

Solvation of gold and rare earths by tributyl phosphate

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Abstract Frozen solution samples were made from gold chloride and $\text{KAu}(\text{CN})_2$ solvated with TBP/xylene. The ^{197}Au Mössbauer parameters were similar to those same species as frozen solutions or adsorbed onto activated carbon. Solvated samples from EuO dissolved in HCl or H_2SO_4 and frozen gave characteristic $\text{Eu}(\text{III})$ spectra. All the spectra were consistent with bonding to the TBP being through hydronium ions or water molecules.

Keywords Solvation · Gold · Europium · Tributyl phosphate · Bonding

1 Introduction

The technique of solvent extraction is commonly used in many industrial processes and separates compounds based on their relative solubilities in two different immiscible liquids. When metals are extracted by solvation, the coordinated water molecules around the metal ion are replaced partially or completely by the extractant, thus forming an organically soluble species. The phosphate ester tri-*n*-butyl phosphate (TBP) is used in many metal extraction processes, including the PUREX process for uranium extraction as $\text{UO}_2(\text{TBP})_2(\text{NO}_3)_2$. TBP initiates association with the solute through the donor electron pair on the $\text{P}=\text{O}$ part of the molecule and works better from nitrate or chloride solutions than from sulphate or phosphate solutions. However, in spite of the widespread data on its uses, much less is known about the mechanisms by which it bonds to particular metal complexes. The extraction systems can be complex and the extracted species are not easily defined.

Our principal aim was to study the extraction of gold from chloride solution, which is an environmentally more attractive system than using cyanide. However, the gold chloride species are easily reduced to the metal, for example in carbon-in-pulp

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processes. We have shown that when using some forms of polyurethane foam as the adsorbent [1, 2], this reduction can be avoided. Polyurethane foams can be loaded with suitable extractants, such as TBP, to improve the adsorption. TBP can also be adsorbed onto carriers such as nanoparticulate magnetite to enable magnetically assisted chemical separation.

2 Sample preparation

The gold chloride systems were prepared by first dissolving metallic gold in aqua regia and then diluting it to a pH of -0.9 . TBP is miscible in most common organic solvents and xylene was chosen as a suitable carrier for the TBP. Two different concentrations of 10% and 50% TBP in xylene were prepared. The TBP/xylene mixture was added to the acid solution, shaken for approximately 5 min and then centrifuged. An aliquot of approximately 0.45 ml of the organic phase was then frozen quickly (>15 K/s) by pipetting into a cylindrical teflon absorber holder held onto a copper block below the surface of liquid nitrogen. Rapid cooling at >10 K/s prevents crystallization and the viscosity of the liquid increases until a metastable glass phase is formed which will have the same composition as the liquid and should have a similar structure. The gold cyanide sample was prepared similarly by dissolving commercial $\text{KAu}(\text{CN})_2$ in water, mixing it with the TBP/xylene, centrifuged, and frozen quickly.

The rare earths are also amenable to extraction with TBP and were selected as possibly providing complementary bonding information to that from the gold. The rare earth samples were prepared by dissolving EuO and Gd_2O_3 in HCl or H_2SO_4 acids of various strengths. In each case, the metal-containing samples were added to the TBP/xylene, centrifuged, and an appropriate amount for the Mössbauer experiments frozen into teflon absorber holders.

3 Results

The ^{197}Au spectrum, taken at 5 K, of gold from chloride solution extracted into 50% TBP in xylene is shown in Fig. 1a and the fitted parameters are $\text{IS} = 1.09(2)$ mm/s (w.r.t. Pt), $\text{QS} = 1.59(3)$ mm/s and $\text{FWHM} = 2.02$ mm/s. The spectrum from 10% TBP in xylene appears to be the same within error, but as the dip is reduced proportional to the fraction of TBP, the spectrum is not as well defined. The spectrum of the gold cyanide sample, also taken at 5 K, showed the characteristic broad splitting and Gol'danskii-Karyagin effect of the $\text{Au}(\text{CN})_2^-$ ion (Fig. 1b) with parameters $\text{IS} = 3.17(4)$ mm/s, $\text{QS} = 10.4(1)$ mm/s, $\text{FWHM} = 1.92$ mm/s and area ratio $A_+/A_- = 0.89$.

The ^{151}Eu spectra at 78 K each showed a typical broadened single line for the unresolved quadrupole splitting, with an effective isomer shift (IS_{eff}) of 0.8 mm/s and FWHM of 3.4 mm/s for the sulphuric acid sample and IS_{eff} of 0.3 mm/s and FWHM of 3.0 mm/s for the hydrochloric acid sample. Although the original oxide was $\text{Eu}(\text{II})$, the IS_{eff} values are clearly $\text{Eu}(\text{III})$. ^{155}Gd spectra taken at 4.2 K of several different samples did not show any measurable absorption. This was unfortunate, since Gd^{3+} is an S-state ion whose IS and QS values usually allow for a good interpretation in terms of the bonding.

