

Viscosity Behaviour of 2-Aryl-2-Dihydronaphtho (1, 8-Ef) (1, 2, 4)-Triazepine-3(4H) Thiones in Different Percentages of Solvent

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ABSTRACT

The viscosities and densities of several 2-Aryl-2-dihydronaphtho(1,8-ef)(1,2,4)-triazepine-3(4H) thiones(VI a-e) have been obtained in good yield after the isomerization N-(1H-naphtho) (1,8-cd) thiadiazepine-3(4H)-ylidene anilines (Va-Ve). The viscosities and densities of these synthesized compounds (VI a-e) in different percentages of acetone- water, ethanol-water, dioxane-water mixtures have been measured. From the data obtained the relative viscosities have been calculated which are used to measure the molecular interactions in the solutions and to study the viscosity behavior of substituted 2-aryl-2-dihydronaphtho(1,8-ef)(1,2,4)-triazepine-3(4H) thiones on the basis of the presence of different substituents.

Key words – Viscosity, Substituted triazepine-3(4H) thiones

I. INTRODUCTION

Triazepinethiones are shown to have utility as a black toning agent for laminated photographs¹. They have also been shown to possess superior bone resorption-inhibitory action and are useful as therapeutic agents for osteoporosis². The present work deals with the study of molecular interactions of substituted triazepine-3(4H) thiones (VI a-e) in different percentages of acetone-water, ethanol-water and dioxane-water mixtures at (29±0.1°C) and their viscosity behavior on the basis of presence of different substituents. Viscosity is one of the important properties of liquids. It implies resistance to flow. Viscosity measurements, like other transport properties of electrolytes, provides useful information about solute-solute and solute-solvent interactions in non aqueous and aqueous solutions³⁻⁵. Molecular interactions of binary mixtures have also been studied by many workers⁶⁻⁹. Many attempts have been made to study viscosities of binary liquid mixtures, but no satisfactory results seems to have been reported⁸.

II. EXPERIMENTAL

Synthesis of 1-(8-Amino naphthalene-1-yl)-3-(4-methyl phenyl) thiourea (IIIa):

1-8-Diamino naphthalene (0.01 mole) was added to phenyl isothiocyanate (0.01 mole). To this mixture 10 ml chloroform was added as solvent. The reaction mixture was reflux for 1 hr. After completion of reaction the

solvent was vacuum distilled when granular solid was obtained. It was crystallized from ethanol m.p. 214°C, other thiocarbamides were prepared by following similar procedure.

Synthesis of 4-Methyl-1-N-(3Z)-1-H-naphtho(1,8-cd) (1,2,6) thiadiazepine-3(4H)-ylidine aniline(Va):

1-(8-Amino naphthalene-1-yl)-3-(4-methyl phenyl) thiourea (IIIa) was made into paste with ethanol. To this iodine solution in ethanol was added dropwise with stirring the reaction mixture. The addition was continued till violet colour of iodine persisted. The reaction mixture was left at room temperature for overnight. The granular solid (IVa) was obtained. On basification of (IVa) with dilute ammonium hydroxide afforded free base (Va).

Isomerization of 4-Methyl-1-N-(3Z)-1-H-naphtho(1,8-cd) (1,2,6) thiadiazepine-3(4H)-ylidine aniline(Va) to 2-(4-methyl phenyl)-1,2-dihydronaphtho (1,8-ef)(1,2,4)-triazepine-3(4H) thione was done by refluxing (Va) with 10 ml 5% ethanolic sodium hydroxide solution for 1 hr. The mixture was poured in cold water. The isolated solid (VIa) was filtered, dried and crystallized from ethanol.

The other compounds (VIb-VIe) were obtained by isomerization of related thiadiazepines(Vb-Ve). Where, a-(4-methyl), b-(3-methyl), c-(2-methyl), d-(H), e-(4-chloro) are substituents.

