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Study of Thermodynamic Parameters and Viscosity Behaviour of Substituted Pyrazolines in 70% Dioxane-Water—Part II*

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Viscosity measurements have been made on system comprising 1-carboxamido-3-(2′-hydroxy-3′-bromo-5′-chlorophenyl)-5-phenyl Δ^2-pyrazoline (ligand **1**) and 1-carboxamido-3-(2′-hydroxy-3′-nitro-5′-chlorophenyl)-5-phenyl-Δ^2-pyrazoline (ligand **2**) in 70% dioxane-water mixture solvent at different temperatures. The data have been used to calculate viscosity and thermodynamic parameters such as ΔG^*, ΔH^* and ΔS^*. We have also studied the effect of solvent on the viscosity at 30°C. It has been found that viscosity increases with increase in the percentage of dioxane. Also viscosity increases due to increase in the concentration of ligand **1** and ligand **2** in 70% dioxane-water mixture. In the presnt investigation β-coefficient value of ligand **2** is greater than the value of ligand **1** in dioxane-water mixture. We have also calculated the thermodynamic parameters ΔG^*, ΔH^* and ΔS^* for ligand **1** and ligand **2** which showed that the process is spontaneous and irreversible.

INTRODUCTION

Viscosity is one of the physical properties of liquids and gases and it implies resistance to flow. The significance of viscosity may be further elucidated by considering the flow of liquid through a narrow pipe. Physical properties of liquid and binary liquid mixture have been the subject of interest in research laboratories[1–6]. The measurements of viscosities of electrolytes in solution provide an excellent method of obtaining data on solute-solvent and solute-solute interaction. These interactions have been studied by many workers in aqueous and non-aqueous solutions but such investigations in mixed solvents are scanty.

The Jone-Dole[7] equation accounts for the observed viscosity-concentration dependence of dilute electrolyte solution, while Bresalu-Miller[8], Vand[9] and Thomson[10] equation accounts for the concentration dependence of viscosity in concentrated electrolyte solution. The present work deals with the study of interaction of 1-carboxamido-3-(2′-hydroxy-3′-bromo-5′-chlorophenyl)-5-phenyl Δ^2-pyrazoline (ligand **1**) and 1-carboxamido-3-(2′-hydroxy-3′-nitro-5′-chlorophenyl)-5-phenyl-Δ^2-pyrazoline (ligand **2**) in 70% dioxane-water mixture at

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different temperature and also to study the effect of percentage of dioxane-water on viscosity by keeping the ligand, concentration constant.

EXPERIMENTAL

1-Carboxamido-3-(2′-hydroxy-3′-bromo-5′-chlorophenyl)-5-phenyl-Δ^2-pyrazoline (ligand **1**) and 1-carboxamido-3-(2′-hydroxy-3′-nitro-5′-chlorophenyl)-5-phenyl-Δ^2-pyrazoline (ligand **2**) were prepared in the laboratory[11] and confirmed by spectral data. Dioxane was purified by standard method of Vogel. Dioxane-water (70%) were mixed by volume and used as a solvent. The different percentages of solvents (70, 75, 80, and 85%) were prepared by change in the volume of solvent and keeping the volume of ligand fixed. The solutions of different molarities ($1 \times 10^{-6} \ldots 2.5 \times 10^{-6}$ M) of ligands were prepared fresh by dissolving an appropriate amount of solvent mixture at 30°C. Densities of mixture were determined by the help of pyknometer having a bulb volume of 10 cm^3 and capillary having an internal diameter 1 mm. Viscosities were measured by means of Ostwald Viscometer. Standard errors in viscosity measurement were less than ±0.2%.

RESULTS AND DISCUSSION

The data of viscosity in the present investigation are presented in Table-1, to study the effect of dioxane-water solvent. It could be seen from Table-1 that viscosity increases with increase in the percentage of dioxane for both ligand 1 and ligand **2**. It could be also seen that the values of viscosity coefficient of ligand **2** are greater than the values of ligand **1**. This may be due to the effect of stronger —NO_2 electron withdrawing group than —Br withdrawing group.

