Solubility in the ternary system MgCl$_2$-FeCl$_2$-H$_2$O at 288 K by conductance method

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Abstract: Experimental studies on the solubility of the ternary system MgCl$_2$-FeCl$_2$-H$_2$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 MgCl$_2$-6H$_2$O, FeCl$_2$-4H$_2$O and solid solution Fe$_2$Cl$_4$·Mg$_2$Cl$_2$·10H$_2$O 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. Furthermore, phase diagrams permit us to study and control important processes such as phase separation, crystallization, solidification, and purification. For these reasons, the study of the solid-liquid equilibrium of the ternary system (MgCl$_2$ - FeCl$_2$ - H$_2$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 MgCl$_2$-H$_2$O, Fe / Cl - H$_2$O (M = K, Na) and MgCl$_2$-H$_2$O. Our purpose is to examine deeply the ternary system MgCl$_2$-FeCl$_2$-H$_2$O behavior at 288 K.

A large amount of experimental data related to the phase diagrams of the binary systems MgCl$_2$-H$_2$O and FeCl$_2$-H$_2$O are available. In our latter study, 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 H$_2$O-MCl$_n$ (M = Mg$^{2+}$, Fe$^{3+}$, Fe$^{2+}$). To estimate solubility, the databases on iron and magnesium mineral’s solubility were taken from the compilations of Linke and Seidell 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 FeCl$_2$·nH$_2$O (n=2, 4, 6) and MgCl$_2$·nH$_2$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 MgCl$_2$-FeCl$_2$-H$_2$O, the first study was conducted by Boeke in 1911. 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 FeCl$_2$MgCl$_2$.8H$_2$O from the temperature of 295.8 K where all solid phases were stoichiometric. Shchedrina et al. 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 MgCl$_2$·6H$_2$O and those based on FeCl$_2$·4H$_2$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 FeCl$_2$·MgCl$_2$.8H$_2$O appears, at 338 K, the double salt...

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DOI: http://dx.doi.org/10.13171/mjc811902523am

Received November 25, 2018
Accepted January 10, 2019
Published February 5, 2019
appears as a stoichiometric phase, and finally, at 343 K they obtained the same results at 338 K with the appearance of the MgCl₂.6H₂O crystallization field. 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 FeCl₂-
MgCl₂-HCl-H₂O 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 FeCl₂-MgCl₂-H₂O at 298 K. In addition to the fields of simple MgCl₂.6H₂O and FeCl₂.4H₂O salts, Balarew and Spassov also found a very narrow field corresponding to the crystallization of the double salt MgCl₂·FeCl₂·8H₂O. 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 {mMgCl₂ + nFeCl₂}(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 Fe²⁺ to Fe³⁺. Table 1 summarizes the information of the key reagents used in the current study, their manufacturer (origins) and their corresponding purity.

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 MgCl₂.6H₂O, and it was preserved in a desiccator in the presence of P₂O₅.

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

![Figure 1. Ternary MgCl₂-FeCl₂-H₂O representation at 288 K (Original ternary MgCl₂-FeCl₂-H₂O representation)](image)
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 FeCl₂·4H₂O and MgCl₂·6H₂O 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 ± 0.2%). The Mg²⁺ concentration was determined with a precision of within ± 0.5% by complexometric titration at pH 9.5–10 (ammonia buffer), using Erichrome black T as the indicator. The Fe²⁺ solution was titrated with a precision of about 0.3% by standard potassium dichromate (K₂Cr₂O₇) 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.

\[
P = 2n_{\text{Mg}^{2+}} + 2n_{\text{Fe}^{2+}} = n_{\text{Cl}^-} ; \quad U = \frac{n_{\text{Mg}^{2+}}}{p} \cdot 200 ; \quad V = \frac{n_{\text{Fe}^{2+}}}{p} \cdot 200 ; \quad Z = \frac{n_{\text{H}_{2}O}}{p} \cdot 100
\]

and \(U + V = 100\)

\(U\): MgCl₂ Jänecke coordinate; \(V\): FeCl₂ Jänecke coordinate; \(Z\): water Jänecke coordinate

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 mS/cm⁻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 CaCl₂-SrCl₂-H₂O 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 MgCl₂-FeCl₂-H₂O 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 taken 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, FeCl₂·4H₂O or MgCl₂·6H₂O”
- Two invariant phase fields liquid + FeCl₂·4H₂O + “solid solution or MgCl₂·6H₂O”

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
This procedure permitted the determination of the entire phase diagram of MgCl₂-FeCl₂-H₂O at 288 K.

