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EFFECT OF TEMPERATURE AND CONTENT OF CHLORURATED SALT OF Cu(II), Mn(II) OR AL(III) ON THE DENSITY OF ACIDIFIED SEAWATER AND WATER MIXES SAMPLES

JUAN SEGOVIA [1], JUAN M SANDOVAL[2] AND VENECIA HERRERA [2]*

[1]*Facultad de Ingeniería y Arquitectura, Universidad Arturo Prat, Casilla 121, Iquique. Chile.*
[2]*Facultad de Ciencias, Universidad Arturo Prat, Av. Arturo Prat 2120, Iquique. Chile.*

ABSTRACT

The relationship between the density of seawater and acidified mixtures samples in the presence of up to a maximum concentrations of 0.18 m for Cu(II), 0.34 m for Mn(II) or 0.6 m for Al(III), in selected temperatures used in the copper leaching process (283.15 - 313.15 K), showed a positive linear behavior with salinity and cation concentration.

The influence of temperature on the density rate changes was similar when comparing the three solutes in acidified solutions of different salinity. The effect of temperature on the change in density did not exceed 1% and by concentration, the greatest influence was due to Al(III) with 5.43%, in agreement with its greater relative quantity.

The data obtained, using a vibrating tube density meter, were used to analyze and correlate to the Apelblat equation that was favorably applied to calculate the isobaric expansibility coefficient. The temperature had an influence on the isobaric expansibility coefficient values, suggesting a making interaction effect due to majority anions present in the seawater and mixture samples ($Cl^- > SO_4^{-2}$), and a breaking interaction effect when the cations Cu(II), Mn(II) or Al(III) were added.

Keywords: Sea water, Density, Expansibility coefficient, Heap leaching, Copper/Manganese/Aluminum ions.

1. INTRODUCTION

Copper mining in the northern regions of Chile is developed in very arid environments of geographical heights between 600 to 4,900 meters above sea level. due to transport costs, Mineral benefit plants are installed close to the extraction sites, where stacked acid leaching process and for high-quality copper production by solvent extraction are common practices. In this process, the crushed ore is irrigated with either continental water resources, saline solutions, or acidified seawater, which dissolves those available materials in their passage through the stack [1-5]. Given the environmental conditions present in this territory, such as water scarcity and high evaporation rate, water must be continuously recirculated, concentrating dissolved ions during this process [6]. The main cations reported in leaching solutions correspond to Al (III), Fe (II) / Fe (III), Mn (II), Cu (II) ions, among other major and trace ions associated with the minerals [5-7].

Hydraulic conductivity is a property of soil-liquid systems that determines the speed with which a fluid circulates through porous soil. This property is impacted by the permeability of the soil, as well as by the density of the solutions that irrigate it [8]. In heap leaching for copper ores, continuous changes in temperature due to heat generation from bio- and chemical reactions [9-10], as well as changes in concentration due to dissolution of metals [5,7], could affect the density.

The density of a solution, as a function of concentration and temperature, is one of the most important properties for calculations of material and energy balances in industrial and metallurgical processes [11,12], as well as to understand the interactions between solutes and their solvents [13-17].

For a better understanding of the molecular interactions in homogeneous mixtures, thermodynamic parameters such as isobaric expandability or apparent molal volume can be determined from solution density experimental data [11,13,14]. Several density studies of aqueous electrolyte solutions have been reported, both in binary and multicomponent systems [18-21], which have developed empirical equations [22-27] that relate density to temperature, solution composition, and pressure. Apelblat [12], carried out a detailed analysis of 634 aqueous solutions, introducing a new two-parameter equation that represents the density of these solutions as a function of composition and temperature. On the other hand, several studies have applied statistical and semi-empirical thermodynamic models adjusting or corroborating density values [28-31]. The preferred method for the determination of density is the vibratory tube assay that allows both adequate control of temperature and accurate analysis of the uncertainty [14,32].

Due to local water scarcity in mining processes, the use of seawater has become an alternative to be considered [1,2,5]. The physicochemical properties of seawater have been extensively studied [32-36], where density value is defined as a function of temperature, pressure, and salinity, with a practical use value of 1,030 kg m^{-3}, even though it can obtain values between 1,022 - 1,027 kg m^{-3} at different latitudes [32-37]. Seawater composition (3.5% w/w) presents various compounds in the form of dissolved ions classified as majority ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- y CO_3^{2-}) and trace elements, mainly metals, metalloids, and a constant ratio of N/P. The total amount of these ions expresses salinity and their composition is considered constant [32,37,38].

