

Effect of pH, Temperature and Time on the Stability of Potassium Ethyl Xanthate

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Summary: Stability of potassium ethyl xanthate is studied as a function of time, temperature (283 and 300 K) and pH (5, 7 and 9). The rate of its decomposition is found to decrease from 2.099 % to 0.451 % with the increase in pH from pH 5 to 9 at 283 K, while it is found to increase from 0.902 % to 4.103 % at pH 7 when the temperature is increased from 283 to 300 K. The maximum rate of decomposition is found to be 6.484 % at 300 K, which is reduced to 2.099 % at 283 K at pH 5.

Introduction

Collectors are used in the mineral processing industry as flotation agents in the recovery of metals. Collectors are organic compounds which render selected minerals water repellent by the adsorption of molecules or ions on to the mineral surface, reducing the stability of the hydrated layer separating the mineral surface from the air-bubble to such a level that attachment of the particle to the bubble can be made on contact [1].

Most collectors are weak acids or bases. They are heteropolar and may be considered to have two functional ends, one ionic, which can be adsorbed at the mineral surface and the other an organic chain, which provides the hydrophobic surface to the mineral. Collectors are generally divided into two main groups, the ionizing collectors and the non-ionizing collectors. The ionizing collectors are further subdivided in two classes, the anionic and cationic. Comparing both, the usage of anionic type of collectors is greater than the cationic type of collectors. Thiol and dithiophosphates are the most widely used anionic collectors in mineral processing.

The most commonly used thiol collectors are xanthates, which are alkali metal (e.g. Na⁺, K⁺) salts of monoalkyl esters of dithiocarbonic acid [2] (e.g. potassium ethyl xanthate: ROCSSK). They are used as flotation agents in the recovery of metal sulphides. The efficiency of xanthates as mineral collectors increases with the length of the carbon chain but results in a decrease in the selective flotation of minerals.

An extensive literature has been reported on the usage of xanthates for the recovery of sulphide

minerals [3-8]. But little has been reported on the factors affecting the stability of potassium ethyl xanthate itself [9-12]. The purpose of the present study is to monitor the effect of pH, temperature and time on the stability of potassium ethyl xanthate.

Results and Discussion

The effects of time, temperature and pH on potassium ethyl xanthate absorbance of concentration (1×10^{-4} M) are given in Tables 1-6. The data show that at 283 K and at pH 9 (Table 1) no appreciable change was observed in the absorbance due to xanthate concentration at 301 nm. By decreasing the pH to 7 and then to 5 the absorbance started decreasing showing that the xanthate concentration

Table-1: Time Effect on Potassium Ethyl Xanthate Composition at pH 9 and at 283 K.

Days	Absorbance at			
	206 nm	215 nm	226 nm	301 nm
0	-	0.577	0.686	1.084
1	-	0.583	0.673	1.080
4	-	0.587	0.680	1.076
5	-	0.579	0.644	1.059
7	-	0.519	0.612	1.057
8	-	0.584	0.664	1.049
10	-	0.496	0.584	1.034
12	-	0.584	0.654	1.028
13	-	0.515	0.639	1.023

decreased with the decrease in pH and increasing time period. Similarly by increasing the temperature to 300 K, the absorbance at this wavelength decreased from 1.084 to 0.747 at pH 9, from 1.079 to 0.534 at pH 7 and from 1.025 to 0.124 at pH 5 in 13 days, showing the xanthate decomposed back to its

Table-2: Time Effect on Potassium Ethyl Xanthate Composition at pH 9 and at 300 K.

Days	Absorbance at			
	206 nm	215 nm	226 nm	301 nm
0	-	0.577	0.686	1.084
1	-	0.596	0.663	1.068
4	-	0.649	0.649	0.991
5	-	0.624	0.624	0.936
7	-	0.549	0.549	0.861
8	-	0.591	0.591	0.855
10	1.176	-	-	0.769
12	1.182	-	-	0.759
13	1.019	0.536	0.536	0.747

Table-3: Time Effect on Potassium Ethyl Xanthate Composition at pH 7 and at 283 K.

