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Measurement of Density, Refractive Index and Conductance of Some Pyrimidine Derivatives in Solutions at 308.15 K.

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Abstract

Some new pyrimidine derivatives have been synthesized and their physicochemical parameters such as density, refractive index and conductance have been measured in N,N-dimethyl formamide and tetrahydrofuran at 308.15 K. It is observed that solvent and structure of compounds have major effect on these studied properties which may be due to different type of interactions in different solvents for different compounds.

Keywords: Density; Refractive Index; Conductance; N, N-Dimethyl Formamide; Tetrahydrofuran

Introduction

Among many heterocyclic compounds, pyrimidine compounds are one of the most prominent structures which attract many chemists and pharmacists due to their therapeutic values [1-10]. The applications of these compounds in drug research have stimulated the invention of wide range of synthetic methods for their preparation and chemical transformations [11-15]. Further, many of these compounds are known to exist in deoxyribonucleic acid and ribonucleic acid which is one of the most essential constituents of all cells and thus of all living matter. As many of these compounds exist in various drugs [16-18], it would be useful to study their physical parameters which are prime factors for the study of these compounds in pharmaceutical field [19-21]. Thus, in the present work, physicochemical parameters such as density, refractive index and conductance of some newly synthesized pyrimidine derivatives such as dihydropyrimidine and dihydropyrimidinthiones have been measured in N,N-dimethyl formamide, dimethylsulphoxide and tetrahydrofuran at 308.15 K.

Experimental

Some new dihydropyrimidine and dihydropyrimidinthiones compounds have been synthesized. The general structures and substitutions in different compounds are given in Figure 1.

pysicochemical Studies

The solvents DMF, DMSO and THF used for physicochemical studies were purified by fractionally distillation by the reported method [22]. For each compound, a series of solutions of different concentrations were prepared in these solvents. The choice of different solvents for dihydropyrimidine and dihydropyrimidinthiones is due to solubility problem. The density and refractive index of pure solvents and solutions were measured by using pycnometer and Abbe refractometer respectively at 308.15 K. The temperature was maintained by circulating water through jacket around the prisms of refractometer from an electronically controlled thermostatic water bath (NOVA NV-8550 E). The uncertainty of temperature was ± 0.1°C. The conductance of each solution was measured by using Elico Conductivity Meter (Model No. CM 180) at 308.15 K. The measured conductance was corrected by subtracting the conductance of pure solvent.

Results and Discussion

Table 1 shows the experimental values of densities and refractive index for all the studied solutions. Using experimental density of solution, density of each compound was calculated using the following relation:

$$\frac{1}{\rho_{12}} = \frac{g_1}{\rho_1} + \frac{g_2}{\rho_2} \quad (1)$$

where ρ_{12} is the density of solution and ρ_1 and ρ_2 are the densities of solvent and solute respectively. g_1 and g_2 are the weight fractions of solvent and solute.

The evaluated densities of all the compounds are listed in (Table 2) along with the theoretical densities which were calculated using the following equation [23]:

Table 1: The density (ρ_{12}) and refractive index (n) of synthesized compounds at 308.15K.