The application of seawater in the hydrometallurgical process of copper generates notable advantages according to studies carried out on copper sulfides, especially with chalcopyrite [2,5,39]. Especially, several investigations over the effect of chloride ion (up to 50 g L^{-1}) on copper leaching at acidic pH, showed that chloride ion contributes to the formation of copper-chloride complexes, which favor the dissolution rate of copper sulfides through cuprous ions [40,41]. However, there is still no information available on the density of acidified seawater in the presence of major and trace ions, for a range of temperatures recorded in mining plants located in the metallogenic band of the foothills and Central Andes from South America.

The objective of this work was to evaluate the thermal behavior (between 283.15 K and 313.15 K) of the density of seawater acidified to pH 2 for six selected molal concentrations (m) of leaching solutions in a density meter oscillating tube assay at 1 atm; in particular, we selected for Cu(II): 0-0.16 m, for Mn (II): 0-0.30 m, and for Al (III): 0-0.60 m, respectively. Trials with pure water and equal parts mixing solutions (1:1), were also included. The isobaric expansibility coefficient for the solutions was determined using the Apelblat equation and a comparison was made with a polynomial equation, obtained by adjusting the density of the solutions as a function of concentration and temperature.

2. MATERIALS AND METHODS

All reagents used were analytical grade or higher: Copper chloride (II) dihydrate (PA) (99.0 %, Merck); Manganese chloride (II) tetrahydrate (PA) (ACS reagent, ≥ 99 %, Sigma Aldrich); Crystallized hexahydrate aluminum chloride (PA) (≥99.0%, Fluka Analytical); Concentrated Hydrochloric acid (PA) (37%, Merck).

Seawater (SW) was obtained from the coastal edge of Huayquique Campus at Arturo Prat University (20.2708° S, 70.1298° W, Iquique, Chile), then filtered with NW50 filters (50 µm, CentriPure), and disinfected by UV treatment with three QL250 sterilizer lamps apparatus (Lifegard Aquatics). Deionized water (DW) was ultrapure in quality (18.2 µS cm^{-1}). A mixture (1:1) was prepared with equal parts SW and DW. The three solutions were acidified at pH 2.00 with concentrated hydrochloric acid at room temperature (20 ± 1° C), and pH measurements were obtained with Orion Star A211 pH-meter (Thermo Scientific).

*Corresponding author email: juan.segovia@unap.cl

Acidified solutions were prepared on molality scale using gravimetric method in glass containers with back cover and refrigerated (6 ± 1° C), prior to measurement. Concentration standards for Cu (II) between 0 to 0.16 mol kg^{-1}; for Mn (II) between 0 to 0.3 mol kg^{-1} and for Al(III) it was between 0 to 0.6 mol kg^{-1}; these intervals were selected based on data from copper mineral benefit processes [3,10].

Mass measurements were performed on a RADLOA6 AS220/C12 analytical balance with an uncertainty of ± 0.0001 g. Density measurements at six temperatures (283.15-313.15 K), at intervals of 5 and 10 K, were carried out at the Mineral Processing Laboratory of the Department of Chemical Engineering and Mineral Processes (University of Antofagasta), using an Anton Paar DSA 5000 M oscillating tube density meter (± $1X10^{-6}$ g cm^{-3} accuracy). For temperature control, the equipment has a Peltier system with ± 0.01 K precision. Experimental measurements of aqueous solutions density and temperature yielded 600 data points, considering the repetitiveness of samples. The data analysis included the statistical description of the measurements, significance, and their adjustment. All correlation analyses were performed through the R 3.6.0 program, using VEGAN, STATS, and GGPLOT211 packages [11].

The percentage change in density (%△ρ), was calculated according to equation 1 as the quotient between the difference in density of the temperature range and the density at the smallest temperature of the range.

$$\%\Delta\rho = \frac{\rho(T_1)-\rho(T_2)}{\rho(T_1)} \times 100 \qquad (1)$$

Where ρ (T1) is the density at the lowest temperature in the range and ρ (T2) is the density at the highest temperature in the range.

The Apelblat equation [12], was used to correlate the experimental density values of the solutions, according to the expression defined by equation (1). Where at a given temperature, ρ represents the density of the solution, ρref represents the density of the reference solution, w is the molar fraction of the ion, while A and B are adjustable parameters. To relate the molar fraction to the molality (m), equation (2) was used, where M is the molar mass of the compound.

$$F(w) = \frac{1}{\rho_{ref}} - \frac{1}{\rho} = Aw + Bw^2 \qquad (2)$$

$$m = \frac{1000w}{[(1-w)M]} \qquad (3)$$

The units used for ρ in this equation was g cm-3 and for molality was mol kg-1. Reference densities were considered to be the density of acidified SW, 1:1 mixture, and DW samples.

