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SOLUBILITIES AND PHYSICAL PROPERTIES OF SATURATED SOLUTIONS IN THE COPPER SULFATE + SULFURIC ACID + SEAWATER SYSTEM AT DIFFERENT TEMPERATURES

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Abstract - In Chile, the most important economic activity is mining, concentrated in the north of the country. This is a desert region with limited water resources; therefore, the mining sector requires research and identification of alternative sources of water. One alternative is seawater, which can be a substitute of the limited fresh water resources in the region. This work determines the influence of seawater on the solid−liquid equilibrium for acid solutions of copper sulfate at different temperatures (293.15 to 318.15 K), and its effect on physical properties (density, viscosity, and solubility). Knowledge of these properties and solubility data are useful in the leaching process and in the design of copper sulfate pentahydrate crystallization plants from the leaching process using seawater by means of the addition of sulfuric acid.

Keywords: Seawater; Copper sulfate; Sulfuric acid.

INTRODUCTION

The most important economic activity in Chile is mining. Currently, there is a worldwide shortage of available fresh water. Therefore, mining industries are developing new methods to optimize water use (Torres *et al*., 2013). In northern Chile, for example, certain mining companies are using raw seawater in their production processes (Rocha *et al*., 2013) and purified seawater by reverse osmosis (Philippe *et al*., 2010). In a mining process, the solid−liquid equilibrium and physical properties of solutions change upon seawater incorporation, especially the density and viscosity; which are used in pipe-sizing and pumping calculations. These properties are related to the cost of energy required to bring seawater to mining operations, usually farther than 120 km (Hernández *et al*., 2012). Copper sulfate pentahydrate (Blue vitriol) is a copper salt with a wide range of commercial applications: in agriculture as a pesticide, fungicide, feed, and soil additive (Milligan and Moyer, 1975); in mining, it is used as a floatation reagent in recovery of zinc and lead (De Juan *et al*., 1999); as a blue and green pigment in dyes, as a print toner in photography, in the production of other copper compounds, and in leather tanning (Richardson, 1997).

Actually, the production process of copper sulfate pentahydrate includes the following steps: 1) Heap leaching, where copper is obtained from oxidized ores using a mixture of sulfuric acid and water; 2) Solvent extraction, where copper is extracted from the leaching solution by mixing with a product called organic; 3) Crystallization, where the copper-loaded organic is discharged using a concentrated acid solution; 4) Re-crystallization, where copper sulfate is

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dissolved in fresh water at a temperature of 80 – 90 °C, and then crystallized by cooling to 25 – 30 °C, in order to remove the impurities (Tabilo, 2012).

Copper sulfate in distilled water solutions has been investigated for crystallization, supersaturation, solid-liquid equilibrium, and properties (De Juan *et al*., 1999; Domic, 2001, and Milligan and Moyer, 1975). In these studies, crystallization conditions of copper sulfate solutions were determined as a function of both temperature and sulfuric acid concentration. In order to optimize the water use, it is interesting to investigate the influence of seawater on the copper sulfate crystallization process. In the literature, there is a publication available of the behavior of copper sulfate in a seawater system (Hernández *et al*., 2012); this paper provides solubilities and physical properties data of $CuSO_4$ in seawater at pH 2. The present work studies the effect of seawater (3.5% salinity) on the solid-liquid equilibrium of copper sulfate in acid solutions at different temperatures (from 293.15 K to 318.15 K). This temperature range was chosen because is within the range in which the crystallization process operates. In addition, the physical properties, density, and viscosity of the saturated solution are experimentally measured and correlated with empirical equations, finding a good agreement.

From the results obtained in this investigation, and in order to minimize the use of fresh water, the next step of this work is to perform the copper sulfate crystallization process from leaching solutions using seawater to study the effect of the ions present in seawater on the habit and size of copper sulfate pentahydrate crystals.

MATERIALS AND METHODS

Reagents

Analytical grade reagents were used (copper (II) sulfate pentahydrate, Merck, 99%; absolute sulfuric acid, Merck, 95 to 97%, absolute). The experiments were performed using filtered natural seawater obtained from San Jorge Bay, Antofagasta, Chile. Table 1 shows the composition of the seawater, obtained by chemical analysis, used in this work (Hernández *et al*., 2012).

Table 1: Individual ions in seawater from Bahía San Jorge, Chile (mg·L^{-1}).

