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STUDY OF ELECTRICAL PROPERTIES AND SOLVENT BEHAVIOUR OF 6-(4-CHLOROPHENYL)-1, 2, 3, 4-TETRAHYDRO-4-OXO-2-THIOXOPYRIMIDINE-5-CARBONITRILE AT DIFFERENT TEMPERATURES

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ABSTRACT
Conductance has been measured in 60% DMSO-water mixture at various concentration in the temperature range 298-313K. The limiting molar conductance (λ^0_m), degree of dissociation (α), dissociation constant (K_d), Walden constant, energy of activation and thermodynamic parameters are evaluated. The results obtained have been interpreted in terms of molecular interactions and solvent properties.
Keywords: Conductivity, 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-4-oxo-2-thioxopyrimidine-5-carbonitrile, Walden Product, Molar Conductivity, Energy of Activation, Thermodynamic Parameters

INTRODUCTION
Physicochemical analysis has provided information about the structure and interactions present in various liquids of different systems.[1] Different properties present in mixture of solvents differ from that of water. Dimethyl sulphoxide is polar aprotic solvent having intramolecular hydrogen bonding in pure state. Presence of trace amount of water changes the solvent structure due to change in hydrogen bonding configuration. On the other hand interactions such as solute- solute and solute–solvent interaction has been of prime importance in different branches such as biochemistry, geochemistry, physical chemistry, surface chemistry, environmental chemistry etc.[2]

Dihydropyrimidine carbonitriles has significant contribution in many biological processes and biological activities.[3-5] The conductometric method plays important role to study interaction with solvent.[6-8] Such analysis is simple, accurate and reliable to study solvent effects, solvent interaction, and structure modification of solvent. Molar conductance variation with temperature at different concentration provides information about solvent viscosity, mobility, hydrogen bonding ability, interaction with solvent. Different molecular associations present in liquid system with respect to variation with concentration and temperature can be studied from thermodynamic data.[9-16]

EXPERIMENTAL
The compound under study was synthesized and purified by recrystallization technique in laboratory[17]. The compound was dissolved in analytical grade (AR) dimethyl sulphoxide of minimum assay of 99.9%. Different solutions required for measurement were prepared from stock solution by dissolving calculated amount of compound. Electrical Conductivities of various concentrations (0.002- 0.010 mol L^{-1}) were measured by digital direct reading conductivity meter (EQ667, EQUIPTRONICS) having range 0.01µS to 200 mS connected with an electrode PVC sleeved (EQ-708A) having cell constant 1.01 cm^{-1}using digital thermostat for obtaining desired temperature (298-313 K) . The flow time was recorded by using digital stop watch.

RESULTS AND DISCUSSION
The molar conductance was calculated from specific conductance data at different temperature as shown in Table-1 by applying relation (1).

$$\lambda_m = \frac{1000XL}{C} \qquad (1)$$

Where, L is the specific conductivities of solution, C is the concentration and λ_m is the molar conductance.

Table-1: Molar Conductance (λ_m) at Different Temperatures.

Conc. (mol L^{-1})	Molar Conductance (S.cm^2/mol) at Temperature (K)			
	298	303	308	313
0.002	24.03	27.42	31.16	34.90
0.004	20.50	22.75	25.05	27.42
0.006	19.27	21.14	23.01	24.88
0.008	17.98	19.44	21.06	22.84
0.010	17.19	18.42	19.86	21.61

From the above table it is clear that values of molar conductance (λ_m) increases with temperature due to high molecular mobility raised from thermal energy, vibrational, rotational and translational energy while decreases with increase in concentration. Also due to increase in concentration number of solute increases decreasing the velocity restricting the movement of solute molecules. While with dilution the values of molar conductance is high shows freedom in the mobility within solution.

The value of limiting molar conductance or molar conductance at infinite dilution (λ^0_m) depends on binary solvent mixtures.

Molar conductance of an electrolyte solution increases with dilution and approaches a limiting value at infinite dilution. It is given by following equation:

$$\lambda_m = \lambda^0_m - (A + B\lambda^0_m) \sqrt{C} \qquad (2)$$

Where, λ^0_m is the molar conductance at infinite dilution, and 'A' and 'B' are the constant and depends on type of solution. The values of molar conductance at infinite dilution or limiting molar conductance (λ^0_m) have been evaluated from intercept of linear plot of λ_m verses $\sqrt{C}$ as shown in fig-1 and the results are tabulated in Table-2. It is clear that molar conductance at infinite dilution decreases with increase in concentration due to low dielectric constant of the medium resulting in decrease in solute-solvent interactions.

