

FULL PAPER

Conductance and solvent behaviour of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxypyrimidine-5-carbonitrile in 60% DMSO at different temperatures

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Conductance of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2,4-dioxypyrimidine-5-carbonitrile has been measured in 60% dimethyl sulphoxide-water mixture at different concentrations from 298 to 313 K. Limiting molar conductance (λ^0_m), degree of dissociation (α), dissociation constant (K_d), Walden constant, energy of activation and thermodynamic parameters were calculated. The results obtained are useful for determining the interactions and solvent properties.

KEYWORDS

Conductivity; 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxypyrimidine-5-carbonitrile; walden product; molar conductivity; energy of activation; thermodynamic parameters.

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Introduction

Physicochemical analysis provides various information for the structure and interactions of liquids in binary and ternary systems [1]. These properties differ from water. Dimethyl sulphoxide is polar aprotic solvent possessing hydrogen bonding. Due to presence of trace amount of water, the solvent structure changes for change in the hydrogen bonding configuration. Interactions like solute-solvent, solute-solute and solvent-solvent plays an important role in various fields of chemistry [2].

Dihydropyrimidine carbonitriles are of paramount importance owing to biological significance and biological activities [3-5]. The conductometric method plays an important role in studying 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 concentrations

provides information about solvent viscosity, mobility, hydrogen bonding ability, interaction with solvent. Molecular associations present in liquid system and its variation with respect to concentration and temperature can be studied by thermodynamic data [9-16].

Material and methods

The compounds under study were prepared and refined by recrystallization [17]. Solutions in various concentrations (0.002 to 0.010 mol L⁻¹) were prepared using dilution method from stock solution in 60% dimethyl sulphoxide solution. To measure density, calibration of pycnometer was done by using triple distilled water and measuring the densities of different solvents. The data obtained was compared with reported literature. The viscosities of test solutions were measured by using Ubbelohde viscometer at different temperatures. Thermally controlled water bath was used

and desired temperature was maintained by circulating water throughout. Digital stop watch was used to measure flow time. Digital direct reading conductivity meter (EQ 667, EQUIPTRONICS) (0.01 μ S to 200 mS) connected with an electrode PVC sleeved (EQ-708A) having cell constant 1.01 cm⁻¹ was used to measure specific conductivities of the solutions.

Results and discussion

TABLE 1. Molar conductance's (λ_m) values at different concentrations for various temperatures

Conc. (mol L ⁻¹)	λ_m (S.cm ² /mol)			
	298 K	303 K	308K	313K
0.002	4.66	5.31	6.02	6.81
0.004	2.64	3.33	4.02	4.52
0.006	1.95	2.65	3.35	3.72
0.008	2.10	2.58	3.00	3.39
0.010	2.16	2.50	2.79	3.17

Molar conductance's (λ_m) increases with temperature showing elevated molecular movement due to different energies like thermal, vibrational, rotational and translational energy and decreases with the increase in concentration. This shows that increase in number of solute molecules decreases the velocity possibly due to hindered mobility while with dilution the values of molar conductance is high which shows freedom in the mobility within the solution. Limiting molar conductance (λ_m^0) values depends on different solvent mixtures. Molar conductance values increases with dilution and reaches to limiting value at infinite dilution.

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

Where, λ_m^0 = molar conductance at infinite dilution, 'A' and 'B' are the constant depending on solution. Limiting molar conductance (λ_m^0) is evaluated from intercept of linear plot of λ_m verses \sqrt{C} as shown in Table 2. The plot of λ_m verses \sqrt{C} are shown in Figure 1. The result obtained in Table 2 shows that λ_m^0 decreases with increase in concentration due to low dielectric constant

Conductivities of test solution of different concentrations ranging from 0.002 to 0.010 (mol L⁻¹) in 60% dimethyl sulphoxide solution at different temperature (298-313 K) with a difference of 5K were measured. The molar conductance is calculated as

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

Where, L = specific conductance's of solution

C = concentration

λ_m = molar conductance.

of the medium which decreases the solute-solvent interactions.

Decreased value in limiting molar conductance indicates that at infinite solution there is neither relaxation nor the electrophoretic effects.

