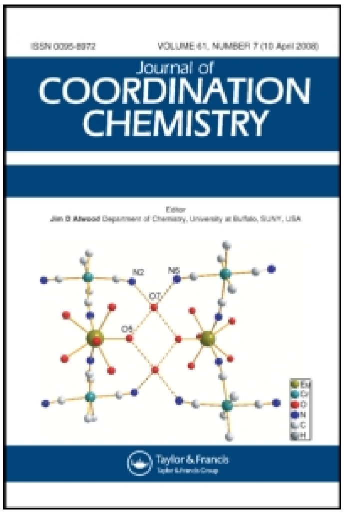

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CYANIDE THERMODYNAMICS. 1. STABILITY CONSTANTS OF CADMIUM(II) AND ZINC(II) CYANIDE COMPLEXES IN AQUEOUS ACETONITRILE MIXTURES

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CYANIDE THERMODYNAMICS.
1. STABILITY CONSTANTS OF CADMIUM(II) AND ZINC(II) CYANIDE COMPLEXES IN AQUEOUS ACETONITRILE MIXTURES

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Stability constants for the cyanide complexes of zinc(II) and cadmium(II) have been determined in five acetonitrile-water mixtures containing up to 70% (v/v) MeCN. The constants were measured at 25°C and an ionic strength of 1M $NaClO_4$ by high precision glass electrode potentiometry. Complexes containing up to four cyanide ions have been detected for both Zn(II) and Cd(II) although the lower order complexes $ZnCN^+$ and $Zn(CN)_2{}^o$ are difficult to quantify because of the sparing solubility of the zinc cyanide salt. The stability constants for both systems increase monotonically with MeCN concentration and show a striking similarity. Evidence for the formation of ternary hydroxocyano-metal ion complexes was obtained at high pH values but their stability constants could not be evaluated because of the lack of quantitative information for the binary $M(II)\text{-}OH^-$ species.

KEYWORDS: zinc(II), cadmium(II), cyanide, stability constants, acetonitrile, water

INTRODUCTION

The cadmium(II) and zinc(II)-cyanide systems have been extensively studied in aqueous solution.[1–4] Apart from some early and almost certainly unreliable polarographic measurements,[5,6] there is general agreement about the existence of $M(Cn)_x{}^{2-x}(aq)$ complexes ($M = Cd,Zn$) with $1 \leq x \leq 4$. Nevertheless, these systems are difficult to investigate because of the sparing solubility of $M(CN)_2$ and $M(OH)_2$ at mid to high pH values and the volatility of HCN at low pH;[1,7] consequently accurate values of their equilibrium (stability) constants remain elusive.[1,2]

As with most complexation reactions, almost nothing is known about the behaviour of metal ion-cyanide equilibria in nonaqueous or mixed solvents.[3,4] This is significant given the potential hydrometallurgical importance of such solutions as demonstrated in particular by Parker and co-workers.[8,9] The behaviour of M^{n+}/CN^- systems in acetonitrile (MeCN)-water mixtures is of special interest in this context because the strength of complexation equilibria may be dramatically altered by even quite small additions of MeCN to water.[10,11] The strength of metal-cyanide complexes in aqueous MeCN solutions is also important for

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understanding and optimizing a recently developed analytical procedure[12,13] to determine "available" cyanide in the complex hydrometallurgical mixtures typically encountered in the extraction of gold from its ores. This method employs ion chromatography, with $MeCN/H_2O$ mixtures as the mobile phase, and its success is critically dependent on the ability of Ni(II) to compete for CN^- with other cyanide-binding species. Finally, the study of the thermodynamics of cyanide equilibria in mixed solvents is of intrinsic interest because of the insights it can provide into the solvation of complex species.[14,15]

Thus, the present paper reports the stability constants of the cadmium(II) – zinc(II)-cyanide systems in $MeCN\text{-}H_2O$ mixtures containing up to 70% (v/v) MeCN obtained by high precision glass electrode potentiometry at $I = 1$ M ($NaClO_4$) and 25°C.

EXPERIMENTAL

1. Reagents

All reagents were of analytical grade and were used without further purification. All solutions were prepared using high purity water (Millipore Milli-Q system) boiled and purged with nitrogen to remove carbon dioxide and oxygen. Stock solutions of 0.1000 M carbonate-free sodium hydroxide were prepared from commercial solutions (BDH, Concentrated Volumetric Standard, stated accuracy ±0.2%), and cross-checked by titration against potassium hydrogen phthalate (Ajax, 99.8–100.2%). Hydroxide solutions were stored tightly sealed to prevent CO_2 contamination and were usually used within two weeks. Stocks solutions of ~1 M $HClO_4$ were prepared from concentrated commercial reagent (UNIVAR) and standardized potentiometrically against NaOH. Stock solutions of ~0.2 M zinc and cadmium were prepared by dissolving zinc oxide (UNIVAR) or cadmium carbonate (BDH), in a small excess of concentrated perchloric acid. These solutions were standardised against commercial 0.02000 M EDTA (BDH, CVS) using Erio-T indicator.[16] The excess of hydrogen ions (necessary to avoid hydrolysis of the cations) was determined against NaOH using Gran plots[17] and the program MAGEC.[18] Solutions of sodium cyanide (BDH, 97%) were prepared daily and were analysed by volumetric titration against silver nitrate (BDH, CVS), by Liebig's method[16]. Sodium perchlorate (BDH, 99.0%) was used to maintain the ionic strength at 1.00 M. High purity acetonitrile (Mallinckrodt, >99.9%) was used for preparing the mixed solvents.

