Kinetics of Xanthate Sorption by Copper Sulphide (CuS)

[1]ABDUL NAEEM*, [1]HAMID ALI, [1]SYED MUSTAFA, [1]SULTANA QAMAR,
[2]SYED TASLEEM AND [1]DILARA BEGUM
[1]*National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan.*
[2]*Department of Chemistry, Kohat University of Science and Technology, Kohat, Pakistan.*

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Summary: A comprehensive kinetic study of the xanthate ions sorption on CuS was performed as a function of different experimental conditions of temperature and concentration. Adsorption kinetics experiments indicated that xanthate adsorption onto the CuS reached steady-state within approximately seven and ten minutes from the start of the experiment in case of high and lower concentration of xanthate anions respectively. Legregran's first order equation was applied for the determination of the rate constant. Temperature had a positive effect on kinetics of the process and from the temperature dependence of the rate constant, energy of activation was calculated.

Introduction

Copper is widely used in electrical appliances, pipes, industrial machinery, coinage and in alloys; its mining is increasing day by day. It generally occurs as oxides or sulphides. The most common oxide ores [1-3] are cuprites (Cu_2O), malachite $CuCO_3.Cu(OH)_2$ and azurite $2CuCO_3.Cu(OH)_2$ while sulphide ores include chalcocite (Cu_2S), covellite (CuS), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and tetrahedrite ($3Cu_2S.Sb_2S_3$).

Adsorption of surfactants on minerals is an important phenomenon in mineral flotation [3-9]. Research in the past studies on xanthate adsorption on metal sulphides has been discussed in a number of publications [10-14]. Kinetics of the adsorption is of great importance for complete understanding of the process [15]. However, the data regarding the kinetics of xanthate adsorption by mineral surface is scarce in the literature. The present work is, therefore, carried out to study the kinetics of xanthate adsorption by copper sulphide.

Results and Discussion

Characterization of CuS

The X-ray diffractometer (XRD) measurement showed that the virgin sample of CuS is crystalline in nature. The diffractogram was compared with standard chart which confirmed that the sample is composed of copper sulphide (CuS) only and no evidence of impurity was obtained.

The point of zero charge (PZC) of the CuS powder was determined in the presence of 0.1M KNO_3 in the temperature range 283-303K. The PZC of the CuS was found to be 5.2, which decreased with the increase in temperature (Fig. 1). Mustafa *et al.* [16, 17] reported similar decreasing trend in PZC with temperature for other solid - solution interface systems. Moreover, the PZC of the CuS in the presence of different concentrations of xanthate was also undertaken. However, no shift in PZC value of sample was observed in the presence of xanthate anions indicating that there is no specific adsorption of xanthate on the CuS surface in presence of NO_3^- anion.

Kinetics of Adsorption

The kinetic studies of xanthate ion sorption on CuS were carried out in the temperature range of 283-293K. The effect of contact time on xanthate ion sorption at different tempera-tures is shown in Figs. 2 and 3. It can be seen from these Figures that in case of low initial xanthate concentration ($2x10^{-4}$M), the equilibrium in the system is established within first 10 minutes, while in case of high concentration of xanthate ($1x10^{-3}$ M) the equilibrium is achieved within seven minutes which can be attributed to the increased probability of the contact of xanthate anions with surface in case of higher xanthate concentration. The data in Figs. 2 and 3 further demonstrate that the sorption of xanthate increases with the increase in time, reaching to a sorption maximum and then decreases with further increase in

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*To whom all correspondence should be addressed.

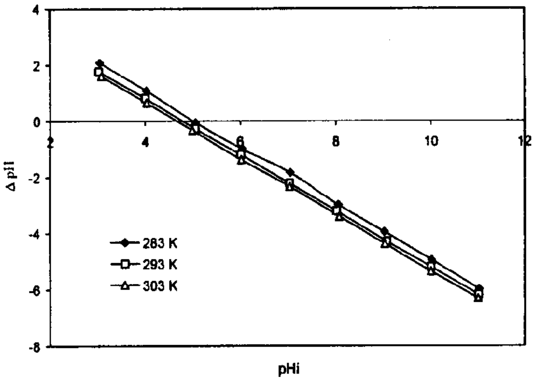

Fig. 1: Temperature effect on P Z C of copper sulphide in the presence of KNO_3 solution.

