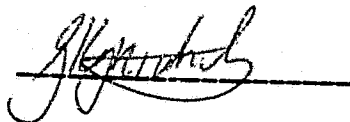An Investigation into Activated Carbon

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

Acknowledgements

An Investigation into Activated Carbon

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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 character-
istics 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 investi-
gated 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
concern 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 hydro-
phobic 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 hydro-
phobic 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 -

$$C_s + H_2O_g \longrightarrow CO_g + H_{2\ g} \qquad \Delta H = 206 \text{ kJmol}^{-1}$$
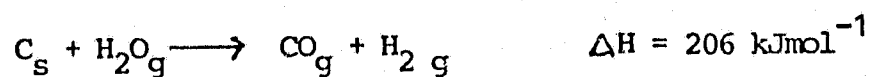
The use of air or molecular oxygen results in a
marked mass loss at lower temperatures which probably
involves the overall reaction shown below -

$$C_s + O_2 \longrightarrow CO_{2\ g}$$
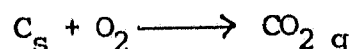
The more reactive portions of the carbon matrix are
preferentially burnt off which further increases the
surface area and pore volume.   According to Dubinin[12]
the pore size distribution of activated carbon may be
divided into three groups.   Macropores (1000 - 2000 Å)
effectively contribute little 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 tha' 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]
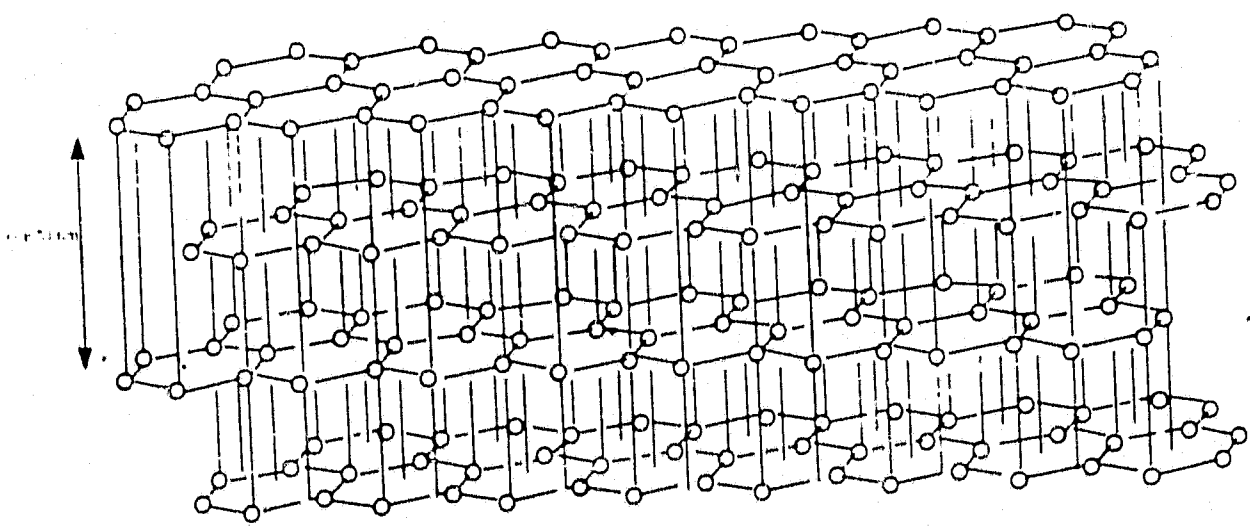
Fig. 1.1 a)   Schematic representation of the structure
              of graphite.   The circles denote the
              positions of carbon atoms, whereas the
              horizontal lines represent carbon-carbon
              bonds.
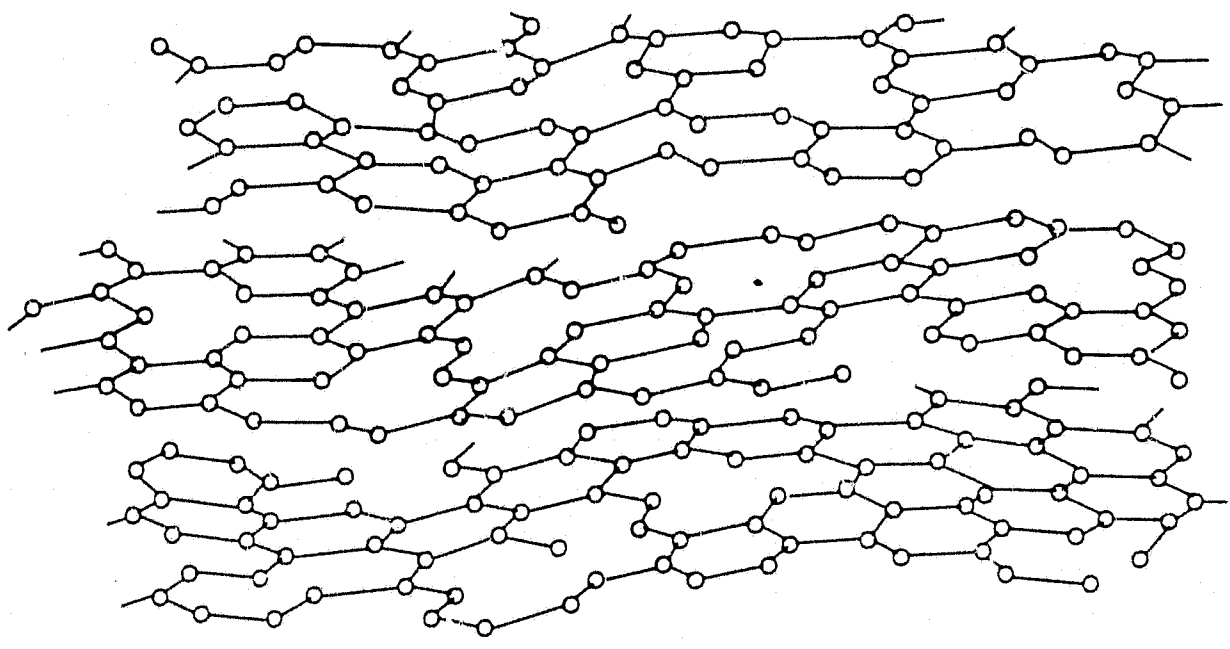
Fig. 1.1 b)   Schematic representation of the proposed
              structure of activated carbon.
              Oxygen-containing organic functional
              groups are located at the edges of
              broken graphitic ring systems.   (After 5)

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 electro-
chemical 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
$Hg(I) + Fe(II) \longrightarrow Hg + Fe(III)$	ClO_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	''
	HCl	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 -

$$CN^- + C(O_2) \longrightarrow CNO^-$$
$$\downarrow$$
$$CO_3^{2+} + NH_3$$
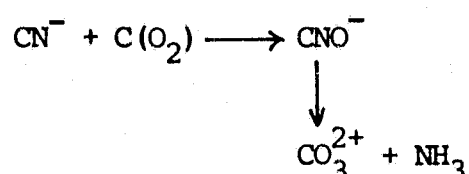
Although this mechanism has not been fully proven
it probably involves a reaction with physisorbed
dioxygen and seems to be continuous, provided that
air is bubbled through the mixture.[40]

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   ransfer 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/race-
mization 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 -

$$Cl0_4^- > NO_3^- > SO_4^{2-}$$
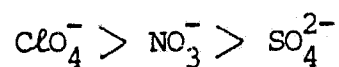
This trend shows that the larger more hydrophobic
ions effectively compete for the cation in solution
to form ion-pairs, thus decreasing the concentration
of ion-pairs at the carbon/aqueous interface. This is
reflected in the retardation·of the rate of racemization.

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

$$Cl0_4^- > SO_4^{2-} > F^- \qquad \text{(as sodium salts)}$$

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 -

$$SCN^- > I^- > NO_3^- > Br^- > C\ell^- > SO_4^{2-}$$
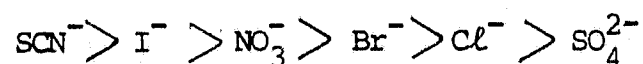
The order of enhancement can be understood assuming the adsorption of ion-pairs or neutral acid-base complexes by carbon. The trend reflects the preference for ion-pairs of low charge and large size (Traube's rule).

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 -

$$H^+ > Al^{3+} > Ca^{2+} > Li^+, Na^+, K^+$$
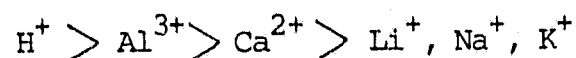
The trend for anion extraction is given by the
series -

$$NO_3^- > Cl^-$$
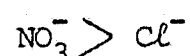
Similarly Snoeyink and Weber[30] reported the following
trend for the adsorption of anions by carbon -

$$ClO_4^- > NO_3^- > SO_4^{2-} > Cl^-$$
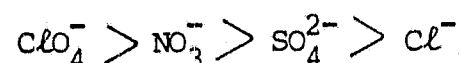
Thus the adsorption is favoured by the formation of
ion-pairs of large size and increasing polarizability.
The larger and therefore more poorly hydrated ion-pairs
show a larger capacity for extraction into the carbon
phase due to increased hydrophobicity.

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 X40W.   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 determind 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
Υ (C≡N) and Υ (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 stopcock 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 distri-
bution 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 investi-
gated 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 equili-
brium 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 ± 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 predeter-
mined 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 tempera-
tures 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 spec-
troscopy.   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 hydro-
sulfide 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]
$\left[M^{m+}\right]\left[Au(CN)_2\right]_n$.

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 -

$$Ca^{2+} > Mg^{2+} > H^+ > Li^+ > Na^+ > K^+$$
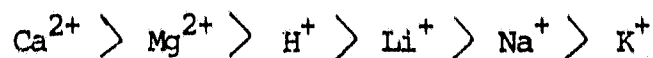
In addition to the so called cation effects McDougall
et al.[24] found that the ionic strength (I) of the additive
also influenced the equilibrium aurocyanide adsorption.

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 and hydrosulfide medium.[23][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 -

$$M^+_{aq} + Au(CN)^-_{2\,aq} \rightleftharpoons \overline{[M^{n+}][Au(CN)_2]}_n$$
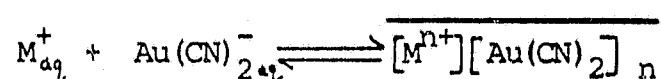
The enhanced loadings observed due to increasing
ionic strength and therefore cation concentration,
shifts the equilibrium to the right hand side as
expected by Le Chatelier's principle.   The depression
of aurocyanide adsorption by anions is probably due
to competition for the cation. The equilibrium 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[24]
changes with surface loading. McDougall et al. 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 $\overset{o}{A}^2$ 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[43] by the Nernst distribution law 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 ∼0,20M after which further additions cause no further
enhancement.   This behaviour is expected by equilibrium

considerations and may be expressed by LeChateliers
principle. The adsorption may be written as -

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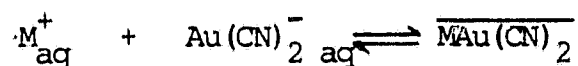
where $K_D = \dfrac{\overline{MAu(CN)_2}}{[M^+][Au(CN)_2^-]}$

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.

1.i) 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 $\ell n K_D$ 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
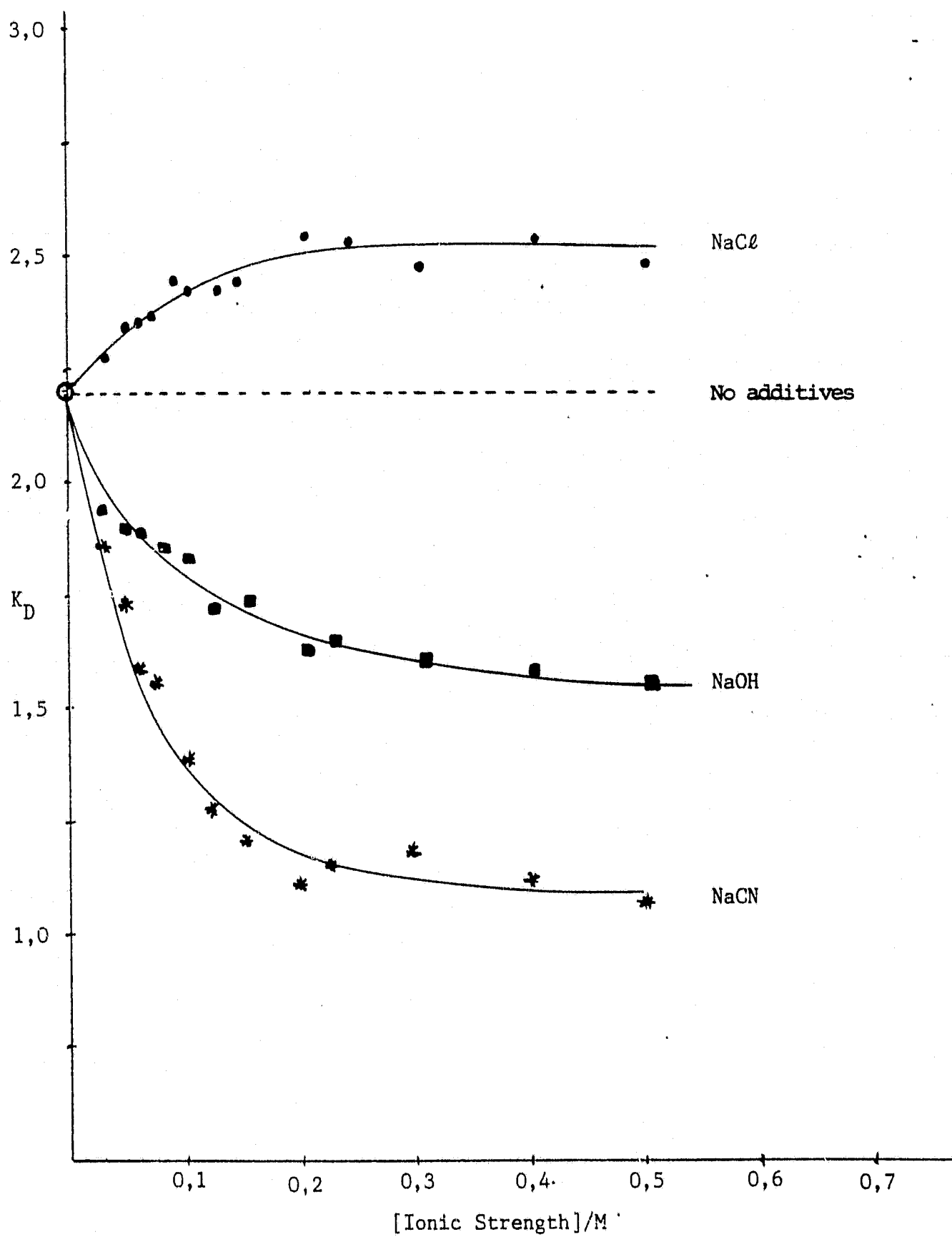
Fig. 3.2

