Empirical models to determine ions concentrations in lithium brines with high ionic strength

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A B S T R A C T

Argentina Puna brines are complex systems in which ions such as Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, and $B_4O_7^{2-}$ are presents. To obtain lithium carbonate from brines, they must be treated in order to increase its lithium concentrations and to eliminate the others ions that are presents in the brines. During concentration some salts can reach their solubility products (kps) and crystallize, producing different solid-liquid equilibriums. In order to design and select the process to purify the brine before lithium salts precipitation, it is necessary to know the other ions concentrations.

Ion concentrations in solutions can be calculated based on the salts coefficient activities using Pitzer's model and its modifications. These methods have the restriction that can only be applied to solutions with ionic strength values up to 6 molal. The state of the art shows that the approach to study the equilibrium in complex system is to consider it as binary, ternary, quaternary and quinary systems. When ionic strength values are higher than 6 m the systems studied are binaries or have symmetrical ions.

Brines of the Argentina Puna have, in general, initial ionic strength values around 6 molal and it increases when the brine is concentrated by evaporation, so the available thermodynamical models cannot be used to determine, beforehand, the final composition of a certain brine. In this work four different brines from four different Puna plateau in Argentina were evaporated to several degrees and ionic strength was calculated from the chemical brine's composition after each evaporation test. Ionic strength was found to correlate with the percentage of eliminated water following two different simple mathematical models, depending on the initial sulphate concentration of the brine and the possibility of its precipitation. Models to estimate the concentration of diluted ions of commercial value such as Li^+, K^+, and Mg^{2+} as function of ionic strength were also proposed. Ion concentrations could be modeled as function of the amount of eliminated water, once the correct relationship between this parameter and the ionic strength of the brine is established. These models correlate accurately ionic strength and ion concentrations for an ionic strength range from 4.8 to 15.4 molal; corresponding to percentages of water evaporated from 0% up to 60%.

With these models it is possible to calculate beforehand the final ions concentrations after a given percentage of evaporated water. It allows to design brines processing and select the purification techniques without exhausting and time-consuming tests. Nowadays there are no tools that allows to do that, in consequence, each company must perform rigorous and numerous tests with its brines. Results of these work show that ionic strength is the parameter that unified brines behavior even if initial composition could be different. In consequence, it could be used as a parameter to describe brine behavior during evaporations.

1. Introduction

Mining is one of the main sources in the production of goods, generation of services and infrastructure development; it also allows improving the quality of life in society [1]. Over time, it is perceived that progress in the area is not only in terms of increased demand but also in the development of new technologies [2,3]. Particularly, lithium-ion batteries have a key role in energy conversion and storage. Nowadays,

world's lifestyle demands mobile power and, in consequence, the development of Li-ion batteries is constantly growing resulting in different designs that adapt for a considerable number of applications [4]. Due to the constant developments in Li-ion batteries technology, lithium carbonate became a commodity. Consumption of lithium in 2022 was projected to be about 134,000 tons, a 41% more than 2021. Worldwide lithium production capacity was estimated to be 130,000 tons per year [5]. Lithium carbonate can be obtained from minerals or brines. South America, most specifically, salars in the Puna regions of Chile, Bolivia, and Argentina, hold about 52% of worlwide lithium resources [5]. Nowadays the majority of these salars, with 200–600 ppm (parts per million) of lithium, are exploited to obtain lithium carbonate. In order to obtain this salt, brine must be processed. This means, to eliminate ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, and $B_4O_7^{2-}$ and concentrate the lithium. The methods to eliminate an ion from a solution depend of several factors, but the main one is their initial concentration. Independently of the selected lithium extraction process, the composition of the brine and specially magnesium concentration is of great importance. The Mg^{2+}/Li^+ ratio is priority to exploit a given salar, a higher ions ratio impedes the obtention of high purity lithium products increasing the cost of lithium recovery [6–10].

Before lithium carbonate precipitation, lithium concentration in the brine must be approximately between to 30,000–50,000 ppm [11]. Even though there are several advances in lithium extraction from brines such as ion sieve-adsorption, solvent extraction, membranes, and electrodyalisis among others [12–15], due to the environmental characteristics of the Puna (high solar radiation, low humidity, and high daily temperature gradients), the common concentration method is solar evaporation which is the most environmentally friendly method [15]. In this process, the brine is pumped into shallow ponds with large surface to increase solar radiation incidence. Also, brine evaporation could be done using an evaporator (forced evaporation) [16]. During evaporation some salts can reach their solubility products (kps) and crystallize, producing different solid-liquid equilibriums. In general, sodium concentrations in brines are near to the saturation; in consequence, sodium chloride precipitate since the first evaporation step. On the other hand, potassium chloride precipitation depends on the amount of water evaporated (around 60%) [17–20]. In brine processing, the term purification refers to the elimination of the other ions present in the brine.

Because of the complexity of the system, each company must perform several concentrations and purifications test with their own brine. In consequence, it could be said that the process is exclusive for a certain brine. This means that if the company expands its zone of exploitation to other salars; the process developed for one brine, not necessarily could be used to exploit other without major modifications. The methods to eliminate an ion from a solution depend of several factors, but the main one is their initial concentration.

Knowing the evolution of the system (brine) during the evaporation is of great practical importance to optimize the industrial process which, at the moment, can not be standardized. There must be a parameter that allows to unify brines behavior during their concentration; this parameter must take into account that during this process different equilibria are reached. Solid-liquid equilibrium of diverse saline systems has been rigorously studied by several authors using synthetic solutions and, in consequence, a variety of models were proposed. The majority of the models are based on the Debye-Hückel theory which was developed for infinitely diluted solutions (concentrations lower than 0.01 m (mol/kg solvent)). This theory introduced the following parameters: activity coefficient (γ) and osmotic coefficient (φ) as a function of ionic strength. These coefficients are temperature dependant and are related to the equilibrium concentration. Once they are determined, the equilibrium concentrations of the system can be calculated. Because the application of the Debye-Hückel theory is restricted to dilute solutions, it can not be used to describe concentrated electrolyte systems.

Different authors modified the Debye-Hückel theory in order to describe more complex ionic systems and to calculate their equilibrium

concentrations. Several empirical models were proposed. The more extended one is Pitzer's Model [20], that describes very well binary, ternary, and even quaternary systems with ionic strength up to 6 m. Pitzer and Simonson [21] developed a mole-fraction-based thermodynamic model for systems containing salts with symmetrically charged ions applicable over the entire concentration range. Clegg and Pitzer [22] extended the model by introducing composition-dependant terms into the Debye-Hückel expression as an additional short-range parameter for the interaction between the solvent and a single anion and cation for highly concentrated solutions. Tests showed that the model was able to represent, within experimental error, osmotic and activity coefficients in single salt and ternary ion solutions containing the species H^+, Na^+, K^+, Cl^-, and NO_3^-.

