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Determination of formation constants and themodynamic parameters of trifluoperazine-metal complexes by potentiometric method

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ABSTRACT

The complex formation constants of Trifluoperazine with Fe (III), Cd (II), Pb (II), Cu (II) and Zn (II) metal ions have been studied by potentiometric measurements. All titrations were performed in aqueous medium at constant ionic strength (0.10 mol·dm^{-3}). The complex formation constants were determined at 25.00 and 35.00 °C by different Computational Methods. The thermodynamic parameters (ΔG, ΔH and ΔS) and the thermodynamic stability constants for all of the investigated complexes were determined.

Keywords: Trifluoperazine, Metal complexes, Formation constant, Thermodynamic Parameters

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INTRODUCTION

Phenothiazines possessing the antipsychotic activity have a three-carbon chain between the nitrogen atoms of the middle ring and the side chain. Trifluoperazine is well known antipsychotic drug [1] of phenothiazine class. However, in recent years coordinating behavior of N-alkyl phenothiazines has gained much importance in the pharmaceuticals and chemical analysis [2, 3]. Literature survey reveals that few studies have been reported on phenothiazines-metal complexes. [4-6].

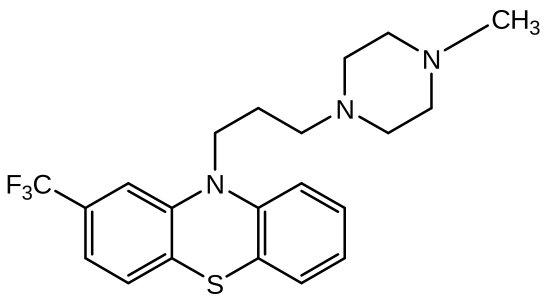

Figure 1: Structure of Trifluoperazine

The present paper deals with the determination of the formation constants of the binary complexes of Fe(III), Cd (II), Pb (II), Cu (II) and Zn (II) metal ions with Trifluoperazine by different Computational methods. The thermodynamic parameters (ΔG, ΔH and ΔS) and the thermodynamic stability constants were determined in aqueous medium at constant ionic strength (0.10 mol·dm^{-3}) and different temperatures 25.00 and 35.00 ^{0}C. The Irving and Rossotti pH-metric titration using Sarin and Munchi technique [7-10] was used to determine the dissociation constants as well as the formation constants for metal complexes.

MATERIALS AND METHODS

All chemicals were purchased from Aldrich and S.d. Fine Ltd, Mumbai (India), and were used without further purification. The solutions of reagents were prepared in double glass distilled water having pH about 6.98 to 7.00. The metal ion concentrations were determined by using sodium salts of ethylene diamine tetra acetic acid (EDTA). The molarity of KOH solution was determined by titrating with known weight of oxalic acid and also with potassium phthalate by using phenolphthalein indicator. In all the systems studied, the metal ion concentration was kept at 4x10 $^{-4}$ M (i.e. 2 ml of 0.01M in 50 ml total volume). Similarly, the ligand concentration was kept at 2x10 $^{-3}$ M in all titrations.

The pH measurements were made using a digital pH meter model L-120 with combined glass electrode (reading accuracy ± 0.001 pH units). The instrument was standardized at different regions of pH using standards buffer (BDH) solutions. The temperature of experimental solution was always maintained during the progress of the titration. The thermostat model Hakkin-1101 was used to maintain the temperature. The reaction mixture (50ml) was taken in cell having an outer thermostatic jacket for circulating water at a constant temperature. The activated combined glass electrode was dipped into the reaction mixture and pre-purified nitrogen gas was bubbled through it during the progress of pH titration. The reaction mixture was continuously stirred with the help of a magnetic stirrer (REMI 1 MLH) to maintain the homogeneity of the reaction mixture.

The following three set of solutions were titrated separately against standard carbonate free KOH solution.

1. Free acid titration (A): HNO_3 (2x10^{-2} M)
2. Free acid + ligand titration (A +L): A (2x10^{-2} M) + L (2x10^{-3} M)
3. Free acid + ligand + metal titration (A +L+M): A (2x10^{-2} M)+L(2x10^{-3} M)+ M(4x10^{-3} M).

RESULTS AND DISCUSSION

The proton-ligand stability constant and metal-ligand stability constants of Trifluoperazine and their complexes with Fe(III), Cd (II), Pb (II), Cu (II) and Zn (II) metal ions have been determined in aqueous medium at constant ionic strength (0.10 mol·dm^{-3}) and different temperatures 25.00 and 35.00 ^{0}C. The proton-ligand formation number nA was calculated by the Irving-Rossotti expression. The pK values of the ligands and formation constants of the complexes were calculated by the algebraic method, point wise calculation and also estimated from formation curves nA VS pH (half integral method) by noted the pH at which nA = 0.5. The pH metric titration curves at different temperature are shown in figure 1 and 2 respectively. The dissociation constant and stability constant of Trifluoperazine at different temperatures are summarized in Table 1 and 2.

