

Surface Chemistry of Carbonaceous Gold Ores, II. Effects of Organic Additives on Gold Adsorption from Cyanide Solution

G.M.K. ABOTSI and K. OSSEO-ASARE

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

(Received January 4, 1984; accepted after revision December 7, 1986)

ABSTRACT

Abotsi, G.M.K. and Osseo-Asare, K., 1987. Surface chemistry of carbonaceous gold ores, II. Effects of organic additives on gold adsorption from cyanide solution. *Int. J. Miner. Process.*, 21: 225-239.

The effects of model surface active organic compounds (dodecylamine (DDA), tricaprylmethylammonium chloride (Aliquat 336), sodium dodecylsulfate (SDS) and dinonylnaphthalene-sulfonic acid (HDNNS)) on gold adsorption by Prestea (Ghana) carbonaceous gold ore were investigated with the aid of adsorption and electrophoretic mobility experiments. The influence of SDS on the uptake of gold by the carbon extract obtained from the ore was also studied. The results indicate that gold uptake in aqueous cyanide solution is enhanced markedly by Aliquat 336 and slightly by DDA or SDS, while HDNNS has a strong opposite effect. Gold loading was also reduced by 37% when pretreatment with hexane was used. The influence of the additives on gold uptake is interpreted in terms of coulombic and hydrophobic interactions between the surfactants and the solid surface, competition between the organic reagents and the aurocyanide complex for interfacial sites, as well as electrostatic and chemical interactions between the adsorbed additives and the aurocyanide complex.

INTRODUCTION

Several techniques have been employed in attempts to counteract the deleterious effects of carbonaceous materials during the recovery of gold (1-5). There are a number of reports in the literature of the use of organic additives, such as kerosene and heavy machine oils, as inhibitors of gold adsorption. However, the experimental conditions and procedures are not adequately documented and the exact mechanisms by which these hydrocarbon solvents inhibit gold adsorption are still obscure. Most of the published data involve complex and poorly characterized organic solvents. For example, kerosene is a mixture of straight chain hydrocarbons, cyclohexanes, cyclopentanes, bicyclic aromatic hydrocarbons (naphthalenes) having twelve to sixteen carbon atoms

per molecule (6, 7). Machine oils also contain a variety of hydrocarbons with sixteen to thirty-five carbon atoms per molecule whose general formula ranges from C_nH_{2n-4} to C_nH_{2n-12} (6, 7).

The present work is therefore aimed at a systematic investigation of the effects of relatively well defined organic additives on aurocyanide uptake by carbonaceous gold ores. The ore used for this research was obtained from the Prestea goldfield of Ghana. The previous paper in this series (8) reported on the characterization of this ore and examined its interaction with aurocyanide solutions. The following surfactants were used as model additives: dodecylamine (DDA), Aliquat 336 (tricaprylmethylammonium chloride, a quaternary amine), sodium dodecylsulfate (SDS) and dinonylnaphthalenesulfonic acid (HDNNS). Dodecylamine and sodium dodecylsulfate are aqueous soluble surfactants whose adsorption behavior at the solid/water interface has been well established in the literature (9–13). Aliquat 336 and HDNNS, which are insoluble in water but readily soluble in organic solvents, have been studied extensively in the solvent extraction literature (14–17).

The organic compounds used in this research were chosen on the basis of their possible interactions with the carbonaceous ore and/or the aurocyanide complex ($Au(CN)_2^-$). Sodium dodecylsulfate (SDS) and dinonylnaphthalenesulfonic acid (HDNNS) were selected with two possible effects in mind. Firstly, it was expected that these compounds would initially adsorb on the solids as anionic species thereby imparting a negative charge to the solid/aqueous interface. The electrostatic repulsion between the highly charged negative solid surfaces and the $Au(CN)_2^-$ anion might then prevent the adsorption of the aurocyanide ion. Secondly, it was expected that these organic additives would coat the surface of the ore and, by limiting the number of available surface sites, inhibit gold uptake. Aliquat 336 was chosen with the view that, being a cationic reagent, it might adsorb preferentially on the negatively charged solid surface, thereby inhibiting $Au(CN)_2^-$ adsorption. It was also of interest to compare the behavior of Aliquat 336 with that of dodecylamine, a surfactant which exhibits pH-dependent ionization behavior (11–13).

EXPERIMENTAL

The characterization of the Prestea (Ghana) carbonaceous gold ore and its derivatives and the preparation of the aurocyanide solution have been presented in the previous paper (8). The material designated as the carbon fraction was obtained by leaching out the inorganic constituents of the carbonaceous ore with concentrated acids. The ground carbonaceous gold ore sample used in this research had a specific surface area of $5.2 \text{ m}^2 \text{ g}^{-1}$; the corresponding value for the carbon extract was $30.2 \text{ m}^2 \text{ g}^{-1}$ (8). Dodecylamine (98%) and sodium dodecylsulfate (99%) were obtained from Aldrich Chemical Company and BHD Chemicals, respectively. The as-received Aliquat 336 (Henkel Corp.)

was purified following the method described by Sato and Watanabe (17) and its concentration was determined using the Volhard method (18). Commercial HDNNS (King Industries) was purified using the method suggested by Danesi et al. (19) and its concentration was obtained by potentiometric titration with standard NaOH solution.

