

Solubility of potassium fluoride in aqueous solution at different temperatures 298.15K–353.15K

J. Faridi and M. El Guendouzi^a

Laboratoire de Chimie Physique, Associé au CNRST-URAC17, Faculté des Sciences Ben M'sik, Université Hassan II Mohammedia-Casablanca, B.P 7955, Casablanca, Maroc.

Abstract. In this investigation, the binary aqueous solutions of Potassium Fluoride have been studied using the hygrometric method at different temperatures 298.15K–353.15K. The water activities are measured at molalities from 0.10 mol kg⁻¹ to saturation. The obtained data allow the deduction of osmotic coefficients. From these measurements, the ionic parameters are determined and used to predict the solute activity coefficients. Thermodynamic characteristics, solubility products K_{sp}° and the standard molar Gibbs energy of dissolution ΔG_{diss}° are given. The predicted solubility isotherms are compared with the literature data.

1. INTRODUCTION

Fluorides are of great interest as the fundamental level at industrial scale. These fluorides in aqueous come in several application areas occupied in industry. Their presence is particularly evident in the phosphate industry, during the production of phosphoric acid. They are also introducing in metallurgy, glass industry and the synthesis of fluorocarbon and fluorosilicates compounds. Alkali fluorides (NaF, KF, KHF₂) are important components in many natural and industrial processes [1–3]. Various chemical processes and industrial problems require thorough knowledge of the properties of aqueous solutions. The study of electrolytes is fundamentally important to understand the properties and behavior of aqueous multicomponent systems. Knowledge of their properties allows understanding of the phenomena governing the industrial processes.

The main objective of this study is the development of thermodynamic model for solution at highly soluble potassium fluoride minerals solubility in KF -H₂O binary and their complex, from 298K to 333K. The solubility modeling approach based on fundamental ionic interaction is employed. We relied on an experimental hygrometric method¹ and thermodynamic considerations based on the ionic interaction [2,3] for the prediction of mineral solubility of potassium fluoride KF at different temperatures.

2. EXPERIMENTAL

The water activity was determined using the hygrometric method previously described in earlier works [4,5]. The apparatus used in this study of aqueous single electrolyte solutions (Figure 1). It is based on the measurement of the water activity over aqueous solution 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.

^a e-mail: elguendouzi@yahoo.fr

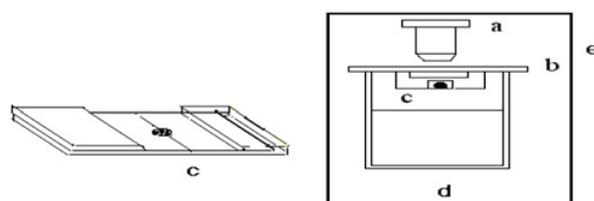
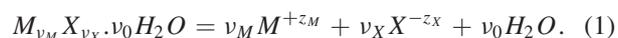


Figure 1. Schematic of the hygrometric apparatus: (a) microscope; (b) lid; (c) support of the drops; (d) cup; (e) wooden box.

3. THEORY AND APPROACH

Several authors, K.S. Pitzer and R.T. Pabalan [2], J.A. Rard and all [3], M. El Guendouzi [5], and C. Christov [6] have constructed models ionic interactions and present a variant of extended model to describe their osmotic coefficient or water activity data for unsaturated and saturated 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



Solubility products K_{sp} formula is

$$K_{sp}(T, P) = \prod_{i=1}^n m_i^{\nu_i} \cdot \prod_{i=1}^n \gamma_i^{\nu_i}. \quad (2)$$

So

$$\ln K_{sp} = \nu_M \ln(m_M \gamma_M) + \nu_X \ln(m_X \gamma_X) + \nu_0 \ln a_w. \quad (3)$$

4. RESULTS

4.1. Water activity, and osmotic coefficients

The water activities are measured at molalities from 0.10 mol kg⁻¹ to saturation of the pure electrolyte for

Table 1. Calculated values of the logarithm of solubility product K_{sp}° , the molality of the saturated binary solutions m_s (mol/kg), Water activities a_w , osmotic coefficient ϕ , activities coefficient γ , and the standard molar Gibbs energy of dissolution ΔG_{diss}° (kJ.mol⁻¹).

T (K)	Solid Phase	m_s (exp)	a_w	ϕ	γ	$\text{Ln}K_{sp}^{\circ}$ (cal)	$^*\Delta G_{diss}^{\circ}$
298.15	KF.2H ₂ O	17.5 17.5 ^a	0.2845	1.993	4.252	6.1	-15.127
313.15	KF.2H ₂ O	20.2	0.2233	2.059	5.727	6.5	-16.924
333.15	KF	24.7	0.1462	2.160	6.908	10.2	-28.457
353.15	KF	25.8	0.1416	2.102	4.528	9.5	-27.942

^a Ref. [7].

