2500.7 2501.6	
Calcium-potassium chloride	5006.4	5054.9/92.1
CaCl ₂ -2H ₂ O/ KCl	2499.7 2506.7	
Calcium-magnesium chloride	4999.1	4979.0/79.6
CaCl ₂ -2H ₂ O/ MgCl ₂ -6H ₂ O	2500.2 2498.9	
Calcium-strontium chloride	5002.1	5047.0/82.5
CaCl ₂ -2H ₂ O/ SrCl ₂ -6H ₂ O	2500.7 2501.4	
Calcium-barium chloride	5000.7	5072.1/82.4
CaCl ₂ -2H ₂ O/ BaCl ₂ -2H ₂ O	2499.8 2500.9	
Strontium chloride	5005.7	5049.5/81.4
SrCl ₂ -6H ₂ O	5005.7	
Strontium chloride	9998.4	10106.3/161.5
SrCl ₂ -6H ₂ O	9998.4	
Barium chloride	10003.8	9987.4/163.0
BaCl ₂ -2H ₂ O	10003.8	
Calcium sulfate-chloride		
CaSO ₄ /	999.6	993.5/11.2
CaCl ₂ -2H ₂ O	4999.6	5026.5/81.8

^aWeighed anion concentration (ppm).

^bDetermined anion concentration (ppm) by the IC.

excellent agreement. The observed differences are within the uncertainty (σ_C) of the IC. The instrumental consistency tests were taken as a confirmation of reasonable analysis of the experimental procedures (e.g., calibration curves, dilution steps, and dilution analysis) [5], and hence, acceptable precipitation data.

The precipitation data for the tested systems along with their error analysis are presented in Tables 2–5. The tabulated precipitation data include the solvents volume ratio (V_R), organic solvent (IPA or EA) volume fractions (θ_3), and precipitation fractions (P) and their associated standard deviations (σ_P).

The precipitation process can be evaluated in terms of the precipitation fraction (P) as a function of the solvents volume ratio (V_R), that is, the ratio of the organic solvent volume to the aqueous volume. Chloride salts, single and binary, were studied at 5000 and 10,000 ppm (Tables 2 and 3) to point out the precipitation capability of both EA and IPA, separately. Fig. 1 reveals the P along with their σ_P of chloride salts at 5000 and 10,000 ppm by both EA and IPA. The P of the chloride salts at 5000 ppm, single and binary, by EA over the studied range of the V_R are nearly identical (e.g., $P = 17\%$ at $V_R = 0.1$ to $P = 59\%$ at $V_R = 2.0$). Fig. 1 also reveals that the P (along with their σ_P) of chloride salts (single: strontium and barium) by IPA at both 5000 and 10,000 ppm are almost identical (e.g., $P = 17\%$ at $V_R = 0.1$ to $P = 59\%$ at $V_R = 2.0$). The small variations in the P of these systems are within their experimental uncertainty. Such precipitation data of the tested chloride salts at 5000 and 10,000 ppm by EA or IPA as precipitation agents are in excellent agreement with our previous experimental findings [5] for chloride salts at 5000 and 10,000 ppm. This would confirm that both IPA and EA

Table 2
Precipitation fractions for chloride ions (5000 ppm) by EA

V_R	θ_3	% P/σ_P						
		Salt 1	Salt 2	Salt 3	Salt 4	Salt 5	Salt 6	Salt 7
0.1	0.09	17.9	16.7	18.7	17.3	18.3	18.8	16.7
		2.0	1.9	1.9	2.0	1.9	1.9	2.0
1.2	0.17	22.4	21.5	22.7	22.4	21.6	21.2	19.9
		1.9	1.8	1.8	1.9	1.8	1.8	1.9
0.4	0.29	31.1	28.4	30.5	27.4	30.7	31.7	29.8
		1.7	1.8	1.7	1.8	1.6	1.8	1.7
0.6	0.38	34.6	34.8	34.1	34.3	33.3	35.4	34.9
		1.6	1.7	1.6	1.6	1.5	1.5	1.6
0.8	0.44	40.7	39.6	40.8	38.6	39.8	39.1	39.3
		1.5	1.4	1.4	1.5	1.4	1.4	1.4
1.0	0.50	44.1	45.3	45.3	44.8	45.1	45.6	44.1
		1.4	1.3	1.3	1.3	1.3	1.3	1.3
1.4	0.58	52.6	52.0	50.8	52.6	52.5	52.1	50.8
		1.2	1.2	1.2	1.2	1.1	1.1	1.2
2.0	0.67	60.0	60.6	60.9	59.1	60.0	61.5	58.3
		1.0	1.1	1.1	1.1	0.9	0.9	1.1

Salt 1: calcium chloride. Salt 2: barium chloride. Salt 3: calcium–sodium chloride. Salt 4: calcium–potassium chloride. Salt 5: calcium–magnesium chloride. Salt 6: calcium–strontium chloride. Salt 7: calcium–barium chloride.

