Solubility in the ternary system MgCl₂-FeCl₂-H₂O at 288 K by conductance method

Abdelkhalek Marrouche [1,*], Brahim Bouargane [1], Assia Mabrouk [2], Mohamed Ghali Biyoune [1,3], Ahmed Bachar [1,3], Ali Atbir [1], Larbi Boukbir [1], Said Mançour-Billah [1], Raddoine Bellajrou [1] and Miloud El Hadek [1]

[1] LGP, Chemical Department, Faculty of Sciences, Université Ibn Zohr, B.P. 8106, Agadir, Morocco

[2] CEMHTI CNRS UPR3079, 1D Av. de la Recherche Scientifque, 45071 Orléans Cedex 2, France

[3] Campus Universitaire-Ait Melloul, Ibn Zohr University, Agadir, Morocco

Abstract: Experimental studies on the solubility of the ternary system MgCl₂-FeCl₂-H₂O at 288 K were determined using a synthetic method based on conductivity measurements. The corresponding solid-liquid phase diagram has been plotted. As can be concluded in the ternary system at 288 K, there are two eutectic points, three crystallization fields corresponding to MgCl₂.6H₂O, FeCl₂.4H₂O and solid solution Fe$_{(1-x)}$Mg$_x$Cl₂.10H₂O) with 0 < x ≤ 0.38 were found. However, no double salt has been formed at the studied temperature.

Keywords: Phase equilibrium; Phase diagram; Solubility; Magnesium chloride; Ferrous chloride; Synthetic method; Conductivity.

Introduction

The study of solubility equilibria between solid salts, salt hydrates and water provides important information for scientific and industrial applications [1–3]. Furthermore, phase diagrams permit us to study and control important processes such as phase separation, crystallization, solidification, purification... For these reasons, the study of the solid-liquid equilibrium of the ternary system (MgCl₂ - FeCl₂ - H₂O) is a promising route for the knowledge of the solubility behavior of magnesium and iron chlorides.

The present study represents a continuation of our previous work focusing on the establishment of the phase diagrams of the ternary systems M, Fe / Cl - H₂O (M = K, Na) [4–6]. Our purpose is to examine deeply the ternary system MgCl₂-FeCl₂-H₂O behavior at 288 K.

A large amount of experimental data related to the phase diagrams of the binary systems MgCl₂-H₂O and FeCl₂-H₂O [7] are available. In our latter study [8], a semi-empirical model in coherence with thermodynamic conditions of equilibrium was used and oriented to the calculation of phase diagrams of the binary systems H₂O-MCln (M = Mg²⁺, Fe²⁺, Fe³⁺). To estimate solubility, the databases on iron and magnesium mineral's solubility were taken from the compilations

of Linke and Seidell [7] and other single determinations.

For each solid phase, the exploitation of the experimental and previously reported data gives a liquidus curve equation comprising a limited number of parameters. The liquidus curves for the hydrated salts FeCl₂·nH₂O (n=2, 4, 6) and MgCl₂·nH₂O (n=2, 4, 6, 8, 12) have been established. They allow estimating with precision the solubility of the stoichiometric solid phase in a large range of temperature and composition.

Concerning the experimental solubility of the ternary system MgCl₂-FeCl₂-H₂O, the first study was conducted by Boeke in 1911 [9]. He has determined the solubility of individual mixtures of these chlorides at 295.8, 316.8 and 345.6 K. He reported the presence of a double salt FeCl₂.MgCl₂.8H₂O from the temperature of 295.8 K where all solid phases were stoichiometric. Shchedrina et al. [10–15] then studied this system at 288, 313, 323, 333, 338 and 343 K. They reported, for the isotherm at 288 K, the presence of two fields of solid solutions of different structures: those based on MgCl₂.6H₂O and those based on FeCl₂.4H₂O; and any double salt has been obtained (Figure 1). For the temperatures 313, 323 and 333 K, a third solid solution field based on the double salt FeCl₂.MgCl₂.8H₂O appears, at 338 K, the double salt

