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Note

THE STABILITY AND THERMODYNAMIC FUNCTIONS OF HEXACHLOROPHENE COMPLEXES WITH ZINC GROUP METAL IONS

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Hexachlorophene has been reported to form chelates with transition metals [1,2]. The antibacterial property of hexachlorophene is due to its ability to form chelates with metal ions. The proton—ligand stability of hexachlorophene and the stabilities of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} have been studied in our laboratory [3]. A comparative study of hexachlorophene complexes of zinc group metals is given in this paper.

EXPERIMENTAL

Due to the insolubility of hexachlorophene in water, the stabilities of its metal complexes have been studied in aqueous ethanol. The standard solution of hexachlorophene (0.05 M) was prepared in absolute alcohol (ethanol). The standard solution (0.01 M) of the metal nitrates of BDH AnalaR grade were prepared in double distilled water. BDH AnalaR $NaClO_4$ solution was used to maintain ionic strength. A standard solution (0.05 M) of AnalaR $HClO_4$ was prepared in double distilled water. A Systronics model 322-1 pH meter having an assembly of glass and calomel electrodes was used for the pH metric titrations, and was calibrated with standard buffers before use. The titrations were carried out at constant temperatures in a water thermostat. The Bjerrum—Calvin pH titration technique [4,5], as modified by Irving and Rossotti [6], was used for the study of the stabilities of the complexes at 25°C with ionic strengths 0.05 M, 0.10 M, 0.20 M, and at 35 and 45°C with 0.10 M ionic strength in aqueous ethanol 50 : 50 (v/v). But at 25°C and ionic strength 0.10 M the composition of the medium was changed from 50 : 50 to 70 : 30 (v/v) in the ethanol—water system to study the effect of the dielectric constant of the medium. The following three solutions were titrated against standard alkali (0.1 M KOH):

(A) 2.0 ml of 0.05 M $HClO_4$;
(B) A + 2.0 ml of 0.05 M ligand;
(C) B + 2.0 ml of 0.01 M metal ion.

In each case the initial total volume was 20 ml in ethanol—water, having medium composition as required. As the titrations were carried out in an ethanol—water system, the appropriate corrections were applied [7] to obtain the correct pH. The pH of the mixture was plotted against the volume of the standard alkali added to reach that pH.

RESULTS AND DISCUSSION

The separation of the titration curves of $HClO_4$, $HClO_4$ + ligand and $HClO_4$ + ligand + metal ion indicates the formation of complexes. The values of $\bar{n}_A$, $\bar{n}$ and pL were obtained using the method of Irving and Rossotti [6]. The values of $\bar{n}$, the average number of ligands bound per metal ion, approach 2. This suggests the formation of 1 : 1 and 1 : 2 complexes of the metals. The stability constants were calculated by interpolation at half $\bar{n}$ values and linear extrapolation methods [8]. These values in terms of log units are given in Table 1. The thermodynamic stability constants were obtained at 25°C by plotting log K_n against $\sqrt{\mu}$ and extrapolating to zero ionic strength. These values are given in Table 2.

The values of free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) associated with the formation of complexes were obtained from the following relations

$$\Delta G = -RT \ln K$$

$$\frac{\Delta H}{RT^2} = \frac{d \ln k}{dT}$$

$$\Delta G = \Delta H - T\Delta S$$

In order to obtain the enthalpy data, log K was plotted against $1/T$. The

TABLE 1

Stability constants of hexachlorophene complexes in ethanol—water at different ionic strengths

Metal ion	Temp. (°C)	Ionic strength	Ethanol—water medium (v/v)	log K_1	log K_2	log β_2
Zn^{2+}	25	0.05 M	50 : 50	9.73	9.37	19.10
		0.10 M	50 : 50	8.57	8.03	16.60
		0.10 M	70 : 30	8.90	8.40	14.04
		0.20 M	50 : 50	7.43	6.60	17.30
	35	0.10	50 : 50	7.90	7.50	15.40
	45	0.10 M	50 : 50	7.17	6.93	14.10
Cd^{2+}	25	0.05 M	50 : 50	8.05	7.25	15.30
		0.10 M	50 : 50	7.52	6.88	14.40
		0.10 M	70 : 30	8.60	7.84	16.44
		0.20 M	50 : 50	6.72	6.12	12.84
	35	0.10 M	50 : 50	7.07	6.33	13.40
	45	0.10 M	50 : 50	6.62	6.02	12.84
Hg^{2+}	25	0.05 M	50 : 50	9.85	9.35	19.20
		0.10 M	50 : 50	8.78	8.26	17.04
		0.10 M	70 : 30	9.17	8.69	17.86
		0.20 M	50 : 50	7.47	6.90	14.37
	35	0.10 M	50 : 50	8.00	7.60	15.60
	45	0.10 M	50 : 50	7.32	6.96	14.28

TABLE 2

Thermodynamic stability constants of hexachlorophene complexes with zinc group metal ions at 25°C in 50 : 50 (v/v) ethanol—water at $\mu = 0$

Metal ion	$\log K_1$	$\log K_2$	$\log \beta_2$	$-\Delta G_1$ (kcal mole^{-1})	$-\Delta G_2$ (kcal mole^{-1})	$-\Delta G = -(\Delta G_1 + \Delta G_2)$ (kcal mole^{-1})
Zn^{2+}	11.92	11.47	23.39	16.36	15.74	32.10
Cd^{2+}	9.22	8.35	17.57	12.66	11.46	24.12
Hg^{2+}	12.20	11.54	23.74	16.75	15.84	32.59

value of ΔH was calculated by the relationship

$$\Delta H = -2.303\ RS_1$$

where S_1 is the slope of the curve. These values are given in Tables 3—5.

