Thermochimica Acta, 144 (1989) 173–175
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

EQUILIBRIUM ANALYSIS OF Nd(III)–NAA, Pr(III)–NAA AND Ce(III)–NAA SYSTEMS

S.S. SAWHNEY, GAMBHIR SINGH CHAUHAN and NARESH CHANDRA
Department of Chemistry, D.A.V. (P.G.) College, Dehra Dun-248001 (U.P.) (India)

(Received 25 July 1988)

INTRODUCTION

Sawhney and co-workers [1–3] have studied the affinity of metals to plant auxins (IBA, IAA, IPA) highlighting their solution chemistry, synthesis, decomposition mechanism, and kinetics. This paper reports on an extension of these studies on the interaction of the metals Nd(III), Pr(III) and Ce(III) with NAA (naphthylacetic acid) in solution.

EXPERIMENTAL

The procedure followed for the study of the metal–NAA systems has been described previously [4]. A Beckman pH meter equipped with glass and calomel electrodes was used.

RESULTS AND DISCUSSION

The entire study was done in 50% acetone in water and at constant ionic strength (0.01-M KNO_3). All experiments were performed at near-infinite dilution so that the activity coefficients of species in solution were reduced to unity and, thereby, the conditions were thermodynamically true.

The protonation constants (${}^{P}K^{H}$) of NAA were calculated for two different temperatures using the equation of Henderson and Hesselback [5]: 5.80 (28 °C) and 4.75 (38 °C). The value of $\bar{n}$ was approximately 3 for the Ce(III)–NAA, Pr(III)–NAA and Nd(III)–NAA systems indicating the presence of 1 : 1, 1 : 2 and 1 : 3 complex species in solution.

The metal ligand curves were well separated from the ligand curves, implying the replacement of the hydrogen atom of the carboxylic group in complexation. The strength of the NAA–metal bond decreased with the successive attachment of the ligand (NAA) molecule ($\log K_1 > \log K_2 >$

0040-6031/89/$03.50

TABLE 1

The stability constants and thermodynamic parameters of the Nd(III)–NAA, Pr(III)–NAA and Ce(III)–NAA systems

System temperature (°C)		log					ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} °C^{-1})
		k_1	k_2	k_1/k_2	k_3	B_3			
Nd(III)–NAA	28	4.18	3.60		3.39	11.17	−15.39	−5.15	
		(4.15)	(3.58)	0.57	(3.30)				
	38	4.16	3.57		3.32	11.05	−15.73		+34.04
		(4.12)	(3.55)	0.57	(3.30)				
Pr(III)–NAA	28	4.78	3.70		3.39	11.87	−16.35	−35.98	
		(4.70)	(3.62)	1.07	(3.30)				
	38	4.16	3.63		3.24	11.03	−15.70		−65.23
		(4.10)	(3.59)	0.51	(3.30)				
Ce(III)–NAA	28	4.16	3.60		3.36	11.12	−15.32	−9.00	
		(4.10)	(3.55)	0.55	(3.30)				
	38	4.08	3.53		3.30	10.91	−15.53		+21.00
		(4.05)	(3.52)	0.53	(3.30)				

log K_3), as is evident from the data given in Table 1 which were determined using a graphical approach. The Bjerrum method [6] could not be used to determine the bond strengths because the data obtained did not satisfy the basic condition of the method (log $k_1/k_2 \geqslant 2.5$). The above energy sequence favours lower temperatures as a necessary condition for the complexation reaction because of the consequent decrease in the number of collisions with the decrease in kinetic energy of the molecules involved.

Evidence of the spontaneity of the reactions could be found in the negative $\Delta G^{\ominus}$ values, which became less negative at higher temperatures in the Pr(III)–NAA and Ce(III)–NAA systems, making the formation of these systems less feasible with increasing temperature; the reverse was observed for the Nd(III)–NAA system. The negative $\Delta H^{\ominus}$ values show that the reactions are endothermic which is in agreement with the conclusions drawn previously on the systems, whereas an increase in the entropy ($+\Delta S^{\ominus}$) of the Nd(III)–NAA and Ce(III)–NAA systems implies spontaneity of the reaction; in the Pr(III)–NAA system the lower negative entropy value ($-\Delta S^{\ominus}$) may be due to solvent effects.

ACKNOWLEDGEMENT

The authors acknowledge the cooperation of the College authorities.

REFERENCES

1 S.S. Sawhney and N. Chandra, Thermochim. Acta, 61 (1983) 357.
2 S.S. Sawhney, N.C. Sharma and N.K. Arora, Thermochim. Acta, 126 (1988) 393.
3 S.S. Sawhney, N. Chandra and A. Gupta, Thermochim. Acta, 125 (1988) 387.
4 S.S. Sawhney and R.M. Sati, Thermochim. Acta, 61 (1983) 365.
5 V.P. Kudesia and S.S. Sawhney, Instrumental Methods of Chemical Analysis, Pragati Prakashan, Meerut, 1983.
6 J. Bjerrum, Metal Amonine Formation in Aqueous solution, P. Hasse and Son, Copenhagen, 1941, p. 298.