appears as a stoichiometric phase, and finally, at 343 K they obtained the same results at 338 K with the
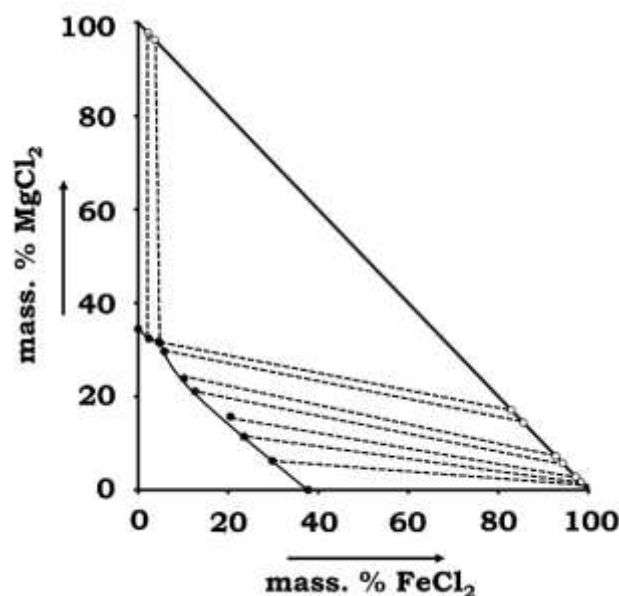
appearance of the $MgCl_2.6H_2O$ crystallization field.

Figure 1. Ternary $MgCl_2$-$FeCl_2$-H_2O representation at 288 K (Original ternary $MgCl_2$-$FeCl_2$-H_2O representation) [10]

Afonichkin et al. [16] took up this system at 273, 288 and 298 K; their results confirm those of Shchedrina et al. [10–15]. Chen et al. studied the $FeCl_2$-$MgCl_2$-HCl-H_2O system at 323 K, no solid solution or double salt were found [17].

In supplementary work, minor changes of the temperature and composition were made by Balarew and Spassov many years ago [18]. They studied the isothermal solubility of $FeCl_2$-$MgCl_2$-H_2O at 298 K. In addition to the fields of simple $MgCl_2.6H_2O$ and $FeCl_2.4H_2O$ salts, Balarew and Spassov also found a very narrow field corresponding to the crystallization of the double salt $MgCl_2.FeCl_2.8H_2O$. However, no solid solution was found.

Christomir Christov has described a Pitzer ion-interaction for thermodynamic analysis model that calculates (solid + liquid) equilibria in the $\{m1MgCl_2 + m2FeCl_2\}$(aq) systems, where m denotes molality at 298 K [19]. All mixed solution parameters are evaluated using experimental solubility data in ternary systems taken from Balarew and Spassov [18]. This thermodynamic model was extended to other systems [20].

Unfortunately, the results from these previous studies show contradictory observations. Significant differences are found in the diagrams of the ternary system at different temperatures. However, the crystallization fields are very different, especially the fields of the double salt and the existence of the solid solution which remain uncertain. No research has yet proved or disproved the previous studies results.

It can be concluded that further experimental studies are necessary in order to clarify this ambiguity of the solid phases present in this ternary system at 15 °C before establishing the quaternary diagram.

Experimental section

Reagents and experimental procedure

The study of this system was carried out at 288 K under a pressure of nitrogen gas of 0.10 MPa, in order to prevent the oxidation of Fe^{2+} to Fe^{3+}. Table 1 summarizes the information of the key reagents used in the current study, their manufacturer (origins) and their corresponding purity

Table 1. Information of chemicals used in this work.

Product name	Chemical/Materials	Grade/Specification	Supplier
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	purity > 99%	Sigma Aldrich
Hydrochloric acid	HCl	purity > 36%	Sigma Aldrich
Metallic Iron	Fe	purity > 99%	Sigma Merck

All the sample solutions were prepared with bi-distilled water (conductivity < 10^{-4} Sm^{-1}). The magnesium chloride used for this study as starting reagents was recrystallized from bidistilled water and was dried at 313 K under water-pump vacuum to get

pure $MgCl_2.6H_2O$, and it was preserved in a desiccator in the presence of P_2O_5.

