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Research Article

DIELECTRIC STUDIES OF HYDROGEN BONDED COMPLEXES OF C=O COMPOUNDS WITH SUBSTITUTED PHENOLS USING FREQUENCY DOMAIN TECHNIQUE

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ABSTRACT

Dielectric studies of H-bonded complexes of acetamide and formamide with 4-aminophenol, 4-bromophenol, 4-chlorophenol and 4-nitrophenol in benzene have been made at 308 K using 9.37 GHz dielectric relaxation set up. Various dielectric parameters like dielectric constant (ε′), dielectric loss factor (ε″) at Microwave frequency, static dielectric constant (ε_0) and dielectric constant at infinite dilution (ε_∞) at optical frequency have been determined. The validity of the single frequency equation of Higasi et al. for multiple relaxation time $\tau_{(1)}$ is found to be function of the hydrogen bonding strength of the phenolic hydrogen, whereas the group rotation relaxation time $\tau_{(2)}$ is a function of the steric interactions of the proton donor. The relaxation time and molar free energy activation of 1:1 molar ratio is greater than other higher molar ratios (i.e. 3:1, 2:1, 1:2, 1:3) confirm that the existence of most likely 1:1 complex formation between the studied systems and also complex formation formed between free hydroxyl group of phenols and carbonyl group of amide.

Keywords: H-bonding, Permittivity, dielectric constant, dielectric loss, relaxation time, activation free energy, X-band microwave.

1. INTRODUCTION

Amides are the simplest molecules containing a peptide linkage and a study of their hydrogen bonding yield into the nature of protein structure [1]. Amides have been the subject of spectroscopic, physical, theoretical investigations to study intermolecular hydrogen bonding. The primary amides like formamide and acetamide are excellent proton donors as well as proton acceptors and hence are strongly associated with intermolecular hydrogen bonds. Dielectric studies have often proved to be a powerful tool to give insights into the mechanisms of association and reorientational dynamics of dipolar liquids [2-4]. The molecule of these compounds has hydrogen bonding sites and can enter into intra and inter molecular hydrogen bonding giving rise to several different conformations. Hydrogen bonds constituted a very interesting class of intermolecular interactions which are of extreme importance in many fields of chemistry and molecular biology. The dielectric investigation of hydrogen-bonded compounds innon-polar solvent provides valuable information regarding molecular interaction of complex formation in solution. The studies of the H-bonds of the type O=H-----O=C occupies a position of considerable importance as it relates to the study of biopolymers. Thus, the study and knowledge of dielectric properties of the mixtures of amide with glycols in non-polar solvents is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest.

Keeping both the industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between free hydroxyl group of phenols and the carbonyl group of amides using dielectric method. This study is expected to provide better understanding of the nature of molecular orientation process. The dielectric relaxation behaviours of amides are expected to be similar to that of n-alcohols [5]. The study of dielectric relaxation of polar liquids in non-polar solvents from the microwave absorption studies give valuable information about various types of the molecular association present in the solutions as microwave can detect weak molecular interactions. Dielectric relaxation study can give precise information on the formation of H-bonded complex when a proton donor is mixed with a proton acceptor in

nonpolar solvent. In our present investigation, the mixed solvents have been used a wide range of chemical, biological pharmaceutical, industrial, biophysics, condensed matter physics, and laboratory applications [6]. The dielectric investigation of hydrogen bonded compounds in non-polar solvent provides valuable information regarding molecular interaction of complex formation in solutions. The study of the H-bonds of the types (O-H, C=O) occupies of position of importance as it relates to the study of biopolymers. Recently, dielectric relaxation behaviour of mixtures of polar molecules under varying conditions of complexation temperature and environ-ment factors has evoked considerable interest [7]. In this work, the proton acceptor ability of formamide and acetamide is investigated by dielectric measurements by computing the dipolar increment of the 1:1 complexes of formamide and acetamide with substituted phenols in Benzene.

