Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Guarnaschelli, C. and Leja, J.(1966) 'Complexes Formed by Quaternary Ammonium Salts with Xanthates, and Synergistic Effects in Adsorption of Xanthate Ions on Reduced Copper Powders', Separation Science and Technology, 1: 4, 413 — 429
To link to this Article: DOI: 10.1080/01496396608049457
URL: http://dx.doi.org/10.1080/01496396608049457

SEPARATION SCIENCE, 1(4), 413–429 (1966)

Complexes Formed by Quaternary Ammonium Salts with Xanthates, and Synergistic Effects in Adsorption of Xanthate Ions on Reduced Copper Powders

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C. GUARNASCHELLI* and J. LEJA†

Summary

Precipitates formed in equimolar solutions of long chain xanthates and alkyl trimethyl ammonium bromides (C_nTAB) have been analyzed by chemical, X-ray diffraction, and infrared spectroscopic methods and were found to consist of a 1:1 complex of long-chain anions and cations. It is inferred that analogous ion-pair complexes, but in a solubilized form, exist in mixed solutions of shorter chain compounds, e.g., potassium ethyl xanthate (KEtX) and $C_{12}TAB$. Tests showed that a reduced copper surface adsorbs xanthate ions from such mixed solutions under anaerobic conditions when no adsorption of uncomplexed xanthate ion is possible. In the temperature range 4 to 20°C, an Arrhenius activation energy of 22.6 kcal/mole was evaluated for adsorption from equimolar solutions KEtX and $C_{12}TAB$. Characteristic changes in the behavior of xanthate due to its complexing with C_nTAB may have important applications in separation of solids by flotation, particularly under oxygen-deficient or reducing conditions, i.e., when normally flotation with xanthate ions is impossible, owing to their inability to adsorb under anaerobic condition.

Xanthate anions are not abstracted by oxygen-free surfaces of metallic copper or lead sulfide (formed as vacuum-deposited films) in a deoxygenated system (*1*). In fact, for xanthate ion adsorption, an oxidized compound must be present either on the surface of the substrate or in the bulk of solution. In contrast to the behavior

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of xanthate ions, an uncharged xanthate species, i.e., dixanthogen, is capable of adsorbing on an unoxidized copper or lead sulfide surface (*1*). Separate experiments (2) showed that the amount of dixanthogen adsorbing under conditions of oxygen deficiency was sufficient to give good flotation of reduced copper powder, using 2-ethyl hexyl alcohol as a frother and nitrogen gas for generating bubbles.

Another way of converting a xanthate anion into a neutral species is by complexing it with a cationic surfactant such as alkyl trimethyl ammonium salt (e.g., bromide; C_nTAB). The first indication that an interaction between xanthates and quaternary ammonium compounds takes place was obtained by Bowcott (*3*), who found that mixed monolayers of long-chain xanthates and C_nTAB stabilized the constituent xanthate molecules against atmospheric oxidation. Buckenham and Schulman (*4*) observed that a 1:1 ratio between xanthates and C_nTAB produced a greater reduction in surface tension than individual solutions of these surfactants, or any other ratios of their mixtures. They also showed that selective flotation of several minerals which otherwise are not always floated by individual surfactants is possible with a judicious mixture of homologues of these two surfactants. Subsequent work carried out in this laboratory by Pomianowski and Leja (*5*) indicated that instead of an expected adsorption of xanthate–C_nTAB complex there is a preferential adsorption of xanthate species, with negligible coadsorption of C_nTAB.

The main objectives of the present work were to extend the study of the adsorption kinetics from mixed solutions of KEtX (potassium ethyl xanthate) and C_{12}TAB (dodecyl trimethyl ammonium bromide) over a range of temperatures and to seek additional evidence on the nature of complexes formed by xanthates/C_nTAB mixtures.

The results show that xanthate anions can adsorb even under anaerobic conditions if complexed with C_nTAB.

EXPERIMENTAL

Materials

Reagent-grade electrolytic copper powder (<60 mesh, as supplied by Fisher Scientific Company) was screened on a 400-mesh Tyler screen to remove the fraction smaller than 38 μ. C_{12}TAB was supplied by K & K Laboratories, Inc., and was subsequently purified by recrystallizations from acetone (four times), extraction with Skellysolve B (to remove soluble impurities), and final recrystallizations from acetone (two times). KEtX was previously prepared in this laboratory and analyzed 99%+ in purity. All KEtX was freshly washed with ether before its use in tests, to remove any dixanthogen formed on storing. Low-conductivity double-distilled water (1.1×10^{-6} ohms^{-1}/cm) was used throughout the experiments.