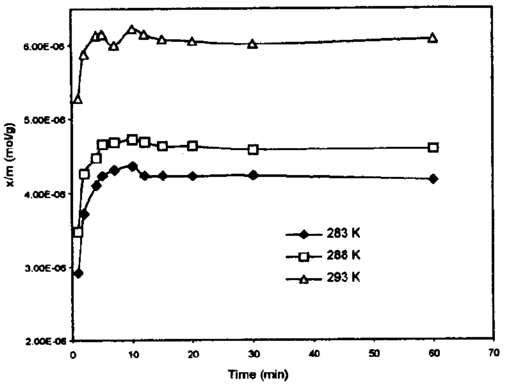

Fig. 2: Temperature effect on adsorption kinetics of $2x10^{-4}$M xanthate solutions at pH 10.

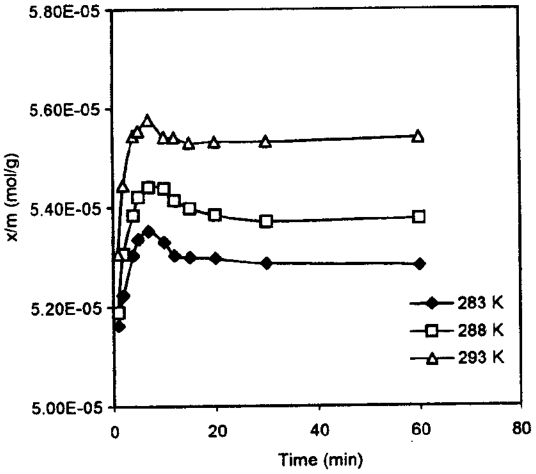

Fig. 3: Temperature effect on adsorption kinetics of $1x10^{-3}$ M xanthate solution at pH 10.

time in both the cases. The adsorption capacity of CuS is also observed to increase with increasing the initial concentration of xanthate in aqueous solution. The initial concentration provides an important driving force to overcome all mass transfer resistance of xanthate ions between the aqueous and solid phases; hence the adsorption capacity of CuS increases with the increase in initial concentration of xanthate anions. As is obvious from Figs. 2 and 3 the rates of initial rapid adsorption increase with the increase in temperature indicating the endothermic nature of the sorption process [18]. Similar findings are also reported elsewhere [7] for other systems. Moreover, almost 80 % of xanthate adsorption is observed within first five minutes in both the cases. This rapid increase in adsorption is in good agreement with the sharp decrease in pH of the sorption. Lagergren s first order equation is applied to the kinetics data in the form mentioned below [3].

$$\log (qe - q) = \log qe - (Ku/2.303)\, t \qquad (1)$$

where qe is the maximum amount of xanthate ions sorbed, q refers to the uptake of xanthate at different times and Ku is the rate constant. The plots of log (qe-q) vs. t give a linear relationship (Fig. 4) indicating the successful application of the equation 1. The values of the rate constants calculated from the slopes (Table-1) are found to increase slightly with the increase in temperature pointing towards the endothermic nature of xanthate adsorption on CuS.

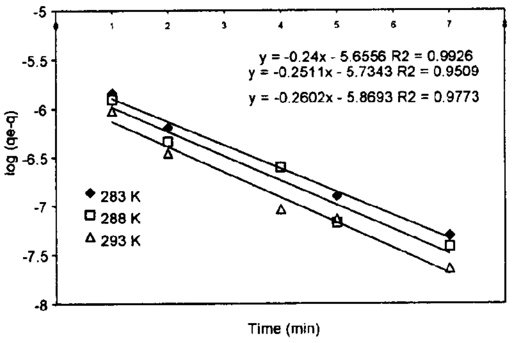

Fig. 4: Plots of log (qe-q) vs. time at different temperatures in the presence of $2x10^{-4}$ M xanthate solution.

The activation energy (Ea) of xanthate ion sorption on copper sulphide is calculated by using the well-known Arrhenius equation in the form, Table-1: Values of the rate constant and activation energy for xanthate sorption on CuS at pH 10.

