Acoustical studies on binary liquid mixtures of some 1,3,4-oxadiazole derivatives with acetone at 303.15 K

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ABSTRACT

The wide spread use of 1,3,4-oxadiazoles as a scaffold in medicinal chemistry establishes this moiety as an important bioactive class of heterocycles. In the present study ultrasonic velocity (u), density (ρ) and viscosity (η) have been measured at frequency 2 MHz in the binary mixtures of 1,3,4-oxadiazole derivatives in acetone at 303.15 K using ultrasonic interferometer technique. The measured value of ultrasonic velocity, density and viscosity have been used to estimate the acoustical parameters namely adiabatic compressibility (β_{ad}), relaxation time (τ), acoustic impedance (Z_i), free length (L_f), free volume (V_f) and internal pressure (π_i), with a view to investigate the nature and strength of molecular interactions. The obtained result support the occurrence of molecular association through hydrogen bonding in the binary liquid mixtures.

Keywords: Acoustical properties; hydrogen bonding; binary mixtures

1. INTRODUCTION

Ultrasonic offer the most exciting and fascinating field of scientific research among the researcher. since the ultrasonic and other related thermo acoustic parameters provide useful information regarding the structure of molecules, molecular order, molecular packing, inter and intra -molecular interaction[1-2] etc. Ultrasonic study of liquid and liquid mixture has gained much importance during the last two decades in assessing the nature of molecular interaction and investigating the physiochemical behavior of system[3-4].

Molecular interaction in liquid mixtures has been extensively studied using ultrasonic technique by many workers[5], because mixed solvents find practical applications in many chemical, biological and industrial processes. 1,3,4-oxadiazole derivatives are heterocyclic compounds containing one oxygen and two nitrogen atoms in a five-membered ring. 1,3,4-oxadiazole derivatives have played a major role in the pharmaceutical chemistry. Therefore the applications of these compounds attract us to study their behaviour in acetone.

We report here the results of study on binary liquid mixture of 1,3,4-oxadiazole derivatives over the entire range of composition at T = 303.15 K. By using the experimentally measured values of ultrasonic velocity (u), density (r) and viscosity (η), various acoustical parameters like excess adiabatic compressibility, excess intermolecular free length, excess acoustic impedance, and excess ultrasonic velocity have been calculated the mixture. The

calculated deviations and excess functions have been explained on the basis of the intermolecular interactions present in these mixtures. The binary liquid systems studied here is

(i)   1-(5-amino-2-phenyl-1,3,4-oxadiazole-3(2H)-yl) ethanone - acetone,

(ii) 1-(5-amino-2-(3-(trifluoromethyl)phenyl)-1,3,4-oxadiazole-3(2H)-yl) ethanone - acetone,

(iii) 1-(5-amino-2-(2,4-dimethoxyphenyl)-1,3,4-oxadiazole-3(2H)-yl) ethanone - acetone.

2. EXPERIMENTAL SECTION

The Compounds were recrystalized before use. The solvent used in the present work of AR grade and were purified according to the standard procedure described in the literature[6]. Solutions of different molarity were prepared for each binary system. The ultrasonic velocity in the mixture was measured using a variable path fixed frequency ultrasonic interferometer working at 2 MHz frequency (Mittal enterprises, New Delhi). The accuracy of sound velocity was ±0.1 ms^{-1}.

The density was determined at the experimental temperature using 10 ml capacity specific gravity bottle immersed in a thermostatic bath (accuracy +0.01 °C). The volume of the bottle at the experimental temperatures, viz. 303.15 K was ascertained using doubly distilled water. The densities of water at these temperatures were obtained from literature. The viscosity of pure liquids and liquid mixtures at 303.15 K were determined using an Ostwald viscometer [30-35].

3. THEORY & CALCULATIONS

The ultrasonic velocity, density and viscosity data described many parameters for understanding solvent interaction and structural effect. Various acoustical parameters like adiabatic compressibility (β_{ad}), intermolecular free length (L_f), specific acoustical impendence (Z_i), Rao's molar sound function (R), Vander Waals constant (b), etc., have been computed using the following standard equations[7-19].