Effect of Cation on Aurocyanide Distribution
in various Ionic Media by Activated Carbon
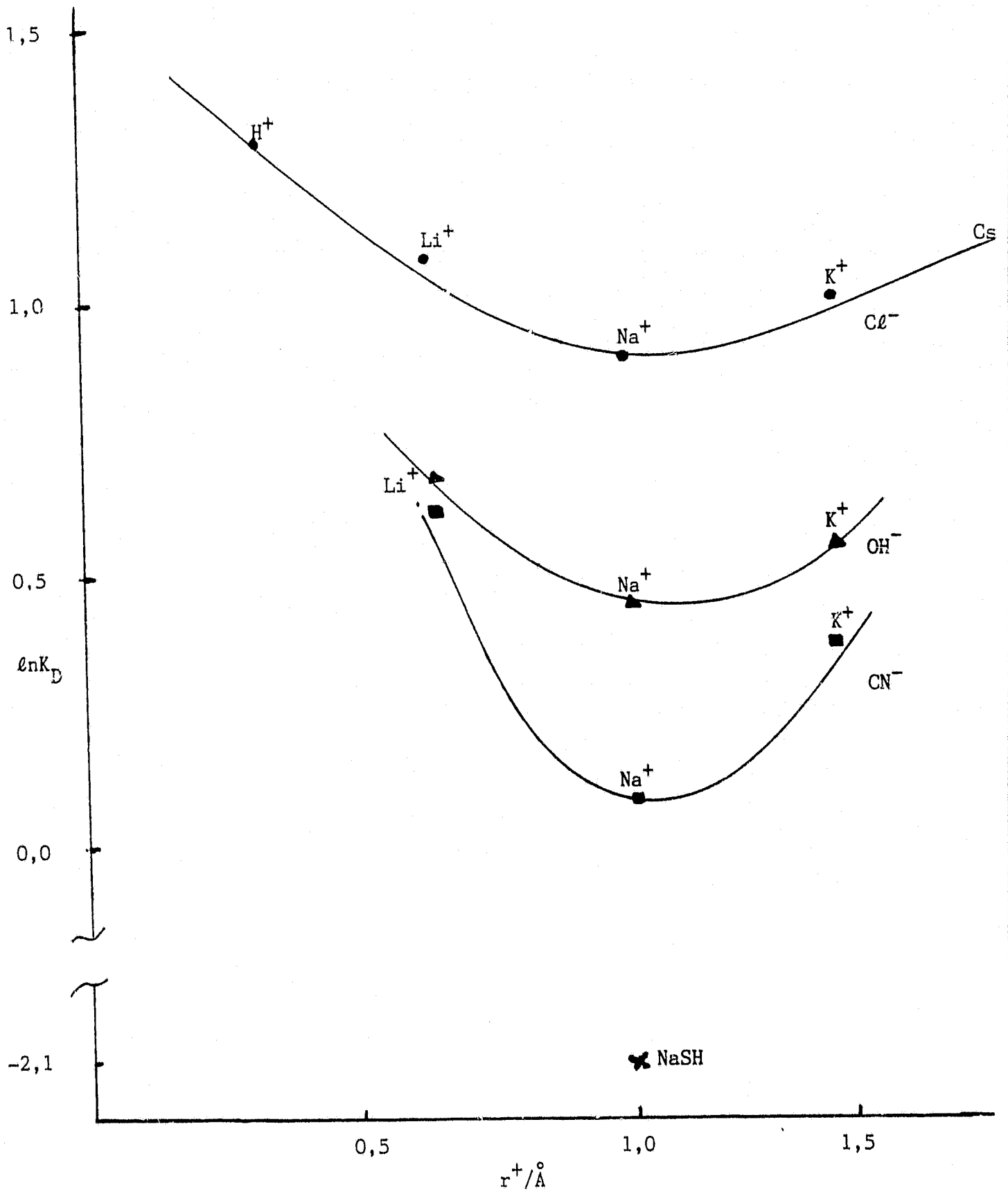
The observed U-shaped curve has a minimum at Na^+ and can be divided into two parts. The left hand side shows that increasing crystallographic radius of cation $(H^+ \longrightarrow Na^+)$ causes a decrease in the extraction coefficient, whereas the right hand side shows that an increasing cationic radius 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:

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

As the Lewis acidity of the cation increases, the fundamental bands of the aurocyanide ion, $\gamma(Au-C)$ and $\gamma(C\equiv N)$ 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 -

$$\text{carbon} \quad N\equiv C - \overset{\delta^+}{Au} - C\equiv N \quad M^+$$
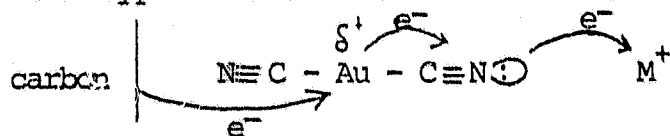
The observed trend for increasing extraction with increasing size of cation can be understood in terms of Traube's rule i.e. increasing hydrophobicity with increasing size. However, examination of the solubility trends for the aurocyanide species shows that the solubility increases with increasing cationic 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

▲ = symetric (Raman)
● = antisymetric (IR)

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

● NH_4^+
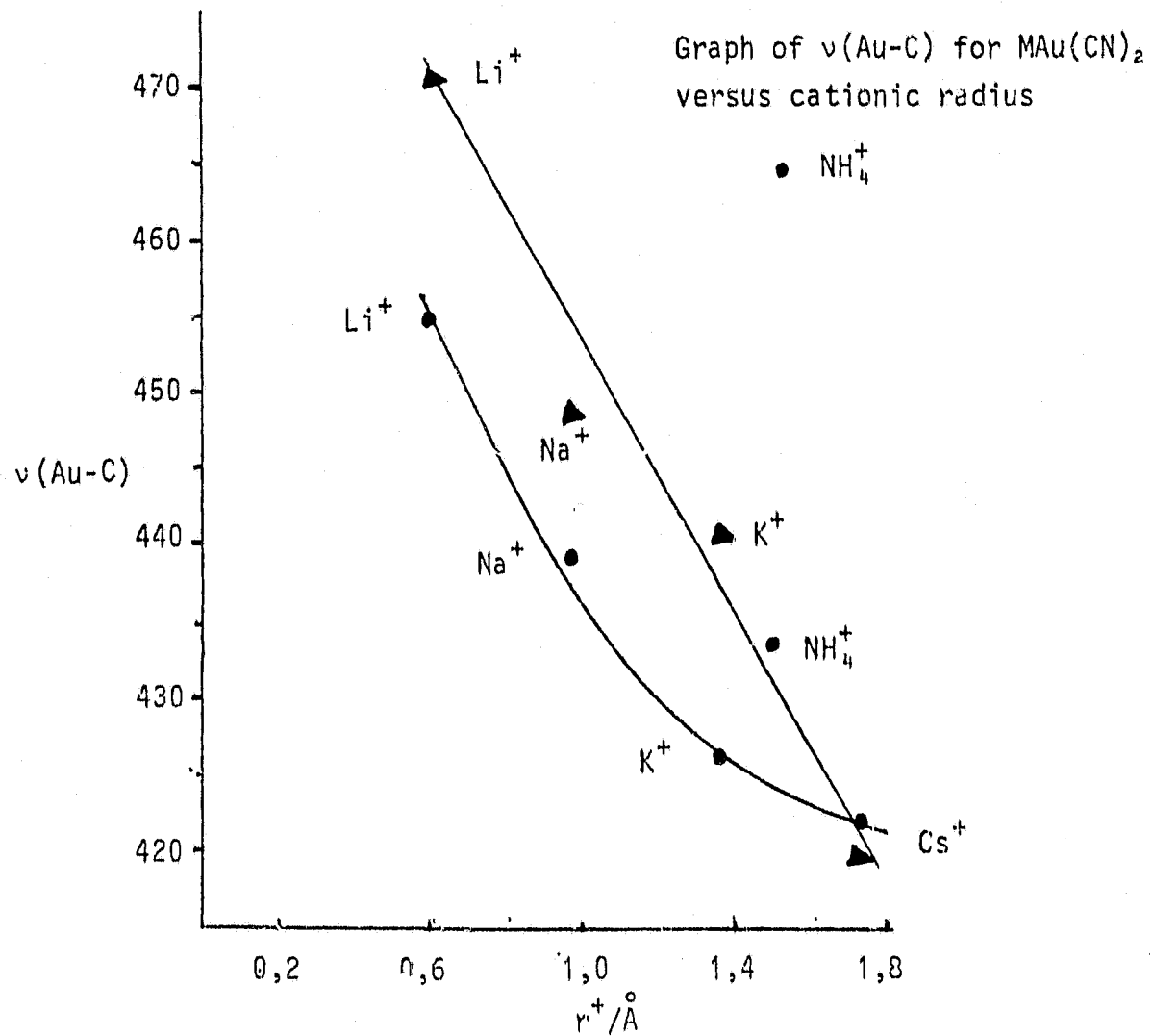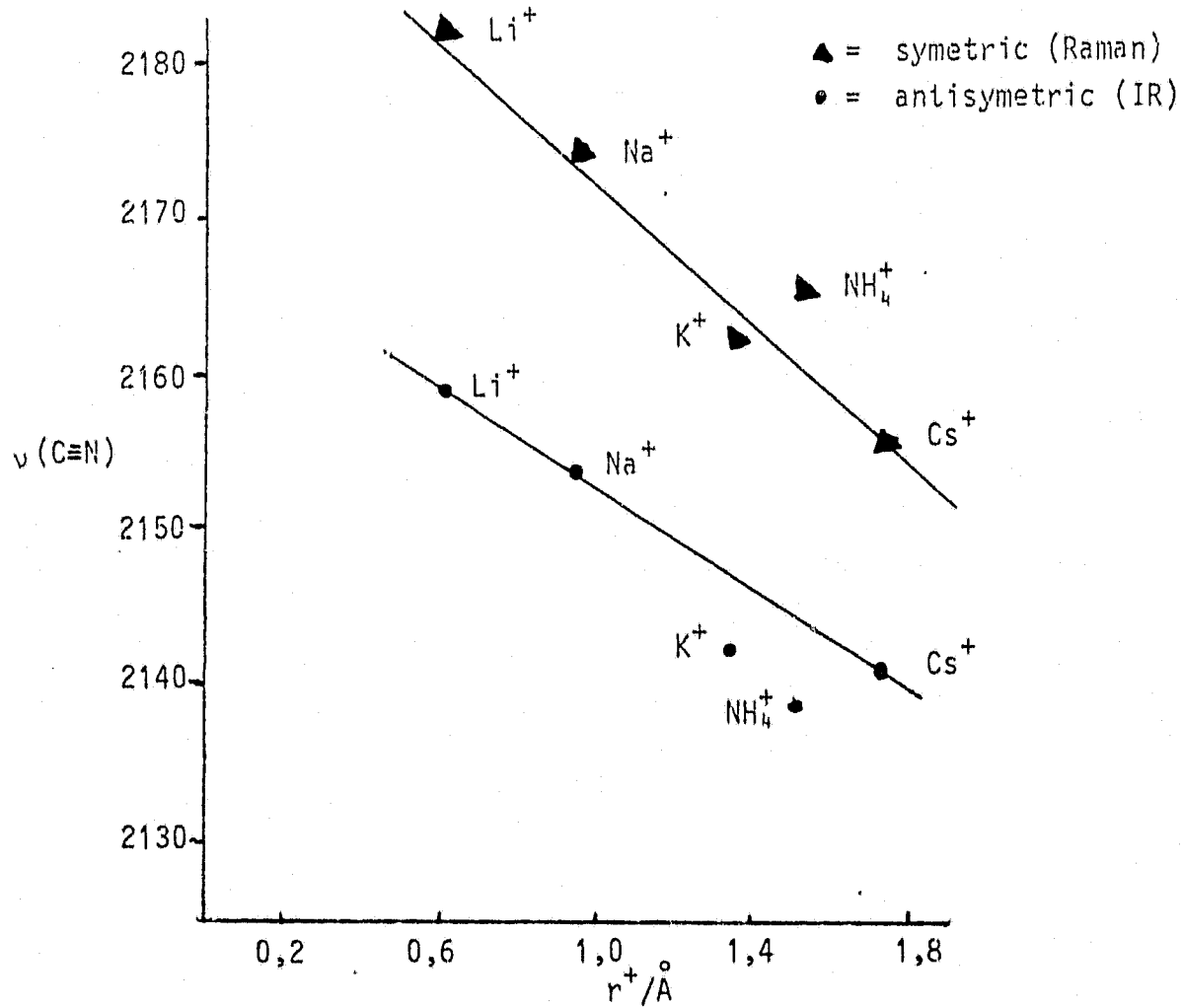
Table 3.1   Molar solubility of various aurocyanide
             salts

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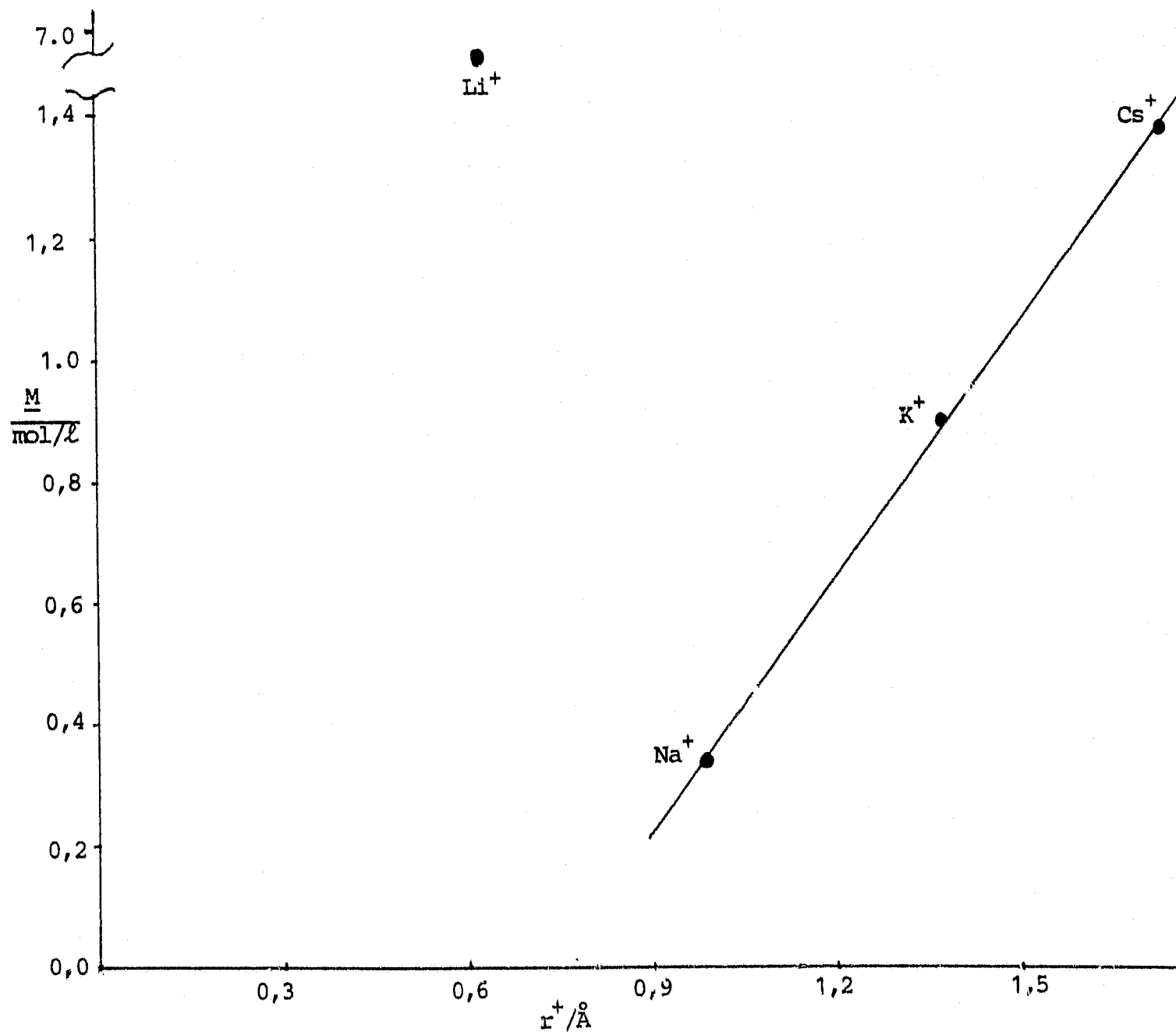
The solubility of a salt is strictly determined by the free energy of solution ΔG_s which may be approximated by the following electrostatic expression.[47]

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

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

$$Li^+ > Na^+ > K^+ > Cs^+$$
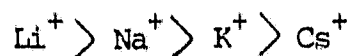
The solubility trend $Li^+ > Na^+$ is in fact observed and presumably the H^+ species would also follow this trend. However, the reverse solubility trend for the larger cations is experimentally observed. Explanation of such an effect is possible considering the form of the resulting ion-pair and its 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.

$$M^+(OH_2) + Au(CN)_2^- \rightleftharpoons M^+(OH_2)Au(CN)_2^- \rightleftharpoons MAu(CN)_2$$

$$\text{solvent} \qquad\qquad \text{contact}$$
$$\text{seperated} \qquad\qquad \text{ion-pair}$$
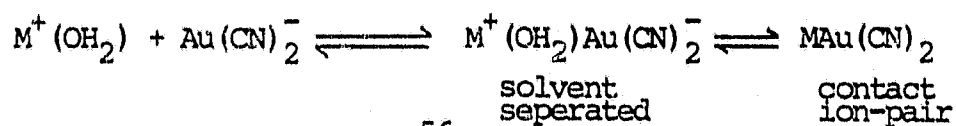
Although no spectroscopic[56] evidence has been found for contact ion-pairs or association reactions for the aurocyanide species in aqueous phase other than for the species $LiAu(CN)_2$,[58] it is probable that the solvent separated species exists in the aqueous phase. The degree of ion-pair formation 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 -

$$Cs^+ > K^+ > Na^+$$
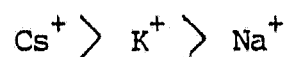
Thus these ion-pairs become increasingly soluble yet
paradoxically increasingly hydrophobic, which is reflected
by the order of extraction into the carbon phase.   The
entropy term therefore largely determines the free energy
of hydration for the large poorly hydrated aurocyanide ion.
Proof of this is 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:

$$Cl^- < SCN^- < OH^- < ClO_4^- < CN^-$$
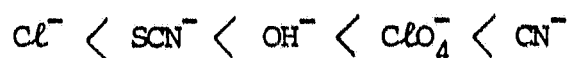
A similar depression due to the hydrosulfide anion[33,34,75]
has been reported, and the depressing effect of
the ClO_4^- ion has recently been redetermined by Adams.[41]

