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Density, viscosity and ultrasonic speed of halogenated symmetric double schiff bases in DMF solutions at 308.15K

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ABSTRACT

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

Keywords: Halogenated Schiff bases,ultrasonic speed, density, viscosity, acoustical parameters, molecular interactions

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INTRODUCTION

Schiff bases are widely used as analytical reagents, fine chemicals, medical substrates and ligands for metal complexes[1]. Schiff bases are well known due to their impressive applications such as the preparation of dyes, liquid crystals, and powerful corrosion inhibitors [2].Symmetric double Schiff bases are also used as starting materials of drugs in pharmaceuticalindustries due to their antitumor, anticancer, anti-inflammatory and antibacterial activities [3].

Ultrasonic technique has become a powerful tool for studying pharmacokinetics of drug and their molecularbehavior in the solutions[4]. This is because of its ability of characterizing physico-chemical behavior of liquid solution. The study of properties of pure solvents and theirsolutions find direct applications in chemical, pharmaceutical, polymer and bio-chemical industries[5-6]. Therefore by measuring density of liquids and their ultrasonic speed many acoustical parameters can be determined [7, 8]. Ultrasonic speed and related thermodynamic parameters useful for characterizing thermodynamic and physico-chemical aspects of binary liquid mixtures such as molecular association or dissociation due to various forces [9]. Density, viscosity and ultrasonic speed, data provide umpteens information about the molecular interaction between ions, dipoles, hydrogen bonding, Vanderwaals forces as well as multipolar and dispersive forces [10]. The ultrasonic speed in a solution is fundamentally related to the binding forces between the atoms or molecules and has been successfully employed in understanding the nature of molecular interactions in pure solvents and their solutions.

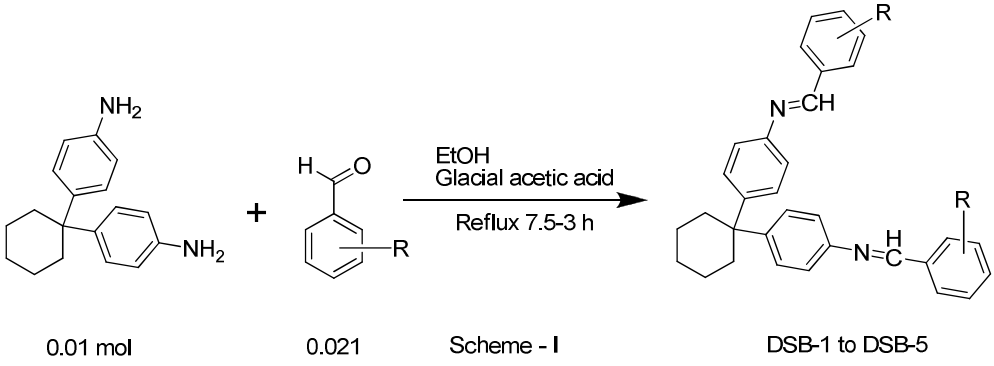
The change in ultrasonicspeed and related parameters enlighten the structural changes associated with the liquid mixtures having strongly interacting components as well as weakly interacting components [11]. Molecular interaction studies can be carried out by both spectroscopic and non-spectroscopictechniques [12]. The physical and chemical properties of polymers in solutionswas studied by number of researchers[13,14] and they correlated the

linear or non-linear variation of density, viscosity, ultrasonic speed, and related acoustical parameters with structural changes occurring in the solutions at constanttemperature and atdifferent concentrations.

In continuation with ultrasonic speedand related study on symmetric double Schiff bases [7,15, 16] here with we have reported determination of ultrasonic speed, density and viscosity of five halogenated symmetric double Schiff bases indimethylformamide at 308.15K. Various acoustical parameters have been determined to understand molecular interactions in the solutions.

MATERIALS AND METHODS

Dimethylformamide used in the present study was supplied by AlliedChemical Corporation Vadodara, and purified according to literature method [17].Schiff bases (DSB-1 to DSB-5) were synthesized (Scheme-I) and crystallized according to our previous work [18].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.



