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Comparison of Molar Refraction and Polarizability Constants of Substituted Benzo-(4,5-d)-2-Arylimino-7-Aryl/Alkylimino-1,3,6-Thiadiazepines in Different Percentages of Solvents

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In different percentages of aetone-water and dioxane-water mixtures the densities and refractive indices of benzo-(4,5-d)-2-phenylimino-7-phenylimino-1,3,6-thiadiazepine (I), benzo(4,5-d)-2-phenylimino-7-*o*-tolylimino-1,3,6-thiadiazepine (II), benzo-(4,5-d)-2-phenylimino-7-*m*-tolylimino-1,3,6-thiadiazepine (III), benzo-(4,5-d)-2-phenylimino-7-*p*-tolylimino-1,3;6-thiadiazepine (IV), benzo-(4,5-d)-2-phenylimino-7-*o*-chlorophenylimino-1,3,6-thiadiazepine (V), benzo(4,5-d)-2-phenylimino-7-*p*-chlorophenylimino-1,3,6-thiadiazepine (VI) and benzo-(4,5-d)-2-phenylimino-7-*t*-butylimino-1,3,6-thiadiazepine (VII) have been measured. From the data the molar refraction and polarizability constants for the compounds have been calculated which have been used to detect the nature of dipoles and to compare the substituted benzo-(4,5-d)-2-arylimino-7-aryl/alkylimino-1,3,6-thiadiazepines on the basis of presence of different substituents.

Key Words: Molar refraction, Polarizability constants, Substituted thiadiazepines.

INTRODUCTION

The properties of liquids such as viscosity, refractive index and ultrasonic velocity of binary mixtures were studied by many workers[1–3]. Refractive indices can be measured easily with a high degree of accuracy. Oswal[4] studied dielectric constants and refractive indices of binary mixtures. Study of refractive indices in mixed solvents has been done by Agrawal *et al.*[5] and Burghate *et al.*[6] The present work deals with the comparative study of molar refraction and polarizability constant of substituted benzo-(4,5-d)-2-arylimino-7-aryl/alkylimino-1,3,6-thiadiazepines **(I–VII)** in different percentages of acetone-water and dioxane-water mixtures and also the comparison of their molar refraction and polarizability constants on the basis of presence of different substituents.

EXPERIMENTAL

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

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o-chlorophenylimino-1,3,6-thiadiazepine (V), benzo-(4,5-d)-2-phenylimino-7-*p*-chlorophenylimino-1,3,6-thiadiazepine (VI) and benzo-(4,5-d)-2-phenylimino-7-*t*-butylimino-1,3,6-thiadiazepine (VII) were prepared by the basification of substituted benzo(4,5-d)-2-arylimino-7-aryl/alkylimino-1,3,6-thiadiazepine hydrochlorides, which were prepared initially by reacting substituted 1-aryl/alkyl-3-(2′-aminophenyl)-thiocarbamides with N-phenyl isocyanodichloride in chloroform. Their structures were established on the basis of elemental analysis, equivalent weight determination and IR and PMR spectral data. The densities of solutions and solvents were determined by a bicapillary pyknometer (±0.2%). The refractive indices of solvent mixtures and solutions were measured by using Abbe's refractometer at (27 ± 0.1°C). The accuracy of Abbe's refractometer was within ±0.001 unit. Acetone-water and dioxane-water mixtures of varying composition (70, 80, 90, 100%) as well as solutions of ligands in different percentages of acetone-water and dioxane-water mixtures were prepared by taking weight. All weighings were made on Shimadzu Japan-BL 2204 balance (±0.001 g). The solvents used were of AR grade and doubly distilled water was used.

RESULTS AND DISCUSSION

The molar refraction of solvents, solvent-water mixtures are determined from

$$R_{S\text{-}W} = X_1R_1 + X_2R_2 \quad \ldots (1)$$

where R_1 and R_2 are molar refractions of solvent and water respectively.

The molar refractions of solutions in solvent-water mixtures are determined from

$$R_{mixture} = [(n^2 - 1)/(n^2 + 2)] \times (X_1M_1 + X_2M_2 + X_3M_3)/d] \quad \ldots (2)$$

where n is the refractive index of solution, d is the density of the solution, X_1, X_2, X_3 are the mole fractions of solvent, water and solute and M_1, M_2, M_3 are the molecular weights of solvent, water and solute respectively.

The molar refraction of solute is calculated as

$$R_{solute} = R_{mixture} - R_{S\text{-}W} \quad \ldots (3)$$

The polarizability constant (α) of solute is calculated as

$$R_{solute} = (4/3)\pi N_0\alpha \quad \ldots (4)$$

where N is Avogadro's number.