The determination of the coefficient of thermal expansion (α_P) was obtained from equation 3 [13], whose density was evaluated using the Apelblat equation.

$$\propto_P = -\frac{1}{\rho}\left(\frac{d\rho}{dT}\right)_P \qquad (4)$$

3. RESULTS AND DISCUSSION

The densities of the aqueous systems, the effect of temperature at the presence of dissolved ions under study are shown in Figures 1-3. It could be determined to see that the density value (g cm^{-3}) decreases as the temperature increases (283.15 - 313.15 K) in the 3 aqueous systems analyzed (SW, 1:1 mixture and PW), this behavior has been previously reported in binary aqueous solutions with different electrolytes using pure water [22,42], seawater [37] and in standard seawater solutions [32].

In particular, the determination of density in the acidified seawater samples presented a range of values of 1,018-1,027 kg cm^{-3} (Fig 1), these results are similar to those published by Garcia [37], who determined that the density of surface seawater in the equatorial zone (294.15 - 295.15 K) presents its minimum value (~ 1,022 g cm^{-3}), while in the polar transect it reaches a maximum value of ~ 1,028 g cm^{-3}. In samples of mixed acidified water (1:1) (Figure 2), the density in the solution showed values in a range of 1.005 - 1.014 g cm^{-3}, indicating that the dilution of seawater affects its thermophysical property under study. In acidified pure water (Figure 3), the density value decreased to a range of 0.992 - 0.999 g cm^{-3}, is consistent with data previously reported [43].

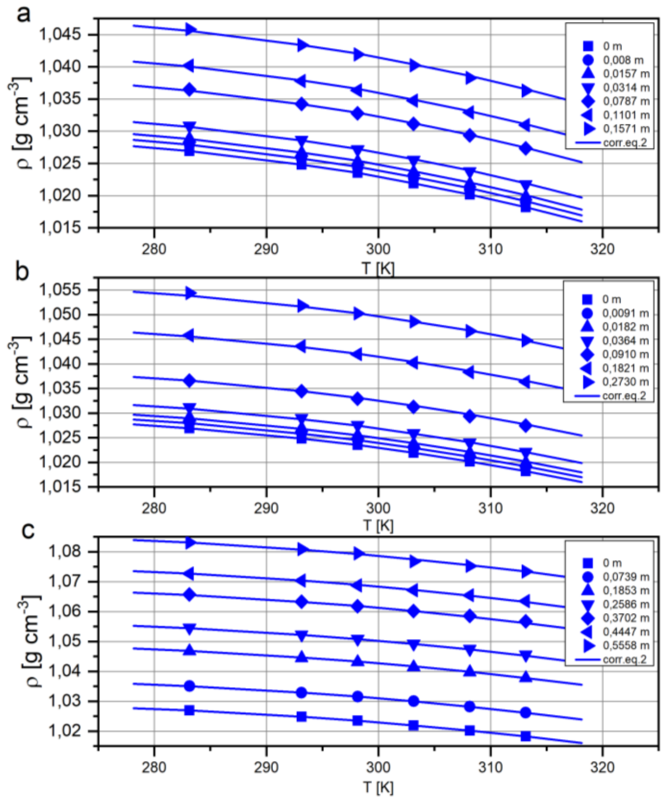

Figure 1. Variation of the density (g cm^{-3}) for acidified seawater with temperature (K), in the presence of molality concentrations (m) of chlorurated (a) Cu(II), (b) Mn(II), and (c) Al(II) salts.

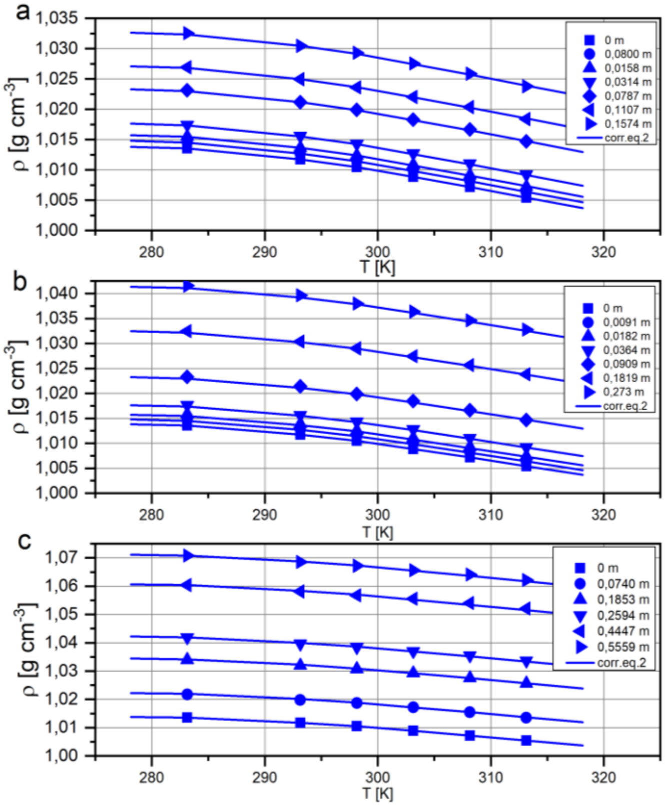

Figure 2. Variation of the density (g cm^{-3}) for acidified 1:1 mixture with temperature (K), in the presence of molality concentrations (m) of chlorurated (a) Cu(II), (b) Mn(II), and (c) Al(II) salts.

