

## Dielectric properties of amino substituted pyridines in dilute solutions of some non-polar solvents at different temperatures

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Microwave dielectric absorption and relaxation behaviour of each of 2-aminopyridine and 4-dimethylaminopyridine in non-polar solvents benzene, carbon tetrachloride and 1,4-dioxane have been studied at 303.15 K, 313.15 K and 323.15 K temperatures. X-band microwave bench operating at 9.1 GHz has been used for determination of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ). The static permittivity ( $\epsilon_0$ ) at 2 MHz and permittivity at optical frequency ( $\epsilon_\infty$ ) have also been determined. The measured values of dielectric permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) have been used to evaluate relaxation time ( $\tau$ ), dipole moment ( $\mu$ ), molar volume ( $V_m$ ) and molar polarization of solute ( $P_2$ ). Present study suggests the existence of intra-molecular and overall rotation of the amino pyridine molecules in the non-polar solvents. The solute-solvent molecular associations have been predicted. The effect of solvent environments on the relaxation behaviour of the amino pyridines has also been discussed.

**Keywords:** Dielectric constant, Dielectric loss, Static permittivity, Relaxation time, Dipole moment

### 1 Introduction

Microwave dielectric absorption studies of polar molecules are very important to understand the nature and size of the different molecules. Dielectric relaxation data of polar solutes (pharmaceutical molecules) in varieties of solvent environments can be used to correlate the relaxation behaviour of a solute in solvent and the solubility of that solute. Many researchers have attempted dielectric relaxation and absorption studies of polar molecules in non-polar solvents at microwave frequencies<sup>1-6</sup>. Poomachandra Rao<sup>7</sup> studied the dielectric behaviour of pyridine in non-polar solvents benzene and carbon tetrachloride. Madan *et al.*<sup>8</sup> studied microwave absorption and dielectric relaxation of some rigid polar molecules pyridine, quinoline and isoquinoline and their mixtures in dilute solutions of benzene in microwave region over a range of temperature. Singh and his co-workers<sup>9</sup> studied the dielectric relaxation of sulfolane in carbon tetrachloride solution from microwave absorption data. Awasthi *et al.*<sup>10</sup> studied the dielectric relaxation behaviour of chlorobenzene and bromobenzene with ethanol in dilute solution of benzene and they observed high value of distribution parameter ( $\alpha$ ). They reported solute-solvent type of interaction in both systems.

The objective of present work is to study microwave dielectric absorption of amino substituted pyridines in dilute solutions of benzene, carbon tetrachloride and 1,4-dioxane at different temperatures and to investigate the effect of solvent environments on the relaxation behaviour of the amino pyridines. One of the amino substituted pyridines under study is 2-aminopyridine which is an organic compound with the formula  $C_5H_6N_2$ . It is one of the three isomeric pyridines. It is a colorless solid that has very large pharmaceutical applications and is used in the production of the drugs piroxicam<sup>11</sup>. Other amino substituted pyridine compound used in present work is 4-dimethylaminopyridine ( $C_7H_{10}N_2$ ) which also has very wide applications in pharmaceuticals and is used as a hypernucleophilic acylation catalyst<sup>12</sup>. Very less existing literature on dielectric studies of amino substituted pyridines in their pure form as well as their solutions in non-polar solvent, and their large pharmaceutical applications are motivation behind the present study. Dielectric, IR and vapor pressure studies were performed on solutions of 2- and 3-amino pyridines and their methyl derivatives by Król *et al.*<sup>13</sup>. They carried out *ab initio* calculations of dipole moments and  $\nu(NH_2)$  frequencies. From these calculations they showed that there are various possible interactions including participation of the  $NH_2$  groups as a proton acceptor. They also

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reinterpreted their results of calculations of frequencies and intensities by using IR spectra. With a view to gain more information in this area, dielectric relaxation of each of 2-aminopyridine and 4-dimethylaminopyridine in dilute solutions of three non-polar solvents benzene, carbon tetrachloride and 1,4-dioxane at single microwave frequency and at different temperatures 303.15 K, 313.15 K and 323.15 K were studied. Results obtained were used to gain information about microwave absorption, relaxation behaviour, solute-solvent molecular interaction, inter and intramolecular hydrogen bonding in relation to the molecular structure of the different solvents. Effects of different solvent environment on the relaxation behaviour of polar molecules have also been discussed.

## 2 Experimental Details

The compounds 2-aminopyridine (2-AMP) (AR grade) and 4-dimethylaminopyridine (4-DMAP) with 99% purity were procured from Ottochemie Pvt Limited, Mumbai, India. Benzene (AR grade), Carbon tetrachloride (AR grade) and 1,4-dioxane (AR grade) were procured from S D Fine Chem Limited, Mumbai, India and were used without further purification. The solutions of different weight fractions were prepared by mixing a certain amount of solute (2-AMP/4-DMAP) in non-polar solvents benzene, CCl<sub>4</sub> or 1,4-dioxane using electronic balance at room temperature.