Different authors applied Pitzer's model and the extended Debye-Hückel theory to determine activity and osmotic coefficients [23–28]. All of these authors work with ionic strength up to 6 m. Weber [29] determined activity and osmotic coefficients for systems containing salts of univalent ion charge such as NaCl, KCl, NaNO₃, and KNO₃. He also determined the thermodynamic parameters for NaCl solutions with ionic strength equal to 12 m. However, this model could be applied only to binary systems where all ions have the same charge. Lovera et al. [30] determined the solubility of the system NaCl–LiCl–H₂O at different temperatures. For a temperature of 100 °C they obtained a good adjustment using solubility data for LiCl up to 25 m.

Rowland et al. [31] performed an extensive study using other authors' data. They analyzed different cases and concluded that Pitzer's model and its modifications can not model complex and concentrated electrolytic systems. Lassin et al. [32] uses a modification on the Pitzer's model to calculate the thermodynamic properties of the system: H–Li–Na–K–Ca–Mg–Cl–H₂O. In order to do so, authors divided the system in binary, ternary, and quaternary subsystems. For the systems containing LiCl the authors work with concentrations over 6 m, while for the other systems concentrations were lower or equal to 6 m. Garcés [33] applied Pitzer's model to determine equilibrium thermodynamic parameters of a natural brine from Chilean salars obtaining a good fit to experimental data due to the fact that the ionic strength of the system is always lower than 6 m. Li et al. [34] worked with a brine used in the petrochemical industry in China. They applied Pitzer's model modified by Harvie and Weare [35] to determined ions concentrations. Results obtained differs from experimental data in some ranges due to the complexity of the system.

Lassin and André [36], studied the CaCl₂–H₂O system up to 250 °C using Pitzer equations and extended their study to the multicomponent HCl–LiCl–NaCl–KCl–MgCl₂–CaCl₂–H₂O system. The authors studied the binary system (CaCl₂–H₂O) from 25 °C to 250° in concentrations range from pure water to 30 M and then apply their results to model ternary systems containing H^+, Li^+, Na^+, K^+, and Mg^{2+}. After analyzed their results, authors concluded that the model is unstable for ternary systems at concentrations close to the solubility limits and above 100 °C.

Keller et al. [37] applied the Pitzer's Model to describe sea water evaporation. They performed different evaporation tests over synthetic NaCl–KCl, NaCl–KCl–CaCl₂, NaCl–KCl–MgCl₂ and three other solutions replicating sea water Na^+, K^+, Cl^-, Mg^{2+}, Ca^{2+} and SO_4^{2-} concentrations. Solutions were evaporated until reach 45 evaporation degree. Authors concluded that their model agrees, in general for the four ions, with the experimental data for ionic strength values up to 10 m. However, when solutions became complex (three ions) and specially when Ca^{2+} was replaced by Mg^{2+} the model had problems describing accurately solutions containing Mg^{2+} and SO_4^{2-} for ionic strength values higher than 10 m.

Is evident that complex systems require an integral and exhausting study. In this paper four different brines were studied. Brines from four different salars of the Argentina Puna Region (Diablillos, Hombre Muerto, Antofalla, and Pozuelos) were concentrated by evaporation at several stages and their ions concentration were measured and analyzed. Data obtained from each step of evaporation were used to calculate the

ionic strength. It was found that brines behavior during evaporations depends on gypsum precipitation affecting the ionic strength evolution. In consequence, this parameter was found to correlate with the percentage of eliminated water following two different simple mathematical models, depending on the initial sulphate concentration of the brine. Models correlate accurately Li^+, K^+, Na^+, and Mg^{2+} concentrations from an ionic strength range of 4.8–15.4 molal. This means ion concentrations could be modeled as function of the amount of eliminated water. Knowing beforehand ion concentrations in brines allow to design industrial process without performing a large number of time consuming tests. On the other hand, the fact that different brines can be group according to its ionic strength evolution during evaporation, means that brines process standardization could be done as function of this parameter.

2. Materials and methods

Brines from four different salars (Table 1) from the Argentinian Puna were selected for this study. Brine I represent the most frequently found composition. Brine II has the lowest content of NaCl. High SO_4^{2-} concentration characterizes brines II and III. Brine IV has a low Li^+ concentration but an extremely high Ca^{2+} content. Boron concentration is unusually high in Brine I.

Brines I and IV were concentrated by several steps of evaporation expressed in percentage of mass of water evaporated. After each evaporation, the solid-liquid system rested 24 h before phases separation. Evaporation tests were performed simulating natural evaporation at room temperature (298.15 K). An amount of brine (100 kg) was placed in a container previously weighed. Container dimensions were 87 cm long, 57 cm wide and 27 cm of height. Brine plus container were placed over an industrial scale capable of weight up to 200 kg. To simulate wind action two fans were placed longitudinally to the container surface at a high such air stream does not generate waves in the brine. During evaporation some salts crystallized due to brine total volume reduction. After each step of evaporation, the solids were carefully harvested and the brine that impregnated them separated by vacuum filtration. After this operation solid mass and brine volume were registered.

Brine obtained after crystals filtration was returned to the container and a liquid sample were took to be analyzed. Crystals were dried at 313.15 K until reached constant weight. These procedures were repeated until evaporate 64.29% of water for Brine I and 60.57% for Brine II.

In each evaporation test, the percentage of mass of water evaporated was calculated as a function of initial and final brine mass, following Equation (1).

$$\% W_{ev.\ i} \frac{m_{bi} - m_{bf}}{m_{bi}} * 100 \tag{1}$$

Where: m_{bi} and m_{bf} are the initial and final brine mass respectively.

The accumulative percentage of water evaporated was determined according to Equation (2):

$$\% W_{ev.\ acc} \frac{w_{ev.\ n} + \sum w_{ev.\ n-1}}{m_{bi}} * 100 \quad n = 1, 2, 3, \ldots, k \tag{2}$$

Where: $m_{ev.n}$ is the mass of water evaporated in the n stage, $m_{ev.n-1}$ is the mass of water evaporated in the (n-1) stage, and m_{bi} is the total initial mass of brine evaporated.

Concentrations of Brines III and IV as well as its pH data were provided by two different industrial companies. Concentrations of Ca^{2+}, Mg^{2+}, Na^+, Li^+ and K^+ were determined by AAS (Shimadzu AA6051F). Ion SO_4^{2-} was analyzed by gravimetry, precipitating $BaSO_4$ by $BaCl_2$ addition. Cl^- was analyzed by volumetry with $AgNO_3$ solution using the Mohr method, while B_2O_3 concentration was determined by titrimetry of boric acid with $Na(OH)$, adding manitol to increase its acidity. Crystallized salts were determined by chemical analysis data, mass balance, and DRX (Philips 3020 radiation $CuK\alpha$, Ni filter (a 35 kV, 40 mA)).