Apparatus

The apparatus, shown in Fig. 1, was a modified version of that used by Pomianowski and Leja (5). The modifications included:

1. Provisions to run the tests under a controlled gas atmosphere.
2. Replacement of a single-disc sample chamber (Fig. 1, No. 8) with one possessing two glass-fritted discs to facilitate the reduction of copper powder in situ by passing H_2 gas at temperatures between 150 and 300°C, using flexible heating tapes.
3. Addition of a refrigerating unit for positive control of the temperature of the circulating solution to ±0.5°C.

Procedure

The adsorption apparatus was cleaned and then rinsed with 3 liters of distilled water followed by a final rinsing with double-distilled water. Copper powder was added to the dried apparatus. The amounts of surface active agents required to give solutions of the order 10^{-3} *M* were weighed on a Micro Gram-Atic balance, dissolved in a 200 ml volumetric flask, and added to the receiving vessel. At regular intervals, samples of the circulating solution were temporarily removed for UV spectrophotometric analysis in a Perkin Elmer 350 model. For runs in a nitrogen atmosphere, the following precautions were taken: (1) oxygen-free water was prepared by passing through double-distilled water a continuous flow of purified premium nitrogen while boiling and quenching; (2) the solution of surface active agents was prepared in a dry box and transferred to the system in a well-stoppered separatory funnel; (3) the apparatus was repeatedly evacuated, filled with purified premium nitrogen, and evacuated through a three-way stopcock;

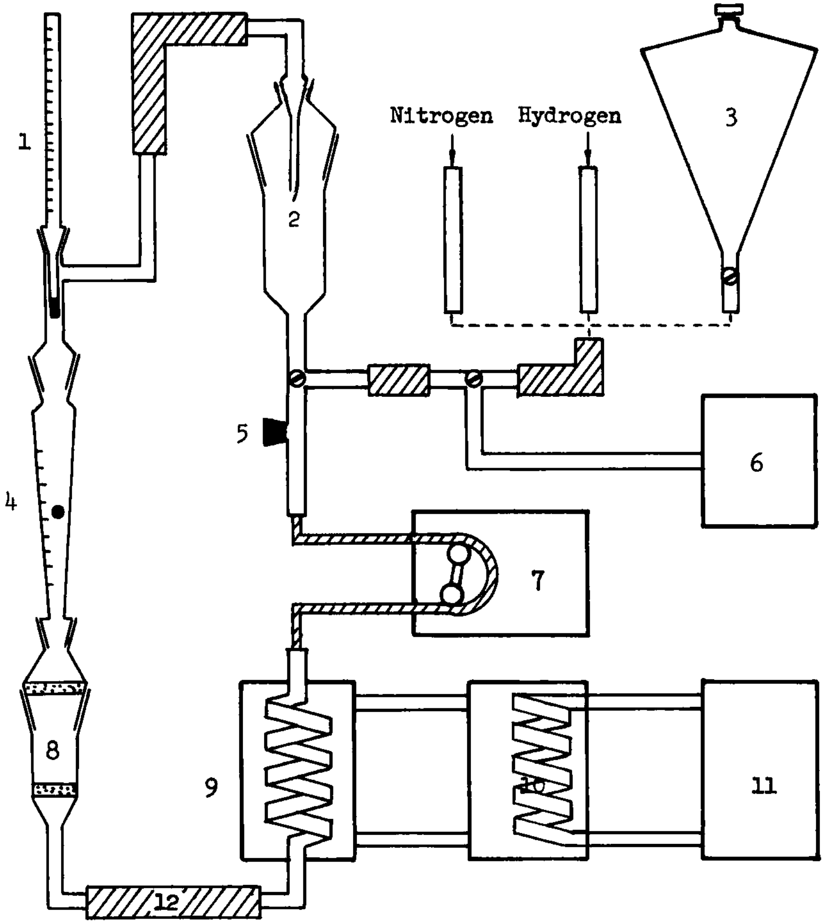

FIG. 1. Arrangement of the adsorption apparatus: 1, thermometer; 2, receiving vessel; 3, separatory funnel; 4, flow meter; 5, sampling stopper; 6, vacuum pump; 7, circulating pump; 8, sample chamber; 9, cooling coil; 10, controlled temperature bath; 11, refrigerating unit; 12, tygon tubing.

and (4) samples removed for spectrophotometric analyses were not returned to the system.

RESULTS

Precipitates in Equimolar Mixtures of Xanthates and C_nTAB

Pomianowski and Leja (5) pointed out that equimolar solutions of nonyl xanthate (KC_9X) and dodecyl-TAB ($C_{12}TAB$) formed a precipitate on mixing. Homologues of higher chain lengths also produced precipitates, whereas a combination of hexyl xanthate (KC_6X) and $C_{12}TAB$ did not precipitate even after standing for a month in a well-stoppered volumetric flask. The precipitates obtained with long-chain homologues were filtered, dried in a vacuum desiccator, chemically analyzed, and their X-ray diffraction patterns compared with those of the original constituents.

