

Acoustical Studies of Schiff Bases in 1, 4-dioxane and Dimethylformamide at 308. 15 K

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Abstract Density, viscosity and ultrasonic velocity of solutions of four Schiff bases in 1, 4-dioxane and dimethylformamide (DMF) were measured at 308. 15 K. Various acoustical properties such as specific impedance (Z), adiabatic compressibility (κ_s), Rao's molar sound function (R_m), the van der Waals constant (b), molar compressibility (W), intermolecular free length (L_f), relaxation strength (r), solvation number (S_n), were calculated. The results are interpreted in terms of molecular interactions occurring in the solutions.

Keywords: Density, Viscosity, Ultrasonic velocity, Schiff bases, 1, 4-dioxane, Dimethylformamide

Various workers have reported the preparation, chemical and physical properties of various Schiff bases [1-5]. Schiff bases are known to be important due to their applications in the preparation of dyes, liquid crystals and powerful corrosion inhibitors. Further more, they are used in the mechanism of many biochemical processes [6-9]. Due to these applications of Schiff bases, the present work was undertaken to study the molecular interactions of these bases in different solvents. The acoustical properties of Schiff bases are studied in 1, 4-dioxane (DO) and dimethylformamide (DMF) at 308. 15 K. The results are interpreted in terms of molecular interactions occurring in the solutions.

1 Experimental

The four Schiff bases were synthesized from 4-amino-antipyrene in our laboratory and purified. IR, NMR and CHN analysis confirmed the structures of these compounds. The structural formulas are shown in Fig. 1. The solvents 1, 4-dioxane and dime-

thylformamide used, were of laboratory grade and were purified prior to use by an appropriate method [10]. The estimated purity was better than 99. 85%, checked by GLC and moisture detection.

Solutions of different concentrations (in molarity, $\text{mol} \cdot \text{dm}^{-3}$) were prepared for each binary system. For GKS-1, measurements could not be carried out in 1, 4-dioxane due to poor solubility. The density, ultrasonic velocity and viscosity of pure solvents and of solutions were measured at 308. 15 K by using a pycnometer, the single frequency interferometer operating at 2 MHz and an Ubbelohde viscometer with an accuracy of $0.0001 \text{ g} \cdot \text{cm}^{-3}$, $\pm 0.01\%$ and $\pm 0.06\%$, respectively. The uncertainty of temperature is $\pm 0.1 \text{ K}$ and that of concentration is $0.001 \text{ mol} \cdot \text{dm}^{-3}$.

2 Results and Discussion

Table 1 shows the experimental data of density, viscosity and ultrasonic velocity of pure solvents and Schiff base solutions at 308. 15 K.

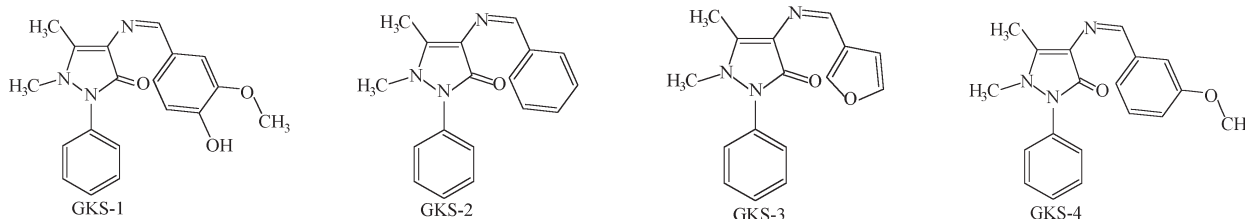


Fig. 1 The structural formulas

GKS-1: 4-[(4'-hydroxy-3'-methoxy-benzylidene)-amino]-1, 5-dimethyl-2-phenyl-1, 2-dihydro-pyrazol-3-one;

GKS-2: 4-(benzylidene-amino)-1, 5-dimethyl-2-phenyl-1, 2-dihydro-pyrazol-3-one;

