Contribution from the Inorganic Chemistry Laboratory,
Oxford University, United Kingdom

Potentiometric Studies in Mixed Solvents.[1] II. Complexes of Nickel(II), Copper(II) and Zinc(II) with Pyridine, Ethylenediamine and Glycine

G. Faraglia,* F. J. C. Rossotti and H. S. Rossotti

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Formation constants for the complexes of pyridine, ethylenediamine and glycinate with protons, nickel(II), copper(II) and zinc(II) were determined potentiometrically in a 0.5 M $(Li)ClO_4$ *medium in water, 54.3% w/w methanol and in 48.1% w/w dioxan at 25°C. The stepwise protonation constants for pyridine decrease in the order water > methanol > dioxan, while both stepwise protonation constants for ethylenediamine follow the order water > dioxan > methanol and both constants for the glycinate ion follow the order dioxan > water, methanol. The first hydrolysis constants for the three ligands, and the second hydrolysis constant for ethylenediamine, all decrease in the order water > methanol > dioxan. For the metal chelate* [illegible] *glycinate complexes than for those of ethylenediamine. The stability constants of pyridine complexes are but little influenced by change in the solvent. For complexes of a given metal cation with ethylenediamine and glycinate, the ratios of successive stability constants are almost independent of the ligand or of the composition of the solvent. The observed trends in the different equilibrium constants are discussed in terms of the number of water molecules released during the reaction and of the estimated free energies of transfer of the various species between an aqueous and a partly organic medium.*

Introduction

Previous work[2] on the effect of composition of mixed aqueous-organic solvents on the magnitude of equilibrium constants has been concerned mainly with the dissociation of organic acids, or of « ion-pairs ». The few metal chelates which have been studied in series of solvent mixtures usually contain oxygen-donor ligands. The stability constants of these complexes, like those of the ligand-proton complexes, increase with increasing organic content of the solvent.[3,4] Scattered reports of preliminary work[2] suggest that the stability of metal-ion complexes of nitrogen-donor ligands is but little influenced by the composition of the solvent.

The present work is part of an investigation[1] of the variation of stability with solvent composition. Stoichiometric stability constants of complexes of copper(II), nickel(II) and zinc(II) with pyridine (py), ethylenediamine (en) and glycine (gly) were determined by potentiometric titration in a 0.5 *M* $(Li)ClO_4$ medium in water, in 54.3% w/w methanol and in 48.1% w/w dioxan at 25°C.

Experimental Section

Reagents. All reagents were of AnalaR grade unless stated otherwise.

Metal perchlorates were prepared from perchloric acid and excess of the metal oxide, carbonate or basic carbonate, and were recrystallized from water. Sufficient perchloric acid was added to stock aqueous solutions of the copper, nickel and zinc salts to repress hydrolysis. The total perchlorate ion concentration was determined by using the ion exchange resin, Amberlite 120, in the hydrogen form. The concentrations of copper, nickel and zinc ions were determined by electrodeposition. Nickel was also determined gravimetrically using dimethylglyoxime. Zinc and copper were also determined volumetrically using EDTA. Silver perchlorate was analysed by titration with sodium chloride.

Lithium hydroxide (British Drug Houses) was dissolved in boiled-out water, filtered and stored under nitrogen.

Glycine was recrystallized,[5] pyridine was redistilled from molecular sieves, and ethylenediamine was redistilled from sodium. Methanol and de-ionized water were purified by redistillation. Dioxan (Fluka, « gereingt nach Hess und Frahm ») was purified first by freezing, and then by refluxing with hydrochloric acid.[5] After being dried over potassium hydroxide and distilled from sodium, it was found to be free from peroxides.

(*) Present address: Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R. - Padova (Italy).

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(2) A. E. Martell and L. G. Sillén, eds., «Stability Constants», 2nd. edn., the Chemical Society, London (1964). R. A. Robinson and R. H. Stokes « Electrolyte Solutions », 2nd edn., Butterworths, London, 1959; R. G. Bates, « Determination of pH, Theory and Practice », Wiley, New York, 1964.

(3) H. Irving and H. Rossotti, *Acta Chem. Scand.*, *10*, 72 (1956).

