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Physicochemical Studies of Some Schiff Bases Derived From 6-Ethylbenzene 1,3-diol

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Abstract The schiff bases were synthesized and their characterization was done by CHN analysis, IR and NMR spectra. The physicochemical properties such as density, refractive index, conductance, heat of solution etc., of these schiff bases were determined

Key words : Physicochemical studies, Schiff base

Introduction

Extensive investigation in the field of schiff bases shows that much have been reported about their preparation, chemical and physical properties.¹⁻³ Some schiff bases are important ligands due to their vivid applications and are known to act as antibacterial, antifungal, insecticidal agents.⁴⁻⁶ This draws our attention to study their physicochemical properties. Thus, in the present work, the physicochemical properties such as density, refractive index, conductance, heat of solution etc., of some schiff bases were determined.

Experimental

The schiff bases were synthesised in our laboratory. Their characterization were done by CHN analysis, IR and NMR.

The solvents dimethylformamide (DMF), dimethylsulphoxide (DMSO) and 1,4-dioxane used for the physicochemical studies were purified by standard methods reported earlier.⁷ All the schiff bases were recrystallized from methanol.

The density and refractive index were measured in DMF and 1,4-dioxane whereas the conductivity was measured in DMF and DMSO. Conductivity in 1,4-dioxane was very less, so dioxane was not used in conductivity measurements. Both the measurements were done at 35°C.

For the determination of density, refractive index and conductance, a series of solutions were prepared of different concentrations for each schiff base in different solvents. The density, conductance and refractive index were measured at 35°C by pycnometer, systronics conductometer (Model No 306) and Abbe refractometer respectively.

The solubility of each schiff base was determined by transferring 25 ml of saturated solution into pre weighed 50 ml beaker and solvent was evaporated to dryness till constant weight is obtained. Three replicate measurements were carried out at a particular temperature and average value of weights was determined. The solubility was determined at 35°C. The amount of solvent in 25 ml solution was calculated by determining the weight of the solution in a stoppered conical flask and the weight of the solute. Finally, the moles of solute and solvent were determined in the liter of saturated solution. The results are given in Table 4.

Result and Discussion

The density of the solution is related with the densities of the solvent, solute and their weight fractions g_1 and g_2 , according to the equation (1)

$$1/\rho_{12} = g_1/\rho_1 + g_2/\rho_2 \text{ -----(1)}$$

where ρ_{12} is the density of the solution and ρ_1 and ρ_2 are the densities of the solvent and solute respectively. The density of each base was determined from the slope of the plot of $1/g_1\rho_{12}$ verses g_2/g_1 . The inverse of the slope gives ρ_2 .

Further, from the knowledge of structural aspects⁸, the density of schiff bases were also calculated by the following equation:

$$\rho = KM/N_A \sum \Delta V_i \text{ -----(2)}$$

where ρ is the density of the compound, K is the packing fraction (=0.681), M is the molecular weight of the compound, N_A is the Avogadro's number and ΔV_i is the volume increment of the atoms and atomic groups present in the compound. The theoretical and calculated densities are given in Table 1.

Table 1 Experimental and calculated densities of all the schiff bases at 35°C.

Compound	Densities g/cm ³		Cal. from eq (2)
	DMF	1,4-dioxane	
SOSR1	1.1429	1.1177	1.1928
SOSR1	1.1842	1.1474	1.1167
SOSR3	1.3271	1.3819	1.1928
SOSR4	1.2235	1.2222	1.1293

The density is not much affected by intermolecular interaction. However, due to polar substituent, there may be changes in the volume as well as in the molecular weight of the compound. It is observed from Table 1 that difference between experimental values from equation (2) in solutions (of DMF and 1,4-dioxane) and between experimental and calculated values may be due to solvation of the ions in solutions.

The molar refractions of pure liquid (MRD) and solutions (MRD)₁₂ are determined according to the equation given by Lorentz and Lorentz.⁹

$$\text{MRD} = (n^2 - 1)/(n^2 + 2) \cdot (M/\rho) \text{ -----(3)}$$

where n and M are the refractive index and molecular weight of the liquid respectively.

$$(\text{MRD})_{12} = (n^2 - 1)/(n^2 + 2) \cdot ((x_1M_1 + x_2M_2)/\rho_{12}) \text{ -----(4)}$$

where n_{12} and ρ_{12} are the refractive index and density of the solutions respectively. x_1 and x_2 are the mole fractions of the solvent and the solute respectively. M_1 and M_2 are the molecular weights of the solvent and solute respectively. From the density and refractive index data, the molar refraction of all the compounds at a specified temperature were determined and are plotted against concentration.