GKS-3: 4-[(furan-3'-methylene)-amino]-1, 5-dimethyl-2-phenyl-1, 2-dihydro-pyrazol-3-one;

GKS-4: 4-[(3'-methoxy-benzylidene)-amino]-1, 5-dimethyl-2-phenyl-1, 2-dihydro-pyrazol-3-one

Table 1 Experimental data of density (ρ), ultrasonic velocity (U) and viscosity (η) of Schiff bases in 1, 4-dioxane (DO) and DMF at 308.15 K

Concentration (mol · dm ⁻³)	GKS-1 + DMF			GKS-2 + DMF			GKS-3 + DMF			GKS-4 + DMF		
	ρ (g · cm ⁻³)	$10^{-5}U$ (cm · s ⁻¹)	$10^2\eta$ (poise)	ρ (g · cm ⁻³)	$10^{-5}U$ (cm · s ⁻¹)	$10^2\eta$ (poise)	ρ (g · cm ⁻³)	$10^{-5}U$ (cm · s ⁻¹)	$10^2\eta$ (poise)	ρ (g · cm ⁻³)	$10^{-5}U$ (cm · s ⁻¹)	$10^2\eta$ (poise)
0.000	0.9368	1.4389	0.9019	0.9368	1.4389	0.9019	0.9368	1.4389	0.9019	0.9368	1.4389	0.9019
0.010	0.9376	1.4816	0.9098	0.9381	1.3972	0.9197	0.9384	1.4200	0.9103	0.9381	1.4490	0.9063
0.020	0.9391	1.4770	0.9299	0.9390	1.4054	0.9482	0.9392	1.4286	0.9268	0.9390	1.4607	0.9285
0.040	0.9408	1.4658	0.9667	0.9307	1.4150	0.9670	0.9414	1.4396	0.9514	0.9393	1.4611	0.9356
0.060	0.9429	1.4602	1.0891	0.9409	1.4221	0.9781	0.9432	1.4458	0.9570	0.9396	1.4690	0.9473
0.080	0.9552	1.4300	1.1774	0.9430	1.4344	0.9946	0.9444	1.4534	0.9693	0.9400	1.4724	0.9537
0.100	0.9564	1.4138	1.2553	0.9449	1.4536	1.0252	0.9456	1.4586	0.9840	0.9430	1.4850	0.9647
	GKS-1 + DO			GKS-2 + DO			GKS-3 + DO			GKS-4 + DO		
0.000	-	-	-	1.0175	1.3362	1.0487	1.0175	1.3362	1.0487	1.0175	1.3362	1.0487
0.010	-	-	-	1.0185	1.3576	1.1307	1.0195	1.3623	1.0100	1.0196	1.3853	1.2092
0.020	-	-	-	1.0189	1.3649	1.1903	1.0203	1.3736	1.1169	1.0212	1.3923	1.2416
0.040	-	-	-	1.0194	1.3821	1.2472	1.0209	1.3822	1.2000	1.0217	1.4021	1.2610
0.060	-	-	-	1.0241	1.3943	1.3811	1.0216	1.3956	1.2398	1.0227	1.4146	1.3010
0.080	-	-	-	1.0259	1.4076	1.4299	1.0240	1.4061	1.2913	1.0242	1.4236	1.3454
0.100	-	-	-	1.0294	1.4124	1.6043	1.0258	1.4181	1.3279	1.0259	1.4332	1.3685

From these experimental data, various acoustical parameters were evaluated using the following standard equations.

$$\text{Specific impedance } (Z)^{[11]}: Z = U\rho$$

where U is the speed of sound and ρ is the density of solution.

$$\text{Adiabatic compressibility } (\kappa_s)^{[12]}: \kappa_s = 1 / (U^2 \rho)$$

$$\text{Rao's molar sound function } (R_m)^{[13]}: R_m = (M_w / \rho) U^{1/3}$$

where M_w is the molecular weight of solution.

