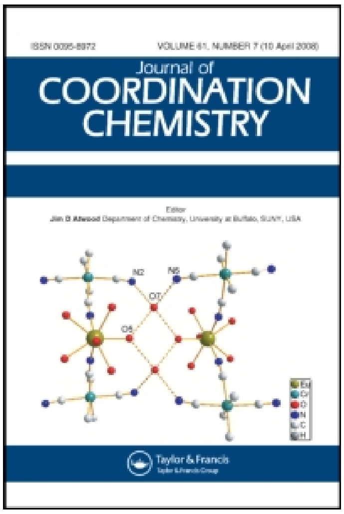

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THE EXISTENCE AND STABILITY OF MIXEDLIGAND COMPLEXES IN AQUEOUS SOLUTIONS CONTAINING ZINC AND CYANIDE IONS AT ELEVATED pH VALUES

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THE EXISTENCE AND STABILITY OF MIXED-LIGAND COMPLEXES IN AQUEOUS SOLUTIONS CONTAINING ZINC AND CYANIDE IONS AT ELEVATED pH VALUES

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The formation and stability of binary Zn^{2+}–CN^- and ternary Zn^{2+}–CN^-–OH^- complexes were studied by glass electrode potentiometry in aqueous solution at 25°C and in a medium of ionic strength 0.1 mol dm^{-3}. The solution pH was varied to cover the range $4 \rightarrow 10$. The potentiometric data were interpreted with the aid of the ESTA suite of computer programs, plots of formation functions, and a novel algorithm for model selection. It is demonstrated that the ternary complex $Zn(CN)_3(OH)^{2-}$ is formed in significant amounts in solutions of pH > 8.5. Some evidence was also obtained for the existence of the five-coordinate species $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CN)_5^{3-}$ in solutions at sub-millimolar concentration levels. No polynuclear complexes were detected under these conditions. Formation constants are reported for both binary Zn^{2+}–CN^- and ternary Zn^{2+}–CN^-–OH^- species.

Keywords: zinc, complexes, cyanide, hydroxide, stability constants

INTRODUCTION

A recent electrochemical study by Nicol *et al.*,[1] of the kinetics and mechanism of the cementation of gold by metallic zinc in cyanide-containing aqueous solutions has shown that the rate of anodic dissolution of zinc increases markedly with cyanide concentration at constant pH, and also with pH value at constant total (analytical) cyanide concentration. It was suggested that hydroxyl ions, through formation of soluble binary zinc-hydroxy complexes of the type $Zn(OH)_4^{2-}$ or ternary zinc-hydroxyl-cyanide complexes participate in the rate-determining step of the dissolution reaction.

The zinc-cyanide system has been studied quite extensively, with a view to determining the species present in solution, and associated formation constants, since 1903. Previous publications[2-19] dealing with this activity are summarized in Table I.

Inspection of this table indicates that uncertainty exists concerning the species

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expected to be present in solution, particularly with regard to $Zn(CN)^+$, $Zn(CN)_5^{3-}$ and $Zn(CN)_6^{4-}$. There have been no reports of ternary Zn–CN–OH species or polynuclear complexes. Furthermore the values of formation constants quoted for the various species vary over a range of 1–2 log units, *i.e.*, by more than would be expected even when account is taken of the effect of ionic strength on the formation constants concerned.

Kunschert[3] and Ferrel *et al.*,[20] report that both zinc and zinc amalgam electrodes are attacked by aqueous cyanide solutions and thus, as pointed out by Izatt *et al.*,[14] results obtained using these electrodes should be considered questionable. Persson[17] however showed that a zinc amalgam electrode can be used provided that oxygen is carefully excluded from the solutions and the cyanide concentration kept low. A combination of zinc amalgam and glass electrode data was used to obtain the value of $\log\beta$ ($ZnCN^+$) shown for this author in Table I.

There has been some apparent disagreement in the literature over the question of whether or not complexes of the form $Zn(CN)_n$ with $n > 4$ exist in solutions containing sufficiently high concentrations of the cyanide ion. Both Pines[4] and Østerud and Prytz[8] deduced the presence of the species $Zn(CN)_5^{3-}$ and $Zn(CN)_6^{4-}$ from polarographic evidence. The latter authors worked with total zinc concentrations in the range 10^{-4} to 10^{-3} mol dm^{-3} and cyanide concentrations from zero up to ~0.6 mol dm^{-3}. They reported four distinct polarographic waves for species other than the zinc aquo ion. The wave assigned to $Zn(CN)_4^{2-}$ was found at a $T_{CN}:T_{Zn}$ ratio of 4:1 upwards, through 24:1 *i.e.*, $[CN^-]_{free} = 0.02$ mol dm^{-3}, but had disappeared by $T_{CN}:T_{Zn} = 120:1$, *i.e.*, $[CN^-]_{free} = 0.12$ mol dm^{-3}. The wave assigned to $Zn(CN)_5^{3-}$, was found to appear at $T_{CN}:T_{Zn} = 8:1$, *i.e.*, $[CN^-]_{free} = 0.004$ mol dm^{-3}. It was still present at $T_{CN}:T_{Zn} = 120:1$, *i.e.*, $[CN^-]_{free} = 0.12$ mol dm^{-3}, but had disappeared by $[CN^-]_{free} = 0.6$ mol dm^{-3}. The wave assigned to $Zn(CN)_6^{4-}$, was distinct at $[CN^-]_{free} = 0.12$ mol dm^{-3} but had also disappeared at $[CN^-]_{free} = 0.6$ mol dm^{-3}. An interesting feature of the polarographic results which was not explained was that the waves assigned to $Zn(CN)_5^{3-}$ and $Zn(CN)_6^{4-}$ apparently both disappeared when the cyanide concentration was raised from ~0.12 mol dm^{-3} to ~0.6 mol dm^{-3}.

Of particular interest in this connection is the elegant infra-red study of this system by Ashurst, Finkelstein and Goold in 1971.[18] In keeping with the requirements of the infra-red technique, they worked with zinc concentrations of the order of 0.25 mol dm^{-3} and total cyanide concentrations of 1.7 to 2.5 mol dm^{-3}. Measurements of the absorbance of free (uncoordinated) cyanide ions were consistent with CN:Zn binding in the ratio 4:1 and not 5:1 or 6:1. It should be noted that, in these measurements, the free cyanide concentrations in the two solutions studied were, respectively, 0.56 and 1.50 mol dm^{-3}.

The results of Ashurst *et al.*, do not appear to necessarily conflict with those of Østerud and Prytz when the absence of polarographic waves for $Zn(CN)_5^{3-}$ and $Zn(CN)_6^{4-}$ at comparable free cyanide concentrations is considered. The metal ion concentrations are also very different in the two studies, which presents the possibility of polynuclearity at higher concentrations. Nevertheless, the speciation of zinc in zinc-cyanide solutions, particularly at high cyanide concentrations (above ~0.01 mol dm^{-3}), cannot be regarded as well understood. Since increasing cyanide concentrations also implies an increase in solution pH, the possibility exists that at least some of these anomalies may be explicable in terms of the formation of ternary Zn–CN–OH complexes in solution at high pH.

The present study was directed primarily towards elucidation of the speciation of zinc-cyanide systems at pH values higher than those attained in previous studies of this system.