Table 3
Precipitation fractions for chloride ions by IPA

V_R	θ_3	% P/σ_P			
		Salt 1	Salt 2	Salt 3	Salt 4
0.1	0.09	15.8	15.9	16.6	17.3
		2.0	2.0	1.9	1.9
0.2	0.17	22.0	21.3	20.4	19.9
		1.9	1.9	1.8	1.8
0.4	0.29	27.4	28.5	28.1	30.1
		1.7	1.6	1.7	1.6
0.6	0.38	34.3	33.2	31.5	33.9
		1.5	1.6	1.6	1.5
0.8	0.44	39.8	37.9	36.8	38.7
		1.4	1.4	1.4	1.4
1.0	0.50	44.3	41.9	41.1	43.9
		1.3	1.3	1.3	1.3
1.4	0.58	51.2	50.3	49.7	51.6
		1.2	1.2	1.2	1.1
2.0	0.67	59.0	58.2	58.4	59.4
		1.1	1.0	1.0	1.0

Salt 1: strontium chloride (chloride: 5000 ppm). Salt 2: barium chloride (chloride: 5000 ppm). Salt 3: strontium chloride (chloride: 10,000 ppm). Salt 4: barium chloride (chloride: 10,000 ppm).

provide nearly identical precipitation trend with the tested chloride salts at 5000 and 10,000 ppm.

Table 4
Precipitation fractions for sulfate and chloride ions by IPA

V_R	θ_3	% P/σ_P			
		Salt 1	Salt 2	Salt 3	Salt 4
0.1	0.09	10.0	55.9	18.1	28.1
		1.4E00	7.0E-1	1.9	1.8
0.2	0.17	50.9	78.7	21.9	32.3
		7.6E-1	3.7E-1	1.8	1.6
0.4	0.29	75.9	93.6	30.2	37.9
		4.0E-1	3.4E-1	1.6	1.5
0.6	0.38	83.1	95.9	32.7	40.9
		3.0E-1	7.1E-2	1.6	1.5
0.8	0.44	88.8	97.8	38.8	45.4
		2.2E-1	3.6E-2	1.4	1.4
1.0	0.50	91.7	99.0	43.2	49.5
		1.8E-1	2.3E-2	1.3	1.3
1.4	0.58	96.1	99.3	49.8	52.8
		1.1E-1	2.3E-2	1.2	1.1
2.0	0.67	98.5	99.4	58.1	62.1
		5.2E-2	2.2E-2	1.0	0.9

Salt 1: % P of sulfate from calcium sulfate (1000 ppm) [5]. Salt 2: % P of sulfate from calcium chloride (5000 ppm)–sulfate (1000 ppm) [this work]. Salt 3: % P of chloride from calcium chloride (5000 ppm) [5]. Salt 4: % P of chloride from calcium chloride (5000 ppm)–sulfate (1000 ppm) [this work].

Table 5

Precipitation fractions of chloride ion from produced water by IPA

V_R	θ_3	% P/σ_p			
		PW1	PW2	PW3	PW4
0.1	0.09	15.6	17.3	20.4	21.0
		1.9	2.0	1.9	1.9
0.2	0.17	18.8	19.4	24.5	24.2
		1.8	1.9	1.8	1.8
0.4	0.29	28.2	27.1	33.2	33.2
		1.7	1.8	1.6	1.6
0.6	0.38	33.5	33.2	38.6	40.5
		1.5	1.6	1.4	1.4
0.8	0.44	37.5	36.2	46.4	44.2
		1.4	1.5	1.3	1.3
1.0	0.50	42.1	43.2	51.1	49.5
		1.3	1.4	1.2	1.2
1.4	0.58	49.0	53.6	57.0	53.6
		1.2	1.2	1.0	1.1
2.0	0.67	58.7	59.1	64.1	63.0
		1.0	1.0	0.9	0.9
3.0	0.75	61.6	66.6	79.0	–
		0.9	0.9	0.5	–
4.0	0.88	64.9	68.3	88.3	–
		0.8	0.8	0.3	–

PW1: produced water (chloride: 10,000 ppm; solvent: IPA). PW2: produced water (chloride: 20,000 ppm; solvent: IPA). PW3: produced water (chloride: 106,654 ppm; solvent: IPA). PW4: produced water (chloride: 106,654 ppm; solvent: EA).

