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Gibbs Free Energy and Activation Free Energy of Complexation of Some Divalent Cations with Ampicillin in Methanol at Different Temperatures

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Abstract: The Complexation reaction between Sodium (2S,5R,6R)-6-{[(2R)-2-amino-2-phenylacetyl]amino}-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate (Ampicillin sodium salt) ligand with Ca^{+2} and Ba^{+2} ions were studied condctometrically in methanol at four different temperatures (293.15K, 298.15K, 303.15K, 308.15K) On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of (1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants, thermodynamic parameters Gibbs free energies and Gibbs free energies of formation of different complexes in methanol were determined.

Keywords: Conductometric Studies, Formation Constant, Gibbs Free Energy, Activation Free Energy, Gibbs Free Energy, Ampicillin, Methanol

1. Introduction

Chemistry of drugs attracts many researchers because of its application in medicinal study. The stability of metal complexes with medicinal drugs plays a major role in the biological and chemical activity. Metal complexes are widely used in various fields, such as biological processes pharmaceuticals, separation techniques, analytical processes etc. [1] Complexes formed by salts of transition and representative elements with thioamides are mentioned in theliterature. [2] prediction of different chemical processes such as isolation, extraction, or preconcentration methods can be of significance in order to using stability constants. [3, 4] Thus, understanding the behavior of ligands and their interaction with metal ions in aqueous solution by the accurate determination of acidity and stability constants values are fundamental. In this paper we have selected antibacterial drug Ampicillin which is a beta-lactam antibiotic that is part of the amino penicillin family and is roughly equivalent to its successor, amoxicillin in terms of spectrum and level of activity [5]. Thermodynamic parameters of ampicillin were studied before [6]. This work was done to study the effect of different divalent cations on Complexation of ampicillin and also to determine free energies of activation of complexes and their thermodynamic paramateres.

2. Experimental

2.1. Materials and Methods

All manipulation was performed under aerobic conditions. The calcium chloride, barium chloride and ampicillin sodium salt were performed from Merck pure and used without any further purification.

2.2. Conductometric Titrations

The Conductometric titration of the $CaCl_2$ and $Bacl_2$ ($1x10^{-3}$) mole/L against AMP ($1x10^{-4}$) mole/L in methanol was performed with 0.5 ml interval additions from $CaCl_2$ or $BaCl_2$ solution. The specific conductance values were recorded using conductivity bridge HANNA, H1 8819Nwith a cell constant equal to 1 cm^{-1}. The conductometer was connected to the type Kottermann 4130 ultra-thermostat. The temperature was adjusted at (293.15K, 298.15K, 303.15K, and 308.15K).

3. Result and Discussion

The specific conductance values (K_s) of different concentrations of $CaCl_2$ and $BaCl_2$ in methanol were measured experimentally in the presence of ligand at (293.15K, 298.15K, 303.15K, 308.15K) The molar conductance (Λ_m) values were calculated [7] using equation(1):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \qquad (1)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} is the cell constant and C is the molar concentration of the $CaCl_2$ or $BaCl_2$ solution. The limiting molar conductance (Λ_m) at infinite dilutions were estimated for each cation in absolute methanol in the presence of the ligand by extrapolating the relation between Λ_m and $\sqrt{C_m}$ to zero concentration. By drawing the relation between molar conductance Λ_m) and the molar ratio of metal to ligand (M/L) concentrations (Fig. 1a-b), different lines are obtained with sharp breaks indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes. The experimental data of (Λ_m) and (Λ_o) were analyzed for the determination of formation constants for each type of the stoichiometric complexes.

