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Note

THE Gd(III), Tb(III) AFFINITY OF FUNCTIONAL GROUPS IN HYDROXY-NAPHTHOQUINONES

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Following earlier reports on the monotropic nature of hydroxy-naphthoquinones, their affinity to metals and the stability and thermodynamics of their systems by Sawhney and his students [1–4], it was thought valid to extend the study to systems involving Gd(III), Tb(III) and hydroxy-naphthoquinones [viz. 2-hydroxy-1,4-naphthoquinone (lawsone), 2-hydroxy-3-(3-methyl-2-butenyl)-11,4-naphthoquinone (lapachol), 5-hydroxy-1,4-naphthoquinone (juglone) and 2-methyl-5-hydroxy-1,4-naphthoquinone (plumbagin)], with a view to gaining insight into the stability and thermodynamics of the respective systems.

EXPERIMENTAL

All the chemicals used were from BDH. The procedure and conditions for studying the systems involved in solution have been described earlier [1].

RESULTS AND DISCUSSION

Calculations of $\bar{n}$ and pL were made by applying the Bjerrum concept [5]. All experiments were conducted in 50% acetone/water at an ionic strength of 0.1 M KNO_3. Concentrations of species involved were chosen to be close to infinite dilution, so that the stability constants of the systems with respect to concentration could be considered as the thermodynamic stability constants.

For metal–ligand stability constants, values of protonation constants ($^{P}K^{H}$) at 35 and 45°C of the studied hydroxy-naphthoquinone were used [1]. Stability constant values evaluated from formation curves ($\bar{n}$ vs. pL) of the Tb–juglone, Tb–plumbagin and Gd-juglone, Gd-plumbagin systems adhered to the conditions laid down by Bjerrum whereas these values for the Tb–lawsone, Tb–lapachol, Gd–lawsone and Gd–lapachol systems deviated considerably, necessitating their calculation by a pointwise calculation method. The solution study data are incorporated in Table 1.

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TABLE 1

Stability constants [a] and thermodynamic parameters of the systems involving Gd(III) and Tb(III) with juglone, plumbagin, lawsone and 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		35°C	45°C
Gd – juglone system							
log k_1	11.71	10.85					
	(11.90)	(10.75)					
log k_2	8.73	8.53					
	(8.80)	(8.65)					
log k_1/k_2	3.10	2.10					
log k_3	6.18	6.26					
	(6.20)	(6.40)					
log β_3	26.67	25.64	−36.36	−36.13	−43.26	−23.13	−23.12
Tb – juglone system							
log k_1	11.44	11.30					
	(11.41)	(11.30)					
log k_2	8.01	8.97					
	(7.90)	(9.15)					
log k_1/k_2	3.50	2.15					
log k_3	5.26	5.91					
	(5.70)	(5.90)					
log β_3	24.67	26.17	−33.64	−36.88	−63.00	10.87	10.51
Gd – plumbagin system							
log k_1	11.05	10.73					
	(11.10)	(10.70)					
log k_3	8.23	7.97					
	(8.20)	(7.80)					
log k_1/k_2	2.90	2.90					
log k_3	5.75	5.69					
	(6.10)	(6.05)					
log β_3	25.03	24.39	−32.24	−34.37	−29.4	9.42	16.13
Tb – plumbagin system							
log k_1	10.68	11.17					
	(11.50)	(10.50)					
log k_2	7.66	9.37					
	(9.50)	(7.71)					
log k_1/k_2	2.00	2.79					
log k_3	5.37	6.81					
	(6.81)	(5.50)					
log β_3	23.71	27.35	−32.33	−38.54	−152.8	−402.6	−371.1
Gd – lawsone system							
log k_1	5.28	5.05					
	(5.10)	(5.30)					
log k_2	4.14	3.84					
	(3.95)	(3.91)					

TABLE 1 (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		35°C	45°C
log k_1/k_2	1.06	1.40					
log k_3	3.63	3.81					
	(3.70)	(3.75)					
log β_3	13.05	13.66	−17.79	−17.93	−13.86	13.18	13.20
Tb–lawsone system							
log k_1	5.58	4.91					
	(5.55)	(4.90)					
log k_2	(3.71)	3.93					
	(3.91)	(3.90)					
log k_1/k_2	1.64	1.00					
log k_3	3.69	3.60					
	(3.70)	(3.71)					
log β_3	12.98	12.44	−17.70	−17.47	−24.36	−22.34	−22.37
Gd-lapachol system							
log k_1	5.73	4.98					
	(5.75)	(4.95)					
log k_2	3.86	3.76					
	(3.80)	(3.90)					
log k_1/k_2	1.95	1.05					
log k_3	3.59	3.57					
	(3.65)	(3.75)					
log β_3	13.18	12.31	−17.97	−17.35	−36.54	−64.39	−62.30
Tb–lapachol system							
log k_1	5.73	4.98					
	(5.75)	(4.95)					
log k_2	3.86	3.76					
	(3.80)	(3.90)					
log k_1/k_2	1.95	1.05					
log k_3	3.59	3.57					
	(3.65)	(3.75)					
log β_3	13.18	12.31	−17.97	−17.35	−36.54	−64.39	−62.30

[a] Values in parentheses are constants due to the Bjerrum half integral method [5].

The value of $\bar{n}$ was near 3 in all the systems studied, suggesting the combination of one mole of either of Tb(III) or Gd(III) with either lawsone, lapachol, juglone or plumbagin in solution under the experimental conditions applied.

Solution data on the stability of the species studied manifested that the bond strength of either molecule of the hydroxy-naphthoquinones studied registered a decreasing trend with decreasing order of stepwise stability constants (Table 1). Further analysis showed a decrease in the values of log $^{P}K^{H}$, log k_1, log k_2 and log k_3 in the Gd(III)–plumbagin,

Gd(III)–lapachol, Tb(III)–lawsone and Tb(III)–lapachol systems with temperature rise; hence, it is concluded that complexation in solution is dependent on low temperature, because of the decrease in number of collisions with decreasing kinetic energy of the molecules involved, favouring a lower stability of the system at higher temperature. In other systems, viz. Gd(III)–lawsone, Gd(III)–juglone, Tb(III)–plumbagin and Tb(III)–juglone, the regular increasing or decreasing phenomenon was not observed. All the complexation reactions are exothermic, in agreement with the inferences drawn on the Gd(III)–plumbagin, Gd(III)–lapachol, Tb(III)–lawsone and Tb(III)–lapachol systems.

Negative ΔG^0 values made the reactions Tb(III)–juglone, Tb(III)–plumbagin, Gd(III)–plumbagin and Gd(III)–lawsone feasible, whereas in other systems the reverse was observed. A high $-\Delta H^0$ value concludes a considerable covalency of the respective systems. The reactions Gd–juglone/lapachol and Tb–plumbagin/lawsone resulted in a decrease in entropy, which can probably be attributed to solvent effects. An increase in entropy (ΔS^0) for the systems listed in Table I, Tb(III)–lawsone, Tb(III)–lapachol, Gd(III)–juglone and Gd(III)–lapachol, helped to distinguish the spontaneity of the reactions.

The higher stability order of metal complexes involving juglone and plumbagin compared to those with lawsone and lapachol occur due to the higher basicity of the former ligands.

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