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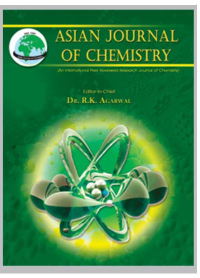

Solubility in Quaternary Systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O

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This paper looks at solubility in systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O at temperatures 25, 60 and 80 ºC. Phase diagrams of these mutual quaternary systems are constructed and crystallization fields of ferrous and zinc mono-, di- or trisubstituted phosphates and chlorides are defined. The new scientific data obtained allows us to justify optimal parameters of processes that take place in such systems. In particular this pertains to preparation of monosubstituted iron and zinc phosphates used in production of anticorrosive phosphate protective coatings.

Key Words: Mutual quaternary systems, Phosphate protective coating, Phase diagram of solubility, Isothermal method, Square Yeneke diagram.

INTRODUCTION

The problem of anticorrosive protection of metals is an essential one today and it calls for a quick solution. Herewith one of ways to manufacture effective phosphate protective coatings is by using waste from chemical-metallurgical manufacturers for that purpose.

It is known that chloride sublimates of chloro-oxidizing roasting of lead-zinc ore contain 28.9 % of chloride-ions, including 38.3 % of $ZnCl_2$ and 6.85 % of $FeCl_2$[1]. After phosphoric-acid treatment of these sublimates in order to obtain phosphating anticorrosive coatings, four-component (quaternary) systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O are formed. Formation of five-component (quinary) system $FeCl_2$-$ZnCl_2$-H_3PO_4-H_2O is possible as well. These processes represent complex chemical-technological systems, including both chemical and phase transformations in equilibrium conditions. Therefore the technology of processing of chloride sublimates with a certain composition using phosphoric acid is impossible to develop without complex physical-chemical analysis of these mutual systems and setting patterns around events taking place in the systems. This analysis is performed by studying properties of a heterogeneous system depending on its composition and parameters and imaging these dependences on state diagrams.

In literature only data available is regarding composition and properties of two-component systems $FeCl_2$-H_2O and $ZnCl_2$-H_2O[2], but it does not correspond with composition of waste in question. Acid-containing ternary systems like $FeCl_2$-HCl-H_2O and $ZnCl_2$-HCl-H_2O, $Fe_3(PO_4)_2$-H_3PO_4-H_2O and $Zn_3(PO_4)_2$-H_3PO_4-H_2O haven't been studied. The only element known is phase equilibrium in a system Fe_2O_3-P_2O_5-H_2O, which has completely different composition with crystallization of ferrous phosphates(III).

The FeO-P_2O_5-H_2O system is examined at 70 ºC in the range of diluted solutions only (less than 5.54 % FeO and 15.1 % P_2O_5) forming amorphous products like $2FeO·P_2O_5·3H_2O$ in solid phase. Hence, information about solubility in the given system is limited and it does not correspond to conditions of process behaviour. Phase equilibrium in quaternary mutual systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O, as well as in quinary system $FeCl_2$-$ZnCl_2$-H_3PO_4-H_2O haven't been studied. There is no data regarding solubility and crystallization fields in these systems even at standard temperature. This predetermined necessity to research system phase composition and properties to determine equilibrium saturation planes and to construct isothermal cross sections for diagrams.

EXPERIMENTAL

In this regard we studied state diagrams of above mentioned quaternary systems, which are the foundation for development of theoretical basis of technological processes that proceed during phosphoric-acid treatment of chloride sublimates. On the basis of constructed solubility diagrams for mutual quaternary systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O one can choose and justify optimal conditions of phosphoric-acid treatment of lead production sublimates and calculate theoretical output of production concentrate. Besides, the results obtained would bring a weighty scientific contribution to fundamental data regarding solubility in above mentioned systems and patterns of processes proceeding in complex physical-chemical systems.

Solubility was investigated by isothermal method which involves mixing solution at constant temperature with solid phase excess until equilibrium is reached. Chemical interaction takes place in systems between initial reagents-phosphoric acid solution with a certain concentration and ferrous(II) chloride or zinc(II) chloride up to establishing an equilibrium according to reaction equations:

$$3FeCl_2 + 2H_3PO_4 = Fe_3(PO_4)_2 + 6HCl \quad (1)$$

$$3ZnCl_2 + 2H_3PO_4 = Zn_3(PO_4)_2 + 6HCl \quad (2)$$

Depending on the degree of acid saturation mono-, di- or tri-substituted phosphates are formed. However to reach the saturation state and to determine system equilibrium composition at a certain temperature it is necessary to input an amount of chlorides exceeding stoichiometric norm for given reactions.