TABLE I

Results of previous studies of formation of complexes of Zn(II) with the cyanide ion in aqueous solution

Date of Study	Temp. /°C	Ionic Strength /mol dm^{-3}	Logarithm to base 10 of the cumulative formation constant, log β (unless otherwise indicated)						Method Used	Reference
			$ZnCN^+$	$Zn(CN)_2$	$Zn(CN)_3^-$	$Zn(CN)_4^{2-}$	$Zn(CN)_5^{3-}$	$Zn(CN)_6^{4-}$		
1903	21	variable				16.9			Zn metal electrode	Euler[2]
1904	18	variable			17.52	evidence			Zn metal electrode	Kunschert[3]
1929	room temp.	variable				16.0	20.17	evidence	Polarography	Pines[4]
1931	18	variable			20.25 or	17.3			Zn metal electrode	Masaki[5]
1932	12.5	variable				18.5 → 20			Zn amalgam electrode	Britton and Dodd[6]
1950	12.5	variable				19			Re-interpretation	Bjerrum[7]
1950	12.5	variable				evidence	evidence	evidence	Polarography	Østerud and Prytz[8]
1951	18	variable				12.60(?)			Zn metal electrode	Stabrovskii[9]
1953	25	Corr. → 0				16.76			Zn amalgam electrode	Suzuki[10]
1958	32	Sat.Na_2SO_4				evidence			Freezing point	Kordes and Langenhoff[11]
1959	25	Corr. → 0				16.72			Zn amalgam electrode	Blackie and Gold[12]
1961	25	variable				evidence			Infrared spectra	Penneman and Jones[13]
1961	25	dil. $K_2Zn(CN)_4$ (?)				log $K_4 = 5$			pH Method	Penneman and Jones[13]
1965	25	Corr. → 0	No evidence	11.07	16.05	19.62			Glass electrode	Izatt *et al*[14]
1969	25	0.1	No evidence	10.64	15.74	19.98			Glass electrode	Martin and Blanc[15]
1971	40	Corr. → 0		10.70	15.20	18.30			Glass electrode	Izatt *et al*[16]
1971	25	3	5.3	11.0	16.7	21.6			Zinc amalgam and glass electrode	Persson[17]
1971	25	variable high concs.					no evidence	no evidence	Spectrophotometry	Ashurst *et al*[18]
1972	25	0.5	4.94	9.7	14.7	18.44			Zn amalgam electrode	Collier *et al*[19]

EXPERIMENTAL

The measurements in this study were made at 25.00 ± 0.05 °C in an aqueous medium of ionic strength made up to $I = 0.10$ mol dm^{-3} with sodium perchlorate as background electrolyte. All volumetric glassware used in this study was "A" grade.

Materials

Stock solutions of strong acid and strong alkali were prepared using analytical reagent grade $HClO_4$ and NaOH respectively. Acid solutions were standardised by titration against freshly recrystallised borax,[21] and alkali solutions were standardised against $HClO_4$, either by use of methyl orange as indicator, or, for the more dilute solutions, potentiometrically, by use of Gran plot techniques,[22–25] which allowed for determination of dissolved carbonate impurity. Alkali solutions were made up and stored under nitrogen in polyethylene bottles. All solutions were made up using freshly-boiled and doubly-distilled water. Zinc perchlorate stock solutions were prepared by dissolving BDH Analar grade ZnO in a slight excess of $HClO_4$. After filtration and dilution, the solution was standardised for Zn^{2+} by titration against standard EDTA with Eriochrome Black T as indicator,[26] and for excess acid by potentiometric titration against standardised NaOH with use of Gran plots. Solutions of sodium cyanide were freshly prepared for each experiment since it is well known[8,16,27,28] that aqueous solutions of cyanide decompose slowly to form among other products CO and NH_3. The NaCN solutions were standardised for CN^- by titration against standard NaCl using the Liebig-Dénigèr's method.[29,30] The NaCN reagent was checked for any NaOH impurity by Gran titration against $HClO_4$ but no such impurity was detected.

Owing to the low concentrations of reactants used in this study (sub-millimolar levels) the background electrolyte $NaClO_4$ had to be as pure as possible. A method of preparation described by Sjöberg,[31] involving neutralisation of $HClO_4$ with sodium carbonate, was used. The stock solutions prepared gave negative results to tests for Cl^-,[32] CO_3^{2-},[33] Fe^{2+}[34] and Fe^{3+}[35]. The solution was standardised for $NaClO_4$ by passing an aliquot of solution through a cation exchange resin (BDH Amberlite 1R − 120(H)) in the protonated form, with subsequent titration of the eluted acid. Reproducibility was around 1%.

Potentiometric Apparatus and Procedure

Potentiometric titrations were carried out in METROHM jacketted glass reaction vessels, type EA880-T-50, fitted with one or more RADIOMETER G202B (low Na error) glass electrodes, a reference electrode/salt bridge assembly, a thermometer, a METROHM EA649 gas bubbler, and a burette tip from a METTLER DV10 automatic burette. The design of the vessel was such that the equilibria could be studied under an inert N_2 atmosphere. The reference electrode and salt bridge were assembled using two INGOLD liquid junction tubes, type 303-95-T-NS, which had been modified so that the assembly could be thermostatted in the same way as the reaction vessel, *i.e.*, by recirculation from a water-bath controlled to 25.00 ± 0.05 °C. The reference electrode consisted of a METROHM silver-silver chloride electrode, type EA-275, inserted into a solution of 0.01 mol dm^{-3} NaCl + 0.09 mol dm^{-3} $NaClO_4$, and saturated with AgCl. The salt bridge was filled with 0.10 mol dm^{-3} $NaClO_4$. The cell EMF was measured using a RADIOMETER PHM64 Research pH meter reading to 0.1 mV. The "high purity" nitrogen used to flush the cell contents during cell calibration was scrubbed of acid and alkaline impurities by passage through

10% NaOH and 10% H_2SO_4 before presaturation through a 0.1 mol dm^{-3} $NaClO_4$ solution. Magnetic stirring was provided. Sodium hydroxide titrant solutions were kept in the solution reservoir of the automatic burette under a continuous flow of N_2 which, in addition to the scrubbing detailed above, was also passed through a U-tube containing soda lime and calcium sulphate.

Cell calibration

The potentiometric cell was calibrated for use of the glass electrode as a hydrogen ion concentration (rather than activity, or pH) probe. When the ionic strength of the solutions used is kept constant, the EMF of a cell such as the one used in this study can be written in the form[24,36–40] shown in (*1*)

$$E_{cell} = E^{\circ\prime}_{cell} + E_j + k\ \log[H^+] \qquad (1)$$

where $E^{\circ\prime}_{cell}$ represents a quantity independent of $[H^+]$ but dependent, *inter alia*, on the activity of Cl^- in the reference electrode, and the activity coefficient of H^+, γ_{H^+}, in the test solution. γ_{H^+} is normally presumed to be constant throughout a titration since background electrolyte is used to keep the ionic strength of the solution very nearly constant. E_j represents the sum of the liquid junction potentials generated across the junction separating the reference electrode filling solution from the salt bridge, and the junction separating the salt bridge from the test solution. In practice, this term places limitations on the degree to which one may approach the two extremes of the pH scale while still maintaining linearity of the E_{cell} *vs* $\log[H^+]$ plot. The constant k represents a constant (termed the "electrode calibration slope") which generally has a value close to (but usually somewhat lower than) that expected from the Nernstian factor, *i.e.*, 2.3026 RT/F. $[H^+]$ represents the concentration of free (uncomplexed) hydrogen ions in solution.

