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Selective Solvation Extraction of Gold from Alkaline Cyanide Solution by Alkyl Phosphorus Esters

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ABSTRACT

Research efforts have shown that solvation extraction of gold from alkaline cyanide solution is possible by alkyl phosphorus esters. Both tributyl phosphate (TBP) and dibutyl butyl phosphonate (DBBP) appear to be effective extractants for gold and exhibit high loading capacities exceeding 30 gpl. Selective solvation extraction of gold from alkaline cyanide solution can be achieved with selectivity factors relative to other cyanoanions as high as 1000 under certain circumstances. Variables influencing the selectivity such as ionic strength, temperature, and extractant structure, are discussed in terms of the extraction chemistry, which seems to involve the solvation of a $\overline{M^+ \cdots Au(CN)_2^-}$ ion pair.

INTRODUCTION

Cyanide leaching of gold and silver ores by conventional techniques has been practiced for over a century. The recovery of gold from these alkaline cyanide solutions is typically accomplished by carbon adsorption or zinc cementation. These and other process alternatives for gold recovery from primary resources have recently been reviewed (1). Also, recovery of gold from secondary sources such as electronic scrap (2) and waste cyanide electroplating solutions is an important technology. Waste gold electroplating solutions containing impurities are not suitable for reuse and must be processed for gold recovery, recycled and/or disposed. In this view, a wide variety of gold-bearing cyanide solutions are processed which include:

Cyanide Solutions	Gold Concentration
Heap Leach Liquors	1-5 ppm
Agitation Leach Liquors	5-10 ppm
Eluates from Activated Carbon	100-2000 ppm
Waste Electroplating Solutions	1000-2000 ppm

Nontraditional process alternatives for gold recovery include resin technology, solvent extraction, and direct reduction. Though solvent extraction is an important process strategy for concentration and purification of many metals, little attention has been given to the solvent extraction of gold from alkaline cyanide solution.

Recent research efforts (3,4) have shown that one possibility for gold recovery from these alkaline solutions is the solvation extraction of a gold cyanide ion pair by alkyl phosphorus esters, such as tributyl phosphate (TBP) and dibutyl butyl phosphonate (DBBP), which have been used for some time for solvation extraction from acid solutions. It was shown that pure TBP and DBBP could extract gold from alkaline cyanide solution. Experimental results indicate that gold is extracted as an ion pair, $\overline{M^+ \cdots Au(CN)_2^-}$, which is rather remarkably solvated by strong Lewis-base alkyl phosphorus esters such as DBBP at modest ionic strength according to the following reaction:

$$M^+ + Au(CN)_2^- \xrightarrow{DBBP} \overline{M^+ \cdots Au(CN)_2^-} \qquad (1)$$

where M^+ = cation, e.g., K^+, Na^+, ..., and the extracted ion pair may remain solvated to some extent by water.

Although both TBP and DBBP appear to be effective extractants for the recovery of gold from alkaline cyanide solutions, stripping with acids or bases does not appear to be feasible as the reaction does not exhibit a significant pH dependence (4). However, it was reported that partial stripping could be accomplished at low ionic strength and high temperature (4). More recently, gold recovery from these loaded organics has been accomplished by direct electrolysis of the organic phase (5). In batch electrolysis experiments, sheet gold was successfully produced from loaded DBBP or TBP at a current density of 8×10^{-4} amp/cm^2 and 55°C from an aqueous/organic mixture. The current efficiency is comparable to that obtained for conventional electrolysis from the aqueous phase.

In order to produce sheet gold of high purity, the selectivity characteristics of this solvation extraction are important, and the study of such characteristics is reported in this contribution. The influence of variables including ionic strength, temperature, and extractant structure have been examined and are discussed in terms of the extraction chemistry.

EXPERIMENTAL

Alkyl phosphorus esters used in this study include tri-n-butyl phosphate (TBP), tri-sec-butyl phosphate (TSBP), tri-n-hexyl phosphate

(THP), tri-n-octyl phosphate (TOP), and di-n-butyl n-butyl phosphonate (DBBP). All these extractants were washed with water (mostly pH 10-11) before use to remove acidic impurities. All reagents used were of reagent-grade quality.

Gold cyanide solutions of appropriate gold concentration were prepared using reagent-grade $KAu(CN)_2 \cdot 2H_2O$. For selectivity tests, metal cyanide solutions were generally prepared from their cyanide salts and KCN. In the case of copper and nickel, the cyanide solutions were prepared from the respective nitrate salts.

Extraction at desired phase ratios was accomplished with a temperature-controlled orbit shaker made by Lab-Line Instruments. Equilibration and separation of the aqueous and organic phases were done at constant temperature. Samples of the aqueous phase were taken after equilibration and analyzed using plasma emission spectroscopy.

