

$$(E^0 = + 0,253V)$$

Table 3.27 shows that similar reactions may be occurring in the case of $Ag(CN)_2^-$.

Table 3.27
Effect of acid and base treatment on the stoichiometry of the adsorbed $Ag(CN)_2^-$ species

Treatment	Concentration, mmol/g		N/Ag
	Ag	N	
Boiled in 4% HCl for 5h	0,0681	0,0111	0,325
Boiled in 4% HCl for 5h then boiled in 0.1 M NaOH for 5h	0,0573	0,0	0,0

After acid-boiling, the ratio of N to Ag is even lower than that of 1 expected for $AgCN$, indicating that a further reaction occurs. A scanning electron micrograph of the surface of this carbon is shown in Figure 3.41. The white grains which are evidently concentrated in the macropores were analysed by Energy Dispersive Spectroscopy (EDS or EDAX) and found to be rich in silver and chloride. X-ray diffractometry enabled the identification of this compound as $AgCl$. None of the peaks characteristic of metallic silver were observed.

The following reactions therefore are evidently occurring on the carbon surface:

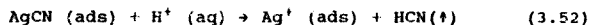
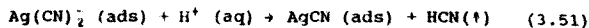
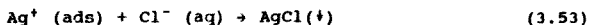


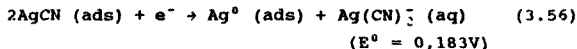
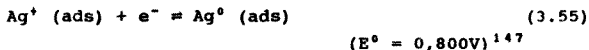
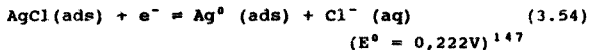


Fig. 3.41 SEM micrograph of an activated carbon surface loaded with argentocyanide and subsequently boiled in 4% HCl for 5 h. (520X magnification)



After subsequently boiling this carbon in 0,1 M NaOH, the ratio of N to Ag is reduced to zero. A scanning electron micrograph of the carbon surface is shown in Figure 3.42. A silver-rich compound was once again found to be precipitated within the macropores. Analysis by EDS indicated that this time no chloride was associated with the silver, and the X-ray diffractogram displayed the peaks characteristic of metallic silver. Moreover, no peaks characteristic of AgCl were evident.

It is thus likely that the following reactions occurred during this process:



The $\text{Ag}(\text{CN})_2^-$ formed via Equation (3.53) appeared in the 0,1 M NaOH solution, being adsorbed more weakly than the $\text{Au}(\text{CN})_2^-$ complex and hence being more easily eluted.

Figure 3.43 shows the structure of one of the metallic silver particles thus formed, located within a macropore. It is noteworthy that this particle appears to be an agglomerate of smaller particles, whereas the equivalent gold particles were found (see section 3.2c) to be dendritic in structure.

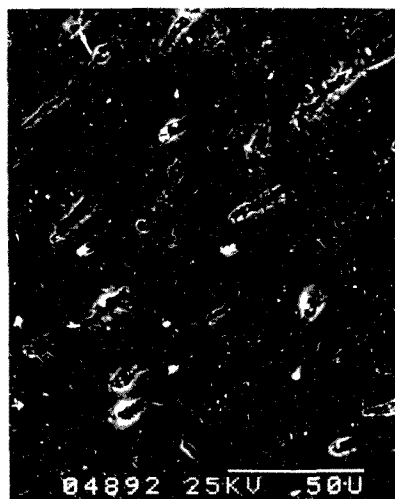


Fig. 3.42 SEM micrograph of the activated carbon surface in Fig. 3.41, subsequently boiled in 0,1 M NaOH for 5 h. (520X magnification)



Fig. 3.43 SEM micrograph of a magnified portion of the activated carbon surface shown in Fig. 3.42, showing the agglomerated structure of a silver particle

(ii) Mechanism of adsorption of Ag^+ onto activated carbon

Nature of the adsorbate

From the reduction potentials for reduction reactions (3.54) and (3.55) shown above, and comparison with reduction potentials reported³² for typical activated carbons of about +0.24 V, it can be predicted that AgCl should theoretically not be reduced to the metal by activated carbon. Moreover, it is likely that any Ag^+ present on the carbon will be reduced to the metal. These facts are consistent with the observations in the previous section.

Figures 3.41 and 3.45 show micrographs of the surface of a carbon loaded with silver from AgNO_3 solution. A combination of EDS and XRD analyses indicated the presence of metallic silver, which appears white in the micrographs, and AgCl , which appears grey in the micrographs. The presence of 500 ppm residual chloride on the activated carbon was verified analytically, thus accounting for the AgCl precipitate.

In an early study of AgNO_3 adsorption onto activated carbon, Bolam and Phillips¹⁴³ postulated a dual mechanism of AgNO_3 adsorption and reduction to metallic silver. It is unlikely, however, that any Ag^+ would remain in the oxidized form on the carbon surface, given the reduction potentials mentioned above. Moreover, it is likely that the activated charcoal used in Bolam and Phillips' 1935 study contained a comparatively larger amount of chloride than that found in modern activated carbons. Therefore the dual mechanism postulated from the results of the present study, of reduction to Ag and precipitation of AgCl , is consistent with the results reported in the literature.

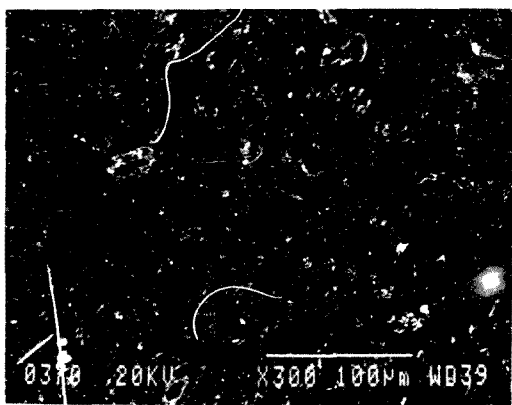
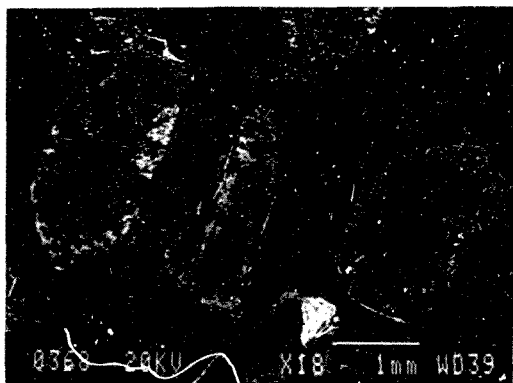


Fig. 3.44 Micrographs showing Ag metal (white) and AgCl precipitate (grey) adsorbed from AgNO_3 solution onto activated carbon

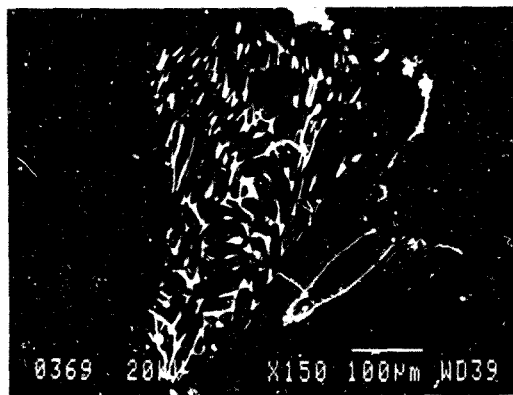
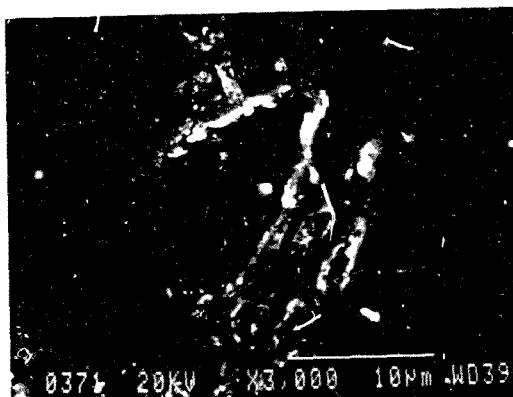


Fig. 3.45 Micrographs showing fine detail of Ag metal (white, and AgCl precipitate (grey) adsorbed from AgNO_3 solution onto activated carbon.
 (a) fine structure within a macropore
 (b) fine structure of Ag metal filling pores

c) *The Mechanisms of Adsorption of $\text{Hg}(\text{CN})_2$ and HgCl_2 onto Activated Carbon*

There are several important applications of the adsorption of mercury species onto activated carbon :

- (i) adsorption of mercury cyanide species onto activated carbon during gold recovery by the carbon-in-pulp process, with subsequent release of toxic mercury vapour during carbon reactivation¹⁵²,
- (ii) removal of mercury species from effluent streams¹⁵³, and
- (iii) use of activated carbon - supported HgCl_2 catalysts for the hydrochlorination of acetylene from vinyl chloride monomer¹⁵⁴.

Earlier work on the mechanism of adsorption of $\text{Hg}(\text{CN})_2$ onto activated carbon³² was aimed more at investigating the competition between $\text{Hg}(\text{CN})_2$ and $\text{Au}(\text{CN})_2^-$ than the mechanism of adsorption of $\text{Hg}(\text{CN})_2$ onto activated carbon. Ibrado and Fuersternau¹⁴⁰ recently correlated the pH dependence of adsorption of mercury onto activated carbon from cyanide solution with the species distribution diagram for the system. Jayson and co-workers¹⁵⁵ investigated adsorption of mercury (II) acetate onto activated carbon cloth and reported that an unspecified mercury compound had precipitated within the cloth. In a study of HgCl_2 adsorption onto activated carbon, Hutchings¹⁵⁴ suggests that the mechanism is similar to that proposed for the adsorption of $\text{M}^{n+}[\text{Au}(\text{CN})_2]^-_n$ ion pairs onto activated carbon. Lopez-Gonzalez and co-workers¹⁵⁶ claim to have detected Hg_2Cl_2 on the surface of activated carbons loaded from HgCl_2 solution, yet neglect to state how this deduction was made.

The present work is aimed at further elucidating the mechanism of adsorption of mercury onto activated carbon from cyanide and chloride solutions, to improve the understanding of all the above-mentioned processes.

- (i) Mechanism of adsorption of $\text{Hg}(\text{CN})_2$ onto activated carbon

Stoichiometry of the adsorbate

Mercury was loaded onto activated carbon from cyanide solutions having the stoichiometries $\text{Hg}(\text{CN})_2$ and $\text{CaHg}(\text{CN})_4$, respectively, and the results are shown in Table 3.28 below.

Table 3.28
Elemental analyses of carbons loaded from various mercuric cyanide solutions

Loading stoichiometry	Elemental analyses (mmol/g)		
	Ca	Hg	$\frac{1}{2}\text{N}$
$\text{Hg}(\text{CN})_2$	0,015	0,513	0,515
$\text{CaHg}(\text{CN})_4$	0,014	0,284	0,215

In both cases, mercury is adsorbed in the form of $\text{Hg}(\text{CN})_2$. These results suggest that $\text{CaHg}(\text{CN})_4$ does not adsorb onto carbon, and the lower extent of mercury loading at higher cyanide concentrations is a reflection of the smaller proportion of mercury in the $\text{Hg}(\text{CN})_2$ form. This aspect will be examined in greater detail in a later section.

Additional information can be obtained from a comparison of values for the standard reduction potentials (as measured against the Standard Hydrogen Electrode), of various

mercury-containing species, shown in Table 3.29.

Table 3.29
Standard reduction potentials of mercury-containing species

Reduction reaction	E°, V	Ref.
$\text{Hg}(\text{CN})_2 + 2\text{e}^- = \text{Hg} + 2\text{CN}^-$	-1,23	83
$\text{Hg}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Hg} + 4\text{CN}^-$	-1,60	83
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- = 2\text{Hg} + 2\text{Cl}^-$	+0,268	65
$\text{Hg}^{2+} + 2\text{e}^- = \text{Hg}$	+0,851	65
$2\text{Hg}^{2+} + 2\text{e}^- = \text{Hg}_2^{2+}$	+0,905	65
$\text{Hg}_2^{2+} + 2\text{e}^- = 2\text{Hg}$	+0,796	65

A comparison of these values with values reported³² for standard reduction potentials of typical activated carbons ($E^\circ \sim +0,24$ V) indicates that it is not thermodynamically feasible for activated carbon to reduce $\text{Hg}(\text{CN})_2$ or $\text{Hg}(\text{CN})_4^{2-}$ to the metal, and this is consistent with the elemental analysis results.

Effect of cyanide concentration

The effect of cyanide concentration on adsorption of mercury onto activated carbon is shown in Figure 3.46. The drop in extraction efficiency with increasing cyanide concentration is much sharper than in the case of silver cyanide, and this is a manifestation of the high stability of the $\text{Hg}(\text{CN})_4^{2-}$ complex at cyanide concentrations above about 0,01 mol/l, as is shown in Figure 3.47. The relevant equilibria are



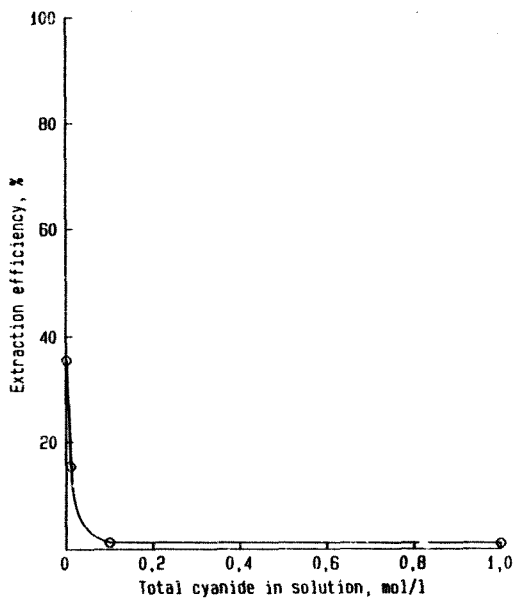


Fig. 3.46 Effect of cyanide concentration on the extraction of mercury by activated carbon.

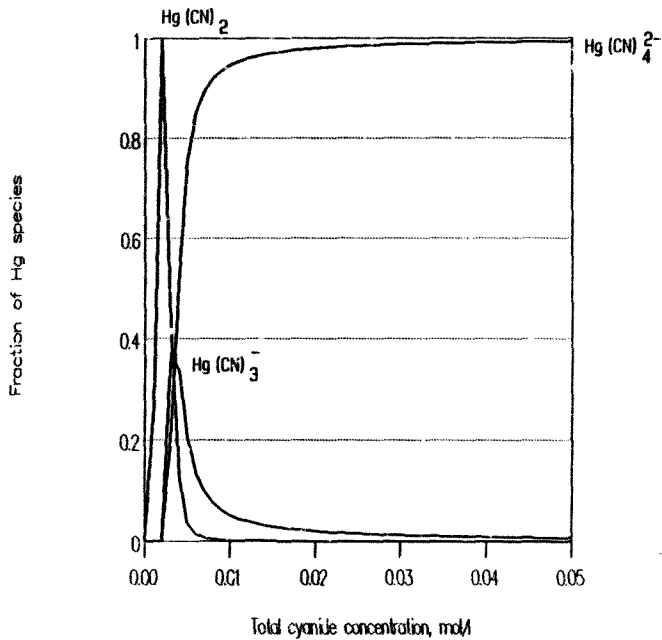
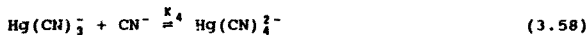


Fig. 3.47 Distribution of mercury species in aqueous solution with increasing cyanide concentration.



where⁸³ $K_3 = 3,64$ and $K_4 = 2,62$. The data in Figure 3.47 were calculated on an IBM microcomputer using the species distribution program HALTAFALL¹⁴⁹. The fact that $\text{Hg}(\text{CN})_4^{2-}$ has a double negative-charge results in a much lower affinity of this species for activated carbon than the neutral $\text{Hg}(\text{CN})_2$ species. This result is consistent with the theory that aurocyanide adsorbs onto carbon in the form of an ion pair of the form $\text{M}^{n+}[\text{Au}(\text{CN})_2]_n^-$, and is also consistent with the previously published observation³² that the latter two species compete for adsorption sites on the carbon surface, as well as with the results of Ibrado and Fuerstenau¹⁴⁰, who showed a correlation between pH dependence of mercury adsorption and calculated distribution of species.

It is noteworthy also that at the $\text{CaHg}(\text{CN})_4$ stoichiometry reported in Table 3.28, the species distribution calculations predict that approximately half of the mercury in the solution is in the form of $\text{Hg}(\text{CN})_2$, which is also consistent with the fact that the amount of mercury loaded from $\text{CaHg}(\text{CN})_4$ solution is half that from $\text{Hg}(\text{CN})_2$ solution.

Infrared spectrophotometric study of adsorbed $\text{Hg}(\text{CN})_2$ species

Infrared spectra showing the $\nu(\text{CN})$ stretching frequencies for mercuric cyanide loaded carbons are shown in Figure 3.48, and the observed values for adsorbed species are compared with those for free species in Table 3.30

It is noteworthy that the observed $\nu(\text{CN})$ band appears at identical frequencies for the species present on the carbons loaded both from $\text{Hg}(\text{CN})_2$ solution and from $\text{CaHg}(\text{CN})_4$ solution. Moreover, the position of the band remains unchanged on samples that were air-dried at 25°C,

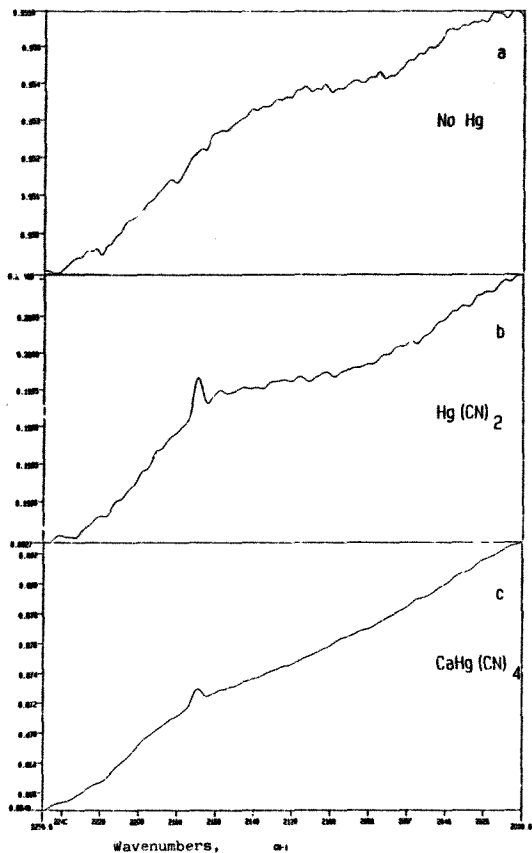


Fig. 3.48 Infrared spectra showing $\nu(\text{CN})$ for mercuric cyanide species adsorbed on activated carbons from solutions of varying stoichiometry:

- a) None
- b) $\text{Hg}(\text{CN})_2$
- c) $\text{CaHg}(\text{CN})_4$

or vacuum-dried at 180°C. Ultimate assignment of the peak is difficult, since it lies between those for the $\text{Hg}(\text{CN})_2$ and $\text{Hg}(\text{CN})_3^-$ species, and the presence of both of these species would result in two peaks, rather than one, being obtained. Moreover, the peak is sufficiently far away from that of the crystalline $\text{Hg}(\text{CN})_2$ to negate any assignment to this species.

Table 3.30
 $\nu(\text{CN})$ stretching frequencies for mercuric cyanide species

Species	$\nu(\text{CN}), \text{cm}^{-1}$	Ref.
Carbon contacted with $\text{Hg}(\text{CN})_2$ solution	2170	This work
Carbon contacted with $\text{CaHg}(\text{CN})_4$ solution	2170	This work
$\text{Hg}(\text{CN})_2$ (s)	2194	This work
$\text{Hg}(\text{CN})_2$ (aq)	2193	157
$\text{Hg}(\text{CN})_3^-$ (aq)	2162	157
$\text{Hg}(\text{CN})_4^{2-}$ (aq)	2143	157

In the light of the stoichiometric and theoretical studies discussed earlier, the peak is assigned to an adsorbed $\text{Hg}(\text{CN})_2$ species. The reason for the shift to lower frequency upon adsorption is unclear at this stage; this may be indicative of a charge-transfer interaction between the metal atom and the carbon surface, as was shown earlier in this Chapter to occur under certain conditions for adsorbed gold species on carbons.

(ii) Mechanism of adsorption of HgCl_2 onto activated carbon

Previous workers¹⁵⁶ have suggested that Hg_2Cl_2 may be formed on the carbon when contacted with HgCl_2 solution. A comparison of the standard reduction potentials in Table 3.29 suggests that this is feasible, since the reduction of Hg^{2+} to Hg_2^{2+} occurs at a much higher potential than the +0,24V of activated carbon, and moreover, if the mercury (I) species is precipitated in the form of Hg_2Cl_2 , it may well be stable as this species has a similar reduction potential (+0,268V) to activated carbon. Table 3.31 confirms that the Hg_2Cl_2 species is very insoluble.

Table 3.31
Solubilities of mercury compounds

Compound	Solubility ¹⁵⁵ , g/100cc	
	Cold water	Hot water
Hg_2Cl_2	0,00020 (25°C)	0,001 (43°C)
HgCl_2	6,9 (20°C)	48 (100°C)
$\text{Hg}(\text{CN})_2$	9,3 (14°C)	33 (100°C)

Figure 3.49 shows a scanning electron micrograph of an activated carbon surface that had been contacted with HgCl_2 solution. The presence of a precipitate is evident in the light coloured specks, and electron dispersive spectroscopic (EDS) analysis confirmed that it contained Hg and Cl. The mechanism of adsorption of mercury from chloride solutions can thus be summarized:





Fig. 3.49 Scanning electron micrograph of the surface of activated carbon contacted with HgCl_2 solution (540x magnification)

2) *The Mechanism of Adsorption of AuCl_4^- onto Activated Carbon*

The fact that AuCl_4^- is reduced to the metal upon contact with activated carbon is a well known phenomenon^{120, 121}, and this is not surprising when the reduction potential for AuCl_4^- (+1.00V against the standard hydrogen electrode) is compared with the average reduction potential for typical activated carbons (+0.24V)³². The micrographs in Figure 3.50 show that reduction occurs only along the particle edge, resulting in a metallic coating on the surface of the particle, in contrast to the crystals of metallic gold formed when aurocyanide-loaded carbons are subjected to acid-boiling prior to contact with hydroxide, and to the spheres of metallic gold produced on heating aurocyanide-loaded carbons at temperatures higher than 270°C.

In previous work⁶², the extraction of AuCl_4^- was found to display a similar dependence on cation to the extraction of $\text{Au}(\text{CN})_2^-$, and it was suggested that ion association also plays a role in the extraction of AuCl_4^- . In section 3.2f of this chapter, it was shown that the AuCl_4^- species adsorbs intact to some extent, particularly in the presence of an oxidant such as nitric acid. Figures 3.51 and 3.52 present ^{197}Au Mössbauer spectra that confirm these findings. The quadrupole due to AuCl_4^- is particularly obvious in the spectrum of the carbon loaded from an aqua regia solution.

These results demonstrate the fact that the adsorption of species onto activated carbon by an ion-pair mechanism is not restricted to aurocyanide, and this lends credence to the mechanism as a whole.

3.4 *Summary and Conclusions*

It was unequivocally shown, using a variety of techniques,

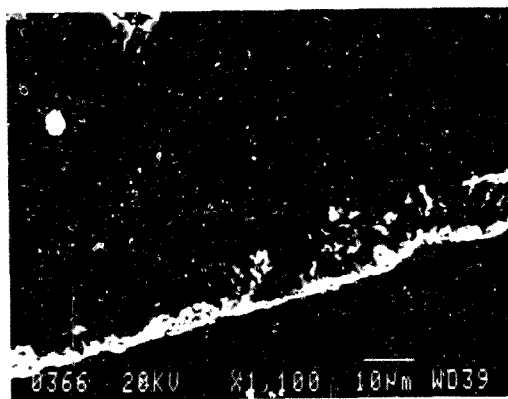
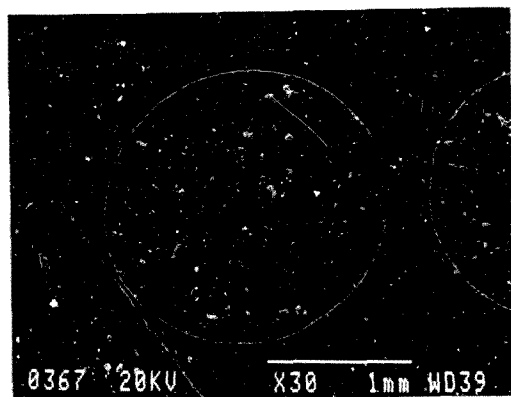


Fig. 3.50 Micrographs showing the reduction of AuCl_4^- to Au metal on the particle edge of activated carbon

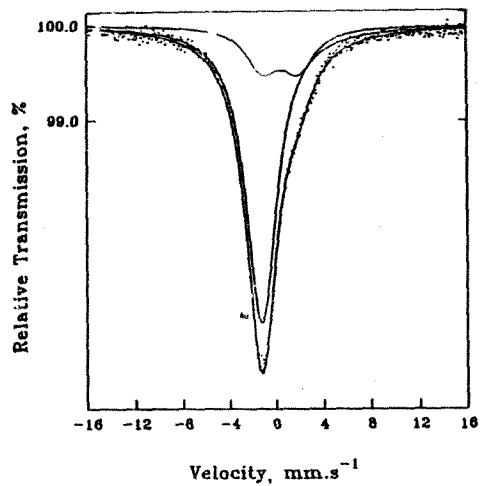


Fig. 3.51 ^{197}Au Mössbauer spectrum of AuCl_4^- adsorbed onto activated carbon from aqueous HAuCl_4 solution. (After Cashion et al.³⁹)

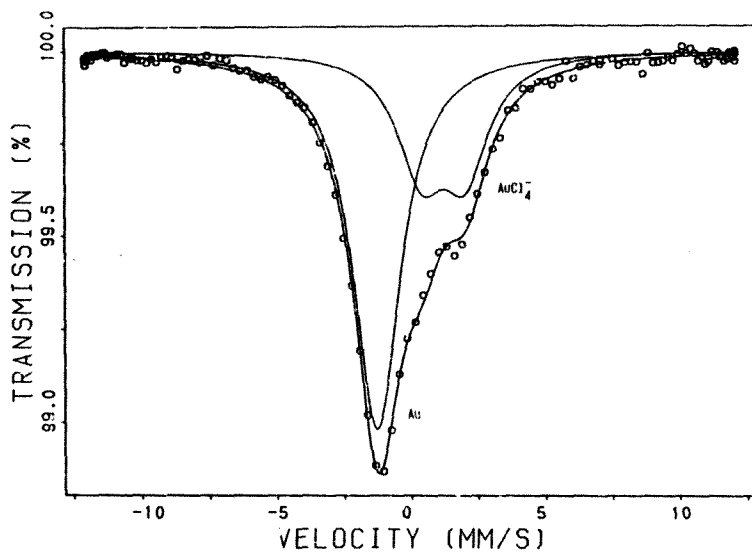
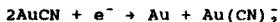


Fig. 3.52 ^{197}Au Mössbauer spectrum of AuCl_4^- adsorbed onto activated carbon from aqua regia

that under alkaline conditions typically encountered in a CIP plant, gold is extracted as an ion pair of the type $M^{n+}[Au(CN)_2]_n$, (where $M^{n+} = Ca^{2+}$, Na^+ , etc). At low pH values (below 3) gold is loaded onto activated carbon predominantly as the aurocyanide acid $HAu(CN)_2$, while, at intermediate pH values, the ion pair and the acid are loaded simultaneously. Partial decomposition of the $HAu(CN)_2$ to an AuCN-type species was shown to occur.

When loaded carbon is heated in strongly acidic solution, aurocyanide decomposition to AuCN is more complete. Evidence from elemental analyses, X-ray diffractometry and Mössbauer spectroscopy is consistent with the AuCN being present in the form of short-chain oligomers. When the carbon is treated subsequently with hydroxide solution, the following reaction occurs:



The standard reduction potential for this reaction is calculated to be 0,252V (vs SHE).

No evidence was found of the formation of AuCN during loading under conditions normally encountered in CIP operations. This reaction would occur to some extent, however, during a high-temperature acid-washing step prior to elution.

These reactions were also studied in aqueous solution in the absence of carbon. The kinetics of AuCN precipitation from acidified aurocyanide solutions were found to be first order, with activation energy 72,5 kJ/mol. Polymeric AuCN was found to be unstable in alkaline solutions, particularly at elevated temperatures. Analysis of the solution for $Au(CN)_2^-$ and CNO^- , and the investigation of the resultant solid phase by XRD enabled the following overall reaction mechanism to be derived:



This novel reaction probably also occurs on the carbon surface.

Aurocyanide adsorbed onto activated carbon from neutral and alkaline solutions is found to remain relatively stable at temperatures up to about 240°C, as concluded from the results of elemental analyses, scanning electron microscopy, X-ray diffractometry and Mössbauer spectroscopic measurements. At higher temperatures the aurocyanide is reduced to the metal, with evolution of gaseous HCN. A portion of the aurocyanide decomposes via an intermediate AuCN-type species. Aurocyanide loaded under acidic conditions decomposes by this mechanism at lower temperatures.

The controversy between different research workers regarding the mechanism of adsorption of aurocyanide onto activated carbon was shown to be due to differences in the experimental conditions employed by different research groups. The present work has shown that several different adsorption mechanisms are possible under varying conditions of ionic strength and pH, and in the presence or absence of oxygen. No evidence for any decomposition of $\text{Au}(\text{CN})_2^-$ to AuCN , NH_4^+ , HCO_3^- , or CNO^- species in neutral or alkaline solutions could be found. The effects of oxygen and ionic strength, and the pH shift that occurs upon adsorption, were found to be interrelated, and can be explained in terms of a dual adsorption mechanism which becomes more prevalent under low ionic strength conditions.

The important conclusions reached in the present work with regard to the mechanism of adsorption, from neutral and alkaline solutions, are summarized below.

Under all practical conditions (high ionic strength),

adsorption of aurocyanide onto activated carbon occurs via an ion-pair mechanism in which ion pairs of the type $M^{n+}[Au(CN)_2]_n$ are adsorbed onto the carbon surface without chemical change. Oxygen has an insignificant effect on gold adsorption under these conditions. Oxygen effects associated with operating carbon-in-pulp plants are more likely due to (i) catalytic oxidation of free cyanide^{89,158}, which results in more favourable conditions for gold adsorption, and (ii) enhancement of gold leaching¹⁵, should this be incomplete.