The values of static permittivity ( $\epsilon_0$ ) of the mixtures have been determined by using capacitive measurement method with a short compensation at 2 MHz. Agilent 4980 A precision LCR meter with a four terminal liquid dielectric test fixture (Agilent 16452A) was used for the capacitance measurement of the cell without and with sample. The measurement accuracy in  $\epsilon_0$  value is  $\pm 0.3\%$ . Dielectric permittivity at optical frequency ( $\epsilon_\infty$ ) of the mixtures were taken as square of the refractive index,  $n_D$ , which was measured with an Abbe refractometer at wavelength of sodium-D light. The maximum measurement error in  $\epsilon_\infty$  value is  $\pm 0.02\%$ . Dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) at microwave frequency 9.1 GHz were measured using microwave test bench using equations already available in literature<sup>14,15</sup>. The relaxation time ( $\tau$ ) was evaluated using Higasi single frequency method<sup>16</sup> and Gopal Krishna's Method<sup>17</sup>. The values of dipole moment ( $\mu$ ) of all the mixtures were calculated by using Higasi's equation<sup>18</sup> and Guggenheim's equation<sup>19</sup>. The density of the mixtures

was determined using a pycnometer by relative measurement method. The pycnometer was calibrated with double distilled water and gave an estimated reproducibility  $\pm 0.0001 \text{ g cm}^{-3}$ . All measurements were carried out at three different temperatures 303.15 K, 313.15 K and 323.15 K and temperature was controlled thermostatically within  $\pm 0.5^\circ \text{C}$ .

The Kirkwood correlation factor ( $g$ ) has been calculated for dilute solutions of polar solute in non-polar solvent using equation<sup>20</sup>:

$$g\mu^2 = \frac{9KT(2\epsilon_m + \epsilon_\infty)^2}{4\pi N f_2 (\epsilon_\infty + 2)^2 (2\epsilon_m + 1)} \left[ \frac{V(\epsilon_m - 1)}{\epsilon_m} - \frac{3V_1 f_1 (\epsilon_1 - 1)}{2\epsilon_m + \epsilon_1} - \dots \right] \quad (1)$$

where,  $\epsilon_m$  is the static permittivity of the solution,  $\epsilon_\infty$  is the square of the refractive index of the solution,  $\epsilon_1$  is the static permittivity of the pure solvent,  $f_1$  is the mole fraction of the solvent,  $f_2$  is the mole fraction of the solute,  $V$  is the molar volume of the solution,  $V_1$  and  $V_2$  are molar volume of the pure solvent and pure solute respectively.  $K$ ,  $T$  and  $N$  are Boltzmann's constant, absolute temperature and Avogadro's number, respectively.

Molar polarization of the solutions<sup>21</sup> is given by:

$$P = f_1 P_1 + f_2 P_2 \quad \dots (2)$$

From Eq. (2) molar polarization of solute is:

$$P_2 = P_1 + \left[ \frac{P - P_1}{f_2} \right] \quad \dots (3)$$

where  $P_1$  is the molar polarization of the solvent, which is given by:

$$P_1 = \left( \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \right) V_1 \quad \dots (4)$$

$P$  is the molar polarization of the solution which is given by:

$$P = \left( \frac{\epsilon_m - 1}{\epsilon_m + 2} \right) V_m \quad \dots (5)$$

$V_m$  is the molar volume of the solution which is given by:

$$V_m = (X_1 M_1 + X_2 M_2) / \rho$$

where  $X_1$ ,  $M_1$  and  $X_2$ ,  $M_2$  are weight fraction and molecular weight of pure solvent and pure solute respectively and  $\rho$  is the density of the solution.

## 3 Results and Discussion

### 3.1 Dilute solutions of 2-AMP in different solvents

Determined parameters  $\epsilon_0$ ,  $\epsilon'$ ,  $\epsilon''$  and  $\epsilon_\infty$  when plotted against the weight fraction of 2-AMP in respective non-polar solvents were found to vary linearly. The slope values of determined parameters

were used to evaluate the distribution parameter ( $\alpha$ ), relaxation time ( $\tau_H$ ) by Higasi's<sup>18</sup> method. The distribution parameter ( $\alpha$ ), relaxation times by Higasi's and Gopal Krishna's method ( $\tau_H$  and  $\tau_G$ ), dipole moment by Higasi's and Guggenheim's method ( $\mu_H$  and  $\mu_G$ ) and thermodynamical parameters ( $\Delta F_E$ ,  $\Delta H_E$  and  $\Delta S_E$ ) at temperatures 303.15 K, 313.15 K and 323.15 K are reported in Table 1. The values of Kirkwood correlation factor ( $g$ ), molar volume ( $V_m$ ), molar polarization of solute ( $P_2$ ) are also presented in the same table.