The calibration constants $E^{\circ\prime}_{cell}$ and k were determined by titration of a solution of a strong acid with a strong base. A typical calibration titration involved titration of a 10^{-3} mol dm^{-3} solution of $HClO_4$ with 10^{-2} mol dm^{-3} NaOH, where all solutions were of course made up to an ionic strength of 0.1 mol dm^{-3} with $NaClO_4$. In most instances points were obtained in the regions $2.3 < p[H] < 2.9$ and $10.8 < p[H] < 11.8$, where p[H] represents $-\log[H^+]$. Within these ranges of p[H] the solutions are sufficiently concentration buffered for reliable cell EMF's to be obtained[40,41] and the junction potential term E_j to be effectively constant. When appropriate correction is made for the effect of carbonate impurities in the sodium hydroxide solutions used,[42] linear plots of E_{cell} *vs* $\log[H^+]$ are obtained. The calibrations were carried out *in situ* at the beginning of each titration. In some instances, values of the calibration slope k for particular electrodes were carried forward from previous calibrations, and the position of the calibration line determined from measurements made in the acid region. The electrode equation (*1*) in the form $E_{cell} = E^{\circ}_{cell} + k\ \log[H^+]$ where $E^{\circ}_{cell} = E^{\circ\prime}_{cell} + E_j$, was found to reproduce the calibration data to a precision typically of the order of ±0.6 mV.

Calculation Techniques

The computer program HALTAFALL[43] was used for calculation of the composition of equilibrium mixtures from known (or assumed) values of formation constants. Otherwise a program ESTA[44,45] was used. This program permits potentiometric titration data to be analyzed using a number of simulation and optimisation procedures. These are described in the following sections.

Formation and deprotonation functions

The hydrogen formation function is defined as

$$\bar{Z}_H = (T_H - [H^+] + [OH^-])/T_L$$

where T_H and T_L are the total concentrations of hydrogen ion and ligand respectively.

The metal formation function is defined† as $\bar{Z}_M = (T_L - A(1 + \Sigma_r \beta_{01r}[H^+]^r))/T_M$ where $A = (T_H - [H^+] + [OH^-])/\Sigma_r r\beta_{01r}[H^+]^r$, T_M = total concentration of metal, and β_{01r} = formation constant of species $M_0L_1H_r$. $\bar{Z}_H$ and $\bar{Z}_M$ were plotted against $p[H] = -\log[H^+]$ and $pA = -\log A$ respectively. The "deprotonation function", $\bar{Q}$, is defined as $\bar{Q} = (T_H^* - T_H)/T_M$ where T_H^* = total hydrogen ion concentration at the observed pH, calculated by ignoring all metal complex formation.

$\bar{Q}$ was plotted against p[H]. $\bar{Q}$ can be regarded as the number of moles of H liberated (from protonated ligand) as a result of complexation, per mole of metal ion. One can also define a hydrogen formation function, $\bar{Z}_H^*$, as $\bar{Z}_H^* = (T_H^* - [H^+] + [OH^-])/T_L$. $\bar{Z}_H^*$ is the value of $\bar{Z}_H$ calculated ignoring the formation of metal complexes. If a solution contains only one predominant complex of formula $M_pL_qH_r$, then the hydrogen stoichiometric coefficient, r, is given by the expression $r = q\bar{Z}_H^* - p\bar{Q}$. This was used to confirm and identify some of the species present in the system.

Point-by-point calculation of formation constants

ESTA permits calculation of a formation constant for a single user-specified complex species at each point in each titration. This is done by making use of the BETA task in the simulation module of the program.[45] The value of such a constant is adjusted to produce agreement with the observed cell EMF at each titration point. Such calculations may be repeated for any number of postulated or trial species. Likely minor species can then be identified by searching for regions in the titrations where a fairly constant value of log β is calculated at a significant number of consecutive points, and where the postulated species is calculated to be present in amounts falling in the range 15–85% and changes rapidly.

Formation constant optimisation

Optimisation was carried out with respect to the objective function, *U*, using task OBJE of the optimisation module. U is given by the expression

$$U = \frac{1}{N - n_p} \sum_{n=1}^{N} W_n (E_n^{obs} - E_n^{calc})^2,$$

where N = number of experimental points, n_p = number of parameters simultaneously optimised, E_n^{obs} = observed electrode potential at the nth data point, $E_n^{calc} = E^\circ + k\log[H^+]$ and E° = electrode intercept and k = electrode calibration slope.

The weighting factor, W_n, was obtained from the formula

$$W_n = \left[\left(\frac{\delta(E_n^{obs} - E_n^{calc})}{\delta V}\right)^2 \sigma_V^2 + \left(\frac{\delta(E_n^{obs} - E_n^{calc})}{\delta E_n^{obs}}\right)^2 \sigma_E^2\right]^{-1}$$

where σ_V and σ_E represent the estimated random errors in the titre volumes and

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† In this paper the symbol β_{pqr} represents the cumulative formation constant of the species $Zn_pCN_qH_r^{(2p+r-q)+}$ and is defined as $\beta_{pqr} = [Zn_pCN_qH_r]/[Zn]^p[CN]^q[H]^r$ where charges are omitted for simplicity. A negative value for r represents hydroxide rather than hydrogen ions.

electrode potentials, chosen as 0.01 cm^3 and 0.1 mV respectively. The derivatives were evaluated analytically. Extended Debye-Hückel type corrections were applied to correct for any ionic strength changes in the titrations. Where values appropriate to $I = 0.1$ mol dm^{-3} were not available, these (denoted by an asterisk in the table) were estimated using a method described recently by Linder and Murray.[46] For these interpolations, the required values of the ion size parameters were either obtained from Kielland[47] or estimated as described by Linder and Murray.[46]

RESULTS

Twelve potentiometric titrations were carried out at various ligand : metal ratios and at various total (analytical) metal ion concentrations. In some instances mixtures of zinc and cyanide ions were titrated with acid; in others a sodium hydroxide titrant was used, and, in a few instances the direction of titration was reversed by switching to a hydroxide titrant after completion of the titration with acid or *vice versa*. Three glass electrodes were used. Total zinc concentrations were varied from 1×10^{-4} to 7×10^{-4} mol dm^{-3} and total cyanide concentrations from 1×10^{-3} to 1×10^{-2} mol dm^{-3}. The ligand to metal quotient T_{CN}/T_{Zn} was varied from 4.4 to 41. In addition, certain titrations were carried out in the absence of zinc ions to allow the pK_a of the cyanide ion to be determined. The contents of the reaction vessel were flushed with nitrogen gas during the calibration step only. No flushing was carried out after addition of cyanide to avoid loss of volatile HCN from the system. The system was, however, kept sealed in the reaction vessel after flushing was discontinued.

Attainment of equilibrium

A criterion for attainment of electrochemical equilibrium adopted in this study was that the cell EMF should remain constant (to ± 0.1 mV) for a minimum period of 5 minutes. To meet this condition, "equilibration" times varied from about 6 minutes per titration point at low pH values (pH = 6 or below) to about 90 minutes per point at the highest pH values studied (~ 11). The latter period seemed rather long and suggests that chemical equilibrium may be approached slowly at high pH values (although glass electrodes are known to require longer equilibration times at high pH).

