

## SOLUBILITY IN THE $\text{CuCl}_2\text{-NaCl-H}_2\text{O}$ SYSTEM AND HYDRATION ANALYSIS IN THE CASE OF COMPLEXATION

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The solubility diagram in the title system was studied at 25 °C. The results were compared with contradictory isotherms of other authors and one isotherm being in error was localized and rejected. The reliable solubility branches were treated with hydration analysis, which brings information on ionic processes in saturated solutions. Formation of coordination anions such as  $[\text{CuCl}_3]^-$  and  $[\text{CuCl}_4]^{2-}$  was found to be the main ionic process in saturated solutions in spite of the non-existence of the corresponding solid phase. The information obtained by this method for systems where hydration of components and complex formation take place simultaneously is demonstrated and discussed for the first time. A possibility of calculation of activity coefficients of the solute on both crystallization branches is discussed.

**Key words:** Solubility; Hydration analysis; Activity coefficients; Crystallization; Copper(II) chloride.

The solubility diagram of the  $\text{CuCl}_2\text{-NaCl-H}_2\text{O}$  system was studied at 25 °C by Kosyakina<sup>1</sup> and more recently by Filippov *et al.*<sup>2</sup>. Kosyakina<sup>1</sup> reports a compound of composition  $\text{CuCl}_2 \cdot \text{NaCl} \cdot 2 \text{H}_2\text{O}$ , which is analogous to phases existing in the systems  $\text{CuCl}_2\text{-MCl-H}_2\text{O}$  (M = Li (ref.<sup>3</sup>), K (ref.<sup>4</sup>),  $\text{NH}_4$  (ref.<sup>5</sup>), Cs (ref.<sup>3</sup>)). According to Filippov *et al.*<sup>2</sup>, the system is eutonic. In addition to solubility isotherms, Filippov *et al.*<sup>2</sup> measured the activity of water in the solutions of the title system and calculated the theoretical isotherm in a way related to the Pitzer concept<sup>6-9</sup>. The solubility data at 25 °C may be compared with solubility isotherms at 30 °C published by Schreinemakers and de Baat<sup>10</sup> and at 50 °C studied by Skripkin and Chernykh<sup>3</sup>. In both these studies, the system was declared to be of eutonic type.

In all the solubility diagrams published, both components are quite well soluble and their crystallization branches are long enough to be analysed by the hydration analysis<sup>11</sup>. This method has been developed to character-

ize the overall difference between the ternary and binary saturated solution of a given solute in terms of the state of water molecules. This characterization is done by means of the parameter  $P$ , which has the physical meaning of the mole fraction of water which, due to the presence of the non-saturating component, acquired properties different from those of water in the binary saturated solution of the solute.

It can be written:

$$P = (w_0^B)_{\text{changed}} / (M_r)_{\text{H}_2\text{O}} (n_0^B + n_1^B + n_2^B),$$

where

$$(w_0^B)_{\text{changed}} = w_0^B - \left( (n_{\text{NaCl}}^B)^{1/2} w_{0,\text{Na}}^A / n_{\text{NaCl}}^A \right) (n_{\text{NaCl}}^B + 2 n_{\text{CuCl}_2}^B)^{1/2},$$

when NaCl is the equilibrium solid phase and

$$(w_0^B)_{\text{changed}} = w_0^B - \left( (n_{\text{CuCl}_2}^B)^{1/3} w_{0,\text{Cu}}^A / 2^{2/3} n_{\text{CuCl}_2}^A \right) (2 n_{\text{CuCl}_2}^B + n_{\text{NaCl}}^B)^{2/3},$$

when  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  is the equilibrium solid phase.

Here, superscript A and B refers to the binary and the ternary saturated solution of the subscript component, respectively.  $(M_r)_{\text{H}_2\text{O}}$  is the relative molecular mass of water,  $n_i$  is the amount of substance and  $w_i$  is wt.% of the subscript component in particular solution.  $w_{0,\text{Na}}^A$  and  $w_{0,\text{Cu}}^A$  are wt.% of water in binary saturated solution of NaCl and  $\text{CuCl}_2$ , respectively. For the sake of clarity, the parameter  $P$  is plotted relative to one mol of the non saturating component, *i.e.*  $P/x_1$ .