Microchemical analyses (by Dr. F. Pascher of Bonn, Germany) are presented in Table 1. The results indicate that the most likely chemical composition of the precipitate is a 1:1 combination of the anionic and cationic molecular species without their corresponding counterions. The oxygen assay is the least reliable, because the precipitates are hygroscopic to various degrees. Further, the discrepancy between the chemical assay values and those of the calculated molecular associations can also be partially attributed to the presence of higher and/or lower chain homologues in the C_nTAB used (although no minimum was found around the critical micelle concentration of this species in surface tension vs. concentration measurements).

X-ray powder-diffraction techniques have been used successfully by Warren and Matthews (6) to identify alcohols by their xanthate

TABLE 1

Comparison between Actual Assay and Calculated Composition of the Precipitate Formed from an Equimolar Mixture of Two Surfactants

	KC_6X and $C_{18}TAB$ precipitate			KC_9X and $C_{12}TAB$ precipitate		
	Actual assay			Actual assay		
Element	Reported, %	Without H_2O, %	Calculated 1:1 composition, %	Reported, %	Without H_2O, %	Calculated 1:1 composition, %
C	65.28	68.2	68.7	64.67	69.0	67.1
H	10.58	11.0	12.1	10.25	10.9	11.9
N	2.33	2.4	2.8	1.96	2.1	3.1
O	5.75	6.0	3.3	4.28	4.6	3.6
S	11.82	12.4	13.1	12.56	13.4	14.3
K	Nil	Nil	Nil	Nil	Nil	Nil
Br	Nil	Nil	Nil	Nil	Nil	Nil
H_2O	4.83	Nil	Nil	5.92	Nil	Nil
	100.59	100.0	100.0	99.64	100.0	100.0

derivatives and by Brock and Hannum (7) for the identification of amines. X-ray diffraction patterns of the individual xanthates and of the quaternary amines used in these experiments were recorded and their *d* spacing compared with those obtained in patterns of the precipitates (Table 2). In no case did the *d* spacings

TABLE 2

X-Ray Diffraction Data

KC$_6$X		KC$_9$X		C$_{12}$TAB		C$_{18}$TAB	
d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
13.8	1.00	17.8	1.00	21.8	1.00	28.0	1.00
6.9	0.08	8.91	0.20	10.9	0.44	14.0	0.74
4.62	0.07	5.93	0.19	5.76	0.36	9.40	0.22
4.51	0.06	4.72	0.01	4.34	0.55	5.64	0.28
4.25	0.01	4.53	0.01	4.21	0.08	4.70	0.50
4.00	0.05	4.46	0.01	3.61	0.29	4.13	0.15
3.26	0.01	4.43	0.02	3.37	0.02	4.03	0.38
3.09	0.03	4.22	0.01	3.09	0.07	3.63	0.09
3.02	0.02	3.56	0.05	2.54	0.01	3.53	0.26
2.92	0.04	3.14	0.01	2.46	0.03	3.14	0.09
		2.97	0.03	2.28	0.02	2.35	0.08
		2.88	0.01	2.08	0.02		
		2.55	0.02				
		2.28	0.01				

KC$_6$X-C$_{18}$TAB		KC$_9$X-C$_{12}$TAB		KC$_9$X-C$_{18}$TAB	
d	I/I_0	*d*	I/I_0	*d*	I/I_0
44±5	1.00	42±5	1.00	32.7	1.00
17.5	0.02	26.1	0.20	11.0	0.03
10.1	0.01	14.2	0.01	8.26	0.05
7.5	0.01	7.07	0.01	6.60	0.15
6.08	0.02	6.70	0.03	5.30	0.03
5.30	0.01	5.40	0.01	4.83	0.03
4.75	0.04	4.98	0.01	4.73	0.05
4.36	0.03	4.48	0.03	4.38	0.21
4.27	0.03	4.33	0.01	3.85	0.12
3.83	0.06	4.09	0.04	3.69	0.03
3.66	0.03	4.02	0.02	3.30	0.04
3.50	0.01	3.85	0.01		
3.04	0.01	3.45	0.01		
2.78	0.01	3.16	0.01		
2.49	0.01				
2.11	0.01				

of the precipitates agree with the *d* spacings of the constituents, thus suggesting that a new complex was formed.

An infrared spectroscopic investigation of precipitates formed by addition of alkyl trimethyl ammonium ions to alkyl xanthate anions has been carried out recently in this department (*8*). The spectra indicate that the precipitates are not simple ion-pair associations of the quaternary ammonium cations and xanthate anions, because slight changes in the characteristic band structures are observed; these changes in band structures suggest a development of weak bonds in addition to the electrostatic bond in ion-pair formation.

