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STUDY OF MOLECULAR INTERACTIONS IN SOLUTIONS OF PHENYL PYRIMIDINE DERIVATIVES IN 1,4-DIOXANE AT 298.15 K

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Abstract— Some new phenyl pyrimidine derivatives have been synthesized and their characterization was done by IR, ^{1}H NMR and Mass spectral data. The density and sound velocity of some newly synthesized phenyl pyrimidine derivatives have been measured in 1, 4-dioxane solutions over a wide range of concentrations (0.01 to 0.1M) at 298.15 K. From these experimental data, some acoustical parameters have been evaluated and correlated with the concentration. The obtained results give useful information about molecular interactions occurring in solution.

Key words: Phenyl pyrimidine derivatives, ultrasonic velocity, molecular interaction, acoustical parameter, 1, 4-dioxane

I. INTRODUCTION

The study of molecular interaction plays a vital role for the understanding of molecular interactions and structural behavior of liquid mixtures and solutions [1-5]. Ultrasonic, a versatile non-destructive technique is a subject of extensive research because of its applications in various fields [6-9]. Further, Ultrasonic velocity measurement is one of the best tools to understand the understanding physicochemical behavior of liquids and solutions i.e., nature of molecular interactions. Ultrasonic velocity together with density and viscosity data furnishes a wealth of information about the interaction between ions, dipoles, hydrogen bonding, dispersive forces etc. [10-12].

Pyrimidine derivatives are an important class of organic compounds and they were reported to possess a broad spectrum of biological activities [13-18].

In view of the medicinal, agricultural, pharmaceutical significance of pyrimidine derivatives, some new phenyl pyrimidine derivatives have been synthesized and their density, sound velocity and viscosity in 1,4-dioxane solutions were measured at 298.15 K over a wide range of concentrations. Further, some acoustical parameters have been evaluated to give useful information about molecular interactions in solution. An attempt is also made to study the effect of substituent at different positions on the acoustic properties.

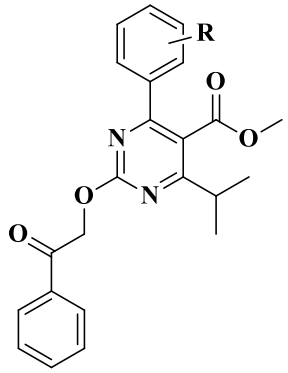
II. EXPERIMENTAL

Some new phenyl pyrimidine derivatives are synthesized in the laboratory and their structure confirmation was done by IR, NMR and mass spectral data. To study acoustical properties, solutions of synthesized compounds were made over a wide range of concentrations in 1,4-dioxane and were kept in air tight bottles.

Ultrasonic velocity and density measurements of pure 1,4-dioxane and solutions of compounds have been done at 298.15 K by using Anton Paar Density and Sound Velocity meter (DSC 5000M) with accuracy of ±0.5 m/s and ±0.000005 g/cm^3 respectively. The instrument was fully automated and the temperature was automatically controlled. Calibration was carried out using Milli-Q-water (Millipore Pvt. Ltd. Bangalore, India).

III. RESULTS AND DISCUSSION

Figure 1 shows general structure of synthesized compound and physical properties of all the synthesized compounds are given in Table 1 with their side chain substitution.



R = Different functional group

Fig. 1: General structure of synthesized compound

Table 1 Physical properties of synthesized phenyl pyrimidine derivatives.

Compound Code	*Substitution R*	*Molecular Formula*	*Molecular Weight*	*Yield (%)*
RPD-1	-4-OCH_3	$C_{24}H_{24}N_2O_4$	420	75
RPD-2	-4-CH_3	$C_{24}H_{24}N_2O_4$	404	84
RPD-3	-H	$C_{23}H_{22}N_2O_4$	390	86
RPD-4	-3-Cl	$C_{23}H_{21}ClN_2O_4$	424	84
RPD-5	-2,5-di-OCH_3	$C_{25}H_{26}N_2O_6$	450	80

Table 2 shows experimental data of density and ultrasonic velocity for the synthesized compounds in 1,4-dioxane at 298.15 K. It is evident from the Table 2 that as concentration increases, density and ultrasonic velocity increases.