Initial xanthate ion Conc. [mol/l]	Temperature (K)	Rate constant (Ku)	Activation energy (Ea) [kJ/mol]
2.0×10^{-4}	283	0.553	
	288	0.578	5.574
	293	0.5992	
1.0×10^{-3}	283	0.578	
	288	0.603	7.085
	293	0.641	

$$\ln Ku = \ln A - Ea/RT \qquad (2)$$

where R is the molar gas constant (8.314 J/mol.K), T is the absolute temperature (K) and A is the Arrhenius factor. The plots of ln Ku vs. 1/T give straight lines with slope equal to Ea/R. The values of the activation energy (Ea) calculated from the slopes of Fig. 5 are given in Table-1. The data represent that the values of Ea increase with the increase in the initial xanthate concentration indicating that more energy is required for the attachment of xanthate onto the copper sulphide surface [3, 6, 7].

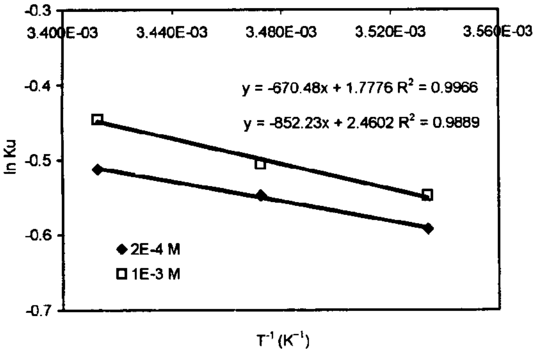

Fig. 5: Concentration effect of xanthate on the plots of ln Ku vs. 1/T.

Experimental

Characterization of CuS

A dry powder of the CuS sample was subjected to the x-ray analysis using X-ray diffractometer model JDX-73 with Mn-filtered Cu-Kα radiation. The spectrum was then analyzed from the resulting peaks.

PZC Determination by Salt Addition Method

Point of zero charge (PZC) of CuS was determined in 0.1M $NaNO_3$ solution at different temperatures. Forty milliliter of 0.1M $NaNO_3$ solution was taken in different titration flasks. The initial pHs of the solution were adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11± 0.20 using HNO_3 and NaOH solutions. The pH of the solution was recorded as initial pH on Orion pH meter model 710A with a combination pH electrode of research grade. CuS (0.2g) was added to each flask and they were shaken for 24 hours on a shaker bath. The final pHs of the solutions were recorded; ΔpH (the difference between initial and final pH) was plotted against initial pH values. The PZC values of the CuS were calculated from the plots of ΔpH vs. initial pH of the suspension.

Preparation of Potassium Ethyl Xanthate (KEX)

Potassium ethyl xanthate was prepared by the method suggested by Rao *et al.* [19], Fuerstenau and Mishra [20] and Mustafa *et al.* [6, 7] according to reaction (3) and the synthesized product was purified twice by recrystallization with diethyl ether from acetone.

$$C_2H_5OH + KOH + CS_2 \rightarrow C_2H_5OCSSK + H_2O \qquad (3)$$

The reactants were mixed in molar ratio according to the above reaction. First of all potassium hydroxide was dissolved in purified ethanol and then the calculated amount of carbon disulfide was added drop wise with constant stirring resulting in the formation of a precipitate. The resultant precipitate was then dissolved in acetone and was reprecipitated with diethyl ether. The process of reprecipitation was repeated two times in order to eliminate the presence of any polysulfide species. The precipitate was then filtered and kept in a glass container. The product obtained was spectrophotometrically (UV) scanned to obtain λ_{max} and was tested for purity. The xanthate thus synthesized was kept in a refrigerator below 293K.

Kinetic Studies

Kinetic studies were carried out by taking 30 ml of different aqueous xanthate solutions (7×10^{-3}, 1×10^{-3} M). To these solutions 0.02 g of CuS sample was added and was shaken for different time intervals in a controlled temperature water bath at temperature range (278, 283, 288 and 293 K). The solutions were filtered. The filtrates were analysed for xanthate determination by passing through UV model 160A Shimadzu Japan at 301 nm [3]. The amount of xanthate adsorbed was calculated from the difference between the initial and final concentrations of the solutions.

Conclusion

The kinetic experiments showed that 10 minutes are enough for the system to reach the equilibrium. The values of Ea showed that more energy is required for the xanthate interaction with the copper sulphide surface. Temperature had a positive effect on kinetics of the process. The kinetics of xanthate adsorption is observed to increase with the increase in temperature indicating more interaction of xanthate with the surface of the CuS at higher temperature.

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