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NOTE

Influence of Dieletric Constants on Complex Equilibra of Sm(III)-Captopril in Dioxane-Water Mixtures

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The interaction between Sm(III) and captopril in different percentage of dioxane-water mixtures at 0.1 M strength and 27 \pm 0.1 °C has been studied pH-metrically. The data obtained can be used to evaluate the proton-ligand and metalligand stability constants for 1:1 and 1:2 complexes. The effect of dielectric constants on the stability of complex equilibrium is also studied.

Key Words: Sm(III), Captopril, Dioxane-water mixtures, Dieletric constants.

It has been repeatedly demonstrated that the equilibrium between metals in non-polar solvents is very sensitive to concentration. Several authors¹⁻³ have studied the equilibrium constants of various metals ions in different aqueous and non-aqueous binary solvents. In this paper, the interaction of Sm(III) with captopril has been investigated pH-metrically in different dioxane-water mixtures at 0.1 M ionic strength.

Standard solutions of 0.1 M NaOH, 0.1 M KNO₃ and nitric acid 0.1 M were prepared by using analytical grade reagent. The aqueous solution samaium nitrate prepared in double distillated water.

The solution of captopril was prepared in aqueous medium. pH meter Elica LI-12 was used for measuring the pH of solution and calibrated by standard buffer solution of pH 4, 7 and 9.

Calvin Bjerrum titration: pH titrations are carried out by using Calvin Bjerrum technique in inert atmosphere. The pH-metric titration in different percentage of dioxane-water mixtures (0, 10, 20, 30 and 50 %) are undertaken (1) nitric acid (10^{-2} M), (2) nitric acid (10^{-2} M) + ligand (20×10^{-4} M) (3) nitric acid (10^{-2} M) + ligand (20×10^{-4} M) + metal (4×10^{-4} M), with standard solution of NaOH (0.1 M) at 27 ± 0.1 °C.

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Proton ligand formation constants: The deviation of (acid + ligand curve) started around pH 3 from acid curves and increasing continuously upto pH 10.50. The average number of Protons associated with the ligand (nA) was determined by Irving-Rassott 's equation⁴. The forming curves were constructed by plotting the values nA against pH at which nA = 0.5 and accurate values were also determined by point wise calculation (Table-1).

TABLE-1
PROTEN LIGAND STABILITY CONSTANT OF CAPTOPRIL IN
DIFFERENT PERCENTAGE OF DIOXANE WATER AT 0.01 M
IONIC STRENGTH

Dioxane (%)	Dielectric constant (D)	1/D	Mole fraction	рК
0	76.00	0.0131	_	3.90
10	67.00	0.0148	0.0125	4.30
20	62.00	0.0161	0.0500	4.65
40	47.00	0.0212	0.1230	5.20
50	43.50	0.0230	0.2000	5.55

Thermodynamic dissociation constant (pK) for the above system are listed in the Table-1. It is observed that pK values increased with increasing the percentage of dioxane in mixture which may be due to increase $d\pi$ -p π interaction.

Initially log K_1 and log K_2 values were obtained by pointwise calculations, since the difference (log K_1 -log K_2) was less than 1, their accurate values were calculated by the method of least squares. The maximum value at 0.1 M ionic strength indicated the 1:1 and 1:2 complex formations are possible. It could be seen from the Table-2 that the values of log k_1 and log K_2 increased with the increasing the percentage of organic solvent this may be due to higher polar nature of the solvent.

TABLE-2 METAL LIGAND STABILITY CAN OF CAPTOPRIL AT DIFFERENT PERCENTAGE OF DIOXANE WATER MIXTURE AT 0.01 M IONIC STRENGTH

Dioxane (%)	Dielectric constant (D)	1/D	log K ₁	log K ₂	$\log K_1 - \log K_2$
0	76.00	0.0131	0.39	0.09	0.30
10	67.00	0.0148	0.89	0.29	0.60
20	62.00	0.0161	1.10	0.35	0.75
40	47.00	0.0212	1.49	0.70	0.79
50	43.50	0.0230	1.84	1.10	0.74

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