2. Instrumentation and Procedures

The titration apparatus and electrodes used were essentially the same as those described by Hefter.[19] Potentiometric titrations were conducted in a tall-form 100 cm^3 titration vessel thermostatted (Haake N7) at 25.0±0.005°C. Glass electrodes (Metrohm model 6.0101.000) were calibrated externally before and after each titration except in the protonation studies when they were calibrated internally.[18] All calibrations were made in terms of $[H^+]$ and so "pH" throughout this paper refers to $-\log[H^+]$. All potentials were measured to ±0.1 mV with a high impedance digital voltmeter relative to a AgCl/Ag reference electrode consisting of a silver wire in contact with solid silver chloride and a solution of 0.95 M $NaClO_4$ and 0.05 M NaCl in the appropriate $MeCN/H_2O$ mixture. The reference electrode was separated from the test solution using a salt bridge containing 1 M $NaClO_4$ also in the appropriate solvent mixture. A low leakage porous glass frit formed the liquid junction. Titrations were conducted using a computer-controlled titration system of in-house construction but employing commercial automatic burettes (Metrohm model 665).[20] Three separate glass electrode/reference electrode combinations were used.

High purity nitrogen, used to protect the cell solution, was first passed through a pre-saturator containing a solution of 1 M $NaClO_4$ in the appropriate $MeCN/H_2O$ mixture. Special precautions were taken to minimise voltalisation of both HCN and acetonitrile. In particular, the titration cell was carefully sealed and, at low pH, degassing was discontinued and stirring minimised.

The cell used in these potentiometric measurements, may be represented as follows

Reference half-cell	‖	Salt bridge	‖	Test solution	
Ag $\mid$ AgCl $\mid$ 0.95 M $NaClO_4$	‖	1 M $NaClO_4$	‖	(1–2*z*) M $NaClO_4$	$\mid$ GE
0.05 M NaCl	‖	v% $MeCN/H_2O$	‖	*x* M NaCN, *y* M NaOH	
v% $MeCN/H_2O$	‖		‖	*z*M $Zn/Cd(ClO_4)_2$	
	‖		‖	*v*% $MeCN/H_2O$	
	E_{j1}		E_{j2}		

where *v*% is the volume percentage (mL MeCN/100 cm^3 solution) in the $MeCN/H_2O$ solvent mixture, GE is a glass electrode, and E_{j1} and E_{j2} are liquid junction potentials (LJPs). This is a constant ionic strength cell and, provided that variation of the ionic strength is minimised and $x,y,z \ll 1$ M, the LJP changes are negligible and may be safely ignored.[21]

Because the pK_a of HCN is quite high (~9) it is usually necessary to titrate M^{n+}/CN^- solutions to high pH values to achieve sufficient competition for the cyanide ion by M^{n+} and H^+. Consequently, it is necessary to know both the dissociation constant of water (K_w), and the dissociation constant of HCN (K_a) in the medium of interest in order to determine the formation constants of the metal-cyanide complexes. These data were obtained by titrations of strong acid ($HClO_4$) with strong base (NaOH) and CN^- respectively, as described in detail elsewhere.[22]

The formation constants of the Cd(II) and Zn(II)-cyanide complexes were determined by titrations with $HClO_4$ at total metal concentrations of (2–5 mM) and cyanide ions (10–25 mM) using mole ratios (R_{T_{CN}/T_M}) of 4, 5 and 6, where T_i represents the total or analytical concentration of the species i. Titrations were started at pH 12–13. No precipitation was observed for the Cd(II)-CN^- system over the entire pH range in any of the $MeCN/H_2O$ solvent mixtures. However, for Zn(II)/CN^-, white precipitates, confirmed to be $Zn(CN)_2$ (in water, $K_s = 3.3 \times 10^{-16}$)[3] by X-ray diffraction, were observed in slightly acidic solutions (pH 5–6). Acid addition was continued until the precipitate completely redissolved. After, restabilisation (~25 minutes), the titrations were continued to about pH 2.5.

3. Data Analysis

Potentiometric data were processed using the ESTA suite of programs.[23,24] For the general equilibrium (the charges are omitted for simplicity)

$$pM + qCN + rH_2O \rightleftharpoons M_p(CN)_q(OH)_r + rH \qquad (1)$$

the overall stability constant of the complex $M_p(CN)_q(OH)_r$ is

$$\beta_{pqr} = \frac{[M_p(CN)_q(OH)_r]K_w^r}{[M]^p[CN]^q[OH]^r} \qquad (2)$$

where

$$K_w = [H][OH] = \beta_{00-1} \qquad (3)$$

is the dissociation constant of water.

Model selection was based primarily on minimisation of the objective function

$$U = (N - n_p)^{-1} \sum_{n=1}^{N} n_e^{-1} \sum_{q=1}^{n_e} W_{nq}(Y_{nq}^{obs} - Y_{nq}^{calc})^2 \qquad (4)$$

in which N is the total number of experimental titration points, n_p is the total number of electrodes, n_c is the number of parameters to be optimised, Y_{nq} is either the total concentration of electrode ion q or the emf of electrode q at the nth titration point. W_{nq} is the weight of the qth residual at the nth point

$$W_{nq} = \left[\sum_p \left(\frac{\delta(Y_{nq}^{obs} - Y_{nq}^{calc}}{\delta p}\right)^2 \sigma_p^2\right] \qquad (5)$$

where p is the optimisation parameter vector, and σ_p in the standard deviation of the titration parameters held constant during the optimisation. Species were accepted in general only if the objective function was significantly reduced (>50%) by their inclusion.

