Viscosity Measurement Of Substituted Schiff's Bases In 70% Water-Dioxane Mixture At Different Temperature And Determination Of Thermodynamic Parameters

Dr.A.D.Khambre[1]

[1]Sant Gadge Baba Amravati University, Amravati

Abstract :-

Viscosities of substituted Schiff's Bases have been determined at different temperature in 70% Water-Dioxane mixture at. Thermodynamic parameters like Free Energy change (ΔG), Enthalpy Change (ΔH) & Entropy Change (ΔS) have been determined. The measurement of viscosity of electrolyte in solutions provides & excellent method of obtaining data on solute-solute & solvent-solvent interaction.The viscosity of a system is determined by how molecules constituting the system interact with each other. The viscosity of a solution depends on the concentration and size of the dissolved substance. Moreover, Schiff bases having their own identity and importance in pharmaceutical, co-ordination and drug chemistry along with medicinal, biotechnological sciences, are an important class of ligands in the field of co-ordination chemistry. The viscosity of a solution depends on the concentration and size of the dissolved substance. Moreover, Schiff bases having their own identity and importance in pharmaceutical, co-ordination and drug chemistry along with medicinal, biotechnological sciences are an important class of ligands in the field of co-ordination chemistry. The properties of Schiff bases have been used to obtain information about intermolecular interaction. The data of A and β-coefficient interactions of viscosity leads in determining the solute-solute and solute-solvent.

Key Words :-

Schiff bases, Density, viscosity, interaction, β-coefficient, Gibb's free energy, Change in entalpy, Change in entropy. etc.

Introduction :-

Viscosity value is dependent on intermolecular forces in the liquid and the molecular complexity of the compound. When large intermolecular forces are present or liquids that have complex molecular structure, a liquid will tend to be thick or highly viscous. Viscosity is one of the important physical properties of liquid and gases and it implies resistance to flow as fluids (liquid and gases) exhibit a characteristic property of flowing under applied force of their own weight (1). In common parlance, a liquid is said to be viscous if its viscosity is substantially greater than that of water; and may be described as mobile if the viscosity is noticeably less than water.

The basic principle of viscosity measurement is to study the interaction between solute and solvent. Polar solute when dissolved in water shows strong interaction while non-polar solute increases the structured-ness of water. The addition of organic co-solvent or mixture of solvents to water also has remarkable effects on the viscosities of the compounds (2).The measurement of viscosity of electrolyte in the solution provides a data on solute-solute, solute-solvent and solvent-solvent interactions. These molecular interaction of electrolyte in binary mixtures of two liquids are measured in terms of 'viscosity coefficient' (3). Researchers have studied the solute-solvent interactions at different concentrations by calculating β-coefficients and thus many related reports. have been published (4-6). Density, viscosity, and ultrasonic speed of halogenated symmetric double Schiff bases in DMF solutions were studied at 308.15K by Gangani B.J. and Parsania P.H. (7). Agrawal (8) have calculated the β-coefficient as a measure of solute-solvent interaction. Viscosity and Density of Two 1-Alkyl-3-methyl-imidazolium Triflate Ionic Liquids at High Pressures and its effect of Alkyl Chain Length was studied by Maria C. M. and co-workers. (9) The properties of Schiff bases have been used to obtain information about intermolecular interaction. They

depend upon the nature of aldehyde/ketone and amines from which these are derived. This provokes to investigate the densities and viscosities of synthesized substituted Schiff's bases (L_1 & L_2) in 70% of 1,4-dioxane-water mixture, at varying temperatures. All ligands were synthesized by standard methods [10]. In the present study, attempt has been made to calculate β-coefficient and viscosity for two ligands at different temperatures of 303, 308, 313, 318 and 323 K in binary mixture of 70% dioxane-water. The study of measurement of viscosities & molecular ineractions in terms of β-coefficient of substituted Schiff's bases as a antibiotic drugs in 70% dioxane-water mixture.

Following antibiotic drugs used in present investigation –
1.2'-Hydroxy,3'-bromo,5'chloro-4-methoxy-N[orthonitrophenyl]Chalcone Imine (L_1)
2 2'-Hydoxy,5'-chloro,4-methoxy-N[orthonitrophenyl] Chalcone Imine (L_2)

Experimental and Instrumentation
Experimental
The drugs Schiff's Bases are synthesized by standard method.The solvents used were of AR grade & doubly distilled water was used. The density and the viscosity measurements of the ligand solutions were done at 303, 308, 313, 318 and 323 K following the standard protocol.The ligands (L_1 & L_2) were recrystallized before use. The solvent 1,4- dioxane was purified using standard procedure. All the working solutions were freshly prepared from the deionized water to avoid any ionic contamination.The 0.01M solution of each ligand was prepared in 70 % of 1,4-dioxane-water mixture.

