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Dielectric relaxation and dipole moment studies of hydrogen bonded complexes for enanthamide and valeramide with halogenated phenols using J-band microwave frequency

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Abstract

Dielectric investigations of hydrogen bonded complexes of Enanthamide and Valeramide with 4-bromophenol, 4-chlorophenol, 4-iodophenol and 4-fluorophenol in benzene were done at 303K, using a J-band (7.22GHz) microwave bench and dielectric relaxation setup. The permittivity of amides with halogenated phenol binary mixtures was measured in the microwave frequency range at temperatures ranging from 298K to 323K. At microwave frequencies; dielectric relaxation of ternary mixes of polar liquids in nonpolar fluids has been explored. Such investigations give useful information about the intermolecular and intramolecular interactions of solutes and solvent molecules. The dipole meter had a measurement frequency of 2MHz. The different parameters of dielectric, relaxation time ($\tau_0$) and the dipole moment ($\mu$) has been evaluated using the single-frequency concentration Higasi approach. The fact that the relaxation time and molar free energy activation of the 1:1 molar ratio are greater than those of other higher molar ratios (i.e. 3:1, 2:1, 1:2, 1:3) confirms the presence of a 1:1 complex structure between the studied systems, as well as a complex formation between the free hydroxyl group of phenols and the carbonyl group of amides. The dielectric relaxation energy parameters ($\Delta F_\varepsilon$, $\Delta H_\varepsilon$ and $\Delta S_\varepsilon$) of amides with halogenated phenols in benzene have been computed and compared with the related viscosity parameters. A comparison of these two sets of characteristics reveals that dielectric relaxation, like viscous flow, may be thought of as rate process.

1. Introduction

Dielectric studies in polar liquids dissolved in nonpolar solvents yield useful information on structural and associational aspects, as well as the formation of molecular complexes in GHz electric fields under various complexation, temperature and environmental parameters. Because microwaves can detect weak chemical associations, it is of great interest to researchers [1–6]. The investigations of the relationship of two polar particles because of hydrogen allotment from the dielectric relaxing estimations at microwave frequencies are exceptional. Dielectric dispersion investigations of polar liquids such as alcohols, amines, and their equimolar binary mixes were performed to identify the nature of the connection between molecules owing to hydrogen bonding, dipole moment, and relaxation behaviour phenomena. The nature of the interaction between the –CH, –OH, –C=O, and –NH groups is crucial in biological systems and drug creation. To reduce the dipole–dipole interaction, dipole moments are estimated for polar liquids diluted in the nonpolar solvent benzene [7–9]. Amides have been studied spectroscopically, physically, and theoretically to see how they can contain intermolecular hydrogen. Many chemical engineering issues, heat and mass transfer calculations, and drug design computations need a comprehensive understanding of thermodynamics and transport characteristics of pure liquids and their binary mixes. [10, 11]. Temperature dependent dielectric relaxation investigations of various polar liquids at different microwave frequency ranges can reveal information about the molecule’s...
structure, inter and intra molecular hydrogen bonding, and dipole orientational polarization [12–22]. Amides include a wide range of important chemical combinations, and their N–H dipoles allow them to function as H-bonded complexes as well [23, 24]. Microwave dielectric relaxation experiments may be used to explore molecular and intramolecular movements, solute–solute interactions, solute–solvent interactions, and their molecular conformations. The dielectric relaxation behaviour of binary mixtures of industrial and biologically useful associating polar solvents in their pure liquid form, as well as non-polar solvents, under varied compositional conditions has piqued the interest of many researchers over the last two decades. The study of the permittivity of polar liquids containing hydrogen bond donor and acceptor group molecules is very useful for a wide range of applications in biological, medical, material science, and technology [25, 26]. For a long time, researchers have been studying the influence of hydrogen bonding in fluid structures and their dielectric behavior. The discovery of hydrogen keeping contributed to the development of multimers, which are associates with a finite number of atoms. Dielectric examines have regularly ended up being an integral asset to give experiences into the components of association and reorientation elements of dipolar fluids [27]. Based on the observations, models of the relaxation process in liquid mixtures have been constructed. There has been little investigation on the coupling of two polar molecules via hydrogen bonding from dielectric relaxation studies at microwave frequencies [28–30]. Antony and Smyth were the first to identify solute–solvent interaction using relaxation time measurements. Amides have been the focus of various structural investigations due to their simplicity as peptide models [31]. To get a better understanding of the dynamic dielectric behaviour of amides in halogenated phenol solutions, the current work examines the dielectric relaxation behavior of Enanthamide and Valeramide mixes with halogenated phenols in benzene. Using a cavity perturbation method, the experiment was carried out at 7.22GHz J-band.

