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An Investigation Into Activated Carbon

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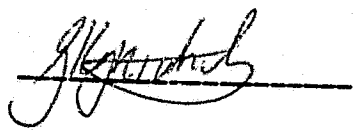
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by G. Kyriakakis

A dissertation Submitted to the Faculty of Science
University of the Witwatersrand, Johannesburg, for
the Degree of Master of Science

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other University.



George Kyriakakis.

Thirty-first day of December, 1984.

Abstract

The extraction of aurocyanide by activated carbon probably involves the adsorption of neutral ion-pair species $\left[M^{n+}\right]\left[Au(CN)_2\right]_n$. The large hydrophobic aurocyanide anion associates with the cation in order to minimize the disruption of the water structure whereby lowering its free energy.

Examination of the adsorption trend suggests the formation of two distinct kinds of ion-pair species. The trend for increasing adsorption with increasing cationic radius is due to the formation of large neutral ion-pair species which are ejected into the carbon phase due to their ease of dehydration. The trend for the smaller more hydrated cations can be understood in terms of a specific ion-pair/carbon interaction. These highly polarizable species may accept charge from the polarized aurocyanide whereby the gold atom is rendered increasingly positive with increasing acceptor strength of Lewis acid. Charge transfer between the polarized ion-pair and the carbon surface results in a donor/acceptor type of surface species.

The aurocyanide ion-pair on the carbon surface is probably stabilized by this charge transfer mechanism particularly at low surface coverages as indicated by the larger heats of adsorption. As the number of available sites diminish with increasing surface coverage any additional adsorbed ion-pair species is not stabilized and undergoes decomposition.

DEDICATION

To my Parents and Yael

DEDICATION

To my Parents and Yael

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1 Introduction

The adsorptive nature of activated carbon has been known for many centuries. In the last 100 years new and varied uses for activated carbon have been developed, the main use appearing to be in waste water purification by the adsorption of organic and inorganic contaminants.[3] The adsorption of aurocyanide by activated carbon has been known since 1894. However, commercial viability has been attained only in the last ten years. The application of this phenomenon is the basis of the carbon in pulp process (CIP), which involves the direct addition of activated carbon to cyanide pulp in a stage-wise counter current unit operation.[5] In practice, gold loading on carbon does not usually exceed the value of 10 000 g Au/t and extremely barren solutions of less than 0,02 mg Au/ℓ are lost as tailing solutions.

This now established extractive hydrometallurgical technique has numerous advantages over the Crown-Merriel process. These include lower capital and operating costs, a significant reduction in soluble gold losses, and often more efficient gold leaching from so called foul pulps.[6] Other important characteristics are the ability of carbon to scaveng aurocyanide from extremely dilute solutions which has found application in waste dump processing. The granular nature of carbon facilitates simple screening of loaded carbon and replaces expensive filtration and de-aeration plant.

The adsorbed gold may be recovered from the carbon by either ashing and then smelting or by desorption using elution columns with hot caustic cyanide.[2,8] The desorbed gold is then recovered via electro-winning or by precipitation using zinc dust. The now barren carbon can be recycled a number of times. However, frequent regeneration is necessary due to poisoning caused by adsorption of silicates, carbonates, and organics such as flotation agents.

Advances in the CIP technology have outstripped fundamental understanding of the interaction between aurocyanide and carbon and, despite a volumous literature fundamentally relativerly little is known about the adsorption mechanism, the adsorbed species, and the nature of the carbon itself. One of the main characteristics of the adsorption process is that the initial rate of adsorption is fast, whereas the attainment of equilibrium is exceedingly slow. CIP technology takes advantage of this and kinetic models have been developed and successfully applied to plant operation and design.[1,7]

Although commercially the CIP process constitutes an advance in the hydrometallurgy of gold it is somewhat disturbing that such an important industry is based on an essentially uncharacterized and poorly understood adsorbant.

In this study the factors influencing the adsorption of aurocyanide by activated carbon were investigated by considering the effects of type and concentration of various cations and anions as well as the effect of surface coverage or loading. The specific adsorption region ($<$40mg Au/g) was further investigated by considering the effect of various cations and anions on the rate and equilibrium of aurocyanide adsorption at various temperatures by activated carbon. The nature of activated carbon was also

investigated by the pyrolysis of coconut char under steam at various temperatures. Factors influencing the aurocyanide adsorption were investigated to establish the effects of pyrolysis temperature, gaseous atmosphere, mass loss and various other parameters. An attempt was made to investigate the nature of the surface oxides or oxygen functional groups via Fourier transform infrared spectroscopy on the pyrolysis products.

1.1 Literature review

Activated carbon has been used for many thousands of years mainly as a purifying agent. Commercially carbon is mainly used in the treatment of effluent and potable water. The adsorptive nature of carbon has also been used in gas scrubbing and air conditioning systems. Hydrometallurgical applications amongst others have included the adsorption of auric chloride,[5] molybdenum blue and silver nitrate.[9] Many other scattered reports have appeared in diverse applications such as heterogenous catalysis and red-ox reactions.[3,4]

Although a voluminous and diverse literature on the subject of activated carbon exists, the bulk of it concerns empirical observations with little emphasis on the mechanisms of such processes. Thus the nature of carbon and the adsorption mechanisms remain largely unknown and poorly understood. The elucidation of the nature of activated carbon similarly proved resistant and much research has been conducted on carbons and chars of varying origin and method of manufacture. These carbons are essentially of unknown nature and purity.

i) Nature of activated carbon

As a first approximation activated carbon may be considered to be a solid but porous carbon matrix which has an extensive pore structure and a large surface area.[3] The bulk of the structure is comprised of amorphous carbon, and is thus essentially hydrophobic in nature. Regions of the matrix have disordered graphitic platelets or microcrystallites whose edge groups have oxygen functionalities which impart a hydrophilic character to the carbon. Thus activated carbon supports domains of hydrophobic and hydrophilic surface and is therefore heterogenous in nature.

Activated carbon can be synthesized from almost any carbonaceous substance,[3] the usual starting materials being coconut shells, peach pips, petroleum char and wood. The first step usually involves slow heating up or pyrolysis at temperatures between 300 - 600°C in an inert atmosphere. The resultant char is primarily amorphous carbon which has some degree of aromatization. A pore structure and surface area develops as a result of the volatile material being driven off. The pore volume and surface area of the resulting char is largely dependant on the origin[10] of the starting material and may be influenced by the ash content which may act as sites for preferential[11] surface oxidation or etching.[17]

The activation[3] of carbon occurs by heating the char between 700 - 1000°C in an oxidizing gaseous environment for a sufficient time interval. Carbon dioxide and steam are good oxidizers and result in a mass loss or burn-off at higher temperatures (800 - 1000°C). The oxidation of carbon essentially involves the water gas reaction -

$$C_s + H_2O_g \longrightarrow CO_g + H_2\ g \qquad \Delta H = 206\ kJmol^{-1}$$

The use of air or molecular oxygen results in a marked mass loss at lower temperatures which probably involves the overall reaction shown below -

$$C_s + O_2 \longrightarrow CO_2\ g$$

The more reactive portions of the carbon matrix are preferentially burnt off which further increases the surface area and pore volume. According to Dubinin[12] the pore size distribution of activated carbon may be divided into three groups. Macropores (1000 - 2000 Å) effectively contribute little to the total surface, the transitional pores (50 - 1000 Å) contribute about

five percent of the total surface whereas micropores ($<$20 Å) contributes about 95 percent of the total surface area.

The formation of microcrystalline carbon is temperature dependant and is observed to occur from about 400°C. These regions consist of disordered graphitic platelets which are a few carbon atoms thick and have a diameter[13] between 20 - 100 Å. These form the so called basal plane regions and it appears that here is little ordering of these stacked planes relative to one another.[16] According to Pinwick[14] and others[15] on pyrolysis, the development of aromaticity occurs from about 350°C which involves nucleation and development of isolated aromatic structures by homolytic cleavage and condensation of free radicals. These planar aromatic systems polymerize on heating and become quite rigid. The condensation of free radicals is found to peak at 550°C after which the H/C ratio suggests the formation of a highly unsaturated system.[15] Simultaneously between temperatures of 600 - 800°C the resistivity of the carbon matrix sharply decreases[10,14] from 10^{7} to 10^{-2} ohm cm^{-1} which is thought to be due to ring closure of the graphitic structure which would allow for the conduction of electrons via the aromatic π system. (See Fig. (1,1)).

The oxidation of carbon by various gases results in a net carbon loss. However, a net gain in oxygen concentration is found and is typically of the order of 3% (M/M) in the final product.[3,8] It appears that the oxygen is almost exclusively concentrated at the edges of the broken graphitic structure and forms the basis of the oxygen functional groups or the so called surface oxides.[3,18]

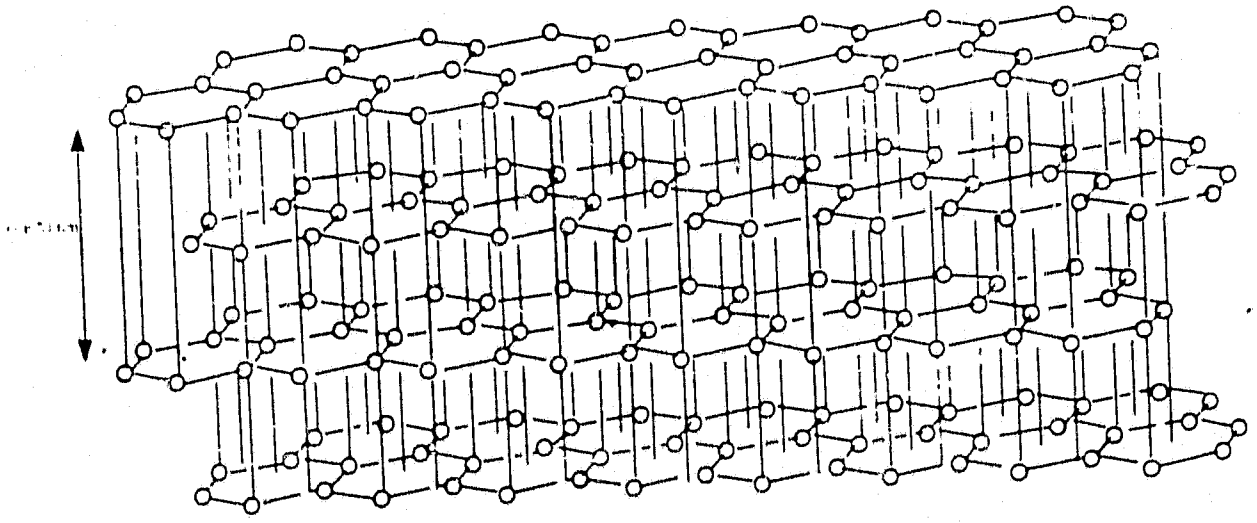


Fig. 1.1 a) Schematic representation of the structure of graphite. The circles denote the positions of carbon atoms, whereas the horizontal lines represent carbon-carbon bonds.

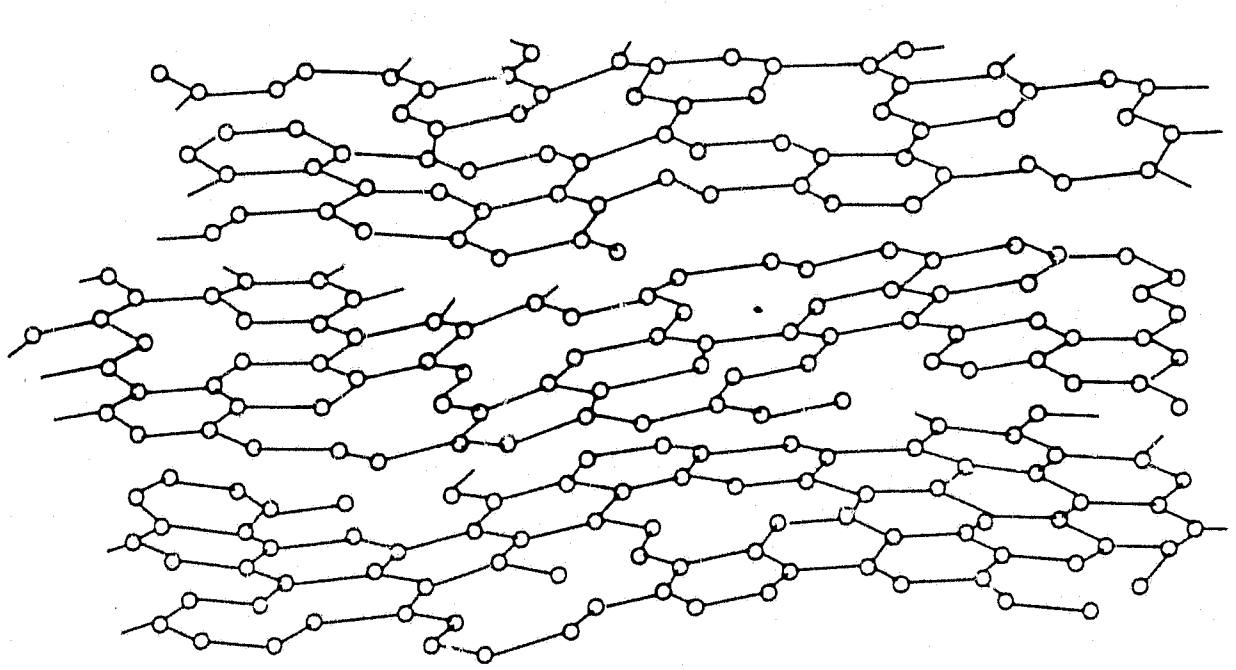


Fig. 1.1 b) Schematic representation of the proposed structure of activated carbon. Oxygen-containing organic functional groups are located at the edges of broken graphitic ring systems. (After 5)

On contact with air, after activation, the carbon further adsorbs molecular oxygen some of which may react with the carbon surface to remove unpaired electrons. The bulk of this fraction appears to involve physisorbed oxygen molecules which can be desorbed reversably.[3]

The characterization of functional groups on the surface of activated carbon has been attempted[18]. However, due to the varying origin of starting materials and varying methods of activation no consensus has been reached as to the exact functionalities. Functional groups such as carboxyl, phenoxy, lactone, lactal, quinone, peroxide and ether groups have been proposed and are expected to influence the properties of the activated carbons. According to Siedlewski et al.[90] oxygen functional groups may be involved in processes such as chemisorption, catalysis, acid/base adsorption, hydrophilic-hydrophobic interactions and ion-exchange mechanisms. Cho and Pitt[39] have suggested that the adsorption of metallocyanide ions may involve chemisorption on the oxygen containing functional groups.

According to Dubinin et al.[12] carbons activated at 900°C using CO_2 as oxidant have about 3 percent oxygen. Thus by simple calculation assuming a mono-molecular layer of oxygen it can be shown that this accounts for about 30 m^2 of surface or about 4 percent of the total surface. Using a volume basis it can be calculated that carbon with a pore volume of 0,8 mℓ/g may have a pore concentration of 3 - 4 M as oxygen on the surface.

The formation of carbon-oxygen complexes on the graphitic structure imparts polarity to the surface and is responsible for the adsorption of polar moietys such as water. According to Youssef et al.[19] the water capacity may be a measure of the modified surface rather than the carbon surface in toto, so that such a surface may be thought of as areas of localised polar solvent in a predominantly hydrophobic environment. The polarity may be further enhanced[20] as the oxygen functionalities are localized on the edge groups of loosely stacked graphitic platelets, and the excess charge of the carbon may be distributed to the surface by such groups.

It is believed that the heterogenous nature of activated carbon is responsible for a remarkable cross section of chemistry reported in the literature. In terms of the above analysis much of the reported chemistry can be rationalized.

ii) Aqueous chemistry

The dual nature of the surface of activated carbon is believed to impart the hydrophilic/hydrophobic balance to the carbon which determines much of the adsorption of molecules from aqueous phase[20]. Water and adsorbate both compete for adsorbant surface so that a predominantly hydrophilic surface would prefer to interact with water molecules, whereas a hydrophobic surface would prefer the adsorbate, depending on its tendancy to be hydrated. The specific nature of the adsorbate and its interaction with water is also of prime importance, so that factors such as charge, moleculer size and polarizability are expected to influence the adsorption chemistry. Physical constraints such as pore size must also be considered as larger molecules are expected to be excluded from being adsorbed due to molecular sieving.

The larger and therefore more hydrophobic molecules are adsorbed by carbon due to their weak interaction with water, which has long been recognized and forms the basis of Traube's rule[3] which states -

> "The adsorption of organic substances onto activated carbon from aqueous phase increases strongly and regularly as we ascend the homologous series."

According to Weber and van Vliet[21] activated carbon and polymeric adsorbants have similar extraction coefficients for the adsorption of high concentration of organics from aqueous solution. This effect has mainly been attributed to forces of the hydrophobic and dispersive type on similar surfaces. The graphitic platelets of activated carbon are hydrophobic and support such interactions, as does the hydrophobic nature of the polymeric adsorbant benzene ring system. At low concentrations of organics however activated carbon has the ability to adsorb small concentrations more effectively than do polymeric adsorbants. This phenomenon is thought to be due to activated carbons dual nature (hydrophilic/hydrophobic) as well as its unique pore structure and pore size distribution. The large concentration of oxygen groups on the edges of the microcrystallites imparts polarity to the surface and is the most probable area for the adsorption of the more polar adsorbates. Molecules with a higher polarity would be expected to have a greater tendency to participate in such interactions, which results in the formation of a donor/acceptor type of surface complex. This type of surface adsorption may be termed as a "specific interaction" between the polar surface and the polar adsorbate.

The nature of the interaction can be further enhanced by electron transfer from the π-electron clouds of the graphitic platelets to the adsorbate provided that the molecular structure of the adsorbate can accommodate such an interaction. The electron transfer is probably effected via the surface oxygen functionalities to the adsorbate which probably retains its hydration sheath. According to Mattson et al.[3] aromatic compounds such as phenols and nitrophenols are thought to accept charge from the carbon surface into their delocalized π systems, thereby forming a surface donor/acceptor complex. It may be speculated that the affinity of the substituted group to withdraw electrons from the aromatic ring may result in an enhanced interaction between the carbon and the adsorbate. Effectively the carbon could donate even more electron density to such moietys.

Electron transfer from the carbon to the adsorbate may be complete or partial, depending on the electrochemical potential of the adsorbate as well as the intrinsic potential of activated carbon. It is believed that this gives rise to catalytic and electrochemical properties in activated carbon.[22] Table (1.1) summarizes a broad spectrum of reactions where the presence of activated carbon or charcoals accelerated the redox reaction. The mechanism of such interactions is not well understood, but probably involves surface catalysis and electron transfer by carbon. Activated carbon is also well known to effect the reduction of various aquo metal complexes. For example, the reduction of auric chloride and silver nitrate results in a surface plating of metal proving that a reductive mechanism is present. McDougall et al.[24] have estimated that activated carbon has a potential of about 0 V(SHE) so that the reduction of the above species can be understood. However, reduction of the aurocyanide species cannot be effected since the reduction potential of this species is -0,61 V(SHE).

Table 1.1 Catalysis by Carbon of various Oxidation-Reduction Reactions (After 22)

Reaction	Medium	Carbon type	Catalysis
$Hg(I) + Fe(II) \longrightarrow Hg + Fe(III)$	$C\ell O_4^-$	Activated Carbon	Positive
$Fe(CN)_6^{3-} + 3I^- \longrightarrow Fe(CN)_6^{4-} + I_3^-$	$K[NO_3]$	Charcoal Graphite	"
$\frac{1}{2}O_2 + 2H^+ + Fe(II) \longrightarrow H_2O + 2Fe(III)$	H_2SO_4	Coconut Carbon	"
	$HC\ell$	Sugar	"
	H_2SO_4	Various-chars	"
$\frac{1}{2}O_2 + pC_6H_6(OH)_2 \longrightarrow H_2O + pC_6H_4O_2$	–	Sugar carbon	"
		Animal-charcoal	"
$\frac{1}{2}O_2 + 2H^+ + 2Fe(CN)_6^{4-} \longrightarrow H_2O + 2Fe(CN)_6^{3-}$	Water	Sugar	"
$O_2 + N_2H_4 \longrightarrow 2H_2O + N_2$	–	Activated carbon	"
$\frac{1}{2}O_2 + HCO_2H \longrightarrow H_2O + CO_2$	–	Various-carbons	"
$\frac{1}{2}O_2 + (CO_2H)_2 \longrightarrow H_2O + 2CO_2$	–	"	"
$H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2$	–	"	"
$O_2 + CH_2(CO_2H)_2 \longrightarrow HO_2 \cdot CHO + CO_2 + H_2O$	–	Sugar carbon	"
$H_2O_2 + HCHO \longrightarrow H_2O + HCO_2H$	–	"	"

Activated carbon has also been shown to have the ability to oxidize free cyanide. According to Bernardin[25] activated carbon catalyses the oxidation via the following reaction -

$$CN^- + C(O_2) \longrightarrow CNO^- \longrightarrow CO_3^{2+} + NH_3$$

Although this mechanism has not been fully proven it probably involves a reaction with physisorbed dioxygen and seems to be continuous, provided that air is bubbled through the mixture.[40]

The role of activated carbon in the catalysed racemization of various cobalt complexes has been reviewed by Basolo and Pearson.[26] Although the understanding is not complete, the catalysis is thought to be effected via ch transfer from the carbon surface to the solvated complex which is not normally adsorbed to any significant extent by carbon. Activated carbon catalyzes the hydrolysis of $[Co(NH_3)_6]^{3+}$ to $[Co(NH_3)_5H_2O]^{3+}$, and the displacement of NH_3 on the complex $[Co(en)_2(NH_3)_2]^{3+}$ by NO_2 to give $[Co(en)_2(NO_2)_2]^{+}$.
Both these species are not readily formed in aqeous phase. However, in the presence of activated carbon a significant reduction in the activation energy results.

Swift and Douglas[27] have studied the racemization of the complexes $[Co(en)_3]^{3+}$ and $[Co(EDTA)]^-$ in the presence of activated carbon. Although the reaction probably involves charge transfer between the solvated complex and the carbon surface the rate of racemization was found to be accelerated or depressed by added electrolytes present in large excess.

It is possible to interpret their results on the assumption that association reactions or ion-pair formation results in the adsorption of a neutral species at the aqueous/carbon interface, prior to the electron exchange reaction on the surface. This also assumes that the electron exchange/racemization reaction is not a rate controlling step.

The retardation of the racemization reaction for the large $[Co(EDTA)]^-$ anion by large hydrophobic anions is given by the following series -

$$ClO_4^- > NO_3^- > SO_4^{2-}$$

This trend shows that the larger more hydrophobic ions effectively compete for the cation in solution to form ion-pairs, thus decreasing the concentration of ion-pairs at the carbon/aqueous interface. This is reflected in the retardation of the rate of racemization.

The cationic $[Co(en)_3]^{3+}$ complex shows an enhancement in the rate with increasing size of anion according to the following series -

$$ClO_4^- > SO_4^{2-} > F^- \qquad \text{(as sodium salts)}$$

The observed trend is expected due to increased hydrophobicity of the resulting ion-pair with increasing size. The retardation of the complex $[Co(en)_3]^{3+}$ by cations is given by the series -

$$Mg^{2+} > Li^+ > Na^+ > K^+ \qquad \text{(as sulfates)}$$

The trend is due to the greater competition for the alkali metal by the sulfate anion, which results in less ion-pair formation between $[Co(en)_3]^{3+}$ and the sulfate anion which is reflected by the lower rate.

Activated carbon is also known to adsorb acid from aqueous solution.[3] Recently Millar[28] has shown that the adsorption of H^+ ions is greatly influenced by the ionic strength of the adsorption medium. In the absence of additives, however, the equilibrium capacity was found to be of the order of 0,2 mmol H^+/g. Mattson and Mark[3] similarly report that the adsorption of acid tends to a maximum for carbons activated at about 850°C in oxidizing atmosphere. This mechanism is not well understood and may involve the protonation of a specific functional group or the neutralization of the ash content (CaO, MgO etc.) formed in the activation process. The concentration of ash in carbon is usually of the order of 3 - 5% (M/M) and it is feasible that this has caused much confusion in this regard as these basic oxides would be neutralized by acid.

The influence of the ionic medium on acid adsorption has similarly been noted by Mattson and Mark,[3] the adsorption of H^+ ions was found to be enhanced in the presence of anions according to the series -

$$SCN^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-}$$

The order of enhancement can be understood assuming the adsorption of ion-pairs or neutral acid-base complexes by carbon. The trend reflects the preference for ion-pairs of low charge and large size (Traube's rule).

The order of enhancement for the adsorption of various cations and anions by activated carbon reported by Maatman et al.[29] can similarly be understood on the assumption that a neutral ion-pair is adsorbed by carbon.

The order reported for the adsorption of cations is given by the series -

$$H^+ > Al^{3+} > Ca^{2+} > Li^+, Na^+, K^+$$

The trend for anion extraction is given by the series -

$$NO_3^- > C\ell^-$$

Similarly Snoeyink and Weber[30] reported the following trend for the adsorption of anions by carbon -

$$C\ell O_4^- > NO_3^- > SO_4^{2-} > C\ell^-$$

Thus the adsorption is favoured by the formation of ion-pairs of large size and increasing polarizability. The larger and therefore more poorly hydrated ion-pairs show a larger capacity for extraction into the carbon phase due to increased hydrophobicity.