DSB-1: R = 2-Cl; DSB-2: R = 3-Cl; DSB-3: R = 4-Cl; DSB-4: R = 3- Br and DSB-5: R = 4-F

Measurements

The density (ρ), viscosity (η) and ultrasonic speed (U) measurements of dimethylformamide (DMF) and Schiff basessolutions (DSB-1 to DSB-5)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 kgm^{-3}, 0.01 mPas and ±0.15%, respectively.

RESULTS AND DISCUSSION

The ρ, η and U of DMF and DSB-1 to DSB-5 solutions are reported in Table 1. Using ρ, η and U data of Schiff bases solutions,various acoustical parameters such as specific acoustical impedance(Z), adiabatic compressibility(K_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 according to our previous work [7, 15, 16] and are reported in Table 1. Various acoustical parameters are correlated with concentration(C) of Schiff bases. The least square equations and correlation coefficients (γ) are presented in Table 2 from which it is observed that fairly good to excellent correlation between a given parameter and concentration of halogenated Schiff bases is observed. From Table 1, it is evident that the density increased with increasing concentration of Schiff base because theincreasingconcentration resulted increase in number of solute molecules in a given volume, which led to shrinkage in volume of the solution and hence density increased [19]. The law of addivity is observed in present case confirming that the density of Schiff bases is greater than that of DMF. It is observed that viscosity increased with increasing concentration of Schiff bases indicating existence of strong molecular interactions, which also supported increase in ultrasonic speed with concentration. The increasing viscosity and ultrasonic speed with increasing concentration of Schiff bases confirmed strong molecular interactionsin the solutionsof DSB-1 to DSB-5 [20].

The predominance of a particular interaction in a particular solution can also be decided byK_a. It is observed that $K_a$decreased with increasing concentration of DSB-1 to DSB-5 indicating the aggregation of solvent molecules around solute molecules [21]. Further the increasing trend of Z supported the possibility of molecular interactions between Schiff bases and DMF and is directly proportional to ultrasonic speed and inversely proportional to K_a [22]. Linear increase in R_m and b suggested absence of any complex formation between Schiff base and DMF. The internal pressure decreased with increasing concentration of DSB-1 to DSB-5 confirming strong molecular interactions between solute and solvent molecules [23]. The decrease in internal pressure is due to loosening of cohesive forces leading to breaking of the structure formed as a result of molecular interactions at higher

concentration due to weakening of intermolecular forces of attraction. Studied acoustical parameters suggested the structure forming tendency of the Schiff bases in DMF. Both intra and intermolecular H-bonding are formed in the solutions. The azomethine proton can form intramolecular H….Cl with DSB-1, while in case of DSB-2 to DSB-5 it can form intermolecular –H---X (X= Cl, Br and F) bonding with methyl protons of DMF. The lone pair of electrons of azomethine can form H-bond with methyl protons of DMF. The dipole-dipole interactions of opposite type can favor structure forming tendency, while of the same type break the structure formed previously. Increasing concentration of the Schiff base may result in increasing solute-solute interaction and as a consequence weakening of the cohesive forces resulted in decreasing internal pressure and increasing free volume.

Table1 Density, viscosity, ultrasonic speed and acoustical parameters of DSB-1 to DSB-5 in DMF at 308.15K