For metal-cyanide systems the formation function, $\bar{Z}_M$, can be formulated as follows

$$\bar{Z}_M = [T_{CN} - A(1 - [H]\beta_{011})]/T_M \qquad (6)$$

where β_{011} is the pK_a of HCN and

$$A = [T_H - [H] + K_w[H]^{-1}/[H]\beta_{011} \qquad (7)$$

was also used to assist in model selection along with the standard deviations of the β_{pqr} values. When only mononuclear metal-ligand complexes (*i.e.* p = 1 in eqn (*1*) are present, A is the free ligand concentration and $\bar{Z}_M$ can be considered as the average number of ligands bound per metal ion.

Once the most likely set of species was determined, the precision of the calculated formation constants was determined using a Monte Carlo method.[25] The titration data for the metal-cyanide systems are summarised as Z_M *vs* pA plots.

RESULTS AND DISCUSSION

1. Dissociation of water and HCN

As noted above, the formation constants of metal-cyanide systems must generally be determined at pH values where the dissociation of HCN and water must be taken into account. Accordingly, the equilibrium constants for these reactions were measured under conditions identical to the present study as described in detail elsewhere.[13,22] For convenience the values obtained are listed in Table I.

No literature values have been reported for either the ionization constant of water (pK_w) or the dissociation constant of HCN in $MeCN/H_2O$ mixtures but the results in aqueous solution are in good agreement with those reported previously in the same medium and the precision is excellent.[1,3,4,26] As can be seen from Table I the values of both pK_w and $pK_a(HCN)$ increase monotonically with increasing MeCN concentration but the magnitude of the changes is quite small even up to 70% MeCN.

2. The cadmium(II)-cyanide system in aqueous solution

The $Cd(II)$-CN^- system will be discussed first as it was not hampered by precipitation; consequently the interpretation of the experimental data is relatively straightforward and indeed can be used in the interpretation of the more difficult $Zn(II)/CN^-$ system. Typical data for the $Cd(II)/CN^-$ system in aqueous solution are summarised in Figure 1.

The "curlbacks" in Figure 1 at low pA (high pH) reflect the existence of ternary $Cd(II)/CN^-/OH^-$ and/or $Cd(II)/OH^-$ complexes. Unfortunately, as no formation constant data are available for the binary $Cd(II)/OH^-$ complexes in $MeCN/H_2O$ mixtures the computational analysis had to be restricted to pH <8.5. Consequently, only the formation constants of the binary $Cd(II)/CN^-$ complexes could be quantified. A similar situation has been described for the $Cd(II)/CN^-$ system at high pH in aqueous NaCl solutions.[1]

The data for the $Cd(II)/CN^-$ system in aqueous solution have been thoroughly reviewed by Verhoeven et al.[1] The most relevant of the available data are collected into Table II along with the present results. Given the differences in ionic strength the agreement is quite satisfactory. The concordance between the calculated and observed data at pH <8.5 is excellent as indicated by the data in Figure 2 and by

Table I Dissociation constants of water and HCN in $MeCN/H_2O$ mixtures at I = 1 M ($NaClO_4$) and 25°C[a].

%MeCN	pK_w	$pK_a(HCN)$
0.0	13.7518(8)	9.0330(10)
10.0	13.9162(10)	9.1209(15)
20.0	14.1920(10)	9.2844(11)
30.0	14.4184(7)	9.4260(20)
50.0	14.9705(9)	9.9338(254)
70.0	15.9189(17)	10.8531(26)

[a] Data from refs. 13 and 22. Values in parentheses are standard deviations in the last significant figure of the constant; the maximum uncertainty is generally an order of magnitude higher.

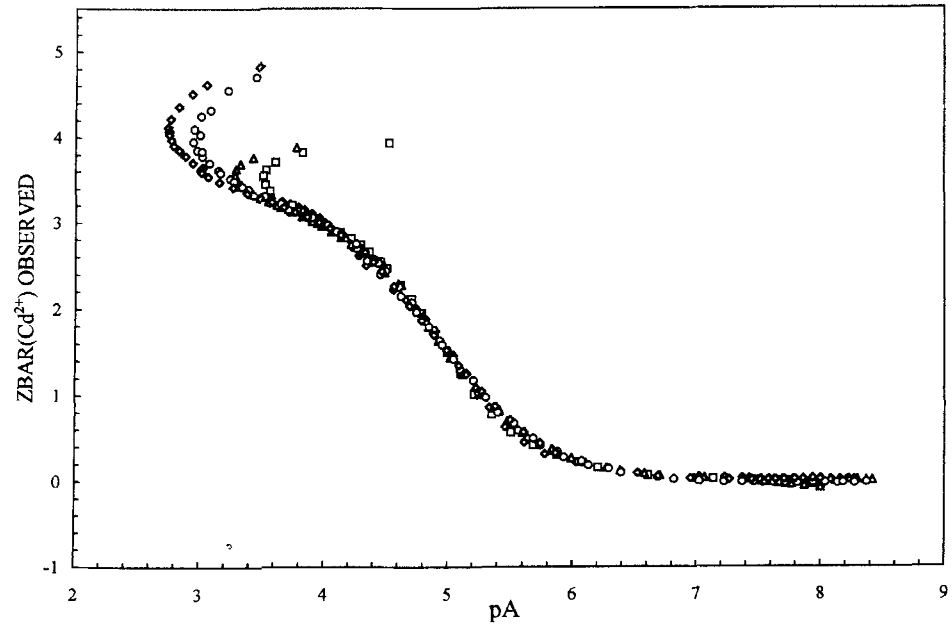

Figure 1 Observed formation function $\bar{Z}_M$ for the Cd(II)/CN$^-$ system in aqueous solution plotted against pA over the (approximate) pH range 2 to 13.

