

CHAPTER 2

Direct Force Measurement between Hydrophobic Glass Sphere and Covellite Electrode in Potassium Ethyl Xanthate Solutions at pH 9.2

2.1 INTRODUCTION

Froth flotation is the most widely used method of separating minerals from one another. The basis of this process is to control the hydrophobicity of the minerals to be separated. The most commonly used measure of hydrophobicity is the water contact angle (θ), which is usually measured on polished mineral surfaces using either sessile drop or captive bubble technique. However, contact angle is a thermodynamic property and, therefore, it is difficult to use it for predicting a kinetic process such as flotation. For this reason, most of the flotation models published in the literature fail to incorporate the role of hydrophobicity. However, recent investigations conducted at Virginia Tech led to the development of a flotation model, which includes contributions from hydrophobic forces [1]. Here the term hydrophobic force should be distinguished from hydrophobicity. Since its first measurement by Israelachvili and Pashley in 1982 [2], many investigators conducted surface force measurements between surfaces of different hydrophobicities. Rabinovich and Yoon [3] and Yoon and Ravishankar [4] reported a relationship between hydrophobic force and θ . Such information is critical for developing reliable flotation models.

Hydrophobic forces can be measured using either the surface force apparatus (SFA) [4-6] or the atomic force microscope (AFM) [3,7-8]. The force measurements are conducted using surfaces hydrophobized by surfactant coating. When θ is in the range of 20-40°, the measured forces (F) can be analyzed using the DLVO theory [9]:

$$F = F_e + F_d, \quad [1]$$

in which F_d is the London-van der Waals dispersion force and F_e is the ion-electrostatic force. The magnitude of the former is represented by the Hamaker constant, while that of the latter is represented by the double-layer potential.

When the contact angle is larger than approximately 40° , it is necessary to extend the DLVO theory by adding an attractive force term (F_h) not considered in the original theory. Thus, Eq. [1] can be extended to include F_h as follows:

$$F = F_e + F_d + F_h. \quad [2]$$

Eq. [2] is referred to as extended DLVO theory, and the additional attractive force term can be described by a power law [8]:

$$F_h = -\frac{KR}{6H^2}, \quad [3]$$

in which R is the radius of curvature of the spherical (or cylindrical) object used for direct force measurement, H is the closest distance separating the two surfaces, and K is a constant. Eq. [3] is of the same form as the one commonly used for the dispersion force. Therefore, K can be compared with the Hamaker constant (A).

Most of the surface force measurements reported in the literature were conducted with surfaces (e.g., of mica, silica and sapphire) coated with long-chain surfactants. Changes in hydrophobic forces with pH [4-6], surfactant concentration [6] and chain length [4] were measured. Several investigators have also conducted force measurements between gold surfaces [10,11] and between precipitated ZnS spheres [12,13]. However, there are no reports of the force measurements conducted with surfaces coated with thiol collectors. Furthermore, no force measurements were

conducted with common sulfide minerals. The difficulty in measuring forces with sulfide minerals is that there are only a few that have well-defined cleavage planes.

In the present work, direct force measurements were conducted with covellite (CuS) surfaces coated with a thiol collector. This mineral cleaves along the {0001} plane to produce a molecularly smooth surface. The force measurements were conducted between cleaved covellite plate and hydrophobized glass sphere ($\theta=109^\circ$) using an AFM. The hydrophobic sphere may simulate the behavior of air bubbles during flotation. The force measurements conducted between hydrophobic glass sphere and silica plate in dodecylammonium chloride solutions showed results that are consistent with flotation data [14]. In the present study, force measurements were conducted as a function of the electrochemical potential of CuS electrode.

2.2 EXPERIMENTAL

2.2 (a) Materials

Pure covellite (source unknown) specimens were obtained from the Museum of Natural History, Smithsonian Institution, Washington, D.C., and used as a plate in AFM force measurements. Glass spheres were obtained from Duke Scientific, hydrophobized by octadecyltrichlorosilane (OTS), and used for the force measurements. The OTS was obtained from Aldrich Chemical Company at 95% purity and used without further purification. The glass spheres, as received, were reacted with OTS in HPLC grade cyclohexane, which was obtained from Aldrich Chemical Company. Flinn, et al. [15] described the process of hydrophobizing glass spheres in detail. The cyclohexane was dried overnight over 3-12 mesh Davidson 3-A molecular sieves before use.

For each experiment, a hydrophobized glass sphere was glued to the end of an

AFM cantilever spring by means of Epon R Resin 1004F from Shell Chemicals Company. The cantilever springs used in the force measurements included Tapping Etched Silicon Probes (TESP) and regular silicon nitride tips, which were obtained from Digital Instruments, Santa Barbara, CA. All experiments were conducted using conductivity water produced from a Barnstead Nanopure II water purification system.

2.2 (b) Apparatus and Procedure

Surface force measurements were conducted using a Digital Instruments Nanoscope III atomic force microscope (AFM) with an electrochemical attachment. The AFM was equipped with a standard liquid cell, which had been modified to have a three-electrode system. Figure 2.1A shows the overall cell assembly, while Figure 2.1B shows the detailed design and dimensions of the sample holder (a). A covellite specimen (b), which is serving as working electrode, is placed in the circular cavity created in the upper part of the plexiglass sample holder. A brass cylinder (c) is glued to the bottom of the sample by means of a colloidal silver paste (obtained from Electron Microscopy Sciences, PA), so that it can provide a conducting path between the working electrode (b) and the potentiostat of the Nanoscope III. In order to prevent the silver paste from reacting with the solution in the liquid cell, the space between the cleaved covellite specimen and the sample holder was filled with a non-conducting adhesive (Epon R Resin 1004F). The whole working electrode assembly was then placed on the Piezoelectric crystal base (d), which is designed to move the sample in x-, y-, and z-directions. A platinum wire (e) placed near the working electrode serves as a reference electrode, while another platinum wire (f) located in the upper part of the liquid cell serves as the counter electrode. A hydrophobized glass sphere of 15-25 μm radius (g) was glued to the end of the cantilever spring (k) using the non-conducting adhesive.

All AFM force measurements were carried out in a manner described by

Rabinovich and Yoon [8]. When the measurements were conducted in Nanopure water, standard triangular silicon nitride (Si_3N_4) cantilevers were used. To measure strong attractive forces, rectangular TESP cantilevers were used. They were calibrated using the technique described by Senden and Ducker [7]. In the present investigation, the potentials of the covellite working electrode were measured against the platinum reference electrode, which in turn was calibrated *vs.* a standard calomel electrode (SCE). All of the potentials measured in the present work were converted to standard hydrogen electrode (SHE) potentials.

