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Thermodynamic studies of 6-(4-chlorophenyl)-1,2,3,4-tetrahydro-2,4-dioxopyrimidine-5-carbonitrile in 60% DMSO in the temperature range 298 to 313 K

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Abstract

Densities and viscosities of 6-(4-chlorophenyl)-1,2,3,4-tetrahydro-2,4-dioxopyrimidine-5-carbonitrile have been measured at different concentration in 60% dimethyl sulphoxide (DMSO) in the temperature range 298 to 313 K. The John-Dole equation was used to determine the viscosity. Gibb's free energy (ΔG), entropy change (ΔS) and enthalpy change (ΔH) were evaluated from relative viscosity. The negative sign of ΔG and ΔH and positive sign of ΔS indicates the spontaneity of reaction according to thermodynamics.

Keywords: *Viscosity, 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile, thermodynamic parameters, Gibb's free energy, enthalpy, entropy*

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INTRODUCTION

Compounds containing pyrimidine ring have significant important owing to many biological significance and biological activities [1-3]. Study of density and viscosity of solutions plays a crucial role in solution chemistry. Apparent molar volume and partial molar volume gives information about various interactions between solute-solute, solute-solvent and solvent-solvent interaction. This interaction provides information about nature of solvent and solute, dielectric properties and polarity of solute and solvent [4-6]. The thermodynamic properties plays vital role in understanding spontaneity of reaction. By measuring viscosity in aqueous solution different parameters like change in Gibb's free energy, entropy and enthalpy at different temperature can be studied [7-9]. Therefore in the present work, the systematic study of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2,4-dioxopyrimidine-5-carbonitrile is done by viscometric studies at temperature range from 298 to 313 K. From viscometric and densitometric data different thermodynamic parameters are determined.

MATERIAL AND METHODS

6-(4-chlorophenyl)-1,2,3,4-tetrahydro-2,4-dioxopyrimidine-5-carbonitrile was prepared and purified by recrystallization [10]. Triple distilled deionized water was adopted for preparation of solution in the concentration range from 0.002 mol L^{-1} to 0.010 mol L^{-1} in 60% DMSO at room temperature. Pycknometer used for measuring density was calibrated using triple distilled water. The viscosity of different solution were measured by using Ubbelohde viscometer at temperature range from 298 to 313 K. The desired temperature was maintained by circulating water through thermally controlled water bath. Digital stop watch was used to measure flow time.

THEORY

The relationship between coefficient of viscosity of liquid and temperature is given by

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

The thermodynamic parameters were determined by using following equations

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

$\log \eta r_2 / \eta r_1 = [\Delta H/2.303\ R]\ [T_2\text{-}T_1/T_1T_2]$ --- (3)

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

RESULT AND DISCUSSION

It is seen that viscosity and density of solution decreases as temperature increases. The values of density and viscosity of solution at different temperature with concentration are tabulated in Table 1 to Table 5. Dynamic viscosity values were incorporated for the calculation of thermodynamic functions. Gibb's free energy values were determined from the slope of graph by plotting log η_r Vs 1/T as shown in Figure 1. It is found that the values of Gibb's free energy are negative for the compounds. The values of change in enthalpy in reaction were determined by using equation (3). Negative values of ΔG and ΔH shows the reaction is spontaneous and exothermic in nature. The value of change in entropy were derived from equation (4) giving positive value again pointing the spontaneity of the reaction which may be achieved due to molecule flipping and destruction of hydrogen bonding of compounds.

Table 1: *Density and Viscosity measurements at 0.002 mol L^{-1} of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile in 60% aqueous DMSO at different temperature.*

Temp	1/T	Density "ρ" (kg m^{-3})	Relative Viscosity "η_r"	log η_r
298	3.356×10^{-3}	1.0893	1.1067	0.04403
303	3.3003×10^{-3}	1.0877	1.0415	0.01765
308	3.2468×10^{-3}	1.0780	1.0474	0.02011
313	3.1949×10^{-3}	1.0675	1.0385	0.02836

Table 2: *Density and Viscosity measurements at 0.004 mol L^{-1} of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile in 60% aqueous DMSO at different temperature.*

Temp	1/T	Density "ρ" (kg m^{-3})	Relative Viscosity "η_r"	log η_r
298	3.356×10^{-3}	1.0887	1.1066	0.04340
303	3.3003×10^{-3}	1.0893	1.0434	0.01845
308	3.2468×10^{-3}	1.0784	1.0500	0.02120
313	3.1949×10^{-3}	1.0677	1.0411	0.01749

Table 3: *Density and Viscosity measurements at 0.006 mol L^{-1} of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile in 60% aqueous DMSO at different temperature.*

Temp	1/T	Density "ρ" (kg m^{-3})	Relative Viscosity "η_r"	log η_r
298	3.356×10^{-3}	1.0898	1.1105	0.04552
303	3.3003×10^{-3}	1.0898	1.0459	0.01949
308	3.2468×10^{-3}	1.0787	1.0524	0.02218
313	3.1949×10^{-3}	1.0679	1.0437	0.01858

CONCLUSION

From the above data the viscous flow of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2,4-dioxopyrimidine-5-carbonitrile in 60% aqueous DMSO at different temperature are thermodynamically spontaneous and exothermic. It is clearly seen that at low concentration the values of change in Gibb's free energy, enthalpy and entropy are high. The magnitude of ΔG, ΔH and ΔS clearly indicate the reaction is spontaneous in accord to thermodynamics.