Table II Stability constants ($\log\beta_{1q0}$) of the Cd(II)-CN$^-$ complexes in aqueous solution at I = 1 M ($NaClO_4$) and 25°C

Species	Formula	This work[a] 1 M ($NaClO_4$)	Persson[b] 3 M ($NaClO_4$)	Leden[c] 3 M ($NaClO_4$)
110	$CdCN^+$	5.487(8)	5.62(5.68)	5.48(5.40)
120	$Cd(CN)_2^{\circ}$	10.353(7)	10.83(10.87)	10.60(10.60)
130	$Cd(Cn)_3^-$	15.085(6)	15.72(15.75)	15.23(15.15)
140	$Cd(CN)_4^{2-}$	18.324(7)	19.20(19.09)	18.78(18.30)

[a] Values in parentheses are standard deviations based on the analysis of 8 titrations with 304 data points; OBJT = 3.84 × 10^{-9}. [b] Values in parentheses are a recalculation[1] of the original data.[7] [c] Values in parentheses are a recalculation[1] of the original data.[27]

the magnitude of the standard deviations of the formation constants and the low value of the unweighted objective function (Table II footnotes).

3. *The cadmium(II)-cyanide system in MeCN/H_2O mixtures*

The data obtained for the Cd(II)/CN$^-$ system in the various MeCN/H_2O solvent mixtures were broadly similar to those obtained in aqueous solution. Representative data are given in Figure 3 and show $\bar{Z}_M$ gradually rising to a value of 4 without any distinct steps, indicative of the presence of overlapping complexes $Cd(CN)_q^{(2-q)+}$ up to q = 4. The $\bar{Z}_M$ curves were always independent of the total metal ion concentration, T_{Cd}, indicating the absence of any polynuclear (p > 1) complexes.

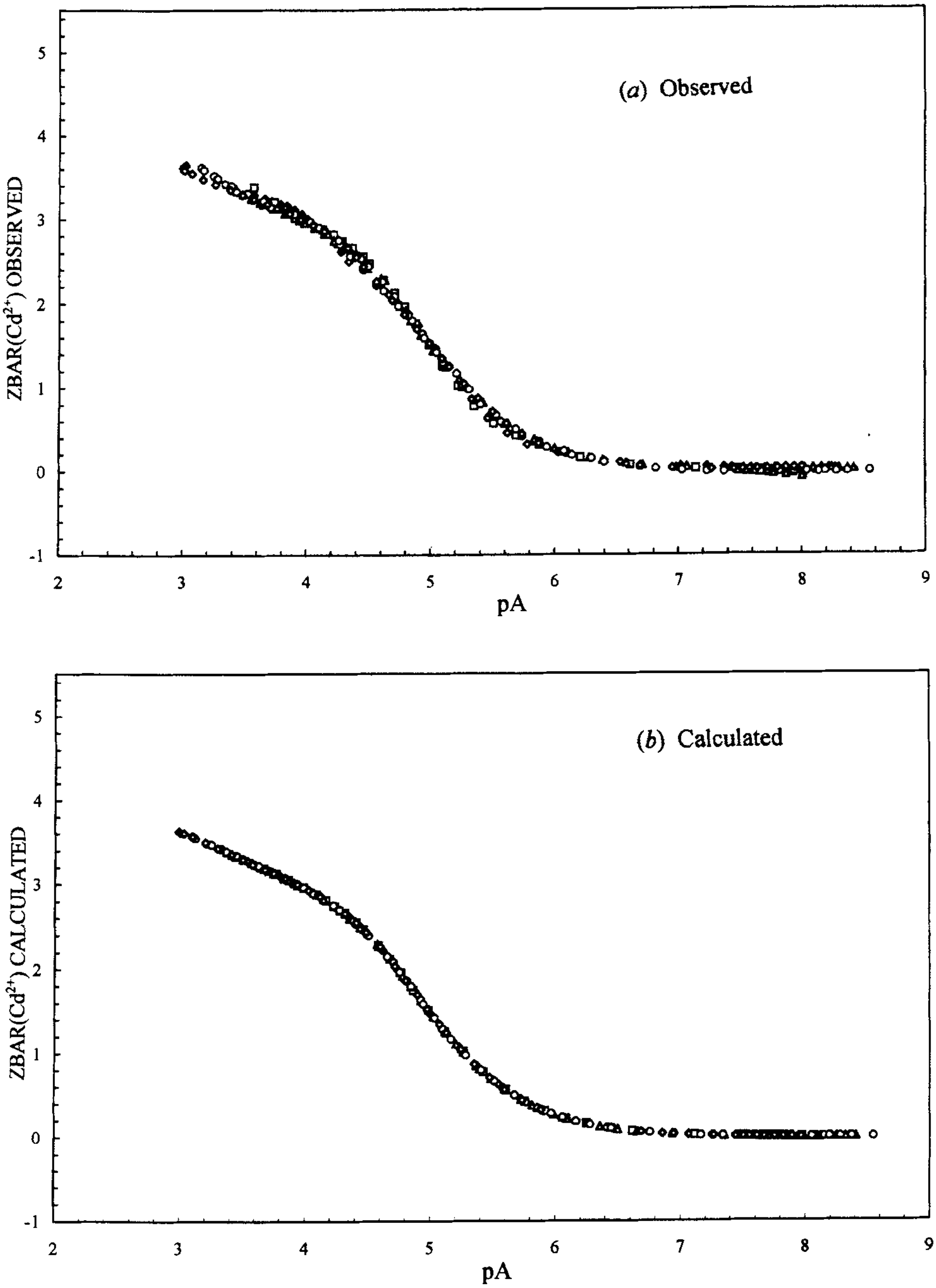

Figure 2 Observed (*a*) and calculated (*b*) formation functions $\bar{Z}_M$ for the Cd(II)/CN$^-$ system in aqueous solution plotted against pA at pH < 8.5.

