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STUDIES ON THE INTERACTION OF Eu(III) WITH LAWSONE (2-HYDROXY-1,4-NAPHTHOQUINONE), LAPACHOL (2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHOQUINONE), JUGLONE (5-HYDROXY-1,4-NAPHTHOQUINONE) AND PLUMBAGIN (2-METHYL-5-HYDROXY-1,4-NAPHTHOQUINONE)

S.S. SAWHNEY and RENU JAIN

Chemistry Department, D.A.V. (P.G.) College, Dehra Dun 248 001 (India)

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ABSTRACT

pH-metric studies show that one mole of Eu(III) interacts with three molecules of each of juglone, plumbagin, lawsone and lapachol in solution. The stability and thermodynamics of these systems (50% aqueous acetone, 0.1 M KNO_3 ionic strength) are discussed and explained.

INTRODUCTION

Hydroxynaphthoquinones have been studied in depth previously [1–6]. Sawhney et al. [7–10] have reported on the metal affinities of some hydroxy-naphthoquinones and the indicator properties of lawsone, lapachol, juglone and plumbagin and recommended their application as pH indicators in neutralization reactions. This study is concerned with the solution investigations of the interaction of Eu(III) with lawsone, lapachol, juglone and plumbagin, and the stability and thermodynamics of these systems.

EXPERIMENTAL

All the chemicals used were of B.D.H./Aldrich/Sigma quality. Solutions of hydroxynaphthoquinones in acetone and $Eu(NO_3)_3 \cdot 6\ H_2O$ in cation free water were prepared. Solutions having an ionic strength of 0.1 M KNO_3 in a 50% aqueous acetone medium were pH-metrically titrated using a Metrohm Herissau pH meter duly calibrated with standard buffers to a sensitivity of ± 0.05 pH.

(a) 4×10^{-3} M HNO_3, 0.10 M KNO_3.
(b) 4×10^{-3} M HNO_3, 0.10 M KNO_3, 4×10^{-4} M ligand.
(c) 4×10^{-3} M HNO_3, 0.10 M KNO_3, 4×10^{-4} M ligand, 8×10^{-5} M Eu(III).

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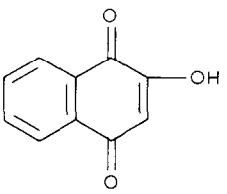
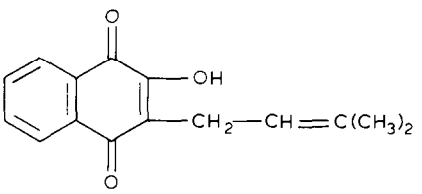
The curves (pH vs. base) after correction following Van Uitert and Haas [11] and for volume, were of usual shape.

RESULTS AND DISCUSSION

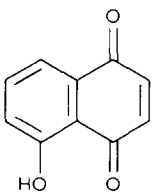
The hydroxynaphthoquinones (**I–IV**) in question are monotropic acids which dissociate in one step.



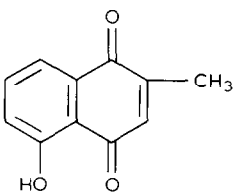
(I) Lawsone



(II) Lapachol



(III) Juglone



(IV) Plumbagin

The average number of H^+ attached to ligands ($\bar{n}_H$) given above, was estimated following the Irving and Rossotti [12] expression and was used for the evaluation of the protonation constants of these ligands using the relationship given in eqn. (1)

$$\log {}^{P}K_n^{H} = \mathrm{pH} + \log_{10}\left[\frac{\bar{n} - (n-1)}{n - \bar{n}}\right] \tag{1}$$

The formation function ($\bar{n}$) approaches 3 in all systems and indicates the existence of 1 : 1, 1 : 2 and 1 : 3 complex species in solution.

TABLE 1

Protonation constants of some Eu(III)–hydroxy-1,4-naphthoquinone systems (50% aqueous acetone, 0.10 M KNO_3 ionic strength)

Ligand	$\log {}^{P}K^{H}$	
	35°C	45°C
Lawsone	5.60	5.00
Lapachol	5.75	5.45
Juglone	11.50	10.70
Plumbagin	11.30	10.60

TABLE 2

Stability constants and thermodynamic parameters of the systems Eu(III)–juglone, Eu(III)–plumbagin, Eu(III)–lawsone and Eu(III)–lapachol (50% aqueous acetone, 0.1 M KNO_3 ionic strength)

