Study of Solubility and Speciation of Iron Sulfates in Phosphoric Acid Milieu

Sara ELJAOUHARI1, Mouna L. BOUAMRANI2, M’hammed EL KOUALI3, Aziz KHEIREDDINE4, Samia YOUSFI5

Département de Chimie, Faculté des Sciences Ben M’Sik, Laboratoire de Chimie Analytique et Physico-Chimie des Matériaux, Université HASAN II de Casablanca.

Abstract: Industrial phosphoric acid contains free metal impurities and/or complexed one. Moreover, each element of the chemical forms and each proportion’s form are still unknown. However, the total contents of each element have been known up to now. It is necessary restraining the elimination or recuperation of the species in solution, to understand their deportment and know what form they may exist. This work examine the behavior and speciation of iron sulfate’s ions by monitoring the kinetics reaction of the iron sulfate’s dissociation in the phosphoric acid in various capacities (1-5.5 M) and by the characterization of the product precipitated by the ray X diffractions. The results obtained have allowed us to determine the equilibrium time of the dissociation reaction of iron sulfates in different phosphoric acid milieu at ambient temperature and the influence of acid content on the sulfate ions (SO$_4^{2-}$) and iron II (Fe$^{2+}$) behavior. This work allowed us to retain the variation of the phosphoric acid content has no significant influence on the equilibrium time of the dissociation reaction of the iron sulfates or on the precipitated product nature and the precipitated structural analysis confirms the absence of iron phosphate (Fe$_3$(PO$_4$)$_2$) and the compound obtained is always iron sulfates (FeSO$_4$).

Keywords: Speciation; Solubility; Speciation, Iron Sulfate; Phosphoric Acid; Solubilization

1. Introduction

Phosphoric acid is a chemical compound that is of great importance at the industrial level because it intervenes in many applications such as, fertilizers phosphate manufacturing, treatment of metal surfaces, organic synthesis, detergents manufacturing, in food industries, etc.

Phosphoric acid is mainly obtained from phosphate rock by the wet process. The obtained phosphoric acid contains most of the impurities previously present in the ore [1].

The common impurities in the phosphate rock are aluminium (Al$^{3+}$), iron (Fe$^{3+}$), magnesium (Mg$^{2+}$), calcium (Ca$^{2+}$), potassium (K$^+$), strontium, chlorides (Cl$^-$) and fluoride (F$^-$). Iron (Fe$^{3+}$) and aluminum (Al$^{3+}$) are often considered as the same category part of impurity. [2]

However phosphoric acid milieu remains very complex and not known enough.

This work examine the behavior and speciation of iron sulfate ions by monitoring the kinetics reaction of the iron sulfate dissociation in the phosphoric acid in various capacities (1-5.5 M) and by the characterization of the product precipitated by the ray X diffractions.

2. Materials and Methods

The dissociation reaction of iron sulfated was performed at ambient temperature and monitoring the kinetics performed by electronic thermometer until stabilization of the temperature of the mixture.

The equilibrium time of the reaction is calculated from the average of the equilibrium time of three similar tests.

Te: Average time equilibrium

Te = Te1 + Te2 + Te3

Te: Average time equilibrium

The residue precipitate is then filtered, washed with acetone and dried temperature at of 40°C.

Test Methods

For the study of the resulting products we performed diffraction analysis X-ray to determine the crystal structure.

3. Results and Discussion

3.1. Probable chemical reaction in the system studied

Chemical reaction in the pur phosphoric acid milieu

H$_3$PO$_4$ + H$_2$O $\leftrightarrow$ H$_2$PO$_4^-$ + H$_3$O$^+$

H$_2$PO$_4^-$ + H$_2$O $\leftrightarrow$ HPO$_4^{2-}$ + H$_3$O$^+$

HPO$_4^{2-}$ + H$_2$O $\leftrightarrow$ PO$_4^{3-}$ + H$_3$O$^+$

Probable chemical reaction in the phosphoric acid milieu containing iron sulfates.

(1)FeSO$_4$ $\leftrightarrow$ Fe$^{2+}$ + SO$_4^{2-}$

(2)2PO$_4^{3-}$ + 3Fe$^{2+}$ $\leftrightarrow$ Fe$_3$(PO$_4$)$_2$

(3)2H$_3$PO$_4$ + 3FeSO$_4$ $\leftrightarrow$ Fe$_3$(PO$_4$)$_2$ + 3H$_2$SO$_4$

In the ion phosphoric milieu acid SO$_4^{2-}$ ions have basic character [3] which results in the production of hydrogen ions HSO$_4^-$:

H$_3$PO$_4$ + SO$_4^{2-}$ $\leftrightarrow$ H$_2$PO$_4^-$ + HSO$_4^-$

Contrary to SO$_4^{2-}$ ions the hydrogen sulfate ions HSO$_4^-$ are deprived of their basic character [3] and thus unable to capture protons to form sulfuric H$_2$SO$_4$ and therefore the acid reaction (3) is not moving in the direction of production of sulfuric acid and ferric phosphate. The precipitates XRD analysis confirms this hypothesis. (Figure 1 and 2)
3.2 Equilibrium time of the reaction of solubility of the iron sulfate in the phosphoric acid milieu.

At a concentration of 5.5M phosphoric acid corresponding to the crude phosphoric acid obtained by a wet process [4], Acid molecules well solvated fail to react with the entire iron sulfate [2] and therefore the solution is rapidly saturated and equilibrium time is equal to the equilibrium time of the dissociation reaction of iron sulfate in desiled water. The variation of the acid concentration has no significant influence on the equilibrium time of the reaction of solubility of the iron sulfate in the phosphoric acid milieu studied.
4. Conclusion

This work allowed us to retain the following:

- The variation of the phosphoric acid content has no significant influence on the equilibrium time of the dissociation reaction of the iron sulfates or on the precipitated product nature.
- The precipitated structural analysis confirms the absence of iron phosphate (Fe₃(PO₄)₂) and the compound obtained is always iron sulfates (FeSO₄).

References