Na^+	Mg^{+2}	Ca^{+2}	K^+	B^{+3}	Cu^{2+}	Cl^-	SO_4^{-2}	HCO_3^-	NO_3^-
9480	1190	386	374	4.6	0.072	18765	2771	142	2.05

Apparatus

The solutions were prepared using an analytical balance (Mettler Toledo Co. model AX204, with 0.07 mg precision). To obtain the phase equilibrium data at different temperatures, a rotary thermostatic bath (to ± 0.1 K, 50 rpm) with a capacity of ten 90 mL glass flasks was used. The densities were measured using a Mettler Toledo DE-50 vibrating tube densimeter with $\pm 5\cdot10^{-2}$ kg·m^{-3} precision.

The kinematic viscosities were obtained using a calibrated micro-Ostwald viscometer with a Schott-Gerate automatic measuring unit (model AVS 310), equipped with a thermostat (Schott-Gerate, model CT 52) for temperature regulation. The absolute viscosities were calculated by multiplying the kinematic viscosity and the respective density.

Procedures

Equilibrium Time Determination

The equilibrium time was determined at 298.15 K. Acidic seawater was prepared by adding sulfuric acid to seawater and stirring the solution until it reached pH 2; this pH was used because it is similar to the pH levels in copper mining operations. The masses of copper (II) sulfate pentahydrate in the solution (seawater at pH 2) were measured. An excess of copper (II) sulfate pentahydrate was added to ensure saturation of the solution. Several saturated solutions ($CuSO_4$ + acid seawater) were placed in closed glass flasks and immersed in a rotary water bath at 298.15 K, these solutions were mechanically shaken. Every hour, the rotation was stopped, one flask was removed from the bath and, maintaining the work temperature (298.15 K) and using a syringe filter (to ensure that no copper sulfate pentahydrate solid was present in the solution), the solution density was measured. The equilibrium time was determined when the solutions that were taken at different times (every one hour), reached constant densities.

Measurement of Physical Properties in Different Conditions

After the equilibrium time was determined, ten solutions ($CuSO_4$ + acid seawater) at different acid concentrations were prepared.

These solutions were stirred in a rotatory water bath for 8 hours (equilibrium time). The rotation was then stopped and the solutions were decanted, maintaining the work temperature. Then, in the thermostatic bath, and using a syringe filter at a slightly elevated temperature (to prevent salt precipitation at lower temperatures), the solutions (without solid) were obtained for each equilibrium point.

Physical properties (density and viscosity) were measured in triplicate for each solution. On the other hand, copper (II) concentration was measured in duplicate by atomic absorption and the $CuSO_4$ solubility was obtained by stoichiometry.

All measurements of the physical properties and solubilities were performed at four different temperatures: 293.15, 298.15, 308.15, and 318.15 K.

RESULTS AND DISCUSSION

Experimental Results

The solubilities, densities, and viscosities are shown in Table 2, for the system studied at different temperatures and acid concentrations.

Solubilities

Table 2 shows the solubility results, expressed as mass fraction of copper sulfate (wCuSO$_4$) for different acid mass fractions (wH$_2$SO$_4$). A significant decrease in solubility was clearly observed with the increase of sulfuric acid in solution; this behavior was observed for all the temperatures. This behavior of the solubility is due to the common ion effect, because copper sulfate and sulfuric acid share the same SO_4^{2-} ion (Cisternas, 2009).

Solubility, expressed as a mass fraction, decreases from approximately 0.1684 to 0.0813 at 293.15 K; 0.1763 to 0.0956 at 298.15 K; 0.2020 to 0.1330 at 308.15 K; and 0.2335 to 0.1526 at 318.15 K. These results show that sulfuric acid might be used as an advantageous co-solvent in the crystallization processes design of copper sulfate pentahydrate.

The solubility results of the saturated solution may be correlated with the sulfuric acid composition by the following equation:

$$s = A + B \times w_2^{0.5} \tag{1}$$

where s is the solubility in mass fraction, w_2 represents H_2SO_4 mass fraction, and A and B are fitting parameters.

Physical Properties

Table 2 presents the densities and viscosities of the saturated solutions for the copper sulfate + seawater + sulfuric acid system.