The aqueous solution of iron (II) chloride, also known as ferrous chloride, was prepared in the

laboratory by addition of iron powder to a solution of concentrated hydrochloric acid. After filtering, iron chloride tetrahydrate was crystallized using vacuum evaporation at the temperature of about 321 K. The obtained crystals were washed with bi-distilled water, dissolved in it and recrystallized again by vacuum evaporation of aqueous solution at 311 K using the processes earlier published [4].

Analytical Methods

The water content of the $FeCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ was determined by chemical analysis. The techniques of analysis have been previously described [4].

The recrystallized product was characterized using several analytical techniques, in order to check its purity. The chloride ions are analyzed by a potentiometric method using silver nitrate (precision $\pm 0.2\%$). The Mg^{2+} concentration was determined with a precision of within $\pm 0.5\%$ by complexometric titration at pH 9.5–10 (ammonia buffer), using Eriochrome black T as the indicator. The Fe^{2+} solution was titrated with a precision of about 0.3% by standard potassium dichromate ($K_2Cr_2O_7$) solution using sodium diphenylamine sulfonate as the indicator.

Synthetic Method

According to the phase equilibrium composition, an appropriate quantity of the salt was dissolved in bi-distilled water first to prepare a few starting solutions. The phase equilibrium was performed in a glass jacket. The jacket temperature was controlled by thermostatic circulating water bath within ± 0.1 K.

The experimental process, as described in the previous papers, consists of determining the solubility by a synthetic method based on conductivity measurements (uncertainty, ± 0.1 mScm^{-1}). The proposed method was successfully applied for direct determination of salts solid-liquid equilibria [21,22]. This technique was used by Tenu et al. to delimit the boundary of the solid solution in the $CaCl_2$-$SrCl_2$-H_2O system [23]. The electric conductivity of the solution in thermodynamic equilibrium is measured when small amounts of water are progressively added to an isothermal saturated mixture of given initial composition using a micro-burette. Each phase changes was indicated by discontinuities in the electric conductivity-composition curve of the saturated solution. The last break corresponds to the dissolution of the last salt crystal. An invariant equilibrium is characterized by a plateau in the curve.

Results and Discussions

Under a pressure of nitrogen gas of 0.10 MPa, the solid-liquid equilibrium solubility data for the ternary system $MgCl_2$-$FeCl_2$-H_2O at 288 K are listed in Table 2. The corresponding phase diagram of the system is built and illustrated graphically in Figure 2 with the Jänecke coordinate. Figure 3 is a right-triangular diagram for the same system with the weight percent. The composition values of the equilibrium solution phase and solid phase were expressed in terms of Jänecke coordinate. The composition of a mixture is related to the total amount of ions P taking into account their charge. Multiple measurements were performed to determine the uncertainty of the measurement.

$$P = 2n_{Mg^{2+}} + 2n_{Fe^{2+}} = n_{Cl^-} \; ; \; U = \frac{n_{Mg^{2+}}}{P} 200 \; ; \; V = \frac{n_{Fe^{2+}}}{P} 200 \; ; \; Z = \frac{n_{H_2O}}{P} 100$$

and $\quad U + V = 100$

U: $MgCl_2$ Jänecke coordinate; V: $FeCl_2$ Jänecke coordinate; Z: water Jänecke coordinate

The evolution of the electric conductivity, when the saturated solution is diluted, can be performed through an indirect method. In particular, the use of the Jänecke coordinate Z, to represent the water volume, displays data in its correct position. This mode of representation has been found to be the most convenient. By way of example, Figure 4 plots the Z (water content) value, added to an initial mixture M, against electric conductivity. The curve gives valuable information about how and where the global composition takes changes.

The results of the conductivity measurements obtained for three ternary mixtures M_8(U=50), M_{12}(U=80) and M_{16}(U=94.97) were presented on Table 3 and reported in Figures 4a, 4b and 4c respectively. The water content vs. conductivity graph of a mixture in a ternary system presents a break at every appearance/disappearance of any phase and a plateau when an invariant equilibrium is reached.

The phase changes was indicated by discontinuities in the graph of water content versus conductivity. The phase boundaries was therefore estimated from the water content of each phase change, and the dotted lines symbolize these boundaries.