As demonstrated later<sup>12</sup>, the ratio of activity coefficients of the solute in ternary and binary saturated solutions  $\gamma/\gamma_0$  can be easily calculated in each point of the solubility curve on the basis of the results of hydration analysis.

In this article, we make a decision between the controversial isotherms of Kosyakina<sup>1</sup> and Filippov *et al.*<sup>2</sup>. After that, the hydration analysis will be applied to the individual solubility branches in the system under investigation. For the first time hydration analysis is applied to a system when not only hydration of ions and competition for water, but also formation of complex ions is possible. The results are discussed from this point of view.

Activity coefficients of the solute on each solubility branch are calculated and the results compared with the activity coefficients derived from the data of Filippov *et al.*<sup>2</sup>.

## EXPERIMENTAL

Recrystallized  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  and NaCl (reagent grade, Lachema Brno) were used in the study. Seven phase complexes were prepared by weighing the components and distilled water and equilibrating them in polyethylene vessels placed in an air thermostat for 4–8 weeks with shaking on a mechanic shaking machine during first 7–10 days. The temperature was kept constant within  $25 \pm 0.1$  °C. The equilibrium was checked by colorimetric determination of the copper contents in saturated solution. After equilibration, the liquid phase was sampled with a pipette into a pre-weighed glass vessel and dried to constant weight at *ca* 200 °C to determine the total content of electrolytes. In addition the copper content in the saturated solution was determined complexometrically. The composition of equilibrium solid phases was derived graphically by connecting the figurative points of the phase complexes and the corresponding saturated solution in ternary diagram. The eutonic character of the system was proved by X-ray diffraction. The respective diffraction diagrams were obtained, at a MIKROMETA2 apparatus (Chirana, Prague), using a cell 57.3 mm in diameter,  $\text{CuK}\alpha$  line and Ni filter ( $U = 30$  kV,  $I = 20$  mA,  $t = 80$  min).

For the calculations of hydration analysis, a universal program was developed using Microsoft Visual Basic Version 5.0. After input of solubility isotherms, either manual or from a medium, a table of all the values obtainable by the method is produced, recorded and passed to SigmaPlot 4.0 program for graphical treatment.

## RESULTS AND DISCUSSION

Our solubility curve in the  $\text{CuCl}_2$ –NaCl– $\text{H}_2\text{O}$  system is compared with the measurements of other authors in Fig. 1. Without any doubt, the isotherm of Kosyakina<sup>1</sup> is wrong and is to be rejected. Probably, not sufficient time was allowed for equilibration in her experiments and no real equilibrium was attained. In Filippov's data<sup>2</sup>, the copper contents seem to have a slight systematical error (*e.g.*, he gives solubility of  $\text{CuCl}_2$  in pure water  $5.69$  mol  $\text{kg}^{-1}$  in comparison with literature value<sup>13</sup> of  $5.75$  mol  $\text{kg}^{-1}$ ) in spite of the fact that the data are both smooth and numerous.

In Figs 2a and 2b, the concentration dependence of the hydration analysis parameter  $P/x_1$  on the solubility branch of  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  and NaCl are depicted, respectively. Here, the evaluational potential of hydration analysis, which may be understood as an additional or alternative use of the method, may be demonstrated. As stated while introducing the method<sup>11</sup> and observed several times in as yet unpublished applications of the method, the hydration analysis is extremely sensitive to the accuracy of analysed isotherms being able to find fine differences among individual sets

of data, which all seem both smooth and reliable at first glance. Here, some scatter may be observed in the isotherm of Schreinemakers and de Baat<sup>10</sup>, highly probably due to the actual potentials of the analytical method when the work was performed. On the other hand, the hydration analysis of Philippov's isotherm<sup>2</sup> yields values close to zero throughout. This "idealized" result can be put into connection both with the systematic error in copper contents and with the fact that the authors' isotherm is reported to be in very good agreement with that calculated using the Pitzer method, in spite of the fact that the points designated as calculated were not involved in hydration analysis. Therefore, the best agreement is found between the hydration analysis of our isotherm and the 50 °C isotherm of Skripkin and Chernykh<sup>3</sup>.

