Original article

Theoretical confirmation of an established experimental phase diagram of ternary system (Cu(SO₄)–Zn(SO₄)–H₂O) at 25 °C: Pitzer parameters determination

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The isotherm phase diagram of the ternary system (Cu(SO₄)–Zn(SO₄)–H₂O) was firstly established at 25 °C using a synthetic method of conductivity measurement. Then, we made use of volumetric dosing, in order to identify solid phases. The obtained isotherm has revealed the presence of two solid phases that having a stable equilibrium with the liquid phase, which are Cu(SO₄)·5H₂O, and the Zn(SO₄)·7H₂O. This study was confirmed numerically while going through the calculation of the binary and ternary Pitzer parameters for the studied salts through a Nelder Mead simplex algorithm. Indeed, the comparison of these with the bibliographic data has confirmed the accuracy of our experimental results.

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1. Introduction

The need for the optoelectronic device with a low cost and high performance had driven by, to the development of thin films of transparent conductive oxides with improved optical and electrical properties. Therefore, electrical materials are currently at the heart of scientific and technological development and their uses are expanded across the most innovative fields of innovation. Such as electrical energy, computing, renewable energy, hydrometallurgy, geochemistry and oceanography. Undoubtedly, photovoltaic cells based on metal oxides are the object of several studies [1–5]. The rational development of such oxides from the corresponding metal salts needs a good knowledge of phase equilibrium in the systems thereby formed.

The first factor involved in the development of thin films of conductive oxide is the temperature. Absolutely, matter changes its physical state, according to this one, which makes diagrams development very useful in this domain because it promotes the explanation of mechanical and thermodynamic properties changes, of metals depending on temperature. In this context comes the present work, where the main objective is to establish the isothermal phase diagram of a ternary system based on metal salts. Furthermore, a theoretical study was approached based on the Pitzer model.
The Cu(SO₄)–Zn(SO₄)–H₂O ternary system investigated in the present work has been the objective of many researches, because of its applicability in different fields. This is particularly relevant to catalyst oxides that are imposed in many applications in several domains. Indeed, the catalysts are chemical species used in most industrial synthesis processes, by allowing them to increase the reaction kinetics while minimizing energy costs [6], as in the case of methane steam reforming [7]. The present paper is, in fact, a start of a larger work about the establishment of the phase diagram for the ZnSO₄–CuSO₄–NiSO₄–H₂O quaternary system, whose knowledge is important in the synthesis of mixed oxides based on the three mentioned metallic ions.

As we know, models have been developed allowing an adequate description of the behavior of concentrated aqueous solutions [8–10]. Pitzer is the most known one proposed for the description of the properties of dense electrolyte solutions in a wide range of temperatures [11], pressures, and compositions. Thus, this one requires the knowledge of interaction parameters between particles. As a matter of fact, Pitzer (1973) has developed his model for an electrolyte, while introducing a set of interaction parameters whether binary or ternary ones.

Hence, comes the second part of our paper in which we have treated the numerical aspect of the established isotherm using the algorithm previously elaborated. We could be able to determine Pitzer parameters for the studied system. The method is based on the comparison between the experimental phase diagram and the one obtained using Pitzer parameters, this comparison has allowed us to confirm that the experimentally developed isotherm is effective.

On the other hand, several methods have been used for the Pitzer parameters determination, except that some are considered expensive in terms of time and money, because of the enormous need for materials, energy, and equipment [12,13].

Clearly, the most known and used way is the iterative calculation based on the determination of the osmotic coefficient experimentally through the isopiestic method. This is an effective method if we could manage to undertake the experimental protocol correctly with low uncertainty.

However, it is considered expensive since the process must be repeated for a large number of modalities’ values.

### 2. Experimental

The analysis of the solution in equilibrium with the different solid phases has been performed with a synthetic method based on conductivity measurements [14–17]. The water is progressively added using a micro-burette Schott Gerate T82/50 under stirring, to a saturated mixture of a given initial composition. After the stirring was stopped and the conductivity of the decanted solution is measured.

The experiment was carried out using a thermostated cell, Fig. 1, in which flows the distilled water maintained at the desired room temperature of 25 °C.

