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Dielectric Relaxation Studies of Alkylacrylates with Ortho-Substituted Benzoic acids in 1, 4 - Dioxane

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Abstract

Dielectric absorption studies of Hydrogen bonded complexes of alkyl acrylates with ortho substituted benzoic acid (2 - Fluoro benzoic acid, 2 - Iodo benzoic acid, 2 - Chloro benzoic acid, 2 - Bromo benzoic acid, and 2 - Nitro benzoic acid) were studied at microwave frequency 9.43GHz in dilute solution of 1,4 - Dioxane at room temperature. Different dielectric parameters like dielectric constant (ϵ') and dielectric loss (ϵ'') at microwave frequency, and static dielectric constant (ϵ_0) and dielectric constant (ϵ_∞) at optical frequency were determined. The validity of the single frequency equation proposed by Higasi et.al., for multiple relaxation time (τ_1) was found to be a function of the hydrogen bonding strength in benzoic acid, whereas the group rotation relaxation time (τ_2) was a function of the steric interaction of proton donor. The relaxation time was maximum at 1:1 molar ratios of alkyl acrylates with ortho substituted benzoic acid.

Keywords: Alkyl Acrylates, Ortho substituted benzoic acids, Dielectric parameters, Dielectric constants, Dielectric relaxation

Introduction

Alkyl acrylates are industrially important chemicals, being precursors in the synthesis of polymers and are also used as adhesives, paints, binders and emulsifiers [1]. Dielectric relaxation of liquid mixtures in the microwave region has been studied to characterize the different types of molecular interactions such as solute-solute, solute-solvent and self association in the solution, because of the capacity of micro waves to detect the weaker molecular interaction [2]. Dielectric relaxation studies of polar molecules in non polar solvents using microwave absorption techniques have been frequently attempted by various researchers [3-6]. Such studies are very useful in understanding the molecular structure and the molecular forces. Sivagurunathan et al. [7] reported the dielectric parameters of Methylacrylate, Ethylacrylate and butylacrylate with primary alcohol using time domain reflectometry. Dielectric parameters for ternary mixtures of alkyl acrylates with phenol derivatives in carbon tetrachloride were reported by Khan et al. [8].

Recently, our research group [9-14] has investigated the complex formation of acrylic esters with proton donors (alcohols) in non-polar solvents using FT-IR spectroscopic method. The study of H-bonds of the type O-H...O=C is of considerable importance as it relates to the study of biopolymers. Thus, the study of dielectric properties of the ternary mixtures of acrylic esters with polar associating liquids in non-polar solvents provides useful and vital process parameters for efficient design of transesterification process 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 benzoic acid and the carboxyl group of ester using dielectric method. This study provides a better understanding of the nature of the molecular orientation process.

Experimental

E- Merck variety of Methyl acrylate, Ethyl acrylate, Butyl acrylate and 1, 4 - Dioxane. And 2 - Fluoro benzoic acid, 2- Iodo benzoic acid, 2 - Chloro benzoic acid, 2 - Bromo benzoic acid, 2 - Nitro benzoic acid were purchased from sigma Aldrich. Chemicals were used without purification. The static

dielectric constants were measured by heterodyne beat method at the room temperature using a Dipole meter (supplied by mittal enterprises – New Delhi). The refractive index was measured by using Abbe's refractometer. The measurement of dielectric constant (ϵ') at an angular frequency and dielectric loss (ϵ'') were carried in the X-band microwave frequency of 9.43GHz. The viscosities were measured with the help of Oswald's viscometer at room temperature. The proton donors (ortho substituted benzoic acid) and the acceptors (alkyl acrylate) under study were separately dissolved at the same molar concentration (0.3mol/L) in the solvent 1,4-Dioxane. Their dielectric constants were measured separately. Then the two solutions were mixed in different proportions at constant measurements. As the maximum deviation of dielectric constant for all the systems occurs at equimolar ratio of the solutes, it is presumed that the deviation is due to the formation of 1:1 complexes.

