Determination of thermodynamic parameters and stability constants of complexes of various dipositively charged metal ions with 2,4-pentanedione-1-(2-chlorophenylhydrazone) PD2CPH using a potentiometric technique

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Abstract

Stability constants of complexes of various dipositively charged metal ions, namely $UO_2(II)$, Cu(II), Pb(II), Zn(II), Cd(II), Ni(II), Co(II) and Mn(II) with 2,4-pentanedione-1-(2-chlorophenylhydrazone) (PD2CPH) have been determined potentiometrically at different ionic strengths and at different temperatures. Thermodynamic parameters, ΔG, ΔH and ΔS, for the complexation reactions have also been evaluated from temperature coefficient data.

INTRODUCTION

Hydrazones have significant biological activity and are therefore of vital importance. They are used in the treatment of several diseases such as tuberculosis, leprosy, mental disorder, cancer, tumours, bacterial infection, etc. [1]. They show spasmolytic activity, hypotensive action and activity against leukaemia, sarcomas and other malignant neoplasma [2]. Hydrazones, containing N, N, N', N'-bis(1,2-ethanedyl)phosphoric diamide moiety, have been found to have anti-cancer activity [3].

Hydrazones have numerous applications in analytical chemistry and their formation is used extensively in estimation and characterisation of carbonyl compounds. Hydrazones have significant chelating power, which has prompted us to undertake the present investigations.

EXPERIMENTAL

Instrumental

A digital pH meter (model PHM83), Radiometer, Copenhagen, in conjunction with a single glass–calomel electrode was used for pH measure-

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ments. The radiometer was standardised with standard radiometer buffer solutions of pH 4 and 7 before performing the titrations.

Chemicals and reagents

2,4-Pentanedione-1-(2-chlorophenylhydrazone) was synthesised by diazotisation of a $0\,^\circ$C-cooled hydrochloric acid solution of O-chloroaniline (0.1 mol) followed by coupling with acetylacetone (0.1 mol) in water and acetone mixture containing crystalline sodium acetate. The temperature was kept between 0 and $5\,^\circ$C throughout the reaction. The crude product thus obtained was filtered and recrystallised from methyl alcohol to give fine yellow needles (m.p., $119\,^\circ$C). The purity of the product, PD2CPH, was checked by TLC and characterised by UV, IR, ^{1}H NMR spectroscopy and elemental analysis. All the metal ion solutions were prepared from their corresponding sulphates or nitrates (AR, BDH) and standardised by conventional methods. Ligand solution was prepared in 100% dioxan, purified by the method of Weissberger et al. [4]. $NaClO_4$ (Fluka) was used to maintain constant ionic strength. Freshly prepared solution of tetramethyl-ammonium hydroxide (TMAH) (Merck) in 50% aqueous dioxan was used as titrant. The potentiometric titrations were carried out in a covered double-walled glass cell in a nitrogen atmosphere (N_2 purity $\approx 99\%$) which was presaturated with 50% (v/v) aqueous dioxan.

The following solution mixtures were titrated against standard 0.1 M TMAH in 50% (v/v) dioxan–H_2O.

(i)   2.5 ml $HClO_4$ (0.02 M) + 2.0 ml $NaClO_4$ (1.0 M) + 0.5 ml K_2SO_4 or KNO_3 (0.02 M) + 5.0 ml H_2O + 10.0 ml dioxan

(ii) 2.5 ml $HClO_4$ (0.02 M) + 2.0 ml $NaClO_4$ (1.0 M) + 0.5 ml K_2SO_4 or KNO_3 (0.02 M) + 5.0 ml H_2O + 10.0 ml ligand (0.01 M) in 100% dioxan

(iii) 2.5 ml $HClO_4$ (0.02 M) + 2.0 ml $NaClO_4$ (1.0 M) + 0.5 ml metal sulphate or nitrate (0.02 M) + 5.0 ml H_2O + 10.0 ml ligand (0.01 M)

In other sets, $NaClO_4$ was added in requisite amounts to maintain the ionic strengths at 0.2, 0.05 or 0.02 M.

In order to determine the thermodynamic parameters, titrations were also performed at various temperatures: 20, 27, 35 and $45 \pm 0.5\,^\circ$C. In all the titrations, the temperature was kept constant ($\pm 0.5\,^\circ$C) using a Julabo (Germany) F20 thermostat which also has a low-temperature facility.

Volume corrections were applied according to the method of Rao and Mathur [5] and the pH values in aqueous organic mixtures were corrected using the method of Van Uitert and Hass [6].