We followed for several poly-phases (liquid + solid) of appropriate composition, the variation of the liquid phase conductivity according to the initial mixture dilution. The electric conductivity–composition curve of the solution has a discontinuity at each phase change. When the identification of the solid phases was too difficult only with the preceding method, the solution and the solid phases of a given mixture composition were submitted to dosages. The compositions of double saturation points are obtained by direct determination of concentration using the wet residues [18] and the “ensembles” methods [19].

The salts used in this work are the Cu(SO₄)·5H₂O (Blue vitriol), the Zn(SO₄)·H₂O. Water was bi-distilled before use. While the conductivity measurements were performed using a Knick 703 device. And the system temperature is maintained constant at 25 °C by using a Julabo F50 thermostat.

The solid phase compositions were determined by a dosage of the Cu and Zn ions in the several sulfates. It is a chemical analysis method whose objective is to confirm the solid phases identified from the conductivity curve.

The Cu ions were measured by iodometry, it is an indirect dosage using potassium iodide (KI) and sodium thiosulfate (Na₂S₂O₃). The Zn ions are titrated by volumetry using the EDTA method and finally the sulfate ions by barium sulfate (BaSO₄) precipitation.

### 3. Pitzer model

The other object of the present work is the Pitzer parameters determination of the ternary system (CuSO₄)–ZnSO₄–H₂O. Hence, the algorithm introduced below was the main tool for this step. In fact, the simplex method has been used to determine both binary and ternary Pitzer parameters.

The Pitzer model is one of the most known models that has known a remarkable success. It is particularly popular with geochemists, waste chemists and engineers, for the prediction of mineral solubilities and phase equilibrium. Pitzer and his colleagues have developed the ionic interaction approach to predict the mean activity coefficients of salts in aqueous solutions of electrolytes as a function of molality as well as the theoretical solubilities of isotherms [8–10].

This ion-interaction model gives an equation for the activity and osmotic coefficient of electrolyte solution depending on four binary parameters, $\psi_{ij}$, $\psi_{ij}$, $\psi_{ij}$, $\psi_{ij}$ and two ternary ones $\psi$ and $\theta$. These parameters allow us the calculation of the equilibrium constant of each component in the systems at different temperature. Indeed, the present work aims to predict Pitzer parameters for the studied system while using our approach that has been developed in a previous work [20].

The method is based on several steps whose most of them move the point of the simplex where the function is maximum to the point where it is minimal. First, we initialize the programs by a set of vectors chosen such that they are not collinear. Then, vectors are ordered while respecting the ascending order of the objective function values. We compute the centroid, these steps are repeated for each iteration. Thereafter, comes the fourth iterative operations that aim to find the minima of the objective function, Reflect, Expand,
Fig. 1 – Illustration of the experimental device.

Fig. 2 – Flowchart of employed algorithm.

Contract and shrink; the method is wide explicit in previous work.

Fig. 2 illustrates the flowchart that generally summarizes all mentioned operations while respecting the conditions and sequences of the algorithm, since the initialization of starting vectors set until we accurate the correct Pitzer parameter values.

• Initialization: we initialize the programs by a vectors set, chosen such that they are not collinear.

\[ P_0 = [X_1, X_2, \ldots, X_{n-1}, X_n] \]

\[ P_i = [X_1, X_2, \ldots, X_{n-1}, X_n] + s_i * E_i; \quad i = 2, \ldots, n \]

where \( E_i = [e_1, e_2, \ldots, e_j, \ldots, e_n] \) is a vector of size \( n - 1 \) With \( \ldots, j = 1 \) if \( i = j \) otherwise \( e_j = 0 \), \( s_i \) is an added step to each parameter of the vector, in order to create \( n+1 \) initial vectors, the \( s_i \) value is chosen such that each parameter \( X_i \) is always between two reasonable values. Previously set by the author.