(4) F. J. C. Rossotti in J. Lewis and R. G. Wilkins, eds., « Modern Coordination Chemistry », Interscience, New York (1960).

(5) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, « Purification of Laboratory Chemicals », Pergamon, Oxford (1966).

Apparatus. Grade A glassware was used for all volumetric work. Titrations were carried out in the potentiometric cell described elsewhere.[6] The silver electrode in the « Wilhelm » reference half-cell was prepared according to Brown.[7] The glass electrode was a Radiometer type G202B (except for some of the titrations of pyridine systems in methanol, where a Beckman electrode AS2LP was used). E.m.f. values were measured to ±0.1 mV using a Radiometer pHM4 potentiometer. There was no difficulty in obtaining steady, reproducible e.m.f. in any of the media studied. The titration vessel was thermostated by a water-bath at 25.00±0.05°C, kept in a room thermostated to 25±1°C.

Solutions. Stock aqueous solutions were made 1.000 M in total perchlorate ion concentration by adding lithium perchlorate. Solutions for potentiometric titration were prepared by adding a volume ν_S of solvent S to 50.0 ml of stock aqueous solution to give a total volume of 100.0 ml. Values of ν_S and mole fractions x_W of water in the resultant solvent mixtures S_M are given in Table I.

Table I. Parameters for Solvent Mixtures

S	Water	Methanol	Dioxan
ν_S, ml	50.0	53.2	52.2
x_W	1.00	0.679	0.819
ω mV M^{-1}	139 ±5	96 ±5	101 ±5
$-\log K_w$	13.568±0.008	13.69 ±0.01	14.82 ±0.02

Cell. The cell

$$-\;\begin{array}{l|l|l|l|l}\text{Glass} & \text{Test} & 0.5\,M\ \text{LiClO}_4 & 0.01\,M\ \text{AgClO}_4 & \text{Ag}\\ \text{electrode} & \text{solution} & \text{in } S_M & 0.49\,M\ \text{LiClO}_4 & \\ & \text{in } S_M & & \text{in } S_M & \\ & & \text{(a)} & & \end{array}\;+ \qquad (1)$$

was used for potentiometric titrations. The composition of the test solution was

H^+, total concentration $H\,M$, free concentration $h\,M$

M^{2+}, total concentration $M\,M$ ($0.004\,M \leqslant M \leqslant 0.025\,M$), free concentration $m\,M$

L, total concentration $L\,M$ ($0.005\,M \leqslant L \leqslant 0.050\,M$), free concentration, $l\,M$

$[\text{Li}^+] = (0.500 - 2M - h + K_w h^{-1})\,M$

$[\text{ClO}_4^-] = 0.500\,M$

The test solution was stirred by oxygen-free nitrogen which had been passed through a solution of 0.5 M LiClO_4 in S_M.

It has previously been shown[1] that total replacement of Li^+ by H^+ has no affect on values of $\gamma_{\pm\text{HCl}}$ in a 0.5 M $(\text{Li}^+ + \text{H}^+)(\text{ClO}_4^- + \text{Cl}^-)$ medium in the solvent mixtures S_M. As the values of M and L are low, the e.m.f. of cell I in mV may be represented by

$$E = E^\circ - 59.15 \log h + E_j \qquad (1)$$

where the term E° includes the asymmetry potential of the glass electrode and E_j is the diffusion potential across the junction (a).

Design of Titrations. Stoichiometric stability constants $K_j = [\text{H}_j\text{L}]/h^j l$ of the acids H_jL were obtained from measurements of $h(H, L)$ for $M = 0$, using the function $\bar{j}(h)$, where

$$\bar{j} = \frac{H - h + K_w h^{-1}}{L} = \frac{\sum_0 jK_j h^j}{\sum_0 K_j h^j} \qquad (2)$$

Measurements of $h(H, L, M)$ gave values of

$$\bar{n} = \frac{L - (H - h + K_w h^{-1})\bar{j}^{-1}}{M} = \frac{\sum_0 n\beta_n l^n}{\sum_0 \beta_n l^n} \qquad (3)$$

and

$$l = \frac{L - \bar{n}M}{\sum_0 K_j h^j} \qquad (4)$$

from which the stoichiometric stability constants $\beta_n = [\text{ML}_n]/ml^n$ of the complexes ML_n were calculated.