2. MATERIAL AND METHOD

The static dielectric constants were measured by heterodyne beat method at 308K using a commercial instrument, Dipole meter DM-01 supplied by Wissenschaijftlich Technische Werksatter, Germany operated by 220V [8]. The refractive indices (n_D) were measured by Abbe's refractometer [9]. All measure-ments were made at 35°C and the temperatures were controlled within ±0.5°C by a thermostat. The uncertainties in the measurements of dielectric constants and refractive indices were ± 0.0005 and ± 0.0002 respectively. The measurements of dielectric constant at an angular frequency (ε') and dielectric loss (ε''), where carried put X-band microwave frequency at 9.37GHz. Ostwald's viscometer is used to measure the viscosities of the liquid. A variable attenuator and a slotted line wave-guide with a slit in the broad face to accommodate a probe were connected with a liquid cell. The signal from the Klystron was fed to the attenuator through a ferrite isolator. This isolator allows free passage of power only in the forward direction and it attenuates the reverse wave strongly. The sample length of liquids was adjustable by the micrometer plunger assembly. The microwave power was transmitted from the slotted line into the liquid through a Teflon window, which has negligible dielectric loss. The probe was a crystal detector, which measured the microwave power. The microwave current was fed to a sensitive spot galvanometer. The temperature of the liquid inside the cell was kept constant by circulating water around it from a thermostat [10]. The physical parameter of all the chemicals used, have been checked against their literature values.

2.1. Dielectric parameters

According to Higasi' smethod [11], the average relaxation time $\tau_{(1)}$ is described by

$$\tau_{(1)} = \frac{a''}{\omega(a'-a_\infty)}$$

While the overall dielectric relaxation $\tau_{(2)}$ is given by

$$\tau_{(2)} = \frac{a_o - a'}{\omega\, a''}$$

$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}}$$

$\tau_{(0)}$ may be called the mean relaxation time. Where ω is the angular frequency ε_0, ε', ε" and ε_∞ are defined by equation (3)

$$\varepsilon_0 = \varepsilon_{01} + a_0 w_2$$

$$\varepsilon' = \varepsilon_1' + a' w_2$$

$$\varepsilon_\infty = \varepsilon_{\infty 1} + a_\infty w_2$$

In which subscript refer to the solvent and 2 refers to the solute, 0 refers to the static frequency and ∞ refers to the infinite or optical frequency measurements and w_2 is the weight fraction of the solute.

The molar free energies have been calculated using the Eyring's equation [12].

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\tau}{RT}\right)$$

$$\eta = \frac{Nh}{V}\exp\left(\frac{\Delta F_\eta}{RT}\right)$$

Where, h-Planck's constant, k-Boltzmann's constant, N-Avagadro number and V- the molar volume.

3. RESULTS AND DISCUSSION

The ternary systems selected were Acetamide and Formamide with proton donors (4-Aminophenol, 4-bromophenol, 4-chlorophenol, 4-nitrophenol) using Benzene as solvents. The value of relaxation times $\tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ for all the systems were calculated by Higasi's method [11]. The relaxation time τ, of amides with proton donors (4-Aminophenol, 4-bromophenol, 4-chlorophenol, 4-nitrophenol) in benzene as solvents at 35°C has been provided in tables 1 & 2. A perusal table

shows that the value of relaxation time τ increases with increasing chain length of amide and acidic nature of phenols. Therefore, there is a possibility of interaction between the positive hydrogen of alcohol group and carbon atom in Benzene. The potential hydrogen bonding nature of benzene molecule may contribute to increasing the relaxation time.