1. Adiabatic compressibility, $\beta_{ad} = 1/u^2\rho$

2. Intermolecular free length, $L_f = K/u\rho^{1/2}$

3. Relative association, $(R.A) = \left(\frac{\rho}{\rho_0}\right)\left(\frac{C_0}{C}\right)^{1/3}$

4. Specific Acoustic impedance, $z_i = P_e/C$

5. Viscous relaxation time, $\tau = \frac{4}{3}\beta\eta$

6. Relaxation strength, $r = 1 - \left(\frac{u}{u_\alpha}\right)^2$

7. Rao's constant or molar sound velocity, $R = Vu^{1/3}$

8. Wada's constant, $B' = \frac{M}{\rho}K_s^{1/7}$

9. Ultrasonic attenuation, $\frac{\alpha}{f^2} = \frac{8\pi^2\eta}{3u^3\rho}$

10. Vander Waal's constant, $b = \frac{M}{\rho}\left\{1 - \left(\frac{RT}{MC^2}\right)\left[1 + \left(\frac{MC^2}{RT}\right)^{1/2} - 1\right]\right\}$

11. Isothermal compressibility, $\beta_T = \frac{1.71\times10^{-3}}{T^{4/9}u^{1/2}\rho^{1/3}}$

12. Isothermal expansion co-efficient, $\alpha = (0.0191\beta_T)^{1/4}$

13. Internal pressure, $\pi_i = \frac{\alpha T}{\beta_T}$

14. Free volume, $V_f = \left(\frac{bRT}{\pi_i}\right)^3\left(\frac{1}{V^2}\right)$

15. Solvation number, $S_n = \left(\frac{n_1}{n_2}\right)\left(1 - \frac{\beta}{\beta_0}\right)$

4. RESULTS AND DISCUSSION

Tables 1 to 3 shows the measured ultrasonic velocity, density and related acoustical parameters of 1,3,4-oxadiazole derivatives with acetone at 303 K. These measured acoustical parameters of 1,3,4-oxadiazole derivatives with acetone at 303 K were also shown graphically in Figure 1 to 9. It is observed that ultrasonic velocity, density, viscosity and acoustic impedance shows nonlinear increasing variation with increase in molar concentration. This indicates the complex formation and intermolecular weak association may be due to hydrogen bond formation[20]. This behaviour is the result of structural changes occurring in the mixture.

Adiabatic compressibility (β_{ad}) shows an inverse behaviour compared to the ultrasonic velocity. Adiabatic compressibility nonlinearly decreases with increase in concentration of 1,3,4-oxadiazole derivatives (shown in Table 2). The decrease in compressibility implies that there is an enhanced molecular association in the system with increase in solute concentration[21-22].

The opposite trend of ultrasonic velocity and adiabatic compressibility indicate association among interacting 1,3,4-oxadiazole derivatives and acetone molecules. In the present systems, free length varies nonlinearly with increase in molar concentration suggest the significant interaction between solute and solvent due to which structural arrangement is also affected[23].

Relaxation time decreases with increase in concentration. The relaxation time which is order of 10^{-12} sec is due to structural relaxation[24-25] process in such a case it is suggested that molecules get rearranged due to co-operative process[26-27].

Table 1. Velocity(u), Density (ρ), Viscosity (η) and Molar volume (Vm) of 2,5-Disubstituted-1,3,4-Oxadiazole derivatives with Acetone at 303.15 K.

Mole fraction	1,3,4-Oxadiazole derivatives			
	u	ρ	$\eta \times 10^3$	$Vm \times 10^6$
X_2	ms^{-1}	kgm^{-3}	$Nm^{-1}sec$	m^3/mol
Compound A1				
0.0063	1290.27	756.37	0.68	78.01
0.0125	1358.20	770.85	0.71	77.74
0.0250	1412.67	787.74	0.74	78.41
0.0500	1433.40	797.65	0.76	82.04
0.1000	1563.00	803.88	0.81	90.56
Compound A2				
0.0063	1227.67	768.31	0.63	77.35
0.0125	1296.73	777.20	0.66	78.20
0.0250	1351.53	788.51	0.70	80.48
0.0500	1429.47	795.49	0.74	86.53
0.1000	1541.53	801.97	0.78	99.24
Compound A3				
0.0063	1305.53	777.96	0.61	76.33
0.0125	1353.60	780.38	0.65	77.75
0.0250	1432.93	787.62	0.68	80.33
0.0500	1495.40	794.98	0.71	86.10
0.1000	1562.33	799.56	0.75	98.56

Table 2. Adiabatic compressibility (βad), intermolecular free length (Lf), Specific acoustic impedance (Zi), Rao's constant (R), Wada's constant (W), Vander waal's constant (b) and Ultrasonic attenuation (α/f^2) of 2,5-Disubstituted-1,3,4-oxadiazole derivatives with Acetone at 303.15 K.