Ionic strengths of the solution were calculated according to Equation (3):

$$I = \frac{1}{2} \sum_1^i m_i z_i^2 \tag{3}$$

where m is the molal concentration of the ion i and z_i is its charge.

3. Results

1. Concentration by evaporation

To determine which compound can precipitate in a given solution, concentration values are often compared with solubility values of pure substances in water. In multicomponent systems, such as brines, solubility of salts changes in presence of other ions due to ion interactions. There are no data about solubility of salts in such multicomponent systems. Because of ionic interaction, using the reported saturation concentrations in water, would not be accurate or representative of the equilibrium that exist in the brines.

Sodium concentrations for the four brines after each evaporation step are shown in Fig. 1.

In Brines I and IV sodium concentration diminishes from the beginning of the evaporation process and solid precipitation was observed. Crystals composition was around 33% Na^+ and 58% Cl^- indicating that NaCl crystallizes; in consequence, these brines are initially saturated in
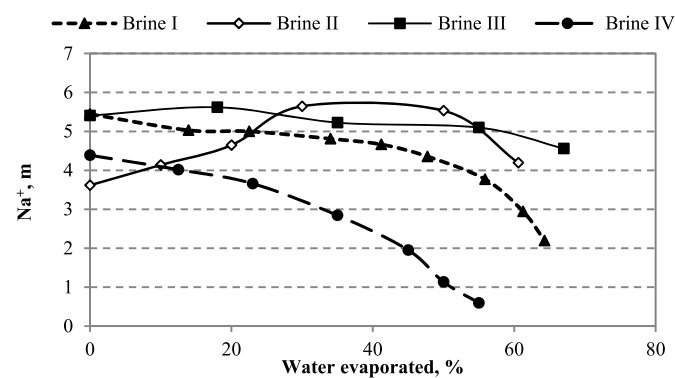

Fig. 1. Sodium concentrations vs. amount of water evaporated.

Table 1
Chemical composition of brines from Pozuelos (I), Diablillos (II), Hombre Muerto (III) and Antofalla (IV) salars.

	Chemical composition, g/100 mL									I	pH
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^-	$B_4O_7^-$	HCO_3^-	mol/kg water	
Brine I	0.08	7.46	0.47	0.22	0.19	13.33	0.17	2.03	0.38	7.09	8.00
Brine II	0.06	5.60	0.58	0.14	0.05	0.59	0.59	0.17	N/D	4.80	7.50
Brine III	0.08	11.07	0.82	0.18	0.07	18.02	1.02	0.21	0.06	6.23	7.23
Brine IV	0.02	8.88	0.14	0.48	2.37	20.78	0.04	0.15	N/D	7.39	6.79

N/D: non determined.

NaCl.

Sodium concentration in Brine II increases up to 30% of evaporation and then start diminishing, while in Brine III it reaches its maximum value when 20% of water is evaporated, from that point sodium concentration diminishes due to precipitation. Therefore, Brines II and III are not initially saturated in NaCl. Notice that Brines I and IV, which are initially saturated in Na^+, have Na^+ concentrations between 4.4 and 5.4 m. Brines II and III, once they reach their saturation, have Na^+ around 5.6 m. These values are lower than its solubility in water (6.12 m) [38]. Sodium and chloride are the major ions that are present in natural brines. For very soluble salts, the presence of other ions has not a significant effect over this salts' solubility; only when ions are present in high concentrations, could affect salts behavior due to the influence over ionic strength [39]. As the rest of ions, in the natural brines studied, have little concentration, it could be considered that they do not influence significantly over the solubilities of the major salts in the beginning of the concentration process. Although all the brines saturate at similar points, at the end of the evaporation Na^+ concentrations differ significantly due to the surge of ions concentration, consequently the increasing of ionic interaction during brine evaporation [39].

Due to the fact that sodium chloride is the major component in brines, figures that show the solubility of Mg^{2+}, Li^+, SO_4^{2-}, and K^+ in NaCl solutions are presented. Fig. 2a, b, and 2c show Li^+, Mg^{2+}, and K^+ solubilities in NaCl solutions. In these figures it is showed that concentrations are lower than those of saturation; the only exception is SO_4^{2-} concentration in brines II and III.

In the case of gypsum, it increases its solubility in NaCl solutions from 0.12% w/w SO_4^{2-} up to values shown in Fig. 3. According to this Figure and considering initial sodium concentration in the brines, gypsum can be expected to precipitate only from Brines II and III, in spite of their relatively low Ca^{2+} concentrations (less than 0.10 g/100 mL) because SO_4^{2-} concentrations values are higher than those given by Linke [40].

Reiss et al. [41] studied gypsum precipitation under saline conditions. Authors found that gypsum solubility in sodium chloride solutions reaches its maximum, at ionic strength values equals to 3.23 m. Also, indicates that this data coincides with those obtained when calcium sulphate precipitates from sea water. Authors stress that ionic strength effect over gypsum depends on the system matrix (solution composition). This explains why for Brines II and III gypsum starts to precipitate at different ionic strength values: 7.25 m and 6.71 m respectively.

To corroborate salts precipitation from Brine II, a solid sample after 50% of water evaporated was analyzed by X-Ray diffraction (DRX). The diffractogram is shown in Fig. 4.

According to Fig. 4, gypsum ($CaSO_4 \cdot 2H_2O$) and Basanite ($CaSO_4 \cdot 0.5H_2O$) are present in the precipitate. As it was expected the main peaks correspond to Halite (NaCl). Small quantities, undetectable by mass balance, of Sylvite (KCl) and Ulexite ($NaCaB_5O_6(OH)_6 \cdot (H_2O)_5$) in the solid phase are probably due to coprecipitation. Lithium and magnesium
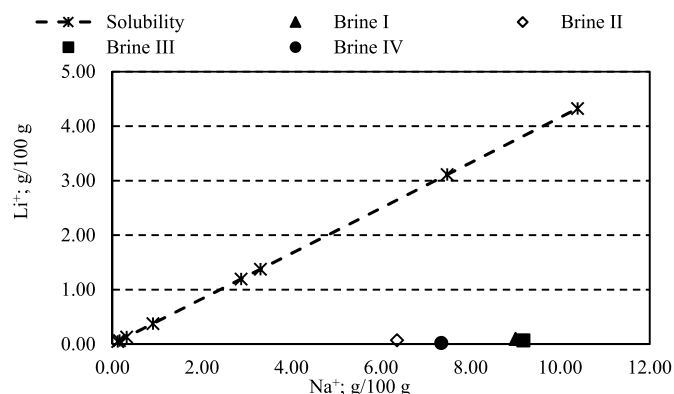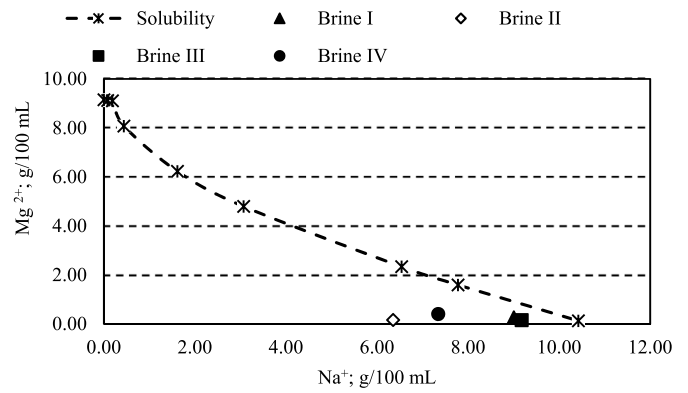

