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Thermodynamics of the complexation of piperazine-*N*,*N*-di-β-propionic acid dihydrochloride with cobalt(II), nickel(II) and copper(II)

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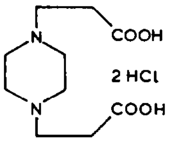
Abstract

Potentiometric studies on the chelation of Co(II), Ni(II) and Cu(II) with piperazine-*N*,*N*-di-β-propionic acid dihydrochloride as as a ligand were carried out in aqueous solution. The effects of the variation of ionic strength and temperature on the proton–ligand and metal–ligand thermodynamic stability constants were calculated. The stability constants of the complexes increase in the order Cu(II) > Ni(II) > Co(II). The thermodynamic parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the chelation processes were also evaluated. The values of these parameters are discussed in terms of the metal ion present.

INTRODUCTION

In spite of the large number of studies on the formation of complexes in solution and the determination of their stability constants by different techniques [1–5], there are relatively few reports describing the effect of the experimental conditions on the formation constants of the complexes [6,7].

The aim of the present work is to examine the influence of changes in the ionic strength *I*, the central metal ion M(II) and the temperature on the thermodynamic stability constants of some complexes formed in aqueous solution as a result of the interaction of piperazine-*N*,*N*-di-β-propionic acid dihydrochloride (p-*N*,*N*-p · 2HCl) as a ligand (A) [8] with Co(II), Ni(II) and Cu(II); the pH titration technique is used. The thermodynamic parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the chelation processes were calculated.



(A)

EXPERIMENTAL

A 0.08 M solution of the ligand (melting point, 261–262° C was prepared in doubly distilled water. Stock solutions of the metals were prepared from the metal nitrates and standardised gravimetrically [9]. Stock solutions were diluted to 0.02 M solution for pH-metric titrations. A standard solution of KNO_3 was used to maintain the required ionic strength. The pH values were measured using a pH meter (Hanna Instruments, Italy) with an expanded scale having an accuracy of ± 0.02 log unit and a sensitivity of ± 0.01. The temperature was controlled with a bath thermostat (± 0.1° C). The following sets of solutions (total volume, 20 ml) were titrated against carbonate-free KOH (0.108 M): (i) 5 ml of 0.08 M solution of the ligand plus the calculated volume of KNO_3 solution to give the required ionic strength; (ii) solutions (i) plus 5 ml of 0.01 M metal salt solution. The metal-to-ligand ratio was

TABLE 1(a)

Influence of ionic strength and temperature on pK_1 values for p-*N*,*N*-p·2HCl

I (mol l^{-1})	T(°C)			
	30	40	50	60
0.02	5.76	5.64	5.46	5.35
0.04	5.78	5.66	5.48	5.37
0.06	5.79	5.68	5.50	5.39
0.08	5.81	5.69	5.52	5.40
0.10	5.83	5.71	5.54	5.42

TABLE 1(b)

Thermodynamic constants and free energy (kJ mol^{-1}) of p-*N*,*N*-p·2HCl at different temperatures

T (°C)	pK_1	$-\Delta G^{\neq}$
30	5.70	32.92
40	5.58	33.31
50	5.39	33.20
60	5.29	33.60

TABLE 1(c)

Thermodynamic function of p-*N*,*N*-p·2HCl at different ionic strengths

	I (mol l^{-1})				
	0.02	0.04	0.06	0.08	0.10
$\Delta H^{\neq}$ (kJ mol l^{-1})	27.01	27.00	26.42	26.81	26.80
$-\Delta S^{\neq}$ (J K^{-1} mol^{-1})	21.27	21.68	23.83	22.90	23.28

TABLE 2(a)

Influence of ionic strength and temperature on pK_2 values for p-N,N-p·2HCl

I (mol l^{-1})	T (°C)			
	30	40	50	60
0.02	10.20	10.04	9.90	9.66
0.04	10.24	10.11	9.94	9.68
0.06	10.26	10.15	9.96	9.70
0.08	10.28	10.18	9.98	9.72
0.10	10.29	10.22	10.02	9.74

TABLE 2(b)

Thermodynamic constants and free energy (kJ mol^{-1}) of p-N,N-p·2HCl at different temperatures

T (°C)	pK_2	$-\Delta G^{\neq}$
30	10.13	58.52
40	9.91	59.10
50	9.81	60.39
60	9.59	60.87

TABLE 2(c)

Thermodynamic function of p-N,N-p·2HCl at different ionic strengths

	I (mol l^{-1})				
	0.02	0.04	0.06	0.08	0.10
$\Delta H^{\neq}$ (kJ mol^{-1})	33.64	35.32	35.68	35.86	35.24
$-\Delta S^{\neq}$ (J K^{-1} mol^{-1})	84.50	80.10	79.41	79.21	81.75

kept at 1 : 8 in all titrations to satisfy the highest coordination number of the respective metal ion.