Evaluation of Dielectric Parameters

According to Higasi et al. [15] method, the average relaxation time τ_1 is described by

$$\tau_1 = \frac{a''}{(a' - a_\infty)}$$

While the overall dielectric relaxation τ_2 and the mean relaxation time τ_0 is given by,

$$\tau_2 = \frac{(a_0 - a')}{\omega a''}$$

$$\tau_0 = \sqrt{\tau_1 \times \tau_2}$$

Where, ω is the angular frequency, a_0 , a' , a'' and a_∞ are defined by the following equations

$$\epsilon_0 = \epsilon_{01} + a_0 w_2$$

$$\epsilon' = \epsilon'_1 + a' w_2$$

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

In the above equations subscript 1 refers to the pure solvent, subscript 2 refers to the solute, subscript 0 refers to the static frequency measurements and W_2 is the mass fraction of the solute.

The molar free energies have been calculated using the Eyring et al. [16] equations,

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

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

Where, h is the Plank's constant, k is the Boltzmann constant, N is the Avogadro number, V is the molar volume, and ΔF_τ , ΔF_η are the molar free energies for the dielectric relaxation process and the viscous flow process respectively.

Result and Discussion

The ternary systems selected were alkyl acrylates (Methyl acrylate (MA), Ethyl acrylate (EA) and Butyl acrylate (BA)) with proton donors (2-Fluro benzoic acid, 2- Iodo benzoic acid, 2- Chloro benzoic acid, 2- Bromo benzoic acid, and 2-Nitro benzoic acid) in a non-polar solvent 1, 4- Dioxane as solvent. The value of relaxation time τ_1, τ_2 and τ_0 for all the systems were calculated by Higasi et al. method [15]. It is observed that the value of relaxation time τ_1, τ_2 and τ_0 increases with increasing chain length of alkyl acrylates and acidity of ortho substituted benzoic acid [16-17] and reported in the Table 1- 3. The increase in relaxation time may be due to the increase in effective radius of the rotating unit. The observed higher value of butyl acrylate (BA) can be attributed to the large size of BA molecule in comparison to methyl acrylate (MA) molecules.

Table -1 Values of dielectric constant and relaxation time of Methyl Acrylate with ortho - substituted benzoic acids in 1,4 - Dioxane at different weight fractions.

Proton donor	Ratio	W ₂	ϵ_0	ϵ'	ϵ''	ϵ_∞	Relaxation Time (ps)		
							τ_1	τ_2	τ_0
2-Nitro benzoic acid	1:3	0.0308	3.1542	3.0389	0.2565	2.1628	5.4950	7.4656	6.4050
	1:2	0.0328	3.2040	3.0467	0.3013	2.1635	6.3947	8.6769	7.4489
	1:1	0.0367	3.2477	3.0527	0.3388	2.1648	7.1474	9.5659	8.2687
	2:1	0.0406	3.1629	3.0493	0.2763	2.1668	5.8695	6.8312	6.3321
	3:1	0.0426	3.1293	3.0467	0.2323	2.1684	4.9619	5.9067	5.4137
2-Fluro	1:3	0.0289	3.0424	2.9058	0.2535	2.1630	6.5556	8.9567	7.6627

benzoic acid	1:2	0.0302	3.0858	2.9203	0.2794	2.1646	7.0775	9.8083	8.3317
	1:1	0.0328	3.1542	2.9330	0.3357	2.1657	8.3643	10.9478	9.5693
	2:1	0.0354	3.0796	2.9216	0.2762	2.1672	7.0154	9.5063	8.1664
	3:1	0.0367	3.0300	2.9118	0.2310	2.1692	5.9758	8.5060	7.1296
2-Iodo benzoic acid	1:3	0.0367	2.9310	2.7880	0.2507	2.1648	7.9662	9.4763	8.6885
	1:2	0.0406	2.9928	2.8136	0.2738	2.1663	8.3168	10.8825	9.5135
	1:1	0.0485	3.0796	2.8308	0.3315	2.1679	9.7917	12.4720	11.0509
	2:1	0.0583	3.0052	2.8201	0.2737	2.1692	8.2583	11.2405	9.6347
	3:1	0.0603	2.9582	2.8156	0.2300	2.1719	7.0334	10.3034	8.5128
2-Chloro benzoic acid	1:3	0.0333	2.8447	2.6637	0.2535	2.1654	10.5829	11.8649	11.2055
	1:2	0.0361	2.8915	2.6735	0.2753	2.1671	11.2623	13.1583	12.1734
	1:1	0.0416	2.9743	2.6783	0.3309	2.1686	13.4281	14.8670	14.1292
	2:1	0.0472	2.8977	2.6707	0.2726	2.1698	11.3051	13.8421	12.5095
	3:1	0.0534	2.8385	2.6668	0.2289	2.1723	9.6494	12.4696	10.9693
2-Bromo benzoic acid	1:3	0.0301	2.8078	2.5650	0.2517	2.1658	13.9848	16.0279	14.9716
	1:2	0.0318	2.8558	2.5677	0.2743	2.1677	15.2006	17.4540	16.2884
	1:1	0.0352	2.9434	2.5639	0.3293	2.1689	18.5598	19.1502	18.8527
	2:1	0.0386	2.8422	2.5469	0.2715	2.1714	16.3872	18.0799	17.2127
	3:1	0.0403	2.7709	2.5423	0.2285	2.1735	14.1318	16.6228	15.3268