The pH dependant adsorption of acetic acid[3] can be similarly rationalized. In the protonated form the neutral acid-base complex or ion-pair can be adsorbed. Above pH5 however the species ionizes to form anions so that negligible adsoption occurs.

McDougall[23] has investigated the adsorption of dicyanamide ($N(CN)_2^-$) by activated carbon. In the protonated form the species $N(CN)_2H$ is quantitatively adsorbed whereas in the ionized form negligible adsorption is observed.

Thus, the adsorption/extraction of various anions and cations by activated carbon can be understood in terms of the formation of ion-pairs or neutral species at the carbon surface. The trend for increasing extraction with increasing size of ion-pair can be understood in terms of increasing hydrophobicity. Such poorly

hydrated complex would be ejected into the carbon phase due to the ease of dehydration.

Aqueous phase adsorption in the polar solvent water, gives rise to adsorbate-solvent interactions such as hydrophilic and hydrophobic effects as above. The nature of the carbon surface, such as the oxygen groups similarly give rise to adsorbate-surface interactions. Polar adsorbates are expected to interact strongly with such polar surfaces. Water, which is in large excess, will have to be displaced prior to the adsorption. Predominantly hydrophobic adsorbates on the other hand would interact with the basal plane area which is largely uniform and hydrophobic.

Thus the dual nature of activated carbon supports both dispersion force interactions on the basal plane and a more polar type of interaction with the oxygen containing surface edge groups.

2 Experimental procedure

2.1 General reagents

a) Metallocyanide salts

Salts of $KAu(CN)_2$ and $KAg(CN)_2$ used in this study were supplied by Johnson Matthy. Salts of aurocyanide (H^+, Li^+, Cs^+, etc.) were prepared by cation exchange resin (Dow W4OX) in columns which were converted to the salt form by passing 0,1 M chloride solution until breakthrough point was reached, after which the column of resin was washed with deionized water until no chlorides could be detected using $AgNO_3$. Pure salts were obtained by evaporating the eluent below 60°C using a rotary evaporator with final drying carried out under vacuum, with P_2O_5. Other metallocyanide salts used were AR grade supplied by BDH.

b) Chloride salts

Chloride salts of group IA and IIA cations used were AR grade.

c) Hydroxide salts

Hydroxide salts of group IA cations were CP grade which were standardized against 0,50 N HCℓ (BDH) by titration.

d) Cyanide salts

Cyanide salts were CP grade except for LiCN which was prepared in columns using Dow X4OW. The cyanide concentration was standardized by titration using AR grade $AgNO_3$ with KI as indicator.

e) Other reagents

Reagents such as nitrates, sulfates and sulfides were AR grade unless otherwise indicated, as were organic solvents such as acetonitrile and acetone. Acetonecyanohydrin was made according to a method given by Vogel.[73]

f) Activated carbons and chars

A number of activated carbons were investigated the main emphasis on a coal based carbon commercially designated KOP. This product was chosen for its inherently low ash content and having been activated in steam between 850 - 900°C.

In general carbons were first washed with deionized water to remove fine particulate carbon, then were copiously washed with hot deionized water to remove soluble salts. Carbons were air dried, then dried in an oven at 90°C to constant weight, and stored in sealed containers.

2.2 Equilibrium adsorption tests

A known mass of carbon was contacted with solutions of known aurocyanide concentration containing the appropriate molarity of additive. The stock solution of aurocyanide was made up containing the appropriate additive and buretted into stoppered glass bottles, then made up to required volume using a second burette containing the appropriate molarity of additive. Mixing was achieved using a linear shaker and contact time was maintained at 96 hours (4 days). The appropriate aliquot was removed at equilibrium and diluted into the range 2 - 8 mg/ℓ and analysed for gold using atomic absorption spectroscopy.

The condition for each adsorption test is shown in Table 2.1 and the carbon used in this study was the KOP product unless otherwise indicated.

Table 2.1 Conditions for equilibrium adsorption tests

Parameter investigated	Conditions	Variable
a) Effect of ionic strength on aurocyanide adsorption	$[V]$ = 100,0 mℓ $[Au]_i$ = 300 mg/ℓ $[Carbon]$ = 0,25g	$[I]$ = 0,0 → 1,0 M NaCℓ NaOH NaCN
b) Effect of cations on aurocyanide adsorption	$[V]$ = 100,0 mℓ $[Au]_i$ = 300 mg/ℓ $[Carbon]$ = 0,25g $[I]$ = 0,30 M	MCℓ M^+ = $\{H^+, Li^+, NA^+, K^+, Cs^+\}$ MOH M^+ = $\{Li^+, Na^+, K^+\}$ MCN M^+ = $\{Li^+, Na^+, K^+\}$ MSH M^+ = $\{Na^+\}$
c) Effect of surface coverage on aurocyanide adsorption	$[V]$ = 100,0 mℓ $[Carbon]$ = 1,000g $[I]$ = 0,30 M	$[Au]_i$ = 50 to 1500 mg/ℓ Additives MCℓ MOH MCN MSH
d) Effect of various metalocyanides on aurocyanide adsorption	$[V]$ = 100,0 mℓ $[Carbon]$ = 1,000g $[I]$ = 0,30 M NaCℓ	$[Au]_i$ = $[MC]_i$ (equimolar) MC = $Ag(CN)_2^-$ $Ni(CN)_4^{2-}$ $Hg(CN)_2$ $Co(CN)_6^{3-}$
e) Effect of surface coverage on aurocyanide adsorption	$[V]$ = 100,0 mℓ $[Carbon]$ = 1,000g $[I]$ = 0,30 M	$[Ag]_i$ = 50 to 1500 mg/ℓ Additives NaCℓ NaOH NaCℓ

2.3 Investigation of adsorbed gold species

i) Direct methods

Carbons with varying gold loadings were prepared by adsorbing varying concentration of aurocyanide in appropriate additive at constant ionic strength. At equilibrium (7 days) the gold remaining in the aqueous phase was dertermind using atomic absorption spectroscopy after which the carbon was separated and copiously washed in deionized water. The carbons were first dried in air overnight, after which complete drying was achieved using a dessicator under vacuum with P_2O_5 as drying agent.

a) X-ray diffraction

Crushed carbons containing gold loadings from 5 - 80 mg Au/g were examined using a Phillips X-ray diffractometer. A spiked carbon was prepared by mixing in a mortar and pestle the appropriate weight of $KAu(CN)_2$ salt to the previously crushed carbon.

b) Fourier transform infrared spectroscopy (FTIR)

The above carbons were investigated via FTIR as KBr pellets. The spectrum between 4000 to 400 cm^{-1} was examined with emphasis on the two fundamental bands $\nu(C\equiv N)$ and $\nu(Au-C)$. A spiked carbon containing 140mg Au/g was also investigated by grinding in the appropriate weight of aurocyanide salt in previously crushed carbon.

c) X-ray Fluorescence

Carbons with varying gold loadings were prepared by dissolving the pure salts of $Ca[Au(CN)_2^-]_2$ and $CsAu(CN)_2$ in deionized water containing no additives.

The gold remaining at equilibrium (7 days) was determined using atomic absorption spectroscopy after which the carbons were separated and dried. The calcium and cesium concentration was determined using a Phillips P.W.1400 fluoroimeter. Standards of these respective cations were prepared by spiking the barren carbons with the appropriate weight of additive as the chloride salts. The method of standard addition was also applied to the loaded carbons using the appropriate aurocyanide salts in well ground carbon.

ii) Indirect methods

a) Non equilibrium (column) elution

Carbons with varying concentrations of gold were placed in columns and eluted at 90 $\pm$ 3°C first using 0,30 M NaOH followed by ~1 M aqueous ammonia. A simple but effective elution column was constructed using a separating funnel with an attached glass U-tube connected to a long rubber hose with stopcock. The gold loaded carbons were placed in the U-tube and packed on either side with glass wool. The whole apparatus was immersed in a thermostatted oil bath. The eluent was added to the separating funnel and when thermal equilibrium was attained the eluent was passed through the bed of carbon by syphon action. The flow rate was controlled by the stop-cock and every 200mℓ of eluent was collected and analysed for the gold content via A.A.S. and the complex was identified using UV spectroscopy. Table (2.2) shows the reaction conditions used. After elution the carbons were collected and ashed at 800°C and the remaining gold was dissolved in aqua regia and analysed via A.A.S.

Table 2.2 Elution conditions for aurocyanide loaded carbons.

Carbon weight	=	5,00g
Volume of eluent	=	1000mℓ NaOH (0,30 M)
then		1000mℓ of ~1 M aqueous ammonia
Temperature	=	90 ± 3°C
Time	=	30 hours

b) Stoichiometric ratio of calcium and gold adsorbed by carbon

The stoichiometric ratio of calcium and gold adsorbed by carbon was determined by contacting carbon with solutions prepared by dissolving the pure $Ca[Au(CN)_2]_2$ salt in deionized water. By keeping constant carbon and varying the aurocyanide concentration the distribution of gold and calcium was determined as a function of surface coverage. To eliminate any contamination due to the ash content, the carbon was copiously washed with hot deionized water until no chlorides could be detected using silver nitrate.

A sample time of 21 days yields carbons with loadings between 5 - 80mg Au/g. The calcium in the aqueous phase was determined using A.A.S. by diluting into the 1 - 5 mg/ℓ range maintaining 0,05 M Lanthanum chloride as background. The gold concentration was determined by diluting into the 1 - 8 mg/ℓ range maintaining a background of 0,05 M NaCℓ.

2.4 Adsorption/desorption tests in the regions of low surface coverage

The adsorption/desorption of aurocyanide was investigated using carbons containing gold loadings between 10 to 30 mg Au/g. By varying the temperature, the desorption of gold was investigated to determine the effects of the initial cation coadsorbed, the type of

anion in the eluent phase, as well as effects due to surface coverage. The rate of approach to equilibrium at a particular temperature was followed with respect to time and the effect of temperature on the distribution of gold at equilibrium was determined in the temperature range between 60 - 95°C.

a) Method I

Accurately known aurocyanide solutions containing the appropriate additive were contacted with known weights of carbon so that equilibrium loadings between 10 - 30 mg Au/g were obtained. The carbons were separated and washed copiously with deionized water and then contacted with eluent in a round bottom flask with condensor. The flask was immersed in an oil bath on a heater/stirrer apparatus where temperature control was better than $\pm$ 1°C. The temperature range investigated was between 60 - 95°C. The rate of approach to equilibrium at a particular temperature was followed with respect to time by withdrawing a small aliquot at predetermined time intervals. The volume of these samples never exceeded 10 percent of the total volume. The desorbed gold was analysed by A.A.S.

Equilibrium at a particular temperature was achieved after 100 minutes reaction time, after which the effect of temperature on the equilibrium was investigated by heating or cooling. The new equilibrium was established after 3 hours.

b) Method II

Once the equilibrium behaviour was established a modified method was used to investigate the system. A known volume of aurocyanide was added to the additive of appropriate molarity and contacted with a known weight of carbon in a round bottom flask. The temperature was increased or decreased and a sample time of 24 hours was maintained.

2.5 The effect of conditions of charring and activating carbon

Coconut char was activated at various temperatures under vigorously controlled conditions. The resulting products were investigated to determine the various factors which influence the aurocyanide capacity.

i) Synthesis of activated carbon

Coconut char was pyrolysed under steam at temperatures ranging from 200 - 1100°C to produce samples for investigation. The char was first sieved to size so that the average particle was 5mm in diameter. The char was then washed to remove fine particles and dried in an oven at 110°C. Accurately weighed samples of about 10g of char were placed in an airtight cylindrical furnace and nitrogen was passed through at a rate of 5ℓ/hr. Air was excluded from the system by a water trap at the exit of the furnace.

The pyrolysis was controlled by a programmable time/temperature device and steam was introduced once the activation temperature was attained.

The flow rate of the nitrogen was then reduced to 0,5ℓ/hr simply to act as a carrier for the steam. The activation temperature was maintained for 60 minutes after which the steam was stopped and the silica tube was removed from the furnace and allowed to cool down to room temperature overnight. The pyrolysis sequence is shown below -

Temp.:	Room temp. —— ——→	Activation temperature	——→ Room temp.
Time :	90 min.	60 min.	overnight
Conditions:	N_2 @ 5ℓ/hr	Equilibrium temp. of 600, 650 etc. to 1000°C 200mℓ of H_2O as steam N_2 @ 0,5ℓ/hr	tube removed N_2 @ 0,5ℓ/hr.

ii) Aurocyanide adsorption experiments

The activated carbons obtained from the pyrolysis experiments were investigated to determine their gold adsorption properties. Two methods were used to evaluate this parameter -

a) % Au adsorbed

Weighed carbon (0,25g) was added to 100mℓ of 200 mg Au/ℓ as $KAu(CN)_2$ with no supporting electrolyte (I = 0). The mixture was reacted for 96 hours on a linear shaker after which the gold remaining in solution was analysed using atomic adsorption spectroscopy. The result was reported as % Au adsorbed/g of carbon.

b) Adsorption of aurocyanide as a function of surface coverage

Known weights of carbon ranging from 0,05g to ~1,5g were added to solutions of 100 mg Au/ℓ as $KAu(CN)_2$ in 0,30 M NaCℓ electrolyte.
The mixture was reacted for 96 hours on a linear shaker after which the gold in solution was analysed by A.A.S.

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2.6 Aspects of aurocyanide chemistry

A short study was conducted into various aspects of aurocyanide chemistry which included the following techniques.

i) Infrared/Raman study of polycrystalline aurocyanide salts

Polycrystalline salts obtained by cation exchange resins were investigated via Infrared and Raman spectroscopy in the range 4000 - 300 cm^{-1} as KBr pellets. Similarly group IA salts of $MAu(CN)_2$ (2,2'-bipyridyl) were investigated, these were prepared by a method given by reference (71). The spectra of the complex $KAu(CN)_2I_2$ were also recorded and was prepared by a method by Jones.[63]

ii) Photoacoustic spectroscopy

Spectra of the yellow complexes $LiAu(CN)_2$ and AuCN as powders were investigated in the visible region from 300 - 800 nm. (Locally-built instrument at Mintek)

iii) Solubility of aurocyanide salts

The molar solubilities of a number of aurocyanide salts were obtained from the literature.[57,48,42] The solubility of $CsAu(CN)_2$ was determined by adding deionized water dropwise to a known mass of the salt at room temperature. At saturation the gold content in aqueous phase was determined by A.A.S.

iv) Solubility of aurocyanide in anhydrous liquid ammonia

Aurocyanide salts were dissolved in anhydrous liquid ammonia and evaporation on a vacuum line. A transient green complex near complete evaporation was observed and upon complete drying the colourless salt was re-obtained which was determined to be a $KAu(CN)_2$ salt from the infrared spectrum.

v) UV study of aqueous $LiAu(CN)_2$

The pure salts of $LiAu(CN)_2$ were dissolved in deionized water and serially diluted. The absorbance of a small charge transfer band at 370 nm was recorded using a Beckman DU 7 single beam spectrophotometer. The instrument was calibrated using water as background.

vi) Some reactions of polymeric AuCN

The polymer AuCN was precipitated by acidifying a boiling solution of $KAu(CN)_2$. The precipitate was separated using a Gooch funnel and then copiously washed with hot deionized water then dried under vacuum and P_2O_5 in a dessicator.

a) Reaction with anhydrous ammonia

AuCN was dissolved in ammonia and then evaporated to dryness using a vacuum line. The resulting white powder was found to be the unstable $AuCNNH_3$ complex which decomposed when exposed to air and moisture. On storage the complex slowly changed

to a green amorphous mass over a period of 3 months and probably is a mixture of AuCN and a general polymeric form $(AuCN)_nNH_3$. On contact with water the white product rapidly decomposed to the yellow AuCN and a green precipitate.

b) Aqueous ammonia

The polymer AuCN can be dissolved in concentrated ammonia solution and appears to be stable for considerable periods. Dilution with water results in the precipitation of the polymer AuCN and a green amorphous mass.

vii) Reaction with hydrosulfide

The polymer AuCN dissolves in solutions of hydrosulfide presumably to form $[Au(CN)(SH)]^-$ however no evidence, spectroscopic or otherwise was found for the existence of this complex. Numerous attempts were made to synthesize the complex $Au(SH)_2^-$ by reacting aqueous hydrosulfide with AuCN or gold metal. Various oxidants such as air and H_2O_2 resulted in the formation of polysulfides by oxidation of the ligand and failed to oxidise the gold metal.

3 Adsorption of aurocyanide by activated carbon

The adsorption of aurocyanide by activated carbon was first seriously studied by Gross and Scott[31] in 1927 and has since been the subject of much debate.[5] In recent years much work has been conducted with regard to the adsorption mechanism which has given rise to numerous theories and postulates. These include complete reduction of aurocyanide to gold metal, polymerization to AuCN or a similar[24] complex and ion-exchange with a positively charged carbonium surface site.[5] Other postulates include adsorption into the electrical double layer[39] and the adsorption of neutral ion-pairs or salts[31,24,74] $[M^{m+}][Au(CN)_2]_n$.

Literature summary and proposed mechanism

The extraction of aurocyanide by activated carbon may be divided into three areas.. Firstly the adsorption/extraction of the aurocyanide species into the carbon phase, secondly the state of the adsorbate and finally how the form of the adsorbate changes as a function of loading or surface coverage.

Davidson[35] amongst others[41] has shown that the extraction of aurocyanide by carbon is enhanced by the cation present in solution. Similar effects have been reported by Cho and Pitt[38] for the adsorption of the argentocyanide species by activated carbon. The order of enhancement for group IA and IIA cations is given by the series -

$$Ca^{2+} > Mg^{2+} > H^{+} > Li^{+} > Na^{+} > K^{+}$$

In addition to the so called cation effects McDougall et al.[24] found that the ionic strength (I) of the additive also influenced the equilibrium aurocyanide adsorption.

Small increases in I greatly enhance the adsorption, although this effect was found to level off after ionic strengths greater than ~0,20 M. Although enhanced aurocyanide adsorption was found in chloride medium, a depression has been noted in hydroxide, cyanide[23] and hydrosulfide medium.[75] The adsorption of argentocyanide is similarly depressed in cyanide medium.[38]

The effect of cation on the adsorption of aurocyanide is probably due to the extraction of neutral ion-pairs by carbon, the equilibrium being given by the following equation -

$$M^{+}_{aq} + Au(CN)^{-}_{2\,aq} \rightleftharpoons \overline{[M^{n+}][Au(CN)_2]}_{n}$$

The enhanced loadings observed due to increasing ionic strength and therefore cation concentration, shifts the equilibrium to the right hand side as expected by Le Chatelier's principle. The depression of aurocyanide adsorption by anions is probably due to competition for the cation. The equilibrium is shifted to the left hand side due to a large excess of these small well hydrated anions.

The desorption of aurocyanide is also favoured by elevated temperatures as well as concentrated basic medium. Davidson[36,37] has shown that hydroxide, cyanide and carbonates at elevated temperatures are effective desorbers of aurocyanide loaded carbons. The cation in the desorption medium was also found to influence the overall extraction, the trend for increasing desorption at constant temperature in hydroxide medium is given by the series -

$$Na^{+} > K^{+} > Li^{+}$$

The effect of temperature is expected, as the adsorption of aurocyanide by activated carbon is exothermic.[39,40,24] However as the solubility of aurocyanide increases with increasing temperature[42] this is also expected to have a role.

Surface coverage effects are known, but not well understood, and it appears that the form of the adsorbate changes with surface loading. McDougall et al.[24] have shown that the gold to nitrogen ratio decreases from 1:2 to 1:1 with increasing surface coverage. This suggests that the aurocyanide species predominates at low surface coverages whereas at loadings higher than 30-40mg Au/g some change occurs to the adsorbate. X-ray diffraction studies[24] of aurocyanide loaded carbons have failed to detect the presence of $Au(CN)_2^-$ and AuCN. This may be due to the absence of a crystalline adsorbate and the highly dispersed state of the adsorbed gold species. On a surface area basis it can be calculated that less than 10 percent of the surface is involved in the adsorption, which is of the order of one gold atom every 650 $\mathring{A}^2$ of surface.

Surface coverage studies have shown that the heat of adsorption decreases with increasing suface coverage. Carbons with gold loadings above 50mg Au/g have heats of adsorption[24] of the order of -40 $kJmol^{-1}$. At low surface coverages Grobbelaar[40] has reported heats of adsorption between -50 to -60 $kJmol^{-1}$ for carbons loaded to 5mg Au/g. The larger heats of adsorption at low gold loadings suggests a more specific interaction between the carbon surface and adsorbate, which is expected as thermodynamically the more energetic sites will be occupied first. Similar results have been reported by Cho and Pitt[38] for the adsorption of argentocyanide by activated carbon.

The nature of the specific interaction has been investigated by McDougall et al.[24] using electron spectroscopy (ESCA). These workers found an apparent reduction in the oxidation state of the adsorbed gold atom. A series of aurocyanide loaded carbons showed an intermediate oxidation state of 0,3 which must involve charge transfer from carbon surface to adsorbed gold species in order to effect such a reduction. More recently Adams[41] using electron spin resonance spectroscopy showed that the number of electron spins in carbon decreased with increasing gold loading. The number of spins decreased up to gold loadings of 40mg Au/g after which gold loaded in increasing amounts without further effecting the number of electron spins. This charge transfer mechanism probably stabilizes the adsorbate and gives rise to a chemisorbed species which is found at low gold loadings ($<$ 40mg Au/g).

As will be shown, much of the adsorption chemistry can be rationalized by the adsorption of the aurocyanide ion-pair into the more polar surface such as the microcrystallite edge of activated carbon. The formation of a donor/acceptor complex on the carbon surface is similar to that proposed by Weber and van Vliet and others for the adsorption of certain organics. The specific adsorption of aurocyanide could involve charge-transfer from the "electron-sink" of the carbon into the polarizable aurocyanide ion. The excess charge could be redistributed into the cyanide ligands of $Au(CN)_2^-$ via π bonds. A highly polarizable cation would induce an even stronger interaction with the carbon surface by withdrawing even more electron density from the gold atom via the lone pairs of electrons on the nitrogen atom, thus enhancing the donor/acceptor surface complex.

Divalent cations being highly polarizable can thus strongly interact by withdrawing even more electron density, which explains the specific cation ordering reported by Davidson[35] and others. The desorption of aurocyanide at elevated temperatures also shows that the distribution of gold favours the aqueous phase as the polarizability of the cation decreases due to the progressively weaker interaction with the carbon surface.

Formation of this type of donor/acceptor complex between carbon and the aurocyanide ion-pair probably stabilizes the adsorbate, although after about 40mg Au/g no more specific adsorption occurs due to the lack of available sites. Additional aurocyanide adsorption above this loading is not stabilized by the specific interaction and it possibly undergoes reduction to gold metal.

3.1 Factors affecting the equilibrium adsorption of aurocyanide by activated carbon

When aurocyanide salts are dissolved in deionized water and subsequently adsorbed into activated carbon an equilibrium is set up between the gold adsorbed by the carbon phase and that remaining in the aqueous phase. The equilibrium may be described by the Nernst distribution law[43] where -

$$K_D = \frac{A_o}{A}$$ where K_D = distribution coefficient

A_o = mg Au/g at equilibrium

A = mg Au/ℓ at equilibrium

The value of A_o and A may be obtained by difference by measuring the gold concentration before and after extraction that is in contact with a known mass of carbon. The value of K_D is not constant and is influenced by parameters such as type and concentration of cation, anion and the degree of surface coverage or aurocyanide loading. By varying one parameter at a time and measuring K_D the effect of the parameter on the whole system can be studied.

3.2 Results and discussion

i) Effect of ionic strength on distribution coefficient

A plot of the distribution coefficient K_D for the extraction of aurocyanide by carbon versus the concentration of sodium ions (as chlorides) is shown in fig. (3.1). As previously reported it was found that small increments of the sodium concentration introduced as the chloride salt enhances the adsorption of aurocyanide up to ionic strengths of $\sim$0,20M after which further additions cause no further enhancement. This behaviour is expected by equilibrium

considerations and may be expressed by LeChatelier's principle. The adsorption may be written as -

$$M^{+}_{aq} + Au(CN)^{-}_{2\ aq} \rightleftharpoons \overline{MAu(CN)_2}$$

where $K_D = \dfrac{\overline{MAu(CN)_2}}{[M^{+}]\,[Au(CN)^{-}_{2}]}$

and $\overline{MAu(CN)_2}$ = adsorbed gold in carbon phase.

The presence of the excess cation drives the equilibrium to the right hand side, thus enhancing the gold loading at equilibrium. The enhancement occurs despite the progressively increasing chloride concentration, fig. (3.1) shows the result for a similar experiment where the sodium concentration was increased using sodium hydroxide and sodium cyanide respectively. The results indicate that both these anions cause a depression of aurocyanide adsorption, which shows that these anions effectively compete with the aurocyanide anion for the cation in solution.

ii.) The effect of specific cations on the distribution coefficient

The effect of specific cation on the distribution coefficient for the adsorption of aurocyanide is shown in fig. (3.2), as a plot of ℓnK_D versus the crystallographic cation radius. The experiment was conducted at constant ionic strength where I = 0,30M for a series of group IA cations as chloride salts.