The functions $\bar{j}(h)$ were determined at several values of L in order to ascertain that species such as H_jL_2 were absent; and measurements of $\bar{n}(l)$ were carried out at various values of M, H and L to check that no mixed, polynuclear or metal hydroxo-complexes were present under the conditions used.

Determination of h. Acid-base titrations when $L = 0$ and $M = 0$ give

$$E^{\circ\prime} = E + 59.15 \log h = E^\circ + E_j \qquad (5)$$

whence

$$\lim_{h \to 0} E^{\circ\prime} = E^\circ$$

It was found that $E_j = \omega h$, where the values of ω are given in Table I. Once E° and ω are known, h can be calculated from E by means of successive approximations, using equation (5). The lower values of ω in organic mixtures are compatible with smaller differences between the mobilities of lithium and hydrogen ions in mixed solvents than in aqueous solution.

Determination of K_w. In alkaline solution, the value of E°_{OH} may be obtained as

$$\lim_{[\text{OH}^-] \to 0} E^{\circ\prime\prime} = E^\circ_{\text{OH}}$$

where

$$E^{\circ\prime\prime} = E - 59.15 \log[\text{OH}^-]$$

Values of

$$-\log K_w = (E^\circ_{\text{OH}} - E^\circ)/59.15 \qquad (6)$$

are given in Table I. Although the value of K_w in dioxan is of comparatively low precision, the values of K_j and β_n are unaffected because $[\text{OH}^-]$ is of little importance under the conditions used.

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(6) F. J. C. Rossotti and H. Rossotti, « The Determination of Stability Constants », McGraw-Hill, New York (1961), and Mir, Moscow (1965).

(7) A. S. Brown, *J. Am. Chem Soc.*, 56, 646 (1934).

Table II. Stability Constants of Ligand-Proton Species

S		Water	Methanol	Dioxan
System				
H^+—py	log K_1	$5.47_5 \pm 0.01$	$4.71_5 \pm 0.01$	4.64 ± 0.01
H^+—en	log K_1	10.01 ± 0.02	9.52 ± 0.02	$9.80_5 \pm 0.01$
	log K_2/K_1	7.31 ± 0.01	6.83 ± 0.01	$6.99_5 \pm 0.01$
H^+—gly	log K_1	9.53 ± 0.01	9.29 ± 0.01	9.58 ± 0.01
	log K_2/K_1	2.39 ± 0.01	2.97 ± 0.01	3.25 ± 0.01

Table III. Stability Constants of Metal-Ligand Complexes

S			Water	Methanol	Dioxan
M	L				
Ni^{II}	py	log β_1	1.88 ± 0.02	1.89 ± 0.02	1.91 ± 0.02
		log β_2/β_1	1.20 ± 0.02	1.23 ± 0.02	1.26 ± 0.02
	en	log β_1	7.36 ± 0.01	7.64 ± 0.02	8.18 ± 0.02
		log β_2/β_1	6.26 ± 0.02	6.54 ± 0.02	7.02 ± 0.01
		log β_3/β_2	4.40 ± 0.03	4.60 ± 0.04	5.02 ± 0.03
	gly	log β_1	5.60 ± 0.01	6.16 ± 0.01	6.51 ± 0.01
		log β_2/β_1	4.74 ± 0.02	5.27 ± 0.02	5.62 ± 0.02
		log β_3/β_2	3.44 ± 0.03	3.91 ± 0.03	4.26 ± 0.02
Cu^{II}	py	log β_1	2.56 ± 0.02	2.46 ± 0.02	2.45 ± 0.01
		log β_2/β_1	1.89 ± 0.02	1.92 ± 0.02	1.83 ± 0.01
	en	log β_1	$10.61_5 \pm 0.01$	$10.82_5 \pm 0.01$	11.24 ± 0.01
		log β_2/β_1	$9.29_5 \pm 0.01$	$9.46_5 \pm 0.01$	9.88 ± 0.01
	gly	log β_1	8.05 ± 0.02	8.82 ± 0.02	9.19 ± 0.01
		log β_2/β_1	6.79 ± 0.02	7.36 ± 0.01	7.65 ± 0.01
Zn^{II}	py	log β_1	0.99 ± 0.01	1.14 ± 0.02	1.06 ± 0.02
		log β_2/β_1	0.28 ± 0.02	—	0.76 ± 0.03
	en	log β_1	5.75 ± 0.01	6.02 ± 0.01	6.52 ± 0.01
		log β_2/β_1	5.09 ± 0.01	5.30 ± 0.02	5.73 ± 0.02
	gly	log β_1	4.81 ± 0.01	5.38 ± 0.02	5.71 ± 0.01
		log β_2/β_1	4.19 ± 0.01	4.75 ± 0.02	5.09 ± 0.02
		log β_3/β_2	2.51 ± 0.01	2.91 ± 0.03	3.21 ± 0.03