Mole fraction	βad $\times 10^9$	$L_f \times 10^{10}$	$Z_i \times 10^6$	$R \times 10^6$	$W \times 10^{-3}$	$b \times 10^6$	$\alpha/f^2 \times 10^{-14}$
X_2	Pa^{-1}	m	$kgm^{-2}s$	$m^{10/3}/kgs^{1/3}mol$	$(m^3/kg.mol)(kg/ms^2)^{-1/7}$	m^3/mol	sec
Compound A1							
0.0063	0.7942	0.5908	0.98	849.30	1.56	72.53	1.1037
0.0125	0.7032	0.5560	1.05	860.93	1.58	72.51	0.9611
0.0250	0.6361	0.5288	1.11	879.78	1.61	73.34	0.8737
0.0500	0.6102	0.5179	1.14	925.07	1.70	76.92	0.8495
0.1000	0.5092	0.4731	1.26	1050.97	1.93	85.49	0.6947
Compound A2							
0.0063	0.8636	0.6161	0.94	828.26	1.53	71.73	1.1689
0.0125	0.7619	0.5799	1.01	852.72	1.57	72.78	1.0271

0.0250	0.6945	0.5525	1.07	889.85	1.64	75.16	0.9455
0.0500	0.6152	0.5200	1.14	974.78	1.79	81.22	0.8373
0.1000	0.5247	0.4803	1.24	1146.37	2.10	93.81	0.6981
Compound A3							
0.0063	0.7542	0.5757	1.02	834.24	1.53	71.02	0.9219
0.0125	0.6994	0.5544	1.06	860.10	1.58	72.53	0.8803
0.0250	0.6184	0.5213	1.13	905.60	1.66	75.24	0.7738
0.0500	0.5625	0.4972	1.19	984.56	1.80	80.98	0.7032
0.1000	0.5124	0.4746	1.25	1143.66	2.09	93.21	0.6459

Table 3. Relaxation strength (r),Viscous relaxation time (τ), Isothermal compressibility (β_T), Isothermal expansion co-efficient (α), Internal pressure (π_i) and Free volume (Vf), Solvation number (Sn) and Relative Association (RA) of 2,5-Disubstituted-1,3,4-Oxadiazole derivatives with Acetone at 303.15 K.

Mole fraction	r	$\tau \times 10^{12}$	$\beta_T \times 10^{14}$	$\alpha \times 10^{-4}$	$\pi_i \times 10^{-12}$	$V_f \times 10^{19}$	$S_n \times 10^{-2}$	R.A
X_2		Sec	m^2N^{-1}	K^{-1}	m^2N^{-1}	m^3mol^{-1}		
Compound A1								
0.0063	0.3497	0.7222	1.1759	1.2242	3.1560	6.6948	3.4533	0.8002
0.0125	0.2794	0.6620	1.0347	1.1857	3.4738	5.0558	2.4686	0.8017
0.0250	0.2205	0.6259	0.9292	1.1542	3.7656	3.9019	1.5031	0.8086
0.0500	0.1974	0.6175	0.8876	1.1411	3.8972	3.2146	0.8035	0.8148
0.1000	0.0457	0.5506	0.7388	1.0899	4.4722	1.7461	0.5028	0.7978
Compound A2								
0.0063	0.4113	0.7277	1.2720	1.2485	2.9754	8.1266	2.3691	0.8264
0.0125	0.3432	0.6754	1.1228	1.2101	3.2674	6.0052	1.9725	0.8208
0.0250	0.2865	0.6480	1.0139	1.1797	3.5272	4.5059	1.2701	0.8214
0.0500	0.2018	0.6070	0.8957	1.1437	3.8707	2.9497	0.7934	0.8133
0.1000	0.0717	0.5457	0.7619	1.0983	4.3700	1.5585	0.4873	0.7996
Compound A3								
0.0063	0.3342	0.6104	1.1062	1.2057	3.3039	6.0956	4.1216	0.8198
0.0125	0.2843	0.6043	1.0248	1.1828	3.4989	4.9462	2.4995	0.8125
0.0250	0.1979	0.5623	0.9033	1.1461	3.8463	3.4886	1.5742	0.8046
0.0500	0.1265	0.5333	0.8192	1.1184	4.1389	2.4370	0.8991	0.8007
0.1000	0.0465	0.5117	0.7448	1.0921	4.4453	1.5010	0.4996	0.7936

