THERMODYNAMIC STUDY OF DIFFERENT CHLORO SUBSTITUTED AZETIDIN-2-ONE AT DIFFERENT CONCENTRATION AND TEMPERATURE IN 90% (ETOH+WATER) SOLVENT BY VISCOMETRICALLY.

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A B S T R A C T

The themodynamic properties such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of different chloro substituted azetidin-2-one have been investigated in 90% (EtOH+water) solvent by the measurement of densities and viscosities at different temperature such as 293K,298K,303K, 308K and 313K. The experimental data study gives the idea about effect of temperature on the molecular interaction and nature of reaction.

Keywords: Density, Relative Viscosity, Specific Viscosity, Thermodynamic Parameters Free energy change, Enthalpy, Entropy

1. Introduction

Study of molecular interactions between solutes molecule and solvent media has got great importance in many fields of science including biochemistry ,medicinal chemistry, industrial processes etc. By the measurement of relative viscosity and ultrasonic velocity of an electrolyte in solutions can be studied the solute solvent and solvent-solvent interactions. The liquids are viscous in nature due to the shearing effect in the liquid which is the movement of liquid layers over each other. The important information regarding solute-solute and solute-solvent interaction in an aqueous and in nonaqueous solution observed by Viscometric study. These compounds have wide range of medicinal and pharmaceutical properties viz. anti-diabetic and anti-oxidant[1] anti-psychotics[2], anti-cancer[3], anti-coccidial[4],cardiovascular[5].The viscometric determination of some drugs including Metform in hydrochloride (MH),Ranitidine hydrochloride (RH), and Tramadol hydrochloride (TH) in aqueous solutions at various temperatures done by Dhondge et al[6]. viscometric studies on N,N-dimethyl acetamide and methanol binary mixtures at various temperatureswas done by Peshwe et al[7]. Densities and Viscosities of (Choline Chloride + Urea) deep eutectic solvent and its aqueous mixtures in the temperature range 293.15 K to 363.15 K studied by Pandey et al. [8].Effect of dilution on the thermodynamic parameters of some transition metal salt by viscometry stuied by Tayade et al [9]. The Estimation of microstructure of titania particulate dispersion through viscosity measured by Lee et al[10]. Viscosity of 2,3,3,3- tetrafluoroprop-1-ene (R1234yf) in the temperature of 243 to 363 observed by X. Meng et al. [11]. Allmendinger et al[12] determined viscosity measurement of protein formulation using capillary electrophoresis instrumentation.

Density and viscosity measurements for 4-aminobutyric acid in different composition in aqueous metformin hydrochloride at various temperature carriedout by Rajagopal et al. [13]. Riyazuddeen et al [14] repored the effects of concentration and temperature on viscosity in (l-alanine/l-threonine/glycylglycine + aqueous d-glucose/aqueous sucrose) systems.Jo et al. [15] has studied the viscosity measurements of multi-walled carbon nanotubes-based high temperature nanofluids.The study of of the (LiF + NaF + KF(eut.)+Na7Zr6F31) fluoride system has been investigated by Peter Barborík et al[16]. Raisuti et al[17] reported viscosity of highly viscous non-Newtonian fluids. Study of density, surface tension, and viscosity of

quaternary ammonium-based ionic liquids ([N222(n)]Tf2N) done by Ghatee et al[18].The density and viscosity of binary 1-hexene + 1-decene mixtures have been simultaneously measured over the temperature range from 298 to 470 K and at pressures up to 196 MPa by Sagdeev et al [19]..The effect of temperature on thermodynamic parameter of s-triazinothiocarbamides in 60% dioxane-water mixture studied by A M Kshirsagar et al[20].

2. Materials and Methods

2.1 Materials and Solutions

Carbon dioxide free double distilled water was used. The entire chemical used of A.R. grade. All weighing were made on Mechaniki Zaktady Precyzying Gdansk Balance [Poland make, (±0.001g)]. The density of solutions were determined by a bicapillary Pyknometer (±0.2%) having a bulb volume of about 10 cm3 and capillary having an internal diameter of 1mm and calibrated with deionised doubly distilled water. The accuracy of density measurements were within ±0.1Kgm-3. The viscosities were measured by means of Ostwald‟s viscometer thoroughly cleaned and dried. The flow time of solutions were measured by using digital clock of racer company having error (±0.01Sec). The 0.1M concentrated solution of compound these were prepared in 90% Ethanol-Water mixture. In the same way 0.075M, 0.05M and 0.025M solutions for the compounds C were prepared. The compound used during investigations is as depicted below,

(C1)3-Chloro-4-(4-hydroxyphenyl)-1-(4-nitrophenyl)azetidin-2-one

(C2)3-chloro-4(4-chlorophenyl)-1-(4-hydroxyphenyl)azetidin-2-one

(C3)3-chloro-1-(4-hydroxyphenyl)-4-phenylazetidin-2-one

2.2Experimental Procedure

The viscometer was kept in Elite thermostatic water bath and temperature variation was maintained at for each measurements, sufficient time was allowed to attain thermal equilibrium between viscometer and water bath. The viscosities were measured by means of Ostwald‟s viscometer thoroughly cleaned and dried and taking the reading of different concentration solutions of C1,C2 and C3.repectively at various temperature.

2.3Observations and Calculations

The present study deals with the investigation of viscosity of Compounds in 90% ethanol–water mixture at different concentration at various temperatures. The results obtained were mentioned in Table 1 to 5

The relative viscosity of each solution during study was determined by formula depicted below

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

Where

ηr = Relative viscosity
ηw = Viscosity of water
ds = Density of solution
dw = Density of water
ts = Flow time for solution
tw = Flow time for water

And the relative viscosities have been analyzed by Jone‟s-Dole equation.