Cyclic voltammetry studies were carried out using a Pine Instrument Model RDE4 double potentiostat. A conventional three electrode system was used for the voltammetric studies with a polished covellite specimen as working electrode, a platinum plate as counter electrode, and a standard calomel electrode (SCE) as reference electrode. All voltammetry experiments were conducted in a 0.01 M NaCl solution whose pH was adjusted to 9.2 by adding aliquots of NaOH solutions. Before each experiment, the surface of the covellite electrode was wet-polished on 600-grit silicon carbide paper.

2.2(c) Contact Angle Measurements

Equilibrium contact angles of a polished covellite electrode were measured using the captive bubble technique by means of a Rame-Hart Model 100 goniometer. The electrode was immersed in 0.01 M NaCl solution of pH 9.2 containing 10^{-3} M KEX, with its polished surface facing down and an air bubble approaching the surface from below. The angles were measured through the aqueous phase, and the electrode potentials were controlled by means of a potentiostat (Pine Instrument Model RDE4).

The contact angle of the hydrophobized glass sphere was determined by conducting the measurement on a glass plate that had been hydrophobized in the same

OTS solution as that used for the glass sphere. The sessile drop technique was used for the measurement.

The sessile drop technique was also used to measure the contact angle of methylene iodide on a polished covellite surface at open circuit. The result was used to calculate the Hamaker constant of the mineral [16, 17].

2.3 RESULTS AND DISCUSSION

2.3 (a) Force Measurements in Nanopure Water

Figure 2.2 shows the results of direct force measurements conducted between a covellite (CuS) plate and a glass sphere in Nanopure water. The water contact angle (θ) of the covellite plate was 28° , while that of the glass sphere was less than 5° . The measured forces F , normalized by the radius of the sphere R , are plotted versus the separation distance H . The solid line in Figure 2.2 represents a DLVO fit of the data. Also shown are the contributions from the ion-electrostatic force (F_e) and the dispersion force (F_d) to F (see Eq. [1]). F_e has been calculated using the constant potential model of Oshima, et al. [18], with ψ_1 (the surface potential of covellite) of -45 mV, ψ_2 (the surface potential of untreated glass sphere) of -60 mV, and κ^{-1} (the Debye length) of 87.7 nm. The value of $\psi_1 = -45$ mV in Nanopure water agrees well with the values of ζ -potentials reported for covellite by Acar and Somasundaran [19]. F_d was obtained using the well-known relationship:

$$F_d = -\frac{RA_{132}}{6H^2}, \quad [4]$$

in which A_{132} is the Hamaker constant for the interaction between covellite **1** and glass **2**

in water **3**, R is the radius of curvature of the glass sphere, and H is the separation distance between the two surfaces. The experimental data can be best fit with a value of $A_{132}=1.1 \times 10^{-20}$ J.

One can substitute the value of A_{132} obtained from the direct force measurement and the value of $A_{232}=0.8 \times 10^{-20}$ J for silica [20] into the geometric mean combining rule:

$$A_{132} = \sqrt{A_{131} \times A_{232}}, \quad [5]$$

and obtain the value of $A_{131}=1.5 \times 10^{-20}$ J. This value may be compared with the experimental value obtained using the methylene iodide contact angle method. In the present work, the contact angle (\mathbf{q}_m) of methylene iodide on polished covellite surface was measured to be 16° . By substituting this experimental value into the equation [16-17]:

$$\mathbf{g}_1^d = \left[(1 + \cos \mathbf{q}_m) \mathbf{g}_m / 2\sqrt{\mathbf{g}_m^d} \right]^2, \quad [6]$$

where γ_m (=50.8 mN/m) is the surface tension of methylene iodide and γ_m^d (=48.5 mN/m) is its dispersion component, one obtains the value γ_1^d (dispersion component of the surface tension of covellite) to be 51.2 mN/m. One can then substitute this value into the following equation [21]:

$$A_{131} = 1.5 \times 10^{-21} (\sqrt{\gamma_1^d} - \sqrt{\gamma_3^d})^2 J \quad [7]$$

where γ_3^d (=21.8 mN/m) is the dispersion component of the surface tension of water, to obtain the value of $A_{131}=0.9 \times 10^{-20}$ J. Thus, the value of $A_{131}=1.5 \times 10^{-20}$ J obtained from the direct force measurement is considerably larger than the experimental value. On the other hand, Visser [22] reported the Hamaker constants (A_{131}) of CdS to be 4.85×10^{-20} J and that of Sb_2S_3 to be in the range of $1.8\text{-}2.4 \times 10^{-19}$ J. These values were determined using the Lifshitz theory. It is possible that the Hamaker constant of CuS determined in

the present work based on q_n underestimated A_{131} . In fact, it is well known that for conducting materials such as gold, a different approach needs to be used to calculate the Hamaker constant [23].

Thus, the force data obtained for the asymmetric interaction between the untreated hydrophilic glass sphere and covellite can be fitted to the DLVO theory. There are no signs of non-DLVO forces. According to Churaev and Derjaguin [9], the DLVO theory is applicable only to the lyophobic colloids whose contact angle is in the range of 20-40°. The covellite sample used in the present work exhibit a contact angle of 28° (Table 2.1). Hence, the absence of non-DLVO forces between the covellite plate and glass sphere in Nanopure water is not surprising.

Figure 2.2 also shows the results of the force measurements conducted in Nanopure water between covellite plate and glass sphere hydrophobized by octadecyltrichlorosilane (OTS). The contact angle of the glass sphere is 109°, as measured on a glass plate that had been hydrophobized in the same batch of OTS solution. Note that the force curve is indistinguishable with that obtained between covellite and untreated glass (hydrophilic) sphere. This finding suggests that silanation does not change the surface potentials (γ_1) of glass or silica, as has been reported by Laskowski and Kitchener [24] and Yoon, et al [20]. This is an interesting finding since Laskowski and Kitchener [24] silanated their silica samples using trimethylchlorosilane (TMCS) while in the present work silanation was done using OTS which has a much longer hydrocarbon chain, i.e., irrespective of the silane used the surface potential of silica remains unchanged.

It is interesting that the interaction between a very hydrophobic glass sphere and hydrophilic covellite showed no evidence of hydrophobic force. Parker and Claesson [25] conducted force measurements between hydrophilic glass plate and hydrophobic silanated glass sphere and found no evidence for long-range attractive forces. Tsao, et

al. [26] observed, on the contrary, long-range attractive forces between hydrophilic and hydrophobic surfaces.