The titrations in which the direction of titration was reversed were used as a further test for attainment of equilibrium. If equilibrium had been attained at each titration point then calculated values of the formation function $\bar{Z}_M$ (defined above) should have the same value for both "forward" and "reverse" titrations at any particular value of pA. This test for attainment of equilibrium is valid provided that no polynuclear or hydrolysed complex species are formed.

It was found that the relevant plots of $\bar{Z}_M$ *vs* pA were superimposable to within experimental error, indicating that electrochemical equilibrium was attained for p[H] values up to at least 9, and also that significant amounts of hydrolysed complex species are not formed below p[H] = 9 in systems having $T_{CN}/T_{Zn} \geqslant 10$. This is more or less in accord with the conclusions of previous workers, who have rarely made measurements at pH values above 8.5.

An examination of solutions containing mixtures of CN^- and HCN by U.V. spectrophotometry indicated that a slow decomposition or possibly oxidation reaction takes place, to produce a species absorbing at $\lambda_{max} = 298$ nm. From the comparative stability of cell EMF values in these solutions it was inferred however that the extent of the side reaction observed was fairly minor in nature.

Data obtained in the region of excess hydroxide

Certain titrations involved the use of an excess of hydroxide over any acid that may have been present at the end of cell calibration, and resulted in the attainment of p[H] values as high as 11.3.

The question as to whether or not the data obtained in the presence of excess hydroxide would be useful for species selection and computation of formation constants was investigated by determining the extent to which the calculated p[H] of the solution depends on the formation constants of complex/es of interest. For this purpose, values of cumulative formation constants taken from the literature[48,49] were used for the binary Zn^{2+}/CN^- and Zn^{2+}/OH^- complexes.

A statistical method proposed by Sharma and Schubert[50] was used to estimate the values $\log \beta_{14-1} = 22.6$, $\log \beta_{13-2} = 21.2$, and $\log \beta_{13-1} = 19.6$ for the ternary species $Zn(CN)_4(OH)^{3-}$, $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CN)_3(OH)^{2-}$, respectively. Simulated potentiometric titration data were calculated by means of the HALTAFALL programme[43], using such literature values and estimates for $\log \beta$.

It was found, for example, that at pH values above 10.5 and at a ligand to metal ratio of 10:1 the solution pH is almost totally insensitive to changes of ±1 log unit in the value of $\log \beta_{13-1}$ for the complex $Zn(CN)_3(OH)^{2-}$. At a pH value of 10, the calculated solution pH changes by about 0.06 units (corresponding to a change of cell EMF of about 3.6 mV), an amount which is uncomfortably close to a realistic estimate of the uncertainty in the value of E°_{cell}. The indications therefore are that when the concentration of free (uncomplexed) OH^- ions becomes comparable to the concentration of free CN^- ions, very great precision of electrode calibration is required in order to distinguish between uncoordinated OH^- and CN^- ions.

The precision of the experimental technique was insufficient to allow ligand replacement reactions of the type

$$Zn(CN)_n(OH)_m^{(2-n-m)+} + OH^- \rightarrow Zn(CN)_{n-1}(OH)_{m+1}^{(2-n-m)+} + CN^-$$

to be followed reliably at pH values above about 10. Consequently, calculations were based on data obtained at pH values below 10.

Model Selection and Calculation of Formation Constants

For the calculations involved in model selection and determination of formation constants, allowance was made for auxiliary equilibria which may be important in the titrations performed. From the titrations carried out in the absence of metal ion, a value of 9.08 ± 0.01 was obtained for the pK_a of HCN. It was assumed that no protonated species other than HCN is formed in such systems. Literature values taken from various data compilations[48,49] for the other constants involved, valid at 25°C and at various ionic strengths, are given in Table II.

Values of the formation function $\bar{Z}_M$(obs) are plotted *versus* pA in Figure 1 for data collected at pH values below 10. For clarity, not all experimental points are shown. Values of T_{Zn} and the ligand-to-metal quotient T_{CN}/T_{Zn} corresponding to each titration are given in Table III.

Reading from right to left in Figure 1, the plot of $\bar{Z}_M$ *vs* pA after an initial increase shows a levelling off at $3.5 < \bar{Z}_M < 4$, followed by a rapid increase with decreasing values of pA. This sudden rapid increase in $\bar{Z}_M$ at low pA values (*i.e.*, high p[H]) is fairly typical for systems in which hydrolysis takes place. It can be easily verified that the $\bar{Z}_M$(obs) *vs* pA plot is very sensitive to small uncertainties in, particularly, the analytical quantity T_H in this high pH region, and also to the value of the pK_a of the ligand, so too much significance should not be accorded to the extreme left hand

TABLE II

Literature values, and values interpolated to I = 0.1 mol dm^{-3} of formation constants used to correct for auxiliary equilibria in the model selection procedure and in calculation of formation constants

Quantity	I = 0	I = 0.1 mol dm^{-3}	I = 3.0 mol dm^{-3}
pK_w		13.78	
log $\beta_1^H(HCO_3^-)$		10.00	
log $K_2^H(H_2CO_3)$		6.16	
log $\beta_{10-1}[Zn(OH)^+]$	5.0	4.6[a]	3.8
log $\beta_{10-2}[Zn(OH)_2]$	10.2	9.6[a]	8.3
log $\beta_{10-3}[Zn(OH)_3^-]$	13.9	13.3[a]	13.7
log $\beta_{10-4}[Zn(OH)_4^{2-}]$	15.6	15.2[a]	18.0
log K[Zn + Zn(OH)]	0.0	0.4[a]	1.7

[a] Values estimated as described in the text.

TABLE III

Analytical (total) zinc concentration T_{Zn} and ligand to metal quotient T_{CN}/T_{Zn} for each potentiometric titration. These quantities vary slightly during the course of each titration. Plotting symbols are those used in Figures 1, 3 and 4

T_{ZN}/mol dm^{-3}	T_{CN}/T_{Zn}	Plotting symbol
4.341×10^{-4}	4.4	△
2.579×10^{-4}	4.5	|
7.141×10^{-4}	6.0	◬
2.922×10^{-4}	9.7	● = forward; ▲ = reverse
2.922×10^{-4}	9.7	⊙ = forward; x = reverse
1.006×10^{-4}	11.0	□
2.664×10^{-4}	15.0	■
1.006×10^{-4}	16.3	△ = forward; ⊡ = reverse
2.579×10^{-4}	20.2	○ = forward; * = reverse

region of the plot. The plot also shows a "curl back" feature to the data from titrations denoted Δ and |, in the former instance occurring at pA ≈ 3.9, and $\bar{Z}_M \approx 4.0$. This feature is also typical of hydrolysis equilibria. The fact that this "curl back" feature occurs early in the plot (reading once again from right to left) accords with the fact that these two titrations were carried out at the lowest ligand-to-metal ratios in this study (see Table III). The lower the ligand-to-metal ratio, the sooner hydrolysis can be expected to occur, when the p[H] of the solution is raised (or the pA lowered).

Another feature of interest in connection with Figure 1 is the degree of superimposability of the $\bar{Z}_M$ *vs* pA curves at varying values of T_{Zn}. Examination of Table III shows that the titrations can be divided into three broad groupings: (a) Titrations having $T_{Zn} \approx 1 \times 10^{-4}$ mol dm^{-3}, (b) Titrations having $T_{Zn} \approx 2.7 \times 10^{-4}$ mol dm^{-3} and (c) Titrations having $T_{Zn} \geqslant 4 \times 10^{-4}$ mol dm^{-3}.