Table 2: Solubility (wCuSO$_4$), density (ρ), and viscosity (η) for saturated solutions of copper sulfate in seawater at various acid concentrations and temperatures.

wH$_2$SO$_4$	wCuSO$_4$	ρ/g·cm^{-3}	η/mPa·s
293.15 K			
0.0036	0.1684	1.21779	2.549
0.0075	0.1669	1.21679	2.514
0.0152	0.1620	1.21807	2.485
0.0235	0.1570	1.21861	2.448
0.0396	0.1506	1.21897	2.379
0.0608	0.1369	1.22326	2.370
0.0828	0.1260	1.22722	2.353
0.1056	0.1179	1.22998	2.342
0.1298	0.1043	1.23603	2.361
0.1810	0.0813	1.25036	2.432
298.15 K			
0.0035	0.1763	1.22742	2.368
0.0071	0.1745	1.22705	2.345
0.0143	0.1705	1.22707	2.293
0.0221	0.1661	1.22731	2.261
0.0375	0.1572	1.22838	2.213
0.0571	0.1477	1.23131	2.175
0.0775	0.1388	1.23369	2.164
0.0994	0.1284	1.23776	2.160
0.1214	0.1182	1.24130	2.165
0.1691	0.0956	1.25438	2.204
308.15 K			
0.0034	0.2020	1.25381	2.113
0.0070	0.1995	1.25379	2.114
0.0142	0.1952	1.25285	2.069
0.0219	0.1898	1.25355	2.032
0.0369	0.1832	1.25575	1.982
0.0561	0.1754	1.25452	1.949
0.0761	0.1659	1.25710	1.927
0.0981	0.1558	1.25794	1.910
0.1183	0.1498	1.26527	1.910
0.1640	0.1330	1.27592	1.937
318.15 K			
0.0032	0.2335	1.28672	2.014
0.0065	0.2316	1.28680	2.004
0.0132	0.2252	1.28478	1.966
0.0203	0.2228	1.28468	1.934
0.0350	0.2076	1.28364	1.866
0.0527	0.2039	1.28466	1.840
0.0711	0.1973	1.28634	1.801
0.0940	0.1758	1.28865	1.777
0.1134	0.1703	1.29342	1.797
0.1579	0.1526	1.30287	1.811

The values for density and viscosity were correlated as a function of copper sulfate and sulfuric acid composition following Equations (2) and (3), respectively:

$$\rho = \exp\left(A + B \times w_1^{0.5} \ln w_1 + C \times w_2^{2.5}\right) \tag{2}$$

$$\eta = \exp\left(A + B \times w_1 + C \times w_2^{2.5} + D \times w_2^{2.5} \times w_1^{3.5}\right) \tag{3}$$

where, w_1 represents the $CuSO_4$ mass fraction, w_2 represents sulfuric acid mass fraction, and A, B, C, and D are fitting parameters. The units for density and viscosity used in these equations are g·cm^{-3} and mPa·s, respectively.

The parameter values were obtained by means of the least squares method, for all experimental data, and are shown in Table 3.The absolute average deviations (AAD) for the fitted parameters are also presented.

Table 3: Parameters values for density, viscosity and solubility for saturated copper sulfate in acidic seawater system.

Property	A	B	C	D	AAD
293.15 K					
ρ/g·cm^{-3}	-0.2322	-0.5861	2.6112		0.0005
η/mPa·s	0.8566	0.5137	1.6012	-1198.5	0.0056
w	0.1905	-0.2353			0.0043
298.15 K					
ρ/g·cm^{-3}	-0.0399	-0.3351	1.9916		0.0004
η/mPa·s	0.9453	-0.4092	-4.2035	-1455.1	0.0029
w	0.1966	-0.2238			0.0038
308.15 K					
ρ/g·cm^{-3}	0.2287	0.0037	1.6397		0.0007
η/mPa·s	0.6205	0.6883	3.2718	-607.6	0.0048
w	0.2181	-0.1980			0.0023
318.15 K					
ρ/g·cm^{-3}	0.3255	0.1054	1.7079		0.0007
η/mPa·s	0.3784	1.4117	7.1461	-311.5	0.0055
w	0.2530	-0.2401			0.0037

$AAD = \left|(s^{\exp} - s^{cal})/n\right|$, where n is the number of experimental points.

The results show that these equations fit satisfactorily the density, viscosity, and solubility experimental data.

The solubility of copper sulfate in acidic seawater with different concentrations of sulfuric acid and physical properties of the saturated solutions, at four different temperatures (293.15, 298.15, 308.15, and 318.15 K) are shown in Figures 1 to 3, along with correlated data.