The values of molar refraction and polarizability constant of different solutes are presented in Tables 1–4. It shows that with increase in the percentage of acetone, the molar refraction as well as polarizability constant of the solute decreases. This may be attributed to the fact that the dipole in the ligand lies perpendicular to the longer axis of the molecules and increase in the percentage of solvent causes decrease in the dielectric constant of the medium; considerable dipole association takes place, resulting in decrease in molar refraction as well as polarizability constant because of the mutual compensation of the dipoles. But with increase in the percentage of dioxane, the molar refraction as well as

polarizability constant of the solute increases, which is due to the increase in dielectric constant of the medium causing dipole dissociation. Also these values are large in acetone due to its greater polarity as compared to non-polar dioxane solvent.

TABLE-1
MOLAR REFRACTION FOR SUBSTITUTED BENZO-(4,5-d)-2-ARYLIMINO-7-ARYL/ ALKYLIMINO-1,3,6-THIADIAZEPINES (I–VII)-ACETONE-WATER MIXTURES

Percentage of acetone (%)	Compounds/molar refraction, [R] $cm^3\ mol^{-1}$ at (27 ± 0.1°C)						
	I	II	III	IV	V	VI	VII
70	0.4918	0.4301	0.4541	0.4147	0.5800	0.5380	0.3501
80	0.3180	0.2785	0.2942	0.2828	0.4290	0.4111	0.2413
90	0.1874	0.1619	0.1687	0.1503	0.2326	0.2147	0.1362
100	0.1120	0.0715	0.0982	0.0622	0.1416	0.1409	0.0492

TABLE-2
MOLAR REFRACTION FOR SUBSTITUTED BENZO-(4,5-d)-2-ARYLIMINO-7-ARYL/ ALKYLIMINO-1,3,6-THIADIAZEPINES (I–VII)-DIOXANE-WATER MIXTURES

Percentage of dioxane (%)	Compounds/molar refraction, [R] $cm^3\ mol^{-1}$ at (27 ± 0.1°C)						
	I	II	III	IV	V	VI	VII
70	0.0837	0.0408	0.0512	0.0341	0.1202	0.1154	0.0204
80	0.1177	0.0911	0.0998	0.0930	0.1573	0.1365	0.0852
90	0.1693	0.1210	0.1362	0.1339	0.2287	0.2123	0.1035
100	0.2533	0.2301	0.2303	02080.	0.3101	0.2914	0.2035

TABLE-3
POLARIZABILITY CONSTANTS FOR SUBSTITUTED BENZO-(4,5-d)-2-ARYLIMINO-7-ARYL/ALKYLIMINO-1,3,6-THIADIAZEPINES (I–VII)-ACETONE-WATER MIXTURES

Percentage of acetone (%)	Compounds/molar refraction, $(\alpha) \times 10^{-24}\ cm^3$ at (27 ± 0.1°C)						
	I	II	III	IV	V	VI	VII
70	0.1948	0.1704	0.1799	0.1643	0.2298	0.2131	0.1387
80	0.1259	0.1103	0.1165	0.1120	0.1699	0.1628	0.0956
90	0.0742	0.0641	0.0668	0.0595	0.0921	0.0850	0.0539
100	0.0443	0.0283	0.0389	0.0246	0.0561	0.0558	0.0194

TABLE-4
POLARIZABILITY CONSTANTS FOR SUBSTITUTED BENZO(4,5-d)-2-ARYLIMINO-7-ARYL/ALKYLIMINO-1,3,6-THIADIAZEPINES (I–VII)-DIOXANE-WATER MIXTURES

Percentage of dioxane (%)	Compounds/molar refraction, $(\alpha) \times 10^{-24}$ cm^3 at (27 ± 0.1°C)						
	I	II	III	IV	V	VI	VII
70	0.0331	0.0161	0.0202	0.0135	0.0476	0.0457	0.0080
80	0.0466	0.0360	0.0395	0.0368	0.0623	0.0540	0.0337
90	0.0670	0.0479	0.0539	0.0530	0.0906	0.0841	0.0410
100	0.1001	0.0911	0.0912	0.0824	0.1228	0.1154	0.0806

It can be seen from Tables 1–4 that the order of molar refraction and polarizability constants in compounds is

V > VI > I > III > II > IV > VII

The increase in molar refraction and polarizability constants of compounds **V** and **VI** may be due the interaction between the electron withdrawing substituent —Cl and solvent resulting in dipole dissociation, while that of decrease in compounds **II, III, IV** and **VII** is due to the presence of electron donating substituents like —CH_3 and —$C(CH_3)_3$, where no such hydrogen bond formation is there but to a lesser extent ion-dipole bonding may occur resulting in dipole association.

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