Thus, T_{Zn}[group (a)] < T_{Zn}[group (b)] < T_{Zn}[group (c)]. There does not appear, in Figure 1, to be any discernable systematic separation or grouping of $\bar{Z}_M$ *vs* pA curves in terms of the value of T_{Zn}. The indications therefore are that polynuclear complexes do not form to any significant extent in this ternary system at metal ion concentrations below 7×10^{-4} mol dm^{-3}.

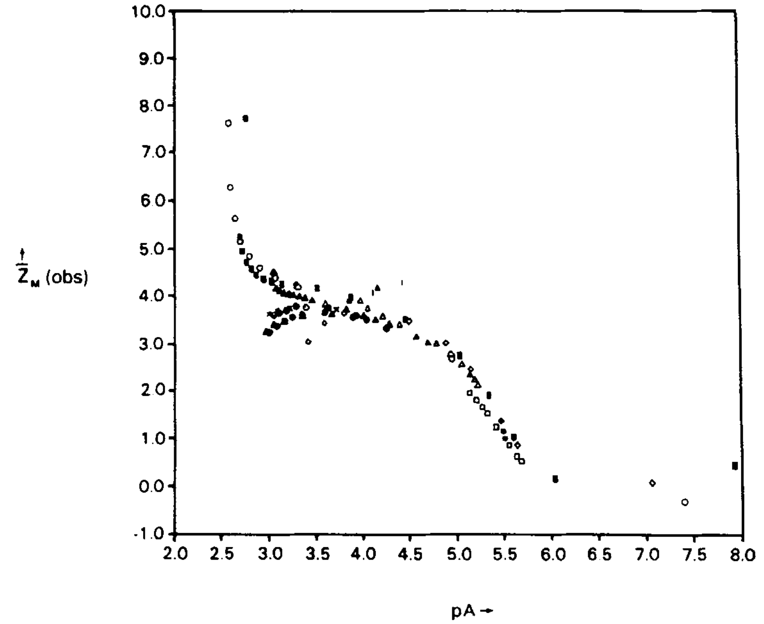
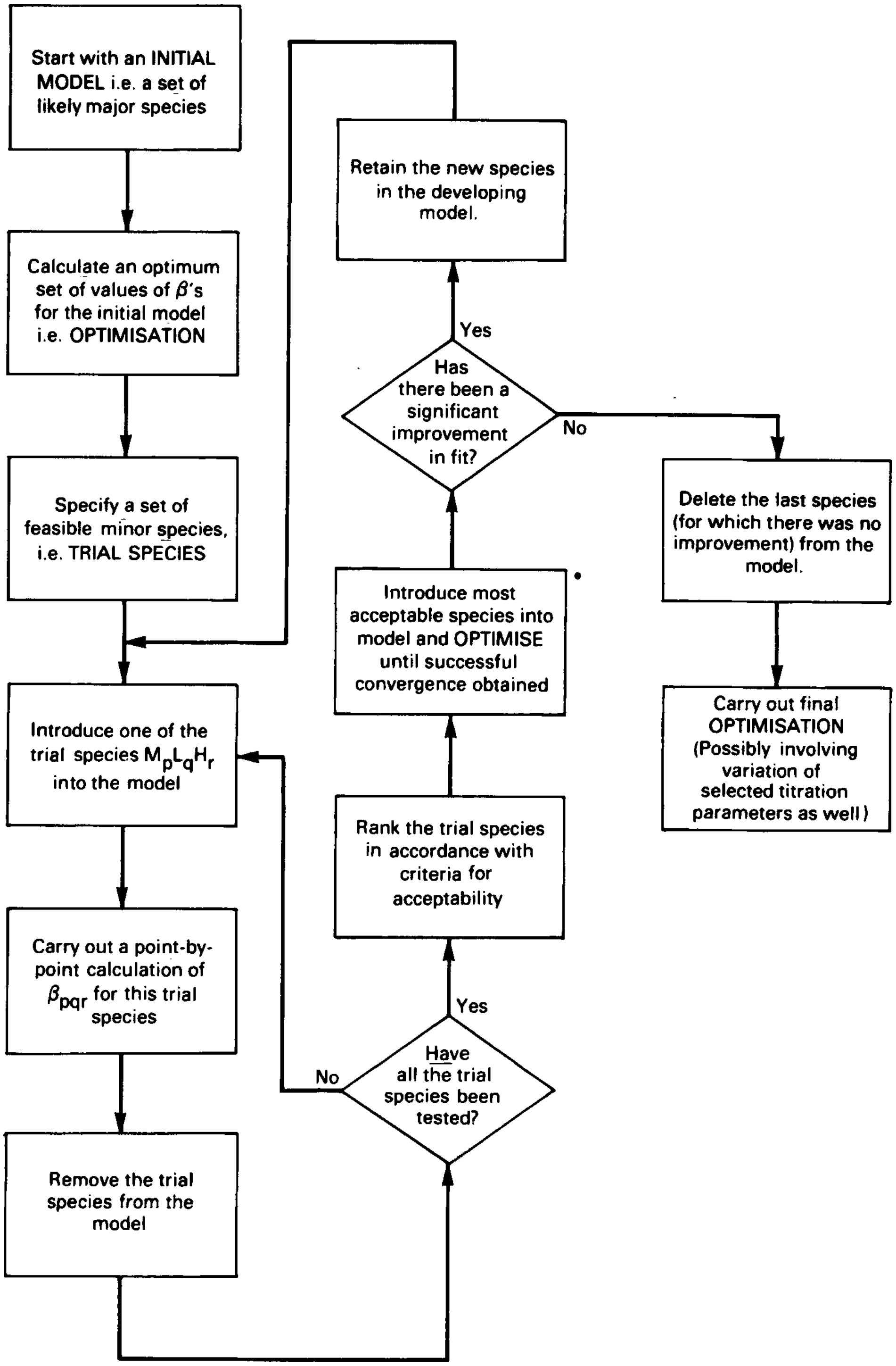


FIGURE 1 The formation function $\bar{Z}_M$(obs) plotted *vs* pA for measurements carried out at p[H] values below 10. Key to the plot symbols used is given in Table III in the text. A value of $pK_a = 9.01$ for HCN was used in the calculation of $\bar{Z}_M$(obs).

Likely species for incorporation into the model for this system were tested for or ranked by use of the BETA facility for point-by-point calculations of formation constants, as referred to earlier. The algorithm used in the model selection phase of this study is summarized in Figure 2. A notable feature of this algorithm is that the inner of the two nested loops involves only single parameter calculations which are much easier and quicker to carry out than the non-linear multiparameter optimisations involved in the outer (and less frequently traversed) loop. Thus, as many as 10 new trial species can be tested for in about the same time as it takes to carry out a single multiparameter optimisation involving a single trial species. Our experience with this algorithm is that the time taken to arrive at a satisfactory model for the system is a factor of 5 to 10 times less than that required by procedures like PQR analysis[31] which involve numerous multiparameter optimisations. Time will tell whether the models obtained using this procedure are as "good" as models obtained by PQR analysis, but recent experience in our laboratory involving variations on both approaches have been most encouraging. It seems prudent, at least until further experience is gathered, to begin with an "initial model", representing the experimenter's guess as to what the major species in the model are likely to be. In the present instance, this initial model was taken to be the set of binary species $Zn(CN)_2$, $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$. The algorithm can then be used to test for the presence or absence of other (presumably minor) species in the system.