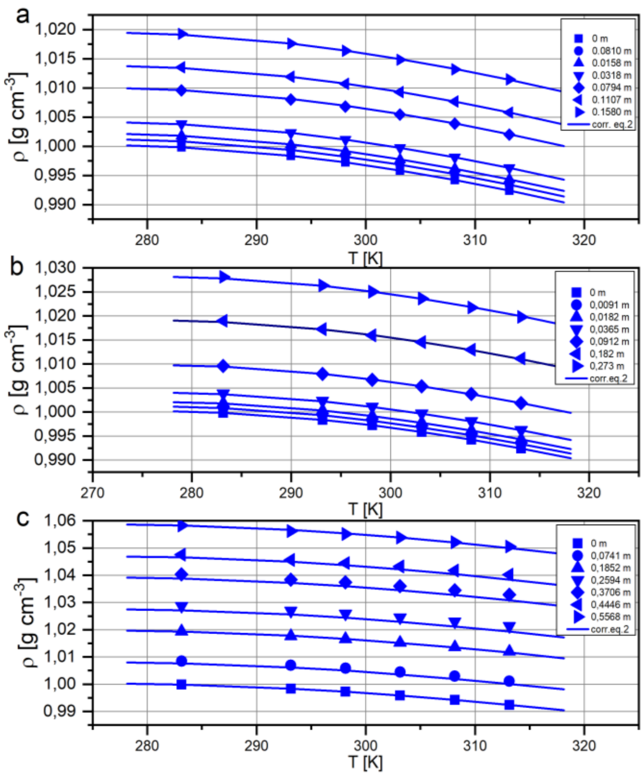

Figure 3. Variation of the density (g cm^{-3}) for pure water with temperature (K), in the presence of molality concentrations (m) of chlorurated (a) Cu(II), (b) Mn(II), and (c) Al(II) salts.

When applying the density calculation model for seawater, proposed by Sharqawy et al [44], no significant differences were observed in the values obtained for samples of acidified waters when they were compared with the non-acidified (<0.43 ± 0.02%, not shown); this allowed us to suggest that the concentration of protons seems to not induce a significant effect on the parameter analyzed.

Due to the scarcity of water resources, mainly in the mining area, it requires the search for other sources such as sea or desalinated water, to meet industrial requirements. In copper leaching processes, any change in the density of the aqueous solution can affect the hydraulic conductivity of it. Figure 1 shows the average effect for density in seawater, when a maximum concentration (m) of selected ions was present, at different temperatures. The water density for the acidified seawater solution with Cu(II) increased by 1.80 ± 0.03% (Figure 1a), regarding the solution without this ion. When Mn(II) was added, the density for acidified seawater increased by 2.62 ± 0.03%; meanwhile for Al(III), this increase reached 5.43 ± 0.04% (Figure 1b-c). When acidified pure water was compared, at the same concentrations of Cu(II), the perceptual density value decreased slightly with increasing temperature (2.58% - 2.71%). For Mn(II), the equivalent comparison indicated a range between 2.43% - 2.60%; meanwhile for Al(III), it was between 2.29% - 2.51%. When the water density was compared with acidified pure water, without dissolved ions, the difference can reach up to 4.60% for Cu(II), 5.50% for Mn(II), and 8.32%, for Al(III). The results of these percentage variations could be decisive in studies of hydraulic conductivity that use seawater, where it is usual to consider the density values of pure water or seawater to simulate the irrigation flow on a heap [4].

Table 1. Percentage change in density (△ρ) for aqueous solutions in the presence of metal ions for the temperatures range 283.15 to 308.15 K.