### Table 2. Data solubility in the ternary system MgCl₂-FeCl₂-H₂O at 288 K.

| N°  | U   | V     | Z₄   | Z₁   | Z₂   | Z₃       | MgCl₂ | FeCl₂ | H₂O   | solid phases |
|-----|-----|-------|------|------|------|---------|-------|-------|-------|-------------|
| 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 MgCl₂ and FeCl₂ is 0.03 and 0.02 in mass %, respectively.

Note: F₄: FeCl₂·4H₂O; SS: solid solution; M₆: MgCl₂·6H₂O; Z₁: solubility limit

Zi (i =1, 2, 3): other phase changes; C₁ and C₂: invariant points

In Figs 2 and 3, points S₁ and S₂ represent the solubility of pure components FeCl₂·4H₂O and MgCl₂·6H₂O, respectively. The ternary phase diagram consists of two co-saturated points C₁ and C₂ of two solids (FeCl₂·4H₂O + solid solution in iron chloride) and (FeCl₂·4H₂O + MgCl₂·6H₂O), 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 FeCl₂·4H₂O or MgCl₂·6H₂O. The largest crystallization field is FeCl₂·4H₂O; the smallest crystallization field is MgCl₂·6H₂O.
- Two invariant triphasic domains (III, V), where a liquid with a defined compositions C₁ and C₂, is in equilibrium with the mixture of "solid solution + FeCl₂·4H₂O", "MgCl₂·6H₂O + FeCl₂·4H₂O", respectively.

S₁C₁, C₂C₂, and C₂S₂ are the isothermal dissolution curves of solid solution, FeCl₂·4H₂O and MgCl₂·6H₂O, respectively at 288 K.

The solubility results are in general in good agreement, especially in the FeCl₂ rich side, with those previously reported by literary. 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 [FeCl₂]₁₋ₓ[MgCl₂]ₓ·10H₂O, i.e. (Fe₁₋ₓMgₓ)₂Cl₂·10H₂O with 0 < x ≤ 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 FeCl₂·MgCl₂·8H₂O have been observed at 298 K.
Table 3. Conductivity Data measurements.

| M₈(U=50) | Z  | σ (mScm⁻¹) | M₁₂(U=80) | Z  | σ (mScm⁻¹) | M₁₆(U=94.97) | Z  | σ (mScm⁻¹) |
|--------|----|-------------|-----------|----|-------------|---------------|----|-------------|
| 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 | 363.77  |
| 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  | 90.0 | 385.40  |
| 95.0   | 351.04 | 122.4 | 497.70  | 89.0 | 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  | 99.0 | 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  | 140.0 | 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 MgCl₂-FeCl₂-H₂O system at 288 K: ●, experiment data in this study. *, literary data.¹⁰,¹⁶ (F₄: FeCl₂.4H₂O; M₆: MgCl₂.6H₂O; U and Z: Jänecke coordinates of MgCl₂ and water respectively)
Figure 3. Phase diagram for the ternary MgCl$_2$-FeCl$_2$-H$_2$O system at 288 K expressed in weight percent: ●, experiment data in this study, •, literary data (F4: FeCl$_2$.4H$_2$O; M6: MgCl$_2$.6H$_2$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 MgCl$_2$-FeCl$_2$-H$_2$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 MgCl$_2$.6H$_2$O, FeCl$_2$.4H$_2$O and solid solution Fe$_{1-x}$Mg$_x$Cl$_2$.10H$_2$O with 0<x≤0.38. 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$_2$O” and “liquid + MgCl$_2$.6H$_2$O”. The smallest crystallization field is MgCl$_2$.6H$_2$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.

References

1 - J.-X. Wu, G.-C. Zhang, B. Zhao, S. Wang and J.-L. Cao, Phase Diagram of the Quaternary System KCl–MgCl$_2$–NH$_4$Cl–H$_2$O 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 des phases du système ternaire KCl–FeCl3–H2O, 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+) et KCl, J. Therm. Anal. Calorim., 2000, 61, 849–860.

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

10 - A. P. Shchedrina and 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. KHIIMII, 1980, 25, 2814–2820.

19 - C. Christov, Pitzer ion-interaction parameters for Fe(II) and Fe(III) in the quinary system, [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-Fe(III)-Cr(III)-Cl-H2O system at 25°C, Acta Sci. Nat., 2018, 5, 6–16.

21 - B. El Goundali, A. Teysnier, M. Kaddami, J.-J. Counioux and C. Goutaudier, Linear behaviour in isothermal equilibrium 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 H2O-CaCl2-2SrCl2-2BaCl2. Méthode d’étude et application au ternaire H2O-CaCl2-2SrCl2, Bull. Soc. Chim. Fr, 1979, 3, 82–85.