Table-2: Limiting Molar Conductance (λ^0_m) at Different Temperatures

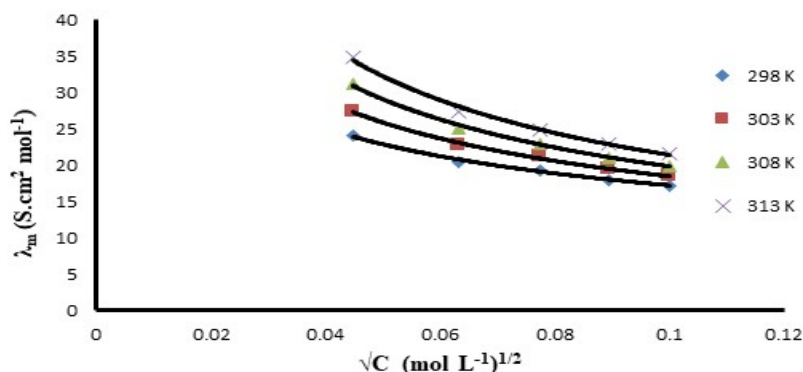| Temperature (K)	Molar Conductance at Infinite Dilution (λ^0_m) (S.cm^2/mol)	Walden Product
298	28.86	97.275
303	33.77	113.823
308	38.97	131.352
313	43.91	148.002

Fig.-1: Plot of λ_m Verses $\sqrt{C}$ at Different Temperature

The decreased in limiting molar conductance indicates that at infinite solution there is neither relaxation nor the electrophoretic effects are effective.

Walden product is useful to understand the interaction between solute and solvent. The variations seen in Walden product give an idea about total solvation. Walden product is given by:

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$\lambda^0_m \eta^0 =$ Walden Product   (3)

Where, η^0 is the viscosity of solvent. The values of Walden product is tabulated in Table-2. It is clearly seen that its value increases with temperature. Thus decrease in conductance is more prominent when the viscosity of solvent increases. The increased value of Walden product indicates weak solvation.

The values of the degree of dissociation (α) and dissociation constant (K_d) is tabulated in Table-3 by applying equation:

$$\alpha = \lambda_m / \lambda^0_m \qquad (4)$$

$$K_d = \left[\frac{\alpha 2}{1-\alpha}\right] C \qquad (5)$$

Where, λ_m is molar conductance, λ^0_m is molar conductance at infinite dilution and C is the concentration (mol L^{-1})

Table-3: Degree of Dissociation (α) and Dissociation Constant (Kd) at Different Concentration

Concentration (mol L^{-1})	Degree of Dissociation (α) and Dissociation Constant (K_d) at Different Temperature (K)							
	298		303		308		313	
	α	K_d x 10^{-3}	α	K_d x 10^{-3}	α	K_d x 10^{-3}	α	K_d x 10^{-3}
0.002	0.83	8.105	0.81	6.906	0.80	6.400	0.79	5.944
0.004	0.71	6.953	0.67	5.441	0.64	4.555	0.62	4.046
0.006	0.67	8.162	0.63	6.436	0.59	5.094	0.57	4.533
0.008	0.62	8.093	0.58	6.408	0.54	5.071	0.52	4.507
0.010	0.60	9.000	0.55	6.722	0.51	5.308	0.49	4.708

The results obtained from Table -3 shows variation in values of K_d due to solvation by solvent molecule. The value of dissociation constant (K_d) with increase in concentration and decreases with temperature indicates endothermic nature of dissociation process.

The effect of temperature on molar conductivity was shown by Arrhenius relation:

$$\log \lambda^0_m = \log A - \frac{E_a}{2.303 \, R.T} \qquad (6)$$

Where, R is the molar gas constant, E_a is the energy of activation which determines the rate of movement of molecule, A is the frequency factor and T is the absolute temperature. The energy of activation was calculated by the plot of $\log \lambda^0_m$ against 1/T as shown in Fig-2. The result obtained is tabular in Table- 4, shows that the value of energy of activation increases with concentration.
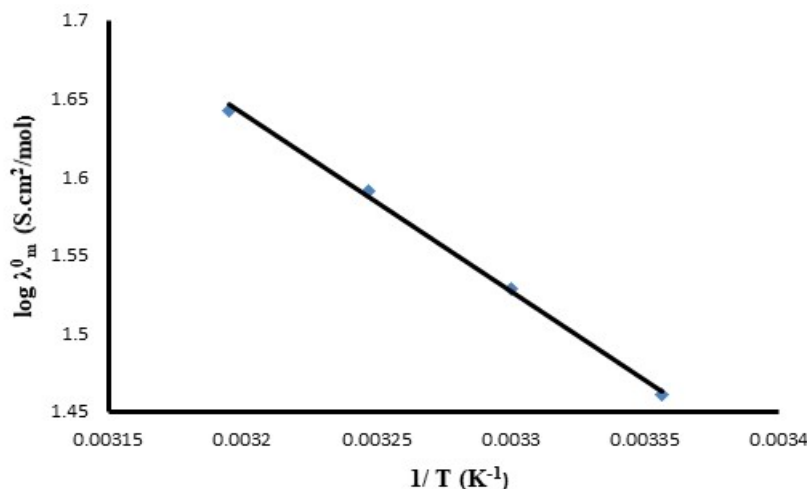