Instrumentation
All Weighing was done on electronic balance, made by Adair Dutt & Co. (T) Pvt. Ltd.(Readability ± 0.001 g).Densities of solutions were determined by a bicapillary Pyknometer (± 0.2%) having a bulb volume of about 10 cm^3 & capillary having an internal diameter of 1mm & calibrated with deionised doubly distilled water (0.9960 gm cm^{-3} at 303.15 K). The viscosities were measured by means of Ostwald's Viscometer (± 0.11% kg m^{-1} s^{-1}) which was kept in equilibrium with elite thermostatic water bath (± 0.1^0C). Both ligands were prepared in 70% dioxane-water mixture.

Result and Discussion
The relative viscosity,Ŋr is given by the ratio of the viscosity of a solution ($η_2$) to the viscosity of the solvent used ($η_1$) and have been analyzed by Jones-Dole equation [11]

$$\eta^{r-1}/\sqrt{C} = A + β\sqrt{C}$$

Where, C = molar concentration of ligands
    A = Falkenhagen coefficient
    β = Jones-Dole coefficient
Falkenhagen coefficient (A) is the measure of ion-ion interactions and Jones-Dole coefficient (β) is the measure of solute-solvent interactions.
'$η_{r-1}/\sqrt{C}$' is also known as 'specific viscosity' denoted by '$η_{sp}$'.
In the present study, the parameters like relative viscosity ($η_r$), density (ρ) of 0.01 M solution of ligands L_1 & L_2, prepared in 70% of 1,4-dioxane-water mixture were calculated at temperature 303, 308, 313, 318 and 323 K.The experimental data obtained was tabulated (table no. 1 to 2) as under-

Table 1 : Measurement of Viscosity At Different Temperatures
System : Ligand L_1

Temp. T(^{0}K)	1/T(K^{-1}) x 10^{-3}	Density (ρ) gm.cm^{-3}	Time Flow Sec	Viscosity $η_l$	Relative Visccosity $Ŋr = Ŋ_l / Ŋ_w$	Log Ŋ
303	3.30	1.0339	24.56	7.465 x 10^{-3}	0.9332	-2.12
308	3.24	1.0290	23.96	6.579 x 10^{-3}	0.9075	-2.18
313	3.19	1.0255	23.03	5.661 x 10^{-3}	0.8709	-2.24
318	3.14	1.0155	22.20	5.080 x 10^{-3}	0.8329	-2.29
323	3.09	1.0086	21.23	4.571 x 10^{-3}	0.8019	-2.34

System : Ligand L_2

Temp. $T(^0K)$	$1/T(K^{-1})$ x 10^{-3}	Density (ρ) gm.cm^{-3}	Time Flow Sec	Viscocity η_l	Relative Visccosity $\eta r = \eta_l / \eta_w$	Log η
303	3.30	1.0368	26.53	8.0876 x 10^{-3}	1.0109	-2.09
308	3.24	1.0338	25.36	6.8711 x 10^{-3}	0.9478	-2.16
313	3.19	1.0305	24.30	6.002 x 10^{-3}	0.9234	-2.22
318	3.14	1.0276	23.16	5.363 x 10^{-3}	0.8792	-2.27
323	3.09	1.0190	22.33	4.793 x 10^{-3}	0.8409	-2.32

From the above table 1, it is seen that as temperature increases the relative viscosity decreases. This shows decrease in solute-solvent interactions. This can be explained in terms of hole theory of liquid where there are vacancies or holes in liquid. The liquid molecules keep on moving continuously into these vacancies. Consequently, the vacancies also keep on moving around, as otherwise the liquid will not be able to flow. This process, however, requires energy. The liquid molecules therefore, need some energy to move into hole. At increasing temperature, the energy becomes increasingly available and so liquid can flow more easily. Thus, the viscosity falls appreciably with rise in temperature.

Addition of macromolecules raises the viscosity of pure solvent to higher value. This occurs because the large molecules which extend across the streaming lines greatly enhance the resistance to flow. As a result, viscosity of macromolecular solution is always greater than that of pure solvent. However, in practice, the viscosity of a solution can be below that of a pure solvent. In fact, negative viscosity was discovered long time ago in variety of binary simple liquid mixtures. It may be regarded as arising from specific interactions between solute and solvent molecules such that a liquid structure of some kind in the solvent is destroyed in the vicinity of solute molecules[12-13]. The values of viscosity 'A' & 'β' coefficients responsible for solute-solute & solvent-solvent interactions are presented in table below. It shows that the interactions between solute-solvent decreases with increasing temperature. β-coefficient values obtained, employing the various equations do not agree well with each other, but they are of the same order. Negative values of β-coefficient are associated with a structure breaking effect of the solutions. It has been suggested, that the viscosity β-coefficient measures of ion-dipole interaction between ions & solvent molecules.