The internal pressure increases & free volume decreases with increases in molar concentration indicate the association through hydrogen bonding. It shows the increasing magnitude of interaction between the 1,3,4-oxadiazole derivatives and acetone. The decrease in free volume shows that the strength of interaction decreases gradually with the increase in

solute concentration. It represents that there is weak interaction[28] between the solute and solvent molecules.
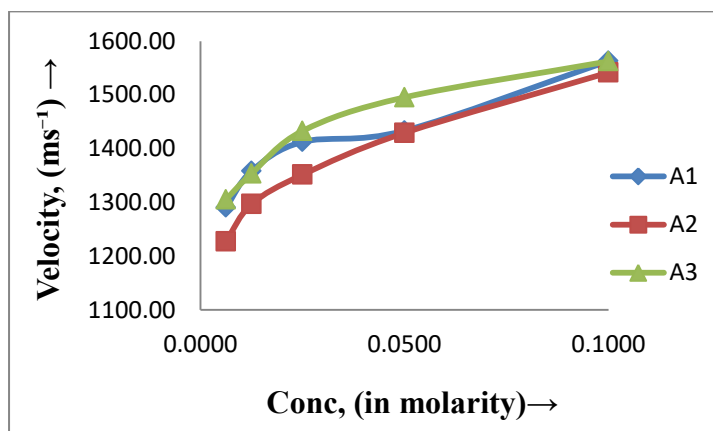

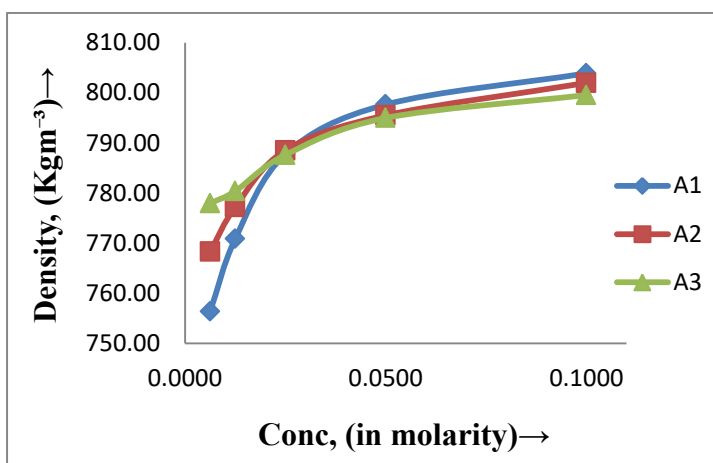**Fig. 1.** Velocity Vs Concentration of AT1, AT2 and AT3 at 303.15 K.

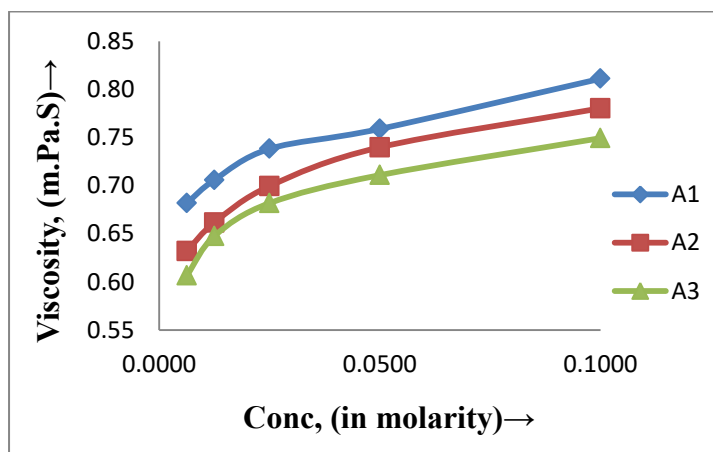**Fig. 2.** Density Vs Concentration of A1, A2 and A3 at 303.15 K.