	SW	Mix 1:1	PW
Cu(II)	0.8876 ± 0.0002	0.8228 ± 0.0002	0.7547 ± 0.0001
Mn(II)	0.8916 ± 0.0002	0.8345 ± 0.0002	0.7680 ± 0.0003
Al(III)	0.8595 ± 0.0003	0.7992 ± 0.0002	0.7215 ± 0.0001

Table 1 shows the calculated values of percentage change in density (%△ρ) for the solutions in a temperature range between 283.15 to 308.15 K, in the presence of metal ions. The values were obtained considering as a reference the measured density of the solutions in study at 283.15 K. The results show a change ≤ 1% in the density value of water samples tested: for acidified seawater (in the presence of Cu(II) or Mn(II) or Al(III) ions) a mean maximum value of 0.88 ± 0.02%; for 1:1 mixture, 0.82 ± 0, 02% and for acidified pure water, 0.75 ± 0.02%. Using the Sharqawy equation [44], similar percentage values of density change were obtained for the unacidified aqueous solutions (seawater, 1:1 mixture, and pure water; with values of 0.89%, 0.83%, and 0.75%, respectively), confirming that the presence of protons in solution does not have an important effect on the density of aqueous solutions. Consequently, the effect on △ρ would depend on the content of major ions [35], It should be noted that the concentrations of Al(III) used were two times higher than those for Mn(II) and approximately ~4 times higher than those for Cu(II).

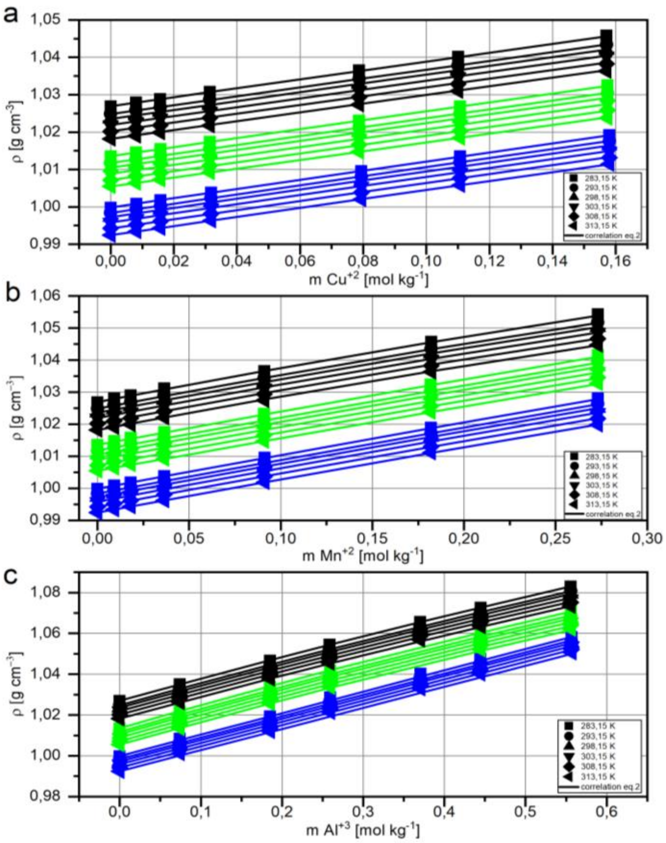

Figure 4. Graphic comparison of the behavior of the density (g cm^{3}) in the temperature interval (K), for the three acidified water solutions (black: seawater, green: 1:1 mixture, and blue: pure water) as a function of molality concentration (mol kg^{-1}) of (a) Cu(II), (b) Mn(II), and (c) Al(II) ions.

The density value at six temperatures, in acidified solutions of seawater, 1:1 mixture, and pure water, depending on the concentration of Cu(II), Mn(II), or Al(III) (expressed in molality) is shown in Figure 4 a-c, respectively. The results showed that the density increases as the salinity and the concentration of the dissolved ion increased, while the effect of temperature on the density of the solutions has little or no influence. For the series of data obtained, a linear regression was applied, obtaining that the density is linearly dependent on the concentration of the dissolved ions. The linear regression coefficients determined were between 0.998319 and 0.999978. The analysis of the slopes, which represent the change in density according to the change in concentration, showed that the presence of Cu(II) ion generates a slightly greater effect (average 0.119 ± 0.002), compared to the slopes obtained for Mn(II) and Al(III) (mean of 0.101 ± 0.0002), which were significantly similar. The influence of ion concentration and temperature can be understood by the intermolecular interactions between solute and solvent, whose volumetric properties are sensitive to these variables (13-17).

Herrington [45], measured the density of aqueous solutions of $MnCl_2$ up to 3 m between 298.15-348.15 K and calculated the apparent molal volume for the solute, reporting values between 19.492 - 20.513 cm^3 mol^{-1}.

