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Studies in Solute-Solute and Solute-Solvent Interaction of Some Substituted Ketimine Drugs in 75 % Dichloromethane Water Mixture under Different Temperature by Viscometric Technique

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Abstract: *The computation of densities, specific viscosities of 5- Bromo-2-hydroxy-4-chloro (p-methyl phenyl) ketimine (L1) and 5- Bromo-2-hydroxy-4-chloro (p-amino phenol) ketimine (L2) drugs in 75% (DCM + water) mixture at the temperature range (308 to 314 K) are reported. The investigational data shows, the effect of temperature on viscosity of solute in DCM + water mixtures which gives idea about the molecular interactions present in different solutions. Considerable molecular interactions have been observed between the substituted ketimines drugs and DCM + water mixture. The experimental data at different temperature range (308 to 314 K) are used to investigate thermodynamic properties such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of substituted ketimines drugs in 75% (DCM + water) mixture. The experimental data gives the idea about effect of temperature on the molecular interaction and structural changes in solute.*

Keywords: Ketimine, dichloromethane (DCM), molecular interaction, free energy change etc.

I. INTRODUCTION

Viscosity measurement like other properties of electrolyte, provide useful information about solute-solute and solute solvent interactions. A fluids viscosity strongly depends upon its temperature. Zarei and Jalili [1] studied measurement of viscosity at different temperature play an important role in compassionate the nature and the extent of the patterns of molecular interactions that exist in binary liquid mixtures and their sensitivities to variations in composition and the molecular structure of the pure components. Viscosity data at different temperature help in consideration of drug action through various kinds of physico-chemical interactions e.g., ionic or covalent, charge-transfer, hydrogen bonding, ionic-dipole interaction, hydrophilic interaction [2-7].

Iqbal and Siddiquah [8] studied effect of temperature on drug solvent molecular interaction plays important role to understand the proper drug action. In the field of biochemistry interaction of macromolecular drug is an important phenomenon which involve complex mechanism. The complex mechanism of drug action within the biological process and the activity of drugs at the molecular level is inappropriate to study directly as the drug solvent interactions are found to vary with temperature as well as addition of co solutes like salt, surfactants, osmolytes, proteins and carbohydrates. One of the well-recognized methods to study these molecular interactions is the use of thermodynamic method [9]. The volumetric and viscous behavior of solutes has been proven to be very useful in elucidating the various interactions occurring in solutions and it is an important key to thermodynamic properties.

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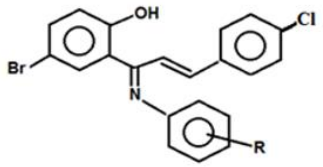
Recently the study of chemistry of ketimines continuously is increasing because of their applications in various biological systems, polymer stabilizer, homogeneous and heterogeneous catalysis, medicine, pharmacy and other technologies [10]. This class of compounds shows wide range of biological activities such as antibacterial, antifungal, anti-inflammatory, antiviral and antipyretics [11-12]. So keeping these views in consideration attempt has been made to study the physiochemical behavior of 5- Bromo-2-hydroxy-4-chloro (p-methyl phenyl) ketimine (L1) and 5- Bromo-2-hydroxy-4-chloro (p-amino phenol) ketimine (L2) drugs in 75% (DCM+water) mixture at the temperature range (308 to 314 K) has been reported.

II. Materials and Methods

In the present article drugs which physiochemical parameters is to be inspect are synthesized by using reported methods. All the chemicals of AR grade were used. All the weighings were made on one pan digital balance (petit balance AD_50B) with an accuracy of (±0.001) gm. For the measurement of densities of pure solvent and solutions of various concentrations at different temperature precalibrated bicapilary pycnometer was used. Viscosities of the solutions were determined with the help of calibrated Ostwald viscometer (± 0.1% Kgm-1s -1). The flow time of solutions were measured by using digital clock of Racer Company having error (±0.01sec).



Where L1 R = 4-CH3
L2 R = 4-OH
Ligand-1 (L1) 5- Bromo-2-hydroxy-4-chloro (p-methyl phenyl) ketimine
Ligand-2 (L2) 5- Bromo-2-hydroxy-4-chloro (p-amino phenol) ketimine

III. Calculations

The relative and specific viscosity, the different concentration of the substituted α, β unsaturated ketimine solutions were measured with help of the following mathematical equation

$$(\eta r) = (ds \times ts / dw \times tw) \times \eta w \quad (1)$$

Where ŋr = Relative viscosity
ŋw = Viscosity of water
ds = Density of solution
dw = Density of water
ts = Flow time for solution
tw = Flow time for water

From the values of relative viscosities (ŋr) and the temperature (T), the graph between log (ŋr) vs 1/T can be plotted. The relative viscosities and density data of ligand solutions at different concentration are presented in table I. The viscosity data have been analyzed by Jones–Dole equation [13].

$$(\eta r - 1) / \sqrt{C} = \eta sp / \sqrt{C} = A + B\sqrt{C} \quad (2)$$

Where A = Falkenhagen coefficient (measures the solute-solute interaction)
B = Jones-Dole coefficient (measures the solute-solvent interaction)
C = Molar concentration of ligand solutions

The thermodynamic parameters i.e. free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) can be determine by using following relation,

$$\Delta G = -2.303 \times R \times slope \quad (3)$$

$$\log \eta r1 - \log \eta r2 = (\Delta H/2.303) \times (1/T1 - 1/T2) \quad (4)$$

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$$\Delta S = (\Delta G - \Delta H)/T \qquad (5)$$

Table 1: Densities (d) gm. /cc and specific viscosities (ŋsp) of substituted ketimines of different concentration in 75% (DCM+ water) solvent at 308K.