Determination of K_j. Ligand was added to the solution in a cell for which E° had been determined. The value of H was varied by titration with $HClO_4$ or LiOH, and the function $\bar{j}(h)$ was calculated using equations (1) and (2). The values of K_1 for pyridine, and the widely separated values of K_1 and K_2/K_1 for glycine were found by comparing the experimental functions $\bar{j}(\log h)$ with the theoretical normalised curve for a monobasic acid.[6] The less-widely separated values of K_1 and K_2/K_1 for ethylenediamine were obtained by the projection-strip method.[8] The values obtained are shown in Table II.

Determination of β_n. The value of E° was determined for a solution in which $H>0$, $M>0$ and $L = 0$. Values of H and L were then varied either by the addition of L and subsequent titration with LiOH or, for pyridine, by titration with a L—LH^+ buffer. The function $\bar{n}(l)$ was obtained by means of equations (3) and (4).

Values of β_1 and β_2 for the Cu^{II}-gly and Cu^{II}-en systems were obtained from the formation curves $\bar{n}(\log l)$ by the projection strip method.[8a] Stability constants of other systems were obtained by successive extrapolation[8b] of the functions $F_t(l)$, where

$$F_t = \sum_{0}^{t-1} \frac{\bar{n}-n}{t-\bar{n}} \beta_n l^{n-t}$$

As the maximum values of $\bar{n}$ achieved in the Zn-py systems were rarely more than 0.4, the stability constants of these complexes were recalculated on an English Electric KDF9 computer using the ALGOL program[9] FAJAF 32. The values obtained are shown in Table III.

Discussion

General Considerations. Suppose that in all three media studied, the formation of H_jL and ML_n can be written as

$$aA\,.\,zH_2O + B\,.\,yH_2O \longrightarrow BA_a\,.\,xH_2O + wH_2O \qquad (7)$$

where w for a particular reaction is independent of solvent, and solvation by methanol or dioxan is negligible.[10,11] If the total concentrations of A and B are

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[8] (a) F. J. C. Rossotti, H. S. Rossotti, and L. G. Sillén, *Acta Chem. Scand.*, *10*, 203 (1956); F. J. C. Rossotti and H. S. Rossotti, *J. Phys. Chem.*, *63*, 1041 (1959); (b) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand*,, *9*, 1155 (1955).

[9] G. Cumming, J. S. Rollett, F. J. C. Rossotti, and R. J. Whewell, unpublished work.

[10] A. Fratiello and D. C. Douglass, *J. Chem. Phys.*, *39*, 2017 (1963).