The formation functions nA , n and pL can be computed from the following eqations:

$$\text{n A} = \gamma - \frac{(V_2 - V_1)(N + \varepsilon^0)}{(V_0 + V_1)T^0L} \qquad \textbf{(1)}$$

$$\text{n} = \frac{(V_3 - V_2)(N + \varepsilon^0)}{(V_0 + V_2)\text{nA } T^0M} \qquad \textbf{(2)}$$

$$\text{PL} = \log \left\{ 1 + \frac{\dfrac{[H^+]}{K_2} + \dfrac{[H^+]^2}{K_1K_2}}{\left(T^0L - T^0M\right)\bar{n}} \text{ X } \frac{\left(V_0 + V_3\right)}{V_0} \right\} \qquad \textbf{(3)}$$

Where,
Vo = Initial volume of the solution.
V_1, V_2 and V_3 = volume of alkali required for the (A), (A + L) **and (A + L + M)** titrations respectively for same pH value
T^0L = Initial concentration of ligand.
ε^0 = Initial concentration of acid (HNO3)
γ = Number of replaceable protons.

Table 1: Proton-ligand stability constants of the ligand (Trifluoperazine)

Temperatures (^{0}C)	pK_1	pK_2
25.00	4.119	8.408
35.00	4.024	8.293

Table 2: Metal ligand stability constant of M-(Trifluoperazine) at different temperature

System	**LogK**							
	25.00 (^{0}C)				35.00 (^{0}C)			
	Computational Methods				**Computational Methods**			
	a	**b**	**c**	**d**	**a**	**b**	**c**	**d**
Cd (II)-TFPZ	3.195	3.186	3.188	3.190	3.155	3.149	3.151	3.144
Pb (II))- TFPZ	3.309	3.316	3.311	3.308	3.228	3.229	3.230	3.233
Fe (III))- TFPZ	4.073	4.079	4.081	4.080	3.885	3.888	3.891	3.880
Cu (II))- TFPZ	3.753	3.759	3.761	3.766	3.465	3.458	3.461	3.466
Zn (II))- TFPZ	3.415	3.418	3.421	3.419	3.336	3.341	3.333	3.328

(a) Interpolation at half n values, (b) Least square method, (c) Linear plot method, (d) Point wise calculation method

It is seen from Table 1and Table 2 that stability constants gradually decreases with rise in temperature showing there by that lower temperature favours the formation of stable complexes.

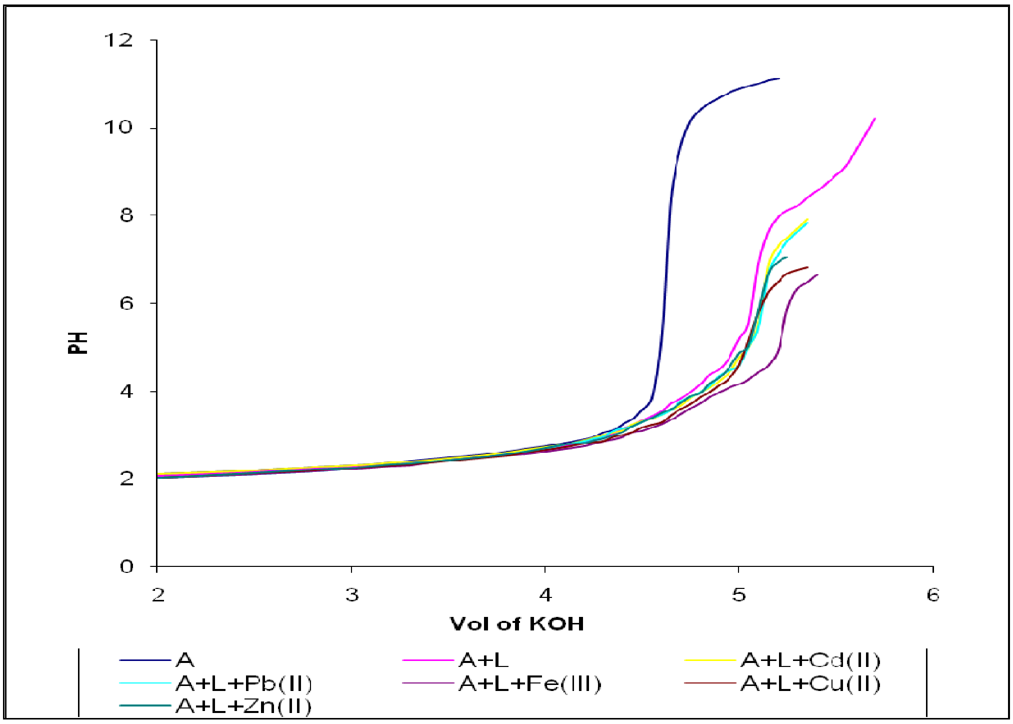

Figure 1: Plot of pH v/s volume of added KOH at 25.00^{0}C

The following thermodynamic parameters: $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined from following equations and are summarized in Table 3.