Fig. 3.1

Effect of Ionic Strength on Aurocyanide Adsorption by Activated Carbon

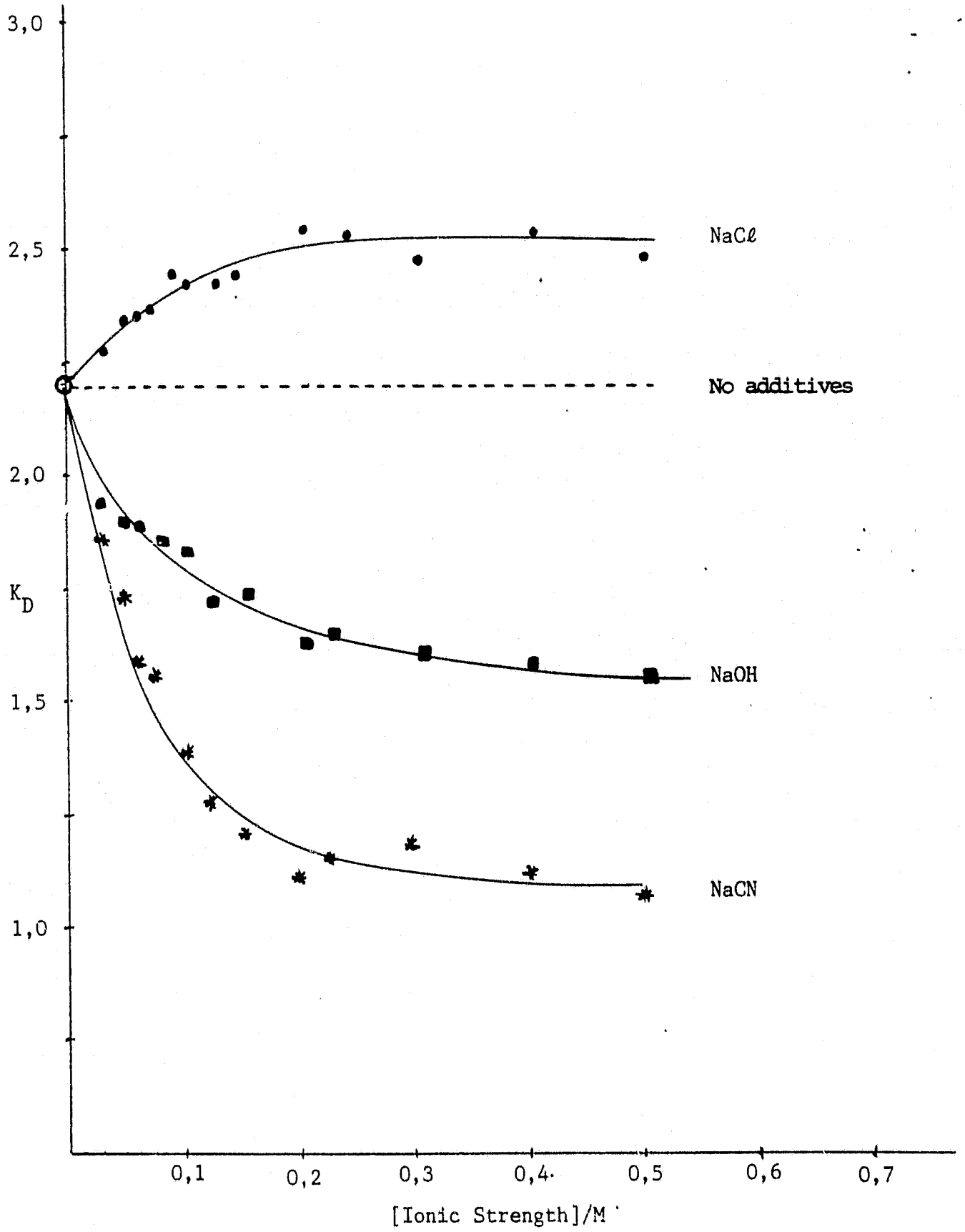
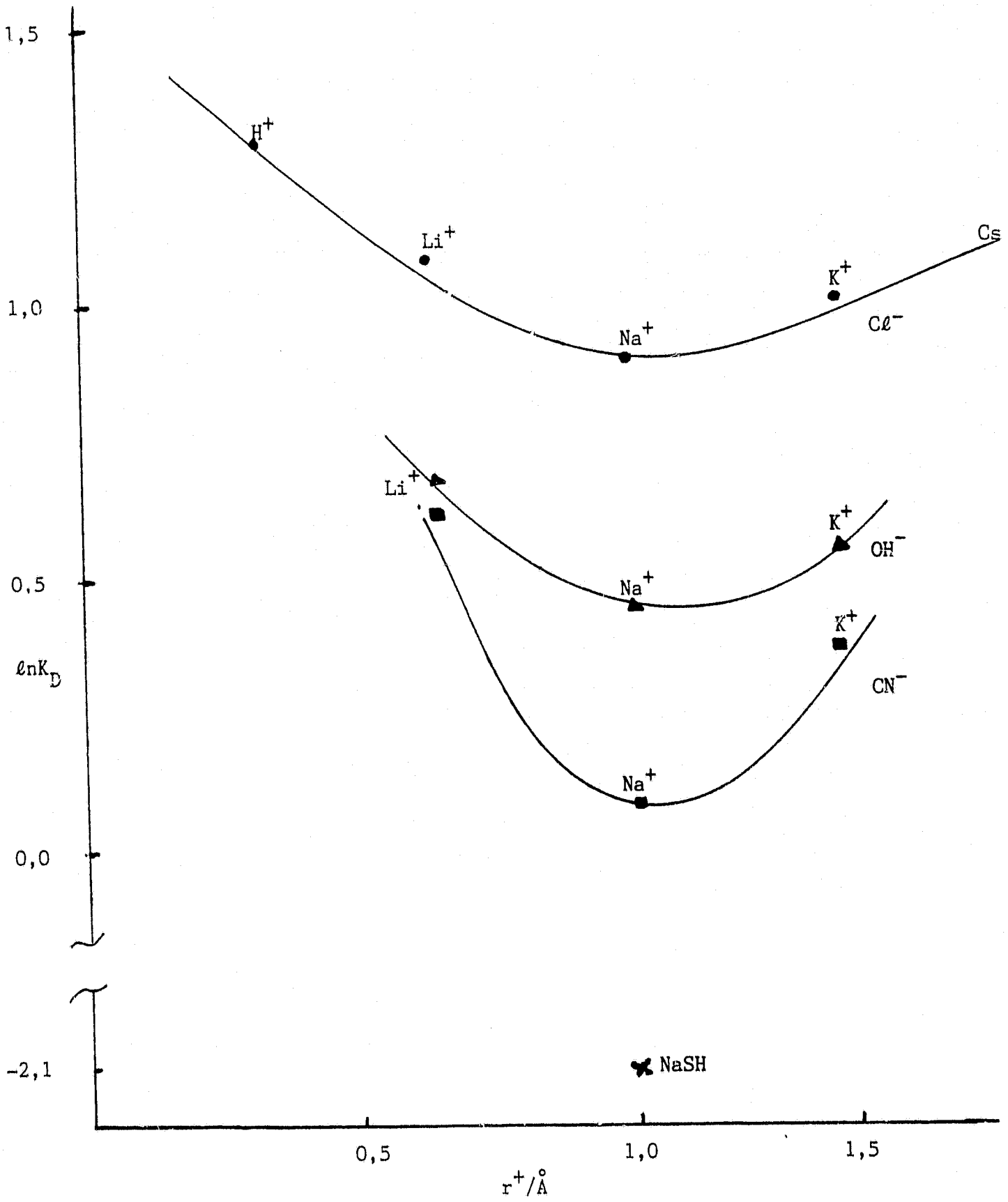


Fig. 3.2

Effect of Cation on Aurocyanide Distribution in various Ionic Media by Activated Carbon



The observed U-shaped curve has a minimum at Na^+ and can be divided into two parts. The left hand side shows that increasing crystallographic radius of cation ($H^+ \longrightarrow Na^+$) causes a decrease in the extraction coefficient, whereas the right hand side shows that an increasing cationic radius results in an enhanced extraction ($Na^+ \longrightarrow Cs^+$). Since the ionic strength has been kept constant throughout, the effect on the distribution coefficient must be due to the specific cation, and the tendency of the ion-pair to be extracted/ adsorbed.

Fig. (3.2) also shows the effect of specific cations on the distribution coefficient in hydroxide and cyanide medium. Similar U-curves are obtained with respect to the cations, although smaller distribution coefficients are observed due to the competing anion. The effect of the cation on the distribution of aurocyanide between aqueous and carbon phase will now be examined.

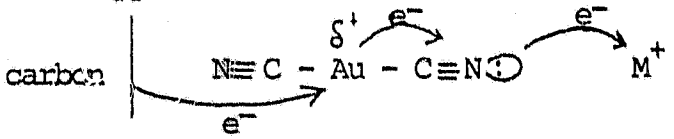
Considering the processes in solution[45,46,51,52] the above U-curves show that both polarizability and size of the resulting ion-pair influences the distribution of gold between the two phases. The trend with increasing size can be attributed to decreasing water phase compatibility, i.e. increasing hydrophobicity with increasing size. The smaller cations, however, show increasing tendency to be extracted with increasing polarizability of the cation. Hydrophobic arguments cannot explain this trend because the enthalpies[52] of hydration of the resulting ion-pairs are expected to decrease with increasing size, whereas the more polar and more hydrophilic ion-pairs have a greater tendency to be extracted.

The polarization of the aurocyanide species by various Lewis acids has been considered by the study of infrared and

Raman spectroscopy of polycrystalline salts. Fig. (3.3) shows the order of increasing polarization of the aurocyanide by the cation. The trend is given by the series:

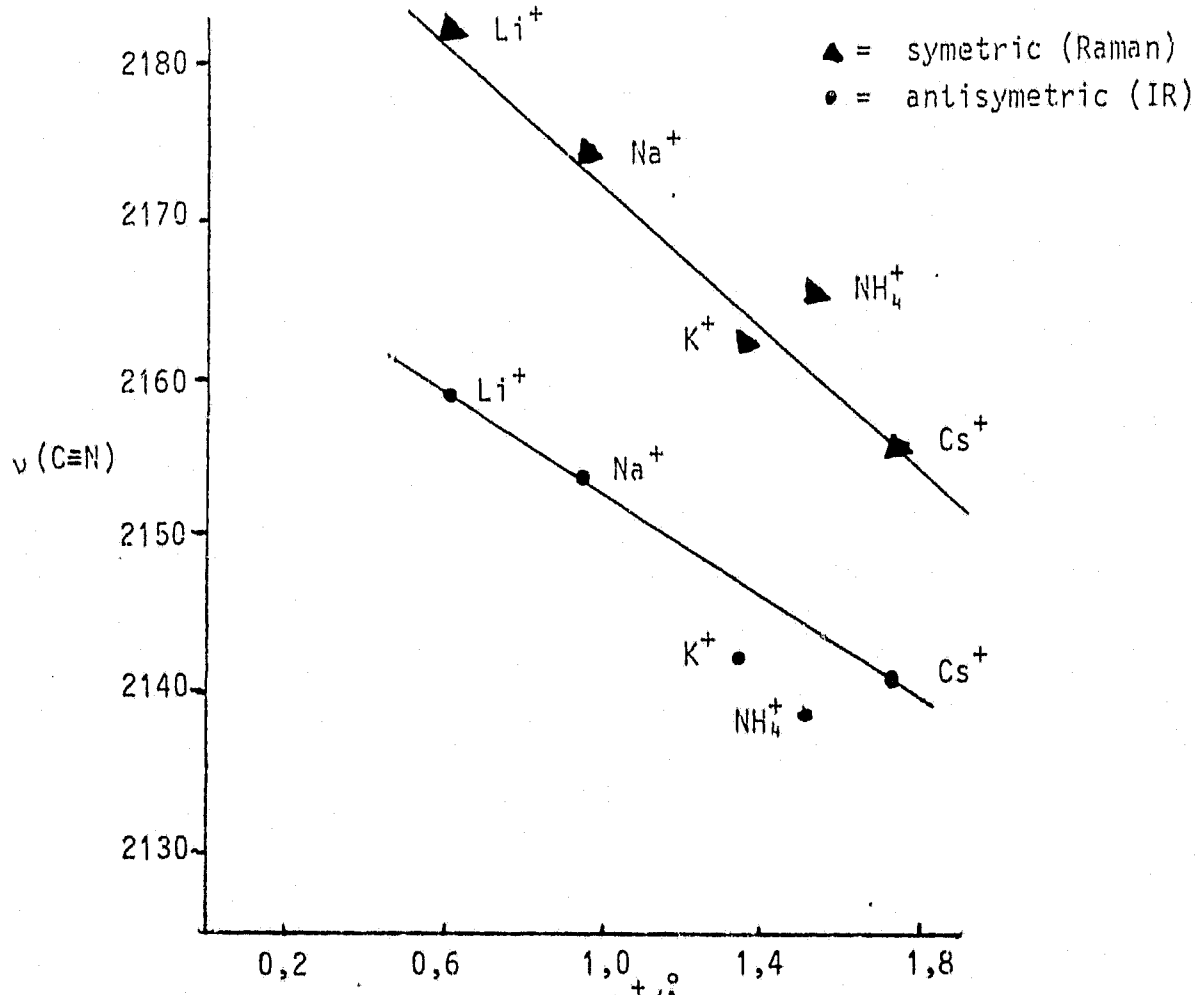
$$Li^+ \rangle\ Na^+ \rangle\ K^+ \rangle\ Cs^+$$

As the Lewis acidity of the cation increases, the fundamental bands of the aurocyanide ion, ν(Au-C) and ν(C≡N) both increase in frequency indicating enhanced acid/base interaction (see appendix (1)). The polarizable aurocyanide anion strongly interacts with the Lewis acid and charge transfer could be effected via the cyanide ligands delocalized π system. This type of interaction is expected to be covalent in nature and for strong Lewis acid/base complexes such as $LiAu(CN)_2$ and $[Be][Au(CN)_2]_2$ involves charge transfer as indicated by their characteristic lemon yellow colour. This type of outer-sphere charge transfer (OSCT) probably results in a residual positive charge on the gold atom relative to the cyanide ligands. The bonding involves d-orbital participation in Au-C σ bonding as well as both π-donor and π-acceptor bonding with the cyanide ligand. The interaction is expected to enhance the carbon/adsorbate interaction as the gold atom is rendered positive with increasing acceptor strength of the Lewis acid. The carbon having a residual negative charge may donate electron density to the gold atom which can be distributed by the cyanide ligands to the Lewis acid. This type of interaction is shown schematically below -



The observed trend for increasing extraction with increasing size of cation can be understood in terms of Traube's rule i.e. increasing hydrophobicity with increasing size. However, examination of the solubility trends for the aurocyanide species shows that the solubility increases with increasing cationic radius. (Table (3.1)). This phenomenon will now be considered.

Fig. 3.3 Graph of $\nu(C\equiv N)$ for $MAu(CN)_2$ versus cationic radius



Graph of ν(Au-C) for $MAu(CN)_2$ versus cationic radius

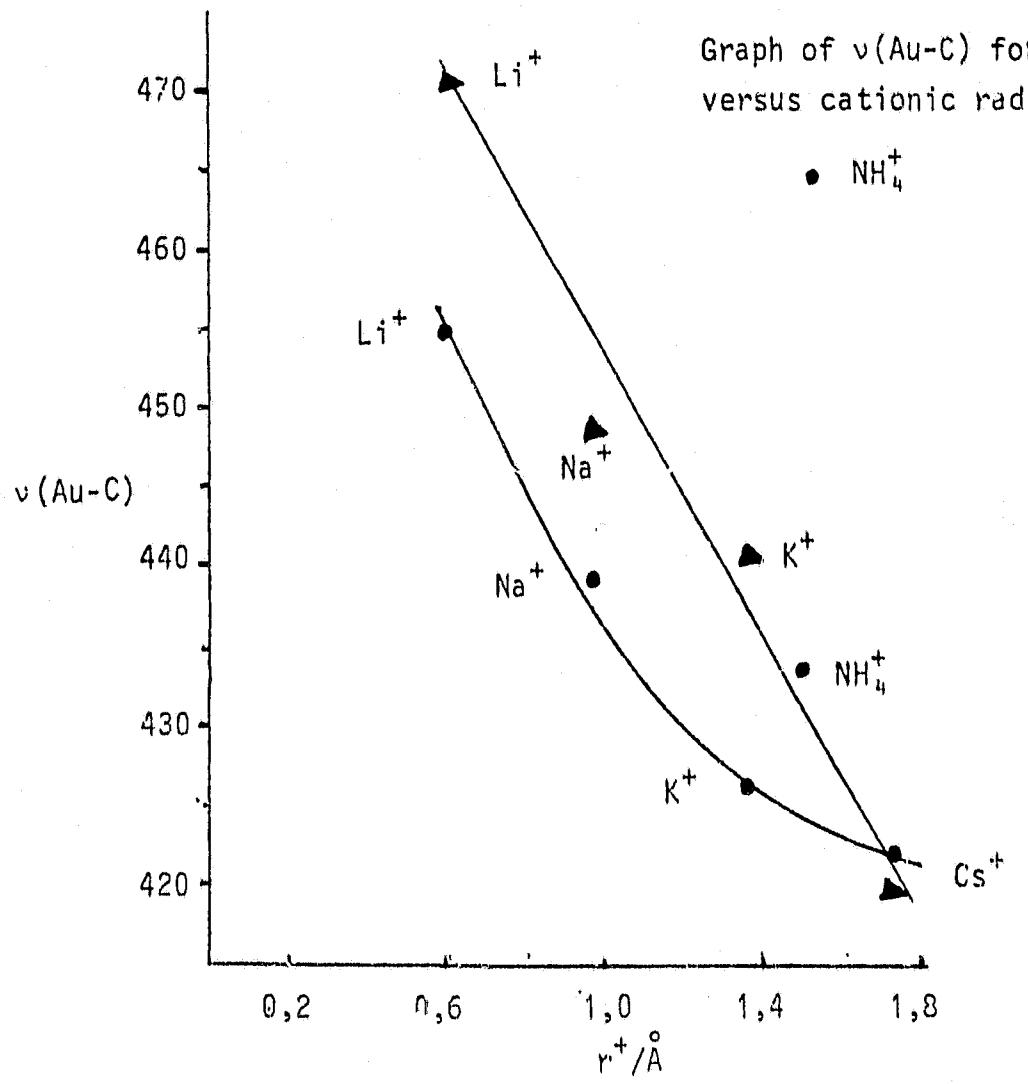
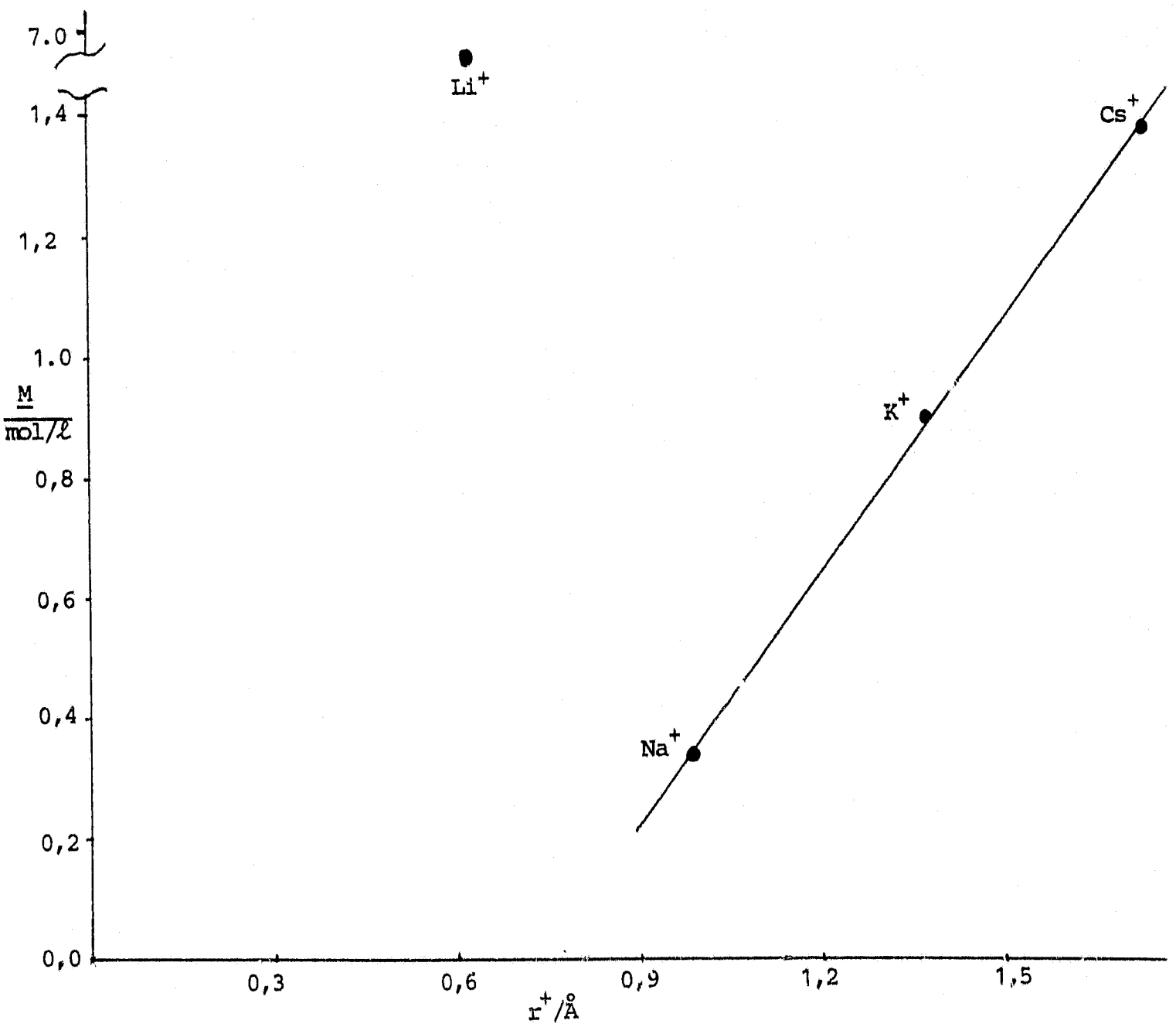


Table 3.1 Molar solubility of various aurocyanide salts

Cation	Molar Solubility mol/ℓ	Comments	reference
H^+	V. Soluble	colourless	59
Li^+	~ 7	lemon yellow	57
Na^+	0,33	colourless	57
K^+	0,85	colourless	52
Cs^+	1,35	colourless	this work
Tl^+	V.insol (0,005)	canary yellow	this work
NH_4^+	V.insol (0,005)	colourless	this work

Fig.3.4 Molar solubility of group IA aurocyanide salts versus cationic radius



The solubility of a salt is strictly determined by the free energy of solution ΔG_s which may be approximated by the following electrostatic expression.[47]

$$\Delta G_s \propto \frac{Z^+}{r^+}$$ where Z^+ is the cationic charge.

This relationship predicts that ΔG_s will decrease with increasing radius of cation and therefore predicts the following solubility trend -

$$Li^+ > Na^+ > K^+ > Cs^+$$

The solubility trend $Li^+ > Na^+$ is in fact observed and presumably the H^+ species would also follow this trend. However, the reverse solubility trend for the larger cations is experimentally observed. Explanation of such an effect is possible considering the form of the resulting ion-pair and its interaction with water. On ion-pair formation, the resulting complex may be solvent separated or a contact ion-pair as shown in the equilibrium below.

$$M^+(OH_2) + Au(CN)_2^- \rightleftharpoons \underset{\text{solvent seperated}}{M^+(OH_2)Au(CN)_2^-} \rightleftharpoons \underset{\text{contact ion-pair}}{MAu(CN)_2}$$

Although no spectroscopic[56] evidence has been found for contact ion-pairs or association reactions for the aurocyanide species in aqueous phase other than for the species $LiAu(CN)_2$,[58] it is probable that the solvent separated species exists in the aqueous phase. The degree of ion-pair formation must depend on the interaction between the cation and the aurocyanide anion in the aqueous phase. According to Frank and Evans[45] very large ions or neutral species which are weakly polarized undergo a hydrophobic hydration in polar water. The reduction in the

number of ions in solution and the neutralization of charge favours the formation of ion-pairs. The forces operative between the weakly polarized ion-pair and water are weak dispersive forces and such weak interactions do not influence the structure of water because there is no primary hydration sheath to orientate the bulk water. Such an interaction can be thought of as hydrophobic hydration. The free energy of solution therefore becomes more negative with increasing ordering which is reflected by the solubility trend -

$$Cs^+ > K^+ > Na^+$$

Thus these ion-pairs become increasingly soluble yet paradoxically increasingly hydrophobic, which is reflected by the order of extraction into the carbon phase. The entropy term therefore largely determines the free energy of hydration for the large poorly hydrated aurocyanide ion. Proof of this is also found in that the solubility[48] of $KAu(CN)_2$ which is 14 times more soluble in hot water than in cold and similarly the species $NaAu(CN)_2$ also increases in solubility with increasing temperature.[42]

iii) Effect of anions

The effect of anions on aurocyanide adsorption have been previously noted. McDougall[23] found that various anions cause a depression of aurocyanide adsorption, the order of depression being given by the series:

$$Cl^- < SCN^- < OH^- < ClO_4^- < CN^-$$

A similar depression due to the hydrosulfide anion[33,34,75] has been reported, and the depressing effect of the ClO_4^- ion has recenty been redetermined by Adams.[41]

Table (3.2) shows the effect of anions on the distribution coefficient for aurocyanide adsorption by carbon. The ionic strength of additive was kept constant at I = 0,30 M as the sodium salt.

