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Note

STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF YTTRIUM(III), RHODIUM(III), INDIUM(III), SAMARIUM(III), GADOLINIUM(III), AND DYSPROSIUM(III) WITH LAPACHOL [2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHOQUINONE]

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Lapachol, a derivative of lawsone, forms metal chelates with a ring structure similar to that of 2,5-dihydroxy-*p*-benzoquinone [1]. Since the literature reveals that the interaction of lapachol with Y(III), Rh(III), In(III), Sm(III), Gd(III) and Dy(III) has not yet been attempted, investigations on the interaction of the metals with lapachol in non-aqueous media at 0.1 M ionic strength (KNO_3) were planned and initiated.

EXPERIMENTAL

All chemicals used were either BDH or Aldrich Analar quality. Solutions of the ligand in EtOH and metal nitrate in CO_2-free conductivity water were prepared. pH Metric titrations were carried out with carbonate-free 0.2 M NaOH. An appropriate quantity of potassium nitrate (M) solution was added to maintain a constant ionic strength of 0.1 M. The estimation of the stability constants of the metals and proton complexes was carried out at 20 ± 0.5°C and 40 ± 0.5°C in a thermostat bath employing the Bjerrum—Calvin technique modified by Irving and Rossotti [2]. The pH was measured using a Metrohm Herisau E-520 pH meter with a sensitivity of ±0.05, which was calibrated with suitable buffers before use. The shapes of the curves (plot of volume of NaOH and corresponding pH) were as expected. Correction following Van Uitert and Haas [3] for 50% v/v(EtOH—water mixture) was also applied.

RESULT AND DISCUSSION

$\overline{n}_H$, $\overline{n}$, and pL were calculated using the relationships derived by Irving and Rossotti. A plot of the degree of formation, $\overline{n}_H$, of the proton complex vs. the pH value was used for the estimation of the proton—ligand stability constant ($\log^P K^H$) with the aid of the Bjerrum half-integral method [4]. The metal—ligand formation curve was obtained by plotting $\overline{n}$ vs. pL. Metal—ligand stability constants could not be obtained by the Bjerrum half-integral

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method, as the difference between log k_1 and log k_2 was far less than 2.5 Thus the aid of point-wise calculation and graphical methods [5], using the following equations, was sought for these determinations

$$\log k_1 = \mathrm{pL} - \log \frac{1-\bar{n}}{\bar{n}}$$

$$\log k_1 = \mathrm{pL} - \log \frac{2-\bar{n}}{\bar{n}-1}$$

$$\log k_3 = \mathrm{pL} - \log \frac{3-\bar{n}}{\bar{n}-2}$$

The well-known temperature coefficient equation and the Gibbs—Helmholtz equation [6] were employed for the determination of the values of overall changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0).

TABLE 1

Protonation constants of the ligand: stepwise and overall metal—ligand stability constants of the complexes and thermodynamic parameters at two temperatures

Metal ion	Protonation constants/ metal—ligand and stability constants	Temperature (°C)		—ΔG (kcal mole^{-1})		ΔH° (kcal mole^{-1}) at 40°C	ΔS° (cal mole^{-1}) at 40°C
		20	40	20°C	40°C		
	log $^{P}k^{H}$	6 45	5.85				
Y^{3+}	log k_1	4.32	4.05	5.79	5.80		
	log k_2	3.57	3.43	4.79	4.91		
	log k_3	3.50	3.28	4.69	4.69		
	log β_3	11.39	10.76	15.27	15.40	—13.22	6.99
Rh^{3+}	log k_1	4.53	4.50	6.07	6.45		
	log k_2	3.59	3.43	4.81	4.91		
	log k_3	3.31	3.28	4.44	4.70		
	log β_3	11.43	11.21	15.32	16.06	—4.62	36.54
In^{3+}	log k_1	4.55	4.48	6.10	6.42		
	log k_2	3.49	3.36	4.68	4.81		
	log k_3	3.31	3.26	4.44	4.67		
	log β_3	11.35	11.10	15.22	15.90	—5.25	34.02
Sm^{3+}	log k_1	4.33	4 09	5.81	5.86		
	log k_2	3.83	3.52	5.14	5.04		
	log k_3	3 49	3.31	4.68	4.74		
	log β_3	11.65	10.92	15.63	15.64	—15.32	1.02
Gd^{3+}	log k_1	3.93	3.73	5.27	5.34		
	log k_2	3.87	3.75	5.19	5.37		
	log β_2	7.80	7.48	10.46	10.71	—6.72	12.74
Dy^{3+}	log k_1	3.66	3.68	4.91	5.27		
	log k_2	3.80	3.88	5.09	5.56		
	log β_2	7.46	7.56	10.00	10.83	+2.1	41.3

Table 1 incorporates the mean value of the protonation constant, stability constants and thermodynamic functions.

The values of $\overline{n}$ approach 3 for Y(III), Rh(III), In(III), and Sm(III) chelates with lapachol, indicating the formation of 1 : 1, 1 : 2 and 1 : 3 complexes. In the case of Gd(III) and Dy(III)—lapachol systems, values of $\overline{n}$ approach 2, showing the existence of 1 : 1 and 1 : 2 complexes. The data for Y(III)—, Rh(III)—, In(III)—, Sm(III)—, and Gd(III)—lapachol systems, reveal a decrease in the value of log ${}^{P}K^{H}$, log k_1, log k_2 and log k_3 with increase in temperature. This indicates that a lower temperature is favourable for complexation because of the decreased number of collisions with the decrease in kinetic energy of molecules, and hence their stabilities are lowered. In the case of the Dy(III)—lapachol system, an increase in the values of log k_1 and log k_2 was observed, thereby indicating that a higher temperature favours the reactions. The formation of complexes, with the exception of the Dy(III)—lapachol reaction, which is endothermic in nature (providing an explanation for the increase in the formation constants with increase in temperature), are exothermic reactions which support the lower value of the formation constant with increase in temperature. The free energies of formation (ΔG^0) have more negative values in all cases as the temperature increases, showing that complex formation is a spontaneous process. The entropy (ΔS^0) values are positive in all cases, indicating a favourable entropy for the formation of complexes.

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