The evidence for a 1:1 complex formed on precipitation suggests that analogous 1:1 complexing, but resulting in solubilized species, might take place in solutions of lower homologues of the two surfactants. Pomianowski (9) found the equivalent conductivities in these mixed solutions of short-chain homologues to be lower than expected for mixtures of unreactive constituents, which would suggest the formation of uncharged solubilized aggregates (dimers or their multiple combinations). In addition, the ability of xanthate species to adsorb from mixtures with C_{12}TAB under anaerobic conditions (when uncomplexed xanthate anions are incapable of adsorption) can also be taken as an indicator of complexing in the form of solubilized species.

Rates of Xanthate-Ion Abstraction

Figure 2 shows the progress of abstraction of EtX^- with time, by unreduced copper powders (i.e., covered with a layer of surface oxides) from solutions of KEtX alone and from an equimolar mixture of KEtX and C_{12}TAB. The curves obtained for 10°C, Fig. 2(a), show the same trend as that obtained by Pomianowski and Leja (5) for 20°C. However, at 4°C, the trend is reversed; i.e., the initial abstraction of EtX^- is slower than the second stage. In all cases, adsorption of xanthate ions from equimolar mixture of KEtX and C_{12}TAB is greater than from solutions of KEtX alone. The same trend, but to a lesser degree, is observed when the receiving vessel (Fig. 1, no. 2) is opened to allow atmospheric oxygen to be continuously supplied to the solution (open system) as compared to the nitrogen atmosphere (closed system).

Effect of Oxygen. A subsequent series of tests with reduced copper powder gave initially rather erratic results even from solutions of

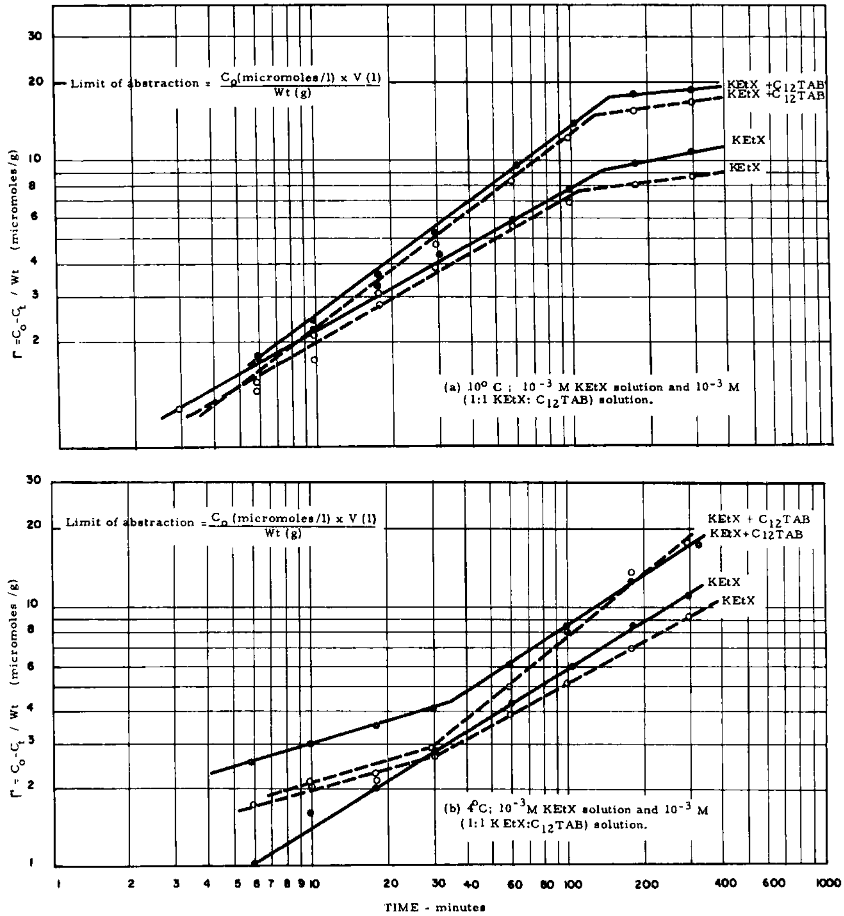

FIG. 2. Abstraction of EtX^- from solutions of KEtX alone and from 1:1 mixtures of KEtX:$C_{12}TAB$ by 10 g of unreduced copper powder, using air (———) and unpurified premium nitrogen (— — —) atmospheres at 10°C (a) and at 4°C (b): (a) 10°C; 10^{-3} *M* KEtX solution and 10^{-3} *M* (1:1 KEtX: $C_{12}TAB$) solution; (b) 4°C; 10^{-3} *M* KEtX solution and 10^{-3} *M* (1:1 KEtX : $C_{12}TAB$ solution.

KEtX alone; the cause of this scattering has been finally traced to varying residual oxygen content in the several cylinders of unpurified nitrogen, which have been alternately used in tests. When an oxygen-removal train was inserted in the line supplying nitrogen to the system, the results became reproducible (Fig. 3).

