Thermochimica Acta, 52 (1982) 371–374
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THERMODYNAMIC FUNCTIONS OF SOME TRANSITION METAL CHELATES WITH PHLOROACETOPHENONE IN 50% METHANOL $-H_2O$

R C. AGARWAL * and S L AGARWAL

Department of Chemistry, Bipin Bihari College, Jhansi-284001 (India)

(Received 30 July 1981)

Aromatic ketones with a hydroxy group in the *ortho* position have the capability of chelation with transition metal ions due to the possible formation of a six-membered chelation ring. The interaction of phloroacetophenone (PAP), i.e. 2,4,6-trihydroxyacetophenone, an aromatic ketone with a hydroxy group in the *ortho* position, with the metal ions has also been studied by the authors [1–3]. In this communication, the interaction of Fe(II), Co(II), Ni(II) and Cu(II) with PAP in 50% methanol $-H_2O$ at three different temperatures, i.e. 25 ± 0.1, 35 ± 0.1 and 45 ± 0.1°C has been investigated at 0.1 M $NaClO_4$ ionic strength. The proton–ligand stability constant of the PAP and metal–ligand stability constants at three different temperatures have been calculated and the overall change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) computated. An attempt is also made to establish and confirm the Irving–Williams Rule [4,5]. The effects of temperature and interaction medium on the chelation are also explained.

EXPERIMENTAL

All experimental details, e.g. the preparation of PAP [1,2], estimation of metal content [3], preparation of sets for pH-metric titrations and calculations etc. [6–8] have already been described. $NaClO_4$ (1 M) was used for maintaining the ionic strength. pH measurements were carried out on Systronix pH meter (Model 322-1) with glass–calomel electrode. In all the titrations, the volume (50 ml), ionic strength, and temperature were kept constant.

RESULTS AND DISCUSSION

The proton–ligand stability constant of PAP at various temperatures are reported in Table 1 and the formation curves are shown in the Fig. 1. The formation curves

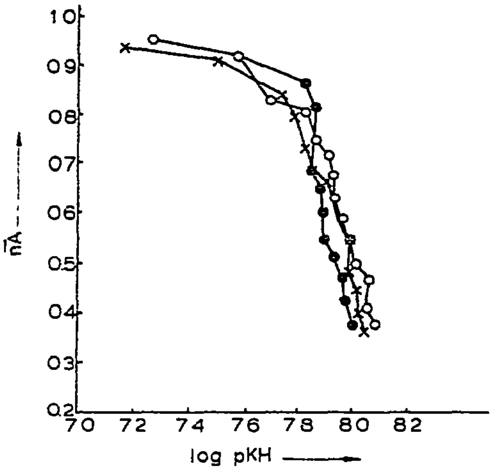
---

* To whom correspondence should be addressed.

TABLE I

Metal–ligand stability constants and thermodynamic functions of the complexes in 50% methanol-H_2O at μ 0 1 M $NaClO_4$

Metal		log k			ΔG (kcal $mole^{-1}$)			ΔH for temp difference	ΔS		
		25°C	35°C	45°C	25°C	35°C	45°C	of 10°C	25°C	35°C	45°C
PAP		8 01	7 98	7 94							
Cu(II)	log k_1	5 65	5 80	5 30	−7 704	−8 175	−7 712				
	log k_2	4 45	3 80	4 25	−6 068	−5 356	−6 184				
	log β	10 10	9 60	9 55	−13 772	−13 531	−13 896	4 395	31 46	29 66	29 87
Ni(II)	log k_1	5 40	5 85	5 10	−7 364	−8 245	−7 421				
	log k_2	4 45	3 55	4 10	−6 068	−5 003	−5 778				
	log β	9 85	9 40	9 20	−13 432	−13 248	−13 199	−3 355	33 81	32 12	30 95
Co(II)	log k_1	5 30	4 85	4 85	−7 227	−6 835	−7 057				
	log k_2	4 30	4 10	3 50	−5 863	−5 778	−5 093				
	log β	9 60	8 95	8 35	−13 090	−12 614	−12 150	−8 681	14 79	12 77	10 91
Fe(II)	log k_1	5 05	5 05	4 60	−6 886	−7 117	−6 693				
	log k_2	4 15	3 85	3 55	−5 659	−5 426	−5 166				
	log β	9 20	8 90	8 75	−12 545	−12 543	−11 859	−0 036	41 97	40 60	37 18