	Conc. moldm^{-3}						
Parameter	**0**	**0.01**	**0.02**	**0.04**	**0.06**	**0.08**	**0.1**
DSB-1-DMF							
ρ, kgm^{-3}	927.5	950.5	954.0	957.1	959.6	962.3	964.5
η, mPa s	0.815	0.866	0.916	0.952	1.009	1.040	1.070
U, ms-1	1458.6	1485.0	1492.4	1505.4	1509.2	1513.0	1519.2
Z x 10-^{6} kg m^{-2}s^{-1}	1.382	1.393	1.401	1.407	1.411	1.415	1.417
κ_α x 10^{10} Pa^{-1}	5.067	4.771	4.706	4.610	4.575	4.539	4.493
R x 10^{4}, m$^{10/3}$ s$^{1/3}$ mol^{-1}	8.935	9.053	9.315	9.870	10.407	10.937	11.474
b x10^{5}, m^{3}	7.764	7.823	8.037	8.495	8.952	9.403	9.855
L$_f$ x10^{11}, m	4.71	4.57	4.54	4.50	4.48	4.46	4.44
πx10^{-8} , Pa	5.037	5.024	5.005	4.756	4.597	4.399	4.218
V$_f$ x 10^{7} m^{3}	-	1.661	1.610	1.680	1.677	1.735	1.794
τ x10^{13} ,s	5.505	5.510	5.752	5.854	6.159	6.306	6.437
(α/f^{2})cl.10^{14}, s^{2}m^{-1}	-	7.317	7.600	7.668	8.047	8.218	8.355
DSB-2- DMF							
ρ, kgm^{-3}	927.5	948.5	952.1	956.3	960.3	963.1	965.6
η, mPa s	0.815	0.880	0.927	0.991	1.032	1.055	1.088
U, ms-1	1458.6	1487.6	1493.2	1501.4	1505.6	1509.0	1513.2
Z x 10-^{6} kg m^{-2}s^{-1}	1.382	1.393	1.401	1.407	1.411	1.414	1.417
κ_α x 10^{10} Pa^{-1}	5.067	4.771	4.706	4.610	4.575	4.539	4.493
R x 10^{4}, m$^{10/3}$ s$^{1/3}$ mol^{-1}	8.935	9.073	9.336	9.870	10.390	10.916	11.443
b x10^{5}, m^{3}	7.764	7.840	8.051	8.502	8.945	9.393	9.841
L$_f$ x10^{11}, m	4.71	4.57	4.54	4.51	4.49	4.47	4.45
πx10^{-8} , Pa	5.037	5.070	5.025	4.855	4.656	4.436	4.256
V$_f$ x 10^{7} m^{3}	-	1.627	1.584	1.577	1.617	1.696	1.751
τ x10^{13} ,s	5.505	5.588	5.823	6.129	6.321	6.414	6.558
(α/f^{2})cl.10^{14}, s^{2}m^{-1}	-	7.408	7.689	8050	8.279	8.382	8.547
DSB-3- DMF							
ρ, kgm^{-3}	927.5	952.6	956.8	959.2	961.9	963.3	964.4
η, mPa s	0.815	0.892	0.934	0.961	0.995	1.031	1.081
U, ms-1	1458.6	1485.2	1495.0	1503.0	1505.4	1509.2	1515.2
Z x 10-^{6} kg m^{-2}s^{-1}	1.382	1.393	1.401	1.407	1.411	1.415	1.417
κ_α x 10^{10} Pa^{-1}	5.067	4.759	4.676	4.615	4.587	4.558	4.517
R x 10^{4}, m$^{10/3}$ s$^{1/3}$ mol^{-1}	8.935	9.033	9.291	9.840	10.369	10.913	11.465
b x10^{5}, m^{3}	7.764	7.805	8.012	8.474	8.927	9.391	9.856
L$_f$ x10^{11}, m	4.71	4.57	4.53	4.50	4.48	4.47	4.45
π x10^{-8} , Pa	5.037	5.125	5.06	4.791	4.577	4.385	4.236
V$_f$ x 10^{7} m^{3}	-	1.589	1.568	1.653	1.708	1.756	1.771
τ x10^{13} ,s	5.505	5.661	5.825	5.914	6.083	6.264	6.510
(α/f^{2})cl.10^{14}, s^{2}m^{-1}	-	7.517	7.684	7..759	7.967	8.184	8.472
DSB-4- DMF							
ρ, kgm^{-3}	927.5	953.3	956.9	960.3	964.1	967.0	969.3
η, mPa s	0.815	0.899	0.968	1.052	1.127	1.186	1.238
U, ms-1	1458.6	1483.2	1489.2	1499.4	1511.0	1519.2	1525.4
Z x 10-^{6} kg m^{-2}s^{-1}	1.382	1.393	1.401	1.407	1.411	1.415	1.417
κ_a x 10^{10} Pa^{-1}	5.067	4.768	4.712	4.632	4.543	4.481	4.433
R x 10^{4}, m$^{10/3}$ s$^{1/3}$ mol^{-1}	8.935	9.138	9.509	10.278	11.039	11.795	12.551
b x10^{5}, m^{3}	7.764	7.900	8.211	8.860	9.496	10.133	10.772
L$_f$ x10^{11}, m	4.71	4.57	4.55	4.51	4.46	4.43	4.41
π x10^{-8} , Pa	5.037	5.075	5.015	4.763	4.521	4.285	4.070
V$_f$ x 10^{7} m^{3}	-	1.597	1.533	1.539	1.567	1.649	1.679
τ x10^{13} ,s	5.505	5.719	6.082	6.499	6.824	7.081	7.317
(α/f^{2})cl.10^{14}, s^{2}m^{-1}	-	7.603	8.053	8.547	8.906	9.198	9.459
DSB-5- DMF							
ρ, kgm^{-3}	927.5	950.0	853.5	956.3	959.1	962.5	964.6
η, mPa s	0.815	0.882	0.937	0.984	1.035	1.073	1.103