To study molecular interactions of compounds in solutions, some acoustical and apparent parameters such as adiabatic compressibility (κ_s), intermolecular free length (L_f), solvation number (S_n), apparent molar compressibility (ϕ_k) and apparent molar volume (ϕ_v) were evaluated using experimental data of ultrasonic velocity (U) and density (ρ) using equations

reported earlier [19]. Some of these parameters are given in Table 2.

Further, the apparent molar compressibility (ϕ_k) of the solutions is fitted to Gucker's relation [20] and is given by:

Table 2: Some acoustical parameters of solutions of phenyl pyrimidine derivatives in 1,4-dioxane at 298.15

Conc. (M)	*Density Kg/m³*	*Velocity m/s*	*$L_f \times 10^{11}$ m*	*$\kappa_s \times 10^{10}$ $m^2.dyne^{-1}$*	*S_n*
RPD-1					
0.00	1027.56	1344.92	4.7708	5.3802	-
0.01	1028.25	1346.55	4.7634	5.3635	6.32
0.02	1028.86	1347.56	4.7584	5.3523	7.57
0.04	1030.04	1348.75	4.7515	5.3367	9.79
0.06	1031.08	1350.26	4.7438	5.3194	10.57
0.08	1032.04	1351.51	4.7372	5.3047	11.43
0.10	1033.89	1352.42	4.7298	5.2880	11.78
RPD-2					
0.01	1027.99	1346.95	4.7626	5.3617	5.27
0.02	1028.27	1348.13	4.7578	5.3509	6.66
0.04	1029.03	1350.15	4.7489	5.3309	7.99
0.06	1029.43	1352.35	4.7403	5.3115	8.66
0.08	1030.26	1354.59	4.7305	5.2897	8.83
0.10	1031.58	1356.10	4.7222	5.2712	9.22
RPD-3					
0.01	1028.15	1345.86	4.7661	5.3695	8.52
0.02	1028.74	1346.48	4.7625	5.3615	9.76
0.04	1029.79	1347.97	4.7548	5.3442	10.19
0.06	1031.15	1348.25	4.7507	5.3350	12.23
0.08	1031.78	1349.56	4.7446	5.3214	12.62
0.10	1033.11	1350.00	4.7400	5.3111	13.51
RPD-4					
0.01	1028.46	1346.74	4.7622	5.3609	5.57
0.02	1029.10	1346.96	4.7600	5.3558	8.83
0.04	1030.43	1347.94	4.7535	5.3411	11.10
0.06	1031.65	1348.54	4.7485	5.3301	13.06
0.08	1032.95	1349.01	4.7439	5.3197	14.53
0.10	1034.42	1349.35	4.7393	5.3094	15.64
RPD-5					
0.01	1028.38	1345.93	4.7653	5.3678	9.75
0.02	1029.31	1346.78	4.7601	5.3562	10.10
0.04	1031.07	1348.43	4.7502	5.3339	10.55
0.06	1032.84	1349.65	4.7419	5.3152	11.35
0.08	1034.85	1351.07	4.7323	5.2937	11.45
0.10	1036.71	1352.25	4.7239	5.2750	11.85

$$\phi_k = \phi^\circ_k + S_k m^{1/2} \qquad (1)$$

Where ϕ°_k and S_k are the limiting apparent molar compressibility at infinite dilutions and interaction parameter respectively. The values of ϕ°_k and S_k are calculated by the least square method.

By using the following Masson relation [21]

$$\phi_v = \phi^\circ_v + S_v m^{1/2} \qquad (2)$$

The values of ϕ°_v and S_v are calculated by the least square method. ϕ°_v is the limiting apparent molar volume at infinite dilution and S_v is measure of solute-solvent interaction.

These calculated parameters are given in Table 3.