In this way, the number of complexes in the model as increased by one each time the outer loop was traversed, and the values of all unknown formation constants were optimised using the OBJE task. A total of 117 data points, grouped into 12 titrations were used in these calculations.



•Occasionally it may be found that the "best" of the trial species is not accepted into the model at the optimisation stage. If so, try the next best trial species etc. until one is accepted (i.e. leads to successful convergence).

FIGURE 2 A flowchart showing the sequence of steps involved in model selection.

Results of these calculations are summarised in Table IV. Values of the objective function U are given in Columns 8, 9 and 10 of the Table. The formation constants given in Column 3 of Table II were incorporated as fixed values (assumed correct) in all the calculations.

Calculations were performed on two data sets, one comprising all the data obtained from the titrations referred to in Table III (117 data points), and the other comprising all the data except those obtained at p[H] values above 6.5 for the titrations denoted ○,* and ■ (giving a total of 94 data points). The omitted data from the latter titrations (corresponding to the rapid increase in $\bar{Z}_M$ on the extreme left-hand side of Figure 1) are known to be very sensitive to small uncertainties in analytical concentrations. Also, the ligand : metal ratios for these titrations (20.2 and 15.0 respectively) are both rather high and make the data from these titrations more than usually sensitive to small systematic errors. For the smaller data set, the pK_a of HCN was optimised in one set of calculations (column 9) and was held fixed at the experimentally determined value of 9.08 in the other set (column 10).

It is clear from Table IV that a simple model comprising only the binary species $Zn(CN)_2$, $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$ fails to account for the present experimental data adequately. The introduction of ternary $Zn/CN^-/OH^-$ species produces a marked improvement in fit between observed and calculated cell EMF values. A smaller improvement in fit is obtained on introduction of the five-coordinate species $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CN)_5^{3-}$, but the improvement appears to be significant, particularly when the 94 data point set is considered. It should be noted that, perhaps not surprisingly, a significant degree of correlation (correlation coefficient above 0.90) exists between the values of log β_{150} and log β_{011}, log β_{130} and log β_{140}, when the pK_a of HCN is treated as an adjustable parameter. However, when the pK_a of HCN is fixed at 9.08, no significantly correlated parameters are found. Attempts to introduce more species into the model were unsuccessful irrespective of whether 117 or 94 data points were used in the calculations. The evidence for inclusion of the five-coordinate species $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CN)_5^{3-}$ in the model is not as firm as the evidence for existence of $Zn(CN)_3(OH)^{2-}$. Nevertheless, in the light of other corroborating evidence to be discussed below, the former two complexes are retained in the model.

Final results based on the 94 data point set for the species present in solution and associated formation constants, together with estimated uncertainty limits obtained by multiplying ESTA – calculated standard deviations by 3, are given in Table V.

Plots of $\bar{Z}_M$(obs) (plotted as discrete points) and $\bar{Z}_M$(calc) (plotted as continuous lines) are shown in Figure 3. Similarly, plots of $\bar{Q}$(obs) and $\bar{Q}$(calc), both plotted *vs* $-\log[H]$, are shown in Figure 4. For clarity, not all experimental points are shown in Figures 3 and 4. Although agreement between observed and calculated formation functions is not perfect, it is felt that, particularly in view of the sub-millimolar concentration levels studied, the level of agreement between observed and calculated formation functions is acceptable. Features of the formation functions, such as the "curl back" displayed by certain titrations in the $\bar{Z}_M$ plot have been reproduced, as well as the relative positions of curves for various titrations on the low p[H] side of the $\bar{Q}$ plot, and the levelling off of the points for the titration denoted | on the high p[H] side of the $\bar{Q}$ plot.

DISCUSSION

To provide a visual representation of the speciation of zinc in zinc/cyanide/hydroxide-containing solutions, a plot of the percentage of zinc in the form of each complex is

TABLE IV

Results of model selection and calculation of formation/hydrolysis constants (expressed as logarithms to base 10)

Cycles through outer loop of algorithm	Species and formation/hydrolysis constants[a]						Goodness of fit, U		
	$Zn(CN)_2$	$Zn(CN)_3^-$	$Zn(CN)_4^{2-}$	$Zn(CN)_3(OH)^{2-}$	$Zn(CN)_3(OH)_2^{2-}$	$Zn(CN)_5^{3-}$	117 data points $pK_a = 9.08$	94 data points pK_a optimized	94 data points $pK_a = 9.08$
0	10.94	16.04	20.53				2610	2796	2960
1	10.98	15.53	20.33	3.81[b]			720	521	596
2	10.83	16.11	20.41	7.08			597	416	447
3	10.85	16.10	20.45	6.82	−3.31		560	355	401
4	10.80	16.12	20.41	6.61	−3.25	22.93	399	249[c]	288

[a] For complexes containing the hydroxide ion, *e.g.*, $Zn(CN)_n(OH)_m$, the values given in the Table represent log $\beta_{1n-m} - mpK_w$. [b] This value refers to the complex $Zn(CN)_2(OH)^-$ which was replaced by $Zn(CN)_3(OH)^{2-}$ at the next cycle. [c] Simultaneous variaton of $pK_a(HCN)$ leads to significant correlation between parameters at cycle 4.

TABLE V

Species present in $Zn^{2+}/CN^-/OH^-(H^+)$ containing solutions at p[H] values below 9.8, together with associated formation constants (expressed as logarithms to base 10)

Species	log β ($\pm 3\sigma$)
$Zn(CN)_2$	10.8 ± 0.1
$Zn(CN)_3^-$	16.12 ± 0.06
$Zn(CN)_4^{2-}$	20.41 ± 0.07
$Zn(CN)_3(OH)^{2-}$	20.4 ± 0.3
$Zn(CN)_3(OH)_2^{3-}$	24.3 ± 0.2
$Zn(CN)_5^{3-}$	22.9 ± 0.2
HCN	9.08 ± 0.01

given as a function of p[H] in Figures 5 and 6 for solutions in which $T_{Zn} = 3 \times 10^{-4}$ mol dm^{-3}, and $T_{CN}/T_{Zn} = 5$ and 10 respectively. At a ligand:metal ratio of 5:1 and p[H] = 9.8, the highest value attained in this study, the predominating species in solution is $Zn(CN)_4^{2-}$, accounting for 53% of the total zinc in solution, followed by the species $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CN)_3(OH)^{2-}$ in roughly equal amounts of 17% each. The remaining zinc occurs in the complexes $Zn(CN)_3^-$ and $Zn(CN)_5^{3-}$. Thus, at a p[H] of 9.8 and ligand:metal ratio of 5:1, mixed ligand complex species account for some 34% of the total zinc content of the solution. At the same p[H] value, but at a $T_{CN}:T_{Zn}$ ratio of 10:1, the binary complexes $Zn(CN)_5^{3-}$ and $Zn(CN)_4^{2-}$ predominate in solution, largely at the expense of the mixed ligand species, which together now account for only about 10% of the total zinc in solution. In both

