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Thermodynamic stabilities. Thermodynamic parameters of some complexes of 4′-morpholinoacetophenone 4-phenyl-3-thiosemicarbazone

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Abstract

The stability constants (ln K) of the Co(II), Ni(II), Cu(II), Ag(I), Cd(II) and Hg(II) complexes with 4′-morpholinoacetophenone 4-phenyl-3-thiosemicarbazone were determined using a spectrophotometric method at different temperatures (25, 30, 35 and 40 ± 0.1°C) and at different ionic strengths (0.05, 0.10 and 0.20 mol dm^{-3}) in 60% (v/v) aqueous dimethylformamide. Plots of thermodynamic stability constants at zero ionic strength (ln K^0) versus T^{-1} gave linear curves, and $\Delta H^\ominus$ and $\Delta S^\ominus$ were also calculated from these plots. Moreover, the changes in free energy for each metal–ligand system were calculated from the equation $\Delta G^\ominus = -RT \ln K^0$.

Keywords: Stability; Thermodynamics; Thiosemicarbazone

1. Introduction

It was reported that the thiosemicarbazones behave as bidentate ligands in most complexes [1–3] and they have been used in the determination of some metals [4–6].

Thermodynamical studies of the complexes of 4′-morpholinoacetophenone thiosemicarbazone [7] and 2-methylindole-3-carboxaldehyde thiosemicarbazone with some transition metal ions have been reported recently [8]. In this study,

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4′-morpholinoacetophenone 4-phenyl-3-thiosemicarbazone (MAPPT) was synthesized for the first time. Here we describe the determination of the thermodynamic stability constants and thermodynamic parameters of the Co(II), Ni(II), Ag(I), Cd(II) and Hg(II) complexes of the ligand.

2. Experimental

2.1. Apparatus

A Crison 2002 pH-ionmeter with a combined glass–calomel electrode, and a Shimadzu UV-160 spectrophotometer, with a 1.0-cm quartz cell and a Lauda MT 3 circulating thermostatic bath, were used.

2.2. Synthesis of MAPPT

In a 250 ml flask were placed 0.6 g of 4′-morpholinoacetophenone (Aldrich), 0.5 g of 4-phenyl-3-thiosemicarbazide (Merck) and 60 ml of water. The mixture was heated until dissolution of the reagents was complete. To this was added 40 ml of acetate buffer solution (1.36 g of sodium acetate and 1.2 ml of glacial acetic acid). The mixture was refluxed for 8 h, and then cooled to room temperature. Yellow crystals were formed. The precipitate was washed with ethanol and hot water, then dried at 120°C (M.P. 185–187°C, yield 70%. Found: 64.43% C, 6.19% H, 15.90% N; calculated for $C_{19}H_{22}ON_4S$: 64.37% C, 6.26% H, 15.81% N). MAPPT does not dissolve in ethanol, carbon disulphide, chloroform, carbon tetrachloride, benzene or hot water, but does dissolve in *N*,*N*-dimethylformamide (DMF), dimethyl sulphoxide and hot ethanol.

2.3. Reagents

Solutions of nickel sulphate, copper(II) sulphate, silver nitrate, mercury(II) nitrate, cobalt nitrate and cadmium nitrate were prepared in distilled water, and standardized according to known methods. The stock metal solution (0.002 M) was prepared from each standardized solution. Buffer solutions of sodium carbonate–sodium bicarbonate (0.55 M, pH 9.3) and potassium nitrate (1 M) were prepared in distilled water. MAPPT solution of concentration 0.2% (w/v) was prepared in DMF. All reagents and solvents were of analytical grade.

2.4. Procedures

2.4.1. Determination of molar absorption coefficients

To a 10 ml volumetric flask, were added 2 ml of buffer solution ($C_T = 0.55$ M, pH 9.3), 2 ml of 1 M potassium nitrate solution and X ml of MAPPT solution ($X = 0.3$ ml for Ag, 0.35 ml for Hg, 0.4 ml for Cd, Co and Ni, and 0.45 ml for Cu; the X values are sufficient volumes for the optimum ligand concentrations). This mixture was diluted to the mark with DMF, and mixed thoroughly; 3 ml of the mixture was transferred to the stoppered quartz cell. The cell was warmed for 15 min at 25 ± 0.1°C in the thermostatic bath. Stock metal solution (10–35 μl) (kept in the same thermostatic bath for the same time) was added to the stoppered quartz cell with a micro pipette, and then shaken (ionic strength, $I = 0.20$). Five mixtures with differing metal concentrations were prepared for each metal. The changes in absorbance at maximum wavelength were recorded against a similar solution containing no metal ion until the reaction was complete.