The values of the stability constants (Table 1) show a decrease with rise in temperature from 25°C to 35°C and from 35°C to 45°C. This suggests that the formation of Zn(II), Cd(II) and Hg(II) complexes of hexachlorophene is favourable at lower temperature. Therefore, the exothermic formation of these complexes may be the result of the effect of change of temperature.

The ionic strength has a pronounced effect on the stability of the complexes (Table 1), which decreases with rise in ionic strength. The activity of a metal ion for complexation with a ligand is decreased by the presence of other ions in the system. The metal ion is screened by the other ions and hence the rate of its interaction with the ligands is decreased. This is in agreement with the observations recorded by Debye [9] for the decrease in stability of complexes with rise in ionic strength.

To study the effect of the dielectric constant of the medium on the stabilities, the composition was changed from 50 : 50 to 70 : 30 in the ethanol—

TABLE 3

Free energy data for hexachlorophene complexes of zinc group metal ions in 50 : 50 (v/v) ethanol—water system at μ = 0.10 M

Metal ion	Temp. (°C)	$-\Delta G_1$ (kcal mole^{-1})	$-\Delta G_2$ (kcal mole^{-1})	$-\Delta G = -(\Delta G_1 + \Delta G_2)$ (kcal mole^{-1})
Zn^{2+}	25	11.76	11.02	22.78
	35	11.21	10.64	21.85
	45	10.50	10.15	20.65
Cd^{2+}	25	10.32	9.44	19.76
	35	10.03	8.98	19.01
	45	9.70	8.82	18.52
Hg^{2+}	25	12.05	11.34	23.39
	35	11.35	10.78	22.13
	45	10.72	10.20	20.92

TABLE 4

Enthalpy data for hexachlorophene complexes of zinc group metal ions

Metal ion	$-\Delta H_1$ (kcal mole^{-1})	$-\Delta H_2$ (kcal mole^{-1})	$-\Delta H = -(\Delta H_1 + \Delta H_2)$ (kcal mole^{-1})
Zn^{2+}	32.51	27.64	60.15
Cd^{2+}	20.99	19.19	40.18
Hg^{2+}	34.20	30.04	64.24

water system (v/v) at 25°C, with 0.10 M ionic strength. With the change of fraction of ethanol from 50 to 70%, the stability of the complexes shows an increase. In the case of oxygen donors the stability constants of the complexes increase linearly with the mole fraction of the component of lower dielectric constant in the water—dioxane mixture [10,11]. Hexachlorophene is an oxygen donor and thus the stability constants of its complexes increase with the increase of mole fraction of ethanol in the solvent system. This also suggests that the ligand associates as an anion with the metal ion.

The stability constants of the complexes are in the order Hg(II) > Zn(II) > Cd(II). The second ionization potential values are 17.96, 16.90, 18.75 eV and the elatronegativity values according to the Pauling Scale are 1.6, 1.7 and 1.9 for Zn, Cd and Hg, respectively. The ionic radii of Zn^{2+}, Cd^{2+} and Hg^{2+} are 0.74, 0.97 and 1.10 Å, respectively. From these values it is apparent that the ionization potential and the electronegativity possess a direct relationship with the stability of the complexes of metal ions, but the stability constants hold an inverse relationship to the ionic radii of ions.

The enthalpy and entropy of complexation are negative in all the present cases. The negative enthalpy supports the lower temperature as the favourable condition for complexation. The negative enthalpy is favourable but negative entropy is unfavourable for the complexation.

The studies show that the stabilities of the hexachlorophene complexes of

TABLE 5

Entropy data for hexachlorophene complexes of zinc group metal ions

Metal ion	Temp. (°C)	ΔS_1 (cal deg^{-1} mole^{-1})	ΔS_2 (cal deg^{-1} mole^{-1})	$\Delta S = \Delta S_1 + \Delta S_2$ (cal deg^{-1} mole^{-1})
Zn^{2+}	25	−69.63	−55.77	−125.40
	35	−69.16	−55.19	−124.35
	45	−69.21	−55.0	−124.21
Cd^{2+}	25	−35.81	−32.72	−68.53
	35	−35.58	−33.15	−68.73
	45	−35.50	−32.61	−68.11
Hg^{2+}	25	−74.33	−62.75	−137.8
	35	−74.19	−62.53	−136.72
	45	−73.84	−62.39	−136.23

zinc group metals are in the order Hg(II) > Zn(II) > Cd(II) and that they decrease with increase in temperature, ionic strength and dielectric constant of the medium.

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