From the titration curves of solution mixtures (i), (ii) and (iii), the parameters, $\bar{n}_H$, the average number of protons bound to the ligand, $\bar{n}$, the average number of ligand molecules bound per metal ion, and pL, the free ligand exponent, were determined using the expression described by Irving

and Rossotti [7,8] in order to evaluate the pK_a values of the ligand and the stability constants of the complexes. These were calculated using a weighted least-squares program based on that of Sullivan et al. [9], computed on an Uptron PC plus computer which determines that set of β_n values which makes the function

$$U, \left\{ U = \sum_{n=0}^{N} (y - x - nz)\beta_n X^n \right\} \tag{1}$$

nearest to zero by minimising S

$$\left\{ S = \sum_{i=1}^{I} W_i U^2(x_i, y_i, z_i) \right\} \tag{2}$$

with respect to variation in β_n. Values of S_{min} are reported for the different metal complexes. S_{min} has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Rydberg and Sullivan [10], and can be equated to χ^2.

RESULTS AND DISCUSSION

The dissociation constant of the ligand and the stability constants of its complexes with metal ions were evaluated at four different ionic strengths (0.2, 0.1, 0.05 and 0.02 M $NaClO_4$) at 35°C, and at four different temperatures (20, 27, 35 and 45°C ± 0.5°C) at 0.1 M $NaClO_4$ ionic strength.

The order of stability constants for the metal complexes of PD2CPH was found to be $UO_2(II) > Cu(II) > Pb(II) > Zn(II) > Cd(II) > Ni(II) > Co(II) > Mn(II)$ which is in good agreement with the order observed by Mellor and Maley [11] and by Irving and Williams [12,13]. The order can be accounted for by the decrease in metal ion radius from Mn to Zn and by the increase in crystal field stabilisation energy along the series. The d orbitals of Zn(II) are completely filled, therefore no stabilisation energy is released in its complex formation; thus, the position of Zn(II) is hard to determine. Log K_1 and S_{min} values are summarised in Tables 1 and 2.

Effect of ionic strength

The values of the dissociation constants of the ligand (pK_a) have been found to decrease with increasing ionic strength of the medium (Table 1) in agreement with the Debye Huckel equation [14]

$$pK_a^{\ominus} - \left[A(\mu)^{1/2}/1 + \alpha(\mu)^{1/2} \right] + C\mu = pK_a \tag{3}$$

A similar variation has been observed in the case of the stability constants of its complexes with various metal ions.

TABLE 1

Stability constants of dipositively charged metal ion complexes of PD2CPH at different ionic strengths (μ) (M NaClO$_4$) at $35 \pm 0.5\,^\circ$C

System	Stability constant	Ionic strength (M NaClO$_4$)			
		0.02	0.05	0.1	0.2
PD2CPH	pK_a	12.55	12.49	12.43	12.28
UO$_2$(II)–PD2CPH	log K_1	10.74	10.64	10.35	9.10
	log K_2	9.63	9.54	9.44	9.18
	S_{min}	0.010	0.012	0.008	0.008
Cu(II)–PD2CPH	log K_1	9.49	9.32	9.02	8.83
	log K_2	8.90	8.68	8.58	8.17
	S_{min}	0.033	0.068	0.039	0.051
Pb(II)–PD2CPH	log K_1	9.25	9.19	8.91	8.51
	log K_2	7.98	7.77	7.49	7.34
	S_{min}	0.042	0.029	0.048	0.087
Zn(II)–PD2CPH	log K_1	8.69	8.44	8.21	7.85
	log K_2	8.03	8.02	8.11	7.60
	S_{min}	0.096	0.045	0.080	0.048
Cd(II)–PD2CPH	log K_1	8.52	8.32	7.95	7.52
	log K_2	8.04	7.92	7.45	6.58
	S_{min}	0.194	0.140	0.165	0.092
Ni(II)–PD2CPH	log K_1	7.57	7.43	7.30	6.99
	log K_2	6.94	6.91	6.25	6.20
	S_{min}	0.102	0.076	0.08	0.072
Co(II)–PD2CPH	log K_1	7.42	7.22	6.98	6.72
	log K_2	6.88	6.94	6.23	6.21
	S_{min}	0.065	0.096	0.048	0.112
Mn(II)–PD2CPH	log K_1	7.06	6.92	6.71	6.39
	log K_2	6.52	6.61	6.50	5.70
	S_{min}	0.016	0.085	0.027	0.061

Effect of temperature

The present investigations have shown clearly that the stability constants decrease with increase in temperature along with the pK_a values (Table 2). These results are in good agreement with those of Pitzer [15].

The thermodynamic parameters, ΔG, ΔH and ΔS, were calculated using the following relationships

$$\Delta G = -RT \ln K \tag{4}$$

$$d \log K / d(1/T) = \Delta H / 2.303K \tag{5}$$

$$\Delta S = (\Delta H - \Delta G) / T \tag{6}$$

The overall free energy, enthalpy and entropy changes are reported in Table 2.