A 10^{-4} kmol m^{-3} aqueous solution of DDA was prepared following the procedure of Joy and Watson (11). The solution was successively diluted to 10^{-8} kmol m^{-3} with doubly distilled water. Similar solutions of SDS in doubly distilled water and Aliquat 336 and HDNNS in hexane were prepared.

Adsorption experiments

To examine the effects of dodecylamine and sodium dodecylsulfate on gold uptake, appropriate volumes of the respective aqueous surfactant solutions were added to measured volumes of gold cyanide solution to obtain 25.0 cm^3 samples containing DDA or SDS and $2.3 \cdot 10^{-3}$ kmol m^{-3} NaCN and $5.3 \cdot 10^{-4}$ kmol m^{-3} Au. Each solution (pH 10) was shaken with 1.0 g of the carbonaceous gold ore for 24 h (at $24 \pm 2^\circ\text{C}$) after which it was filtered, and the filtrate analyzed for gold using atomic absorption spectrophotometry. The experiment was repeated with 0.172 g of the carbon extract in SDS solution containing the same CN^- and Au concentrations as above.

In the case of Aliquat 336 and HDNNS, 1.0 g of the ore sample was agitated with 25.0 cm^3 of the respective hexane solutions for 24 h after which each solution was distilled off using a rotary evaporator. The solids were dried (12 h) at room temperature ($24 \pm 2^\circ\text{C}$) and 25.0 cm^3 of the gold cyanide solution ($2.3 \cdot 10^{-3}$ kmol m^{-3} NaCN and $5.3 \cdot 10^{-4}$ kmol m^{-3} Au) added to each of the surfactant-pretreated carbonaceous ore samples (1.0 g each). Each slurry was adjusted to pH 10, using reagent grade KOH solution. The samples were then equilibrated by shaking them for 24 h. After the 24 h conditioning period, the mixtures were filtered and each filtrate was analyzed for its gold content using atomic absorption spectrophotometry. Pretreatment of the ore with Aliquat 336 or HDNNS before gold cyanide adsorption, a technique which was an adaptation of the method used by Dorfman (5), was necessary to ensure adequate contact of the ore particles with the organic phase.

Electrophoretic mobility measurements

The effects of the organic additives (DDA, Aliquat 336, SDS and HDNNS) on the surface charge of the carbonaceous gold ore were determined by conducting electrophoretic mobility measurements on the ore samples. In the case of DDA and SDS, 25.0 cm^3 aqueous solutions containing various concentrations of the surfactants and 1.0 g each of the ore were shaken for 24 h (to enable adsorption of the organic additives onto the solids) followed by filtration and

drying ($24 \pm 2^\circ\text{C}$) of the particles for about 12 h. Organic solutions (25.0 cm^3 , different concentrations, hexane as solvent) of Aliquat 336 and HDNNS were similarly treated (24 h agitation) with 1.0 g each of the ore followed by vacuum distillation of the solvent and drying ($24 \pm 2^\circ\text{C}$, about 12 h) of the solids. After drying, 100 mg of each pretreated solid sample was dispersed in 1000 cm^3 of aqueous solution containing $10^{-3}\text{ kmol m}^{-3}\text{ KNO}_3$ for ionic strength control. A 75.0 cm^3 portion of each slurry was taken and its pH adjusted to pH 10 with KOH solution. These slurries were then equilibrated by shaking them for 3 h after which electrophoretic mobilities were obtained as described previously (8).

RESULTS

Fig. 1 presents the effects of the various organic reagents on gold adsorption by the carbonaceous ore. As can be observed from these results, the organic additives investigated produced three distinct effects on gold uptake: the presence of dodecylamine or sodium dodecylsulfate led to only a slight increase in gold uptake, Aliquat 336 enhanced gold adsorption, while HDNNS had a pronounced adverse effect on gold uptake. A striking feature of these results is that in the absence of the surfactants, gold uptake is decreased by about 37% when hexane pretreatment is used, the gold adsorption densities being 26.7 and $42.3\text{ }\mu\text{mol m}^{-2}$, respectively, with and without the hexane pretreatment. The effect of SDS concentration on the adsorption of gold by the carbonaceous ore and the carbon extract is shown in Fig. 2. In these adsorption experiments, both samples had the same total surface areas. Fig. 2 therefore indicates that the carbonaceous ore is more active as a gold adsorbent than the carbon extract in the presence of SDS and, by extrapolation, in its absence as well. The less active behavior of the carbon extract has been attributed to the modification of the surface functional groups by the extraction process used to isolate it from the carbonaceous ore (8). Fig. 2 further demonstrates the previous observation (see Fig. 1) that the presence of SDS enhances gold uptake from cyanide solution.