The infrared spectra were determined with a Nicolet 7000 series Fourier Transform Infrared Spectrometer (6000 bench) at 1 cm^{-1} resolution. A germanium-coated KBr beam-splitter and a liquid nitrogen-cooled Hg-Cd-Te detector were used, and each sample was scanned 200 times. For liquid organic samples, a variable-pathlength cell was used. An aliquot of sample was spread between two CaF_2 windows, and the thickness of the film was adjusted in the cylindrical chamber with a Vernier scale.

Solvation Extraction by TBP and DBBP

Both TBP and DBBP have been proved to be effective solvating extractants for gold from alkaline cyanide solution provided the ionic strength is sufficient (3,4). As had been reported previously, this phenomenon is most significant for TBP. The effect of NaCN concentration on gold extraction by pure TBP and DBBP has been examined and is presented in Figure 1. Percent gold extraction increases slightly with an increase in NaCN concentration, when the ionic strength has been established with 0.1 M NaOH. Without any NaOH addition, gold extraction increases significantly with NaCN addition due to the increase in ionic strength. For example, extraction of gold by pure TBP is only 50% at 0.015 M NaCN solution but increases to 93% at 0.3 M NaCN.

Figure 2 shows gold and potassium extraction from a $KAu(CN)_2$ solution in terms of concentration in DBBP vs. pH. The concave nature of the curve for gold extraction is due to the ionic strength effect. Minimum gold extraction occurs near the natural pH of the solution (minimum ionic strength), and the increased extraction at lower or higher pH is due to the increase in ionic strength from the addition of acid (H_2SO_4) or base (NaOH) for pH adjustment. If the ionic strength is fixed with an indifferent electrolyte, the extraction is complete at all pH values (4). In the absence of ionic strength control, as in Figure 2, it is interesting to note that an equimolar amount of potassium was extracted with gold from the potassium aurocyanide solution above pH 7. However, below pH 3 where essentially complete gold extraction occurs, there is a dramatic decrease in potas-

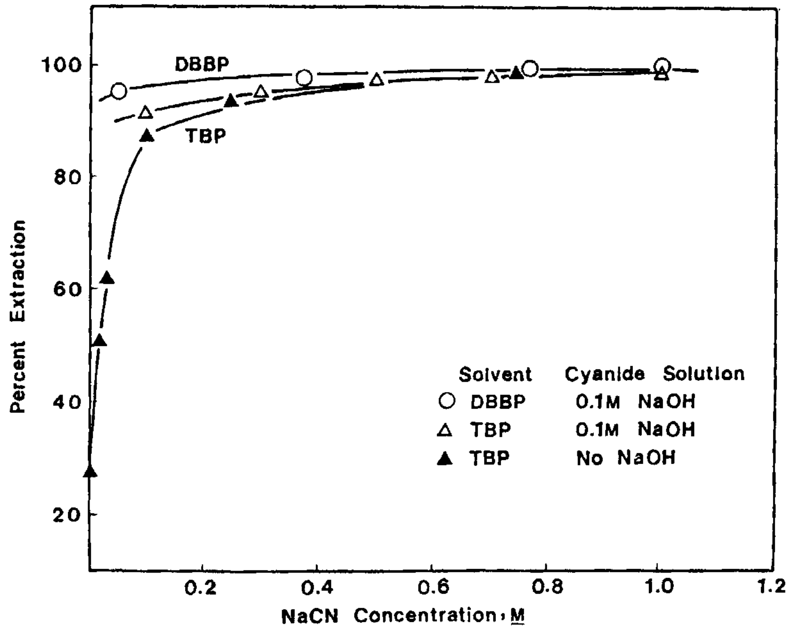

Figure 1. The effect of NaCN concentration on the extraction of gold (0.00507 M) from $KAu(CN)_2$ solution by DBBP and TBP.

sium extraction. Presumably, gold is extracted as the protonated $HAu(CN)_2$ species at low pH. These results are consistent with previous findings at high ionic strength for which the extraction was independent of pH and support the notion that solvation extraction occurs due to a "salting-out" effect (4).

Equilibrium Isotherms

Gold recovery from alkaline cyanide solution is of interest in the processing of heap leach liquors (1-5 ppm), agitation leach liquors (5-10 ppm), eluates from carbon strip (100-2000 ppm), and waste electroplating solutions (1000-2000 ppm); consequently a wide range of gold concentrations was considered. Figure 3 is the equilibrium isotherm for gold extraction from alkaline cyanide solution by pure TBP and DBBP. The data indicate that low-gold raffinates can be obtained using either TBP or DBBP. The ultimate loading capacity of pure TBP or DBBP for this solvation extraction is rather high and has not yet been reached at 30 gpl. The gold distribution coefficient varies from about 155 to 17 for DBBP, and from about 55 to 6 for TBP, under these conditions.