The value  $P/x_1 < 0$  found in both cases corresponds to all presumptions on which the method is based: in formation of complex ions such as  $[\text{CuCl}_3]^-$  and  $[\text{CuCl}_4]^{2-}$ , water molecules originally held in hydration spheres of involved simple ions are released. Naturally, the sodium ions added form their hydration sphere simultaneously. The overall effect, however, is characterized by water bonding of a smaller intensity than with saturated solutions of both  $\text{NaCl}$  and  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ .

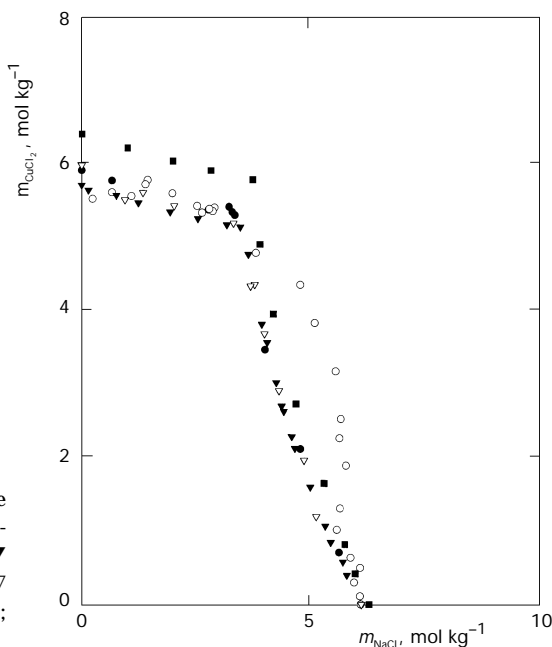


FIG. 1  
Solubility isotherms in the  $\text{CuCl}_2\text{-NaCl-H}_2\text{O}$  system. ● Our measurements, 25 °C; ○ Kosyakina<sup>1</sup>, 25 °C; ▼ Philippov *et al.*<sup>2</sup>, 25 °C; ▽ Schreinemakers and de Baat<sup>10</sup>, 30 °C; ■ Skripkin and Chernykh<sup>3</sup>, 50 °C

In Figs 3a and 3b, the concentration dependence of  $P/x_1$  is depicted together with the ratio  $m_{\text{Cl}}/m_{\text{Cu}}$ . Such way of presentation seems to be more informative than giving the number of available water molecules, which is to be presented in systems where competition for hydration water is the main process. In Figs 3a and 3b, a rise in the absolute value of  $P/x_1$  with rising  $m_{\text{Cl}}/m_{\text{Cu}}$  ratio can be observed. This is in full agreement with the generally accepted equilibrium treatment, where a rise of the  $m_{\text{Cl}}/m_{\text{Cu}}$  ratio must lead to the enhancement of complex formation. The observation can be understood as next support for the statement that in saturated solutions in the  $\text{CuCl}_2\text{-NaCl-H}_2\text{O}$  system formation of coordination anions is the main ionic process in spite of the fact that no corresponding solid phase exists.

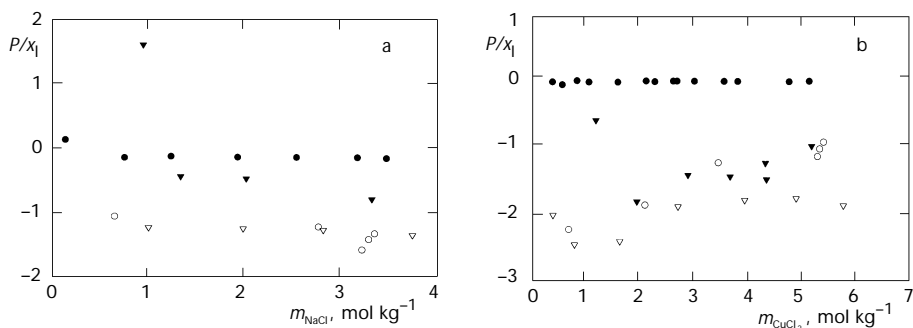


FIG. 2

Hydration analysis in the  $\text{CuCl}_2\text{-NaCl-H}_2\text{O}$  system: a solubility branch of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , b solubility branch of  $\text{NaCl}$ .  $\circ$  Based on our measurements, 25 °C;  $\bullet$  based on the measurements of Filippov *et al.*<sup>2</sup>, 25 °C;  $\blacktriangledown$  based on the measurements of Schreinemakers and de Baat<sup>10</sup>, 30 °C;  $\nabla$  based on the measurements of Skripkin and Chernykh<sup>3</sup>, 50 °C