Fig.-2: Plot between log limiting Molar Conductance (λ^0_m) Versus 1/T

Table-4: Energy of Activation and Frequency Factor

Temperature (K)	1/ T	Energy of Activation (E_a) KJ mole^{-1}	Frequency Factor (A)
298	3.356×10^{-3}		
303	3.3003×10^{-3}	21.738	1.875×10^5
308	3.2468×10^{-3}		
313	3.1949×10^{-3}		

Free energy change of activation (ΔG) refers to the maximum amount of energy available to do work. It can be calculated from following relation:

$$\Delta G^* = 2.303 \ RT \log K_d \qquad (7)$$

The enthalpy change of activation ΔH^* was calculated by equation:

$$\Delta H^* = E_a^* - R.T \qquad (8)$$

The entropy change (ΔS^*) which measure the randomness or disorder of a system is significantly connected with solvent structure is calculated by the relation:

$$\Delta S^* = \Delta H^* - \Delta G^*/ T \qquad (9)$$

Table-5 to Table-9 shows the values of thermodynamic parameters such as free energy change of activation (ΔG^*), enthalpy change of activation (ΔH^*) and entropy change of activation (ΔS^*) for different concentration at different temperature. The negative value of ΔG^*, ΔH^* and ΔS^* indicates the spontaneity of reaction and increases with concentration and temperature.

Table-5: Thermodynamic Parameters for 0.002 (mol L^{-1}) at Different Temperatures

Temperature (K)	ΔG^* (KJ mole^{-1})	ΔH^* (KJ mole^{-1})	ΔS^* (KJ mole^{-1})
298	- 11.932	-19.260	-0.02459
303	-12.536	-19.218	-0.02205
308	-12.938	-19.177	-0.02025
313	-13.340	-19.136	-0.01852

Table-6: Thermodynamic Parameters for 0.004 (mol L^{-1}) at Different Temperatures

Temperature (K)	ΔG^* (KJ mole^{-1})	ΔH^* (KJ mole^{-1})	ΔS^* (KJ mole^{-1})
298	-12.312	-19.260	-0.02332
303	-13.137	-19.218	-0.02006
308	-13.809	-19.177	-0.01743
313	-14.341	-19.136	-0.01532

Table-7: Thermodynamic Parameters for 0.006 (mol L^{-1}) at Different Temperatures

Temperature (K)	ΔG^* (KJ mole^{-1})	ΔH^* (KJ mole^{-1})	ΔS^* (KJ mole^{-1})
298	-11.915	-19.260	-0.02465
303	-12.713	-19.218	-0.02147
308	-13.522	-19.177	-0.01836
313	-14.045	-19.136	-0.01627

Table-8: Thermodynamic Parameters for 0.008 (mol L^{-1}) at Different Temperatures

Temperature (K)	ΔG^* (KJ mole^{-1})	ΔH^* (KJ mole^{-1})	ΔS^* (KJ mole^{-1})
298	-11.936	-19.260	-0.02458
303	-12.724	-19.218	-0.02143
308	-13.534	-19.177	-0.01832
313	-14.060	-19.136	-0.01622

Table-9: Thermodynamic Parameters for 0.010 (mol L^{-1}) at Different Temperatures

Temperature (K)	ΔG^* (KJ mole^{-1})	ΔH^* (KJ mole^{-1})	ΔS^* (KJ mole^{-1})
298	-11.672	-19.260	-0.02546
303	-12.604	-19.218	-0.02183
308	-13.417	-19.177	-0.01870
313	-13.947	-19.136	-0.01658

CONCLUSION

It was concluded that molar conductance increases with temperature and decreases with concentration due to increase in mobility. Increased value of Walden constant with increased concentration shows strong interaction with solvent molecule and strong hydrogen bonding between the solvent molecules. Due to strong interaction degree of dissociation decreases. Thermodynamic parameter also confirms the spontaneity of reaction and strong molecular interaction between the molecules and solvent.

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