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Research Article

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Ultrasonic speed and related acoustical parameters of symmetric double Schiff bases solutions at 308.15K

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ABSTRACT

Thedensity (ρ), viscosity (η) and ultrasonic speed (U) (2MHz) of DMF solutions of symmetric double Schiff bases were determined at 308.15K.Various acoustical parameters such as specific acoustical impedance (Z), adiabatic compressibility (κ_a), Rao's molar sound function (R_m), Vander Waals constant (b), internal pressure (π), free volume (V_f), intermolecular free path length (L_f), classical absorption coefficient ($(\alpha/f^2)_{Cl}$), and viscous relaxation time (τ)were determined usingρ, η and U data. Linear increase of U, Z, R, b, V_f, $(\alpha/f^2)_{Cl}$, τ and linear decrease of κ_a, L_f and π with increasing concentration of Schiff bases supported presence of strong molecular interactions in the solutions and hence solvophilic nature of the Schiff bases. Further solvation number (S_n) also supported solvophilic nature of Schiff bases. The position and nature of substituent also affected molecular interactions.

Keywords: Symmetric double Schiff bases, Ultrasonic speed, Acoustical studies, Solvation number, Molecular interaction in DMF

INTRODUCTION

Symmetric double Schiff bases or imines or azomethines have played vital role in the progress of chemical sciences [1] and used as fine chemicals, medical substrates and ligands for metal complexes [2] having industrial importance as antifungal and biological applications [3]. They are also useful as a starting material for the synthesis of drugs like antibiotics, antiallergic, antiphlogistic, anti-inflammatory, anticancer and antitumor [4, 5].

Ultrasonic technique is one of the most useful techniqueto study the molecular interactions so many researchers have observed close relation between ultrasonic speed and chemical or structural characteristic properties in solution [6, 7]. The ultrasonic speed and viscosity measurements have proved important for studying molecular and structural properties of liquid solutions [8].Therefore by measuring density of liquid and its ultrasonic speed many acoustical parameters can be determined [9]. Acoustical parameters provide information about molecular interactions, the nature and strength of interactions (solute-solute and solute-solvent interactions) in pure solvents and their solutions. It is observed that various kinds of physico-chemical interactions such as ionic or covalent, charge-transfer, hydrogen bonding, solute-solvent and solvent–solvent, ionic-dipole, etc. affect the physiological action of the drugs [10, 11]. Various pharmacokineticsprocesses involve transport of drugs across biological membrane, which can be understood by ultrasonic speed, viscosity, diffusion and thermal conductivity [12-15].