$$-\Delta G° = 2.303\, RT \log K \qquad \textbf{(4)}$$

Where, R = universal gas constant, T = absolute temperature and $\log K$ = stability constant of the complex.

$$\Delta H^0 = 2.303\ RT_1T_2 \left\{ \frac{(\log K_2 - \log K_1)}{T_2 - T_1} \right\} \qquad \textbf{(5)}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad \textbf{(6)}$$

Where, $\log K_1$ and $\log K_2$ are the respective stability constants of the complex at the absolute temperatures T and T_2 respectively.

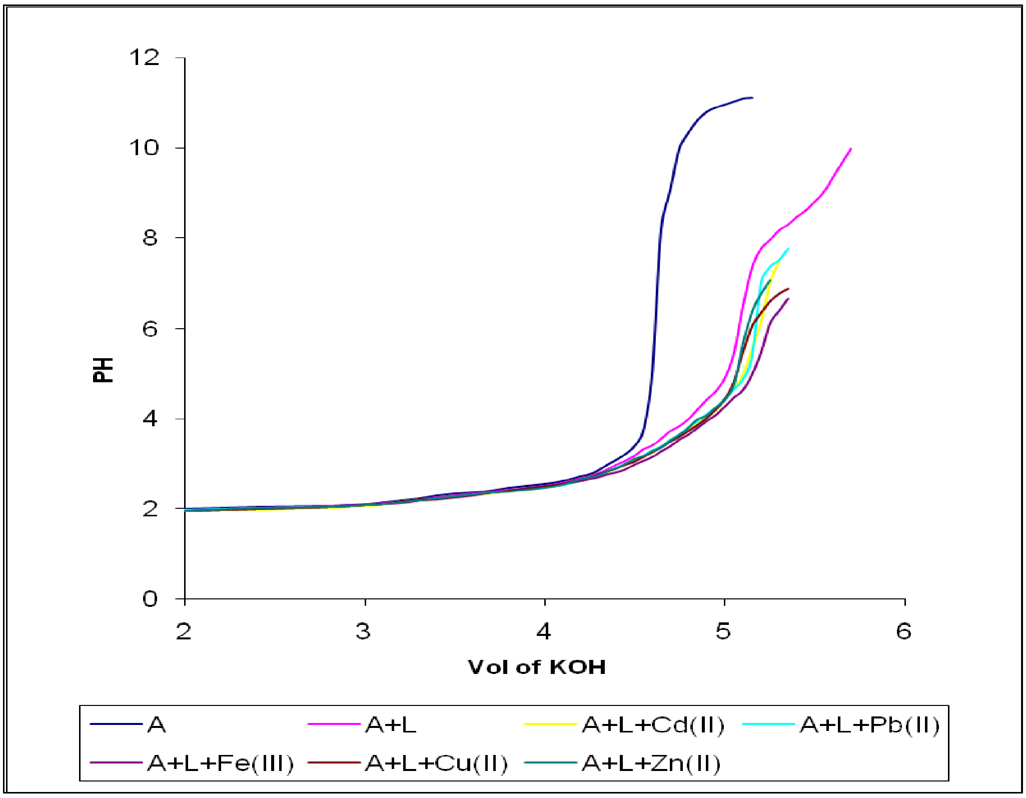

Figure 2: Plot of pH v/s volume of added KOH at 35.00^{0}C

Table 3. Thermodynamic activation parameters for the formation of 1:1 complex of Trifluperazine in aqueous media medium at 0.1 M ionic strength

Metal ions	-ΔG KJ/mol	-ΔH KJ/mol	-ΔS KJ/mol
Cd(II)	18.22	7.00	0.037
Pb(II)	18.87	14.17	0.015
Fe(III)	23.23	32.90	0.032
Cu(II)	21.41	50.40	0.097
Zn(II)	19.48	13.82	0.019

The negative value of (ΔH) indicate the exothermic nature of reaction process in fair agreement with increasing stability suggesting lower temperature favours the chelation process. The entropy values indicate that complexation is favoured by enthalpy and entropy factors.

CONCLUSION

The results obtained from the potentiometric measurements, the values of pKa were found to decrease with increasing temperature. The values of the thermodynamic functions ΔG, ΔH and ΔS were calculated. The values of stability constants reveal that the stability constants decrease with increasing temperature, along with the pKa value.

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