STUDY OF VISCOSITY BEHAVIOR OF SCHIFF BASE N–(2-HYDROXYBENZYLIDENE) PYRIDINE-2-AMINE AND ITS DERIVATIVES IN DIFFERENT PERCENTAGE OF 1,4-DIOXANE-WATER AT 293, 297 AND 300 K

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ABSTRACT

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 properties of Schiff bases have been used to obtain information about intermolecular interaction. This provokes to investigate the densities and viscosities of synthesized substituted Schiff's bases and measurements of 0.01 M solution of N–(2-hydroxybenzylidene) pyridine-2-amine and its derivatives in different percentage of 1,4-dioxane-water at varying temperatures. The β-coefficient and viscosity were calculated for all four ligands at different temperatures of 293, 297 and 300 K. The molecular interactions were studied from β-coefficient values.

KEYWORDS

Schiff bases, Density, viscosity, interaction, β-coefficient, parameters.

1. 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 (A_1-A_4) in different percentage of 1,4-dioxane-water mixture, at varying temperatures. N–(2-hydroxybenzylidene) pyridine-2-amine and its substituted derivatives were synthesized in the laboratory preferring microwave radiations over conventional route (10). In the present study, attempt has been made to calculate β-coefficient and viscosity for all four ligands at different temperatures of 293, 297 and 300 K in binary mixture of dioxane-water.

Following is the structure of the ligand –
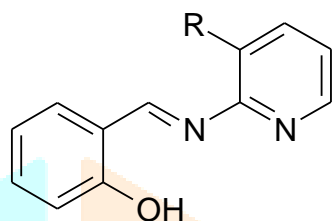
N - (2 - hydroxybenzylidene)
pyridine - 2 - amine

Where,
R = -H, -OH, -NO_2, -CH_3
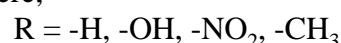
1. N-(2'-hydroxybenzylidene) pyridine-2-amine (A_1)
2. N-(2'-hydroxybenzylidene)-3-hydroxy pyridine-2-amine (A_2)
3. N-(2'-hydroxybenzylidene)-3-nitropyridine-2-amine (A_3)
4. N-(2'-hydroxybenzylidene)-3-methylpyridine-2-amine (A_4)

2. Experimental and Instrumentation

2.1 Experimental

The chemicals used for synthesis were of L.R. grade. The ligands (A1-A4) 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 different percentage (75%, 80%, 85%, 90%, 95% and 100%) of 1,4-dioxane-water mixture. The density and the viscosity measurements of the ligand solutions were done at 293, 297 and 300 K following the standard protocol.

2.2 Instrumentation

All the weighing in the present study was made on Citizen CY 104 one pan digital balance. The densities of the solution were determined by standardize capillary pyknometer having a bulb of volume of about 10 cm^3 and capillary having an internal diameter of 1 mm. The viscosities of the ligand solutions were measured with the help of Oswald's viscometer. The viscometer was kept in elite thermostatic water bath (±0.10C) to maintain the temperature constant.

3. Result and Discussion

The relative viscosity, η_r 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)--

$$\frac{\eta_r - 1}{\sqrt{C}} = A + \beta \sqrt{C}$$

where, C = molar concentration of ligands

A = Falkenhagen coefficient

β = Jones-Dole coefficient

Falkenhagen coefficient (A) is the measure of solute-solute interactions and Jones-Dole coefficient (β) is the measure of solute-solvent interactions.

'$\eta_r-1 /\sqrt{C}$' is also known as 'specific viscosity' denoted by 'η_{sp}'.

In the present study, the parameters like relative viscosity, density and specific viscosity of 0.01 M solution of ligands A1, A2, A3 and A4, prepared in different percentages of 1,4-dioxane-water mixture were calculated at temperature 293, 297 and 300 K. The experimental data obtained was tabulated (table no. 1 to 4) as under-

Table 1: Ligand A₁ in 1,4-dioxane-water mixture at 293 K, 297 K and 300 K

% Dioxane	Density ds x 10³ (kg m⁻³)	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10³ (kg m⁻³)	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10³ (kg m⁻³)	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})
	293 K				297 K				300 K			
75	0.99882	88	0.920959	-0.79041	1.00131	74	0.776373	-2.23627	0.99747	71	0.742042	-2.57958
80	0.99859	84	0.951287	-0.48713	0.99891	73	0.826979	-1.73021	0.99693	68	0.76881	-2.3119
85	0.99855	78	0.915346	-0.84654	0.99861	73	0.856722	-1.43278	0.99588	67	0.784157	-2.15843
90	0.99703	65	0.763549	-2.36451	0.99727	66	0.775483	-2.24517	0.99517	59	0.691775	-3.08225
95	0.99562	64	0.809095	-1.90905	0.99722	60	0.759745	-2.40255	0.99456	52	0.656689	-3.43311
100	0.99547	62	0.793803	-2.06197	0.9962	53	0.679071	-3.20929	0.99436	49	0.626661	-3.73339