Under conditions of low ionic strength, the adsorption of aurocyanide onto activated carbon occurs via two mechanisms, the relative contributions of which depend on the presence of oxygen:

- (i) adsorption of $M^{n+}[Au(CN)_2]$ ion pairs, which occurs to a greater extent in the absence of oxygen, and
- (ii) formation of ion-exchange sites that coordinate aurocyanide by simple electrostatic ion-exchange. This mechanism occurs to a greater extent in the presence of oxygen.

The $Au(CN)_4^-$ species was found to adsorb onto activated carbon by a similar mechanism to that postulated for $Au(CN)_2^-$, i.e. as an ion pair of the type $M^{n+}[Au(CN)_4]_n$. The affinity of $Au(CN)_4^-$ for adsorption onto carbon proved to be greater than that for $Au(CN)_2^-$, which is also consistent with the ion-pair mechanism.

A Mössbauer spectroscopic investigation confirmed that $Au(CN)_4^-$ is the adsorbed species from both acidic and neutral solutions. A carbon that was loaded with $Au(CN)_4^-$ and subsequently acid-boiled, was found to contain $Au(CN)_2Cl_2$, $Au(CN)_2^-$ and $AuCN$, which are products of the decomposition of $Au(CN)_4^-$ by boiling hydrochloric acid.

Silver is adsorbed onto activated carbon from potassium cyanide solution in the form of the $K^+Ag(CN)_2^-$ ion pair. These species undergo further chemical change to AgCN and AgCl after boiling in hydrochloric acid. Subsequent treatment with hot sodium hydroxide solution results in reduction of all silver on the carbon to the metallic state, with some desorption of $Ag(CN)_2^-$.

When silver is loaded onto activated carbon from a silver nitrate solution, adsorption takes place via a dual mechanism, with reduction to metallic silver and precipitation of AgCl both taking place on the carbon surface.

Mercury is found to adsorb onto activated carbon in the form of $Hg(CN)_2$ from cyanide solution. The $Hg(CN)_2$ species adsorbs to a negligible extent, indicating the possibility of eluting adsorbed mercury with cold caustic cyanide solution. The adsorption of mercury from chloride solution occurs via the reduction to mercury(I) species, with subsequent precipitation of insoluble Hg_2Cl_2 within the carbon pores.

CHAPTER 4 ION ASSOCIATION OF $\text{MAu}(\text{CN})_2$ SALTS IN VARIOUS SOLVENTS

Knowledge of extent of association in $\text{MAu}(\text{CN})_2$ solutions and the nature and structure of complex species involved is important in understanding the influence of ion-pairing effects on extraction processes.

Work presented in the previous chapter has yielded evidence that the gold species adsorbed onto activated carbon from cyanide solution is the $\text{M}^{\text{n}+}[\text{Au}(\text{CN})_2]_n$ ion pair. This ion pair has also been invoked in extraction of aurocyanide by solvents such as 1-pentanol⁴⁵ and tributyl phosphate¹⁵⁹, as well as polymeric adsorbent resins^{80,132}, and the loading of gold onto deprotonated weak-base ion-exchange resins at high pH.

The ion associate of $\text{Au}(\text{CN})_2^-$ with the tetraphenylarsonium cation $(\text{C}_6\text{H}_5)_4\text{As}^+$ dissolved in an organic solvent provides the liquid membrane for an aurocyanide-specific ion-selective electrode¹⁶⁰. Another analytical technique that involves aurocyanide ion pairs is ion-pair chromatography¹⁶¹, in which the tetrabutylammonium ion pair is partitioned between a hydrophilic mobile phase and a hydrophobic surface.

This chapter presents a detailed study, using various techniques, of the association of $\text{MAu}(\text{CN})_2$ salts in various solvents. The factors influencing the extraction of ion pairs are also elucidated.

4.1 Ion Association of $\text{MAu}(\text{CN})_2$ Salts in Various Solvents - A Literature Survey

Perusal of the literature pertaining to stability constants^{83-85,147} reveals that much work has been done on the ion association behaviour of the iron cyanides and cobaltcyanide, and almost nothing on the other complex metal cyanide salts.

The dissociation constant of $\text{HAu}(\text{CN})_2$ has been reported¹⁶² to be 4.5×10^{-3} mol/l, which means that in aqueous solutions of low pH the gold will be almost entirely in the form of the associated $\text{HAu}(\text{CN})_2$ species. This is in agreement with other workers¹⁶³ who postulate dimerization to $[\text{HAu}(\text{CN})_2]_2$ in the aqueous phase at high concentrations.

Jones¹⁶⁴ explained effects in Raman spectra of concentrated aqueous $\text{LiAu}(\text{CN})_2$ solutions in terms of an ion association interaction between Li^+ and $\text{Au}(\text{CN})_2^-$. Some doubt as to this interpretation was raised by subsequent workers, however¹⁶⁵.

Ion pairs of the form $\text{MAg}(\text{CN})_2$, $\text{MAg}(\text{CN})_3^-$ and $\text{MAg}_2(\text{CN})_3^{2-}$ ($\text{M} = \text{Na}^+$, K^+) have been postulated¹⁶⁵ to exist in liquid ammonia solutions, as interpreted from Raman spectra.

The presence of ion pairs of the form $\text{MCo}(\text{CN})_6^{2-}$ in aqueous solutions ($\text{M} = \text{H}^+$, Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NR_4^+) has been indicated by variations in the cobalt-59 NMR chemical shift^{166,167}. The interpretation of the results in terms of polarization of cyanide ligands and solvent molecules in the presence of small cations, and a solvation effect in the presence of large cations, is similar to that independently postulated for aurocyanide ion-pairs⁴⁵.

Stability constants of ferrocyanide and ferricyanide ion pairs involving numerous cations have been determined⁸³⁻⁸⁵

by a number of different techniques.

4.2 The Study of Ion Association - A Literature Survey

There are numerous techniques¹⁶⁸⁻¹⁷¹ that have been used to quantitatively study ion association, although the suitability of a technique depends on the characteristics of the system to be studied. Various aspects of the system may be studied by a range of techniques. The more widely-used ones are summarised below.

a) Conductivity Measurements

Several methods^{168,173} exist for calculation of association constant K_a and limiting conductance Λ_0 for electrolytes from conductance/concentration data. The technique has been used for numerous solvents and electrolytes.

b) Ion-Selective Electrodes

This technique is still in its infancy, but is seeing an increasing number of applications to the study of ion association¹⁷⁴. However, application of ion-selective electrodes to nonaqueous solutions is still rather limited¹⁷⁵, due to variations in liquid-junction potentials and solvent attack on the membranes. Moreover, investigations are limited to one specific ion for each electrode.

The method has, however, given consistent values¹⁷⁶ for aqueous phase association of $KFe(CN)_6^{3-}$ and $KFe(CN)_6^{2-}$, where an appreciable degree of association occurs at relatively low concentrations.

c) *Ultraviolet-Visible Spectrophotometry*

In cases where there is some measure of orbital overlap occurring, and the spectrum of the ion pair differs from that of the unpaired ions, valuable information regarding environment and association of ions can be gained, both for aqueous¹⁷⁷ and nonaqueous¹⁷⁸ solutions. However, this additional information on the environment of the ions may become a disadvantage when the ion pair cannot be isolated and its spectrum analyzed.

d) *Infrared Spectrophotometry*

Information has been obtained on association and solvation of ions by infrared spectrophotometry^{179,180}. However, this technique is limited by the very large absorption due to water, and in solutions containing even a relatively small amount of water, the technique may prove useless.

e) *Raman Spectrophotometry*

Raman spectrophotometry is normally only useful when some measure of covalency exists between the ions. This limitation is somewhat balanced, when the ion pair does show Raman lines, by the fact that unlike infrared spectrophotometry, Raman scattering is not influenced by the presence of water molecules.

f) *NMR Measurements*

If one of the ions is paramagnetic, NMR measurements (for example, relaxation, chemical shifts, spin-spin coupling) can provide useful information on ion association interactions¹⁸¹. The chemical shift of the ^{23}Na nucleus has been taken to be a measure of solvating power of solvents towards Na^+ , by virtue of the linear relationship between $\delta^{23}\text{Na}$ and DN, the solvent donor number.

g) *Ion-Pair Solvent Extraction*

Distribution measurements can be used¹⁸² to generate values for association constant and extraction equilibrium constant as long as the assumption of zero association in the aqueous phase is valid, and the associated species is only assumed to be formed on mutual contact of the ions with the organic phase. The possibility of side reactions such as triple ion formation and dimerization must also be taken into account. When this is the case, reasonable agreement¹⁸³ with conductivity measurements can be obtained.

The two methods may also be combined¹⁸⁴, to provide association constants for both phases, as well as extraction constants which take the distribution of both neutral and ionic species into account.

h) *Ion-Exchange Studies*

In the case where an ion association constant is either known or negligible, ion-exchange studies with mixtures of the salt of interest and a salt containing a common ion can be used to determine association constants¹⁸⁵. The disadvantage is that a mixed electrolyte must be used.

Another area¹⁸⁶ involves the uptake of an anion such as AuCl_4^- by cation-exchange resin, via the formation of Li^+ or H^+ ion pairs¹⁸⁷.

i) *Other Methods*

In certain cases, other methods such as polarography^{188,189}, reaction kinetics^{188,189}, solubility determinations¹⁸⁹, polarimetry¹⁸⁹, x-ray scattering¹⁸⁸, ESR spectroscopy¹⁸⁹, ebulliometry¹⁹⁰ (changes in boiling temperature of the solvent due to ion association), ultrasonic absorption^{188,191}, have all been found to be

useful in the study of ion association and solvation. The characteristics of the system in question should be taken into account before any of these methods are attempted, however.

4.3 Ion Association of $\text{MAu}(\text{CN})_2$ Salts in Aqueous Solution

As discussed earlier, the only association data for an $\text{MAu}(\text{CN})_2$ species found in the literature is that reported by Ford-Smith, et al.¹⁶², who deduced a value of $4,5 \times 10^{-3}$ mol/l as the dissociation constant for $\text{HAu}(\text{CN})_2$ in aqueous solution. This value is possibly incorrect, as will be discussed below.

a) Potentiometric Titration of Aqueous Solution of $\text{HAu}(\text{CN})_2$

A fresh solution of $\text{HAu}(\text{CN})_2$ was prepared and titrated against standardized NaOH solution. The titration curve is shown in Figure 4.1. A value for pK (acid dissociation constant) of $1,52 \pm 0,02$ was computed using points 2 to 7 of the data shown in Table 4.1. The points further on in the titration were not usable because the acid was virtually completely dissociated at that stage ($\alpha > 0,965$; see Table 4.1) and titrant additions served mainly to adjust the pH. The initial points correspond to a sufficiently low degree of dissociation to ensure that an accurate result can be calculated.

The stoichiometric end-point of the titration enabled the determination of total acid content of the initial solution as $0,005087$ mol/l. This can be compared with the gold concentration of $0,005056$ mol/l calculated from the mass of $\text{KAu}(\text{CN})_2$ initially used to prepare the solution, corresponding to a variance of only 0,6 per cent.

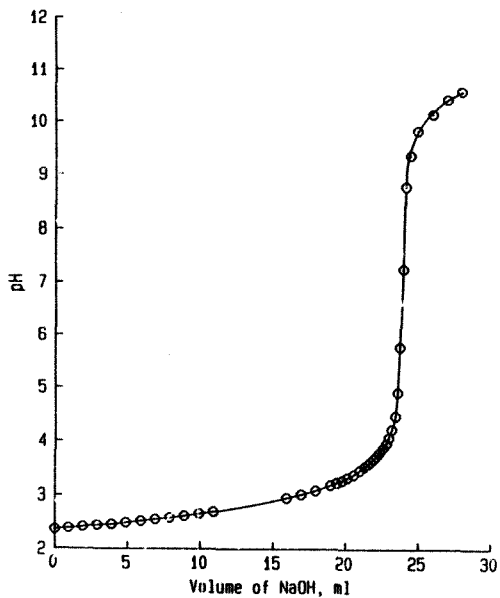
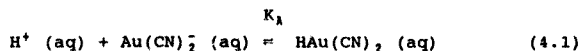


Fig. 4.1 Potentiometric titration of $\text{H[Au(CN)}_2\text{]}$ with NaOH

Table 4.1
Values of pK_a and α (Degree of Dissociation)
for Titration Data in Figure 4.1

No.	pH	α	pK_a
2	2,410	0,8774	1,555
3	2,463	0,8966	1,525
4	2,523	0,9093	1,522
5	2,590	0,9186	1,538
6	2,657	0,9356	1,495
7	2,943	0,9623	1,536
8	3,093	0,9657	1,643
9	3,270	0,9724	1,723
10	3,450	0,9742	1,873
11	3,660	0,9788	1,995
12	4,063	0,9835	2,288

A value for the association constant of HAu(CN)_2 can be calculated from the titration results, i.e



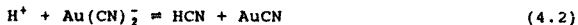
$$K_A = 33,8 \text{ l/mol}$$

This can be compared with the value $K_A = 222,2 \text{ l/mol}$ obtained by Ford-Smith et al.¹⁶², by a similar potentiometric titration. Their result is possibly in error owing to simplifications in their calculation; for example, they assumed that the pK_a was equal to the pH of half-neutralization, an assumption that is justified only if the acid is very weak, or very dilute¹⁹². This is tantamount to assuming that, when exactly half the equivalent amount of NaOH has been added, the

concentrations of HAu(CN)_2 and Au(CN)_2^- are equal, and this is only true if the initial solution was mainly in the associated form. Calculation shows that this was not the case in Ford-Smith's experiment, and applying the same erroneous calculation to the present data yields an erroneous value for K_A of similar magnitude. Moreover, any calculation based solely on one data point would not be expected to yield as accurate a value as one based on several points.

A species distribution diagram for acidified aurocyanide solutions as a function of pH is shown in Figure 4.2. The associated HAu(CN)_2 species clearly predominates in solutions of $\text{pH} < 1.5$, and essentially all of the aurocyanide will be in the associated form in 1.0 mol/l acid solution. This effect should be taken into account whenever acidified aurocyanide solutions are being used.

A final point regarding these results is the possibility that the HAu(CN)_2 solution degraded to some extent, forming the insoluble AuCN polymer:



This reaction proceeds almost quantitatively at temperatures exceeding about 60°C , as shown in Chapter 3, but the rate and the extent of this reaction has not been determined under conditions pertinent to the present experiment. To address this problem, a volume of 250 ml of acidified aurocyanide-containing solution was placed in a glass bottle and shaken thoroughly. Samples of the solution were taken periodically, filtered with Whatman 542 filter paper and analysed for gold by atomic absorption spectrophotometry. The results are shown in Table 4.2, and demonstrate that the solution remained quite stable within the time period required to perform the titration.

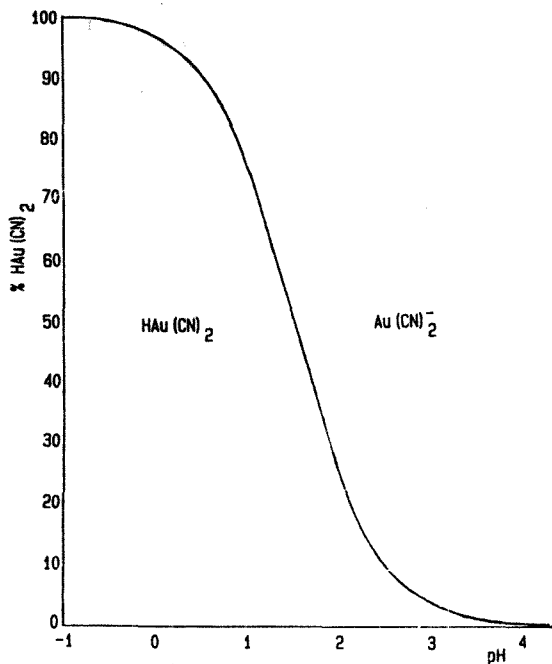


Fig. 4.2 Species distribution diagram for acidified aurocyanide solutions

Table 4.2
Stability of $\text{HAu}(\text{CN})_2$ Solutions with Time

Time h	Gold concentration in solution, mg/l	
	$\text{HAu}(\text{CN})_2$ solution prepared by ion-exchange	Solution of $\text{KAu}(\text{CN})_2$ in 0,16 M HCl
0	255	893
1	256	896
4	255	893
24	259	854
48	266	830
72	262	845
96	255	-

Yellow AuCN appeared on the plastic lid of the bottle in the second experiment after about 24 hours. Only a faint trace of AuCN was seen in the first experiment. Plastic containers and synthetic polymeric adsorbents are known⁸⁰ to catalyze reaction 4.2 to some extent, so the stability of the solution in the all-glass container used in the titration should be acceptable.

*b) Conductimetric Study of Aqueous Solutions of
 $\text{KAu}(\text{CN})_2$ and $\text{NaAu}(\text{CN})_2$*

Equivalent conductances of the above-mentioned salts in aqueous solution are presented in Table 4.3. The data was analysed using the Shedlovsky extrapolation technique¹⁹³, which is based on the equation

$$1/\Lambda S(z) = 1/\Lambda_0 + (K_A/\Lambda_0^2) (cAf_{\pm}S(z)) \quad (4.3)$$

in which Λ is the measured equivalent conductance, Λ_0 is the equivalent conductance at infinite dilution, K_A is the association constant, c is the concentration, and f is the activity coefficient calculated using the Debye-Huckel limiting Law equation,

$$-\log f_{\pm} = a (ac)^{1/2} \quad (4.4)$$

In Equation 4.4, a is a constant that depends on dielectric constant and temperature, and α is the degree of dissociation.

The function $S(z)$ in Equation 4.3 has the form

$$S(z) = (z/2 + (1 + (z/2)^2)^{1/2})^2 \quad (4.5)$$

where

$$z = \Lambda(c\Lambda)^{1/2}/\Lambda_0^{3/2} \quad (4.6)$$

in which Λ is the Onsager constant, a function of the dielectric constant, viscosity and temperature of the solution.

The calculation was performed on an Apple IIe computer. Convergence normally occurred after two iterations. The calculation effectively involves the linear least squares analysis of a plot of $1/\Lambda S(z)$ against $c\Lambda f_{\pm} S(z)$ (Equation 4.3).

Table 4.4 presents results for analysis of the conductance data. The Shedlovsky technique is not the most modern conductance equation, but can be expected¹⁹⁵ to yield values of K_A and Λ_0 sufficiently close to those obtained by other equations to suit the purposes of this Thesis.

Table 4.3
Concentrations and corresponding equivalent
conductances for MAu(CN)₂ salts in aqueous solution

Salt	$10^4 c$ (mol/l)	Λ (Scm ² /mol)
KAu(CN) ₂	7,8737	118,88
	15,225	117,67
	23,637	117,19
	32,198	116,35
	49,169	115,00
	61,706	114,40
	71,694	113,45
	79,909	112,72
	88,381	112,53
	97,020	112,17
NaAu(CN) ₂	7,5110	100,53
	17,886	98,95
	27,465	97,94
	34,925	97,35
	49,294	96,64

Table 4.4
Constants derived using equation 4.3

Salt	K_A l/mol	Λ_0 Scm ² /mol	λ_0^+ Scm ² /mol ^a	λ_0^- Scm ² /mol
KAu(CN) ₂	1,40	121,49	73,50	48,0
NaAu(CN) ₂	1,64	102,70	50,10	52,6

^a Literature values obtained from Robinson and Stokes¹⁹⁴

The values of K_A for $\text{KAu}(\text{CN})_2$ and $\text{NaAu}(\text{CN})_2$ in aqueous solution of about 1,5 indicate a modest degree of association in aqueous solution, with the sodium salt exhibiting a slightly higher degree of association than the potassium one. Figure 4.3 presents a species distribution diagram for $\text{KAu}(\text{CN})_2$ and $\text{NaAu}(\text{CN})_2$ as a function of cation concentration. These findings are consistent with the previously postulated mechanisms of extraction of $\text{MAu}(\text{CN})_2$ ion pairs by activated carbon⁶², polymeric adsorbents⁸⁰ and organic solvents⁴⁵. A reasonable correlation for the equivalent ionic conductance at infinite dilution for the $\text{Au}(\text{CN})_2^-$ ion (λ_0^-) was obtained from the $\text{KAu}(\text{CN})_2$ and $\text{NaAu}(\text{CN})_2$ data. A value of 48,0 Scm^2/mol can be taken for this parameter, based on the 9-point determination of $\text{KAu}(\text{CN})_2$. This value can be compared with that obtained¹⁹⁵ for $\text{Ag}(\text{CN})_2^-$, of 66,5 Scm^2/mol , and fits into the expected trend of decreasing ionic conductance with decreasing ionic radius, as shown in Table 4.5

This trend is consistent with that expected for the mobilities of large, effectively unhydrated ions in aqueous solution, following the trend predicted by the Stokes equation, which relates hydrated radius and limiting specific conductance of ions:

$$r_s = z_+ F^2 / (6\pi L \eta \lambda_0) \quad (4.7)$$

where z is the ionic charge, F is the Faraday constant, L is Avogadro's number and η is the solution viscosity.

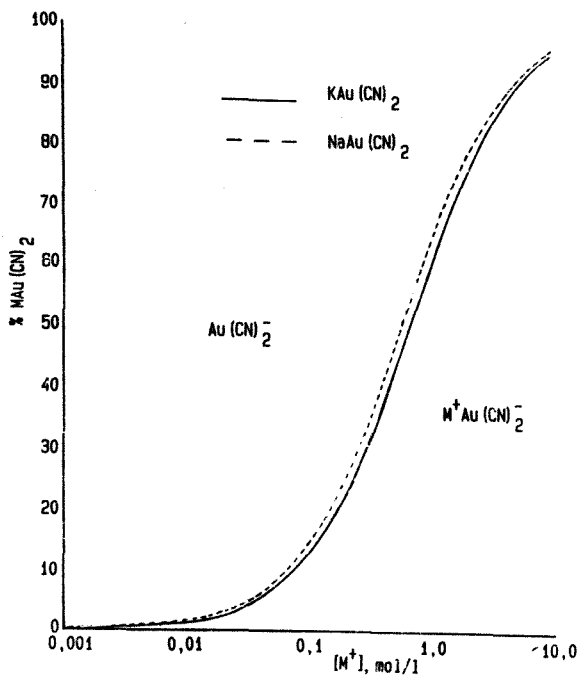


Fig. 4.3 Species distribution diagram for potassium and sodium aurocyanide with variation in cation concentration

Table 4.5
Specific ionic conductances and ionic radii
for some anions in aqueous solution

Anion	λ_0 (S cm^2/mol)	r_c (Å)	Ref
ClO_4^-	67,3	2,36	194
I^-	76,8	2,16	194
Br^-	78,2	1,95	194
Picrate	30,4		194
Butyrate	32,6		194
Propionate	35,8		194
Acetate	40,9		194
Formate	54,5		194
$\text{Au}(\text{CN})_2^-$	48,0		This work
$\text{Ag}(\text{CN})_2^-$	66,5		196

Values for the Stokes radii were calculated (see Table 4.6) for the $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ ions, using the values for λ_0 in Table 4.5. It should, however, be emphasized that Equation 4.7 is strictly only valid for symmetrical ions, whereas these ions are linear. Calculations for the "effective" ionic radii of the ions, based upon their estimated ionic volumes, yield values also presented in Table 4.6. (See Appendix 2 for details).

The similarities in the two ionic radii, for both salts, confirms the lack of hydration of the $\text{Au}(\text{CN})_2^-$ ions in aqueous solution, despite the various estimations involved.

Table 4.6
Comparison of estimated effective ionic radii
with Stokes radii for $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$
in aqueous solution

Anion	r_{eff} (Å)	r_s (Å)
$\text{Au}(\text{CN})_2^-$	2,33	1,9
$\text{Ag}(\text{CN})_2^-$	2,28	1,4

4.4 Ion Association of $\text{MAu}(\text{CN})_2$ Salts in Organic Solvents

To predict the effect of organic solvents on the degree of association, it is necessary to turn to one of the numerous theories for ion association.

The Bjerrum theory¹⁹⁷ yields an indication of the important parameters that influence ion association. The Bjerrum equation has the form

$$K_A = \frac{4\pi L}{1000} \left[\frac{z_+ z_- e_0^2}{\epsilon k_B T} \right]^3 \int_2^b e^{y^4} dy \quad (4.8)$$

where L is Avogadro's number, z_+ and z_- are the charges on the ions, e_0 is the electronic charge, ϵ the dielectric constant of the solvent, k_B is Boltzmann's constant, and T is the temperature. The constant b is

$$b = z_+ z_- e_0^2 / \epsilon a k_B T \quad (4.9)$$

where a is the interionic distance.

From Equation 4.8 it can be seen that an increased association constant can be expected for (i) solvents of lower dielectric constant, (ii) small ionic radii, which result in a small value for a and hence a large value for b in the integral, and (iii) large z_+ and z_- .

This theory gives no indication of the effects of solvation, covalent bonding, polarization, and non-spherical ions, all of which could be expected to play a role in solutions of $\text{MAu}(\text{CN})_2$ salts in organic solvents.

a) *Infrared Spectra of $\text{MAu}(\text{CN})_2$ salts in organic solvents*

Infrared measurements were made in the cyanide stretch $\nu(\text{CN})$ region ($2000 - 2300 \text{ cm}^{-1}$), which was found to be almost free of solvent absorption for both solvents studied.

Infrared studies of the analogous systems of lithium and sodium thiocyanates in aprotic organic solvents, including THF and MEK, have been the subject of several studies in the past^{129, 198-200}, all of which interpreted spectral changes in terms of ion association and higher aggregation, with the help of evidence from other techniques, such as ultrasonic spectroscopy¹⁹⁸.

Infrared spectra of $\text{LiAu}(\text{CN})_2$ solutions in THF and MEK are shown in Figures 4.4 and 4.5 respectively. The spectra for $\text{LiAu}(\text{CN})_2$ in THF show dramatic changes occurring in the two obvious absorbance bands with change in total electrolyte concentration. Four absorbance bands are apparent in the spectrum of $\text{LiAu}(\text{CN})_2$ in MEK.

Spectral data obtained for $\text{LiAu}(\text{CN})_2$ solutions are presented in Table 4.7, along with assignments of bands and

proposed structures of species. The CN stretch for $\text{Au}(\text{CN})_2^-$ in aqueous solution has been reported²⁰¹ to occur at 2146 cm^{-1} . In the THF solution no such absorbance band occurs; however, a strong band at 2152 cm^{-1} is evident. (This is analogous to a similar shift that occurs, from "free" SCN^- in THF¹²⁹ at 2052 cm^{-1} to LiSCN ion pairs¹²⁹, at 2065 cm^{-1}). Figure 4.4 shows a prominent band at 2172 cm^{-1} that grows in intensity, relative to the 2052 cm^{-1} band, with increasing electrolyte concentration. This is attributable to $[\text{LiAu}(\text{CN})_2]_2$ dimers, having a structure similar to that shown in Table 4.7. The small shoulder at 2177 cm^{-1} is attributable to the CN stretch of the non-bonded CN group, although the distinction between the two CN groups of $\text{Li}\dots\text{N}-\text{C}-\text{Au}-\text{C}-\text{N}$ is not clear at this stage.

The effects discussed above are clearer on examination of the spectra of $\text{LiAu}(\text{CN})_2$ in MEK (Figure 4.5). A band at 2145 cm^{-1} is present in this case, and is attributable to free $\text{Au}(\text{CN})_2^-$, or solvent-separated $\text{Li}^+\text{S}_x\text{Au}(\text{CN})_2^-$ ion pairs. It is not possible to distinguish between the two by IR spectrophotometry, since orbital overlap is required in order to observe an effect. An interesting feature is that the intensity of the 2145 cm^{-1} band decreases relative to that of the 2152 cm^{-1} ion-pair band as the electrolyte concentration increases. This behaviour is expected for an ion association equilibrium.

The fact that the 2145 cm^{-1} band is observable when MEK is the solvent, and not when THF is the solvent indicates a lesser degree of contact ion-pairing in MEK ($\epsilon = 18.0$), as compared with THF ($\epsilon = 7.4$). This observation is in compliance with the trends predicted by the Bjerrum equation (4.8) for ion association with varying dielectric constant, as discussed earlier.

The dimer band at 2172 cm^{-1} is also relatively weaker than the ion-pair band at 2152 cm^{-1} , when the MEK spectra (Figure 4.5) are compared with the THF spectra (Figure 4.4). This

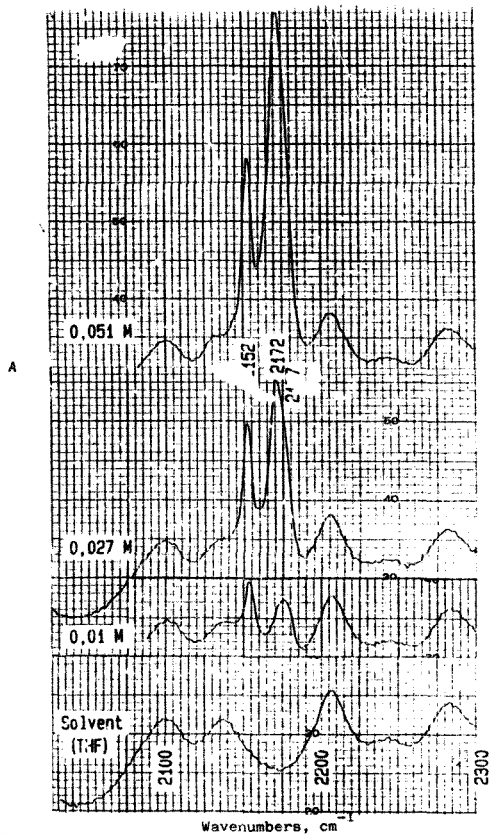


Fig. 4.4 Infrared spectra showing the CN stretch bands of LiAu(CN)_2 in THF at various concentrations

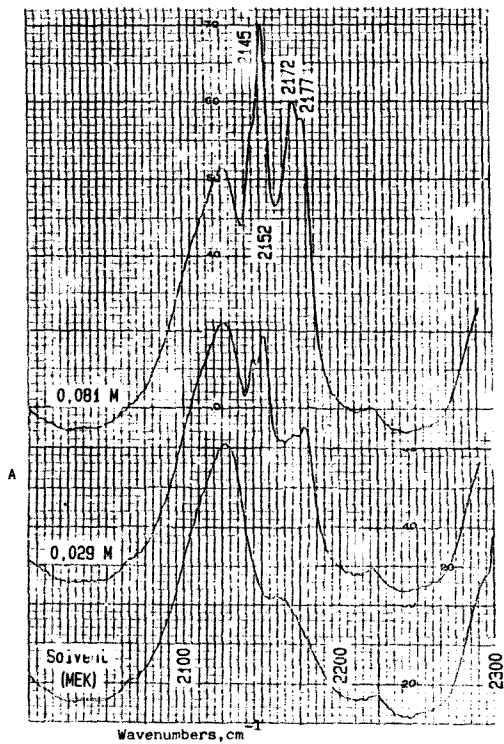


Fig. 4.5 Infrared spectra showing the CN stretch bands of LiAu(CN), in MEK at various concentrations

is indicative of a lesser degree of dimerization in the solvent of lower dielectric constant, a trend once more expected from theory.