Table – 2 Values of dielectric constant and relaxation time of Ethyl Acrylate with ortho - substituted benzoic acids in 1,4 - Dioxane at different weight fractions

Proton donor	Ratio	W ₂	ϵ_0	ϵ'	ϵ''	ϵ_∞	Relaxation Time (ps)		
							τ_1	τ_2	τ_0
2-Nitro benzoic acid	1:3	0.0339	3.0448	2.9166	0.2484	2.1631	6.3206	8.5814	7.3647
	1:2	0.0355	3.0870	2.9282	0.2874	2.1643	7.1975	9.1871	8.1317
	1:1	0.0388	3.1754	2.9428	0.3343	2.1651	8.2020	11.5614	9.7379
	2:1	0.0420	3.0635	2.9330	0.2747	2.1672	6.8590	7.8915	7.3571
	3:1	0.0436	3.0101	2.9158	0.2315	2.1687	5.9887	6.7889	6.6201
2-Fluro benzoic acid	1:3	0.0319	2.9063	2.7434	0.2495	2.1635	8.6430	10.8502	9.6839
	1:2	0.0329	2.9607	2.7597	0.2856	2.1651	9.6009	11.6946	10.5962
	1:1	0.0348	3.0610	2.7763	0.3318	2.1662	10.8119	14.2597	12.4167
	2:1	0.0368	2.9730	2.7717	0.2726	2.1679	8.9944	12.2750	10.5074
	3:1	0.0377	2.9285	2.7713	0.2296	2.1695	7.6081	11.3823	9.3058
2-Iodo benzoic acid	1:3	0.0398	2.7955	2.5631	0.2455	2.1651	13.6964	15.7285	14.6773
	1:2	0.0434	2.8595	2.5754	0.2812	2.1668	15.1489	16.7935	15.9500
	1:1	0.0505	2.9569	2.5819	0.3202	2.1685	16.9826	19.4694	18.1835
	2:1	0.0577	2.8398	2.5723	0.2725	2.1698	14.9783	16.3111	15.6305
	3:1	0.0613	2.7685	2.5608	0.2226	2.1735	12.8790	15.5014	14.1295
2-Chloro benzoic acid	1:3	0.0363	2.7832	2.5145	0.2421	2.1661	16.2034	18.4441	17.2875
	1:2	0.0388	2.8459	2.5232	0.2774	2.1672	18.0190	19.3340	18.6649
	1:1	0.0437	2.9446	2.5271	0.3181	2.1689	20.4817	21.8178	21.1392

	2:1	0.0486	2.8656	2.5259	0.2713	2.1708	17.6763	20.8096	19.1791
	3:1	0.0510	2.7979	2.5247	0.2349	2.1742	15.5919	19.3370	17.3638
2-Bromo benzoic acid	1:3	0.0331	2.7709	2.4672	0.2350	2.1671	19.5194	21.4817	20.4770
	1:2	0.0345	2.8299	2.4736	0.2535	2.1682	20.5156	23.3597	21.8915
	1:1	0.0372	2.9335	2.4851	0.3033	2.1695	23.3909	24.5696	23.9730
	2:1	0.0400	2.8484	2.4777	0.2593	2.1716	20.9107	23.7603	22.2900
	3:1	0.0413	2.7807	2.4767	0.2416	2.1756	19.9792	20.9169	20.4427

Table – 3 Value of dielectric constants and relaxation times of Butyl Acrylate with ortho - substituted benzoic acids in 1,4 - Dioxane at different weight fractions