Table 3.2 Effect of anions on aurocyanide adsorption

Anion	ℓnK_D
Cl^-	0,924
No additive	0,788
OH^-	0,464
CN^-	0,086
SH^-	~0

A trend of increasing depression is observed with increasing size and polarizability of anion in the aqueous phase. It should be noted however that a large excess of anion is necessary to cause any depression as shown by Fig. (3.2) shown on page 41.

iv) Effect of aurocyanide concentration

The distribution of aurocyanide between aqueous and carbon phase increases with increasing cation concentration and tends to a maximum when I ~0,20 M. This behaviour is expected from LeChatelier's principle and is just a manifestation of equilibrium. When the concentration of cation is kept constant and in large excess, the distribution of aurocyanide between aqueous phase and carbon phase depends on the gold to carbon ratio, that is to say the surface coverage.

At low surface coverages the distribution coefficient increases with increasing aurocyanide concentration up to equilibrium gold loading of approximately 30mg Au/g, after which, the distribution coefficient decreases with increasing aurocyanide concentration (table 3.3).
A similar effect has also been reported by Gross and Scott.[31]

Table 3.3 Effect of aurocyanide concentration on the extraction by activated carbon

Cation	$Au(CN)_2^-$ mg/ℓ	K_D	Gold loading mg Au/g
Na^+	0,556	8,89	4,94
	0,642	15,47	9,94
	0,836	23,83	19,92
	1,332	22,40	29,87
	2,668	14,89	39,73
	4,975	9,95	49,50
K^+	0,691	14,44	9,97
	0,700	28,36	19,76
	1,110	26,87	29,89
	3,056	16,26	49,69

The variation of the adsorption coefficient with gold loading or surface coverage is expected, as the heat of adsorption is not constant due to changing adsorption site energy.

The variation of site energy for the adsorption of aurocyanide and argentocyanide by activated carbon has been extensively investigated via the Langmuir,[38,39] Temkin[33,34] and Freundlich[35] isotherms. Each model implicitly assumes that certain conditions are met by both the adsorbate and the adsorbant.

The Temkin model assumes that the site energies vary linearly with surface coverage whereas the Freundlich model assumes an exponential relationship. Adsorption of aurocyanide by carbon has been modelled using both the Langmuir and the Temkin isotherms. Deviations from the assumed model at low surface coverages has been observed by McDougall[23] and more recently by Adams[41] using the Freundlich model. This effect must be due to the variation of site energy with surface coverage, which will be examined next.

3.3 Surface coverage effects

The adsorption of aurocyanide by activated carbon as a function of surface coverage was investigated in various additive solutions as shown in table 3.4 . The effect on the equilibrium adsorption was investigated by varying both the cation and anion of additive but maintaining constant ionic strenth (I=0,30). The effect of surface coverage was simultaneously investigated by varying the gold to carbon ratio.

The effect of metallocyanide on aurocyanide adsorption was also investigated by keeping constant ionic medium and varying the metal to carbon ratio in which equimolar aurocyanide and metallocyanide concentration was maintained.

This system was further used to investigate the effects of sodium salts of chloride, hydroxide and cyanide on argento-cyanide adsorption.

Table 3.4 Effect of additives on metallocyanide adsorption

Metallocyanide	Additive (I = 0,30M)
$Au(CN)_2^-$	MCℓ M = {Li^+, Na^+, K^+, Cs^+} MOH M = {Li^+, Na^+, K^+} MCN M = {Li^+, Na^+, K^+} MSH M = {Na^+}
$Ag(CN)_2^-$ $Ni(CN)_4^{2-}$ $Hg(CN)_2$ $Cu(CN)_4^{3-}$ $Fe(CN)_6^{3-}$	Equimolar ratios of $[Au(CN)_2^-]$: $[M(CN)_x^y]$
$Ag(CN)_2^-$	Additive (I = 0,30M) NaCℓ NaOH NACN

3.4 Results and discussion

i) Effect of cations and anions on aurocyanide adsorption

Fig. (3.5) shows the Langmuir plot for the adsorption of aurocyanide at constant ionic strength for a series of group IA cations (as chloride salts). For surface coverages (θ) between $0,3 > \theta < 0,8$, the equilibrium constant decreases linearly with increasing surface coverage, although at low gold loadings the model cannot be applied. The effect of cation on the

Fig. 3.5 Langmuir Model

Equilibrium Constant K versus Surface Coverage θ

for Aurocyanide Adsorption in I=0,30M MCℓ

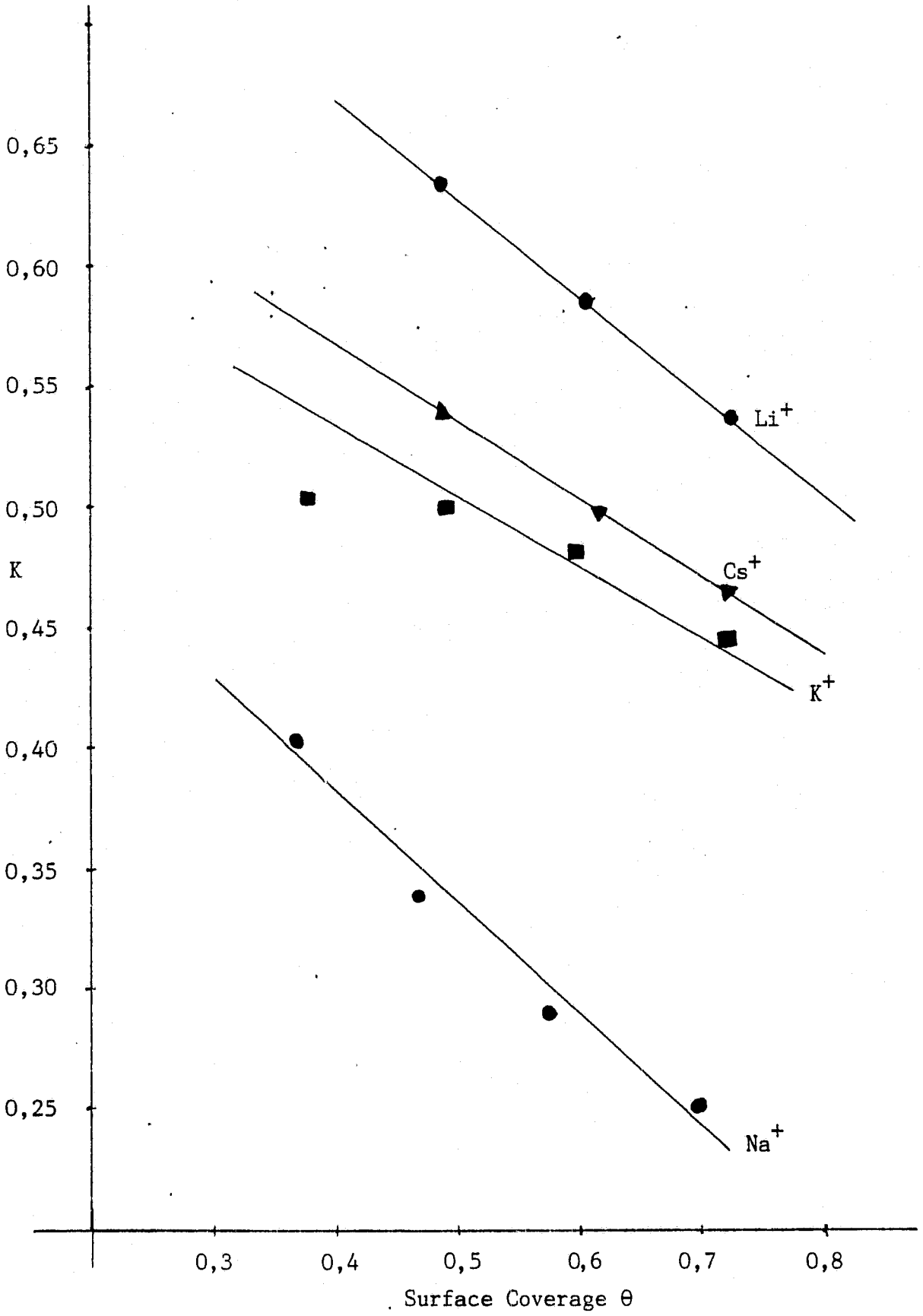
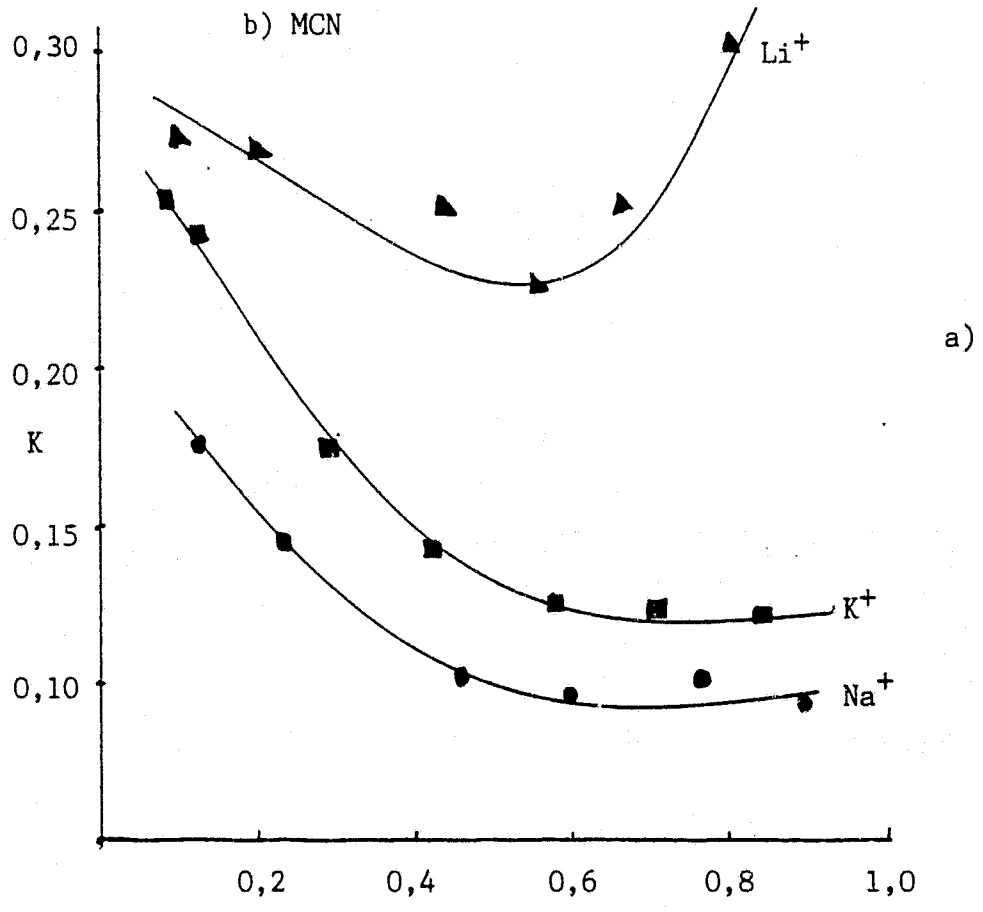


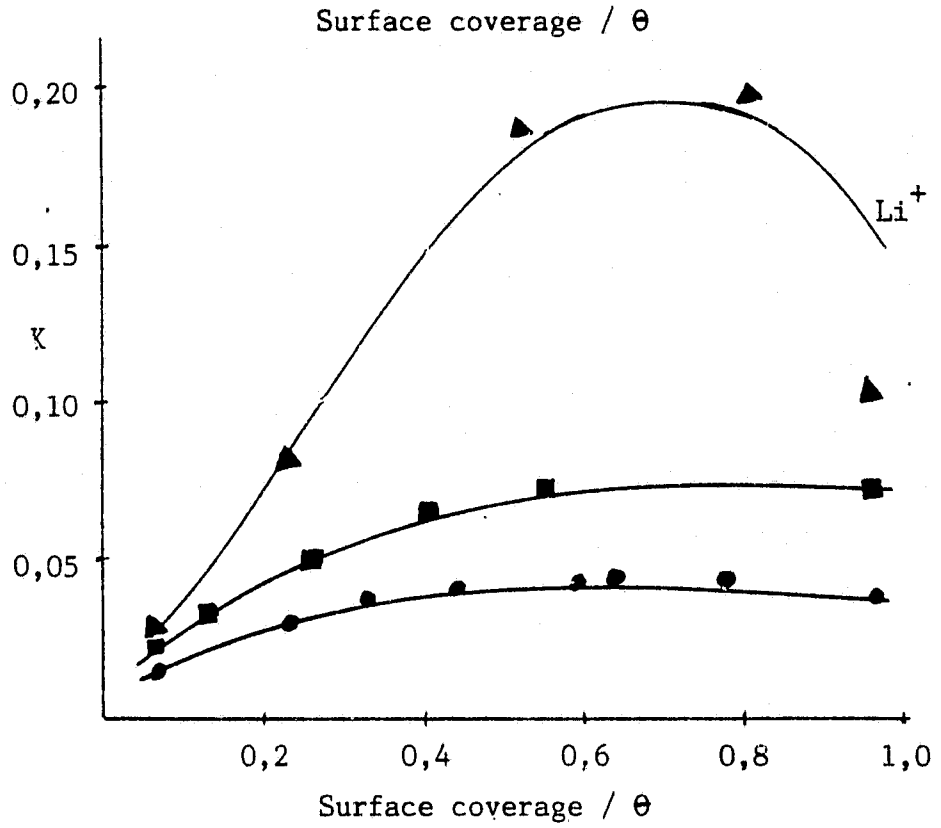
Fig. 3.6 Langmuir Model

Equilibrium constant K verses surface coverage O in constant ionic medium (I=0,30M)

a) MOH
b) MCN



a)



b)

adsorption of aurocyanide is given by the following trend -

$$Li^+ > Cs^+ > K^+ > Na^+$$

The Langmuir model cannot be applied to the adsorption of aurocyanide in hydroxide, cyanide and hydrosulfide medium due to deviations from linearity. (Figs. (3.6 a) and (3.6 b))

Fig. (3.7) shows the Temkin plot for Group IA cations at constant ionic strength (as chlorides). Two linear regions are obtained with a distinct break at ~30mg Au/g. The magnitude of the slopes indicates that the initial adsorption sites are higher in energy. Figs. (3.8) and (3.9) show the Temkin plot for the adsorption of aurocyanide in hydroxide and cyanide medium. In both cases the model applies particularly well at low surface coverages. Some curvature is observed corresponding to a large depression of aurocyanide.

The effect of hydrosulfide on aurocyanide adsorption is shown in Fig. (3.10) as a Temkin plot. The adsorption of aurocyanide is greatly depressed by this large polarizable anion. In addition, activated carbon oxidizes the anion to form polysulfides which may also displace adsorbed aurocyanide due to the formation of polymers of low charge and large size.
The case with no additives is shown in Fig. (3.11) and is plotted according to the Temkin isotherm. The resulting linear relationship ends abruptly at ~40mg Au/g below which no detectable amounts of gold remain in solution. However, in constant ionic medium little, but still sufficient gold remained in solution for accurate analysis. This