2. Materials and methods

Aldrich Ltd assortments of Enanthamide and Valeramide with 4-bromophenol, 4-chlorophenol, 4-iodophenol and 4-fluorophenol were utilized. Benzene was used as solvent. The proton donors (phenols) and the acceptors (amides) were separately dissolved at the same concentration (0.3moles/litre) in Benzene. Their dielectric constants were measured separately. The molar proportions of the amide-phenol tertiary mixtures were continually varied in the ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 in any case maintaining the solute complex in benzene constant. Using a J-band bench, the dielectric constant (ε’) and dielectric loss (ε”) were estimated. The static dielectric constants were calculated at 303K utilizing a standard equipment, the Dipole metre DM-01 from Wissenschaftlich Technische Werksatter, Germany, which was powered by 220V [32]. The binary system’s refractive index was calculated using an Abbe’s refractometer with sodium D light as the source. Refractometer observations yield a high frequency of dielectric constant (ε∞ = n2) for the pure and binary systems, and the measurements for ε” are correct to ±1 and ±5, respectively [33]. All measurements were taken at 35 °C, with the temperature being held within 0.5 °C by a thermostat. The calculation of dielectric constants and refractive indices had uncertainties of ±0.0005 and ±0.0002, respectively. Densities were calculated using a 10 ml specific gravity bottle, and weights were calculated using an Anamed electronic scale. The sample’s losses due to evaporation were reduced. The viscosities of liquids are measured using Ostwald’s viscometer. A liquid cell was used to link a variable attenuator and a slotted line waveguide with a probe slit in the wide face. A ferrite isolator carried the signal from the Klystron to the attenuator. This isolator only allows power to flow freely in one direction: forward and it strongly attenuates the reverse wave. The microwave power was transmitted into the liquid via a Teflon window with negligible dielectric loss from the slotted line. The microwave power is measured by the probe which is a crystal detector. A sensitive spot galvanometer receives the microwave current as shown in (figure 1) schematic diagram [34].
Table 1 compares experimental results for permittivity ($\varepsilon_0$), refractive index ($n_D$), dipole moment ($\mu$ in Debye) of pure liquids to available literature data [35–39]. Many of the chemicals used here had their physical parameters tested against their literature values.

3. Dielectric analysis

From Higasi’s method [39], the average relaxation time $\tau_{(1)}$ is described by

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

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

$$\tau(2) = \frac{a_0 - a'}{\omega a''} \quad (2)$$

$$\tau(0) = \sqrt{\tau(1)\tau(2)} \quad (3)$$

The Debye’s equation in terms of $a_0$, $a'$, $a_{\infty}$ and $a$ yields two independent equations [40].

$$\varepsilon_0 = \varepsilon_{01} + a_0w_2 \quad (4)$$

$$\varepsilon' = \varepsilon'_1 + a'w_2 \quad (5)$$

$$\varepsilon'' = a''w_2 \quad (6)$$

$$\varepsilon_{\infty} = \varepsilon_{\infty1} + a_{\infty}w_2 \quad (7)$$

Eyring’s equations [41] were used to quantify the free energy of activation for dielectric relaxation $\Delta F_\tau$ and viscous flow $\Delta F_f$ similarly excess entropy $\Delta S_f$ will be calculated.
\[ h_{kT}F \exp (t) = D_{t}F_{H}S \]

\[ \Delta F_{\varepsilon} = \Delta H_{\varepsilon} - \Delta S_{\varepsilon} \]

\[ \eta = \frac{Nh}{V} \exp \left( \frac{\Delta F_{\varepsilon}}{R T} \right) \]

\[ \Delta F_{\tau} = \Delta H_{\tau} - \Delta S_{\tau} \]

Where \( \tau \), \( h \), \( K \), \( T \), \( V \), \( R \) is relaxation time, Planck’s constant, Boltzmann constant, temperature in Kelvin, molar volume of the solvent and gas constant, respectively. \( \Delta F_{\varepsilon}, \Delta H_{\varepsilon}, \Delta S_{\varepsilon} \) are the free energy, enthalpy and the entropy of activation for the relaxation process and \( \Delta F_{\tau}, \Delta H_{\tau}, \Delta S_{\tau} \) are the corresponding parameters for the viscous flow of benzene. As required by equations (9) and (11), which showed the applicability of these equations to our relaxation time and viscosity data.