A sample of ferrous(II) chloride or zinc(II) chloride (reagent-grade) was added to the phosphoric acid solution of a certain concentration in amount that would salt-saturate the solution at the end of the reaction. This state was defined by excess amount of salt left in solid phase. After saturation was reached samples of liquid phase were sampled every 0.5 h using a thermostated sampler. The samples were subjected to chemical analysis to determine content of chloride-ions in liquid phase. We determined the time of reaching equilibrium by constant content of chloride-ions in last 2-3 samples. At the same time we analyzed solid phase samples to determine chloride-ions and P_2O_5 content in it. Chemical analyses of preliminary dried crystals were carried out using standard techniques.

Solubility was calculated on the basis of 3-4 parallel experiment results at allowable discrepancy less than 0.5 % between two parallel analyses of liquid phase in every experiment. It is established experimentally that equilibrium in systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O is reached in 2.5 h at any temperature. Solubility is studied in phosphoric acid concentration interval from 5 to 55 % of H_3PO_4 at temperatures 25, 60 and 80 ºC. The latter ones correspond to conditions of chloride sublimate processing.

RESULTS AND DISCUSSION

In mutual quaternary systems consist of water and two salts without a common ion, in order to illustrate such systems a tetragonal pyramid is used. The vertex of the pyramid represents figurative point of water composition and the base is the reflection of composition of waterless system consisting of salt pairs $3FeCl_2$-$2H_3PO_4$ and $Fe_3(PO_4)_2$-6HCl, $3ZnCl_2$-$2H_3PO_4$ and $Zn_3(PO_4)_2$-6HCl[3]. Solubility is more visually depicted in such systems using projections of isothermal sections of space diagram onto the pyramid base as a square. Herewith only points of composition of solution and solid phase salt mass are plotted on the diagram and such projection doesn't contain any information about water content in the system. To reflect water content it is necessary to construct additionally the water projection diagram.

To construct solubility isotherms for mutual quaternary systems on flat square Yeneke diagram the ionic salt composition of the system is expressed in Yeneke indexes. The indexes are determined on the basis of equality of the sum of cation and anion moles. So for the $FeCl_2$-H_3PO_4-H_2O system the sum of cation moles $3Fe^{2+}$ (bounded as chlorides and phosphates in the solution) and $6H^+$ (bounded as phosphoric acid and hydrochloric acid) should be equal to the sum of anion moles $6Cl^-$ and $2PO_4^{3-}$, which are bounded as matched salts and acids. On this basis the ionic composition of the system at any point of the diagram is determined as a molar ratio of one of the anions to the sum of anions and as a molar ratio of hydrogen-ions $6H^+$ to the sum of cations.

For this purpose we recalculated the obtained experimental result of equilibrium composition of systems by taking into account chemical reactions (1) and (2). Herewith chloride-ion content in the solution takes into account its presence both in ferrous chloride and in hydrogen chloride composition. High content of these ions in diluted phosphoric acid solutions (5-15 % of H_3PO_4 at 25 ºC) shows that there is $FeCl_2$ salt present in equilibrium with the stable salt pair $Fe_3(PO_4)_2$-6HCl and free H_3PO_4 is absent in this system. At higher temperatures the range of such composition of equilibrium system is expanded up to 20 and 25 % at 60-80 ºC in match. For the $ZnCl_2$-H_3PO_4-H_2O system such composition is characteristic for all temperature intervals in the range of phosphoric acid solution concentrations of 5-25 % of H_3PO_4. This is the case when $ZnCl_2$ salt is in equilibrium with the stable salt pair $Zn_3(PO_4)_2$-6HCl. This shows that solubility in the given system does not practically depend on temperature in the interval 25-80 ºC, whereas for the $FeCl_2$-H_3PO_4-H_2O system there is temperature dependence-temperature increase causes solubility increase and the ternary eutonic point is displaced to the range of higher concentrations.

Recalculation of component content in the system taking into account proceeding chemical reactions shows that starting with inflection point up to maximal H_3PO_4 concentration, phosphoric acid is in equilibrium with the stable salt pair. It gives evidence of wide crystallization range of ferrous and zinc phosphates. On the basis of obtained results we calculated point coordinates on solubility isotherms. When we plotted specific composition of saturated solutions (X_{PO_4}, XH) on the Yeneke diagram, we obtained lines of solubility isotherms in examined systems at 25, 60 and 80 ºC (Figs. 1 and 2).

According to obtained data crystallization fields of salts in systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O are constructed on the diagrams taking into account probable formation of mono- and disubstituted ferrous and zinc phosphates. Composition of these salts is labeled by points F_1 and F_2 accordingly in Figs. 1 and 2. Graphic representation of solubility isotherms shows that there is no temperature dependence of solubility in the $ZnCl_2$-H_3PO_4-H_2O system. Isotherms for all temperatures practically coincide and this points to impossibility of polythermal crystallization in this system.