Table 2: Ligand A₂ in 1,4-dioxane-water mixture at 293 K, 297 K and 300 K

% Dioxane	Density ds x 10³ (kg m⁻³)	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10³ (kg m⁻³)	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10³ (kg m⁻³)	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})
	293 K				297 K				300 K			
75	1.00168	95	0.997064	-0.02936	0.99902	76	0.795533	-2.04467	0.99726	72	0.752335	-2.47665
80	1.0007	89	1.010041	0.100414	0.99835	76	0.860482	-1.39518	0.99702	68	0.768879	-2.31121
85	1.00052	82	0.964185	-0.35815	0.99744	72	0.843996	-1.56004	0.99647	66	0.77291	-2.2709
90	0.99907	77	0.906363	-0.93637	0.99664	67	0.786735	-2.13265	0.99598	57	0.668869	-3.31131
95	0.99714	72	0.911621	-0.88379	0.99525	56	0.707695	-2.92305	0.99533	51	0.644559	-3.55441
100	0.99599	70	0.896698	-1.03302	0.9947	49	0.626875	-3.73125	0.99476	48	0.614119	-3.85881

Table 3: Ligand A₃ in 1,4-dioxane-water mixture at 293 K, 297 K and 300 K

% Dioxane	Density ds x 10^3 (kg m^{-3})	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10^3 (kg m^{-3})	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10^3 (kg m^{-3})	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})
75	0.99903	96	1.004893	0.048934	1.00613	78	0.822279	-1.77721	0.99923	75	0.78523	-2.1477
80	0.99878	92	1.042085	0.420845	1.00119	77	0.874284	-1.25716	0.99839	70	0.792581	-2.07419
85	0.99863	88	1.032781	0.32781	0.99904	75	0.880572	-1.19428	0.99764	67	0.785542	-2.14458
90	0.99744	79	0.928388	-0.71612	0.99643	62	0.72787	-2.7213	0.99747	58	0.681622	-3.18378
95	0.99577	75	0.9483	-0.517	0.99555	57	0.720549	-2.79451	0.99724	54	0.683784	-3.16216
100	0.99535	72	0.921725	-0.78275	0.99479	54	0.690905	-3.09095	0.99635	50	0.64073	-3.5927

Table 4: Ligand A₄ in 1,4-dioxane-water mixture at 293 K, 297 K and 300 K

% Dioxane	Density ds x 10^3 (kg m^{-3})	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10^3 (kg m^{-3})	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})	Density ds x 10^3 (kg m^{-3})	Time flow t_s (sec)	Relative viscosity (η_r)	Specific viscosity (η_{sp})
75	1.00086	95	0.996247	-0.03753	1.00203	78	0.818928	-1.81072	0.99875	76	0.795318	-2.04682
80	0.9993	90	1.019961	0.199612	1.00037	76	0.862223	-1.37777	0.99834	69	0.781219	-2.18781
85	0.99795	89	1.043806	0.438059	0.99823	69	0.80947	-1.9053	0.997	67	0.785038	-2.14962
90	0.99667	83	0.974642	-0.25358	0.99728	64	0.751991	-2.48009	0.99624	59	0.692519	-3.07481
95	0.99655	77	0.974351	-0.25649	0.99533	59	0.745667	-2.54333	0.99606	54	0.682975	-3.17025
100	0.99552	72	0.921882	-0.78118	0.99455	51	0.652364	-3.47636	0.99569	52	0.665918	-3.34082

