STABILITIES OF NICKEL(II) COMPLEXES WITH SOME
C-ALKYLETHYLENEDIAMINES

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Näsänen et al.[1] have reported equilibrium data for nickel(II)–pn‡ complexes in aqueous $NaClO_4$ media, $I =. 0 \cdot 05$–$2 \cdot 0M$, and Carlson et al.[2] and Edwards[3] have reported data for $0 \cdot 5M$ KCl (30°) and 1M KCl (25°) respectively. Basolo et al.[4] have reported data for the nickel(II)–pn and nickel(II)–ibn complexes in aqueous KNO_3–$Ba(NO_3)_2$, $I = 0 \cdot 65M$. There appear to be no other reported equilibrium data for nickel(II) complexes with C-alkylethylenediamines.[3] This paper presents further data for the complexes with pn and ibn and the first data for complexes with eten; data are given for $NaClO_4$–$Ba(ClO_4)_2$ media in the ionic strength range $0 \cdot 04$–$0 \cdot 35M$. The data reported are concentration quotients, $K_n = [NiL_n]/[L][NiL_{n-1}]$, and the thermodynamic formation constants $K°_n$ obtained by extrapolation of K_n data to zero ionic strength.

Experimental and Results

Concentration quotients were determined using the technique and apparatus described previously.[5,6] The method for calibration of the cell glass electrode || solution | calomel electrode against solutions of known [H+] has recently been discussed in detail.[7] Syntheses of the amines have been reported.[5] At each point in the titration curve the equilibrium ligand concentration was calculated from

$$[L] = ([\text{acid}] - [H^+] + K_w/[H^+])/(k_1[H^+] + 2k_1k_2[H^+]^2)$$

in which k_1 and k_2 are concentration quotients for ligand protonation,[5] [acid] is the total concentration of ionizable acid present, and $K_w/[H^+]$ is the acid produced by (ligand) hydrolysis

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‡ Abbreviations used: pn, propane-1,2-diamine; ibn, 2-methylpropane-1,2-diamine; eten, butane-1,2-diamine; en, ethylenediamine.

[1] Näsänen, R., Meriläinen, P., and Heinänen, E., Suomen Kem. (B), 1962, **35**, 15.

[2] Carlson, G. A., McReynolds, J. P., and Verhoek, F. H., J. Am. chem. Soc., 1945, **67**, 1334.

[3] "Stability Constants." Special Publication Nos 17 and 25. (Chemical Society: London 1964 and 1971.)

[4] Basolo, F., Chen, Y. T., and Murmann, R. K., J. Am. chem. Soc., 1954, **76**, 956.

[5] Powell, H. K. J., and Curtis, N. F., J. chem. Soc. (B), 1966, 1205.

[6] Powell, H. K. J., and Curtis, N. F., J. chem. Soc. (A), 1967, 1441.

[7] Hedwig, G. R., and Powell, H. K. J., Analyt. Chem., 1971, **43**, 1206.

of water; data for $K_w = [H^+][OH^-]$ were taken for NaCl solutions[8] and assumed valid in the system employed. Values of $[L]_{\bar{n}=n-1/2}$ ($n = 1, 2,$ and 3) were interpolated from plots of $\bar{n}$ against $[L]$, and $\log K_n$ values were calculated by Bjerrum's method of successive approximations.[9] Errors in all K_n were assessed as $\pm 3\%$.

Values of $\log K^{\circ}_n$ were obtained by graphical extrapolation to zero ionic strength from plots of $\log K_n$ against I. Data are given in Table 1. For pn these data agree well with Näsänen's $\log K^{\circ}_1$ (7·29) and $\log K^{\circ}_2$ (6·14), but $\log K^{\circ}_3$ (4·18) is at variance.