In our previous work [5], the P of sulfate salts were studied at 1000 ppm. The P of the sulfate ion from the calcium sulfate system is very high (10–99%) while the P of the sulfate ion from the magnesium sulfate system (15–60%) are significantly lower than the P of the calcium sulfate system. On the other hand, the P of the sulfate ion from the calcium–magnesium sulfate system (20–77%) are lower than the P of the calcium sulfate system, but they are higher than the P of the magnesium sulfate system. However, the P of the sulfate ion from the calcium–sodium sulfate or calcium–potassium sulfate systems are higher than the P that was resulted from the calcium–magnesium sulfate or magnesium sulfate systems, but lower than the P of calcium sulfate. Such precipitation trends may be attributed to the phenomenon that the aqueous solubility of calcium sulfate increases in the presence of other cations in form of sulfate with higher aqueous solubilities (exhibits a negative effect on the P) [5], and the increase is higher in the presence of alkaline earth cations (e.g., magnesium) than in the presence of alkali earth cations (e.g., sodium or potassium) [5,6]. Fig. 2 depicts the P along with their σ_p of sulfate salts by IPA [5].

In this work, the P of a combined salt contains sulfate ion at 1000 ppm and chloride ion at 5000 ppm in form of calcium was studied using IPA as a precipitation solvent. Fig. 3 reveals the P along with their σ_p of sulfate and chloride ions from calcium sulfate, calcium chloride and calcium chloride–sulfate systems using IPA. The P of the

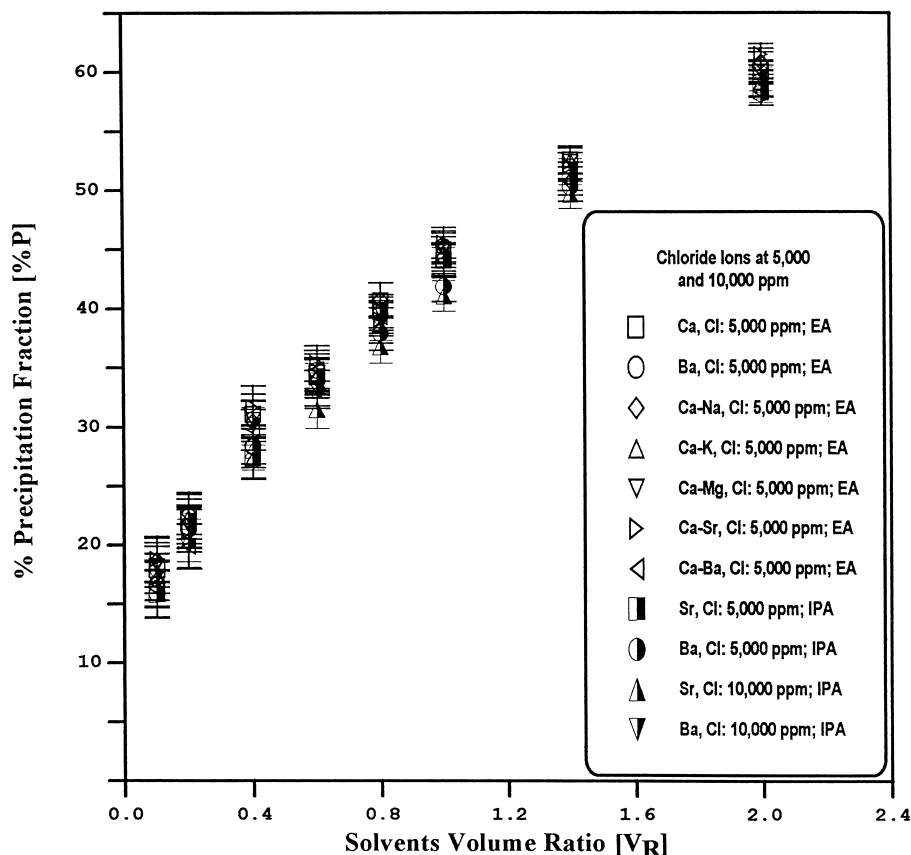


Fig. 1. Precipitation fractions of chloride salts using EA or IPA.

sulfate ion at 1000 ppm from the calcium chloride–sulfate system is significantly higher than the P of sulfate ion at 1000 ppm from calcium sulfate system [5], particularly at the lower values of V_R : 0.1–1.0 (Table 4). The P of chloride ion at 5000 ppm from calcium sulfate–chloride system is relatively higher than the P of chloride ion at 5000 ppm from calcium chloride system [5], particularly at V_R values of 0.1–1.0 (Table 4). Such precipitation trends suggest that the presence of combined sulfate and chloride ions in form of calcium has a positive significant impact on the P of sulfate ion, and to a lesser extent on the P of chloride ion. This would also indicate that the presence of other alkaline earth cations in form of sulfate with significantly lower aqueous solubility limits (e.g., strontium sulfate: 0.1 ppm; barium sulfate: 2.4 ppm [7]) than calcium sulfate (2400 ppm [7]) should lead to significant precipitation and removal of these cations in form of sulfate (a very critical issue in certain applications such as the DOE waste streams).