[11] J. Padova, *J. Phys. Chem.*, *72*, 796 (1968).

low, we may assume that Owen's secondary medium effect[12] is negligible, *i.e.* that the activity coefficients $_W\gamma$ and $_M\gamma$ in aqueous solution and in the mixed solvent depend only on the medium (solvent mixture and background salt). If we now define the standard state so that all $_W\gamma$ are unity, the activity coefficients $_M\gamma$ represent Owen's primary medium effect.[12]

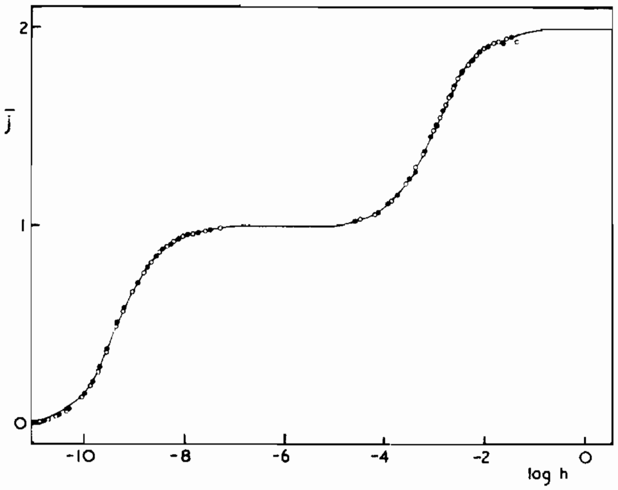

Figure 1. The formation curve $\bar{j}(\log h)$ for the gly—H$^+$ system in aqueous methanol. The experimental points refer to initial concentrations of $L = 0.040\,M$ (full circles) and $0.025\,M$ (open circles). The full curve is calculated using the values of K_1 and K_2/K_1 given in Table II. Experimental data for all other L—H$^+$ systems are of similar precision.

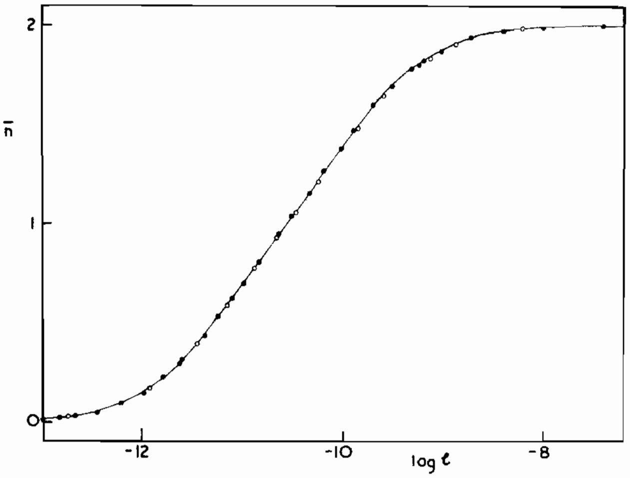

Figure 2. The formation curve $\bar{n}(\log l)$ for the Cu^{II}-en system in aqueous dioxan. The experimental points refer to initial values of $M = 0.0288\,M$ (open circles) and $0.0127\,M$ (full circles). The full curve is calculated using the values of β_1 and β_2 given in Table III. Experimental data for all other M—L systems are of similar precision.

Let $_WK'$ and $_MK'$ be the stoichiometric equilibrium constants for reaction (7) in water, and in S_M. Then

$$\ln \frac{_WK'}{_MK'} = \ln \frac{[BA_a]_W[H_2O]_W^w}{[B]_W[A]_W{}^a} - \ln \frac{[BA_a]_M[H_2O]_M^w}{[B]_M[A]_M{}^a} =$$

$$\ln \frac{_M\gamma_{BA_a} \cdot {_M\gamma}_{H_2O}^{w}}{_M\gamma_B \cdot {_M\gamma_A}^a} \qquad (8)$$

whence

$$RT \ln \frac{_WK'}{_MK'} = \Delta G^t_{BA_a} + w\Delta G^t_{H_2O} - \Delta G^t_B - a\Delta G^t_A = \Delta G^t_R \qquad (9)$$

Here $\Delta G_i{}^t$ is the molar free energy of transfer of the species i from medium W to medium M; and $\Delta G_R{}^t$ is the sum of $\Delta G_i{}^t$ for the products of reaction (7) minus the sum of $\Delta G_i{}^t$ for the reactants. The conventional stoichiometric stability constants $K = K'[H_2O]^{-w}$ which do not involve the concentration of water, may be substituted into equation (9) to give

$$\log \frac{_WK}{_MK} = \frac{\Delta G_R{}^t}{2.303\ RT} + w \log \frac{[H_2O]_M}{[H_2O]_W} \qquad (10)$$

