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Solubility of Malladrite Na_2SiF_6 and K_2SiF_6 in aqueous solutions

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Abstract. The water activities of binary solutions Na_2SiF_6-H_2O and K_2SiF_6-H_2O are measured from dilution to saturation using the hygrometric method at temperature 353 K. From these experimental data, the activity coefficients of solute were calculated using parameters of ionic interaction model. These coefficients are used to predict the solubility products of the K°_{sp}, the free energy ΔG°_{diss} of dissolution and also the characterization of the precipitated phases to saturation of the system containing Na_2SiF_6 or K_2SiF_6. The analyzed of solid phase obtained from saturated solution is made by Xray- diffraction.

1. INTRODUCTION

Hexafluorosilicates are used widely in research and industry, for a selective removal of surface acidity in zeolite [1], in photovoltaic applications [2], for an effective dealumination of zeolite [3] and ferrietite [4], as active agents in the formulation of mouthwashes and dentifrices [5], and as catalysis products in the frosted glass industry [6].

In phosphate industry, during the acid attack reaction, the highly soluble phosphoric acid generates complex aqueous systems, the dissolved species and the resulting physicochemical interactions are closely dependant on the variability of both the phosphate rock quality and the operating conditions of the process. Precipitation of the salts of hexafluorosilicate is considerable on scaling minerals [7] Fig. 1. The literature contains little information on solubility equilibria of the fluosilicates and the amount of solubility data is limited.

The prediction of the solubility in aqueous electrolyte solutions is important for a variety of applications in the chemical industry processes. The study of solubility of binary electrolyte solutions allows a better understanding of the properties and behavior of multicomponent aqueous systems. Studies of solubility diagrams of binary and multicomponent solutions are of importance for many applications.

The main objectives of this work the thermodynamic properties of the binary solutions aqueous Na_2SiF_6-H_2O and K_2SiF_6-H_2O using the hygrometric method at temperature 353 K. Also, the measured and predict solubility of the precipitated phases are determined. The analyzed of solid phase obtained from saturated solution is made by Xray-diffraction.

2. EXPERIMENTAL

The solutions of Na_2SiF_6 and K_2SiF_6, in water were prepared from crystalline materiel (extrapur-grade chemicals, mass fraction <0.99) and deionised distilled water. The reference solutions is NaCl(aq).

Figure 1. Precipitation of compounds containing salts of Hexafluorosilicate on the pipes during the production of phosphoric acid.

The water activity was determined using the hygrometric method described in our earlier work [8,9]. The apparatus used in this study of mixed electrolyte solutions is essentially the same as that used for the investigation of aqueous binary and ternary electrolyte solutions. It is based on the measurement of the water activity over aqueous solutions containing non-volatile electrolytes. The apparatus used is a hygrometer in which a droplet of salt solution is maintained on a thin thread. The diameter measurement of the previously calibrated droplet permits therefore the knowledge of the water activity of aqueous solutions.

The droplets of a reference solution of NaCl (aq) are deposited on the spider thin thread by pulverization. This thread is kept tense over a perspex support, which is fixed to a cup containing the selected solution to be studied. The cup is then placed in a thermostatted box. The droplet diameter is measured by a microscope with an ocular equipped with the micrometric screw.

From measurements of reference droplet diameters, $D(a_w(ref))$, above the reference solution and the corresponding diameters $D(a_w)$ above the studied solution, we calculate the growth ratio and then graphically determine the water activity using the variation of the ratio K as

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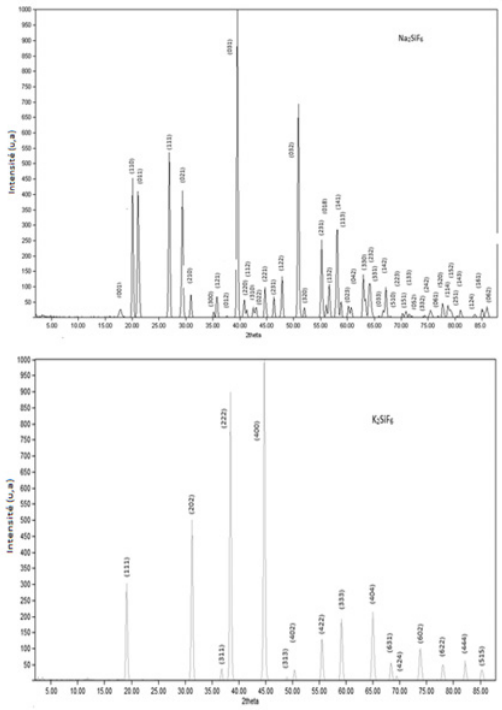

Figure 2. Powder X-ray diffraction of Na_2SiF_6 and K_2SiF_6.

Table 1. Calculated values of the logarithm of solubility product, the molality of the saturated binary solutions m_s, activities coeffitient γ, and the standard molar Gibbs energy of dissolution at 353 K.

Solid Phase	$\mathbf{m_s(exp)}$	$\boldsymbol{\gamma}$	$\mathbf{LnK^{\circ}_{sp}}$ **(calculed)**	$\mathbf{\Delta G^{\circ}_{diss}}$ **(KJ · mol^{-1})**
Na_2SiF_6	0.25	0.674	−3.9562	11.617
K_2SiF_6	0.30	0.150	−7.9170	23.247

a function of the water activity of NaCl(aq) reference solution.

$$K = \frac{D(a_w)}{D(0.84)}. \quad (1)$$

3. THEORY AND APPROACH

Several authors, K.S. Pitzer and R.T. Pabalan [10], J.A. Rard and all [11], C. Christov [12], and M. El Guendouzi [13], have constructed models ionic interactions and present a variant of extended model to describe their osmotic coefficient or water activity data for unsaturated solutions. The key parameter to be determined in order to deduce the solubility using this approach is the activity coefficient and experimental molality of saturation for each temperature.

In the equilibria

$$M_{V_M}X_{V_X} \cdot \nu_0 H_2O = \nu_M M^{+z_M} + \nu_X X^{2z_x} + \nu_0 H_2O. \quad (2)$$

Solubility products Ksp formula is

$$K_k(T, P) = \prod_{t-1}^{M} m_t^{v\cdot\omega} \prod_{t-1}^{M} \gamma_t^{v\cdot\omega}. \quad (3)$$

4. RESULTS: SOLUBILITY PREDICTION

The component solubilities of the binary aqueous system containing Malladrite Na_2SiF_6 or K_2SiF_6 at temperature 353 K were calculated using an ionic interaction model. The water activity at total molality from dilution to saturation for binary is used to evaluate the osmotic coefficients of the solutions. From the experimental data, the activity coefficients of the solute were calculated using ionic mixing parameters.

These parameters are used to predict the solubility in this system at 353 K. The precipitated solid phase is analyzed by X-ray diffraction, (Used Lambda=1.5406; Anode=Cu). The powder X-ray diffraction of Na_2SiF_6 and K_2SiF_6 are presented in the Fig. 2.

The values of the pure electrolyte and mixing ionic-interaction parameters which give the best fit of the activity data in binary solutions and solubility data are tabulated. Thermodynamic characteristics, solubility products $K^{\circ}sp$ and the standard molar Gibbs energy of formation ΔG° diss of the crystallizing solids are given in Table 1. The predicted solubility isotherms are compared with the literature data.

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