

## Solubility in the ternary system $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$ at 288 K by conductance method

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**Abstract:** Experimental studies on the solubility of the ternary system  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  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  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and solid solution  $\text{Fe}_{(1-x)}\text{Mg}_x\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  with  $0 < x \leq 0.38$  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 <sup>1-3</sup>. 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 ( $\text{MgCl}_2 - \text{FeCl}_2 - \text{H}_2\text{O}$ ) 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 -  $\text{H}_2\text{O}$  (M = K, Na) <sup>4-6</sup>. Our purpose is to examine deeply the ternary system  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  behavior at 288 K.

A large amount of experimental data related to the phase diagrams of the binary systems  $\text{MgCl}_2\text{-H}_2\text{O}$  and  $\text{FeCl}_2\text{-H}_2\text{O}$  <sup>7</sup> are available. In our latter study <sup>8</sup>, 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  $\text{H}_2\text{O-MCl}_n$  (M =  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ). To estimate solubility, the databases on iron and magnesium mineral's solubility were taken from the compilations

of Linke and Seidell <sup>7</sup> 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  $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$  (n=2, 4, 6) and  $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$  (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.

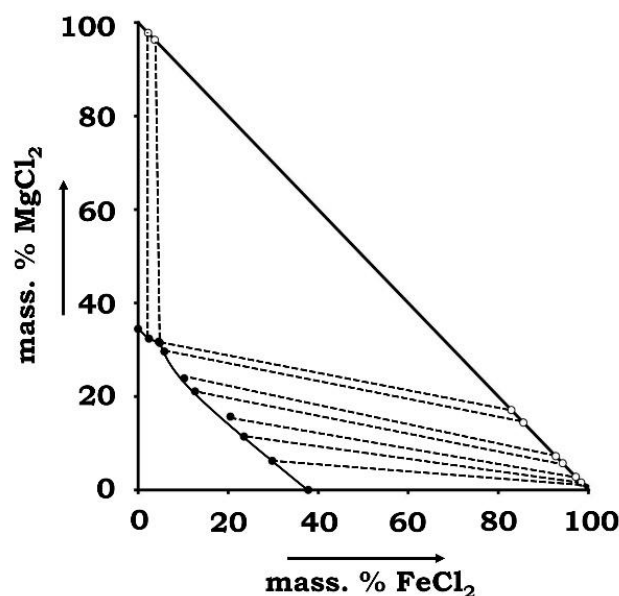
Concerning the experimental solubility of the ternary system  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$ , the first study was conducted by Boeke in 1911 <sup>9</sup>. He has determined the solubility of individual mixtures of these chlorides at 295.8, 316.8 and 345.6 K. He reported the presence of a double salt  $\text{FeCl}_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  from the temperature of 295.8 K where all solid phases were stoichiometric. Shchedrina et al. <sup>10-15</sup> 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  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and those based on  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ; 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  $\text{FeCl}_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  appears, at 338 K, the double salt

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appears as a stoichiometric phase, and finally, at 343 K they obtained the same results at 338 K with the

appearance of the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  crystallization field.



**Figure 1.** Ternary  $\text{MgCl}_2$ - $\text{FeCl}_2$ - $\text{H}_2\text{O}$  representation at 288 K (Original ternary  $\text{MgCl}_2$ - $\text{FeCl}_2$ - $\text{H}_2\text{O}$  representation)<sup>10</sup>

Afonichkin et al.<sup>16</sup> took up this system at 273, 288 and 298 K; their results confirm those of Shchedrina et al.<sup>10-15</sup>. Chen et al. studied the  $\text{FeCl}_2$ - $\text{MgCl}_2$ - $\text{HCl}$ - $\text{H}_2\text{O}$  system at 323 K, no solid solution or double salt were found<sup>17</sup>.