In most oil-field-produced waters, the dominant anion is chloride with the exception of a few cases where sulfate and bicarbonate exceed chloride by weight [8]. Chloride-rich produced waters, however, are divided into two major subtypes: (1) those in which

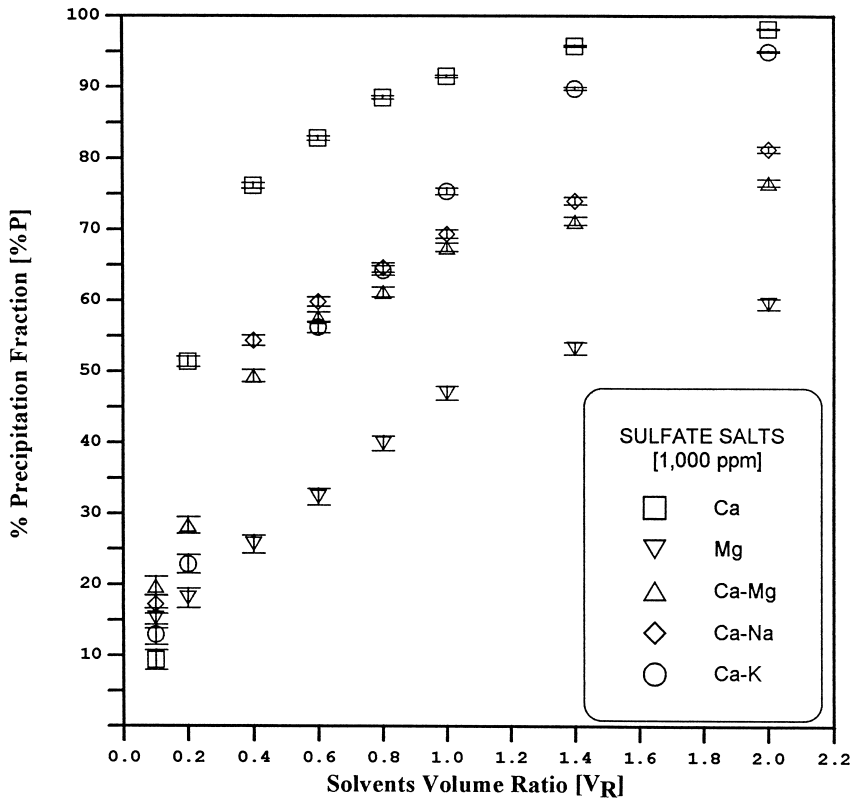


Fig. 2. Precipitation fractions of sulphate salts using IPA [5].

sodium is dominant over calcium; and (2) those in which calcium is relatively abundant [8]. Chloride-rich produced waters that are high in calcium are generally high in alkaline earth cations such as strontium, barium, and, in some cases, radium. The availability of radium in chloride-rich produced waters suggests that the decay chain of radium (NORM) are common, and, thus, such waters can become radioactive.

The P of chloride and sulfate ions from oil-field-produced waters containing 106,654 ppm of chloride ion and 435 ppm of sulfate were also studied using both IPA and EA as precipitation solvents. The sulfate ion was completely precipitated in the first stage at a V_R of 0.1 by both IPA and EA. As shown in Table 5, however, the P of chloride ion by IPA over the studied range of V_R extended from 0.1 to 4.0 were 20.4–88.3%. A similar P trend was observed for chloride ion at 106,654 ppm from produced water using EA as a precipitation agent at a V_R range of 0.1 (P : 21.0%) to 2.0 (P : 63.0%). When the produced water was diluted to 20,000 ppm, and then to 10,000 ppm of chloride ion, sulfate ion was completely precipitated by IPA in the first stage ($V_R = 0.1$) for both cases. The P of chloride ion by IPA at a V_R range extended from 0.1 to 4.0 were 17.3–68.3% for chloride ion at 20,000 ppm, and 15.6–64.9% for chloride ion at 10,000