From the above table, 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 graphs are plotted between $(\eta_r - 1)/\sqrt{C}$ vs % composition (fig 1 to 3). The graph for each system gives a linear straight line showing validity of Jones-Dole equation. The slope of the straight line gives values of β-coefficient and from the intercept of that line; 'A' can be known.
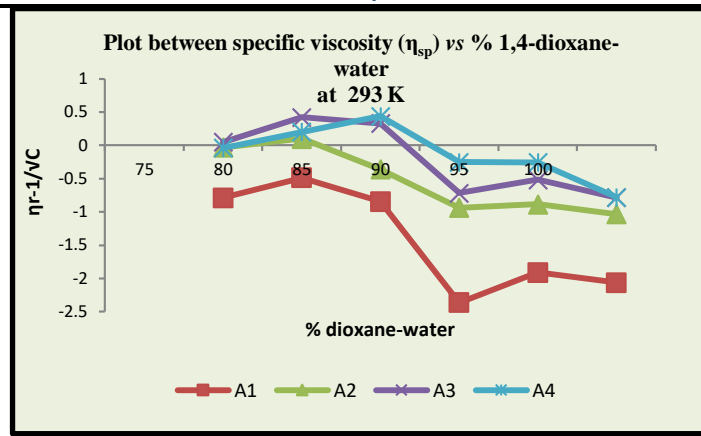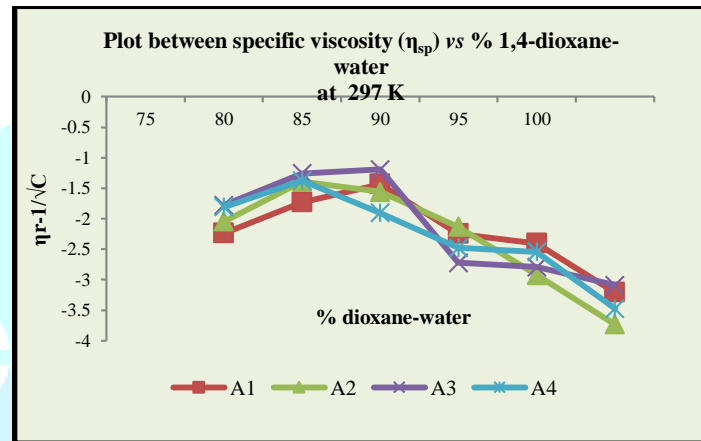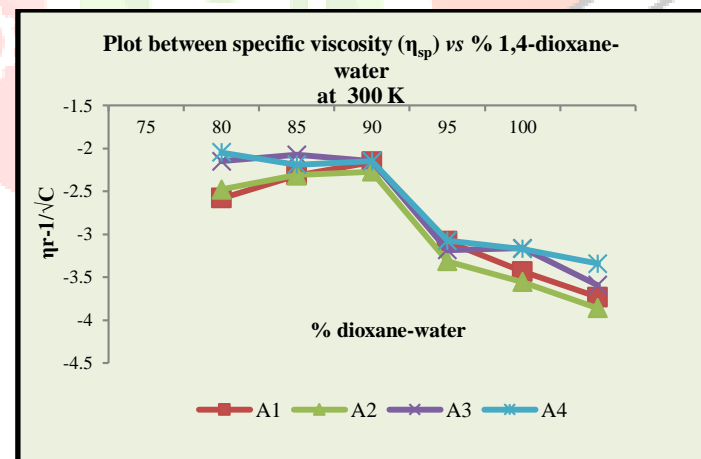
Fig. 1

Fig. 2

Fig. 3

From the graphs $(\eta_r-1)/\sqrt{c}$ *vs* % composition, 'A' which is the measure of solute-solute interactions and 'β' which is the measure of solute-solvent interactions has been calculated. 'A' is known as the Falkenhagen coefficient which characterizes the ionic interaction and 'β' is the Jones-Dole or viscosity β-coefficient which depends on the size of solute and the nature of solute-solvent interaction (14). The large and small values of A shows the stronger and weaker solute-solute Interactions respectively as listed in table 5.

Table 5 : β-Coefficient and 'A' values in 1,4-dioxane at different temperatures

Ligands	293 K		297 K		300 K	
	A-Coefficient	β-coefficient	A-Coefficient	β-Coefficient	A-Coefficient	β-Coefficient
A_1	4.6608	-0.0694	1.6379	-0.044	2.1451	-0.0575
A_2	3.7512	-0.0489	4.4967	-0.0777	2.8765	-0.0667
A_3	3.8049	-0.0458	4.2146	-0.0726	3.0465	-0.0659
A_4	2.7739	-0.033	3.9342	-0.0709	2.5096	-0.0591

From table 5, 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 A-coefficient at 293 K are in the following order -

$$A_1 > A_3 > A_2 > A_4$$

This shows that the solute-solute interaction is highest among the molecules of ligand A1 and so they tend to interact with solvent molecule to lesser extent leading decrease in solute-solvent interaction which is shown by lowest β-coefficient value.

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

Thus the β-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 293, 297 and 300 K may indicate strong ionic interaction.

The data of A and β-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 the three temperatures.

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