Table 2. Experimental Dipole moment(\( \mu \)) and Permittivity(\( \varepsilon_{0} \)) at 20 MHz and their binary mixtures at different temperatures.

| T/K   | \( \varepsilon_{0} \)     | \( \mu \) in Debye |
|-------|---------------------------|-------------------|
| 298K  | 6.2708                    | 2.72D             |
| 303K  | 6.2671                    | 2.70D             |
| 308K  | 6.2662                    | 2.66D             |
| 313K  | 6.2638                    | 2.63D             |
| 318K  | 6.2606                    | 2.64D             |
| 323K  | 6.2594                    | 2.62D             |

* Standard uncertainties u are \( u(\varepsilon_{0}) = 2\%–3\% \) and \( \mu = \pm 0.04 \) respectively. References [40, 42]
halogenated phenols such as 4-bromophenol, 4-chlorophenol, 4-iodophenol, and 4-fluorophenol. Higasi’s approach was used to compute the relaxation times $\tau (1), \tau (2)$ and $\tau (0)$ for both processes [42]. In benzene, tables 3 and 4 show the relaxation time of amides with proton donors (4-bromophenol, 4-chlorophenol, 4-iodophenol, and 4-fluorophenol) at 35 °C. The dipole moment ($\mu$) and permittivity ($\varepsilon_0$) (measured at 20 MHz) of Enanthamide, Valeramide with halogenated phenols and their equimolar binary mixture at different temperature from 298 K to 323 K are tabulated in table 2. Table 2 shows that the dipole moment and permittivity of pure liquids agree well with the reported literature values. The measured values of the dipole moment differ slightly from the literature values, which may be due to the electron density cloud of benzene in the liquid system. The presence of hydrogen bonding between amides and phenols molecules causes an increase in the value of the dipole moment of the equimolar binary system when compared to pure liquids, as expected. The increase in the binary system’s dipole moment as a result of the environment associated with the liquid system [43]. The net dipole moment of pure liquids and binary systems decreases as temperature is raised. The increase in thermal energy disrupts the alignment of the dipoles in the field direction, resulting in a decrease in the dipole moment value.

According to figure 2, permittivity ($\varepsilon_0$) increases with increasing concentration of amides and phenols liquid medium and decreases with increasing temperature. The increase in permittivity ($\varepsilon_0$) is caused by an increase in dipolar association in the liquid mixture, which increases dielectric susceptibility. This graph’s nonlinear response indicates that heteromolecular interaction exists in liquid mixtures (figure 2). The decrease in permittivity with increasing temperature caused by the breakage of hydrogen bond networks in the solution causes a decrease in the system’s permittivity [44]. Figure 3 depicts the frequency and concentration dependent complex permittivity spectra of binary mixes at 303 K. Below 0.1 GHz, the real part ($\varepsilon’$, $\varepsilon’’$) of the complex permittivity spectrum of amide–phenol combinations was practically frequency independent. As a result, static permittivity values from the low frequency range were recovered [45]. There was a single loss peak in the investigated frequency range for each concentration, suggesting co-operation in the binary mixes; the complicated permittivity loss peaks changed to higher frequencies with increasing halogenated phenols concentration, indicating decreasing relaxation time (figure 3).