The relaxation time of 2-AMP in all the three solvents decreases with rise in temperature (Table 1). The relaxation time obtained for 2-AMP in benzene from Higasi's method is 5.28 ps at 303.15 K while from Gopal Krishna's method; it is 5.1 ps at the same temperature. This type of discrepancy is found in relaxation time values of 2-AMP in all solvents at all the temperatures. This is may be due to different methods used for calculating the relaxation time. Non-zero values of distribution parameter  $\alpha$  is obtained for dilute solutions of 2-AMP in all the three solvents at all temperatures. This indicates that besides the overall rotation, there is contribution of group rotation to the relaxation processes. Vyas and Rana<sup>22</sup> studied dielectric relaxation of pyridine in benzene solution at different temperatures. They obtained relaxation time of pyridine in benzene solution, 4.1 ps and 3.5 ps at 303 K and 313 K, respectively by Higasi's single frequency method, whereas in present study, the relaxation time of 2-AMP in benzene solution is 5.28 ps at 303.15 K and 4.67 ps at 313.15 K temperature. This indicates that substitution of amino group to pyridine ring structure increases the relaxation time of molecule.

The value of  $g > 1$  indicates parallel orientation of dipoles whose dipole-dipole interaction lead to a positive correlation called as  $\alpha$ -multimers while  $g < 1$  indicates anti-parallel orientation of dipoles called as  $\beta$ -multimers<sup>23,24</sup>. The variation of value of  $g$  with weight fraction of 2-AMP in benzene are reported in Table 1. The  $g$  values of 2-AMP in benzene solutions are greater than 1 at 303.15 K and 313.15 K which indicates the parallel orientation of dipoles and at the same temperatures, the  $g$  values decrease gradually with increasing weight fraction of 2-AMP. It is a clear indication of conversion of more and more  $\alpha$ -multimers into  $\beta$ -multimers. At 323.15 K temperature, the  $g$  value does not change much with weight fraction of 2-AMP which indicates that the

ratio of  $\alpha$ - and  $\beta$ -multimers remain the same at this temperature. The values of dipole moment ( $\mu$ ) for dilute solutions of 2-AMP in benzene are determined by two different methods such as Guggenheim and Higasi. They are presented in Table 1. From the table, it can be seen that there is small difference in dipole moment values obtained by Higasi and Guggenheim methods. At 303.15 K temperature the value of dipole moment by Higasi's method ( $\mu_H$ ) is 1.9 D while by the Guggenheim method ( $\mu_G$ ), it is 2.1 D. Discrepancy in dipole moment values is may be due to different methods applied for calculating the dipole moment. Król *et al.*<sup>13</sup> found that the dipole moment value  $\mu_M$  for the 2-AMP in benzene solution is 1.98 D at 25 °C, which is in very close agreement with present result at the temperature of 303.15 K. From the Table 1, it can also be seen that the value of  $\mu_G$  is higher than the value of  $\mu_H$  at 303.15 K and 313.15 K, whereas at 323.15 K the values of  $\mu_G$  and  $\mu_H$  are nearly equal.

The molar polarization  $P_2$  (cc) of an unassociated solute in non-polar solvent usually decreases with increase of concentration<sup>25</sup> and similar behaviour is observed in case of 2-AMP in benzene. The behaviour of molar polarization of solute ( $P_2$ ) indicates solute-solvent interaction. The molecular association between the 2-AMP and benzene molecules as shown in Fig. 1 can be predicted, which may arise because of the interaction between delocalized positive charge on the pyridine ring and  $\pi$ -delocalized electron cloud of the benzene ring<sup>26</sup>. The density of the solution of the 2-AMP in benzene increases with increase in weight fraction of 2-AMP, which results in decrease in the molar volume ( $V_m$ ) of the solution. The decrease in molar volume ( $V_m$ ) suggests the close packing of the molecules, which indicates the increase in the magnitude of interaction<sup>27</sup>. Moreover, molar volume ( $V_m$ ) increases with increase in temperature, which is may be due to the fact that thermal energy facilitates an increase in the molecular separation in the liquid mixtures which leads to an increase in molar volume<sup>28</sup> ( $V_m$ ).

It has also been observed that the relaxation time ( $\tau_G$  and  $\tau_H$ ), both are small for 2-AMP in benzene solution as compared to the relaxation time ( $\tau_G$  and  $\tau_H$ ) of 2-AMP in 1,4-dioxane solution (Table 1). Higher values of relaxation time ( $\tau_G$  and  $\tau_H$ ) of 2-AMP in 1,4-dioxane solution may be because of large hindrance offered by slightly polar 1,4-dioxane molecules to reorient the 2-AMP molecules as compared to the benzene molecules. There is a

Table 1 — Values of Kirkwood correlation factor( $g$ ), molar volume ( $V_m$ ), molar polarization of solute ( $P_2$ ), relaxation time ( $\tau$ ), dipole moment ( $\mu$ ), molar free energy of activation ( $\Delta F_E$ ), molar enthalpy of activation ( $\Delta H_E$ ) and molar entropy of activation ( $\Delta S_E$ ) of 2-AMP in benzene, 1,4-dioxane and carbon tetra chloride at 303.15 K, 313.15 K and 323.15 K temperatures (*contd.*)