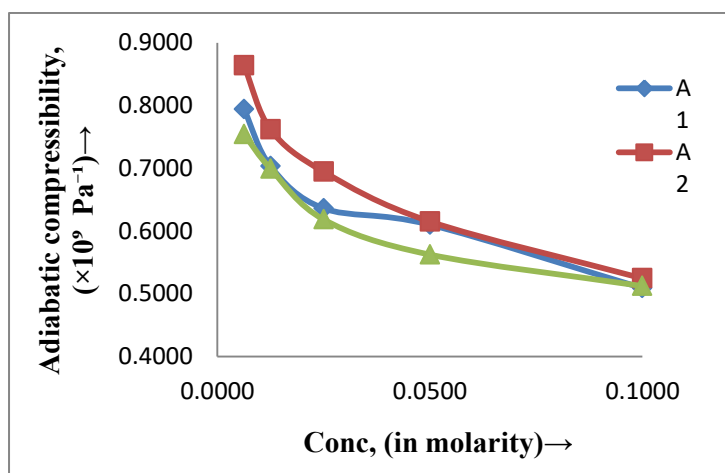**Fig. 3.** Viscosity Vs Concentration of A1, A2 and A3 at 303.15 K.

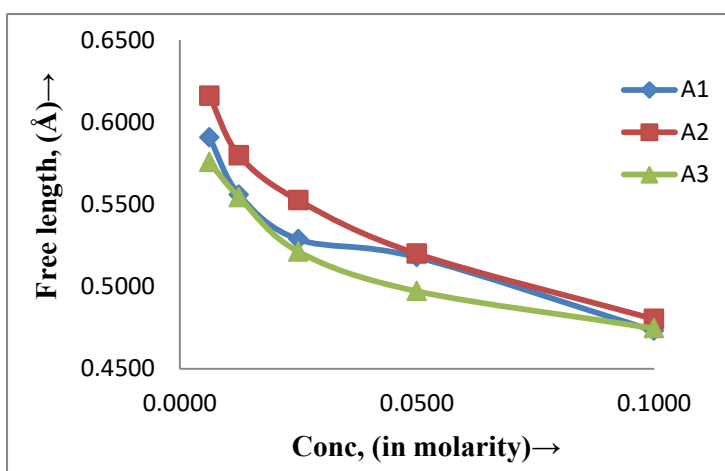**Fig. 4.** Adiabatic compressibility Vs Concentration of A1, A2 and A3 at 303.15 K.

Fig. 5. Free length Vs Concentration of A1, AT2 and AT3 at 303.15 K.
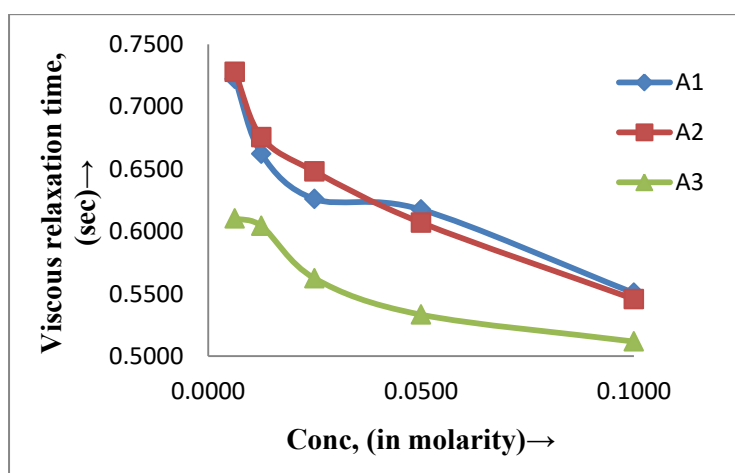
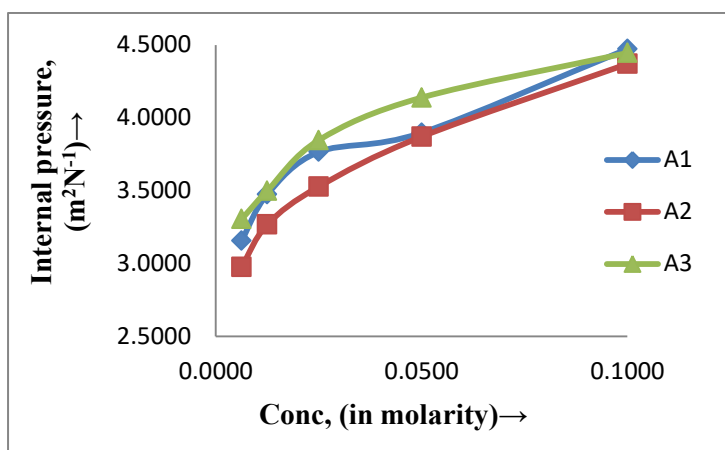**Fig. 6.** Viscous relaxation time Vs Concentration of A1, A2 and A3 at 303.15 K.