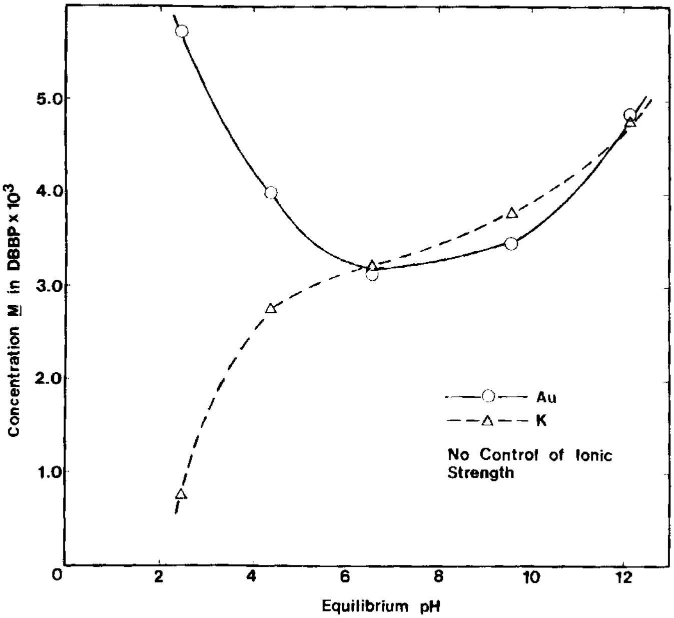

Figure 2. Extraction of gold and potassium by pure DBBP from $KAu(CN)_2$ solution. Initial concentration 0.00507 M.

The slope of such plots shown in Figure 3 could reveal the stoichiometry of the extracted species which is expected to be unity as indicated in Equation (1). However, the slopes were deduced by a best-fit statistical analysis of the experimental data and were found to be approximately 0.8 which is less than the expected value of 1.0. The deviation from the expected value may reflect a continual change in the capacity of the organic phase and/or the nature of the mixed solvation structure either of which phenomena may cause a systematic change in the activity coefficient of the extracted ion pair with increase in concentration. Under certain conditions, such a log/log plot as presented in Figure 3 could remain linear with a slope less than unity. Interesting, a similar dependence was observed for gold adsorption from alkaline cyanide solution by neutral polymeric adsorbents (6).

Selectivity Characteristics

In cyanide leaching or electroplating solutions, there are a host of complex cyanoanions that can be found. In this study, the following cyanoanions were considered: $Ag(CN)_2^-$, $Cu(CN)_4^{2-}$, $Zn(CN)_4^{2-}$, $Ni(CN)_4^{2-}$, and $Fe(CN)_6^{3-}$. Gold selectivity with respect to these anions

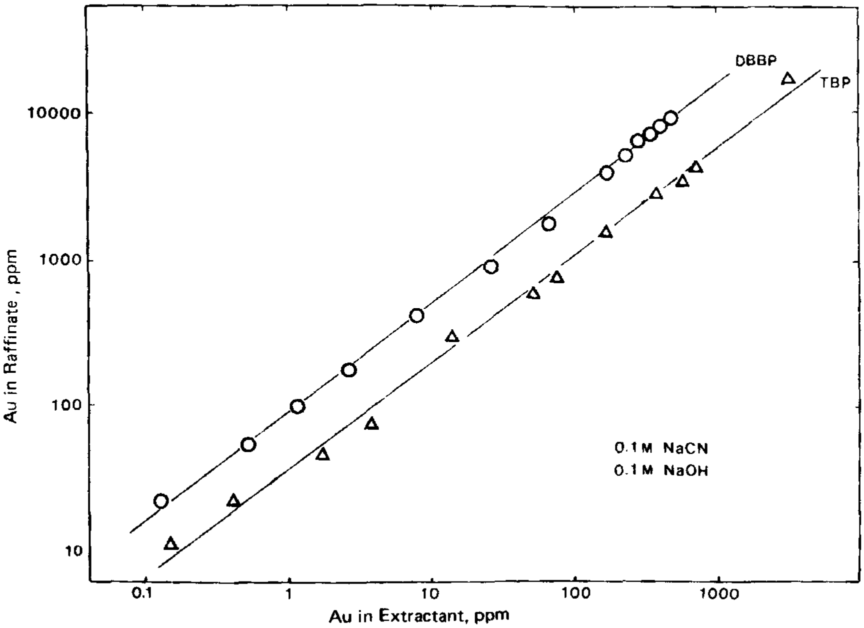

Figure 3. Equilibrium isotherm for gold extraction by pure TBP and DBBP from alkaline cyanide solution.

was determined for variables such as ionic strength, temperature, and extractant structure.