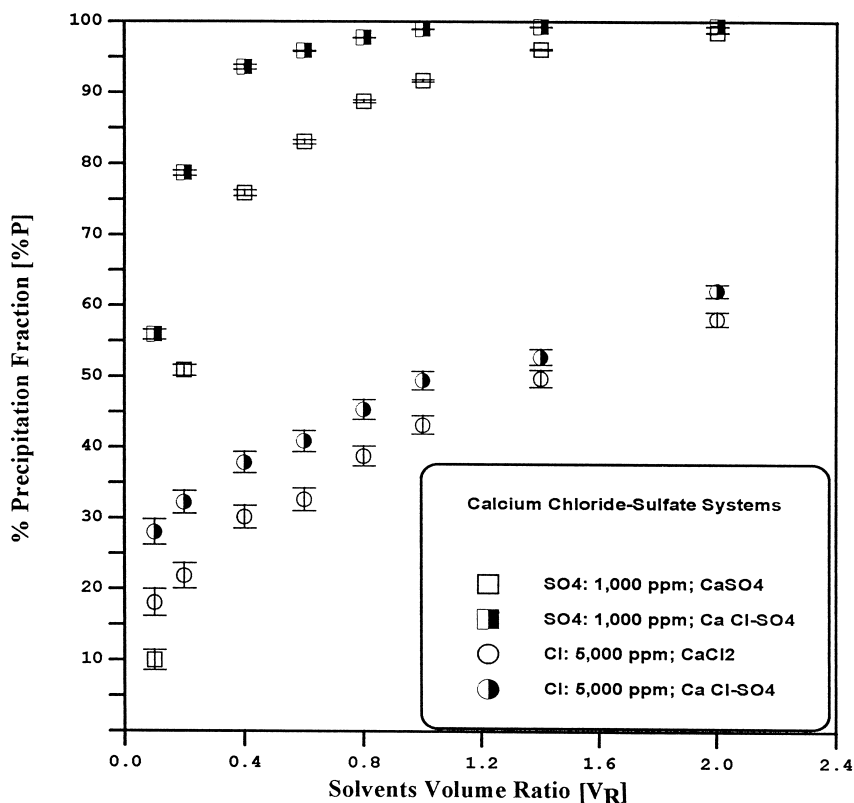


Fig. 3. Precipitation fractions of chloride and sulphate ions using IPA.

ppm, which were lower than the P of chloride ion at 106,654 ppm. However, the P of chloride ion at 10,000 and 20,000 ppm by IPA at a V_R range of 0.1–2.0 were relatively identical to the observed P trends of chloride ions at 5000 and 10,000 ppm (as shown in Fig. 1). Fig. 4 reveals the P along with their σ_p of chloride ion at 106,654, 20,000, and 10,000 ppm from oil-field-produced waters by both IPA and EA.

3.2. Presentation and evaluation of the framework equations

The amount of experimental data required can be dramatically reduced when a practical model with minimum empiricism (few adjustable parameters suitable for generalization), and reliable correlation and prediction capabilities is developed. As such, we have developed a framework derived from basic thermodynamic principles of SLE criteria to correlate and predict the precipitation of salts from aqueous solutions using organic solvents [4]. The solubility of a given salt in a mixed-solvent mixture was related to solubilities of such a salt in each of the pure solvents (water and organic). Two

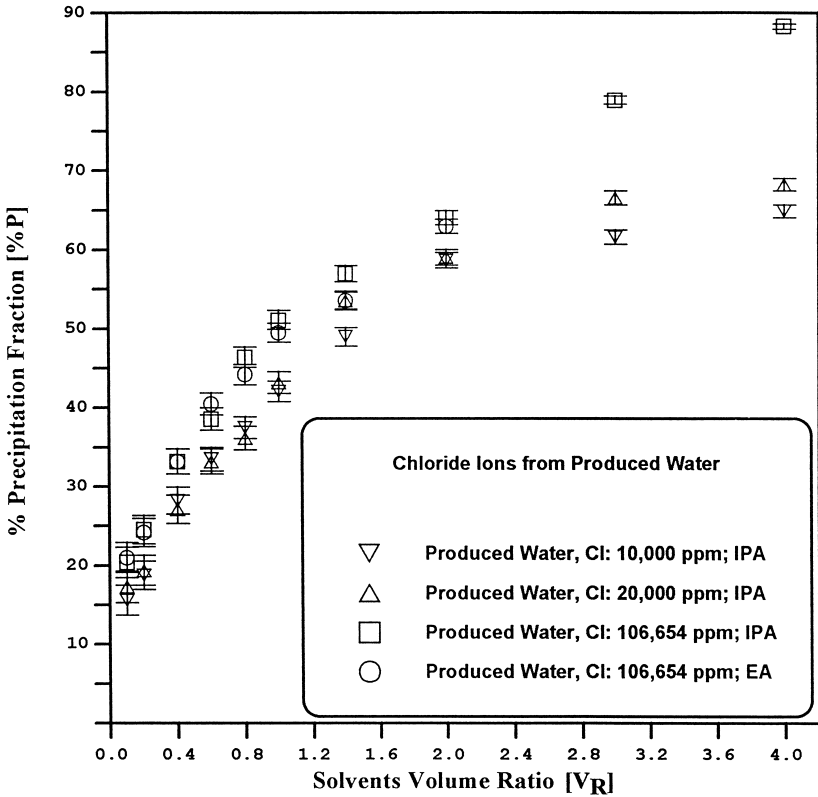


Fig. 4. Precipitation fractions of chloride ions from produced water using IPA or EA.

optimum equations were derived: the 2-Suffix equation (two-regressed parameters: $x_{1,3}$ and Λ_{32}) [4]:

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

and the 3-Suffix equation (three-regressed parameters: $x_{1,3}$, Λ_{32} and Λ_{23}) [4]:

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

where $x_{1,m}$ is the solubility (mole fraction) of a given anion in mixed-solvents media (water and organic), $x_{1,2}$ is the solubility of a given anion in water solvent, $x_{1,3}$ is solubility of a given anion in organic solvent, θ_3 is the salt-free volume fraction of organic solvent, θ_2 is the salt-free volume fraction of water solvent, v_i is the molar volume of species i (1: anion; 2: water; 3: organic solvent), and Λ_{32} and Λ_{23} are solvent–solvent (water–organic) interaction parameters.