Stability constants		Temp.		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} deg^{-1})
		35°C	45°C	35°C	45°C		45°C
Juglone							
log k_1	I	10.65	10.35				
	II	10.54	10.24				
	III	10.70	10.65				
	mean	10.63	10.41				
log k_2	I	7.40	7.60				
	II	7.18	7.48				
	III	7.45	7.95				
	mean	7.34	7.68				
log k_1/k_2	I	3.25	2.75				
log k_3	I	4.30	5.35				
	II	4.38	5.20				
	III	4.40	5.45				
	mean	4.36	5.33				
log β_3	I	22.35	22.30				
	II	22.10	22.92				
	III	22.55	24.05				
	mean	22.33	23.06	−31.47	−33.56	−32.72	+2.64
Plumbagin							
log k_1	I	11.20	10.55				
	II	11.26	10.67				
	III	11.25	10.60				
	mean	11.23	10.60				
log k_2	I	8.76	8.00				
	II	8.73	8.03				
	III	8.65	8.00				
	mean	8.71	8.01				
log k_1/k_2	I	2.44	2.55				
log k_3	I	6.55	4.52				
	II	6.98	4.69				
	III	6.45	4.60				
	mean	6.66	4.60				
log β_3	I	26.51	23.07				
	II	26.97	23.39				
	III	26.35	23.20				
	mean	26.61	23.22	−37.50	−33.80	−151.94	−371.49

TABLE 2 (continued)

Stability constants		Temp.		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} deg^{-1})
		35°C	45°C	35°C	45°C		45°C
Lawsone							
log k_1	I	5.55	5.0				
	II	5.72	5.14				
	III	5.65	5.1				
	mean	5.64	5.08				
log k_2	I	4.05	3.90				
	II	4.11	3.94				
	III	4.0	3.85				
	mean	4.05	3.89				
log k_1/k_2		1.50	1.10				
log k_3	I	3.70	3.70				
	II	3.71	3.70				
	III	3.70	3.65				
	mean	3.70	3.68				
log β_3	I	13.30	12.60				
	II	13.54	12.78				
	III	13.35	12.60				
	mean	13.39	12.66	−18.87	−18.42	−32.72	−44.94
Lapachol							
log k_1	I	5.80	5.35				
	II	5.75	5.58				
	III	5.15	5.55				
	mean	5.56	5.49				
log k_2	I	4.06	4.05				
	II	4.38	4.08				
	III	4.35	4.05				
	mean	4.26	4.06				
log k_1/k_2		1.74	1.30				
log k_3	I	3.70	3.70				
	II	3.70	3.70				
	III	3.70	3.65				
	mean	3.70	3.68				
log β_3	I	13.56	13.10				
	II	13.83	13.36				
	III	13.20	13.25				
	mean	13.53	13.23	−19.07	−19.25	−13.45	+18.26

The free ligand exponent (pL) [eqn. (2)] and $\bar{n}$ were calculated according to Bjerrum's concept [13]

$$pL = \log_{10}\left[\frac{1 + 10^{-pH}\,{}^{P}K^{H}}{\Delta NaOH}\right] \quad (2)$$

From the formation curves (pL vs. $\bar{n}$) of the systems, completed at both ends, adherence to Bjerrum's condition ($\log k_1/k_2 \geqslant 2.5$) was indicated in the case of the systems Eu(III)–juglone and Eu(III)–plumbagin; for the systems Eu(III)–lawsone and Eu(III)–lapachol, $\log k_1/k_2$ was in the range 1.10–1.70, necessitating the calculation of these constants by dependable methods of stepwise calculation and using graphical methods.

It was further seen (Tables 1 and 2) that $\log {}^{P}K^{H}$, $\log k_1$, $\log k_2$ and $\log k_3$ of the systems Eu(III)–plumbagin, Eu(III)–lawsone and Eu(III)–lapachol decrease with increasing temperature indicating that low temperatures are favoured for complexation because of the decrease in the number of collisions with the decrease in kinetic energy of the molecules and, thus, the stability of the systems is lowered. The Eu(III)–juglone system showed a decrease in $\log {}^{P}K^{H}$ and $\log k_1$ whereas $\log k_2$ and $\log k_3$ were increased at a higher temperature (45°C). The negative value of the free energy change (ΔG^0) points to the feasibility of the reactions which assumed a decreasing trend for the systems Eu(III)–juglone, Eu(III)–plumbagin and Eu(III)–lawsone with a rise in temperature. Enthalpy change values for all the systems ($-\Delta H^0$) point to the exothermic nature of the reactions, which agrees with the fact that low temperatures are favourable for complexation.

The complexation process between Eu(III) and juglone and lapachol was accompanied by an increase in entropy ($+\Delta S^0$) and tends to be spontaneous. A decrease in $-\Delta S^0$ for the systems Eu(III)–plumbagin and Eu(III)–lawsone is probably due to solvent effects.

Juglone and plumbagin with a higher basic strength than that of lawsone and lapachol form more stable chelates of Eu(III), agreeing with the concept of Calvin and Wilson following the order of stability plumbagin > juglone > lapachol > lawsone.

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