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	$\ell n K_D$
$C\ell^-$	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 $I \sim 0,20$ M. This behaviour is expected from LeChateliers 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 =	$\{Na^+\}$
$Ag(CN)_2^-$			
$Ni(CN)_4^{2-}$			
$Hg(CN)_2$	Equimolar ratios of $\left[Au(CN)_2^-\right] : \left[M(CN)_x^y\right]$		
$Cu(CN)_4^{3-}$			
$Fe(CN)_6^{3-}$			
$Ag(CN)_2^-$	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
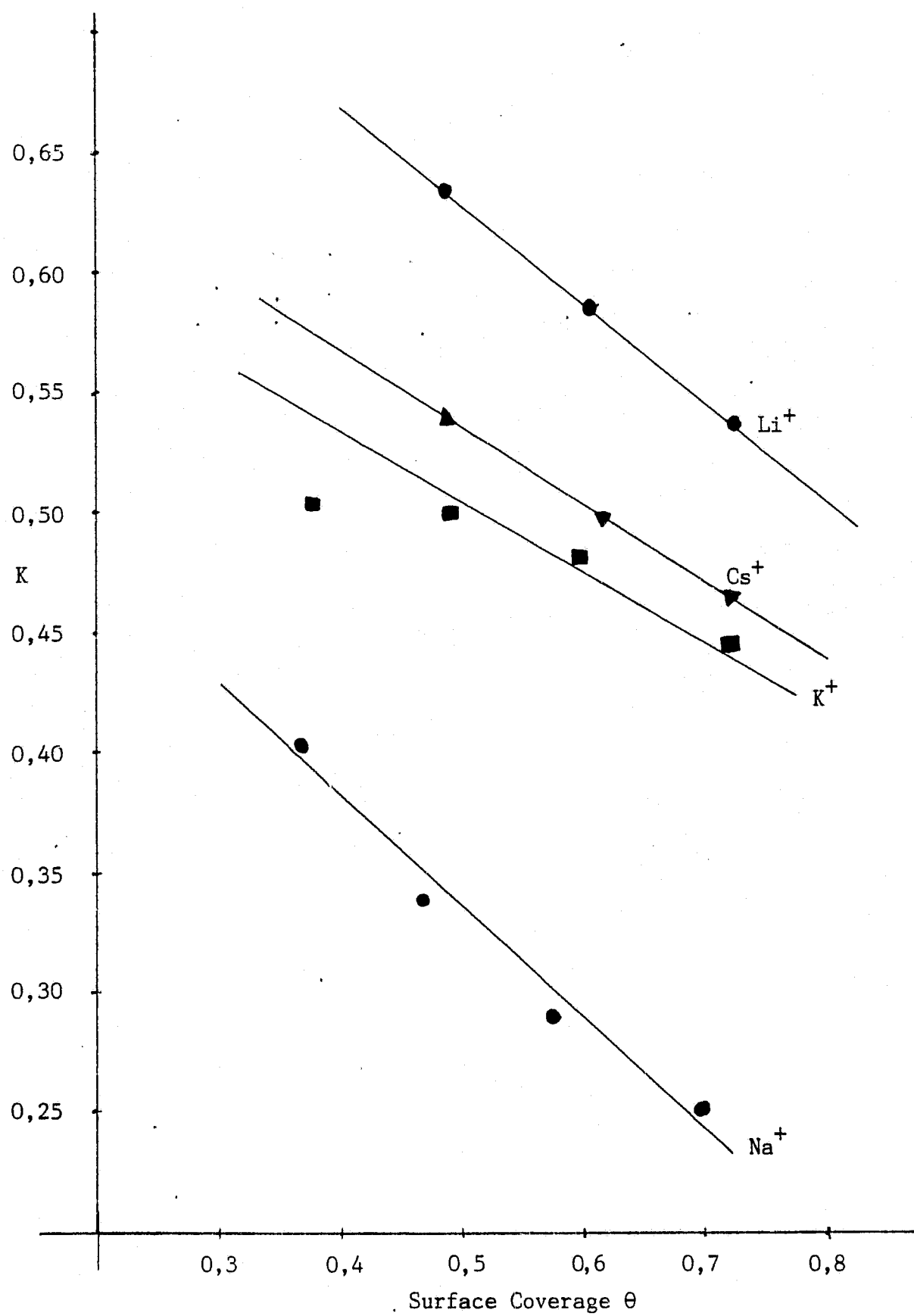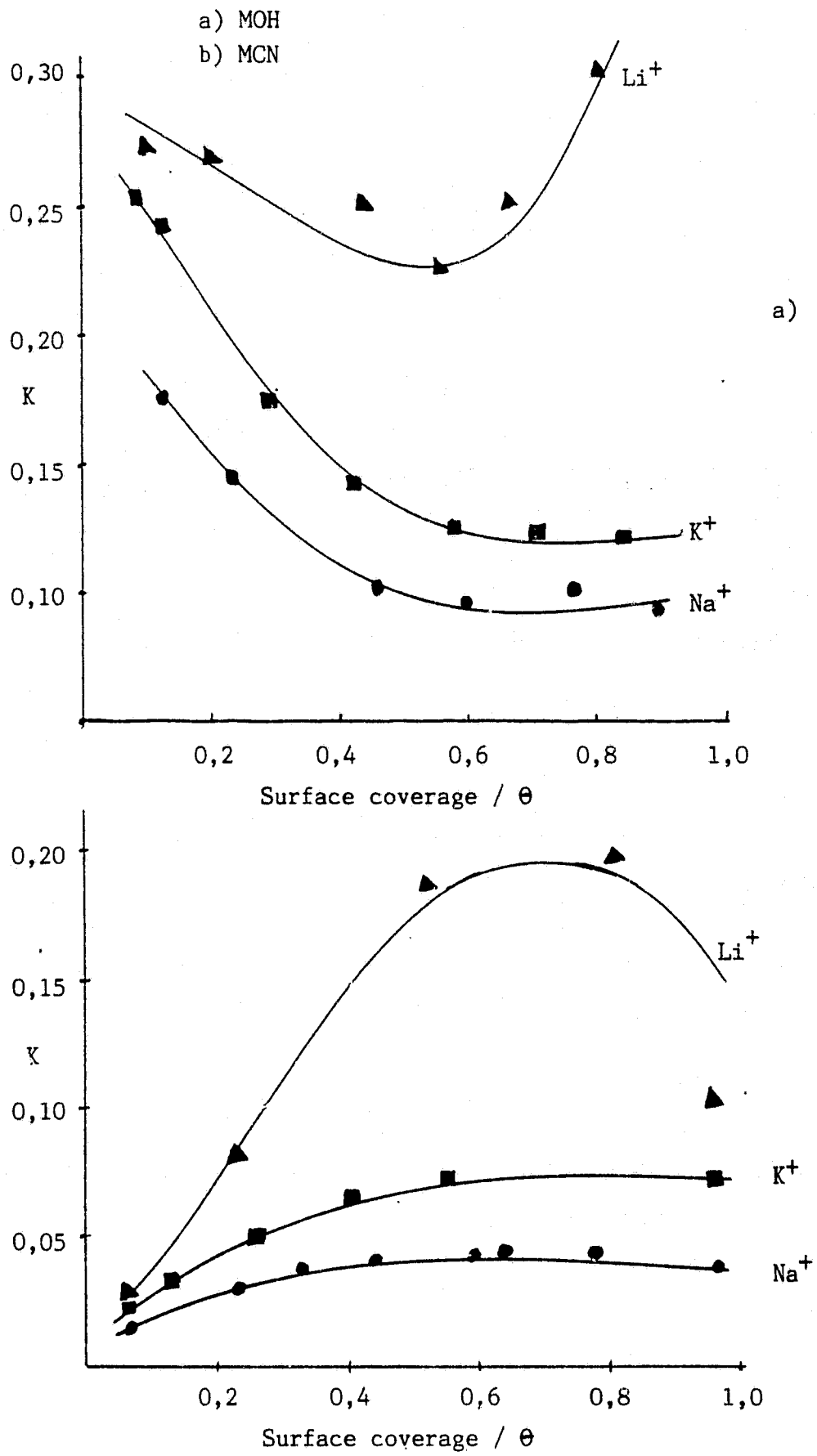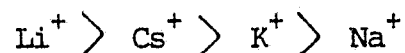
for Aurocyanide Adsorption in I=0,30M MCℓ

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)

Surface coverage / θ

Surface coverage / θ

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

$I = 0,30M\ MC\ell$
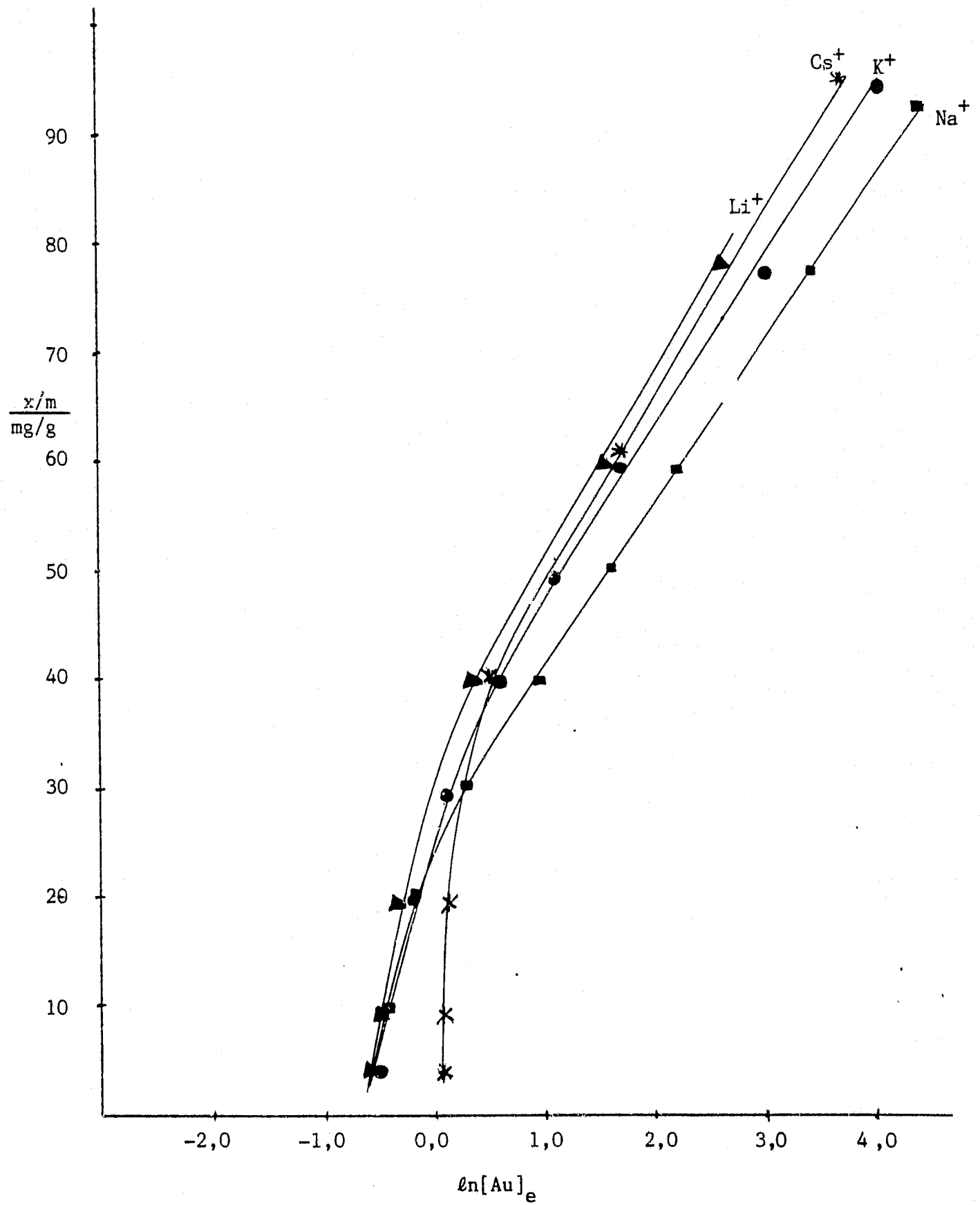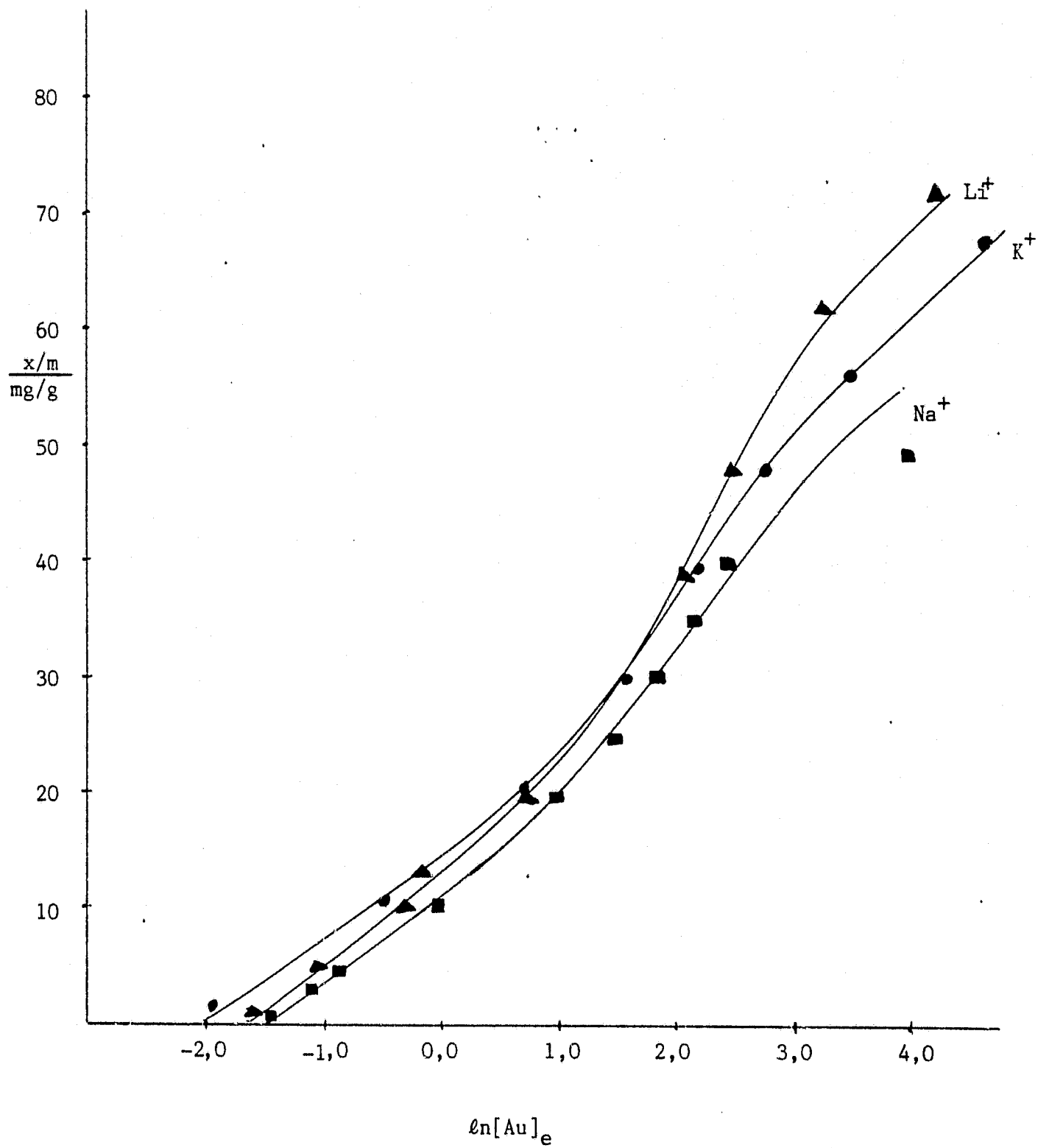
Fig. 3.8   Temkin Model