2.3 (b) Force Measurements in Xanthate Solutions

Figure 2.3 shows two force curves obtained between covellite plate and glass sphere in a 10^{-3} M KEX solution at pH 9.2. One was made with an untreated (hydrophilic) glass sphere with $\theta < 5^\circ$, and the other with OTS-treated glass sphere with $\theta = 109^\circ$. Each measurement was conducted after 30 minutes of equilibration. The force curve obtained with the hydrophilic glass sphere (the upper curve) can be fitted to the classical DLVO theory with $\psi_1 = -67$ mV for covellite, $\psi_2 = -60$ mV for the glass sphere and $k^1 = 8.3$ nm. Contributions from the ion-electrostatic (F_e) and dispersion forces (F_d) are also shown. Note here that the Debye length is substantially smaller than that obtained in Nanopure water ($\kappa^{-1} = 87.7$ nm) (Figure 2.2), which can be attributed to the double-layer compression in the presence of 10^{-3} M KEX. Note also that ψ_1 of -67 mV in the xanthate solution is substantially more negative than in Nanopure water ($\psi_1 = -45$ mV) (Figure 2.1). This is not surprising because xanthate is an anionic collector. To confirm this, ζ -potential measurements were conducted on a pulverized covellite sample. The ζ -potential was -40 mV in Nanopure water, which increased to -69 mV when 10^{-3} M KEX was added. A similar observation was made by Lekki and Laskowski [27] with chalcocite.

The lower force curve in Figure 2.3 represents the results obtained between covellite plate and hydrophobized glass sphere with $\theta = 109^\circ$. This measurement is designed to simulate bubble-particle interactions in flotation, considering that air bubble is hydrophobic. Yoon and Aksoy [28, 29] showed the changes in hydrophobic force at the air/water interface as functions of cationic and anionic surfactants. It is not likely, however, that the presence of xanthate affect the hydrophobicity of the hydrophobized

glass sphere because ethyl xanthate is a short-chain surfactant. This was confirmed by the results of contact angle measurements conducted on a silanated silica plate ($\theta=109^\circ$), which showed no change in the contact angle with the addition of 10^{-3} M KEX. Thus, the force curve may give information concerning the surface forces between air bubble and covellite hydrophobized in the xanthate solution. As shown, the measured forces are net-attractive, indicating the presence of an attractive force not considered in the DLVO theory. The data can be fitted to the extended DLVO theory (Eq. [2]), which includes a hydrophobic force term. In the present work, the hydrophobic force is represented by a power law (Eq. [3]), with K_{132} representing a constant for the interaction between covellite **1** and silica **2** in water **3**. The force data were fitted with a value of $K_{132}=1.5\times 10^{-18}$ J, which is roughly 136-times larger than the Hamaker constant ($A_{132}=1.1\times 10^{-20}$ J). The increase in hydrophobic force in the presence of 10^{-3} M KEX is accompanied by an increase in θ from 28° in Nanopure water to 60° in the xanthate solution (see Table 2.1).

2.3 (c) Force Measurements in Xanthate Solutions Under Controlled Potential Conditions

Force measurements were also conducted by controlling the electrochemical potential of the covellite surface in a 10^{-3} M KEX solution at pH 9.2. Sodium chloride (0.01 M) was added to make the solution sufficiently conducting, and the pH was controlled by NaOH solution. In each experiment, the electrode was held at a given potential for 30 minutes to allow for xanthate to adsorb on the mineral surface, after which the circuit was open and the force measurement conducted immediately. Figure 2.4 shows the data obtained at potentials of 145, 445 and 595 mV (SHE). As shown, the measured forces are net-attractive at all potentials, indicating that xanthate adsorption rendered the surface hydrophobic. Also shown in Figure 2.4 is the force curve obtained at open circuit, in which case the potential of the covellite electrode was controlled by the mixed potential between xanthate oxidation (adsorption) and oxygen

reduction. The open circuit potential of the covellite electrode in the 0.01 M NaCl solution containing 10^{-3} M KEX at pH 9.2 was -60 mV.

At 0.01 M NaCl, the Debye length is approximately 3 nm. Therefore, the double-layer force becomes negligible at distances larger than three-times the Debye length, i.e., ~9 nm. Also, the van der Waals force becomes negligibly small at $H > 15$ nm (see Fig. 3). Therefore, the attractive forces measured at $H > 20$ nm should be considered due to hydrophobic interactions. In the present work, a power law (Eq. [3]) has been used to represent the hydrophobic force. The data obtained at open circuit, 145, 445 and 595 mV (SHE) have been fitted to Eq.[3] with $K_{132} = 1.5 \times 10^{-18}$, 4×10^{-18} , 4×10^{-17} and 7×10^{-18} J, respectively.

The hydrophobic force constants (K_{132}) obtained from the direct force measurements conducted in the present work are for the asymmetric interactions between two surfaces, i.e., glass sphere and covellite plate, having different hydrophobicities. It may be useful to convert these values to symmetric force constants, K_{131} , between covellite surfaces. This can be accomplished by using the combining rule for hydrophobic forces [20]:

$$K_{132} = \sqrt{K_{131} K_{232}} \quad [9]$$

In the present work, the value of K_{232} was determined by conducting force measurement between a glass sphere and a fused silica plate, both of which have the same water contact angle of 109° . The results showed that $K_{232} = 2 \times 10^{-16}$ J, which is somewhat smaller than the value of 2.7×10^{-16} J reported previously [20]. Substituting the values of K_{132} obtained from the force measurements and the value of K_{232} determined in the present work, the values of K_{131} have been calculated and are given in Table 2.1.

The value of $K_{131}=1.1\times 10^{-20}$ J obtained at open circuit is comparable to the Hamaker constant of the covellite ($A_{131}=1.5\times 10^{-20}$ J) estimated from the direct force measurement conducted in the present work. Note here that the value of A_{131} was obtained for the covellite in Nanopure water. In the presence of 10^{-3} M xanthate, however, its value could be lower. As the electrochemical potential was raised to 145 mV so that more xanthate could adsorb on the covellite surface, K_{131} increased to 8×10^{-20} J, which is 5.3 times larger than A_{131} . As the potential was further increased to 445 mV, where xanthate adsorption should be higher, K_{131} increased to 8×10^{-18} J, which is 533 times larger than A_{131} . These results show that xanthate adsorption renders the covellite surface hydrophobic, and that the hydrophobic force increases with increasing the adsorption density of xanthate.

Note that the K_{131} values given in Table 2.1 for the covellite-KEX system are comparable to those obtained with other solids immersed in various long-chain surfactants [8]. It is well established that short-chain thiols can adsorb on sulfide mineral surfaces forming multi-layers, which are conducive for rendering the mineral more hydrophobic [30,31]. This is different from the case of hydrophobizing oxides by adsorbing long-chain surfactants. With these surfactants, multi-layer formation is detrimental to hydrophobization because of the inverse orientation in the second layer. It is not likely that short-chain thiols such as ethyl xanthate would have inverse orientation because of the weak association between the short hydrocarbon chains. Furthermore, metal xanthates by themselves are hydrophobic [31]; therefore, multi-layer formation of metal xanthates (and/or dixanthogen) should increase water contact angle and, hence, the hydrophobic force.