It might be expected that the solvation extraction of cation-cyanoanion ion pairs would be nonselective, since they are all rather soft bases and specific chemical bonding seems to be absent. Nevertheless, good selectivity was found, and it appears that unique solvent specificity for the aurocyanide ion pair occurs. Figure 4 shows percent extraction as a function of cyanide concentration at 0.1 M NaOH for various cyanoanions by pure DBBP. The initial concentrations of the various cyanoanions in aqueous solution are all $5x10^{-3}$ M.

The selectivity factors based on the experimental results obtained for the extraction of cyanoanions by DBBP gives the following order of selectivity:

$$Au(CN)_2^- >> Ag(CN)_2^- >> Cu(CN)_4^{2-} > Zn(CN)_4^{2-},\ Ni(CN)_4^{2-},\ Fe(CN)_6^{3-}$$

The selectivity sequence for this solvation extraction may be explained by consideration of charge and size effects; the extraction of anions is noted to increase with decreasing charge. Singly charged

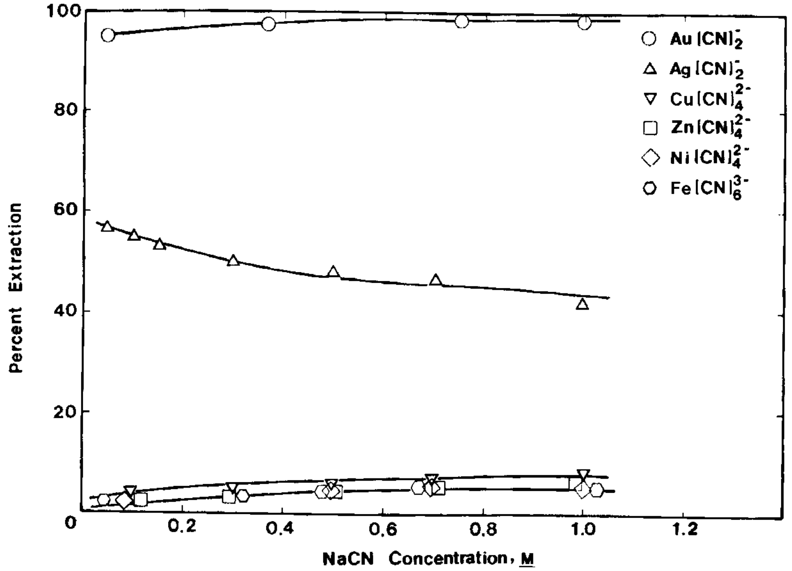

Figure 4. Percent extraction of various cyanoanions (0.00507 M) by DBBP as a function of NaCN concentration at 0.1 M NaOH.

anions are extracted to a greater extent than the doubly charged anions, while the highly charged anions show little affinity for DBBP. For a given anion charge, an increase in the size of the anion favors partition in the organic phase; thus $Au(CN)_2^-$ is extracted over $Ag(CN)_2^-$.

The extraction results in Figure 4 demonstrate that pure DBBP does not extract silver to the same extent as gold which had been reported previously (4). Interestingly, it should be noted that the amount of silver extraction decreases with increasing cyanide concentration. These results are indicative of the fact that at high cyanide concentrations, silver may add another ligand to form $Ag(CN)_3^{2-}$,

$$Ag(CN)_2^- + CN^- = Ag(CN)_3^{2-} \qquad K = 35.5\ (7) \qquad (2)$$

The higher charge of $Ag(CN)_3^{2-}$ complex reduces the extent of silver extraction as expected from the hypothesis advanced. Further evidence for this proposition is found in Figure 5 where, at fixed cyanide concentration, the concentrations of $Ag(CN)_2^-$ and $Ag(CN)_3^{2-}$ are fixed, and silver extraction increases with an increase in sodium hydroxide concentration due to the increase in ionic strength.

Under these circumstances, significant discrimination between the extraction of $Au(CN)_2^-$ and other cyanoanions can be achieved, as shown in Figure 6. It is important to note that the selectivity factor for gold over other transition metal cyanoanions is as high as 1000.