Proton donor	Ratio	W ₂	ϵ_0	ϵ'	ϵ''	ϵ_∞	Relaxation Time (ps)		
							τ_1	τ_2	τ_0
2-Nitro benzoic acid	1:3	0.0400	2.894	2.7434	0.2224	2.1642	7.7171	11.2482	9.3168
	1:2	0.0409	2.952	2.7545	0.2513	2.1654	8.5437	13.0631	10.5644
	1:1	0.0428	3.0027	2.7625	0.2831	2.1661	9.4813	14.1013	11.5628
	2:1	0.0447	2.9112	2.7538	0.2391	2.1679	8.1811	10.9431	9.4619
	3:1	0.0457	2.8570	2.7415	0.2071	2.1692	7.2920	9.2679	8.2208
2-Fluro benzoic acid	1:3	0.0380	2.8078	2.6254	0.2191	2.1648	10.1043	13.8314	11.8219
	1:2	0.0383	2.8693	2.6330	0.2482	2.1659	11.2417	15.8258	13.3382
	1:1	0.0389	2.9158	2.6370	0.2741	2.1668	12.3089	16.9089	14.4267
	2:1	0.0395	2.8378	2.6290	0.2253	2.1685	10.3894	15.4061	12.6515
	3:1	0.0398	2.8002	2.6268	0.2006	2.1698	9.3434	14.3621	11.5841
2-Iodo benzoic acid	1:3	0.0459	2.7558	2.4999	0.2053	2.1655	14.5610	20.7189	17.3691
	1:2	0.0488	2.8297	2.5061	0.2393	2.1672	16.6564	22.4698	19.3460
	1:1	0.0546	2.8815	2.5079	0.2601	2.1689	18.0888	23.8763	20.7820
	2:1	0.0604	2.8007	2.4934	0.2119	2.1709	15.8328	24.1044	19.5356
	3:1	0.0633	2.7586	2.4916	0.1939	2.1742	14.8344	23.0970	18.5103
2-Chloro benzoic acid	1:3	0.0425	2.7219	2.4500	0.1928	2.1667	17.4955	23.4317	20.2472
	1:2	0.0442	2.8121	2.4542	0.2400	2.1675	21.3753	24.7856	23.0174
	1:1	0.0478	2.8691	2.4570	0.2528	2.1692	22.3805	27.0942	24.6248
	2:1	0.0513	2.7605	2.4412	0.2085	2.1712	20.3907	25.4911	22.7987
	3:1	0.0530	2.7068	2.4404	0.1963	2.1745	19.6748	23.5944	21.5457
2-Bromo benzoic acid	1:3	0.0392	2.7011	2.4125	0.1945	2.1679	22.3596	24.6631	23.4837
	1:2	0.0399	2.7575	2.4178	0.2167	2.1685	24.1339	26.0526	25.0749
	1:1	0.0413	2.8009	2.4269	0.2291	2.1699	27.7957	28.5832	28.1867
	2:1	0.0422	2.7265	2.4195	0.2075	2.1721	23.4000	26.1831	24.7525
	3:1	0.0434	2.6605	2.4047	0.1768	2.1762	22.5274	23.7956	23.1528

Table 1-3 presents the value of τ_2 which is significantly higher than τ_1 and τ_0 for all the systems. Higher value of τ_2 indicates that the contribution of intermolecular or overall molecular relaxation is larger in comparison to intramolecular or individual

molecular relaxation in the systems [18]. In the present systems, it has been observed that the relaxation time of ternary mixtures (ortho substituted benzoic acid with alkyl acrylate in 1,4 - Dioxane) is much greater than the binary mixture

(ortho substituted benzoic acid with solvent (or) alkyl acrylate with 1,4- Dioxane) This result indicates that there is a formation of hydrogen bond between the OH group of ortho substituted benzoic acid and the carbonyl group of alkyl acrylate as shown in Figure 1.