$$\text{van der Waals constant } (b)^{[14]}:$$

$$b = (M_w / \rho) (1 - RT / M_w U^2 (\sqrt{1 + M_w U^2 / 3RT} - 1))$$

where R is gas constant and T is absolute temperature.

$$\text{Molar compressibility } (W)^{[15]}: W = (M_w / \rho) \kappa_s^{-1/7}$$

$$\text{Intermolecular free length } (L_f)^{[16]}: L_f = K \kappa_s^{1/2}$$

where K is Jacobson constant ($= 6.0816 \times 10^4$).

$$\text{Relaxation strength } (r)^{[17]}: r = 1 - (U / U_\infty)^2$$

where $U_\infty = 1.6 \times 10^5 \text{ cm} \cdot \text{s}^{-1}$.

$$\text{Solvation number } (S_n)^{[18]}:$$

$$S_n = M_{w2} / M_{w1} [1 - \kappa_s / \kappa_{s1}] [(100 - X) / X]$$

where X is the number of grams of solute in 100 g of the solution. M_{w1} , M_{w2} , κ_s and κ_{s1} are the molecular weights and adiabatic compressibility of solvent and solute respectively.

Some of these parameters are given in Table 2 and Table 3. It is observed that in 1, 4-dioxane, ultrasonic velocity and acoustic impedance are observed to increase with concentration of solute whereas adiabatic compressibility and intermolecular free length decrease with concentration. The increase of intermolecular free length causes a decrease in velocity (U) and vice versa. The decrease in intermolecular free length is due to solute-solvent interactions, which causes velocity to increase. Fig. 2 shows variation of ultrasonic velocity with concentration in the both solvents. It is observed from Table 3 that in 1, 4-dioxane, κ_s

decreases with concentration for all the three bases. The solute - solvent interaction is further supported by decrease in relaxation strength (r) in 1, 4-dioxane systems.

However, in DMF (Table 2), except GKS-1, velocity and acoustic impedance are observed to increase with concentration of solute. In case of GKS-1, both velocity and acoustic impedance decrease with the concentration. The adiabatic compressibility and intermolecular free length are observed to increase for GKS-1 but decrease for other three bases with concentration. The decrease in intermolecular free length and increase in velocity suggest the presence of solvent-solute interactions in GKS-2, GKS-3, and GKS-4, which is supported by decrease in relaxation strength in these three systems. The decrease in κ_s might be due to aggregation of solvent molecules around solute molecules indicating strong solvent-solute interaction. For GKS-1 system, increase in intermolecular free length, adiabatic compressibility and relaxation strength suggest the presence of solute-solute interactions in this system.

The linear change in W , R_m and b in all the bases (Table 2 and Table 3) suggest the absence of any complex formation in both 1, 4-dioxane and DMF systems. The viscosity is also observed to increase for all the bases in both the solvents.

The structure forming or structure breaking tendency of a solute in a particular solvent is further confirmed by their solvation number S_n . It is observed from Table 2 that in DMF solutions, S_n values are observed to decrease for GKS-1 whereas for GKS-2 and GKS-3, these values increase. For GKS-4, it decreases with concentration initially then becomes almost constant. The increase in S_n values suggests structure-forming tendency of solute whereas decrease in S_n is due to structure breaking ten-

Table 2 Variation of acoustical parameters with concentration for Schiff bases in DMF at 308. 15 K