Fig. 3 indicates that the electrophoretic mobility of the Prestea carbonaceous gold ore is independent of DDA concentration. On the other hand, the solid surface becomes less negatively charged with increase in the concentration of Aliquat 336, while the opposite effect is observed for increasing concentrations of SDS and HDNNS. At higher concentrations, HDNNS depresses the electrophoretic mobility more than SDS. Further, it can be seen from Fig. 3 that at low organic reagent concentrations (e.g. $10^{-7}\text{ kmol m}^{-3}$) and for pH values in the range 9–10, the electrophoretic mobility is approximately the same (i.e. about $-2.7\text{ }\mu\text{m s}^{-1}\text{ per V cm}^{-1}$) for both the pretreated and untreated ore particles.

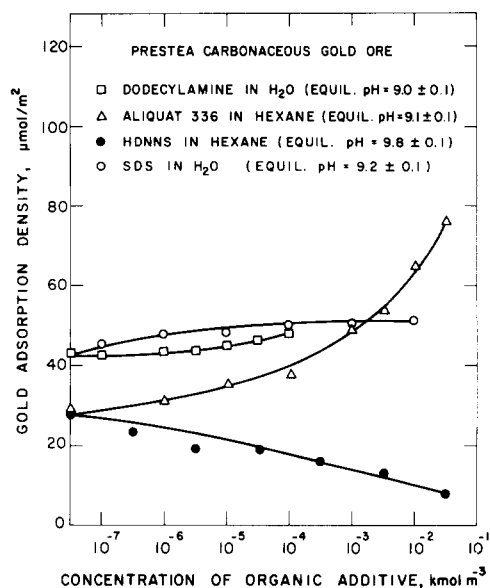


Fig. 1. Effects of the model organic additives on gold adsorption by Prestea carbonaceous gold ore. Initial conditions: $[\text{Au}] = 5.3 \cdot 10^{-3} \text{ kmol m}^{-3}$, $[\text{CN}^-] = 2.3 \cdot 10^{-4} \text{ kmol m}^{-3}$, pH = 10.

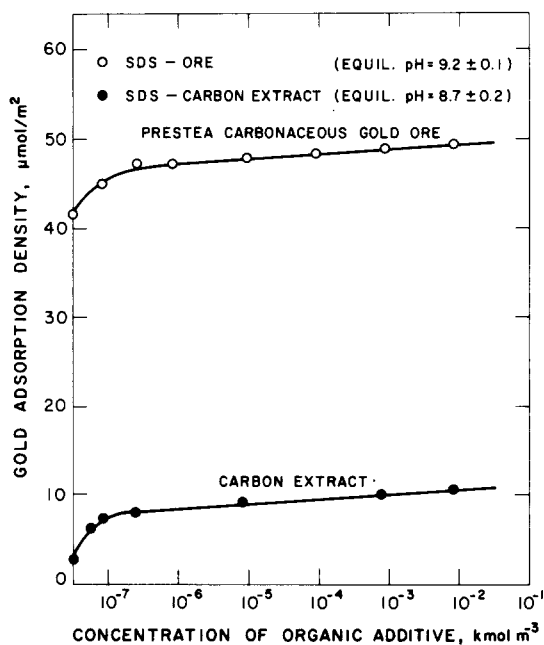


Fig. 2. Effects of sodium dodecylsulfate on gold cyanide adsorption by Prestea carbonaceous gold ore and its carbon extract. Initial conditions: $[\text{Au}] = 5.3 \cdot 10^{-4} \text{ kmol m}^{-3}$, $[\text{CN}^-] = 2.3 \cdot 10^{-3} \text{ kmol m}^{-3}$, pH = 10.

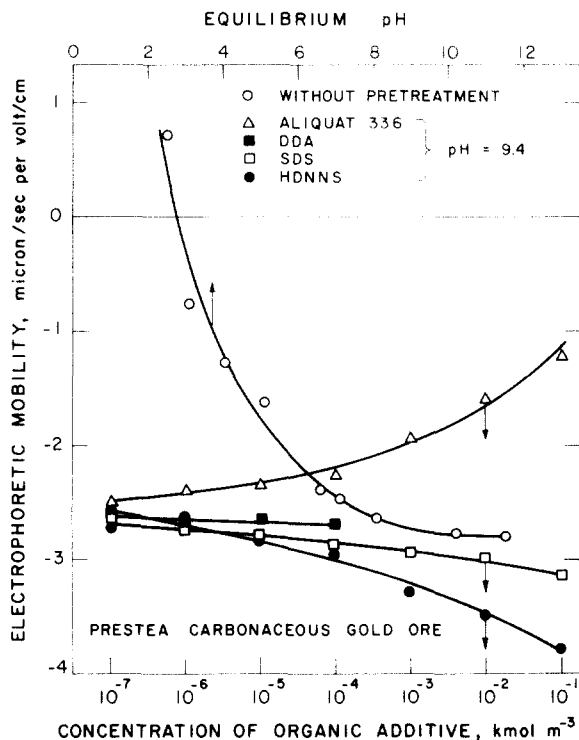


Fig. 3. Electrophoretic mobility of Prestea carbonaceous gold ore as a function of pH or surfactant concentration.