Table 4.7

Infrared spectral data for $\text{LiAu}(\text{CN})_2$ species in tetrahydrofuran (THF) and methyl ethyl ketone (MEK)

Species	Proposed Structure	$\nu(\text{CN})(\text{cm}^{-1})$	Solution
Free ion or solvent-separated ion pair	$\text{Au}(\text{CN})_2^-$ or $\text{Li}^+\text{S}_x\text{Au}(\text{CN})_2^-$	2145	$\text{LiAu}(\text{CN})_2$ in MEK
Contact ion pair	$\text{Li} \cdots \text{N} \equiv \text{C} - \text{Au} - \text{C} \equiv \text{N}$	2152 2177	$\text{LiAu}(\text{CN})_2$ in MEK or THF
Contact dimer	$ \begin{array}{ccc} & \text{N} \equiv \text{C} - \text{Au} - \text{C} \equiv \text{N} & \\ & & \\ \text{Li} & & \text{Li} \\ & & \\ & \text{N} \equiv \text{C} - \text{Au} - \text{C} \equiv \text{N} & \end{array} $	2172	$\text{LiAu}(\text{CN})_2$ in MEK or THF

The fact that only one band is associated with the dimer indicates that all four CN groups have similar environments; hence the structure assigned in Table 4.7. It should be pointed out that polycrystalline $\text{LiAu}(\text{CN})_2$ exhibits the $\nu(\text{CN})$ at 2152 cm^{-1} , with no higher frequency bands¹²⁶ such as occur in THF and MEK solutions. The

observed effects can therefore not be attributed to the presence of colloidal LiAu(CN)_2 crystals.

The spectra of $\text{NBu}_4\text{Au(CN)}_2$ in both THF and MEK (Figures 4.6 and 4.7 respectively) display only one major absorbance band, at 2145 cm^{-1} , that is attributable to $\nu_3(\text{CN})$. The small bands observable in very concentrated solutions at 2102 cm^{-1} and 2165 cm^{-1} in both solvents are attributable to $\nu_2(\text{CN})$ in $[\text{N}^{13}\text{CAuCN}]^-$ and $\nu_1(\text{CN})$ respectively¹²⁶. Tetrabutylammonium salts are known¹²⁹ to be associated in THF, and the lack of infrared bands is a manifestation of the negligible orbital overlap occurring in these systems. The bulky NBu_4^+ cation is suggested¹²⁹ to bring negligible perturbations to the relevant anion; hence no effect is observable.

Figures 4.8 and 4.9 show the effect of adding 1-2 drops of de-ionized water to MEK and THF solutions of comparable concentration to those discussed earlier. No effect on the $\text{NBu}_4\text{Au(CN)}_2$ solutions is observed. However, for LiAu(CN)_2 solutions in both THF and MEK, all the ion-pair and dimer bands disappear, leaving only the 2145 cm^{-1} band attributable to the free ion, or solvent-separated ion-pair. The small amount of water is effectively hydrating the ions, thereby removing the contact interaction. They will still be associated, as solvent-separated ion-pairs (water being the solvent in this case), as will be discussed in the following section.

4.5 Distribution of MAu(CN)_2 Salts between Aqueous Solutions and Organic Solvents

Distribution of MAu(CN)_2 salts into organic solvents such as 1-pentanol⁴⁴ and TBP^{159, 202} has recently been the topic of some attention, with the mechanism involving extraction of ion-pair species. Distribution of HAu(CN)_2 into some ketones and alcohols has also been studied in the past.

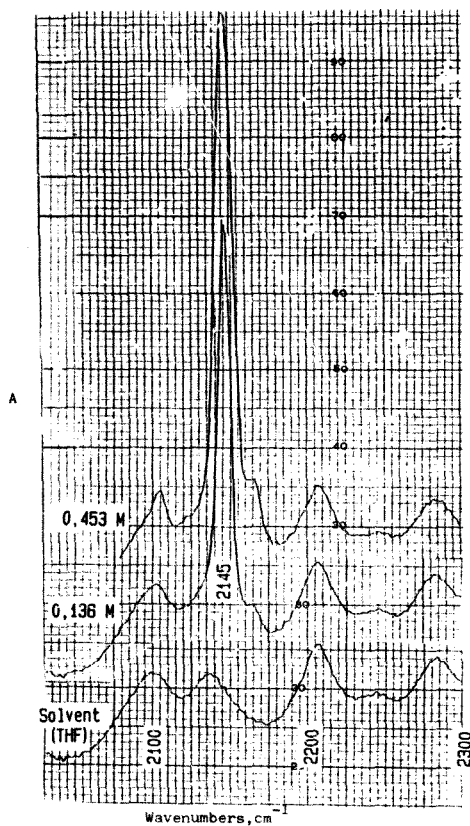


Fig. 4.6 Infrared spectra showing the CN stretch bands of $\text{NBu}_4\text{Au}(\text{CN})_4$ in THF at various concentrations

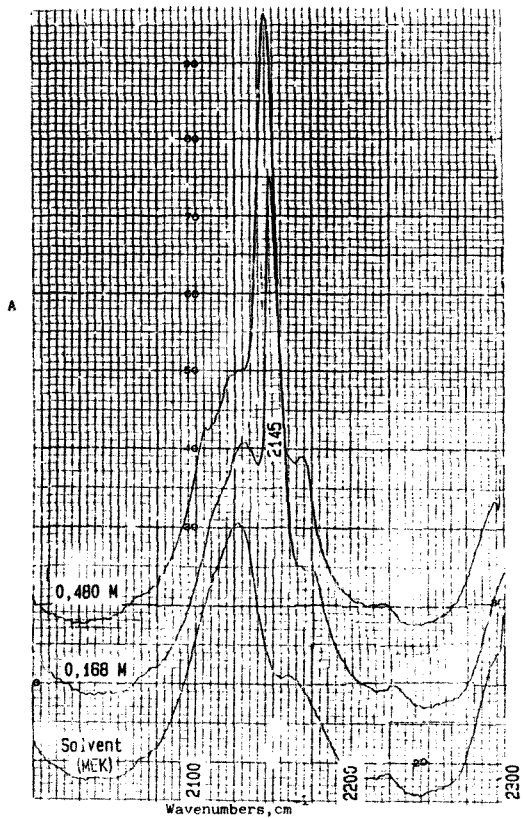


Fig. 4.7 Infrared spectra showing the CN stretch bands of $\text{NBu}_4\text{Au}(\text{CN})_2$ in MEK at various concentrations

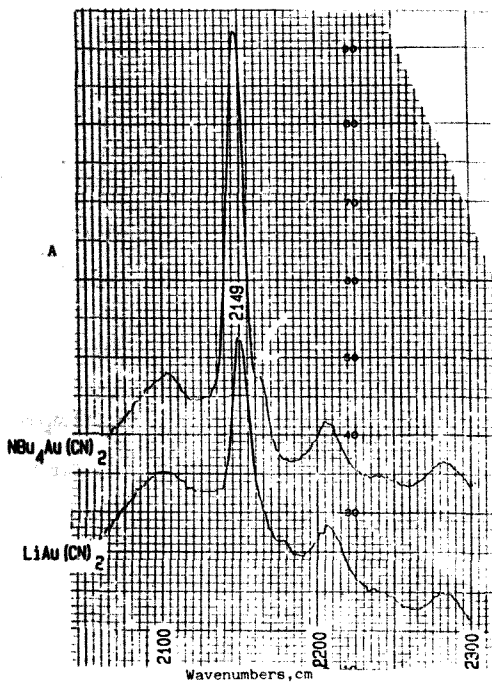


Fig. 4.8 Infrared spectra showing the effect of water on the CN stretch bands of $\text{LiAu}(\text{CN})_2$ and $\text{NBu}_4\text{Au}(\text{CN})_2$ in THF

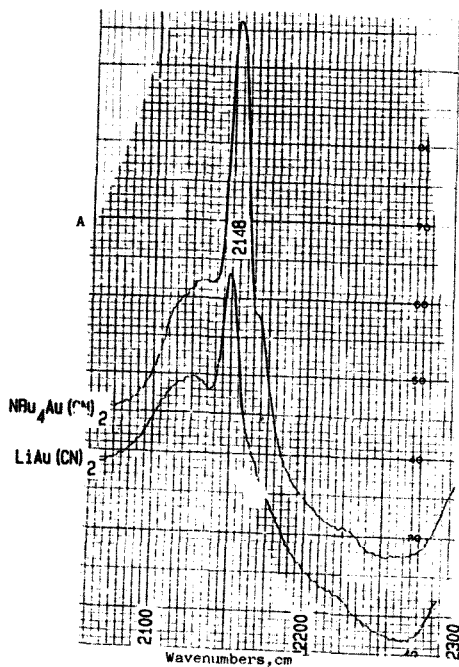
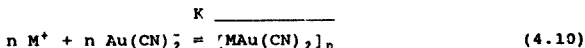


Fig. 4.9 Infrared spectra showing the effect of water on the CN stretch bands of $\text{LiAu}(\text{CN})_2$ and $\text{NBu}_4\text{Au}(\text{CN})_2$ in MEK

Distribution of MAu(CN)_2 into an immiscible solvent can be represented as follows:



where overscoring denotes species in the organic phase. This model assumes there to be one species $[\text{MAu(CN)}_2]_n$ in the organic phase. This assumption has no theoretical basis but is a useful tool in interpreting distribution data.

The equilibrium constant K for reaction (4.10) can be written as follows:

$$K = \frac{[\text{MAu(CN)}_2]_n}{[\text{M}^+]^n [\text{Au(CN)}_2^-]^n} \quad (4.11)$$

The logarithmic form is:

$$\log [\text{MAu(CN)}_2]_n = n \log [\text{M}^+] + n \log [\text{Au(CN)}_2^-] + \log K \quad (4.12)$$

In the present series of experiments, $[\text{M}^+]$ is kept constant at 0,1M (as MCl). Thus, $n \log [\text{M}^+]$ remains constant. If c_o denotes the total gold concentration in the solvent phase at equilibrium, and c_a denotes that in the aqueous phase at equilibrium, then a plot of $\ln c_o$ against $\ln c_a$ would yield n , the aggregation number, which is equal to the slope. An example of such a plot is shown in Figure 4.10, and the value of $n = 0,69$ obtained indicates that the simple model of Equations 4.10 to 4.12 above does not hold in this instance. Miller, et al.¹⁵⁹ report a similar effect for KAu(CN)_2 extraction into TBP from an aqueous solution containing 0,1 M $\text{NaCN}/0,1$ M NaOH , and they ascribe the behaviour to "a continual change in the capacity of the organic phase and/or the nature of the mixed solvation

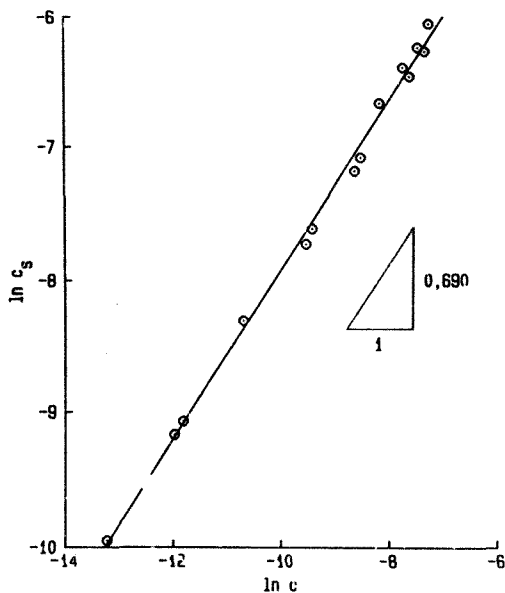


Fig. 4.10 Total gold concentration in the organic phase versus that in the aqueous phase for the distribution of $\text{KAu}(\text{CN})_2$ between TBP and 0,1 M KCl solution

structure".

In the light of the present study, an interpretation based simply on dissociation of $\text{MAu}(\text{CN})_2$ species in the organic phase is used. Conductance measurements on the solutions used to generate the data in Figure 4.11 have confirmed this premise. Dissociation of salts in water-saturated organic solvents has been suggested in numerous studies²⁰³, particularly in solvents of higher bulk dielectric constant. Müller and Diamond²⁰⁴ present similar curves for triauryllamine. Data on HCl salts in organic solvents (where values of n ranged from less than 1 to greater than 2) was interpreted in terms of dissociation ranging through to aggregation. The interpretation was confirmed by osmometric measurements. Maddock et al²⁰⁵ report the dissociation of HAuCl_4 in various organic phases, as shown by distribution measurements and confirmed by migration experiments.

A different situation arises when the solvent is 1-pentanol, as shown in Figure 4.11. Apart from the behaviour discussed above, a break in the curve exists and at lower concentrations, a slope of $n = 1$ is obtained. This is the reverse of the predicted situation, where the degree of association would be expected to increase with increasing concentration. Zvyagintsev, et al¹⁶³, report similar behaviour for distribution of $\text{HAu}(\text{CN})_2$ into 1-pentanol, which they interpret in terms of aqueous phase dimerization, forming non-extractable $[\text{HAu}(\text{CN})_2]_2$ species in the aqueous phase. Dimerization is not likely to occur in media of such high dielectric constant, however, and the following interpretation seems more reasonable.

The background electrolyte, in this case KCl, has been found to distribute into the 1-pentanol phase to a modest degree. Potentiometric titrations for Cl^- were performed on aliquots of 1-pentanol that had been contacted with aqueous solutions with varying KCl concentrations. The

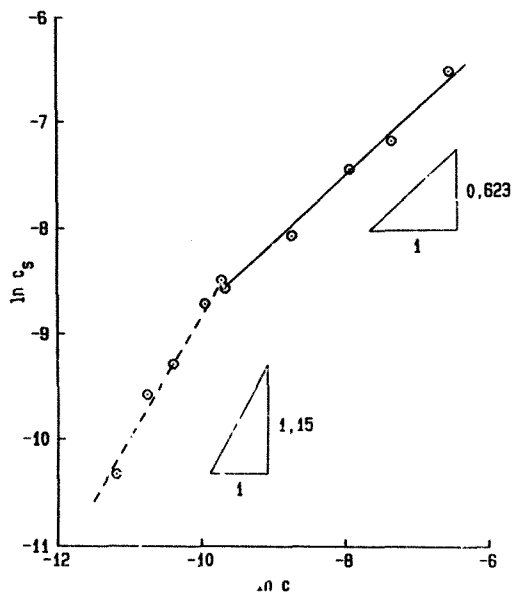


Fig. 4.11 Total gold concentration in the organic phase versus that in the aqueous phase for the distribution of KAu(CN)_2 between 1-pentanol and 0,1 M KCl solution

chloride concentration in the 1-pentanol phase which had been contacted with aqueous 0.1 M KCl, was found to be about 2×10^{-4} M. This corresponds approximately with the location of the break in the $\ln c_o - \ln c$ curve (Figure 4.10), at about 1×10^{-4} M.

The behaviour at low gold concentrations is simply an ion exchange between Cl^- and $\text{Au}(\text{CN})_2^-$. The very much higher affinity of the latter ion for the solvent phase ensures the complete exchange of $\text{Au}(\text{CN})_2^-$ for Cl^- . Once this point has been reached, no further ion exchange can occur, and extraction of $\text{K}^+\text{Au}(\text{CN})_2^-$ takes place, as discussed for the TBP case. In TBP solution (Figure 4.10), the concentration of chloride was found to be about 2×10^{-5} M; therefore the break in the $\ln c_o - \ln c$ curve was fortuitously not observed in the concentration region studied.

A similar behaviour was observed in the $\text{HAu}(\text{CN})_2^-$ / 1-pentanol system (Figure 4.12). A value of $[\text{Cl}^-]_o$ of 0.0034 M can be compared with the location of the break in the curve, which occurs at $c_o = 0.0025$ M.

The slope of $n = 1$ found for concentrations of gold less than that for Cl^- in the organic phase is to be expected from the ion-exchange mechanism discussed above, and can be derived mathematically^{206,207}.

The association constant for $\text{MAu}(\text{CN})_2$ in the organic phase can be calculated from distribution data at varying total concentrations of gold, from which Figures 4.10 to 4.12 were derived. Association behaviour in these water-saturated solvents will be discussed in terms of extraction of $\text{MAu}(\text{CN})_2$ salts from aqueous solution by various extractants. Background knowledge of association behaviour of these species in aqueous (section 4.3) and pure organic solution (section 4.4) will prove invaluable in interpreting the results.

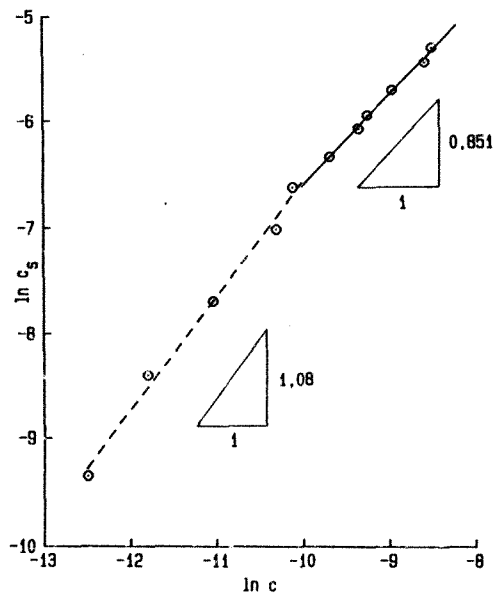


Fig. 4.12 Total gold concentration in the organic phase versus that in the aqueous phase for the distribution of HAu(CN)_2 between 1-pentanol and 0,1 M HCl solution

The extraction constant for a species QX between two phases is given¹⁸² as:

$$K_{ox}^{1p} (QX) = \frac{a_o (QX)}{a_v (Q^+) a_v (X^-)} \quad (4.13)$$

where a_o and a_v refer to activities of species in organic and aqueous phases respectively. In dilute solutions of QX containing only Q^+ , X^- ions and QX ion pairs, the association constant in the organic phase is given as

$$K_A (QX) = \frac{a_o (QX)}{a_o (Q^+) a_o (X^-)} \quad (4.14)$$

From Equations 4.13 and 4.14, a relationship between distribution ratio D^* and aqueous concentrations can be deduced¹⁸²:

$$D^* + D_{corr} = (a_v (Q^+) a_v (X^-))^{1/2} K_{ox}^{1p} (QX) + (K_{ox}^{1p} (QX)/K_A (QX))^{1/2} \quad (4.15)$$

where D^* is defined as

$$D^* = c_o / (a_v (Q^+) a_v (X^-))^{1/2} \quad (4.16)$$

and D_{corr} is a correction term:

$$D_{corr} = (1 - 1/f_o) (K_{ox}^{1p} (QX)/K_A (QX))^{1/2} \quad (4.17)$$

In Equation 4.17, f_o is the mean activity coefficient in the organic layer. The D_{corr} term was found to be small and rather unimportant for the calculation, except in the cases cited later.

It is obvious that Equation 4.13 assumes that the aqueous ions distribute into the organic phase in the form of the ion pair alone. The possibility of the free ions distributing into the organic phase as such necessitates the definition of an ionic extraction constant:

$$K_{ex}^{ION} (QX) \frac{a_s (Q^+) a_s (X^-)}{a_v (Q^+) a_v (X^-)} \quad (4.18)$$

If this is combined with Equation 4.14, we obtain Equation 4.19:

$$K_{ex}^{ION} = K_{ex}^{IP} / K_A \quad (4.19)$$

The total extraction constant, which includes extraction of both ions and ion pairs, will be defined in a similar manner to that of Iwamoto, et al¹⁸⁴:

$$K_{ex}^{TOT} = K_{ex}^{ION} \cdot K_{ex}^{IP} \quad (4.20)$$

Equation 4.15 was solved using a linear least squares program on an Apple IIe microcomputer, enabling the calculation of K_A , K_{ex}^{TOT} , K_{ex}^{IP} and K_{ex}^{ION} .

a) *Effect of solvent*

(i) *Water content*

Values of K_A , K_{ex}^{TOT} , K_{ex}^{ION} and K_{ex}^{IP} were obtained for $KAu(CN)_2$ in various solvents from distribution data similar to that shown in Figures 4.10 to 4.12. A correlation between these parameters and the water content of the organic phase expressed in terms of x_v , the mole fraction of water, is shown in Figures 4.13 to 4.16. The association constant (Figure 4.13) decreases exponentially as the water content of the organic phase increases. This is consistent with the findings from the infrared study reported in the previous section, and suggests that species in the organic phase are preferentially hydrated. Abundant evidence exists^{184,203,204,208-210} regarding preferential hydration of salts in organic solvents originating from distribution experiments.

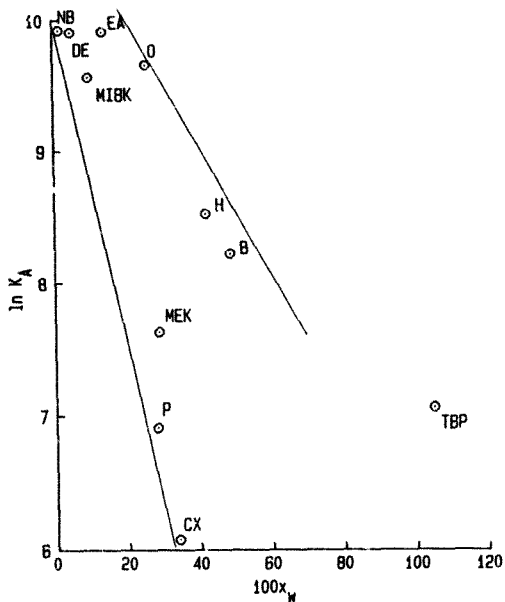


Fig. 4.13 Effect of water content of solvent on K_A for $\text{Au}(\text{CN})_2$ in water-saturated solvents

- NB - Nitrobenzene
- DE - Diethyl ether
- EA - Ethyl acetate
- O - Octanol
- H - Hexanol
- B - Butanol
- MIBK - Methyl isobutyl ketone
- MEK - Methyl ethyl ketone
- P - 1-Pentanol
- CX - Cyclohexanone
- TBP - Tributyl phosphate

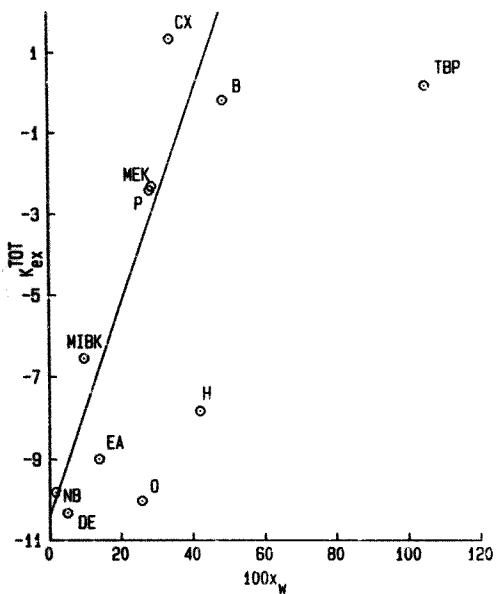


Fig. 4.14 Effect of water content of solvent on K_{ex}^{TOT} for the distribution of $KAu(CN)_2$ between various solvents and 0,1 M KCl solution

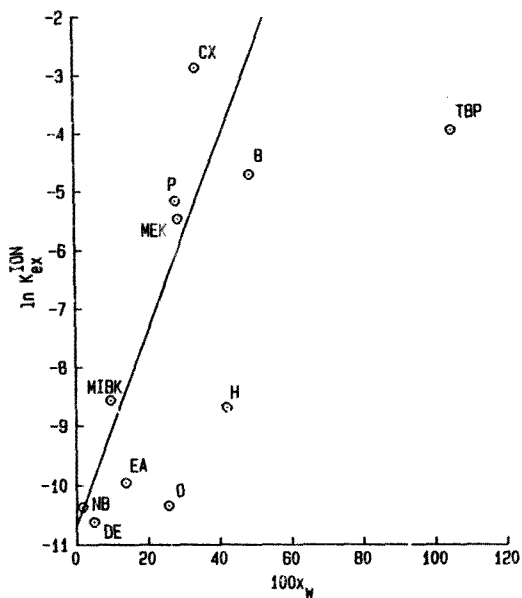


Fig. 4.15 Effect of water content of solvent on K_{ex}^{ION} for the distribution of $KAu(CN)_2$ between various solvents and 0.1 M KCl solution

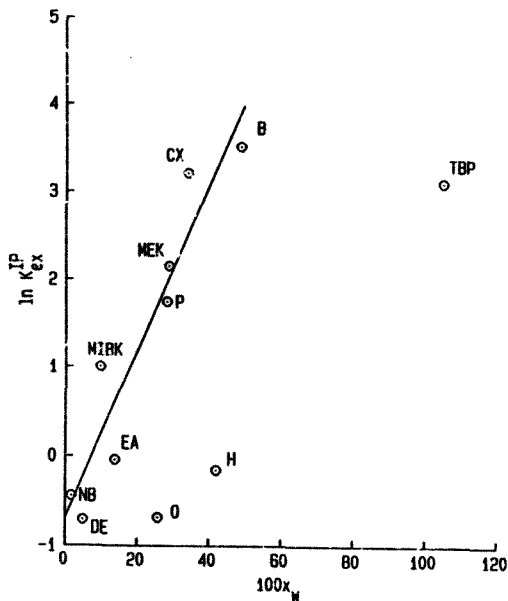


Fig. 4.16 Effect of water content of solvent on K_{ex}^D for the distribution of $KAu(CN)_2$ between various solvents and 0.1 M KCl solution

The correlation of the extraction constants with $100 x_w$ is reasonable. The low values obtained for hexanol and octanol can possibly be ascribed to the high viscosity of these solvents resulting in equilibrium not being reached in twenty minutes. The distribution data obtained for these two solvents was more scattered than for any other solvent studied.

The correlation of K_A with $100 x_w$ (Figure 4.13) is obviously not as good as that for the extraction constants (Figures 4.14 to 4.16). This indicates that even though the water content of the organic phase proves to be a factor affecting the association constant, other factors are also important. Some of these are discussed in the following sections.

The effect shown in Figure 4.13 is simply a manifestation of decreasing hydration forcing the ions to associate in order to fulfill the coordination requirements. The trend of increasing extraction of species as the water content increases (Figures 4.14 to 4.16) is also a manifestation of this effect. In general, solvents with a high water content are more able to solvate, and therefore extract, ions and ion pairs effectively.

A notable exception to these trends occurs when the solvent is TBP. TBP was the only solvent for which the correction for $f_{\pm}$, the activity coefficient of the free ions in the organic phase, made any real difference to the results. However, negative values were obtained for the constants upon application of the Debye-Hückel equation. The results have no physical significance, and this is probably due to the limitations of the simple equation used. Application of more complex activity equations to the data would probably not be useful due to limitations in the accuracy of data obtained in distribution experiments.

Alternatively, evidence²⁰³ suggests that a 1:1 TBP:H₂O

adduct is formed, accounting for the high water content. Moreover, Marcus and Kertes¹⁰³ assign TBP to a Group II class of solvents, whereas all the oxygen-containing hydrocarbon type solvents are assigned to Group I. In Group II solvents the solvent itself is involved in solvating the dissolved species, which is not the case for Group I solvents. The anomalous behaviour of TBP may thus be due to a different extraction mechanism, in which a mixed TBP-H₂O solvate exists. Such a species has been postulated¹¹¹ previously to occur in the TBP-H₂O-KAu(CN)₂ system. Moolman¹¹¹ found that both $\nu(\text{CN})$ and $\nu(\text{P=O})$ for these solutions remained the same as the pure compounds. The lack of an effect on $\nu(\text{CN})$ is consistent with the findings in the present work when water was added. It was also shown earlier in this chapter that Au(CN)₂ remains largely unhydrated. It is therefore likely that only the associated cation is solvated in the organic phase, and if such a mixed solvate as KAuC(CN)₂·xTBP·yH₂O exists, then the concentration of solvating TBP would be negligible in comparison with the concentration of non-solvating TBP, and no effect could be expected to be observed on $\nu(\text{P=O})$.

(ii) Dielectric Constant

Figure 4.17 shows the effect of solvent dielectric constant on the association constant. The solid line is the theoretical trend due to the Bjerrum equation (4.8). The correlation is poor, but it should be pointed out that the solvent water content, dielectric constant and donor number DN (see next section) are all interrelated and will all have an effect on the system.

Table 4.8 shows constants obtained for several isodielectric solvents. A comparison of association and extraction constants within each group confirms that a simple Bjerrum-type dependence on dielectric constant does not hold for these systems.

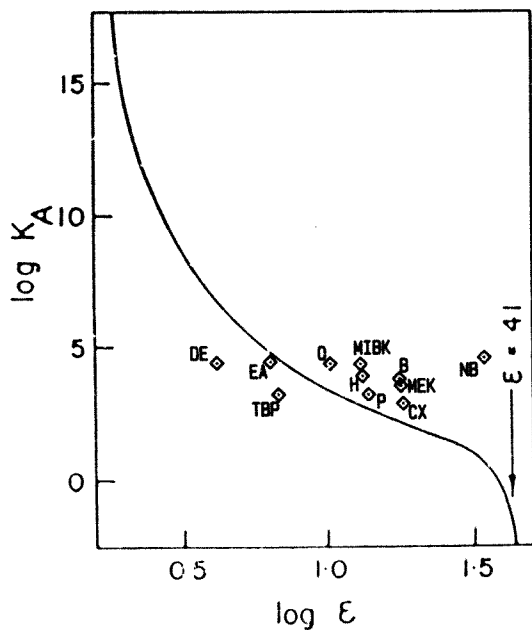


Fig. 4.17 Plot of $\log K_A$ versus $\log \epsilon$ for KAu(CN)_2 in water-saturated solvents. (Solid line is the theoretical Bjerrum relation (4.8) for 1:1 salts, after Bockris and Reddy⁹⁷)

Table 4.8
Association and extraction constants for $KAu(CN)_2$ in
several isodielectric solvents

Solvent	ϵ	n^a	K_A	$10^4 K_{ex}^{TOT}$	$10^4 K_{ex}^{ION}$	K_{ex}^{IP}	DN^b	δ^c
1-Butanol (B)	17,5	(1,34) 0,82	3 739	2 976	89,22	33,36	19,5 24,0	13,6
Methyl ethyl ketone (MEK)	18,0	0,68	2 052	365	42,14	8,65	17,4	
Cyclohexanone (CX)	18,3	0,60	437	13 878	563,4	24,63	17,8	9,9
1-Pentanol (P)	13,9	(1,00) 0,60	1 004	331	57,39	5,76		11,6
Methyl isobutyl ketone (MIBK)	17,1	0,81	14 186	5,25	1,92	2,73		
Ethyl acetate (EA)	6,02	0,92	20 165	0,459	0,477	0,962	17,1	
Tributyl phosphate (TBP)	6,8	0,63	1 160	4 134	188,8	21,90	23,7	

^a Slope of a $\ln c_s - \ln c$ plot (Aggregation number). When two numbers are given, the top one reflects the ion-exchange region.

