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Solubility of Ferrate(VI) in NaOH−KOH Mixtures at Different Temperatures

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The solubility of potassium ferrate(VI) (K_2FeO_4) was measured in a mixture solution containing various molar ratios of KOH and NaOH at a total concentration of 14 M from (10 to 60) °C. The solubility of K_2FeO_4 decreased necause of the presence of K^+ in the solution mixture. The solubility (S^*) was expressed as $\log S^* = 5.830 - 2019/T - 5.845X_{K^+}{}^{0.5} + 1.595X_{K^+} + 724X_{K^+}{}^{0.5}/T$ ($\sigma = 0.024$), where X_{K^+} is the mole fraction of K^+ in the solution mixture and T is in Kelvin. A comparison of the values of S^* in different alkali metal hydroxide solutions showed that the solubility of K_2FeO_4 was diminished in KOH and CsOH and similarly in LiOH and NaOH solutions. The solubility product constant (K_{sp}^*), calculated from the solubility measurements, was given as $\log K_{sp}^* = 18.10 - 6055/T - 17.535X_{K^+}{}^{0.5} + 4.785X_{K^+} + 2171X_{K^+}{}^{0.5}/T$ ($\sigma = 0.061$). The heat of dissolution (ΔH_{diss}) decreased linearly with an increase in the mole fraction of K^+ ions. The significance of the solubility results is briefly discussed.

Introduction

Iron usually exists in metallic (Fe(0)), ferrous (Fe(II)), and ferric (Fe(III)) forms; however, the plus six oxidation state of iron, called ferrate(VI) in the form of $Fe^{VI}O_4{}^{2-}$, has recently attracted attention because of its potential use in high-energy density rechargeable batteries and in environmentally benign processes for organic synthesis.[1,2] There is also a marked increase in applications of ferrate(VI) in the remediation of pollutants and toxins in water and wastewaters.[3−6,6−8] Ferrate(VI) has also shown promise in oxidative transformations of estrogens and antibiotics in the environment.[9−14] The byproduct of ferrate(VI) is nontoxic, iron(III), making it a cleaner ("greener") chemical for various applications. Of the several salts of ferrate(VI), potassium ferrate(VI) (K_2FeO_4) is the most promising in applications. This compound is generally prepared indirectly by first synthesizing the sodium salt of ferrate(VI) (Na_2FeO_4) and then converting it into K_2FeO_4 by adding solid KOH ($Na_2FeO_4 + KOH \rightarrow K_2FeO_4 + NaOH$).[6,15] The sodium salt is highly soluble, and an addition of K^+ ions results in much less soluble K_2FeO_4. However, the amount of K^+ ions needed to efficiently obtain the solid product of K_2FeO_4 under ferrate(VI) synthesis conditions is still missing from the literature.

Generally, three kinds of techniques are used to synthesize ferrate(VI): thermal, chemical, and electrochemical.[16−18] The electrochemical technique is the most promising because it uses electrons as "clean" reactants and produces a pure dissolved Fe(VI) product. Several studies demonstrated that the use of 14 M NaOH solution was the most efficient reactant condition to produce ferrate(VI).[19] The information on the amount of KOH needed to add to NaOH solutions at a 14 M ionic strength to separate solid ferrate(VI) from the solution is critical. Thus, this demands knowing the solubility of ferrate(VI) in NaOH−KOH mixtures. A solubility study done earlier used impure K_2FeO_4 (~72 %).[20] The use of an impure salt of ferrate(VI) can be subjected to a substantial degree of error, since the impurities increase the decomposition of ferrate(VI) in the solution. Furthermore, the solubility data were determined at a 12 M hydroxide concentration and are not relevant to the ferrate(VI) synthesis conditions.

The solubility measurements made in this study were performed with a high purity ferrate(VI) (+98 %) in 14 M solutions at various compositions of NaOH and KOH and temperatures to assist in understanding the separation of the solid ferrate(VI) product from the synthetic solution. The compositions of the solutions were 14:0, 11:3, 7:7, 3:11, and 0:14 ([NaOH]:[KOH]), and the temperature was varied in the range from (20 to 60) °C, which corresponds to the temperature of the ferrate(VI) synthesis.