Conc. M	ρ_{12} g.cm^{-3}	n	ρ_{12} g.cm^{-3}	n
Dihydropyrimidinthiones				
	DMF		**THF**	
SSN-1				
0.00	0.9338	1.4239	0.8798	1.4016
0.01	0.9413	1.4241	0.8832	1.4038
0.02	0.9433	1.4249	0.8868	1.4043
0.04	0.9470	1.4261	0.8898	1.4059
0.06	0.9481	1.4275	0.8941	1.4076
0.08	0.9523	1.4289	0.8972	1.4082
0.10	0.9569	1.4313	0.9005	1.4097
SSN -2				
0.01	0.9427	1.4242	0.8822	1.4032
0.02	0.9447	1.4248	0.8843	1.4041
0.04	0.9453	1.4259	0.8863	1.4057
0.06	0.9466	1.4273	0.8891	1.4063
0.08	0.9485	1.4291	0.8925	1.4076
0.10	0.9494	1.4308	0.8962	1.4082
SSN -3				
0.01	0.9409	1.4243	0.8840	1.4035
0.02	0.9418	1.4248	0.8864	1.4053
0.04	0.9462	1.4257	0.8886	1.4069
0.06	0.9484	1.4268	0.8917	1.4083
0.08	0.9495	1.4289	0.8941	1.4098
0.10	0.9553	1.4292	0.8978	1.4111
SSN -4				
0.01	0.9434	1.4247	0.8832	1.4031
0.02	0.9457	1.4255	0.8861	1.4044
0.04	0.9471	1.4265	0.8900	1.4069
0.06	0.9485	1.4277	0.8948	1.4087
0.08	0.9504	1.4286	0.8981	1.4093
0.10	0.9527	1.4298	0.9002	1.4118
SSN -5				
0.01	0.9421	1.4249	0.8845	1.4056
0.02	0.9438	1.4256	0.8872	1.4061
0.04	0.9468	1.4269	0.8898	1.4082
0.06	0.9479	1.4289	0.8925	1.4092
0.08	0.9494	1.4292	0.8960	1.4122
0.10	0.9512	1.4311	0.8991	1.4138
SSN -6				
0.00	0.9338	1.4239	0.8798	1.4016
0.01	0.9431	1.4250	0.8812	1.4036
0.02	0.9448	1.4258	0.8862	1.4052
0.04	0.9454	1.4270	0.8904	1.4065

0.06	0.9481	1.4282	0.8935	1.4079
0.08	0.9521	1.4291	0.8962	1.4091
0.10	0.9574	1.4305	0.8992	1.4108
SSN -7				
0.01	0.9431	1.4253	0.8836	1.4034
0.02	0.9454	1.4264	0.8865	1.4049
0.04	0.9471	1.4276	0.8905	1.4059
0.06	0.9489	1.4290	0.8954	1.4070
0.08	0.9506	1.4308	0.8982	1.4082
0.10	0.9514	1.4320	0.9022	1.4098
SSN -8				
0.01	0.9413	1.4242	0.8871	1.4031
0.02	0.9437	1.4247	0.8894	1.4046
0.04	0.9450	1.4269	0.8924	1.4056
0.06	0.9486	1.4289	0.8947	1.4079
0.08	0.9533	1.4295	0.8981	1.4086
0.10	0.9552	1.4312	0.9002	1.4112
SSN -9				
0.01	0.9420	1.4243	0.8864	1.4034
0.02	0.9456	1.4269	0.8892	1.4048
0.04	0.9482	1.4272	0.8942	1.4058
0.06	0.9512	1.4281	0.8974	1.4066
0.08	0.9532	1.4309	0.9005	1.4079
0.10	0.9563	1.4320	0.9044	1.4091
Dihydropyrimidine				
	DMF		**DMSO**	
SNO-1				
0.00	0.9338	1.4239	1.0959	1.4716
0.01	0.9494	1.4261	1.0971	1.4719
0.02	0.9506	1.4274	1.0982	1.4729
0.04	0. 9531	1.4291	1.0989	1.4733
0.06	0.9555	1.4308	1.0998	1.4739
0.08	0.9577	1.4321	1.1004	1.4745
0.10	0.9584	1.4336	1.1012	1.4779
SNO -2				
0.01	0.9485	1.4237	1.0971	1.4722
0.02	0.9498	1.4248	1.0987	1.4729
0.04	0.9516	1.4257	1.0992	1.4732
0.06	0.9536	1.4275	1.1005	1.4739
0.08	0.9554	1.4283	1.1017	1.4746
0.10	0.9571	1.4308	1.1023	1.4759
SNO -3				
0.01	0.9488	1.4223	1.0965	1.4728
0.02	0.9490	1.4231	1.0973	1.4733
0.04	0.9520	1.4235	1.1002	1.4741
0.06	0.9527	1.4241	1.1009	1.4749