Walden product is helpful to know interaction between solute and solvent highlighting the total solvation changes. It is given as product of λ_m^0 and viscosity of solvent as

$$\text{Walden Product} = \lambda_m^0 \eta^0 \quad (3)$$

Where, η^0 = viscosity of solvent. Walden product values are tabulated in Table 2 which increases with temperature. Therefore, decrease in conductance is more as viscosity of solvent increases. An increased value of Walden product indicates weak solvation.

The values of " α " and " K_d " are calculated by applying equations as

$$\alpha = \lambda_m / \lambda_m^0 \quad (4)$$

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

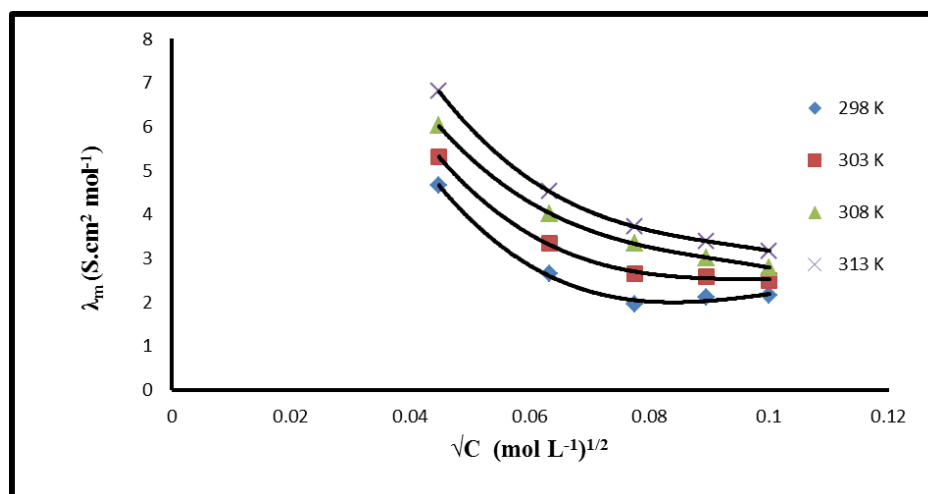
Where, λ_m = molar conductance

λ_m^0 = molar conductance at infinite dilutions

C = concentrations

TABLE 2. Limiting molar conductance (λ^0_m) and Walden product at various temperatures

Temperature (K)	λ^0_m (S.cm ² /mol)	Walden product
298	5.97	20.122
303	6.96	20.818
308	8.10	20.927
313	9.13	21.396

**FIGURE 1.** Plot of λ_m versus \sqrt{C} at various temperatures**TABLE 3.** 'α' and 'K_d' values for different concentrations at various temperatures

Concentration (mol L ⁻¹)	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	0.78	5.531	0.76	4.813	0.74	4.212	0.75	4.500
0.004	0.44	1.383	0.48	1.772	0.49	1.883	0.50	2.000
0.006	0.32	0.904	0.38	1.397	0.41	1.709	0.41	1.709
0.008	0.35	0.151	0.37	1.738	0.37	1.738	0.37	1.738
0.010	0.36	0.203	0.36	2.025	0.34	1.752	0.35	1.885

The results obtained from Table 3 shows variation in values of K_d due to solvation by solvent molecule. K_d values increase with concentration and decrease with temperature indicating endothermic nature of dissociation process.

Arrhenius relation shows effect of temperature on molar conductivity as

$$\log \lambda^0_m = \log A - \frac{E_a}{2.303 RT} \quad (6)$$

Where, R = molar gas constant

E_a = energy of activation

A = frequency factor

T = temperature in Kelvin.

The energy of activation can be evaluated from plot of $\log \lambda^0_m$ Vs $1/T$. The values are tabularized in Table 4, showing increase in energy of activation with concentration.