^b Gutmann's^{212,213} donor number, from refs 214,215.

^c Solubility parameter, from Weast⁶⁵.

A comparison of values obtained for n , the slope of a $\ln c_s - \ln c$ plot confirms the fact that lower n values correspond to a higher degree of dissociation. In fact, for both diethyl ether and nitrobenzene, two solvents of

very different dielectric constant (Table 4.9), values of $n=1$ were obtained and association constants proved to be large, indicating that for these solvents, the ion pair is the predominant species. It should be noted that the ion-exchange mechanism discussed earlier does not account for these results, since effectively no chloride could be detected in the organic phases.

Table 4.9
Association and extraction constants for KAu(CN)_2 in
diethyl ether and nitrobenzene

Solvent	ϵ	n^a	K_A	$10^4 K_{\text{ex}}^{\text{TOT}}$	$10^4 K_{\text{ex}}^{\text{ION}}$	$K_{\text{ex}}^{\text{IP}}$	$[\text{Cl}^-]_e$ (mol/l) ^b	DN^d	δ^e
Diethyl ether (DE)	4,2	0,91	20 103	0,121	0,245	0,493	0 ^c	19,2	7,4
Nitrobenzene (NB)	34,82	0,99	20 403	0,203	0,315	0,643	6×10^{-6}	4,4	10,0

^a Slope of a $\ln c_e - \ln c$ plot. (Aggregation number)

^b Determined by potentiometric titration with AgNO_3 solution

^c None detectable

^d Gutmann's^{212,213} donor number, from refs 214,215

^e Solubility parameter, from Weast⁶⁵

(iii) Donor number (DN), and solubility parameter (δ)

Tables 4.8 and 4.9 show that neither solvent DN^{212,213} nor δ are the most important parameters influencing the association and extraction constants, once again

confirming the importance of water content on the association and distribution behaviour of the system. Empirical relationships have been established²¹⁶ between association constants and other parameters, such as solubility products. It is likely that this as well as other parameters not discussed also have some effect on association constants in different solvents. Lack of available data negates any quantitative calculations along these lines, however.

b) Effect of diluent

Benzene and cyclohexane were found to extract no measurable quantity of gold from a 0,003 M $\text{KAu}(\text{CN})_2$ aqueous solution in the presence of 0,1 M KCl, and are thus effectively inert solvents.

The effect of these inert diluents (1:1 mole ratios with 1-pentanol) on the distribution of $\text{KAu}(\text{CN})_2$ was investigated. Figures 4.18 and 4.19 show $\ln c_1$ - $\ln c_2$ plots for benzene and cyclohexane respectively as diluents. Table 4.10 summarizes the relevant properties of these mixtures.

Aggregation numbers exceeding $n = 1,0$ indicate that aggregation beyond the ion pair is occurring, e.g.

$$K_d = \frac{2 [\text{K}^+\text{Au}(\text{CN})_2^-]}{[\text{K}^+\text{Au}(\text{CN})_2]_2} \quad (4.21)$$

The fact that the aggregation number lies between 1 and 2 indicates that a mixture of ion pairs and dimers is probably present. The species are presumably all hydrated, forming solvent-separated ion pairs and dimers, unlike the contact species found to exist in anhydrous solvents (Section 4.4).

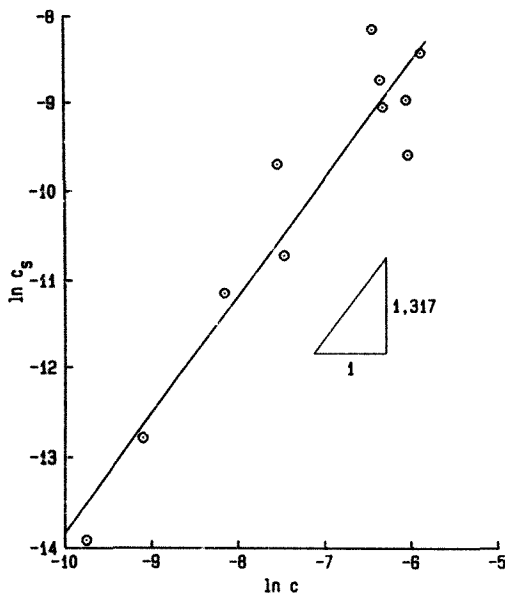


Fig. 4.18 Total gold concentration in the organic phase versus that in the aqueous phase for the distribution of $\text{KAu}(\text{CN})_2$ between 1-pentanol/benzene mixtures (molar ratio 1:1) and 0,1 M KCl solution

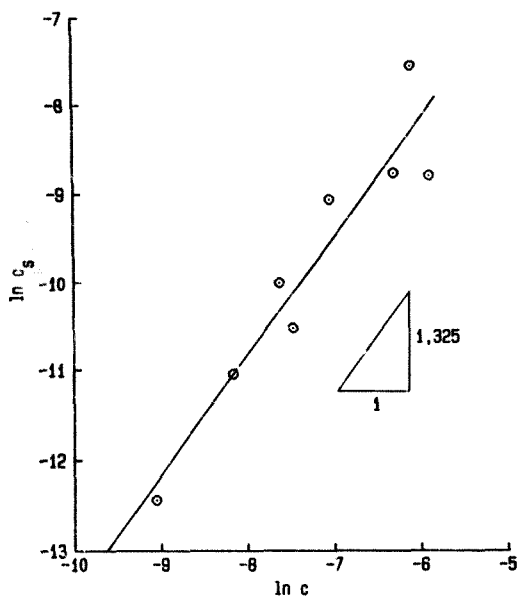


Fig. 4.19 Total gold concentration in the organic phase versus that in the aqueous phase for the distribution of $\text{KAu}(\text{CN})_2$ between 1-pentanol/cyclohexane mixtures (molar ratio 1:1) and 0,1 M KCl solution

Table 4.10
Aggregation numbers and relevant properties of
solvent mixtures

Solvent mixture (1:1 molar ratio)	n ^a	ε ^b	100x _w ^c	wt % w ^d	ρ (g/ml)
Pentanol/benzene	1,317	9,5	5,4	1,17	0,841
Pentanol/cyclo- hexane	1,325	5,5	4,0	0,82	0,794
Pentanol	0,60	13,9	28,3	7,5	0,814
Benzene	- ^e	2,28	0,31	0,072	0,879
Cyclohexane	- ^e	2,03	0,48	0,072	0,779

^a Slope of $\ln c_s - \ln c$ plot (Aggregation number)

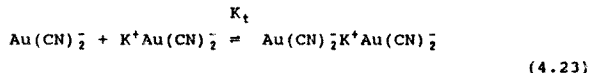
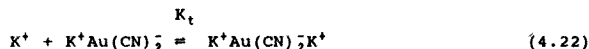
^b Mixtures - this work

^c x_w refers to the mole fraction of water in the water-saturated mixture

^d Weight % water in organic phase

^e Densities of the water-saturated mixtures are reported, and compares well with theoretical values for the pure mixtures (See Appendix 1)

Interpretation of these results in terms of triple ion formation, i.e.



cannot be discounted. However, the existence of triple ions has recently been questioned^{217,218}, because the conductivity effects which led initially to triple ions

being postulated can in several instances be explained in terms of the effects of concentration on permittivity. Moreover, the presence of any ionic species in media of such low dielectric constant and water content is dubious.

Table 4.10 shows that the dielectric constant of the solution is about half that of pure 1-pentanol; however, the water content has been reduced by a factor of about six. Water content is once again the most important factor which influences the ion-pair formation and aggregation in the $\text{KAu}(\text{CN})_2$ system.

The presence of species such as dimers in mixtures of solvents and diluents also serves to explain certain anomalous behaviour reported previously. In an attempt to assign a solvation number to the extracted species, Mooiman²¹⁹ reports an upward curvature to a plot of $\log D$ against $\log [\text{TBP}]$ for the distribution of $\text{KAu}(\text{CN})_2$ between an aqueous solution and a TBP solution with o-xylene as diluant ($\epsilon = 2,568$). Under these conditions, dimerization would be expected to occur to some extent, and this probably explains Mooiman's²¹⁹ anomalous result. Thus, analysis based on an assumption that the only species in the organic phase is the ion pair may be invalid under conditions of low ionic strength.

c) *Effect of Cation*

The effect of cation on the distribution and association parameters for $\text{KAu}(\text{CN})_2$ in five different solvents are shown in Figures 4.20 to 4.23.

The effect of cationic radius on the total extraction constant, $K_{\text{x}}^{\text{TOT}}$, is similar for several different solvents, as shown in Figure 4.20. The total extraction constant goes through a minimum at K^+ , with $K_{\text{x}}^{\text{TOT}}$ increasing towards both lower cationic radius (Li^+ , H^+), as

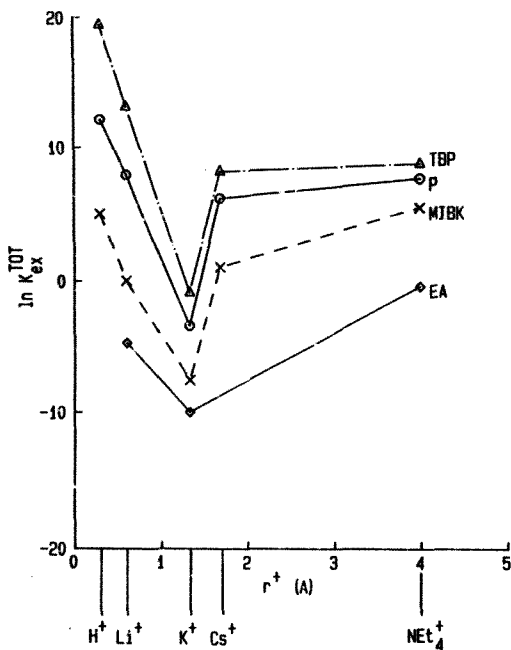


Fig. 4.20 Effect of cationic radius on K_{ex}^{TOT} for the distribution of $MAu(CN)_2$ between various solvents and 0,1 M NaCl solution

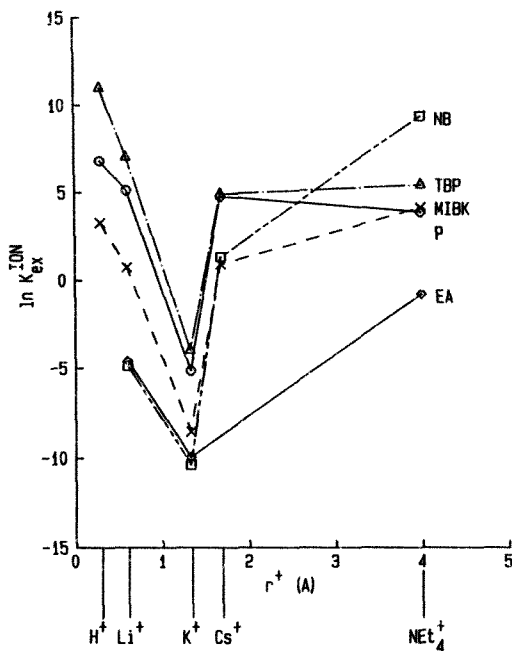


Fig. 4.21 Effect of cationic radius on K_{ex}^{ION} for the distribution of $MAu(CN)_2$ between various solvents and 0.1 M MCl solution

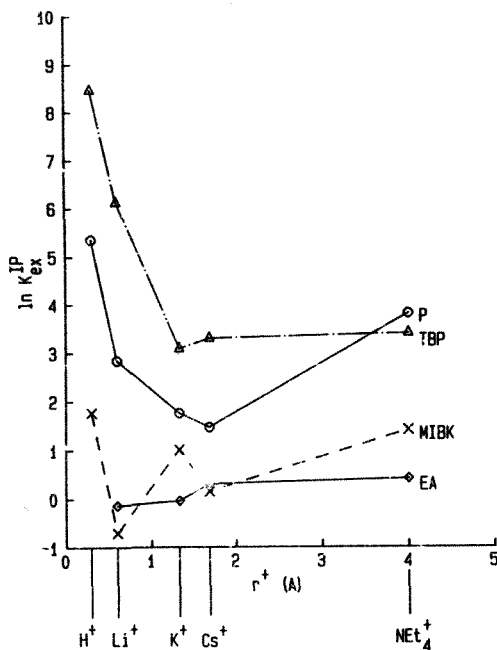


Fig. 4.22 Effect of cationic radius on K_{ex}^{IP} for the distribution of $MAu(CN)_2$ between various solvents and 0,1 M MCl solution

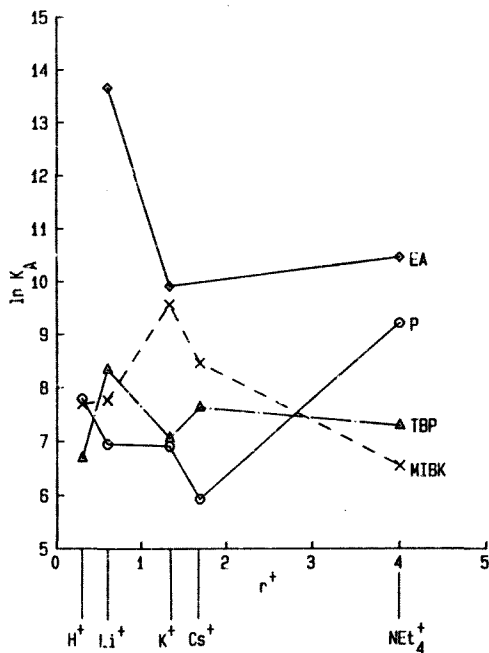


Fig. 4.23 Effect of cationic radius on K_A for $MAu(CN)_2$ in various water-saturated solvents

well as higher cationic radius (Cs^+ , NEt_4^+). (It should be pointed out that the use of the crystallographic radius on the abscissa has no practical implication, and merely represents a convenient scale for comparison. No cognizance has been taken in Figure 4.20 of hydrated or solvated radii, these being somewhat difficult to quantify). A similar trend has been established in previous work⁴⁵ on the distribution of aurocyanide ion-pairs into 1-pentanol.

The fact that a similar trend is evident in solvents of such varying dielectric constant and water content suggests a similar mechanism for extraction of $\text{KAu}(\text{CN})_2$ by each of these solvents.

The trend to greater K_{ex}^{TOT} as one ascends the series K^+ , Li^+ , H^+ is probably a manifestation of the structure of the hydrated species in each case. Diamond²²⁰ discusses a related effect observed in the extraction of HInCl_4 into organic solvents. Water molecules are much smaller than solvent molecules and hence more water molecules can pack around a cation to form a primary hydration shell. This fact, coupled with the greater solvation energy of ion-water interactions as compared to ion-organic solvent interactions, means that to extract into the solvent without great loss in solvation energy, the cation must retain its primary hydration shell, and undergo further solvation of this hydrated species in the organic phase. Table 4.11 gives some values for enthalpies of hydration and ionic radii for the pertinent ions.

The situation is different for larger cations, such as Cs^+ and NEt_4^+ , which have smaller hydration enthalpies and virtually no primary hydration shell. Such ions displace a considerable volume of the hydrogen-bonded water structure in the aqueous phase, and are hydrophobic, being squeezed out into the organic phase. This hydrophobic effect is also evidenced by the aqueous solubilities of

aurocyanide salts, listed in Table 4.12.

Table 4.11
Ionic radii and absolute hydration enthalpies of
some ions

Ion	Ionic radius, Å (Pauling)	ΔH_{hyd} , kJ/mol ^a
H ⁺	0,30 ^b	-1091
Li ⁺	0,60	- 519
K ⁺	1,33	- 322
Cs ⁺	1,69	- 264
NEt ₄ ⁺	4,00 ^c	

^a All data from Cotton and Wilkinson²²¹, unless otherwise stated

^b Estimated in previous work⁴⁵

^c From Marcus²²²

Table 4.12
Solubility of aurocyanide salts in aqueous solution

Salt	Solubility at 25°C mol/l	Ref.
LiAu(CN) ₂	7	130
NaAu(CN) ₂	0,16	130
KAu(CN) ₂	0,87	130
NBu ₄ Au(CN) ₂	0,003	45

It is significant that the order of decreasing extractability in Figure 4.20, i.e.

TBP > 1-pentanol > MIBK > ethyl acetate

is also the order of decreasing water content of the saturated solvents.

The effect of cation on K_{ex}^{ION} is shown in Figure 4.21, and from the similarity to the effect on K_{ex}^{TOT} , it is clear that the ionic component contributes considerably to the total extraction trend shown in Figure 4.20.

The data for nitrobenzene in some cases yielded slightly negative values, indicating complete dissociation in the organic phase. (See Appendix 3). Moreover, in these cases the aggregation number, n , proved to be very close to 0.5 which is the theoretical value obtained when dissociation is complete. This is a manifestation of the high dielectric constant of nitrobenzene ($\epsilon = 34$,²²), and the inverse dependence of K_A on ϵ (Equation 4.8). Therefore, K_{ex}^{TOT} and K_{ex}^{IP} data for nitrobenzene do not appear in Figures 4.20 and 4.22. The data for K_{ex}^{ION} , however, has physical significance, and appears in Figure 4.21. A similar trend to the other solvents is evident, except in the case of NET_4^+ , which displays a markedly higher extraction into nitrobenzene. Nitrobenzene is relatively non-coordinating, being a poor donor solvent, and therefore has a low water content, thus providing a medium more compatible for the non-hydrated tetraethylammonium cation than a solvent with a higher water content. Moreover, large hydrophobic cations such as NET_4^+ behave as "structure makers" in aqueous solution²²³, so a 0.1 M NET_4Cl background in the aqueous phase would result in a loss of entropy and increase in enthalpy of water, resulting in an enhanced "squeezing out" of the hydrophobic $NET_4^+Au(CN)_2^-$ ion pair from the aqueous phase.

The effect of cationic radius on both K_{ex}^{IP} and K_A does not show as clearcut a trend as the effect on K_{ex}^{ION} and K_{ex}^{TOT} . The effect on K_{ex}^{IP} is qualitatively similar, displaying a minimum. However, the difference in solvation of the

various ion pairs must be considerable and could account for the shifting minimum.

In Figure 4.23 a general trend to lower K_1 is observed as the cationic radius increases, and this is in agreement with data for association of tetraalkylammonium halides in various solvents²¹⁴ and is consistent with the theoretical dependence of K_1 on a , the interionic distance in the Bjerrum equation (4.8). The anomalous behaviour of the $\text{NET}_4^+\text{Au}(\text{CN})_2^-$ ion pair in 1-pentanol is probably a manifestation of the hydrogen-bonded structure of the alcohol, making it water-like and therefore subject to the same thermodynamic considerations as discussed above for the aqueous phase.

The effect of solvent water content on the values of extraction and association constants obtained for the H^+ , Li^+ , Cs^+ and NET_4^+ systems with $\text{Au}(\text{CN})_2^-$ are shown in Figures 4.24 to 4.27 respectively. The behaviour observed for the extraction of $\text{HAu}(\text{CN})_2$ and $\text{LiAu}(\text{CN})_2$ (Figures 4.24 and 4.25 respectively) is similar to that for the extraction of $\text{KAu}(\text{CN})_2$, with solvent water content being the most important solvent parameter influencing the extraction and association constants, as discussed in section 4.5 a). For the larger, less hydrated Cs^+ and NET_4^+ cations, (Figures 4.26 and 4.27 respectively), a similar trend does not exist, and other specific solvent properties, such as dielectric constant and hydrogen-bonding ability play a role, as discussed above.

The distribution and association of $\text{MAu}(\text{CN})_2$ has proven to be complex; however the most important factors influencing the observed behaviour have been isolated and discussed above.

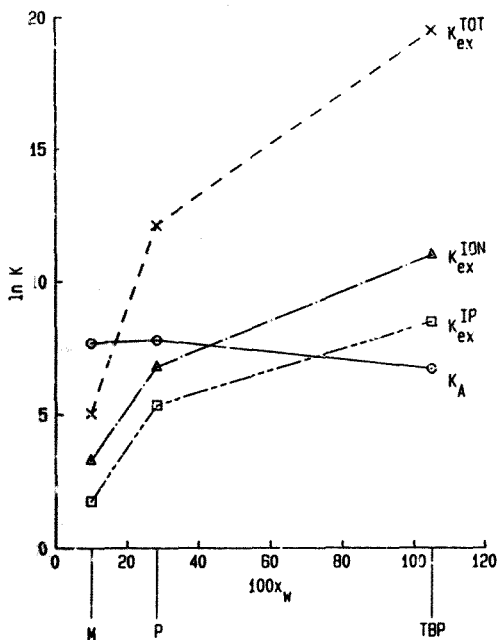


Fig. 4.24 Effect of water content of solvent on the distribution and association constants for $H[Au(CN)_2]$ between various solvents and 0.1 M HCl solution

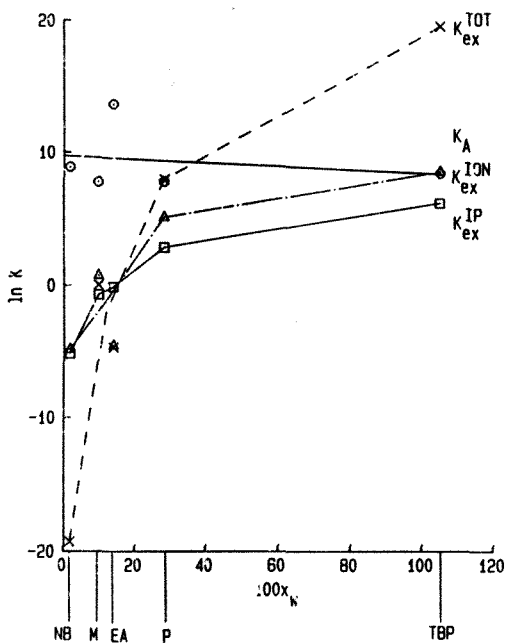


Fig. 4.25 Effect of water content of solvent on the distribution and association constants for $LiAu(CN)_2$ between various solvents and 0.1 M LiCl solution

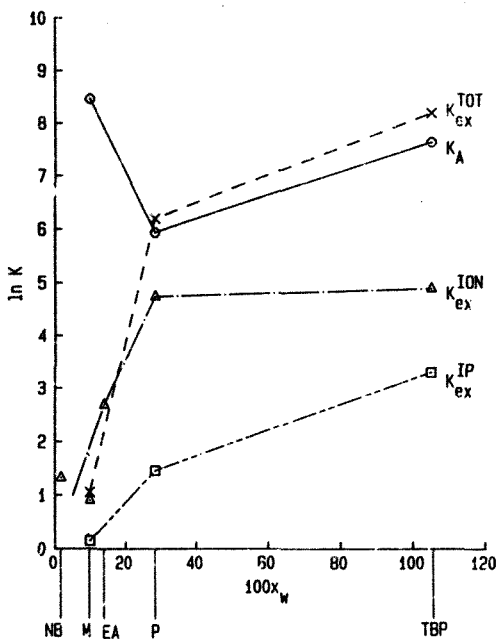


Fig. 4.26 Effect of water content of solvent on the distribution and association constants for $CsAu(CN)_2$ between various solvents and 0.1 M $CsCl$ solution

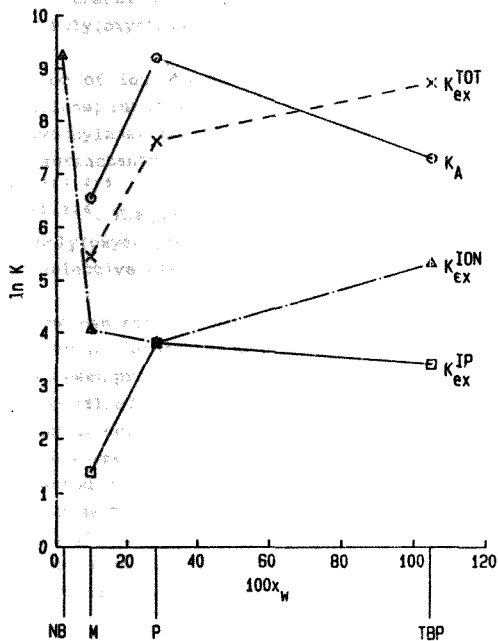


Fig. 4.27 Effect of water content of solvent on the distribution and association constants for $\text{Net}_4\text{Au}(\text{CN})_2$ between various solvents and 0.1 M Net_4Cl solution

4.6 Extraction of Aurocyanide Ion Pairs by Poly(oxyethylene) Extractants

Extraction of ions by extractants containing the poly(oxyethylene) functional group is a well known phenomenon. Poly(oxyethylene) extractants may take the form of non-ionic surfactants dissolved in a water-immiscible solvent^{224,225} or polyether-based polyurethane foams^{151,226}. The phenomenon has also been applied to the use of poly(oxyethylene) derivatives as neutral carriers in ion-selective electrodes²²⁷.

Several mechanisms have been postulated¹⁵¹ for extraction of ions by polyether-based polyurethane foams, and one which has been proposed¹⁵¹ to be the most likely candidate is the so-called "cation-chelation mechanism", in which the cation is coordinated by oxygen atoms within a helical structure formed by the poly(oxyethylene) chain, and the co-extracted anion lies outside the helix. Yanagida *et al*²²⁴ suggest that the helical conformation is energetically favourable for a non-ionic surfactant dissolved in an organic solvent, and propose a similar extraction mechanism for the liquid phase situation.

Some evidence for this type of complexation occurring in the crystalline state is given by Saenger *et al*²²⁸, who present the crystal structure of the RbI complex of 18-hexaoxaicosane. In this complex, the polyether chain wraps smoothly around the Rb⁺ ion in a helical fashion. However, Siddiqui and Wright²²⁹ suggest that molecular structures of long-chain poly(oxyethylene)-alkali salt complexes are uncertain. The uncomplexed poly(oxyethylene) chain in the crystalline state²³⁰ forms a helical structure containing seven units in two turns.

Raman spectroscopic studies²³¹ have indicated that the helical structure is maintained to some extent for the uncomplexed chain in aqueous solution. The conformation in

organic solutions remains unknown.

Solvent extraction of $\text{Na}^+\text{AuCl}_4^-$ ion pairs by poly(oxyethylene) derivatives of organic carbonates has been reported by Rollat et al.²³². They concluded from infrared spectrophotometric studies that complexation occurs through strong ligand-sodium interactions. Solvent extraction of $\text{M}^+\text{Au}(\text{CN})_2^-$ ion pairs by poly(oxyethylene) derivatives has not yet been examined; however, their extraction into solvents such as 1-pentanol⁴⁵ and tributylphosphate¹⁵⁵ has been reported. Extraction of aurocyanide by polyether-based polyurethane foam has been briefly examined by Braun and Farag²³³.

The present section examines the mechanism of solvent extraction of aurocyanide ion pairs by poly(oxyethylene) derivatives, using liquid-liquid distribution techniques and molecular mechanics calculations. Particular attention is given to the role of coiling of the polyether chain in solvents of differing dielectric constant, and to what extent possible pre-organization of the chain influences extraction efficiency.

a) Solvent Extraction of $\text{M}^+\text{Au}(\text{CN})_2^-$ Ion Pairs
by Triton X-100

(i) Effect of counter-cation and solvent

Extraction efficiencies for various combinations of counter-cations and solvents are shown in Table 4.13.

Table 4.13
Efficiencies of extraction of $M^+Au(CN)_2^-$ ion pairs
($M^+ = Li^+, K^+, Cs^+$) by Triton X-100 dissolved in
various solvents

Solvent	ϵ	Extraction efficiency, %					
		Li^+		K^+		Cs^+	
		Pure solvent*	0.1M Triton X-100	Pure solvent*	0.1M Triton X-100	Pure solvent*	0.1M Triton X-100
Benzene	2,28	0,0	0,0	2,4	5,8	2,4	9,6
1-Pentanol	13,90	84,9	89,8	66,8	92,3	76,3	92,4
Nitro-benzene	34,82	0,0	77,4	16,8	99,8	19,4	99,8

* i.e. no Triton X-100 added

While there remains only a small degree of extraction into benzene upon addition of the polyether, the effect of Triton X-100 addition to nitrobenzene is an increase in extraction efficiency to 99,8% when potassium or caesium are present. This effect is explicable from the results of the molecular mechanics calculations, and will be discussed in detail later.

(ii) Effect of the solubility of water in
the solvent phase

The case of 1-pentanol is clearly an anomaly, as a comparison between the extractions into the three pure solvents shows. Only 1-pentanol displays any marked extraction of gold in the absence of the polyether. The trend towards a minimum at potassium has been described previously⁴⁵, and explained in terms of polarization and hydrophobic effects. Table 4.14 shows solubilities of water in both pure and polyether-containing solvents.

Table 4.14
Solubilities of water in the various solvent phases

Solvent	Pure solvent ^a		0,1 M Triton X-100	
	Wt % W ^b	100 X _H ^c	Wt % W ^b	100 X _H ^c
Benzene	0,072	0,31	0,35	1,50
1-Pentanol	7,5	28,3	8,62	31,59
Nitrobenzene	0,25	1,71	0,41	2,74

^a Data for the solubilities of water in the pure solvents are from Marcus and Kertes¹⁸⁶.

^b Percentage (by mass) of water in the water-saturated solvent phase.

^c Mole fraction of water in the solvent phase.

The fact that the solubility of water in 1-pentanol is more than an order of magnitude higher than that in both benzene and nitrobenzene explains the anomaly. The extensively hydrogen-bonded, hydrated network present in this case provides an environment similar to that present in the aqueous phase, probably in the form of microdomains which are solvated by the hydrophilic ends of 1-pentanol molecules. It is also noteworthy that the extra amount of water which can dissolve in the solvent when 0,1 M Triton X-100 is added, is negligible, corresponding to about one water molecule for each polyether chain, eleven oxygens in length. This suggests that the polyether is effectively not hydrated in the solvent phase, for all three solvents studied.

One other point of interest which is evident in Table 4.13 is the similarity in extraction efficiencies between potassium and caesium when the polyether is present. The trend is

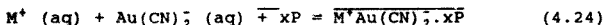


for all three solvents. Once again, this effect is explicable in the light of the molecular mechanics calculations and will be discussed in detail in that section.

(iii) Effect of cation concentration

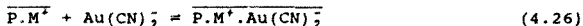
Extraction of $M^+Au(CN)_2^-$ by the polyether can be thought of as occurring by one of two distinct processes¹⁵¹, viz.

- (1) solvation of $M^+Au(CN)_2^-$ ion pairs, similar to that occurring in their extraction by pure solvents such as 1-pentanol⁴⁴, or TBP¹⁵⁹:



(Overscoring denotes species in the solvent phase; the polyether is represented as P). The driving force is solvation of the entire ion pair.