Fig. 3.7 Temkin Model
Adsorption of Aurocyanide in
I=0,30M MCℓ

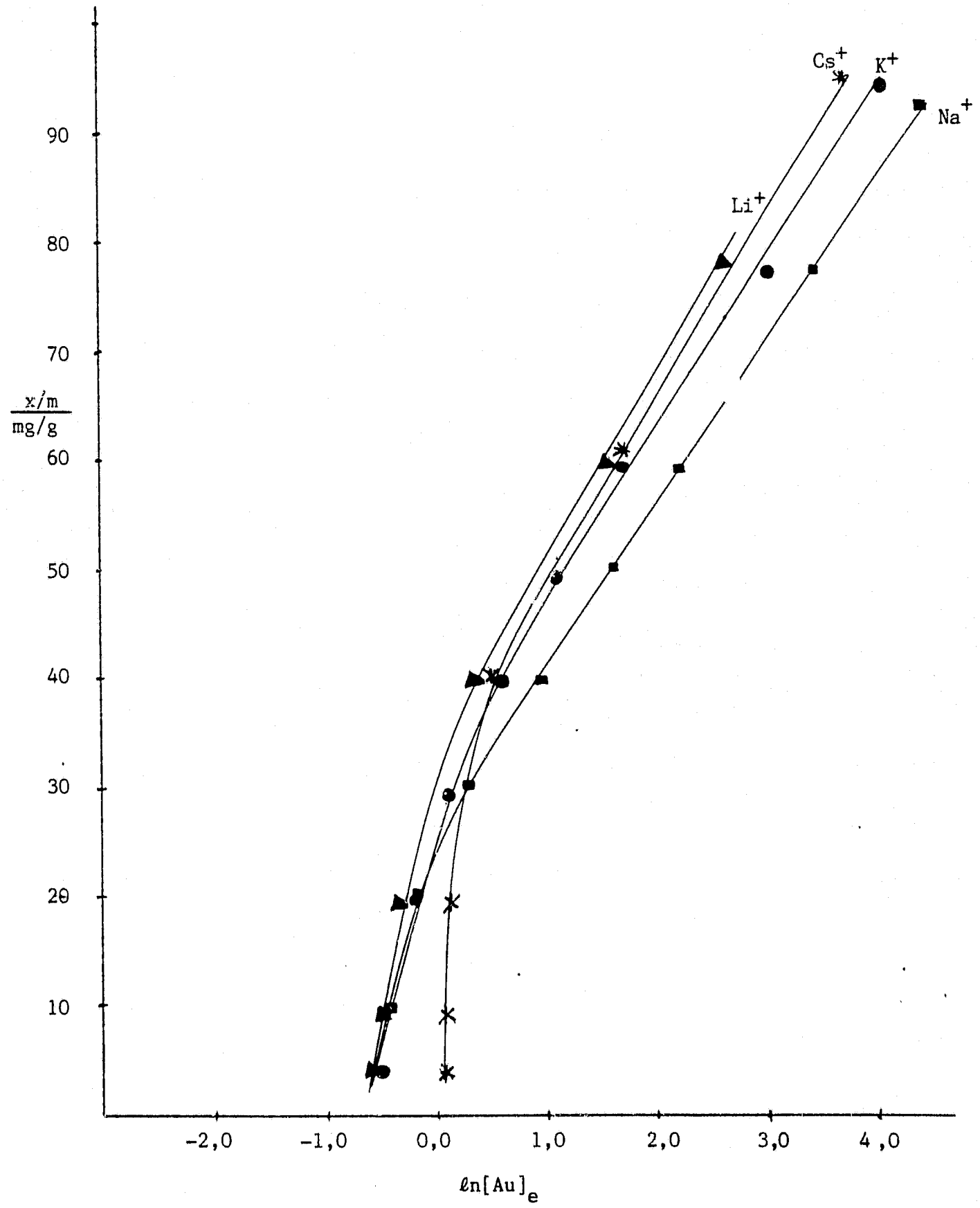


Fig. 3.8 Temkin Model

Adsorption of Aurocyanide in
I=0,30 M MOH

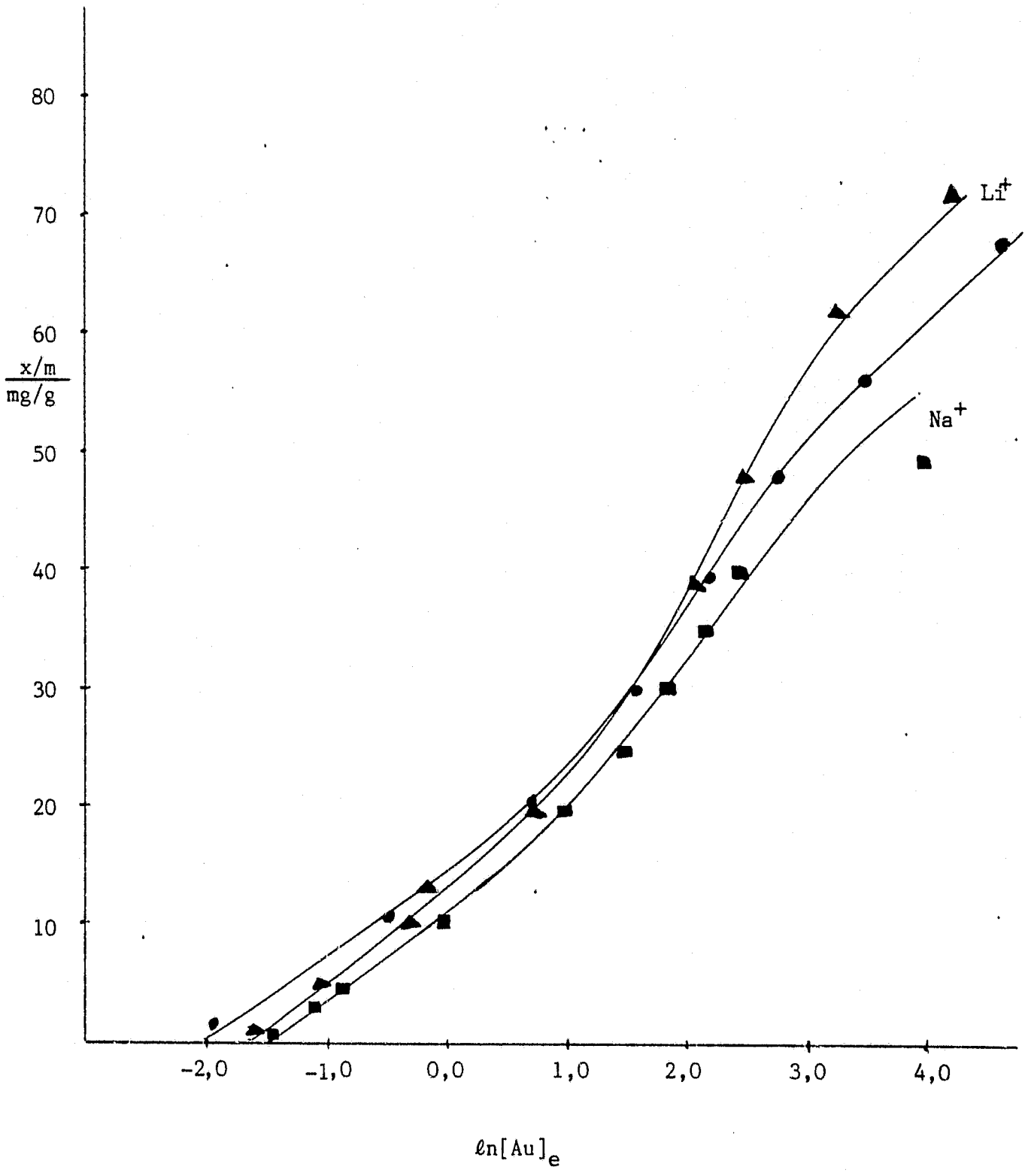


Fig. 3.9 Temkin Model
Adsorption of Aurocyanide in
I=0,30 M MCN

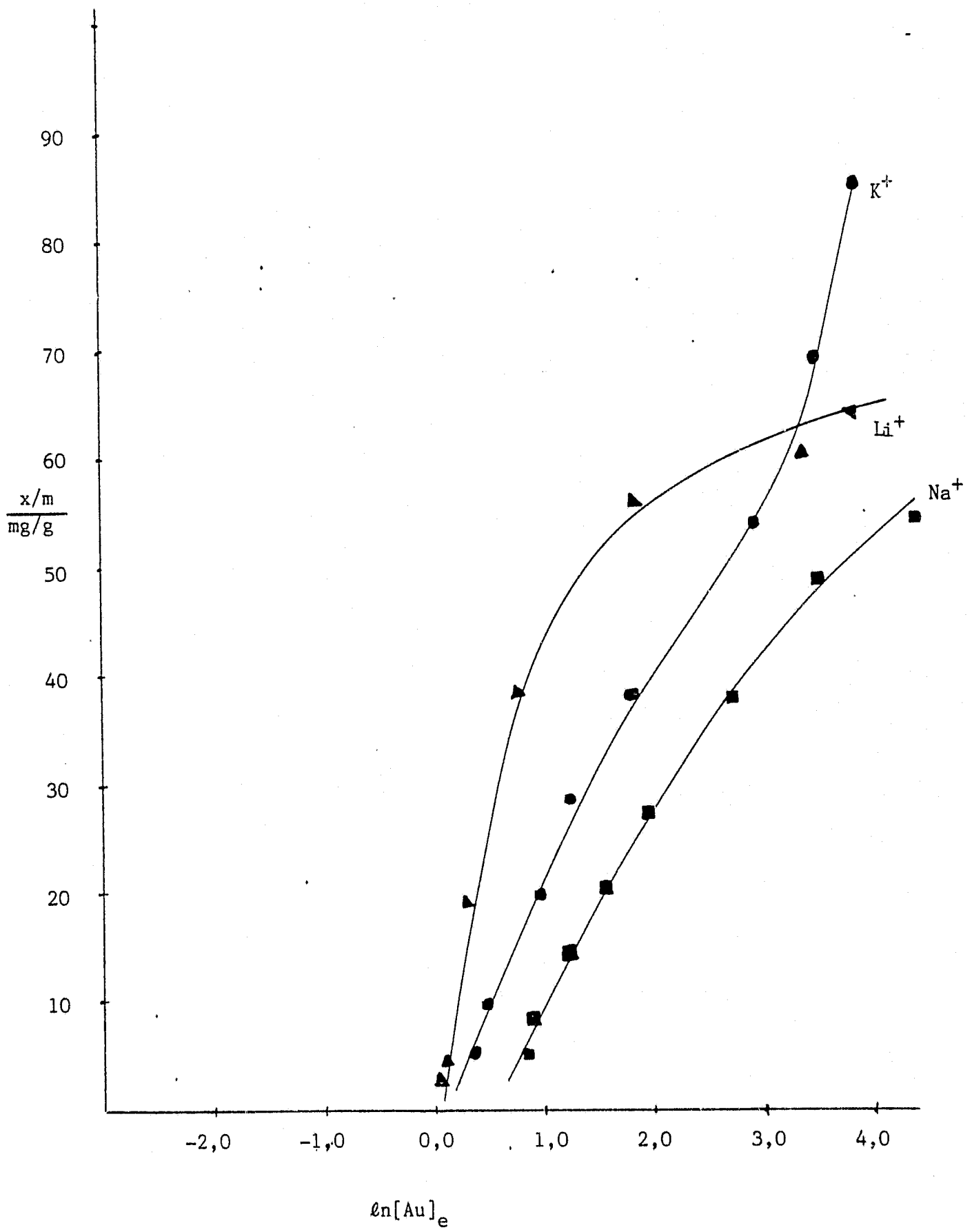


Fig. 3.10 Temkin Model

Adsorption of Aurocyanide in
I=0,30 M NaSH

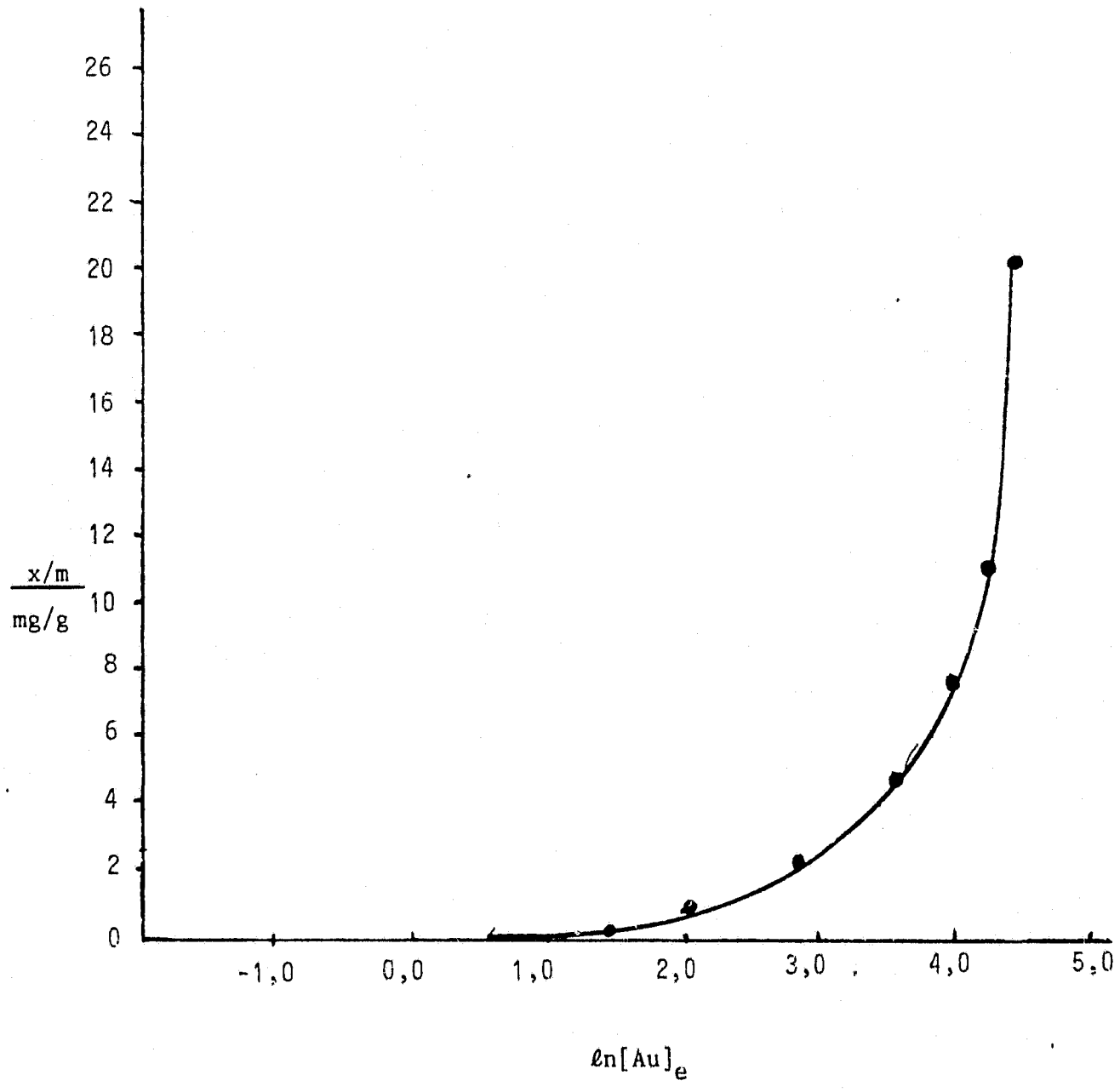
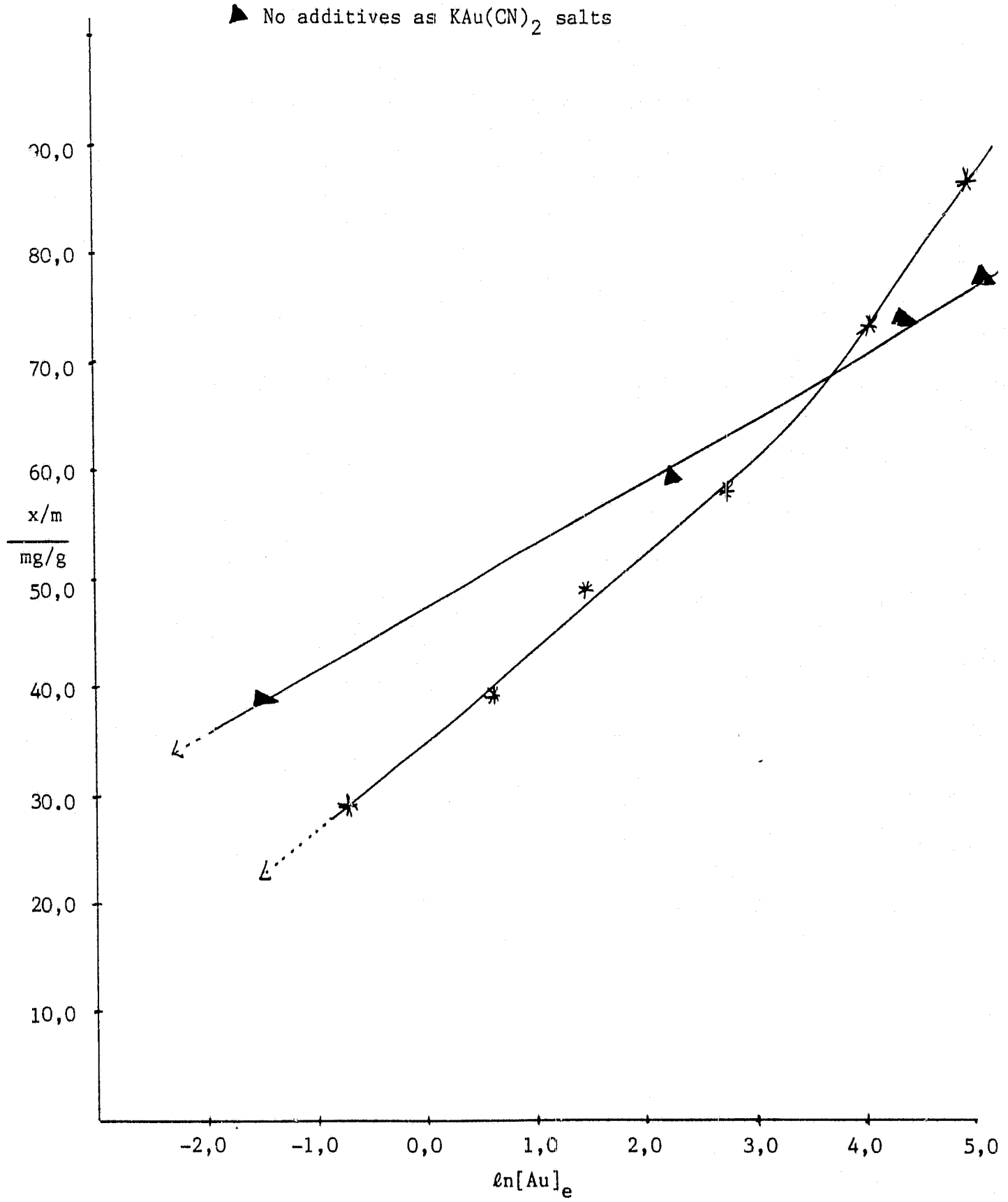


Fig. 3.11 Temkin Model

Adsorption of aurocyanide in deionized water

* No additives as $Ca[Au(CN)_2]_2$ salts

▲ No additives as $KAu(CN)_2$ salts



behaviour must be due to the higher site energy observed at low surface coverages and is responsible for the scavenging ability of activated carbon at low gold concentration.

The equilibrium adsorption of aurocyanide onto activated carbon initially involves a more specific type of interaction with the carbon surface. As the loading or site coverage increases a less specific interaction occurs.[39] Cho and Pitt report a similar trend where the heat of adsorption was found to decrease with increasing gold loading.[40] Grobbelaar has found similar results calorimetrically for the adsorption of aurocyanide by carbon.

The Temkin model approximates the equilibrium adsorption data particularly at low surface coverage. A large depression in aurocyanide is observed due to the specific anion that must compete with the aurocyanide for both cation and surface. The large excess of these anions shifts the equilibrium to the aqueous phase, which effect will be futher exanined in Chapter 5.

ii) Effect of metallocyanide on aurocyanide adsorption

Although it is well known that metallocyanides are co-adsorbed with aurocyanide onto activated carbon, the effects on the equilibrium are not well established. In complex cyanide pulp, activated carbon displays a remarkable selectivity towards aurocyanide despite the large stoichiometric excess of complex metallocyanides present. The only serious competitor for adsorption seems to be argentocyanide species. According to

Fleming,[49] adsorbed gold and silver can be reverably desorbed in a cyclic manner under CIP conditions which demonstrates that at low surface coverages the adsorption process is fully reversible.

Fig. (3.12) shows the Temkin plot for the adsorption of aurocyanide in various additives. The effect of metallocyanides on aurocyanide adsorption was investigated for the whole range of surface coverages in which the concentration of the metallocyanide was stoichiometrically equal to the aurocyanide concentration. The ionic strength of the medium was kept constant at I = 0,30 M using NaCℓ salts. Two distinct effects are observed, firstly the specific region of adsorption shows little effect on the aurocyanide adsorption due to metallocyanides being present. However as surface coverage increases the metallocyanides have an increasing tendency to depress aurocyanide adsorption. The order of aurocyanide depression on an equimolar basis is given by the series:

$$Ag(CN)_2^- > Ni(CN)_4^{2-} > Hg(CN)_2 \ggg Cu(CN)_4^{3-} > Fe(CN)_6^{3-}$$

Under these conditions, very little depression was observed for the copper and iron complexes; thus the adsorption isotherms have not been plotted.

McDougall[23] et al have reported a similar sequence for the adsorption capacity of various metallocyanides by activated carbon. The trend is given by the series:

$$Hg(CN)_2 > Au(CN)_2^- > Hg(CN)_4^{2-} > Ag(CN)_2^- > Ni(CN)_4^{2-} > Co(CN)_6^{3-}$$

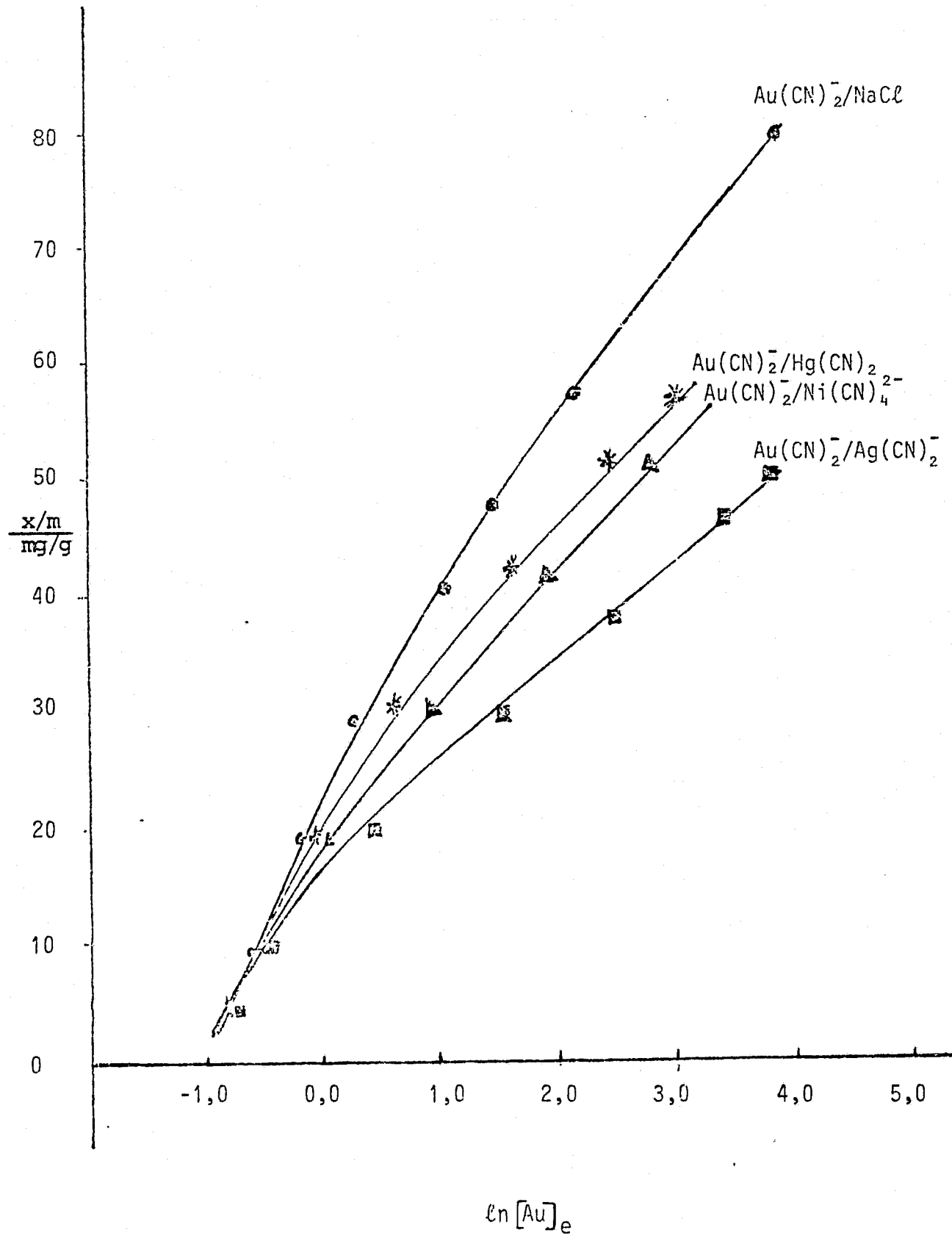
This shows that the carbon has a preference for the adsorption of a species of low charge and large size.

The large neutral $Hg(CN)_2$ complex has been found to be a strong competitor for adsorption and in fact displaces adsorbed aurocyanide[23]. Similar effects have been noted by Fleming[49], where argentocyanide is displaced by aurocyanide in CIP circuits.

The trend reported in this work shows a seemingly anomalous result for the $Hg(CN)_2$ species since this large neutral molecule is expected to cause an even larger aurocyanide depression than observed. However, as the adsorption was conducted in a large excess of chloride ions, the formation of the species $[Hg(CN)_2 Cl_2]^-$ possibly explains the result (see appendix 1A).

Fig. 3.12

The effect on aurocyanide adsorption of equimolar metalocyanides in constant ionic strenth medium I=0,30 NaCℓ



iii) Effects of argentocyanide on aurocyanide adsorption

The effects of equimolar argentocyanide and aurocyanide in excess NaCℓ medium on their respective isotherms is shown in Fig. (3.13) where both these linear metallocyanides show a depression in their adsorption. The depression is marked particularly at higher surface coverages. An indication of the strength of adsorption is given by the slope k of the Temkin isotherm. For the adsorption of aurocyanide, a large depression occurs at high surface coverages, which is expected since the site energies in this region have a lower strength of adsorption. At low surface coverages very little aurocyanide depression is observed which must be due to a more specific type of interaction.

For the adsorption of aurocyanide, the slope k, of the Temkin model for the two types of surface gives an indication of the strength of interaction with the carbon surface where -

$k_i > k_f$ $\quad k_i$ = slope of initial isotherm, k_f = slope of final isotherm

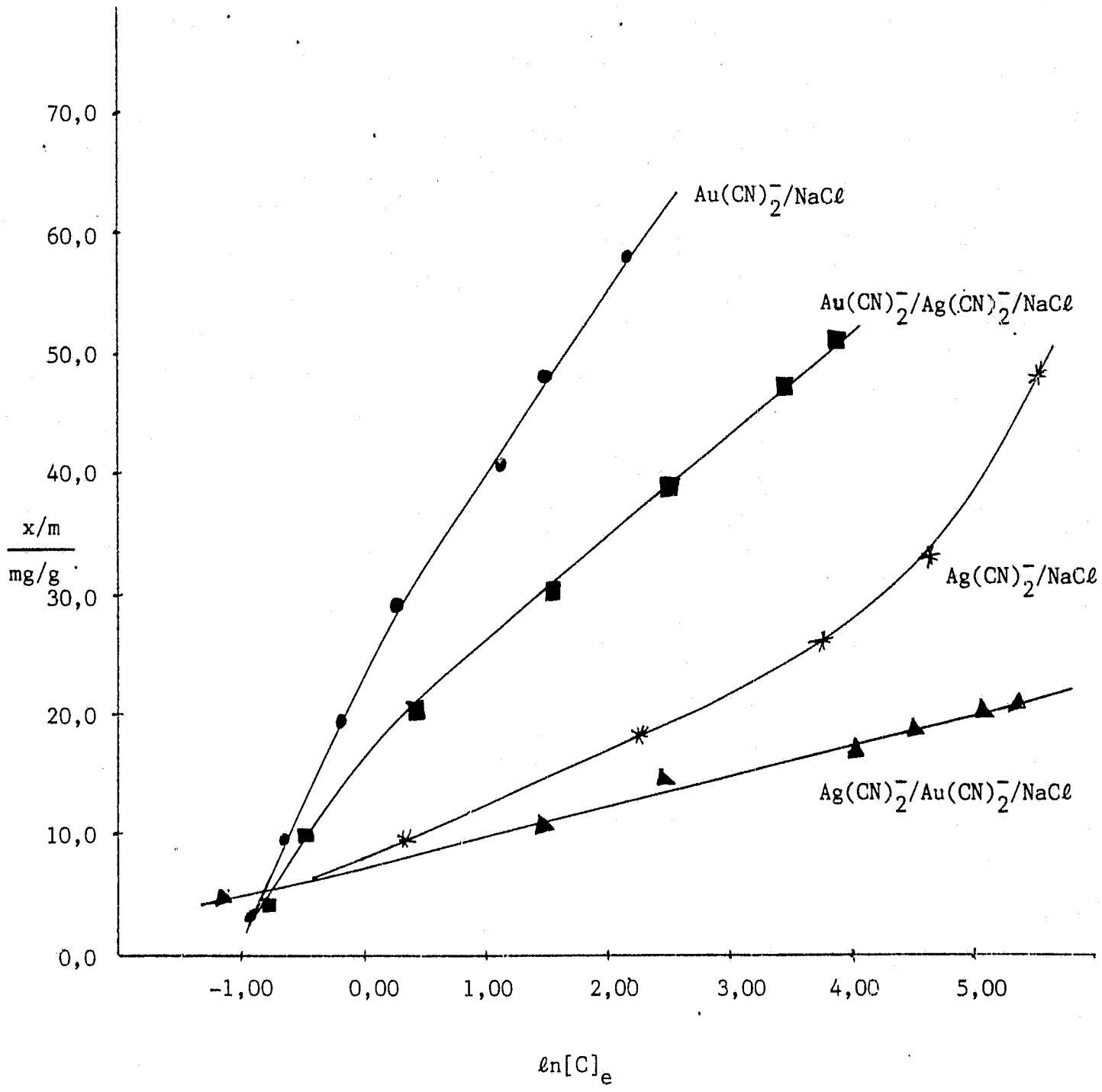
The adsorption of argentocyanide also shows competitive effects at higher surface coverages. However, overall the strenth of interaction with the carbon surface is much lower than the aurocyanide species since-

$$k_{Au(CN)_2^-} > k_{Ag(CN)_2^-}$$

Both the aurocyanide and argentocyanide species are polarized due to metal to ligand charge transfer.[60,61] However, the aurocyanide species having a larger d-orbital participation in M-C σ bonding as well as π-donor and π-acceptor bonding due to a higher effective nuclear shielding can thus more readily

Fig. 3.13 Temkin Model

Effect of aurocyanide and argentocyanide on their adsorption isotherm at equimolar metallocyanide concentrations in constant ionic strenth medium I=0,30 NaCℓ



undergo this type of transition. Effectively the aurocyanide species can thus participate in a donor/acceptor surface species with carbon more readily than the argentocyanide species due to the effective relative positive charge on the Au and Ag atoms respectively. This possibly accounts for the differences in the capacity of carbon for these two linear metallocyanides.

iv) Adsorption of argentocyanide by activated carbon

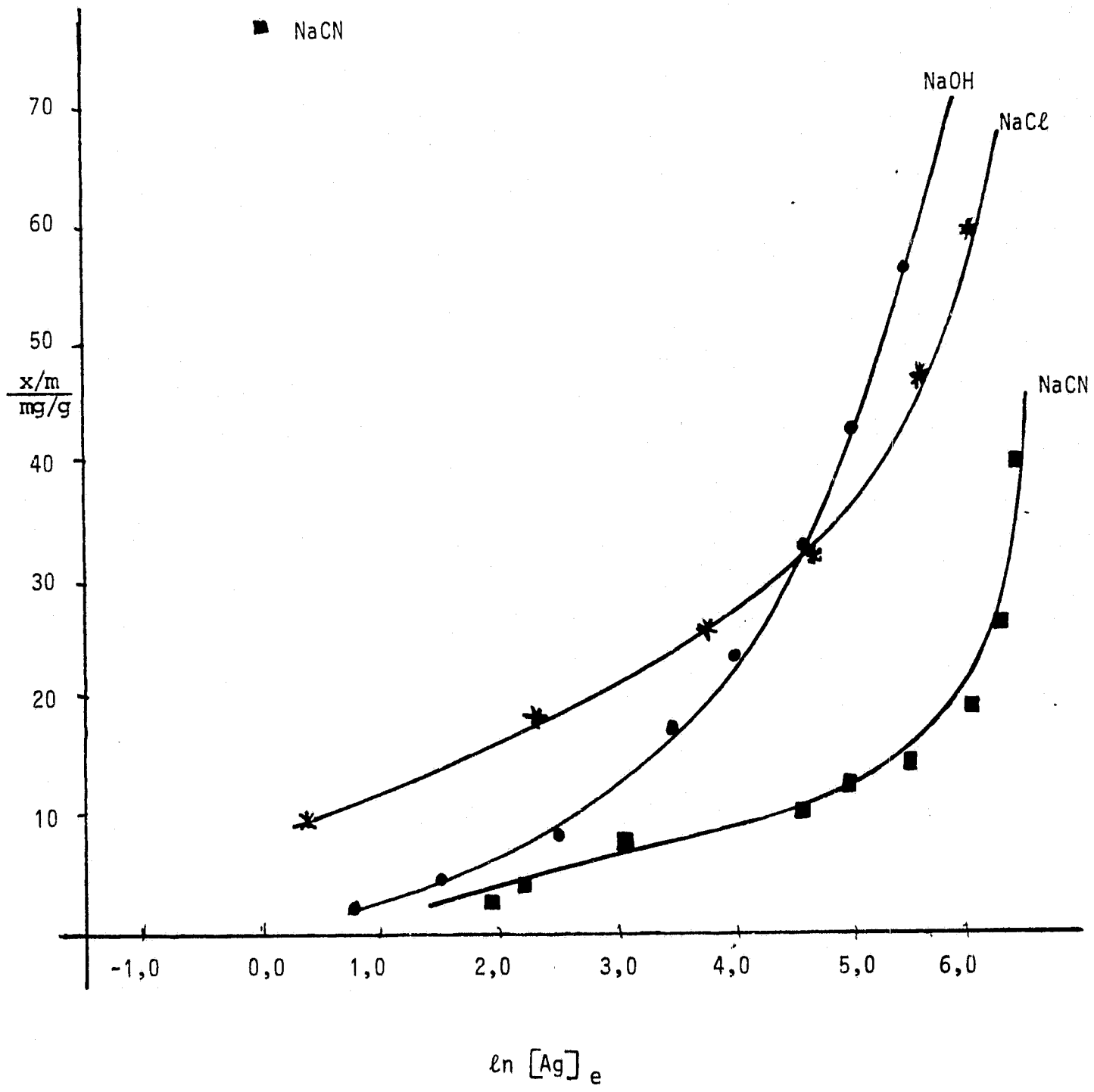
The adsorption of argentocyanide is shown in Fig. (3.14) where a Temkin plot for the adsorption of this linear metallocyanide is shown in various ionic media, as the sodium salt. As in the adsorption of aurocyanide, argentocyanide is depressed by a large excess of anions, the order of depression is given by the series -

$$Cl^- < OH^- < CN^-$$

Complex formation between the argentocyanide and the cyanide ligand results in the formation of higher charged species such as $[Ag(CN)_3]^{-2}$. The adsorption isotherm thus consists of a number of equilibria and is quite complex in nature.