It is possible to note that, for all the temperatures, the solubility decreases with increasing acid concentration. Also, the figure shows that solubility levels increased with temperature; this is because, as the solution temperature increases, the average kinetic energy of the molecules that make up the solution also increases. This increase allows the solvent molecules to break apart the solute molecules more effectively that are held together by intermolecular attractions.

Figure 2 compares the density of saturated solutions of copper sulfate in acid seawater at four different temperatures (293.15, 298.15, 308.15, and 318.15 K).

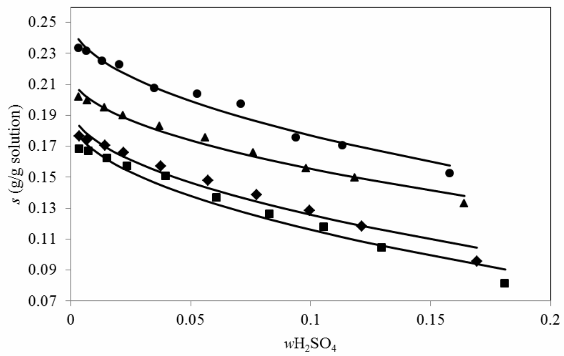

Figure 1: Solubility for the saturated solutions ($CuSO_4$ + acid seawater): ■, 293.15; ♦, 298.15 K; ▲, 308.15 K; ●, 318.15 K; ─, correlations with Eq. (1).

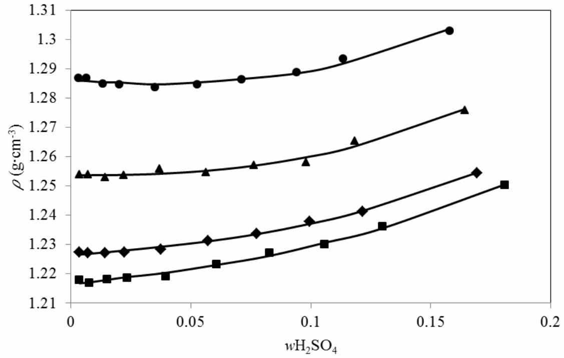

Figure 2: Density for the saturated solutions ($CuSO_4$ + acid seawater): ■, 293.15 K; ♦, 298.15 K; ▲, 308.15 K; ●, 318.15 K; ─, correlations with Eq. (2).

As can be seen, there is a slight decrease in the density of the solutions at low acid concentrations. However, at a certain point, it begins to increase. This behavior is better observed at higher temperatures (at low temperatures this decrease is not clear).

This phenomenon could be attributed, at low acid concentrations, to the copper sulfate solubility decrease, and therefore, the density; however, as the acid concentration increases, the solution density begins to increase, due to the high density of the sulfuric acid.

Figure 2 shows that the density values increased slightly with temperature.

Figure 3 compares the viscosity of saturated solutions of copper sulfate in acid seawater at four different temperatures (293.15, 298.15, 308.15, and 318.15 K).

It is possible to note that, for all the temperatures, viscosity values decrease with increasing acid concentration. Also, the figure shows that viscosity levels decrease slightly with increasing temperature. This behavior is expected, as observed in the work of

Hernández, Hotlos and Price (Hotlos and Jaskula, 1988; Price and Davenport, 1980; Hernández *et al.*, 2012).

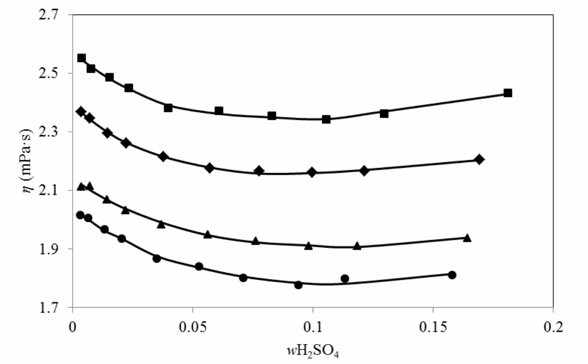

Figure 3: Viscosity for the saturated solutions ($CuSO_4$ + acid seawater): ■, 293.15 K; ♦, 298.15 K; ▲, 308.15 K; ●, 318.15 K; —, correlations with Eq. (3).