Adsorption of Aurocyanide in
I=0,30 M MOH

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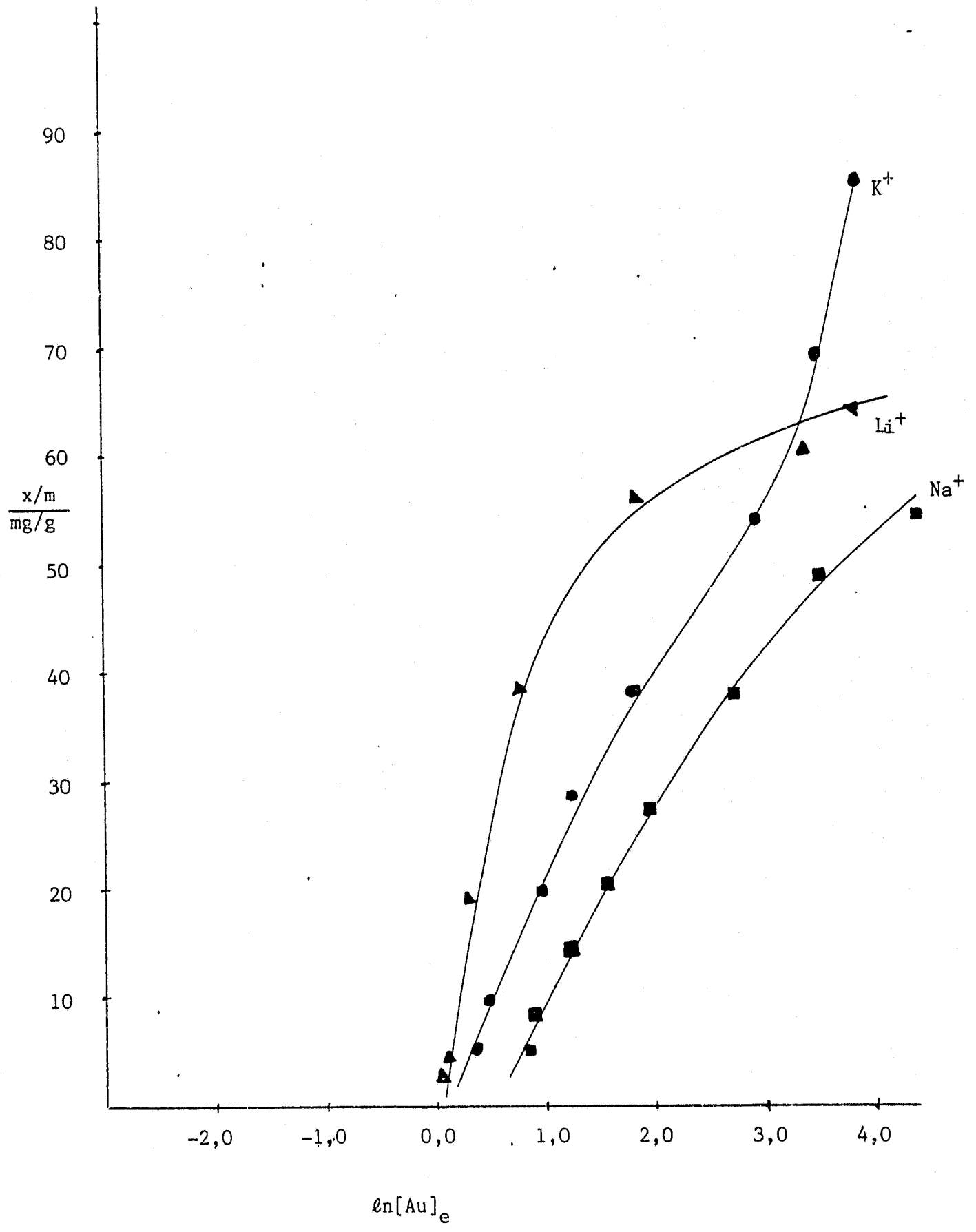Adsorption of Aurocyanide in
I=0,30 M MCN

Fig. 3.10   Temkin Model
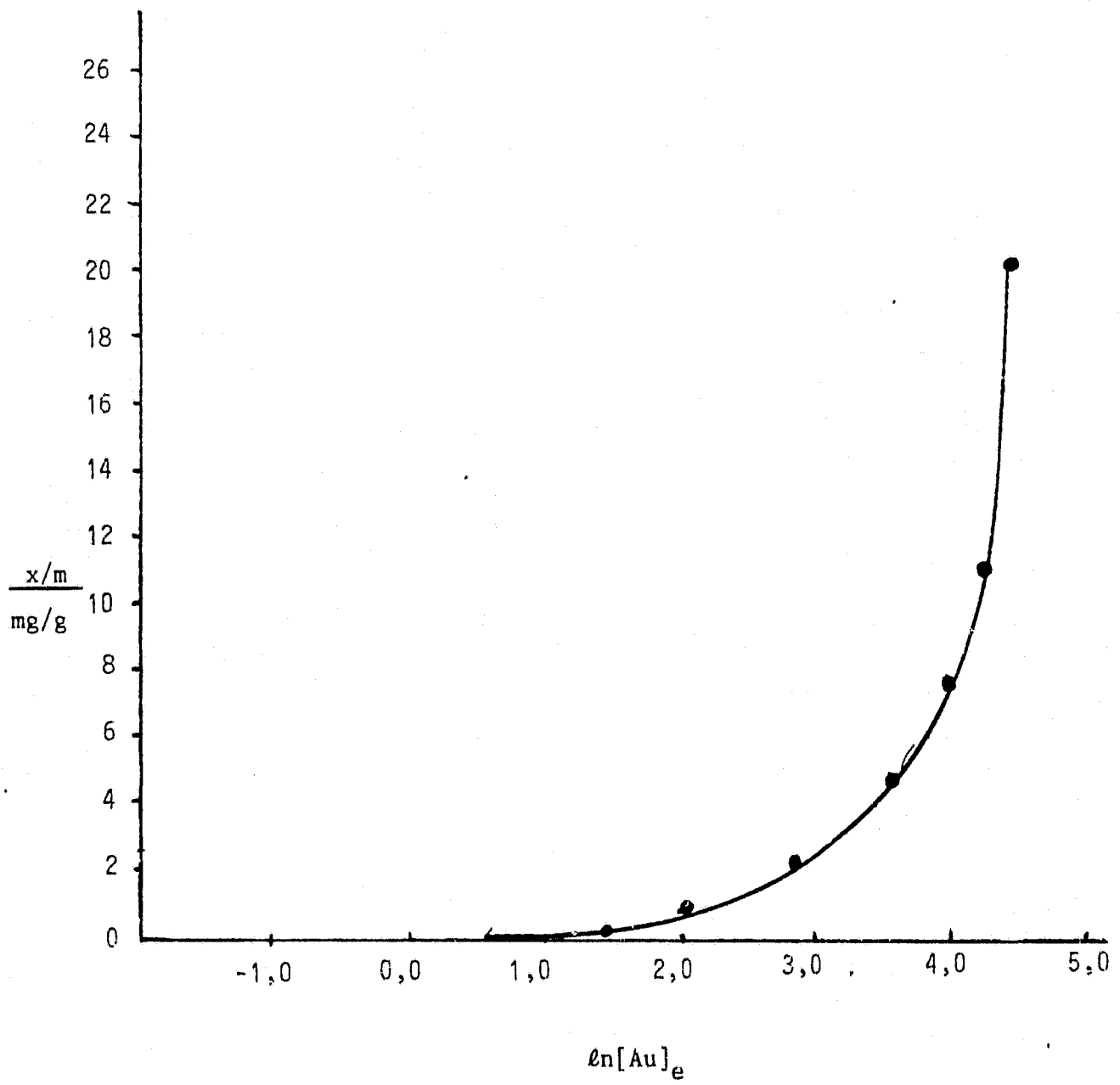
Adsorption of Aurocyanide in
I=0,30 M NaSH

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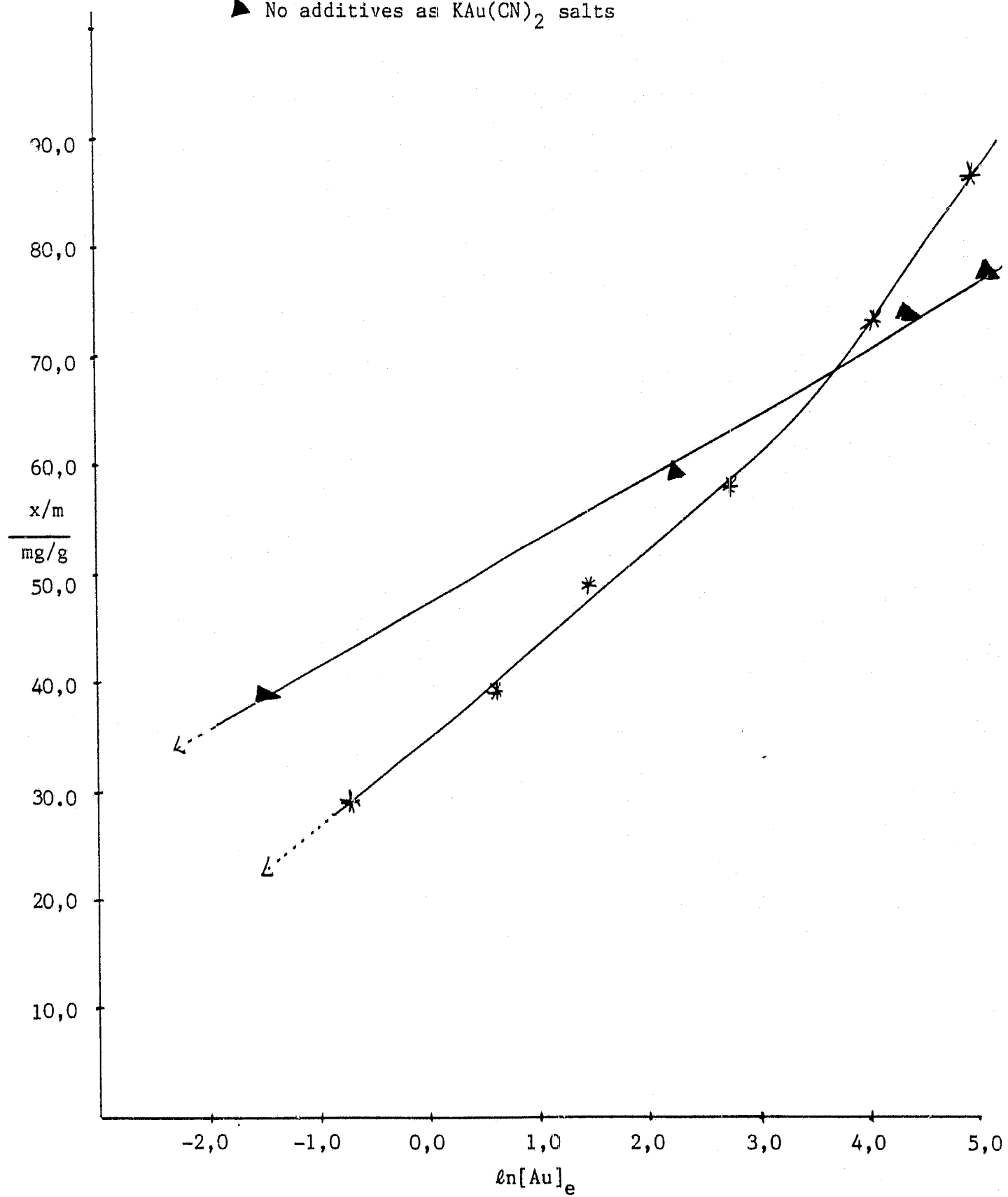
behaviour must be due to the higher site energy
observed at low surface coverages and is responsible
for the scavenging ability of activated carbon at
low gold concentration.

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.   Cho and Pitt[39] report a similar
trend where the heat of adsorption was found to
decrease with increasing gold loading.   Grobbelaar[40]
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 examined 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 $NaC\ell$ 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:

$$Ag(CN)_2^- > Ni(CN)_4^{2-} > Hg(CN)_2 \ggg \quad Cu(CN)_4^{3-} > Fe(CN)_6^{3-}$$
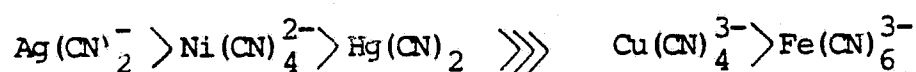
Under these conditions, very little depression was
observed for the copper and iron complexes; thus the
adsorption isotherms have not been plotted.

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:

$$Hg(CN)_2 > Au(CN)_2^- > Hg(CN)_4^{2-} > Ag(CN)_2^- > Ni(CN)_4^{2-} > Co(CN)_6^{3-}$$
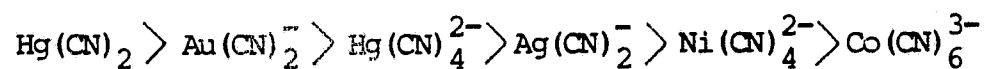
This shows that the carbon has a preference for the
adsorption of a species of low charge and large size.

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 argento-cyanide 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 $[Hg(CN)_2Cl_2]^-$ 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

ℓn $[Au]_e$
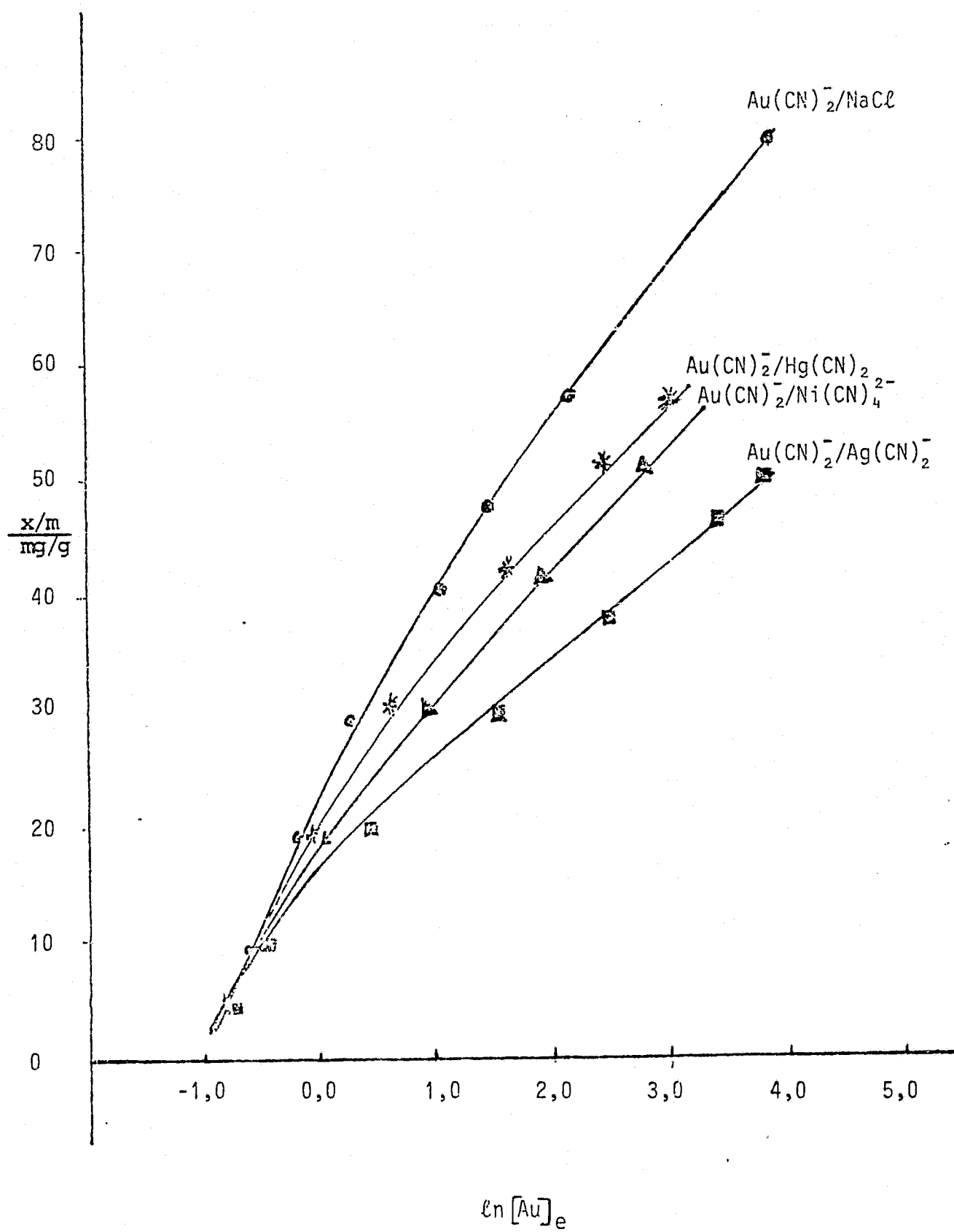
iii)   Effects of argentocyanide on aurocyanide adsorption