Table 4: *Density and Viscosity measurements at 0.008 mol L^{-1} of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile in 60% aqueous DMSO at different temperature.*

Temp	1/T	Density "ρ" (kg m^{-3})	Relative Viscosity "η_r"	log η_r
298	3.356×10^{-3}	1.0898	1.1119	0.04607
303	3.3003×10^{-3}	1.0909	1.0476	0.02020
308	3.2468×10^{-3}	1.0788	1.0545	0.02305
313	3.1949×10^{-3}	1.0681	1.0464	0.019670

Table 5: *Density and Viscosity measurements at 0.010 mol L^{-1} of 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile in 60% aqueous DMSO at different temperature.*

Temp	1/T	Density "ρ" (kg m^{-3})	Relative Viscosity "η_r"	log η_r
298	3.356×10^{-3}	1.0899	1.1135	0.04669
303	3.3003×10^{-3}	1.0911	1.0495	0.02098
308	3.2468×10^{-3}	1.0788	1.0567	0.02395
313	3.1949×10^{-3}	1.0684	1.0492	0.02086

Table 6: *Values of thermodynamic parameters for 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrilein 60% aqueous DMSO.*

Conc.(mol L^{-1})	ΔG (J mol^{-1} K^{-1})	ΔH (J mol^{-1} K^{-1})	ΔS (J K^{-1})
0.002	-1329.6541	-476.3883	2.8161
0.004	-2702.0447	-450.5643	7.4306
0.006	-2815.7787	-470.0677	7.7416
0.008	-2752.4017	-467.1783	7.5420
0.010	-2687.3014	-464.2889	7.3367

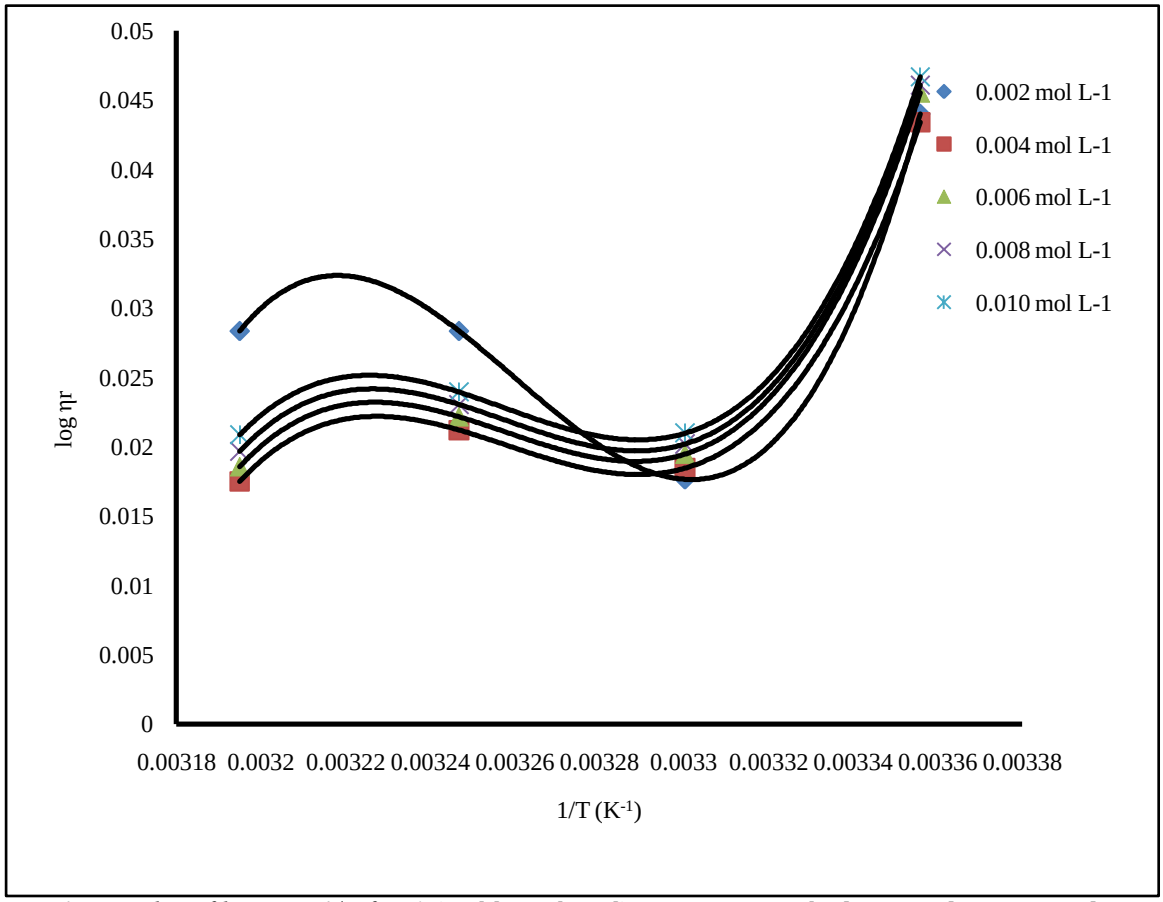

Fig. 1: *Plot of log η vs 1/T for 6-(4-chlorophenyl)-1, 2, 3, 4-tetrahydro-2, 4-dioxopyrimidine-5-carbonitrile at different concentration.*

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