From the least square analysis, the value of molar refraction were determined from the intercepts. From the density and molar refraction data, the refractive index of each schiff base was calculated from equation (3). The refractive index and molar refraction for each schiff base are given in Table 2. The conductivities of schiff base in DMF and DMSO solutions are given in Table 3. Further, the equivalent conductance (λ_c) of each solution was determined by the equation :

$$\lambda_c = 1000K/C \text{----(5)}$$

where K is the specific conductance and C is the concentration (g.equiv/lit) of the solution respectively.

Table 2 Molar refraction ((MRD)₂) and refractive index (n) for all the schiff bases at 35°C.

Compound	(MRD) ₂	n
SOSR1	94.00	1.4919
SOSR2	122.5	1.3419
SOSR3	84.00	1.4581
SOSR4	86.00	1.5096

Table 3 The conductance (κ) and equivalent conductance (λ_c) of all schiff bases in DMF and DMSO at 35°C.

Conc. C (g.eq./lit)	$\kappa \cdot 10^5$ (Ω) ⁻¹	λ_c (cm ² / Ω . equiv.)	$\kappa \cdot 10^5$ (Ω) ⁻¹	λ_c (cm ² / Ω . equiv.)	$\kappa \cdot 10^5$ (Ω) ⁻¹	λ_c (cm ² / Ω . equiv.)	$\kappa \cdot 10^5$ (Ω) ⁻¹	λ_c (cm ² / Ω . equiv.)
	SOSR1		SOSR2		SOSR3		SOSR4	
DMF								
0.000	1.62	--	1.62	--	1.62	--	1.62	--
0.002	3.13	6.1155	1.69	0.2835	1.86	0.9720	1.90	1.3770
0.004	4.23	5.2853	1.81	0.3848	1.98	0.7290	2.60	1.9845
0.006	5.30	4.9680	2.30	0.9180	2.12	0.6750	3.29	2.2545
0.008	6.35	4.7891	2.70	1.0935	2.20	0.5873	3.72	2.1263
0.010	6.86	4.2444	3.01	1.1259	2.33	0.5751	4.20	2.0898
0.020	7.38	2.3328	3.58	0.7938	2.81	0.4820	6.49	1.9724
0.040	8.35	1.3628	4.93	0.6703	3.46	0.3726	7.73	1.2373
0.060	9.45	1.0571	5.91	0.5792	3.90	0.3078	8.03	0.8654
0.080	11.4	0.9912	6.25	0.4688	4.30	0.2714	9.33	0.7800
0.100	12.1	0.8497	6.79	0.4188	4.82	0.2592	10.8	0.7444
DMSO								
0.000	0.763	--	0.763	--	0.763	--	0.763	--
0.002	2.59	7.3994	1.28	2.0939	1.35	2.3774	3.97	12.9884
0.004	4.21	6.9803	1.62	1.7354	1.77	2.0393	4.59	7.7497
0.006	4.65	5.2475	1.86	1.4810	1.94	1.5890	4.72	5.3420
0.008	5.11	4.4013	2.16	1.4145	2.23	1.4853	5.80	5.0999
0.010	5.62	3.9342	2.24	1.1964	2.32	1.2612	6.19	4.3959
0.020	5.97	2.1089	2.84	0.8412	2.93	0.8776	7.90	2.8905
0.040	6.37	1.1354	4.55	0.7687	3.10	0.4732	12.0	2.2755
0.060	6.42	0.7637	6.06	0.7151	3.77	0.4060	15.5	1.9895
0.080	6.87	0.6183	6.15	0.5454	4.69	0.3976	16.4	1.5833
0.100	7.03	0.5078	6.81	0.4898	4.92	0.3367	16.8	1.2989

The equivalent conductance values for all schiff bases are reported in Table 3. The equivalent conductance is plotted against \sqrt{C} and is shown in Fig. 1 for DMF and DMSO systems. It is observed that in DMF, λ_c curves for SOSR2 and SOSR4 do not increase uninterruptedly but bend downward at low concentrations giving rise to a maximum at 0.0064 and 0.0042 M concentration. However, the normal behavior i.e., increase of equivalent conductance with dilution is observed for SOSR1 and SOSR3 bases in DMF. This typical behavior of SOSR2 and SOSR4 can be explained in terms of specific solvation characteristics. Both SOSR2 and SOSR4 have methyl groups, which may form hydrogen bonding within

the molecule thereby causing constriction within the molecule. Similar behavior was observed for polyions by Singh et al¹⁰. In DMSO, all the schiff bases show normal behavior i.e., equivalent conductance increases with decreasing concentration.