Concentration (mol · dm ⁻³)	10 ⁻⁵ Z/g · cm ⁻²	10 ¹⁶ κ _s /cm ² · N ⁻¹	L _f /pm	S _n	b	10 ⁻³ R _m	10 ⁻³ W	r
0.000	1.3479	5.1556	43.66	—	73.33	4.0884	2.3008	0.1912
0.010	1.3891	4.8584	42.39	73.69	74.35	4.1785	2.3485	0.1424
0.020	1.3870	4.8809	42.48	33.98	75.19	4.2207	2.3731	0.1477
0.040	1.3790	4.9468	42.77	12.80	76.96	4.3082	2.4238	0.1606
GKS-1 0.060	1.3768	4.9737	42.89	7.42	78.70	4.3980	2.4756	0.1678
0.080	1.3659	5.1195	43.51	1.11	79.43	4.4091	2.4889	0.2012
0.100	1.3552	5.2309	43.98	-1.84	81.14	4.4577	2.5351	0.2192
0.010	1.3107	5.4605	44.94	-75.67	73.82	4.0803	2.2999	0.2374
0.020	1.3197	5.3915	44.65	-29.21	74.46	4.1217	2.3229	0.2284
0.040	1.3311	5.3089	44.31	-9.45	75.73	4.1982	2.3659	0.2178
GKS-2 0.060	1.3380	5.2551	44.08	-4.06	77.11	4.2790	2.4109	0.2099
0.080	1.3527	5.1534	43.65	0.07	78.34	4.3560	2.4541	0.1961
0.100	1.3735	5.0086	43.04	3.57	79.29	4.4405	2.5008	0.1746
0.010	1.3325	5.2848	44.21	-32.08	73.80	4.0989	2.3083	0.2123
0.020	1.3417	5.2169	43.92	-7.59	74.39	4.1374	2.3300	0.2027
0.040	1.3552	5.1255	43.54	1.86	75.52	4.2073	2.3693	0.1904
GKS-3 0.060	1.3675	5.0714	43.30	3.45	76.65	4.2740	2.4070	0.1833
0.080	1.3725	5.0127	43.05	4.37	77.83	4.3446	2.4466	0.1748
0.100	1.3792	4.9704	42.87	4.51	79.00	4.4127	2.4850	0.1688
0.010	1.3594	5.0759	43.32	19.77	74.13	4.1394	2.3295	0.1796
0.020	1.3716	4.9911	42.96	20.35	74.96	4.1944	2.3596	0.1665
0.040	1.3724	4.9865	42.94	10.39	76.67	4.2884	2.4125	0.1660
GKS-4 0.060	1.3803	4.9313	42.70	9.13	78.41	4.3899	2.4691	0.1569
0.080	1.3840	4.9070	42.60	7.54	80.12	4.4863	2.5232	0.1531
0.100	1.4005	4.8077	42.16	8.41	81.60	4.5785	2.5752	0.1383

Z: acoustical impedance; κ_s: adiabatic compressibility; L_f: free length; S_n: solvation number; b: van der Waals constant; R_m: Rao's molar sound function; W: molar compressibility; r: relaxation strength

Table 3 Variation of acoustical parameters with concentration for Schiff bases in 1, 4-dioxane at 308. 15 K