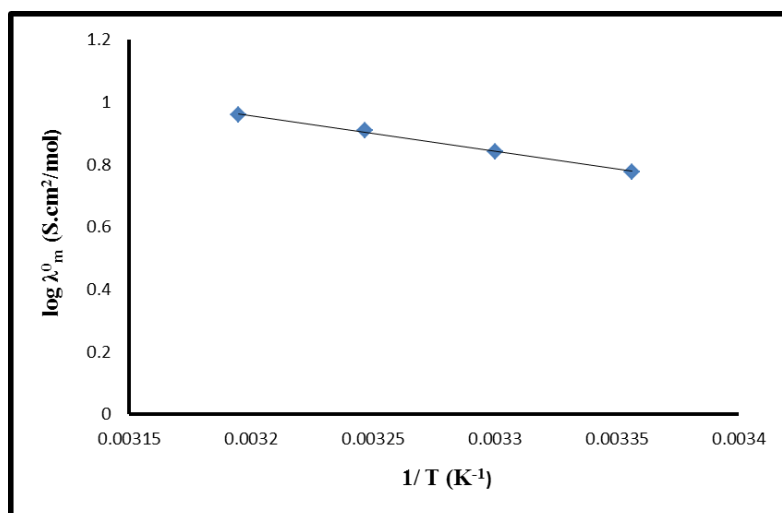


FIGURE 2. Limiting molar conductance (λ_m^0) versus $1/T$ at various temperatures

TABLE 4. “ E_a ” and “ A ” values at various temperatures

Temperature (K)	1/T	E_a (KJ mole ⁻¹)	A
298	3.356×10^{-3}	22.105	4.4895×10^4
303	3.3003×10^{-3}		
308	3.2468×10^{-3}		
313	3.1949×10^{-3}		

Free energy change of activation (ΔG) is defined as maximum amount of energy available to do work. It can be calculated from following relation

$$\Delta G^*(\text{in KJ mole}^{-1}) = 2.303 T \log K_d \quad (7)$$

Enthalpy change of activation ΔH^* can be evaluated by equation

$$\Delta H^*(\text{in KJ mole}^{-1}) = E_a^* - R \cdot T \quad (8)$$

Change (ΔS^*) measures the disorder in system which relates the solvent structure. It is determined from relation

$$\Delta S^*(\text{in KJ mole}^{-1}) = \Delta H^* - \Delta G^* / T \quad (9)$$

Tables 5-9 shows the values of ΔG^* , ΔH^* and ΔS^* for different concentrations at different temperature. The negative value of thermodynamic parameters shows spontaneity of reaction and increases with concentrations and temperature.

TABLE 5. Thermodynamic parameters for 0.002 (mol L⁻¹) at various temperatures

Temperature	ΔG^*	ΔH^*	ΔS^*
298	-12.879	-19.627	-0.02264
303	-13.446	-19.586	-0.02026
308	-14.009	-19.544	-0.01797
313	-14.064	-19.503	-0.01738

TABLE 6. Thermodynamic parameters for 0.004 (mol L⁻¹) at various temperatures

Temperature	ΔG^*	ΔH^*	ΔS^*
298	-12.312	-19.627	-0.02455
303	-13.137	-19.586	-0.02128
308	-13.809	-19.544	-0.01862
313	-14.341	-19.503	-0.01649

TABLE 7. Thermodynamic parameters for 0.006 (mol L⁻¹) at various temperatures

Temperature	ΔG^*	ΔH^*	ΔS^*
298	-17.037	-19.627	-0.000869
303	-16.562	-19.586	-0.009980
308	-16.319	-19.544	-0.010471
313	-16.584	-19.503	-0.009326

TABLE 8. Thermodynamic parameters for 0.008 (mol L⁻¹) at various temperatures

Temperature	ΔG^*	ΔH^*	ΔS^*
298	-21.80	-19.627	-0.007291
303	-16.012	-19.586	-0.011795
308	-16.276	-19.544	-0.010610
313	-16.540	-19.503	-0.009467

TABLE 9. Thermodynamic parameters for 0.010 (mol L⁻¹) at various temperatures

Temperature	ΔG^*	ΔH^*	ΔS^*
298	-21.069	-19.627	-0.004839
303	-15.627	-19.586	-0.013066
308	-16.256	-19.544	-0.010675
313	-16.329	-19.503	-0.010141

Conclusion

It is seen that molar conductance of compound increases with temperature and decreases with concentration due to increase in mobility. Increased values of Walden constant with increased concentration shows strong interaction with solvent molecule and strong hydrogen bonding between the solvent molecules. Due to strong interactions, the 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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