### Table 3. Values of Valeramide + 4FP + 4CP + 4BP + 4IP in Benzene (J-band) at 303K [Static dielectric frequency ($\varepsilon_0$), Dielectric Constant ($\varepsilon’$), Dielectric Loss ($\varepsilon’’$), optical frequency ($\varepsilon’’$) and relaxation times ($\tau$)] for various weight fractions.

| Ratio | $w_2$ | $\varepsilon_0$ | $\varepsilon’$ | $\varepsilon’’$ | $\tau_1$ | $\tau_2$ | $\tau_3$ |
|-------|-------|-----------------|---------------|---------------|----------|----------|----------|
| Valeramide + 4FP + ben | | | | | | | |
| 1:3 | 0.03745 | 6.1157 | 2.9653 | 0.9625 | 2.6283 | 20.19 | 20.56 | 20.23 |
| 1:2 | 0.03714 | 6.1232 | 2.9623 | 0.9615 | 2.6247 | 19.52 | 20.25 | 19.88 |
| 1:1 | 0.03652 | 6.1467 | 3.0008 | 0.9560 | 2.6365 | 20.05 | 21.08 | 20.56 |
| 2:1 | 0.03589 | 6.1265 | 2.9642 | 0.9616 | 2.6276 | 19.56 | 19.35 | 19.45 |
| 3:1 | 0.03558 | 6.1167 | 2.9648 | 0.9654 | 2.6233 | 18.98 | 20.09 | 19.78 |
| Valeramide + 4CP + ben | | | | | | | |
| 1:3 | 0.04168 | 6.1382 | 2.9786 | 0.9527 | 2.6367 | 20.12 | 19.18 | 19.65 |
| 1:2 | 0.04091 | 6.1312 | 2.9734 | 0.9508 | 2.6287 | 19.44 | 19.43 | 19.43 |
| 1:1 | 0.03933 | 6.1555 | 3.0069 | 0.9560 | 2.6358 | 19.72 | 19.98 | 19.85 |
| 2:1 | 0.03777 | 6.1303 | 2.9775 | 0.9616 | 2.6282 | 19.17 | 19.56 | 19.37 |
| 3:1 | 0.03699 | 6.1305 | 2.9698 | 0.9764 | 2.6485 | 20.23 | 19.33 | 19.56 |
| Valeramide + 4BP + ben | | | | | | | |
| 1:3 | 0.05312 | 6.1399 | 3.0738 | 0.9458 | 2.6347 | 19.19 | 19.56 | 19.23 |
| 1:2 | 0.05105 | 6.1405 | 3.0476 | 0.9042 | 2.6412 | 19.52 | 19.25 | 19.13 |
| 1:1 | 0.04695 | 6.1630 | 3.0547 | 0.9250 | 2.6434 | 19.05 | 20.08 | 19.56 |
| 2:1 | 0.04284 | 6.1408 | 3.0612 | 0.9479 | 2.6476 | 19.56 | 19.35 | 19.15 |
| 3:1 | 0.04079 | 6.1345 | 3.0590 | 0.9647 | 2.6314 | 18.98 | 19.09 | 19.33 |
| Valeramide + 4IP + ben | | | | | | | |
| 1:3 | 0.06517 | 6.1409 | 3.1145 | 0.9556 | 2.6345 | 19.16 | 19.53 | 19.29 |
| 1:2 | 0.06178 | 6.1433 | 3.1075 | 0.9448 | 2.6304 | 19.08 | 19.21 | 19.04 |
| 1:1 | 0.05499 | 6.1785 | 3.1849 | 0.9344 | 2.6447 | 19.35 | 19.42 | 19.33 |
| 2:1 | 0.04821 | 6.1424 | 3.1012 | 0.9476 | 2.6330 | 18.27 | 19.93 | 19.11 |
| 3:1 | 0.04482 | 6.1361 | 3.0804 | 0.9642 | 2.6389 | 19.47 | 19.14 | 19.22 |
concentration increases at 1:1 complexes. As a result, connection between the phenol group frequency, dielectric constant, and dielectric loss at microwave frequency all the values increases as mixture of phenolic compounds, according to a table. The static dielectric constant, dielectric constant at optical τ, might lead to a greater relaxation time. As the 4- and the carbon molecule in Benzene is feasible. The possibility of hydrogen bonding in the benzene molecule dependent, as well as the chain length of the proton donor molecules.

The unoccupied turn of C=O and N—H in Formamide and acetamide should happen limited because of this. The unoccupied turn of C=O and N—H in Formamide and acetamide should happen limited because of this. The unoccupied turn of C=O and N—H in Formamide and acetamide should happen limited because of this. The unoccupied turn of C=O and N—H in Formamide and acetamide should happen limited because of this.