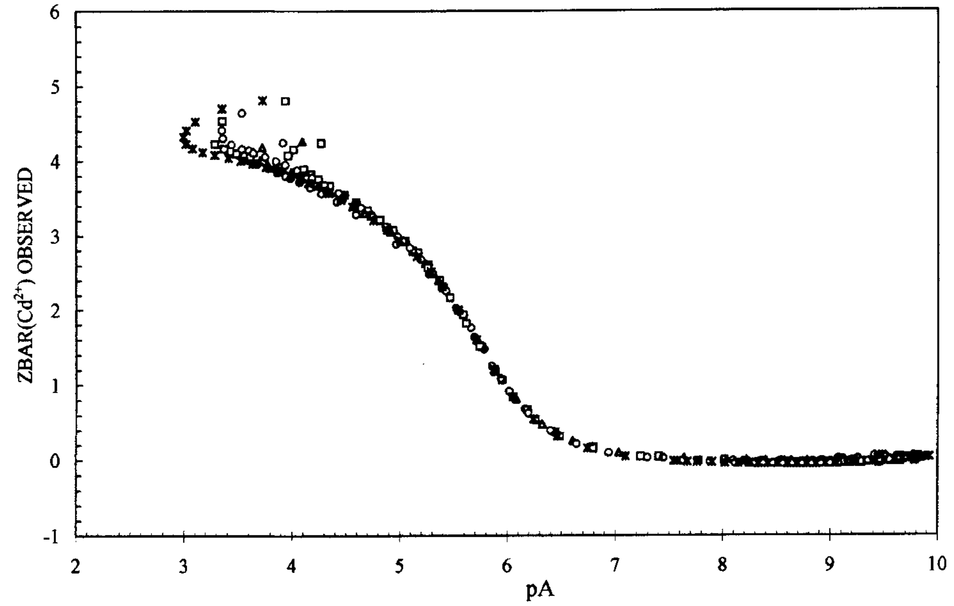

Figure 3 Representative formation function data for the Cd(II)/CN$^-$ system in MeCN/H_2O mixtures.

On the other hand, the "curl-backs" characteristic of mixed Cd(II)/CN$^-$/OH$^-$ and/or Cd(II)/OH$^-$ complexes were also always observed (Figure 3) but, for the reasons outlined above, such data had to be excluded from the computational analysis. The "best-estimate" values for β_{1q0} are given in Table III. No previous measurements for this system in MeCN/H_2O mixtures have been reported so no direct comparisons are possible. However, the absence of major systematic errors in the data was confirmed by establishing that small changes in the local optimized titration parameters had no significant effect on the OBJT function or the optimized β_{1q0} values.

4. *The zinc(II)-cyanide system in aqueous solution*

Although the accessible pH range for the zinc(II)-cyanide system was limited by the precipitation of $Zn(CN)_2(s)$, corresponding to the gap in the $\bar{Z}_M$ *vs* pA plots, it was generally possible to obtain some data at low pH after the precipitate redissolved (Figure 4). As with the aqueous Cd(II)/CN$^-$ system a maximum $\bar{Z}_M$ of 4 corresponding to $Zn(CN)_4{}^{2-}$ was observed and the $\bar{Z}_M$ plots were independent of T_{Zn}. The "curl-backs" characteristic of ternary and/or hydroxo complexes were also present (Figure 4) as observed previously for this system by Verhoeven *et al.* in 3 M NaCl[1]. Again, the absence of the stability constants for the Zn(II)/OH$^-$ complexes in the present medium meant that the high pH (low pA) data had to be excluded from the computational analysis so that only β_{1q0} constants were

Table III Stability constants of the Cd(II)/CN^- complexes in MeCN/H_2O mixtures at I = 1 M ($NaClO_4$) and 25°C

MeCN %	Species	Log β^a_{pqr}	Standard deviation	OBJT	No. of titrations	No. of data points
10.0	110	5.5046	0.0118	7.2E-09	8	271
	120	10.4448	0.0117			
	130	15.2936	0.0087			
	140	18.9045	0.0091			
20.0	110	5.6301	0.0103	3.4E-09	8	236
	120	10.8425	0.0086			
	130	15.8528	0.0074			
	140	19.9092	0.0065			
30.0	110	5.6629	0.0119	4.2E-09	8	246
	120	11.0277	0.0098			
	130	16.1684	0.0080			
	140	20.4119	0.0068			
50.0	110	5.9335	0.0156	5.0E-09	8	283
	120	11.7484	0.0096			
	130	17.1904	0.0089			
	140	21.7887	0.0077			
70.0	110	6.4588	0.0185	4.4E-09	8	232
	120	13.0679	0.0082			
	130	19.1390	0.0082			
	140	24.2632	0.0072			

determined. The "best estimates" of the formation constants are given in Table IV along with relevant literature data.

The restricted pH range created difficulties in determining the formation constants and will therefore be discussed in some detail. Model selection began by assuming only those species for which the chemical evidence is unquestionable:[1,2,7] $Zn(CN)_2{}^0$, $Zn(CN)_3{}^-$ and $Zn(CN)_4{}^{2-}$. The only other species considered likely to be present, at low pH, was $ZnCN^+$. As a rule of thumb, a species was accepted into the model only if the unweighted objective function OBJT was significantly reduced (by ≥50%) and the standard deviations of the already accepted equilibrium constants remained the same or improved.