In the $FeCl_2$-H_3PO_4-H_2O system displacement of the ternary eutonic point is observed (as mentioned above), as well as solubility increase and widening of the cocrystallization range of salts $Fe_3(PO_4)_2$ and $FeCl_2$ when temperature increases.

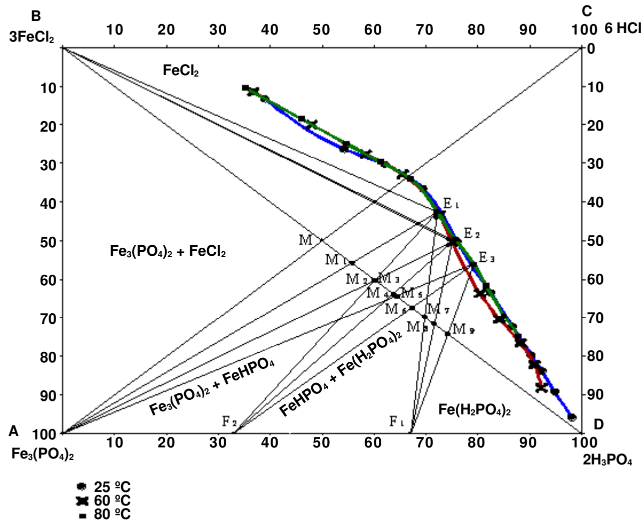

Fig. 1. Solubility in system $FeCl_2$-H_3PO_4-H_2O

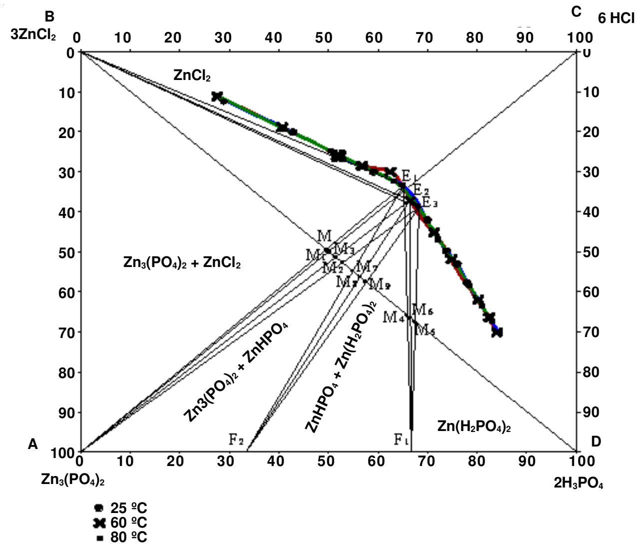

Fig. 2. Solubility in system $ZnCl_2$-H_3PO_4-H_2O

However, fields of ferrous and zinc phosphates crystallization are reduced and therefore this affects the choice of optimal conditions for preparation of monosubstituted ferrous and zinc phosphates. Points of ternary eutonics E_1, E_2 and E_3 are defined by an extreme point in saturated solution composition at given temperature. They are confirmed by solid phase composition, which was determined by phosphate- and chloride-ion content in it (Tables 1 and 2). Some deviations in solid phase composition in the range of small concentrations of phosphoric acid are obviously related to formation of ferrous chloride crystalline hydrate $FeCl_2 \cdot 4H_2O$, which results in chloride-ion content decrease.

The calculation of preparation processes of monosubstituted ferrous and zinc phosphates is performed on the basis of constructed phase diagrams of systems $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O. According to the rule of the connecting line the process of chloride and phosphoric acid interaction is illustrated on the diagram by line BD, connecting points of initial pure reagent composition. To form the target product-ferrous or zinc dihydrophosphate it is necessary to carry out the process with such mass ratio of initial compounds that the figurative point of system composition is on the crystallization ray of salts $Fe(H_2PO_4)_2$ and $Zn(H_2PO_4)_2$, which connects points of their composition F_1 and eutonic points. When the process takes place at 80 ºC, the unknown point M_5 is determined by the intersection of line of initial reagent interaction and crystallization ray F_1E_3 because it provides maximal product output.

To obtain given system composition we determined the consumption of phosphoric acid solution according to the rule of segments and then more precisely by means of mass balance calculation. As a result of calculations we determined output of target products-salts $Fe(H_2PO_4)_2$ and $Zn(H_2PO_4)_2$. Thus we established optimal consumption of phosphoric acid solution for given product output from a unit of mass (1 kg) of ferrous chloride-2.69 kg and of 1 kg of zinc chloride -2.115 kg. We have also determined maximal possible output of target product in given conditions of the process from a unit of mass of ferrous chloride -0.977 kg and from a unit of mass of zinc chloride -0.818 kg.

