



Thermodynamics Studies for 6-(4-chlorophenyl)-1,2,3,4-tetrahydro-4-oxo-2-thioxopyrimidine-5-carbonitrile in 60% Dimethyl Sulphoxide at Different Temperatures

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ABSTRACT

Viscometric studies for ternary mixture of 6-(4-chlorophenyl)-1,2,3,4-tetrahydro-4-oxo-2-thioxopyrimidine-5-carbonitrile in 60% dimethyl sulphoxide was carried out at different temperatures ranging between 298 and 313 K over different concentration. From viscometric data ΔG , ΔS and ΔH were evaluated. The result shows that the magnitude of ΔG and ΔH are negative while ΔS is positive showing spontaneity of reaction according to thermodynamics pointing structure breaking takes place between solute and solvent. As ΔH is negative and ΔS positive, the reaction is spontaneous at low temperatures (decreasing the magnitude of the entropy term). The thermodynamic study reveals that as concentration increases spontaneity of reaction decreases.

Keywords: Viscosity, 6-(4-chlorophenyl)-1,2,3,4-tetrahydro-4-oxo-2-thioxopyrimidine-5-carbonitrile, ΔG , ΔS , ΔH , Spontaneity, Molecular association.

INTRODUCTION

Heterocyclic compounds possessing cyclic pyrimidine ring have attracted significant importance due to many biological activities¹⁻³. On other hand, density and viscosity studies of solution plays important role in solution chemistry. By evaluating parameters like apparent molar volume, Jones Dole coefficients 'A' and 'B' different interactions such as solute-solute, solute-solvent and solvent-solvent interaction present within the solution can be studied. Such interaction provides helpful information to understand nature of solute, solvent, dielectric properties and polarity⁴⁻⁶.

Thermodynamic properties plays vital role in understanding spontaneity of reaction. By measuring viscosity of solute in aqueous solution, parameters such as Gibbs free energy, entropy and enthalpy change at different temperatures can be studied⁷⁻⁹.

Therefore in our present work we have systematically studied viscometric measurement for different concentrations at temperatures range from 298 to 313 K. From these data different thermodynamic parameters are determined which gives important information about structure making or structure breaking in the solution. We have also



studies the relationship between concentration of solution with the spontaneity for the reaction of ternary mixture.

MATERIAL AND METHODS

The compounds under study was synthesized, purified by recrystallization technique and characterized by IR and ^1H NMR spectroscopy¹⁰. Different concentration of solutions ranging from 0.002 to 0.010 mol L⁻¹ in 60% dimethyl sulphoxide was prepared using triple distilled deionized water at room temperature. The calibration of pycnometer used to determine density was done by measuring the densities of different solvents like distilled water, acetone, toluene and carbon tetrachloride. The data obtained was compared with reported literature. The viscosity of test solutions were measured by using Ubbelohde viscometer at temperatures ranging from 298 to 313 K. Thermally controlled water bath was used and desired temperature was maintained by circulating water throughout. Digital stop watch was used to measure flow time.

Theory

Coefficient of viscosity of liquid and temperature are correlated by following equation

$$\eta_r = A \cdot e^{-\Delta G/RT} \quad (1)$$

The thermodynamic parameters are evaluated from following equations

$$\Delta G = -2.303R \times \text{slope} \quad (2)$$

$$\log \eta_{r2}/\eta_{r1} = [\Delta H/2.303 R] [T_2 - T_1/T_1 T_2] \quad (3)$$

$$\Delta S = ([\Delta H - \Delta G] / T) \quad (4)$$

RESULT AND DISCUSSION

From viscometric studies it is observed that rise in temperature decreases and viscosity of the solution. The values of viscosity of solution at various temperatures with concentration are represented in Table 1 and 2. Gibb's free energy are determined from the slope of graph by plotting $\log \eta$ Vs $1/T$ as shown in Fig. 1. It is found that compound possess negative value of Gibb's free energy. The values of change in enthalpy in reaction were determined by using equation (3). The system showed negative values indicating the reaction is highly exothermic and spontaneous in nature. The value of change in entropy were determined from equation (4). The value of entropy change is positive which shows spontaneity in the reaction achieved by molecule flipping over each other and destruction of hydrogen bonding of compounds.

Table 1: Relative viscosity for different concentrations at various temperatures

Temp. K	1/T x 10 ⁻³	0.002 mol L ⁻¹		0.004 mol L ⁻¹		0.006 mol L ⁻¹		0.008 mol L ⁻¹		0.010 mol L ⁻¹	
		η_r	$\log \eta_r$	η_r	$\log \eta_r$	η_r	$\log \eta_r$	η_r	$\log \eta_r$	η_r	$\log \eta_r$
298	3.3560	1.1001	0.04143	1.1018	0.04210	1.1039	0.04293	1.1053	0.04348	1.1073	0.04427
303	3.3003	1.0321	0.01372	1.0342	0.01460	1.0362	0.01544	1.0380	0.01620	1.0401	0.01708
308	3.2468	1.0290	0.01242	1.0325	0.01389	1.0360	0.01536	1.0367	0.01565	1.0375	0.01599
313	3.1949	1.0257	0.01102	1.0284	0.01216	1.0315	0.01347	1.0342	0.01461	1.0371	0.01582

Table 2: Values of thermodynamic parameters at different concentrations

Conc. (mol L ⁻¹)	ΔG (J mol ⁻¹ K ⁻¹)	ΔH (J mol ⁻¹ K ⁻¹)	ΔS (J K ⁻¹)
0.002	-3333.90	-500.41	9.35
0.004	-3261.91	-496.61	9.13
0.006	-3188.00	-496.43	8.88
0.008	-3142.43	-492.64	8.75
0.010	-3117.54	-491.02	8.67

CONCLUSION

From the above data the viscous flow for different compounds in 60% aqueous dimethyl sulphoxide at different temperatures are

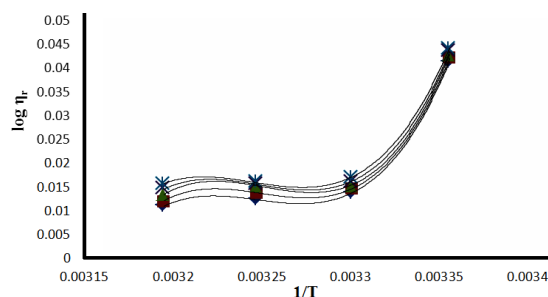


Fig.1. Graph of $\log \eta_r$ against $1/T$ for different concentrations

thermodynamically spontaneous and exothermic. We found decrease in ΔG , ΔH and ΔS with increase in concentration. The magnitude of these thermodynamic parameters clearly indicates that the reaction is spontaneous according to

thermodynamics. The study reveals that there is structure breaking between solute and solvent along with decrease in spontaneity with concentration. This shows strong molecular interaction between the molecules and solvent i.e. solute-solvent interaction is high rather than solute-solute and solvent-solvent interactions.

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Conflict of Interest

There is no conflict of interest.

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