Experimental Section

Chemicals. All chemicals were of reagent grade or better (Sigma-Aldrich) and were used without further purification. Solutions were prepared with water that had been distilled and passed through an 18 MΩ Milli-Q cm water purification system. Solid potassium ferrate (K_2FeO_4) of high purity (98 % plus) was prepared by the wet method.[21]

Apparatus and Procedure. In the solubility experiments, the crystals of K_2FeO_4 were added to 10 mL of the studied hydroxide solution. The amount of K_2FeO_4 was about three times that of the estimated solubility. The solution was then placed into a temperature-controlled cell and continuously stirred with a magnetic stirrer. The temperature was controlled within ± 0.1 °C by a Fischer Scientific Isotemp 3016 circulating water bath. The solution was allowed to mix for 2 h, which was sufficient to establish solubility equilibrium, which was confirmed independently by measuring the ferrate(VI) concentration at different times. After 2 h, the solution was immediately filtered using a membrane Omnipore filter (Millipore, USA).

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Table 1. Solubility (S^*) and Solubility Product Constants (K_{sp}^*) of K_2FeO_4 in NaOH−KOH Mixture Solution at Different Temperatures

KOH	NaOH		10 °C	20 °C	30 °C	40 °C	50 °C	60 °C
M	M	X_{K^+}	$S^*/10^{-2}/M$					
14	0	1.00	0.104	0.149	0.204	0.284	0.372	0.505
11	3	0.25	0.114	0.158	0.229	0.317	0.439	0.619
7	7	0.50	0.145	0.210	0.330	0.494	0.683	0.960
3	11	0.75	0.311	0.482	0.661	1.00	1.47	2.27
0	14	0.00	4.72	9.60	14.16			
			$K_{sp}^*/10^{-8}$ M^3					
14	0	1.00	0.448	1.33	3.42	9.13	20.6	51.4
11	3	0.25	0.600	1.57	4.82	12.7	33.9	94.7
7	7	0.50	1.21	3.73	14.4	48.2	127.5	353.8
3	11	0.75	12.0	44.7	115.7	399.4	1260	4686
0	14	0.00	41955	354025	1136431			

A temperature-controlled unit was applied to filter the ferrate solution. The diagram of the unit is shown in Figure S1 of the Supporting Information. It was important to use this apparatus; otherwise, filtration at room temperature would have changed the solubility during filtration and resulted in an error in the measurements. The concentration of ferrate(VI) in the filtrate was determined using two methods. For the filtrate which had a $5 \cdot 10^{-3}$ M concentration, a chromite method was used.[21] For concentrations of ferrate(VI) in solution of more than $5 \cdot 10^{-3}$ M, the concentration was determined by measuring the absorbance at 510 nm and using the molar absorption coefficient $\varepsilon_{510nm} = 1150\ M^{-1} \cdot cm^{-1}$ at pH 9.0.[22] The solubility measurements were reproducible within 2.8 %. This corresponds to percentage errors in the values of K_{sp} within 8.4 %.

Results and Discussion

The measured values of molar solubility of K_2FeO_4 in NaOH−KOH mixtures (S^*) at different temperatures are tabulated in Table 1. The results are shown as a plot of log S^* versus the square root of the mole fraction of K^+ ions in the solution mixtures (X_{K^+}) (Figure 1). The solubility greatly diminished with the addition of K^+ into the NaOH solution (Figure 1). This decrease was profound at a low level of K^+ ions and then slowed further with an increase of concentration of the K^+ ion in the solution mixture. The solubility of K_2FeO_4 increased with an increase in temperature, and the trend was similar at all temperatures (Figure 1). The solubility of K_2FeO_4 (S^*/M) was related to X_{K^+} at different temperatures by eq 1.

$$\log S^* = 5.830 - 2019/T - 5.845X_{K^+}^{0.5} + 1.595X_{K^+} + 724X_{K^+}^{0.5}/T \quad (1)$$

where T is in Kelvin. The standard error of the fit (σ) was 0.037. The solid lines drawn using eq 1 fit the experimental data nicely (Figure 1).

