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Ultrasonic study of some synthesized pyrazolines at different concentration in 70% of 1, 4-dioxane-water mixture

V. D. Mane[*1], D. T. Mahajan[2] and P. R. Rajput[2]

[1]*Department of Chemistry, Shankarlal Khandelwal College, Akola, India*
[2]*Department of Chemistry, Vidyabharti Mahavidyalaya, Amaravti, India*

ABSTRACT

The ultrasonic velocity study of the heterocyclic compounds i.e. ultrasonic velocity, adiabatic compressibility, apparent molal volume, apparent molal compressibility have been determined for the synthesized pyrazolines at different concentrations in the dioxane-water mixture by using ultrasonic interferometer at 1 MHz frequency. The variations in acoustical properties with increasing in concentration of the heterocyclic compounds have been used to understand the changes in molecular interactions between solute and solvent to know the structure making and breaking property of solute molecules with increase in concentration of pyrazolines.

Keywords: adiabatic compressibility, acoustic properties, ultrasonic velocity, apparent molal volume, apparent molal compressibility.

INTRODUCTION

The synthetic heterocyclic compounds found their application in various field like antibacterial, antimycobacterial, trypanocidal, anti HIV activity, genotoxic, herbicidal, analgesic, antinflammatory, muscle relaxant, antileishmanial agents, anticonvulsant, anticancer, antimalerial, antifungal and lipid peroxidation inhibitor, antitubercular, hypnotics, anti depressant, antitumoral, anthelmintic, and insecticidal agent[1-6]. Number of important biochemical molecules and drugs obtained from natural resources contains heterocyclic rings. Presence of heterocyclic rings has profound effect on physiological activity of heterocyclic ring containing compounds and has lead to wide variety of modern drugs.

Substituted pyrazoline have been reported to exhibit antioxidant[7], anticancer[8], fungicidal[9], anti-inflammatory[10], analgesic[11], insecticidal[12], antiarthritic[13], cerebroprotective[14], antidepressant[15], activities. Apart from their biological activities pyrazolines exhibited fluorescent and luminescent[16] activities.

Ultrasonic velocity measurement is one of the highly powerful and sensitive method that reveals the nature and strength of intermolecular interactions occurring in the solutions. So in the recent days there is a vast study going on regarding to analyze the intermolecular interaction in solutions, molecular structures by using ultrasonic velocity techniques and some properties such as adiabatic compressibility, apparent molal volume, and apparent molal compressibility. Theses study provides a new avenue for the understanding intermolecular interaction of various solvent with water. Literature survey shows that many researchers[17-23] have done the acoustical study by the measurement of density and ultrasonic velocity of different aqueous and non-aqueous systems like dioxane, ethanol etc at different temperatures. Adiabatic compressibility in aqueous solutions of alkali metal chlorides have been studied by Hisashi Uedaira and Yasuko Suzuki[24].In view of the importance of these parameters, an attempt is made to determine the density and ultrasonic velocity of pyrazolines and isoxazoline in different percentage of dioxane-water mixtures at a particular temperature.

MATERIALS AND METHODS

The substituted 2-hydroxy pyrazolines has been synthesized by known methods in the laboratory and their structure are confirmed by on the basis of their analytical data. 1, 4-dioxane was purified by Vogel's standard method[25]. The double distilled water is used for solution preparation of solution of metal salt. The solution of pyrazoline was prepared in pure dioxane. The densities of solutions containing different concentration of ligand in absence and in presence of metal ion were measured by using digital density meter (Aton Paar make). The ultrasonic velocity of the solutions were measured by using ultrasonic interferometer having frequency 1MHz (Mittal Enterprises, Model No F-81) .The constant temperature was mentained by circulating water through the double wall measuring cell made up of steel. In the current study we determined the value of adiabatic compressibility (βs), apparent molal volume (ϕv), apparent molal compressibility ($\phi\kappa$).The apparent molal volume and apparent molal compressibility have been calculated from following equations.

The following pyrazolines are used for ultrasonic study
i) 3-(2-Hydtroxy-3, 5-dichlorophenyl)-5-(4-chlorophenyl)-1-phenylpyrazoline (HCPPA)**L1**
ii)3-(2-Hydtroxy-3, 5-dichlorophenyl)-5-(2, 4-dichlorophenyl)-1-Phenylpyrazoline. (HDPPB)**L2**

The apparent molal volumes, adiabatic compressibility and apparent molal adiabatic compressibility were determined by using following formulas.