Table 2.1 gives the water contact angles of the covellite electrode at different potentials. There is a reasonable correlation between the contact angles and the hydrophobic force constants, except at open circuit. In general, the higher the contact angle is, the larger the values of K_{131} and K_{132} . As the potential was increased from 145

to 445 mV, contact angle increased from 41° to 91°. This was accompanied by a ten-fold increase in K_{132} and a 100-fold increase in K_{131} . This observation can be attributed to the increased xanthate adsorption at the higher potential, as will be discussed later. When the potential was further increased to 595 mV, the contact angle decreased to 85° and K_{132} and K_{131} decreased to 7.0×10^{-18} J and 2.45×10^{-19} J, respectively. This decrease in hydrophobicity may be attributed to the oxidation of the mineral, which renders it hydrophilic due to the formation of hydrophilic oxidation product such as $\text{Cu}(\text{OH})_2$. Note that the K_{131} value observed at 145 mV was 7.3-times larger than at the open circuit; however, the contact angle decreased from 60° to 41°. This discrepancy is difficult to explain without further research.

The data given in Figure 2.4 and Table 2.1 show that hydrophobic force reaches a maximum at 445 mV. This finding agrees well with the results of the flotation tests conducted by Roos, et al. [32]. As shown in Figure 2.5, covellite begins to float at 50 mV, and reaches a maximum in the potential range of 345-445 mV. The values of K_{132} also reaches maximum in this potential range. Thus, there is a good correlation between the flotation data and the hydrophobic forces measured in the present work

Figure 2.6 shows the voltammograms of a covellite electrode obtained in a 0.01 M NaCl solution at pH 9.2 in the presence and absence of KEX. Also shown are the equilibrium contact angles measured on the covellite electrode at different potentials. The voltammogram obtained in the absence of KEX shows a sharp increase in anodic current beginning at approximately 250 mV, which is close to the reversible potential for the following reaction:



The reversible potential was calculated based on the thermodynamic data listed by Bertoci and Wagman [33]. It is possible, however, that the sulfur oxidation product

could be in the form of polysulfide rather than elemental sulfur.

In the presence of KEX, three distinct anodic waves (labeled A_1 , A_2 and A_3) that may be related to the adsorption of xanthate are observed. The anodic waves A_2 and A_3 begin at potentials of approximately 250 mV, which is close to the reversible potentials of the following reactions:



where X and X_2 represent ethyl xanthate and ethyl dixanthogen, respectively. The reversible potentials were calculated based on the thermodynamic data given by Young, et al. [34]. Therefore, the sharp increase in current above 250 mV may be attributed to either or both of these two reactions, representing copper-xanthate and dixanthate formation on the surface of covellite. The negative-going scan after the anodic sweep shows well-defined reduction waves, indicating the reduction (or desorption) of the oxidation (or adsorption) product(s) on the covellite surface.

The anodic wave A_1 is much smaller than A_2 and A_3 . However, there are unequivocal evidences that it is due to xanthate adsorption. *First*, the contact angle begins to increase at the foot of A_1 . *Second*, the cyclic voltammograms obtained with narrower scan limits (see Figure 2.7) reveal similar behavior as observed with other minerals and metals that show chemisorption of xanthates [35-37]. Thus, the anodic wave A_1 beginning at -270 mV may be due to *chemisorption*, which is the term frequently used to describe the adsorption of xanthate below thermodynamic potentials.

The results obtained in the present work represent the first direct force measurements conducted with xanthate-coated sulfide mineral surfaces. The results are

consistent with what is known on the basis of the mixed-potential theory of xanthate adsorption. The hydrophobic forces appear in the potential region where the adsorption of the collector is expected to occur. It is interesting to note that the adsorption of a short-chain thiol such as KEX can produce large hydrophobic forces. Work is currently under way to study the effects of chain length.

2.4 SUMMARY AND CONCLUSIONS

An atomic force microscope (AFM) has been used to measure the surface forces between a cleaved covellite plate and a hydrophobic glass sphere whose water contact angle is 109° . The latter may simulate the behavior of air bubbles in flotation. The forces measured in 10^{-3} M KEX solution at pH 9.2 cannot be fitted to the DLVO theory due to the large hydrophobic forces created by the adsorption of xanthate. The results show that the hydrophobic force increases with increasing electrochemical potential of the mineral electrode. From the asymmetric hydrophobic force constants K_{132} , determined from the force measurement, symmetric hydrophobic force constants K_{131} , were calculated using the geometric mean combining rule. The results showed that K_{131} changes sharply with the electrochemical potential of the covellite electrode, which in turn controls the xanthate adsorption on the mineral surface.

The voltammogram of a covellite electrode obtained in 10^{-3} M KEX solution shows an anodic wave beginning at -270 mV SHE, which corresponds to the potential at which contact angle begins to increase. At potentials above 250 mV, which is close to the thermodynamic potentials for the formation of copper ethyl xanthate and ethyl dixanthogen, both the anodic current and contact angle increase sharply. These results suggest that xanthate begins to chemisorb on covellite at -270 mV and additional xanthate adsorb above 250 mV in the form of copper ethyl xanthate and/or dixanthogen. The results of the voltammetry and contact angle measurements correlate well with the

hydrophobic force constants derived from the direct force measurements conducted in the present work. The potential at which the hydrophobic force constant reaches a maximum corresponds to the optimum potential for the flotation of covellite reported in the literature.

2.5 REFERENCES

1. Yoon, R.-H., and Mao, L., *J. Colloid Interface Sci.* **181** (1996) 613
2. Israelachvili, J. N., and Pashley, R. M., *Nature* **300** (1982) 341
3. Rabinovich, Ya. I., and Yoon, R.-H., *Colloids Surf.* **93** (1994) 263
4. Yoon, R.-H., and Ravishankar, S. A., *J. Colloid Interface Sci.* **179** (1996) 391
5. Israelachvili, J. N., and Adams, G. E., *J. Chem. Soc. Faraday Trans. I* **74** (1978) 975
6. Yoon, R.-H., and Ravishankar, S. A., *J. Colloid Interface Sci.* **166** (1994) 215
7. Senden, T. J and Ducker, W. A., *Langmuir* **10** (1994) 1003
8. Rabinovich, Ya. I., and Yoon, R.-H., *Langmuir* **10** (1994) 1903
9. Churaev, N. V and Derjaguin, B. V., *J. Colloid Interface Sci.* **103** (1985) 542
10. Biggs, S., Mulvaney, P., Zukoski, C. F., and Grieser, F., *J. Am. Chem. Soc.* **116** (1994) 9150