0.08	0.9543	1.4249	1.1010	1.4762
0.10	0.9565	1.4265	1.1026	1.4779
SNO -4				
0.01	0.9470	1.4219	1.0974	1.4728
0.02	0.9474	1.4226	1.0982	1.4735
0.04	0.9478	1.4231	1.0992	1.4748
0.06	0.9484	1.4238	1.0996	1.4762
0.08	0.9489	1.4249	1.1010	1.4778
0.10	0.9505	1.4255	1.1027	1.4783
SNO -5				
0.01	0.9494	1.4225	1.0969	1.4719
0.02	0.9517	1.4234	1.0985	1.4723
0.04	0.9530	1.4243	1.0996	1.4729
0.06	0.9555	1.4253	1.1003	1.4741
0.08	0.9577	1.4258	1.1017	1.4749
0.10	0.9597	1.4283	1.1036	1.4756
SNO -6				
0.00	0.9453	1.4218	1.0971	1.4722
0.01	0.9487	1.4219	1.0987	1.4729
0.02	0.9505	1.4227	1.0992	1.4732
0.04	0.9518	1.4233	1.1005	1.4739
0.06	0.9547	1.4249	1.1017	1.4746
0.08	0.9554	1.4259	1.1023	1.4759
0.10	0.9566	1.4273	1.0971	1.4722
SNO -7				
0.01	0.9485	1.4253	0.8836	1.4034
0.02	0.9500	1.4264	0.8865	1.4049
0.04	0.9515	1.4276	0.8905	1.4059
0.06	0.9528	1.4290	0.8954	1.4070
0.08	0.9535	1.4308	0.8982	1.4082
0.10	0.9546	1.4320	0.9022	1.4098
SNO -8				
0.01	0.9505	1.4219	0.8871	1.4031
0.02	0.9523	1.4224	0.8894	1.4046
0.04	0.9558	1.4230	0.8924	1.4056
0.06	0.9581	1.4236	0.8947	1.4079
0.08	0.9587	1.4241	0.8981	1.4086
0.10	0.9595	1.4249	0.9002	1.4112
SNO -9				
0.01	0.9508	1.4224	0.8864	1.4034
0.02	0.9524	1.4232	0.8892	1.4048
0.04	0.9558	1.4239	0.8942	1.4058
0.06	0.9576	1.4252	0.8974	1.4066
0.08	0.9605	1.4268	0.9005	1.4079
0.10	0.9617	1.4281	0.9044	1.4091

Table 2: Experimental and theoretical densities of compounds at 308.15 K.

Dihydropyrimidinthiones			
Compound Code	**Experimental Density (g.cm^{-3})**		**Theoretical Density (g.cm^{-3})**
	DMF	***THF***	
SSN -1	1.7358	1.6886	1.3512
SSN -2	1.3335	1.4658	1.3682
SSN -3	1.6717	1.4804	1.3782
SSN -4	1.4420	1.7781	1.4649
SSN -5	1.4205	1.5618	1.4731
SSN -6	1.6642	1.6393	1.4689
SSN -7	1.3714	1.7655	1.4689
SSN -8	1.6753	1.5265	1.4714
SSN -9	1.6554	1.8272	1.5120
Dihydropyrimidine			
	DMF	***DMSO***	
SNO-1	1.3746	1.2347	1.0526
SNO -2	1.3226	1.3201	1.0749
SNO -3	1.2560	1.3168	1.1127
SNO -4	1.0622	1.3006	1.0749
SNO -5	1.1847	1.3355	1.0526
SNO -6	1.2962	1.3029	1.1319
SNO -7	1.2596	1.2999	1.1127
SNO -8	1.3454	1.3186	1.1588
SNO -9	1.3263	1.2204	1.1695

$$\rho = KM/N_A \sum \Delta V_i \quad (2)$$

where ρ is the density of the compound, K is packing fraction (0.599), 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.

