

Viscosity Behaviour of Substituted Benzo-1,3,6-Thiadiazepines in Different Percentages of Solvents

PRADIP P. DEOHATE*, PRATIBHA B. AGRAWAL and B.N. BERAD

Postgraduate Department of Chemistry,
Shri Shivaji Science College, Amravati-444603, India

The viscosities and densities of benzo-(4,5-d)-2,7-diphenylimino-1,3,6-thiadiazepine (I), benzo-(4,5-d)-2,7-di-*o*-tolylimino-1,3,6-thiadiazepine (II), benzo-(4,5-d)-2,7-di-*m*-tolylimino-1,3,6-thiadiazepine (III), benzo-(4,5-d)-2,7-di-*p*-tolylimino-1,3,6-thiadiazepine (IV), benzo-(4,5d)-2,7-di-*o*-chlorophenylimino-1,3,6-thiadiazepine (V), benzo-(4,5-d)-2,7-di-*p*-chlorophenylimino-1,3,6-thiadiazepine (VI), benzo-(4,5-d)-2,7-di-*t*-butylimino-1,3,6-thiadiazepine (VII) in different percentages of acetone-water, ethanol-water and dioxane-water mixtures have been measured. From the data the relative viscosities have been calculated which are used to measure the molecular interactions in the solutions and to study the viscosity behaviour of substituted benzo-1,3,6-thiadiazepines on the basis of the presence of different substituents.

Key Words: Viscosity, Substituted benzo-1,3,6-thiadiazepines.

INTRODUCTION

Viscosity is one of the important properties of liquids. It implies resistance to flow. Viscosity measurement, like other transport properties of electrolytes, provides useful information about solute-solute and solute-solvent interactions in non-aqueous and aqueous solutions¹⁻³. Molecular interactions of binary mixtures have also been studied by many workers⁴⁻⁷. Many attempts have been made to study viscosities of binary liquid mixtures, but no satisfactory result seems to have been obtained⁸. The present work deals with the study of molecular interactions of substituted benzo-1,3,6-thiadiazepines (I-VII) in different percentages of acetone-water, ethanol-water and dioxane-water mixtures at (29 ± 0.1°C) and their viscosity behaviour on the basis of the presence of different substituents.

EXPERIMENTAL

Benzo-(4,5-d)-2,7-diphenylimino-1,3,6-thiadiazepine (I), benzo-(4,5-d)-2,7-di-*o*-tolylimino-1,3,6-thiadiazepine (II), benzo-(4,5-d)-2,7-di-*m*-tolylimino-1,3,6-thiadiazepine (III), benzo-(4,5-d)-2,7-di-*p*-tolylimino-1,3,6-thiadiazepine (IV), benzo-(4,5-d)-2,7-di-*o*-chlorophenylimino-1,3,6-thiadiazepine (V), benzo-

*Address: Sant Krupa, Prakash Colony, Morshi-444 905, Amravati (Maharashtra), India.

(4,5-d)-2,7-di-*p*-chlorophenylimino-1,3,6-thiadiazepine (VI), benzo(4,5-d)-2,7-di-*t*-butylimino-1,3,6-thiadiazepine (VII) were prepared by the cyclization of some substituted 1,2-bis(aryl/alkyl thiocarbamido-*N*-)benzene by ethanolic iodine in presence of potassium iodide and alkali. Their structures 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 of Ostwald's viscometer ($\pm 0.11\%$ $\text{kg m}^{-1} \text{s}^{-1}$) which was kept in equilibrium with Elite thermostatic water bath ($\pm 0.1^\circ\text{C}$). 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 was allowed to maintain constant temperature by attaining thermal equilibrium in a thermostat.

RESULTS AND DISCUSSION

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

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

where η_r is 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 tabulated in Tables 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^{9,10}. Relative viscosities follow the order:

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.

It can also be seen from Tables 1 to 3 that the order of relative viscosities in compounds is V > VI > I > III > II > IV > VII. The increase in viscosity of compounds V and VI may be due to the presence of more number of free ions across the fluid stream which is because of the interaction between the electron withdrawing substituent —Cl and solvent resulting in ionic dissociation, while that of decrease in viscosity of compounds II, III, IV and VII is due to the presence of electron donating substituents like —CH₃ and —C(CH₃)₃, where no such interaction is there but to a lesser extent ion-dipole bonding may occur resulting in ionic association and decrease in number of free ions across the fluid

stream. Free ions present across the fluid stream always tend to rotate and absorb the energy, resulting in increase in the relative viscosity.

TABLE-1
VISCOSITY DATA FOR SUBSTITUTED BENZO-1,3,6-THIADIAZINES (I-VII)
ACETONE-WATER MIXTURES

Percentage of acetone	Compounds/Relative viscosity (η_r) at (29 \pm 0.1°C)						
	I	II	III	IV	V	VI	VII
70	1.2312	1.2039	1.2129	1.2027	1.2641	1.2566	0.9641
80	1.1771	0.1495	1.1508	1.1437	1.2264	1.2175	0.9239
90	0.1564	0.0901	1.1349	1.1159	1.1896	1.1772	0.8871
100	0.1007	0.0792	1.0939	1.0648	1.1474	1.1317	0.8483

TABLE-2
VISCOSITY DATA FOR SUBSTITUTED BENZO-1,3,6-THIADIAZINES (I-VII)
ETHANOL-WATER MIXTURES

Percentage of ethanol	Compounds/Relative viscosity (η_r) at (29 \pm 0.1°C)						
	I	II	III	IV	V	VI	VII
70	1.1603	1.1110	0.1361	0.1193	1.1921	1.1805	0.9500
80	1.1435	1.0854	1.1183	1.0853	1.1643	1.1536	0.8117
90	1.1004	1.0680	1.1265	1.0552	1.1314	1.1156	0.6360
100	1.0650	1.0286	1.0540	1.0355	1.0733	1.0735	0.6136

TABLE -3
VISCOSITY DATA FOR SUBSTITUTED BENZO-1,3,6-THIADIAZINES (I-VII)
DIOXANE-WATER MIXTURES

Percentage of dioxane	Compounds/Relative viscosity (η_r) at (29 \pm 0.1°C)						
	I	II	III	IV	V	VI	VII
70	1.0088	0.9755	0.9803	0.9710	1.0437	1.0318	0.8491
80	0.9643	0.9368	0.9418	0.9318	1.0037	0.9988	0.8033
90	0.9295	0.8972	0.9079	0.8957	1.9353	0.9054	0.7236
100	0.8778	0.8415	0.8522	0.8381	1.8940	0.8868	0.7207

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Contact:
Per Kolsaker
Chemistry Department, University of Oslo
Tel: +47 22 85 56 07 Fax: +47 22 85 41
E-mail: esor-9@kjemi.uio.no
<http://www.kjemi.uio.no/esor9/>