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Note

SOLUTION STUDIES ON TRIS(2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHALENEDIONE SEMICARBAZONATO) M^{3+} (M = PRASEODYMIUM OR NEODYMIUM)

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Hydroxynaphthalenediones have been extensively explored [1–10]. The interaction of 2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthalenedione with semicarbazide hydrochloride has been attempted and studied. The first reporting on its synthesis supported by mass spectral investigation and its affinity to metals, viz. Eu(III), Gd(III) and Tb(III), was made by Sawhney et. al. [11]. This note covers the affinity of Pr(III) and Nd(III) to the title compound (hereafter abbreviated as 2-HMBNS) in solution under thermodynamic conditions.

EXPERIMENTAL

All the chemicals used were of analytical grade. All procedural details on solution study are covered in our earlier report [11].

RESULTS AND DISCUSSION

Formation functions, viz. $\bar{n}$, pL were worked out following Bjerrum's concepts [12]. The earlier reported value of the protonation constant of 2-HMBNS, monoprotic in nature, has been used for the calculation of pL values ($\log {}^{\mathrm{P}}K^{\mathrm{H}} = 4.75$ (35 °C) and 5.75 (45 °C)).

The whole determination has been made under a thermodynamic environment (near infinite dilution, constant ionic strength (0.1 M KNO_3). From the plots of $\bar{n}$ against pL, the observed difference between $\log k_1$ and $\log k_2$ was far less than 2.5, ruling out the applicability of Bjerrum's approach to evaluate the constants; pointwise calculation and graphical methods were relied upon for data reliability, and the subsequent thermodynamic data on the systems involved.

As a result of the decreasing trend of the stepwise stability constants ($\log k_1 > \log k_2 > \log k_3$), a decrease bond strength of 2-HMBNS with

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TABLE 1

Stability and thermodynamics[a] of Pr(III)- and Nd(III)-2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthalenedionesemicarbozone systems

	Pr(III)		Nd(III)	
	35 °C	45 °C	35 °C	45 °C
Log k_1	4.63	6.45	4.50	5.35
Log k_2	3.86	5.56	3.93	4.09
Log k_3	3.75	3.63	3.61	3.72
Log β_3	12.24	15.65	12.04	13.16
ΔG^0	−17.25	−22.77	−16.97	−19.15
ΔH^0		+152.83		+50.20
ΔS^0		+552		+218

[a] ΔG^0 and ΔH^0 in kcal mol^{-1}; ΔS^0 in cal mol^{-1} K^{-1}.

reference to Pr/Nd with successive attachment of ligand is inferred. Furthermore, the stability data indicated an increase in logarithmic values of the protonation constant and stepwise formation constants of the 2-HMBNS–Nd system with a rise in temperature. It led us to believe that the complexation reaction is temperature dependent at high temperatures because of the increase in the number of collisions with an increase in kinetic energy of the molecules involved. The first two stepwise constants of the Pr–2-HMBNS system, increased as the temperature rose, and the value of log k_3 at 45 °C was slightly less than the one observed at 35 °C. The reactions are endothermic ($+\Delta H^\circ$), aiding the increase in the constants at higher temperatures. As ΔG° assumed a negative value, the reaction was feasible, and it became more feasible at higher temperature as ΔG^0 assumed a more negative value. The reactions are accompanied by an increase in entropy ($+\Delta S^0$) and tend to be spontaneous.

Under the solution conditions, the formation curves were complete at both ends. With $\bar{n}$ assuming a value close to 3, the presence of species with 1 : 1, 1 : 2, 1 : 3 stoichiometries is concluded.

Table 1 gives the stability and thermodynamic data on the systems studied.

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