Comparison of densities values showed that theoretical density values are different from those evaluated from experimental data. Further, for the same compound, density in the two solvents is different. This suggests that solvent plays an important role. In solutions, compounds interact differently depending upon their substitution, structure and nature of solvent. These molecular interactions affect volume which causes change in density.

Further, the molar refraction of a pure liquid (MRD)1 were calculated by the following equation:

$$(MRD)_1 = \left[\frac{n^2-1}{n^2+1}\right]\frac{M}{\rho} \quad (3)$$

where n, M and ρ are refractive index, molecular weight and density pure liquid respectively.

For solutions, the following equation was used to determining molar refraction:

$$(MRD)_{12} = \left[\frac{n_{12}^2-1}{n_{12}^2+1}\right]\left[\frac{X_1M_1 + X_2M_2}{\rho_{12}}\right] \quad (4)$$

where n_{12} and ρ_{12} are refractive index and density of solution respectively. X_1 and X_2 are the mole fractions and M_1 and M_2 are the molecular weight of the solvent and solute respectively.

From the values of the molar refraction of solution and pure solvent, molar refraction of solid compounds was determined by following equation:

$$(MRD)_{12} = X_1(MRD)_1 + X_2(MRD)_2 \quad (5)$$

From the density and molar refraction data, the refractive indexes of all the compounds were calculated from equation (5). The molar refraction $(MRD)_2$ and refractive index of all the compounds are reported in Table 3 for 0.1M solution.

It is evident from Table 3 that both $(MRD)_2$ and refractive index of compounds are different in each solvent. This again proves that in different solvents, intermolecular interactions are different, which affect these parameters. In some solvents, there may be interaction between solute and solvent molecules where as in others breakage of bonds may take place. As refractive index and molar refraction depends not only upon atomic refraction but also upon single, double or triple bonds, these parameters are affected by the type of interactions taking place in solution. Further, bond polarity also causes change in molar refraction. Thus, type of solvent affects the refractive index and molar refraction of a solute. The measured conductance (k) of each solution after correction is listed in Table 4. It is observed that for all the studied compounds, conductance increases with concentration in all the solvents. For

dihydropyrimidinthiones compounds, conductance is lower in THF than that of DMF which may be due to greater electro relaxation effect owing to the higher permittivity of THF, which contributes interionic repulsions to a larger extent [24]. For dihydropyrimidine, conductivity is less in DMSO than that in DMF.

Table 3: Molar refraction $(MRD)_2$ and refractive index (n) of 0.1 M solutions of compounds at 308.15 K.

Dihydropyrimidinthiones				
Compounds	Solvents			
	DMF		THF	
	(MRD_2)	n	(MRD_2)	n
SSN -1	91.0744	1.6724	102.4883	1.7566
SSN -2	100.7345	1.6012	98.1486	1.6551
SSN -3	80.0690	1.5734	113.1660	1.7628
SSN -4	91.4046	1.5561	111.3178	1.9494
SSN -5	101.7629	1.6267	124.5989	1.9328
SSN -6	86.6130	1.5919	113.1603	1.8205
SSN -7	113.8506	1.6333	102.4138	1.7656
SSN -8	96.2845	1.6817	112.5131	1.7397
SSN -9	100.4741	1.6862	92.4797	1.7004
Dihydropyrimidine				
	DMF	DMSO		
	(MRD_2)	n	(MRD_2)	n
SNO-1	133.61	1.4336	129.88	1.4779
SNO -2	118.08	1.4308	102.81	1.4759
SNO -3	102.37	1.4265	117.35	1.4779
SNO -4	107.93	1.4255	114.02	1.4783
SNO -5	181.09	1.4283	102.03	1.4756
SNO -6	106.33	1.4273	117.85	1.4781
SNO -7	105.32	1.4269	112.75	1.4779
SNO -8	95.20	1.4249	124.21	1.4784
SNO -9	106.18	1.4281	131.64	1.4787

Table 4: Molar refraction $(MRD)_2$ and refractive index (n) of 0.1 M solutions of compounds at 308.15 K.