Fig.3.14

Adsorption of $Ag(CN)_2^-$ by activated carbon in constant ionic medium (I = 0,30)



3.5 Summary and conclusions

The extraction/adsorption of aurocyanide by carbon appears to involve the formation of ion-pairs at the carbon/aqueous interface where the association constant must largely depend on the specific cation present and the nature of the resultant ion-pair. The U-curve shown in Fig. (3.2) seems to be the result of the formation of two different kinds of ion-pair species.

The trend for increasing extraction into the carbon phase with increasing cationic radius can be understood in terms of the hydrophobicity of the cation since, as the cationic radius increases, the more weakly solvated it becomes. When two large oppositely charged poorly hydrated ions are present in aqueous phase, the minimization of their free energy occurs by the combination of these ions, whereby the neutralization of charge occurs and the disruption of the structure of water is minimized (hydrophobic hydration). The formation of a large neutral poorly hydrated ion-pair thus becomes increasingly compatible with the carbon phase rather than as dissociated ions in the aqueous phase. This hydrophobic effect can be related to Traube's rule which states:

> "The adsorption of organic substances onto activated carbon from aqueous solution increases strongly and regularly as we ascend the homologous series."

For the smaller well hydrated cations, the above hydrophobic arguments cannot rationalize the observed order of extraction. An increased interaction between the adsorbed ion-pair and the

carbon surface must be invoked to explain the result. The smaller cations being highly polarizable are expected to accept charge from the polarized aurocyanide ion whereby the gold atom is rendered increasingly positive by the increasing acceptor strength of Lewis acid. Charge transfer between the polarized ion-pair and the carbon surface results in a donor/acceptor type of adsorbate on the surface.

Anions present in large excess in the aqueous phase result in the depression of aurocyanide adsorption. This is expected since these anions must compete with the aurocyanide anion for both cation and carbon surface. The trend follows that of increasing aurocyanide depression with increasing size of anion and polarizability. This is expected due to the formation of increasingly hydrophobic ion-pairs with increasing size of anion as well as the result of an enhanced interaction between the carbon surface as the polarizability of the adsorbed species increases.

The adsorption of aurocyanide is similarly depressed by competing metallocyanide anions, particularly at higher surface coverages. This is expected due to the variation of site energy with increasing gold loading. The trend follows that for the adsorption of a species of low charge and increasing hydrophobicity with increasing size.

The extraction of aurocyanide by activated carbon shows that the site energy varies with surface coverage. Although the adsorption of aurocyanide by carbon can be modelled by the Langmuir, Temkin and Freundlich isotherms, the low surface coverage is best described by the Temkin model. This model assumes that the variation in site energy

decreases linearly with increasing surface coverage. The region of low loading ($<$40 mg/g) is the region of industrial importance since in CIP practice, gold loadings of the order of 10 mg Au/g are encountered. This region of surface coverage will be considered in detail in Chapter 5.

4 Characterization of adsorbed gold complex on activated carbon

The formation of neutral ion-pairs at the aqueous/carbon interface is an essential step for the transition of the aurocyanide complex between the two phases. Once the probably neutral complex is adsorbed onto the carbon surface the subsequent events have not been fully characterized.[5,24] Firstly the identity of the actual gold complex has not been established nor has the presence of the cation.[31,38,39] Secondly the effect of surface coverage on the form of the adsorbate has not been fully resolved.[24]

Many postulates on the identity of the adsorbate have been made, which include:

A) Adsorption of the ion-pair
B) Adsorption of the anion
C) Partial degredation of aurocyanide to the polymeric form $(AuCN)_p$ or the formation of a surface complex such as (carbon/-AuCN) which may be formed via a ligand replacement reaction.
D) Reduction to gold metal.

A series of aurocyanide loaded carbons were prepared in chloride medium so that at equilibrium carbons containing between 1mg to 80mg Au/g were obtained in the following additives: HCl, $NaCl$, $CsCl$ and $CaCl_2$.

The initial approach for the characterization of the adsorbed gold species included the following direct methods.

4.1 Results and discussion

i) X-ray diffraction

The X-ray diffraction study of the loaded carbons showed no characteristic lines due to AuCN, $Au(CN)_2^-$ nor gold metal

irrespective of surfact coverage or ionic medium in the adsorption phase. Carbons spiked with as little as 10mg Au/g as $K[Au(CN)_2]_s$ showed the characteristic bands expected for the aurocyanide complex.

This method depends on a crystalline structure for the diffraction of X-rays. It appears that the gold adsorbed by the carbon is either in a highly dispersed state or not crystalline in nature.

ii) Fourier transform infrafred spectroscopy (FTIR)

In appendix (1) it is shown that the aurocyanide salts with group IA cations have characteristic frequencies for both the $\nu(C\equiv N)$ and $\nu(Au-C)$ bands. It was therefore speculated that the specific salt, the anion or the polymeric products could be distinguished via this technique provided a powerful enough instrument was used. Activated carbon, being black and energy adsorptive, is not idealy suited for an investigation of this type. Nevertheless, numerous carbons were studied. No bands due to aurocyanide or $(AuCN)_p$ were found irrespective of gold loading or adsorption medium. A spiked sample (140mg Au/g) as $K\,Au(CN)_2$ readily yielded the characteristic adsorption band at $2140cm^{-1}$. The failure to detect any of the expected bands may be attributed to the highly dispersed state of the adsorbed gold complex, the large surface area of carbon, and, in the main, the low extinction coefficients (ε = 24 ℓ/mol cm) of the cyanide complexes.

iii) X-ray fluorescence

This method was used to determine both the gold and cation concentration on carbons loaded from $Ca[Au(CN)_2]_2$ and $CsAu(CN)_2$ salts in deionized water. Sample preparation proved to be difficult possibly due to small surface concentrations, and reproducibility on the same sample was not readily achieved.

Statistical analysis showed that the error bars especially in the regions of low gold loading were large and therefore not really useful. Overall the gold cation ratio is less than that expected from stoichiometric considerations, and the adsorption of the neutral ion-pair is not realized over the surface coverage investigated. The above direct methods failed to yield any conclusive information as to the actual species on the carbon surface.

4.2 Indirect characterization of gold complex of carbon

Davidson,[36,37] amongst others, has shown that hydroxide solutions at elevated temperatures can readily elute gold loaded carbons. This approach was adapted and proved to be a remarkably simple method for the characterization of the gold species on the carbon by examining the eluted gold species by UV spectroscopy. The success of this method depends on the fact that the hydroxide anion is non-complexing for gold under all conditions. Fig. (4.1) shows the elution sequence employed where each step gives conclusive information as to the desorbed species.

Carbons were loaded from 1 - 80mg Au/g in the following adsorption media: $NaCl$, $CaCl_2$, HCl. Each carbon was then eluted in a column using 0,30 M NaOH at 90°C in a thermostatted bath. A slow flow rate of 5 bed volumes/hr was used and a total of 200 bed volumes were passed. The total volume of the eluent was collected and the gold concentration was determined via atomic absorption spectroscopy. The desorbed gold species was quantitatively identified using UV spectroscopy and checked against the result obtained from A.A.S.

The same carbon was then subsequently eluted with 1 M NH_3 to complex any possible $(AuCN)_p$ type of adsorbate according to the following reaction -

$$(AuCN)_p + \text{excess } NH_3 \longrightarrow Au(CN)(NH_3)$$

Fig. 4.1

Choice of eluant :

Hydroxide and cyanide are both known eluants; however, the use of cyanide yields no information as to the surface complex as both the adsorbed and desorbed complex will involve the aurocyanide species.

Using hydroxide followed by aqueous ammonia as eluant yields useful information according to the following scheme :

Assume the following species exist on the carbon surface -

$Au(CN)_2^-$ / M $Au(CN)_2$; AuCN/carbon ; $(AuCN)_p$ and $\overset{\circ}{Au}$

gold loaded carbon

OH^- @ 90°C

aqueous phase

$Au(CN)_2^-$

M $Au(CN)_2$

Identification via UV.

carbon phase

$(AuCN)_p$; AuCN/carbon ; $\overset{\circ}{Au}$

NH_3 @ 90°C

aqueous phase

$Au(CN)(NH_3)$

Eluted gold species was stabilized by the addition of cyanide

carbon phase

$\overset{\circ}{Au}$

ash at 800°C

aqua regia —— A.A.S.

$(AuCl_4^-)$

The carbons were then ashed at 800°C and the remaining gold taken up in aqua regia and analysed via A.A.S. as a check on the mass balance.

Results and discussion

A plot of the percentage gold desorbed or eluted from the carbon versus the initial gold loading using hydroxide eluent at 90°C is shown in Fig. (4.2), The carbons with initial loadings of less than 40mg Au/g were eluted in excess of 90 percent, after which, as the initial gold loading increased, the overall extraction decreased. No effect on the elution due to the initial cation present from loading was noted, although in acidic medium a drastic decrease in the elutability of gold was noted with increasing loading.

Examination of the UV spectrum of the hydroxide eluant, neutralized to approximately pH7 shows maxima at 239, 229 and 210 nm which is characteristic[62] of the aurocyanide anion. This species must be the form of the adsorbed gold complex on the carbon surface.

Subsequent elution of the same carbon using ~1 M aqueous ammonia effectively removed only traces of gold. This effectively discounts the formation of the polymer $(AuCN)_p$ on the carbon surface. The gold that remains on the carbon surface after the aurocyanide is displaced by the hydroxide anion is possibly gold matal which seems to increase in concentration as the gold loading increases. However, this does not exclude the possibility of the formation of an activated carbon-AuCN type of complex, since ammonia being a poor donor ligand possibly cannot replace the stronger carbon-Au bond to form the complex $Au(CN)(NH_3)$.

The acid loaded carbons on elution with hydroxide failed to desorb any significant amounts of aurocyanide,

particularly with increasing gold loading. This may be expected as adsorption of aurocyanide in acidic medium would result in the formation of the neutral $HAu(CN)_2$ ion-pair on the surface. On heating this species is expected to degrade to form AuCN which is a well known route for the preparation of this polymer. The overall reaction is given by the following equation -

$$H^+_{excess} + (Au(CN)^-_2)_n \xrightarrow{65°C} n(AuCN) + n(HCN) \qquad (4.2)$$
$$n > 1$$

Subsequent elution using aqueous ammonia however failed to form the complex $Au(CN)(NH_3)$ so that degradation to the metal is probable. The polymerization reaction 4.2 also assumes a localized aurocyanide concentration at the surface. This is unlikely as X-ray diffraction results suggest the presence of more evenly spread sites.

Fig. (4.3) shows some results due to McDougall.[23] This shows that for aurocyanide loaded carbons below loadings of about 40 mg Au/g, the ratio of gold to nitrogen suggests the presence of the aurocyanide anion. At higher loadings the data suggests that some degredation occurs.

Graph of % Au desorbed as aurocyanide versus initial loading onto activated carbon

Fig. 4.2

Eluent = 0,30 M NaOH at 90°C

Loading medium

Key ● NaCℓ

✱ $CaCℓ_2$

■ HCℓ

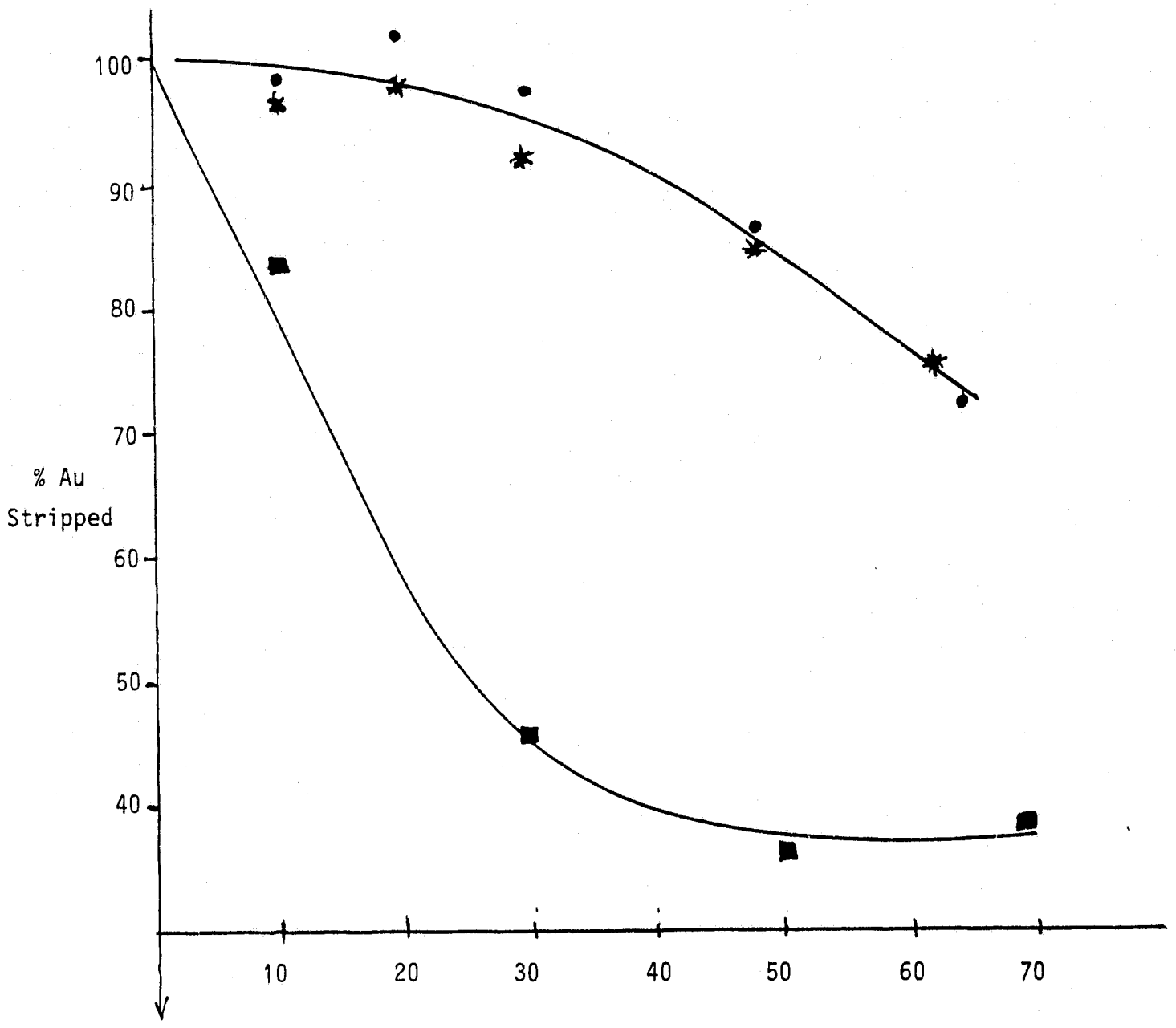
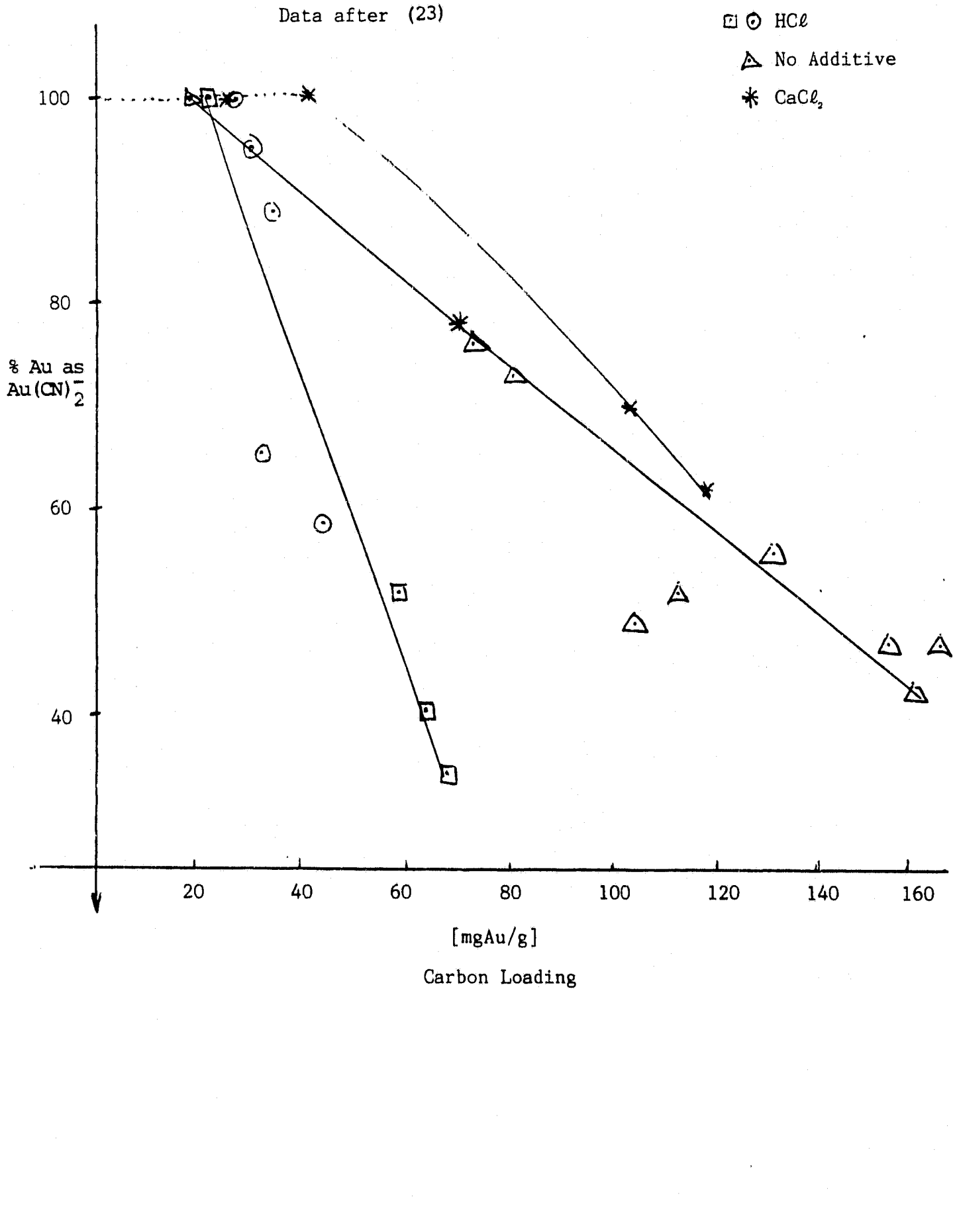


Fig. 4.3 Percentage Au on Carbon as $Au(CN)_2^-$ assuming all N is bound vs. Carbon loading



4.3 Stoichiometric ratio of Ca and Au adsorbed by carbon

In the previous section it was shown that the form of the adsorbate on the carbon surface depends on the gold loading of surface coverage. Gold loadings below about 40mg Au/g the aurocyanide species seems to predominate. However, little was discovered concerning the stoichiometry of the cation which is necessary for the adsorption of the ion-pair. Adsorption of the $Ca[Au(CN)_2]_2$ salts dissolved in deionized water was carried out. The equilibrium concentration of both Ca^{2+} and gold was determined after 21 days, and, knowing the initial concentration of both cation and anion, the loadings were calculated by difference.

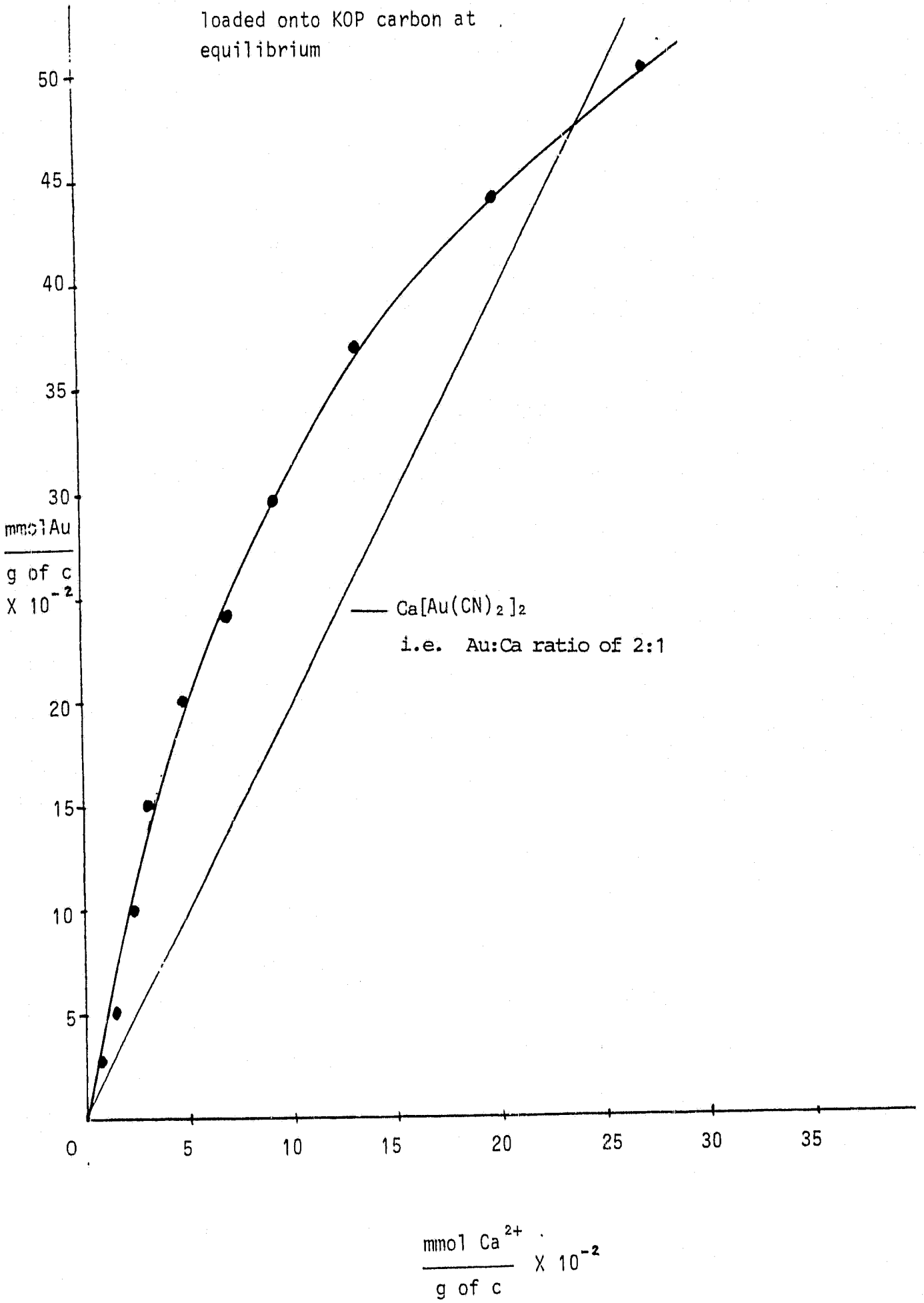
Results and discussion

Fig.(4.4) shows a plot of the equilibrium gold adsorbed versus the equilibrium calcium adsorbed from solutions containing only these ions. The stoichiometric ratio for the adsorption of the ion-pair $Ca[Au(CN)_2]_2$ is never realized and a large concentration of calcium ions are found in solution at equilibrium.

The initial region of loading is linear up to approximately 0,2mmol Au/g, this region corresponds to loadings of less than 40mg Au/g. The slope of this region gives the ratio of gold to calcium adsorbed and has the value of approximately four, therefore only half of the adsorbed aurocyanide exists as the ion-pair. As the gold loading increases the gold to calcium ratio tends towards that of the ion-pair as the uptake of calcium ions increases whereas the gold uptake decreases. This is probably indicative of the decomposition of aurocyanide, probably to the metal.

Fig. 4.4

Graph of the Au to Ca^{2+} ratio loaded onto KOP carbon at equilibrium



The increased adsorption of calcium ions with gold loading may be due to complex formation with the degradation products of aurocyanide such as CN^- or CO_3^{2-}.