DISCUSSION

Adsorption of organic compounds at the solid/oil and solid/water interfaces

The adsorption of a surfactant onto a solid is controlled by the free energy change (20, 21):

$$\Delta G_{\text{ads}} = \Delta G_{\text{coul}} + \Delta G_{\text{spec}} \quad (1)$$

The electrostatic term, ΔG_{coul} , has been defined previously (8) and is due to the interaction between the charge of the adsorbate and the electrical double layer potential. The specific adsorption energy term, ΔG_{spec} , consists of several contributing terms (20, 21):

$$\Delta G_{\text{spec}} = \Delta G_{\text{HM}} + \Delta G_{\text{CH}_2} + \Delta G_{\text{H}} + \Delta G_{\text{solv}} + \Delta G_{\text{chem}} \quad (2)$$

where ΔG_{HM} accounts for the interactions between the adsorbed hydrocarbon chains, ΔG_{CH_2} is a contribution arising from the hydrophobic interaction of the hydrocarbon chains with the solid surface and ΔG_{H} is due to hydrogen bonding between the surface sites and the functional groups on the organic compounds.

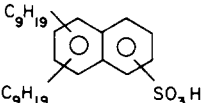
ORGANIC ADDITIVE	STRUCTURE	MOLECULAR WEIGHT
DDA	$\text{CH}_3 (\text{CH}_2)_{11} \text{NH}_2$	185.4
SDS	$\text{CH}_3 (\text{CH}_2)_{11} \text{OSO}_3 \text{Na}$	288.4
ALIQUAT 336	$\left[\begin{array}{cc} \text{R} & \text{R} \\ & \text{N} \\ \text{R} & \text{CH}_3 \end{array} \right]^+ \text{Cl}^-$ $\text{R} = \text{C}_8 \text{ OR } \text{C}_{10}$	442 (AVG.)
HDNNS		460.1

Fig. 4. Structures of the organic compounds used in this study.

The solvation (ΔG_{solv}) and chemical (ΔG_{chem}) terms retain their previous meanings (8).

The interaction of the organic compounds studied in this research with the surfaces of the carbonaceous ore and the carbon extract may be better understood from a knowledge of their chemical structures (as depicted in Fig. 4) and their solution chemistry. The molecular weights range from $185.4 \text{ g gmol}^{-1}$ for dodecylamine to $460.1 \text{ g gmol}^{-1}$ for HDNNS. It must be recalled that DDA and SDS are both aqueous soluble whereas Aliquat 336 and HDNNS are aqueous insoluble surfactants. Several reports have shown that SDS is adsorbed by a variety of solids such as hematite (9) and activated carbon (10), and that sodium laurate (22) and sodium dodecylsulfonate (23) are adsorbed by quartz and alumina, respectively. The adsorption of alkylbenzenesulfonates on activated carbon has also been reported (24). Similarly, DDA is known to adsorb on oxides such as hematite and quartz (11–13), and HDNNS is adsorbed by Fe(III) and Ni(III) oxides (26).

In their study of the adsorption of SDS on hematite, Shergold and Mellgren (9) observed that the zeta-potential of hematite becomes more negative as the concentration of SDS is raised and that SDS is specifically adsorbed, with the ΔG_{HM} and ΔG_{chem} terms dominating. On the contrary, the adsorption of sodium dodecylsulfonate on alumina (23) is controlled by the coulombic energy term, ΔG_{coul} , arising from the attraction between the positively charged alumina surface and the negatively charged sulfonate polar groups. Thus whereas SDS adsorbs on hematite at pH values above the isoelectric point (iep), sodium dodecylsulfonate adsorption on alumina occurs only below the corresponding

iep. It is clear, therefore, that specific effects are operating in the SDS-hematite system while they are absent in the case of the sodium dodecylsulfonate-alumina system. The hydrolytic behavior of DDA has a strong influence on its interfacial activity (11-13,25). Joy and Watson (11) observed that at low pH values, DDA is protonated to form dodecylammonium ions, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+$, whose adsorption on hematite between pH 5.8 (iep) and pH 7.0 is principally due to the ΔG_{coul} contribution, while the adsorption of neutral DDA molecules on negatively charged hematite particles at high pH values is controlled by the hydrogen bonding, ΔG_{H} , term. Fuerstenau (13) has also shown by zeta-potential measurements that the adsorption of dodecylammonium acetate at the quartz/solution interface is strongly dependent on pH. The zeta-potential steadily decreased from zero (at pH 3.7) to about -120 mV at pH 9, became positive between pH 9 and pH 10 and then reversed to negative values above pH 11. According to Fuerstenau (13), adsorption of dodecylammonium cations occurs below pH 10, and the presence of large quantities of these cations in the Stern layer enables hemi-micelle formation between pH 9 and pH 10, thereby imparting a positive charge to the quartz surface. The reversal of the zeta-potential to negative values above pH 11 is attributable (13) to the predominance of neutral dodecylamine molecules in this pH range. Other investigators (12) have reported that maximum flotation of quartz with dodecylamine occurs around pH 10 and that at this pH, maximum amounts of both cationic aminium dimer and amine-aminium complexes are formed.