Conc. M	$k.10^5$mho									
Dihydropyrimidinthiones										
DMF										
	SSN -1	SSN -2	SSN -3	SSN -4	SSN -5	SSN -6	SSN -7	SSN -8	SSN -9	SSN-10
0.000	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200
0.001	0.325	0.420	0.380	0.715	1.200	0.900	0.568	0.817	0.418	0.665
0.002	0.391	0.624	0.480	0.910	2.040	1.420	0.614	1.020	0.577	1.000
0.004	0.550	0.997	0.605	1.320	3.720	1.780	0.728	1.080	0.752	1.610
0.006	0.656	1.340	0.610	1.580	5.000	1.830	0.880	1.380	0.830	2.120
0.008	0.790	1.700	0.612	1.820	5.410	1.900	0.980	1.410	0.980	2.570
0.010	0.900	1.910	0.630	2.090	5.700	2.050	1.090	1.620	1.000	2.980
0.020	1.500	3.350	1.030	3.500	8.800	3.190	1.630	2.500	1.500	3.530
0.040	2.500	5.900	1.740	5.900	14.800	4.800	2.240	4.000	2.500	4.970
0.060	3.500	8.450	2.410	6.300	19.300	5.620	3.000	5.000	3.400	6.390
0.080	4.300	10.800	2.820	6.800	23.500	6.010	3.130	5.500	4.500	7.680
0.100	4.900	12.800	3.300	7.200	24.000	6.600	3.440	6.250	5.600	8.270
THF										
0.000	0.024	0.024	0.024	0.024	0.024	0.024	0.024	0.024	0.024	0.024
0.001	0.098	0.101	0.185	0.169	0.132	0.187	0.127	0.367	0.282	0.287
0.002	0.101	0.107	0.318	0.181	0.224	0.292	0.144	0.594	0.454	0.450
0.004	0.146	0.133	0.425	0.209	0.385	0.380	0.168	0.972	0.729	0.684
0.006	0.177	0.173	0.498	0.285	0.507	0.504	0.188	1.240	0.828	0.853
0.008	0.192	0.195	0.535	0.341	0.551	0.595	0.210	1.540	0.945	0.972
0.010	0.207	0.200	0.580	0.390	0.570	0.660	0.235	1.670	1.040	1.010
0.020	0.377	0.320	1.030	0.620	0.880	1.120	0.372	2.650	1.520	1.720
0.040	0.701	0.590	1.740	1.010	1.480	1.720	0.561	3.940	2.690	2.220
0.060	0.886	0.860	2.410	1.260	1.930	2.270	0.725	4.210	3.420	2.860
0.080	0.955	1.080	2.840	1.590	2.350	2.730	0.878	4.970	4.280	3.440