Our result shows that the relaxation time is larger at 1:1 mole ratio of amide with phenols. The relaxation time conspicuously decreases for the others mole ratios but are higher than either of the components. Saxena et al. [13] studied the H-bonding in pyridine/phenol and quinoline/phenol systems in different compositions. They also observed that the relaxation time of ternary mixtures is always much greater than either of the polar solutes in the inert solvent. Further if the complex is rigid, the distribution parameter is larger, the two relaxation times are well separated, one representing the rotation of the complex as a whole, while the other representing the rotation of one of the interacting polar solute molecules. The relaxation time for dilute solution of p-cresol, p-chlorophenol, 2, 4-dichlorophenol and p-nitrophenol observed in the present study ranges between 4.5 and 34 ps. With excess of phenols, the relaxation time of amide/phenol systems shows slight increase. This result is in agreement with the earlier investigations of Tucker et al. [14]. The result also shows that the molecular association between amide and phenols is maximum at 50:50 mol% ratio and then decreases at other mol%. From this we conclude that the 1:1 complexe is dominant in the amide/phenol systems. The relaxation time t_0 increases with increasing acidity of proton donor in complex systems. But in amides with 4-aminophenol systems, the t_0 values are greater than other phenol complexes due to steric hindrance and inductive effect as shown in tables.

Parthiban [15] studied the H-bonding in some carbonyl + phenols system in different compositions. They also observed that the relaxation times of ternary mixtures is always much greater than either of the polar solutes in the inert solvent. The result also shows that the molecular association between amide and phenols is maximum at 50:50 mol% ratio and then decreases at other mol%.

Table 1: Value of dielectric constants and relaxation times for various weight fractions, Acetamide with substituted Phenols in Benzene

Ratio	Weight fraction W_2	ε_0	ε'	ε''	ε_∞	Relaxation Time (ps) using Higasi's Method			Activation energy (KJ mol^{-1})	
						τ_1	τ_2	τ_0	$\Delta f\tau$	$\Delta f\eta$
***Acetamide*+4AP+Benzene**										
1:3	0.0319	5.2419	2.6521	0.7471	2.3228	17.52	18.56	18.04	25.58	25.71
1:2	0.0300	5.2987	2.6282	0.6882	2.3289	18.41	18.94	18.28	25.69	25.83
1:1	0.0263	5.3559	2.6155	0.6647	2.3312	19.05	19.19	19.12	25.81	25.95
2:1	0.0227	5.3845	2.6302	0.6957	2.3296	18.82	18.77	18.08	25.67	25.89
3:1	0.0209	5.4479	2.6334	0.7231	2.3266	17.62	18.09	17.66	25.58	25.69
***Acetamide*+4NP+Benzene**										
1:3	0.0396	5.3101	2.6302	0.6960	2.3188	17.12	18.31	17.42	25.49	25.69
1:2	0.0369	5.3903	2.6116	0.6592	2.3201	17.44	18.71	17.58	25.61	25.81
1:1	0.0315	5.4595	2.6008	0.6177	2.3252	18.72	18.96	18.84	25.76	25.92
2:1	0.0262	5.4975	2.6105	0.6498	2.3197	17.97	18.95	17.51	25.59	25.86
3:1	0.0235	5.5501	2.6142	0.6780	2.3159	17.22	17.01	17.13	25.52	25.66
***Acetamide*+4CP+Benzene**										
1:3	0.0369	5.3903	2.6080	0.6642	2.3178	16.53	18.16	17.04	25.41	25.63
1:2	0.0344	5.4537	2.5912	0.6412	2.3198	17.20	17.68	17.14	25.57	25.78
1:1	0.0297	5.5117	2.5855	0.5752	2.3205	18.56	18.50	18.53	25.67	25.86
2:1	0.0249	5.5247	2.5903	0.6066	2.3192	17.93	17.09	17.21	25.58	25.81
3:1	0.0122	5.5408	2.6080	0.6733	2.3135	16.12	15.85	16.49	25.38	25.58
***Acetamide*+4BP+Benzene**										
1:3	0.0482	5.4421	2.5860	0.6087	2.3132	15.15	17.62	16.39	25.02	25.29
1:2	0.0446	5.5175	2.5767	0.6009	2.3169	16.88	15.50	16.41	25.21	25.39
1:1	0.0373	5.5408	2.5653	0.5669	2.3199	17.54	16.53	17.04	25.34	25.52
2:1	0.0300	5.5568	2.5704	0.5740	2.3157	16.87	15.89	16.34	25.24	25.42
3:1	0.0263	5.5747	2.5847	0.6039	2.3101	15.89	14.70	15.29	25.19	25.35