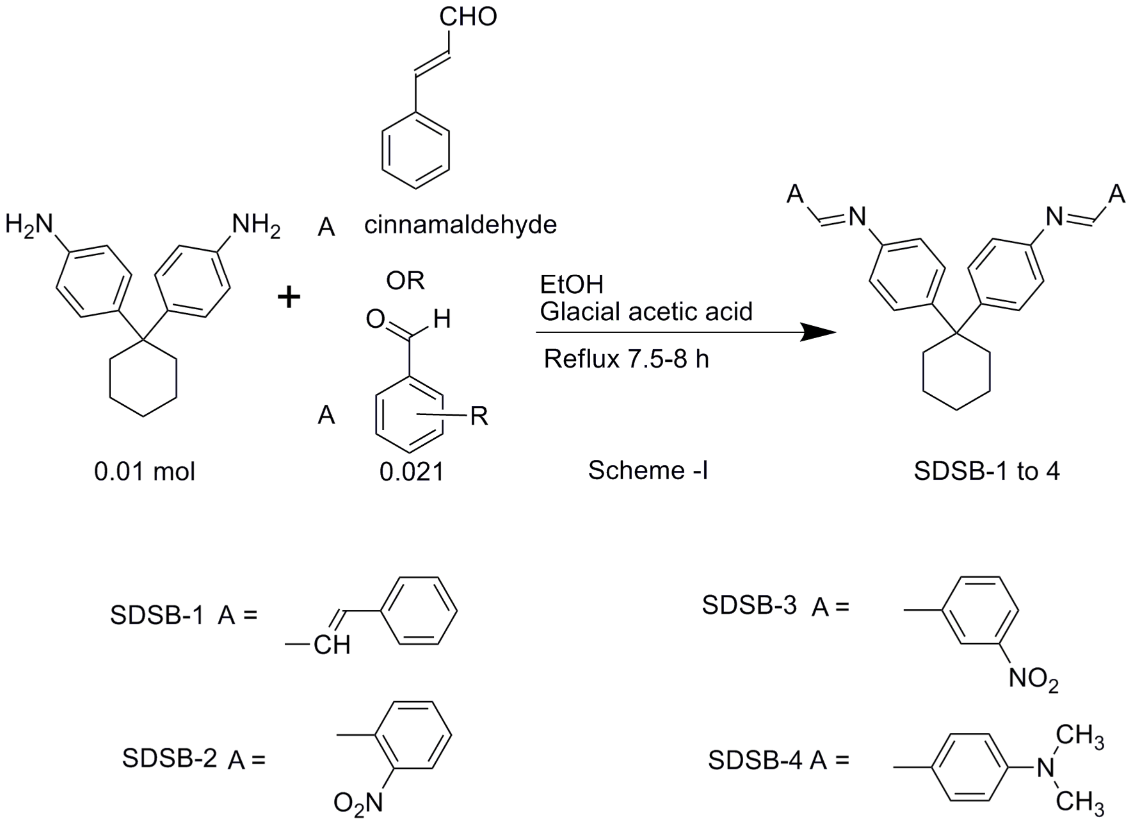
In continuation with ultrasonic speed and related study on symmetric doubleSchiff baseshere with we have reported determination of ultrasonic speed, density and viscosity of four symmetric double Schiff bases indimethylformamide at308.15K. Various acoustical parameters have been determined to understand molecular interactions in the solutions.

EXPERIMENTAL SECTION

Dimethylformamide used in the present study was of laboratory grade and purified according to literature method [16].Schiff bases (SDSB-1 to SDSB-4) were synthesized(Scheme-I)and crystallized according to our previous work [17].Fresh 0.10 mol Schiff bases solutions were prepared at room temperature and from them a series of solutions were prepared in air tight flasks.

Measurements

The density (ρ), viscosity (η) and ultrasonic speed (U) measurements of dimethylformamide (DMF) and Schiff basessolutions (SDSB-1 to SDSB-4)were measured at 308.15K by using specific gravity bottle, Ubbelohde suspended level viscometer and Mittal Enterprise Interferometer (New Delhi) Model No F-81, operating at 2 MHz, respectively. The ρ, η and U measurements were accurate to ±0.1 kg m^{-3}, 0.01 m Pa s and ±0.15%, respectively.



Scheme -I

RESULTS AND DISCUSSION

The ρ, η and U of DMFand SDSB-1 to SDSB-4 solutionsare reported in Table 1. Various acoustical parameters such as specific acoustical impedance (Z), adiabatic compressibility (κ_a), Rao's molar sound function (R_m), Vander Waals constant (b), internal pressure (π), free volume (V_f), intermolecular free path length (L_f), classical absorption coefficient ($(\alpha/f^2)_{Cl}$), viscous relaxation time (τ) and solvation number (S_n) were determined by using ρ, η and U data of Schiff bases solutionsaccording to our previous work [9] and are reported in Table2. All these parameters were correlated with concentration(C) of Schiff bases. The least squares equations andcorrelation coefficients (γ) are presented in Table3 from which it is observed that very good to excellent correlation between a given parameters and concentration of Schiff bases is observed.