On the basis of these two criteria the evidence for the existence of $ZnCN^+$ was inconclusive. Thus, inclusion of $ZnCN^+$ improved OBJT by only 10%, consistent with the limited number and modest scatter of the data points (Figure 4) at high pA (low pH) where $ZnCN^+$ is likely to exist in significant amounts. It should also be remembered that the experimental data in this region are likely to be less reliable because of the increased risk of volatilisation of HCN from acidic solution.

Table IV Stability constants (log β_{1q0}) of the Zn(II)/CN^- complexes in aqueous solution at I = 1 M ($NaClO_4$) and 25°C

Species	Formula	This work[a] 1 M($NaClO_4$)	Persson[b] 3 M($NaClO_4$)	Marsicano *et al.*[2] 0.1 M ($NaClO_4$)
110	$ZnCN^+$	5.438(70)	5.34(5.19)	
120	$Zn(CN)_2{}^0$	11.356(38)	11.03(11.04)	10.8
130	$Zn(CN)_3{}^-$	16.334(36)	16.68(16.65)	16.12
140	$Zn(Cn)_4{}^{2-}$	20.728(33)	21.57(21.49)	20.41

[a] Values in parentheses are standard deviations; 6 titrations/206 data points; OBJT = 3.9×10^{-9}.
[b] Values in parentheses are a recalculation[1] of the original data.[7]

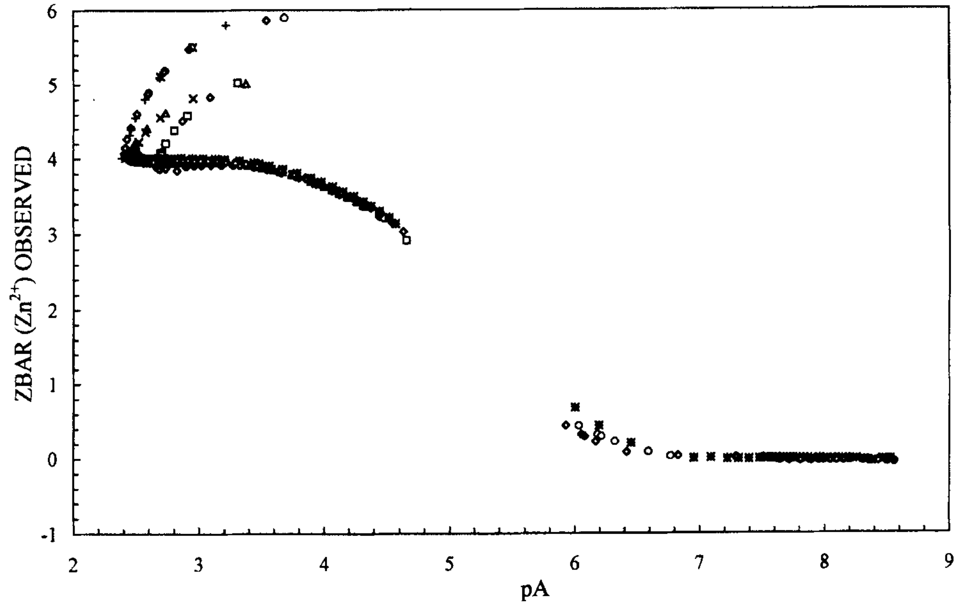

Figure 4 Observed formation function $\bar{Z}_M$ for the Zn(II)/CN$^-$ system in aqueous solution plotted against pA over the (approximate) pH range 2 to 13.

Although the value of β_{110} obtained here was not completely satisfactory, as shown by a very high standard deviation (0.07), its value is in good agreement with the literature data (Table IV). Hence, the ZnCN$^+$ species was included in the final model. The large standard deviation for the β_{110} obtained here was similar to that reported by Verhoeven *et al.*[1] in 3 M NaCl, who also concluded that evidence for ZnCN$^+$ was marginal.

The inclusion of Zn(CN)$_2$$^\circ$ in the model improved the fit by 96% and provided the value of β_{120} = 11.36 in good agreement with the literature results (Table IV). The remaining complexes, Zn(CN)$_3$$^-$ and Zn(CN)$_4$$^{2-}$ were well represented in the data and the results are consistent with literature data (Table IV).

5. The zinc(II)-cyanide system in MeCN/H$_2$O mixtures

The data obtained for the Zn(II)-cyanide system in the various MeCN/H$_2$O mixtures (Figure 5) were similar to those in aqueous solution except that the "gap" in the titration curves due to Zn(CN)$_2$(s) precipitation was rather greater, especially at higher MeCN concentrations ($\geq$50%). Consequently, as can be seen from the $\bar{Z}_M$ plots (Figure 5), almost no data could be obtained for ZnCN$^+$ and Zn(CN)$_2$$^\circ$. As previously, the absence of the formation constants for the Zn(II)/OH$^-$ complexes under the conditions used here restricted the computational analysis to pH $\leq$ 8.5 so that only the formation constants of simple Zn(II)/CN$^-$ complexes could be determined.