The effects of equimolar argentocyanide and auro-
cyanide 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 -

$$k_i \; > \; k_f$$

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-

$$k_{Au(CN)_2^-} \; > \; k_?$$

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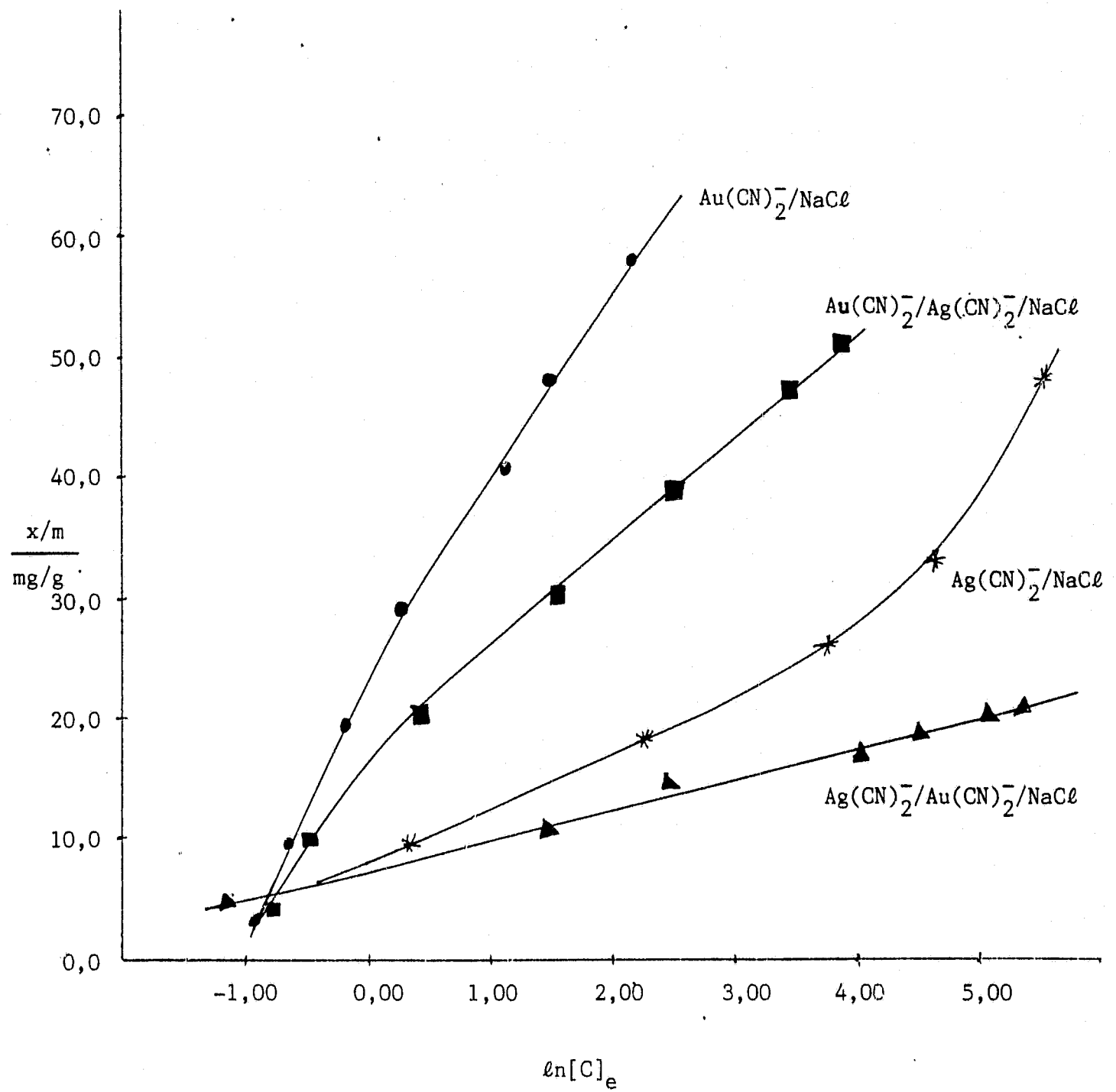
undergo this type of transition. Effectively
the aurocyanide species can thus participate in
a donor/acceptor surface species with carbon
more readily than the argentocyanide species due
to the effective relative positive charge on the
Au and Ag atoms respectively. This possibly
accounts for the differences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

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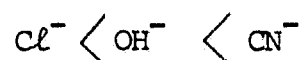
Complex formation between the argentocyanide and
the cyanide ligand results in the formation of
higher charged species such as $[Ag(CN)_3]^{-2}$.
The adsorption isotherm thus consists of a number
of equilibria and is quite complex in nature.

Fig.3.14

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

Loading medium

Key   * NaCℓ

● NaOH

■ NaCN

$\ell n\ [Ag]_e$
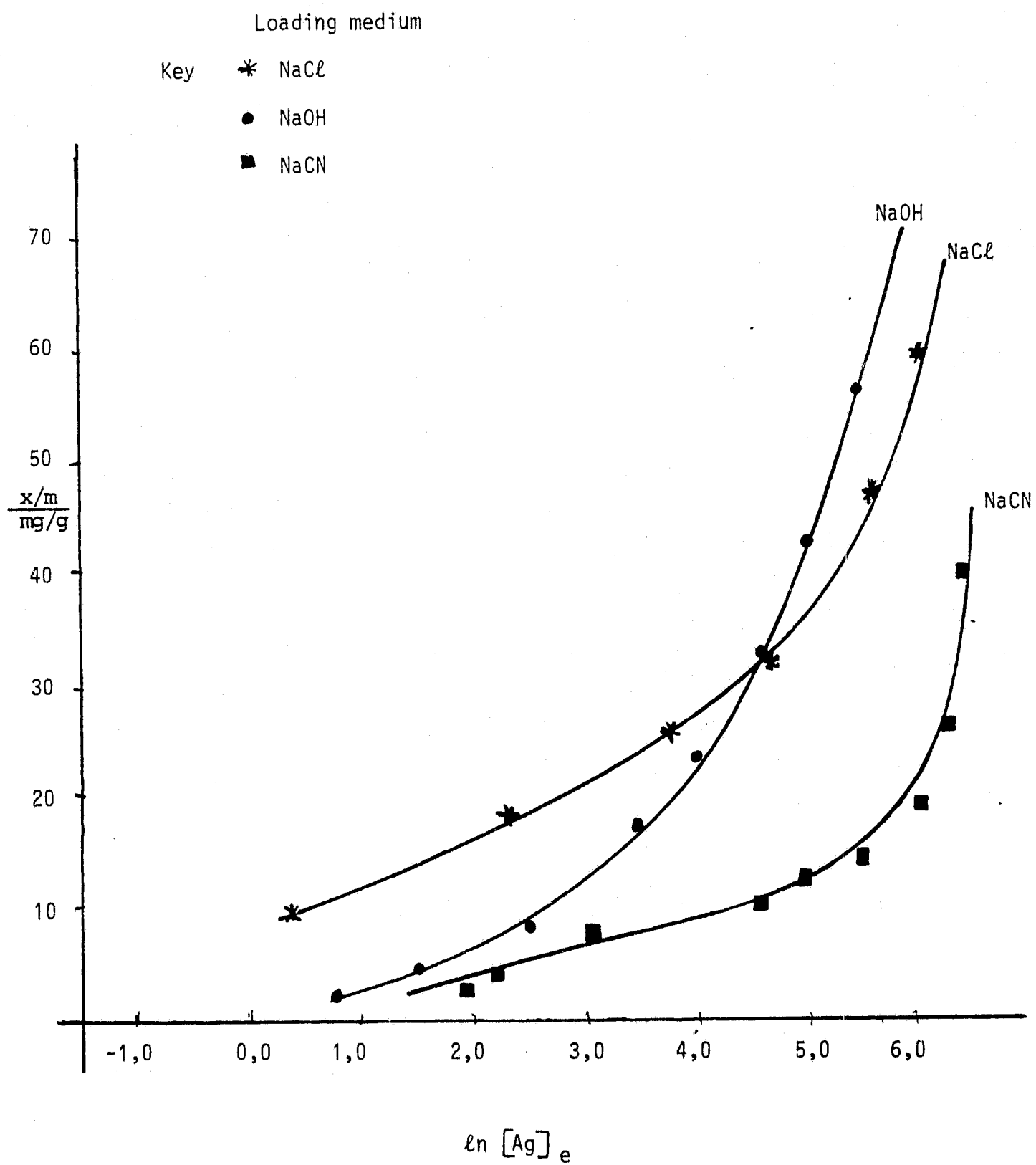
3.5   Summary and conclusions

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 inter-
action between the adsorbed ion-pair and the

carbon surface must be invoked to explain the
result.   The smaller cations being highly polar-
izable 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: $HC\ell$, $NaC\ell$, $CsC\ell$ and $CaC\ell_2$.

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 surface coverage or ionic medium in the
adsorption phase. Carbons spiked with as little as 10mg Au/g
as $[KAu(CN)_2]_s$ 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 $\gamma(C \equiv N)$ and $\gamma(Au-C)$ 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 $2140 cm^{-1}$. 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
($\mathcal{E} = 24$ 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 charac-
terization 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 -

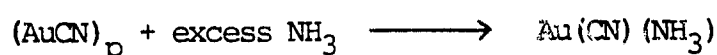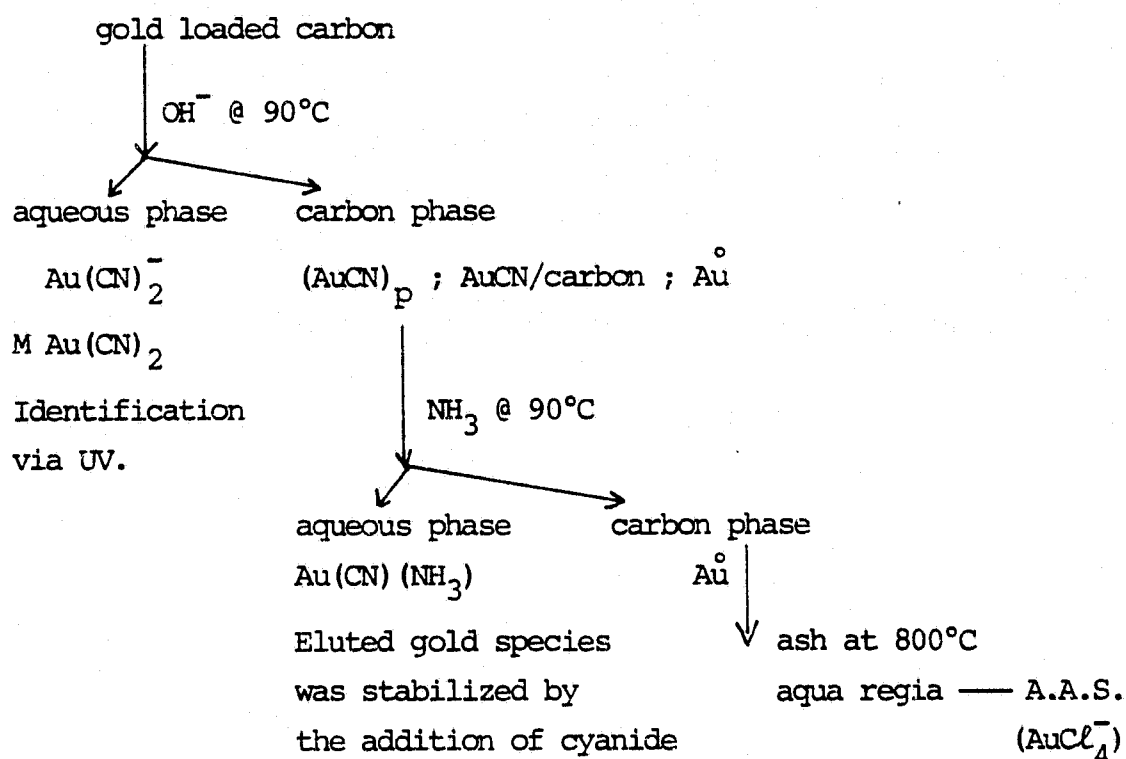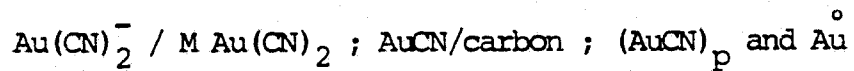$$(AuCN)_p + excess\ NH_3 \longrightarrow Au(CN)(NH_3)$$

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 Au^o

gold loaded carbon

OH^- @ 90°C

aqueous phase   carbon phase

$Au(CN)_2^-$ $(AuCN)_p$; $AuCN$/carbon ; Au^o

$M Au(CN)_2$

Identification NH_3 @ 90°C

via UV.

          aqueous phase   carbon phase

          $Au(CN)(NH_3)$ Au^o

          Eluted gold species   ash at 800°C

          was stabilized by   aqua regia —— A.A.S.

          the addition of cyanide $(AuCl_4^-)$

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 metal 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 -

$$H^+_{excess} + (Au(CN)_2^-)_n \xrightarrow{65°C} n(AuCN) + n(HCN) \qquad (4.2)$$
$$n > 1$$
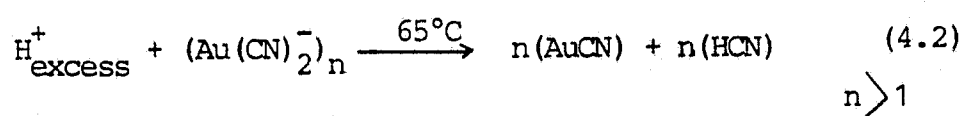
Subsequent elution using aqueous ammonia however
failed to form the complex $Au(CN)(NH_3)$ so that
degradation to the metal is probable.   The
polymerization reaction 4.2   also assumes a localized
aurocyanide concentration at the surface. This is
unlikely as X-ray diffraction results suggest the
presence 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