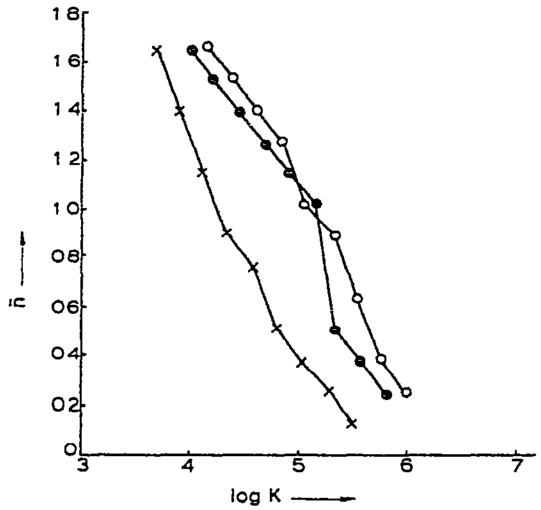
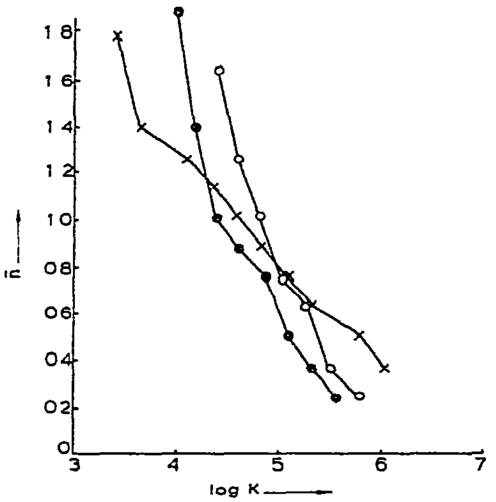


Fig 1 Formation curves of proton–ligand stability constant of PAP at 25 (○), 35 (×) and 45°C (●)

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

for metal–PAP chelates are shown in the Figs. 2–5 and the stepwise stability constants and overall stability constant (log β) and thermodynamic functions are reported in the Table 1.

On going through the values of the stability constants for the metal–PAP chelates from Table 1 and also from Figs. 2–5, it is evident that the chelation takes place stepwise, i.e. 1 : 1 and 1 : 2. It is also obvious that the stability constant of the chelates follow the order Cu(II) > Ni(II) > Co(II) > Fe(II).



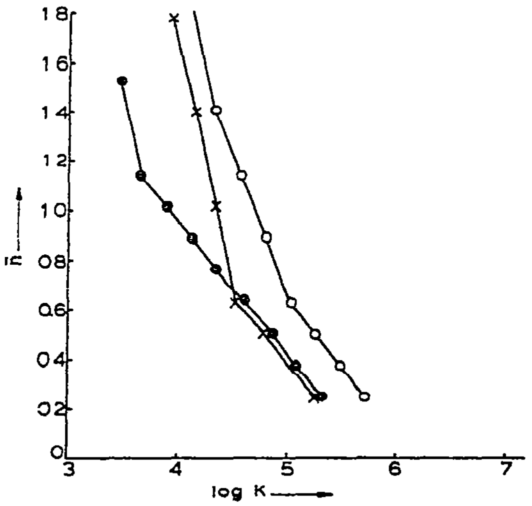


Fig 3 Formation curves of Ni(II)–PAP chelates at 25 (○), 35 (×) and 45°C (●)

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

This stability constant order is generally obeyed by these metals and is commonly known as the Irving–Williams Rule [4,5]. It is also observed from Table 1, and from chelates in the 50% ethanol $-H_2O$ system [3], that stability constants decrease with the change of interaction medium. Thus, it can be concluded that the ability of the metal ions to interact with ligand depends upon the medium of interaction, i.e. on the dielectric constant of the solvent. The stability constants of all the chelates decreases with increase in temperature, and therefore low temperature is favourable for chelation.

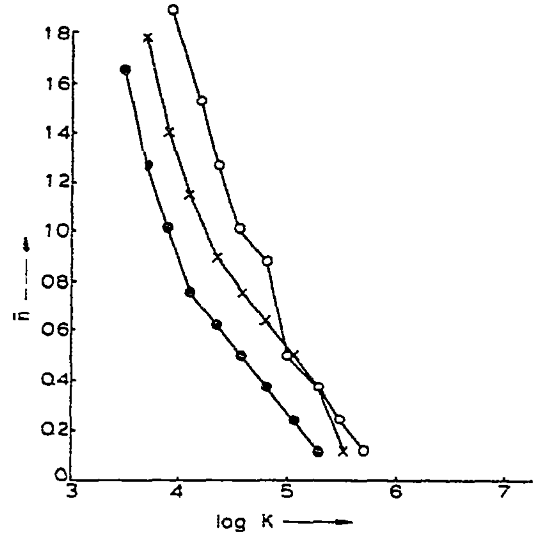


Fig 5 Formation curves of Fe(II)–PAP chelates at 25 (○), 35 (×) and 45°C (●)

ACKNOWLEDGEMENT

The authors are grateful to the college authorities for providing the necessary facilities for performing this work.

REFERENCES

1 R.C Agarwal, J Indian Chem Soc, 51 (1974) 727
2 R C Agarwal, J Indian Chem. Soc, 55 (1978) 984
3 R.C Agarwal and S L Agarwal, Thermochim Acta, 47 (1981) 99.
4 H Irving and R J P Williams, J Chem Soc, (1953) 3192
5 H Irving and R J.P Williams, Nature (London), 162 (1948) 746
6 R C Agarwal, R P. Khandelwal and P C. Singhal, J Indian Chem Soc., 53 (1976) 977
7 R C. Agarwal, J Indian Chem. Soc., 55 (1978) 220
8 R C. Agarwal and S L Agarwal, Thermochim. Acta, 44 (1981) 121