1. Apparent Molal Volume (ϕ_V)

$$(\phi_V) = (M / ds) + [(do - ds)\ x10^3] / m\ do\ ds \quad \text{---- (1)}$$

Whereas M = Molecular weight of Solute.
d_O = Density of a solvent. ds = Density of solution.
m = molality of the solution.

2. Adiabatic Compressibility (β_o & β_s)

i) For Solvent $\beta_o = 1/Uo^2\ d_o$ -----(2)
ii)For solution $\beta_s = 1/Us^2\ d_s$ -----(3)

Were U_o and U_s are ultrasonic velocity in the solvent and solution respectively. d_o and d_s are density of the solvent and solute respectively.
β_o and β_s are adiabatic compressibility of the solvent and solution respectively.

2. Apparent Molal adiabatic compressibility (ϕ_{ks})

$$(\phi_{ks}) = \frac{1000(B_s d_o - B_o d_s)}{m\ d_s.d_o} + \frac{B_s.M}{d_s} \quad \text{---------- (4)}$$

4. The graphs of ϕ_v Vs $\sqrt{m}$ were plotted and presented in fig. 8.2.1 to 8.2.11 as per the value of limiting molal volume of the solution ϕ^0_v at m = 0 and slope S_v were calculated using Mason equation.

$$\phi_v = \phi^o_v + S_v m^{1/2} \quad \text{----------(5)}$$

Where S_v is the slope of the plot which measures solute-solute interaction. ϕ^o_v measures solute-solvent interaction at infinite dilution.

5. The graphs of ϕ_{ks} Vs $\sqrt{m}$ were plotted and are presented in fig. 8.2.2 to 8.2.12 The value of limiting molal adiabatic compressibility ϕ^o_{ks} of the solute at m = 0 and slope S_k were calculated by employing following equation.

$$\phi_{ks} = \phi^o_{ks} + S_k m^{1/2} \quad \text{----------(6)}$$

Where S_k is the slope of the plot, which measure solute-solute interaction. ϕ^o_{ks} is the measures of solute-solvent interaction at infinite dilution.

RESULTS AND DISCUSSION

The present density measurement study shows that the partial molal volume for all ligands are negative this indicates weak solute-solvent interactions. With increase in concentration of the ligand, the partial molal volume is found to be increased this suggested that the solute-solvent interaction though weak are slightly increased. At higher concentration (m = 0.006), all ligands shows positive value of partial molal volume indicating strong solute-solvent interaction. This might be due to electrostriction of the ligand molecules of higher concentration by the solvent molecules. Only at such higher concentration the ligands shows structure breaking property. The partial molal volume of each ligand in presence of Cu (II) ion at lower concentration of ligand are negative suggesting weak solute-solvent interaction. With increase in concentration of HCPP, the partial molal volume of HCPP is increased suggesting increase in solute-solvent interaction. The partial molal volume of HCPP in presence of Cu (II) ion is higher than that ion absence of Cu(II) ions at all different concentration of HCPP. This suggested that the solute-solvent interaction are enhanced in presence of Cu (II) ions the partial molal volume of HDPP in presence of Cu (II) ion up to certain concentration of HDPP (m=0.04472) is higher than that in absence of Cu(II) ions. Above this concentration the partial molal volume of HDPP in presence of Cu (II)ions is lower than that in absence of Cu (II) ion indicating relatively lower solute-solvent interactions. The partial molal volume of HDPL in peresence of Cu (II) ion as compared to in absence of Cu (II) ion is observed, this might be due to continuous structural changes around HDPI molecules in presence of Cu (II) ions than that in absence of Cu (II) ions.

The large negative values of ϕ^{o}_{v} indicate that at infinite dilution , the solute solvent interactions are almost absent hence the solute is acting as structure makers might be due to presence of solute-solute interaction as indicated by positive values of S_v in all systems.

