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Note

Fe(II), Co(II), Ni(II) AND Cu(II) CHELATES WITH PHLOROACETOPHENONE IN 50% ETHANOL —H_2O

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Ketones having an —OH group in the *ortho*-position are generally strong chelating agents owing to the possibility of the formation of a six-membered chelation ring. A number of *ortho*-hydroxyacetophenones and their oximes have already been studied for their interaction with the metal ions. The interaction of phloroacetophenone (2,4,6-trihydroxyacetophenone) with the metal ions have also been studied [1,2]. The literature survey reveals that the interaction of phloroacetophenone (PAP) with Fe(II), Co(II), Ni(II) and Cu(II) in 50% ethanol —H_2O has not yet been studied. This communication reports the interaction of Fe(II), Co(II), Ni(II) and Cu(II) with PAP in 50% ethanol —H_2O at three different temperatures, i.e. 25 ± 0.1, 35 ± 0.1 and $45 \pm 0.1°C$, and at three different ionic strengths (μ), 0.05 M, 0.075 M and 0.10 M $NaClO_4$. The proton—ligand stability constant of PAP and the metal—ligand stability constants at three different temperatures have been calculated, and the overall change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been computed. An attempt is also made to establish and confirm the Irving—Williams Rule [3,4]. The effects of temperature and ionic strength (μ) on the chelation are also explained on the basis of previous publications.

EXPERIMENTAL

PAP was prepared as described previously [1,2]. The absolute alcohol was distilled twice. The metal content of the metal salts was estimated gravimetrically [5]. $NaClO_4$ (1 M) was used for maintaining the ionic strength. pH-Measurements were carried out on a Systronix pH-meter (Model 322-1) with glass—calomel electrodes. The experimental procedure involved a series of pH-titrations of PAP 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. [6—8].

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TABLE 1

Metal—ligand stability constants and thermodynamic functions of the complexes in 50% ethanol—H_2O at $\mu = 0.1$ M $NaClO_4$

Metal		log k			ΔG (kcal mole^{-1})			ΔH for temp. difference of 10°C	ΔS		
		25°C	35°C	45°C	25°C	35°C	45°C		25°C	35°C	45°C
PAP		8.310	8.295	8 065							
Cu(II)	log k_1	7.15	6.35	6.15	−9 750	−8.949	−8.949				
	log k_2	4 15	4.15	3.80	−5 659	−5.849	−5.530				
	log β	11.30	10.50	9.95	−15.409	−14.798	−14.479	−11.143	14.31	11.86	10.49
Ni(II)	log k_1	6.65	6.15	5.70	−9.068	−8.667	−8 294				
	log k_2	4.30	3.85	4.20	−5.864	−5.427	−6.112				
	log β	10.95	10.00	9.90	−14 932	−14.094	−14.406	−15.283	−1.18	−3.86	−2.76
Co(II)	log k_1	7.05	5.25	5.15	−9.614	−7.399	−7.494				
	log k_2	3.65	4.50	4.30	−4.977	−6.342	−6.257				
	log β	10.70	9.75	9.45	−14.591	−13.741	−13.751	−15.501	−3.05	−4.57	−5.50
Fe(II)	log k_1	5.65	5.85	5.40	−7.704	−8.245	−7 858				
	log k_2	4.55	3.65	3.35	−6.205	−5.144	−4.874				
	log β	10.20	9.50	8.75	−13.909	−13.389	−12.732	−9.483	14.85	12.68	10.22