Regressions of the acquired data were performed using the weighted least squares objective function (SS). A Marquardt non-linear regression procedure was employed in the precipitation calculations [9]. The objective function, SS, used for the evaluation of the framework equations is given as follows:

$$SS = \sum_{i=1}^{NP} \left[\frac{Y_{\text{cal}} - Y_{\text{exp}}}{Y_{\text{exp}}} \right]^2 \quad (4)$$

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

$$Y = \ln[1 - P] \quad (5)$$

According to Eq. (4), the root mean square error (RMSE) provides an appropriate measure for the overall performance of the model for a given data set more so than the percent average absolute deviation (%AAD).

A summary of the evaluation results of Eqs. (2) and (3), applied to the acquired precipitation data, is presented in Tables 6 and 7. Eqs. (2), with two regressed parameters, provides an adequate representation of the precipitation measurements.

Table 6

The 2-Suffix equation (Eq. 2) representation of the tested systems

$C_1 = \ln[x_{1,3}/x_{1,2}]$; $C_2 = A_{32}$.

System	Model's parameters		RMSE	%AAD	NP
	C_1	C_2			
<i>Chloride salts: 5000 ppm; solvent: EA</i>					
Calcium	-1.1458	-1.0790	0.0528	8.18	8
Barium	-1.2506	0.1884	0.0484	7.48	8
Calcium-sodium	-1.1563	-0.9400	0.0577	7.55	8
Calcium-potassium	-1.2114	0.0172	0.0480	9.04	8
Calcium-magnesium	-1.1996	0.3631	0.0504	8.18	8
Calcium-strontium	-1.2132	-0.4463	0.0577	7.69	8
Calcium-barium	-1.1456	-0.4105	0.0307	4.20	8
<i>Chloride salts: 5000 and 10,000 ppm; solvent: IPA</i>					
Strontium (5000 ppm)	-1.1901	-0.2180	0.0441	7.95	8
Barium (5000 ppm)	-1.0952	-0.9411	0.0534	8.58	8
Strontium (10,000 ppm)	-1.0963	-0.3541	0.0622	9.94	8
Barium (10,000 ppm)	-1.2305	0.2721	0.0518	7.58	8
<i>Calcium sulfate (1000 ppm)-chloride (5000 ppm); Solvent: IPA</i>					
Calcium sulfate	-6.8307	-7.3640	0.1878	4.03	8
Calcium chloride	-0.8248	-8.6046	0.0754	9.50	8
<i>Produced water-chloride: 106,654, 20,000, 10,000 ppm; solvents: IPA and EA</i>					
Chloride (100,000 ppm; IPA)	-1.0977	-4.8955	0.0678	10.72	10
Chloride (100,000 ppm; EA)	-0.9469	-4.909	0.0714	10.26	8
Chloride (20,000 ppm; IPA)	-1.0011	-2.399	0.0786	14.22	10
Chloride (10,000 ppm; IPA)	-0.9412	-2.9954	0.0668	10.97	10