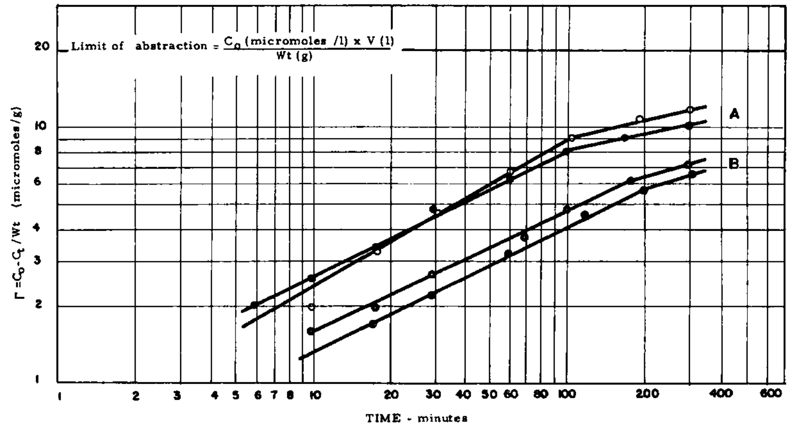

FIG. 3. Reproducibility of the EtX^- adsorption from solutions of KEtX on unreduced copper powder at 15°C (A) and from a mixture of KEtX and $C_{12}TAB$ on reduced copper powder at 10°C (B).

No abstraction of EtX^- was detected with reduced copper in a purified nitrogen atmosphere if the system contained xanthate solution alone, but a progressive adsorption of EtX^- from equimolar solution of KEtX and $C_{12}TAB$ has been obtained (Fig. 7). This indicates clearly that, when complexed with $C_{12}TAB$, the EtX^-

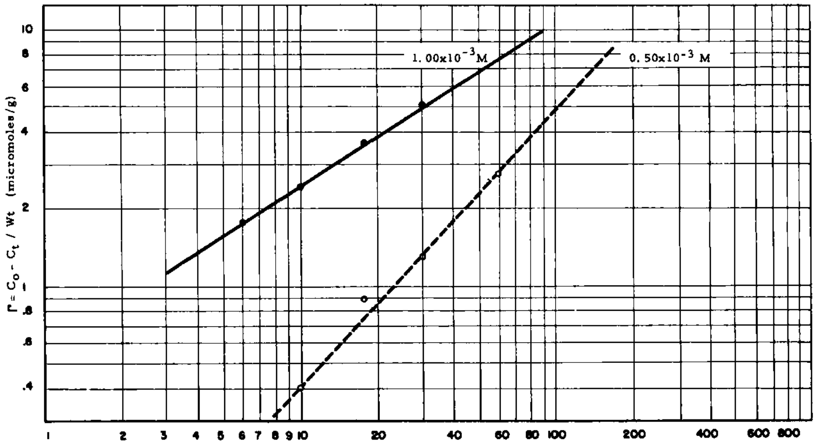

FIG. 4. Effect of a change in xanthate concentration on abstraction of EtX^- from a 1:1 mixture of $KEtX:C_{12}TAB$ by 10 g of unreduced copper powder in a system open to the atmosphere at 10°C.

ions do penetrate the electrical double layer at the surface of reduced copper and are adsorbed thereon.

Effect of Gases on Adsorption of EtX^- Ions. Plaksin et al. in Klassen and Mokrousov (*10*) have found that different gases exert pronounced effects on the reactivity of various mineral surfaces with water (hydration of surfaces) and with flotation reagents, thus strongly affecting the flotation of these minerals. Similar effects of gases have been obtained in the adsorption of EtX^- anions from equimolar solutions of KEtX and C_{12}TAB on reduced copper powder, as shown in Fig. 5. Residual oxygen in unpurified nitrogen increases the amounts of EtX^- abstracted by reduced copper powder when compared to those abstracted in purified nitrogen. In addition, there is a slight but definite effect on the amount adsorbed when argon is substituted for nitrogen, leaving unaffected the *rate* of EtX^- abstraction.

Effect of Temperature. The effect of temperature on the rates of EtX^- abstraction by unreduced copper powder from solutions of KEtX alone is shown in Fig. 6. This should be contrasted with the effect of temperature in the case of reduced copper powder abstracting EtX^- from equimolar solutions of KEtX and C_{12}TAB in a purified nitrogen atmosphere, Fig. 7. It is seen that in the former case, as the temperature increases, the rates of abstraction (slopes of the lines) become progressively smaller, whereas in the latter case the slopes are not affected by temperature.

