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Note

SOLUTION STUDY ON LANTHANUM(III)-, PRASEODYMIUM(III)-, EUROPIUM(III)-, AND GADOLINIUM(III)-PHENYLMETHYL PENICILLIN SYSTEMS

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The pharmacodynamics of penicillins are appreciably recognized. Sawhney and Bansal [1], Tiwari et al. [2–4], and Chakrawarti et al. [5] have contributed work on the metal–penicillins interactions. In this note a report on the solution studies of La(III)-, Pr(III)-, Eu(III) and Gd(III)–phenylmethyl penicillin systems is presented.

EXPERIMENTAL

All the chemicals used were of BDH quality. Phenylmethyl penicillin (sodium salt) was medicinally pure. The metal nitrates were prepared in distilled water, and their metal contents were determined by standard methods. A Beckman model H-2 pH-meter (accuracy $\pm$ 0.05) was employed for all pH measurements. Titrations were carried out in 50% acetone solutions at 25 ± 1 and 35 ± 1°C. An appropriate quantity of KNO_3 (M) solution was added to maintain a constant ionic strength of 0.1 M. Correction of pH for non-aqueous media was applied following the procedure of Van Uitert and Haas [6].

RESULTS AND DISCUSSION

$\bar{n}_H$ was evaluated at various pH values using the Irving–Rossotti expression [7]. The proton–ligand stability constant was determined using eqn. (1) together with the linear plot method [log $\bar{n}_H/(1 - \bar{n}_H)$ vs. pH].

Equation (1) holds good at each point falling on the linear plot. With the maximum limit of $\bar{n}_H$ being less than one ($\bar{n}_H < 1$), one-step dissociation of phenylmethyl penicillin is concluded.

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

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The free ligand exponent (pL) was calculated following the Bjerrum–Calvin titration technique [8]

$$pL = \log_{10}\left[\frac{1 + (H^+)\,{}^{P}K^{H}}{\Delta NaOH}\right] \quad (2)$$

where ΔNaOH corresponds to the extent of complexation, which can be determined from the separation of the metal–ligand curve from the acid curve.

On the progressive addition of 1 M NaOH during pH titration a precipitate was obtained in each case. The pH of precipitation in the different systems involving different metals is

	pH of precipitation	
	25°C	35°C
La(III)	5.8	5.9
Pr(III)	6.0	6.1
Eu(III)	5.6	5.7
Gd(III)	5.9	6.0

Therefore calculations for $\bar{n}$ and pL were carried out below the pH of

TABLE 1

Stability constants and thermodynamics of La(III)-, Pr(III)-, Eu(III)-, and Gd(III)-phenylmethyl penicillin systems

Metal ion	Temp. (°C)	$\log {}^{P}K^{H}$	$\log K_1$	ΔG^0 (kcal mole^{-1})	ΔH^0 (kcal mole^{-1})	ΔS^0 (cal mole^{-1} deg^{-1})
	25	10.84				
	35	10.40				
La(III)	25		9.24 (9.34)	−12.60		
	35		8.39 (8.34)	−11.82	−35.70	−77.53
Pr(III)	25		8.67 (8.68)	−11.82		
	35		8.08 (8.08)	−11.39	−24.78	−43.47
Eu(III)	25		9.25 (9.52)	−12.61		
	35		8.55 (8.69)	−12.05	−29.40	−56.33
Gd(III)	25		8.96 (8.60)	−12.22		
	35		8.20 (8.20)	−11.56	−31.92	−66.10

Values in parentheses are due to point-wise calculation method [eqn. (3)].

precipitation in all cases. The overall concentration of phenylmethyl penicillin in each case was 3×10^{-3} M which, being very dilute, rules out the possibility of the formation of polynuclear complexes.

The metal–ligand stability constants were obtained from the formation curve [$\bar{n}$ vs. pL] using interpolation at half $\bar{n}$ values [8]. Pointwise calculation method together with eqn. (3) was also employed for the purpose.

$$\log K_n = \text{pL} + \log\left[\frac{\bar{n} - (n-1)}{n - \bar{n}}\right] \qquad (3)$$

Table 1 contains the data obtained. Under the experimental conditions $\bar{n}$ did not exceed one ($\bar{n} \leqq 1$), indicating the 1 : 1 stoichiometry of the complex species formed between the metals La(III), Pr(III), Eu(III) and Gd(III) and phenylmethyl penicillin.

Table 1 shows that log $^{P}K^{H}$ and log K_1, decrease as the temperature increases, indicating lower temperatures to be favourable for the interaction of metals with phenylmethyl penicillin because of the decreased number of collisions with the decrease in kinetic energy, and hence their stabilities are lowered. Further the $-\Delta H^0$ values indicate that the reaction is exothermic in nature and provide an explanation for the decrease in stability constant as the temperature rises. The high values of $-\Delta H^0$ also give some idea about the appreciable degree of covalency in the metal–phenylmethyl penicillin bond which in all probability involves metal–nitrogen bonding. The entropy change (ΔS^0) in all systems appeared to be negative which may be due to the effect of solvent; therefore the reactions of La(III), Pr(III), Eu(III), and Gd(III) with phenylmethyl penicillin are enthalpy controlled. ΔG^0 values at 25 and 35°C revealed these reactions as spontaneous processes.

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