U, ms-1	1458.6	1511.6	1518.8	1524.8	1529.4	1535.2	1539.0
Z x 10-^{6} kg m^{-2}s^{-1}	1.382	1.393	1.401	1.407	1.411	1.415	1.417
κ_a x 10^{10} Pa^{-1}	5.067	4.607	4.547	4.498	4.457	4.408	4.377
R x 10^{4}, m$^{10/3}$ s$^{1/3}$ mol^{-1}	8.935	9.047	9.298	9.769	10.232	10.686	11.147
b x10^{5}, m^{3}	7.764	7.795	7.977	8.373	8.764	9.143	9.533
L_f x10^{11}, m	4.71	4.49	4.46	4.44	4.42	4.40	4.38
π x10^{-8} , Pa	5.037	5.065	5.061	4.880	4.710	4.578	4.414
V_f x 10^{7} m^{3}	-	1.708	1.581	1.594	1.596	1.629	1.673
τ x10^{13} ,s	5.505	5.417	5.677	5.899	6.150	6.303	6.438
(α/f^2)cl.10^{14}, s^{2}m^{-1}	-	7.067	7.371	7.629	7.929	8.096	8.249

Table 2: The Least square equations and correlation coefficients for DSB- 1 to DSB- 5 inDMF at 308.15K

Parameter	Least square equations (Correlation coefficients, γ)				
	DSB-1	**DSB-2**	**DSB-3**	**DSB-4**	**DSB-5**
ρ, kg.m^{-3}	147.78 C+950.36 (0.987)	186.33C+948.02 (0.988)	96.5C+955.33 (0.984)	173.56C+952.86 (0.990)	156.38 C+949.59 (0.991)
η, mPa s	2.2458C+0.8608 (0.988)	2.2184 C+0.8809 (0.975)	1.9392C+ 0.8821 (0.993)	3.6899C+0.8877 (0.990)	2.3732C+0.8797 (0.985)
U, ms^{-1}	306C+1489.5 (0.965)	272.11 C+1487.6 (0.977)	292.66C+1487 (0.956)	478.74C+ 1479.8 (0.995)	289.21C+1511.5 (0.985)
Z x 10^{-6}, kg.m^{-2} s^{-1}	0.2 C+ 1.3982 (0.953)	0.2447C+1.3945 (0.958)	0.2C+1.3982 (0.985)	0.2C+1.3982 (0.985)	0.2493C+1.3945 (0.959)
κ_ax10^{+10}, Pa^{-1}	-2.9107 C+4.7661 (-0.996)	-2.5868C+4.7653 (-0.980)	-2.3863C+4.742 (-0.955)	-3.7542C+4.7888 (-0.993)	-2.4384C+4.6083 (- 0.986)
R x10^{4}, m$^{10/3}$ s$^{1/3}$mol^{-1}	26.934C +8.7844 (1)	26.286C +8.814 (1)	27.018C +8.7559 (0.999)	37.979C +8.756 (1)	23.251C +8.8225 (0.999)
b x10^{5}, m^{3}	22.647 C+7.59 (1)	22.277 C+7.611 (1)	22.859C+ 7.5631 (0.999)	31.945C+7.5782 (1)	19.416 C+7.5815 (0.999)
L_f x10^{11}, m	-1.3781C+4.5695 (-0.978)	-1.2575C+4.57 (-0.983)	-0.95C+4.543 (-0.985)	-1.8548 C+4.584 (-0.991)	-1.137 C+4.4904 (- 0.986)
π x10^{-8}, Pa	-9.2868C+5.1463 (-0.997)	-9.3408C+ 5.1989 (-0.997)	-10.282C+5.2269 (-0.996)	-11.519 C+5.217 (-0.999)	-7.5512C+5.1748 (-0.996)
V_fx 10^{7}, m^{3}	2.115 C+ 1.5723 (0.968)	29.107C^2 -1.2279C+1.5906 (0.988)	2.545C+1.5385 (0.971)	36.032C^2-2.6073C +1.596 (0.964)	1.095C+1.5489 (0.932)
τ x10^{13}, s	10.042C+5.4842 (0.985)	8.775 C+5.7225 (0.975)	8.7932C+5.5885 (0.991)	-112.86C^2 + 29.397C +5.4838 (0.997)	10.965C+5.4141 (0.982)
$(\alpha/f^2)_{cl}$.10^{14}, s^{2}m^{-1}	10.3C+7.3596 (0.978)	10.24C+7.575 (0.973)	9.977C+7.415 (0.988)	-1444C^2+ 35.454C +7.3278 (0.997)	12.704C+7.0671 (0.981)