These Figures show a typical shape of the curves, which bound:

✓ One phase field "liquid",
✓ Two phases liquid+solid "solid solution, $FeCl_2.4H_2O$ or $MgCl_2.6H_2O$"
✓ Two invariant phase fields liquid + $FeCl_2.4H_2O$ + "solid solution or $MgCl_2.6H_2O$"

The analysis of the different ternary mixtures, suitably chosen, allowed us to confirm the nature of the solid phases, which are manifested, to delimit the mono-, di- and three-phase stability domains and to

determine the composition of the invariant solutions. This procedure permitted the determination of the

entire phase diagram of $MgCl_2$-$FeCl_2$-H_2O at 288 K.

Table 2. Data solubility in the ternary system $MgCl_2$-$FeCl_2$-H_2O at 288 K.

N°	U	V	Z_L	Z_1	Z_2	Z_3	$MgCl_2$	$FeCl_2$	H_2O	solid phases
			Jänecke coordinate				**Composition of the solution (Mass %)**			
1	0.00	100.00	576.04				0.00	37.93	62.07	F4
2	20.00	80.00	573.10	496.00			5.83	31.03	63.14	SS
3	24.99	75.01	567.74				7.36	29.41	63.23	"
4	30.00	70.00	568.60				8,87	27.56	63.57	"
5	30.00	70.00	573.92				8.82	27.39	63.79	"
6	35.00	65.00	577.40	468.00	499.86		10.30	25.46	64.24	"
7	45.00	55.00	565.30				13.55	22.06	64.39	"
8	50.00	50.00	566.50	532.50	470.00	340	15.12	20.12	64.76	"
9	55.00	45.00	566.00	538.00	501.00		16.72	18.21	65.07	"
10	60.00	40.00	569.68	550.00	532.00		18.25	16.20	65.54	"
11; C1	65.00	35.00	561.00	384.10			20.21	14.49	65.31	F4+SS
12	80.00	20.00	513.20	418.20			26.60	8.86	64.54	F4
13	85.00	15.00	495.60	428.20			29.07	6.83	64.10	"
14	90.00	10.00	462.45	456.00			32.35	4.79	62.86	"
C2	91.75	8.25	450.00				33.59	4.02	59.97	F4+M6
15	92.49	7.51	459.30	440.00			33.49	3.62	62.39	M6
16	94.97	5.03	460.80	386.90			34.42	2.43	63.15	"
17	97.83	2.17	477.50				34.78	1.03	64.19	"
18	97.50	2.50	477.60				34.64	1.18	64.17	"
19	100.00	0.00	487.10				35.19	0.00	64.81	"

Standard uncertainties u are u(T) = 0.1 K, u(w) for $MgCl_2$ and $FeCl_2$ is 0.03 and 0.02 in mass %, respectively.

Note: F4: $FeCl_2.4H_2O$; SS: solid solution ; M6: $MgCl_2.6H_2O$; Z_L: solubility limit
Zi (I =1, 2, 3): other phase changes; C1 and C2: invariant points

In Figs 2 and 3, points S_1 and S_2 represent the solubility of pure components $FeCl_2.4H_2O$ and $MgCl_2.6H_2O$, respectively. The ternary phase diagram consists of two co-saturated points C_1 and C_2 of two solids ($FeCl_2.4H_2O$ + solid solution rich in iron chloride) and ($FeCl_2.4H_2O$ + $MgCl_2.6H_2O$), respectively. The compositions of the invariant points are listed in Table 2.

The ternary phase diagram is composed of six crystallization fields including:

- One domain where only one liquid phase is observed.
- Three monovariant diphasic fields (II, IV, VI), where a liquid phase is in equilibrium with a solid phase: liquid + solid solution or $FeCl_2.4H_2O$ or $MgCl_2.6H_2O$. The largest crystallization field is $FeCl_2.4H_2O$; the smallest crystallization field is $MgCl_2·6H_2O$.
- Two invariant triphasic domains (III, V), where a liquid with a defined compositions C_1 and C_2, is in equilibrium with the mixture of "solid solution +

$FeCl_2.4H_2O$", "$MgCl_2.6H_2O$ + $FeCl_2.4H_2O$", respectively.