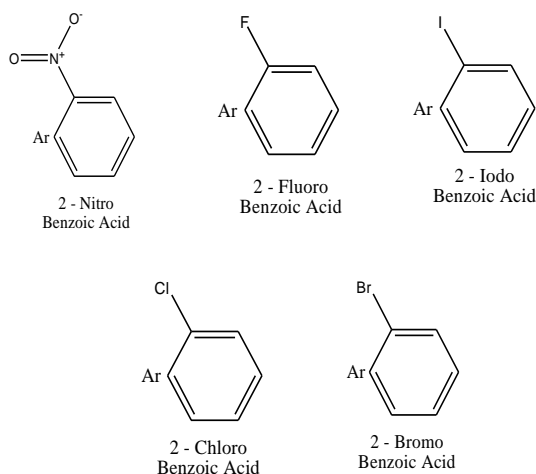
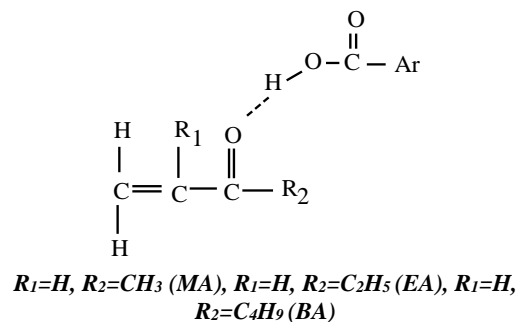
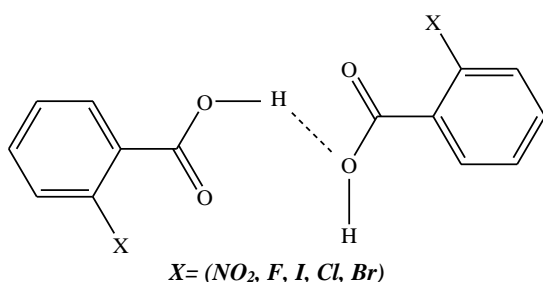


Figure 1 Hydrogen bonding between ortho substituted benzoic acids and alkyl acrylates.

In the system, the complex formation is likely to occur between $H^{\delta+}$ of benzoic acid and $O^{\delta-}$ of $C=O$ group of alkyl acrylate. Oxygen atom is sp^3 hybridized and in the alkyl acrylate structure there is a lot of voids for O-H to penetrate and enter into complexation components. The other possibility of intermolecular H-bond between ortho substituted benzoic acid molecules of the same species are shown in Figure 2.



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Figure 2 Intramolecular hydrogen bonding between Ortho substituted benzoic acid of the same species

1, 4 - Dioxane is a symmetrical non polar molecule with two bridging oxygen atoms having at least a lone pair of electrons on each. These lone pairs are being highly electronegative, polarizable with the neighbor protic substance, which leads to increasing relaxation time. In suitable combination of ortho substituted benzoic acid and alkyl acrylates, having an OH group of and $C=O$ group there is a possibility of dipolar interaction with 1,4 - Dioxane. Both inter and intra molecular H-bonds are possible between ortho substituted benzoic acid with 1, 4 - Dioxane as shown in Figure 3.

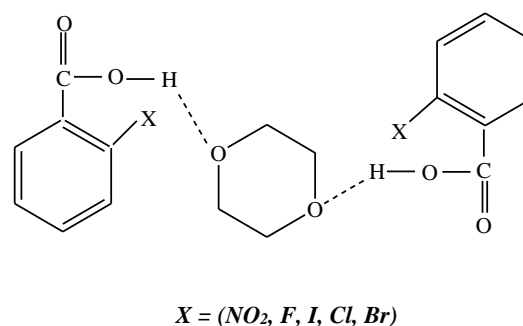


Figure 3: Intermolecular hydrogen bonding between ortho substituted benzoic acid and 1, 4-Dioxane

The dielectric relaxation time shows continuous increase with chain length of alkyl acrylate and acidity of proton donors (ortho substituted benzoic acid) and offers hindrance to the rotation of the molecule. The increase in relaxation time with chain length is expected as hydroxyl group reorientation depends to some extent on the length of the alkyl group, and the viscosity of the liquid. Our result shows that the relaxation time is larger at 1:1 molar ratio of acrylates with ortho substituted benzoic acid. Figs 4, 5 and 6 shows the variation of mean relaxation time with ratio of ortho substituted benzoic acid and alkyl acrylate and maximum variation is observed at 1:1 ratio for all ortho substituted benzoic acid with individual alkyl acrylate. The relaxation time decreases for other molar ratios but it is higher than either of the components. In the present study the relaxation time for dilute solution of ortho substituted benzoic acid were observed in the ranges between 6 and 26 ps. With the excess of benzoic acid, the relaxation time of alkyl acrylate + ortho substituted benzoic acid

system shows a slight increase. This result is in agreement with the earlier investigations of Tucker et al. [17]. The result also shows that the molecular association between alkyl acrylate and ortho substituted benzoic acid is maximum at 1:1 (molar ratio) and lesser in other molar ratios. From this we conclude that the 1:1 complex is dominant in alkyl acrylate + ortho substituted benzoic acid systems.