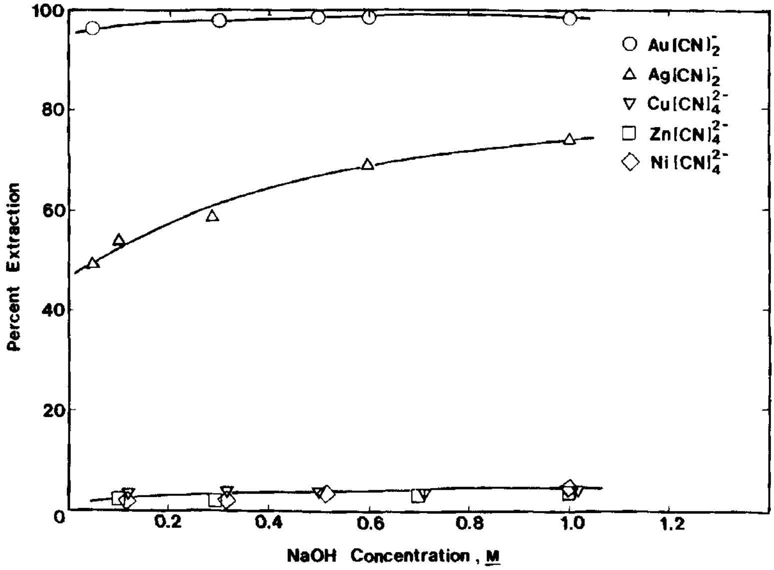

Figure 5. Percent extraction of various cyanoanions (0.00507M) by DBBP as a function of NaOH concentration at 0.1 M NaCN.

In addition to the charge/size effect, the hydration energy of the ion pair may be important. These solvation extractants such as DBBP have the capacity to displace water and the extracted ion pair may become less hydrated, i.e., more readily extracted. It is imagined that a mixed solvation structure (H_2O and DBBP) of some unique character accounts for the selectivity of the $M^+\cdots Au(CN)_2^-$ ion pair. The strong affinity of the $M^+\cdots Au(CN)_2^-$ ion pair for the organic phases may be explained, in part, by the fact that the aurocyanide anion is considered to be weakly hydrated (8).

Temperature Effect

Temperature is perhaps the most complex and the least understood factor affecting the equilibrium in a solvent extraction process. Also, temperature can affect the complexation reactions in the aqueous phase. Figure 7 shows that the extraction of both $Au(CN)_2^-$ and $Ag(CN)_2^-$ by DBBP decreases as a function of temperature. With high ionic-strength solutions (e.g., 0.1 M NaCN and 0.1 M NaOH), the extraction of $Au(CN)_2^-$ decreases from 99% to 55% as the temperature increases from 5°C to 80°C, while $Ag(CN)_2^-$ decreases from 68% to 12%. For a low ionic strength $KAu(CN)_2$ solution, an increase in temperature also markedly decreases the percent gold extraction to 10% at an elevated temperature of 80°C.

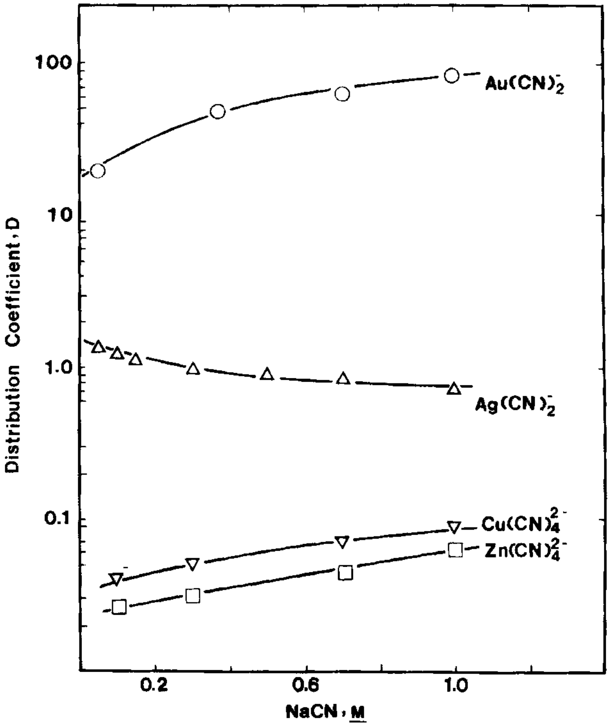

Figure 6. Distribution coefficient for the extraction of cyanoanions by DBBP (0.00507 M) as a function of NaCN concentration at 0.1 M NaOH.

One approach in the analysis of these results is to consider the nature of ion pair formation because the degree of extraction depends on the extent of ion pairing. The extent of ion pair formation decreases with an increase of temperature which is predicted by the Bjerrum Equation, involving temperature, dielectric constant, charge, and distance of separation. The equilibrium between free ions and the ion pair

$$M^+ + X^- = (M^+ \cdots X^-) \qquad K_A \qquad (3)$$

is determined by the ion association constant, K_A, which is inversely dependent on temperature.