2.4.2. Determination of stability constants of the complexes

To a 10 ml volumetric flask were added 2 ml of buffer solution, 2 ml of 1 M potassium nitrate solution, and 0.05–0.10 ml of MAPPT. This mixture was diluted to the mark with DMF, and then mixed thoroughly. Five mixtures with differing MAPPT concentrations were prepared. 3 ml of each mixture was transferred to the stoppered quartz cells. The cells were warmed for 15 min at 25 ± 0.1°C in the thermostatic bath. Keeping the ligand/metal mole ratio at about 2, the reaction was initiated by adding the stock metal solution (kept in the same thermostatic bath for the same time) to each mixture ($I = 0.20$). The absorbances were recorded in the same way as for the determination of the molar absorption coefficients.

Each experiment was repeated three times.

At 0.20 ionic strength, the experiments performed for the determinations of the molar absorption coefficients and stability constants were repeated at 30, 35 and 40 ± 0.1°C by preparing the mixtures afresh.

The experiments were performed at ionic strengths of 0.20, 0.10 and 0.05 at each of these temperatures.

3. Results and discussion

The complexes of Co(II), Ni(II), Cu(II), Ag(I), Cd(II) and Hg(II) with MAPPT are yellow-green in colour. The maximum absorption wavelengths $\lambda_{\max}$, molar absorption coefficients ε at various ionic strengths ($I/(\text{mol dm}^{-3})$) and optimum pH values of these complexes are given in Table 1.

Table 1
The specrophotometric characteristics of the complexes

Complex	$\lambda_{\max}$ in nm	ε in $\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$			Optimum pH range
		$I = 0.05$	$I = 0.10$	$I = 0.20$	
Co-MAPPT	400	13760	13920	14240	9.0–9.6
Ni-MAPPT	398	12350	12550	12940	9.0–9.6
Cu-MAPPT	390	18760	18850	19030	4.0–9.6
Ag-MAPPT	391	5010	5140	5390	4.0–9.6
Cd-MAPPT	385	14000	14150	14450	9.0–9.6
Hg-MAPPT	387	9870	10000	10250	4.0–9.6

Changes in temperature do not modify appreciably the molar absorption coefficients of the complexes, but the absorbances increase slightly with ionic strength and are pH-dependent, as in our studies [7,8]. The Cu(II), Ag(I) and Hg(II) complexes have maximum absorption in the pH range 4.0–9.6, and these complexes are formed practically at once. The formation of the Cd(II), Co(II) and Ni(II) complexes is very slow at pH 4.0. To increase the formation rates of these complexes, pH values were increased. As the precipitate is formed at pH ≥ 10, these experiments were carried out at pH 9.3. At this pH, the formation rates of the Co(II) and Cd(II) complexes are rapid, but that of the Ni(II) is slow. For complete formation of the latter complex, 20 min is required.

For the six complexes, the metal:ligand mole ratio was found to be 1:2 using the Job method. This result shows that MAPPT is a bidentate ligand.

The stability constants $\ln K$ were calculated from measured absorbances, as described elsewhere [7]. It was found that the average values of the stability constants ($\ln K$) of the metal complexes are proportional to the ionic strength and inversely proportional to the temperature. The thermodynamic stability constants $\ln K^0$ (Table 2) and the thermodynamic parameters of the complexes were calculated from the average values of $\ln K$, as described elsewhere [7]. Values of $\Delta C_p^{\ominus}$ associated with the metal–ligand reactions were found to be equal to zero and a temperature-independent heat of association as evident by the $\ln K^0$ versus T^{-1} plots. The negative values of $\Delta H^{\ominus}$ (Table 3) predicted the exothermic nature of the

Table 2
Values of the thermodynamic stability constants at different temperatures

Complex	$\ln K^0$ at different temperatures			
	25°C	30°C	35°C	40°C
Co-MAPPT	23.28	23.11	22.93	22.73
Ni-MAPPT	24.19	23.89	23.63	23.35
Cu-MAPPT	27.62	27.36	27.12	26.81
Ag-MAPPT	22.89	22.75	22.60	22.42
Cd-MAPPT	25.63	25.42	25.15	24.91
Hg-MAPPT	26.90	26.60	26.29	25.92

Table 3
Thermodynamic parameters of the complexes

Complex	$-\Delta G_{25}^{\ominus}$ in kJ mol^{-1}	$-\Delta H^{\ominus}$ in kJ mol^{-1}	$+\Delta S^{\ominus}$ in J mol^{-1} K^{-1}
Co-MAPPT	57.71	28.32	98.61
Ni-MAPPT	59.96	43.04	56.72
Cu-MAPPT	68.47	41.31	91.18
Ag-MAPPT	56.74	24.13	109.46
Cd-MAPPT	63.53	37.60	87.08
Hg-MAPPT	66.68	50.28	55.17

metal–ligand interaction. Sufficiently large negative values of $\Delta G^{\ominus}$ also showed spontaneous formation of the complexes and the values followed the order Cu > Hg > Cd > Ni > Co > Ag (Table 3). The spontaneous formation of the complexes was further confirmed by the positive values of $\Delta S^{\ominus}$.

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