From Table 1, it is evident that the density increased with increase in concentration of Schiff bases because the increase in concentration resulted increase in number of solute molecules in a given volume, which led to shrinkage in volume of the solution and hence density increased [18]. It is observed that viscosity increased with increase in concentration of Schiff bases indicating existence of strong molecular interactions, which also supported increase in ultrasonic speed with concentration.The predominance of a particular interaction in a particular solution can also be decided byκ_a. It is observed that $\kappa_a$decreased with increase in concentration of SDSB-1to SDSB-4 except SDSB-2, indicating the aggregation of solvent molecules around solute molecules [19]. Further the increasing trend of Z supported the possibility of molecular interaction between Schiff bases and DMF and is directly proportional to ultrasonic speed and inversely proportional to κ_a [20]. Linear increase in R_m and b suggested absence of any complex formation between Schiff base and DMF. The internal pressure decreased with increase in concentration of SDSB-1 to SDSB-4 confirmed that there is a strong interaction between solute and solvent molecules [21]. The decrease in internal pressure may be due to loosening of cohesive forces leading to breaking the structure of the solute at higher concentration due to weakening of intermolecular forces of attraction and as a consequence the internal pressure should fall.SDSB-1 to SDSB-4 showed a strongsolvent-solute interaction over the concentration range studied.

Free volume is the average volume in which the center of molecule can move due to repulsion of the surrounding molecules. Free volume increased with increase in concentration of SDSB-1 to SDSB-4. The increase in molecular association caused a decrease in free volume. The increase in free volume may be due to lose packing of the molecules inside the shield, which may be brought about by weak molecular interactions [22]. Thus free volume is an inverse function of internal pressure and hence decreases in internal pressure led to increase in free volume [23] indicating weak solute–solvent interaction. The structure forming tendency is observed due to intramolecular hydrogen bonding between proton of azomethine and polar oxygen of nitro group present in ortho position, the intermolecular H-bonding is observed in other Schiff bases. It is observed that L_f decreased with the increase in concentration of SDSB-1 to SDSB-4. Decrease in intermolecular free path length led to positive deviation in ultrasonic speed and negative deviation in adiabatic compressibility. Decrease in L_f indicated that the molecules are nearer in the system [24]. The values of intermolecular free path length also supported solute-solvent interactions. Both$(\alpha/f^2)_{cl}$ and τ depend on ρ, η and U at a given temperature. Increase of $(\alpha/f^2)_{cl}$ and τ with C can be explained in terms of motion of intermolecular forces. A contribution of acoustical relaxation is accounted due to entropy fluctuation associated in solution of dynamically formed physical entity. The presences of polar groups in the solute molecule enhanced molecular interactions. Thus, various acoustical parameters suggested the solvophilic nature of Schiff bases in DMF and it is further supported by positive values S_n (Table4). A solvation number is the number of the solvent molecules attached to the central atom or ion by their translational degree of freedom. The positive values of Sn indicated appreciable solvation of solutes, which confirmed structure forming nature of the solutes. It is observed that Sn increased with increase in concentration of Schiff bases, which supported increasing solute-solvent interaction.As solute concentration increases, attraction between solute and solvent increases. The concentration and dielectric constant of the medium play an important role in the determining molecular interactions occurring in the solutions [25].

Table1 Density, viscosity and ultrasonic speed of DMF and SDSB-1 to SDSB-4 solutions at 308.15K