- (2) cation chelation of M^+ by the polyether¹⁵⁰, with concomitant ion exchange of the anion:



The driving force is complexation of the cation with one polyether molecule

The results shown in Figure 4.28 shed some light on this aspect. The effect of increasing the concentration of KCl as a background electrolyte should result in increasing extraction efficiencies if reactions (4.24) or (4.25) are

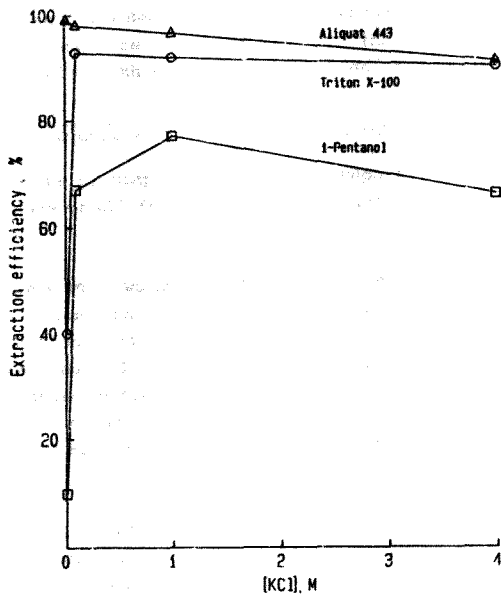
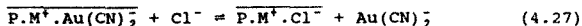


Fig. 4.28 Effect of concentration of potassium chloride on the extraction of $M'Au(CN)_2$ ion pairs by solvents, polyethers and ion-exchangers

important, and decreasing extraction efficiencies if the ion-exchange reaction (4.26) is important, due to competition with chloride ion at high concentrations:



This type of competition has been reported¹⁵ in the ion exchange of Cl^- for $Au(CN)_2^-$ on a typical anion-exchange resin.

Figure 4.28 shows that for Aliquat 443, which is the strong-base anion exchanger, methyltriocetylammmonium chloride, extraction efficiency consistently decreases with increasing KCl concentration. For pure 1-pentanol an increasing extraction efficiency is observed, with a decrease evident only in the presence of 4M KCl. The ion-exchange reaction (4.27) is thus not a dominant one in this case.

In the presence of the polyether, the introduction of a small excess (0.1 M KCl) of K^+ ions results in a marked increase in extraction efficiency, which is consistent with formation of complexed cationic sites (reaction 4.25). At higher K^+ concentrations, the extraction efficiency curve closely follows that for Aliquat 443, suggesting that the ion-exchange competition reaction (4.27) is coming into play at higher ionic strengths.

These results strongly suggest that the second possible mechanism mentioned above more adequately describes the system, i.e. cation chelation of M^+ by the polyether, with concomitant ion exchange of the anion. This is borne out by the molecular mechanics calculations in the following section.

b) Molecular Mechanics Calculations of the
Complexation of Alkali Metal Cations by
Polyethers

(i) Uncomplexed polyether

Strain energies for various conformations of the
uncomplexed polyether are shown in Table 4.15.

Table 4.15

Strain energies of conformations of uncomplexed
poly(oxyethylene) in media of low dielectric constant
($\epsilon=r_{ij}$), high dielectric constant ($\epsilon=4r_{ij}$) and
infinite dielectric constant

C-C-O-C-C-O conformation	Strain energy, kcal.mol ⁻¹		
	$\epsilon=r_{ij}$	$\epsilon=4r_{ij}$	$\epsilon=\infty$
t-t-t-t-t-t (linear)	87,9	16,6	-7,4
g-t-g-g-t-t (tight helical)	92,2	15,0	-21,7
g-t-t-g-t-t (open helical)	117,8	24,1	-9,1

It is not surprising that the linear conformation has the lowest strain in the solvent of lowest dielectric constant, since the *trans* O-C-C-O unit has a lower strain energy than *gauche* or *cis*-rotamers. It is in the *trans* condition that the 0..0 nonbonded and electrostatic interactions are lowest. It is surprising, however, that the tight helical conformation has the lowest energy in solvents of high dielectric constant, whereas the uncomplexed polyether has the open helical conformation in the crystalline state¹³⁰,

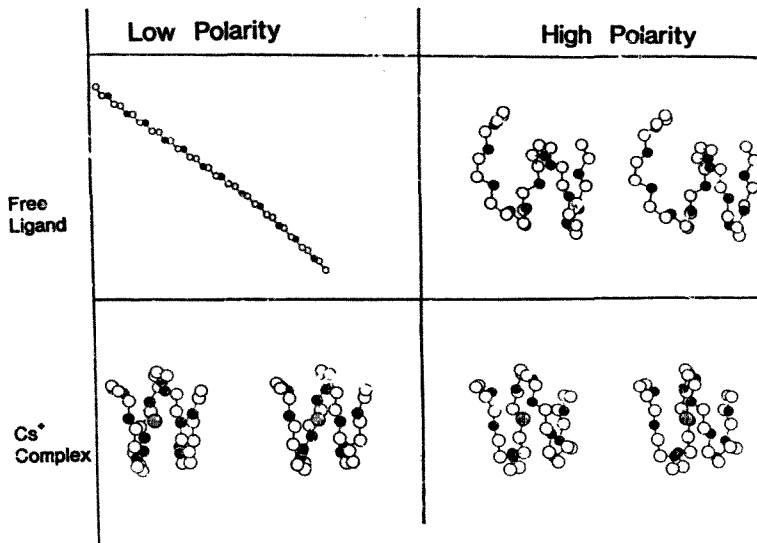
which is expected to be a low polarity environment. 18C6 crystallizes in the conformation that it adopts in solvents of low polarity⁵⁵ in an attempt to minimize intramolecular dipole-dipole interactions^{1,6}, and it is expected that the acyclic polyethers would do the same. The reason is probably that in the crystalline state the intermolecular dipole-dipole interactions are minimized. The refined tight helical polyether is seen to have unwound slightly (Figure 4.29), although the ratios of *g*, *g* and *t* angles are still the same as in the metal complexes.

(ii) Polyether complexes with alkali metals

Since the process of complexation involves not only attachment of metal to polyether, but also dehydration of the ions (reaction (4.24) above) and solvation of the anion, the hydration enthalpies of the metals²³⁴ were subtracted from the calculated internal energies of the complexes, to represent the relative complexation energies of the metals in the same environment. To compare the complexation of metals in environments of differing polarities, it is necessary to subtract the relative energies of the ligands in each solvent. The hydration enthalpy of the large $\text{Au}(\text{CN})_2^-$ anion was assumed to be negligible, on the basis of the calculations in section 4.3, and was thus not included in the calculations. Solvation enthalpies of $\text{Au}(\text{CN})_2^-$ in benzene and in nitrobenzene were calculated by the method of Abraham and Liszi^{208,225,236}, in which the solvation enthalpy is considered to be comprised of an electrostatic and a neutral contribution,

$$\Delta H_s^0 = \Delta H_e^0 + \Delta H_n^0 \quad (4.28)$$

The electrostatic free energy component is calculated via a modified Born equation²⁰⁸ in which the distance-dependent dielectric constant is corrected for by assuming $\epsilon_1 = 2,0$



4.29 Minimum-energy structures of $\text{CH}_3(\text{CH}_2\text{OCH}_2)_{12}\text{CH}_3$ and its Cs^+ complex. Dark atoms represent oxygen, light atoms represent carbon, and shaded atoms represent metals.

for the primary solvation shell:

$$\Delta G_e = \frac{Z^2}{2} \left[\left(\frac{1}{\epsilon_1} - 1 \right) \left(\frac{1}{a} - \frac{1}{b} \right) + \left(\frac{1}{\epsilon} - 1 \right) \frac{1}{b} \right], \quad (4.29)$$

where ϵ is the bulk dielectric constant, a is the ionic radius, Z is the ionic charge, and the thickness of the local layer is $(b-a) = r$, the solvent radius.

The neutral free energy contribution was calculated using the equation

$$\Delta G_n^0 = pa + q, \quad (4.30)$$

where the values of p and q are²³⁵
 -3,2503 and 9,8205 for benzene, and
 -3,2165 and 10,1899 for nitrobenzene.

The ionic radius of $\text{Au}(\text{CN})_2^-$ was estimated earlier in this Chapter to be 2.11 Å, on the basis of theoretical calculations and conductivity measurements.

The electrostatic entropic contribution is calculated²³⁶ using the equation

$$\Delta S_e^0 = \frac{Z^2}{2} \left[\left(\frac{b-a}{ab} \right) \frac{1}{\epsilon_1^2} \frac{\partial \epsilon_1}{\partial T} + \frac{1}{b} \frac{1}{\epsilon^2} \frac{\partial \epsilon}{\partial T} \right] \quad (4.31)$$

where the variation of local dielectric constant with temperature, $\partial \epsilon_1 / \partial T$ is set equal to -0.00160 for all

solvents²³⁶. Values²³⁶ for the variation of bulk dielectric constant with temperature, $\partial\epsilon/\partial T$ are -0,00199 for benzene and -0,180 for nitrobenzene.

The neutral entropic contribution, $-\Delta S_n^0$, was calculated²³⁶ using the equation

$$-\Delta S_n^0 = 6,96\Delta + 1,2 \quad (4.32)$$

The results of the calculations are shown in the tables below:

Table 4.16
Strain energies of metal complexes of
poly(oxyethylene) in benzene (low polarity medium;
 $\epsilon = \epsilon_{ij}$)

Metal Ion:	Li ⁺	K ⁺	Cs ⁺
Complex energy (kcal.mol ⁻¹)	25,7	43,4	53,7
Ligand energy:	87,9	87,9	87,9
Enthalpy of complexation	-62,2	-44,5	-34,2
Anionic solvation energy	-52,4	-52,4	-52,4
Cationic hydration energy:	-133,5	-86,1	-75,2
Enthalpy of extraction	18,9	-10,8	-11,4
% Extraction	0,0	2,4	9,6
Complex E relative to Li ⁺ :	0,0	-29,7	-30,3
% E relative to Li ⁺ :	0,0	2,4	9,6

Table 4.17
Strain energies of metal complexes of
poly(oxyethylene) in nitrobenzene (high polarity
medium; $\epsilon = 4\epsilon_{11}$)

Metal Ion:	Li ⁺	K ⁺	Cs ⁺
Complex energy (kcal.mol ⁻¹)	-51,2	-27,8	-20,9
Ligand energy:	15,0	15,0	15,0
Enthalpy of complexation	-67,2	-42,8	-35,9
Anionic solvation energy	-61,6	-61,6	-61,6
Cationic hydration energy	-133,5	-86,1	-75,2
Enthalpy of extration	5,7	-18,3	-22,3
% Extraction	77,4	99,8	99,8
Complex E relative to Li ⁺ :	0,0	-24,0	-28,3
% E relative to Li ⁺	0,0	22,4	22,4

In both polar and nonpolar media, the Cs⁺ complex has a slightly lower energy than that of the K⁺ complex, both of which have lower energies than that of the Li⁺ complex.

Figure 4.29 shows the lowest energy structures of both the free polyether and its Cs⁺ complex in low- and high-dielectric environments, as determined from molecular mechanics calculations. The complexed and uncomplexed polyether in high-dielectric environment are similar in structure, whereas in low-dielectric environment, the polyether has to undergo striking modifications to complex the Cs⁺ ion. This phenomenon of similarity of ligand conformation before and after complexation has been referred to by Cram¹²⁷ as "pre-organization". The better pre-organized the ligand, the more favourable the complexation thermodynamics, and this is reflected in the unfavourable (positive) energies of complexation in the low-dielectric solvent (Table 4.16), as compared with the favourable (negative) energies of complexation in the high-dielectric solvent (Table 4.17). Even in the high-dielectric solvent, energies of complexation of the

cations are less negative than the hydration energies, indicating that the cations would prefer to remain hydrated.

Figure 4.30 shows minimum energy conformations of the Li^+ , K^+ and Cs^+ complexes of the polyether in high-dielectric environment. A qualitative impression can be gained of the relative strain induced by the coordinated metal by the amount of distortion the ligand experiences upon complexation. The uncomplexed ligand is most pre-organized with respect to the Cs^+ complex. The K^+ complex shows some distortion of the polyether, and the Li^+ complex is the most distorted, which is a reflection of the fact that ligand had to invest a large amount of energy in order to complex this metal ion. This energy investment would detract from the complexation energy, and reduce the proportion of ligated metal in solution.

These results are in accordance with the solvent extraction data, in which the extraction of the $[\text{Cs}(\text{Triton X-100})]^+$ complex into benzene is greater than that of the K^+ complex, and the extraction of the Li^+ complex into benzene is negligible. The percentage extraction of the K^+ and Cs^+ complexes into nitrobenzene is identical at effectively maximum extraction, whereas the extraction of the Li^+ complex into nitrobenzene is only about 80 per cent.

The results of the molecular mechanics complexation energy calculations do not explain the absolute difference in extraction between solvents of differing polarity - there is very little difference in complexation energies of each metal ion in the solvent of high polarity, as compared with one of low polarity, (see Tables 4.16 and 4.17), whereas there is a substantial difference in extraction efficiencies.

The effect is explained by the comparatively large difference between the calculated solvation energies of

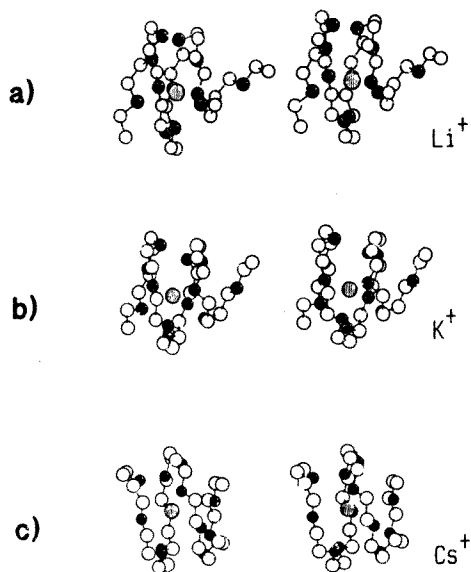


Fig. 4.30 Stereo views of the minimum energy structures of the (a) Li^+ , (b) K^+ and (c) Cs^+ complexes of $\text{CH}_3-(\text{CH}_2-\text{O}-\text{CH}_2)_{12}-\text{CH}_3$ in a high-dielectric environment. Dark atoms represent oxygen, light atoms represent carbon and shaded atoms represent metals.

$\text{Au}(\text{CN})_2^-$ in nitrobenzene and benzene. It is evident that the preferential extraction of the ion pair into high-polarity solvents results more from the preferential solvation of the aurocyanide anion by high-polarity solvents than from the lower complex energy. This conclusion is borne out by the similar dependence of the extraction of $\text{NET}_4^+\text{Au}(\text{CN})_2^-$ ion pairs on the dielectric constant of the solvent, as was shown earlier. The effect is readily attributable to preferential secondary solvation²¹⁰.

These effects would result in an increase in stability of the complexes in the high polarity organic solvent relative to the stability in the low polarity solvent, by the same amount for each metal. The great jump in extraction of the Li^+ complex is thus explained, and the small difference in extraction of the K^+ and Cs^+ complexes is explained by noting that the extraction of these metal complexes is already at a maximum, i.e. it cannot increase beyond 100 per cent.

4.7 Summary and Conclusions

Aqueous solutions of $\text{KAu}(\text{CN})_2$ and $\text{NaAu}(\text{CN})_2$ are found to display a modest degree of association ($K_A \sim 1$), and aqueous $\text{HAu}(\text{CN})_2$ shows a higher degree of association ($K_A \sim 30$). Evidence from infrared spectroscopic data suggests the presence of contact ion pairs and dimers in anhydrous THF and MEK solutions. Addition of a small amount of water effectively hydrates these species, forming solvent-separated ion pairs and free ions.

Distribution experiments confirm the presence of associated and free species in water-saturated solvents. Correlations with organic phase water content are found to exist for association constant K_A as well as extraction constant K_{ex} for distribution of aurocyanide into various

solvents from H^+ , Li^+ and K^+ solutions. For larger, less hydrated cations such as Cs^+ and NEt_4^+ , however, other solvent properties such as dielectric constant and hydrogen-bonding ability begin to play a role.

Aurocyanide ion pairs are also extracted efficiently into organic phases by long-chain polyethers. The polyether is shown to coordinate to the alkali metal cation via ether oxygen atoms, wrapping around the ion in a helical configuration. High extraction efficiencies are obtained with high-dielectric solvents, which tend to stabilize the helical polyether-cation complex. Preferential secondary solvation of the aurocyanide anion by high-dielectric solvents is also an important factor that influences the extraction efficiency.

This fundamental study has several more practical ramifications:

- (i) The presence of ion pairs in aqueous solutions of high ionic strength or low pH will affect the properties of any system relying on aqueous phase ionic concentrations. The presence of $HAu(CN)_2$ in solutions of low pH, for example, probably contributes to the decrease in loading capacity of aurocyanide onto ion-exchange resins observed¹³⁴ in acidic solutions.
- (ii) The mechanism of extraction of aurocyanide by activated carbon has been established in the previous Chapter to involve the adsorption of $M^{n+}[Au(CN)_2]_n$ ion pairs under practical conditions. The work presented in the present Chapter provides a fundamental confirmation of this hypothesis, the presence of $MAu(CN)_2$ ion pairs in both aqueous and organic solutions having now been established. It is suggested that the interior of a micropore in activated

carbon functions in a similar manner to a polar solvent, and acts by solvating the adsorbed ion pair. This confirmation also extends to other systems in which $\text{MAu}(\text{CN})_2$ ion association has been postulated to play a role, for example in the extraction of aurocyanide by polymeric adsorbent resins^{80,132}, as well as by new weak-base ion exchange resins under high pH conditions¹³⁴. At this stage, it is pertinent to comment on the nature of the $\text{MAu}(\text{CN})_2$ ion pair species adsorbed on the surface of activated carbon. The specific effect of cation on the adsorption of aurocyanide by carbon can now be confirmed as being due to the ionic association effects and solvation effects discussed in this Chapter.

- (iii) Existing applications of aurocyanide ion pairs include ion-selective electrodes for $\text{Au}(\text{CN})_2^-$ and ion-pair chromatography for $\text{Au}(\text{CN})_2^-$. The results presented in this Chapter suggest that an enhanced selectivity for aurocyanide could be achieved by the correct choice of solvent and cation.
- (iv) The specificity of the ion association reactions for $\text{Au}(\text{CN})_2^-$ may lead to improved extractants for aurocyanide. For example, a recent contribution¹³³ describes the ion-pair extraction of $\text{KAu}(\text{CN})_2$ by a resin containing phosphonate ester groups. Polyether-based extractants such as were studied here may also have application for the selective extraction of gold.

CHAPTER 5 THE MECHANISM OF ELUTION OF AUROCYNANIDE FROM ACTIVATED CARBON

5.1 Introduction

Adsorptive properties of activated carbon for aurocyanide have been recognized since the last century⁶. In the first serious study of the phenomenon³, attempts were made to elute the adsorbed gold from the activated carbon, but it was not until 1952 that a viable elution process was demonstrated⁸. It was this development that enabled the carbon-in-pulp process to become an economically viable alternative to Merrill-Crowe zinc precipitation, and resulted in the commercialization of the CIP process.

a) *Processes for the Elution of Aurocyanide from Activated Carbon*

Elution of gold and other metals that are adsorbed onto activated carbon is achieved in practice by one of four main procedures, as follows:

(i) The Zadra Process

This involves⁸ the circulation of a hot caustic cyanide solution through an elution column and several electrowinning cells in series. The solution normally contains about 0.5% NaCN and 1.0 to 2.0% NaOH. Temperatures of 85°C to 95°C may be employed, and about 50 hours are usually required for an acceptable elution at these temperatures. An alternative is the use, in some plants, of pressurized vessels or steam heat exchangers to achieve higher column temperatures and hence more efficient elution.

(ii) The Anglo American Research Laboratory
(AARL) Process

This involves²³⁸ the pre-treatment of carbon by a hot caustic cyanide solution, typically containing 2 to 3% NaCN and 2% NaOH. This step may be performed under pressure and lasts for around thirty minutes. It is followed by an eight hour elution with hot deionized water.

(iii) Organic Solvent Processes

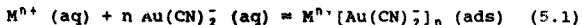
These^{239, 240} are variations of the Zadra or AARL procedures in which the eluant contains large amounts of organic solvents such as methanol, ethanol or acetonitrile. Elution is typically completed within an eight hour period.

(iv) Continuous Elution Processes

In view of the continuous nature of the adsorption circuit, several methods are being developed for continuous elution of gold from activated carbon. Two methods are being developed^{238, 241} that utilize the AARL procedure, whilst another method^{242, 243} utilizes a pressurized continuous elution, which enables 20 to 22 tonnes of carbon per day to be eluted.

b) *The Chemistry and Mechanism of Elution of
Aurocyanide from Activated Carbon*

The mechanism of adsorption of aurocyanide onto activated carbon was discussed in detail in Chapter 3, in which it was shown that under typical plant conditions, aurocyanide is adsorbed as a chemically unchanged ion pair of the form $M^{n+}[Au(CN)_2^-]_n$, by the following reaction:



In the absence of additional factors, such as acid-boiling of the loaded carbon, the adsorption process described by Equation (5.1) is thermodynamically reversible. Thus, chemical and physical factors that inhibit adsorption will enhance elution, and vice versa. These factors form the basis of the elution procedures described above, which are currently used on most full-scale CIP plants. The main factors that influence the elution rate are:

- (i) temperature
- (ii) ionic strength
- (iii) cyanide and hydroxide concentrations, and
- (iv) organic solvents.

The effect of these parameters on elution rate, and their relation to elution methods, will be discussed later in this chapter.

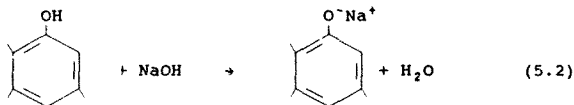
The elution mechanism itself has not been studied in any detail. Muir et al.²³⁹ proffer a mechanism based on their adsorption mechanism, which consists of ion exchange followed by decomposition to AuCN. This mechanism does not adequately describe the system, however, as was shown in Chapter 3. An elution theory that is consistent with all the observations, as well as the theory developed thus far, will be presented in the following section.

5.2 Novel Studies on the Mechanism of Elution of Aurocyanide from Activated Carbon

To gain insight into the mechanism of elution, several synthetic polymeric adsorbents were selected as models for activated carbon. Loading experiments were carried out using three polymeric adsorbents, S-761, S-862 and XAD-8, and the extraction of sodium and aurocyanide ions was monitored in sodium chloride and sodium hydroxide solutions. The results are presented in Table 5.1, and show that, with S-761, substantially less gold and more sodium are extracted with sodium hydroxide than with sodium chloride solution, whereas with S-862 and XAD-8, gold is extracted more strongly from sodium hydroxide than from sodium chloride solution.

These three resins have been characterized previously⁸⁰ and, while S-761 consists of a phenylformaldehyde matrix, both S-862 and XAD-8 consist, essentially, of polystyrene matrices. It seems likely, therefore, that the trends observed for S-761 in Table 5.1 can be ascribed to the presence of phenol-type groups in this resin.

The pK_a of S-761²⁴⁴ is 8.5, and the effect of sodium hydroxide can therefore be represented as



The lower affinity of the resin for aurocyanide in sodium hydroxide solution can thus be attributed to the creation of a higher effective dielectric constant within the resin pores, as well as a hydrophilic, negatively charged surface, with a resultant decrease in affinity for neutral species, as well as anions.

Table 5.1
Extraction of aurocyanide and sodium ions from aqueous
solutions by polymeric adsorbents

Conditions

Adsorbent mass 1,0g (dry)

solution volume 50 ml

initial gold in solution 0,508 mmol/l

time 20 h

Solution	S-761		S-862		XAD-8	
	a	b	a	b	a	b
Nil		0,078		0,074		4,52
0,1 M NaCl	0,74	4,48	0,09	3,61	0,91	4,13
0,1 M NaOH	0,22	439,0	0,17	9,13	1,0	12,1

^a Gold concentration on the adsorbent (10^{-2} mmol/g)

^b Sodium concentration on the adsorbent (10^{-2} mmol/g)

In an experiment with activated carbon, the carbon was contacted with 0,1M sodium hydroxide solution for different periods of time, and the carbon was analysed for sodium while the solution was analysed for hydroxide. The results, which are presented in Table 5.2, indicate that a 1:1 relationship exists between the extraction of Na^+ and OH^- by carbon under these conditions. This result, coupled to the earlier observation that sodium hydroxide is an effective eluant for aurocyanide on carbon (Table 3.4), suggests that a mechanism similar to that shown in Equation (5.2) is operative at the carbon surface under elution conditions.

Table 5.2

Extraction of sodium and hydroxide ions from sodium hydroxide solution by activated carbon at 25°C

Conditions

Carbon mass 25,0g

solution volume 250 ml

initial NaOH concentration 0,2M

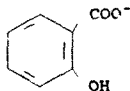
Time	Loading on carbon, mmol/g	
	[Na ⁺] _c observed	[OH ⁻] _c calculated ^a
5 min	0,256	0,252
24 h	0,332	0,360
43 h	0,396	0,392

^a In this instance, [OH⁻]_c does not necessarily refer to specifically adsorbed OH⁻ ion, but refers to the decrease in hydroxide concentration in solution as a result of reaction with activated carbon.

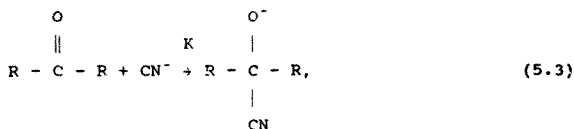
Evidence in support of this mechanism is provided by the results of zeta-potential studies^{75,245,246}, which show that the negative potentials of activated carbons increase with increasing pH. It can be argued that this could be due to the specific adsorption of H⁺ ions onto the carbon surface, with Na⁺ ions located in the outer Helmholtz layer. However, if this were the case, the effect would be greatest for the large, weakly hydrated perchlorate anion and, as pointed out earlier, this anion has been shown⁶² to be ineffective as an eluant for gold.

It is noteworthy also that phenolic groups on the surfaces of carbons have been found^{26,247} to be about 2 meq/g. This provides sufficient sites for the loading of sodium hydroxide on G210 activated carbon (0,4 meq/g, Table 5.2) via reaction (5.2).

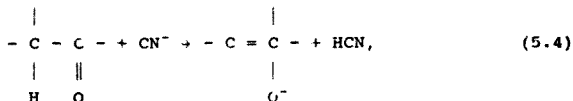
The pK_a of phenol⁶⁵ is 9.89. Therefore, it might be argued that phenolic groups on the carbon surface would be partially ionized at the normal operating pH of the CIP plant (pH 10.0 to 10.5), and that this would lead to poor gold adsorption. However, it has been suggested²⁴, on the basis of an investigation by internal-reflection infrared spectrophotometry (IRS), that phenolic and carboxylic groups are probably both present on the surface of activated carbon, and it is well known that the pK_a values of phenol groups are very sensitive to their chemical environment. For example, the pK_a of the phenolic group in the following species has been reported²⁴⁸ to be 13.4:



Finally, it is interesting to speculate on the reason for the enhanced elution of gold from carbon in the presence of free cyanide in solution. Tsuchida and co-workers⁷³⁻⁷⁵ explain this on the basis of competitive ion exchange of CN^- for $Au(CN)_2^-$, and suggest that the further enhancement that occurs in the presence of polar organic solvents can be attributed to an increase in the activity of the CN^- ion in polar solvents relative to water. However, on the basis of the mechanism suggested in the present work, the ion-exchange mechanism is believed to be relatively unimportant under high ionic strength conditions, and it is suggested that cyanide is involved in a specific chemical reaction at the carbon surface. For example, the equilibrium constant for the formation of cyanohydrin from ketones,



has been found²⁴⁹ to be large, particularly for cyclohexanone ($K \sim 11\,000$). Alternatively, the cyclohexanone ion is listed²⁵⁰ as one of the strongest nucleophiles, and the acid-base reaction at the β -carbon,



could well occur on the carbon surface. It is possible that either or both of these reactions take place with carbonyl groups on the carbon surface under elution conditions, thereby increasing the negative charge density on the surface, and resulting in faster elution kinetics for cyanide than hydroxide. Figure 5.1 shows that the uptake of sodium ions by carbon increases when cyanide is added to a sodium hydroxide solution (at the same total concentration of sodium ions in both cases), which is in support of the above argument. The loss of cyanide ions from the solution exceeded the sodium-ion uptake, but this is attributable⁹⁹ to a certain amount of oxidation to cyanate, catalyzed by activated carbon. Nitrogen analysis of the carbon samples showed that the nitrogen concentration on the carbon also increased in the course of this experiment. The nitrogen concentration after 30 hours (after correction for the nitrogen present on the carbon at the start of the experiment) was 0.19 mmol/g. This is in approximate agreement with the enhanced sodium uptake of 0.18 mmol/g when cyanide is added (see Figure 5.1). This amount is well within the concentration of 2.81 mmol/g cited²⁴⁷ for carbonyl groups present on the surface of a

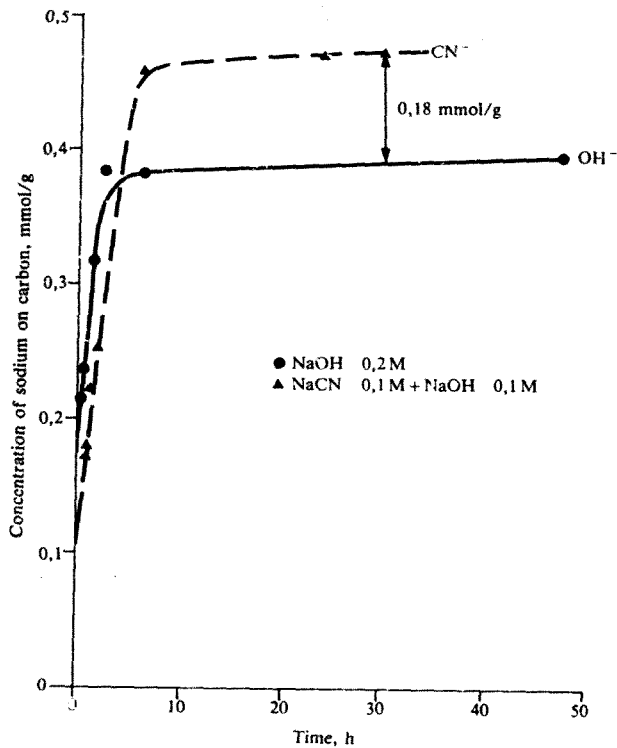


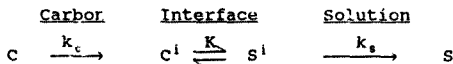
Fig. 5.1 Extraction of sodium ions by activated carbon at 25°C in the presence of cyanide or hydroxide ions

carbon

5.3 The Kinetics of Elution of Aurocyanide from Activated Carbon

Elution is a slow process that, depending on the method employed, requires from 8 to 48 hours for completion, even at elevated temperatures. This is due to slow diffusion of aurocyanide ion within the micropores of the relatively large particles of activated carbon. The kinetics of elution have received very little attention other than the publication of elution profiles under various conditions. It is therefore desirable to derive a kinetic model that can successfully describe the elution over a variety of conditions. Nicol and co-workers²⁵¹ have recently derived such a model for the adsorption of aurocyanide onto activated carbon, and found it to apply to plant data as well as laboratory-scale data. The simplicity of the model is conducive to its application to the reverse operation, viz., elution.