*Specified with relation $\text{Ln}K_{sp} = -\Delta G_{diss}/RT$.

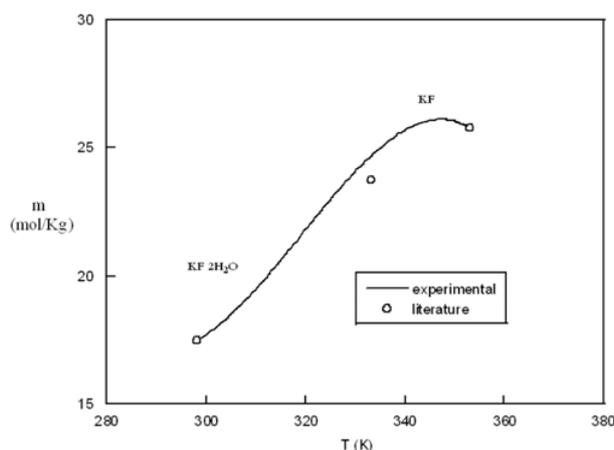


Figure 2. Phase diagram of KF-H₂O system.

binary system KF-H₂O are listed in the table 1. Using the obtained experimental results of the water activity, the osmotic coefficients of the water have been evaluated by Eq (4).

$$\phi = -\frac{1000}{M_w \sum v_i m_i} \ln a_w. \quad (4)$$

4.2. Activity coefficients and solubility

From the results of measurements of water activities for the molality range from dilution to saturation for binary electrolyte solution KF(aq), the osmotic coefficients of the solvent are evaluated for the solutions. The parameters for this binary system are also determined. These parameters were fitted from osmotic coefficients using the ionic-interaction model. Then, the binary parameters for the entire molality range to the saturation are used for the prediction of solubility.

The thermodynamic solubility product ($\text{Ln}K_{sp}^{\circ}$) for the crystalline hydrates was calculated using ionic-interaction model with our parameters. Also, the standard molar Gibbs energy of dissolution ΔG_{diss}° from saturated binary solutions was calculated on the basis of $\text{Ln}K_{sp}^{\circ}$ values. These results are shown in Table 1. The solubility at different temperature are presented in Fig. 2. The results are compared with the literature data. Good agreement is

obtained between the reported values for the electrolytes KF(aq) and the literature data [8]. The methodology used in our laboratory is to identify the precipitated phases by XRD, but it is difficult for some cases of very hygroscopic powders to do such as potassium fluoride. XRD Phases of potassium fluoride are obtained from the literature [8–13].

The variation of γ , $\text{Ln}K^{\circ}$ and ΔG_{diss} at different temperatures (table 1) shows that at $T = 333.15$, the irregular evolution is observed. Is it probably an intermediate hydrate could be existing at this temperature. There is a phase change between 313.15K and 333.15K, the phase diagram of KF shows that from the temperature 318.15K, the phase precipitated is only anhydrous phase [14]. Also, we must take into consideration the loss of the water molecules in the calculation, in addition to temperature.

References

- [1] R. Azougen, M. EL Guendouzi, A. Rifai, J. Faridi. CALPHAD. **34**, 36 (2010).
- [2] R.T. Pabalan, K.S. Pitzer, Geochim. Cosmochim. Acta. **51**, 2429 (1987).
- [3] J.A. Rard, D.G. Archer, J. Chem. Eng. Data. **40**, 170 (1995).
- [4] M. El Guendouzi, A. Errougui, J. Chem. Eng. Data. **54**, 376 (2009).
- [5] C. Christov, J. Chem. Thermodyn. **37**, 1036 (2005).
- [6] M. El Guendouzi, M. Marouani, J. Solution Chem. **32**, 535 (2003).
- [7] W.J. Hamer, Y.C. Wu, J. Phys. Chem. Ref. Data. **1**, 1047 (1972).
- [8] O. Söhnel, P. Novotny, Physical Science Data, (Elsevier, Amsterdam, and New York, 1985).
- [9] A.N. Campbell, A.J. Campbell. Trans. Faraday Soc. **35**, 241 (1939).
- [10] G. Clark. J. Am. Chem. Soc. **41**, 1477 (1919).
- [11] E.N. Pinaevskaya, N.P. Golubchenko. Zh. Prikl. Khim. **26**, 101 (1953).
- [12] D.S. Terekhova, A.I. Ryss, I.V. Radchenko. J. Structural Chemistry Y. **10**(5), 807 (1970).
- [13] H.M. Haendler, A.W. Jache. J. Am. Chem. Soc., **72**(9), 4137 (1950).
- [14] K. Thomsen. Report concerning the second project contribution from Aqueous Solutions; ForskEL project (no. 2008-1-0111), 2009.