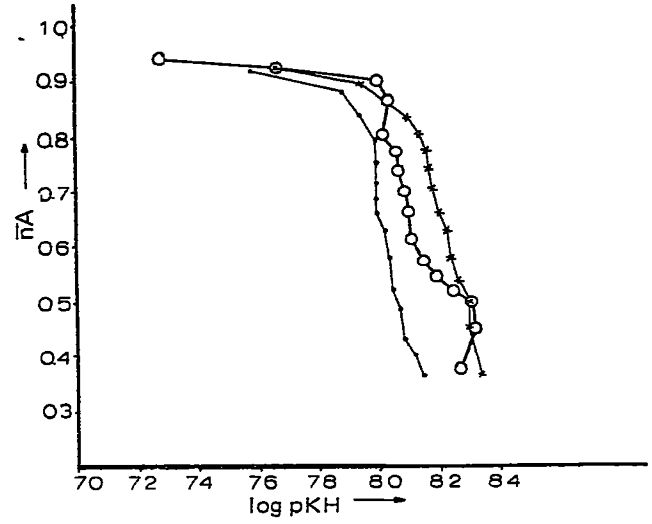

Fig. 1. Formation curves of the proton—ligand stability constant of PAP at 25 (○), 35 (×), and 45°C (⊛).

RESULTS AND DISCUSSION

The proton—ligand stability constants of PAP at various temperatures are reported in Table 1 and those for different ionic strengths are taken from unpublished data of the authors. The formation curves for the proton—ligands are shown in Fig. 1. The formation curves for the metal—PAP chelates are shown in Figs. 2—5, and the stability constants and overall stability constants (log β) are reported in Table 1.

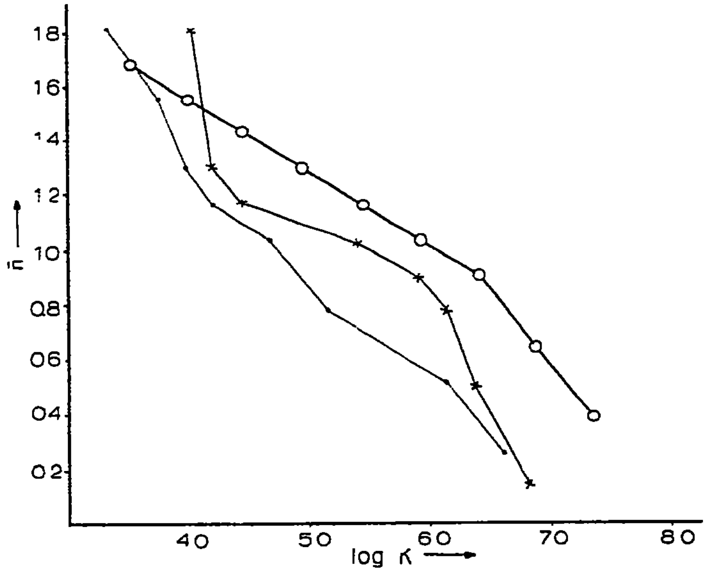

Fig. 2. Formation curves of Cu(II)—PAP chelates at 25 (○), 35 (×) and 45°C (⊛).

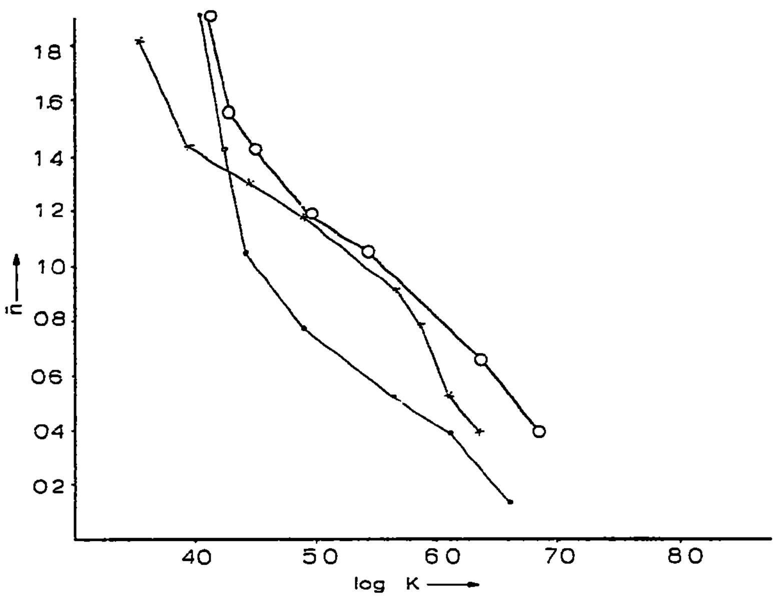

Fig. 3. Formation curves of Ni(II)—PAP chelates at 25 (○), 35 (×) and 45°C (●).