S_1C_1, C_1C_2, and C_2S_2 are the isothermal dissolution curves of solid solution, $FeCl_2.4H_2O$ and $MgCl_2.6H_2O$, respectively at 288 K.

The solubility results are in general in good agreement, especially in the $FeCl_2$ rich side, with those previously reported by literary [10,16]. The synthetic method allowed us to draw, in the FeCcl2 rich side, the tie lines of the solid solutions and to determine its chemical formula, which is $[FeCl_2]_{(1-x)}[MgCl_2]_x.10H_2O$, i.e. $(Fe_{(1-x)}Mg_xCl_2.10H_2O)$ with $0 < x \leq 0.38$.

However, our investigations indicate that no solid solution areas were defined in the system at a high concentration of magnesium chloride. Also, the existence of the double salt was not found in this isothermal phase diagram at a temperature of 288 K. These results contradict those published in previously phase diagrams in which the double salt $FeCl_2.MgCl_2.8H_2O$ have been observed at 298 K [18].

Table 3. Conductivity Data measurements.

$M_8(U=50)$				$M_{12}(U=80)$		$M_{16}(U=94.97)$	
σ (mScm^{-1})	Z	σ (mScm^{-1})	Z	σ (mScm^{-1})	Z	σ (mScm^{-1})	Z
87.4	323.54	122.4	461.03	88.4	352.68	88.6	358.35
87.4	327.20	122.6	470.20	88.6	357.00	88.5	367.37
87.4	332.70	122.6	479.37	88.6	365.65	88.6	376.38
88.8	341.87	122.9	488.53	88.9	376.46	90	385.40
95.0	351.04	122.4	497.70	89	398.07	91.6	403.44
100.5	360.20	122.4	506.87	90.3	419.69	93.3	421.48
105.2	369.37	122.3	512.36	99	441.30	94.4	439.52
109.6	378.54	122.6	516.03	106.6	462.91	95.6	457.55
112.7	387.70	122.1	525.20	112.3	484.53	102.8	475.59
115.2	396.87	122.2	534.36	117.4	506.14	107.1	484.61
116.8	406.03	122.3	543.53	122.8	527.76	111.7	493.63
118.4	415.20	121.9	552.70	132.2	549.37	116.5	502.65
120.3	428.03	121.6	561.86	136.1	560.18	120.4	511.66
120.5	433.53	122.9	571.03	140	570.99		
120.8	437.20	126.3	580.20	143.8	581.80		
121.4	442.70	130.2	589.36				
122.2	455.53						

Standard uncertainties u are u(σ) = 0.1 mScm^{-1}, u(Z) = 0.05.

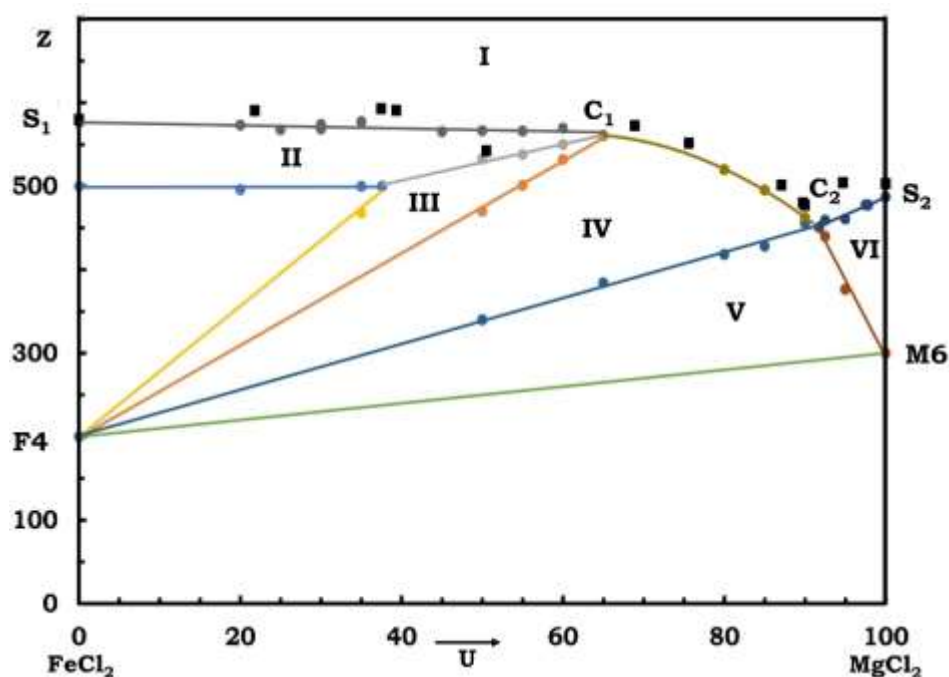**Figure 2**. Phase diagram for the ternary MgCl$_2$-FeCl$_2$-H$_2$O system at 288 K: ●, experiment data in this study. ▪, literary data [10,16] (F4: FeCl$_2$.4H$_2$O; M6: MgCl$_2$.6H$_2$O; U and Z: Jänecke coordinates of MgCl$_2$ and water respectively)