- Centroid: \( M = \frac{1}{n} \sum_{i=1}^{n} p_i \)
- Reflect: \( P^R_n = 2 * M + P_n \)
- Expand: \( P^E_n = 2 * P^R_n - M \)
- Contract: \( P^C_n = \frac{3}{2} (M - P_n)P^R_n - \frac{1}{2} (M + P_n) \)
- Shrink: \( V_i = \frac{3}{2} (P_0 - P_i) \) if \( i = 1 \) otherwise \( V_j = 0 \)
The objective function $f$ is in terms of the standard deviation between the fitting of experimental points and the theoretical function.

$$f(X) = Y_{exp} - Y_{the}$$

The calculated ($Y_{exp}$) is obtained by fitting the experimental points, the theoretical function ($Y_{the}$) is established after the adjustment of the theoretical points found using the Pitzer model at 25°C. Indeed, the equilibrium constant ($K$) for the binary system, is calculated for an initial guess of Pitzer parameters. Then, the ternary equilibrium constant ($K_t$) is calculated for the same initial guess, in order to define the theoretical pairs of solubility limits of the ternary system. The method consists essentially of equalizing the equilibrium constant of the binary ($K_b$) and the ternary system ($K_t$) corresponding to the same solid phase [21], while varying the molality of cation and anion as well as the water quantity.

$$\omega = \sum_{i=1}^{N_{pts}} (K_t(m_c, m_a, n_{w}) - K_b)^2$$

where $N_{pts}$: number of data points in the solubility isotherm; $m_c, m_a$: molality of cation; $n_{w}$: molality of anion; $n_{w}$: water quantity.

### Table 1 – The measured solubility data of the ternary system (Cu(SO$_4$)–Zn(SO$_4$)–H$_2$O) at 25°C.

<table>
<thead>
<tr>
<th>W(Cu(SO$_4$))</th>
<th>W(Zn(SO$_4$))</th>
<th>Limit domains</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35.51</td>
<td>Zn$_7$ + Liq</td>
</tr>
<tr>
<td>5.03</td>
<td>28.33</td>
<td>–</td>
</tr>
<tr>
<td>7.61</td>
<td>24.99</td>
<td>Cu$_3$ + Zn$_7$ + Liq</td>
</tr>
<tr>
<td>8.35</td>
<td>21.82</td>
<td>Cu$_4$ + Liq</td>
</tr>
<tr>
<td>9.13</td>
<td>19.27</td>
<td>–</td>
</tr>
<tr>
<td>11.02</td>
<td>15.51</td>
<td>–</td>
</tr>
<tr>
<td>12.42</td>
<td>11.65</td>
<td>–</td>
</tr>
<tr>
<td>13.81</td>
<td>8.33</td>
<td>–</td>
</tr>
<tr>
<td>15.41</td>
<td>5.41</td>
<td>–</td>
</tr>
<tr>
<td>16.53</td>
<td>2.58</td>
<td>–</td>
</tr>
<tr>
<td>18.48</td>
<td>0</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 2 – Weight composition coordinate of eutectic points for the studied ternary system.

<table>
<thead>
<tr>
<th>W(Cu(SO$_4$))</th>
<th>W(Zn(SO$_4$))</th>
<th>Domain limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.61</td>
<td>24.99</td>
<td>Cu$_3$ + Zn$_7$ + Liq</td>
</tr>
</tbody>
</table>

### Table 3 – Single-salts calculated and existing Pitzer ion interaction parameters.

<table>
<thead>
<tr>
<th>Salts</th>
<th>Calculated</th>
<th>Literature</th>
<th>$\rho^0$</th>
<th>$\rho^1$</th>
<th>$r^0$</th>
<th>$r^1$</th>
<th>$\rho_b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(SO$_4$)</td>
<td>0.195</td>
<td>0.2358</td>
<td>2.4</td>
<td>2.485</td>
<td>-0.002</td>
<td>-0.012</td>
<td>-50.12</td>
<td>[24]</td>
</tr>
<tr>
<td>Literature</td>
<td>0.2340</td>
<td>0.21757</td>
<td>2.527</td>
<td>2.62597</td>
<td>0.0044</td>
<td>0.013756</td>
<td>-48.33</td>
<td>[25]</td>
</tr>
<tr>
<td>Zn(SO$_4$)</td>
<td>0.14</td>
<td>0.1949</td>
<td>2.88</td>
<td>2.88</td>
<td>0.05</td>
<td>0.02896</td>
<td>-32.70</td>
<td>[26]</td>
</tr>
</tbody>
</table>

### Table 4 – Calculated ternary Pitzer ion interaction parameters.

<table>
<thead>
<tr>
<th>Ternary parameters</th>
<th>$\theta_{Cu,Zn}$</th>
<th>$\psi_{Cu,Zn,SO_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>0.314</td>
<td>-0.025</td>
</tr>
</tbody>
</table>