Table 1 (ϕ_V) and (ϕ_{ks}) values in 70% dioxane –water mixture
System: (HCPP-A) L_1 Temp = 30 ± 0. 1°C
Ultrasonic frequency = 1 MHz

Sr. No.	Concentration of ligand m/10^{-3} mol.kg^{-1}	ϕ_{ks}/10^{-2} m^3 mol^{-1} pa^{-1}	ϕ_V /10^{-6}m^{3}mol^{-1}
1	0.50	-10.09	-2953.5695
2	1.00	-91.40	-1183.0926
3	2.00	-5.40	-437.4667
4	4.00	-0.188	-18.116
5	6.00	-0.451	152.76

Table 2 (ϕ_V) and (ϕ_{ks}) values in 70% dioxane –water mixture
System :(HCPP-A) L_1+Cu (II)
Temp =30 ± 0.1°C Ultrasonic frequency = 1 MHz

Sr. No.	Concentration of ligand m/10^{-3} mol.kg^{-1}	ϕ_{ks}/10^{-2} m^3 mol^{-1} pa^{-1}	ϕ_V /10^{-6}m^{3}mol^{-1}
1	0.50	-1.423	-1836.3642
2	1.00	-0.530	-810.6133
3	2.00	-2.386	-251.1852
4	4.00	0.226	-18.27052
5	6.00	-3.34	214.815

Table 3 (ϕ_V) and (ϕ_{ks}) values in 70% dioxane –water mixture
System: (HDPP-B) L_2
Temp =30 ± 0.1°C Ultrasonic frequency = 1 MHz

Sr. No.	Concentration of ligand m/10^{-3} mol.kg^{-1}	ϕ_{ks}/10^{-2} m^3 mol^{-1} pa^{-1}	ϕ_V /10^{-6}m^{3}mol^{-1}
1	0.50	0.4278	-1616.2569
2	1.00	-1.3521	-1242.4097
3	2.00	-0.8723	-357.19063
4	4.00	3.5180	155.5152
5	6.00	-4.8168	133.9166

Table 4 (ϕ_V) and (ϕ_{ks}) values in 70% dioxane –water mixture
System: - (HDPP-B) L_2 + Cu (II)
Temp =30 ± 0.1°C Ultrasonic frequency = 1 MHz

Sr. No.	Concentration of ligand m/10^{-3} mol.kg^{-1}	ϕ_{ks}/10^{-2} m^3 mol^{-1} pa^{-1}	ϕ_V /10^{-6}m^{3}mol^{-1}
1	0.50	2.868	-1617.2569
2	1.00	-3.788	-683.6713
3	2.00	0.7270	-264.0016
4	4.00	-0.1738	62.248

ϕ_{ks} value in all systems shows continuous variation with increase in concentration of the ligands. In case of ligand HCPP-L_1, the ϕ_{ks} values increase with increases in concentration of the ligand. But for the ligand HDPP-L_2 the ϕ_{ks} values are decreasing with increase in concentration of the ligand. This suggested the decrease in compressibility due to weak solute - solvent interactions. The L_1+Cu (II) and L_2+Cu (II) system shows decrease in ϕ_{ks} values because of increasing solute-solvent weak interactions. The L_3+Cu (II) system shows increasing ϕ_{ks} values with increasing in concentration of the ligand. This might be due to decrease in solute-solvent interactions the negative ϕ^{o}_{ks} values for L_1+Cu (II) systems indicates decrease in compressibility due to increased solute-solvent interaction, where as the positive ϕ^{o}_{ks} value for L_2+Cu(II) systems suggested increase in compressibility due to decreased solute-solvent interactions at infinite dilution. The negative ϕ_{ks} values for L_1-Cu (II) and L_2- Cu (II) systems indicates absence of solute-solute interaction.

Table 7 $\phi^{o}v$, $\phi^{o}Ks$, S_v and S_k values for ligand system

Ligands	$\phi^{o}v/10^{-6}\ m^3\ mol^{-1}$	$S_v/10^4 kg^{1/2}m^3\ mol^{-3/2}$	$\phi^{o}Ks/10^{-12}m^3\ mol^{-1}Pa^{-1}$	S_k / $kg^{1/2}m^3\ mol^{-3/2}Pa^{-1}$
L_1	-2200	2.80	-14	200
L_2	-2111	4.25	1.4	-94.44