Pogue [46,47][1,2][1,2], obtained the densities of aqueous solutions of various salts, including $CuCl_2$ and $MnCl_2$, and derived the molal partial volume using the equation developed by Redlich-Meyer for solutions between 0.0 - 3.5 m, at temperatures between 288.15-328.15 K, showing that the molar volume 8.9 - 10.76 cm^3 mol^{-1} for Cu(II) is less than the molal volume for Mn (II) (17.9 - 18.13 cm^3 mol^{-1}). Given that density relates to the mass and volume of a compound, and considering that the molar mass of $CuCl_2$ is greater than $MnCl_2$, the change in density for the solution with $CuCl_2$ must be greater than the solution with $MnCl_2$, this conclusion is consistent with the slopes obtained from the curves in Figure 4. There is no scientific information available to compare these variables in the presence of aluminum salts. For their part, the values of the intercept of the lines are close to the density values of the acidified solvents (SW, mixture, and PW) in the absence of Cu(II), Mn(II), or Al(III) ions.

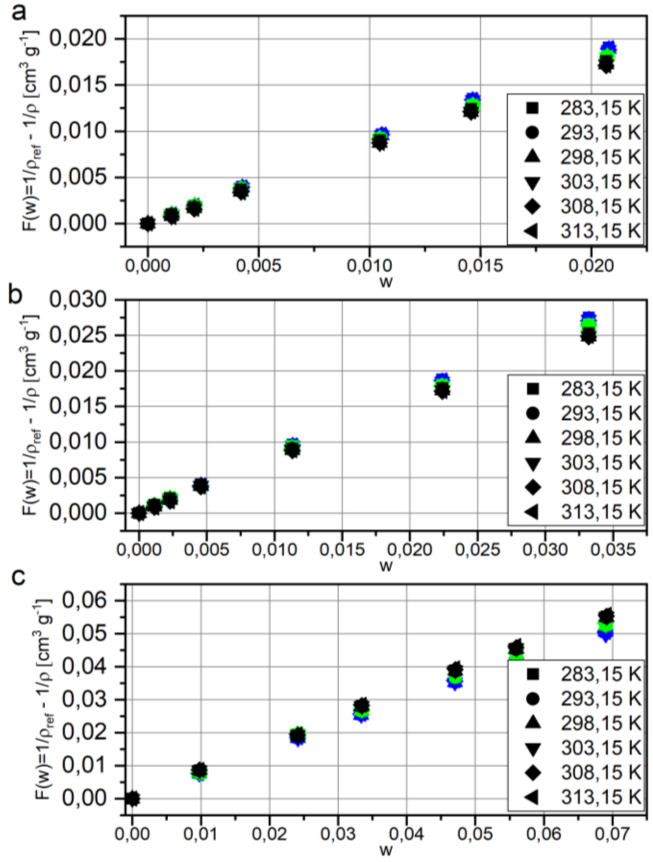

Figure 5. Relationship between the function F(W) and the physical concentration of (a) Cu(II), (b) Mn(II), and (c) Al(II), for acidified water solutions (black: seawater; green: 1:1 mixture, and blue: pure water) at different temperatures (K).

An important number of algebraic expressions have been developed for the correlation and prediction of the density of a great variety of aqueous binary solutions [12]. The two-parameter equation (2), indicated in the methodology, used in binary solutions for various solutes (such as inorganic electrolytes, ionic liquids, amino acids, organic acids among others), determines the effect of concentration as dominant over the influence of the temperature [12]. The results obtained from the function F(w) of the saline solutions under this study, as shown in figure 5, was dependent only on the mass fraction of the solute and not on the temperature, corroborating that at different temperatures the relationship between the inverses of the reference density and the experimental density, it obtains similar values when varying the amount of solute.

These results have been observed and reported in various types of aqueous solutions [48]. The values of parameters A and B for all the study solutions were ordered according to salinity in Table 2. These parameters are dimensionless, independent of temperature and ionic composition. The results obtained for the values of A and B are in agreement with those obtained by Apelblat [12], which proposed equation is applied to binary aqueous solutions; for the parameter A, our results fluctuated between 0.30098 to 1.73878 (average of 0.84 ± 0.04).

Table 2. Parameters A and B of two-parameter equation of Apelblat for aqueous solutions (SW, Mix 1:1, and PW) in the presence of ion metals. AAD (absolute average deviation) represents the experimental average deviation in relation to the calculated value from the model described by Hernandez y cols [23].

	Cu(II)			**Mn(II)**			**Al(III)**		
	A	B	AAD	A	B	AAD	A	B	AAD
SW	0.8465	-0.2720	0.00009	0.8283	-2.3845	0.00002	0.7890	-0.8329	0.00002
Mix 1:1	0.8763	-0.4688	0.00005	0.8124	-0.8143	0.00020	0.8397	-1.0961	0.00002
PW	0.9269	-0.7992	0.00003	0.8474	-0.8538	0.00004	0.7902	0.1338	0.00087

The values determined for the parameter B in the Apelblat works, presented a range between -2.11640 and 3.28950; in this work, the results showed for B a minimum value of -2.3845 and a maximum value of 0.1338. The absolute mean deviation (AMD) for the correlation of the equation, describes satisfactorily the system and these results support the relevance of the model used in seawater and diluted seawater samples tested.