Days	Absorbance at			
	206 nm	215 nm	226 nm	301 nm
0	-	0.624	0.706	1.079
1	-	-	-	1.075
2	0.495	-	0.625	1.065
4	-	-	-	1.057
5	-	-	-	1.037
7	-	-	-	1.028
8	-	-	-	1.020
10	-	-	-	0.977
12	-	-	-	0.965
13	-	-	-	0.960

Table-4: Time Effect on Potassium Ethyl Xanthate Composition at pH 7 and at 300 K.

Days	Absorbance at			
	206 nm	215 nm	226 nm	301 nm
0	-	0.624	0.706	1.079
1	-	0.631	0.668	1.030
2	0.902	0.546	0.592	0.969
4	1.015	0.608	0.628	0.925
5	1.055	-	-	0.817
7	1.061	-	-	0.698
8	1.058	-	-	0.688
10	1.013	-	-	0.566
12	0.925	-	-	0.560
13	0.922	-	-	0.534

Table-5: Time Effect on Potassium Ethyl Xanthate Composition at pH 5 and at 283 K.

Days	Absorbance at			
	206 nm	215 nm	226 nm	301 nm
0	-	-	-	1.025
1	-	-	-	0.790
2	-	-	-	0.768
4	-	-	-	0.703
5	-	-	-	0.659
7	-	-	-	0.601
8	-	-	-	0.599
10	-	-	-	0.566
12	-	-	-	0.546
13	-	-	-	0.537

Table-6: Time Effect on Potassium Ethyl Xanthate Composition at pH 5 and at 300 K.

Days	Absorbance at			
	206 nm	215 nm	226 nm	301 nm
0	-	-	-	1.025
1	-	-	-	0.805
2	-	-	-	0.728
4	-	-	-	0.675
5	-	-	-	0.544
7	-	-	-	0.305
8	-	-	-	0.268
10	-	-	-	0.215
12	-	-	-	0.152
13	1.736	-	-	0.124

reactants. The rate of % decomposition was determined by using the equation in the form:

$$dx / dt = Kx \quad (1)$$

where x is the amount of xanthate decomposed at time t . According to this equation, a linear relationship is observed (Fig.1) by plotting (%) decomposition of xanthate vs. time. The values of the rate of decomposition calculated from the slopes of the plots are listed in Table 7. The data in table show that at pH 9 the rate of decomposition come out to be 2.587 % at 300 K and 0.451 % at 283 K, while the rate of decomposition at pH 7 was observed to be 4.103% at 300 K and 0.9024% at 283 K. Similarly, at pH 5 the values were found to be 6.484% at 300 and 2.099% at 283 K. Similar rates of decomposition for sodium ethyl xanthate at 303 K were also reported by R. Crozier [9]. Though, all the three parameters contributed in the decomposition of potassium ethyl xanthate but the major role was played by the pH of the system. It is pertinent to mention here that in acidic medium the decomposition started instantly.

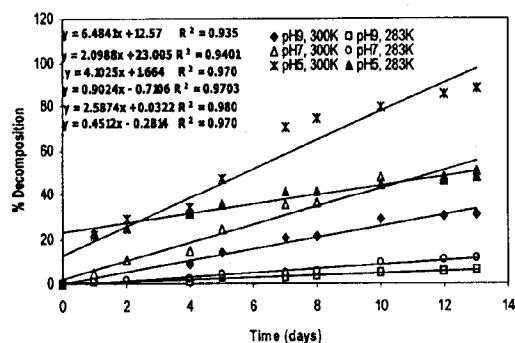


Fig. 1: Rate of Decomposition of 1×10^{-4} M Potassium Ethyl Xanthate at Different Temperature and pH.

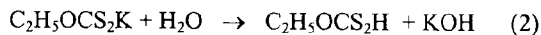
Table-7: Temperature and pH Effect on the Rate of Decomposition of Potassium Ethyl Xanthate.