Temperature (K)	Weight fraction	$g$	$V_m$ (cm <sup>3</sup> /mol)	$P_2$ (cc)	Relaxation time (ps)	Dipole moment (D)	$\Delta F_E$ (kJ/mol)	$\Delta H_E$ (kJ/mol)	$\Delta S_E$ (J/mol/ K)
2-AMP + Benzene									
303.15	0.009	1.65	90.29	151.73	$\tau_H=5.28$	$\mu_H=1.9$	8.75	6.48	-0.007
	0.019	1.34	90.27	122.97	$\tau_G=5.1$	$\mu_G=2.1$			
	0.028	1.32	90.25	121.61					
	0.039	1.21	90.13	111.14					
	0.048	1.11	90.06	103.11					
313.15	0.009	1.28	91.04	132.45	$\tau_H=4.67$	$\mu_H=1.8$	8.82		-0.007
	0.019	1.22	90.77	114.35	$\tau_G=4.53$	$\mu_G=1.9$			
	0.028	1.17	90.67	110.69					
	0.039	1.13	90.54	101.52					
	0.048	1.09	90.35	97.42					
323.15	0.009	1.00	91.68	107.98	$\tau_H=3.95$	$\mu_H=1.7$	8.90		-0.007
	0.019	0.99	91.22	97.45	$\tau_G=4.08$	$\mu_G=1.7$			
	0.028	0.98	91.11	97.10					
	0.039	0.96	90.91	94.36					
	0.048	0.95	90.72	90.63					
2-AMP+1,4-dioxane									
303.15	0.010	1.80	84.31	316.52	$\tau_H=5.61$	$\mu_H=2.9$	8.92	3.87	-0.017
	0.020	1.06	83.69	193.96	$\tau_G=5.44$	$\mu_G=3.0$			
	0.030	0.85	83.16	159.98					
	0.040	0.77	82.91	145.22					
	0.050	0.72	82.54	136.73					
313.15	0.010	1.73	84.77	302.78	$\tau_H=5.19$	$\mu_H=2.8$	9.09		-0.017
	0.020	1.04	84.16	191.63	$\tau_G=5.03$	$\mu_G=2.9$			
	0.030	0.80	83.56	149.20					
	0.040	0.71	83.16	133.22					
	0.050	0.67	82.9	126.31					
323.15	0.010	1.69	85.2	284.16	$\tau_H=4.68$	$\mu_H=2.7$	9.25		-0.017
	0.020	1.04	85.16	186.66	$\tau_G=4.64$	$\mu_G=2.8$			
	0.030	0.77	84.51	140.80					
	0.040	0.69	84.03	126.48					
	0.050	0.65	83.85	120.68					
2-AMP+Carbon tetra chloride									
303.15	0.010	3.35	95.97	1994.53	$\tau_H=6.20$	$\mu_H=3.2$	9.20	5.32	-0.013
	0.020	1.80	95.86	1040.37	$\tau_G=6.10$	$\mu_G=3.3$			
	0.030	1.29	95.73	719.90					
	0.040	1.04	95.65	561.72					
	0.049	0.90	95.56	478.08					

(contd.)

Table 1 — Values of Kirkwood correlation factor ( $g$ ), molar volume ( $V_m$ ), molar polarization of solute ( $P_2$ ), relaxation time ( $\tau$ ), dipole moment ( $\mu$ ), molar free energy of activation ( $\Delta F_E$ ), molar enthalpy of activation ( $\Delta H_E$ ) and molar entropy of activation ( $\Delta S_E$ ) of 2-AMP in benzene, 1,4-dioxane and carbon tetra chloride at 303.15 K, 313.15 K and 323.15 K temperatures

Temperature (K)	Weight fraction	$g$	$V_m$ (cm <sup>3</sup> /mol)	$P_2$ (cc)	Relaxation time (ps)	Dipole moment (D)	$\Delta F_E$ (kJ/mol)	$\Delta H_E$ (kJ/mol)	$\Delta S_E$ (J/mol/K)
313.15	0.010	3.02	96.06	1899.89	$\tau_H=5.71$	$\mu_H=3.1$	9.37		-0.013
	0.020	1.62	95.7	995.28	$\tau_G=5.60$	$\mu_G=3.2$			
	0.030	1.15	95.49	692.52					
	0.040	0.95	95.07	543.32					
	0.049	0.82	94.68	463.54					
323.15	0.010	2.77	96.6	1848.72	$\tau_H=5.13$	$\mu_H=2.9$	9.46		-0.013
	0.020	1.52	96.29	968.60	$\tau_G=5.02$	$\mu_G=2.8$			
	0.030	1.09	95.94	674.38					
	0.040	0.90	95.53	528.89					
	0.049	0.79	95.08	449.06					

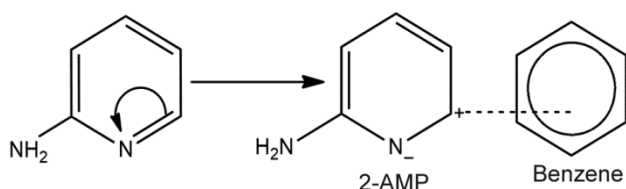


Fig. 1 — Solute-solvent molecular association between 2-AMP and benzene.