These results confirmed the good fit between experimental values for concentrations of the salt and the physical properties of the saturated solutions at four temperature levels, in a broad range of acid concentrations.

On the other hand, looking for a single equation that includes the effect of different temperatures, we used the empirical models proposed in the work of Milligan (Milligan and Moyer, 1975); to estimate the density and solubility of the system $CuSO_4$ - H_2SO_4 - H_2O at different temperatures (Equations (4) and (5)). The parameters of these equations were adjusted in acid seawater; for Y_0, solubility values of $CuSO_4{\cdot}5H_2O$ in fresh water from the literature (Linke and Seidell, 1965) were utilized.

The proposed equations are shown below:

$$\rho = \frac{1}{C_2}\ln\left[e^{C_2 A_2} + e^{C_2((a_2)X+B_2)}\right] \tag{4}$$

$$Y = \frac{1}{C_1}\ln\left[e^{C_1(A_1\cdot X+Y_0)} - e^{C_1(A_1\cdot X+B_1)} + e^{C_1 B_1}\right] \tag{5}$$

where:

Y = mass percentage of $CuSO_4{\cdot}5H_2O$ in saturated solution

ρ = density of saturated solution in $g{\cdot}cm^{-3}$

X = mass percentage of H_2SO_4 in solution

T = temperature in °C

$Y_0 = 20.37e^{0.01316T}$ = mass percentage of $CuSO_4{\cdot}5H_2O$ in saturated solution with no acid content

$$A_1 = -a_1 e^{(b_1)T} \tag{6}$$

$$B_1 = C_1\left[1 + e^{(-d_1)(T-e_1)}\right]^{-1} \tag{7}$$

$$C_1 = f_1\left[1 + g_1(T-h_1)^2\right]^{-1} \tag{8}$$

$$A_2 = b_2 e^{(c_2)T^{(d2)}} \tag{9}$$

$$B_2 = e_2 + f_2^T \tag{10}$$

$$C_2 = g_2\left[1 + h_2(T-i_2)^2\right]^{-1} \tag{11}$$

The parameter values are shown in Table 4. The absolute average deviations (AAD) for the fitted parameters are also presented.

Table 4: Parameter values for density and solubility for saturated copper sulfate in acidic seawater system.

Property	Parameters		Temperature	AAD
Solubility	a_1	0.1165	293.15 K	0.2222
	b_1	0.0943		
	c_1	21.7293	298.15 K	0.3287
	d_1	0.0931		
	e_1	30.6388	308.15 K	0.2861
	f_1	16.7409		
	g_1	2.0939	318.15 K	0.4501
	h_1	15.0081		
Density	a_2	0.0094	293.15 K	0.0008
	b_2	1.187		
	c_2	0.00017	298.15 K	0.0005
	d_2	1.5986		
	e_2	0.9897	308.15 K	0.0011
	f_2	0.00162		
	g_2	15.51	318.15 K	0.0014
	h_2	0.00038		
	i_2	34.16		

$AAD = \left|(s^{\exp} - s^{cal})/n\right|$, where n is the number of experimental points.

In Figures 4 and 5, the density and solubility values of saturated solutions of copper sulfate in acid seawater at four different temperatures (293.15, 298.15, 308.15, and 318.15 K), and the correlations with the Equations (4) and (5) can be seen.

The experimental values for density, and solubility in the saturated solutions were correlated adequately using Equations (4) and (5) shown previously.

Also, the comparison between experimental values of solubility for saturated solutions of copper sulfate in seawater, with data of copper sulfate in fresh water presented by Milligan and Moyer (1975) as a function of acid concentration at four different temperatures 293.15 K, 298.15 K, 308.15 K, and 318.15 K is performed and the results are shown in Figure 6.

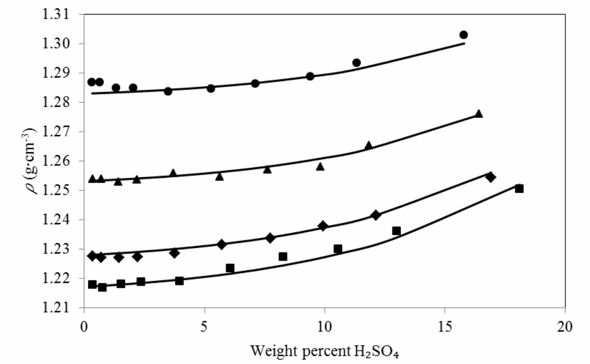

Figure 4: Density for the saturated solutions ($CuSO_4$ + acid seawater): ■, 293.15 K; ♦, 298.15 K; ▲, 308.15 K; ●, 318.15 K; ─, correlations with Eq. (4) (Milligan and Moyer, 1975).