Temperature (K)	pH	Rate of decomposition (% decomposition. Day ⁻¹)
283	5	2.0988
300		6.4841
283	7	0.9024
300		4.1025
283	9	0.4512
300		2.5874

Interestingly, new peaks with appreciable amount of absorbance having intensity 1.02 to 1.18 appeared at 206 nm at pH 9 and 300 K after 9 days and are reported in Table 1 while on pH 7 at 300 K after one day the same peak was observed having the intensity 0.902 which increased to 1.061 on the 7th day, as tabulated in Table 4. This peak may be assigned to C₂H₅OH as similar peak was observed by running aqueous ethanol solution, confirming the decomposition of potassium ethyl xanthate back to its reactants. This behaviour showed that at neutral and basic pH the decomposition products included the ethanol.

The peak at 226 nm disappeared with the decrease in pH to the acidic side (Table 6). Our study thus confirms the results of Mielczarski [11] and Harris and Finkelstein [12] that monothiocarbonate peak appeared when the pH was raised above 5.5. According to Fornasiero *et al* [10] also the peak around 221 nm is due to the ethyl monothiocarbonate.

The decomposition reaction thus in acidic medium occurs according to reaction 2.



i.e. in acidic aqueous medium potassium ethyl xanthate decomposition results in the formation of xanthic acid and potassium hydroxide, which changes to reaction 3 in the basic medium



This study thus shows that xanthate stability decreases with increase in temperature, pH and time. So it is recommended to keep the xanthate solution below 293 K and secondly the pH of the stalk solution should be adjusted to pH 10 in order to increase its shelf life.

Experimental

Reagents

Analytical grade reagents were used without further purification. All the solutions and mixtures were prepared in double distilled water.

Potassium Ethyl Xanthate (KEX) Preparation

Potassium ethyl xanthate was synthesized and then purified by recrystallization from acetone by the usual method given by Rao [13], Fuerstenau and Mishra [14]. The purity of the product obtained was tested spectrophotometrically. The xanthate thus synthesized was kept in a refrigerator below 293 K.

Potassium Ethyl Xanthate Stability

Potassium ethyl xanthate of concentration $1 \times 10^{-4} \text{M}$ was taken in two different 250 ml volumetric flasks. Solution pH was adjusted to 9 with the help of KOH and HNO₃. The flasks were then kept at 283 and 300K respectively. Each day both the solutions were scanned on UV (UV-160A SHIMADZU Japan) between 200 and 1000 nm. The changes in the solution composition were thus recorded each day.

References

1. B.A. Wills, "Mineral Processing Technology", 3rd Ed. 380 (1984).
2. P.J. Harris, "Reagents in Mineral Technology" (Eds. P. Somasundaran and B.M. Moudgil). Marcel Dekker: New York. Ch 11, 371 (1988).
3. E. Ahlberg. and A.E. Broo, *Inter.J. Mineral Processing*, **46**, 73 (1996).
4. J.R. Roos, J.P. Celis and A.S. Sundarsono, *Inter. J. Mineral Processing*, **28**, 231 (1990).
5. J.O. Leppinen, C.I. Basilio and R.H. Yoon, *Inter. J. Mineral Processing*, **26**, 259 (1989).
6. J.M. Cases, M. Kongolo, P. de Donato, L.J. Michot and R. Erre, *Inter. J. Mineral Processing*, **38**, 267 (1993).
7. X.J. Wang, *J. Colloid Interface Sci.*, **171**, 413 (1995).
8. M. McNeil, S.R. Rao and J.A. Finch, *Can. Metall. Quart.*, **23**, 165 (1994).
9. R. Crozier, Plant Reagents- Part 1: "Changing Patterns in the Supply of Flotation Reagents", *Mixing Magazine*, 201(1984).
10. D. Fornasiero, M. Montalti and J. Ralston,

- J. Colloid Interface Sci.*, **172**, 467 (1995).
11. J. Mielczarski, *J. Colloid Surf.*, **17**, 251(1986).
 12. P.J. Harris and N.P.Finkelstein, *Int. J. Miner. Process.* **2**, 77 (1975).
 13. S.R.Rao, Xanthates and related Compounds, Marcel Dekker, New York, pp. 504(1971).
 14. D.W.Fuerstenau, and R.K.Mishra, On the mechanism of pyrite flotation with xanthate collectors, in Complex Sulphide Ores, (ed. M.J.Jones), I.M.M. London (1980).