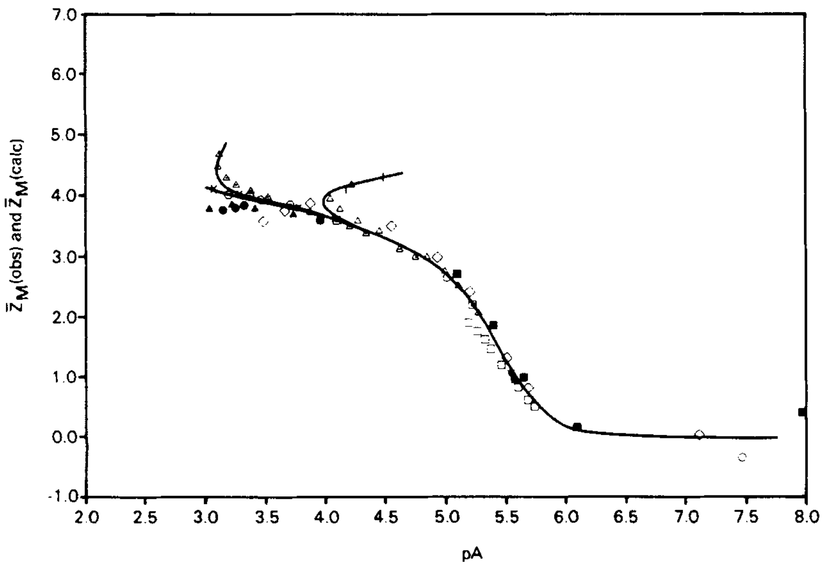


FIGURE 3 The formation functions $\bar{Z}_M$(obs) (discrete points) and $\bar{Z}_M$(calc) (continuous curves) plotted *vs* pA. For titrations ○, ● and ■ only data obtained below pH = 6.5 are included. $\bar{Z}_M$(calc) was obtained using the model and formation constants given in Table V in the text.

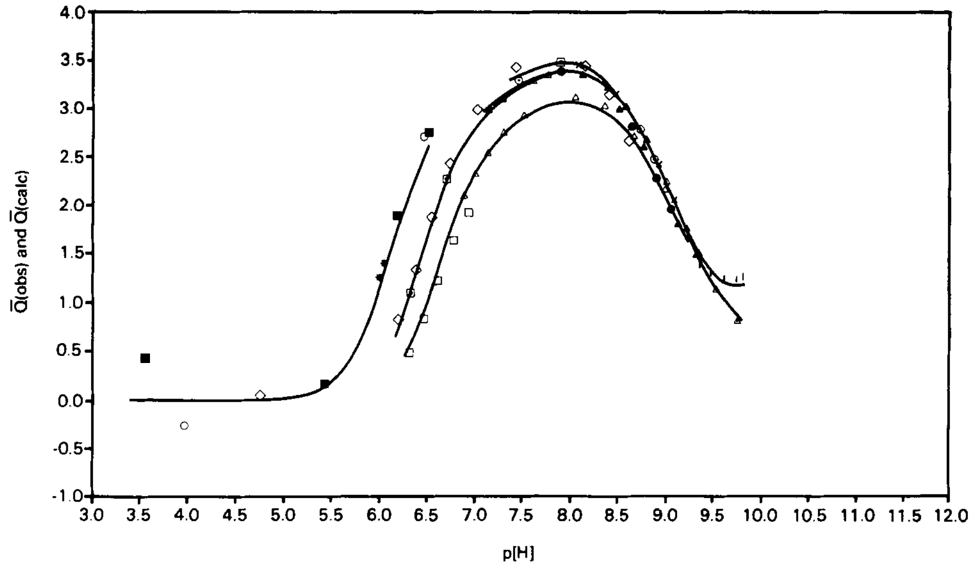


FIGURE 4 The deprotonation functions $\bar{Q}$(obs) (discrete points) and $\bar{Q}$(calc) (continuous curves) plotted *vs* p[H]. For titrations ○, * and ■, only data obtained below pH = 6.5 are included. $\bar{Q}$(calc) was obtained using the model and formation constants given in Table V in the text.

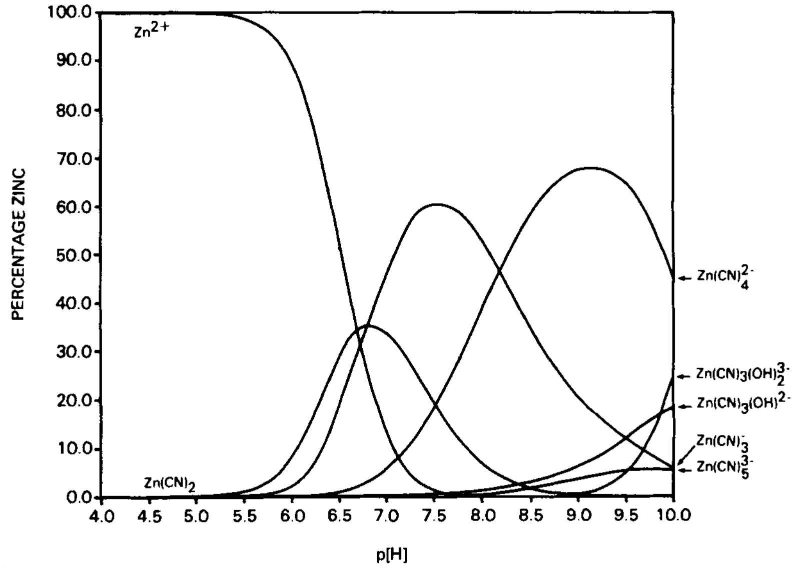


FIGURE 5 Speciation of zinc in Zn–CN–OH solutions as a function of p[H] for $T_{Zn} = 3 \times 10^{-4}$ mol dm^{-3} and $T_{CN}/T_{Zn} = 5$. Formation percentages were calculated using formation constants given in Table V in the text.

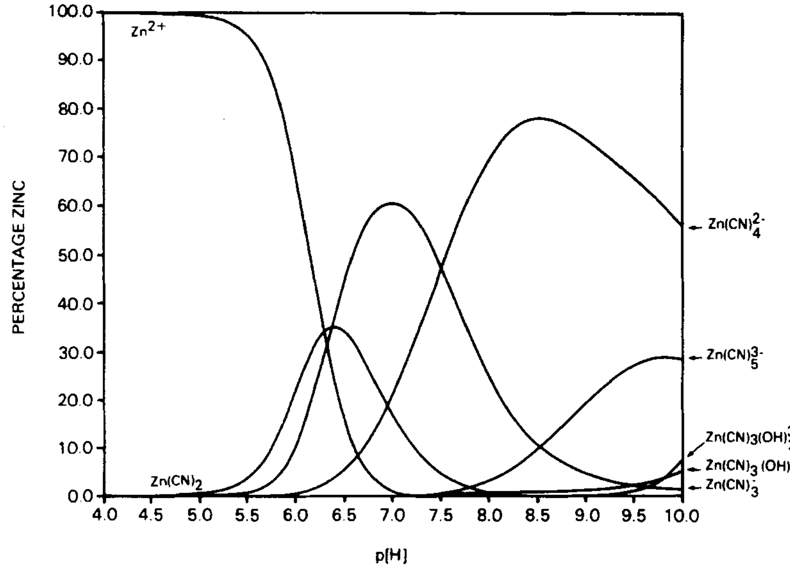


FIGURE 6 Speciation of zinc in Zn−CN−OH solutions as a function of p[H] for $T_{Zn} = 3 \times 10^{-4}$ mol dm^{-3} and $T_{CN}/T_{Zn} = 10$. Formation percentages were calculated using formation constants given in Table V in the text.

instances, calculations show that binary zinc-hydroxy complexes of the type $Zn_m(OH)_n$ do not form to any appreciable extent under these conditions.