From the foregoing discussions, it is clear that (a) adsorption of positively charged organic compounds on negatively charged solids or vice versa is dominated by the ΔG_{coul} contribution arising from the oppositely charged species, and (b) the ΔG_{spec} term is more important when the adsorbate is uncharged or when the solid and the organic adsorbent have similar charges.

As previously reported (8), the carbonaceous gold ore used in this research contains a variety of inorganic minerals such as quartz and aluminosilicates (52.6% SiO_2 , 14.6% Al_2O_3 , 6% Fe_2O_3) and about 5% total carbon. The major carbonaceous fraction is the carbon extract (3.9%) followed by the hydrocarbon extract (0.27%). The carbon extract contains 59.4% C and 10.6% Al_2O_3 , while the hydrocarbon extract analyzes 66.9% C, 10.5% H, 1.7% O and 18.2% S. The infrared spectrum of the hydrocarbon extract showed the presence of CH_3 , CH_2 , CH and C=O groups (8). Thus the surfaces of the carbonaceous gold ore and the carbon extract consist of a composite of organic and inorganic materials. Therefore on the basis of the adsorption results reported in the literature for activated carbon and various oxides (9-13, 20-26) it would be expected that the surfactants used in this work (i.e., SDS, HDNNS, DDA and Aliquat 336) would adsorb on carbonaceous gold ores. The electrophoretic mobility and the gold uptake results (Figs. 1-3) confirm this.

Effect of hexane

As was noted above, gold uptake is depressed by 37% when, during the pretreatment operation, hexane is used as the solvent instead of water. Hexane must have been adsorbed onto the ore, the free energy change for the adsorption being mainly due to the ΔG_{CH_2} term, since the hydrocarbon molecules (hexane, $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$) will be adsorbed onto the solid as a result of hydrophobic interaction between the molecule and the organic groups on the solid surface. Being hydrophobic, the adsorbed hexane molecules will prevent the approach of the hydrophilic $\text{Au}(\text{CN})_2^-$ anion onto the solid surface. In addition, there is no mechanism by which the $\text{Au}(\text{CN})_2^-$ complex can hydrogen bond with the adsorbed hexane species.

Effects of dodecylamine and Aliquat 336

Figure 1 indicates that gold adsorption increases rapidly as the Aliquat 336 concentration is raised whereas only a slight increase is observed in the case of DDA. The different effects of the two amines could be due to two factors: (a) the nature (whether neutral or charged) of the adsorbed organic surfactant, and (b) the amount of surfactant adsorbed.

At pH values below about 10.5, DDA exists as positively charged aminium ions, aminium dimers and amine-aminium complexes as well as neutral undissociated molecules (11–13). Thus the interaction of this surfactant with the carbonaceous gold ore particles would be expected to involve several mechanisms such as hydrophobic interactions with the organic groups on the ore surface, hydrogen bonding between the nitrogens of the amine and the aminium complexes and electronegative atoms (such as inorganic and organic oxygen atoms) on the ore surface and attractive coulombic interactions between the positively charged species (i.e. the aminium ions, the aminium dimers and the amine-aminium complexes) and the negatively charged ore surface. Thus after the pretreatment steps the ore surface can be visualized as containing adsorbed neutral DDA molecules as well as positively charged derivatives of DDA. As in the case of DDA, the adsorption of Aliquat 336 by the ore particles will involve both specific and coulombic energy terms. A major difference however arises from the fact that whereas the extent of ionization of DDA is pH-dependent, Aliquat 336 is cationic over the entire pH range. The ore surface will become less negatively charged due to the electrostatic attraction between the positively charged quaternary ammonium ion of Aliquat 336 and the negative ore surface. According to the electrophoretic mobility results (Fig. 3), Aliquat 336 adsorption results in a less negatively charged surface. On the other hand, DDA has very little effect on the surface charge density of the ore particles. It should be noted that while the adsorption experiments were conducted with DDA-containing aurocyanide solutions, the electrophoretic

mobility experiments used DDA-free aurocyanide solutions and carbonaceous ore particles containing pre-adsorbed DDA. It may be argued that the insignificant effect of DDA on the electrophoretic mobility of the ore particles is attributable to the desorption of the amine species into the originally DDA-free solution. However, similar electrophoretic mobility trends were obtained when DDA-containing aurocyanide solutions were used with a different batch of carbonaceous ore (27). Thus it is believed that the different effects of DDA and Aliquat 336 on the electrophoretic mobility reflect, in part, the greater cationic nature of the quaternary amine. The electrophoretic mobility results also suggest that there is a greater adsorption of Aliquat 336 in comparison with DDA. According to Traube's rule (28), the extent of adsorption of an organic compound on a solid is directly related to the chain length (or size) of the organic adsorbate. Comparison of the sizes of DDA (mol. wt. = 185.4) and Aliquat 336 (average mol. wt. = 442) shows that the latter compound is far larger than DDA and Aliquat 336 should therefore adsorb onto the ore to a greater extent than the primary amine (DDA) and its derivatives.