Fig. 2b. Magnesium chloride solubility in the presence of NaCl (T = 25 °C) [40].
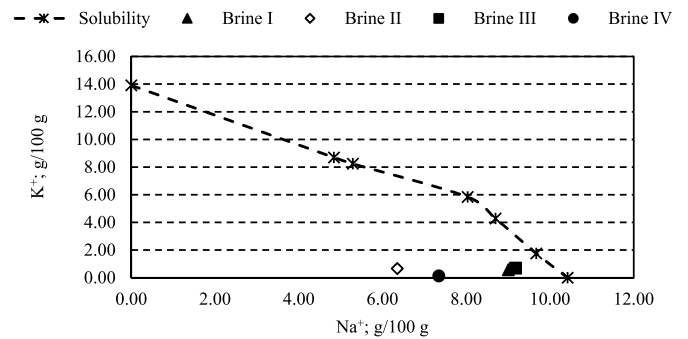

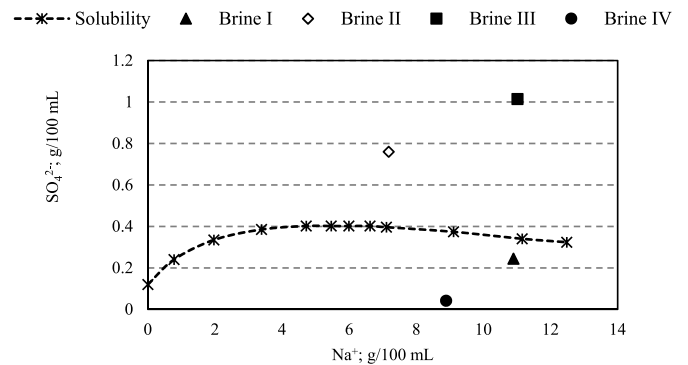Fig. 2c. Potassium chloride solubility in the presence of NaCl (T = 25 °C) [40].

Fig. 3. Gypsum solubility in the presence of NaCl (T = 25 °C) [40].

are not present in the diffractogram showing that these ions increase their concentration without precipitating.

Although in Brine I and III Mg^{2+} concentration is near equilibrium curve [39], it is confirmed by mass balance that $MgCl_2$ does not precipitate. Experimental data for $MgCl_2$ - NaCl – H_2O and $MgCl_2$ - KCl – H_2O ternary systems at 298.15 K, indicates that $MgCl_2 \cdot 6H_2O$ solubility is almost constant around to 0.09 (molar fraction) when NaCl solubility increases from 0.000 to 0.004 (molar fraction), or for KCl concentrations from 0.000 to 0.002 (molar fraction); for sodium and potassium concentrations higher than those reported, magnesium chloride is soluble. In the studied brines, sodium and potassium concentrations are much higher than those informed by Tanveer et al. [42]; confirming that magnesium chloride does not precipitate during brines evaporation.

According to Zhou et al. [43] in all the brines studied, NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$ concentrations are insufficient for $MgSO_4$ and Na_2SO_4 precipitation; this fact maintains for all the evaporations stages. Also,

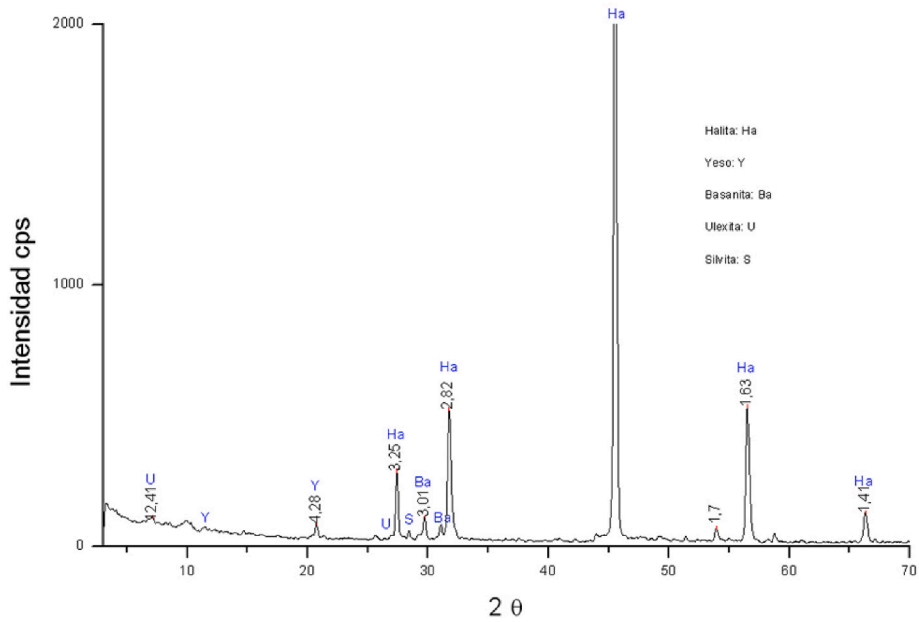Fig. 2A. Lithium chloride solubility in the presence of NaCl (T = 25 °C) [40].

Fig. 4. Diffractogram of the solid sample obtained after 50% of water evaporation of Brine II.

brines contain other ions such as, $B_4O_7^{2-}$ HCO_3^-, which do not saturate and, in consequence, do not precipitate either.

Ion concentrations evolutions during brine evaporation are shown in Figs. 15–18 along with model adjustment.

2. Ionic strength modeling

The Pitzer parameters represent the interactions between different ions in solution and can be used to calculate concentrations for other systems in which the same ions are present. However, Pitzer's model and its modifications has the ionic strength (no higher than 6 m) or complexity of the system as a limitation.