11. Arai, T., and Fujihira, M., *J. Vac. Sci. Technol. B* 14(2), Mar/Apr (1996)
12. Toikka, G., Hayes, R. A., and Ralston, J., *Langmuir* **12** (1996) 3783
13. Atkins, D. T., and Pashley, R. M., *Langmuir* , 9, (1993) 2232
14. Flinn, D. H., *Ph.D. Dissertation*, Virginia Polytech. Institute & State Univ., (1996)
15. Flinn, D. H., Guzonas, D. A., and Yoon, R.-H., *J. Colloids and Surf.* **87** (1994) 163
16. Xu, Z., and Yoon, R.-H., *J. Colloid Interface Sci.* **132** (1989) 532
17. Fowkes, F. M., *Ind. Eng. Chem.* **56**, (1964) 40
18. Oshima., H., Healy, T. W., and White, L. R., *J. Colloid Interface Sci.* **89** (1992) 484
19. Acar, S., and Somasundaran, P., *Minerals Engineering*, 5 No 1 (1992) 27
20. Yoon, R.-H., Flinn, D.H., Rabinovich, Y.I., ., *J. Colloid Interface Sci.* **185** (1997) 363
21. Fowkes, F. M., and Pugh, R. J., in E.D. Goodard and B. Vincent (Eds.), *Polymeric Adsorption and Dispersion Stability*. American Chemical Society, Washington D.C. 1984, p331

22. Visser, J., *Advan. Colloid. Interface Sci.* **3** (1972) 331
23. Israelachvili, J. N., "Intermolecular and Surface Forces." Academic Press (1990)
24. Laskowski, J., and Kitchener, J.A., *J. Colloid Interface Sci.* **29** (1969) 670
25. Parker, J.L., and Claesson, P.M., *Langmuir* **10**, (1994), 635.
26. Tsao, Y. H., Evans, F. D., and Wennerstrom, H., *Langmuir* **9** (1993) 779
27. Lekki ,J., and Laskowski, J., "On the Organic Effect of Frother-Collector Joint Actions in Flotation" *Trans. IMM* **80** (1971) 174
28. Yoon, R-H., and Aksoy, S., To be presented at XX International Mineral Processing Congress, Aachen, Germany, September 21-26, 1997
29. Yoon, R-H., and Aksoy, S., To be published
30. Mielczarski, J., and Yoon, R-H., in Dobby, G, S., and Rao, S, R., (Eds), *Processing of Complex Ores, Proceedings of the International Symposium on Processing of Complex Ores*, Permagon Press, 1989, Halifax
31. Poling, G, W., in Fuerstenau, M,C (Ed)., *Flotation, Vol.1*, American Institute of Mining , Metallurgical, and Petroleum Engineers, Inc., New York, 1976, Chapter 11.
32. Roos, J. R., Celis. J. P., and Sudarsono, A. S., *Int. J. Minerals. Processing*, **29** (1990) 17
33. Bertoci,U., and Wagman, D., In: Bard, J.A., Parsons,R., Jordan, J., "Standard Potentials in Aqueous Solution", IUPAC- Marcel-Deker,Inc., New York 1985
34. Young, C.A., Basilio, C.I., and Yoon, R-H., *Int. J. Minerals. Processing*, **31** (1990) 265
35. Woods, R., Young, C,A., and Yoon, R-H., *Int. J. Minerals. Processing*, **30** (1990) 17
36. Woods, R., Chen, Z., and Yoon, R-H., *Int. J. Minerals. Processing*, **50** (1997) 47
37. Woods, R., Basilio, C,I., Kim, D,S., and Yoon, R-H., *J. Electroanal. Chem.* **328** (1992) 179

Table 2.1. Effects of Electrochemical Potential on the Contact Angle of a Polished Covellite Electrode

Solution Condition	Applied Potential (mV, SHE)	Equilibrium Contact Angle (θ)	Hydrophobic Force Constants	
			$K_{132} \times 10^{18}$ J	$K_{131} \times 10^{19}$ J
Nanopure Water	-	28°	-	-
10 ⁻³ M KEX	-	60°	1.5	0.11
10 ⁻³ M KEX	145	41°	4.0	0.8
10 ⁻³ M KEX	445	91°	40	80
10 ⁻³ M KEX	595	85°	7.0	2.45

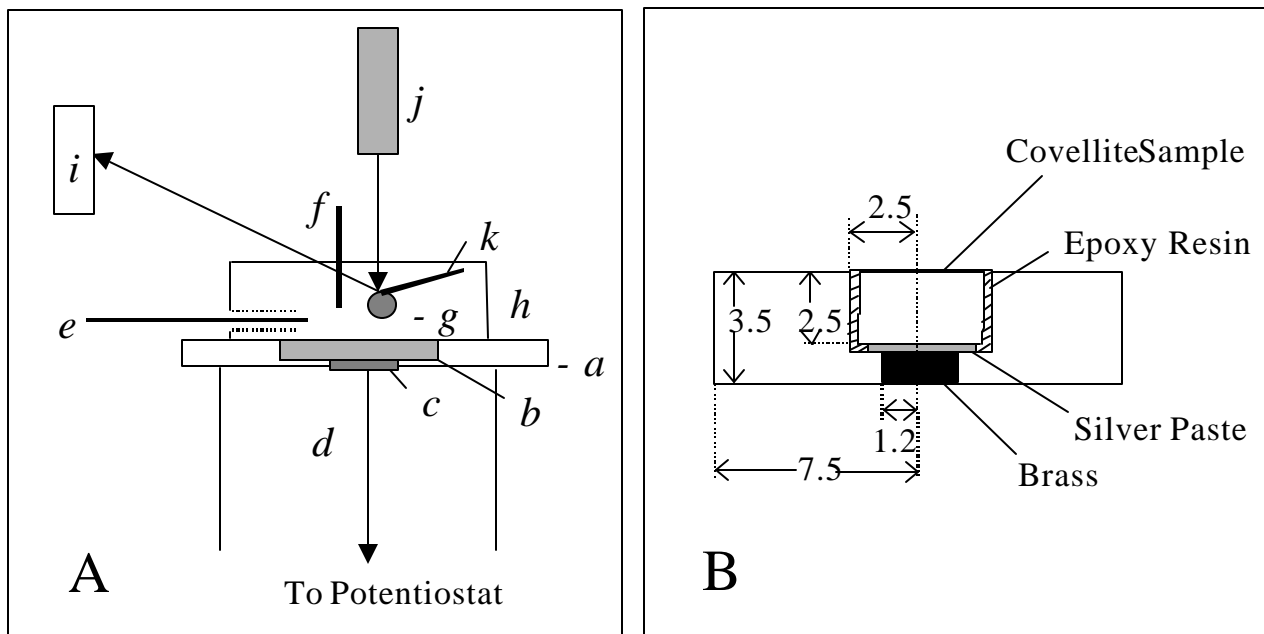


Figure 2.1. A) A schematic representation of the electrochemical AFM: a, sample holder; b, covellite sample; c, brass cylinder; d, piezo-electric base; e, Pt-reference electrode; f, Pt-counter electrode; g, hydrophobic glass sphere; h, fluid cell; i, photodetector; j, laser source; k, cantilever.
 B) Dimensions (in millimetres) of the sample holder.