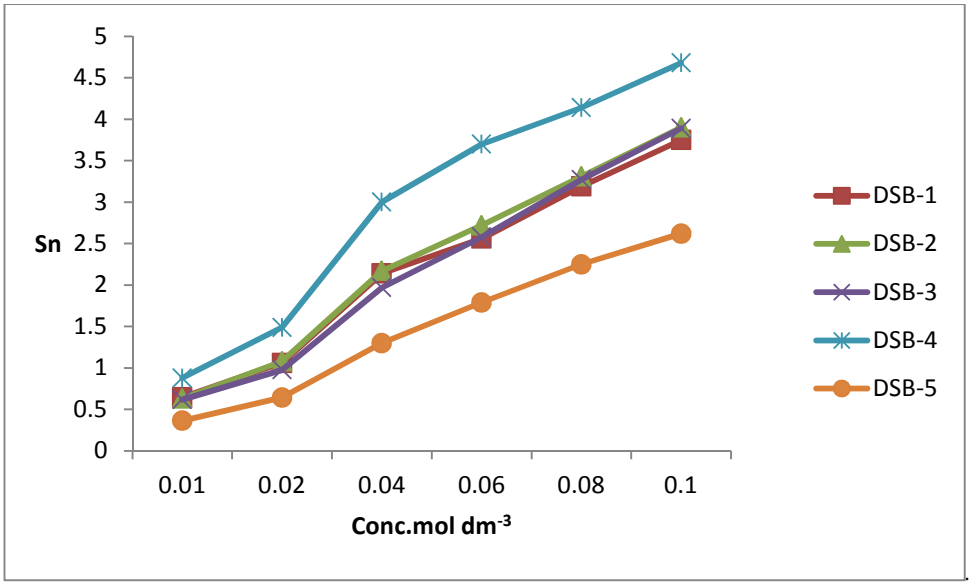


Fig-1 The plots of solvation number against the concentration of Schiff bases at 308.15K

It is observed that L_f decreased with the increasing concentration of DSB-1 to DSB-5. Decrease in intermolecular free path length led to positive deviation in ultrasonic speed and negative deviation in adiabatic compressibility [24]. Decrease in L_f indicated that the molecules are nearer in the system [25]. 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 agiven 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 presence 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 (Fig.1). The interaction of solute and solvent molecules is also a measure of solvation number (S_n), which is the number of the solvent molecules attached to the central atom or ion by their translational degree of freedom. It is observed that$S_n$increased with increase in concentration suggesting structure forming tendency of Schiff bases [26]. The positive values of S_n indicated appreciable solvation of DSB-1 to DSB-5and this in turns confirmed structure forming nature of halogenated symmetric double Schiff basesin DMF.This indicated that as solute concentration increased, attraction between solute and solvent increased.At constant temperature, the concentration and dielectric constant of the medium play an important role in determining the interaction occurring in the solution, which is reflected in S_n values [27].

CONCLUSION

From the experimental findings, it is observed that the acoustical and solvation number suggested the structure forming tendency of the Schiff bases and hence existence of strong molecular interactions the solutions.

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