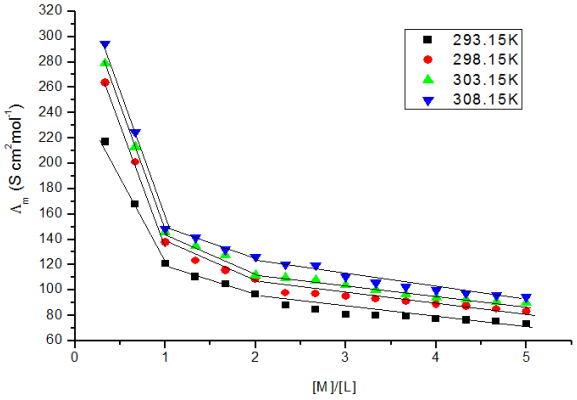

Fig. 1. *The relation between molar conductance (Λ_m) and the [M]/[L] molar ratio of $CaCl_2$ to ampicillin in methanol at different temperatures.*

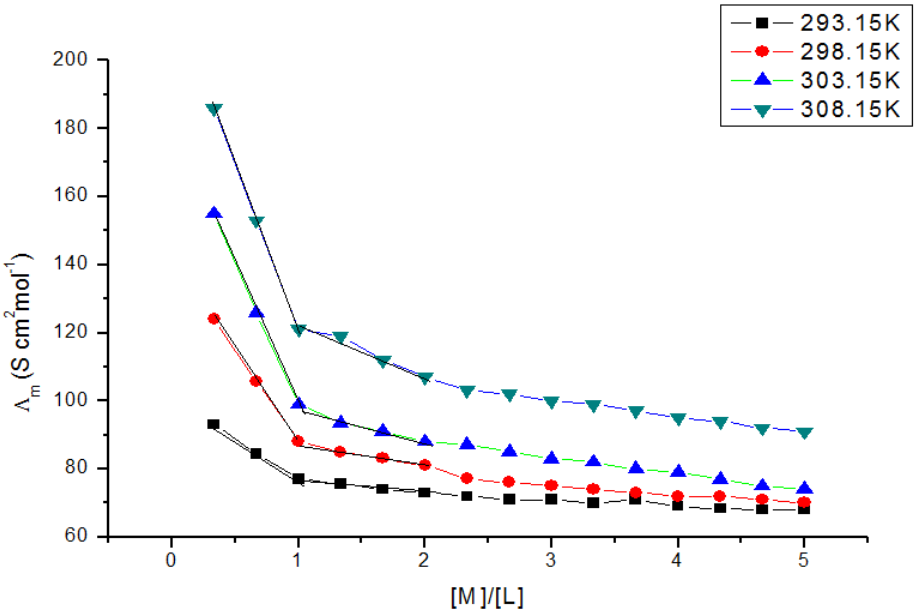

Fig. 2. *The relation between molar conductance (Λ_m) and the [M]/[L] molar ratio of $BaCl_2$ to ampicillin in methanol at different temperatures.*

The formation constants (K_f) for $CaCl_2$ and $BaCl_2$ complexes were calculated for each type of complexes (1:1) and (2:1) (M:L) [9, 10] by using equation(2):

$$K_f = \frac{[ML]}{[M][L]} = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (2)$$

Where Λ_m is the limiting molar conductance of the $CaCl_2$ or $BaCl_2$ alone, $\Lambda_{obs.}$ is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complex. The obtained values (Kf) for $CaCl_2$-ligand or $BaCl_2$-ligand stoichiometric complexes are presented in Tables (1 - 4)

The Gibbs of free energy change of association (ΔG_f) of different ratios of the metal ligand MeOH were calculated [8-13] from the formation constant (K_f) by using equation(3).

$$\Delta Gf = - 2.303\ RT \log Kf \quad (3)$$

Where R is the gas constant (8.341 J) and T is the absolute temperature.