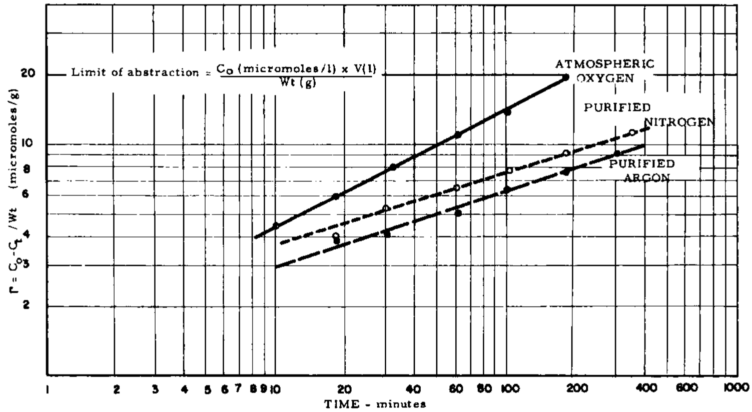

FIG. 5. Influence of various gases on adsorption of EtX^- from a mixture of KEtX and C_{12}TAB on 10 g of reduced copper powder at 10°C.

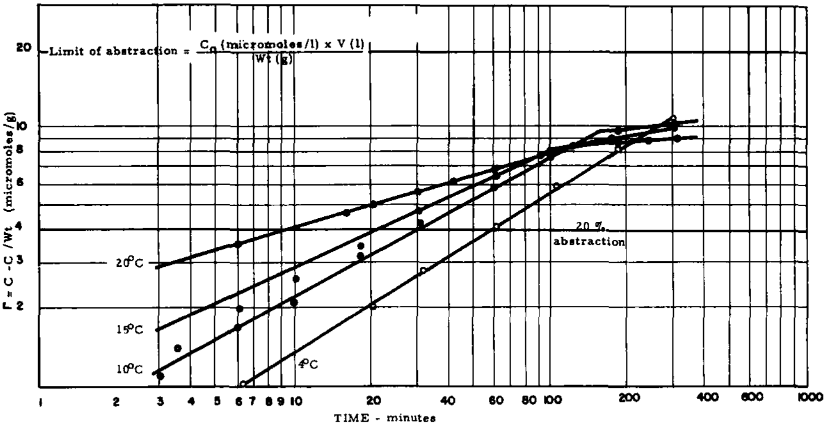

FIG. 6. Adsorption of KEtX on 10 g of unreduced copper powder from solutions of KEtX (10^{-3} M) in systems open to the atmosphere.

Evaluation of Abstraction Results

Using the half-life method (see the Appendix) and the values of half-life determined from data in Fig. 4, the reaction order was found to be approximately 1 for the abstraction of EtX^- by unreduced copper powder from equimolar solutions of KEtX and $C_{12}TAB$. An independent confirmation that the adsorption from a

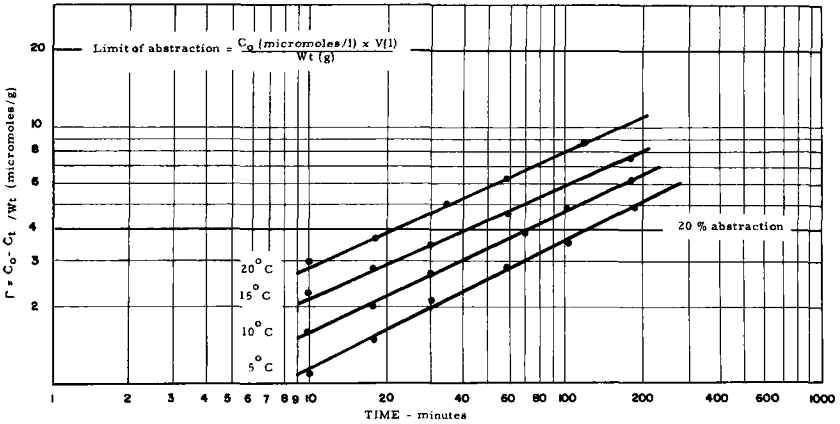

FIG. 7. Adsorption of KEtX on 10 g of copper (reduced) from mixtures of KEtX (10^{-3} M) and $C_{12}TAB$ (10^{-3} M) in purified nitrogen atmospheres.

mixture of C_{12}TAB and ethyl xanthate is indeed a first-order reaction is presented in Fig. 8; for a reaction of first order, $-dC/dt = k_T C$, the following relationship is derived: $k_T t = \ln (C_0/C_t)$; adsorption data, $\ln (C_0/C_t)$ vs. time, for a mixture of C_{12}TAB and EtX^- plot as straight lines for both reduced and unreduced copper powder systems (lines C and B, respectively), whereas analogous data for adsorption by unreduced copper powder in a solution of *xanthate alone* depart from linearity (curve A). The curvature of the latter indicates that neither k_T nor the order of reaction is constant at a given temperature. Once the reaction order is known, the specific rate constant can be evaluated for each temperature recorded in Fig. 7. The plot of $\ln k_T$ vs. $1/T$, presented in Fig. 9, shows that the Arrhenius activation energy E_a (from $k_T = Ae^{-E_a RT}$) is constant at 22.6 kcal/mode for the given range of temperatures.