Table 8 $\phi^{o}v$, $\phi^{o}Ks$, S_v and S_k values for ligand + metal system

Ligands	$\phi^{o}v/10^{-6}m^3mol^{-1}$	$S_v/10^4 kg^{1/2}m^3\ mol^{-3/2}$	$\phi^{o}Ks/10^{-12}m^3\ mol^{-1}Pa^{-1}$	S_k / $kg^{1/2}m^3\ mol^{-3/2}Pa^{-1}$
L_1+ Cu(II)	-1889	3.57	-0.620	-37.6
L_2+ Cu(II)	-1500	6.80	3.8	-70.58

PLOT OF (ϕ_V) AND (ϕ_{ks}) Vs MOLE FRACTION

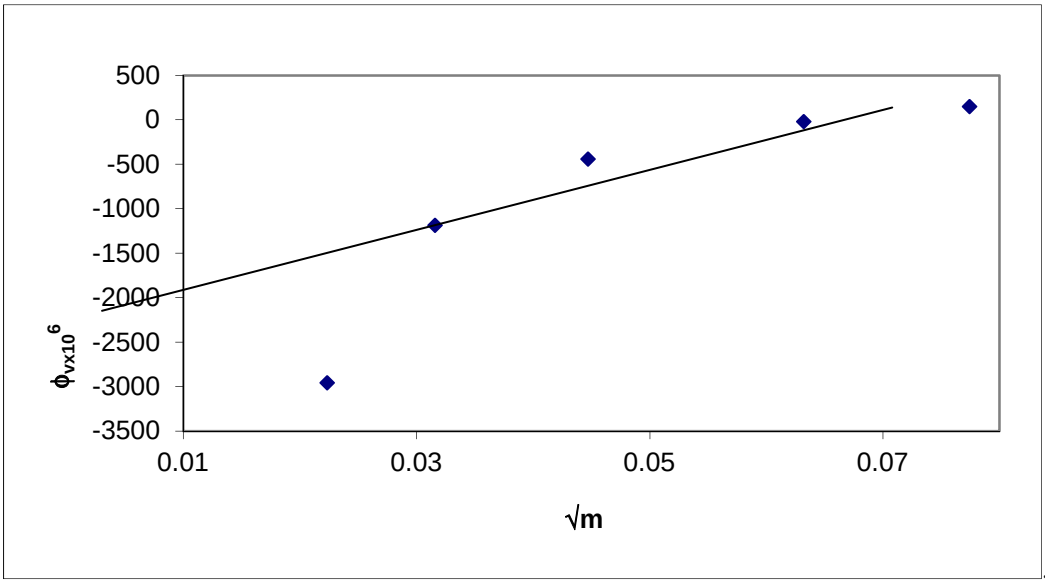

Fig. 1 system-HCPP-L_1 (ϕ_V) Vs √m

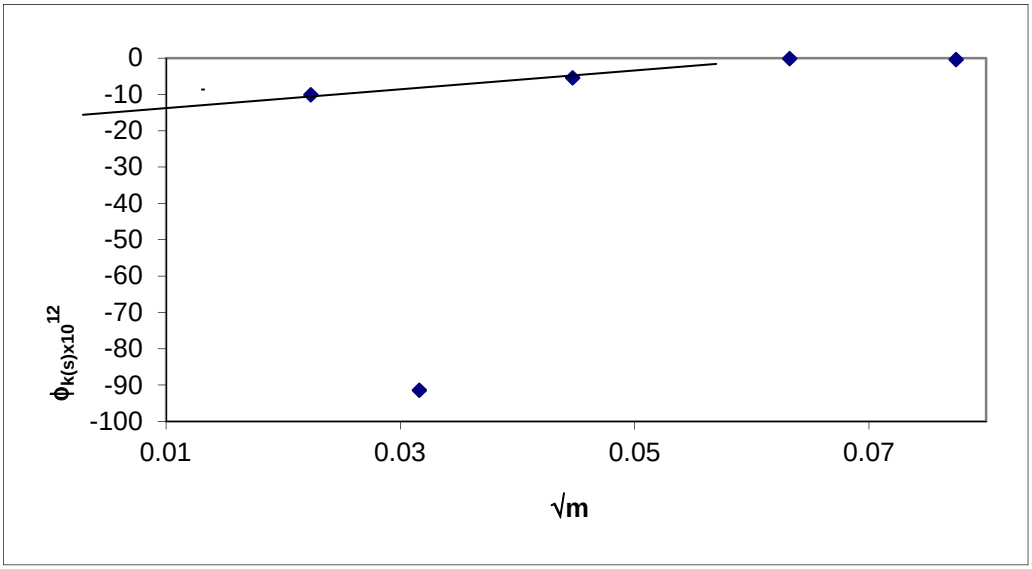

Fig. 2 system-HCPP-L_1 (ϕ_{ks}) Vs √m

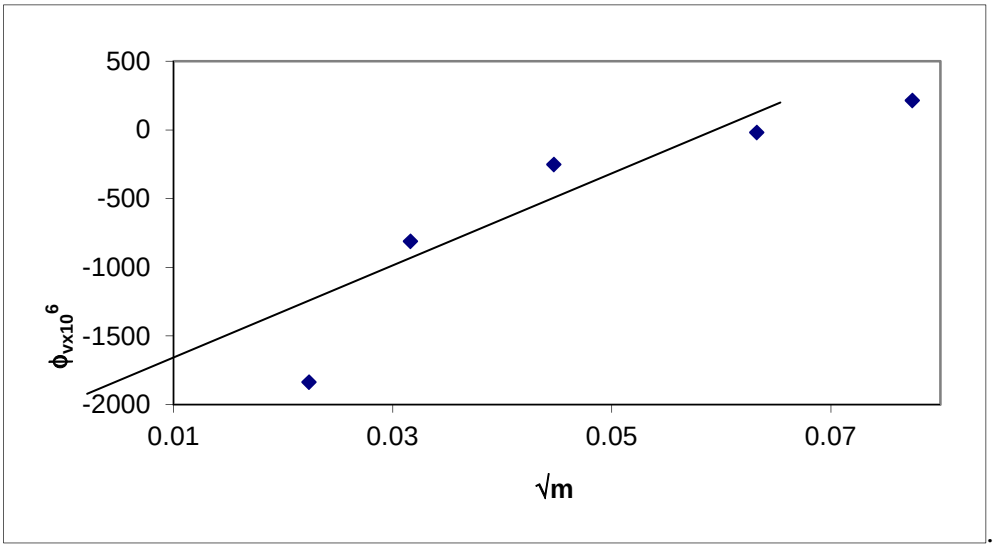

Fig. 3 system- HCPP-L_1+ Cu (II) (ϕ_v) Vs √m

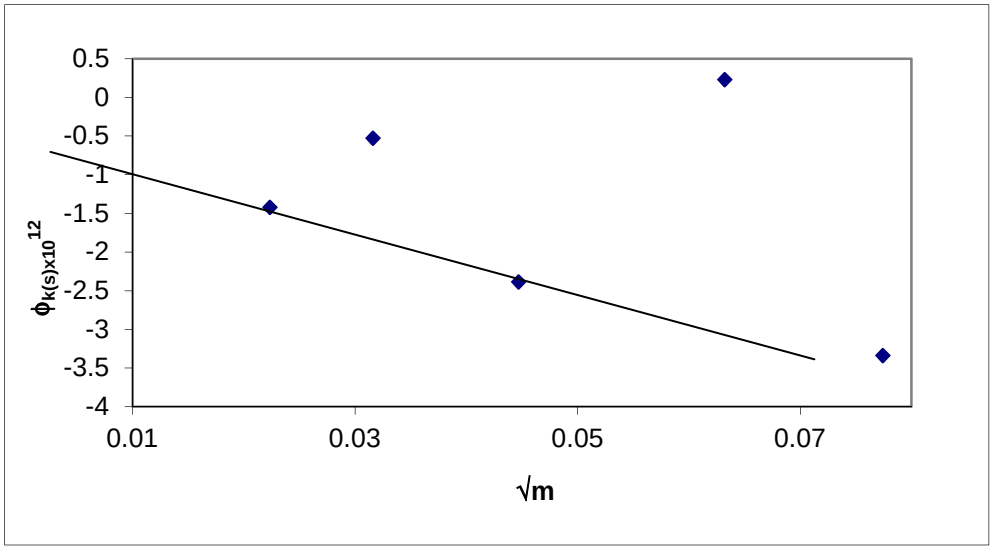

Fig. 4 system- HCPP-L_1+Cu (II) (ϕ_{ks}) Vs √m

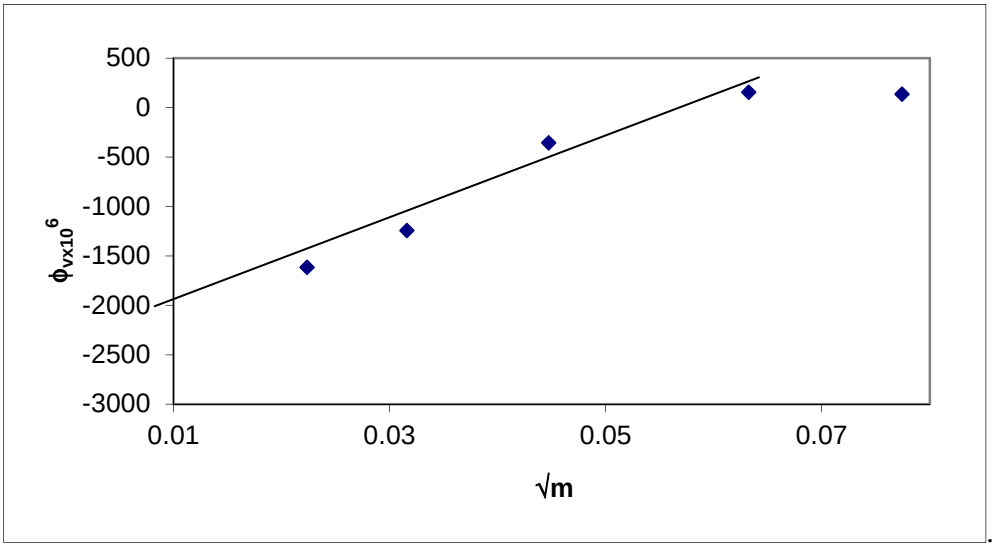