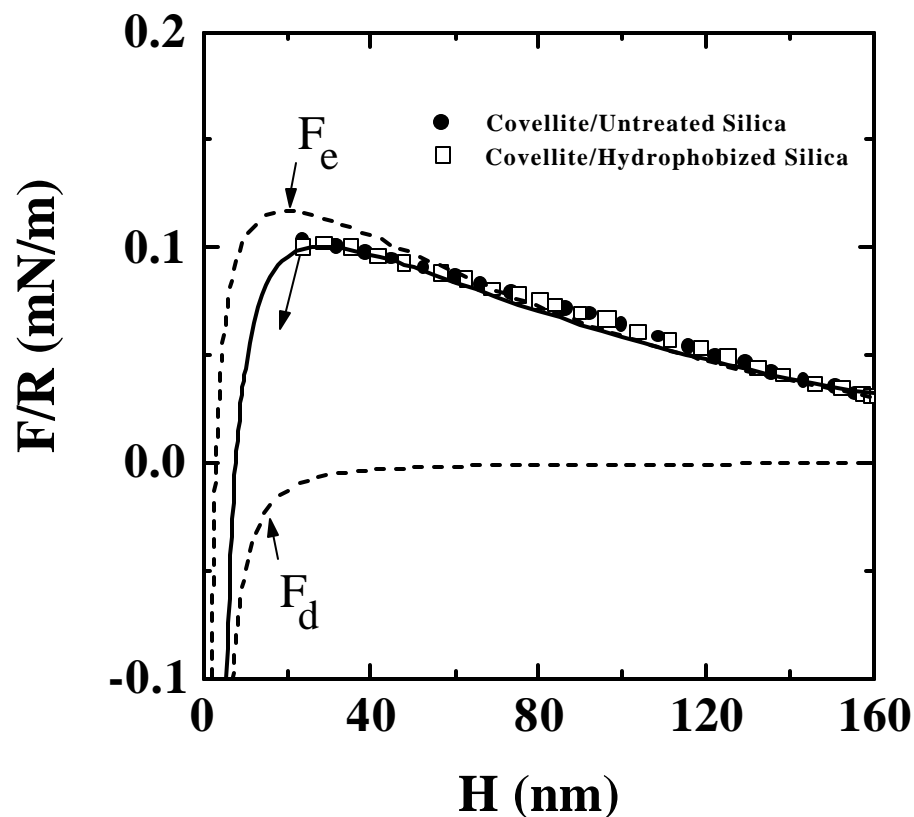


Figure 2.2. Results of the AFM force measurements conducted between i) a covellite plate ($\theta=28^\circ$) and a glass sphere ($\theta=5^\circ$) (●) and ii) a covellite plate and a hydrophobic glass sphere ($\theta=109^\circ$) (□) in Nanopure water. The force F was normalized by the radius of the sphere R and plotted versus separation distance H . The solid line represents the DLVO fit to the experimental data (constant potential model) with $\Psi_1=-45$ mV for covellite, $\Psi_2=-60$ mV for the glass sphere, $k^1=87.7$ nm and $A_{132}=1.1\times 10^{-20}$ J. The dashed lines represent the contributions from the ion-electrostatic (F_e) and dispersion (F_d) forces to F . No additional attractive force was observed.

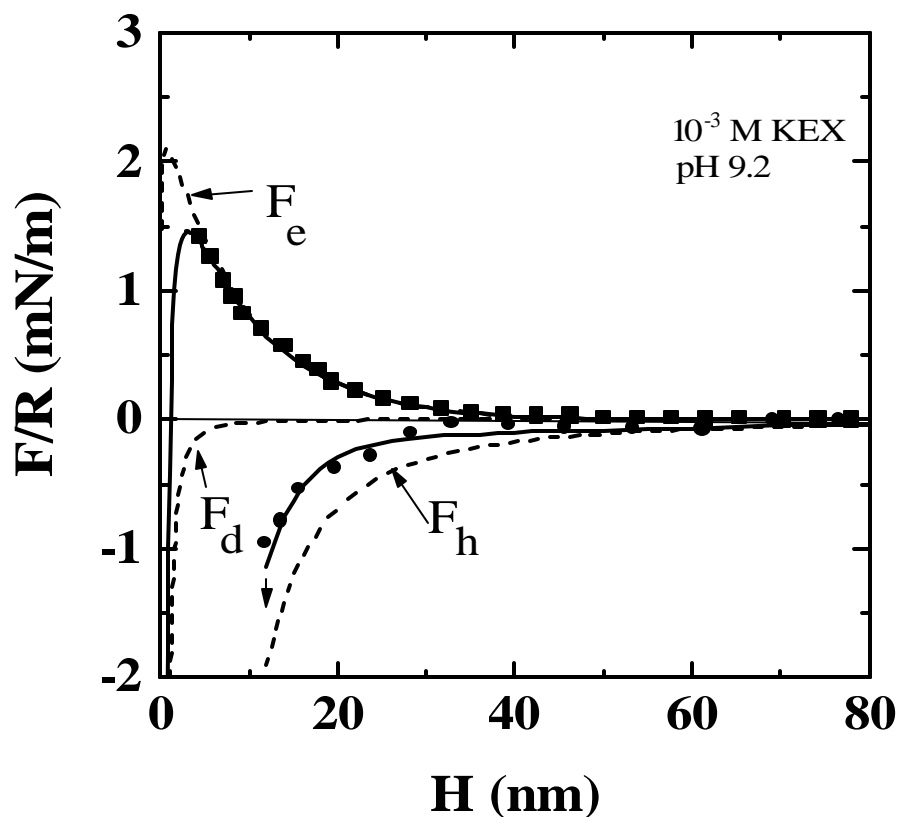


Figure 2.3. F/R vs. H curves obtained between i) ■, a covellite plate and an untreated glass sphere ($\theta < 5^\circ$), and ii) ●, a covellite plate and a hydrophobic glass sphere ($\theta = 109^\circ$) in 10^{-3} M KEX solution at pH 9.2. The force data obtained with the untreated glass sphere can be fitted to the DLVO theory with $\mathbf{Y}_1 = -67$ mV for covellite, $\mathbf{Y}_2 = -60$ mV for glass sphere and $\mathbf{k}^1 = 8.3$ nm. The results obtained with the hydrophobic glass sphere show a net attractive force due to the hydrophobic force not considered in the DLVO theory. The hydrophobic force can be fitted with a power law (Eq. [3]), with $K_{132} = 1.5 \times 10^{-18}$ J. The dashed lines represent the contributions from the ion-electrostatic force (F_e), dispersion force (F_d), and hydrophobic force (F_h).