Different authors simulated a variety of systems, calculating Pitzer parameters for solutions with ionic strength less or up to 6 m. For system with higher ionic strength, authors studied binary or ternary systems in which ions had the same electrical charge [20–32].

As was said before brines are not ideal solutions, and ionic strength would take an important role and can influence ions solubilities and brines behavior during evaporation. In consequence, ionic strength was chosen as a common parameter to predict the evolution of ions concentration in the studied natural brines.

Values of Ionic strength were calculated using Equation (3) based on experimental data. In a first attempt, ionic strength evolution was modeled using PHREEQC software which used Pitzer's model [44]. This was made in order to corroborate Pitzer's model limitations or to see if this model could be used to explain brine behavior in the range of the Puna brines ionic strength values. Results are showed in Figs. 5–8.

Model adjustment using Pitzer is bad for brines I and II. For brines III and IV model adjust experimental data for up to 40% of water evaporated; from this point model deviation is important. Model is represented by a full line while experimental data is plotted in dots.

Ionic strength increases from values around 5 up to 16 m, depending on the brine. These values of ionic strength are out of range for Pitzer's model application [20–32]. Figs. 5–9 shows ionic strengths evolution for the studied brines.

In Brines II and III ionic strength seem to follow a straight line with positive slope, while data from Brines I and IV show that ionic strength increases exponentially. This difference is due to gypsum precipitation during evaporations in Brines II and III along with NaCl. According to Equation (1), ionic strength diminishes as divalent ions concentrations
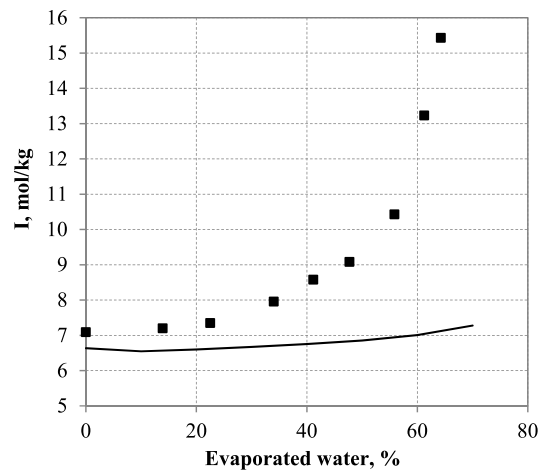

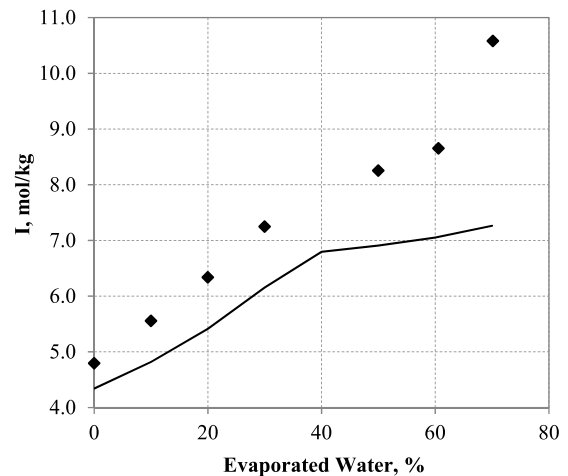**Fig. 5.** I vs. evaporated water Brine I.

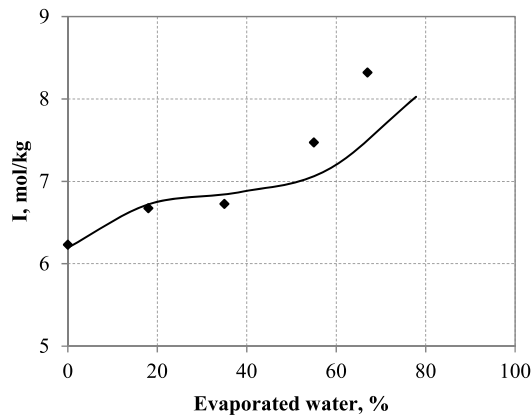**Fig. 6.** I vs. evaporated water. Brine II.

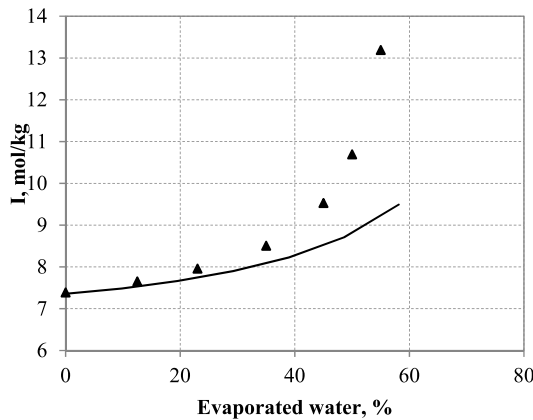**Fig. 7.** I vs evaporated water. Brine III.

Fig. 8. I vs. evaporated water. Brine IV.

in the brine decrease. Both pairs of brines show that ionic strength evolution is independent of the individual ions concentration and is only dependent of the overall concentration variations [39].

Both kinds of systems can be represented by simple mathematical models, as shown in Figs. 10 and 11. These models were obtained using XLSTAT software, the fit in both cases being of more than 80%. Brines II and III show only a linear increase of their ionic strength due to the gradual elimination of part of the divalent ions by precipitation as $CaSO_4$.

Models' adjustment is shown in Fig. 12a and b. The adjustment was made using Pearson correlation.

For Brine I and IV the non-lineal model is represented by Equation (4) while for brines II and III is represented by Equation (5).

$$I = 7,212 + 0,0518 - 0,00291x^2 + 0,0000621x^3 \qquad (4)$$

$$I = 5,328 + 0,0550x \qquad (5)$$

In these equations, x represents the percentage of water evaporated.
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3. Ion Concentrations modeling

A model to predict the evolution of ions concentration could be formulated using one of the ionic strength models obtained above.