Table 2 : A & β Coefficient Values

System	A	β (lit/mole)
L_1	18.50	-1.36
L_2	16.90	-1.08

From table 2, it is clear that, all ligands possess negative values of β-coefficient at 293, 297 and 300 K. This shows weaker interaction between solute and solvent. The solute with negative β-coefficient is characterized as 'structure breakers'.

Values of $\boldsymbol{\beta}$ -coefficient at in the order - $L_2 > L_1$

This shows that the solute-solute interaction is highest among the molecules of ligand L_1 and L_2 so they tend to interact with solvent molecule to lesser extent leading to decrease in solute-solvent interaction which is shown by lowest $\boldsymbol{\beta}$ -coefficient value.

The positive 'A' values of ligands at all temperatures may indicate the presence of very strong ionic interactions.

Thus the $\boldsymbol{\beta}$-coefficient values for all the ligands are negative indicating weak solute-solvent interaction. Whereas the positive values of 'A' for all the ligands in 1,4-dioxane at temperature 303, 308, 313, 318 and 323 K may indicate strong ionic interaction.

The data of A and $\boldsymbol{\beta}$-coefficient of viscosity leads in determining the solute-solute and solute-solvent interactions.

Thus, from the present study and observations, it can be concluded that in 1,4-dioxane-water mixture, ligands show weak solute-solvent interaction and very strong ionic interactions at all   temperatures.

The thermodynamic parameters like free energy change (ΔG), Enthalpy Change (ΔH) & Entropy Change (ΔS) have been determined to study in various interaction taking place in solution of ligand.

Table 3 : Values of Thermodynamic Parameters

System	ΔG(J Mole^{-1} deg^{-1})	ΔH (J Mole^{-1} deg^{-1})	ΔS (J Mole^{-1} deg^{-1})
L_1	-21183.45	520.97	-71.6317
L_2	-41804.51	1201.86	-141.935

The values of thermodynamic parameters (ΔG, ΔH, ΔS) are presented in table 3. It is seen from table 3 that negative values of ΔG shows evolution of energy.

Conclusion :-

It is conclude that as the temperature increases the relative viscosity decreases. This shows decrease in solute-solvent interactions. All ligands possess negative values of β-coefficient at 293, 297 and 300 K. This shows weaker interaction between solute and solvent. The solute with negative β-coefficient is characterized as 'structure breakers'. Negative values of ΔG shows evolution of energy. A resulting data may be helpful for a possible correlation between drugs activities & viscosities.

REFERENCES

1. http://www.merriam-webster.com/dictionary/viscosity.
2. Frank F. and Ives D.S.G., *Quart. Rev.*, 20(1), (1966).
3. Naik A.B., *Ph.D. Thesis* S.G.B.A.U., Amravati (2007).
4. Deshmukh C.N., Doshi A.G., Raghuwanshi P.B., *Asian J. Chem.*, 12 (3), 899, (2000).
5. Arbad B.R., Patil C.S., Shankarwar A.G., *Asian J. Chem.*, 13 (1), 231, (2001).
6. Jauhar S.P., Sandhu S., *Ind. J. Chem.*, 39 (4), 392, (2000).
7. Gangani B.J., Parsania P.H., *Arch. of App. Sci. Res.*, 7 (1), 10-14, (2015).
8. Agrawal P.B., *Ph.D. Thesis* S.G.B.A.U., Amravati (2001).
9. Maria C. M. Sequeira, Helena M. N. T. Avelino, Fernando J. P. Caetano, and João M. N. A. Fareleira, J. Chem. Eng. Data, 66, 4, 1763–1772, (2021)
10. Mahajan M. M. and Raghuwanshi P. B., Int. Res. J. of Natural and App. Sci., 3 (7), 127-137, (2016).
11. Wagh S.P., *Int. J. of Chem. and Phy. Sci.*, 4, 69-72, (2015).
12. Parthasarathi S., Saravanakumar K., Buskaran R.., Kubendran T. R.., *Int. J. of Sci. and Tech.*, 1(2), 96-101 (2011).
13. Serdyuk I. N., Zaccai N. R.., Zaccai J., *Methods in Molecular Biophysics: Structure, Dynamics, Function*, Cambridge University Press, (2007).
14. Dash U.N., Roy G.S., Talikdar M., Moharatha D., *Ind. J. Pure and Appl. Phys.,* 48, 651-657, (2010).