The low loading regions (<40mg Au/g) show a deficiency of cation for the adsorption of the ion-pair. However, elemental analysis of carbon shows that the non-extractable ash content might adequately account for the missing cations. A blank solution containing only carbon showed that no calcium was extracted into the aqueous phase. Thus it is possible that the residual ash content of carbon might be fixed or complexed by the carbon matrix. A similar result for the adsorption of argentocyanide has been reported by Cho and Pitt[38].

4.4 Summary and conclusion

The elution of aurocyanide loaded carbons using hydroxide at elevated temperatures displaced in excess of 90 percent of the adsorbed gold for loadings of less than 40mg Au/g. Examination of the UV spectrum of the eluent confirmed the presence of the aurocyanide species. As the loading increased, the elutability of the gold decreased and some decomposition to gold metal probably occurs. The formation of AuCN type of surface species seems unlikely since this fraction could not be eluted by aqueous ammonia. These results are consistent with those found by McDougall et al.[23,24] who reported that for carbon loadings below 40mg Au/g the gold to nitrogen ratio of about 0,5 was found. This corresponds to that of the aurocyanide species. However, as the gold loading increased the ratio was found to tend to about 1 which corresponds to that of AuCN. This result may well be an average for a mixture of gold metal and the aurocyanide anion. The results of the X-ray diffraction also suggests that no AuCN type of adsorbate is formed on the carbon surface.

The adsorption of the ion-pair is not realized when conducted from solutions containing only these ions. In the initial region of adsorption only half of the aurocyanide can be accounted for as the ion-pair species. The inherent ash content of activated carbon, however, can more than account for the discrepancy of cation.

Adsorption of aurocyanide in excess cation concentration is expected to drive the equilibrium, thus favouring the adsorption of ion-pairs.

5 The adsorption/desorption of aurocyanide at low loadings

The adsorption of aurocyanide by activated carbon under typical CIP operation rarely exceeds the value of about 10mg Au/g. The adsorption therefore involves the low surface coverage region and the interaction between the aurocyanide ion and the carbon surface must involve a specific type of interaction. It appears that the majority of researchers have not recognized this fact and much work has been conducted on carbon with loadings in excess of 30mg Au/g, this has probably contributed to much of the confusion with regard to the mechanism.

Literature review

The desorption of gold has mainly been studied using elution columns in which packed beds of aurocyanide loaded carbons are subjected to aqueous solutions containing anions such as hydroxide and cyanide at elevated temperatures (~98°C). Empirically,[2,8,36] it has been found that solutions of caustic cyanide as the sodium salt are good desorbers of gold. It has also been found that the desorption process is strongly dependent on temperature[8]. More recently Davidson[37] reported that pre-treatments are most beneficial for the elution process. Pre-soaking the loaded carbon in basic medium such as K_2CO_3/KOH, KOH, NaOH and LiOH followed by copious amounts of good quality deionized water at elevated temperatures, led to the carbon being eluted at faster rates. The cation in the pre-soak medium was also found to influence the overall extraction. On this and other work Davidson proposed that the strength of attachment of the adsorbed gold species influenced the elutability. Davidson reports the order of elution for aurocyanide salts adsorbed on carbon to be;

$$Ca^{2+} < Mg^{2+} < H^{+} < Li^{+} < Na^{+} < K^{+},$$

The above series shows that as the polarizability of the cation decreases, the strength of the interaction between the ion-pair and the carbon also decreases. Similarly using hydroxide eluent Davidson[37] found that the less polarizing the cation of the medium the higher the overall desorption, according to the following trend: LiOH < KOH < NaOH. Surface coverage also influences the elutability. Davidson[36,37] reported that for carbons loaded from 3,3 to 6,3 mg Au/g approximately 90 - 95 percent of the gold could be desorbed, whereas for carbons loaded between 40 - 60 mg Au/g less than 85 percent of the gold could be desorbed. These results are consistent with those reported in section 4.2 where the overall decrease must be due to the decomposition of the aurocyanide ion-pair. In the low surface coverage regions the adsorbed gold complex, the aurocyanide ion-pair, must be stabilized by the specific interaction between the adsorbate and the carbon surface. This accounts for the overall differences in the extraction with surface coverage.

5.1 Factors influencing the adsorption/desorption of aurocyanide by activated carbon

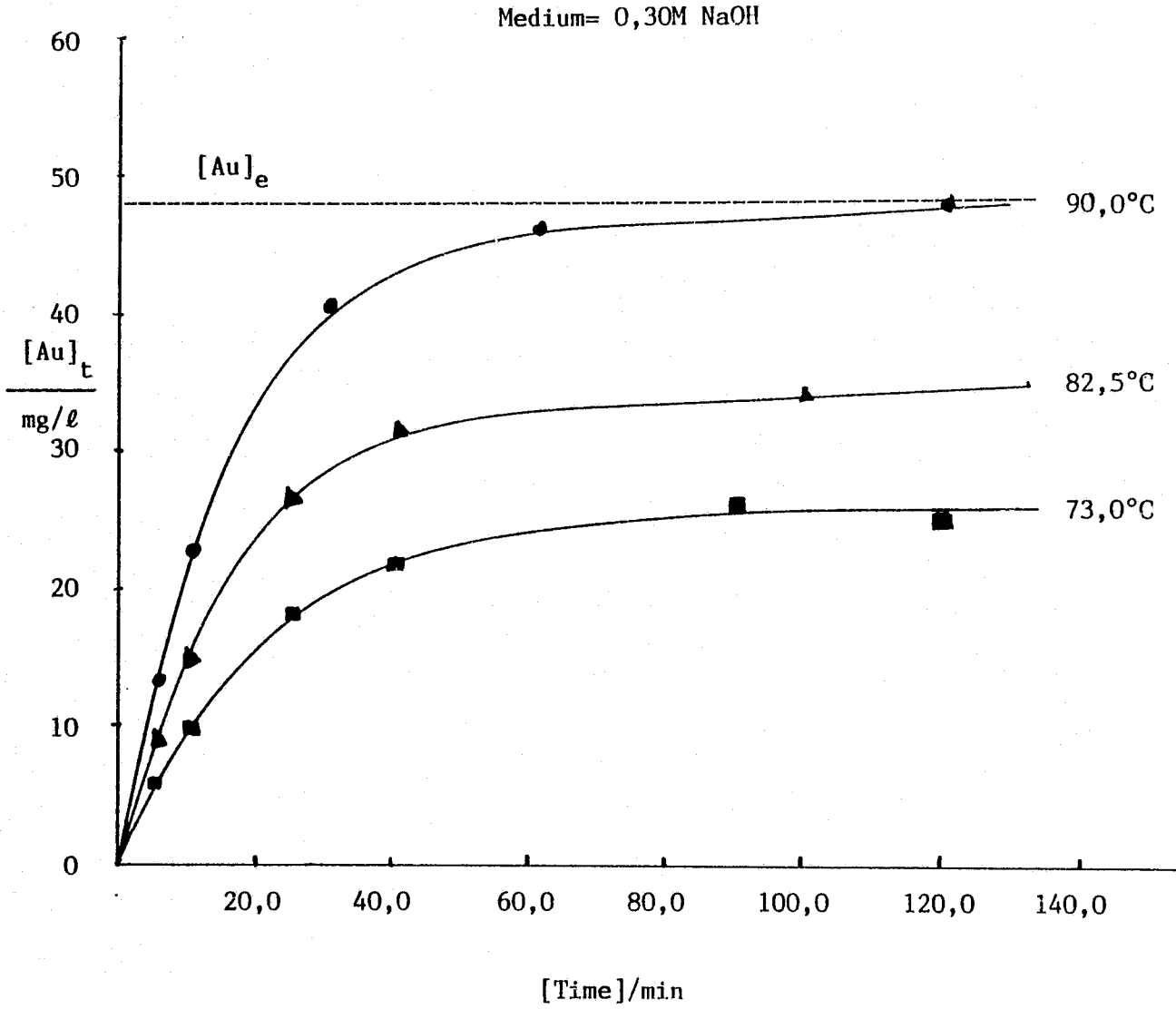
In the light of the new understanding of the interaction of aurocyanide with activated carbon, various factors which influence the desorption of gold were investigated. Emphasis was placed on carbons with low surface coverages where the specific type of adsorption mechanism is operative.

Carbons containing between 10 - 30 mg Au/g were prepared from solutions containing accurately known aurocyanide concentration in large excess of additive, thus ensuring the adsorption of the ion-pair on the carbon surface. The loaded carbon was then subjected to desorption whereby the influence of temperature, the initially loaded cation, the cation in the desorption medium, as well as the effect of various anions in the desorption medium was investigated. The effect of these parameters were investigated with respect to the rate and equilibrium of the process. Table 5.1 shows

Rate of Aurocyanide Desorption from Carbon Fig. 5.1

Initally loaded to 10mg/g

Medium= 0,30M NaOH



the additives used in the adsorption and desorption media used in this series of experiments.

Table 5.1
Additives used in the adsorption and desorption medium

Adsorption medium	Elution medium
MCl M = H^+,Li^+,Na^+,K^+,Cs^+	MOH M^+ = Li^+,Na^+,K^+
MCl_2 M = Ca^{2+}	MCN M^+ = Na^+,K^+
No additives	MSH M^+ = Na^+

5.2 Results and discussion

i) Factors influencing the rate of desorption in hydroxide medium

The rate of desorption of aurocyanide from carbon was followed with respect to time at constant temperature. Fig.(5.1) shows the appearance of gold in solution with respect to time for carbon loaded to 10mg Au/g and eluted with 0,30M NaOH. The desorption of gold was investigated over a temperature range between 60-95°C. The desorbed gold was characterized to be the aurocyanide species via its characteristic UV spectrum.

The rate data was found to obey first order kinetics and is described by the following mathematical function -

$$[Au]_t = [Au]_e \ (1-e^{-kt}) \qquad (5.1)$$

where

$[Au]_t$ = gold concentration mg Au/ℓ at time t

$[Au]_e$ = equilibrium gold concentration

k = rate constant

t = time in minutes

The desorption of gold from carbon was found to tend to an equilibrium value after approximately 100 minutes when $[Au]_e$ = constant, at constant temperature.

Rearranging equation 5.1 and taking logarithms, the linear form of the rate expression is obtained -

$$\ell n([Au]_e - [Au]_t) = -kt + \ell n[Au]_e \qquad (5.2)$$

The plot of $\ell n([Au]_e - [Au]_t)$ versus t is linear and has slope equal to -k and intercept $\ell n[Au]_e$. The rate constant at various temperatures was determined and the Arrhenius rate law was then applied.

where

$$k = Ae^{-E/RT}$$

and A = pre-exponential or frequency factor

E = activation energy of the process

Taking logarithms we obtain the linear form -

$$\ell nk = -E/RT + \ell nA \qquad (5.3)$$

A plot of ℓnk versus 1/T has slope equal to -E/R and intercept ℓnA.

ii) Effect of cation on the desorption of aurocyanide

The effect of temperature on the rate of desorption for various aurocyanide loaded carbons is shown in Figs. (5.2) , (5.3) and (5.4). The plot of ℓnk versus 1/T shows the effect of cation which is common to both adsorption and desorption medium.

The rate of desorption for this system depends on the cation and shows a general trend of increasing rate with decreasing polarization of the cation.

The activated energy E_a for the desorption of aurocyanide is shown in Table (5.2) , these values are approximate due to deviation from linearity. This may possibly be due to changes in the site energy with surface coverage. The activation energy E_a, for the desorption process suggests that the rate is governed by a truly chemical step.[84] The order of the activation energy is larger than that expected for difusion control in the aqueous phase. In addition to this, the rate was unaffected by better agitation.

Table 5.2
Effect of cation on the activation energy E_a and frequency factor for the desorption of aurocyanide

Cation	System	E_a kJmol^{-1}	A s^{-1}
Na^+	No add./NaOH	13,08	4,82
	NaCℓ/NaOH	15,65	11,44
K^+	NaCℓ/KOH	18,13	24,89
	KCℓ/KOH	15,20	8,88
Li^+	NaCℓ/LiOH	21,57	65,06
	LiCℓ/LiOH	18,17	22,11

Due to the observed curvature, the pre-exponential factor A is only an apparent one. However, a general trend is observed in that as the activation energy increases, the number of successful collisions or encounters decreases dramatically. This may be thought of as a caging effect[45,50] and is expected in the case of an ion or neutral molecules in a polar solvent.[45] Changes in polarity during the course of the action between solvent molecules, carbon surface and

Fig. 5.2 Graph of ℓnk versus 1/T for NaOH eluent

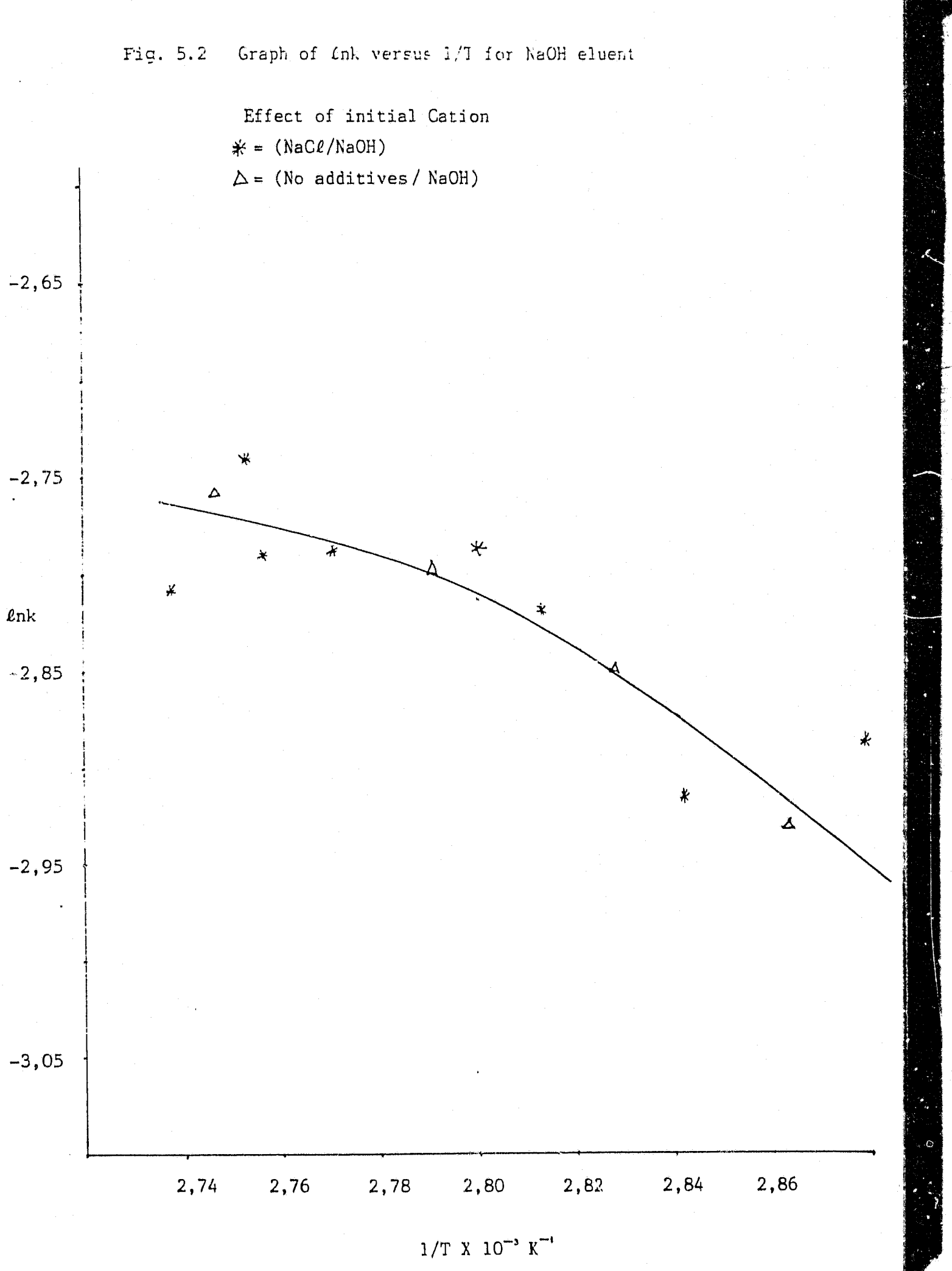


Fig. 5.3 Graph of ℓnk versus 1/T for KOH eluent

Effect of initial Cation

O = (KCℓ/KOH)

✱ = (NaCℓ/KOH)

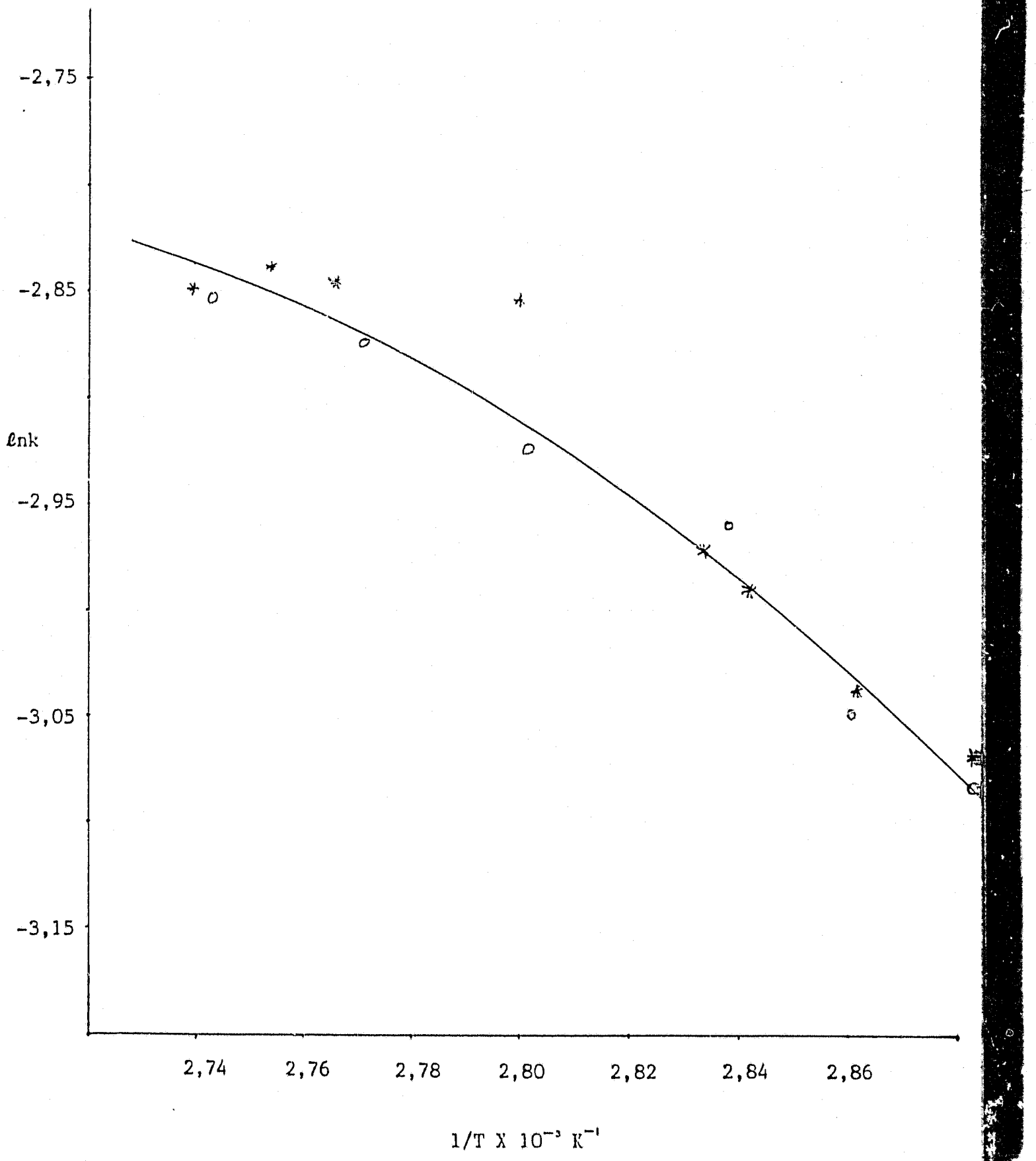


Fig. 5.4 Graph of ln k versus 1/T for LiOH eluent

Effect of initial Cation

△ = (LiCℓ/LiOH)

✳ = (NaCℓ/LiOH)

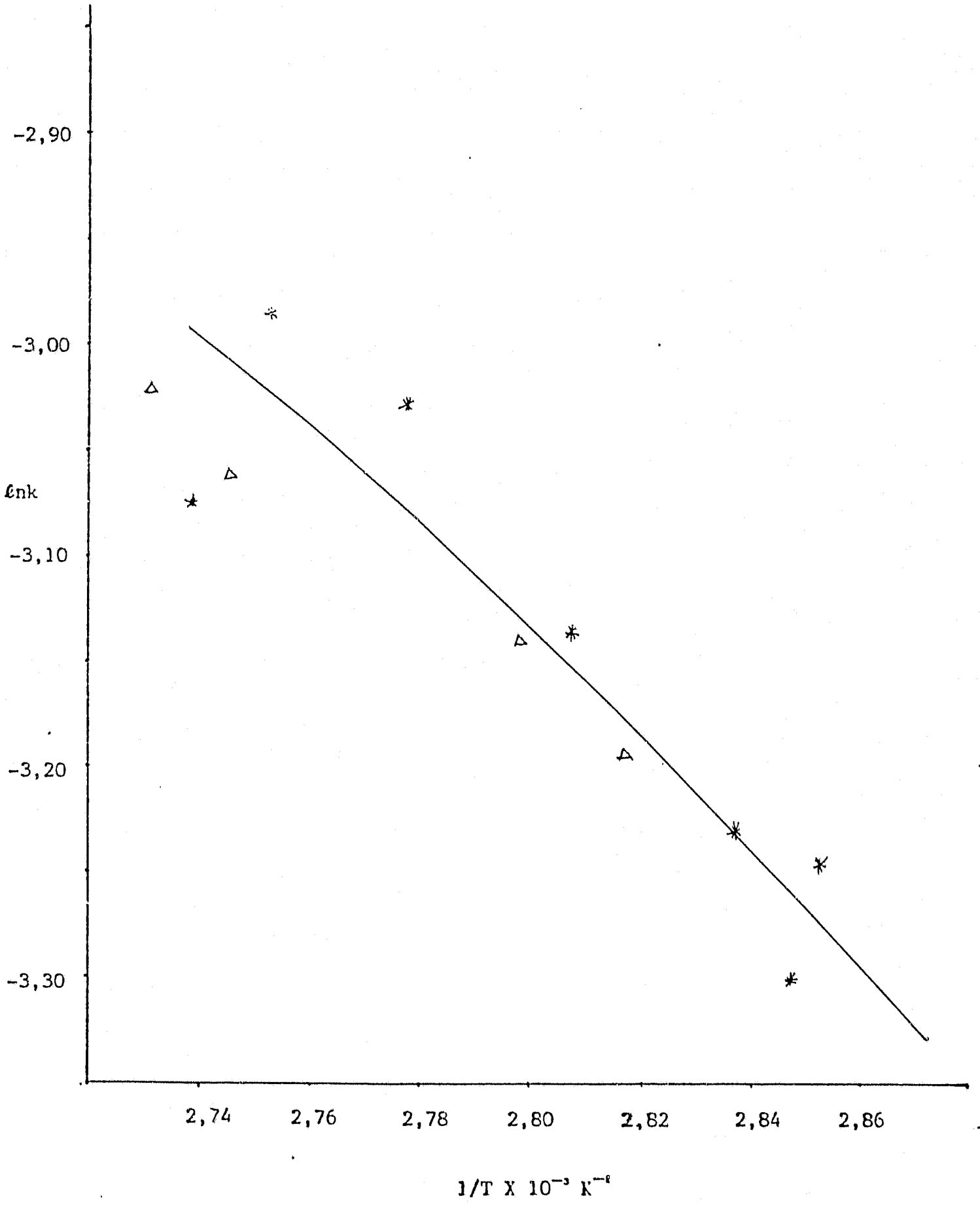
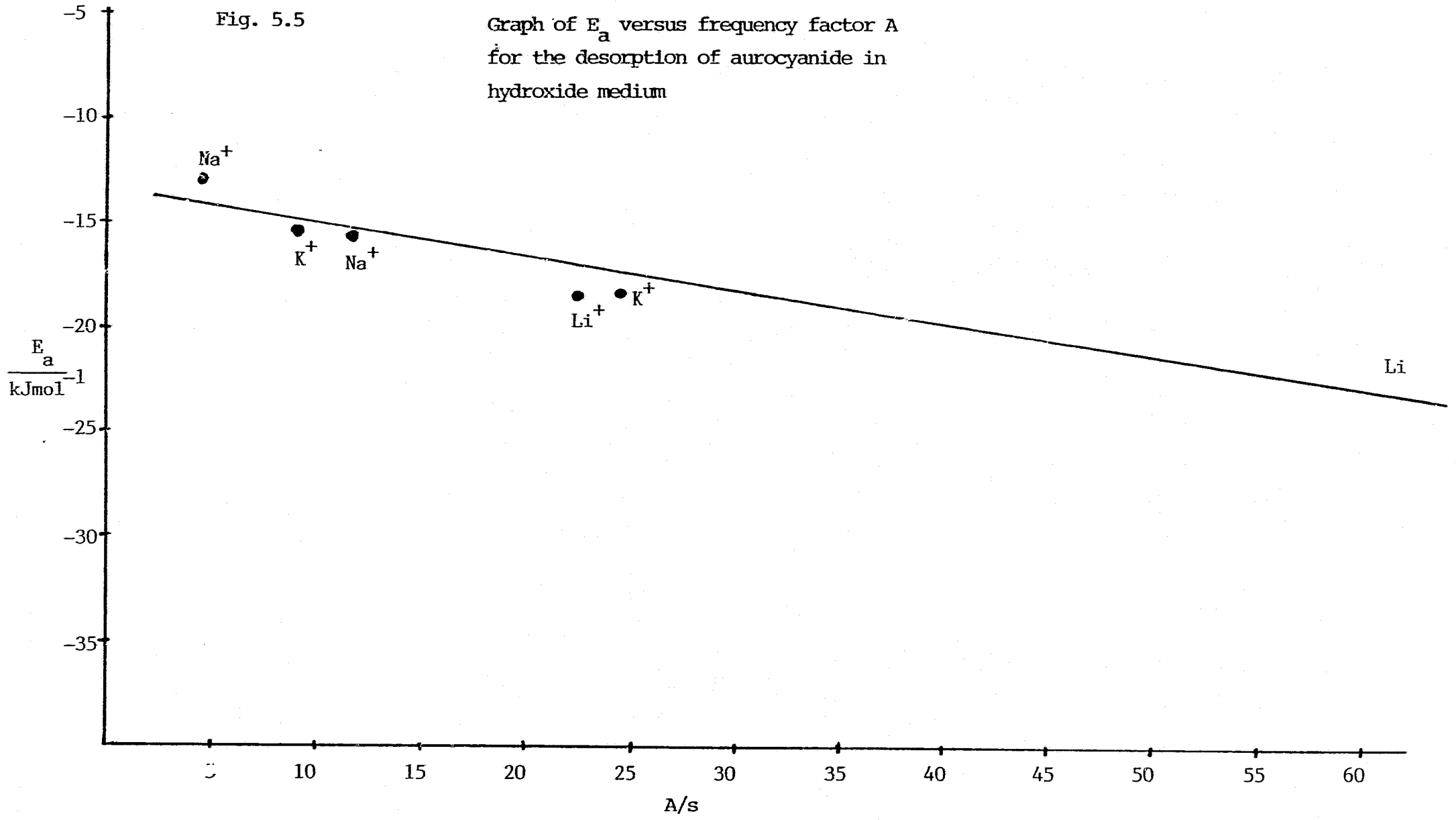


Fig. 5.5

Graph of E_a versus frequency factor A for the desorption of aurocyanide in hydroxide medium



the ion-pair will cause reorientation of solvent molecules which will affect the entropy of activation (i.e. pre-exponential factor). This is summarized in Fig.(5.5) where a plot of E_a versus frequency factor shows this effect.