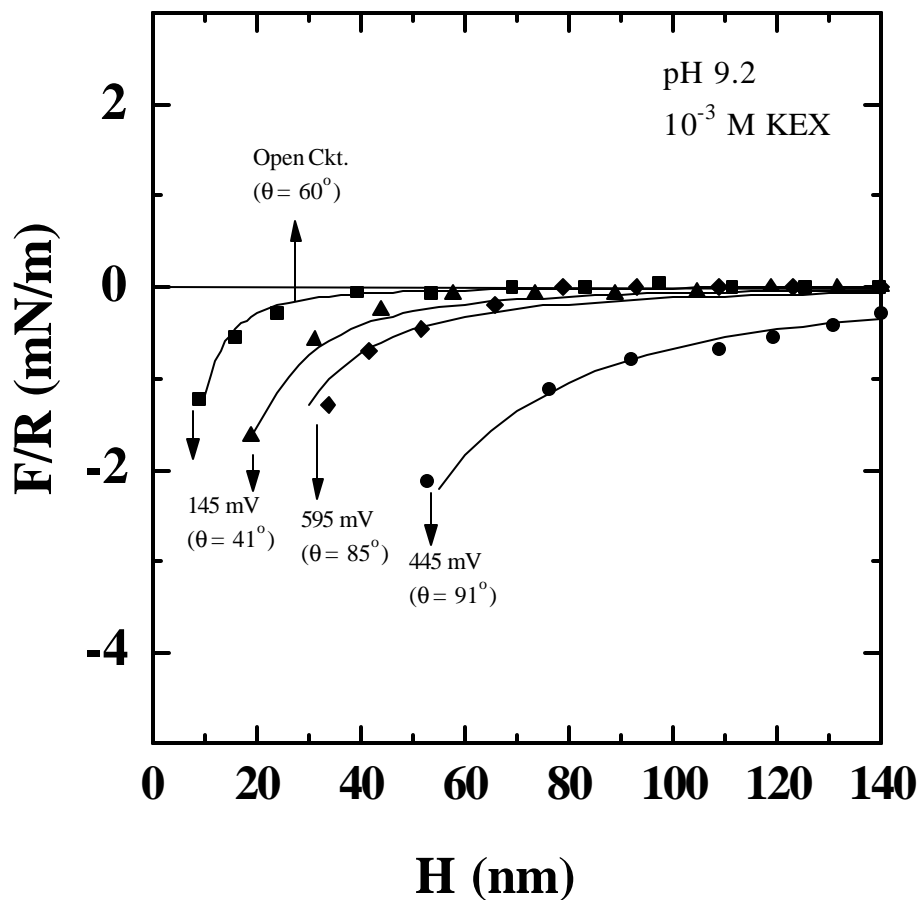


Figure 2.4. F/R vs. H curves obtained between a silanated glass sphere and a covellite plate in 10^{-3} M KEX solutions at pH 9.2 under different applied potential conditions. The hydrophobic forces have been fitted with a power law (Eq. [3]), with $K_{132} = 1.5 \times 10^{-18}$, 4×10^{-18} , 4×10^{-17} and 7×10^{-18} J at open circuit, 145, 445 and 595 mV (SHE), respectively. The values of the equilibrium contact angles on covellite at different potentials are given in Table 2.1.

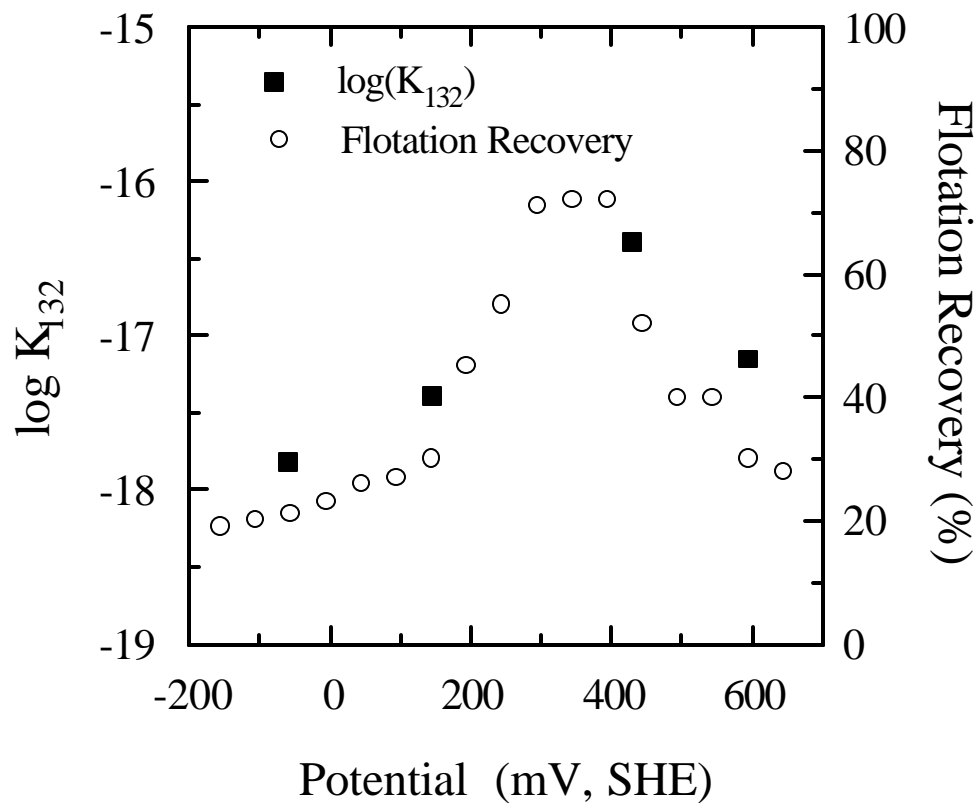


Figure 2.5. The hydrophobic force constants, K_{132} , for the asymmetric interactions between covellite **1** and silanated glass sphere **2** in water **3**, plotted versus the potential applied to the covellite electrode. Also shown for comparison are the recoveries of covellite floated at different applied potentials [32].