Table 2: Value of dielectric constants and relaxation times for various weight fractions, Formamide with substituted Phenols in Benzene

Ratio	Weight fraction W_2	ε_0	ε'	ε''	ε_∞	Relaxation Time (ps) using Higasi's Method			Activation energy (KJ mol^{-1})	
						τ_1	τ_2	τ_0	$\Delta f\tau$	$\Delta f\eta$
Formamide+4AP+Benzene										
1:3	0.0331	5.5231	2.8421	0.8421	2.5081	17.53	17.73	17.97	26.01	26.23
1:2	0.0316	5.5437	2.8326	0.8262	2.5132	17.87	19.44	18.89	26.39	26.63
1:1	0.0288	5.5640	2.8255	0.7648	2.5231	21.44	21.75	21.63	26.68	26.96
2:1	0.0259	5.5745	2.8320	0.8369	2.5134	18.53	18.58	18.56	26.47	25.69
3:1	0.0245	5.5979	2.8432	0.8238	2.5072	17.86	16.77	17.71	26.08	26.26
Formamide+4NP+Benzene										
1:3	0.0408	5.6043	2.8571	0.8532	2.5092	17.44	17.82	17.62	25.39	25.79
1:2	0.0385	5.6132	2.8435	0.8372	2.5152	17.82	19.66	18.66	25.57	26.02
1:1	0.0174	5.6395	2.8302	0.7759	2.5254	20.69	20.98	20.86	26.06	26.52
2:1	0.0293	5.6575	2.8416	0.8464	2.5144	17.97	17.88	17.93	25.69	26.09
3:1	0.0155	5.6701	2.8493	0.8362	2.5089	17.92	16.83	17.21	25.52	25.84
Formamide+4CP+Benzene										
1:3	0.0381	5.6903	2.8608	0.8671	2.5132	17.74	16.68	17.31	24.72	25.02
1:2	0.0361	5.7037	2.8581	0.8467	2.5163	16.84	18.81	17.83	25.07	25.58
1:1	0.0321	5.7117	2.8402	0.7852	2.5268	20.76	19.64	20.21	25.67	25.96
2:1	0.0281	5.7110	2.8580	0.8526	2.5158	17.90	17.54	17.72	25.58	25.61
3:1	0.0262	5.7154	2.8628	0.8462	2.5112	17.86	15.91	16.89	24.79	25.08
Formamide+4BP+Benzene										
1:3	0.0495	5.7281	2.8759	0.8822	2.5168	17.62	16.73	17.18	24.02	24.29
1:2	0.0462	5.7297	2.8658	0.8656	2.5175	16.18	18.93	17.56	24.21	24.39
1:1	0.0397	5.7300	2.8557	0.827	2.5283	19.68	19.53	19.61	24.54	24.82
2:1	0.0300	5.7258	2.8657	0.8688	2.5179	17.71	16.56	17.14	24.24	24.41
3:1	0.0321	5.7241	2.8754	0.8785	2.5153	16.94	15.88	16.41	24.19	24.35

From this we conclude that the 1:1 complex is dominant in amide in phenols as shown in fig 1 & 2. The increasing relaxation time is due to increasing chain length of phenols and amides which offers hindrance to the rotation of the molecule. The increase in relaxation time may be due to the increases in effective radius of the rotating unit. At high concentration phenols in the mixtures, there is large number of phenols molecule surrounding the amide molecules. Thus dipole-dipole interactionsoccur in such a way that the effective dipole moment gets increased and linear α-multimers are formed. The dipole-dipole interactions are the interaction of the -OH group of the phenols with C=O of amide. At low concentrations of phenols in the mixtures, other is only a small number of phenols molecule to enable dipole-dipole interaction through hydrogen bonding with non-associative amide molecules [16, 17].

The relaxation time increases with increasing chain length of amide and acidity of proton donor (phenols), indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases. The relaxation time increases with increasing chain length with the fact that the relaxation time is directly related to the size of the molecules [18-23].