RESULTS AND DISCUSSION

In order to obtain information about the influence of ionic strength and temperature on the dissociation process of piperazine-N,N-di-β-propionic acid dihydrochloride, we recorded the potentiometric curves of aqueous solutions of p-N,N-p · 2HCl (8×10^{-2} M) at temperatures of 30, 40, 50 and 60 °C and ionic strengths of 0.02, 0.04, 0.06, 0.08 and 0.10 M (KNO_3). From these curves and by application of Bjerrum's method [10] and its modifications [11,12], we obtained the pK_1 and pK_2 values reported in Tables 1(a) and 2(a) respectively. These results indicate that on increasing the ionic strength I the values of pK_1 and pK_2 also increase.

TABLE 3(a)

Stability constant log K_1 of 1 : 1 M^{2+}–p-N,N-p·2HCl complexes at different ionic strengths and temperatures

I (mol l^{-1})	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
	At 30 °C			At 40 °C		
0.02	4.63	5.51	7.69	4.48	5.21	7.39
0.04	4.53	5.49	7.67	4.36	5.19	7.36
0.06	4.47	5.43	7.64	4.30	5.17	7.34
0.08	4.36	5.38	7.59	4.26	5.15	7.32
0.10	4.27	5.27	7.56	4.23	5.12	7.29
	At 50 °C			At 60 °C		
0.02	4.27	5.01	7.16	4.01	4.76	6.90
0.04	4.24	4.98	7.14	3.99	4.74	6.88
0.06	4.21	4.95	7.12	3.96	4.72	6.87
0.08	4.20	4.92	7.10	3.94	4.69	6.86
0.10	4.19	4.90	7.08	3.90	4.68	6.85

TABLE 3(b)

Thermodynamics constants log K_1 and free energy $\Delta G^{\neq}$ (kJ mol^{-1}) of complexes with p-N,N-p·2HCl at different temperatures

Metal ion	30 °C		40 °C		50 °C		60 °C	
	log K_1	$-\Delta G^{\neq}$	log K_1	$-\Delta G^{\neq}$	log K_1	$-\Delta G^{\neq}$	log K_1	$-\Delta G^{\neq}$
Co(II)	6.04	34.86	5.41	32.25	4.58	28.20	4.44	28.18
Ni(II)	6.64	37.30	5.56	33.17	5.45	33.55	5.09	32.32
Cu(II)	8.23	47.52	7.77	46.35	7.48	46.03	7.09	44.98

TABLE 3(c)

Enthalpy (kJ mol^{-1}) and entropy (J K^{-1} mol^{-1}) of metal p-N,N-p·2HCl complexes at different ionic strengths

Metal ion	I (mol l^{-1})				
	0.02	0.04	0.06	0.08	0.10
	$-\Delta H^{\neq}$				
Co(II)	39.38	33.13	30.84	25.05	22.08
Ni(II)	46.93	46.83	45.03	43.83	37.93
Cu(II)	49.56	49.37	48.22	45.93	44.60
	$+\Delta S^{\neq}$				
Co(II)	41.1	22.64	16.36	1.1	9.76
Ni(II)	50.14	50.65	45.19	42.12	24.32
Cu(II)	17.25	17.08	13.86	7.13	3.35

TABLE 4(a)

Stability constants $\log K_2$ of 1 : 1 M^{2+}–p-N,N-p·2HCl complexes at different ionic strengths and temperatures

I (mol l^{-1})	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
	At 30 °C			At 40 °C		
0.02	2.52	3.31	4.80	2.43	3.10	4.60
0.04	2.46	3.26	4.76	2.41	2.96	4.57
0.06	2.40	3.20	4.73	2.39	2.94	4.55
0.08	2.37	3.14	4.70	2.32	2.87	4.52
0.10	2.28	2.96	4.68	2.31	2.82	4.49
	At 50 °C			At 60 °C		
0.02	2.29	2.94	4.47	2.07	2.82	4.25
0.04	2.28	2.40	4.44	2.06	2.76	4.22
0.06	2.27	2.88	4.42	2.05	2.74	4.21
0.08	2.26	2.80	4.39	2.03	2.72	4.19
0.10	2.25	2.72	4.37	2.01	2.68	4.18

TABLE 4(b)

Thermodynamic constants $\log K_2$ and $\Delta G^{\neq}$ (kJ mol^{-1}) of metal ion with p-N,N-p·2HCl at different temperatures