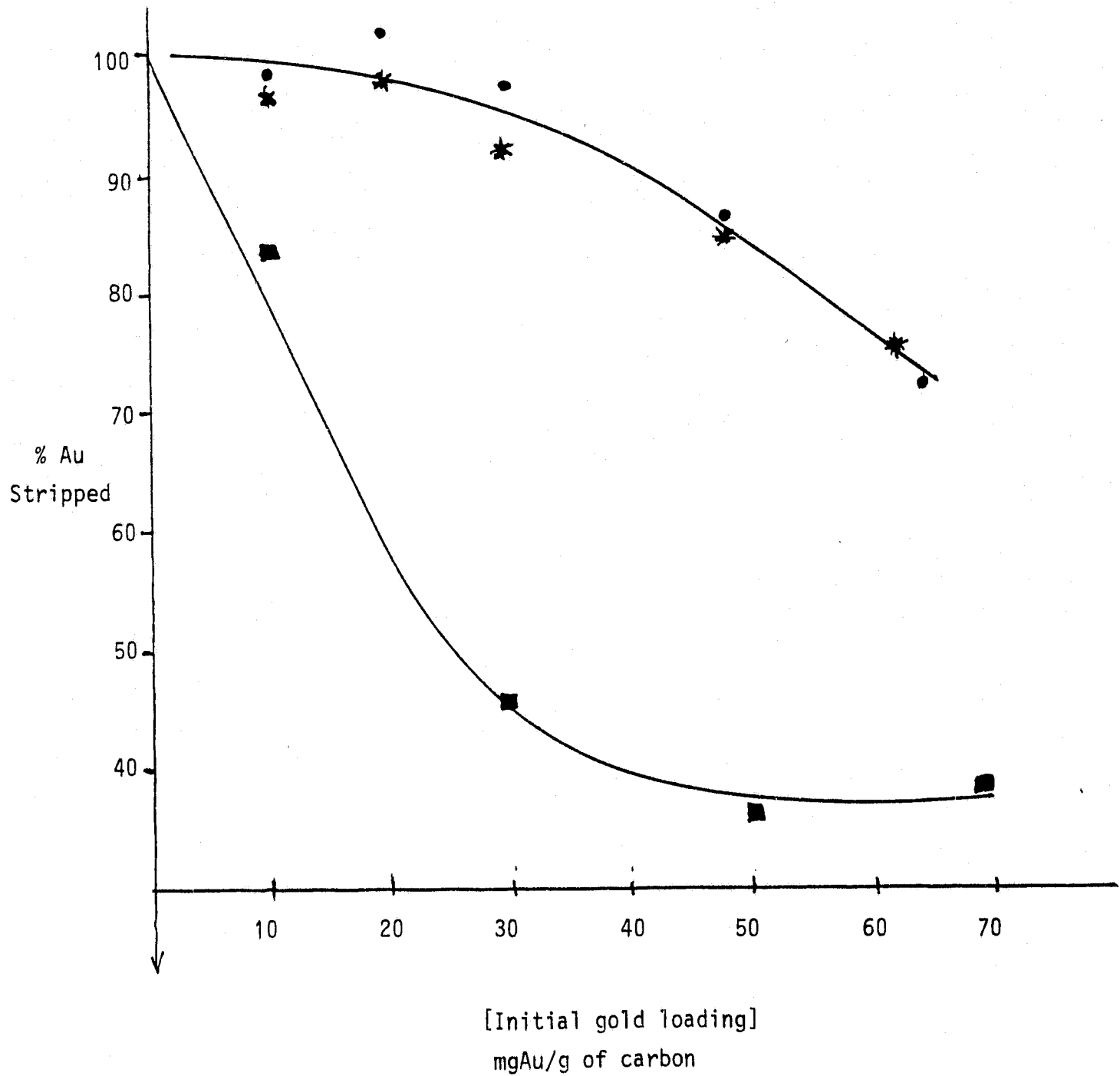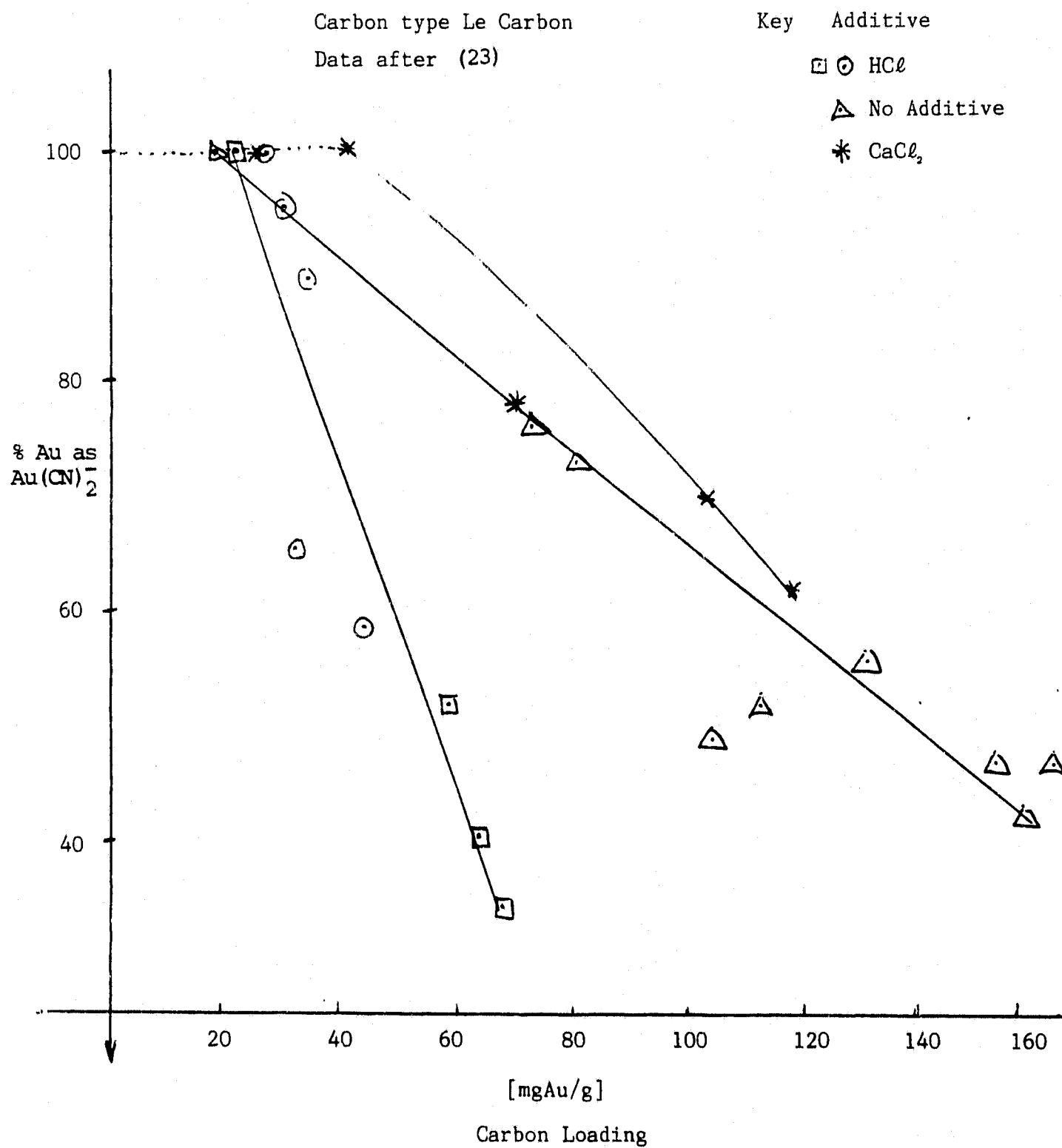Loading medium

Key   ●   NaCℓ

       ✳   CaCℓ₂

       ■   HCℓ

% Au
Stripped

[Initial gold loading]

mgAu/g of carbon

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
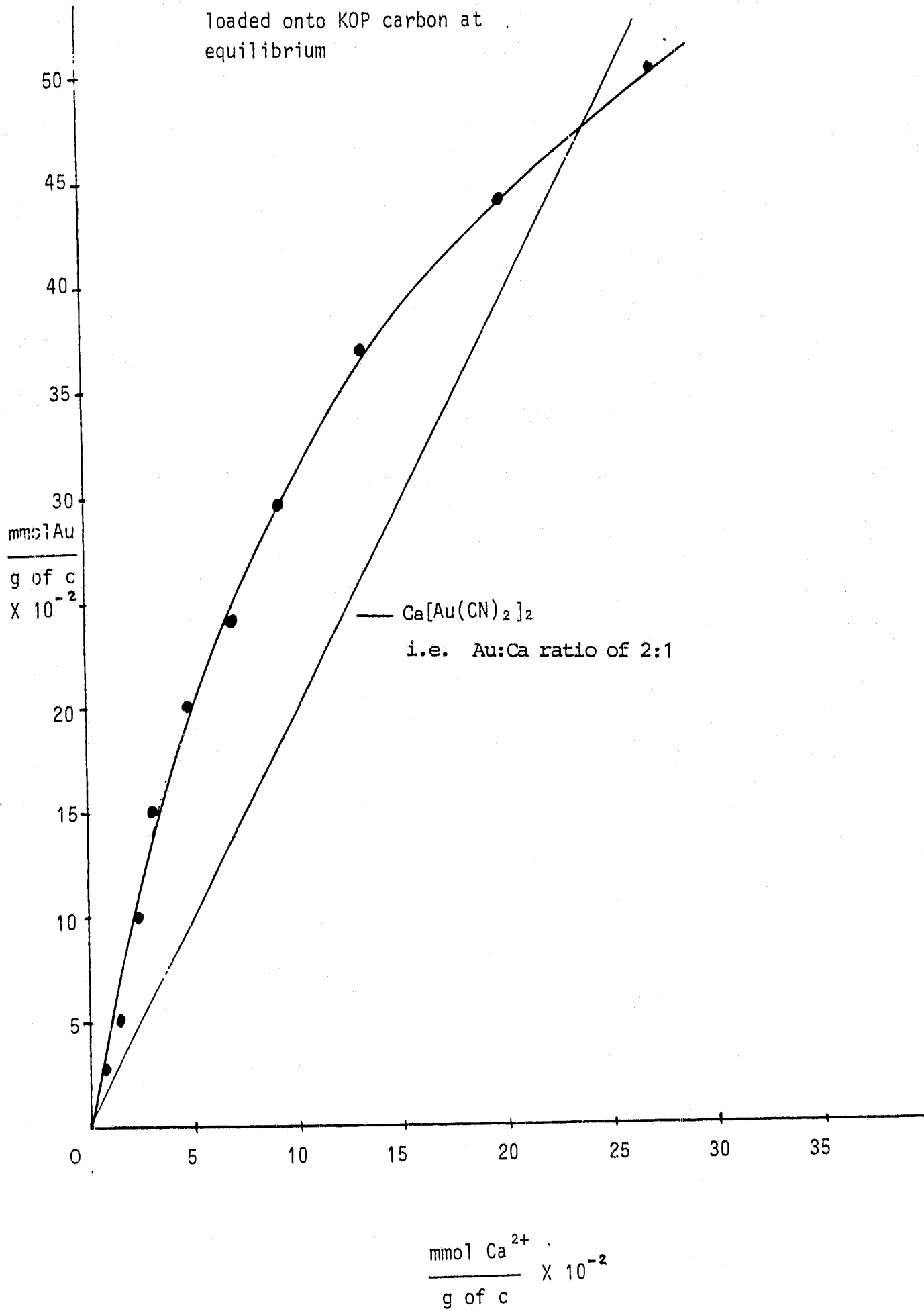of both cation and anion, the loadings were calculated
by difference.

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

— $Ca[Au(CN)_2]_2$

i.e. Au:Ca ratio of 2:1

$\dfrac{mmol\ Au}{g\ of\ c}\ X\ 10^{-2}$

$\dfrac{mmol\ Ca^{2+}}{g\ of\ c}\ X\ 10^{-2}$

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.who[23,24] 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 ($\sim$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;

$$Ca^{2+} < Mg^{2+} < H^+ < Li^+ < Na^+ < K^+,$$
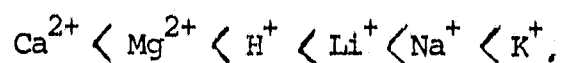
The above series shows that as the polarizability of
the cation decreases, the strength of the interaction
between the ion-pair and the carbon also decreases.
Similarly using hydroxide eluent Davidson[37] found that
the less polarizing the cation of the medium the higher
the overall desorption, according 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
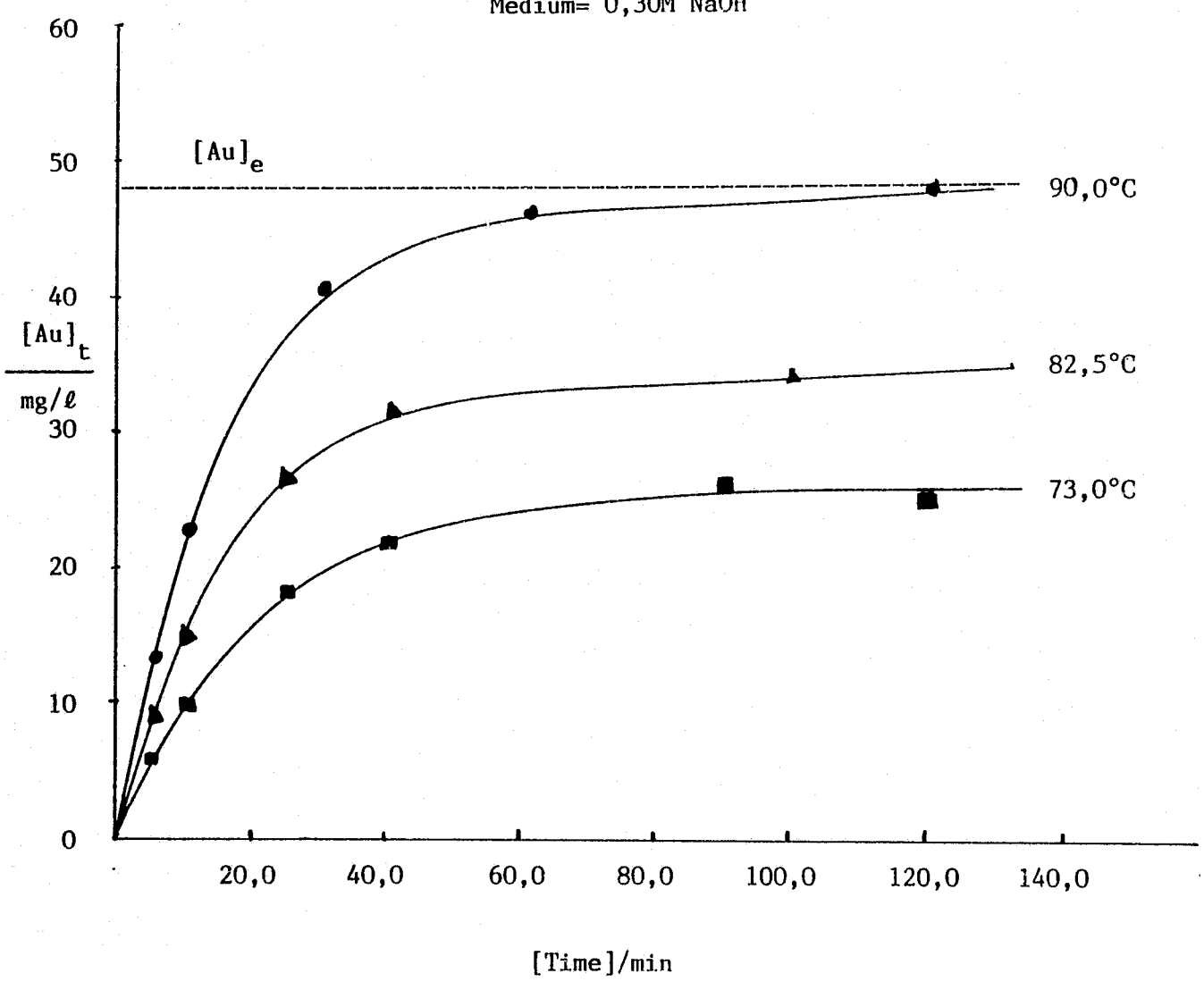
the additives used in the adsorption and desorption
media used in this series of experiments.