The ions of interest during the brine processing are Li^+, Mg^{2+} and K^+. The interest in lithium is because of lithium carbonate uses and price. Magnesium is also important because the kps of magnesium carbonate is two orders lower than lithium carbonate. In consequence, it precipitates first, so it is necessary to know final magnesium concentration after each evaporation step in order to eliminate it before precipitating lithium carbonate. Potassium could be recovered as a by-product to be used as raw material in different industries; therefore, it is also important to know its concentration in the brine after evaporation. By chemical analysis of the solids and liquid and by mass balance it was determined
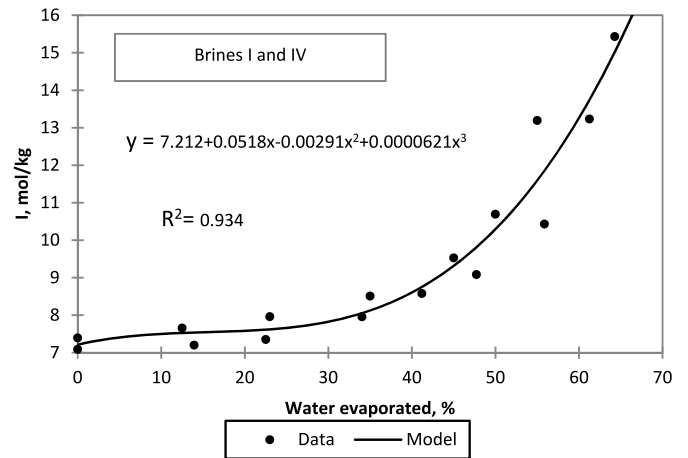

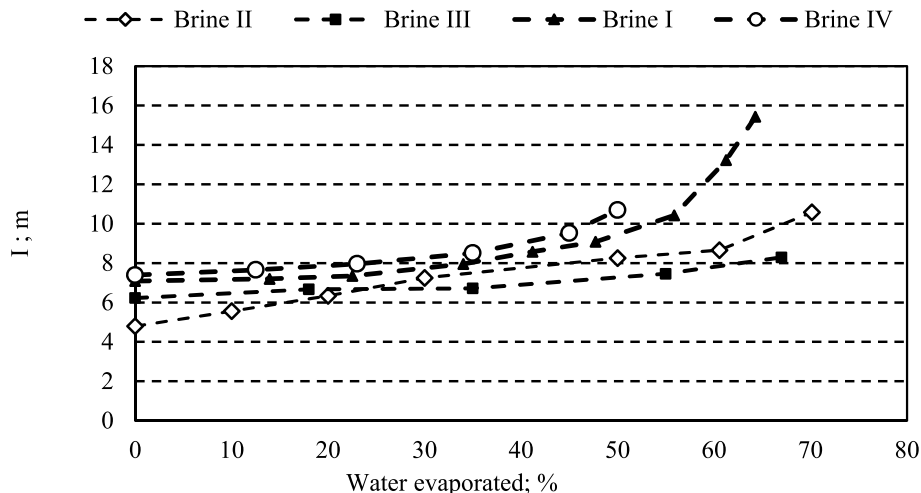**Fig. 10.** Model for ionic strength data of Brines I and IV.

Fig. 9. Ionic strength vs. evaporated water for the four natural brines.
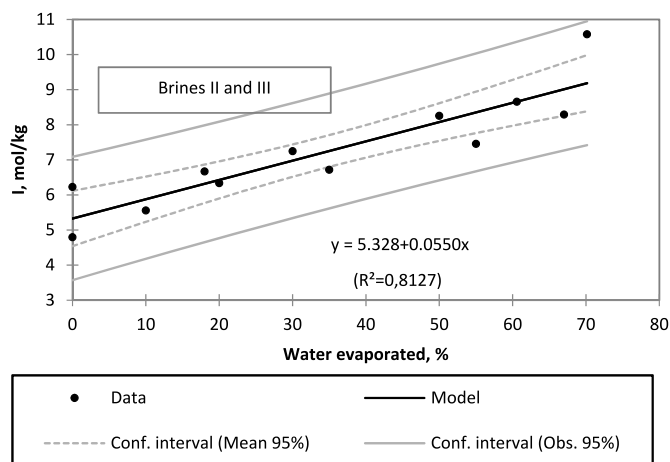
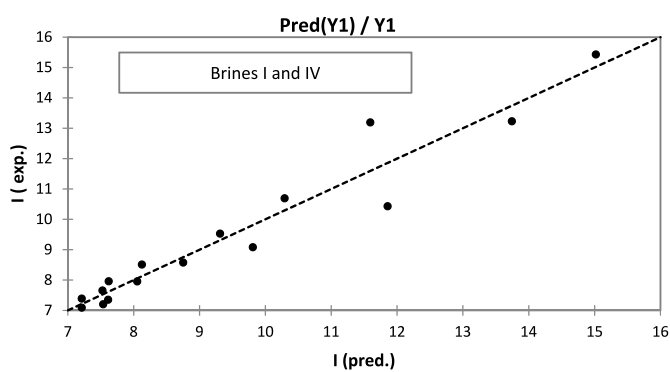**Fig. 11.** Model for ionic strength data of Brines II and III.

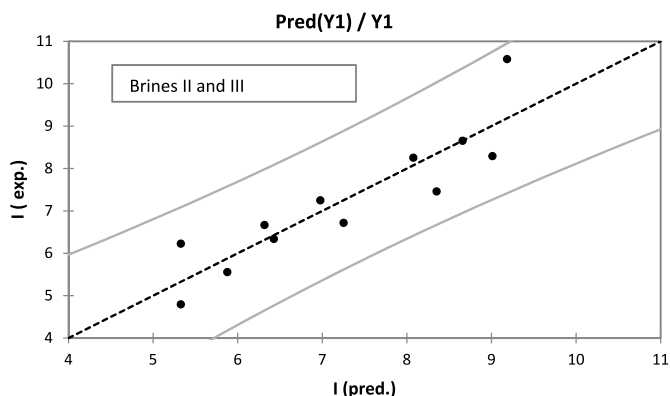**Fig. 12A.** Model adjustment for Brines I and IV.

Fig. 12b. Model adjustment for Brines II and III.

that in Brine I, KCl saturates at 60% of water evaporated (KCl concentration equal to 1.313 mol/kg). This result coincided with those reported by Silva et al. [17]. They evaporated a natural brine from the north of Argentina to recovered KCl and determined that this salt precipitate after 59% of water was evaporated along to NaCl. Li et al. [34] evaporated a brine containing NaCl–KCl–SrCl$_2$ at 298.155 K and conducted computer simulation of isothermal evaporation and brine separation. They reported that pure KCl precipitated at 67,81% of evaporated water when KCl concentration was equal to 1.3089 mol/kg. In Brines II, III and IV, concentration of KCl is lower than saturation point and it would precipitate at higher percentage of water evaporation.

For each studied brine, it was found that Li$^+$ and K$^+$ had the same

behavior, responding to a particular model. For Brines I and IV it was found that Mg^{2+} concentration can be adjusted to a single model. On the other hand, for Brines II and III, Mg^{2+} concentrations could not be represented by a single model. Concentrations model adjustment for Li$^+$, K$^+$ and Mg^{2+} is shown in Figs. 13 and 14.

In Table 2 it is shown the equations that represent ions concentration evolution along with ionic strength.

Empirical ionic strength models obtained for the different brines were used to calculate final ion concentrations vs. amount of water evaporated, being this parameter the most easily measured. Model were obtained by replacing Equations (4) and (5) in those on Table 2.