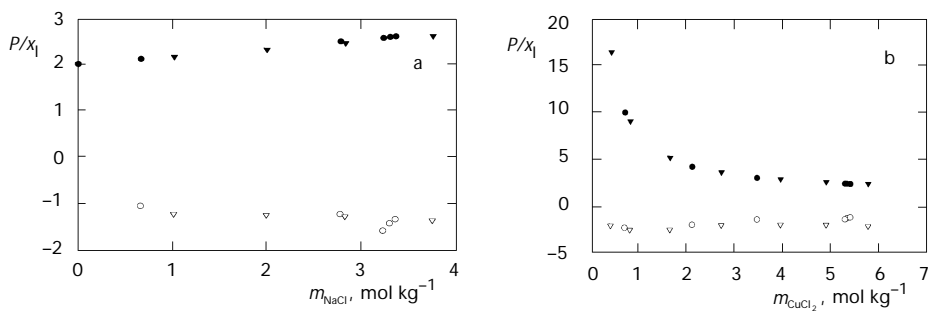


FIG. 3

The ratios  $m_{\text{Cl}}/m_{\text{Cu}}$  ( $\bullet$ ,  $\blacktriangledown$ ) and  $P/x_1$  ( $\circ$ ,  $\nabla$ ) in the  $\text{CuCl}_2\text{-NaCl-H}_2\text{O}$  system: a solubility branch of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , b solubility branch of  $\text{NaCl}$ .  $\circ$ ,  $\bullet$  Based on our measurements, 25 °C;  $\nabla$ ,  $\blacktriangledown$  based on the measurements of Skripkin and Chernykh<sup>3</sup>, 50 °C

In Table I, the activity coefficients of NaCl, calculated on the way described in ref.<sup>12</sup>, in its saturated solutions in the CuCl<sub>2</sub>-NaCl-H<sub>2</sub>O system at 25 °C are summarized. The value of  $\gamma_0$  has been taken from Silvester and Pitzer<sup>14</sup>. In the case of CuCl<sub>2</sub>, the value of  $\gamma_0$  was not available, as Pitzer's virial coefficients are reported to be valid only up to the concentration of 2 mol kg<sup>-1</sup> H<sub>2</sub>O. In Filippov's article<sup>2</sup>, an additional term was introduced in one of Pitzer's equations and calculation based on Filippov's solubility isotherm is reported to be valid up to saturation. With regard to the systematic error in copper concentration on the respective isotherms, the calculations of activity coefficients of CuCl<sub>2</sub> using  $\gamma_0$  derived from Filippov's results was not performed and only the ratio  $\gamma/\gamma_0$  is given in Table II.

TABLE I

Activity coefficient of NaCl in its saturated solutions in the CuCl<sub>2</sub>-NaCl-H<sub>2</sub>O system at 25 °C

$m_{\text{CuCl}_2}$	0.00	0.71	2.11	3.46	5.33	5.40	5.29
$(\gamma/\gamma_0)_{\text{NaCl}}$	1.0000	0.9723	0.9336	0.9278	0.9090	0.9164	0.9014
$\gamma_{\text{NaCl}}$	1.0080	0.9800	0.9411	0.9352	0.9163	0.9237	0.9086

TABLE II

Activity coefficient of CuCl<sub>2</sub> in its saturated solutions in the CuCl<sub>2</sub>-NaCl-H<sub>2</sub>O system at 25 °C

$m_{\text{NaCl}}$	0.00	0.66	2.77	3.29	3.22	3.35
$(\gamma/\gamma_0)_{\text{CuCl}_2}$	1.0000	0.9877	0.9433	0.9239	0.9175	0.9275

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