It was shown in Chapter 3 that adsorption of gold from cyanide solutions by activated carbon does not involve any slow chemical reactions, so the slow steps in the process are associated with mass transport in the solution and solid phases. It can therefore be expected that the rate of elution could be governed by similar considerations and, as applied to elution, the model can be pictured as shown below:



where C is the concentration of gold on the carbon at time t , and C^i is the concentration of gold on the carbon at the interface with the solution. Similarly, the S terms

represent gold in the solution. The equilibrium constant K is defined as

$$K = S^I / C^I, \quad (5.5)$$

where the values of S^I and C^I may be approximated by the bulk values S and C . The equilibrium constant K can thus be measured by batch equilibration tests under elution conditions, and is represented by the slope of the curve in Figure 5.2.

Thus, carbon is considered to be a homogeneous phase through which aurocyanide is transported by diffusion with a mass transport coefficient k_c to an interface where equilibration with aurocyanide in solution is assumed to be rapid. Diffusion of gold from the interface into the bulk of the solution occurs with a mass transport coefficient k_s .

For adsorption, the rate equation

$$\frac{dC}{dt} = k(KS - C) \quad (5.6)$$

is that used by Nicol, Fleming and Cromberge²⁵¹. The term k is the intrinsic rate constant for the process. For elution, this can be written

$$-\frac{dC}{dt} = k(C - KS) \quad (5.7)$$

and can be incorporated into the mass-balance equation for any particular elution system.

In the present study, the reactor is regarded as a small continuous stirred tank reactor (CSTR) into which fresh eluate enters, and the concentration of gold in the eluate

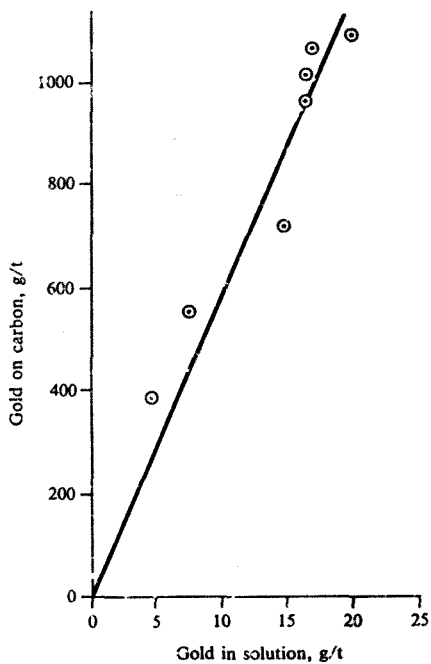


Fig. 5.2 Equilibrium isotherm for the distribution of aurocyanide between activated carbon and a solution containing 0,2M NaOH and 0,2M NaCN at 95°C

leaving the reactor is analysed as a function of time. In terms of the mass-balance for the system,

$$-M_c \frac{dC}{dt} = V_s \cdot S + M_s \cdot \frac{dS}{dt} \quad (5.8)$$

where M_c is the mass of carbon in the elution column, M_s is the mass of solution in the elution column, and V_s is the flowrate of eluant solution through the column. The experimental arrangement is such that M_s , the mass of eluant in the reactor, is small, so that

$$M_s \frac{dC}{dt} \ll V_s \cdot S$$

and the equation can be simplified to

$$- \frac{dC}{dt} = \frac{V_s \cdot S}{M_c} \quad (5.9)$$

Substitution of the rate equation (5.7) in this expression and rearrangement yields

$$S = kM_c C / V_s + kM_c \quad (5.10)$$

and differentiation with respect to time, substitution into equation (5.4), and integration of the resulting equation yields

$$\ln S = \ln(kM_c C_0 / (V_s + kM_c)) - k't, \quad (5.11)$$

where

$$k' = k \cdot V_s / (V_s + kM_c) \quad (5.12)$$

Equation (5.11) predicts a linear relationship between the logarithm of the concentration of gold in the eluant and

time. Results of a typical laboratory elution under these conditions are shown in Figure 5.3. It can be seen that the simple first-order model above describes the experimental data well, down to residual concentrations of gold on the carbon of less than 10 g/t (after 50 hours). The slope of the line yields an estimate of the constant k' from which the rate constant k can be obtained after measurement of the equilibrium constant K by batch equilibration tests under the same conditions, as described earlier. Additional verification of the model can be obtained via the rearrangement of Equation (5.12):

$$1/k' = K(M_c/V_s) + 1/k \quad (5.13)$$

A plot of $1/k'$ against M_c/V_s yields a linear relationship, as predicted by Equation (5.13). The value of $K = 63 \pm 3$ obtained is comparable with that of 55 ± 3 measured from batch tests (Figure 5.4).

It should be noted that the experimental conditions above are similar to those used for the Zadra method. The AARL technique can be partially simulated by pre-treatment of the carbon with a caustic cyanide solution, draining of the solution, and elution with deionized water. The results of such an experiment are shown in Figure 5.5, from which it is apparent that the kinetics do not follow the predicted linear dependence. This is not unexpected since, although draining removes a large proportion of the pretreatment solution, there is still an amount of occluded caustic cyanide present, that is only completely removed after several bed-volumes of water have passed through the system.

The ionic strength of the eluant is therefore continuously decreasing, and this will result in the greater-than-predicted rate observed during the later stages of elution, as will be shown in the following section. This phenomenon makes simulation of the AARL technique very difficult, and

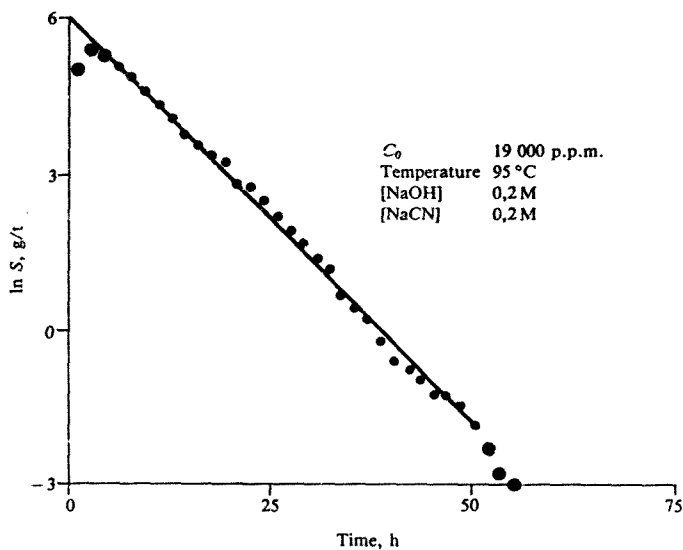


Fig. 5.3 Rate of elution of gold from activated carbon at 95°C

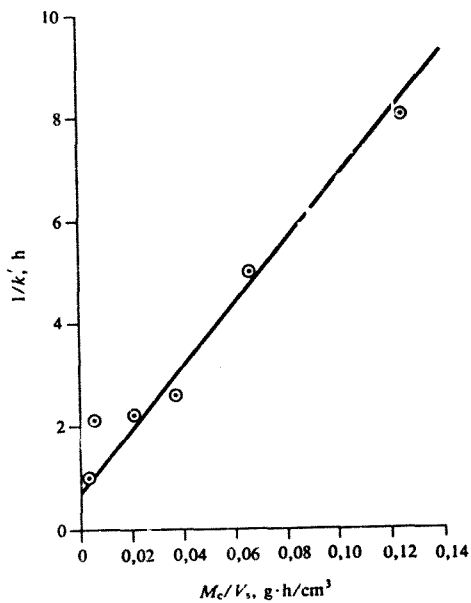


Fig. 5.4 Variation of the rate of elution with the mass of carbon and flowrate of the eluant

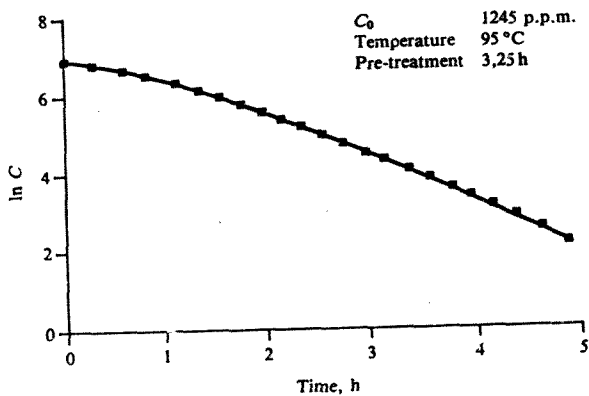


Fig. 5.5 Rate of elution of gold from activated carbon by the AARL procedure

it is not surprising that there are no published reports of attempts to do so.

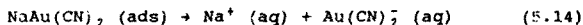
The above-mentioned work examined a single-pass elution of a fluidized carbon bed with fresh eluant solution containing no gold (i.e., $S_{in} = 0$). In practice, however, the Zadra process utilizes a carbon column as opposed to a fluidized bed, and moreover, recirculation of eluate through electrowinning cells results in a variable amount of gold being present in the eluant feed.

a) *Effect of a Finite, Constant Concentration of Gold in the Eluant Feed*

As a first approximation to the practical situation, the effect of a constant concentration of gold in the eluant feed ($S_{in} = \text{constant}$) was examined.

These experiments comprised a single-pass elution similar to that described earlier, with the exception that several constant gold concentrations in the eluant feed (S_{in}) were considered here. The results are shown in Figure 5.6, which indicates a decrease in elution rate.

This effect is explicable in that an increase in the aurocyanide concentration of the eluant feed will push the elution equilibrium in Equation (5.14) to the left:



This would result in the observed decrease in elution rate.

At concentrations of gold in the eluate of 15 mg/l or more, adsorption was found to occur initially (Figure 5.7), despite the fact that the carbon had been brought to the elution temperature in the presence of cyanide and hydroxide before any contact with feed solution was made.

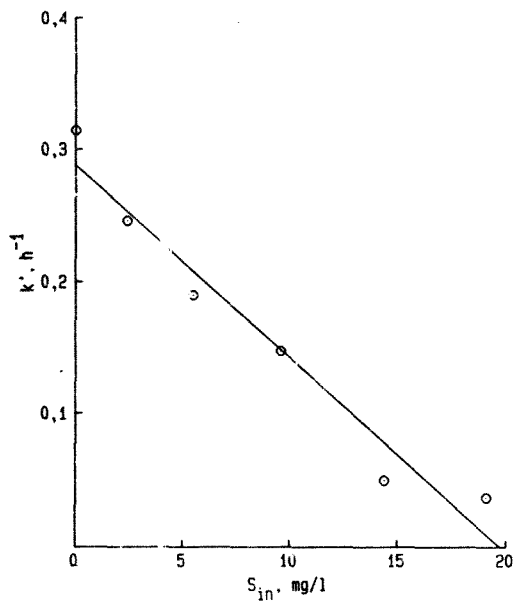


Fig. 5.6 Effect of aurocyanide concentration in the eluant feed on the rate of elution at 95°C

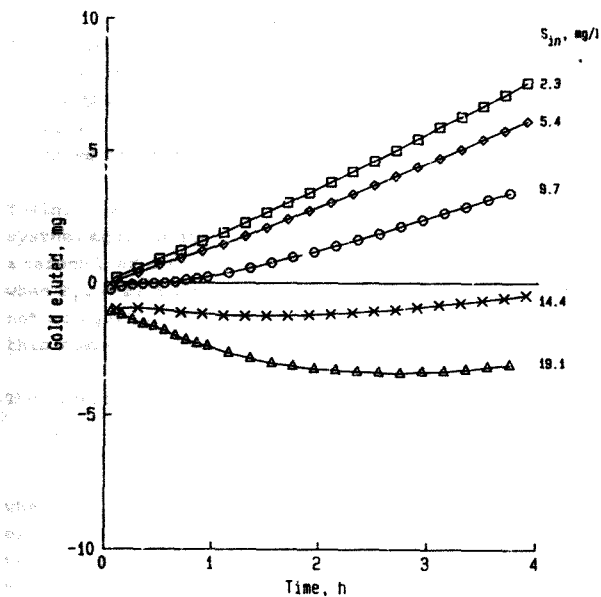


Fig. 5.7 Plot of gold eluted against time for elutions with varying aurocyanide concentrations in the eluant feed

The results shown in Figure 5.7 suggest that it takes some time for the reagents to diffuse through the carbon pores before these reactions between cyanide, hydroxide and the surface functional groups (Equations 5.2 and 5.3) have occurred to a sufficient extent for elution to take place.

Taking a value of 55 for the equilibrium constant K for the system, equilibrium conditions (and hence no elution), for a carbon loaded to 1245 g/t gold should theoretically occur when $S_{in} = 22,6$ mg/l. Given the fact that the system was not at equilibrium, the results in Figure 5.7 show that this number is approximately correct.

The elution model can be written as Equation (5.15) below:

$$-\frac{dC}{dt} = k(C - KS_{out}) \quad (5.15)$$

where S_{out} is the concentration of gold in the solution exiting from the carbon bed at time t . Application of the mass balance for a single-pass flow-through and solving the mathematics results in Equations (5.16) and (5.17), which describe the concentrations of gold in solution and on the carbon at any time t :

$$\ln C = \ln C_0 - k't \quad (5.16)$$

$$\ln S_{out} = \ln C_0 - \ln \left(\frac{V_s + kKM_c}{kM_c} \right) - k't \quad (5.17)$$

where V_s is the flowrate, M_c is the mass of carbon, and

$$k' = \frac{k V_s}{V_s + kKM_c} \quad (5.18)$$

is the first-order rate constant. These equations do not take into account the possibility of any gold being present in the eluant feed. It is now possible to simulate the true situation in which eluate is recirculated through an electrowinning cell back to the carbon column, and to incorporate a constant gold concentration in the eluant feed, S_{in} , into the mass balance for the system. This results in the following relationships:

$$\ln (C-KS_{in}) = \ln (C_0-KS_{in}) - k't \quad (5.19)$$

$$\ln (S-S_{in}) = \ln (C_0-KS_{in}) - \ln \left(\frac{V_s + kKM_c}{kM_c} \right) - k't \quad (5.20)$$

(These reduce to Equations (5.16) and (5.17) when $S_{in} = 0$.)

A plot of either $\ln (C-KS_{in})$ or $\ln (S_{out}-S_{in})$ against time should yield a straight line of slope k' . Table 5.3 compares the measured values for k' and the intercept obtained from these graphical plots, with calculated values. The calculated values for k' and the intercept were obtained from Equations (5.19) and (5.20) and the experimentally determined values of $K = 55$ and $k = 2 \text{ h}^{-1}$.

At higher S_{in} , the elution rate becomes too slow to be accurately measurable, S_{out} being close to S_{in} .

Values for the calculated intercepts of the plots correlate well with the observed ones. The k'_{calc} values, however,

are somewhat higher than the observed values. (When no gold was present in the feed, a good correlation was obtained.) This result could be due to the fact that the system had not come to equilibrium prior to contact with the eluant.

Table 5.3

Comparison between observed and calculated values for k' and the intercept for Equations (5.19) and (5.20)

Conditions:

carbon mass (M_c) 1,35g
 temperature 95°C
 initial gold on carbon (C_0) 1245 g/t
 [NaCN] 0,2M
 [NaOH] 0,2M
 flowrate (V_0) 39 ml/h

S_{in} (mg/l)	k'_{obs}	k'_{calc}	Intercept from		Intercept from	
			plot of equation (5.19)		plot of equation (5.20)	
			obs	calc	obs	calc
3,30	0,287	0,376	6,98	6,97	2,50	2,74
6,41	0,261	0,377	6,89	6,80	2,37	2,56

b) *Effect of a Variable Gold Concentration in the Eluant Feed*

The integration of an electrowinning cell of constant single-pass extraction efficiency (i.e., $S_{in} = S_{out}(1-E)$) into a circuit with a carbon bed was simulated experimentally by dilution of the eluant feed as described in the experimental section. The other conditions were the same as those for a constant gold concentration in the

feed.

Table 5.4 shows that as the single-pass extraction efficiency is decreased, the amount of gold left on the carbon after elution increases.

Table 5.4
Gold concentrations on the carbon after 16 hours
elution for simulated electrolytic extractions
of differing single-pass efficiency

E	C (μg/g)
0,83	19
0,71	31
0,57	64
0,19	321

Theoretically, one can apply a treatment similar to that of the constant $S_{i,n}$ case. By assuming $S_{i,n}$ to be constant over a period Δt between sample $(i - 1)$ and sample i (and effectively integrating), one obtains similar equations to (5.19) and (5.20) i.e.,

$$\ln (C_i - KS_{i-1, in}) = \ln (C_{i-1} - KS_{i-1, in}) - k' \Delta t \quad (5.21)$$

$$\ln (S_{i, out} - S_{i-1, in}) = \ln (C_{i-1} - KS_{i-1, in})$$

$$- \ln \left(\frac{V_s + kKM_c}{KM_c} \right) - k' \Delta t \quad (5.22)$$

From the mass balance,

$$S_{i, out} = S_{i, in} (1 - E) \quad (5.23)$$

where $S_{i,out}$ and $S_{i,in}$ refer to the solution concentrations out of and into the carbon bed respectively, at time t .

An Apple IIe microcomputer was used to calculate gold concentrations for Zadra-type elutions as predicted by the above equations, using values of k and K equal to 2 h^{-1} and 55, respectively. Calculations commenced at $t=0$ and a value of the increment $\Delta t = 0,1\text{ h}$ was used. This value was considered to be adequately small for the assumption of a constant S_{in} over the period Δt to be valid. The calculated carbon and solution concentrations at time t became the input values for time $(t + \Delta t)$, and in this manner, elution profiles for both carbon and solution concentrations could be obtained.

Figure 5.8 shows carbon (a) and solution (b) concentration profiles for elution of aurocyanide from a 5 ml bed of carbon, with a single-pass extraction efficiency of 0,42. Profiles calculated according to the above analysis provide a reasonable fit to the observed data points, with the discrepancy probably being due to the small scale on which the experiment was carried out.

c) *Elution of Aurocyanide from Carbon in a Packed Column*

Equations for the mathematical modelling of the elution of aurocyanide from carbon in a packed bed column have been derived by Nicol²⁵², but never tested. Comparison between the predictions of the model and experimentally observed results from the present work, is made in this section.

Application of this model to experimental data is shown in Figure 5.9. A 25 ml column containing carbon and deionized water was heated to 85°C before effectively starting the elution by pumping the caustic cyanide eluant solution

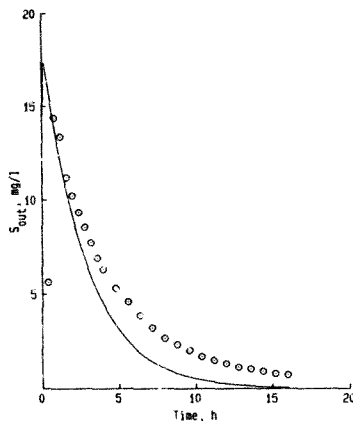
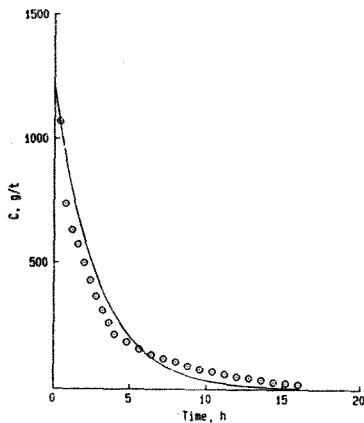


Fig. 5.8 Elution of aurocyanide from a 5ml carbon bed by the Zadra method, with a single-pass extraction efficiency of 0,42. (The solid line refers to the theoretical concentration profile calculated using Equations (5.20) to (5.22))

- a) Plot of gold concentration on the carbon against time.
- b) Plot of gold concentration in the eluate solution against time.

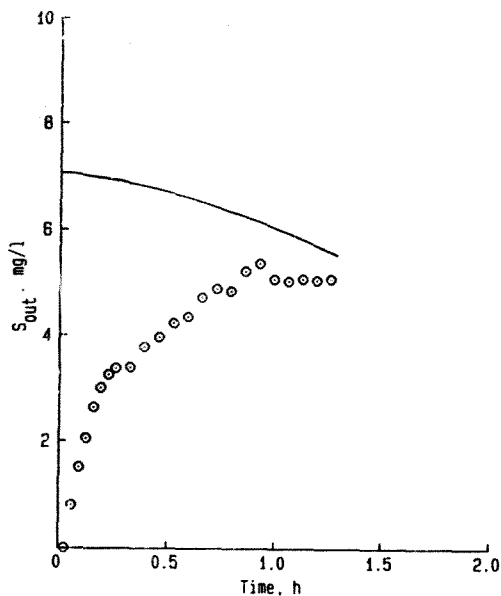


Fig. 5.9 Elution of aurocyanide from a 25ml carbon column with no pre-equilibration prior to elution. The solid line refers to the theoretical concentration profile calculated according to the model. (Flowrate $V_s = 2.5$ BV/h)

through at 2,3 BV/h. The observed solution concentrations differ from the calculated ones in that the latter assume that equilibrium between loaded carbon and eluate is attained instantaneously, whereas it was shown earlier that a period of time is required for eluate to diffuse into the carbon pores. This effect can be eliminated by equilibration of the column with eluant solution at 95°C for two hours prior to elution at 95°C, as shown in Figure 5.10. This procedure ensured that elution would commence with carbon in equilibrium with eluate solution - i.e. containing a concentration of gold dictated by the equilibrium condition:

$$S_{out} = KC \quad (5.24)$$

The equilibration time of two hours was considered to be ample, from a knowledge of the equilibrium constant for the system, $K = 55$, and from the solution analyses. One can derive the following equations for gold on the carbon and in solution based on the mass balance and the equilibrium condition:

$$C_{eq} = \frac{K R_m C_o}{1 + K R_m} \quad (5.25)$$

$$S_{eq, out} = \frac{R_m C_o}{1 + K R_m} \quad (5.26)$$

where $R_m = M_c/M_s$ is the ratio of carbon mass to solution mass in the column.

Figure 5.10 shows that the model (solid line) predicts the experimental points quite well for the elution of a 25 ml carbon column under the conditions shown.

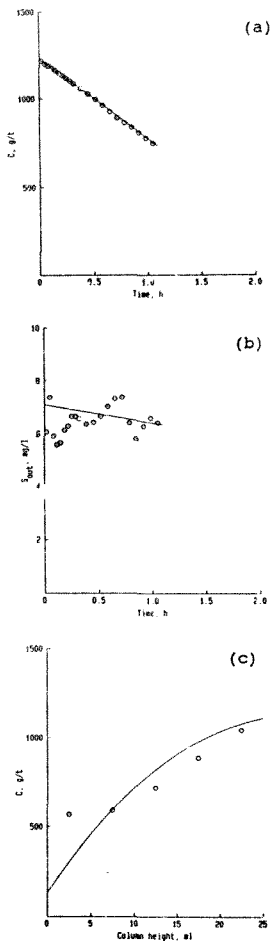


Fig. 5.10 Elution of aurocyanide from a 25 ml carbon column equilibrated with eluant solution prior to elution. The solid line refers to the profile calculated according to the model. (Flowrate $V_s = 23.5$ BV/h)

- (a) Plot of average carbon concentration against time
- (b) Plot of solution concentration out of column against time
- (c) Gold concentration profile across the carbon column

Figure 5.11 compares experimental and predicted curves for gold on carbon and in solution as a function of time, for elution of a 5 ml carbon column by an eluant flowing through the column at several different flowrates. At very high flowrates (Figures. 5.11a and 5.11b), factors such as channelling of eluant through the column almost certainly account for the poorer elutions than predicted - the model fits the data better at more normal flowrates. (Figures 5.11c and 5.11d). The extremely small scale on which the experiment was performed is probably an additional source of error, as a better fit was obtained for a 25ml column (Figure 5.10).

5.4 Factors Influencing the Elution of Gold from Activated Carbon

The most important factors that influence the elution were mentioned earlier. Since the rate of elution is the crucial aspect, the effect of these factors will be discussed in terms of the rate constant k' in Equation (5.11) above.

a) Effect of Temperature

This is probably the most important variable. An increase in temperature results in a significant decrease in the adsorptive power of carbon⁶². The exothermic nature of the loading of gold is typical of most heterogeneous adsorptive processes. Thus, all operating elution procedures are carried out at elevated temperatures.

The effect of temperature on the rate constant k' is shown as an Arrhenius plot in Figure 5.12. The non-linear nature of the plot is not unexpected because, according to Equation (5.12), k' is the non-linear function of both k and K , each of which is temperature dependent. The data at

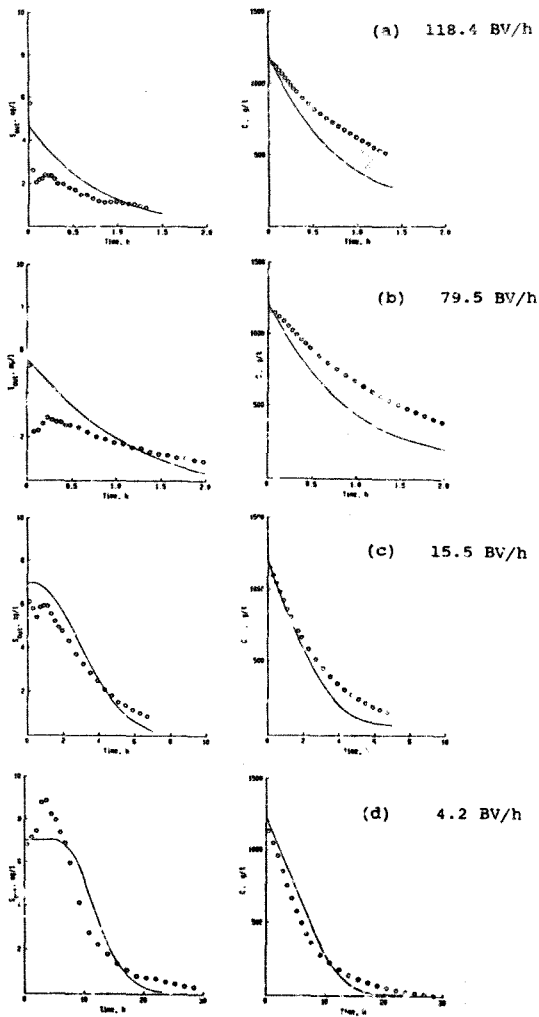


Fig. 5.11 Elution of aurocyanide from a 5ml carbon column, pre-equilibrated with eluent solution, at various flow-rates.

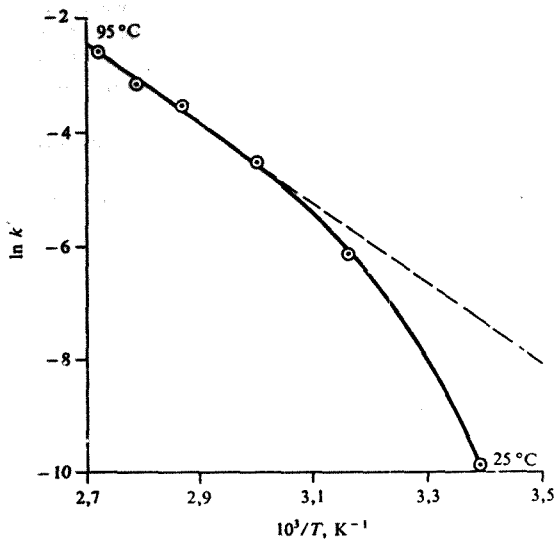


Fig. 5.12 Variation of the rate of elution with temperature

high temperatures are reasonably linear, from which an apparent activation energy of 58 kJ/mol can be calculated; this value can be used for estimation of the effect of temperature on elution kinetics.

b) *Effect of Ionic Strength*

The presence of dissolved solids in the adsorption medium generally results in an increase in the loading capacity of carbon¹¹ and this effect has been found to depend on the type of cation, and concentration of cation⁶².

As discussed earlier, these effects have been interpreted in terms of the adsorption of ion pairs of the type $M^{n+}[Au(CN)_2]_n$. Hence, desorption is favoured by conditions of low ionic strength and the absence of ions like Ca^{2+} and Mg^{2+} , which enhance gold adsorption. This forms the basis of the AARL elution procedure in which the pretreatment with hot caustic cyanide converts the calcium ion pair into the less-strongly adsorbed $Na^+Au(CN)_2^-$, which is then eluted under the conditions of low ionic strength produced by the use of deionized water.

An increase in ionic strength results in a decrease in elution rate, as shown in Figure 5.13.

c) *Effect of Cyanide and Hydroxide Concentrations*

The capacity of carbon for gold adsorption decreases with increasing cyanide, and to a lesser extent, hydroxide concentrations¹¹, and this forms the basis for the Zadra elution procedure, in which caustic cyanide at high pH is used to displace the adsorption equilibrium.

The results presented in Chapter 3 showed that complete elution can be achieved in the absence of cyanide using

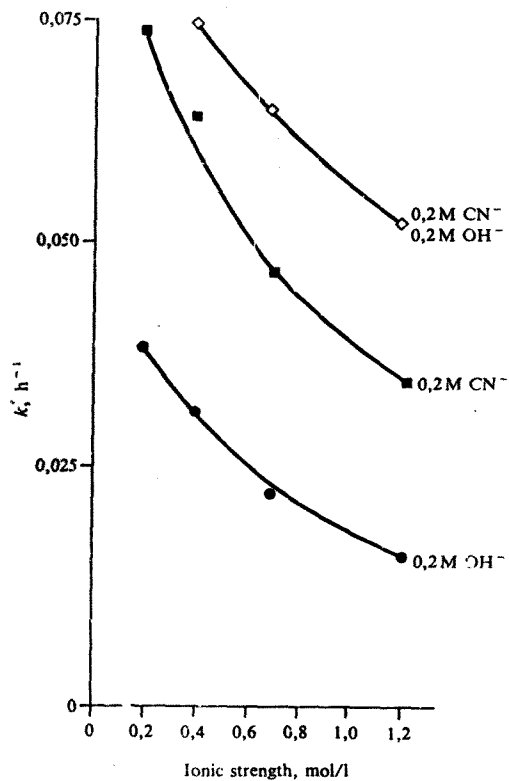


Fig. 5.13 The effect of the ionic strength of the eluant on the rate of elution at 95°C

sodium hydroxide as the eluant, and some mines are using cyanide-free eluants in practice.