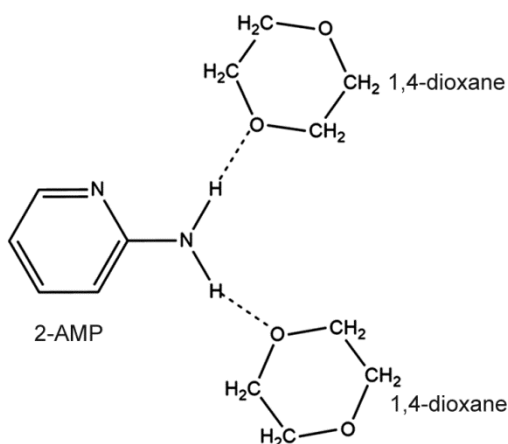


Fig. 2 — Solute-solvent molecular association between 2-AMP and 1,4-dioxane.

possibility of H-bond interaction between the hydrogen of amino group in 2-AMP and lone pair electrons at the sight of oxygen in the 1,4-dioxane molecule (Fig. 2). Similar type of H-bonding was shown between amino group of each of *o*- and *m*-acetophenon and 1,4-dioxane by Ghanbahadur *et al.*<sup>29</sup>. This H-bonded interaction between the solute-solvent molecules is responsible for the hindered motion of 2-AMP in 1,4-dioxane.

The values of dipole moment of 2-AMP in benzene solution is 1.9 D and in 1,4-dioxane, it is 2.9 D from the Higasi method at 303.15 K temperature. Furthermore, the values of dipole moment changes with temperature. This is due to the fact that the association between polar molecule and non-polar solvent molecule depends upon the temperature. Temperature dependent variation of dipole moment also suggests solute-solvent type of molecular association between 2-AMP and 1,4-dioxane.

The values of Kirkwood correlation factor ( $g$ ) for 2-AMP in 1,4-dioxane are shown in Table 1. Up to 0.02 weight fraction of 2-AMP in 1,4-dioxane solvent, the  $g$  values are greater than unity whereas for 0.03 to 0.05 weight fractions of 2-AMP in 1,4-dioxane, the  $g$  values are less than unity. This type of behaviour shows that these molecule associate to form multimers with parallel dipole moment and also with antiparallel dipole moment. The values of  $g$  indicate that  $\alpha$ -multimers are converted in to  $\beta$ -multimers with increase in the concentration of 2-AMP in 1,4-dioxane. The trend of molar polarization of solute ( $P_2$ ) follows the Kirkwood correlation factor. Gupta *et al.*<sup>21</sup> have shown similar type of behaviour between molar polarization of the solute ( $P_2$ ) and Kirkwood correlation factor ( $g$ ) for the system of cyclohexylamine in non-polar solvent benzene, *n*-heptane and 1,4-dioxane.

From Table 1 it can be seen that the values of relaxation time of 2-AMP in dilute solutions of different solvents are in the order of  $\text{CCl}_4 > 1,4\text{-dioxane} > \text{benzene}$  at all studied temperatures by both the methods. Some researchers<sup>30,31</sup> also found similar

type of solvent effects in dilute solutions of polar solute in non-polar solvents. The difference between the relaxation time values of 2-AMP in benzene, 1,4-dioxane and  $\text{CCl}_4$  solvents are may be because of the large difference in the densities of these solvents. Higher values of density of  $\text{CCl}_4$  in comparison to the densities of benzene and 1,4-dioxane produces large hindrance and there is increase in relaxation time value in bulky solvent. Sengwa<sup>31</sup> reported similar effect of bulky solvent on average relaxation time of polyethylene glycols. The values of dipole moment ( $\mu_G$  and  $\mu_H$ ) of 2-AMP in  $\text{CCl}_4$  solutions are also higher as compared to the 2-AMP in benzene and 1,4-dioxane solutions. The value of dipole moment  $\mu_H$  (Higasi method) in the present investigation is 3.16 D at 303.15 K temperature. Reported value of dipole moment of 2-AMP in  $\text{CCl}_4$  by Król *et al.*<sup>13</sup> is 3.1 D at 25 °C, which is in close agreement with present result. The dipole moment of dilute solutions of 2-AMP in  $\text{CCl}_4$  decreases with increase of temperature, which indicates presence of solute-solvent molecular interactions.