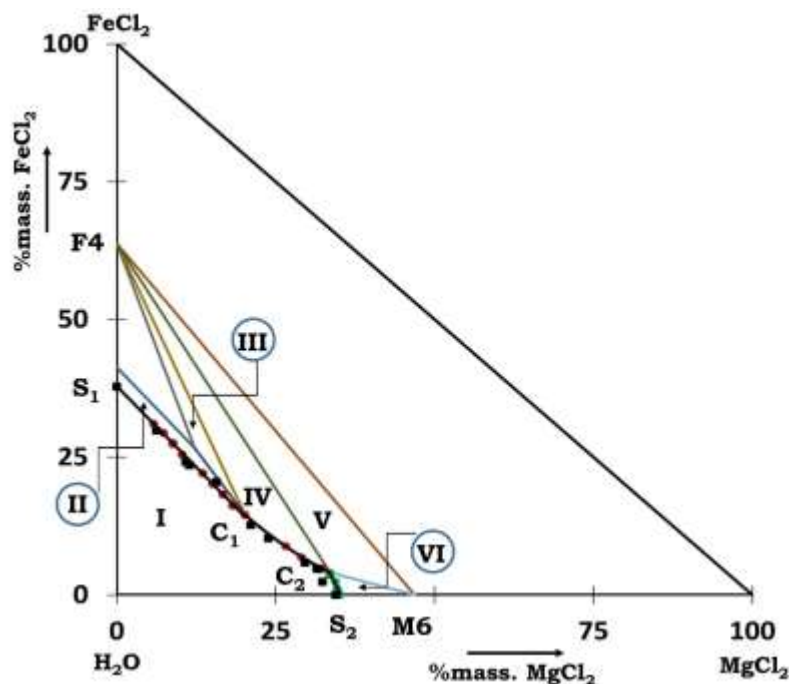**Figure 3**. Phase diagram for the ternary $MgCl_2$-$FeCl_2$-H_2O system at 288 K expressed in weight percent: ●,experiment data in this study, ▪, literary data [10,16] (F4: $FeCl_2.4H_2O$; M6: $MgCl_2.6H_2O$).
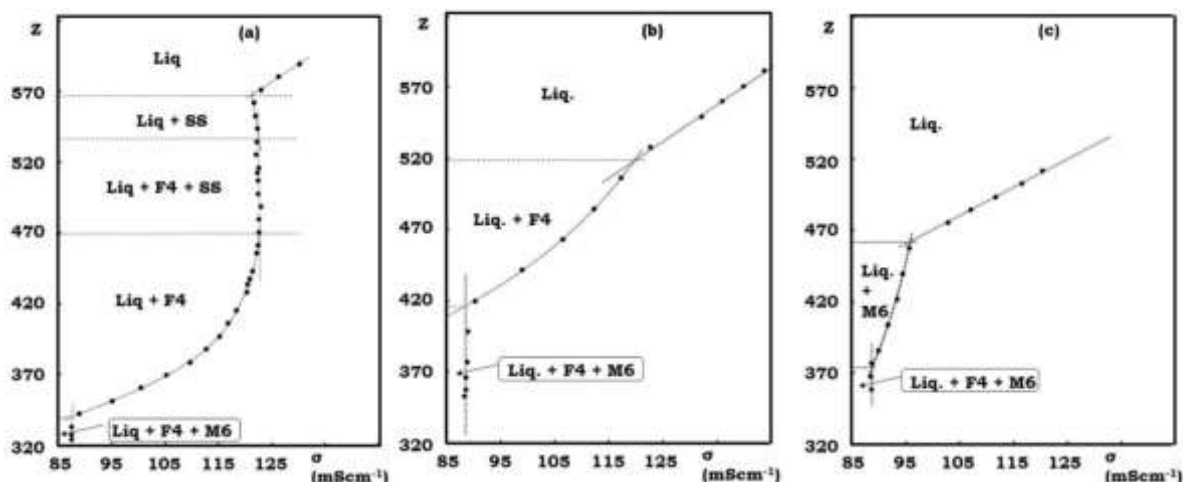