Extraction of the ion pair might be considered in more detail according to Equation (4):

$$M^+ + Au(CN)_2^- + m\,\overline{RPO} + n\,\overline{H_2O} = \overline{M^+ \quad Au(CN)_2^-\ m\ RPO\ n\ H_2O} \qquad (4)$$

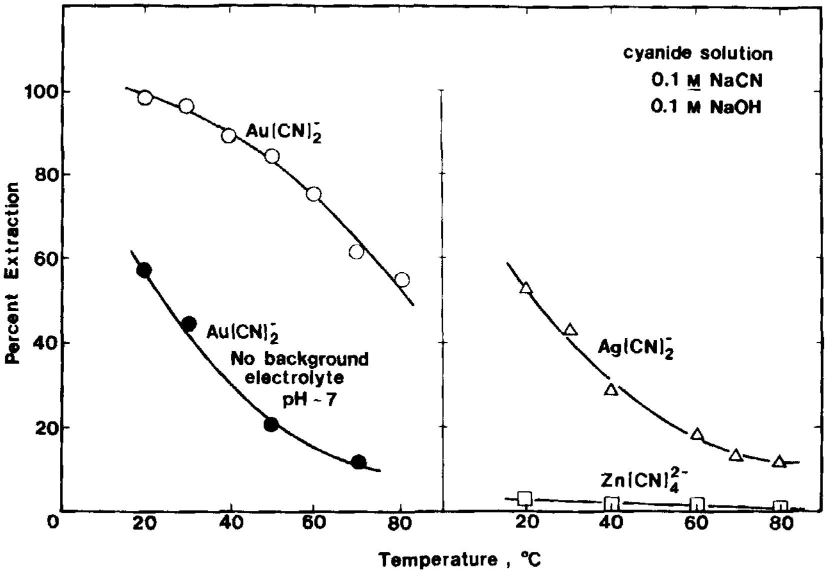

Figure 7. Percent extraction of cyanoanions (0.00507 M) by DBBP as a function of temperature.

The experimental results can be explained from a thermodynamic analysis in terms of the stability of the mixed solvation structure (H_2O and DBBP). The van't Hoff equation can be rewritten in terms of the distribution coefficient,

$$\log D = - \frac{\Delta H^0}{2.303\ RT} + C^* \qquad (5)$$

where D is the distribution coefficient, ΔH^0 is the enthalpy change for the extraction reaction and C* is the integration constant which includes the equilibrium constant for Equation (4), activity and activity coefficient for other components which are assumed to be invariant under the experimental conditions. A plot of log D vs. 1/T according to Equation (5) is presented in Figure 8 from which the enthalpies for gold and silver extraction have been found to be -15.2 Kcal/mole and -7.7 Kcal/mole respectively. The standard free energy for the ion pair extraction reaction (Equation (4)) can be estimated from the equilibrium constant by making certain assumptions (9):

$$K = \frac{[\overline{M^+\ \ Au(CN)_2^-\ m\ RPO\ n\ H_2O}]}{[M^+][Au(CN)_2^-\ ][\overline{RPO}]^m\ [\overline{H_2O}]^n} \qquad (6)$$

Under these conditions, the standard free energy was found to be approximately ΔF° = -6.7 kcal/mol (9). On this basis, ΔS° was calcu-

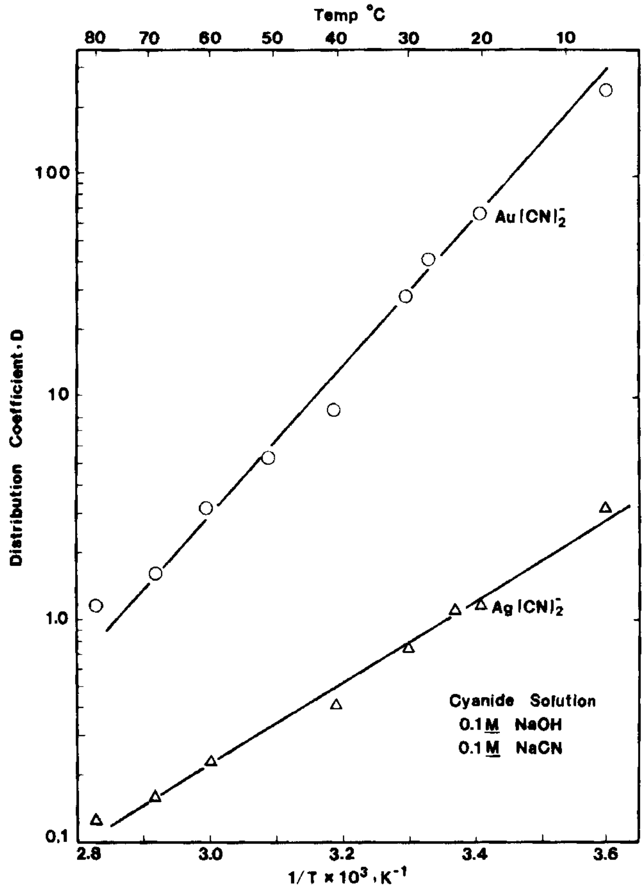

Figure 8. Distribution coefficient versus 1/T for solvation extraction of Au(CN)$_2^-$ (0.00507 M) and Ag(CN)$_2^-$ (0.00507 M) by DBBP.