Metal ion	30 °C		40 °C		50.° C		60 °C	
	$\log K_1$	$-\Delta G^{\neq}$	$\log K_1$	$-\Delta G^{\neq}$	$\log K_1$	$-\Delta G^{\neq}$	$\log K_1$	$-\Delta G^{\neq}$
Co(II)	3.42	19.76	2.84	16.93	2.45	15.07	2.31	14.60
Ni(II)	4.62	26.68	4.10	24.46	3.80	23.35	3.32	21.05
Cu(II)	5.27	30.44	5.03	29.99	4.86	29.94	4.51	28.65

TABLE 4(c)

Enthalpy (kJ mol^{-1}) and entropy (J K^{-1} mol^{-1}) of metal p-N,N-p·2HCl complexes at different ionic strengths

Metal ion	I (mol l^{-1})				
	0.02	0.04	0.06	0.08	0.10
	$-\Delta H^{\neq}$				
Co(II)	28.31	24.19	22.13	21.89	20.22
Ni(II)	31.07	29.73	27.45	25.35	17.92
Cu(II)	33.93	33.35	31.59	31.44	30.88
	$+\Delta S^{\neq}$				
Co(II)	44.74	32.42	26.26	25.63	20.58
Ni(II)	35.88	37.05	30.42	24.91	3.16
Cu(II)	20.53	19.34	14.99	14.48	12.83

The values of the dissociation constants decrease with increasing temperature in accordance with the weak acid nature of p-N,N-p · 2HCl. The log K_1 and K_2 values for the ligand at the four temperatures were plotted against $I^{1/2}$ and extrapolated to zero ionic strength to obtain the thermodynamic constants and free energy $\Delta G^{\neq}$ for the dissociation processes, which are summarised in Tables 1(b) and 2(b). By plotting log K values vs. 1/T we obtained a straight line, which was adjusted by the least-squares method. From the slope and the ordinate of this line, values of the enthalpy and entropy changes were calculated. These values are given in Tables 1(c) and 2(c). The enthalpy values are positive, as for the dissociation of a weak acid (endothermic process); $\Delta G^{\neq}$ and $\Delta S^{\neq}$ values are negative owing to a spontaneous reaction and to the increased order produced by the solvation process respectively. The potentiometric titration curves of solutions containing Co(II), Ni(II) and Cu(II) and p-N,N-p · 2HCl at 30, 40, 50 and 60 °C and 0.02, 0.04, 0.06, 0.08 and 0.10 M ionic strength were recorded. The stepwise stability constants log K_1 and log K_2 of the formed complexes obtained by application of Bjerrum's method and its modifications to these curves are presented in Tables 3(a) and 4(a). From these values the following observations may be made.

(i) Log K_1 and log K_2 decrease with increasing ionic strength and temperature; this fact indicates that the lower temperature and ionic strength are favourable for complexation. This observation may be due to the decrease in the metal ion activity for complexation with the ligand in the presence of other ions in the system (i.e. the metal ion is screened by other ions). This is in accordance with similar findings reported by Hückel [13] and others [14–17] that the stability decreases with increasing ionic strength of the medium.

(ii) The stability constants of the complexes increase in the order Cu(II) > Ni(II) > Co(II), which is in accordance with the Irving–Williams rule [1,18].

The thermodynamic stability constants of the complexes were obtained at 30, 40, 50 and 60 °C by plotting log K_1 (or log K_2) against $I^{1/2}$ and extrapolating to zero ionic strength. These values are reported in Tables 3(b) and 4(b). The corresponding values of $\Delta G^{\neq}$ for the complexation process were calculated by the relation

$$\Delta G^{\neq} = -2.303\mathrm{RT} \log \mathrm{K}$$

In all cases $\Delta G^{\neq}$ is negative, which means that the complexation processes are spontaneous. By comparing the values of ΔG for Co(II), Ni(II) and Cu(II) it is found that the value is lowest (most negative) for Cu(II), which suggests that this ion has the highest tendency for interaction with the ligand.

By plotting log K_1 (or K_2) vs. $1/T$ we have calculated the corresponding enthalpy and entropy changes for each complexation process according to the relation

$$\log K = -\frac{\Delta H^{\neq}}{2.303RT} + \frac{\Delta S^{\neq}}{2.303R}$$

The resulting values are given in Tables 3(c) and 4(c), and from these values the following observations may be made.

(i) The enthalpy changes ($\Delta H^{\neq}$) are negative, which supports the idea that the lower temperature is favourable for complexation.

(ii) The values of the entropy change $\Delta S^{\neq}$ for all complexes are positive, which suggest that on account of the complexation process the disorder of the system increases much more rapidly than the increase in the order taking place in the complexation reactions.

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