Figure 4. Water content (Z) evolution according to electrical conductivity of saturated solution (a), (b) and (c) correspond to mixtures N° 8, 12 and 16, respectively

Conclusions

In this study, the solubility isotherm of $MgCl_2$-$FeCl_2$-H_2O system at 288 K was established using the synthetic method based on conductivity measurements. It was found that only three solubility branches are corresponding to $MgCl_2.6H_2O$, $FeCl_2.4H_2O$ and solid solution $Fe_{(1-x)}Mg_xCl_2.10H_2O$ with $0<x\leq0.38$. The compositions, in Jänecke coordinate, of the two invariant points, are:

C_1: 65% $MgCl_2$; 35% $FeCl_2$; Z=561

C_2: 91.75% $MgCl_2$; 8.25% $FeCl_2$; Z=450.6

Three diphasic fields, where a solid phase coexists in equilibrium with liquid: "liquid + solid solution", "liquid + $FeCl_2.4H_2O$" and "liquid +

$MgCl_2.6H_2O$". The smallest crystallization field is $MgCl_2·6H_2O$. According to our experimental data, no double salt was formed at 288 K.

It seems that the synthetic method based on conductivity measurements is an important tool to investigate the solid solution in ternary aqueous phase diagrams.

References

1 - J.-X. Wu, G.-C. Zhang, B. Zhao, S. Wang and J.-L. Cao, Phase Diagram of the Quaternary System KCl–MgCl2–NH4Cl–H2O at t = 60.00 °C and Their Application, *J. Solution Chem.*, **2017**, 46, 58–69.

2 - R. G. da Silva, M. Seckler, S. D. F. Rocha,

D. Saturnino and É. D. de Oliveira, Thermodynamic modeling of phases equilibrium in aqueous systems to recover potassium chloride from natural brines, *J. Mater. Res. Technol.*, **2017**, 6, 57–64.

3 - A. Sunil Dhoot, A. Naha, J. Priya and N. Xalxo, Phase Diagrams for Three Component Mixtures in Pharmaceuticals and its Applications, *J. Young Pharm.*, **2018**, 10, 132–137.

4 - A. Atbir, M. El Hadek and R. Cohen-Adad, Solid-liquid equilibria in the quaternary system NaCl–FeCl2–FeCl3–H2O, *Fluid Phase Equilib.*, **2001**, 181, 187–194.

5 - A. Atbir, M. El Hadek and R. Cohen-Adad, Diagramme de phases du système ternaire KCl-FeCl ₃ -H ₂ O. Isothermes 15 et 30 °C, *Le J. Phys. IV*, **2001**, 11, Pr10-187-Pr10-190.

6 - A. Atbir, S. Mançour-Billah and M. El Hadek, Solid-liquid equilibria in the quaternary system K+, Fe2+, Fe3+/Cl--H2O at 288.15 K, *Fluid Phase Equilib.*, **2004**, 215, 97–103.

7 - A. Seidell and W. F. Linke, *Solubilities Inorganic and Metal-organic Compounds: A Compilation of Solubility Data from the Periodical Literature. K-Z*, Van Nostrand, New York, 4th edn., **1965**.