Thus as a result of the favorable electrostatic interaction, adsorption of the anionic aurocyanide complex would be enhanced by the presence of the pre-adsorbed cationic Aliquat 336. In this way, this quaternary ammonium surfactant acts as an activator (20) for gold cyanide adsorption. On the other hand, the presumed smaller interfacial concentration of DDA species coupled with the smaller fraction of cationic DDA species compared with Aliquat 336, apparently results in a lower tendency for the aurocyanide ion to adsorb onto the DDA-pretreated ore.

Effects of SDS and HDNNS

Unlike DDA which forms cationic and neutral species in solution and Aliquat 336 which is entirely cationic, both SDS and HDNNS are anionic. In aqueous environments, these surfactants will dissociate according to:



Since the carbonaceous ore is negatively charged, there will be electrostatic repulsion between the anionic polar groups of the surfactant molecules and the solid surface. Consequently, SDS and HDNNS will encounter an unfavorable electrostatic energy situation in the presence of the negatively charged solid surfaces and positive adsorption will therefore depend heavily on specific interactions.

Both SDS and HDNNS will be adsorbed through hydrophobic interactions among their respective non-polar radicals and between the non-polar groups and the organic groups on the solid surfaces. Comparison of the SDS and

TABLE I

Typical composition of a waste paper-mill solution (29)

Material	Percent
Lignin (as lignosulfate)	50-65
Sugars	15-22
Sugar sulfonic acids	5- 8
Calcium (as CaO)	7-10
Sulfur (as SO ₂)	8-12
Volatile organic acids	3

HDNNS structures (Fig. 4) shows that the latter compound is the larger of the two. It should also be noted that HDNNS has two benzene rings (SDS has none) and that the effect of each benzene ring on enhancing the adsorption of a surfactant is roughly equal to three times the effect of one CH₂ group in the alkyl chain (20). HDNNS should therefore adsorb onto the ore particles to a greater extent than SDS, a prediction which is confirmed by the electrophoretic mobility results (Fig. 3): for example, the ore particles are much more negatively charged at 10^{-2} kmol m⁻³ surfactant concentration in the presence of HDNNS, than in the case of SDS. The smaller negative charge on the SDS-treated ore could also be due in part to desorption of some of the adsorbed aqueous soluble SDS molecules from the surface of the SDS-pretreated ore particles when they were dispersed in water for the electrophoretic mobility measurements. However, as was found in the case of DDA, use of SDS-containing aurocyanide solution gave a similar trend in electrophoretic mobility behavior, i.e., the presence of SDS in the aurocyanide solution had little effect on the surface charge of the particles (27). The forces responsible for the reduced gold adsorption in the presence of HDNNS must be the coulombic repulsion between the Au(CN)₂⁻ anion and the strongly negatively-charged surface of the HDNNS-treated solid.

The effect of HDNNS on gold uptake is similar to that observed for waste paper-mill liquors, which also decrease gold adsorption as was observed by Leaver and Woolf (4). Table I presents a typical composition of a waste paper-mill solution (29). As can be observed from this table, such liquors contain high amounts of organosulfates and organosulfonic acids. There are also different types of sugars, the simplest being glucose (C₆H₁₂O₆) (30). More complex sugars, such as lignin, can be derived from the polymerization of glucose; polymers of glucose have the general structure (C₆H₁₀O₅)_n where $n=1000$ or more (30). Thus a waste paper-making solution can be visualized as containing high molecular weight organo-sulfates and organo-sulfonic acids, which should have high adsorption densities on carbonaceous gold ores, with the consequent high magnitudes of negative charge densities on the ores.

Since SDS adsorbs to a lesser extent than HDNNS (see Fig. 3) one would not expect this aqueous-soluble surfactant to decrease gold adsorption substantially. The apparent increase in gold uptake in the presence of SDS (see Fig. 1) is, however, unexpected. This behavior suggests possible interaction between the aurocyanide complex and SDS. As explained previously (8), aurocyanide adsorption onto a negatively charged solid surface is a result of specific chemical interactions between this anionic complex and oxygen containing functional groups on the surface. The possibility of the gold cyanide complex being converted to neutral, less soluble compounds of the type $M^{n+} [Au(CN)_2]_n$ where $M = Na^+, K^+, H^+$ or Ca^{2+} and subsequently adsorbed, or the neutral compounds being reduced to gold cluster complexes, $Au(CN)_{(x)}$ (where $0.2 \leq x \leq 0.33$) after adsorption, has been discussed (8, 31). Zaitseva et al. (32) have also proposed that $Au(CN)_2^-$ forms complexes of the type $Na_2Au(CN)_2RX$ in the presence of humic acids where X is COO^- or CO^- . In the present investigation a specific chemical interaction between $Au(CN)_2^-$ and the functional groups of the adsorbed organic additives cannot be ruled out and may explain the gold adsorption behavior in the case of SDS, since Na^+ ions (from dissociation of adsorbed SDS) will be available for the formation of compounds of the form $Na_2Au(CN)_2RX$, where X, in this case, is $-OSO_3^-$. Such neutral compounds would be adsorbed onto the carbonaceous gold ore and the carbon extract, in accordance with the proposals of McDougall et al. (31) and Zaitseva et al. (32). For gold cyanide adsorption in the presence of HDNNS, H^+ ions would not be available for the formation of $H_2[Au(CN)_2]_n$ since any H^+ dissociated from HDNNS would be neutralized by the alkaline medium (equilibrium pH for the ore-HDNNS- $Au(CN)_2^-$ system was 9.8). In addition, steric hindrance due to the bulky naphthalene rings might discourage the formation of $H_2Au(CN)_2RSO_3$ complexes.