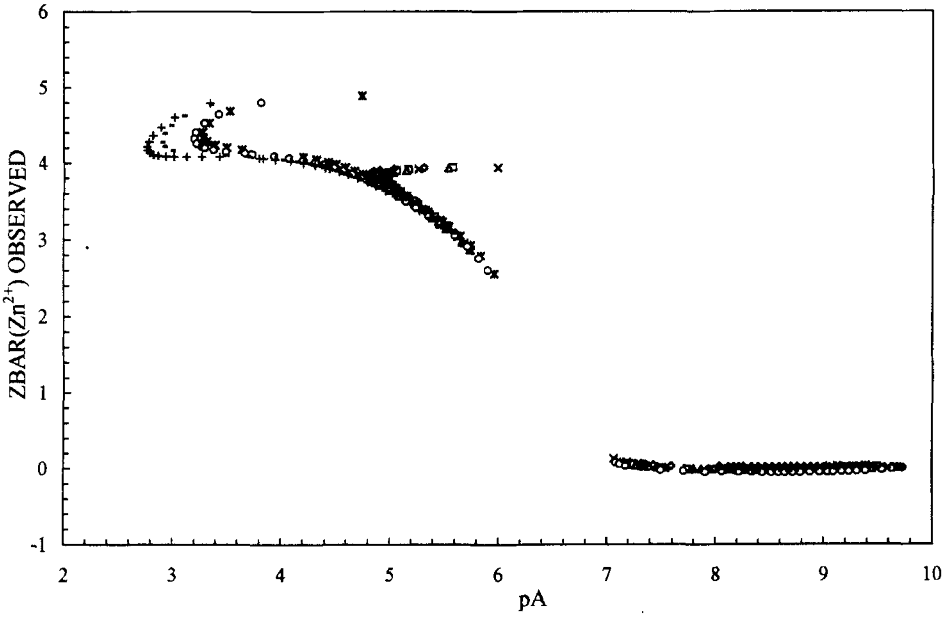

Figure 5 Representative formation function data for the Zn(II)/CN^- system in MeCN/H_2O mixtures.

Model selection for this system in the mixed solvent solutions was initially based on the species $ZnCN^+$, $Zn(CN)_2^o$, $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$ derived for aqueous solutions (see above). However, attempts to include all four complexes into the model simultaneously resulted in non-convergence, indicating that not all of the four complexes exist in significant amounts within the accessible pH range. Reasonable fits were obtained when either the $Zn(CN)_2^o$ or $ZnCN^+$ species was separately combined with $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$. Thus, inclusion of $Zn(CN)_2^o$ improved OBJT by 31, 42, 58, 65 and 52% for 10, 20, 30, 50 and 70% MeCN mixtures respectively. Consistent with the difficulty of its detection similar, but somewhat smaller, improvements in OBJT were obtained when $ZnCN^+$ was (separately) included in the model. However, in both cases significant changes in β_{130} and β_{140} *and* their standard deviations were observed. For these reasons an alternative strategy was applied. This involved holding β_{110} and β_{120} constant and optimizing β_{130} and β_{140} only. The appropriate values of β_{110} and β_{120} for each MeCN/H_2O mixture were obtained by assuming that their change from H_2O to MeCN/H_2O was the same as that measured for the corresponding Cd(II) complexes. That is

$$(\log\beta^{Zn}_{1q0})_{S2} - (\log\beta^{Zn}_{1q0})_{S1} = \Delta\,(\log\beta^{Zn}_{1q0})_{S1\to S2} \approx \Delta(\log\beta^{Cd}_{1q0})_{S1\to S2} \qquad (8)$$

where $(\log\beta^{M}_{1q0})_{S1\to S2}$ is the change in (the logarithm of) the formation constant of the complex $M(CN)_q^{2-q}$ in going from H_2O (S1) to the particular MeCN/H_2O mixture (S2). The values of $\log\beta^{Cd}_{1q0}$ in S1 and S2 were taken from Tables II and III respectively and those for $(\log\beta^{Zn}_{1q0})_{H_2O}$ from Table IV.

The inclusion of the fixed values of β_{110} and β_{120} in the models for the Zn(II)/CN$^-$ system in 10, 20, 30, 50 and 70% MeCN improved the objective function by 37, 20, 49, 58 and 44%, respectively. The lack of a large improvement in the fit is due mainly to the very small amount of, and modest scatter in, the data in the region where ZnCN$^+$ and Zn(CN)$_2^0$ might be expected to be significant. Nevertheless, it is interesting to note that the β^{Zn}_{1q0} (q = 1,2) values calculated in this way are in quite good agreement with the values obtained by (separate) optimization of the experimental data as shown in Table V.

Table V Comparison between the calculated (*via* eqn (*8*) and computer optimized stability constants of the Zn(II)/CN$^-$ system in MeCN/H$_2$O mixtures

MeCN %	log β_{110} calculated	log β_{110} computer optimization	log β_{120} calculated	log β_{120} computer optimization
10.0	(5.46)	5.61	(11.45)	11.58
20.0	(5.58)	5.39	(11.85)	11.60
30.0	(5.61)	5.73	(12.03)	12.05
50.0	(5.89)	6.04	(12.75)	12.87
70.0	(6.41)	6.80	(14.07)	14.77

The results obtained for the Zn(II)/CN$^-$ system in the various MeCN/H$_2$O mixtures are summarized in Table VI. It is obvious from a comparison of Tables III and VI that although the objective functions are similar for the Zn(II)/CN$^-$ and Cd(II)/CN$^-$ systems, the uncertainties in the formation constants of the former are

Table VI Stability constants of the Zn(II)-cyanide complexes in MeCN/H$_2$O mixtures at 25°C and I = 1 M (NaClO$_4$)

MeCN/H$_2$O %	Species	Log β^a_{pqr}	Standard deviation	OBJT	Number of titrations	Number of data points
10.0	110	(5.456)		1.01E-08	10	432
	120	(11.448)				
	130	16.817	0.0256			
	140	21.917	0.013			
20.0	110	(5.582)		1.43E-09	10	432
	120	(11.846)				
	130	17.063	0.033			
	140	22.225	0.014			
30.0	110	(5.615)		6.90E-09	10	316
	120	(12.031)				
	130	17.639	0.015			
	140	22.867	0.007			
50.0	110	(5.885)		4.66E-09	8	326
	120	(12.752)				
	130	18.733	0.014			
	140	24.116	0.009			
70.0	110	(6.411)		1.74E-09	8	278
	120	(14.071)				
	130	20.629	0.019			
	140	26.484	0.014			

[a] Values in parentheses have been fixed as described in the text.