lated to be -28.7 kcal/degree mole, which suggests that the formation and extraction of the $\overline{M^+\ Au(CN)_2}$ ion pair results in the formation of a complex ordered structure of rather large size (9) and that this unique solvation structure accounts for the specificity observed for gold extraction from alkaline cyanide solution. The extent of extraction decreases appreciably at higher temperature as expected, because of the large negative entropy term.

The solvation extraction can be considered from one other perspective. If the extracted ion pair is solvated by the formation of a mixed solvation structure, then the extent of extraction may be determined by the water activity in the organic phase. If a mixed solvation structure accounts for the selective gold extraction according to Equation (4) then the equilibrium point of the solvation extraction should be determined by the water activity of the organic phase. In this regard, the temperature dependence of the solvation extraction may be explained by a decrease of water concentration in TBP with an increase in temperature as is reported in the literature (10). Along this line of discussion, it will be noted in the following section that the solvation extraction decreases significantly with an increase in chain length as shown in Figure 9. Although these results may be considered from the standpoint of steric hindrance and dielectric constant, it is also expected that the water activity will decrease significantly with an increase in extractant chain length. In this regard the results presented in Figure 9 would also tend to support the hypothesis of a mixed solvation structure for the extracted ion pair.

Chain Length and Structure of Alkyl Group

The degree of solvent extraction is determined to some extent by the special configuration of both ligand and metal ion to be extracted. However, steric considerations including shielding, conformational, and spatial effects are also important and are determined by the composition, structure, and configuration of the extractant. The chain length and structure of the alkyl groups are two important extractant features.

In addition to TBP, tri-sec-butyl phosphate (TSBP) also shows excellent solvation extraction of gold over the entire pH range as shown in Figure 9 (11). It seems that branching of the butyl group, with an expected decrease in dielectric constant, has little effect on the solvation extraction. On the other hand, chain length has quite a significant effect. Tri-n-hexyl phosphate (THP) and tri-n-octyl phosphate (TOP) are less effective than TSBP as shown in Figure 9. One explanation is that an increase in chain length results in an increase in steric hindrance which inhibits extraction. Alternately, the decrease in solvation extraction may be related to a decrease in water solubility in the organic phase, thus preventing the formation of the unique mixed solvation structure. Further research will be necessary to distinguish between these effects. Nevertheless, the alkyl groups are an important feature of the solvation extractant and both steric effects and compositional effects must be considered in the analysis of the extraction reaction.

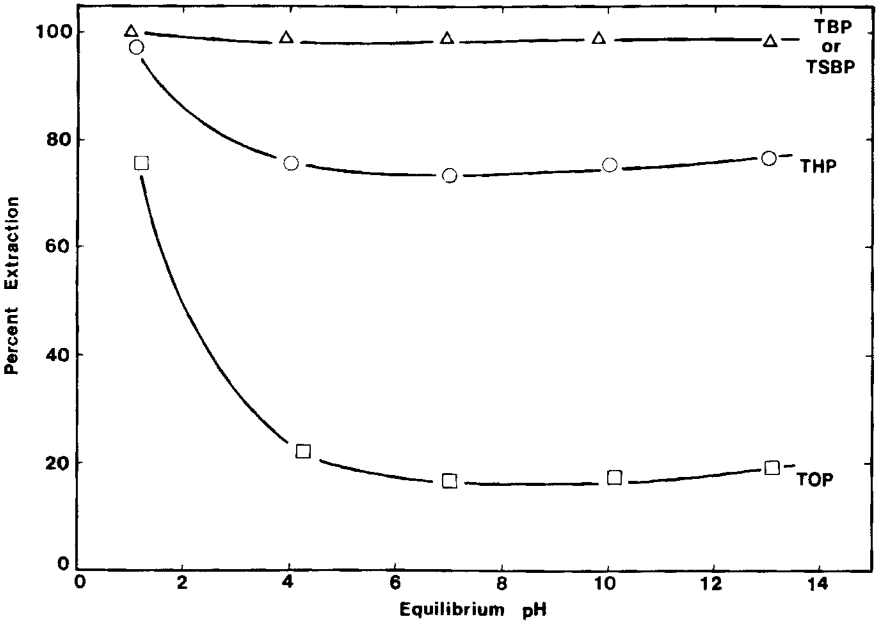

Figure 9. The effect of extractant structure on the extraction of aurocyanide at 0.5 M Na_2SO_4 solution.