The comparison of the solubility of K_2FeO_4 in different alkali metal hydroxides (MOH) is shown in Figure 2.[23,24] The results obtained by different workers are in reasonable agreement with each other. The solubility decreased with an increase in the concentration of hydroxide in solution. Generally, the solubility of K_2FeO_4 in different hydroxides showed a linear negative relationship with the concentration of hydroxide, which can be expressed by eq 2.

$$\log S^*(\mathrm{MOH}) = 0.6832 - b[\mathrm{OH}^-] \quad (2)$$

where $b = 0.1000$, 0.2629, and 0.2901 for NaOH, KOH, and CsOH, respectively. The intercept of eq 2 gives the molar solubility of K_2FeO_4 in water (S) as 4.822 mol·L^{-1} at 22 °C.

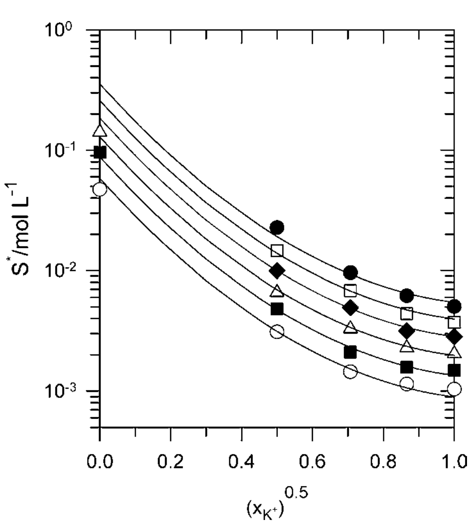

Figure 1. A plot of log S^* versus the square root of the mole fraction of K^+ in NaOH−KOH mixtures at different temperatures. Solid lines were drawn using eq 1. ○, 10 °C; ■, 20 °C; △, 30 °C; ◆, 40 °C; □, 50 °C; and ●, 60 °C.

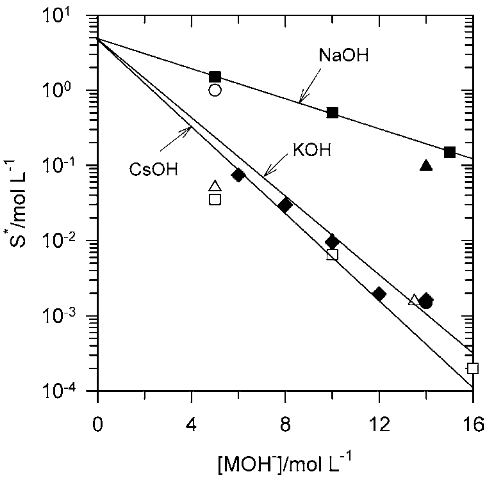

Figure 2. Dependence of the solubility of K_2FeO_4 on the concentration of hydroxide ion in different electrolytes. The linear solid line for NaOH solution represents the best fitted line, and the lines for KOH and CsOH solutions were drawn using the value in water obtained from the dependence of solubility in NaOH solution. ○, LiOH, 22 °C;[23] ■, NaOH, 22 °C;[23] △, KOH, 22 °C;[23] ◆, KOH, 25 °C;[24] □, CsOH, 22 °C;[23] ▲, NaOH, 20 °C (this study); and ●, KOH, 20 °C (this study).

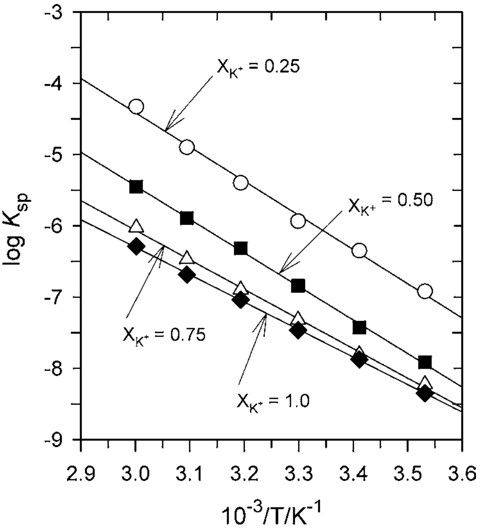

Figure 3. A plot of log K_{sp}* versus 1/T at different mole fractions of K^+ in NaOH−KOH mixtures.