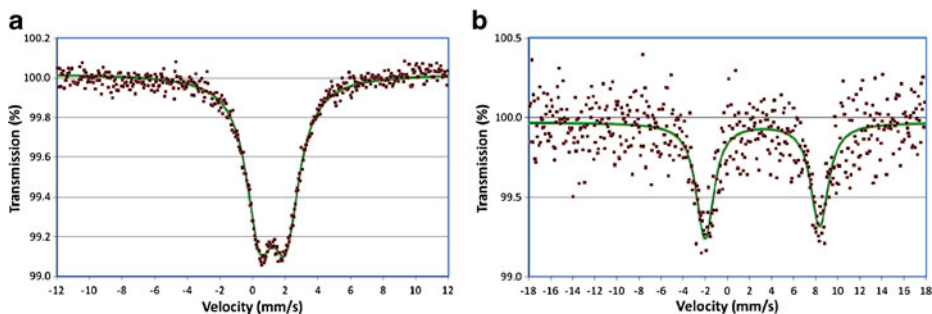


Fig. 1 ^{197}Au Mössbauer spectra of **a** frozen TBP/xylene/ $[\text{AuCl}_4]^-$ and **b** frozen TBP/xylene/ $\text{Au}(\text{CN})_2^-$ complexes, both taken at 5 K

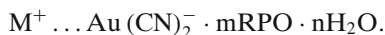
4 Discussion

TBP itself is not basic enough to take a proton out of the aqueous phase. Water, a stronger base than TBP, can acquire protons from the aqueous phase to form the hydronium ion, H_3O^+ . TBP extracts hydronium ions or partially hydrated hydronium ions out of the aqueous phase [3]. Each TBP molecule is hydrogen bonded to one of the hydrogen atoms of the hydronium ion or of a water molecule. The overall positive charge of the hydronium ion attracts the negatively charged gold species, $[\text{AuCl}_4]^-$. This results in species of the form [4]



The IS and QS agree with the parameters of the $[\text{AuCl}_4]^-$ species adsorbed onto polyurethane foams observed by Cashion et al. [1, 2] which had IS = 1.06–1.09 mm/s and QS = 1.58–1.63 mm/s.

Wan and Miller [5] reported no shift in the infrared spectrum of $\text{Au}(\text{CN})_2^-$ with alkyl phosphorous esters and concluded that the extracted species are in the form of an ion pair



The linear N-C-Au-C-N molecule has negatively charged ends which are attracted to the hydronium ions as described above. One notable feature of Mössbauer spectra of the $\text{Au}(\text{CN})_2^-$ ion is that all crystalline or frozen solution samples produce a strong Gol'danskii-Karyagin effect [6], while samples adsorbed onto activated carbon or polyurethane foams do not [6, 7]. This is because, in the former case, the bonding of the molecule is only at the negatively charged nitrogen ends, allowing the gold atom to vibrate more strongly perpendicular to the molecule. For the adsorbed molecules the additional bonding at the gold atom limits the perpendicular vibration. The presence of a Gol'danskii-Karyagin effect in the frozen $\text{Au}(\text{CN})_2^-$ —TBP complex is consistent with the other frozen solution samples and shows that the $\text{Au}(\text{CN})_2^-$ ion is only bonded to the complex at either one or both ends.

Comparison of the parameters with those from the prior samples just described [6, 7] and discussed in ref. [8], shows that the IS is the same as for crystalline $\text{KAu}(\text{CN})_2^-$ and smaller than that for the adsorbed species, implying that there is negligible bonding at the gold atom in agreement with the previous paragraph. The

QS is slightly larger than that of the crystalline species, suggesting a slight change in the length of the molecule.

The parameters of the Eu-Cl sample were almost identical to those obtained for frozen EuCl_3 solutions [9] inferring close association with water. $\text{Eu}(\text{NO}_3)_3$ complexed with TBP has been shown [10] to have 3 TBP molecules with one water molecule in low $[\text{HNO}_3]$ and no water molecules at high $[\text{HNO}_3]$. Ma et al. [11] evaluated the efficiency of TBP for extracting trivalent rare earths from $\text{HNO}_3/\text{LiNO}_3$ solutions and showed that it reached a local maximum at Eu before dropping by a factor of 1.5 to Gd. Since TBP extracts divalent actinide and rare earth ions more efficiently than trivalent ones, it is probable that the absence of a Gd absorption was due to a reduced extraction compared to the Eu sample, rather than to the much higher energy gamma rays (86.5 keV, compared to 21.6 keV) and consequent reduced recoilless fraction.

5 Conclusions

Solutions of gold chloride and $\text{KAu}(\text{CN})_2$ were added to a TBP/xylene mixture and the solvated species frozen rapidly. The $[\text{AuCl}_4]^-$ species showed Mössbauer parameters very similar to those obtained following adsorption onto activated carbon. The $\text{Au}(\text{CN})_2^-$ species showed a strong Gol'danskii-Karyagin effect which, together with the IS, indicated that there was no bonding at the gold atom. These spectra, and those from Eu(III) complexes, were consistent with bonding to the TBP being through hydronium ions or water molecules.

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