The expansibility or isobaric expansion coefficient (α_p) was determined, which expresses the rate of change in volume to temperature (equation 4), and are shown in Figures 6 and 7, for acidified samples of seawater and 1:1 mixture, respectively, in the absence and presence of different molal concentrations of metal ions. For a better interpretation, both graphs included the pure water curve data obtained from Robinson and Stokes [49]. Figure 6, also includes the curve for an internal standard seawater sample (salinity of 42.11 g kg^{-1}, slightly alkaline pH), whose data were calculated using the Sharqawy equation [44]. Additionally, Figure 7 contains a curve for an internal standard 1: 1 mixture solution (salinity of 21.1 g kg^{-1}, not acidified).

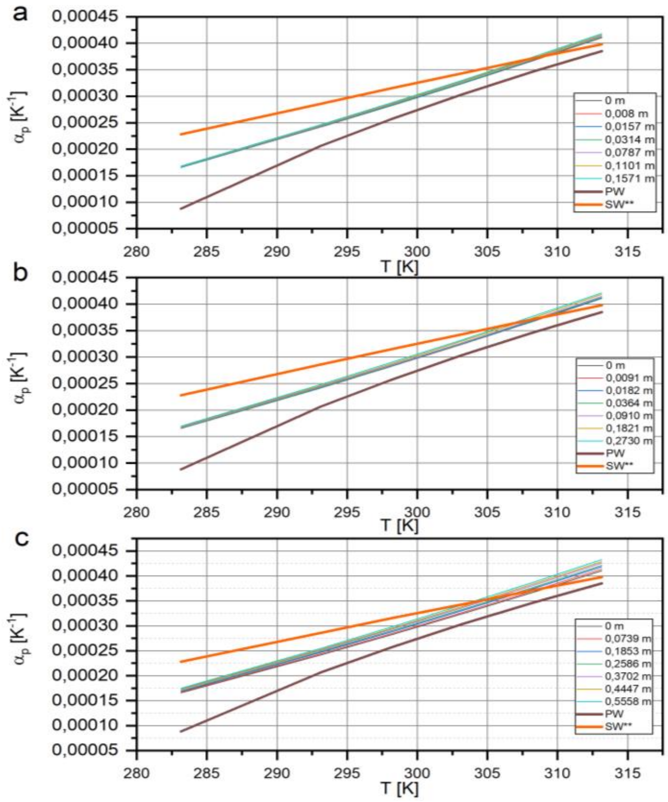

Figure 6. Effect of temperature (K) on the isobaric expansibility coefficient (α_p/K^{-1}) for acidified seawater solutions in the presence of molal (m) concentrations of (a) Cu(II), (b) Mn(II), and (c) Al(II). PW (pure water), and SW** (internal standard seawater sample (salinity of 42.11 g kg^{-1}, slightly alkaline pH))

The effect of temperature on the expansibility of acidified seawater solutions in the presence of Cu(II), Mn(II), and Al(III) is shown in Figure 6 a-c, respectively. It was observed that the expansibility increases with increasing temperature and slightly with increasing cation concentration. At low temperatures, the expansibility for the acidified seawater solution (which includes ions) showed higher values compared to pure water, but it is lower than the internal standard seawater sample included; increasing temperature decreases these differences. The result obtained can be explained from the behavior of the ions contained in an aqueous solution, in this way, the increase in the expansibility of seawater is due to the breaking effect of Cl^- and a lesser extent for SO_4^{-2} [50]. This behavior decreases with increasing temperature, possibly due to the depletion of the water structure [14]. Additionally, the cations Cu(II), Mn(II), or Al(III), generate a making effect at low temperatures in acidified seawater, which corresponds to the maintenance of the water structure; it is important to note that Marcus [50], has previously reported that the making effect depends on the ion analyzed (with lower intensity for Al(III), compared to Mn(II) and Cu(II) which were similar), attenuating the effect generated by the anion Cl^-. As can be seen in Figure 6, when the temperature increases, the high concentration of Cl^- anion allows to maintain the tendency of the solution to break the structure of water, exceeding the expansibility threshold of seawater from temperatures between 305.0 - 310.0 K, an effect concentration-dependent by Cu(II), Mn(II) or Al(III) ions.