The relaxation time increases with increasing acidity of proton donor in complex system. The relaxation times of alkyl acrylate with 2 - Nitro benzoic acid is less than that of alkyl acrylate with other ortho substituted benzoic acid complex due to peripheral effect and greater I^- effect. Relaxation time of the substituted benzoic acid is in the following order $\text{NO}_2 < \text{F} < \text{I} < \text{Cl} < \text{Br}$.

At high concentration of substituted benzoic acid in the mixtures, there are large numbers of alcohol molecules surrounding the alkyl acrylate molecules. The associative OH molecules in benzoic acid act as proton donors enabling hydrogen bonding with alkyl acrylate molecules. Thus dipole-dipole interaction occurs in such a way that effective dipole moment gets increased and linear α -multimers are formed [19]. The dipole-dipole interaction is the interaction of the -OH group of alcohol with $\text{C}=\text{O}$ of alkyl acrylate. At lower concentration of benzoic acid in the mixtures, there are only a lesser number of OH molecules in benzoic acid to enable dipole-dipole interaction through hydrogen bonding with the non-associative alkyl acrylate molecules. As a result, intermolecular interaction is weak. The relaxation time increases with increasing alkyl chain length of alkyl acrylate and acidity of proton donor (substituted benzoic acid) indicating that the degree of co-operativity for reorientation of the molecules increases with increasing chain length and the bulk of cluster increases. These effects are due to: (i) the increase of viscosity as chain length increases and (ii) the increase of molecular size as the chain length increases [20-22]. The higher value of relaxation time observed for 2- Bromo benzoic acid with alkyl acrylate suggests that 2 - Bromo benzoic acid is more acidic than other substituted benzoic acid

Table – 4 Activation energies of alkyl acrylates with ortho substituted benzoic acids in 1, 4- Dioxane at 1:1 stoichiometric ratio

Systems	Activation energy	
	Δf_τ	Δf_η
MA+2–Nitro benzoic acid	10.42	13.01
MA+2–Fluro benzoic acid	10.97	13.62
MA+2–Iodo benzoic acid	11.18	14.02
MA+2–Chloro benzoic acid	11.57	14.12
MA+2–Bromo benzoic acid	11.79	14.22
EA+2–Nitro benzoic acid	11.12	13.46
EA+2– Fluro benzoic acid	11.32	13.76
EA+2–Iodo benzoic acid	11.65	14.14
EA+2–Chloro benzoic acid	12.02	14.24
EA+2 – Bromo benzoic acid	12.18	14.32
BA+2– Nitro benzoic acid	11.25	13.52
BA+2 – Fluro benzoic acid	11.52	13.89
BA+2– Iodo benzoic acid	11.76	14.25
BA+2– Chloro benzoic acid	12.18	14.66
BA+2– Bromo benzoic acid	12.32	15.02

The molar free energy of activation for viscous flow Δf_η and the molar free energy of dielectric relaxation Δf_τ are calculated for alkyl acrylate with ortho substituted benzoic acid in 1,4 - Dioxane and presented in Table 4. It is evident from our data that the $\Delta f_\eta > \Delta f_\tau$. This is in agreement with the fact that the process of viscous flow, which involves both the rotational and translational forms of motion, faced greater interference from neighbors than dielectric relaxation, which takes place by rotation only [23]. Smyth et al. [24] 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.

Conclusions

The hydrogen bonded complexes of substituted benzoic acid (2 - Fluro benzoic acid, 2 - Iodo benzoic acid, 2 - Chloro benzoic acid, 2 - Bromo benzoic acid, and 2 - Nitro benzoic acid) and acrylic esters (Methyl acrylate, Ethyl acrylate and Butyl acrylate) have been studied in a dilute non-polar solvent of 1,4 - Dioxane using dielectric method. The dielectric parameters show significant changes with concentration; the alkyl chain length of the alkyl acrylate and the acidities of the substituted benzoic acid. From these studies, it may be concluded that the alkyl chain length of esters and acidity of substituted benzoic acid play an important role in the determination of strength of hydrogen bond formation.

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