Concentration (mol · dm ⁻³)	10 ⁻⁵ Z/g · cm ⁻²	10 ¹⁶ κ _s /cm ² · N ⁻¹	L _f /pm	S _n	b	10 ⁻³ R _m	10 ⁻³ W	r
0.000	1.3362	5.5041	45.11	—	81.46	4.4268	2.5297	0.3025
0.010	1.3827	5.3271	44.38	13.09	82.00	4.4754	2.5560	0.2800
0.020	1.3907	5.2682	44.14	15.11	82.54	4.5110	2.5757	0.2722
0.040	1.4090	5.1349	43.57	16.68	83.55	4.5859	2.6172	0.2538
GKS-2 0.060	1.4280	5.0224	43.09	19.18	84.37	4.6361	2.6464	0.2405
0.080	1.4442	4.9193	42.65	24.63	85.34	4.7008	2.6828	0.2260
0.100	1.4540	4.8692	42.43	37.36	86.12	4.7472	2.7102	0.2207
0.010	1.3889	5.2848	44.21	13.50	81.89	4.4738	2.5550	0.2749
0.020	1.4015	5.1942	43.83	14.57	82.36	4.5094	2.5746	0.2629
0.040	1.4111	5.1268	43.54	16.51	83.34	4.5699	2.6086	0.2536
GKS-3 0.060	1.4257	5.0254	43.11	19.61	84.32	4.6353	2.6445	0.2391
0.080	1.4399	4.9389	42.73	32.36	85.15	4.6894	2.6757	0.2276
0.100	1.4547	4.8471	42.34	45.86	86.02	4.7478	2.7087	0.2143
0.010	1.4125	5.1102	43.47	15.54	82.14	4.5086	2.5728	0.2503
0.020	1.4220	5.0506	43.20	17.65	82.71	4.5458	2.5946	0.2427
0.040	1.4325	4.9783	42.91	21.30	84.09	4.6290	2.6408	0.2320
GKS-4 0.060	1.4467	4.9313	42.51	27.32	85.42	4.7125	2.6877	0.2182
0.080	1.4580	4.9070	42.21	47.39	86.80	4.7896	2.7314	0.2083
0.100	1.4703	4.8077	41.89	82.44	87.95	4.8663	2.7749	0.1975

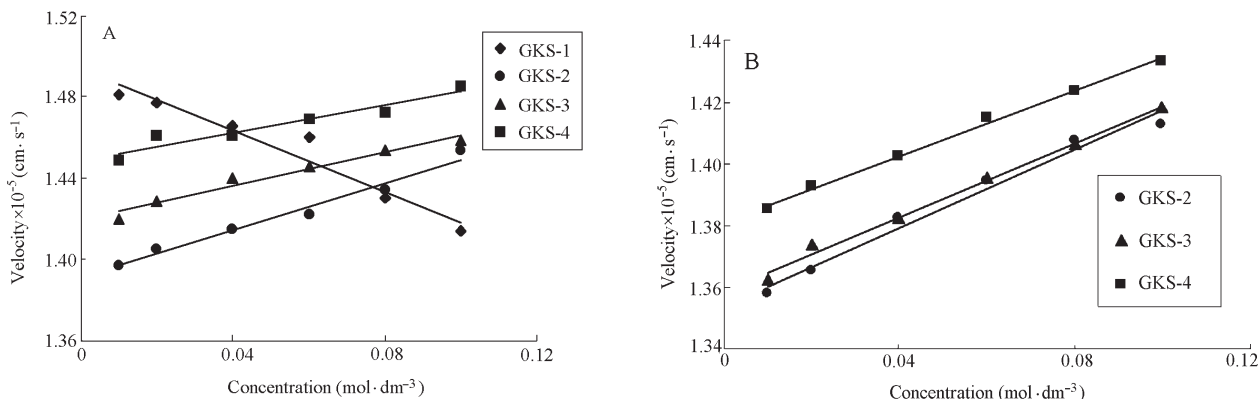


Fig. 2 Variation of velocity with concentration for Schiff bases in (A) DMF and (B) 1,4-dioxane at 308.15 K

density. The decrease in GKS-4 suggests that some acoustical properties show solute-solvent interaction, solute-solute interaction also exists, which is confirmed by S_n values. For all the three Schiff bases in 1,4-dioxane solutions (Table 3), solvation number increases with increase in concentration.

For GKS-2, GKS-3 and GKS-4 in both solvents, viscosity (Table 1) is observed to increase which further confirms the association between solute and solvent molecules. For GKS-1 in DMF solution, although structure-breaking tendency is observed, its viscosity increases with concentration. This suggests that both solute-solute and solute-solvent interactions exist in the solution. However, solute-solute interactions dominate due to which velocity and solvation number are observed to decrease in DMF solution of GKS-1.

In conclusion, solute-solvent interactions exist in both the solvents, for GKS-2, GKS-3 and GKS-4. However, GKS-1 shows structure-breaking tendency in DMF due to dominating solute-solute interactions.

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