The effects of eluant composition on rate of elution are complex, with the opposing influences of cyanide and hydroxide concentrations on the one hand and ionic strength on the other. The results in Figure 5.14 were therefore obtained with eluants containing only cyanide or hydroxide, confirming that cyanide is more effective an eluant than hydroxide, and that there is an optimum concentration close to 0,2 mol/l (or 1% NaCN). The decrease in rate at higher concentrations is due to the increasing ionic strength, as demonstrated by the results shown in Figure 5.13. It is noteworthy also that a mixture of cyanide and caustic is more effective than either alone. The elimination of variations owing to the ionic strength shows (Figure 5.15) that the rate of elution increases with increasing concentration of either cyanide or hydroxide, at constant ionic strength.

d) *Effect of Organic Solvents*

Several studies have been made in which various organic solvents have been added to the aqueous solution to promote more efficient desorption of gold. Thus, even at low temperatures, gold can be desorbed in the presence of high concentrations of certain solvents, as shown by the results in Table 5.5.

Several mechanisms have been proposed for the action of these organic solvents in suppressing adsorption of gold. That proposed by Muir et al.²³⁹ is interesting in that it assumes that competition by the cyanide ion for adsorption sites is the major factor involved. They postulate that the main effect of organic solvents is to substantially increase the activity of small anions like CN^- (increases of up to 10^6 have been measured) whereas large complex

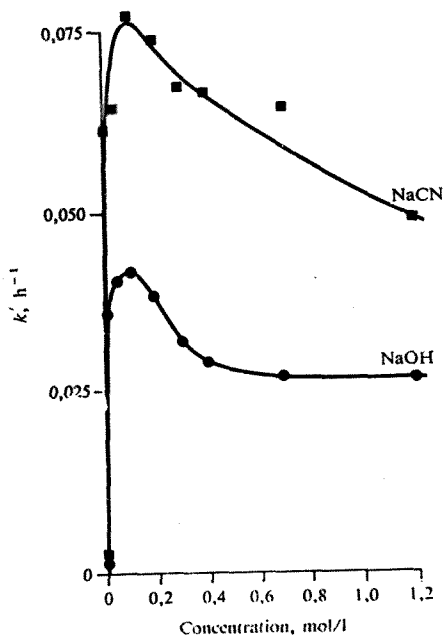


Fig. 5.14 The effects of the concentration of cyanide or hydroxide on the rate of elution at 95°C

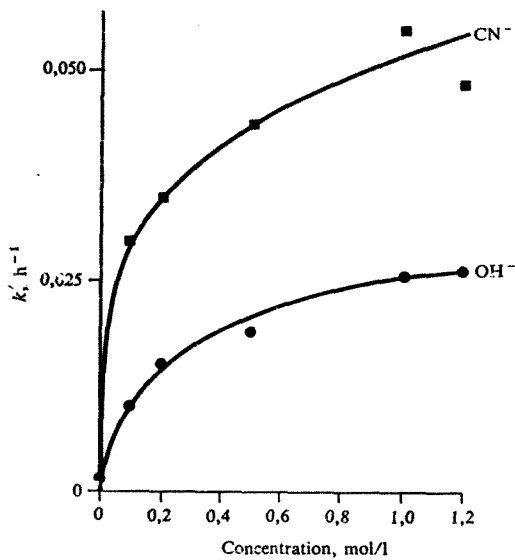


Fig. 5.15 Variation of the rate of elution with eluant concentration at a constant ionic strength of 1,2 at 95°C

anions like Au(CN)_2^- are relatively unaffected. This proposal assumes that the adsorption of aurocyanide onto activated carbon is due to simple ion exchange onto positively-charged surface sites. However, the evidence provided in this Thesis shows that ion exchange does not play a major part in the adsorption under typical plant conditions. It is suggested that the action of organic solvents on the elution is better explained by the preferential adsorption of the organics on the surface of carbon, displacing the adsorbed $\text{M}^{n+}[\text{Au(CN)}_2^-]_n$ species. This is consistent with the observed²⁹ displacement of adsorbed mineral acids from carbons by organics.

Table 5.5
Elution of gold by organic solvents at 25°C
(after Nicol et al²⁵¹)

Solvent 40% (V/V)	NaCN (g/l)	Gold loading (kg/t)	% Eluted in	
			1h	24h
Ethanol	10	5,5	5	12
Acetone	10	5,5	25	70
Acetonitrile	10	5,5	25	75
Acetonitrile	50	5,5	50	95

5.5 Other Aspects of the Elution Process

Certain other aspects of elution have not received attention. Some of these aspects play a profound role in the practical application of the elution procedures mentioned above.

a) *Effect of Acid washing Prior to Elution*

Many plants utilize an acid-washing step of some kind prior to elution of gold from the carbon. The main advantage of this procedure is removal of precipitated calcium carbonate from the carbon pores, which increases the intraparticle diffusion coefficient. It is reported²⁵³ that a cold acid-wash (typically 1 bed-volume of 3% v/v hydrochloric acid, although a wide variation of conditions are in use) will remove calcium from the carbon. A hot (90°C) acid-wash has been found²³⁸ to remove zinc, nickel, iron and silica, in addition to calcium.

One aspect of acid-washing that has for the first time come to light in the present work (Chapter 3), concerns the effect of acid on the adsorbed gold species. Cold acid-washing results in the limited formation of insoluble AuCN, while the reaction occurs to a much greater extent when hot acid-washing is employed:



AuCN thus formed on the carbon was found in Chapter 3 to decompose in alkaline solution, forming gold metal (see Figure 3.2) and aurocyanide:

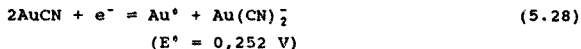


Table 5.6 shows that acid-boiling the loaded carbon for six hours does not influence the elution kinetics significantly when the eluant contains 0,2M NaCN. The aurocyanide species is evidently reformed rapidly when 0,2M NaCN is present.

In contrast, when the eluant contains 0,2M NaOH and no cyanide, the elution rate from acid-boiled carbon is only

half that for untreated carbon. It was pointed out in Chapter 3 that under these conditions, half of the gold has been reduced (via reaction (5.28)) to the metallic form, which does not form a strong complex with the hydroxide ion, and thus cannot be eluted by 0,2M NaOH solution.

Table 5.6
Effect of acid treatment on the elution rate

Elution conditions: carbon mass 26,7g
temperature 95°C
initial gold on carbon (C_0) 1245 g/t

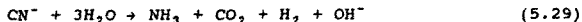
Acid treatment	Eluant	$k' (h^{-1})$
None	0,2M NaOH	0,0937
0,1M HCl wash, 24h		0,1026
0,1M HCl boil, 1h		0,0503
None	0,2M NaOH/0,2M NaCN	0,1663
0,1M HCl wash, 24h		0,1746
1,1M HCl boil, 6h		0,1846

Several CIP plants around the world, particularly in Canada, have designed elution plants in which gold is stripped from the carbon with hydroxide, with no cyanide added to the eluant. The above results indicate that care will have to be taken on these plants not to produce AuCN during acid-washing, if this "cyanide free" elution process is to be successful.

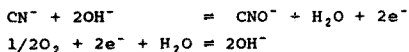
b) *Effect of Cyanide Decomposition on
Gold Elution Efficiency*

It is well known^{238,254} that cyanide decomposes during a typical Zadra elution, to the extent that little cyanide

remains in the eluate on completion of elution. It has been shown^{89,255} that the hydrolysis of cyanide to carbon dioxide and ammonia, via an ammonium formate intermediate, is the reaction responsible for the rapid cyanide loss under elution conditions:



A high rate of cyanide loss also occurs²⁵⁶ in the electrowinning cell, due to anodic oxidation:



Activated carbon itself is known^{89,158} to catalyze reaction (5.30), but neither this reaction, nor the hydrolysis reaction



which occurs at low (less than 9) pH values, are important under elution conditions⁸⁹.

The data in Figure 5.16 show the result of a batch experiment in which carbon loaded with gold was contacted with an aqueous caustic cyanide solution at 95°C for 200 hours. During this period the concentration of cyanide in solution decreased from an initial value of 5240 mg/l (0.2M) to 3 mg/l, mainly as a result of the hydrolytic decomposition reaction. It can be seen in Figure 5.16 that the loss of cyanide from solution has a marked effect on the concentration of gold in solution, which initially increases, to reach a maximum value after about 24 hours, and then gradually decreases over the remainder of the period. Readsorption of gold occurs as a result of cyanide loss from solution, and is a reflection of the different

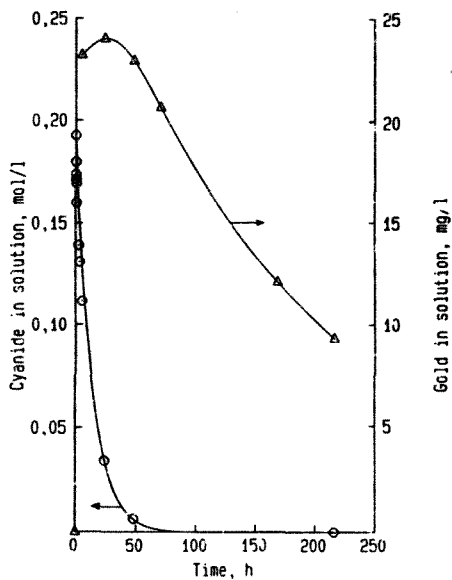


Fig. 5.16 Effect of cyanide decomposition on the elution of aurocyanide from activated carbon at 95°C in a batch reactor. ($C_0 = 1300$ g/t)

equilibrium constant for elution with hydroxide compared with cyanide. It should be noted that, because this was a batch elution experiment, the actual elution efficiencies represented in Figure 5.16 are very low.

c) *Effect of Removal of Cyanide from
Eluant Solution*

Figure 5.16 shows that even when the cyanide concentration has been reduced to a negligible value, some gold remains in solution. It was shown in Chapter 3 that complete elution can be achieved using a sodium hydroxide eluant with no cyanide present. Several full-scale plants are currently using a cyanide-free caustic eluant. The slower kinetics of elution with hydroxide as against cyanide is a disadvantage of this approach; however, Figure 5.14 shows that only a small (c. 0.01M) concentration of cyanide is required in order to improve the elution kinetics to around the level expected for a high-cyanide eluant. Figure 5.17 shows that this is also true in the presence of 0.2M NaOH, i.e. conditions approximating those used in practice for Zadra elutions.

The presence of an acid-washing step in the circuit prior to elution could well complicate the situation, since any gold that is present on the carbon in the metallic form (via reactions (5.27) and (5.28)) is not eluted by hydroxide (see Chapter 3), and a high-cyanide eluant would probably be necessary in such cases.

d) *Selective Elution of Copper and Mercury*

Copper dissolves in cyanide solution as the copper(I) complex and, depending on the ratio of cyanide to copper and the pH, the following complexes predominate in solution: $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$, and $\text{Cu}(\text{CN})_4^{3-}$. The relevant species

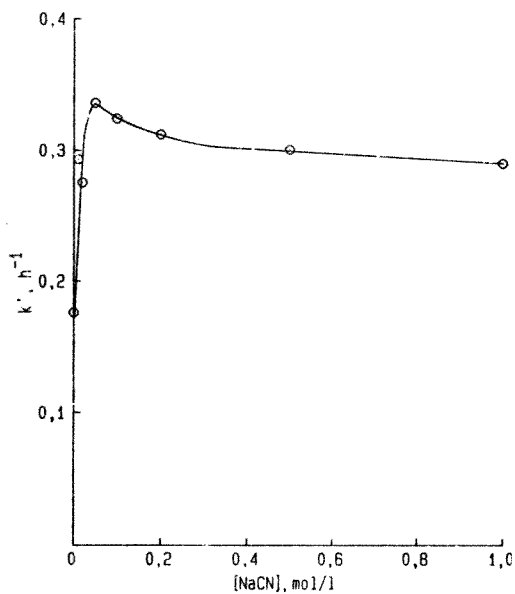


Fig. 5.17 Effect of cyanide concentration on the rate of elution at 95°C in the presence of 0.2M NaOH

distribution diagrams, as calculated by the HALTAFALL¹⁴⁹ program on an IBM PC II personal computer, are shown in Figures 5.18 and 5.19, for fixed pH values of 10 and 7, respectively. (The copper concentration is fixed at 0.0001571 M, i.e., 10 mg Cu/l.) The $\text{Cu}(\text{CN})_2$ species and CuCN precipitate predominate at low cyanide concentrations and low pH values, whereas $\text{Cu}(\text{CN})_3^{2-}$ is the predominant species at high cyanide concentrations. It has been shown⁶⁸ that the $\text{Cu}(\text{CN})_2$ species is loaded very strongly onto activated carbon, yet that $\text{Cu}(\text{CN})_3^{2-}$ is hardly loaded at all. The loading behaviour of copper in a plant situation can therefore be influenced by varying the concentration of free cyanide. For significant reduction of the copper loading, however, high levels of free cyanide (higher than 500 p.p.m.) have to be maintained, and this may not always be economically viable. An alternative approach therefore is this - the copper can be allowed to build up on the carbon in the CIP extraction stages and the loaded carbon can then be treated with cyanide at low temperatures. This converts the $\text{Cu}(\text{CN})_2$ species to the less strongly adsorbed $\text{Cu}(\text{CN})_3^{2-}$ species, which is eluted.

The results of laboratory tests on loaded carbons are shown in Table 5.7. It is apparent that copper can be selectively eluted by this procedure, and that problems with electrowinning or cementation, or both, can be avoided in cases where excessive loading of copper occurs.

The presence of mercury on loaded carbons from certain plants in the U.S.A. poses an environmental problem, since the mercury vaporizes in the regeneration furnace¹⁵². The results presented in Figures 3.46 and 3.47 suggest that the conversion of mercury from the strongly adsorbed $\text{Hg}(\text{CN})_2$ species to the weakly adsorbed $\text{Hg}(\text{CN})_3^{2-}$ species could circumvent this problem in a similar way to that described above for the $\text{Cu}(\text{CN})_2$ species.

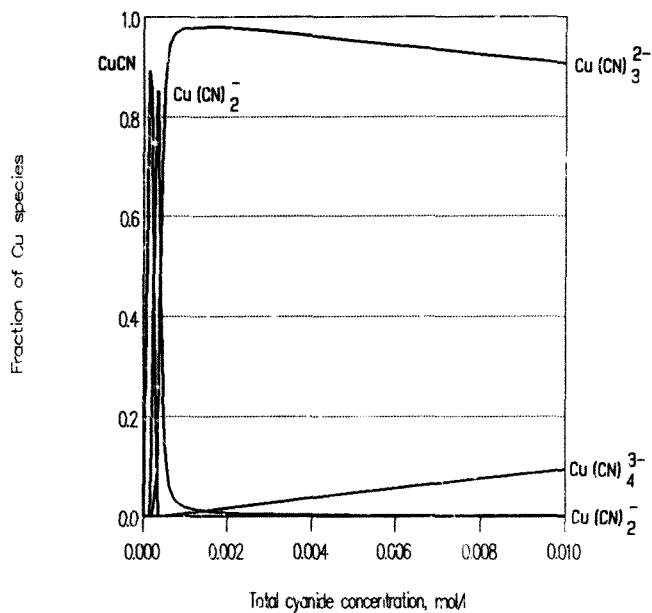


Fig. 5.18 Distribution of copper species at pH 10 with variation in cyanide concentration

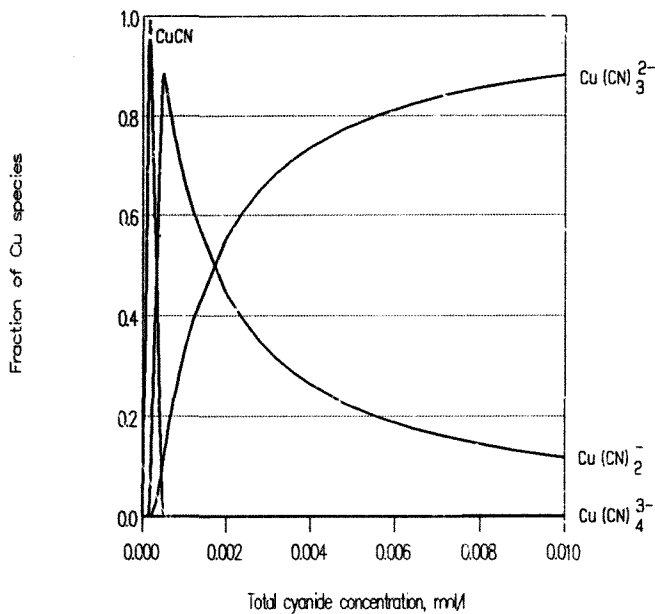


Fig. 5.19 Distribution of copper species at pH 7 with variation in cyanide concentration

Table 5.7
Elution of gold, silver and copper with sodium cyanide
at 20°C (after Fleming and Nicol⁶⁸)

Carbon sample	Metal	Metal on loaded carbon p.p.m.	% metal eluted in 20 BV			
			NaCN 1g/l		NaCN 10g/l	
A	Au	1490	0		0	
A	Ag	4400	1,5		6,1	
A	Cu	6400	88		100	
B	Au	1460	0		0	
B	Ag	3740	2,9		6,2	
B	Cu	24800	78		100	

5.6 Conclusions

Evidence has been presented which suggests that the mechanism of elution involves ionization of phenolic-type groups on the surface of activated carbon in strongly alkaline solution. This causes the carbon surface to be negatively charged, hydrophilic, and incompatible with adsorption of the aurocyanide ion pair. The catalytic effect of cyanide in the elution process is ascribed to a similar mechanism, in which the cyanide ion reacts with surface carbonyl groups, resulting in the formation of additional negatively charged O⁻ sites on the surface.

A kinetic model was developed for elution of aurocyanide from activated carbon, and was shown to successfully describe the kinetics of elution for several configurations, including the recirculation of depleted eluate, and flow through a carbon column.

Several chemical influences on the Zadra elution, were also

examined. Hot acid-washing the carbon prior to elution was shown to slow down the elution kinetics (when no cyanide is present), due to the formation of metallic gold on the carbon. The extent of acid-washing is a compromise between maximum calcium removal and minimum formation of metallic gold. Decomposition of cyanide during elution was shown to be extensive; however, this has a significant deleterious effect on the elution only after long time periods not normally experienced in plant operations. This rapid loss of cyanide, together with the fact that complete elution can be achieved with no cyanide present in the eluant, suggests that cyanide concentrations an order of magnitude lower (c. 0.05% NaCN, i.e. 0.01M) than those presently used (c. 0.5% NaCN, i.e. 0.1M), would be economically advantageous. The presence of this small amount of cyanide is sufficient to enhance the elution kinetics markedly, as well as being necessary to leach small amounts of insoluble AuCN formed during the acid-washing step. If hot acid-washing is employed, however, it would probably be necessary to use the more concentrated (0.1M) cyanide eluant to leach the larger amounts of AuCN formed.

The elution step is an important one in the CIP process as a whole, and it is only recently that an understanding of it is being gained on a fundamental level. A knowledge of how the important factors influence the elution, viz. temperature, ionic strength, cyanide and hydroxide concentrations, organic additives and gold in the eluant feed, is essential to the effective utilization of the principles.

Application of kinetic models to plant data could also assist in the actual operation, as could a knowledge of other factors that influence elution, such as cyanide decomposition, the effect of acid-washing, and the selective elution of copper and mercury.

There are without doubt, many improvements that can be made to the relatively lengthy, energy-inefficient methods currently used for elution of gold from activated carbon, and the need for a fast, low temperature elution procedure has never been greater.

CHAPTER 6 **THE INFLUENCE OF ACTIVATED CARBON**
SURFACE CHEMISTRY AND STRUCTURE ON
THE ADSORPTION OF AUROCYNANIDE

Adsorption of aurocyanide onto activated carbon has been the subject of much study and speculation in recent years, particularly with regard to the mechanism of adsorption^{11,62,77,78,92,111}. The emphasis has been on the elucidation of the nature of the aurocyanide adsorbate, rather than the role of the activated carbon itself.

The surface chemistry of activated carbon remains the topic of much debate, and most studies of the adsorption of aurocyanide onto activated carbon make mention of the oxygen-containing functional groups present on activated carbon surfaces. The influence of carbon pore structure on aspects of the process has also been brought to light from time to time. However, it is uncertain which properties of the carbon are of primary importance for the effective adsorption of aurocyanide.

This Chapter aims at elucidating the main physical and chemical characteristics of the carbon that are influential on the adsorption and elution processes.

6.1 Influence of Activation Conditions and Starting
Material on Surface Chemistry, Structure and Gold
Adsorption Activity of Activated Carbon

The activation process should perhaps more accurately be regarded as the net result of a set of complex physical and chemical processes that occur simultaneously as the raw material is heated to the required activation temperature,

in the presence of the gases that make up the activation atmosphere. In the only previous attempt⁶² to isolate activation parameters of importance to gold adsorption, it was established that activation temperature had the greatest influence on the affinity of carbon for aurocyanide.

In the present study, carbons were produced from the pyrolysis, under various conditions, of S-761 polymeric adsorbent, which is essentially a phenol-formaldehyde matrix. A set of four commercial activated carbons made from different starting materials were also investigated. The influence of activation conditions on various chemical and physical properties of the carbons was investigated.

a, *Gold Adsorption Activity*

A marked increase in aurocyanide capacity in the 650 to 850°C region is apparent, as shown in Figure 6.1. The capacity is increased by a factor of ten from 650 to 850°C. Gross and Scott³ report a similar effect of activation temperature for carbon made by the pyrolysis in air of pine wood, with a large increase in the capacity for gold in the 750°C region. It should be noted that the higher temperature products (> 850°C) were found to have gold activities comparable with those of the commercial carbons studied. Gold activities are reported as percentage extraction after twenty hours. This set of results also appears in earlier work⁶², in which the carbons were not characterized as rigorously as in the present work.

Table 6.1 shows that similar gold adsorption activities result from activations under atmospheres of nitrogen, steam, carbon dioxide and air, and for activation times of both one hour and four hours. Moreover, gold adsorption activities of the carbons made from coconut shells, peat and coal were similar, with the wood carbon (Norit C) being

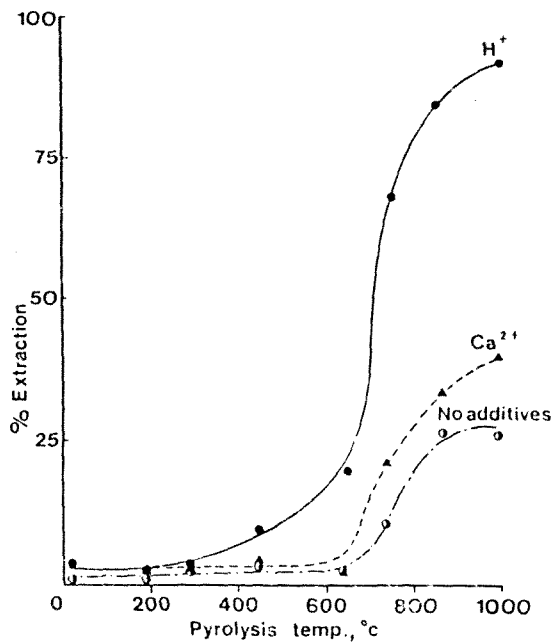


Fig. 6.1 Effect of pyrolysis temperature of S-761 polymeric adsorbent on aurocyanide capacity (after Adams et al.⁸²)

the only one which was found to be markedly inferior. This is the only carbon which was activated at low temperatures, in a phosphoric acid process²⁵⁷.

Table 6.1
Gold adsorption activities of synthetic and
commercial activated carbons

Carbon	Gold adsorption after 24 h, %		
	No additives	0,033M CaCl ₂	0,1M HCl
850/H ₂ O	19,8	28,5	84,2
850/CO ₂	18,3	21,2	78,1
850/N ₂	19,1	21,5	77,0
850/1h	19,0	24,2	80,8
G210	16,4	32,7	79,4
K00-15	22,7	33,4	80,1
AURC	20,4	31,6	74,9
Norit C	7,8	22,0	23,0

b) Activated Carbon Structure

The effects of pyrolysis temperature on skeletal densities, micropore volumes and surface areas of the carbons produced, are shown in Figures 6.2, 6.3 and 6.4 respectively. The marked increase in skeletal density at 750°C is consistent with the graphitization process which occurs in this region³⁰, since the density of pure graphite (2,25 g/cm³)⁶⁵ is approximated in the high temperature region. Skeletal densities of the carbons produced under different atmospheres and from different starting materials are all similar, as shown in Table 6.2. The exception is again Norit C, the low temperature carbon, which has a much lower skeletal density.

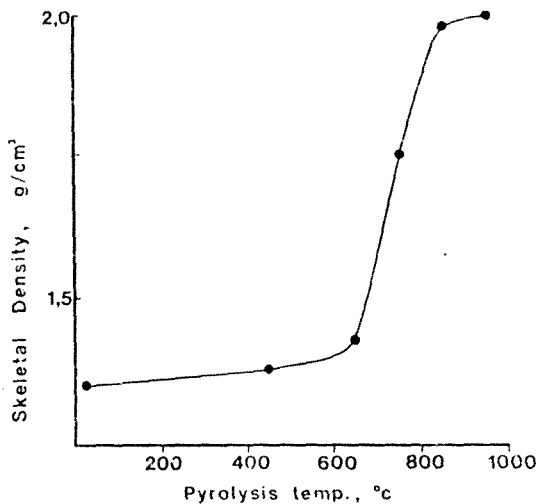


Fig. 6.2 Effect of pyrolysis temperature of S-761 polymeric adsorbent on skeletal density

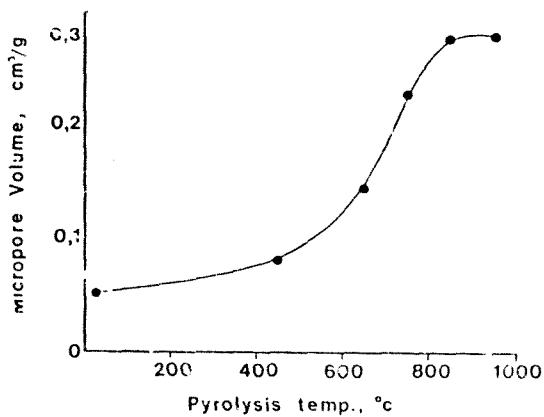


Fig. 6.3 Effect of pyrolysis temperature of S-761 polymeric adsorbent on micropore volume

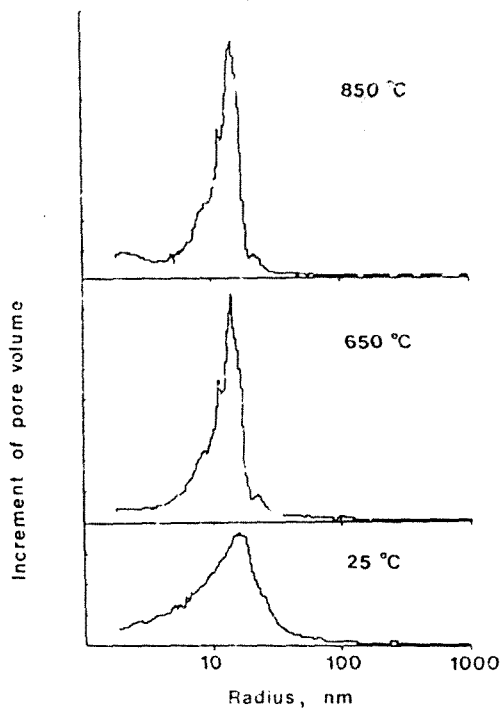


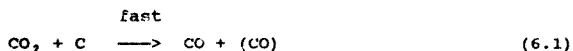
Fig. 6.4 Effect of pyrolysis temperature of S-761 polymeric adsorbent on pore size distribution

Table 6.2
Structural properties of synthetic and
commercial activated carbons

Carbon	Skeletal density g/cm ³	Pore volume, cm ³ /g				Surface area m ² /g
		Micro- pore $D_p < 2\text{nm}$	meso- pore $2 < D_p < 30\text{nm}$	macro- pore $D_p > 30\text{nm}$	Total	
850/H ₂ O	2,0433	0,3311	0,1803	0,0252	0,4794	722
850/CO ₂	1,9443	0,2530	0,2017	0,0247	0,5366	480
850/N ₂	2,0165	0,2694	0,1999	0,0246	0,4939	490
850/1h	2,0080	0,2647	0,5499	0,0084	0,8230	660
G210	2,086	0,3916	0,1250	0,1343	0,6509	1000
RO3515	2,184	0,3711	0,0338	0,3189	0,7238	1160
AURC	2,166	0,3691	0,1258	0,2562	0,7511	1160
Norit C	1,600	0,1926	0,6419	0,9289	1,7634	1200

The micropore volume (Figure 6.3) displays a similar sharp increase over the 650°C to 850°C range, which is consistent with the suggestion²⁵⁸ that the micropores are in effect gaps between graphitic microcrystallites and between graphitic planes within microcrystallites. Once again the only carbon with a low micropore volume is Norit C, as shown

in Table 6.2. It is noteworthy that the pore structure of the pyrolyzed polymeric adsorbent remains very similar throughout, being mesoporic, as shown in Figure 5.4, and that despite the variance in the mesopore and macropore volumes of the four commercial carbons, their micropore volumes are similar (see Table 6.2). Comparison of the micropore volumes and skeletal densities of the four carbons made under various activation conditions shows that the graphitization process is aided by the presence of water vapour, and depressed by the presence of CO_2 , which is consistent with the previously postulated schemes²⁵⁹ for the reaction of CO_2 with carbon:



(where (CO) represents intermediate surface functional groups), and the reaction of H_2O with carbon:



Reaction with steam results in removal of more carbon as CO and CO_2 than the reaction with CO_2 .

Another observation is that the surface area, *per se*, is not

the most important parameter for high gold adsorption activities.

The effect of pyrolysis temperature on surface area is shown in Figure 6.5. Unlike the gold activity curve in Figure 6.1, no sharp increase at about 750°C is observed, the curve being much shallower. The surface areas of the four commercial carbons are all very similar, which is consistent with the similarities in their other properties. The variance in surface areas of the four carbons produced under different activation atmospheres is at odds with their similar gold adsorption activities, again discounting surface area as the most important property for gold adsorption. It is not surprising that activation under a nitrogen blanket resulted in the generation of a relatively low surface area carbon, due to the reactions



being pushed to the left hand side by the lower oxygen partial pressure. An increase in the CO_2 partial pressure evidently has a similar effect. Activation at 850°C in air for one hour results in a somewhat lower surface area than for the four-hour activation. Moreover, carbons activated at 850°C in the presence of nitrogen or carbon dioxide both have lower surface areas than the carbon activated at 650°C in the presence of air, yet display markedly higher gold adsorption activities. It is therefore the activation temperature, rather than the activation atmosphere, that is important in producing a good activated carbon for gold.