The variation of ultrasonic velocity and intermolecular free length (L_f) with concentration are shown in Figures 2 and 3 respectively. It is clear from these figures that ultrasonic velocity increases with concentration for all the compounds whereas intermolecular free length (L_f) decreases with increases in concentration. Thus, ultrasonic velocity is reverse of intermolecular free length (L_f). The decrease of intermolecular free length (L_f) with increase of concentration suggests the decrease of distance between solute and solvent molecules due to solute-solvent interactions which causes velocity to increase.

Table 4: Coefficients of Gucker and Masson equations for phenyl pyrimidine derivatives at 298.15 K

Coefficient	*RPD-1*	*RPD-2*	*RPD-3*	*RPD-4*	*RPD-5*
$-\phi^\circ_k x\ 10^7$ $dyn^{-1}mol^{-1}$	2.12	2.18	1.46	2.23	1.74
$S_k x\ 10^7$ $m^3.mol^{-1}$	3.3	3.83	1.7	4.3	0.70
$-\phi^\circ_v$ $dyn^{-1}m^3mol^{-1}$	74	39.7	61.9	76	82.4
S_v dyn^{-1} $m^{-3/2}.mol^{-3/2}$	78.14	40	40	30.90	18.55

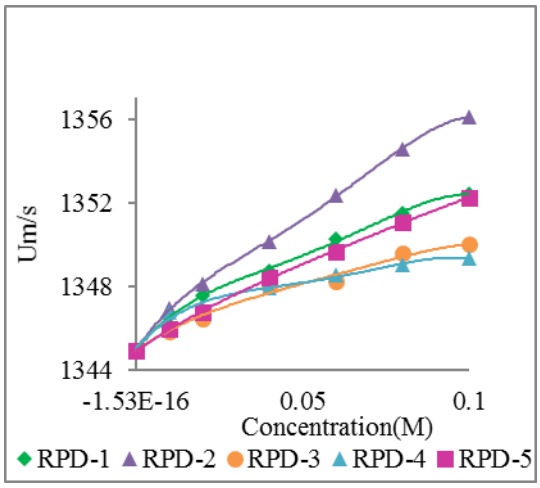


Figure 2: The variation of ultrasonic velocity (U) with concentration of phenyl pyrimidine derivatives in1,4-dioxane at 298.15 K

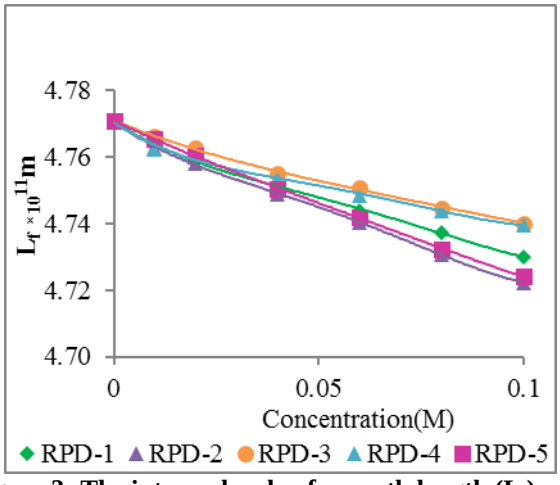


Figure 3: The intermolecular free path length (L_f) with concentration of phenyl pyrimidine derivatives in1,4-dioxane at 298.15 K

Figure 4 shows the variation of adiabatic compressibility (κ_s) with concentration which is found to decrease with increase in concentration. The decrease in adiabatic compressibility again

proves that there is strong interaction between solvent and solute molecules. By increase in concentration of solute, molecular associations are enhanced and newly formed aggregates cause adiabatic compressibility to decrease.