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

A = Falkenhagen coefficient
B = Jones-Dole coefficient
C = concentration of solutions

The Falkenhagen coefficient (A) measures the solute-solute interaction while Jones-Dole coefficient (B) measures the solute-solvent interaction.The thermodynamic parameters i.e. free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) can be determine by using following relation,

$$\Delta G = -2.303\times R\times slope \quad (4)$$

$$\log \eta r1-\log \eta r2=(\Delta H/2.303)\times(1/T1 -1/T2) \quad (5)$$

$$\Delta S = (\Delta G - \Delta H)/T \quad (6)$$

Table 1- Determination of Densities and Relative Viscosities at Different Concentrations at 308K Temperatures in 90% EtOH –Water mixture For C1, C2 & C3.

C1		C2		C3		
Conc C Mole/lit	Density gm/cc	Relative Viscosity ŋr	Density gm/cc	Relative Viscosity ŋr	Density gm/cc	Relative Viscosity ŋr
0.1	1.04947	1.782	1.0414	1.7534	1.02928	1.6739
0.075	1.04382	1.7574	1.03574	1.7339	1.02363	1.65
0.05	1.04008	1.7412	1.03201	1.7178	1.01989	1.6342
0.025	1.03595	1.7244	1.02787	1.706	1.01575	1.613

Table 2 -Determination of Densities and Relative Viscosities at Different Concentrations at 313K Temperatures in 90% EtOH –Water mixture For C1, C2 & C3.

C1		**C2**		**C3**		
Conc C Mole/lit	**Density gm/cc**	**Relative Viscosity ŋr**	**Density gm/cc**	**Relative Viscosity ŋr**	**Density gm/cc**	**Relative Viscosity ŋr**
0.1	1.04902	1.7799	1.04092	1.7505	1.02876	1.6736
0.075	1.04324	1.7544	1.03514	1.7305	1.02299	1.6489
0.05	1.03919	1.7321	1.03109	1.7134	1.01894	1.6271
0.025	1.03514	1.715	1.02704	1.6964	1.01489	1.6105

There are plotted between √ C versus ŋsp/√C**.** The graph for each system gave linear straight line showing validity of Jone‟s –Dole equation. The slope of straight line gave value of b coefficient.

Table 3- A and β Co-Efficient Value from Fig. 1 to 6 at various Temperatures for 90% Ethanol-Water Mixture.

Temp in K	**C1**		**C2**		**C3**	
A	**b**	**A**	**b**	**A**	**b**	
308	6.537	-13.39	6.392	-13.20	5.501	-11.10
313	6.420	-13.03	6.289	-12.88	5.457	-10.97

Table 4- Densities (d) gm/cc and relative viscosities (ŋr) of Different chloro substituted azetidin-2-one of 0.1M concentration in 90% (EtOH+ water) solvent at different temperature (293,298, 303,308 and 313) K

C1		**C2**		**C3**		
Temp. in K	**Density gm/cc**	**Relative Viscosity ŋr**	**Density gm/cc**	**Relative Viscosity ŋr**	**Density gm/cc**	**Relative Viscosity ŋr**
293	1.05014	1.8092	1.04213	1.76	0.3162	1.6871
298	1.05009	1.7959	1.0421	1.7592	0.3162	1.6799
303	1.0497	1.7875	1.0417	1.7547	1.0296	1.6776
308	1.04947	1.782	1.0414	1.7534	1.02928	1.6739
313	1.04902	1.7799	1.04092	1.7505	1.02876	1.6736

There are plotting between log nr versus 1/T for C1, C2 & C3. The slope of straight line value putting in eq. no 4 we get free energy change (ΔG) and from eq no. 5 and 6 gives enthalpy change (ΔH) and entropy change (ΔS) respectively.

Table 5- Values of Thermodynamic Parameters for temperature difference 293K-313K

System	**ΔG (J mol-1 K-1)**	**ΔH (J mol-1 K-1)**	**ΔS (J mol-1 K-1)**
C1	-619.79	5.8851	-1.999
C2	-215.21	39.2817	-254.5
C3	-301.38	-43.151	-0.825

3. Results and Discussion

As the temperature increases the value of relative viscosity and density decreases shown in table IV. Due to increase in temperature the interaction between solute such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of Different chloro substituted azetidin-2-one are calculated by plotting graph betweenThermodynamic parameter mentioned in table 5. From the results in **Table 1-5,** it is observed that, the decreasing concentration of compound decreasing density of solution and relative viscosity respectively for compounds in 90% ethanol-water mixture. Relative viscosity of all compounds is inversely proportional to temperatures. Among all three compounds, C3 has smallest relative viscosity due to absence of electron-withdrawing group as compare to other two compounds. The negative values of "A" and β-coefficient characterized as „structure-breaker" indicating a weak solute-solvent interaction which is good for interactions in between the drug and the drug receptors shows best drug activity and drug effect and it fevers pharmacokinetics and pharmacodynamics of drug. The value of A coefficient show that, the solute-solvent interaction is highest in compound C1 at 308K for 90% ethanol-water mixture and so they tend to interact with solvent molecules to lesser extent leading decrease in solute-solvent Interaction.

Conclusion

Values of β-coefficient for all compounds decrease with increasing the temperature which indicates that increasing the solute-solvent interaction. This study is an important for biochemical, pharmaceutical and medicinal sciences which directly focus on drug interaction with solvent at various temperature .The negative value Thermodynamic Parameters interpreted that reaction of solute and solvent are spontaneous and exothermic. This study gave information regarding pharmacodynamics and pharmacokinetics of compounds.

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