As a result of the microporosity of activated carbons, the term "surface area" has little physical meaning, and it is preferable²⁴⁰ to refer to pore volume. Recent measurements^{258,259} of the heat of adsorption at low

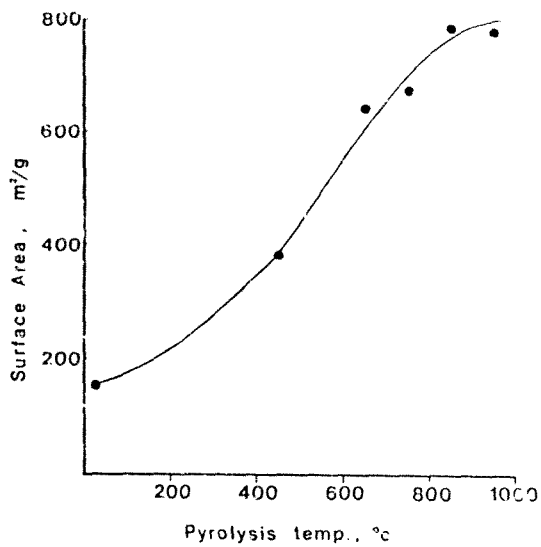


Fig. 6.5 Effect of pyrolysis temperature of S-761 polymeric adsorbent on surface area

surface coverage of various hydrocarbons on microporous carbons and non-porous carbon blacks show that adsorption energy in micropores is enhanced by a factor of about 2 as compared with adsorption on a flat surface. This enhancement factor is consistent with that predicted by adsorption potential theory for slit-shaped pores^{258,259}, whereby the interaction energy between the adsorbate molecule and the solid surface is enhanced as a consequence of overlap of adsorption field from neighbouring walls.

These ideas are consistent with the fact that Freundlich plots of gold adsorption data on carbon are usually non-linear⁶² - at low equilibrium values of aqueous gold concentrations, the adsorption site energies are much greater than expected from an exponential variation model such as the Freundlich equation. High energy surface sites, such as micropores of the correct size, should be the first to be taken up by adsorbate molecules. Measurements of the enthalpies of adsorption of aurocyanide onto activated carbon at different loadings shows that higher energy interactions (-75,0 kJ/mol) are involved at low loadings (20 mg Au/g) than at higher loadings (54 mg Au/g), where the enthalpy of adsorption was determined⁶² to be -35,0 kJ/mol.

A further measure of the degree of graphitization of an activated carbon is conductivity, and this parameter follows a trend similar to that of skeletal density as activation temperature is increased, as shown in Figure 6.6. The high temperature commercial carbons all have high conductivities, whereas the low temperature Norit C carbon has a very low conductivity, as shown in Table 6.3. The carbons produced under different activation atmospheres all display similar conductivities. These trends are consistent with the onset of graphitization at around 750°C, as discussed earlier. The relation between electronic conductivity and chemical reactivity in graphites has been discussed previously²⁵⁹.

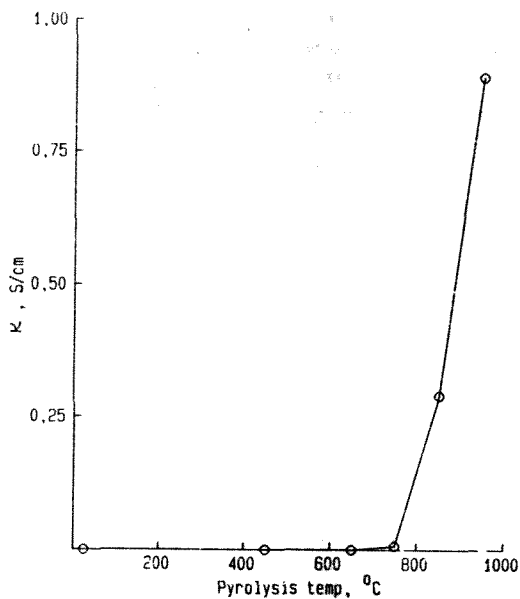


Fig. 6.6 Effect of pyrolysis temperature of S-761 polymeric adsorbent on conductivity

Table 6.3
Conductivities of synthetic and commercial
activated carbons

Carbon	κ , S/cm
850/H ₂ O	0,20
850/CO ₂	0,42
850/N ₂	0,39
850/1h	0,18
G210	3,8
RO3515	8,0
AURC	5,4
Norit C	$<7 \times 10^{-8}$

The graphitization process can be studied further by examination of the X-ray diffractograms of the various activated carbons. X-ray diffractograms of S-761 polymeric adsorbent pyrolysed at different temperatures were measured previously²², but not analysed. Peak intensities do not provide a quantitative comparison due to discrepancies resulting from differences in sample packing. However, peak positions and widths can be used to determine the microcrystallite diameters (L_a) and heights (L_c), assuming that the microcrystallites are approximately cylindrical in shape. The method used was that described by Biscoe and Warren²⁶¹. An X-ray diffractogram of a typical activated carbon (Le Carbone G210) appears in Figure 6.7. The L_c term is derived from the (002) peak width at half the maximum intensity (β_{002} , expressed in radians):

$$L_c = \frac{1,0 \lambda}{\beta_{002} \cos \theta}, \quad (6.11)$$

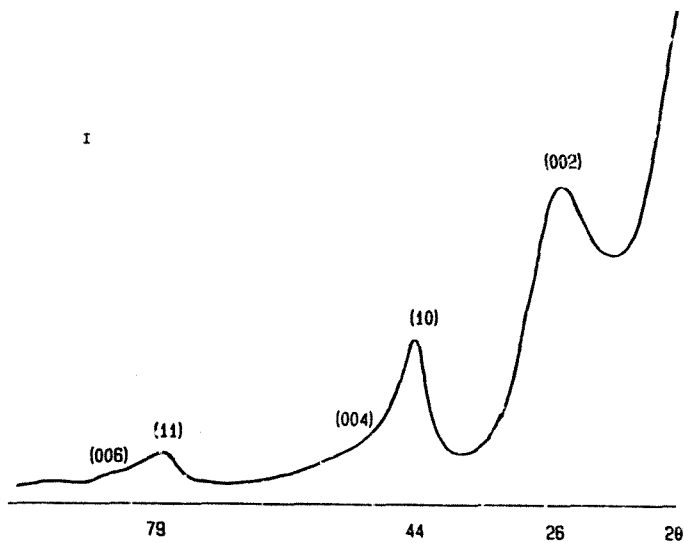


Fig. 6.7 X-ray diffractogram of a typical activated carbon (Le Carbone G210)

where θ is the incident angle corresponding to the peak maximum, and λ is the wavelength of the radiation employed, in this case $\text{Cu K}\alpha_1$ radiation ($\lambda = 1,54178 \text{ \AA}$).

The L_c term is similarly calculated from the (10) peak width and position:

$$L_c = \frac{1,84 \lambda}{B_{10} \cos \theta} \quad (6.12)$$

No graphitic peaks were observed for unheated or 450°C -heated polymeric adsorbent. Thereafter, both (002) and (10) peaks were observed, which increased in intensity with pyrolysis temperature, as reported previously²². The derived parameters of L_c and L_a for the carbons appear in Table 6.4. The microcrystallites are somewhat smaller in both height and diameter in the 650°C - pyrolyzed carbon, and thereafter approximately constant values of $L_c = 9 \text{ \AA}$ and $L_a = 30 \text{ \AA}$ are observed. The slightly larger microcrystallites observed for the steam-heated carbon are coincident with the slight enhancement in gold adsorption activity for this carbon. Both the nitrogen-activated carbon and the carbon activated for a shorter time display similar microcrystallite heights but smaller diameters. In polycrystalline graphite, the distance between planes is cited²⁶¹ as $3,349 \text{ \AA}$, and that between carbon atoms as $2,456 \text{ \AA}$. An average microcrystallite in activated carbon therefore consists of two disordered planes, about twelve aromatic rings in diameter. The distance between the graphitic planes in activated carbons has been determined²⁶² to be about $3,7 \text{ \AA}$, i.e. larger than in graphite.

Table 6.4
Microcrystallite dimensions of synthetic and
commercial activated carbons, from XRD peak data

Carbon	L_c , Å	L_a , Å
25	- ^a	-
450	-	-
650	6,9	28,2
750	9,1	31,8
850	9,0	29,7
950	9,5	34,5
850/H ₂ O	10,4	37,5
850/CO ₂	9,5	34,5
850/N ₂	9,7	27,8
850/1h	9,4	26,2
G210	10,2	43,2
RO3515	9,6	47,9
AURC	12,3	47,9
Norit C	-	-
Graphite	150,5	86,5

^aNo graphitic peaks observed.

The three commercial high-temperature activated carbons have L_c (height) dimensions of about 10 Å, which are similar to those of the synthetic carbons, and L_a dimensions of about 45 Å, which are somewhat larger than in the case of the synthetic carbons. The low-temperature Norit C carbon did not display any observable graphitic peaks. It is interesting to compare the values in Table 6.4 with those of a typical sample of graphite. Both L_c and L_a dimensions are much larger than for the activated carbons, but the largest difference between the two is the large microcrystallite height dimension, which implies that the graphite sample has, on average, 22 stacked graphitic planes per crystallite, as opposed to activated carbon, with only two or at most three.

The marked correlations between gold adsorption activity

and micropore volume, as well as the degree of graphitization, should be discussed in terms of the physical structure of carbon. There is considerable evidence^{258,260} that a large part of the microporosity is in the form of an interconnected network of slit-shaped pores formed by the spaces between the carbon layer planes and the gaps between the stacks. These pores have widths of between about 3,4 Å and 8 Å. These dimensions are commensurate with dimensions of adsorbate molecules both organic and inorganic, and the observed²² decrease in aurocyanide adsorption with large cations such as tetrabutylammonium ($r^+ = 4,94$ Å) as opposed to potassium ($r^+ = 1,33$ Å) for example, is consistent with this hypothesis. The effective radius of $\text{Au}(\text{CN})_2^-$, based on an estimate of its molar volume, was calculated in Chapter 4 to be 1,9 Å, and this is close to the measured Stokes radius of 2,4 Å. Tetrabutylammonium aurocyanide will therefore be excluded from entering a typical micropore due to size effects. McEnaney²⁵⁸ suggests that strong adsorption of gases at low pressures in micropores is caused by the enhancement in adsorption potential due to overlap of force fields of opposite pore walls. This may explain why a similar effect is observed²² in adsorption of aurocyanide onto activated carbon from dilute solutions, as discussed earlier. Moreover, this interaction is suggested⁶² to involve a charge-transfer interaction between the carbon and the gold nucleus under certain conditions on the basis of the collected evidence from electron spin resonance (ESR)⁶² and X-ray photoelectron spectroscopic (XPS) measurements (see also Chapter 3). Recent Mössbauer measurements are also consistent with an increased charge density around the gold nucleus in the adsorbed aurocyanide species. (See Chapter 3). Similar charge-transfer interactions have been proposed to occur between carbon and other adsorbates^{24,262-264}.

c) *Activated Carbon Surface Chemistry*

The identities of many of the oxygen-containing functional groups on activated carbon surfaces remains a contentious issue²⁶, although there is qualitative evidence from various techniques for the presence of carbonyl, phenol, carboxylic acid and lactone groups. Table 6.5 details some relevant chemical properties of the synthetic and commercial activated carbons used in this study. The high-temperature activated carbons are all characterized by high carbon contents (~ 90%) and low hydrogen contents (~ 1%). There is a gradual trend in both of these values as the activation temperature is increased.

Table 6.5
Chemical characteristics of synthetic and commercial
activated carbons

Carbon	Elemental analyses, %			E V (vs SHE)	Phenol adsorption after 24 h, %	ΔpH in water
	C	H	O			
25	68,3	5,0	-	+0,334	44,9	-3,40
450	73,3	4,1	-	+0,328	37,5	-2,75
650	85,9	3,2	6,1	+0,319	78,5	-1,79
750	88,3	2,2	2,9	+0,278	94,8	-1,56
850	90,8	1,6	2,4	+0,259	96,7	-1,26
950	92,4	1,2	1,6	+0,229	96,5	-0,87
850/H ₂ O	93,4	1,3	2,0	+0,245	89,0	+0,22
850/CO ₂	94,9	1,2	1,0	+0,259	93,7	+0,01
850/H ₂	93,7	1,5	1,1	+0,242	90,3	+0,31
850/1h	92,8	1,4	2,5	+0,260	92,7	+0,67
G210	92,5	0,9	1,7	+0,188	92,7	+3,76
RO3515	89,2	0,8	3,0	+0,208	94,8	+3,42
AURC	85,4	0,9	5,3	+0,193	92,5	+2,74
Norit C	69,4	3,4	4,6	+0,356	39,7	-3,89

-Not determinable

The oxygen content of the synthetic carbons steadily decreases as the activation temperature increases. It is also lower when activated in the presence of N_2 or CO_2 , corresponding with the activated carbons where less micropore formation was evident. The oxygen content of a carbon is not a reliable measure of the gold adsorption activity, however - AURC has both a high oxygen content and gold adsorption activity. In this case, the anomalous oxygen content could be due to the coal base, or to the binder used in the extruding process.

An integral part of the surface chemistry of activated carbon is its electrochemical behaviour. The reduction potential of the series of carbons was measured using a technique reported previously³². A graphite rod electrode was contacted with several of the carbon particles after fifteen minutes of immersion in a 0,01 M NaCl solution, kept at a pH value of 5,0. The potential was measured against a saturated calomel electrode. The effect of activation temperature on this property is shown in Figure 6.8, and it is evident that the functional groups imparting the potential to the carbon only appear at activation temperatures of 750°C or higher, corresponding to the increase in gold adsorption activity at the same temperature. Activation under different atmospheres has little influence on reduction potential (see Table 6.5). The commercial high-temperature activated carbons all have relatively low reduction potentials, which is indicative of higher reducing power, whereas Norit C has a rather positive potential, corresponding to its low gold adsorption activity.

It should be noted that these values are not absolute, and merely reflect an arbitrary point from which a reasonable comparison can be made. Figure 6.9 shows the variation in measured reduction potential with time for R03515 activated carbon. The fact that the potential tends to that

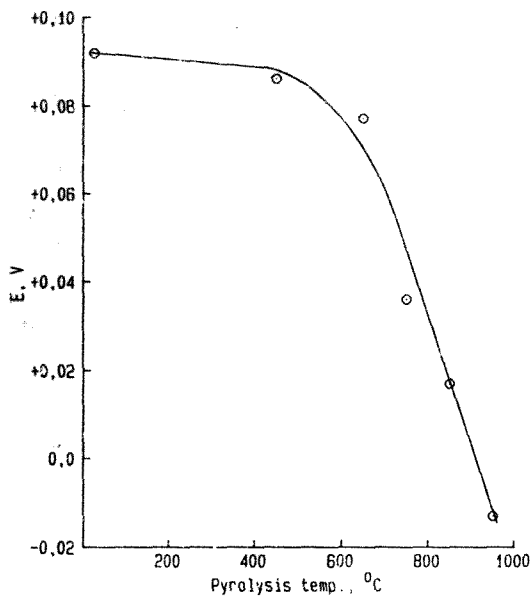


Fig. 6 8 Effect of pyrolysis temperature of S-761 polymeric adsorbent on reduction potential

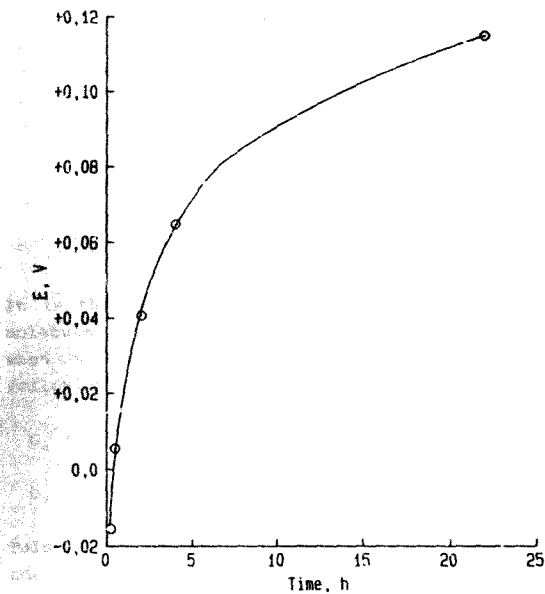
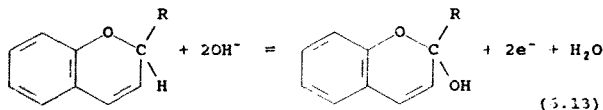
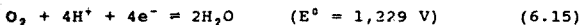
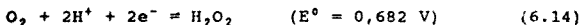


Fig. 6.9 Variation of measured reduction potential for R03515 activated carbon with time of measurement

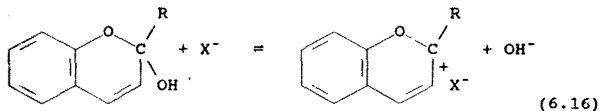
measured for the solution with no carbon present, suggests that the functional groups responsible for the reducing power of the carbon are gradually oxidized in aqueous solution. An example of such a reaction is the oxidation of the chromene group:



It is thermodynamically feasible for the reduction of molecular oxygen to occur as the reduction half-reaction, when comparing the measured reduction potentials with the following:

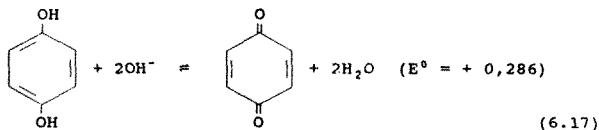


This set of reactions has been postulated^{6,9} to occur upon adsorption of anions from solution, by an ion-exchange mechanism:



The fact that the pH of the solution used in these measurements continually had to be adjusted with acid, is consistent with this mechanism.

The quinone/hydroquinone couple has also been postulated^{2,4} in this regard:



An interesting comparison with gold adsorption activity is that of phenol adsorption activity. Both aurocyanide⁶² and phenol²⁴ have been proposed to adsorb on the activated carbon surface via a charge transfer interaction. The effect of activation temperature on phenol adsorption is shown in Figure 6.10, and is clearly similar to the effect of temperature on gold adsorption (Figure 6.1). Moreover, the trends for adsorption of phenol onto the commercial activated carbons and the carbons activated under different atmospheres (Table 6.5) are similar to those for the adsorption of gold, shown in Table 6.1. It is well known that organic compounds can desorb a substantial fraction of adsorbed aurocyanide from activated carbons and it was suggested in Chapter 5 that this desorption is due to a competition between the organic and aurocyanide for the same adsorption sites. This is the origin of the effect of poisoning of CIP plant activated carbons by organics in the pulp.

The final column in Table 6.5 shows the pH change upon contact of the activated carbons with water. The high-temperature carbons, particularly the commercial ones, all undergo significant positive shifts in pH, and the low-temperature carbons display negative shifts. The discrepancy in the synthetic high temperature carbons is due to a somewhat more alkaline water being used for these tests. These results are consistent with the well documented^{24,29} presence of basic functional groups on the surface of high-temperature carbons, and acidic groups on the surface of low-temperature carbons.

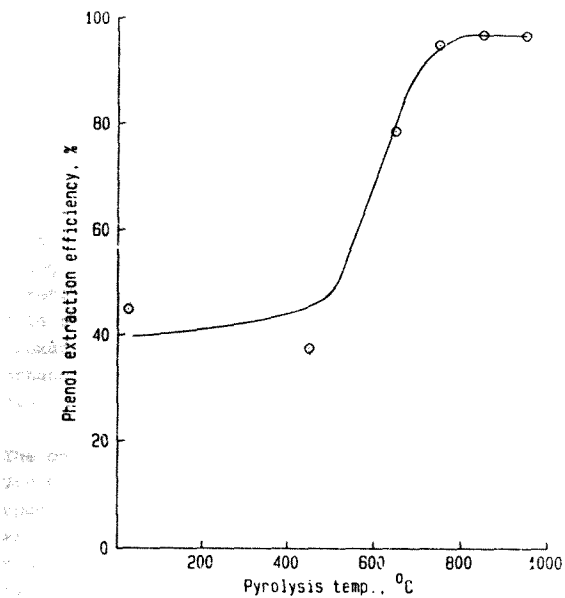


Fig. 6.10 Effect of pyrolysis temperature of S-761 polymeric adsorbent on phenol activity

Infrared spectra of the pyrolysis products of S-761 polymeric adsorbent are shown in Figure 6.11. It is evident that changes in the chemical nature of the adsorbent start occurring after heating at 450°C, with the bands at 1654 cm⁻¹ and 1012 cm⁻¹, assigned to β -diketone groups²⁶⁵, decreasing in intensity and a new band at 1720 cm⁻¹, assigned to carboxyl groups^{265,266}, appearing.

Further heating, to 650°C, results in further marked changes in the chemical structure of the adsorbent. The O-H stretch band at 3558 cm⁻¹ and the aryl-O stretch band at 1216 cm⁻¹ are now greatly reduced in intensity and the aromatic C-H stretch band at 3052 cm⁻¹ is somewhat enhanced, as well as the aromatic C-H bands at 700 to 900 cm⁻¹.

The onset of aromatization at temperatures greater than 750°C is clearly evidenced by the lack of resolution of the spectra, with the only discernable features being the aromatic C=C stretch at 1580 cm⁻¹ and a broad C-O stretch band^{265,266} between 1000 and 1300 cm⁻¹. Moreover, the slanting shape of these spectra, with almost complete absorption at high wavenumbers, i.e. close to the near-IR region, is typical for highly-aromatized systems such as carbons and graphites. This effect has been attributed²⁶⁷ to the absorption edge of the lower-energy side of the $\pi \rightarrow \pi^*$ electronic transition.

The spectra of the carbons produced under atmospheres of CO₂, H₂O and N₂ were indistinguishable from those of the high-temperature carbons in Figure 6.11, as was that for the carbon activated in air for one hour.

Infrared spectra of the four commercial carbons studied are shown in Figure 6.12. Once again, the spectra of the high-temperature carbons are indistinguishable from each other, with the exception of the low-temperature carbon, Norit C. This spectrum contains a significant O-H stretch band,

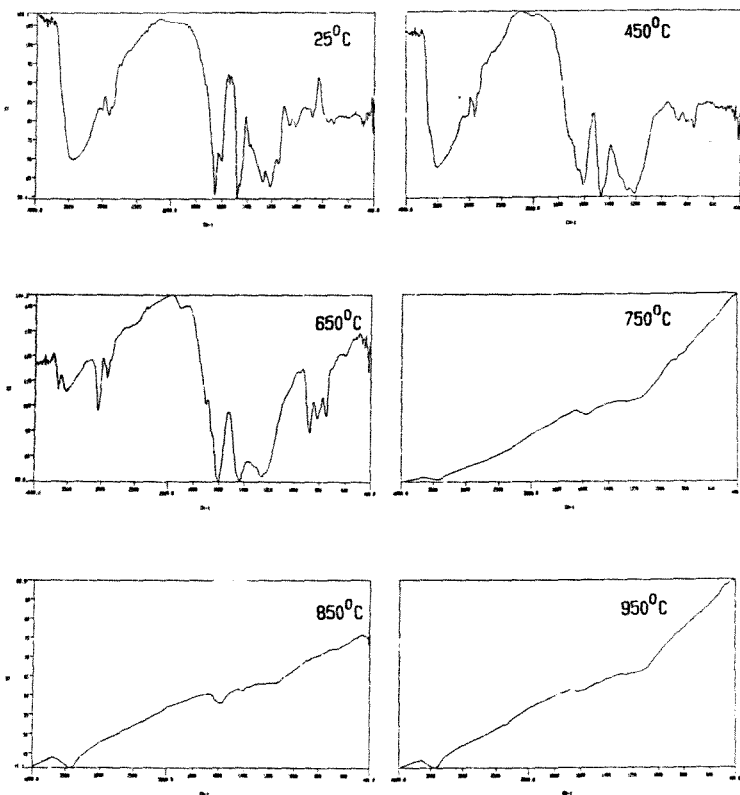


Fig. 6.11 Infrared spectra of pyrolysis products of S-761 polymeric adsorbent after activation at different temperatures

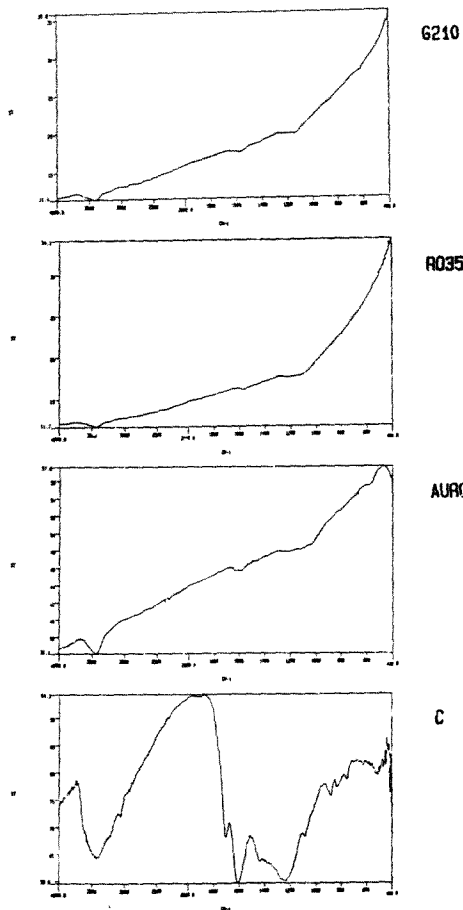


Fig. 6.12 Infrared spectra of commercial activated carbons studied

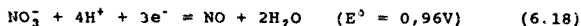
which confirms that the material was not heated to temperatures as high as 650°C. Other features are a strong C=O stretch band at 1705 cm⁻¹ attributable²⁶⁶ to carboxyl groups and a significant band at 1450 cm⁻¹ attributable²⁶⁶ to methylene groups.

6.2 Effect of Surface Oxidation on Surface Chemistry, Structure and Gold Adsorption Activity of Activated Carbon

In an effort to further evaluate the contribution of surface chemical effects on the adsorptive properties of the carbon, the effects of surface activation on various physical and chemical properties were evaluated. It has previously been reported^{11,77,268} that surface oxidation of activated carbon can result in lower gold adsorption activities; however, no reasons for this have yet been proffered. Moreover, the oxidative processes used^{16-18,269} to deactivate the preg-robbing component of carbonaceous ores have been used on a commercial scale without any attempts being made to explain the observation.

a) Gold Adsorption Activity

The results in Table 6.6 confirm the fact that surface oxidation in general reduces the gold adsorption activity of activated carbons. The magnitude of this reduction in activity is dependent on the harshness of the oxidizing conditions used. Boiling in 1M NaOCl for one hour had only a slight effect, which was enhanced by substituting HNO₃ for NaOCl, a reflection of the greater reduction potential for the reaction



than for the reaction

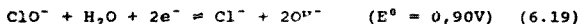
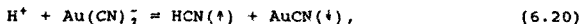


Table 6.6
Effect of surface oxidation on gold
adsorption activity of Le Carbone G210 activated
carbon

Oxidation conditions	Gold adsorption after 24 h, %		
	No additives 0,033M CaCl ₂ 0,1M HCl		
None	16,4	32,7	79,4
Boiled in 1M NaOCl, 1h	12,2	29,2	39,1
Boiled in 1M HNO ₃ , 1h	10,4	24,9	35,4
Boiled in 1:1 HNO ₃ : H ₂ SO ₄ , 2h	9,6	12,9	16,8
Soaked in 20% H ₂ O ₂ for 1 week at 25°C	19,3	34,9	31,8

The depressing effect on gold adsorption activity in acidic (0,1M HCl) solution is far more marked, even with NaOCl as the oxidant. It has previously⁸⁰ been shown that the precipitation of AuCN from acidic aurocyanide solution,



occurs preferentially on hydrophobic surfaces. Oxidation would yield a less hydrophobic surface, so evidently this reaction is more sensitive to surface oxidation than adsorption of aurocyanide from neutral and alkaline solutions.

Finally, it is significant that hydrogen peroxide results in enhanced gold extraction except for 0,1M HCl. Claus and Weiss²⁶⁸ observed that the presence of peroxide in the

adsorption medium was beneficial to gold loading. This effect may be similar to that reported in section 3.2e for the enhancement of gold adsorption activity in the presence of molecular oxygen.

b) *Activated Carbon Structure*

Table 6.7 shows that oxidation under moderate conditions with NaOCl, HNO₃ and H₂O₂ all resulted in a slight increase in both micropore volume and surface area, presumably as a result of micropore widening due to reactions with pendant hydrocarbon chains at the edges of the microcrystallites. No significant change in skeletal density was observed for these three carbons. However, marked changes occurred in the case of the carbon oxidized in the concentrated acid. The marked increase in the pore volume, together with the large decrease in surface area and skeletal density, suggests that extensive erosion of the micropores has occurred in this case, resulting in the presence of fewer micropores of larger diameter. These conditions are not conducive to gold adsorption, as discussed earlier.

The effects of surface oxidation on the conductivity and microcrystallite dimensions of activated carbon are shown in Table 6.8. The conductivity remains virtually unchanged for all the oxidation treatments, with the exception of the harsh treatment, viz. boiling in 1:1 HNO₃:H₂SO₄ for two hours, which caused a marked enhancement in conductivity. It is proposed that this is due to the removal of aliphatic hydrocarbon chains from between the microcrystallites, thus ensuring closer contact between graphitic regions. This explanation is also compatible with the surface area and micropore volume results.

Table 6.7
Structural properties of oxidized Le Carbone
G210 activated carbon

Oxidation conditions	Skeletal density g/cm ³	Pore volume, cm ³ /g				Surface area m ² /g
		Micro-pore	Meso-pore	Macro-pore	Total	
None	2,086	0,3916	0,1250	0,1343	0,6509	1000
Boiled in 1M NaOCl for 1h	2,215	0,3823	0,1508	0,1697	0,7028	1000
Boiled in 1M HNO ₃ for 1 h	2,185	0,4372	0,1454	0,1546	0,7372	1180
Boiled in 1:1 HNO ₃ :H ₂ SO ₄ for 2 hrs	1,803	0,5649	0,1671	0,1401	0,8721	860
Soaked in 20% H ₂ O ₂ for 1 week	2,179	0,4459	0,1459	0,1436	0,7354	1160

Table 6.8
The effect of surface oxidation on the conductivity
and microcrystallite dimensions of Le Carbone G210
activated carbon

Oxidation conditions	κ , S/cm	L_c , Å	L_a , Å
None	3,8	10,2	43,2
Boiled in 1M NaOCl, 1h	2,6	9,2	40,1
Boiled in 1M HNO ₃ , 1h	4,0	9,5	39,2
Boiled in 1:1 HNO ₃ :H ₂ SO ₄ , 2h	0,14	10,2	41,1
Soaked in 20% H ₂ O ₂ for 1 week at 25°C	5,7	9,8	35,9

Author Adams Michael David

Name of thesis The Chemistry Of The Carbon-in-pulp Process. 1989

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