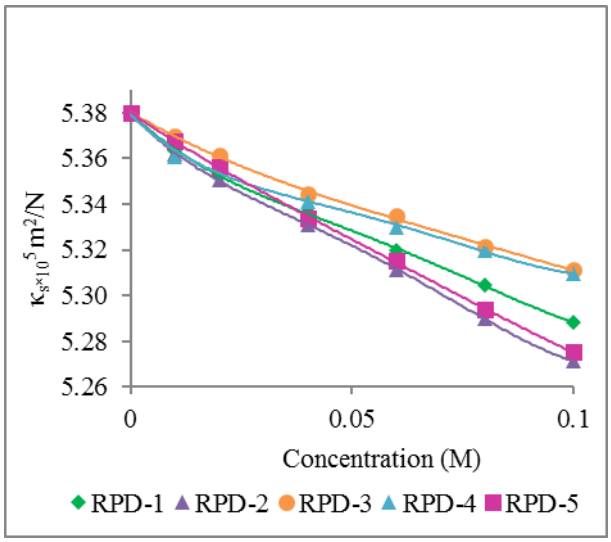


Figure 4: Variation of adiabatic compressibility (κ_s) with concentration of phenyl pyrimidine derivatives in 1,4-dioxane at 298.15 K.

Further, it is observed that for all the five synthesized compounds, maximum solute-solvent interactions are observed for RPD-2 and minimum for RPD-4. The type and magnitude of interaction depends upon structure of compound as well as solvent. In the present study, solvent is same for all the compounds so different structure is responsible for magnitude of molecular interactions. For all the compounds, central moiety is same but side chains are different. Table 1 shows that compound containing p-methyl group (RPD-2) exhibited maximum molecular interaction in 1,4-dioxane whereas minimum molecular interaction is observed for RPD-4 containing 3-Cl group. This suggests that electro negativity of groups play an important role in 1,4-dioxane solution of studied compounds. Lower the electro negativity, maximum is the molecular interaction.

The type of interactions between solute and solvent molecules can also be suggested by a parameter solvation number (S_n), which is the number of solvent molecules attached to the solute molecule. It gives the information about structure forming tendency or structure breaking tendency of a compound in solutions. Depending upon structure of compound, the solvation number is either positive or negative. Figure 5 shows that for the studied compounds, the solvation numbers are positive and increases with increase in concentration.

The positive solvation number (S_n) indicates structure forming tendency of compound in solution. Thus, solvation number again proves that there is strong solute-solvent interaction between solute and solvent molecules which causes an increase in solvation number [22].

As shown in Table 4, values of ϕ^0_k and ϕ°_v values are negative whereas S_k and S_v values are positive for all the synthesized compounds. In a solution, when solute causes electrostriction in a solution, it causes decrease in compressibility which is reflected by negative ϕ^0_k values. Thus, ϕ°_v also decreases, thus negative values are observed. The positive S_k and S_v values again confirms the existence of solute-solvent interactions in the studied systems.

Thus, it is concluded that in 1,4-dioxane solutions, for all the studied compounds, solute-solvent interactions exists which increases with concentration. The solute-solvent interactions are affected by different side chains present in the compound. The electro negativity of the substitution present as a side chain in the compound and temperature affect molecular interactions.

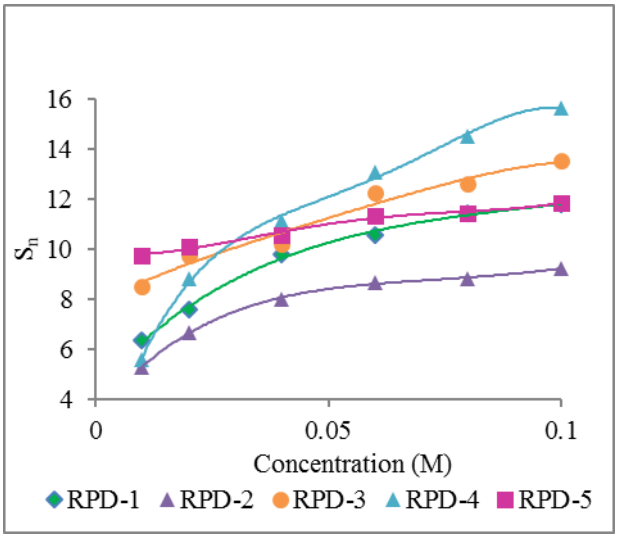


Figure 5: Variation of solvation number (S_n) with concentration of phenyl pyrimidine derivatives in 1,4-dioxane at 298.15 K.

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