Thermochimica Acta, 115 (1987) 385–387
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

EQUILIBRIUM ANALYSIS OF La(III)– AND Pr(III)–3-METHYL-5-HYDROXY-1,4-NAPHTHALENEDIONE SYSTEMS

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(Received 22 September 1986)

Hydroxynaphthalenediones have been widely studied for their affinity to metals in solution by Sawhney et al. [1–10]. This contribution is devoted to the study of the solution chemistry of La(III)– and Rh(III)–3-methyl-5-hydroxy-1,4-naphthalenedione systems.

EXPERIMENTAL

All the chemicals used were of analytical grade. The procedural details relevant to solution study were reported earlier [11,12].

RESULTS AND DISCUSSION

pH curves displaying the separation of the metal–ligand curve from the ligand curve indicated the release of protons in solution due to metal–ligand interactions, and participation of the anion of the ligand in question.

Examination of the formation curves ($\bar{n}$ vs. pL; the formation functions were calculated following the usual Bjerrum procedure) indicated that the stepwise formation tended to decrease, concluding a weakening of bond strength with the successive attachment of the 3-methyl-5-hydroxy-1,4-naphthalenedione molecule to the metal (La or Rh).

$\bar{n}$ neared 3 in both the systems favouring the formation of 1 : 1, 1 : 2 and 1 : 3 complex species under the experimental conditions; the liberation of protons under the limiting conditions of a 1 : 4 mixture (metal/ligand) demonstrated the above results.

The formation curves of the systems (complete at both ends) are based on Bjerrum procedure and warranted Bjerrum's basic conditions [13].

Metal hydrolysis was prevented by keeping a 5 : 1 (ligand/metal) ratio in each set. The whole study near infinite dilution and at constant ionic strength (0.1 M KNO_3) reduced the activity coefficient of the species

0040-6031/87/$03.50

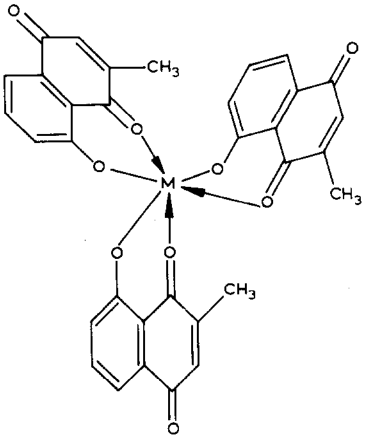
TABLE 1

Stability and thermodynamic data for La(III)– and Rh(III)–3-methyl-5-hydroxy-1,4-naphthalenedione systems

Stability constants	Temp. (° C)		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} deg^{-1}) at 45 ° C
	35	45	35 ° C	45 ° C		
La(III) – 3-methyl-5-hydroxy-1,4-naphthalenedione						
log k_1	10.65	9.25				
log k_2	8.25	5.75				
log k_3	6.00	5.20				
log β_3	24.90	20.20	−35.10	−29.40	−31.37	−7.30
Rh(III) – 3-methyl-5-hydroxy-1,4-naphthalenedione						
log k_1	11.00	10.50				
log k_2	8.10	8.00				
log k_3	5.85	5.65				
log β_3	24.95	24.10	−35.17	−35.07	−38.10	−9.50

involved to unity, demonstrating that the stability data were thermodynamically true.

The decreasing stability constants with increasing temperature suggests that a low temperature is favourable for both reactions. This observation indicates a decrease in kinetic energy for the molecules involved, indicating a lowering of the stability of the systems as temperature rises. The less negative ΔG^0 value at high temperatures made the enthalpy-controlled reactions less feasible. Higher $-\Delta H^0$ data indicated a considerable degree of covalency in the metal complexes studied. Solvent effects might have been responsible for the negative entropy of these systems.



Scheme 1. Tris(3-methyl-5-hydroxy-1,4-naphthalenedionato)–M(II) (M = La, Rh).

In the light of solution data, the metal (La or Rh) in these complexes may be visualized as shown in Scheme 1.

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