The effect of NaCN concentration on gold extraction for TOP is similar to that for TBP. High ionic strength enhances the solvation extraction as shown in Figure 10 but the degree of extraction is influenced to a greater extent by the chain length of the solvating extractants, as shown in Figure 9. The percent gold extraction at high ionic strength with TOP is only 28%.

Infrared Spectroscopic Analysis

The reported cyanide stretching frequencies are 2140 cm^{-1} for crystalline potassium aurocyanide (12) and 2145 cm^{-1} for the aurocyanide complex in aqueous solution (13). Penneman et al. (14) determined the IR spectra of solid anhydrous aurocyanic acid, $HAu(CN)_2$, and reported a single cyanide stretching frequency at 2146 cm^{-1}. However, this finding does not agree with the value, 2212 cm^{-1}, reported by Evans et al. (15) who found the cyanide stretching frequency of the acid is greater than that of the corresponding potassium salt by about 60 cm^{-1}.

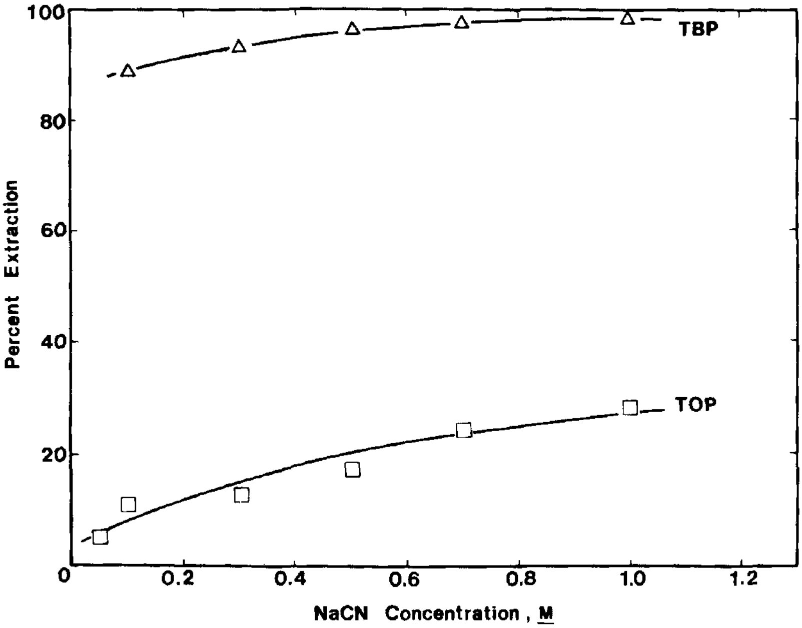

Figure 10. Percent extraction of gold from $KAu(CN)_2$ solution (0.00507 M) by TBP and TOP as a function of NaCN concentration at 0.1 M NaOH.

In this regard, it was found in our laboratory that the spectra of DBBP loaded with $KAu(CN)_2$, from a 0.1 M NaCN and 0.1 M NaOH solution gives a cyanide stretching frequency at 2146 cm^{-1}. In another experiment, the DBBP was loaded with $KAu(CN)_2$ from a pH 2 solution and the cyanide stretching frequency was found to remain unchanged at 2146 cm^{-1}. In view of the results presented in Figure 2 which provide strong evidence for the presence of the $HAu(CN)_2$ species at pH 2, it would seem that in DBBP solution the spectral data confirm the findings of Penneman et al. (14).

SUMMARY

Research efforts have shown that selective solvation extraction of gold from alkaline cyanide solution is possible by certain esters of phosphoric and phosphonic acid. Both TBP and DBBP appear to be effective extractants for gold cyanide and exhibit high loading capacities. Equilibrium isotherms for gold extraction from alkaline cyanide solution are reported with distribution coefficients that range from 155 to 17 for DBBP and 55 to 6 for TBP. These extractants can load gold to rather high levels, even in excess of 30 gpl.

The effect of ionic strength and temperature on the extraction of gold indicates that the solvation reaction involves the extraction of an ion pair. High temperature and low ionic strength (especially for TBP) will inhibit the solvation extraction.

Significant discrimination between the extraction of $Au(CN)_2^-$ and other cyanoanions can be obtained. It seems that unique specificity of alkyl phosphorus esters for the alkali cation-aurocyanide ion pair may involve a mixed solvation structure. The selectivity factor for gold with respect to other cyanoanions was found to be as high as 1000.

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