Conc., mol lit^{-1}	**Density ρ, kg m^{-3}**	**Viscosity η,mPa s**	**U, ms^{-1}**	**Conc., mol lit^{-1}**	**Density ρ, kg m^{-3}**	**Viscosity η,mPa s**	**U, ms^{-1}**
0	927.5	0.815	1458.6	**0**	927.5	0.815	1458.6
DMF-SDSB-1				**DMF-SDSB-2**			
0.01	952.9	0.871	1485.8	**0.01**	954.1	0.945	1485.2
0.02	955.3	0.918	1492.0	**0.02**	957.7	1.004	1492.4
0.04	957.1	0.965	1498.8	**0.04**	960.5	1.076	1499.2
0.06	959.8	0.998	1505.4	**0.06**	963.5	1.127	1507.2
0.08	962.0	1.044	1513.0	**0.08**	965.9	1.175	1515.4
0.10	963.3	1.082	1518.8	**0.10**	967.8	1.206	1521
DMF-SDSB-3				**DMF-SDSB-4**			
0.01	955.9	0.947	1485.2	**0.01**	950.4	0.916	1483.4
0.02	957.7	1.004	1492.4	**0.02**	953.0	0.970	1489.2
0.04	961.0	1.077	1499.2	**0.04**	956.7	1.027	1496.8
0.06	963.6	1.127	1507.2	**0.06**	960.1	1.069	1504.8
0.08	966.1	1.175	1515.4	**0.08**	962.7	1.097	1509.4
0.10	968.6	1.206	1521.0	**0.10**	965.1	1.135	1515.2

Table2 Acoustical parameters of SDSB-1 to SDSB-4 in DMF at 308.15K

Conc., mol lit^{-1}	**Z x 10^{-6}, kgm^{-2} s^{-1}**	**κ_ax10^{+10}, Pa $^{-1}$**	**R_m x10 ^{4}, m$^{10/3}$ s$^{1/3}$mol^{-1}**	**b x10^5, m^3**	**L_f x10^{11}, m**	**π x10^{-8}, Pa**	**V_fx 10^7, m^3**	**τ x10^{13}, s**	**$(\alpha/f^2)_{cl.}10^{14}$, s^{2}m^{-1}**
	1.382	5.505	8.935	7.764	4.71	5.037	-	5.505	-
DMF-SDSB-1									
0.01	1.393	4.754	9.012	7.685	4.57	5.077	1.643	5.521	7.328
0.02	1.401	4.702	9.261	7.991	4.54	5.038	1.596	5.753	7.603
0.04	1.407	4.651	9.776	8.426	4.52	4.843	1.618	5.981	7.869
0.06	1.411	4.597	10.277	8.848	4.49	4.637	1.672	6.115	8.009
0.08	1.415	4.541	10.783	9.271	4.46	4.478	1.692	6.323	8.241
0.10	1.147	4.500	11.295	9.701	4.44	4.313	1.731	6.49	8.426
DMF-SDSB-2									
0.01	1.393	5.989	9.044	7.814	4.56	5.264	1.463	5.989	7.952
0.02	1.401	6.279	9.338	8.048	4.53	5.221	1.414	6.279	8.296
0.04	1.407	6.648	9.918	8.548	4.51	5.021	1.41	6.648	8.744
0.06	1.411	6.866	10.504	9.041	4.48	4.795	1.449	6.866	8.982
0.08	1.415	7.062	11.094	9.535	4.45	4.585	1.491	7.062	9.189
0.10	1.147	7.183	11.680	10.029	4.42	4.389	1.559	7.183	9.312
DMF-SDSB-3									
0.01	1.393	4.742	9.026	7.799	4.56	5.276	1.459	5.989	7.952
0.02	1.401	4.688	9.328	8.048	4.53	5.221	1.414	6.278	8.296
0.04	1.407	4.63	9.913	8.543	4.51	5.025	1.409	6.648	8.745
0.06	1.411	4.569	10.503	9.040	4.48	4.568	1.449	6.865	8.982
0.08	1.415	4.507	11.091	9.532	4.45	4.507	1.491	7.062	9.189
0.10	1.417	4.463	11.668	10.019	4.42	4.463	1.558	7.178	9.306
DMF-SDSB-4									
0.01	1.396	4.78	9.072	7.841	4.58	5.172	1.532	5.837	7.759
0.02	1.401	4.732	9.36	8.082	4.55	5.124	1.484	6.119	8.103
0.04	1.407	4.665	9.938	8.569	4.52	4.789	1.509	6.386	8.413
0.06	1.411	4.6	10.513	9.053	4.49	4.676	1.558	6.56	8.597
0.08	1.415	4.559	11.085	9.539	4.47	4.444	1.638	6.669	8.712
0.10	1.417	4.516	11.658	10.022	4.45	4.254	1.691	6.827	8.885