CONCLUSIONS

From the current study of the effects of four model organic additives on gold adsorption from aurocyanide solutions, a number of conclusions can be drawn.

(1) Aliquat 336 and dodecylamine enhanced gold adsorption onto the Pres-tea carbonaceous gold ore. Aliquat 336, which is completely cationic and adsorbs via both electrostatic and hydrophobic interactions, produced the greater effect, presumably by acting as an activator linking the negatively charged aurocyanide complex to the negatively charged solid surface. For gold adsorption in the presence of Aliquat 336 the free energy of adsorption is probably dominated by the ΔG_{coul} term since electrophoretic mobility studies show that the ore particles become less negatively charged in the presence of this surfactant. Enhanced gold uptake by the DDA-pretreated material was less dramatic apparently because of the lower degree of ionization and the lower extent of adsorption of this surfactant, compared with Aliquat 336.

(2) The presence of HDNNS caused a marked increase in the negative charge of the carbonaceous solid/water interface; the effect of SDS was less pronounced, indicating that HDNNS is the more strongly adsorbed of the two anionic surfactants. Since the solid surface is originally negatively charged (8), the adsorption of the anionic sulfonate reagents suggests the presence of specific (hydrophobic and chemical) interactions between the surfactants and the ore surface. HDNNS depressed gold loading onto the carbonaceous ore as a result of the repulsion between the adsorbed $-\text{SO}_3^-$ groups on the ore and the $\text{Au}(\text{CN})_2^-$ anion. The slight increase in gold uptake in the presence of SDS is probably a result of the formation and subsequent adsorption of the neutral compound $\text{Na}_2\text{Au}(\text{CN})_2\text{RSO}_3$.

(3) Gold adsorption is reduced by about 37% when, during the pretreatment operation, hexane is used as the solvent instead of water. The hydrophobic character of the hexane-treated solid hinders the approach of the charged $\text{Au}(\text{CN})_2^-$ onto the solid surface.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant Nos. INT-8017213 and INT-8313427. K.O.A. thanks the Director, Institute of Mining and Mineral Engineering, University of Science and Technology, Kumasi, Ghana, and the Director, Ghana Geological Survey for their cooperation with this research. The authors also thank the management of the State Gold Mining Corporation of Ghana for providing the sample used in this research, and Dr. A.O. Barnafo and Ghana National Manganese Corporation for logistic assistance. Discussions with P.M. Afenya are gratefully acknowledged.

REFERENCES

- 1 Addison, R., 1980. Gold and silver extraction from sulfide ores. *Min. Congr. J.*, 66(10): 47-54.
- 2 Nice, R.W., 1971. Recovery of gold from active carbonaceous ores at McIntyre. *Can. Min. J.*, 49-49.
- 3 Guay, W.J., 1981. The treatment of refractory gold ores containing carbonaceous material and sulfides. In: W.J. Schlitt, W.C. Larson and J.B. Hiskey (Editors), *Gold and Silver Leaching Recovery and Economics. SME-AIME*, p. 17.
- 4 Leaver, E.S. and Woolf, J.A., 1930. Re-treatment of Mother Lode (California) carbonaceous slime tailings. *Bur. Mines, Tech. Pap.*, 481: 1-20.
- 5 Dorfman, A., 1922. On the metallurgy of carbonaceous gold ores. *Bull. Can. Inst. Min. Metall.*, 15: 383-395.
- 6 Gruse, W.A. and Stevens, D.R., 1960. *Chemical Technology of Petroleum*. McGraw-Hill, New York, N.Y., 3rd ed., p. 487 (1960).
- 7 Rossini, F.D., Mair, B.J. and Streiff, A.J., 1953. *Hydrocarbons from Petroleum*. Reinhold, New York, N.Y., p. 88.