The Kirkwood correlation factor  $g$  of 2-AMP in  $\text{CCl}_4$  solution is shown in Table 1. The values of Kirkwood correlation factor  $g$  are greater than unity up to the weight fraction 0.03 of 2-AMP in  $\text{CCl}_4$  solution. At 0.03 to 0.05 weight fractions, the values of  $g$  are less than unity. This type of behaviour indicates that up to the 0.03 weight fraction, the molecules of these compound associate to form multimers with parallel dipole and at higher weight fraction the molecules associate to form antiparallel alignment of the dipole. The  $g$  values for 2-AMP in  $\text{CCl}_4$  solution are comparatively higher than those of solutions in benzene and 1,4-dioxane. In all the three solvents, molar polarization of the solute ( $P_2$ ) follows the Kirkwood correlation factor ( $g$ ) behaviour; higher values of  $g$  for 2-AMP in  $\text{CCl}_4$  show large  $P_2$  values, while for lower  $g$  values, the  $P_2$  values are also lower.

The values of free energy of activation ( $\Delta F_E$ ), enthalpy of activation ( $\Delta H_E$ ) and entropy of activation evaluated using the Eyring's equation<sup>32</sup> are presented in Table 1. The activation energy ( $\Delta F_E$ ) increases with increase in temperature in all the three systems. This is because as temperature increases thermal agitation increases and the molecules require more energy to overcome the energy barrier separating the two mean equilibrium positions. The values of molar enthalpy are less compared to the  $\Delta F_E$  values which results in the negative value of molar entropy of activation ( $\Delta S_E$ ). The negative values of ( $\Delta S_E$ ) shows that the

activated state is more ordered as compare to the normal state because of better alignment of the dipoles in the activated state. The value of molar enthalpy ( $\Delta H_E$ ) for 2-AMP in  $\text{CCl}_4$  solvent is the highest among the three solvents. This suggests that 2-AMP forms larger relaxing units in  $\text{CCl}_4$ .

### 3.2 Dilute solutions of 4-DMAP in different solvents

The values of Kirkwood correlation factor ( $g$ ), molar volume ( $V_m$ ) and molar polarization of solute ( $P_2$ ) of 4-DMAP in dilute solutions of benzene, 1,4-dioxane and  $\text{CCl}_4$  at 303.15 K, 313.15 K and 323.15 K temperatures are presented in Table 2. The relaxation time by Higasi's and Gopal Krishna's method ( $\tau_H$  and  $\tau_G$ ), dipole moment by Higasi's and Guggenheim's method ( $\mu_H$  and  $\mu_G$ ) and thermodynamical parameters  $\Delta F_E$ ,  $\Delta H_E$  and  $\Delta S_E$  at 303.15 K, 313.15 K and 323.15 K temperatures are reported in the same table.

The relaxation time of 4-DMAP in all the three solvents decreases with rise in temperature, which is a usual behaviour of polar solute in non-polar solvent. From Tables 1 and 2 it can be seen that the relaxation time for 4-DMAP is higher than the relaxation time of 2-AMP in respective non-polar solvents at all temperatures. This is due to the larger molecular size of 4-DMAP in comparison with 2-AMP. The value of relaxation time  $\tau_H$  for 4-DMAP in 1,4-dioxane is 6.26 ps (Table 2) at 303.15 K, while for 4-DMAP in benzene solution, the values of  $\tau_H$  is 5.87 ps at the same temperature. The higher value of relaxation time in dioxane is due to significant interaction of 4-DMAP with dioxane. The average relaxation time ( $\tau_G$  and  $\tau_H$ ) of 4-DMAP in different solvents is in the order  $\text{CCl}_4 > 1,4\text{-dioxane} > \text{benzene}$  at all studied temperatures. The difference between the relaxation time values in different solvents is evidently because of the large difference in the densities of these solvents.

Non-zero values of distribution parameter  $\alpha$  is obtained for 4-DMAP in all the three solvents at all studied temperatures. This indicates that besides the overall rotation, there is contribution of group rotation to the relaxation processes. The values of Kirkwood correlation factor  $g$  are found to be greater than unity up to the weight fraction of 0.02 of 4-DMAP in benzene solution, which indicates that the molecules of these compounds associate to form multimers with parallel alignment of dipoles. While for the weight fraction 0.03, 0.04 and 0.05, the values of  $g$  are less than unity at 303.15 K temperature which indicates

Table 2 — Values of Kirkwood correlation factor ( $g$ ), molar volume ( $V_m$ ), molar polarization of solute ( $P_2$ ), relaxation time ( $\tau$ ), dipole moment ( $\mu$ ), molar free energy of activation ( $\Delta F_E$ ), molar enthalpy of activation ( $\Delta H_E$ ) and molar entropy of activation ( $\Delta S_E$ ) of 4-DMAP in benzene, 1,4-dioxane and carbon tetra chloride at 303.15 K, 313.15 K and 323.15 K temperatures (*contd.*)

