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Note

STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF Y(III), Rh(III), Sm(III), Gd(III) and Dy(III) WITH JUGLONE (5-HYDROXY-1,4-NAPHTHOQUINONE)

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Hydroxynapthoquinones, with an anionic functionality (—OH) and a carboxyl group as coordinating sites, received attention in recent years as chelating agents [1—5]. Little work appears to have been done on metal—juglone systems. The present paper deals with the study of complexes of Y(III), Rh(III), Sm(III), Gd(III) and Dy(III) with juglone in a 50% v/v EtOH—water mixture at 0.1 ionic strength (KNO_3).

EXPERIMENTAL

All chemicals used were either of B.D.H. or Aldrich AnalaR quality. The solutions of ligand and metal nitrates were prepared in ethanol and CO_2-free conductivity water, respectively. The concentration of ligand was always 1×10^{-3} M and that of metal 0.8×10^{-5} M. An appropriate quantity of KNO_3, to maintain an ionic strength of 0.1 M, was added. Estimation of stability constants of metals and proton complexes was carried out at 20 ± 0.5°C and 40 ± 0.5°C employing the Calvin—Bjerrum pH titration technique. The pH was measured on a Metrohm-Herisau E-520 pH-meter having a sensitivity of ±0.05 and was calibrated before use with suitable buffers. The shapes of the curves (plot of volume of NaOH vs. corresponding pH) were as expected. Volume correction due to Van Uitert and Haas [6] for the 50% v/v EtOH—water system was applied.

RESULTS AND DISCUSSION

The expression of Bjerrum [7] was used for calculating $\bar{n}_H$, $\bar{n}$ and pL. For proton—ligand formation curves the degree of formation ($\bar{n}_H$) or the proton complex was plotted against the pH value. The proton—ligand stability, log ${}^{P}k^{H}$ (hydroxy group), of the ligand was determined by the Bjerrum half integral [7] and graphical methods. Metal—ligand stability constants were

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determined by point-wise and graphical methods [8] [eqns. (1)—(3)], and eqn. (4) due to Bjerrum [7] for a higher complexity system ($N = 3$) was employed.

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

$$\log k_2 = \mathrm{pL} - \log \frac{2 - \bar{n}}{\bar{n} - 1} \tag{2}$$

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

$$\frac{\bar{n}}{(\bar{n} - 1)\mathrm{L}} + k_1 + \frac{\bar{n} - 2}{\bar{n} - 1} \cdot (L) k_1 k_2 + \frac{\bar{n} - 3}{\bar{n} - 1} (L)^2 k_1 k_2 k_3 = 0 \, . \tag{4}$$

The values of overall changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were estimated with the aid of the well-known temperature coefficient and Gibbs—Helmholtz equation [9]. Table 1 contains the mean values of protonation constants and thermodynamic functions.

TABLE 1

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

Metal ion	Protonation constant/ metal—ligand stability constant	Temp.		$-\Delta G^0$ (kcal mole^{-1})		ΔH^0 (kcal mole^{-1}) 40°C	ΔS^0 (cal mole^{-1}) 40°C
		20°C	40°C	20°C	40°C		
Y^{3+}	$\log {}^{p}k^{H}$	9.90	9.50				
	$\log k_1$	6.34	7.03	8.50	10.06		
	$\log k_2$	5.07	5.74	6.80	8.22		
	$\log k_3$	4.53	5.01	6.07	7.18		
	$\log \beta_3$	15.94	17.78	21.37	25.46	+38.61	204.73
Rh^{3+}	$\log k_1$	7.94	6.66	10.65	9.54		
	$\log k_2$	5.94	5.63	7.96	8.06		
	$\log k_3$	4.48	4.43	6.00	6.35		
	$\log \beta_3$	18.36	16.72	24.62	23.95	—34.41	—33.42
Sm^{3+}	$\log k_1$	6.36	6.49	8.53	9.30		
	$\log k_2$	5.48	5.47	7.35	7.84		
	$\log k_3$	3.56	4.56	4.77	6.53		
	$\log \beta_3$	15.40	16.52	20.65	23.67	+23.50	150.67
Gd^{3+}	$\log k_1$	7.43	7.36	9.96	10.54		
	$\log k_2$	6.59	5.75	8.84	8.24		
	$\log k_3$	5.50	5.77	7.37	8.26		
	$\log \beta_3$	19.52	18.88	26.17	27.04	—13.43	43.49
Dy^{3+}	$\log k_1$	8.38	7.32	11.24	10.48		
	$\log k_2$	6.00	5.98	8.04	8.57		
	$\log k_3$	5.46	4.87	7.32	6.97		
	$\log \beta_3$	19.84	18.17	26.60	26.02	—35.04	—28.81

The average number of ligands per metal ion, $\bar{n}$, approaches 3 as maximum value for Y(III), Rh(III), Sm(III), Gd(III) and Dy(III) chelates with juglone when the concentration of juglone increases, indicating the formation of 1 : 1, 1 : 2 and 1 : 3 complexes. Further confirmation was available from pH-titrations of juglone alone and metal—juglone mixtures prepared in the ratios 1 : 1, 1 : 2, 1 : 3 and 1 : 4. The nature of the curves led to the conclusion that the reaction takes place with the liberation of protons. The limiting condition was reached with the 1 : 3 metal—juglone mixture (for all systems). Beyond this, overlapping of the curves takes place, thereby showing that a maximum of three protons is liberated per metal ion in the reaction, which supports the above conclusion. A decrease in the values of log ${}^{P}k^{H}$, log k_1, log k_2 and log k_3 of the Rh(III), Gd(III) and Dy(III)—juglone systems with increase in temperature shows that a low temperature is favourable for the formation of complexes, because of a decrease in number of collisions with decrease in the kinetic energy of the molecules. However, a higher temperature favours the complexation of Y(III) and Sm(III) with juglone, as an increase in log k_1, log k_2 and log k_3 was observed. The free energies of formation (ΔG^0) have more negative values with increase in temperature, with the exception of Rh(III)—, Dy(III)—juglone systems, indicating that complex formation is a spontaneous process. ΔH^0 values for the systems, with the exception of Y(III)— and Sm(III)—juglone systems which are endothermic (ΔH^0 being positive), are negative, indicating the exothermic nature of complexation. With the exception of Rh(III)— and Dy(III)—juglone systems, the systems have positive ΔS^0 values, indicating a favourable entropy for complex formation.

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