In supplementary work, minor changes of the temperature and composition were made by Balarew and Spassov many years ago<sup>18</sup>. They studied the isothermal solubility of  $\text{FeCl}_2$ - $\text{MgCl}_2$ - $\text{H}_2\text{O}$  at 298 K. In addition to the fields of simple  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  salts, Balarew and Spassov also found a very narrow field corresponding to the crystallization of the double salt  $\text{MgCl}_2 \cdot \text{FeCl}_2 \cdot 8\text{H}_2\text{O}$ . 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  $\{m_1\text{MgCl}_2 + m_2\text{FeCl}_2\}$ (aq) systems, where *m* denotes molality at 298 K<sup>19</sup>. All mixed solution parameters are evaluated using experimental solubility data in ternary systems taken from Balarew and Spassov<sup>18</sup>. This thermodynamic model was extended to other systems<sup>20</sup>.

**Table 1.** Information of chemicals used in this work.

Product name	Chemical/Materials	Grade/Specification	Supplier
Magnesium chloride hexahydrate	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	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 <  $10^{-4} \text{ Sm}^{-1}$ ). 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

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  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Table 1 summarizes the information of the key reagents used in the current study, their manufacturer (origins) and their corresponding purity

pure  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and it was preserved in a desiccator in the presence of  $\text{P}_2\text{O}_5$ .

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<sup>4</sup>.

### Analytical Methods

The water content of the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was determined by chemical analysis. The techniques of analysis have been previously described<sup>4</sup>.

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  $\text{Mg}^{2+}$  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  $\text{Fe}^{2+}$  solution was titrated with a precision of about 0.3% by standard potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) 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  $\pm 0.1$  K.

$$P = 2n_{\text{Mg}^{2+}} + 2n_{\text{Fe}^{2+}} + n_{\text{Cl}^-}; \quad U = \frac{n_{\text{Mg}^{2+}}}{P} 200; \quad V = \frac{n_{\text{Fe}^{2+}}}{P} 200; \quad Z = \frac{n_{\text{H}_2\text{O}}}{P} 100$$

and  $U + V = 100$

U:  $\text{MgCl}_2$  Jänecke coordinate; V:  $\text{FeCl}_2$  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 experimental process, as described in the previous papers, consists of determining the solubility by a synthetic method based on conductivity measurements (uncertainty,  $\pm 0.1 \text{ mScm}^{-1}$ ). The proposed method was successfully applied for direct determination of salts solid-liquid equilibria<sup>21,22</sup>. This technique was used by Tenu et al. to delimit the boundary of the solid solution in the  $\text{CaCl}_2$ - $\text{SrCl}_2$ - $\text{H}_2\text{O}$  system<sup>23</sup>. 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  $\text{MgCl}_2$ - $\text{FeCl}_2$ - $\text{H}_2\text{O}$  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.

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,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ”
- ✓ Two invariant phase fields liquid +  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  + “solid solution or  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ”

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  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  at 288 K.

**Table 2.** Data solubility in the ternary system  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  at 288 K.

N°	Jänecke coordinate						Composition of the solution (Mass %)			solid phases
	U	V	Z <sub>L</sub>	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>	MgCl <sub>2</sub>	FeCl <sub>2</sub>	H <sub>2</sub> O	
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  $\text{MgCl}_2$  and  $\text{FeCl}_2$  is 0.03 and 0.02 in mass %, respectively.

Note: F4:  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  ; SS: solid solution ; M6:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  ; Z<sub>L</sub>: solubility limit  
Z<sub>i</sub> (i = 1, 2, 3): other phase changes; C1 and C2: invariant points

In Figs 2 and 3, points S<sub>1</sub> and S<sub>2</sub> represent the solubility of pure components  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , respectively. The ternary phase diagram consists of two co-saturated points C<sub>1</sub> and C<sub>2</sub> of two solids ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  + solid solution rich in iron chloride) and ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  +  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), 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  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The largest crystallization field is  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ; the smallest crystallization field is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .
- Two invariant triphasic domains (III, V), where a liquid with a defined compositions C<sub>1</sub> and C<sub>2</sub>, is in equilibrium with the mixture of “solid solution +

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ”, “ $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  +  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ”, respectively.

S<sub>1</sub>C<sub>1</sub>, C<sub>1</sub>C<sub>2</sub>, and C<sub>2</sub>S<sub>2</sub> are the isothermal dissolution curves of solid solution,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , respectively at 288 K.