Temperature (K)	Weight fraction	$g$	$V_m$ ( $\text{cm}^3/\text{mol}$ )	$P_2$ (cc)	Relaxation time (ps)	Dipole moment (D)	$\Delta F_E$ (kJ/mol)	$\Delta H_E$ (kJ/mol)	$\Delta S_E$ (J/mol/ K)
4-DMAP + Benzene									
303.15	0.010	2.60	91.50	339.05	$\tau_H=5.87$	$\mu_H=2.3$	9.11	6.38	-0.009
	0.020	1.28	91.19	183.26	$\tau_G=5.79$	$\mu_G=2.4$			
	0.030	0.90	90.22	133.00					
	0.040	0.86	90.17	129.11					
	0.050	0.75	90.13	119.38					
313.15	0.010	2.10	91.62	283.35	$\tau_H=5.14$	$\mu_H=2.2$	9.15		-0.009
	0.020	1.20	91.46	172.42	$\tau_G=5.08$	$\mu_G=2.3$			
	0.030	0.85	91.40	136.11					
	0.040	0.83	91.37	128.78					
	0.050	0.70	90.89	113.06					
323.15	0.010	1.57	91.77	258.38	$\tau_H=4.71$	$\mu_H=2.0$	9.29		-0.009
	0.020	0.90	91.66	146.96	$\tau_G=4.63$	$\mu_G=2.2$			
	0.030	0.80	91.54	128.18					
	0.040	0.73	91.39	115.22					
	0.050	0.63	91.26	104.83					
4-DMAP+1,4-dioxane									
303.15	0.010	4.74	88.03	1038.41	$\tau_H=6.26$	$\mu_H=3.4$	9.20	6.49	-0.009
	0.020	2.57	87.95	595.77	$\tau_G=6.09$	$\mu_G=3.5$			
	0.030	1.83	87.89	434.95					
	0.040	1.46	87.85	356.07					
	0.050	1.22	87.79	305.23					
313.15	0.010	4.55	88.65	961.5	$\tau_H=5.62$	$\mu_H=3.3$	9.30		-0.009
	0.020	2.47	88.46	529.48	$\tau_G=5.45$	$\mu_G=3.4$			
	0.030	1.76	88.37	382.26					
	0.040	1.42	88.28	309.45					
	0.050	1.19	88.17	262.69					
323.15	0.010	4.41	89.35	901.22	$\tau_H=5.02$	$\mu_H=3.2$	9.38		-0.009
	0.020	2.42	89.33	502.48	$\tau_G=4.87$	$\mu_G=3.1$			
	0.030	1.74	89.21	365.87					
	0.040	1.38	89.12	294.03					
	0.050	1.16	88.99	250.04					
4-DMAP+Carbon tetra chloride									
303.15	0.010	5.73	96.66	1994.53	$\tau_H=6.65$	$\mu_H=3.6$	9.36	4.27	-0.017
	0.020	2.99	96.73	1040.37	$\tau_G=6.50$	$\mu_G=3.6$			
	0.030	2.06	96.79	719.90					
	0.040	1.60	96.89	561.72					
	0.049	1.36	96.97	478.08					

*(contd.)*

Table 2 — Values of Kirkwood correlation factor ( $g$ ), molar volume ( $V_m$ ), molar polarization of solute ( $P_2$ ), relaxation time ( $\tau$ ), dipole moment ( $\mu$ ), molar free energy of activation ( $\Delta F_E$ ), molar enthalpy of activation ( $\Delta H_E$ ) and molar entropy of activation ( $\Delta S_E$ ) of 4-DMAP in benzene, 1,4-dioxane and carbon tetra chloride at 303.15 K, 313.15 K and 323.15 K temperatures

Temperature (K)	Weight fraction	$g$	$V_m$ (cm <sup>3</sup> /mol)	$P_2$ (cc)	Relaxation time (ps)	Dipole moment (D)	$\Delta F_E$ (kJ/mol)	$\Delta H_E$ (kJ/mol)	$\Delta S_E$ (J/mol/ K)
313.15	0.010	5.59	96.83	1899.89	$\tau_H=6.14$	$\mu_H=3.4$	9.54		-0.017
	0.020	2.92	96.90	995.28	$\tau_G=5.99$	$\mu_G=3.5$			
	0.030	2.02	97.05	692.52					
	0.040	1.58	97.25	543.32					
	0.049	1.35	97.46	463.54					
323.15	0.010	5.55	97.39	1848.72	$\tau_H=5.57$	$\mu_H=3.2$	9.70		-0.017
	0.020	2.90	97.51	968.60	$\tau_G=5.49$	$\mu_G=3.3$			
	0.030	2.01	97.57	674.38					
	0.040	1.57	97.65	528.89					
	0.049	1.33	97.70	449.06					