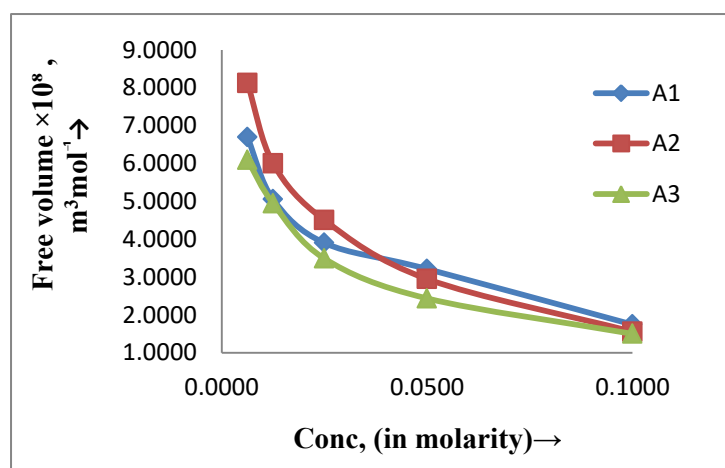**Fig. 7.** Internal pressure Vs Concentration of A1, A2 and A3 at 303.15 K.

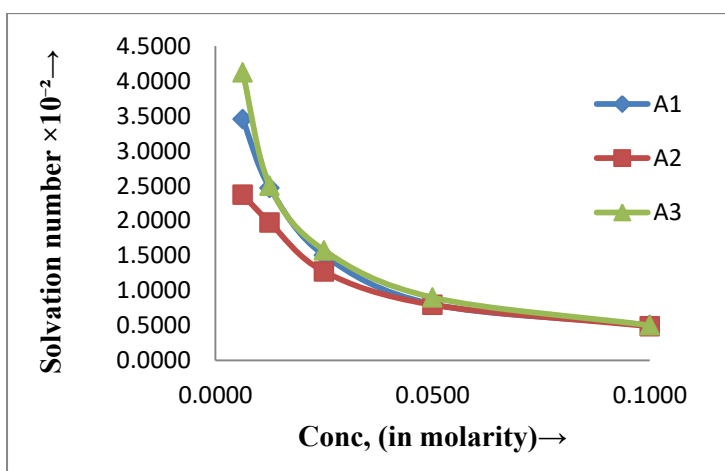**Fig. 8.** Free volume Vs Concentration of A1, A2 and A3 at 303.15 K.

Fig. 9. Solvation number Vs Concentration of A1, A2 and A3 at 303.15 K.

The interactions occurring in different solutions can also be confirmed by the solvation number (Sn), which is measure of structure forming or structure breaking tendency of solute in a solution. Fig. 8 shows the variation of solvation number (Sn) with molefractions for all the compounds in acetone. Sn values are found decrease with concentration of solute in acetone (shown in Table 3). Sn clearly represents the solvation of solute in solvent causes interactions giving rise to increase the solubility of solute[29].

This weak association is further confirmed by low relative association value (RA), this is almost same for all compounds (Table 3). The decrease of relative association with concentration substantiate that the solvent structure breaks up.

5. CONCLUSION

All the computed acoustical parameters and their values point to the presence of specific molecular interaction in the liquid mixtures of 1-(5-amino-2-phenyl-1,3,4-oxadiazole-3(2H)-yl) ethanone, 1-(5-amino-2-(3-(trifluoromethyl)phenyl)-1,3,4-oxadiazole-3(2H)-yl) ethanone, 1-(5-amino-2-(2,4-dimethoxyphenyl)-1,3,4-oxadiazole-3(2H)-yl) ethanone. Hence it is concluded that the association in these mixtures is the result of Hydrogen bonding between the molecule and acetone.

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