Conclusion

The calculation on the basis of experimental results Yeneke indexes and constructed phase state diagrams of the $FeCl_2$-H_3PO_4-H_2O and $ZnCl_2$-H_3PO_4-H_2O systems at 25, 60 and 80 ºC represent new scientific data about solubility in mutual quaternary systems. This data widens essentially the area of knowledge in physical-chemical analysis of multicomponent systems and it is the theoretical base for analysis and justification of optimal parameters of processes that take place in researched systems.

TABLE-1
COMPOSITION OF SOLID PHASE IN EQUILIBRIUM WITH SOLUTIONIN THE SYSTEM $FeCl_2$-H_3PO_4-H_2O

Composition ofan acid,% H_3PO_4	P_2O_5/Clamount in solid phase (%) at temperature			Composition of equilibrium solid phase (%) at temperature		
	25 (ºC)	60 (ºC)	80 (ºC)	25 (ºC)	60 (ºC)	80 (ºC)
5	0/37.2	0/39.1	0/42.2	$FeCl_2 \cdot H_2O$	$FeCl_2 \cdot H_2O$	$FeCl_2 \cdot H_2O$
10	0/45.1	0/40.4	0/47.7	$FeCl_2 \cdot H_2O$	$FeCl_2$	$FeCl_2$
15	3.0/43.5	0/46.9	0/50.3	$FeCl_2+Fe_3(PO_4)_2$	$FeCl_2$	$FeCl_2$
20	29.2/16.1	0/51.2	0/50.2	$FeCl_2+ Fe_3(PO_4)_2$	$FeCl_2$	$FeCl_2$
25	38.7/1.3	28.7/12.1	0/48.9	$FeCl_2+Fe_3(PO_4)_2+FeHPO_4$	$FeCl_2+Fe_3(PO_4)_2$	$FeCl_2$
30	50.3/0	42.0/0	27.7/10.4	$Fe_3(PO_4)_2+ FeHPO_4$	$Fe_3(PO_4)_2+FeHPO_4$	$FeCl_2+Fe_3(PO_4)_2$
35	51.9/0	52.1/0	40.9/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe_3(PO_4)_2+ FeHPO_4$
40	54.3/0	55.0/0	50.5/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$
45	53.8/0	53.5/0	53.7/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$
50	53.0/0	53.9/0	54.4/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$
55	54.1/0	54.0/0	53.1/0	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$	$Fe(H_2PO_4)_2$

TABLE-2
COMPOSITION OF SOLID PHASE IN EQUILIBRIUM WITH SOLUTIONIN THE SYSTEM $ZnCl_2$-H_3PO_4-H_2O

Composition ofan acid,% H_3PO_4	P_2O_5/Clamount in solid phase (%) at temperature			Composition of equilibrium solid phase (%) at temperature		
	25 (°C)	60 (°C)	80 (°C)	25 (°C)	60 (°C)	80 (°C)
5	0/47.1	0/47.7	0/49.2	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$
10	0/48.0	0/47.8	0/48.6	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$
15	0/49.2	0/49.0	0/49.0	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$
20	0/47.5	0/49.3	0/47.0	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$
25	24.4/13.4	0/48.8	0/48.3	$ZnCl_2$+ $Zn_3(PO_4)_2$	$ZnCl_2$	$ZnCl_2$
30	34.5/2.5	25.6/12.9	31.0/13.7	$ZnCl_2$+ $Zn_3(PO_4)_2$	$ZnCl_2$+$Zn_3(PO_4)_2$	$ZnCl_2$+$Zn_3(PO_4)_2$
35	38.8/0	35.9/0	37.1/0	$Zn_3(PO_4)_2$+ $ZnHPO_4$	$Zn_3(PO_4)_2$	$Zn_3(PO_4)_2$+$ZnHPO_4$
40	43.5/0	39.9/0	44.0/0	$ZnHPO_4$	$Zn_3(PO_4)_2$+ $ZnHPO_4$	$ZnHPO_4$
45	53.1/0	52.2/0	52.9/0	$Zn(H_2PO_4)_2$	$Zn(H_2PO_4)_2$	$Zn(H_2PO_4)_2$
50	54.1/0	54.0/0	54.2/0	$Zn(H_2PO_4)_2$	$Zn(H_2PO_4)_2$	$Zn(H_2PO_4)_2$
55	54.5/0	54.5/0	53.9/0	$Zn(H_2PO_4)_2$	$Zn(H_2PO_4)_2$	$Zn(H_2PO_4)_2$

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