Table 7

The 3-Suffix equation (Eq. 3) representation of the tested systems

$$C_1 = \ln[x_{1,3} / x_{1,2}]; C_2 = \Lambda_{32}; C_3 = \Lambda_{23}.$$

Systems	Model's parameters			RMSE	%AAD	NP
	C ₁	C ₂	C ₃			
<i>Chloride salts: 5000 ppm; solvent: EA</i>						
Calcium	-2.6559	3.0207	4.5129	0.0118	1.78	8
Barium	-2.6849	4.2005	4.6132	0.0107	1.60	8
Calcium-sodium	-2.7486	3.3783	4.8106	0.0151	2.30	8
Calcium-potassium	-2.7737	4.1994	4.9790	0.0234	3.71	8
Calcium-magnesium	-2.6627	3.6832	4.5553	0.0164	2.62	8
Calcium-strontium	-2.6240	3.5987	4.3597	0.0142	2.57	8
Calcium-barium	-1.7513	1.3558	1.8231	0.0135	2.19	8
<i>Chloride salts: 5000 and 10,000 ppm; solvent: IPA</i>						
Strontium (5000 ppm)	-2.6089	4.7672	4.4758	0.0157	3.03	8
Barium (5000 ppm)	-2.6327	4.5217	4.6908	0.0077	0.91	8
Strontium (10,000 ppm)	-2.8138	5.8820	5.3675	0.0093	1.72	8
Barium (10,000 ppm)	-2.5229	5.1844	4.1598	0.0098	1.93	8
<i>Calcium sulfate (1000 ppm)-chloride (5000 ppm); solvent: IPA</i>						
Calcium sulfate	-4.3980	-9.7539	-3.9837	0.1445	3.20	8
Calcium chloride	-3.1110	-2.1886	5.5196	0.0192	2.86	8
<i>Produced water -chloride: 106,654, 20,000, 10,000 ppm; solvents: IPA and EA</i>						
Chloride (100,000 ppm; IPA)	-3.3016	4.7406	5.9877	0.0352	6.55	10
Chloride (100,000 ppm; EA)	-3.0552	2.0824	5.3814	0.0282	6.35	8
Chloride (20,000 ppm; IPA)	-3.3111	7.9970	6.7840	0.0380	7.37	10
Chloride (10,000 ppm; IPA)	-2.7513	5.3825	5.0973	0.0138	4.15	10

However, significant improvements were achieved when Eq. (3), with three regressed parameters, was used (e.g., for calcium chloride at 5000 ppm by EA; Eq. (2) RMSE = 0.0528, %AAD = 8.18; Eq. (3) RMSE = 0.0118, %AAD = 1.78). Such improvements were attributed to the unsymmetric form of Eq. (3) with respect to θ_3 [4].

Fig. 5, as a demonstration case (produced water, chloride ion at 106,654 ppm by EA), illustrates the abilities of Eqs. (2) and (3) in correlating the precipitation data. The figure shows a plot of the left-hand side of Eqs. (2) and (3), $\ln[1 - P]$, vs. θ_3 . Without the addition of the precipitation agent, the left-hand side of Eqs. (2) and (3) is zero since P is equal to 0. Without the use of the interaction parameters (Λ_{32} and/or Λ_{23}), the precipitation data can fit a straight line, which is equivalent to the ideal mixture solubility [10,11]. These interaction parameters, however, are needed to account for the non-ideality of the systems at higher values of θ_3 [4].

As a demonstration case, a comparison of the experimental P at different V_R along with their uncertainties (σ_p) of chloride ion from produced water at 106,654 ppm using EA as a precipitation solvent, and the predicted P by the optimum predictive equation, Eq. (3), is shown in Fig. 6. The comparison indicates that the P of chloride ion from produced water at 106,654 ppm using EA is accurately predicted by Eq. (3). The

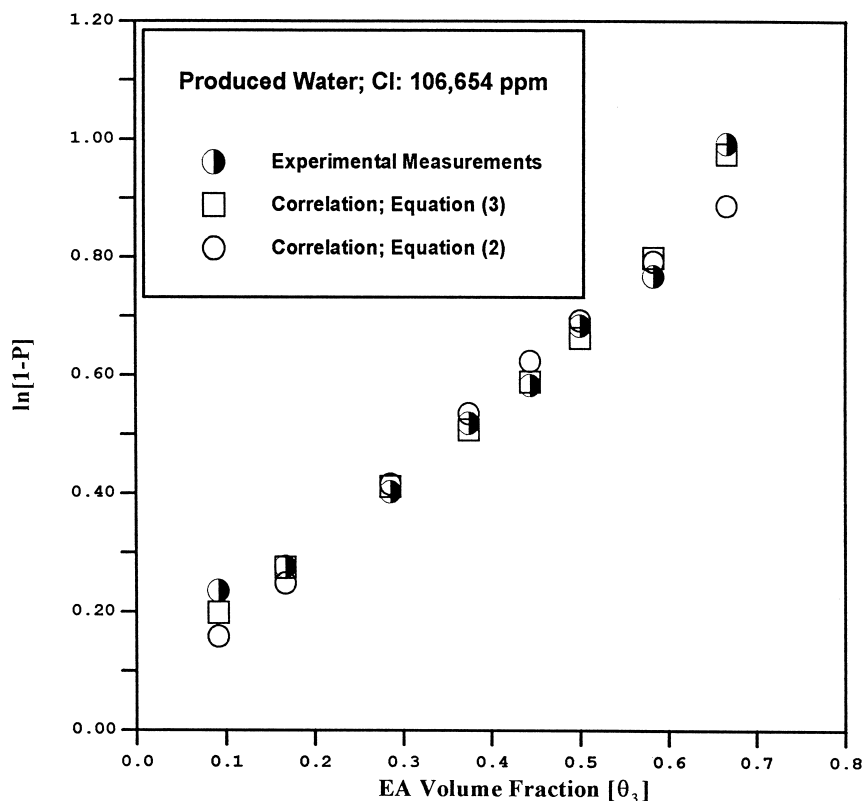


Fig. 5. Precipitation of chloride ion from produced water using EA.

resultant interaction parameters were also employed to predict the P at higher values of V_R (3.0 and 4.0) where no experimental precipitation data were available. It appears that Eq. (3) is capable of predicting the expected precipitation data and providing acceptable estimates at V_R values of 3.0 ($P = 73.6\%$) and 4.0 ($P = 79.3\%$).