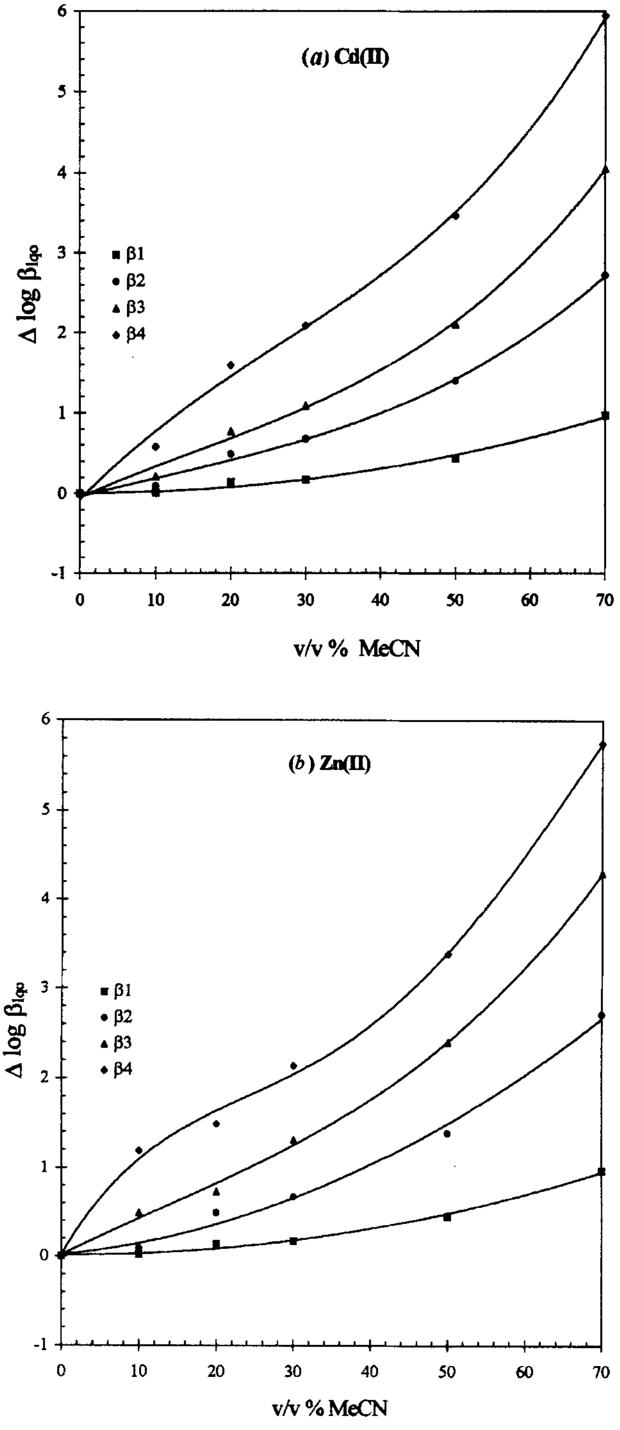

Figure 6 The variation in Δ (log $\beta_{1q0}(M(CN)_q^{(2-q)+}))_{S1\rightarrow S2}$ for the cyanide complexes of (*a*) Cd(II) and (*b*) Zn(II) in MeCN/H_2O mixtures.

greater. Again, this is a reflection of the difficulties of obtaining sufficient reliable data for the Zn(II)/CN^- system over the appropriate concentration ranges.

6. *General comments*

The variation of the stability constants of the Cd(II) and Zn(II) cyanide complexes with solvent composition in MeCN/H_2O mixtures (Tables II–VI) is illustrated in Figure 6 which plots the change in the equilibrium constant ($\Delta \log \beta_{1q0})_{S1 \rightarrow S2}$ as a function of solvent composition. In general, all the stability constants show a monotonic increase with increasing MeCN concentrations. Insofar as comparisons are possible (Tables II–VI), the changes for the Zn(II) and Cd(II) complexes are remarkably similar. This is a little surprising because it might have been expected that the "softer" Cd^{2+} would be rather better solvated by the "soft" MeCN co-solvent. Unfortunately, no quantitative data are available regarding the solvation of Cd^{2+} in MeCN/H_2O mixtures although Zn^{2+} has been shown to be less well solvated in such mixtures than in water over the whole composition range.[29] Presumably, any enhanced solvation of Cd^{2+} over Zn^{2+} in MeCN/H_2O mixtures is counterbalanced by a similar effect for the complex ions.

As can be seen from Figure 6 the change in stability for both the Zn(II) and Cd(II) cyanide systems increases with the number of CN^- ligands, *i.e.*, $\Delta \log \beta_{140} > \Delta \log \beta_{130} > \Delta \log \beta_{120} > \Delta \log \beta_{110}$. A similar effect was observed[11] for the Zn(II)Cl^- system in MeCN/H_2O, which was shown to be due to the far less favourable solvation of Cl^- in the mixtures compared with H_2O. The Gibbs energy of transfer of CN^- from H_2O to MeCN/H_2O is also unfavourable[29] although not as much as for Cl^-, which is consistent with the much smaller effect of MeCN concentration on the stability constants of the metal ion-cyanide complexes. Further discussion of these results requires a more detailed knowledge of the solvation characteristics of all the species involved, both simple and complex.

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