Table 1. *Limiting molar conductance (Λo), formation constant (Kf), free energy change (ΔGf) for CaCl2 and ampicillin complex (1:1 M/L) formation in methanol at different temperatures.*

Temperature	Λ_o (S cm^2.mol^{-1})	$\Lambda_{obs.}$ (S cm^2.mol^{-1})	K_f	ΔG_f (kJ mol^{-1})
293.15 K	298.96	111.73	5.693E+05	-32.2987
298.15 K	338.41	124.04	5.891E+05	-32.9345
303.15 K	376.05	144.66	1.262E+06	-35.4064
308.15 K	379.71	152.25	4.835E+05	-33.5327

Table 2. *Limiting molar conductance (Λ_o), formation constant (K_f), free energy change (ΔG_f) for $CaCl_2$ and ampicillin complex (2:1 M/L) formation in methanol at difrrent temperatures.*

Temperature	Λ_o (S cm^2.mol^{-1})	$\Lambda_{obs.}$ (S cm^2.mol^{-1})	K_f	ΔG_f (kJ mol^{-1})
293.15 K	298.96	101.072	1.199E+05	-28.5021
298.15 K	338.41	108.53	1.554E+05	-29.6308
303.15 K	376.05	119.32	8.721E+04	-28.672
308.15 K	379.71	125.17	6.622E+04	-28.4397

Table 3. *Limiting molar conductance (Λ_o), formation constant (K_f), free energy change (ΔG_f) for $BaCl_2$ and ampicillin complex (1:1 M/L) formation in methanol at difrrent temperatures.*

Temperature	Λ_o (S cm^2.mol^{-1})	$\Lambda_{obs.}$ (S cm^2.mol^{-1})	K_f	ΔG_f (kJ mol^{-1})
293.15 K	136.21	77.74	3.06E+04	-25.1734
298.15 K	170.74	88.96	3.34E+04	-25.82
303.15 K	223.23	101.93	7.99E+04	-28.4508
308.15 K	276.25	121.38	1.20E+05	-29.9635

Table 4. *Limiting molar conductance (Λ_o), formation constant (K_f), free energy change (ΔG_f) for $BaCl_2$ and ampicillin complex (2:1 M/L) formation in methanol at different temperatures.*

Temperature	Λ_o (S cm^2.mol^{-1})	$\Lambda_{obs.}$ (S cm^2.mol^{-1})	K_f	ΔG_f (kJ mol^{-1})
293.15 K	136.21	72.82	2.39E+04	-24.5714
298.15 K	170.74	72.08	2.94E+04	-25.5031
303.15 K	223.23	87.39	3.50E+04	-26.374
308.15 K	276.25	106.49	5.31E+04	-27.8758

Previous tables shows that decreasing in Gibbs free energy of complexaion by increasing in temperatures indicating more spontaneous process also this values is case of (1:1 M/L) is smaller than in case of (2:1 M/L) for each salt used. also limiting molar conductance increases buy increasing temperatures also its values for (1:1 M/L) is higher than that in case of (2:1 M/L). the date shows that complex formation is more exothermic using barium salt than calcium. also (2:1) complex is more stable for using each cation.

The enthalpy (ΔH_f) for the metal salt complexes were calculated for each type of complexes, (1:1) and (2:1) (M/L) by using van 't Hoff equation (4):

$$\frac{dlnK}{dT} = \frac{\Delta H_A^o}{RT^2} \quad (4)$$

Where *R* is the gas constant (8.341 J) and T is the absolute temperature. By drawing the relation between log K_f and 1/T, different lines are obtained for the formation of 1:1 and 2:1 (M/L) stoichiometric complexes for, $BaCl_2$ and $CaCl_2$ with ampicillin.

From the relation between log K and 1/T, ΔH_f can be calculated for each type of complexes from the slope of each line ($-\Delta H_f/2.303R$). The entropy (ΔS_f) for complexes were calculated for each type of complexes (1:1) and (2:1) (M/L) tables (5-6)by using equation (5):

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (5)$$

Where (S) is the entropy of system.