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	$\dfrac{E_a}{kJmol^{-1}}$	$\dfrac{A}{s^{-1}}$
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

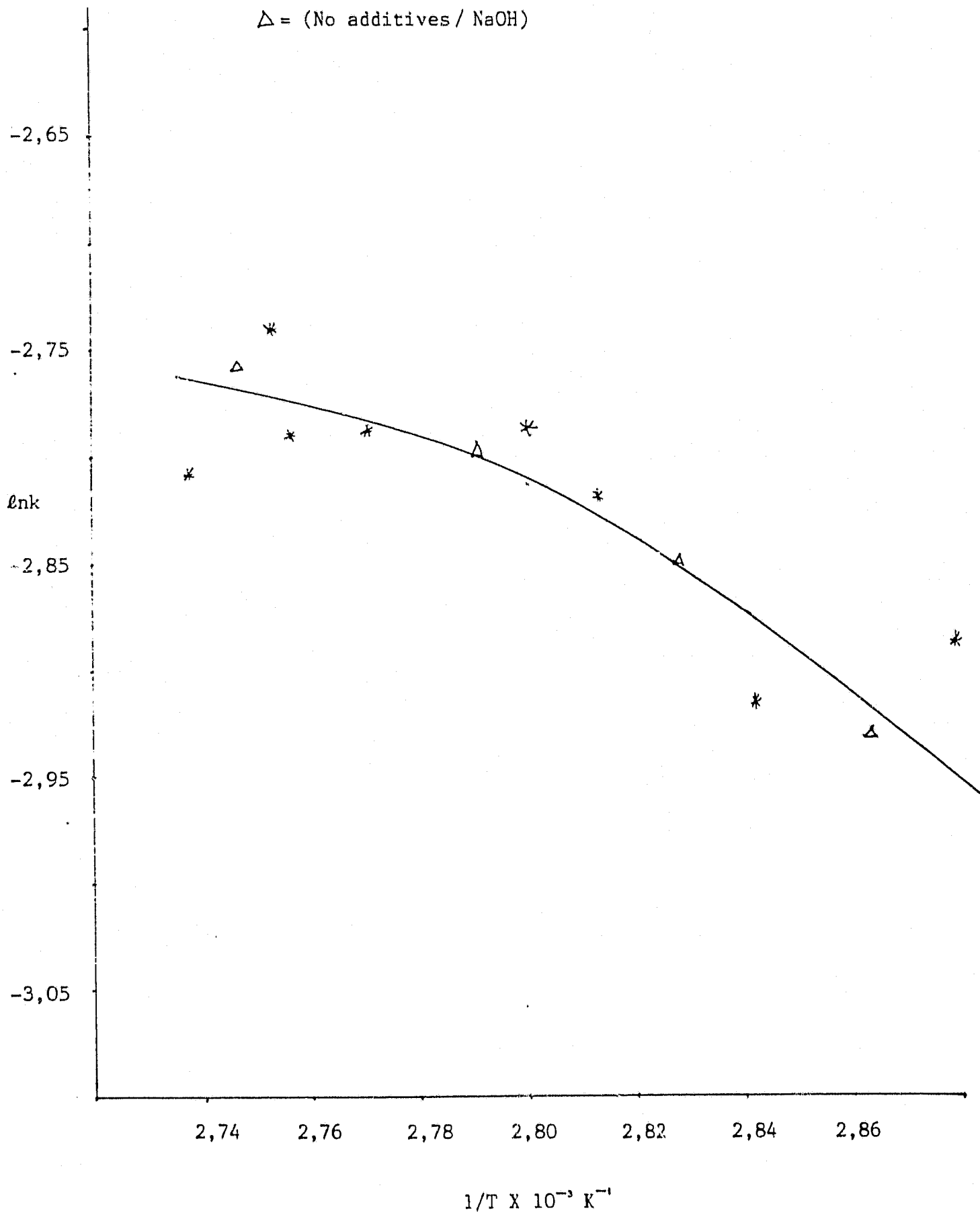Effect of initial Cation
＊ = (NaCℓ/NaOH)
△ = (No additives / NaOH)

$1/T \times 10^{-3} \ K^{-1}$

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

Effect of initial Cation

O = (KCℓ/KOH)

＊ = (NaCℓ/KOH)

ℓnk

-2,75

-2,85

-2,95

-3,05

-3,15

2,74   2,76   2,78   2,80   2,82   2,84   2,86

$1/T \times 10^{-3} \text{ K}^{-1}$
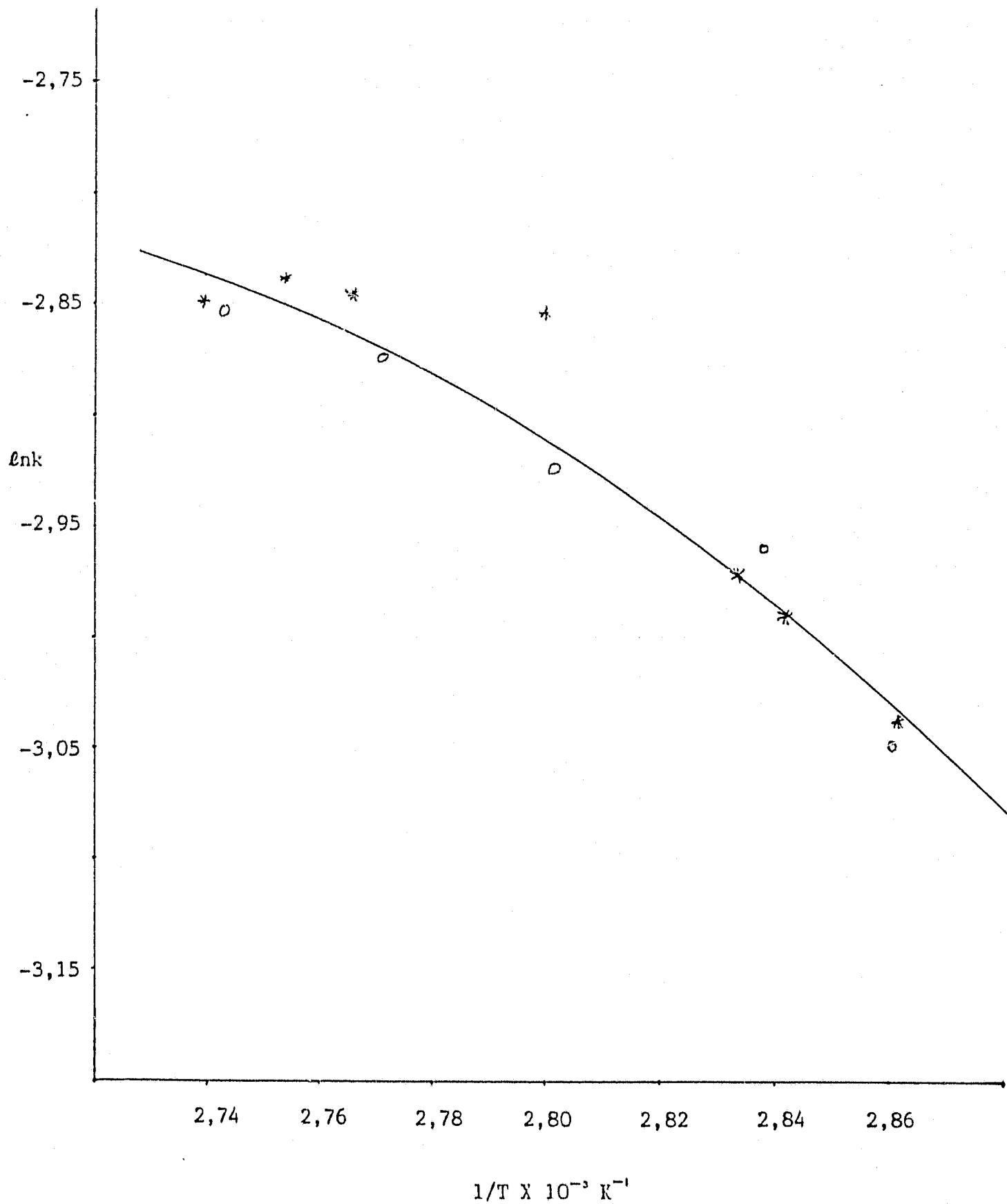
Fig. 5.4   Graph of ℓnk versus 1/T for LiOH eluent

Effect of initial Cation
$\triangle$ = (LiCℓ/LiOH)
$*$ = (NaCℓ/LiOH)

1/T X 10^{-3} K^{-1}
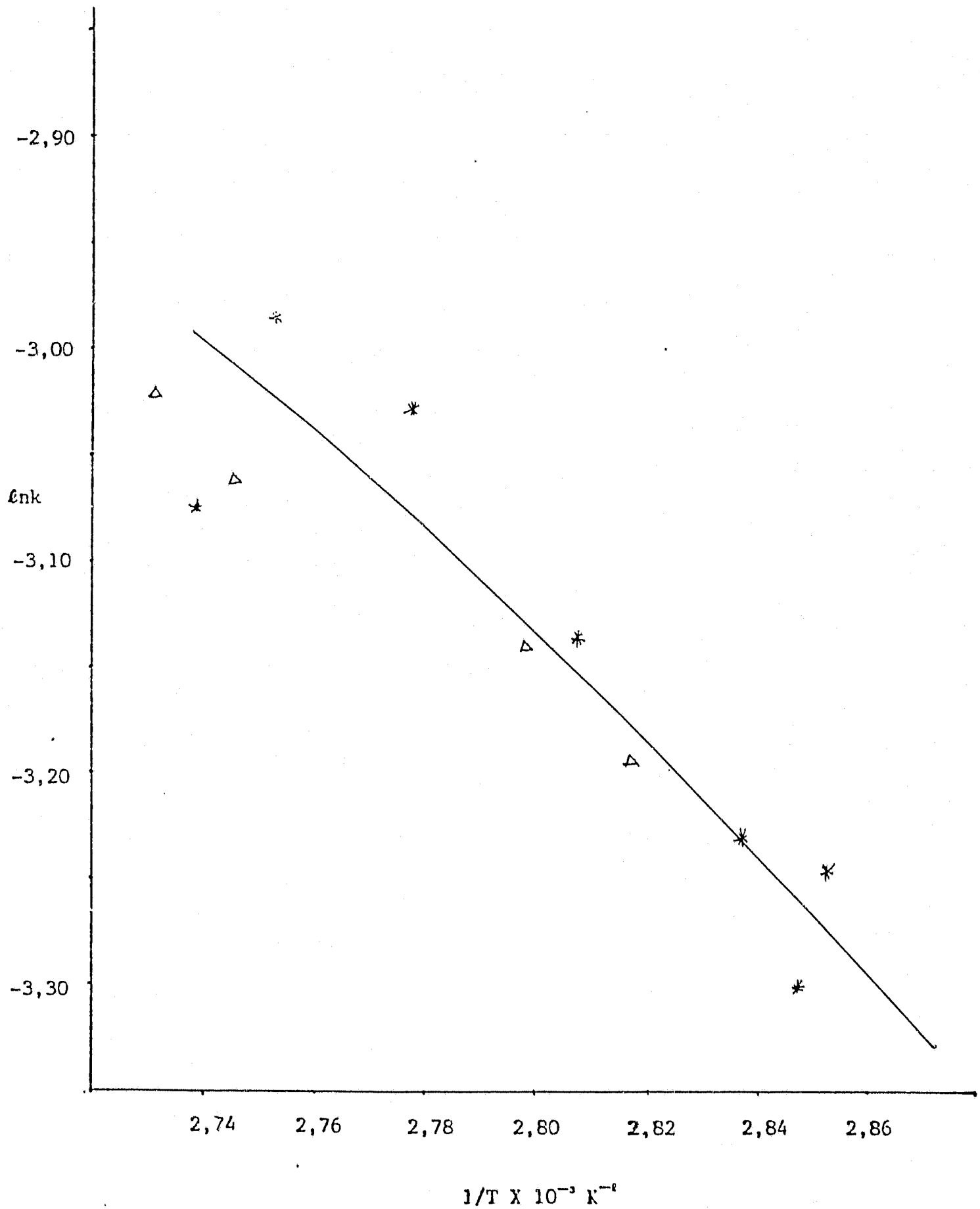
Fig. 5.5

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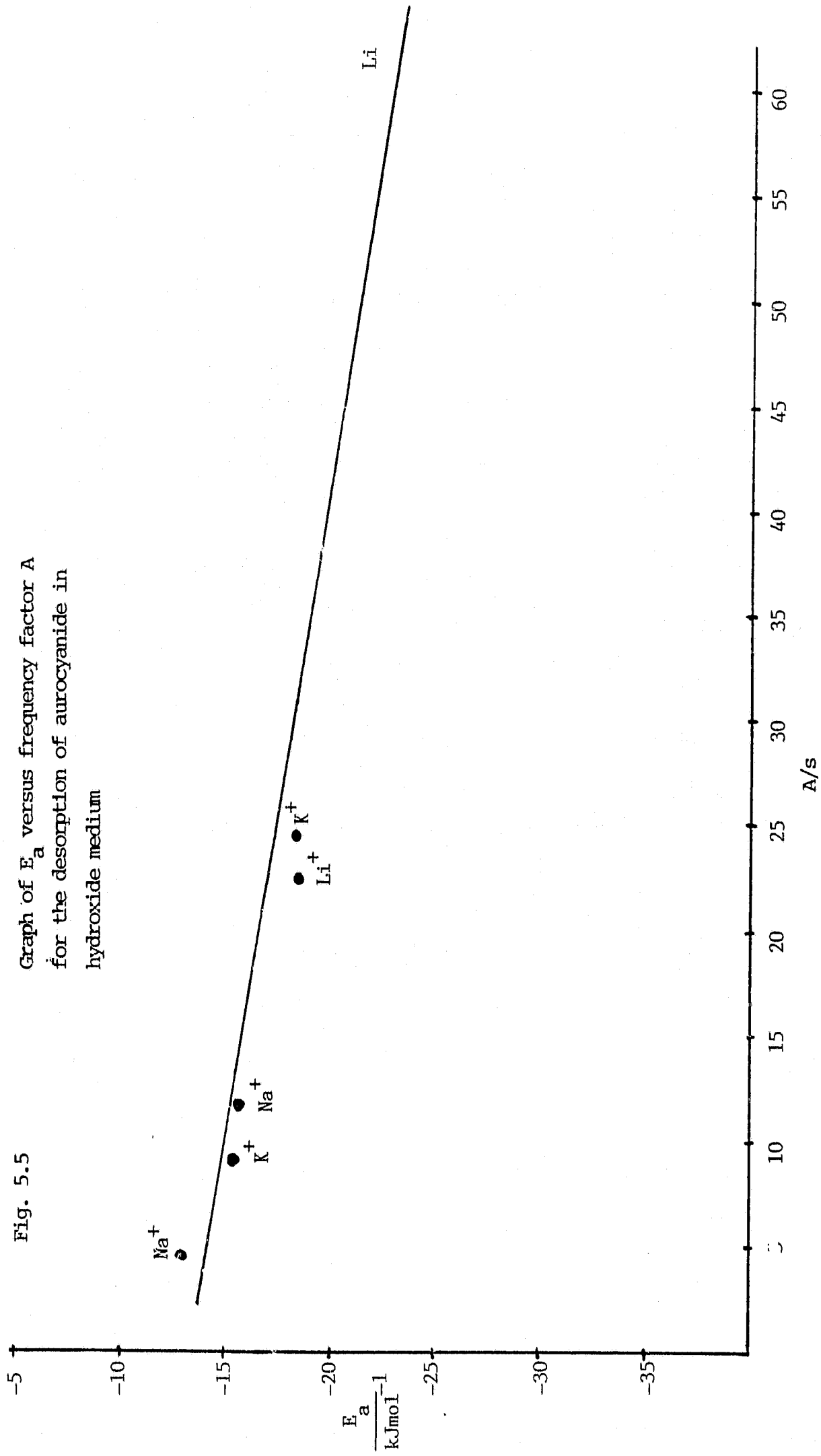
the ion-pair will cause reorientation of solvent molecules which will affect the entropy of activation (i.e. pre-exponential factor). This is summarized in Fig.(5.5) where a plot of E_a versus frequency factor shows this effect.