that molecules may form multimers with antiparallel alignment of dipoles (Table 2). This type of mixed behaviour is shown by 4-DMAP in benzene solution at all studied temperatures. The values of Kirkwood correlation factor ( $g$ ) for the 4-DMAP in 1,4-dioxane and in CCl<sub>4</sub> solution decrease with increase in weight fraction of 4-DMAP and are greater than unity, which indicate that molecules of this system tend to orient themselves with the parallel dipole alignments. The values of  $g$  vary with change in temperature indicating that temperature change produces appreciable structural change. The values of  $g$  for 4-DMAP are higher as compared to 2-AMP in 1,4-dioxane solution at all temperatures. From Table 2, it can be seen that the value of  $\mu_G$  for 4-DMAP in benzene is 2.4 D at 303.15 K while the value of  $\mu_H$  is 2.3 D at the same temperature. Discrepancy in dipole moment values may be due to different methods applied for calculating the dipole moment. The value of dipole moment of 4-DMAP is higher than 2-AMP in all the three solvents, which indicates that 4-DMAP is more polar than 2-AMP. The value of dipole moment decreases with increase in temperature in all the three solvents, which suggests solute-solvent type of interaction between 4-DMAP and solvent molecules. The predicted molecular association between the 4-DMAP and respective solvents are shown in Fig. 3.

From the Table 2, it can be seen that the molar polarization values decrease with increasing weight fraction of 4-DMAP in all the three solvents at all studied temperatures which indicates solute-solvent interactions of an unassociated solute 4-DMAP

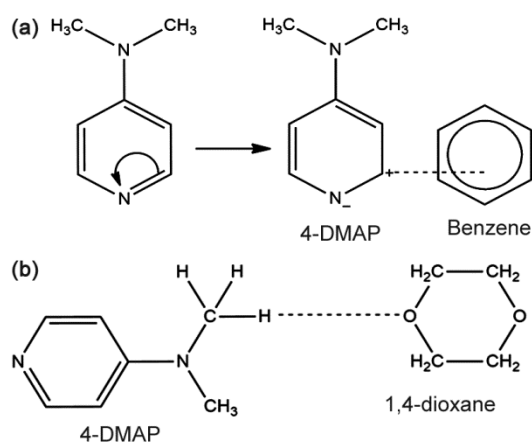


Fig. 3 — Solute-solvent molecular association between (a) 4-DMAP and benzene, and (b) 4-DMAP and 1,4-dioxane.

molecules with the solvent molecules. The molar polarization ( $P_2$ ) of 4-DMAP in CCl<sub>4</sub> solution is higher in comparison with benzene and 1,4-dioxane solution. The values of density ( $d$ ) increase and molar volume ( $V_m$ ) decreases with increase in weight fractions of 4-DMAP in all the three solvents (Table 2). As compared to 4-DMAP in benzene system, the molar volume ( $V_m$ ) of 4-DMAP in 1,4-dioxane system is relatively small. The density values decrease with increase in temperature due to thermal agitation of component molecules.

The values of energy of activation ( $\Delta F_E$ ), enthalpy of activation ( $\Delta H_E$ ) and entropy of activation ( $\Delta S_E$ ) for 4-DMAP in benzene, 1,4-dioxane and CCl<sub>4</sub> at different temperatures are presented in Table 2. The molar enthalpy ( $\Delta H_E$ ) for 4-DMAP in CCl<sub>4</sub> solvent is the highest among the three solvents which suggest



that 4-DMAP form larger relaxing units in  $\text{CCl}_4$ . The negative values of entropy in this system show that activated state is more ordered as compared to the normal state.

#### 4 Conclusions

In this paper, results of a systematic study of dielectric properties, dielectric relaxation and thermodynamic properties of two polar solutes 2-AMP and 4-DMAP with each of the three non-polar solvents benzene, 1,4-dioxane and  $\text{CCl}_4$  at 303.15 K, 313.15 K and 323.15 K temperatures, have been reported. The study provides the values of relaxation time, dipole moments, Kirkwood correlation factor, thermodynamical parameters, molar polarization and molar volume. Dielectric relaxation behaviour of 2-AMP and 4-DMAP in corresponding solvents has been compared. Effect of solvent environments and temperature on the dielectric relaxation behaviour of 2-AMP and 4-DMAP was discussed. The linear variation of  $\epsilon'$  and  $\epsilon''$  ensures the applicability of Debye theory and hence Gopalkrishna's and Higasi's methods were used to calculate the relaxation time. It is observed that the intra-molecular and overall orientations are present in the studied systems at all studied temperatures. The value of relaxation times  $\tau_G$  and  $\tau_H$  for each of 2-AMP and 4-DMAP are in the order of  $\text{CCl}_4 > 1,4\text{-dioxane} > \text{benzene}$  at all studied temperatures. The dipole moment values also show similar trend. In all three solvents variation of molar polarization ( $P_2$ ) of the solute follows the same trend as Kirkwood correlation factor ( $g$ ). The values of activation energy  $\Delta F_E$  are the highest for solutions of 2-AMP and 4-DMAP in  $\text{CCl}_4$ . The values of entropy are negative for all systems at all studied temperatures, which indicates that fewer configurations are possible in activated state and for these configurations the activated state is more ordered than the normal state.

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