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Note

STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF Fe(II), Co(II), Ni(II) AND Cu(II) COMPLEXES WITH 5-SULFOSALICYLIC ACID

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Like salicylic acid, 5-sulfosalicylic acid is a very good chelating agent. A survey of the literature reveals that the study of the interaction of 5-sulfosalicylic acid (referred to herein as SSA) with Fe(II), Co(II), Ni(II) and Cu(II) is not complete. Therefore, in this communication the interaction of Fe(II), Co(II), Ni(II) and Cu(II) with SSA at two different temperatures (25 ± 0.1 and 35 ± 0.1°C) and 0.1 M $NaClO_4$ ionic strength (μ) is studied. The proton-ligand stability constant of SSA, and the metal-ligand stability constants at 25 ± 0.1 and 35 ± 0.1°C are calculated, and the overall change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), are computed. An attempt is also made to establish and confirm the Irving–Williams Rule [1,2]. The effect of temperature on the complexes is explained.

EXPERIMENTAL

SSA was commercially obtained. The metal contents of the metal salts were estimated gravimetrically [3]. $NaClO_4$ (1 M) was used for maintaining the ionic strength. Measurement of the pH was carried out on a Systronix pH-meter (Model 322-1) with glass calomel electrodes. The experimental procedure involved a series of pH-titrations of SSA in the absence of and in the presence of metal ions. In all the titrations, the volume (50 ml), ionic strength and temperature were kept constant. Other experimental details regarding preparation of sets for titration and calculation have been described previously by Agarwal et al. [4–6].

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TABLE 1

Metal-ligand stability constants and thermodynamic function of the complexes at $\mu = 0.1$ M $NaClO_4$

Metal		log K		ΔG (kcal mole^{-1})		ΔH for temp. difference of	ΔS	
		25°C	35°C	25°C	35°C	10°C	25°C	35°C
log pK_1H		2.86	3.19					
log pK_2H		2.79	3.02					
log p$K\beta H$		5.65	6.21					
Cu(II)	log K_1	5.36	5.50	−7.296	−7.752			
	log K_2	4.10	4.25	−5 591	−5.990			
	log β	9.46	9.75	−12.887	−13.742	5.471	61.604	62.379
Ni(II)	log K_1	5.05	5.20	−6 886	−7.329			
	log K_2	4.05	4.30	−5.523	−6.060			
	log β	9.10	9.50	−12.409	−13.389	7.295	66.120	67 156
Co(II)	log K_1	5.40	5.65	−7.364	−7.963			
	log K_2	3.45	3.75	−4.705	−5.285			
	log β	8.85	9.40	−12.069	−13.248	10.030	74.157	75 578
Fe(II)	log K_1	4.85	5.05	−6.614	−7.118			
	log K_2	3.85	3.90	−5.250	−5.497			
	log β	8.70	8.95	−11 864	−12.615	4.559	55.111	55.759

RESULTS AND DISCUSSION

The proton-ligand stability constants of SSA at 25 ± 0.1 and $35 \pm 0.1°C$ are reported in Table 1. The thermodynamic functions of the chelates were calculated using the relationships

$$\Delta G = -RT \log K$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

and

$$\Delta G = \Delta H - T \Delta S$$

It is evident from Table 1 that the dissociation of H^+ ion from SSA and chelation take place stepwise, i.e. 1:1 and 1:2. It is also obvious that the stability constants of the chelates follow the order

$$Cu(II) > Ni(II) > Co(II) > Fe(II)$$

This order is generally obeyed by these metals and is commonly known as the Irving–Williams Rule [1,2]. It is also observed from Table 1 that the proton-ligand stability constant of SSA increases with increase of temperature, as do the metal-ligand stability constants. Thus, it can be concluded that the higher temperature is favourable for complexation.

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