Table3 The least square equations and correlation coefficients for SDSB- 1 to SDSB- 4 in DMFat 308.15K

Parameter, Y	**Correlation equations (Correlation coefficients, γ),**			
	DMF-SDSB-1	**DMF-SDSB-2**	**DMF-SDSB-3**	**DMF-SDSB-4**
ρ, kgm^{-3}	113.92 C+952.51(0.990)	145.67 C+954.06(0.984)	139.81 C+954.90.998)	161.75 C+949.64(0.993)
η, mPa s	2.2312C+ 0.8644(0.992)	2.8359C+0.9423(0.983)	2.51C+0.9672(0.989)	2.2986C+0.9761(0.961)
U, ms^{-1}	358.52C+1483.8(0.997)	390.9C+1483.2(0.995)	390.9C+ 1483.2(0.995)	347.18C+1481.9(0.980)
Z x 10^{-6}, kg.m^{-2} s^{-1}	0.2493C+1.3945(0.959)	0.2C+ 1.3982(0.985)	0.2C+1.3982(0.995)	0.2288C+1.396(0.978)
κ_ax10^{+10}, Pa $^{-1}$	-2.757C+4.7666(- 0.995)	-3.0907C+4.7619(-0.993)	-3.0523 C+4.7575(-0.996)	-2.903C+4.792(-0.991)
R_m x10 ^{4}, m$^{10/3}$s$^{1/3}$mol^{-1}	25.324C +8.7582(1)	29.285C +8.7499(1)	29.359C +8.7379(1)	28.483C +8.8294(1)
b x10^5,m ^{3}	21.984 C+7.5178(0.999)	24.669C+7.5613(1)	24.687C+7.5547(1)	24.247 C+7.598(1)
L_f x10^{11},m	-1.4027C+4.5758(- 0.993)	-1.4822C+4.5682(-0.996)	-1.4822C+4.5682(-0.996)	-1.3973 C+4.5822(-0.987)
π x10^{-8},Pa	-8.811 C+5.18 62(-0.996)	-10.067 C+5.3993(-0.998)	-10.243C+5.3726(-0.957)	-10.557C+5.3041(-0.998)
V_fx 10^7,m^3	1.72C+1.5586(0.991)	1.855 C +1.3533(0.946)	1.85C+ 1.3532(0.946)	2.715C+1.4131(0.986)
τ x10 ^{13},s	9.08C+5.5876(0.998)	11.11C+6.141(0.980)	11.07C+ 6.142(0.979)	8.495 C+6.0025(0.987)
$(\alpha/f^2)_{cl.}10^{14}$,s^{2}m^{-1}	-55.341C^2+7.437C+7.216(0.992)	12.385C+8.1615(0.972)	12.32C+8.1644(0.971)	9.315C+7.9831(0.983)

Table4 The solvation number of SDSB-1 to SDSB-4 in DMF at 308.15K.

Conc., mollit^{-1}	**Solvation number (S_n)**			
	DMF-SDSB-1	**DMF-SDSB-2**	**DMF-SDSB-3**	**DMF-SDSB-4**
0.01	0.568	0.654	0.635	0.715
0.02	0.98	1.09	1.09	1.22
0.04	1.98	2.2	2.2	2.46
0.06	2.62	2.9	2.89	3.11
0.08	3.12	3.41	3.4	3.59
0.1	3.51	3.84	3.83	4.17

CONCLUSION

Studied acoustical parameters confirmed solvophilic nature of the Schiff bases under investigation. The nature of solvent and solute both played an important role in understanding molecular interactions in the solutions.

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