0.100	1.180	1.280	3.340	1.900	2.400	2.990	1.000	5.550	5.070	3.510
Dihydropyrimidine										
DMF										
	SNO -1	SNO -2	SNO -3	SNO -4	SNO -5	SNO -6	SNO -7	SNO -8	SNO -9	SNO-10
0.000	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200
0.001	0.390	0.322	0.400	0.422	0.300	0.310	0.422	0.320	0.261	0.550
0.002	0.461	0.390	0.530	0.640	0.354	0.415	0.591	0.440	0.304	0.781
0.004	0.672	0.532	0.847	0.993	0.494	0.552	0.982	0.622	0.377	1.142
0.006	0.866	0.686	1.200	1.410	0.592	0.774	1.342	0.792	0.446	1.480
0.008	0.993	0.863	1.491	1.820	0.690	0.983	1.751	0.984	0.521	1.843
0.010	1.180	1.075	1.844	2.190	0.811	1.231	2.090	1.131	0.617	2.150
0.020	2.140	1.674	3.420	5.700	1.151	2.090	3.630	2.160	0.833	3.210
0.040	3.830	3.060	5.560	10.220	1.925	3.510	6.240	3.600	1.121	4.220
0.060	5.190	4.100	7.230	14.800	2.360	4.620	9.090	4.740	1.324	5.960
0.080	6.180	4.950	7.820	18.800	2.750	5.720	11.130	4.980	1.567	7.310
0.100	7.030	5.700	8.520	22.600	3.200	6.410	13.440	5.300	1.775	9.22
DMSO										
0.000	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016
0.001	0.134	0.124	0.191	0.117	0.291	0.027	0.023	0.022	0.030	0.023
0.002	0.237	0.177	0.286	0.197	0.524	0.038	0.028	0.029	0.045	0.027
0.004	0.425	0.288	0.497	0.382	0.980	0.060	0.036	0.039	0.084	0.039
0.006	0.652	0.375	0.678	0.548	1.350	0.082	0.045	0.050	0.121	0.051
0.008	0.871	0.473	0.870	0.760	1.670	0.104	0.053	0.062	0.154	0.061
0.010	1.010	0.520	1.070	1.020	2.040	0.124	0.159	0.078	0.214	0.110
0.020	1.560	0.770	1.750	1.680	3.570	0.356	0.243	0.137	0.282	0.192
0.040	2.700	1.320	3.070	3.020	3.780	0.567	0.385	0.248	0.371	0.301
0.060	3.770	1.780	4.080	4.160	4.070	0.785	0.554	0.361	0.497	0.438
0.080	5.370	2.260	5.010	5.340	4.530	0.883	0.718	0.451	0.620	0.562
0.100	6.330	2.890	5.910	6.810	4.680	0.996	0.910	0.522	0.801	0.756

From corrected conductance, specific conductance (κ) and equivalent conductance (λ_c) are calculated using the following equations:

$$\kappa = k\theta \quad (6)$$

$$\lambda_c = 1000\frac{\kappa}{C} \quad (7)$$

where θ is the cell constant (0.96 cm^{-1}) and c is the concentration (g. equi. /lit.) of solution.

Table 5: The limiting equivalent conductance (λ0) of some synthesized compounds at 308.15 K.

Compound code	**λ_0 mho.cm². equi. $^{-1}$**	
Dihydropyrimidinthiones		
	DMF	**THF**
SSN -1	2.8	1.5
SSN -2	5.2	1.68
SSN -3	3.6	2.3
SSN -4	-	2.5
SSN -5	12.7	1.5
SSN -6	8.5	2.29
SSN -7	4.7	2.52
SSN -8	-	-
SSN -9	3.1	3.5
SSN-10	6	-
Dihydropyrimidine		
	DMF	**DMSO**
SNO-1	-	1.2
SNO -2	1.51	-
SNO -3	-	-
SNO -4	2.4	1.1
SNO -5	-	3
SNO -6	-	0.5
SNO -7	1.26	0.2
SNO -8	2.45	0.2
SNO -9	1.46	0.14
SNO-10	0.92	0.12

The equivalent conductance (λ_c) is plotted against $\sqrt{C}$ for all compounds as shown in (Figures 1 & 2). For all the dihydropyrimidinthiones and dihydropyrimidine, the equivalent conductance increases with concentration in both the solvents. It is obvious from figures that some of the compounds behave as strong electrolytes whereas others exhibited weak electrolytic behavior. The behavior is different in different solvents. For weak electrolytes, it is difficult to determine λ_0. However, for some of the compounds in the studied solutions of compounds, λ_0 values are evaluated approximately by extrapolation method and are reported in Table 5.