TABLE-1
VISCOSITY OF LIGAND **1** AND **2** IN DIFFERENT PERCENTAGE OF DIOXANE-WATER AT 303 K

Percentage of solvent	Viscosity in poise	
	Dioxane-water-ligand **1**	Dioxane-water-ligand **2**
70	0.007565	0.009027
75	0.008516	0.010200
80	0.009310	0.011150
85	0.010790	0.012900

The determination of viscosities at different temperatures (303, 308, 313, 318, and 323 K) in 70% dioxane-water mixture solvent for ligand 1 and 2 has been done in the present investigation with a limited aim to evaluate the thermodynamic parameters such as ΔG^*, ΔH^* and ΔS^*. The data of viscosity obtained at different temperatures for ligand **1** and **2** are presented in Table-2. It could be seen from Table-2 that viscosity increases with increase in the concentration of ligands because interaction of ligand (solute)-solvent increased with respect to change in the concentration. The data evaluated in the present work of ΔG^*,

ΔH^* and ΔS^* are presented in Table-3. It is seen from Table-3 that there is gradual increase in the value of ΔG^* and ΔS^* for ligand **1** and **2** system whereas the values ΔS^* are found to decrease in case of ligand **2** system. This may be attributed to the presence of stronger electron withdrawing —NO_2 group. It is also observed from Table-3 that the values of ΔG^* are found to be positive and those of ΔS^* are found to be negative ($\Delta G^* > 0$ and $\Delta S^* < 0$) which shows in that the process is spontaneous and irreversible. It could also be seen from same Table-3 that there is no appreciable difference between the values of ΔG^*, ΔH^* and ΔS^* for both the systems. This may be because of the presence of —Br and —NO_2 electron withdrawing groups in ligand **1** and **2** respectively.

TABLE-2
VISCOSITY OF LIGAND **1** AND **2** AT DIFFERENT TEMPERATURES

Concentration mole lit^{-1}	303 K	308 K	313 K	318 K	323 K
Ligand **1**					
1×10^{-6}	0.007964	0.007753	0.007477	0.007411	0.007278
1.5×10^{-6}	0.008290	0.008216	0.008082	0.007867	0.007793
2×10^{-6}	0.008647	0.008341	0.008274	0.008036	0.007983
2.5×10^{-6}	0.009371	0.008781	0.008673	0.008534	0.008366
Ligand **2**					
1×10^{-6}	0.008474	0.008298	0.008231	0.007941	0.007948
1.5×10^{-6}	0.008917	0.008745	0.008692	0.008662	0.008519
2×10^{-6}	0.009376	0.009237	0.009017	0.008881	0.008744
2.5×10^{-6}	0.009488	0.009352	0.009200	0.009064	0.008934

TABLE-3
DATA OF THERMODYNAMIC PARAMETERS IN J/mole FOR LIGAND **1** AND **2**

Concentration mole lit^{-1}	Ligand **1**			Ligand **2**		
	ΔG^*	ΔH^*	ΔS^*	ΔG^*	ΔH^*	ΔS^*
1×10^{-6}	20675.21	76.55	–67.98	20928.53	53.93	–68.89
1.5×10^{-6}	20901.81	57.41	–66.59	20994.59	41.75	–69.15
2×10^{-6}	20933.84	66.11	–66.07	21037.64	67.85	–69.20
2.5×10^{-6}	20998.22	59.32	–65.85	21057.41	53.93	–69.31

β-Coeffcient value: The relative viscosity (n_r) and specific viscosity ($n_r - 1$) were calculated. Jone-Doles have applied the equation $\frac{n_r - 1}{\sqrt{c}} = A + B\sqrt{c}$ and investigated the role of solute-solvent interaction. In the present investigation, β-coefficient value of ligand **2** (0.6211×10^5) is greater than

the β-coefficient value of ligand **1** (0.4568×10^5) in dioxane-water mixture. This shows greater interaction between ligand **2** (solute) and dioxane (solvent).

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