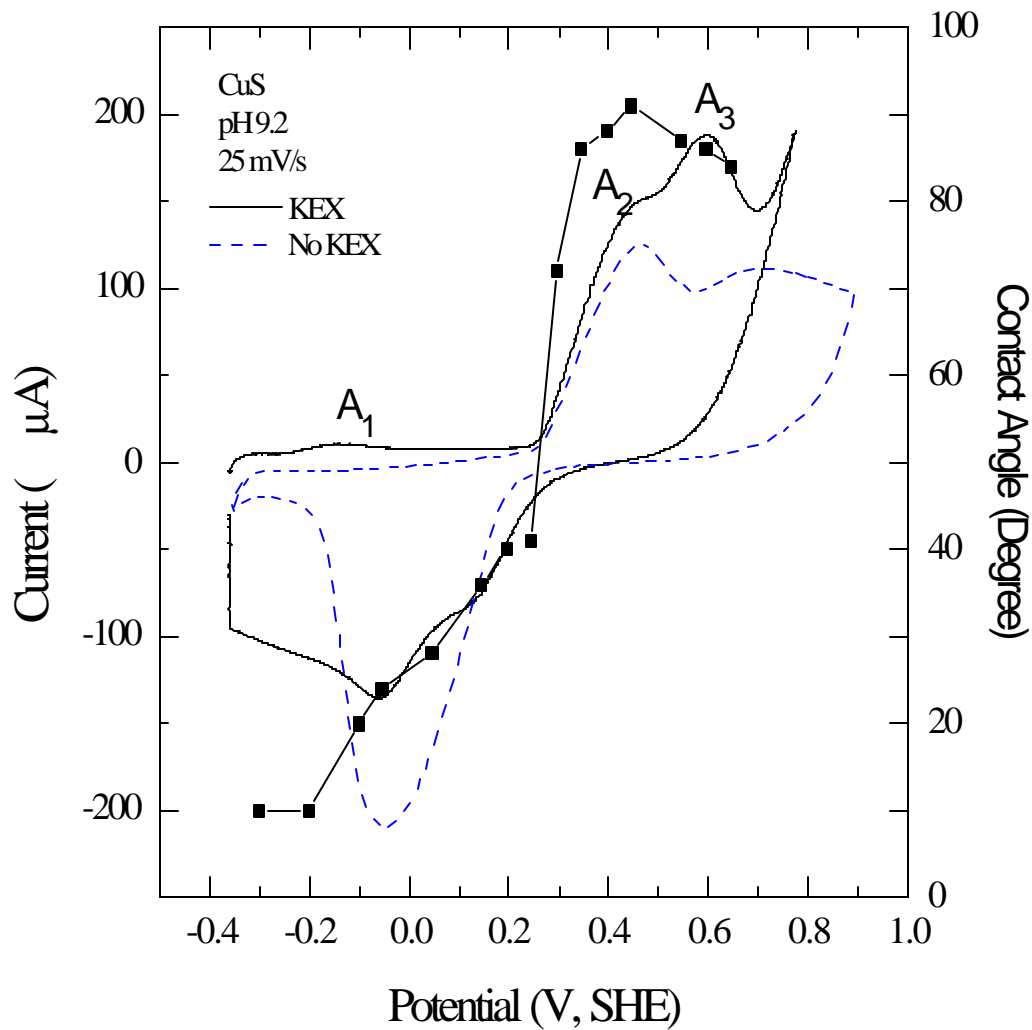


Figure 2.6. The voltammograms obtained at a 25 mV/s scan speed in 0.01 M NaCl solutions at pH 9.2. The contact angles of the covellite electrode measured at different potentials are superimposed.

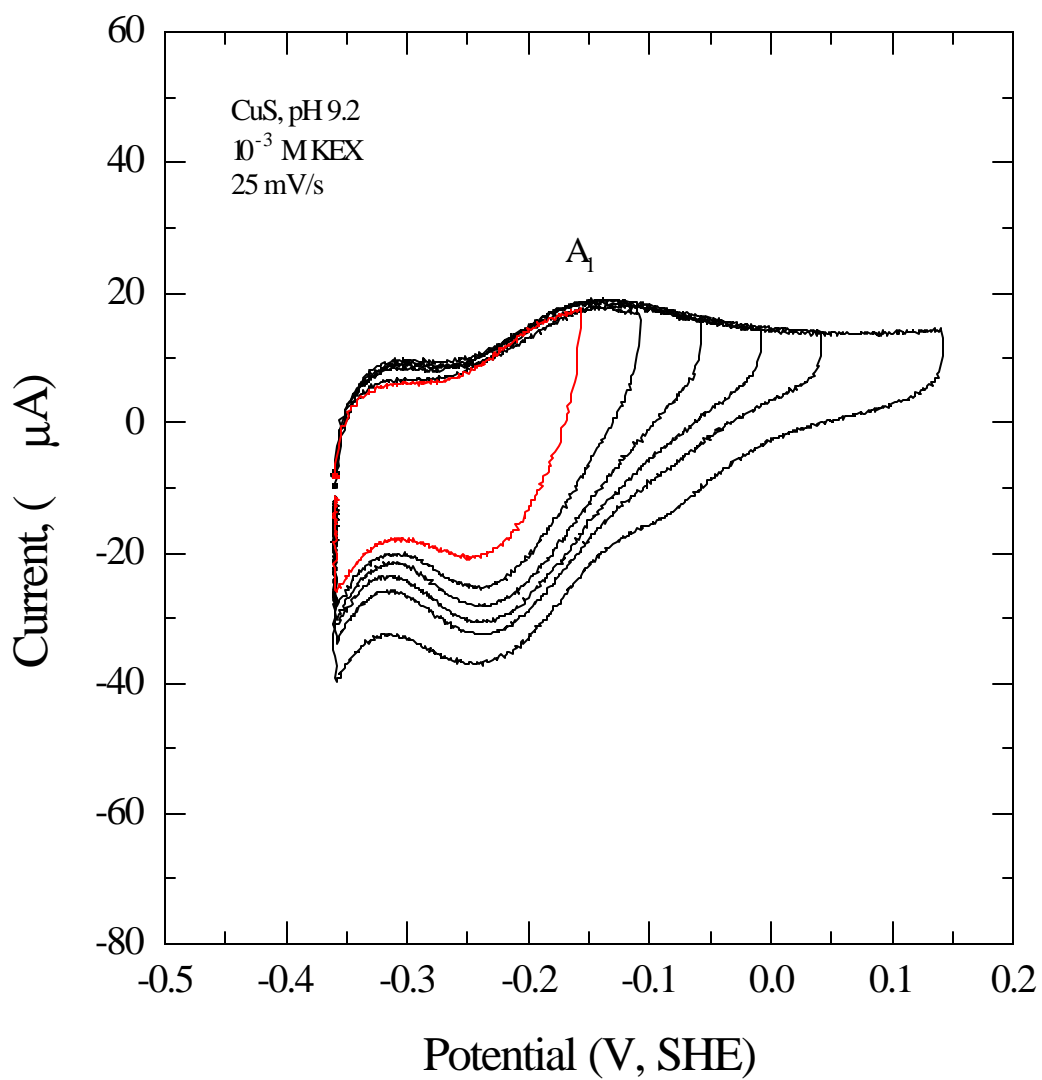


Figure 2.7. Cyclic voltammograms of a covellite electrode obtained at a 25 mV/s scan speed in 10^{-3} M KEX at pH 9.2 with different upper potential limits.