A close perusal of equivalent conductance curves of schiff bases shows the following order of λ_c :

In DMF : SOSR1 > SOSR4 > SOSR2 > SOSR3

In DMSO : SOSR4 > SOSR1 > SOSR2 \approx SOSR3

SOSR1 and SOSR3 have the same molecular weight but in DMF, high λ_c values are observed for SOSR1 whereas minimum λ_c values are observed for SOSR3. In DMSO, no regular trend is observed. SOSR4 has lowest molecular weight but shows highest λ_c values. Next higher values are for SOSR1, which has larger molecular weight. The lowest values are for SOSR2 and SOSR3 bases. SOSR3 has higher molecular weight (equal to SOSR1) whereas SOSR2 has intermediate molecular weight. This ensures that λ_c is based largely on the solvent and nature of solute under study rather than on its molecular weight¹⁰

Further, it is obvious from figure that all the schiff bases behave as weak electrolytes. So equivalent conductance at infinite dilution (λ_0) can not be determined by extrapolation of the plot of λ_c verses \sqrt{C} . Thus, an alternative procedure¹⁰ for extrapolation is considered by using the equation:

$$\kappa = \kappa_0 + \lambda_0 C + C \phi(c) \quad \text{-----(6)}$$

where κ and κ_0 are the electrolytic conductivities of the solutions and solvent respectively. C is the equivalent concentration and the function $\phi(c)$ denotes the effect of interionic interactions. The slope $d\kappa/dc$ of the plot of κ verses C approximates the limiting conductivity (λ_0), provided other derivatives $d\kappa_0/dC$ and $d[C\phi(c)]/dC$ in the differential form of equation (7) are neglected as compared to λ_0 . However, λ_0 can be determined from conductivity data obtained at extreme dilution, provided the κ verses C curve is linear over a sufficiently wide range of concentration¹¹

$$d\kappa/dC = d\kappa_0/dC + \lambda_0 + d/dC[C\phi(c)] \quad \text{-----(7)}$$

The concentration dependence of electrolytic conductivity (κ) in DMF system is shown in Fig. 2. This shows that the term $d\kappa_0/dC$ has a dominating influence on eq. (7) due to the presence of polyion. All the systems have considerable interionic interactions through out the wide range studied. Therefore, the derivative $d[C\phi(c)]/dC$ cannot be ignored in comparison to λ_0 . Despite these restrictions, limiting equivalent conductivities were evaluated from the limiting slope of small linear portions of the κ verses C curve, assuming that the interionic interactions in this range of concentration are limited. The calculated λ_0 values for all the systems are given in Table 4. The accuracy of the evaluated λ_0 values appeared highly questionable and erroneous throughout this treatment.

Table 4 The limiting equivalent conductance (λ_0) for all the schiff bases in DMF and DMSO at 35°C

Compound code.	DMF		DMSO	
	λ_0 (cm ² /Ω.equiv.)	λ_0 (cm ² /Ω.equiv.) calc. by eq. (7)	λ_0 (cm ² /Ω.equiv.)	λ_0 (cm ² /Ω.equiv.) calc. by eq. (7)
SOSR1	4.79	7.50	3.31	10.05
SOSR2	1.78	-	1.25	2.70
SOSR3	0.58	1.35	1.16	3.30
SOSR4	2.86	-	2.83	-

The solubility of each schiff base was determined in DMF and 1,4-dioxane at different temperatures and is given in Table 5. It is evident from the Table that solubility of schiff bases decreases with temperature in both the solvents. The heat of solution is determined by the following equation:

$$\log N_2 = (\Delta H/2.303R)[T-T_m/TT_m] \text{ -----(8)}$$

where ΔH is the heat of solution, R is gas constant, N_2 is the mole fraction and T and T_m are the temperature of the experiment and melting temperature of the schiff base.

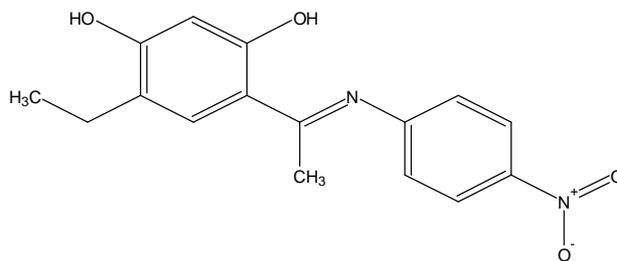
The heat of solution for schiff bases in DMF and 1,4-dioxane are given in Table 5. It is observed from Table 5 that heat of solution is negative. Thus, the dissolution of a schiff base in the solvent is accompanied by the evolution of heat indicating thereby exothermic behavior of schiff bases.

Table 5 The solubility and heat of solution of all schiff bases in DMF and 1, 4- dioxane at different temperatures.