4. Conclusions

A database for the precipitation of chloride and sulfate salts in univalent and divalent cation forms from aqueous streams was generated using IPA and EA as precipitation agents. Experimentally consistent precipitation data were obtained. The P of all chloride salts (at 5000 and 10,000 ppm) over the studied range of V_R by both IPA and EA are nearly identical. The P of sulfate ion at 1000 ppm from calcium sulfate–chloride system by IPA are appreciably higher than the P of sulfate ion at 1000 ppm from calcium sulfate system, while the P of chloride ion at 5000 ppm from calcium sulfate–chloride system by IPA are relatively higher than the P of chloride ion at 5000 ppm from calcium chloride system. The P of chloride ion from produced water at 106,654 ppm by both IPA and EA are higher than the P of chloride ion at 20,000 and 10,000 ppm,

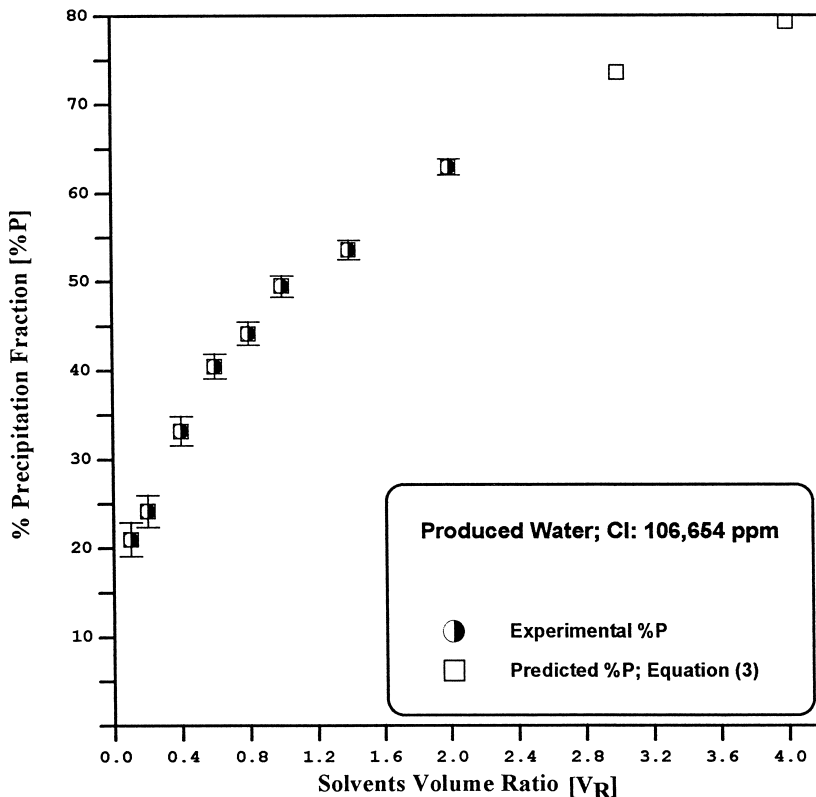


Fig. 6. Experimental and predicted precipitation fractions of chloride ions from produced water using EA.

especially at V_R values of 3.0 and 4.0. Two model equations (2-Suffix and 3-Suffix) based on the criteria of the SLE were employed to evaluate the precipitation data. The acquired precipitation data were adequately correlated by both equations. Optimum interaction parameters were provided. Such parameters can be used to estimate the P for the tested systems when no experimental data are available (e.g., different anion concentrations and/or different organic solvent volumes).

Notation

%AAD	Percent average absolute deviation
$C_{1,2}$	Concentration of anion i in standard sample (water)
$C_{1,m}$	Concentration of anion i in filtered sample (mixed solvents: water–organic)
NP	Number of points
P	Precipitation fraction
RMSE	Root mean square error
SS	Objective function

V_R	Solvents volume ratio (organic/water: V_3/V_2)
v_i	Molar volume of solvent i
V_i	Volume of solvent i
x_i	Mole fraction of anion i in liquid solution
$x_{i,j}$	Mole fraction of anion i in solvent j
$x_{i,m}$	Mole fraction of anion i in mixed-solvents mixture m

Greek symbols

Λ_{ij}	Interaction parameters of solvent i with solvent j
θ_i	Volume fraction of solvent i
σ	Standard deviation

Subscripts

1	Anion
2	Water
3	Organic solvent
cal	Calculated
exp	Experimental
m	Mixed-solvents mixture (water–organic)

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