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Note

ON THE INTERACTION OF Ce(IV) AND Th(IV) WITH PHENOXYMETHYL PENICILLIN IN SOLUTION

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Metal–phenoxymethyl penicillin systems have been scarcely explored in solution [1–4]. A report on the affinity of Ce(IV) and Th(IV) to phenoxymethyl penicillin is presented.

EXPERIMENTAL

All the reagents used were of analytical grade. The solutions under investigation, in 50% v/v acetone–water are: (a) 4×10^{-3} M HNO_3, 1×10^{-1} M KNO_3; (b) 4×10^{-3} M HNO_3, 1×10^{-3} M KNO_3 and 3×10^{-3} M phenoxymethyl penicillin (Na^+); (c) 4×10^{-3} M HNO_3, 1×10^{-3} M KNO_3, 3×10^{-3} M phenoxymethyl penicillin (Na^+) and 4×10^{-4} M metal ion. The pH was measured with a Beckman pH-meter (Model H-2; sensitivity $\pm$ 0.5 pH) duly standardised with standard buffers. The ensuing curves (pH vs. NaOH) were of usual shapes; pH was duly corrected following Van Uitert and Haas [5] and for volume of the titrant added.

RESULTS AND DISCUSSION

The Irving and Rossotti expression [6] was applied to estimate the average number of H^+ ions attached to phenoxymethyl penicillin; value of $\bar{n}_H$ at 0.5 from the curve ($\bar{n}_H$ vs. pH) was taken as the value of log ${}^pK^H$ (log ${}^pK^H = 10.82$ and 10.50 at 25 and 35°C, respectively). The free ligand exponent (pL) was estimated using Bjerrum's expression [7]

$$pL = \log\left[\frac{1 + 10^{-pH\ {}^pK^H}}{\Delta NaOH}\right] \quad (1)$$

where the terms have the usual meanings. The formation curves were obtained by plotting pL against $\bar{n}$; pL values at $\bar{n} = 0.5$ were taken as the values of log k_1/log β_1. During the titrations the solutions became turbid at both temperatures with pH ranging from 5.7 to 6.0. These observations

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TABLE 1

Stability and thermodynamic data of the Th(IV)– and Ce(IV)–phenoxymethyl penicillin systems

System	Temp. (°C)	$\log k_1/\log \beta_1$	ΔG^0 (kcal mol^{-1})	ΔH^0	ΔS^0 (cal mol^{-1} deg^{-1})
Th(IV)	25	9.88	−13.47		
	35	9.86	−13.90	−0.84	+42.40
Ce(IV)	25	9.02	−12.30		
	35	9.64	−13.59	+26.04	−40.43

entailed the following restrictions limiting calculations below the pH of precipitation

	pH of precipitation	
	25°C	35°C
Th(IV)	5.70	5.90
Ce(IV)	6.0	5.70

For both the systems $\bar{n}$ approaches 1 indicating the combination of a mole of Ce(IV)/Th(IV) with a mole of phenoxymethyl penicillin in solution. A gradual increase in $\bar{n}$ value with increasing pH indicates the participation of the anionic form of phenoxymethyl penicillin. The values of log ${}^{P}K^{H}$ and log k_1 of the Th(IV)–phenoxymethyl penicillin system decrease with the increase in temperature indicating that a low temperature favours the reaction because of the decrease in the number of collisions with the decrease of kinetic energy of the molecules and thus the stability of the system is lowered. For the Ce(IV)–phenoxymethyl penicillin system an increase in log k_1 was noticed with the rise of temperature. The free energy change, assuming a negative sign at both the temperatures, indicated the feasibility of the reactions; the data further indicated the appreciation in the feasibility of the reactions at 35°C.

ΔH^0 values (Table 1) for Ce(IV)– and Th(IV)–phenoxymethyl penicillin systems corroborate the previous inferences. The negative ΔS^0 value for the former system appears to be due to solvent effect; its value for the latter system favours complex formation.

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