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Note

FORMATION CONSTANTS AND THERMODYNAMIC FUNCTIONS OF Cd(II), Zn(II), Pb(II), VO^{2+} AND Ce(IV) WITH LAPACHOL

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Sawhney and co-workers [1–4] have demonstrated pH-metrically the chelating tendency of lapachol[2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone] in solution. This note concerns the interaction of Cd(II), Zn(II), Pb(II), VO^{2+} and Ce(IV) with lapachol in non-aqueous media (50% by volume of EtOH and water) and at 0.1 M ionic strength (KNO_3), and subsequent estimation of the stoichiometry, formation constants and thermodynamic functions of the systems.

EXPERIMENTAL

All chemicals used were either BDH or Aldrich analar quality. Potentiometric titrations were performed using a Beckman H-2 model 8509 pH meter. Buffer solutions of pH 4 and 9.2 were used to standardize the electrodes. Ionic strength was maintained at 0.1 M with KNO_3. All work was at 20 ± 1°C and 40 ± 1°C. The shapes of the curves after correction following Van Uitert and Haas [5] for non-aqueous media were as usual. Formation constants of the different systems were estimated by various methods.

RESULTS AND DISCUSSION

Formation functions, $\bar{n}_H$, $\bar{n}$ and pL were calculated using the expressions of Irving and Rossotti [6]. For proton–ligand stability constants, a plot of $\bar{n}_H$ vs. pH together with the Bjerrum half integral method [7], and the use of eqn. (1) were employed.

$$\log {}^{p}K^{H} = B + \log[\bar{n}_H - (n-1)]/(n-\bar{n}_H) \quad (1)$$

The difference between $\log k_1$ and $\log k_2$ was much less than 2.5; under these conditions, employment of the Bjerrum half integral method for stability constants could not be justified. Pointwise and graphical methods using eqn. (2) were used for the purpose

$$\log k_n = \mathrm{pL} + \log[\bar{n} - (n-1)]/(n-\bar{n}) \quad (2)$$

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TABLE 1

Protonation consant of the ligand, ligand stability constants of the complexes and thermodynamic functions at 20 and 40°C

Metal ion	Constants	Temperature (°C)		$-\Delta G^0$ (kcal mole^{-1})		ΔH^0 (kcal mole^{-1}) at 40°C	ΔS^0 (cal mole^{-1}) at 40°C
		20	40	20°C	40°C		
	$\log {}^{P}K^{H}$	6 45	5 85				
Cd^{2+}	$\log k_1$	3 51	3 49				
	$\log k_2$	2 71	2 70	8 34	8 84	−73 5	28 00
Zn^{2+}	$\log k_1$	3 52	3 50				
	$\log k_2$	2 70	2 68	8 34	8 85	−58 82	28 09
VO^{2+}	$\log k_1$	2 48	2 49				
	$\log k_2$	2 74	2 70	8 34	8 87	−44 10	28 18
Pb^{2+}	$\log k_1$	3 41	3 38				
	$\log k_2$	2 70	2 69	8 19	8 70	−59 90	27 55
Ce^{4+}	$\log k_1$	3 50	3 41				
	$\log k_2$	2 71	2 70	8 33	8 84	−58 90	28 05

The $\bar{n}$ values approach 2 for all the systems, indicating that under these experimental conditions 1 : 2 complexes are formed. Conductometric titrations also supported the pH-metrically concluded stoichiometry of the complexes.

Values of thermodynamic functions have been calculated from the well-known temperature coefficient and the Gibbs–Helmholtz equation [8]. Table 1 contains the mean values of the protonation constant ($^{P}K^{H}$), formation constants and thermodynamic functions, and shows that the values of $\log {}^{P}K^{H}$, $\log k_1$ and $\log k_2$ decrease as the temperature increases, indicating that a lower temperature favours complexation because of the decrease in kinetic energy of molecules, and thus their stabilities are lowered. Interaction of the ligand and metal is a spontaneous process as the free energies of formation (ΔG^0) have a more negative value in all cases with the rise in temperature. The entropy (ΔS^0) is favourable for complex formation in all cases since it has a positive value.

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