Table 5. *Enthalpy of association (ΔH_a), ($T\Delta S_a$) and entropies (ΔS_a) for $CaCl_2$ in presence of ampicillin in MeOH solvent at different temperatures.*

Temperature	ΔH_a kJ.mol^{-1}	$T\Delta S_a$ kJ.mol^{-1}	ΔS_a kJ.mol^{-1}
293.15K	20.423	37.887	0.1292
298.15K	20.423	36.176	0.1213
303.15K	20.423	38.589	0.1272
308.15K	20.423	38.685	0.1255

Table 6. *Enthalpy of association (ΔH_a), ($T\Delta S_a$) and entropies (ΔS_a) for $BaCl_2$ in presence of ampicillin in MeOH solvent at different temperatures.*

Temperature	ΔH_a kJ.mol^{-1}	$T\Delta S_a$ kJ.mol^{-1}	ΔS_a kJ.mol^{-1}
293.15K	10.211	29.329	0.1000
298.15K	10.211	29.150	0.0977
303.15K	10.211	29.604	0.0976
308.15K	10.211	29.757	0.0965

The tables show that complex formation is favored at lower temperatures.

Since the conductance of an ion depends mainly on its mobility, it is quite reasonable to treat the conductance data similar to the one that employed for the rate process taking place with the change of temperature on the basis of equation (6).

$$\Lambda_0 = A\, e^{-Ea/RT} \quad (6)$$

Where A is the frequency factor, (R) is the gas constant and (E_a) is the Arrhenius activation energy of transport process. Therefore, on plotting of log (Λ_o) versus 1/T straight lines are obtained from their slopes the (E_a) values are evaluated and also their thermodynamic parameters represented in Tables (7-8).

Table 7. *Activation energy (E_a), Gibbs free energy change (ΔG*) and entropy change (ΔS*) of activation for $CaCl_2$ and ampicillin complex (1:1 M/L) formation in methanol at different temperatures.*

Temperature	E_a (kJ mol^{-1})	ΔG* (kJ mol^{-1})	TΔS* (kJ mol^{-1})	ΔS* (kJ mol^{-1}K^{-1})
293.15 K	16.3859	-13.8931	30.2790	0.1053
298.15 K	16.3859	-14.4373	30.8232	0.1034
303.15 K	16.3859	-14.9452	31.3311	0.1034
308.15 K	16.3859	-15.2165	31.6024	0.1026

Table 8. *Activation energy (E_a), Gibbs free energy change (ΔG*) and entropy change (ΔS*) of activation for $BaCl_2$ and ampicillin complex (1:1 M/L) formation in methanol at different temperatures.*

Temperature	E_a (kJ mol^{-1})	ΔG* (kJ mol^{-1})	TΔS* (kJ mol^{-1})	ΔS* (kJ mol^{-1}K^{-1})
293.15 K	34.7249	-11.9771	46.7020	0.1593
298.15 K	34.7249	-12.7415	47.4664	0.1592
303.15 K	34.7249	-13.6308	48.3557	0.1595
308.15 K	34.7249	-14.4016	49.1264	0.1594

A perusal of Tables shows that the value of E_a (+ve). This indicates higher mobility of ions in solutions and hence Λ_o increases with increasing temperatures. activation free energy is more in case of using barium salt.

4. Conclusion

We study the complexation reaction between Ampicillin sodium salt with Ca^{+2} and Ba^{+2} ions condctometrically in methanol at four different temperatures (293.15K, 298.15K, 303.15K, 308.15K) data obtained indicates the formation of 1:1 and 2:1 (M/L) stoichiometric complexes. Negative values of gibbs free energy f complexation indicates that the reaction is spontaneous. It's shown that formation constant increases by increasing temperatures and decreasing in Gibbs free energy of complexaion by increasing in temperatures indicating more spontaneous process also this values is case of (1:1 M/L) is smaller than in case of (2:1 M/L) for each salt used. also limiting molar conductance increases buy increasing temperatures also its values for (1:1 M/L) is higher than that in case of (2:1 M/L). Values of E_a (+ve). This indicates higher mobility of ions in solutions and hence Λ_o increases with increasing temperatures.

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