Table 2. Enthalpy of Dissolution (ΔH_{diss}*) of K_2FeO_4 in NaOH, KOH, and NaOH−KOH Mixture Solutions

KOH M	NaOH M	X_{K^+}	ΔH_{diss}* kJ·mol^{-1}	ref
14	0	1.00	73.9 ± 0.8	this study
11	3	0.75	79.4 ± 1.9	this study
7	7	0.50	90.0 ± 1.5	this study
3	11	0.25	91.9 ± 3.2	this study
0	14	0.00	118 ± 1.9	this study
10			91.3 ± 36.7	23
satd.			80.2 ± 15.0	24

The order of the molar solubility of K_2FeO_4 in different alkali metal hydroxides was LiOH ≈ NaOH > KOH > CsOH (Figure 2).

The solubility product constant in water (K_{sp}) and in NaOH−KOH mixture solutions (K_{sp}*/M^3) can be obtained from the solubility measurements. The expressions for the constants are as follows:

$$K_{sp} = 4S^3 \tag{3}$$

$$K_{sp}^* = 4S^{*3} \tag{4}$$

The value of K_{sp} was obtained as 4.42·10^2 M^3 at 22 °C. The calculated values of K_{sp}* at different mole fractions of K^+ ions and temperature are given in Table 1.

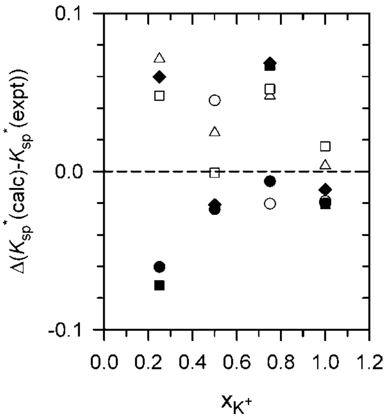

Figure 4. A plot of $\Delta(K_{sp}^*(\text{calc}) - K_{sp}^*(\text{expt}))$ versus the mole fraction of K^+ in NaOH−KOH mixtures at different temperatures. ○, 10 °C; ■, 20 °C; △, 30 °C; ◆, 40 °C; □, 50 °C; and ●, 60 °C.

The values of K_{sp}* at different temperatures in NaOH−KOH mixture solutions are shown in Figure 3. The slopes of the linear fits of the plots of log K_{sp}* versus 1/T were used to determine the heat of dissolution of K_2FeO_4 (ΔH_{diss}*). The values are given in Table 2. The value of ΔH_{diss}* in 14 M KOH solutions in the present study is in reasonable agreement with the values calculated from the temperature dependence solubility measurements in 10 M and saturated KOH solutions (Table 2). With an increase in mole fraction of K^+ ions in the mixture, ΔH_{diss}* decreased (Table 2). This is consistent with a higher ΔH_{diss}* in 14 M NaOH solution compared to a 14 KOH solution.[23,24] The values of ΔH_{diss}* in the NaOH−KOH mixture were linearly related to the square root of mole fraction of K^+ ions (ΔH_{diss}* = 117.1 − 43.0X_{K^+}; r^2 = 0.998).

All of the results of K_{sp}* were fitted to eq 5.

$$\log K_{sp}^* = 18.10 - 6055/T - 17.53X_{K^+}^{0.5} + 4.785X_{K^+} + 2171X_{K^+}^{0.5}/T \tag{5}$$

This equation has a standard error of 0.061 in log K_{sp}*. The calculated values of the log K_{sp}* from eq 5 are in reasonable agreement with the experimental values as is shown in Figure 4, since most of the measurements at different temperatures fall with the standard error of the fit.

Conclusions

Experimental measurements of solubility and K_{sp}* of K_2FeO_4 in NaOH−KOH mixture solutions could be fitted reasonably to equations, which can determine values of S* and K_{sp}*, at different mole fractions of K^+ ions in the temperature range from (10 to 60) °C. The values of S* decreased sharply at X_{K^+} by less than 0.25, which suggests that FeO_4^{2-} ions in the solution of NaOH can be separated in the solid form of K_2FeO_4 by adding a small amount of KOH. Therefore, only small amounts of KOH relative to NaOH will be needed to precipitate K_2FeO_4 from a solution of NaOH containing FeO_4^{2-} ions. Overall, the results of the study are useful in synthesizing a solid salt of K_2FeO_4 efficiently.

Supporting Information Available:

Diagram of the temperature controlled filtration unit. This material is available free of charge via the Internet at http://pubs.acs.org.

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