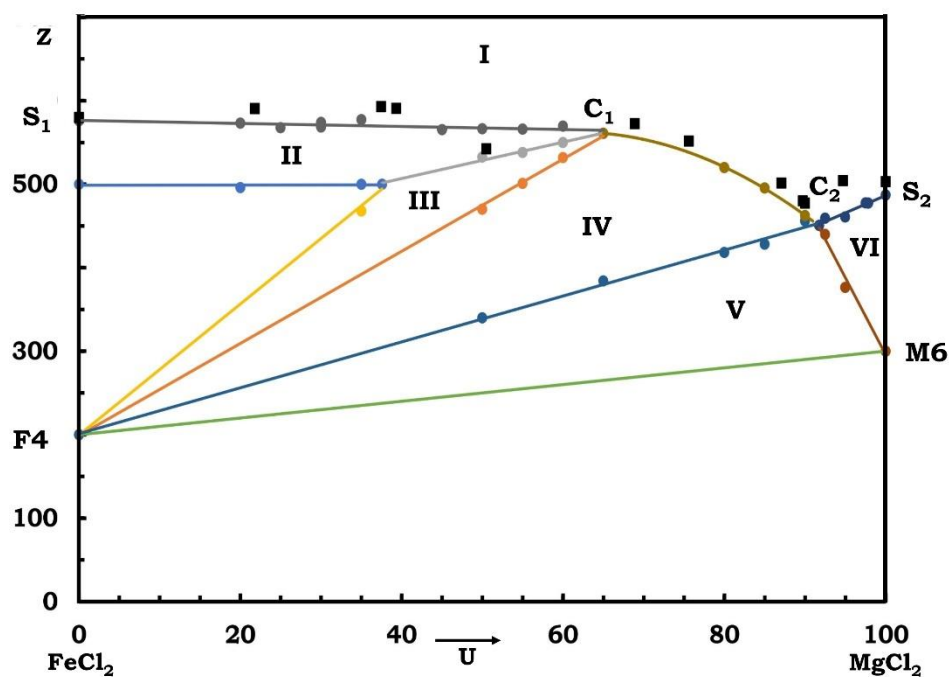
The solubility results are in general in good agreement, especially in the  $\text{FeCl}_2$  rich side, with those previously reported by literary<sup>10,16</sup>. The synthetic method allowed us to draw, in the  $\text{FeCl}_2$  rich side, the tie lines of the solid solutions and to determine its chemical formula, which is  $[\text{FeCl}_2]_{(1-x)}[\text{MgCl}_2]_x \cdot 10\text{H}_2\text{O}$ , i.e.  $(\text{Fe}_{(1-x)}\text{Mg}_x\text{Cl}_2 \cdot 10\text{H}_2\text{O})$  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  $\text{FeCl}_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  have been observed at 298 K<sup>18</sup>.

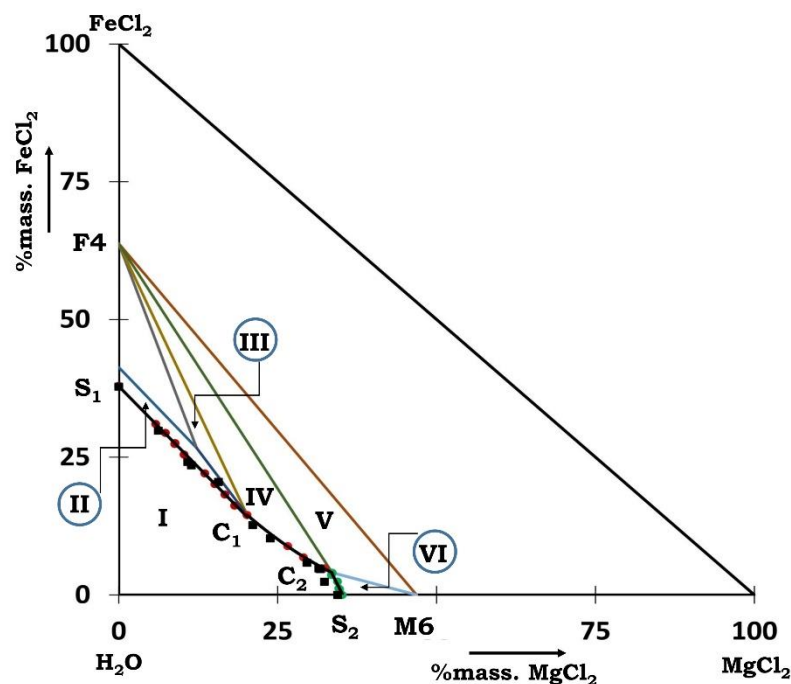
**Table 3.** Conductivity Data measurements.