The structure of these compounds were established on the basis of elemental analysis, equivalent weight determination, IR and PMR spectral data. The solvents used were of AR grade and doubly distilled water was used. Weighing was made on Shimadzu Japan BL-2204 balance (± 0.001 g). The densities of ligand solutions and solvents were determined by a bicapillary pycnometer ($\pm 0.2\%$). The viscosities were measured by means Ostwald's viscometer ($\pm 0.11\%$ Kgm⁻¹s⁻¹) which was kept in equilibrium Elite thermostatic water bath ($\pm 0.1^\circ$ C). The solutions were prepared in different percentages (70,80,90 and 100%) of acetone-water, ethanol-water and dioxane-water mixtures. For each measurement sufficient time allowed to maintain constant temperature by attaining thermal equilibrium in a thermostat.

III. RESULTS AND DISCUSSION

The relative viscosity of each of the ligand solution is determined by using the empirical formula,

$$n_r = d_s \times t_s / d_b \times t_b$$

Where n_r indicates relative viscosity of ligand solution, d_s is density of ligand solution and d_b is density of respective solvent; t_s is time of flow for ligand solution and t_b is time of flow for respective solvent.

The relative viscosity and density data for ternary mixtures in different percentages of solvents are obtained in Table 1 to 3. It can be seen that relative viscosity increases with decrease in the percentage of acetone, ethanol and dioxane, which may be due to increase in molecular interactions. Also change in the structure of solvent or solution as a result of hydrogen bond formation or disruption leads to decrease or increase in interactions. Solutes can occupy interstitial spaces in the solvent. The increase in viscosity arises from the fact that solute particles lie across the fluid stream lines and are subjected to torsional force^{11,12}.

Acetone-Water > Ethanol-Water > Dioxane-Water

This may be due to the effect of greater polarity of acetone as compared to the less polar ethanol and non-polar dioxane solvent. The polar compounds are having more viscosity than non-polar compounds. In polar compounds cohesive forces attributed to the presence of different types of intermolecular forces which results increase in viscosity.

It can be seen from Tables 1 to 3 that the order of relative viscosities in compounds is VIe>VIa>VIc > VIb>VIId.

Also as molecular weight increases, viscosity increases and is related to density. Molecular weight is directly proportional to density as the density increases distance between ligand molecules decreases. That result cohesive forces between molecules increases and viscosity of liquid increases.

Table-1 Viscosity Data for Substituted Triazepine-3(4H)-thiones (VIa-VIe) Acetone-Water Mixtures

Compounds/Relative viscosity (n_r) at ($29 \pm 0.1^\circ\text{C}$).						
Percentage of acetone	VIa	VIb	VIc	VIId	VIe	
70	1.2615	1.2412		1.2448	1.2310	1.2941
80	1.2334	1.2110		1.2123	1.985	1.2549
90	1.1825	1.1771		1.1882	1.1620	1.2013
100	1.1189	1.1028		1.1030	1.1022	1.1238

Table-2 Viscosity Data for Substituted Triazepine-3(4H)-thiones (VIa-VIe) Ethanol-Water Mixtures

Compounds/Relative viscosity (n_r) at ($29 \pm 0.1^\circ\text{C}$).						
Percentage of ethanol	VIa	VIb	VIc	VIId	VIe	
70	1.1532	1.1321		1.1449	1.1120	1.1648
80	1.1270	1.1112		1.1123	1.1079	1.1383
90	1.1069	1.1012		1.1023	1.0076	1.1114
100	1.0117	1.0103		1.0108	1.0094	1.0125

Table-3 Viscosity Data for Substituted Triazepine-3(4H)-thiones (VIa-VIe) Dioxane-Water Mixtures

Compounds/Relative viscosity (n_r) at ($29 \pm 0.1^\circ\text{C}$).						
Percentage of dioxane	VIa	VIb	VIc	VIId	VIe	
70	1.1421	1.1301		1.1336	1.1217	1.1598
80	1.1224	1.1202		1.1210	1.1122	1.1367
90	1.1172	1.1022		1.1092	1.1036	1.1223
100	1.1075	1.1021		1.1026	1.1002	1.1125

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