The effect of the initial cation loaded on the rate of desorption is shown in Figs.(5.6) , (5.7) and (5.8). Superimposition of the curve in which the desorption medium is common to both is found and no effects due to the initial cation are apparent. The cation in the aqueous phase therefore determines the rate of desorption, which is probably due to the large concentration excess which would be expected to drive the cation exchange reaction postulated by Davidson.[35,37] The short lifetime of the ion-pair probably also has a role.

5.3 Factors influencing the equilibrium distribution of aurocyanide at low surface coverages

At equilibrium when $[Au]_t = [Au]_e$, the distribution of aurocyanide between the aqueous phase and the carbon phase was found to be dependant on the temperature, the cation, and the anion of the desorption medium. By varying one parameter at a time, the effect of that parameter on the system was determined using the Nernst distribution coefficient which is given by -

$$K_D = \frac{[\text{mg Au/g}]_e}{[\text{mg Au/}\ell]_e}$$

The analysis of the gold in solution at constant temperature enables the calculation of the distribution coefficient by difference since the initial gold loading is accurately known.

5.4 Results and discussion

i) Effect of temperature

The effect of temperature on the distribution ratio allows for the calculation of the enthalpy of the adsorption/desorption process by the application of the Van't Hoff relationship -

where $\Delta G = -RT\ell nK_D$

and $\Delta G = \Delta H - T\Delta S$

$\therefore \quad \ell nK_D = \frac{-\Delta H}{RT} + \frac{T\Delta S}{R}$ (5.4)

where ΔH = enthalpy for the adsorpted aurocyanide species

and ΔS = entropy for the process

A plot of ℓnK_D versus $1/T$ has slope = $-\Delta H/R$ and intercept = $\Delta S/R$

Fig. (5.6) shows the effect of temperature on the distribution of aurocyanide between the aqueous and carbon phase for carbons which were initially loaded to 10mg Au/g. The desorption medium contains 0,30M hydroxide and the Van't Hoff plot for the system is linear in the lower temperature range for the various cations investigated. As the temperature increases, deviations from linearity are observed and show that the heat of adsorption is not constant for this region of surface coverage. The initial heat of adsorption is of the order of -40 $kJmol^{-1}$ and increases to approximately -80 $kJmol^{-1}$ at lower surface coverages. For each hydroxide system investigated, a distinct curve is observed each associated with the cation in the hydroxide medium.

Fig. 5.6
Effect of Temperature on distribution of $Au(CN)_2^-$ for Hydroxide eluents

Graph of ℓnK_D versus 1/T

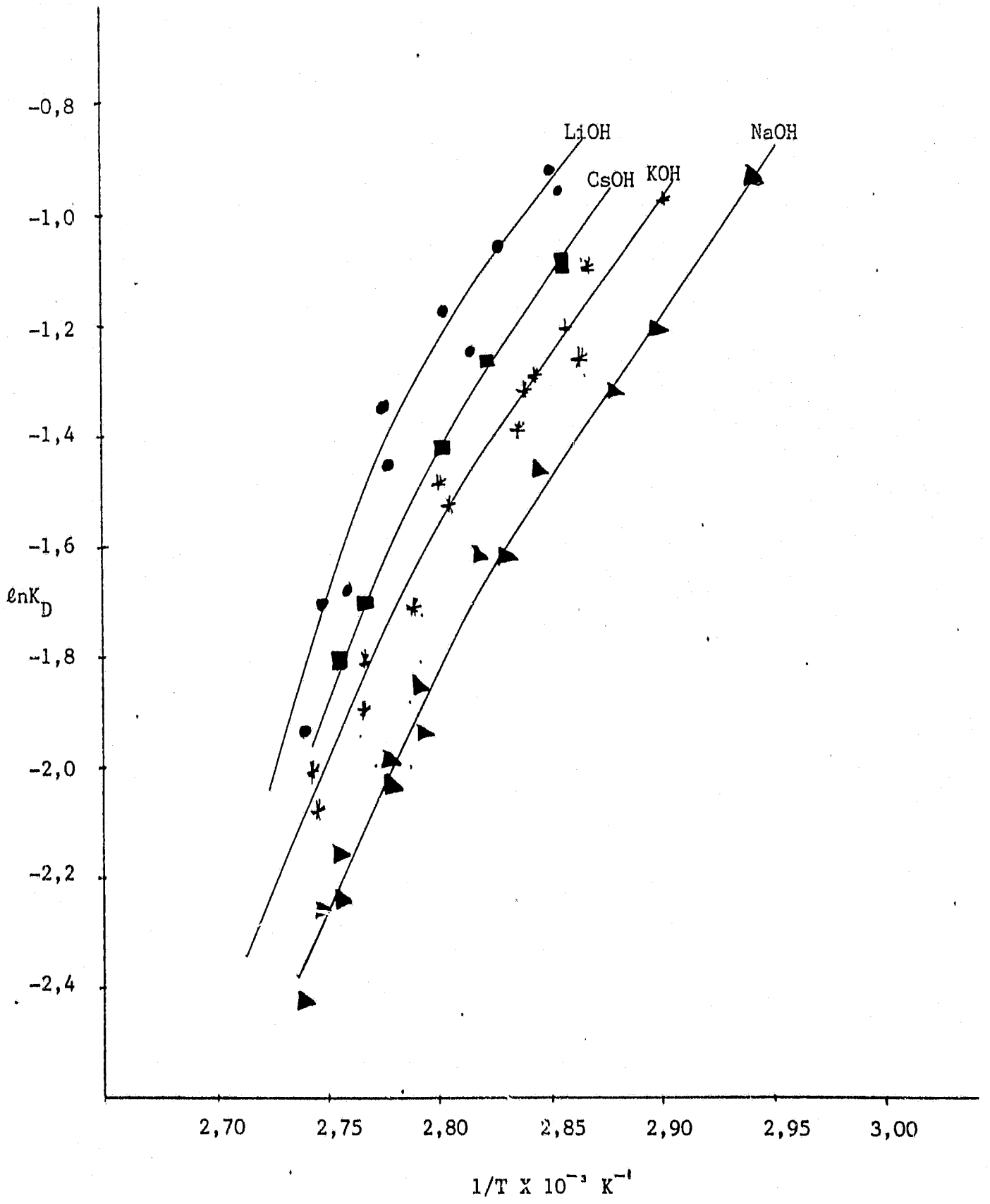


Fig. 5.7 Graph of ℓnK_D versus 1/T for CsOH medium

● = Heating
▲ = Cooling

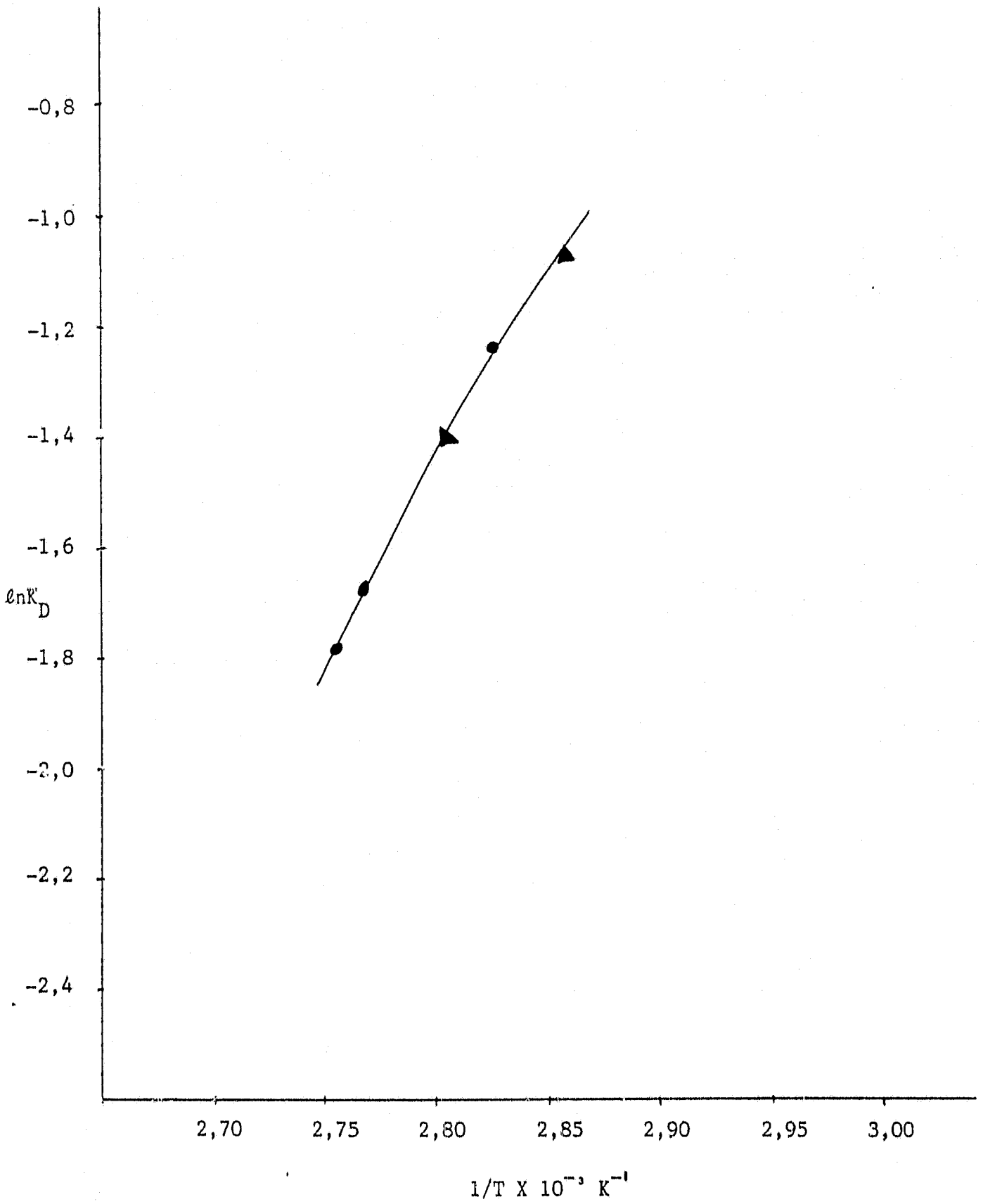


Fig.(5.7) shows the effect of heating and cooling on the distribution coefficient for the CsOH system. No hysteresis was found by increasing or decreasing the temperature, which implies that the equilibrium is a reversible one.

ii) Effect of cation on distribution coefficient of aurocyanide

Fig.(5.8) shows the equilibrium distribution of aurocyanide between aqueous and carbon phase at constant temperature versus the cationic radius for some group IA hydroxide media investigated. The characteristic U-curve shows that the distribution is dependent on the cation and, as previously found, two trends are apparent-

$$Li^+ > Na^+ \qquad 1.$$

$$Cs^+ > K^+ > Na^+ \qquad 2.$$

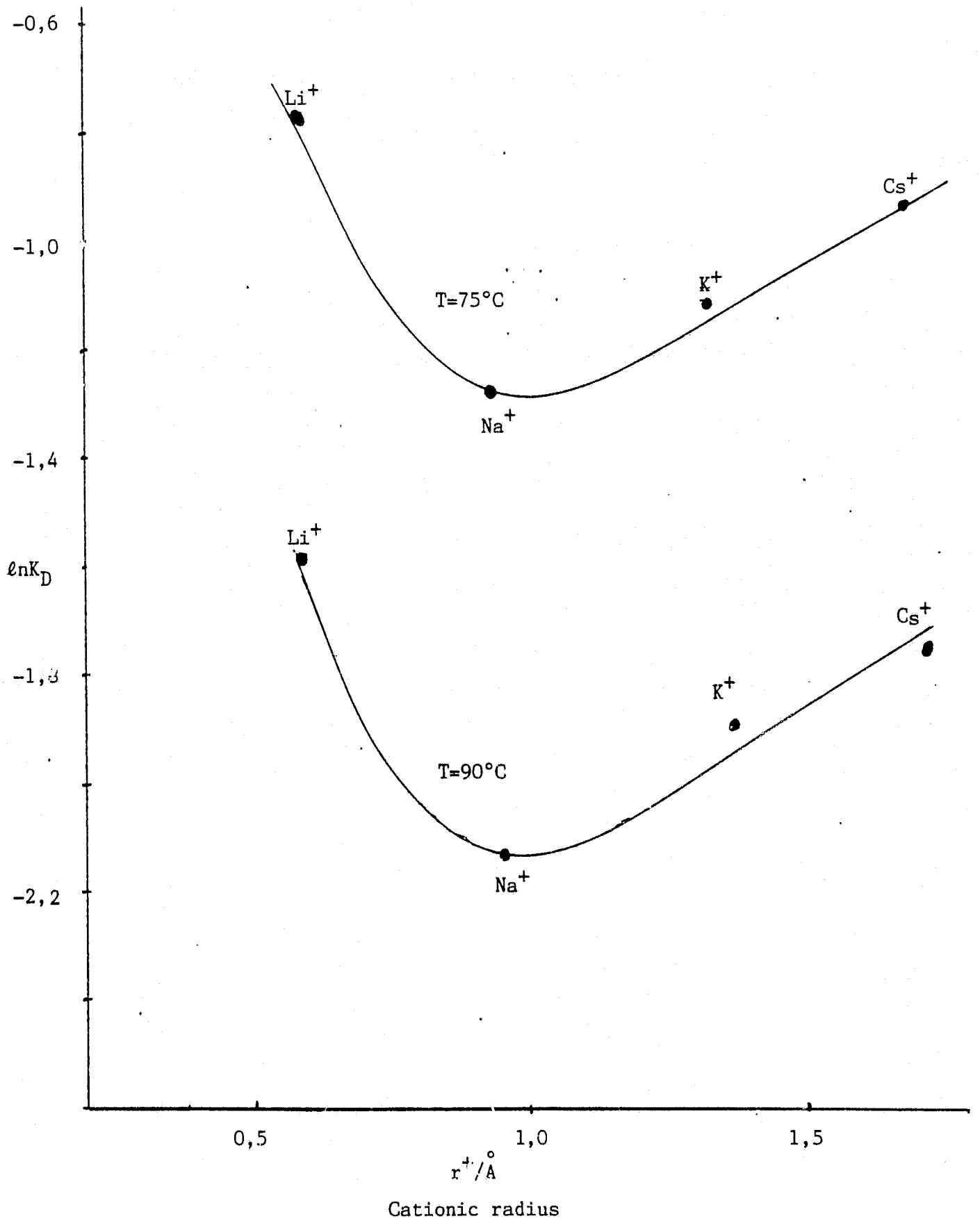
The effect on the distribution of aurocyanide by the cation must be due to the assocation or ion-pair formation at the carbon surface. The equilibrium reaction may be written -

$$\overline{MAu(CN)_2} \rightleftharpoons M^+ + OH^- \rightleftharpoons M^+ + Au(CN)_2^-$$

Where M^+ is the cation of the hydroxide medium which largely determines the distribution coefficient between the aqueous phase and the carbon phase.

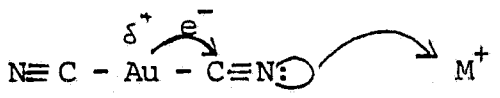
Trend 2 can be understood in terms of the hydrophobicity of the large ion-pair where such poorly hydrated ion-pairs would prefer the carbon phase. The trend for the small hydrophilic cations, however, cannot be rationalized by these arguments, and must involve a specific interaction between the carbon surface and the polarized ion-pair.

Fig. 5.8 Graph of ℓnK_D vs. r^+ at constant Temperature

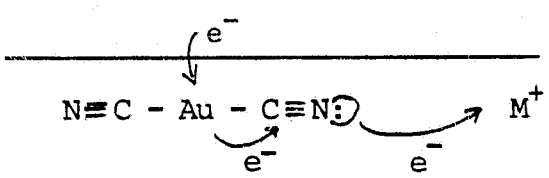


The order of affinity for the carbon phase $Li^+ > Na^+$ (and presumably the H^+ cation would follow this trend if it were not unstable) can only be explained by the polarizability of the cation and the resulting interaction with the aurocyanide anion and the carbon surface.

These polarizable Lewis acids may accept electron density from the aurocyanide anion via the gold-carbon bond of the polarizable cyanide ligand, thus rendering the gold atom positive.



The positive centre of the ion-pair can be stabilized by accepting electron density from the carbon surface thus forming a donor/acceptor complex.



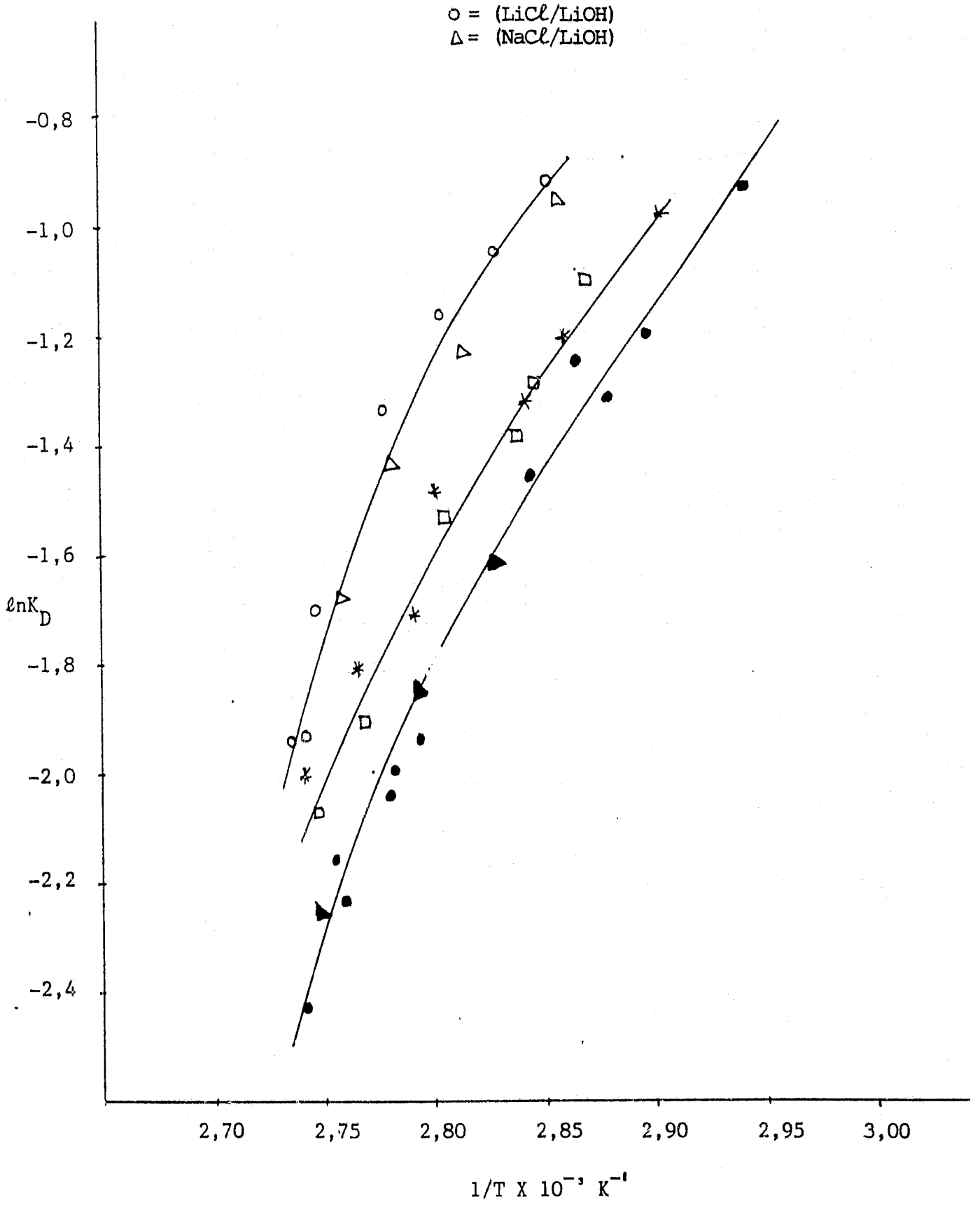
This type of specific adsorption between the aurocyanide ion-pair and the carbon surface stabilizes the adsorbate up to gold loadings of 40mg Au/g.

For the large hydrophobic ion-pairs, the trend for increasing distribution onto carbon is expected with the formation of increasingly hydrophobic ion-pairs with increasing size.

Fig. (5.9) shows the effect of the initial cation loaded on the distribution of aurocyanide in various hydroxide media, where no effects due to the initial cation are found. The equilibrium therefore depends on the cation present in large excess in the aqueous phase as expected.

Fig.5.9 Effect of initial cation on the equilibrium distribution of aurocyanide

● = (NaCℓ/NaOH)
▲ = (No additives/NaOH)
✱ = (KCℓ/KOH)
□ = (NaCℓ/KOH)
○ = (LiCℓ/LiOH)
△ = (NaCℓ/LiOH)



The energetics of ion-pair formation suggests that the enthalpy of the interaction is small because of the water molecules separating the charged species.[79] The main driving force for ion-pair or association reaction must be due to a large favourable entropy changes from the loss of hydration.[80] The hydrated cation produces an ordering effect on the solvent, when complex formation occurs, hydration of the cation is lost, which must result in an increase of the disorder of the system.[81] Entropies depend more than enthalpies on changes in size and sign of charge. Thus entropy favours the solubility of salts containing large ions of low charge.

The effect of specific cation on the system is further demonstrated in Fig. (5.10) where the desorption of aurocyanide in aqueous ammonia is shown with respect to time. The reflux condenser was removed after about 40 minutes which resulted in the readsorption of aurocyanide, due to the reduced concentration of the ammonium cation according to the following equilibrium -

$$NH_3^+ + OH^- \rightleftharpoons NH_3\uparrow + H_2O$$

iii) Effect of anions on the distribution coefficient of aurocyanide

Fig. (5.11) shows the effect of hydroxide and cyanide anions (as sodium salts) on the distribution of aurocyanide between aqueous phase and carbon phase for the temperature range between 60 - 95°C.

The large concentration of cyanide anions (I = 0,30 M) depresses aurocyanide adsorption. The Van't Hoff plot for this system is linear for the temperature range investigated and the heat of adsorption is of the order of -40 $kJmol^{-1}$. This indicates that a chemisorption or a specific interaction occurs between the aurocyanide ion-pair and the carbon surface.

Author Kyriakakis G
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