Ion concentrations for Brines II and III, where SO$_4^{2-}$ precipitated, could not be modeled accurately by a single model such as the case of Brines I and IV.

Models' adjustment is shown in Figs. 15–18. Models are represented in a full line.

Empirical model adjustment is very good for brines I and IV considering that brines had very different initial concentrations. Unfortunately, model adjustment for Brine III was bad. Due to the fact that concentrations data for this brine was provided, we could not repeat evaporation tests in order to determine the motives of the discrepancy between ion concentration and the models. However, for Brine II, model represents accurately ions concentrations.

4. Conclusions

Equilibrium and ions concentration evolutions during evaporation process of non-ideal solutions such as natural brines, require systematic data collection in order to describe correctly the systems. Brines compositions are widely different, and models must be established accordingly. Various salts can precipitate at different stages of the evaporation process, according to their solubility products. In consequence, it affects ionic strength evolution. The state of the art shows that the approach to study the equilibrium in complex system is to consider it as binary, ternary, quaternary and quinary systems. When ionic strength values are higher than 6 m the systems are reduced to binaries or have symmetrical ions. In this paper it was studied four natural brines with mono and divalent ions and initial ionic strength values from 4.8 to 7.3 m.

Results show that it is possible to adjust two different models that describe accurately ionic strength behavior for these brines. Models were obtained as a function of the percentage of water evaporated and they are valid up to 60%. It is noticeable that, industrially, it is not recommended to evaporate such amount of water. At this point, the amount of brine is scarce and it is difficult to separate from the solids that precipitate.

It was found that ionic strength models were lineal or non-lineal depending on the initial sulphate concentrations in the brines. Also, it was stablished that for sulphate concentrations higher than 0.4 g/100 mL gypsum could precipitate during brine evaporation.

Models to estimate the concentration of diluted ions of commercial value such as Li$^+$, K$^+$, and Mg^{2+} as function of ionic strength were also proposed. Finally, the models of ionic strength and concentration were combined in order to predict ions concentrations as functions of the amount of water evaporated up to 60%.

For each brine where sulphate do not precipitate during evaporation, it was possible to adjust a single model that predicts Li$^+$ and K$^+$ concentrations with a minimum error. On the other hand, a single model to predict Mg^{2+} concentration for both brines was adjust. These results are independent from the initial brine concentrations but dependent from sulphate initial concentration. Brines where sulphate precipitates are more complex systems and it was difficult to adjust a single model to determine ions concentration.

With these models it is possible to calculate beforehand the final ions concentrations after a given percentage of evaporated water. It allows to design brines processing and select the purification techniques without exhausting and time-consuming tests. Nowadays there are no tools that
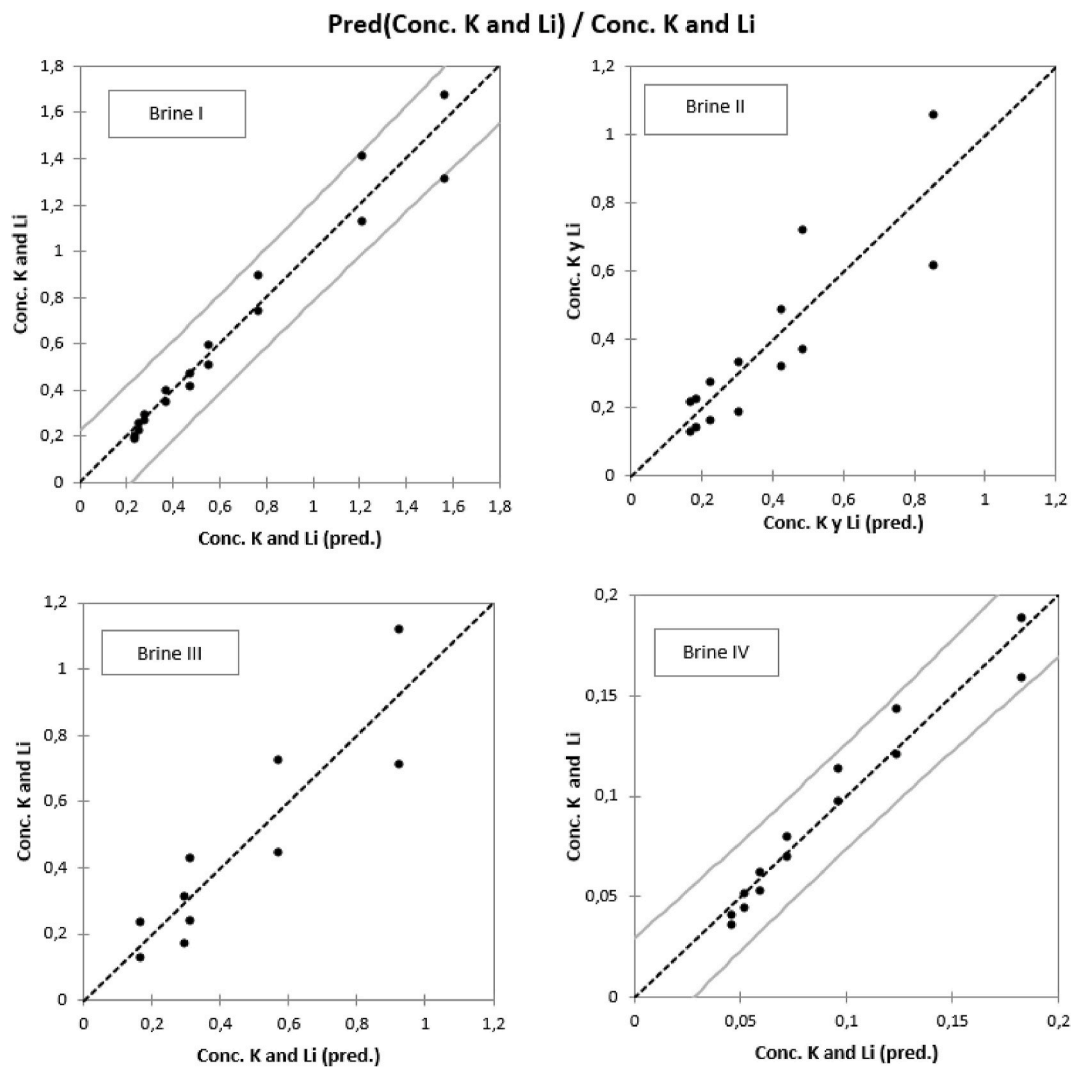
Pred(Conc. K and Li) / Conc. K and Li