$M_8(U=50)$				$M_{12}(U=80)$		$M_{16}(U=94.97)$	
$\sigma$ (mScm <sup>-1</sup> )	Z	$\sigma$ (mScm <sup>-1</sup> )	Z	$\sigma$ (mScm <sup>-1</sup> )	Z	$\sigma$ (mScm <sup>-1</sup> )	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						

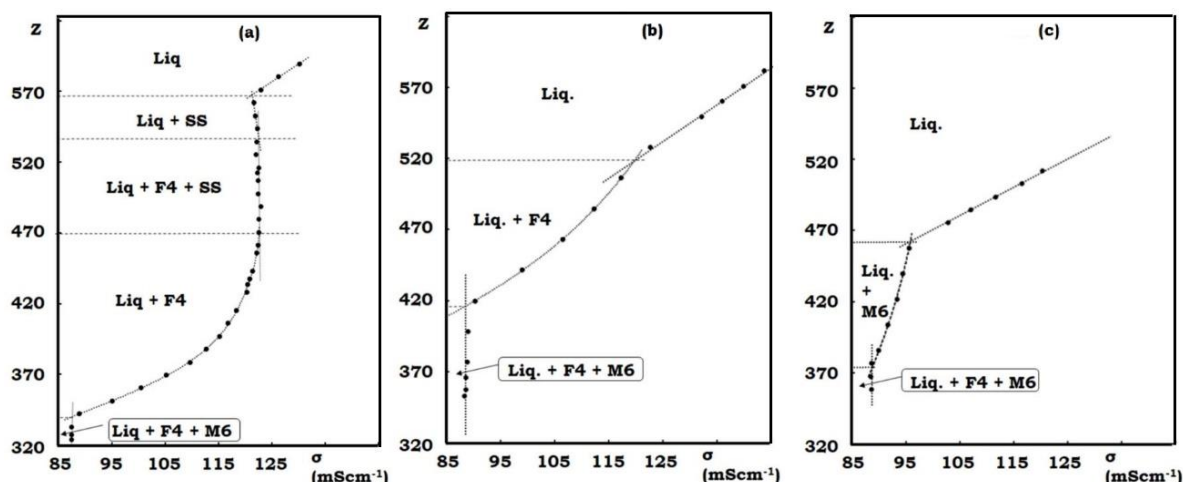
Standard uncertainties  $u$  are  $u(\sigma) = 0.1 \text{ mScm}^{-1}$ ,  $u(Z) = 0.05$ .



**Figure 2.** Phase diagram for the ternary  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  system at 288 K: ●, experiment data in this study. ■, literary data <sup>10,16</sup> (F4:  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ ; M6:  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ; U and Z: Jänecke coordinates of  $\text{MgCl}_2$  and water respectively)



**Figure 3.** Phase diagram for the ternary  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  system at 288 K expressed in weight percent: ●, experimental data in this study, ■, literary data <sup>10,16</sup> (F4:  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ; M6:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ).



**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  $\text{MgCl}_2\text{-FeCl}_2\text{-H}_2\text{O}$  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  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and solid solution  $\text{Fe}_{(1-x)}\text{Mg}_x\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  with  $0 < x \leq 0.38$ . The compositions, in Jänecke coordinate, of the two invariant points, are:

$C_1$ : 65%  $\text{MgCl}_2$  ; 35%  $\text{FeCl}_2$  ;  $Z=561$

$C_2$ : 91.75%  $\text{MgCl}_2$  ; 8.25%  $\text{FeCl}_2$  ;  $Z=450.6$

Three diphasic fields, where a solid phase coexists in equilibrium with liquid: “liquid + solid solution”, “liquid +  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ” and “liquid +

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ”. The smallest crystallization field is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . 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.

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