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Thermodynamic Stabilities & Thermodynamic Parameters of Some Complexes of Benzamidothiosemicarbazide with Divalent Metal Ions

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Cobalt(II), Ni(II), Zn(II) and Cd(II) form 1:2 (metal-ligand) complexes with benzamidothiosemicarbazide. The stability constants of these complexes in aq. ethanol (80:20, v/v) have been determined at different ionic strengths and temperatures (25° and 30°) to evaluate the thermodynamic stability constants. Thermodynamic parameters, ΔG°, ΔH°, and ΔS° have also been calculated.

In continuation of our earlier work[1-3] on the complexing behaviour of benzamidothiosemicarbazide, we report herein the thermodynamic stability constants and thermodynamic parameters of Co(II), Ni(II), Zn(II) and Cd(II) complexes with this ligand.

Stock solution of benzamidothiosemicarbazide (abbreviated as BTSC) was prepared in 80:20 ethanol-water (v/v). Stock solutions of cobalt chloride, nickel chloride, zinc acetate, cadmium acetate, potassium chloride and potassium hydroxide were prepared from AR reagents (BDH) in doubly distilled CO_2-free water and standardized by recommended methods[4].

Following series of solutions (total vol. 30 ml in each case) were titrated against carbonate-free 0.1*N* KOH at 25° and 30° ± 0.1°C using a Toshniwal *p*H-meter fitted with glass-SCE electrode assembly: (i) 20 ml of 0.02 *M* BTSC + X ml of 2 *M* KCl; and (ii) 20 ml of 0.02 *M* + X ml of 2 *M* KCl + Y ml of 0.02 *M* metal salt (X = 1,2 and 3 ml, Y = 1, 1.5 and 2 ml).

The *p*H-meter readings were corrected for mixed solvents according to the method of Van Uitert *et al.*[5]

Physicochemical investigations revealed 1:2 stoichiometry for these complexes (loc. cit). The *p*K values of BTSC were determined *p*H-metrically at 25° and 30° at different ionic strengths and the values were found almost similar. The titration curves of metal-ligand mixtures, ligand and metal separately against 0.1 *M* KOH, showed lowering of *p*H, indicating the liberation of protons as a result of complex formation. Furthermore, maximum lowering in the case of 1:2 metal-BTSC mixtures and the inflection corresponding to 2 mol of KOH to 1 mol of metal indicated 1:2 metal-ligand ratio in the complexes.

Table 1—Values of log *K* at Different Ionic Strengths

Temp °C	log *K* at ionic strengths (mol dm^{-3})			
	0.067	0.133	0.200	0.00
		Co-BTSC		
25	8.67	8.83	8.99	8.49
30	8.48	8.57	8.68	8.37
		Ni-BTSC		
25	8.80	8.95	9.13	8.63
30	8.69	8.84	9.04	8.50
		Zn-BTSC		
25	8.24	8.40	8.60	8.02
30	8.08	8.21	8.41	7.92
		Cd-BTSC		
25	8.50	8.70	8.86	8.33
30	8.37	8.50	8.67	8.22

Table 2—Thermodynamic Parameters at 25°C

Complex	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (JK^{-1}mol^{-1})
Co-BTSC	−48.44	−41.49	+23.32
Ni-BTSC	−49.24	−44.95	+14.40
Zn-BTSC	−45.76	−34.58	+37.52
Cd-BTSC	−47.53	−38.04	+31.84

*p*H-titrations of BTSC + KCl alone and in the presence of different concentrations of metal ions at different ionic strengths (0.067, 0.133, 0.20 mol dm^{-3} KCl) and temperatures (25° and 30°) were performed according to the method of Calvin and Melchior[6]. From the titration curves, at different *p*H values, different sets of $\bar{n}$ values were determined and the corresponding concentration of free ligand ($\bar{L}$) was calculated and normal formation curves were obtained for all the metals. The values of *pK* at $\bar{n} = 0.5$ and 1.5 gave log K_1 and log K_2 respectively (Table 1).

Values of log *K* at 25° and 30° were plotted against ionic strengths for each metal-ligand system and the curves were extrapolated to zero ionic strength to give thermodynamic stability constants, log K° (Table 1).

From the knowledge of thermodynamic stability constants, the changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) accompanying the metal-ligand complexation reactions, were calculated at 25°

(Table 2) using the well known relations. The data in Table 2 show that ΔG° values are negative indicating spontaneous reactions. ΔG° values follow the order: Ni(II) > Co(II) > Cd(II) > Zn(II). This further suggests decrease in reaction rate also in the same order and is in accordance with findings of Glasstone[7]. The ΔS° values are all positive indicating that change in entropy favours complex formation. Further negative values of ΔH° predicts the exothermic nature of the complex reactions. In comparison to ΔS°, ΔH° is very large and is mainly responsible for the complexation.

References

1 Bhardwaj Shreesh, Jain M C, Ansari M N, Kaushik R D & Malik W U, *J Indian chem Soc*, **60** (1983) 445.

2 Ansari M N, Jain M C, Kaushik R D & Malik W U, *J Indian chem Soc*, **59** (1982) 419.

3 Bhardwaj Shreesh, Ansari M N, Jain M C & Malik W U, *J Indian chem Soc*, **60** (1983) 929.

4 Vogel I, *Text book of quantitative inorganic analysis* (ELBS, London), 1973, 479, 530, 532, 493.

5 Van Uitert L G & Hass C G, *J Am chem Soc*, **75** (1953) 451.

6 Calvin M C & Melchior N C, *J Am chem Soc*, **70** (1948) 3270.

7 Glasstone S, *Thermodynamics for chemists* (Van Nostrand, New Jersey), 1969, 286.