TABLE 1

CONCENTRATION QUOTIENTS FOR NICKEL(II) COMPLEXES WITH SOME C-ALKYLETHYLENEDIAMINES IN AQUEOUS NaClO$_4$–Ba(ClO$_4$)$_2$ MEDIUM, AT 25°

Uncertainty in $\log K_n$, $\pm 0\cdot015$. $\log K^{\circ}_n$ obtained by extrapolation from plot of $\log K_n$ against I

Constant	I (mol l^{-1})	Ligand			
		en[a]	pn	eten	ibn
$\log K_1$	0·35		7·33		
	0·20		7·33	7·32$_5$	6·59$_5$
	0·15		7·28	7·28$_5$	6·56$_5$
	0·10		7·29$_5$	7·28$_5$	6·54$_5$
	0·04		7·31	7·24	6·50
$\log K^{\circ}_1$	0·00	7·32	7·30	7·23$_5$	6·48
$\log K_2$	0·35		6·38		
	0·20		6·31	6·61$_5$	5·95
	0·15		6·29	6·68	6·01$_5$
	0·10		6·28$_5$	6·62	6·00
	0·04		6·31	6·80	6·18$_5$
$\log K^{\circ}_2$	0·00	6·06	b	6·85	(6·25)[c]
$\log K_3$	0·35		4·73$_5$		
	0·20		4·86$_5$	5·14$_5$	2·89$_5$
	0·15		4·92	5·24	3·02
	0·10		4·87$_5$	5·18$_5$	3·06
	0·04		4·92	5·21$_5$	3·46$_5$
$\log K^{\circ}_3$	0·00	4·1	4·98	5·23$_5$	(3·7)[b]
$\log k^{\circ}_1$ [d]	0·00	9·92	9·72	9·39	9·42
$\log k^{\circ}_2$ [d]	0·00	6·86	6·61	6·40	6·18

[a] Data valid for $I = 0\cdot015$M; from Davies, T., Singer, S. S., and Stavely, L. A. K., *J. chem. Soc.*, 1954, 2304.

[b] Extrapolated value uncertain because of irregular trend in $\log K_n$ data.

[c] Extrapolated value uncertain because the bis complex involves high spin and low spin species in equilibrium and the ratio of their concentrations is dependent on the anion and on the ionic strength (Leussing, D. L., Harris, J., and Wood, P., *J. phys. Chem.*, 1962, **66**, 1544; Curtis, N. F., unpublished data).

[d] Equilibrium constants for ligand protonation; ref. 5.

Discussion

The basicities of the C-alkylethylenediamines decrease slightly with increased C l substitution[5] (see Table 1). This trend in ligand basicity is reflected quantitatively

[8] Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolyte Solutions." 3rd Edn, p. 752. Am. chem. Soc. Monograph Ser. (Reinhold: New York 1957.)

[9] Sen, B., *Analytica chim. Acta*, 1962, **27**, 515.

by the stabilities of the mono and bis(diamine)copper(II) complexes[6] and qualitatively by the mono(diamine)nickel(II) complexes. However, for the bis and tris(diamine)-nickel(II) complexes the trend is reversed. There is an extra stability arising for the ligands with C-alkyl substituents; this stability is particuarly marked for the bis and tris complexes with eten and the tris complex with pn. (For ibn the issue is less clear as K_2 refers to a system with high spin and low spin states in equilibrium (see Table 1, footnote) and the low value for K_3 reflects the strong interligand (methyl–methyl) interaction occurring in the coordination sphere of the tris complex.)

The extra complex stability which occurs with increased ligand substitution may arise from the ability of the coordinated diamine to disrupt the solvent lattice and increase solvent entropy. Also ligand substituents will increase solvent entropy by increasing the charge insulation which the ligand effects between the metal ion and the solvent. Data for related systems support this view. For example, although 2,2-dimethylpropane-1,3-diamine is a weaker base than propane-1,3-diamine, it forms slightly more stable mono and bis complexes with copper(II); the higher stabilities arise solely from more favourable entropy terms.[10]

[10] Hares, G. B., Fernelius, W. C., and Douglas, B. C., *J. Am. chem. Soc.*, 1956, **78**, 1816.