A full interpretation of the variation of equilibrium constants with solvent therefore requires a knowledge of the number, w, of water molecules released during the reaction[13,14] and the free energies of transfer of all participating species. Although values for most of these quantities are not known, the signs and approximate magnitudes of $\Delta G_i{}^t$ have been estimated for some simple species.[16-20] If these estimates are accepted, the sign of $\Delta G_R{}^t$ for a particular reaction can be predicted, and compared with the experimental value of

$$Y_W = \log {_WK} - \log {_MK} - w \log[H_2O]_M/[H_2O]_W \qquad (11)$$

calculated for $[H_2O]_M/[H_2O]_W = \frac{1}{2}$, using a likely value of w. If w has been correctly chosen, then $RTY_W \ln 10 = \Delta G_R{}^t$.

Ligand-proton Systems. The values (see Table II) of K_1 for pyridine, and of K_1 and K_2/K_1 for ethylenediamine, are all lower in the mixed solvents than in water, in agreement with the observation that the strengths of nitrogen bases pass through a minimum at some intermediate solvent composition.[15,21-23] However, the values of K_1 for glycine fall in the order $_MK_{\text{dioxan}} > {_WK} > {_MK_{\text{methanol}}}$. Thus values of $Y_o = \log {_WK} - \log {_MK}$ are positive for all systems except for those involving glycine and for these systems Y_W is positive for the first protonation step if one or more water molecules is released, *i.e.* if $w \geqslant 1$.

According to Feakins and coworkers,[16-19] $\Delta G^t_{\text{cation}}$ is negative, the effect being smaller the smaller the cation. A smaller negative value of ΔG^t has also been invoked for uncharged species; but here the effect is thought to increase with increasing size of the molecule. These estimates suggest that, since $\Delta G_L{}^t$ and $(\Delta G^t{}_{H^+} - \Delta G^t{}_{HL^+})$ appear to be negative, the term $\Sigma\Delta G^t$ is positive for the formation of pyH$^+$ and enH$^+$.

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(12) H S. Harned and B. B. Owen, « Physical Chemistry of Electrolyte Solutions », 3rd. ed., Reinhold, New York (1958).

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(22) G. Douhéret, *Bull. Soc. Chim. Francc*, 1967, 1412.

(23) M. Paabo, R. G. Bates and R. A. Robinson, *J. Phys. Chem.*, *70*, 247 (1966).

This is compatible with the observed value of Y_W, which is positive for any value of $w > 0$ for the addition of a proton to enH^+. No estimates of ΔG^t are available for divalent ions, but if $w \geqslant 0$ for the addition of a proton to enH^+, the observed positive value of Y_W would indicate that $\Delta G^t_{enH_2^{2+}} > (\Delta G^t_{H^+} + \Delta G^t_{enH^+})$.

If $\Delta G^t_{L^-}$ for the glycinate ion is, like the values for other anions,[16-19] positive and greater than $-\Delta G^t_{H^+}$, the term $(\Delta G^t_{H^+} + G^t_{L^-})$ is positive. The observed positive value of Y_w for $w \geqslant 0$ implies that $\Delta G^t_{HL^-}$ must be positive, and greater than $(\Delta G^t_{H^+} + \Delta G^t_{L^-})$. The observed negative value of Y_1 for the addition of a second proton in the H^+-gly system implies that, if $w = 1$, then $\Delta G^t_{H^+} > \Delta G^t_{+HL^-}$. If, however, $w \geqslant 2$, then Y_w becomes positive, and the converse arguement applies.

It is of interest that the equilibrium constants $\chi_1 = K_1 K_w [H_2O]^{-1}$ for the reactions

$$L + H_2O \rightleftharpoons HL + OH^- \qquad \chi_1$$

fall in the order $\chi_{water} > \chi_{methanol} > \chi_{dioxan}$ for the three ligands studied as does the constant $\chi_2 = K_2 K_w K_1^{-1} [H_2O]^{-1}$ for the reaction

$$Hen^+ + H_2O \rightleftharpoons H_2en^{2+} + OH^-$$

It would indeed be expected that an increase in the dielectric constant of the medium would decrease the stability of an H^+—OH^- complex relative to that of H^+—L, where L is an uncharged ligand.