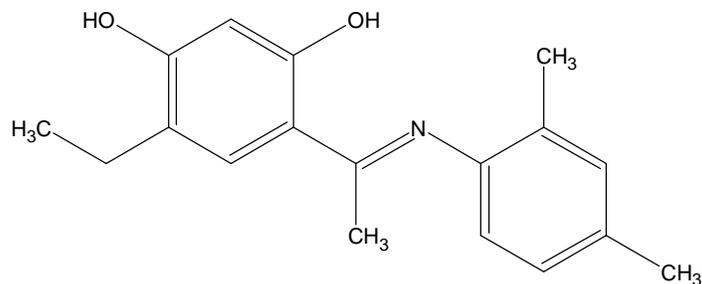
Temp. °C	N_2	ΔH_s Kcals/mol	N_2	ΔH_s Kcals/mol
	SOSM1 + DMF		SOSM2 + DMF	
35	0.0214	-7.0314	0.0107	-7.7759
45	0.0167	-8.2539	0.0078	-9.1228
55	0.0152	-9.3565	0.0049	-10.9817
	SOSM3+DMF		SOSM4+DMF	
35	0.0067	-8.1078	0.0086	-8.2750
45	0.0047	-9.4731	0.0055	-9.9524
55	0.0017	-12.3665	0.0023	-12.8251
	SOSM1+DO		SOSM2+DO	
35	0.0099	-8.4442	0.0049	-9.1262
45	0.0071	-9.9757	0.0037	-10.5147
55	0.0061	-11.3983	0.0036	-11.6623
	SOSM3+DO		SOSM4+DO	
35	0.0028	-9.5468	0.0037	-9.7526
45	0.0017	-11.2323	0.0029	-11.1866
55	0.0012	-12.9155	0.0016	-13.5441

Figure 1

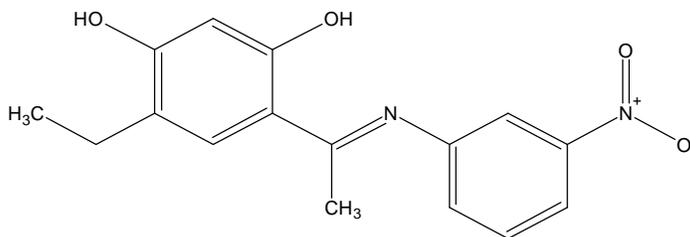
SOSR1: 4-[2-aza-1-methyl-2-(4-nitro-phenyl)vinyl]-6-ethylbenzene-1,3-diol



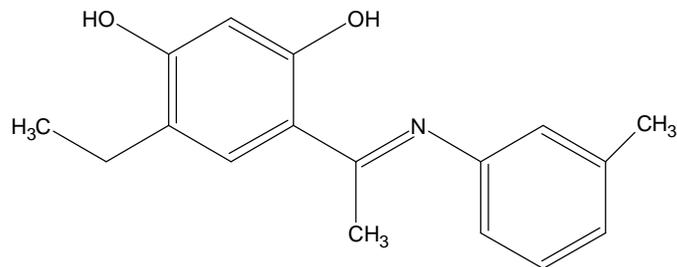
SOSR2: 4-[2-aza-2-(3,4-dimethylphenyl)-1-methyl vinyl]-6-ethylbenzene-1,3-diol



SOSR3: 4-[2-aza-1-methyl-2-(3-nitro-phenyl)vinyl]-6-ethylbenzene-1,3-diol



SOSR4: 4-[2-aza-2-(3,4-dimethylphenyl)-1-methyl vinyl]-6-ethylbenzene-1,3-diol



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Reference

1. Bayer E, *Ber.*, 1975,90, 2325.
2. Asadi M and Sarvestani A H, *Can. J. Chem.*, 2001, 79, 1360.
3. Rieder M I, Kranse R, Bird I R and Dekaban G A, *J. Acquired Immune defic. Syndr., Hum. Retrovirol.* 1995, 8, 134.
4. Nath M and Yadav R, *Bull. Chem. Soc. Jpn.*, 1997, 70, 1331.

5. **Kabeer S A, Baseer M A and Mote N A, *Asian J. Chem.*, 2001, 13, 496.**
6. **Rao S and Mitra A S, *J. Ind. Chem. Soc.*, 1978, 55, 420.**
7. **Riddick J A, Bunger W B and Sakano T, *Organic Solvents-Physical Properties and methods of purification, Fourth Edition.*, Techniques of Chemistry, Vol II, A Wiley-Interscience Publication, John Wiley.**
8. **Slonimskii G I, Askadshii A A and Kitaigorodskii A. I, *Vysokomol. Soyed.* 1970, A12, 494.**
9. **Lorentz H A, *Theory of Electronics*, Leipzig 1906.**
10. **Singh M, Kumer A Easo S and Prasad B B, *Can. J Chem.*, 1997, 75, 1403.**
11. **Vink H, *J Chem. Soc., Faraday Trans.* 1981, 1, 77, 2439; 1983, 79, 1403; 1987, 83, 801.**



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