It should be noted that the cyanide concentrations used, as well as the upper limit of pH attained in these titrations, were substantially lower than those used in the electrochemical studies of Nicol *et al.*[1] To provide some basis for comparison however, speciation calculations were carried out for the pH range 4→12 for a solution in which $T_{Zn} = 3 \times 10^{-4}$ mol dm^{-3} and $T_{CN} = 0.01$ mol dm^{-3}, *i.e.*, $T_{CN}/T_{Zn} = 33$. The results indicate that at the relatively high cyanide concentration of 0.01 mol dm^{-3} $[Zn(CN)_5^{3-}] \gg [Zn(CN)_4^{2-}] > [Zn(CN)_3(OH)_2^{3-}]$ at pH values below 11.0. At pH values above 11.0 $[Zn(CN)_3(OH)_2^{3-}] > [Zn(CN)_5^{3-}] > [Zn(CN)_4^{2-}] \geqslant [Zn(CN)_3(OH)^{2-}]$. It is of course entirely possible that other species not detected in this study may appear at pH values substantially above 10, and may even predominate at sufficiently high pH values. Nevertheless, the relative *order* of concentrations of the species $Zn(CN)_5^{3-}$, $Zn(CN)_4^{2-}$, $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CH)_3(OH)^{2-}$ given above will probably still be applicable.

With respect to the existence or otherwise of species of the form $Zn(CN)_n$ with $n > 4$, this study seems to corroborate the conclusion drawn by Pines[4] and Østerud and Prytz[8] on the basis of polarographic evidence, that such species are formed at sufficiently high cyanide concentrations. The latter authors worked at T_{Zn} concentrations in the range 10^{-4} to 10^{-3} mol dm^{-3} as in the present study, and presumably, at the natural pH of solutions formed at various cyanide levels. They reported a polarographic wave, assigned to $Zn(CN)_5^{3-}$, at a $T_{CN} : T_{Zn}$ ratio of 8 : 1 which persisted up to a ligand : metal ratio of 120 : 1. Speciation calculations carried out using the constants given in Table V, and the program HALTAFALL,[43] indicate that $Zn(CN)_5^{3-}$ is formed to an extent of 20% of total zinc in solution (at a natural pH of ~9.8) at a ligand : metal ratio of 8 : 1 in apparent accord with the observations (and deductions) of Østerud and Prytz.

Other recent studies of the $Zn^{2+} + CN^-$ system involving glass electrode potentiometry, such as those of Martin and Blanc[15] and Persson[17] in which the data were interpreted in terms of complexes $Zn(CN)_2$, $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$ only (see Table I), were carried out at pH values not exceeding ~8.5. Under such conditions one would expect, on the basis of the constants given in Table V, no more than about 2% of the total zinc in solution to be present as the $Zn(CN)_5^{3-}$ complex, and this may explain why these authors did not find it necessary to postulate the existence of this (and other other ternary) complex.

Although the formation of the mixed ligand species $Zn(CN)_3(OH)^{2-}$ has been established with some confidence in this study, one can be less certain about the five-coordinate species $Zn(CN)_3(OH)_2^{3-}$ and $Zn(CN)_5^{3-}$. However, considered in conjunction with the polarographic evidence of Østerud and Prytz, there are reasonable grounds for believing that such species do form in dilute solutions.

It is of interest that Østerud and Prytz report that at a T_{CN}/T_{Zn} ratio of 600:1, (*i.e.*, at a natural pH of ~11) the polarographic waves assigned to $Zn(CN)_5^{3-}$ and $Zn(CN)_6^{4-}$ both disappear. This observation may be significant in relation to the observations of Ashurst *et al.*,[18] that at free cyanide concentrations (and natural pH values) significantly higher than the highest value used by Østerud and Prytz, the free cyanide concentration in solution is consistent with a bound-cyanide:zinc ratio of 4:1. It would seem that although the species $Zn(CN)_5^{3-}$ (and, according to Østerud and Prytz,[8] $Zn(CN)_6^{4-}$) may form in solutions of sufficiently high cyanide concentrations, a point is reached when further reactions are induced which have the effect of *liberating* cyanide to the solution. Indeed, when this additional reaction is well advanced (as it presumably must have been in the experiments described by Ashurst *et al.*[18]), the bound cyanide:metal ratio drops to around 4:1.

The precise nature of the supposed cyanide-liberating reaction referred to above is a matter of speculation at present. Among the possibilities that exist, one may include the formation of polymeric species in solution involving cyanide and zinc in the ratio 4:1 with cyanide or hydroxide ions acting as bridging ligands, or the formation of some form of colloidal precipitate involving cyanide and zinc in the ratio 4:1 and possibly also the hydroxide ion.

With regard to the ternary complexes reported in Table V, it is of interest to compare the value of $\log \beta = 20.4$ for $Zn(CN)_3(OH)^{2-}$ with the corresponding values of $\log \beta = 20.41$ for $Zn(CN)_4^{2-}$ and $\log \beta = 15.2$ for $Zn(OH)_4^{2-}$ – all values referred to an ionic strength of 0.1 mol dm^{-3}. Other factors being equal, mixed ligand complexes are stabilised by comparison to the corresponding binary complexes involving the same total number of ligands, since there are statistically more ways of making up a mixed ligand complex than the corresponding binary complexes. As discussed by Sharma and Schubert[50] the statistical factor tending to stabilise the mixed ligand complex $ML_xL'_yL''_z\ldots$ can be calculated from $S = n!/(x!\,y!\,z!\ldots)$ where n represents the total number of ligands in the complex. If the total number of ligands on the complexes considered is less than the maximum possible coordination number of the metal ion concerned, this should presumably stabilise both the mixed ligand and the corresponding binary complexes to the same extent and therefore produce no net effect. The logarithm of the formation constant of a mononuclear mixed ligand complex $ML_xL'_y$ can then be estimated by use of the relation (*2*).

$$\log \beta(ML_xL'_y) \simeq \frac{x}{x+y}\log \beta(ML_{x+y}) + \frac{y}{x+y}\log \beta(ML'_{x+y}) + \log S \qquad (2)$$

Application of this relationship leads to a prediction of $\log \beta[Zn(CN)_3(OH)^{2-}] \simeq 19.7$.

Comparison with the experimental value of 20.4 ± 0.3 indicates a "ligand enhancement factor"[50] $\Delta \log \beta = 0.7 \pm 0.3$ for this complex, *i.e.*, after correction for statistical effects, this mixed ligand complex shows an enhanced stability of some 0.7 log units. This observation, together with the equation may prove useful when estimating formation constants of other mixed ligand complexes like $Zn(CN)_2(OH)^-$, $Zn(CN)(OH)$ *etc.*, any or all of which may form under appropriate experimental conditions, e.g. low cyanide:zinc ratios.

There are indications that, in addition to involvement in the metallurgy of gold extraction, the zinc cyanide system and the constants that describe it are likely to be important in other fields such as industrial electroplating and metal reclamation, the modelling of body fluids, and speciation research into radioactive waste disposal.

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