Metal Ion Complexes. Values of β_1, $\beta_2\beta_1^{-1}$ and $\beta_3\beta_2^{-1}$ (see Table III) show that the stability of all the chelate complexes studied increases in the order water < methanol < dioxan, although there is not a corresponding increase in the stability of the ligand-proton complexes. The stability constants of the non-chelated metal-py complexes are not very sensitive to the composition of the solvent so for these systems too the effect of change of solvent on K_1 is not reflected in the values of β_1.

The effect of solvent on the relative values of K_1 and β_1 may be discussed in terms of the equilibrium constants χ' for the reactions

$$M + HL \rightleftharpoons ML + H^+ + dH_2O \qquad \chi'$$

where $d = w - w'$ is the difference between the numbers of water molecules released during the reactions

$$M + L \rightleftharpoons ML + wH_2O$$

and

$$H + L \rightleftharpoons HL + w'H_2O$$

The values of $\chi' = \beta_1 [H_2O]^d K_1^{-1}$ for all nine systems, and with $d = 0$, 1 or 2 fall in the order $\chi'_{water} < \chi'_{methanol} < \chi'_{dioxan}$, with $(\log\chi'_{methanol} - \log\chi'_{water})_{d=0} \sim 0.8$ and $(\log\chi'_{dioxan} - \log\chi'_{methanol})_{d=0}$ ranging from $+0.26$ to -0.03. Thus although release of water on complex formation clearly leads to increased stability on increasing the organic content of the solvent, the small differencces in χ' for different M and L in the same solvent indicate that more specific factors are also involved.

Now it has been shown[24,25] that $w = 2$ for many M-en and M-gly complexes; and that $w = 1$ for many complexes of metal ions and unidentate ligands. Substitution of $w = 1$ into equation (11) gives positive values of Y_1 for pyridine complexes. Since ΔG^t_{py} is probably negative, a positive value of Y_1 gives no information about the relative values of ΔG^t for complexed and uncomplexed metal ion. However, by analogy with values for singly charged cations, it is likely that $(\Delta G^t_{Mpy^{2+}} - \Delta G^t_{M^{2+}})$ would have a small positive value.

If the same arguments apply to en complexes as to py ones, the value of Y_2 for the M-en systems would also be expected to be positive. This is observed for the M-en complexes in aqueous methanol. In aqueous dioxan, however, Y_2 for Cu-en is approximately zero, while Y_2 for Ni-en and Zn-en have small negative values.

Values of Y_2 for M-gly complexes are negative (except for Ni-gly and Zn-gly in aqueous methanol, where $Y_2 \sim 0$). This is compatible with the large positive value of ΔG^t expected for an anionic ligand.

In the absence of more information about hydration and free energies of transfer, the significance of Y_w values cannot be discussed in more detail; nor can much be inferred from the experimental values of the stepwise stability constants β_2/β_1 and β_3/β_2. However, it is of interest that the ratios K_1^2/K_2 and β_1^2/β_2 are almost independent of the solvent, both for H_jL and ML_n complexes. These ratios are, of course, the ratios of the stepwise stability constants for the first two complexes, and the equilibrium constants for the reactions

$$H_2L + L \rightleftharpoons 2HL$$

and

$$ML_2 + M \rightleftharpoons 2ML$$

which do not involve the release of any water molecules. For ethylenediamine and glycine, the ratios are roughly independent of the ligand, as well as of the solvent, although they vary with the nature of the cation. This implies that

$$\Delta G^t_{HL} = \tfrac{1}{2}(\Delta G^t_H + \Delta G^t_{H_2L})$$

and

$$\Delta G^t_{ML} = \tfrac{1}{2}(\Delta G^t_M + \Delta G^t_{ML_2})$$

have similar values in the two solvent mixtures studied, and also that ΔG^t_{HL} and ΔG^t_{ML} for the en and gly systems are of similar value for complexes of the same cation with each of the bidentate ligands.

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