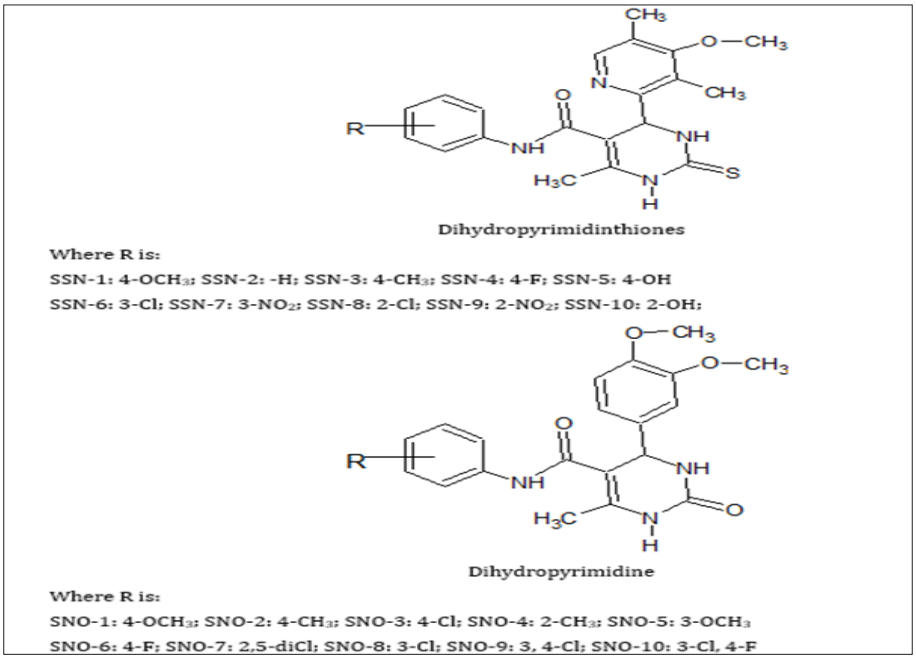

Figure 1: General structure of synthesized different pyrimidine derivatives.

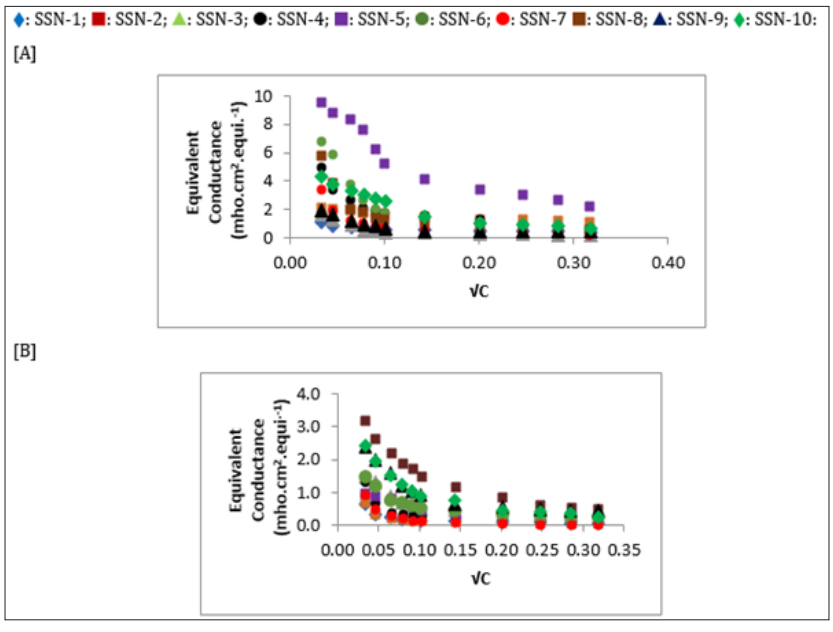

Figure 2: The variation of equivalent conductance with C for Dihydro pyrimidinones in [A] DMF and [B] DMSO at 308.15 K.

Conclusion

It is observed that physicochemical parameters of compounds in solution depends not only on the structure and substitution of the compound but also on the nature of solvent in which it is dissolved. The molecular interactions occurring in the solution affect volume which in turn causes a small change in density and refractive index. Depending upon the nature of solvent, the conductance i.e., electrolytic behavior of compounds also changes.

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