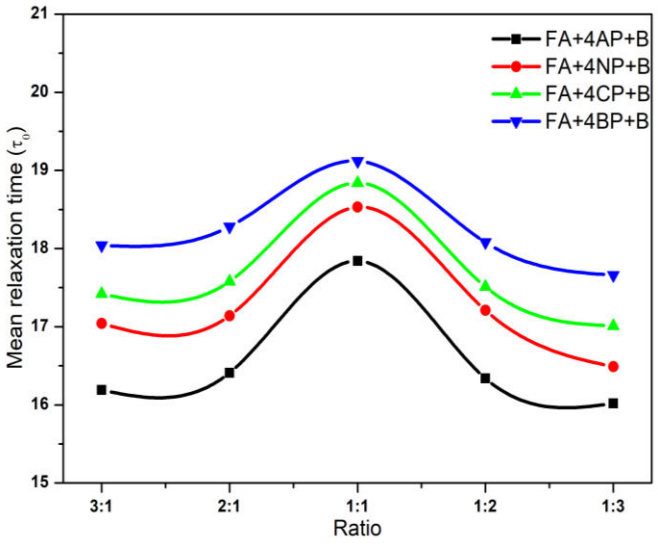

Fig. 1: Variation of mean relaxation time with ratio of substituted phenols with Acetamide in Benzene

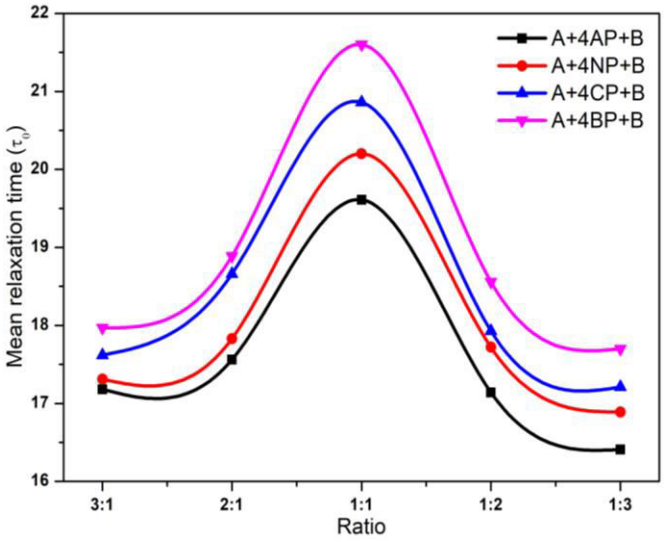

Fig. 2: Variation of mean relaxation time with ratio of substituted phenols with Formamide in Benzene

The higher values of relaxation time observed for p-bromophenol with alkyl methacrylate, suggested that p-bromophenol is more acidic than other phenols. The molar free energy of activation for viscous flow $\Delta F\eta$ and the free energy $\Delta F\tau$ are calculated for acetamide and formamide with substituted phenols (4-aminophenol, 4-bromophenol, 4-chlorophenol, 4-nitrophenol) using benzene and given in table. It is evident from our data that the $\Delta F\ \eta > \Delta F\tau$.

This is in agreement with the fact that the process viscous flow, which involves both the rotational translational forms of motion, faced greater interference from neighbour than dielectric relaxation, which take place by rotation only [24, 25]. Smyth [26] pointed out that the relaxation time of a proton donor increases as the acceptor ability of the solvent environment increases. Similarly, for a given proton acceptor, the relaxation time must increase with the proton donor ability of the donor solute. Our results are in accordance with this conclusion.

4. CONCLUSION

The hydrogen bonded complexes of Acetamide and Formamide with substituted Phenols (4-Aminophenol, 4-bromophenol, 4-chlorophenol, 4-nitrophenol) have been suited dilute solutions of benzene using dielectric method. The dielectric properties of the above systems studied are depending on the alkyl chain length of phenols and amides. The most likely association between phenols and amide is 1:1 complex through the free hydroxyl group of the phenols and the carbonyl group of amides. From the above result it may be conclude that, the proton accepting ability of amides is in decreasing order: formamide <acetamide.

Conflict of interest

None declared

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