TABLE 2

Stability constants and thermodynamic parameters of dipositively charged metal ion complexes of PD2CPH at different temperatures (°C), $\mu = 0.1$ M NaClO$_4$

System	Stability constant	Temperature (°C)				$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (kJ mol^{-1}K^{-1})
		20 ± 0.5	27 ± 0.5	35 ± 0.5	45 ± 0.5			
PD2CPH	pK_a	12.79	12.60	12.43	12.20			
UO$_2$(II)–PD2CPH	$\log K_1$	10.79	10.68	10.35	10.09	60.64	58.67	0.056
	$\log K_2$	9.69	9.62	9.45	9.35			
	S_{min}	0.042	0.008	0.008	0.010			
Cu(II)–PD2CPH	$\log K_1$	9.58	9.27	9.02	8.52	52.81	70.93	−0.517
	$\log K_2$	8.65	7.21	8.58	8.15			
	S_{min}	0.047	0.087	0.039	0.040			
Pb(II)–PD2CPH	$\log K_1$	9.24	9.01	8.91	8.38	52.18	60.01	−0.223
	$\log K_2$	7.29	8.20	7.49	7.23			
	S_{min}	0.071	0.087	0.048	0.084			
Zn(II)–PD2CPH	$\log K_1$	8.71	8.36	8.21	7.96	48.08	58.67	−0.302
	$\log K_2$	8.21	7.83	8.11	7.68			
	S_{min}	0.083	0.030	0.080	0.078			
Cd(II)–PD2CPH	$\log K_1$	8.35	8.05	7.95	7.34	46.57	61.35	−0.422
	$\log K_2$	8.04	7.74	7.45	7.23			
	S_{min}	0.029	0.032	0.165	0.056			
Ni(II)–PD2CPH	$\log K_1$	7.70	7.53	7.30	6.92	42.77	55.82	−0.372
	$\log K_2$	7.19	6.63	6.25	6.20			
	S_{min}	0.077	0.073	0.081	0.076			
Co(II)–PD2CPH	$\log K_1$	7.60	7.40	6.98	6.79	40.88	62.69	−0.623
	$\log K_2$	6.88	6.31	6.23	5.86			
	S_{min}	0.055	0.060	0.048	0.077			
Mn(II)–PD2CPH	$\log K_1$	7.34	6.98	6.71	6.46	39.29	62.69	−0.668
	$\log K_2$	6.72	6.53	6.56	5.92			
	S_{min}	0.015	0.054	0.027	0.023			

TABLE 3

$Er(Mn-Zn)$ and δH values for complexes of PD2CPH

Parameters (kcal mol^{-1})	Metal ions				
	Mn^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cu^{2+}
log $K_1^{\ominus}$ [a]	7.34	7.62	7.75	8.95	9.72
ΔF [b]	43.10	44.65	45.40	52.34	56.91
ΔF_R [c]	–	1.54	2.30	9.33	13.8
ΔH_H [d]	–	179.95	259.47	196.69	263.65
ΔH_L [e]	–	181.49	261.77	206.02	277.46
$(n-5)/5 Er$ [f]	–	82.40	123.58	–	167.31
δH [g]	–	99.10	138.18	–	112.66

[a] Values obtained by extrapolating the log K_1 against $\mu^{1/2}$ plot to zero ionic strength.
[b] Free energy change on complexation, $\Delta F = 2.303RT$ log $K_1^{\ominus}$, where R, T and $K_1^{\ominus}$ have the usual meanings and $T = 308$ K.
[c] Change in heat content for the formation of the complex in solution relative to Mn^{2+}.
[d] Heat of hydration of metal ions relative to Mn^{2+}.
[e] Heat of complexation, referred to metal ion in gaseous state and ligand in solution state.
[f] Lattice energy difference for Zn^{2+} and Mn^{2+} complexes, where n is the number of electrons in the 3d orbital.
[g] Thermodynamic stabilisation energy.

Thermodynamic stability constants, obtained by extrapolating the straight line plots of log K against $(\mu)^{1/2}$ to zero ionic strength, are given in Table 3 along with the thermodynamic stabilisation energy δH. The δH and $Er(Mn-Zn)$ values were calculated according to the method of George and McClure [16] are listed in Table 3. The hydration energies are those given by George and McClure [16]. The order of δH is: Co < Ni > Cu.

The above results indicate that the complexation reactions are spontaneous. The entropy is, however, negative for all the complexation reactions except for UO$_2$ (II), showing that entropy is not favourable for most of the complexation reactions.

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