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Note

STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF CADMIUM(II), PRASEODYMIUM(III), AND NEODYMIUM(III) WITH JUGLONE (5-HYDROXY-1,4-NAPHTHOQUINONE)

B.M.L. BHATIA *

Additives Laboratory, Indian Institute of Petroleum, Dehra Dun 248005, U.P. (India)

S.D. KAPILA, K.K. PATHAK and RANJANA CHAKRABORTY

Instruments Research and Development Establishment, Raipur, Dehra Dun 248008, U.P. (India)

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Juglone forms co-ordination complexes with metal ions [1,2]. Earlier, Bhatia et al. [3,4] reported the complexes of juglone with UO_2(II), Y(III), Rh(III), Sm(III), Gd(III) and Dy(III). The present paper investigates the interaction of juglone with different metal ions such as Cd(II), Pr(III), and Nd(III) in 50% v/v acetone–water mixture at 0.1 M ionic strength, and provides information concerning stoichiometry, stability and thermodynamic parameters.

EXPERIMENTAL

All chemicals used were either BDH or Aldrich Analar quality. The solutions of ligand and metal nitrate were prepared in acetone and CO_2-free conductivity water, respectively. pH-metric titrations were carried out with carbonate-free 0.1 M NaOH. The concentration of the ligand was always 1×10^{-3} M and that of the metal ion 1×10^{-4} M. An appropriate quantity of KNO_3 (1.0 M) was added to maintain an ionic strength of 0.1 M. Estimations of the stability constants of the metals and proton complexes were determined at 20 ± 0.5°C and 40 ± 0.5°C in a thermostat bath using the Calvin–Bjerrum [5] titration technique. pH measurement was made on an Emco digital pH meter (type EE330A), with a sensitivity of ±0.01 and was calibrated before use with suitable buffers. The shapes of the curves

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* To whom correspondence should be addressed.

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(plot of volume of NaOH and corresponding pH) were as usual. Volume correction due to van Uitert and Haas [6] was also applied.

RESULTS AND DISCUSSION

$\bar{n}_H$, $\bar{n}$ and pL were calculated using the expressions of Bjerrum [5]. The proton–ligand formation curve was obtained by plotting the degree of formation, $\bar{n}_H$, of the proton complex against pH. The Proton–ligand stability constant, ${}^{\mathrm{p}}K^{\mathrm{H}}$, of the ligand was determined using the Bjerrum half-integral and graphical methods [7]. Metal stability constants were determined by point-wise calculation and graphical method using the equations

$$\log k_1 = \mathrm{pL} - \log\left(\frac{1-\bar{n}}{\bar{n}}\right)$$

$$\log k_2 = \mathrm{pL} - \log\left(\frac{2-\bar{n}}{\bar{n}-1}\right)$$

The values of overall changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were estimated using the well-known temperature coefficient and Gibbs–Helmholtz equation [8]. Table 1 contains the mean values of stability constants and thermodynamic functions.

The average number of ligands bound per metal ion, $\bar{n}$, approaches 2 as maximum value for Cd(II), Nd(III), and Pr(III) complexes with increasing

TABLE 1

Stepwise and overall metal–ligand stability constants of the complexes and thermodynamic parameters at 20 and 40°C

Metal ion	Protonation constant [a], metal–ligand and stability constants	Temp.		$-\Delta G^0$ (kcal mole^{-1})		ΔH^0 (kcal mole^{-1}) at 40°C	ΔS^0 (cal mole^{-1}) at 40°C
		20°C	40°C	20°C	40°C		
Cd^{2+}	$\log k_1$	4.31	4.47				
	$\log k_2$	4.10	4.17				
	$\log \beta_2$	8.41	8.64	11.275	12.375	48.260	54.95
Pr^{3+}	$\log k_1$	7.35	8.08				
	$\log k_2$	5.20	6.51				
	$\log \beta_2$	12.55	14.59	16.826	20.897	42.805	203.02
Nd^{3+}	$\log k_1$	8.48	7.36				
	$\log k_2$	6.62	5.37				
	$\log \beta_2$	15.10	12.73	20.245	18.233	−49.729	−100.62

[a] Protonation constants of the ligand at 20 and 40°C are reported in an earlier paper [3].

concentration of juglone, indicating the formation of 1 : 1 and 1 : 2 complexes. This was further confirmed by pH-metric titrations of juglone alone and metal–juglone mixtures prepared in the ratios 1 : 1, 1 : 2 and 1 : 3. The nature of the curves obtained led to the conclusion that the reaction took place with the liberation of protons. The limiting condition was reached with the 1 : 2 metal–juglone mixture, beyond which overlapping took place, thereby showing that a maximum of 2 protons were liberated per metal ion in the reaction, which supports the conclusion made above.

The data show an increase in the values of log k_1 and log k_2 with increase in temperature for Cd(II)–juglone and Pr(III)–juglone systems. This shows that higher temperatures favour the formation of the complexes since an increase in the number of collisions results in an increase in the kinetic energy of the molecules and hence their stabilities were enhanced. On the other hand, a decrease in the values of log k_1 and log k_2 was observed for the Nd(III)–juglone system. The values of free energy of formation (ΔG^0) have more negative values with increase in temperature, with the exception of the Nd(III)–juglone system, indicating that complex formation is a spontaneous process. The ΔH^0 values for Cd(II)– and Pr(III)–juglone systems are positive, thus indicating the endothermic nature of complexation In the case of Nd(III)–juglone, the reaction is exothermic, ΔH^0 being negative. With the exception of the Nd(III)–juglone system, all the systems have positive ΔS^0 values, indicating a favourable entropy for complexation.

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