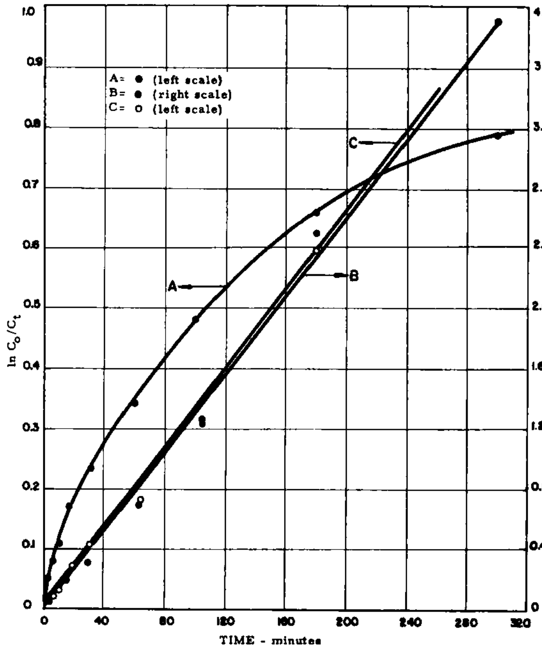

FIG. 8. First-order plots of the adsorption of EtX^- from a solution of KEtX alone on unreduced copper powder (A), the adsorption of EtX^- from a mixture of KEtX and C_{12}TAB on unreduced copper powder (B), and the adsorption of EtX^- from a mixture of KEtX and C_{12}TAB on reduced copper powder (C), all at 10°C. A = ● (left scale); B = ⊙ (right scale); C = ○ (left scale).

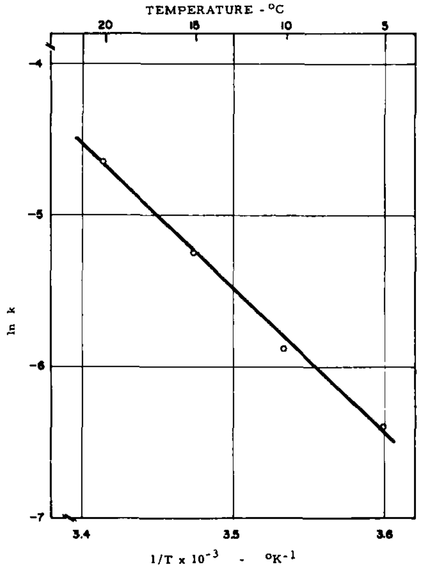

FIG. 9. Temperature independence of the Arrhenius activation energy for the adsorption of EtX^- from an equimolar solution of KEtX and $C_{12}TAB$ in a purified nitrogen atmosphere.

It is also instructive to evaluate the entropy of activation from the results obtained in this study. The method is again outlined in the Appendix. The value obtained for the entropy of activation in the adsorption of xanthate complex on reduced copper powder from equimolar solutions of KEtX and $C_{12}TAB$ was −0.73 cal/deg mole.

DISCUSSION

Chemical analyses, X-ray diffraction, and infrared spectroscopy of the precipitates formed in equimolar solutions of long-chain homologues of potassium alkyl xanthates and alkyl trimethyl ammonium bromides indicate a 1:1 complex formation between anionic and cationic species, without the inclusion of corresponding counterions (present in the original constituents). The formation of an analogous but solubilized complex between ethyl xanthate and $C_{12}TAB$ is inferred from a decrease in equivalent conductivities, but has not been checked yet by other techniques (e.g., light scattering).

The most striking result in the adsorption data presented above is the ability of un-ionized xanthate species from equimolar mixture (presumed to be a 1:1 cation:anion complex) to adsorb on unoxidized (reduced) copper surfaces while *uncomplexed xanthate ion* is *incapable* of adsorption on the same surface under identical conditions. Stringent control of residual oxygen content in the system is required to differentiate between these two behaviors, but the reproducibility of tests makes this difference in adsorptive action real and significant (Fig. 3).