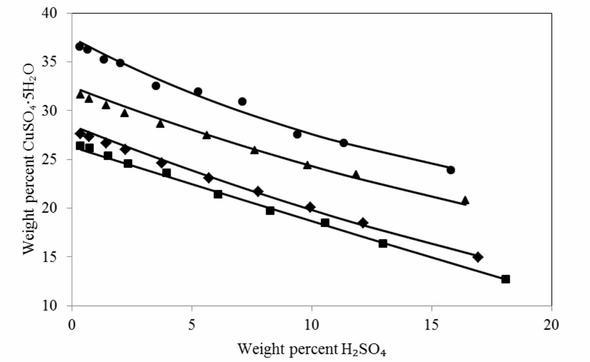

Figure 5: Solubility for the saturated solutions ($CuSO_4$ + acid seawater): ■, 293.15; ♦, 298.15 K; ▲, 308.15 K; ●, 318.15 K; ─, correlations with Eq. (5) (Milligan and Moyer, 1975).

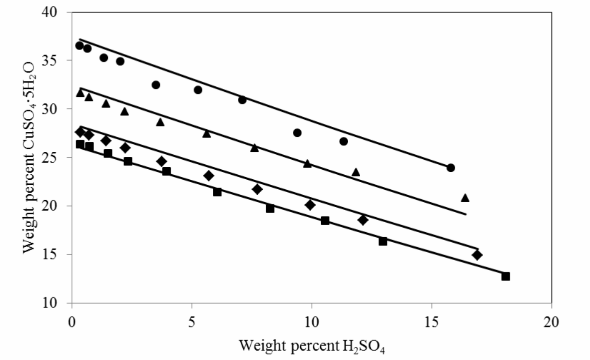

Figure 6: Solubility for the saturated solutions ($CuSO_4$ + acid seawater): ■, 293.15; ♦, 298.15 K; ▲, 308.15 K; ●, 318.15 K. Black lines show fresh water data at different temperatures (Milligan and Moyer, 1975).

It is possible to note that the solubility of copper sulfate pentahydrate in seawater is lower than the solubility of this salt in fresh water. This phenomenon is due to the presence of salts in seawater, which contribute to decrease the solubility of copper sulfate. This is because the water activity of seawater is lower than the water activity of fresh water and therefore the solubility is lower. Furthermore, as mentioned in Table 1, seawater composition presents 2771 mg·L^{-1} of SO_4^{2-} ion, which could be responsible of the decrease in the copper sulfate solubility in this medium, due to the common ion effect. This can be the reason why the average deviation is higher with this equation with respect to the equation proposed in this work.

CONCLUSIONS

With increasing temperature and acid concentration, an increase is observed in the density of the solutions, and there is a slight decrease in the density of the solutions at low acid concentrations.

With increasing acid concentration and temperature, there is a decrease in the solution viscosity.

With increasing acid concentration, there is a decrease in the solubility; on the other hand, when the temperature increases, the solubility increases.

The experimental values for density, viscosity, and solubility in the saturated solutions, were adequately correlated using Equations (1) to (3) proposed in this work, with absolute average deviations for density, viscosity, and solubility of 0.0005, 0.0056, and, 0.0043, respectively, at 293.15 K; 0.0004, 0.0029 and, 0.0038, respectively, at 298.15 K; 0.0007, 0.0048, and 0.0023, respectively, at 308.15 K; and 0.0007, 0.0055, and 0.0037, respectively, at 318.15 K.

The experimental values for density, and solubility in the saturated solutions were correlated adequately using Equations (4) and (5), with absolute average deviations for density, and solubility of 0.0008, and 0.2222, respectively, at 293.15 K; 0.0005, and 0.3287, respectively, at 298.15 K; 0.0011, and 0.2861, respectively, at 308.15 K; and 0.0014, and 0.4501, respectively, at 318.15 K.

The solubility of copper sulfate pentahydrate in seawater is lower than the solubility in fresh water due to the presence of salts in seawater, which contribute to decrease the solubility of copper sulfate.

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