8 - A. Atbir, A. Marrouche, H. Atif, L. Boukbir, M. El Hadek and R. Cohen-Adad, Calcul Des Diagrammes De Phases Des Systemes Binaires H2O–MCln (M=Mg2+, Fe2+, Fe3+), *J. Therm. Anal. Calorim.*, **2000**, 61, 849–860.

9 - H. E. Boeke, Über die Eisensalze in den Kalisalzlagerstâtten, *N. Jb. Miner. Geol.*, **1911**, 1, 48–76.

10 - A. P. Shchedrina, M. N. Ozerova and K. G. Khomyakov, The FeCl2-MgCl2-H2O System at 15°C, *Russ. J. Inorg. Chem*, **1964**, 9, 400–401.

11 - A. P. Shchedrina, L. I. Krasnova and M. N. Ozerova, The FeCl2-MgCl2-H2O System at 40°C, *Russ. J. Inorg. Chem*, **1969**, 14, 138–139.

12 - A. P. Shchedrina and L. I. Krasnova, The FeCl2-MgCl2-H2O System at 50°C, *Russ. J. Inorg. Chem*, **1969**, 14, 122–123.

13 - A. P. Shchedrina, L. I. Krasnova and L. M. Mel'nichenko, The FeCl2-MgCl2-H2O System at 60°C, *Russ. J. Inorg. Chem*, **1970**, 15,

991–992.

14 - A. P. Shchedrina and L. I. Krasnova, The FeCl2-MgCl2-H2O System at 65°C, *Russ. J. Inorg. Chem*, **1972**, 17, 122–123.

15 - A. P. Shchedrina and L. M. Mel'nichenko, The FeCl2-MgCl2-H2O System at 70°C, *Russ. J. Inorg. Chem*, **1974**, 19, 897–899.

16 - O. V. Afonichkin and T. I. Gaidukova, SOLUBILITÉ DES SELS DANS LES SYSTÈMES NaCl-Fecl2-H2O et MgCl2-Fecl2-H2O, *Zh. Khim.*, **1976**, 74, 30–34.

17 - E. C. Chen, G. McGuire and H. Y. Lee, Solubility isotherm of the ferric chloride-magnesium chloride-hydrogen chloride-water system, *J. Chem. Eng. Data*, **1970**, 15, 448–449.

18 - C. Balarew and D. Spasov, FORMATION OF DOUBLE SALTS FROM DIVALENT METAL CHLORIDES, *ZHURNAL Neorg. KHIMII*, **1980**, 25, 2814–2820.

19 - C. Christov, Pitzer ion-interaction parameters for Fe(II) and Fe(III) in the quinary {Na + K + Mg + Cl + SO4 + H2O} system at T=298.15 K, *J. Chem. Thermodyn.*, **2004**, 36, 223–235.

20 - L. André, C. Christov, A. Lassin and M. Azaroual, Thermodynamic model for solution behavior and solid-liquid equilibrium in Na-Al(III)-Fe(III)-Cr(III)-Cl-H2O system at 25°C, *Acta Sci. Nat.*, **2018**, 5, 6–16.

21 - B. El Goundali, A. Teyssier, M. Kaddami, J.-J. Counioux and C. Goutaudier, Linear behaviour in isothermal equilibria involving saturated electrolyte solutions: The H2O–Co(NO3)2–Ni(NO3)2 ternary system at low temperature, *J. Chem. Thermodyn.*, **2016**, 101, 343–350.

22 - J. Maous and M. Kaddami, Solid-liquid equilibria of the binary system (Mn(NO3)2 + H2O) and the ternary system (Mn(NO3)2 + Fe(NO3)3 + H2O) at 0 °C and 20 °C, *Fluid Phase Equilib.*, **2018**, 467, 1–7.

23 - R. Tenu, J.-J. Counioux and R. Cohen-Adad, Détermination conductimétrique de l'isotherme 45 C du système H ₂ O-CaCl ₂-SrCl ₂-BaCl ₂. Méthode d'étude et application au ternaire H ₂ O-CaCl ₂-SrCl ₂, *Bull. Soc. Chim. Fr*, **1979**, 3, 82–85.