Fig. 5 system-HDPP-L_2 (ϕ_v) Vs √m

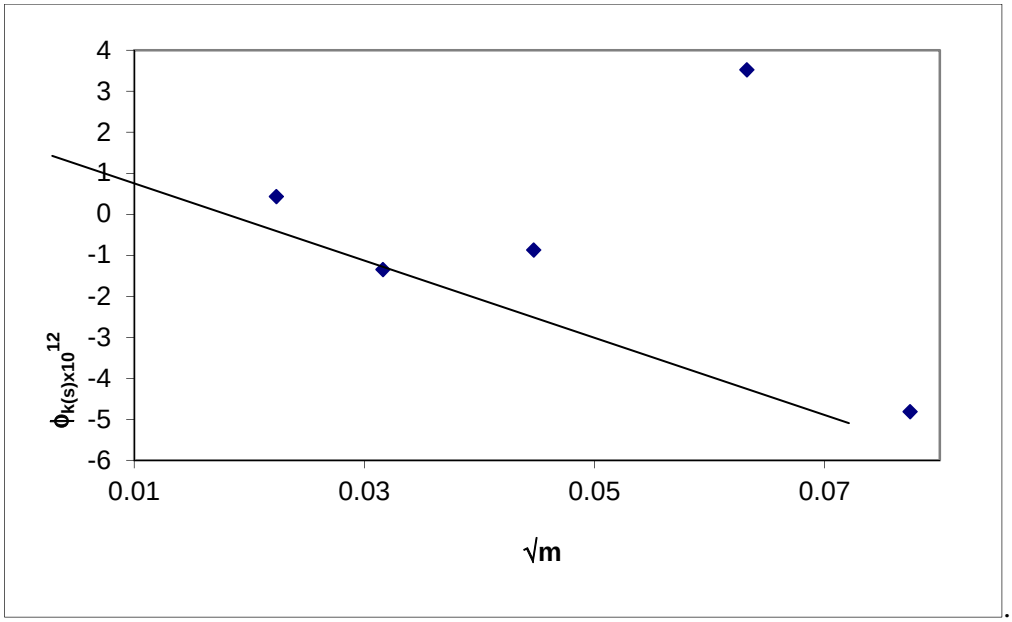

Fig. 6 system-HDPP-L_2(ϕ_{ks}) Vs √m

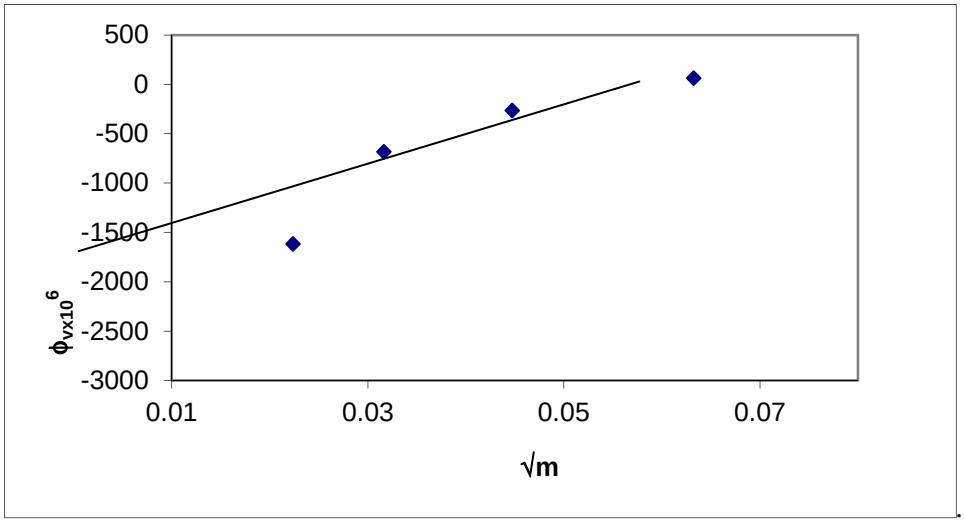

Fig. 7 system-HDPP-L_2- Cu (II) (ϕ_v) Vs √m

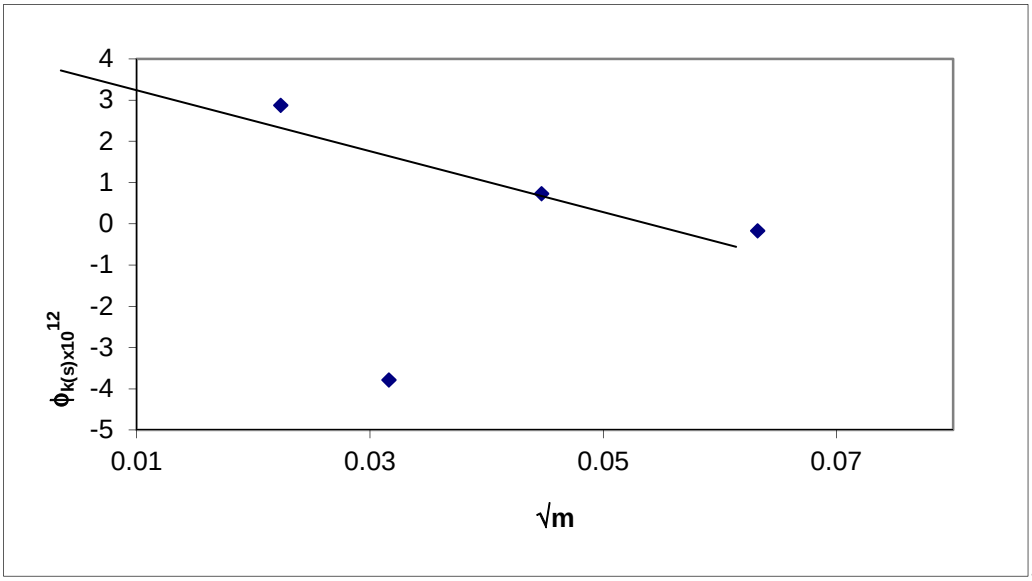

Fig. 8 system-HDPP-L_2- Cu (II) (ϕ_{ks}) Vs √m

CONCLUSION

The substituted 2-hydroxy pyrazoline has been synthesized from chalcone, when it was reacted with phenyl hydrazine hydrochloride in ethanol respectively. Acoustical properties were measured for these heterocyclic compounds in 1,4-dioxane at constant temperature. The result from graph shows that these is good solute- solvent interaction take place

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