### 4. Results and discussion

#### 4.1. The experimental isotherm

The weight composition coordinates of considered mixture points were calculated using the following expressions:

$$W(Cu(SO_4)) = \frac{m(Cu(SO_4))}{m_t}$$

$$W(Zn(SO_4)) = \frac{m(Zn(SO_4))}{m_t}$$

$$m_t = m(Cu(SO_4)) + m(Zn(SO_4)) + m(H_2O)$$

The solids phases encountered in this work are:
- Cu(SO$_4$·5H$_2$O) (Cu$_5$)
- Zn(SO$_4$·5H$_2$O) (Zn$_1$)

The experimental results of the solubility isotherm obtained at 25°C are given in Table 1. The results that have been found are exploited to find the isothermal curves of the ternary systems. In fact, we have introduced a triangular representation based on the conversion of rectangular coordinates to triangular ones (Tables 2–4).

The conversion of the orthogonal reference to a triangular one on a 45° angle is as follows:

$$X_{tri} = X_{rec} + 0.5 * Y_{rec} \text{ and } Y_{tri} = Y_{rec}$$

Fig. 3 illustrates the isotherm of Cu(SO$_4$)–Zn(SO$_4$)–H$_2$O system, according to the triangular representation. The existing domains in the curve are explicit as follows:

- (I): the liquid field.
- (II): the saturated solution is in equilibrium with a stable Zn(SO$_4$·7H$_2$O) solid phase.
- (III): the solid phases in equilibrium with the saturated solution is Cu(SO$_4$·5H$_2$O).
- (IV): the solid phases in equilibrium with their saturated solution are Zn(SO$_4$·7H$_2$O and Cu(SO$_4$·5H$_2$O).
Otherwise, only one invariant isotherm and isobar is found at 25 °C with the following weight composition coordinates:

4.2. Theoretical isotherm

In this part, our approach is to determine the Pitzer parameters for the studied solid phases using the algorithm previously confirmed while exploiting the isothermal curve of the stake ternary system, a comparison was made between the results of our program and existing data in literature as will be shown in tables.

The ternary Pitzer parameters of the studied system are not available in literature. Therefore, we have been able to find their values thanks to our used approach.

The main object of this part is to confirm our experimental work. As we have previously seen in this paper, the algorithm is based essentially on the isothermal curve, especially the experimental points of solubility limits. We made use of these points to find the Pitzer parameters numerically. Then, the comparison was made to discover how much we are near to the literature data.

Fig. 4 shows the solubility limits calculated from the developed method, it is a triangular representation of the mass fractions. As it is clearly shown in the curve, the results that we found from the Simplex method based on the Pitzer calculation model are identical to those we found experimentally, which confirms the certainty of our experimental curve.

As it will be shown in Table 5, a comparison was made between experimental data and theoretical points established from the used method, it has proved the efficiency of the approach based on Nelder Mead Simplex.

The most interesting issue about this method is that it can also be used inversely. Thus, this work has been dedicated to determine the binary and ternary Pitzer parameters of the metallic salt system, while basing it on experimental results that has been established before. In a reversible way, the experimental points that define the isotherm can be elaborated from known Pitzer parameters while making these last the fixed starting values of the simplex method, that has been used in a previous work [22] and with the same protocol we will search for the function that represents the isotherm, by minimizing the Gibbs energy [23]. The discovery of this option about our program represents a major gain in the field of experimental and theoretical chemistry, because being able to simulate the experiment without having to invest in terms of time, energy as well as chemicals, is already a remarkable progress in the present discipline, which comes to reduce and optimize significant expenses.

5. Conclusion

With this investment, we have proved that the used algorithm is efficient for the studied system. In our case, we have opted for two different aspects: In the first place the isotherm of the ternary system Cu(SO₄)–Zn(SO₄)–H₂O was determined using the experimental protocol seen above, then a numerical study was conducted to confirm our experimental result while comparing the obtained Pitzer parameters with literature.

In fact, this identification allowed us to conclude that the obtained isotherm is 100 percent correct. Furthermore, we have justified that the algorithm previously established can
be useful, to elaborate a phase diagram from Pitzer parameters, which means less investment in terms of time, money and energy.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgment

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