Fig. 13. Concentrations model adjustment for Li^+ and K^+.
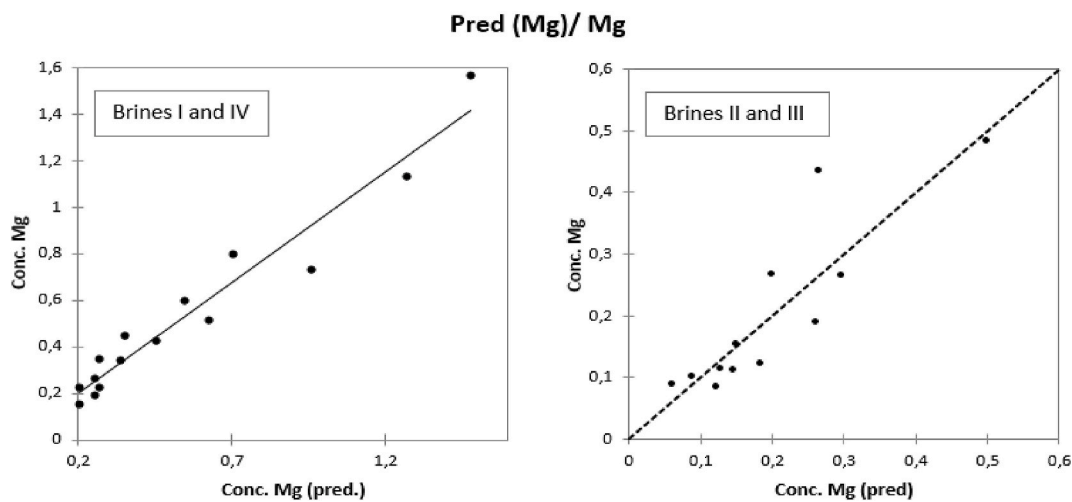
Pred (Mg)/ Mg

Fig. 14. Concentrations model adjustment for Mg^{2+}.

allows to do that, in consequence, each company must perform rigorous and numerous tests with its brines. Results of these work show that ionic strength is the parameter that unified brines behavior even if initial composition could be different. In consequence, it could be used as a parameter to describe brine behavior during evaporations.

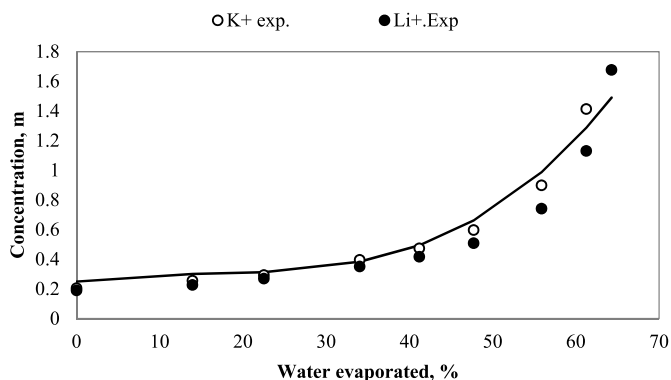Using the models obtained in this work has the advantage of

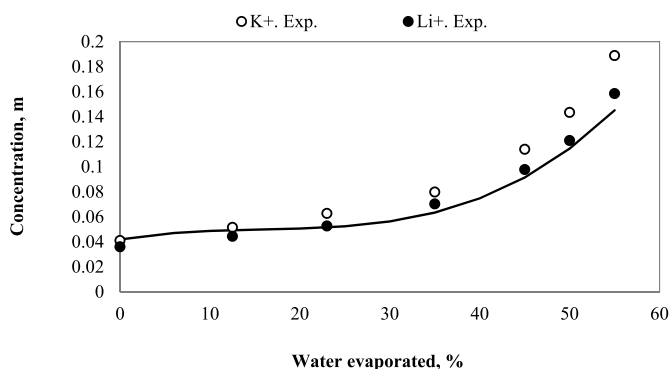**Fig. 15.** Model adjustment for Li$^+$ and K$^+$ concentration for Brine I.

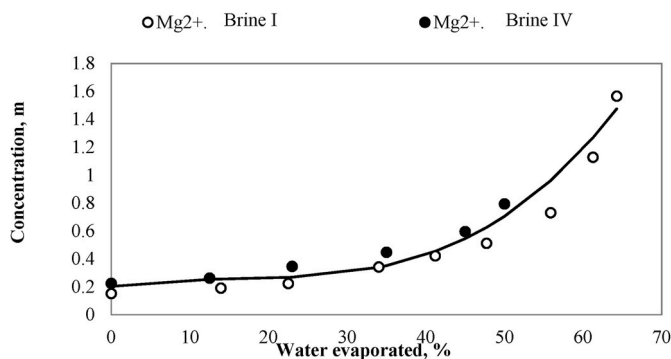**Fig. 16.** Model adjustment for Li$^+$ and K$^+$ concentration for Brine IV.

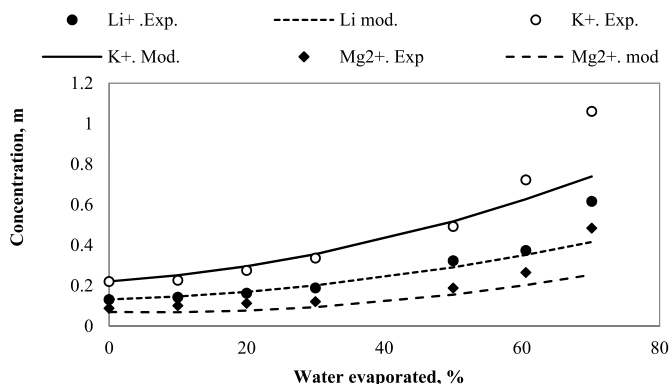**Fig. 17.** Model adjustment for Mg^{2+} concentration for Brines I and IV.

Fig. 18. Model adjustment for Li$^+$, K$^+$, and Mg^{2+} concentration for Brine II.

Table 2
Ion concentration vs. Ionic strength for the four studied brines.

Brine	Model: ion concentration vs. I	R^2
I	Li$^+$, K$^+$ = 0.160 I − 0.897	0.958
II	Li$^+$, K$^+$ = 0.019 I^2 − 0.174 I − 0.562	0.769
III	Li$^+$, K$^+$ = 0.048 I^2 − 0.331 I − 0.367	0.815
IV	Li$^+$, K$^+$ = 0.0236 I − 0.129	0.946
I and IV	Mg^{2+} = 0.163 I − 0.972	0.996
II and III	Mg^{2+} = −0.0414 I^2 + 0.00763I + 0.084	0.767

estimating ion concentrations for a given percentage of evaporated water, reducing the amount of evaporation tests necessaries to design the brine processing.

The fact that for two different brines a single model represent accurately ionic strength and ions behavior during evaporations, imply that brine processing could be standardize. However, in order to do so, other brines must be studied to adjust the proposed models.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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