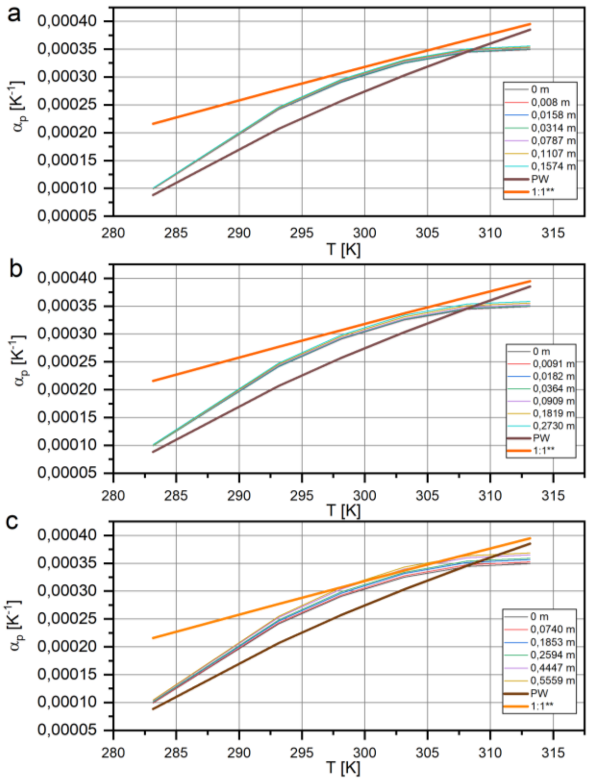

Figure 7. Effect of temperature (K) on the isobaric expansibility coefficient (α_p/K^{-1}) for acidified 1:1 water mixture solutions in the presence of molal (m) concentrations of (a) Cu(II), (b) Mn(II), and (c) Al(II). PW (pure water), and 1:1** (internal standard 1: 1 mixture solution (salinity of 21.1 g kg^{-1}, not acidified)).

Figure 7 a-c, shows the expandability values for the water mixture 1:1 assays, in the presence of Cu(II), Mn(II), and Al(III), respectively. It was determined that the expandability values present similar behavior when compared with the samples of acidified seawater in the presence of ions (Figure 6), they increased as the temperature is increased, with a slightly increment when a higher concentration of ions was added. Graphically, the curves obtained for the 1:1 mixture samples that included ions crossed the expandability curve for pure water, between 307.0 - 310.0 K, with a maximum expandability value (~ 0.00035 K^{-1} on average); after these temperatures, the expandability values for the mixture solutions were lower than those obtained for pure water, showing the importance of the making effect generated by Cu(II), Mn(II), and/or A(III) cations, at higher temperatures [13,50]. In general, at temperatures below 307.0 K, a combination of breaking (due to major anions) and making (due to metal ions) effects that maintain the expandability values for the experimental solutions above of those obtained for pure water; however, the expansibility values were lower than those determined for the internal 1:1 standard mixture solution included in the analysis. These results scan be explained due to the dominant breaking effect generated by Cl^-, present in standard mixture solution. When comparing the expandability results of the experimental samples with respect to pure water, it is observed that they are higher in a wide range of temperatures (283.15 - 307.0 K), this effect can be explained by the breaking effect of chloride ion, which decreases at higher temperatures. Water in its liquid state has a highly structured organization, and the Gibbs free energy is set relative to the average number of hydrogen bonds, the loss of the structure of water (breaking effect) is due to lower intermolecular interactions and a decrease in Gibbs free energy. As a counterpart, an increase in this energy indicates that hydrogen bonds are being formed on average (making effect). When solutions are cooled, molecular arrangements generally occur and in the case of an increase in temperature, expansibility takes place [13]. The decrease in the breaking effect is considered to be due to the breakdown of water structure at high temperatures, in particular for samples of diluted seawater, a process that is compensated by the equalization of expansibilities. The seawater salinity is represented by the content of the majority ions, among these, Cl^- and Na^+ exceed 50% [35]; however, in Marcus' ionic classification, Na^+ ions does not generate appreciable effects on the structure of the water [50].

CONCLUSION

The densities of acidified seawater and mixture samples, decrease slightly at increased temperatures when different concentrations of Cu(II), Mn(II) or Al(III) ions, which are present during copper leaching process, reaching variations of less than 1%.

The increase in salinity and cations concentration, produced an increase in density, where the greatest effect was determined by Al(III) (+5.43%), consistent with its high relative content. The results of the linear correlation analysis determined that the change in rates of density were similar when comparing the three ions assessed.

The isobaric expansibility coefficient values as a function of temperature, salinity, and the presence of cations, calculated using the Apelblat equation, were consistent with the classification developed by Marcus (2009) for major and trace ions. The presence of Cl^- and SO_4^{-2} ions, decrease the density change value due to the braking effect, as opposed to the making effect caused by Cu(II), Mn(II), or Al(III) ions.

The use of seawater in a copper leaching process could affect the permeability in the heap, it is recommended to work with the diluted resource and must include other thermophysical properties in future studies and simulations.

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