The thermodynamic functions of the chelates were calculated using the relationships

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

$$\log \frac{k_2}{k_1} = \frac{\Delta H}{R} \, \frac{T_2 - T_1}{T_1 T_2}$$

and are reported in Table 1.

From an examination of the values of stability constants for the metal—PAP chelates given in Table 1 (and also from Figs. 2—5), it is evident that

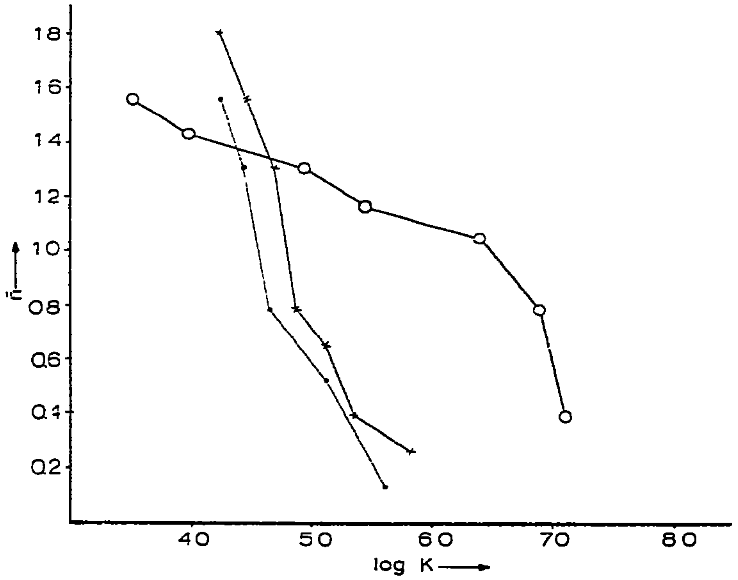

Fig. 4. Formation curves of Co(II)—PAP chelates at 25 (○), 35 (×) and 45°C (●).

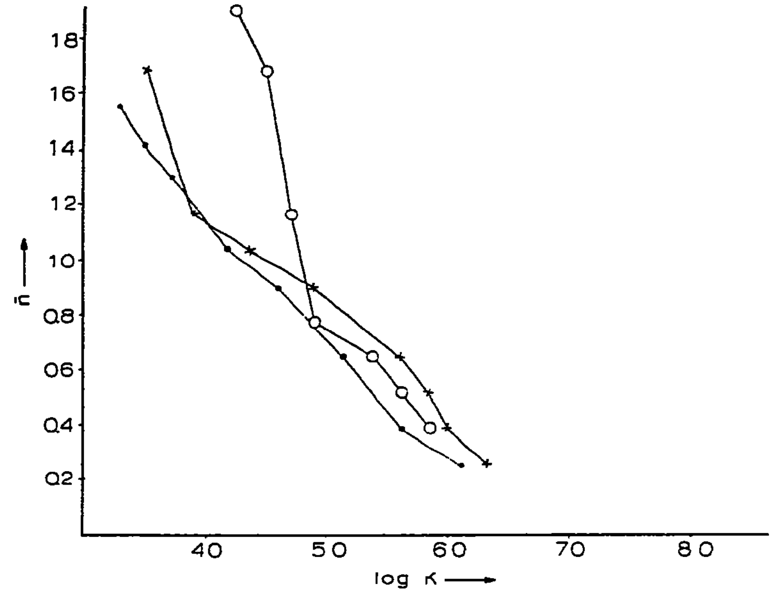

Fig. 5. Formation curves of Fe(II)—PAP chelates at 25 (○), 35 (×) and 45°C (●)

stepwise chelation takes place, 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 [3,4]. It is also observed from Table 1 that the stability constants of the chelates decrease with increase in ionic strength. Thus, it can be concluded that the activity of the metal ions to interact with the ligand decreases with increase in ionic strength. This is also in accordance with the earlier findings by Debye [9]. The stability constants of all the chelates decrease with rise in temperature; therefore, low temperature is favourable for chelation.

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