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Note

pH-METRIC STUDIES ON THE INTERACTION OF SOME LANTHANONS–PHENOXYMETHYL PENICILLIN SYSTEMS

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Penicillins, the life saving drugs, are well recognized. Very little data is available on the penicillin derivatives' affinity for metal ions [1–5]. An attempt has been made to study pH-metrically in solution the stability and thermodynamics of Eu(III)– and Gd(III)–phenoxymethyl penicillin systems.

EXPERIMENTAL

All the reagents were of analytical grade. Phenoxymethyl penicillin (Na^+) and metal nitrates were prepared in cation free water; the latter were standardized by standard methods. Solutions having identical concentrations of the common ingredient were prepared in three sets according to Bjerrum [6]: (a) 4×10^{-3} M HNO_3, 1×10^{-1} M KNO_3; (b) 4×10^{-3} M HNO_3, 1×10^{-1} M KNO_3, 3×10^{-3} M phenoxymethyl penicillin; (c) 4×10^{-3} M HNO_3, 1×10^{-1} M KNO_3, 3×10^{-3} M phenoxymethyl penicillin, 4×10^{-4} M metal. The pH was corrected for non-aqueous media (50%, v/v, acetone–water) according to van Uitert and Haas [7] and was measured on a Beckman pH-meter, model H-2, with a sensitivity of ± 0.5 pH units and calibrated with standard buffers. The ionic strength was maintained at 0.1 M KNO_3. The curves (pH vs. base) were of usual shapes.

RESULTS AND DISCUSSION

The average number of H^+ attached to the ligand ($\bar{n}_H$) was estimated through the Irving and Rossotti expression [8]; the linear plot of log $\bar{n}/(1-\bar{n})$ against B (pH-meter reading) following eqn. (1) gave the value of the protonation constant (pK^H) of phenoxymethyl penicillin which dissociates in one step

$$\log {}^{P}K_n^H = B + \log \frac{[\bar{n} - (n-1)]}{[n - \bar{n}]} \quad (1)$$

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The formation function of the system ($\bar{n}$) and free ligand exponent (pL) (eqn. 2) were determined according to Bjerrum's concept [6]

$$pL = \log \frac{[1 + 10^{-pH} \cdot {}^{P}K^{H}]}{\Delta NaOH} \quad (2)$$

Where $\Delta NaOH$ corresponds to the extent to which complexation occurs in solution. For metal–phenoxymethyl penicillin systems, the stability constants, and hence thermodynamic parameters (Table 1), were determined by applying Bjerrum's half integral method; the curves were complete at both ends. The metal–ligand titration curves were found to separate from the ligand curve showing that the phenoxymethyl penicillin anion is involved in complexation. In each set, a ratio of five parts of phenoxymethyl penicillin to one part of metal ion was maintained to avoid the hydrolysis of the metal.

The formation function ($\bar{n}$) of all the systems neared a value of one indicating that a 1 : 1 complex exists only in solution under the experimental conditions. During titration with NaOH the mixture in all cases turned turbid. The calculations under these conditions were restricted to below the pH of precipitation.

	pH of precipitation at 25°C	pH of precipitation at 35°C
Eu(III)	5.6	5.8
Gd(III)	6.1	5.9

Further analysis of Table 1 shows that $\log {}^{P}K^{H}$ and $\log k_1$ of the Eu(III)–phenoxymethyl penicillin system decrease with a decrease in temperature showing that a low temperature is favourable for interaction because of the decreased number of collisions with a decreased kinetic energy of the molecules and hence a stable system is obtained. An increase in these constants was observed for the Gd(III)–phenoxymethyl penicillin system. ΔG^0 assumed negative values for both systems at both temperatures indicating the feasibility of the reactions. With the more negative values of ΔG^0 of both systems at 35°C, the feasibility of the reaction increases with the rise of temperature. The ΔH^0 value for the Gd(III)–phenoxymethyl penicillin system was +32.34 kcal mol^{-1} which points to the fact that a high temperature

TABLE 1
Stability constants and thermodynamic parameters of some lanthanons–phenoxymethyl penicillin systems

System	Temp. (°C)	$\log {}^{P}K^{H}$	$\log k_1$	$\log \beta_1$	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} $deg.^{-1}$)
Eu^{3+}	25	10.82	9.68	9.68	−13.20		
	35	10.50	9.58	9.58	−13.50	−4.20	+30.20
Gd^{3+}	25	10.82	9.63	9.63	−13.13		
	35	10.50	10.40	10.40	−14.70	+32.24	−57.30

favours the reaction. For the Eu(III)–phenoxymethyl penicillin system the ΔH^0 value (-4.20 kcal mol^{-1}) favours a low temperature for the interaction of Eu(III) and phenoxymethyl penicillin. The entropy change (ΔS^0) for the Gd(III)–phenoxymethyl penicillin system is, in all probability, due to solvent effect. The positive entropy change for the Eu(III)–phenoxymethyl penicillin system indicates a favourable entropy for complex formation.

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