Concentration (C) Mole/lit	L1		L2	
	Density gm/cc	Relative Viscosity ŋr = ŋ/ŋ0	Density gm/cc	Relative Viscosity ŋr = ŋ/ŋ0
0.01	1.22419	1.605	1.22057	1.592
0.008	1.22329	1.566	1.21967	1.544
0.006	1.22238	1.555	1.21967	1.485
0.004	1.22148	1.502	1.21876	1.389
0.002	1.21604	1.367	1.21786	1.277

Table 2: A = Falkenhagen coefficient, B= Jones-Dole coefficient values

Ligand + 70%DMF-Water	A	B (Lit/mol)
L1	10.32	-42.464
L2	6.4397	-4.1696

Table 3: Densities (d) gm/cc Relative and relative viscosities (ŋr) of substituted ketimines in 75% (DCM+ water) solvent at different temperature (308, 310,312 and 314) K

Temp (K)	L1		L2	
	Density (Kgm-3)	Relative Viscosity ŋr	Density (Kgm-3)	Relative Viscosity ŋr
308	1.22419	1.6085	1.2205	1.6036
310	1.22406	1.5731	1.2199	1.5938
312	1.22396	1.5619	1.2192	1.5831
314	1.22385	1.5143	1.2187	1.5638

Table 4: Values of Thermodynamic Parameters for temperature difference 314K – 308°K

System	ΔG (J mol-1 K-1)	ΔH (J mol-1 K-1)	ΔS (J mol-1 K-1)
Ligand 1	-7557.95	-8083.52	-1.6738
Ligand 2	-3301.92	-997.17	7.339984

The value of A = Falkenhagen coefficient, B= Jones-Dole coefficient is calculated by ploting the graph between of √ C Vs ŋsp/√C of all substituted ketimines.

IV. Result and Discussion

The relative viscosity and density data are presented in table 1. The data shows that relative viscosity of substituted ketimines (L1 and L2) decreases with decrease in concentration of solution. The increase in concentration with increase in viscosity of substituted ketimines may be attributed due to increase in solute solvent interactions. The graphs are plotted between (ŋsp/√C) Vs (√C) presented in fig. 1-3. These graphs validate Jones-Dole equation for both the ligands by showing linear straight lines. From the graphs values of Falkenhagen coefficient ie coefficient A and Johne-Dole ie coefficient B are obtained. The coefficient A is the intercept while coefficient B is the slope of graph (ŋsp/√C) Vs (√C). The positive and negative values of coefficient B shows order and disorder produced by solute in solvent respectively.

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The coefficient B often measure the effective hydrodynamic volume of solute which signifies ion solvent interactions. In the present study values of coefficient B for both the ligands (L1 & L2) are negative which indicate moderate interactions between solute and solvent. The Falkenhagen coefficient i.e. coefficient A is the intercept of graphs which measures solute solute interactions. From table 2 the values of coefficient A for L1 and L2 are positive of the order of ligands L1 > L2.

The properties such as viscosity and densities are mostly affected by polar nature of substituents attached to ligand molecule. From the table I values of relative viscosity and density decreases with decrees in concentration of solution. Hence order of relative viscosity of ligands L1 > L2 due to more polar substituent of L1.

The molecular interactions of solute also affected on account of increase or decrease in temperature of system. The solute-solute and solute-solvent interaction decreases with increase in temperature. Which also account on the basis of different thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) these are calculated from the graph 1/T Vrs log ŋr (fig. 4-6). The values of free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) are presented in table IV. The negative values of free energy change (ΔG)for both the ligands shows reaction is feasible, while negative values of enthalpy change (ΔH) indicate reaction are spontaneous and exothermic and negative value of entropy change (ΔS) indicate that, randomness of solute molecule in solvent decreases

V. CONCLUSION

The properties such as densities and viscosities of solutions of 5- Bromo-2-hydroxy-4-chloro (p-methyl phenyl) ketimine (L1) and 5- Bromo-2-hydroxy-4-chloro (p-amino phenol) ketimine (L2) drugs in 75% (DCM+water) mixture at the temperature range (308 to 314 K) were reported. From the experimental data, various parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) Falkenhagen Coefficient, A, Jones–Dole coefficient, B, were calculated. The results indicate that there exist strong solute-solute and solute–solvent (hydrophilic-ionic group and hydrophilic-hydrophilic group) interactions increase with increase of ketimine concentration.

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