- 8 Abotsi, G.M.K. and Osseo-Asare, K., 1986. Surface chemistry of carbonaceous gold ores. I. *Int. J. Miner. Process.*, 18: 217-236.
- 9 Shergold, H.L. and Mellgren, O., 1969. Concentration of minerals at the oil/water interface: hematite-isooctane-water system in the presence of sodium dodecylsulfate. *Trans. Inst. Min. Metall.*, 78: C121-C132.
- 10 Day, R.E., Greenwood, F.G. and Parfitt, G.D., 1967. Effect of heat treatment on the adsorption of sodium dodecyl sulfate from aqueous solution on spheron 6. *Proc. 4th Int. Cong. on Surface Activity*, II: 1005.
- 11 Joy, A.S. and Watson, D., 1964. Adsorption of collector and potential determining ions in the flotation of hematite with dodecylamine. *Trans. Inst. Min. Metall.*, 73: 323-335.
- 12 Ananthpadmanabhan, K., Somasundarana, P. and Healy, T.W., 1978. Chemistry of oleate and amine solutions in relation to flotation. *Trans. AIME*, 266: 2003-2009.
- 13 Fuerstenau, D.W., 1956. Streaming potential studies on quartz in solutions of aminium acetates in relation to the formation of hemi-micelles at the quartz-solution interface. *J. Phys. Chem.*, 60: 981-985.
- 14 Chiarizia, R., Danesi, P.R., D'Alessandro, G. and Scuppa, B., 1976. Interfacial behavior of dinonylnaphthalenesulfonic acid at the toluene-HClO₄ interface. *J. Inorg. Nucl. Chem.*, 38: 1367-1369.
- 15 Osseo-Asare, K. and Keeney, M.E., 1980. Aspects of the interfacial chemistry of nickel extraction with LIX63-HDNNS mixtures. *Metall. Trans. B.*, 11: 63-67.
- 16 Marcus, Y. and Kertes, A.S., 1969. *Ion Exchange and Solvent Extraction of Metal Complexes*. Wiley, New York, N.Y., p. 164.
- 17 Sato, T. and Wanatabe, H., 1970. The extraction of zirconium (IV) from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat 336). *Anal. Chim. Acta*, 49: 463-471.
- 18 Skoog, D.A. and West, D.M., 1969. *Fundamentals of Analytical Chemistry*. Holt Rinehart and Wintone, New York, N.Y., 2nd ed., p. 233.
- 19 Danesi, P.R., Chiarizia, R. and Scibona, G., 1973. A simple purification method for the liquid cation exchanger dinonylnaphthalenesulfonic acid (HDNNS). *J. Inorg. Nucl. Chem.*, 35: 3926-3928.
- 20 Fuerstenau, D.W., 1971. The adsorption of surfactants at solid-water interfaces. In: M.L. Hair (Editor), *Chemistry of Biosurfaces*, 1. Marcel Dekker, New York, N.Y., p. 376.
- 21 Osseo-Asare, K., Fuerstenau, D.W. and Ottewill, R.H., 1975. Mechanism of sulfonate adsorption at the silver iodide-solution interface. In: *Adsorption at Interfaces*. ACS Symp. Ser., 8: 63-78.
- 22 Gaudin, A.M. and Chang, M.C., 1952. Adsorption on quartz from an aqueous solution of barium and laurate ions. *Trans. AIME*, 193: 193-196.
- 23 Wakamatsu, T. and Fuerstenau, D.W., 1968. The effect of hydrocarbon chain length on the adsorption of sulfonates at the solid water interface. *Adv. Chem. Ser.*, 79: 161-172.
- 24 Weber Jr., W.J. and Morris, J.C., 1971. Effects of particle size on the adsorption of anionic benzenesulfonates. In: J.S. Mattson and H.B. Mark Jr. (Editors), *Activated Carbon, Surface Chemistry and Adsorption from Solution*. Marcel Dekker, New York, N.Y., pp. 201-205.
- 25 deBruyn, P.L., 1955. Flotation of quartz by cationic collectors. *Trans. AIME*, 202: 291-298.
- 26 Kennedy, P., Petronio, M. and Gisser, H., 1970. The adsorption of dinonylnaphthalenesulphonates on metal oxide powders. *J. Phys. Chem.*, 74: 102-107.
- 27 Abotsi, G.M.K. and Osseo-Asare, K., unpublished research.
- 28 Adamson, A.W., 1976. *Physical Chemistry of Surfaces*. Wiley, New York, N.Y., 3rd ed., p. 389.
- 29 Calkin, J.B. and Witham, G.S., 1957. *Modern Pulp and Paper Making*. Reinhold, New York, N.Y., 3rd ed., p. 116.

- 30 Morrison, R.T. and Boyd, R.N., 1973. *Organic Chemistry*, Allyn and Bacon, Boston, Mass., 3rd ed., p. 671.
- 31 McDougall, G.J., Hancock, R.D., Nicol, M.J., Wellington, O.L. and Copperwaite, R.G., 1980. The mechanism of the adsorption of gold cyanide on activated carbon. *J. S. Afr. Inst. Min. Metall.*, 80: 344-356.
- 32 Zaitseva, M.L., Ivanoskii, M.D. and Larina, N.K., 1973. An examination of the sorption properties of carbonaceous gold ores. *Sov. J. Non-Ferrous Met.*, 14(1): 78-80.