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 –

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

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

$\therefore$ $\ell nK_D = \dfrac{-\Delta H}{RT} + \dfrac{T\Delta S}{R}$ (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
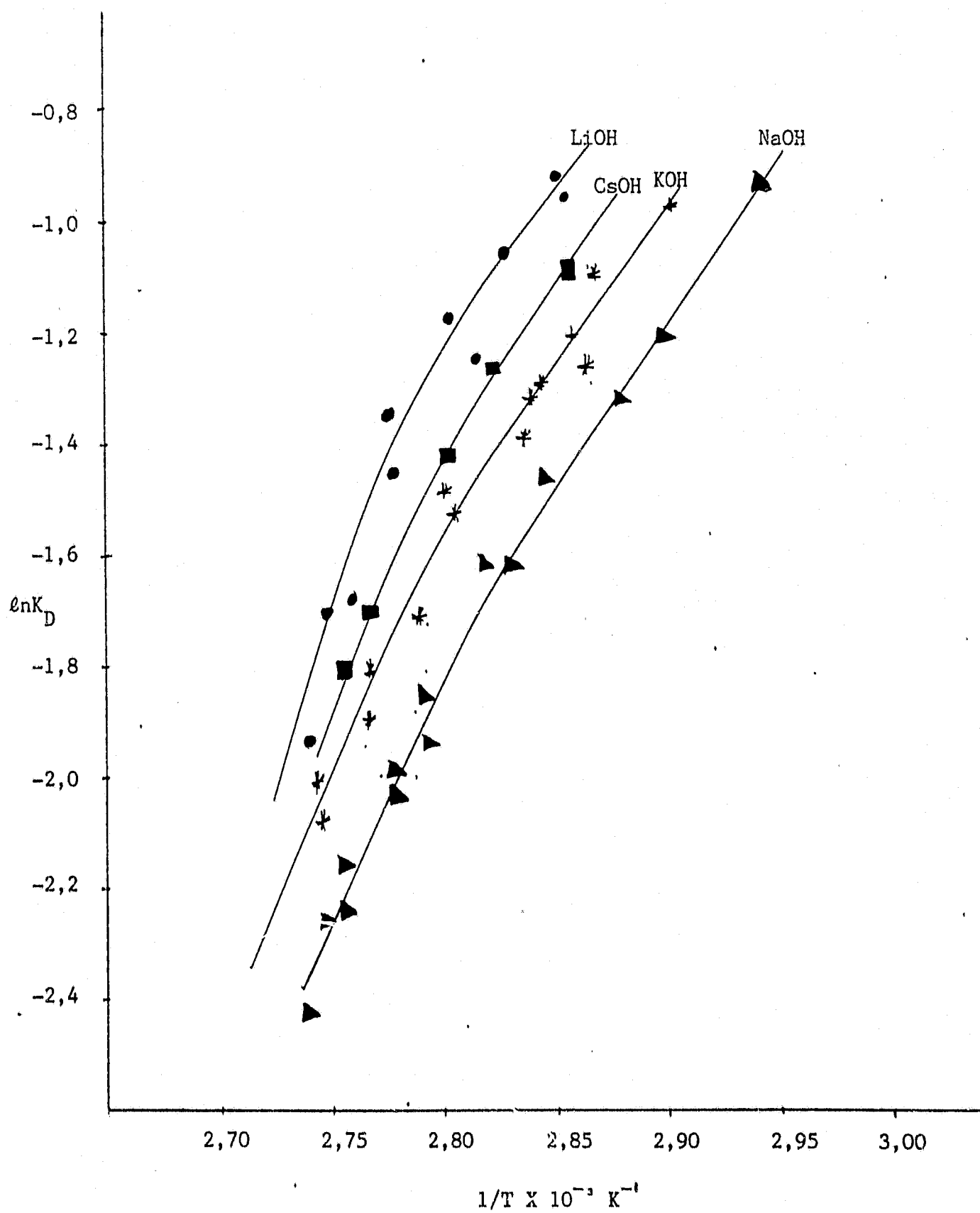$Au(CN)_2^-$ for Hydroxide eluents

Graph of $\ln K_D$ versus $1/T$

Fig. 5.7   Graph of $\ln K_D$ versus 1/T for CsOH medium
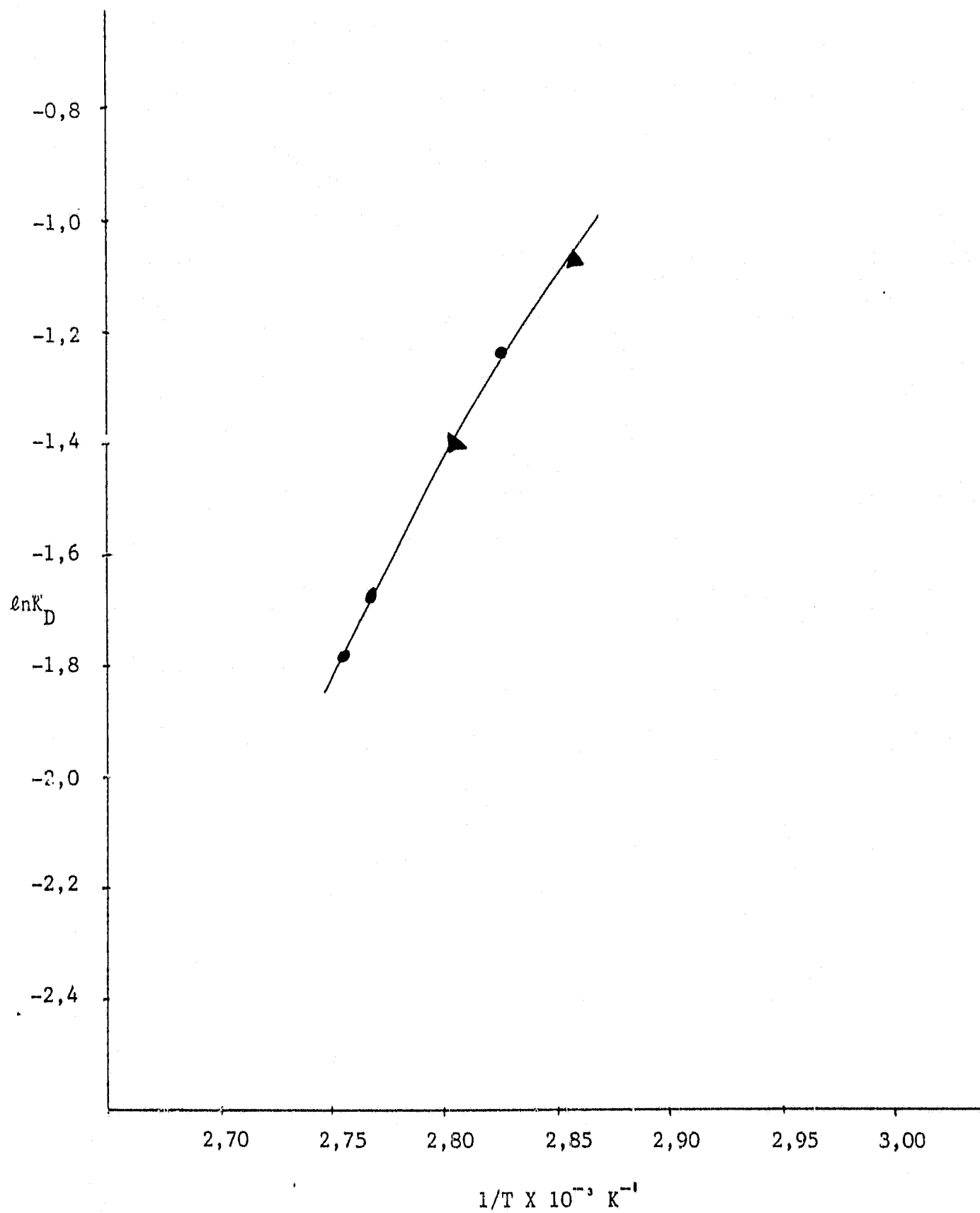
● = Heating
▲ = Cooling

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 auro-
cyanide 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-

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

$$Cs^+ > K^+ > Na^+ \qquad 2.$$
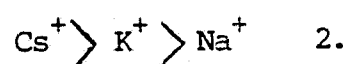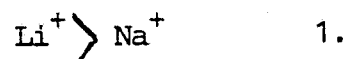
The effect on the distribution of aurocyanide by the
cation must be due to the assocation or ion-pair formation
at the carbon surface.   The equilibrium reaction may be
written -

$$\overline{MAu(CN)_2} \underset{\xrightarrow{\hspace{2cm}}}{\xleftarrow{\hspace{2cm}}}^{M^+ + OH^-} M^+ + Au(CN)_2^-$$
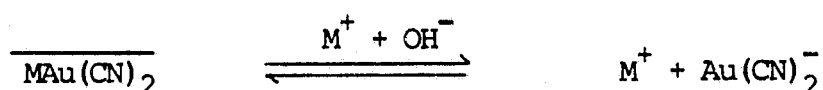
Where M^+ is the cation of the hydroxide medium which
largely determines the distribution coefficient between
the aqueous phase and the carbon phase.

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
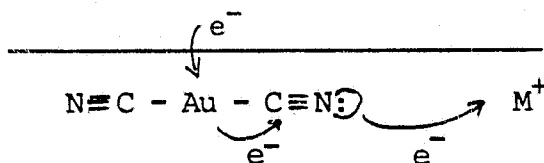between the carbon surface and the polarized ion-pair.

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

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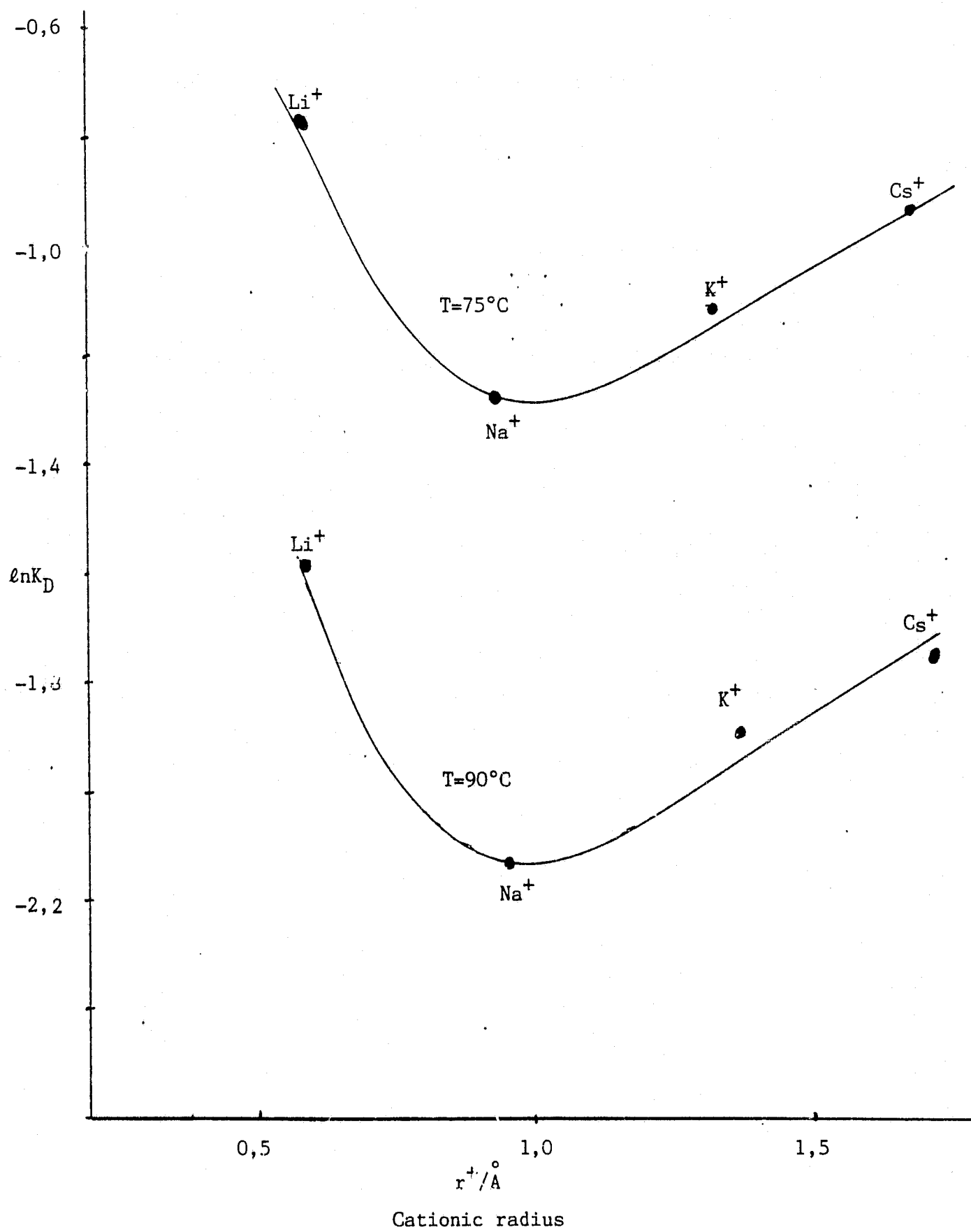
The order of affinity for the carbon phase $Li^+ > Na^+$
(and presumably the H^+ cation would follow this trend
if it were not unstable) can only be explained by the
polarizability of the cation and the resulting inter-
action with the aurocyanide anion and the carbon surface.

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.

$$N \equiv C - \overset{\delta^+}{Au} \overset{e^-}{\longrightarrow} C \equiv N \quad \longrightarrow \quad M^+$$
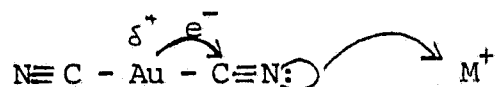
The positive centre of the ion-pair can be stabilized
by accepting electron density from the carbon surface
thus forming a donor/acceptor complex.

$$N \equiv C - Au - C \equiv N \quad \longrightarrow \quad M^+$$

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)

$1/T \times 10^{-3} \ K^{-1}$
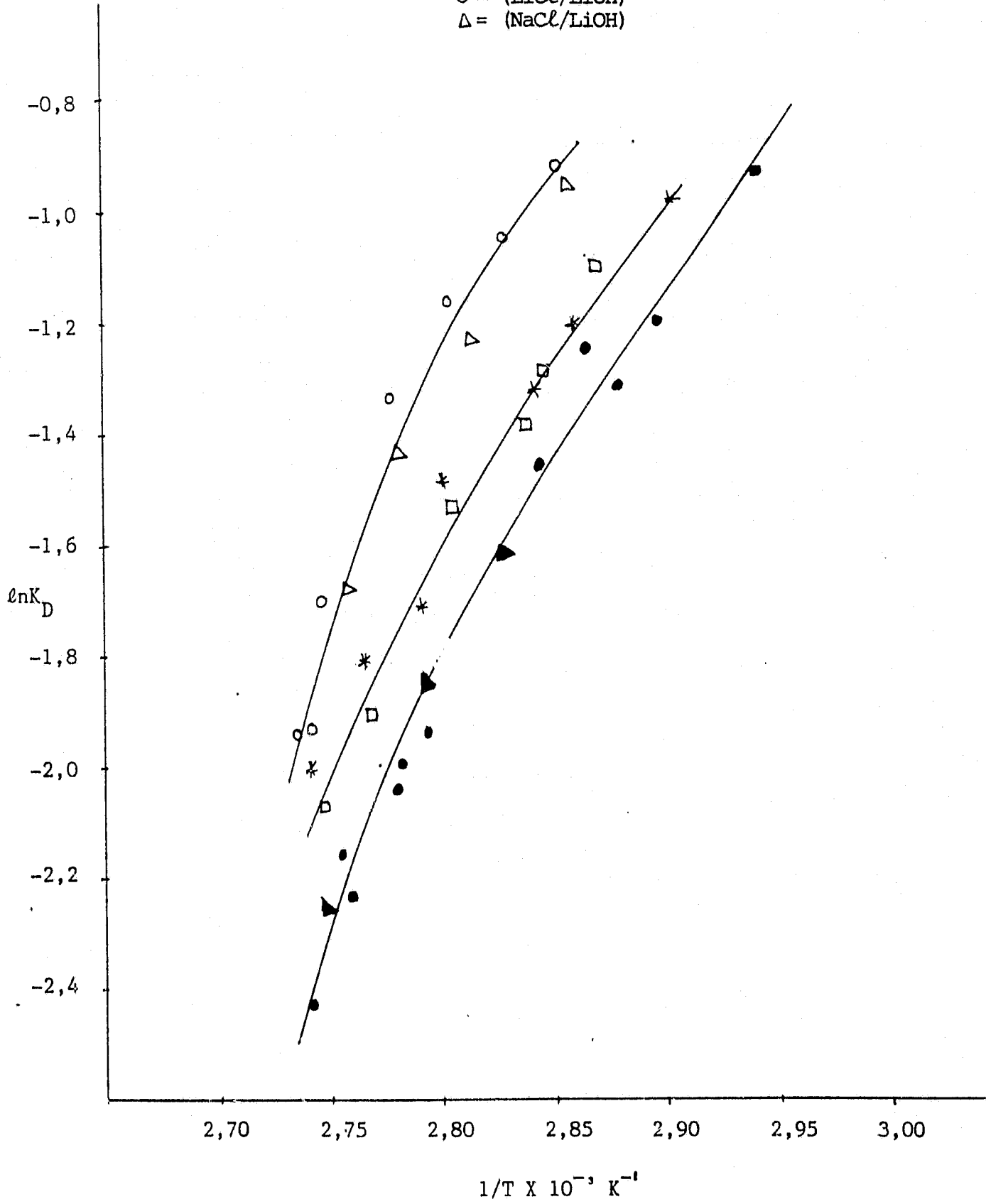
The energetics of ion-pair formation suggests that
the enthalpy of the interaction is small because
of the water molecules separating the charged species.[79]
The main driving force for ion-pair or association
reaction must be due to a large favourable entropy
changes from the loss of hydration.[80]
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 –

$$NH_3^+ + OH^- \rightleftharpoons NH_3\uparrow + H_2O$$
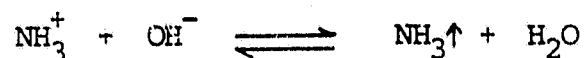
iii)   Effect of anions on the distribution coefficient
of aurocyanide

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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