The results reported by Pomianowski and Leja (5) for oxidized copper powder have been confirmed in that the rate of abstraction of xanthate species from equimolar solutions of KEtX and C_{12}TAB is always greater (Figs. 2 and 3) than that from solutions of KEtX alone; for unoxidized copper surfaces the difference between the mixture and KEtX alone is even more pronounced: no adsorption of uncomplexed ion whereas complexed xanthate species adsorbs in appreciable quantities. In addition, the energy and entropy of activation for adsorption from equimolar mixture on reduced copper have been evaluated. Within the range studied, Fig. 7 shows that in the system with reduced copper powder the rate of abstraction is not appreciably affected by temperature, whereas with the oxidized copper surfaces the rate of EtX^- abstraction is decreasing with rising temperature (Fig. 6). This effect of decreasing rate of abstraction may be due to solubility of the adsorbed layer increasing with the rise in temperature. As shown previously by infrared techniques (*1*) the adsorbed layer formed on oxidized copper surfaces (Fig. 6) consists of a multilayer mixture of cuprous xanthate and dixanthogen adhering to a monolayer of adsorbed xanthate. Although the monolayer itself is not readily removed by solvents dissolving bulk cuprous xanthate, a rise in temperature will definitely increase the solubility of the overlaying multilayer mixture of cuprous xanthate and dixanthogen, thus decreasing the over-all abstraction rate. No infrared spectroscopic work has yet been done on the adsorbed layer abstracted from equimolar solutions of KEtX and C_{12}TAB by reduced copper surfaces. The UV spectroscopic results reported previously (5) seem to indicate that xanthate species is being abstracted preferentially, leaving the bulk of C_{12}TAB in solution.

With regard to the mechanism of adsorption, the magnitude of the activation energy, 22.6 kcal/mole, suggests that chemisorption and not physical adsorption is involved. The negative value of the entropy of activation (−0.73 eu) indicates that the degree of ordering in the adsorbed layer is increased. Finally, the apparent preferential adsorption of xanthate species on copper surfaces suggests that the 1:1 complex is not permanently adsorbed on the surface but is readily decomposed (after diffusing through the electrical double layer at the interface) and allows the C_{12}TAB cation either to diffuse back to the bulk solution or to act as a link in the subsequent transfer of EtX^- anions in analogous fashion to proton transfer mechanisms. It is now obvious that a complete elucidation of the mechanism of adsorption from complexing solutions will require further work in infrared-spectroscopic examination of adsorbed species as well as additional electrochemical and electrokinetic studies.

The feasibility of selective flotation using equimolar mixtures of alkyl xanthates and C_nTAB has already been demonstrated by Buckenham and Schulman (*4*). The ability of these complexes to adsorb on unoxidized surfaces under anaerobic conditions may have interesting applications in flotation processes, particularly if other combinations of anionic and cationic surfactants are judiciously employed.

APPENDIX

Reaction Order

The rate equation for a decrease in xanthate-ion concentration resulting from abstraction by solid powders can be written in a general form:

$$-\frac{dC}{dt} = k_T C^n \qquad \text{(A)}$$

where k_T = specific rate constant (mole^{-1}/min), C = concentration (moles/liter), t = time (min), and n = reaction order. The half-life, or time τ, during which the initial concentration C_0 is reduced to $\frac{1}{2} C_0$, is expressed

$$\tau = \frac{2^{n-1} - 1}{k_T(n-1)(C_0^{\,n-1})} \qquad \text{(B)}$$

It can be shown that even for $n = 1$ the above relationship holds and gives a determinate τ, viz., $\tau = \ln 2/k_T$. Given two concentrations, C_1 and C_2, and their respective half-lives, τ_1 and τ_2, the reaction order, n, can be evaluated using the equation

$$n = \frac{\ln (\tau_1/\tau_2)}{\ln (C_2/C_1)} + 1 \tag{C}$$

which is easily derived from (B). From the data of Fig. 4 the reaction order for equimolar mixtures of KEtX and $C_{12}TAB$ is found to be

$$n = \frac{\ln (106/92)}{\ln (1.00/0.50)} + 1 = 1.2$$

Entropy of Activation

The expression for the reaction rate (k_T) in terms of the entropy ($\Delta S^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) is

$$k_T = kT/h \exp(\Delta S^{\neq}/R) \exp(-\Delta H^{\neq}/RT)$$

or

$$k_T = kT/h \exp(\Delta S^{\neq}/R) \exp [-(E_a - RT)/RT], \text{ since } \Delta H^{\neq} = E_a - RT$$

where k = Boltzmann's constant, h = Planck's constant, and R = gas constant. Taking logarithms and rearranging,

$$\Delta S^{\neq} = \left(\ln k_T + \frac{E_a - RT}{RT} - \ln \frac{kT}{h}\right) R$$

The value for the entropy of activation with an Arrhenius activation energy of 22,600 calories is −0.73 cal/deg mole.

Acknowledgments

The authors wish to thank Dr. R. W. Scowen and Dr. W. V. Youdelis for extensive discussions of the present work, and Mr. J. Wojno for technical assistance.

An unsolicited research grant which has been provided by The Consolidated Mining and Smelting Company of Canada Limited, Trail, B.C., financed both this investigation and Mr. Guarnaschelli's scholarship, and is gratefully acknowledged.

The work has been carried out in the University of Alberta, Department of Mining and Metallurgy.

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Received by editor May 17, 1966
Submitted for publication June 8, 1966