As the ratio of the electron - deficient amide was decreased gradually, the hydrogen bonded complexes stabilised by splitting in resonance form. This mechanism is aided by the solvent action of benzene, which has a higher Hydrogen bonding capacity with phenols than the amides’ own identity Hydrogen bonding capability. The amides carbonyl oxygen functions as a hydrogen bond acceptor, while the amides NH group acts as a hydrogen bond donor. The contact between the carbonyl oxygen and the OH group of phenols as well as the interaction between the NH group of amides and the oxygen of phenol is the main hydrogen bonding interaction. However, hydrogen bonding between the CH group and the carbonyl oxygen or phenols oxygen are also crucial for the complexes overall stability. Enanthamide is a more efficient proton donor than Valeramide, and it is more soluble in benzene because of resonance in benzene ring. This is why Enanthamide has a longer relaxation time in benzene than Valeramide at the same concentration. Amides basicity is determined by the substituent linked to the carbonyl group. When the benzene group bonds with the carbonyl group, the resonance is extended. As a result, the lone pairs of N are accessible for protonation. As a result, benzamide is more basic than acetamide, and likewise our results too same.

H-bonding in pyridine/phenol and quinoline/phenol structures now various conformations were investigated by Saxena et al. They found that tertiary mixtures have a significantly longer relaxation time.

| Ratio     | Weight fraction | ε₀   | ε'   | ε'' | ε∞   | τ₁   | τ₂   | τ₀   |
|-----------|----------------|------|------|-----|------|------|------|------|
| Enanthamide +4FP + ben 1:3 | 0.03985 | 6.2137 | 3.1918 | 1.0847 | 2.6735 | 22.56 | 22.48 | 22.52 |
| 1:2 | 0.04034 | 6.2318 | 3.1876 | 1.0738 | 2.6768 | 22.47 | 22.57 | 22.52 |
| 1:1 | 0.04132 | 6.2671 | 3.2035 | 1.1675 | 2.6758 | 22.96 | 23.36 | 23.16 |
| 2:1 | 0.04229 | 6.2342 | 3.1840 | 1.0724 | 2.6793 | 22.77 | 22.76 | 22.76 |
| 3:1 | 0.04278 | 6.2123 | 3.1974 | 1.0874 | 2.6748 | 22.58 | 22.85 | 22.71 |
| Enanthamide +4CP + ben 1:3 | 0.04048 | 6.2211 | 3.1952 | 1.0853 | 2.6897 | 22.43 | 21.05 | 21.75 |
| 1:2 | 0.04412 | 6.2436 | 3.1898 | 1.0616 | 2.6806 | 22.93 | 21.09 | 22.01 |
| 1:1 | 0.04414 | 6.2638 | 3.1712 | 1.0544 | 2.6988 | 22.21 | 22.39 | 22.86 |
| 2:1 | 0.04417 | 6.2432 | 3.1996 | 1.0902 | 2.6812 | 22.14 | 21.71 | 21.92 |
| 3:1 | 0.04419 | 6.2238 | 3.1839 | 1.1135 | 2.6787 | 22.76 | 21.86 | 22.31 |
| Enanthamide +4BP + ben 1:3 | 0.05551 | 6.2321 | 3.2088 | 1.0745 | 2.6886 | 21.02 | 21.24 | 21.13 |
| 1:2 | 0.05425 | 6.2475 | 3.2201 | 1.0539 | 2.6937 | 21.21 | 21.01 | 21.11 |
| 1:1 | 0.05175 | 6.2662 | 3.2365 | 1.0477 | 2.6958 | 22.53 | 22.26 | 22.14 |
| 2:1 | 0.04925 | 6.2489 | 3.2439 | 1.0598 | 2.6985 | 21.32 | 21.03 | 21.61 |
| 3:1 | 0.04872 | 6.2387 | 3.2314 | 1.0883 | 2.6794 | 21.70 | 21.14 | 21.91 |
| Enanthamide +4IP + ben 1:3 | 0.06757 | 6.2402 | 3.2004 | 1.0908 | 2.6812 | 20.59 | 20.32 | 20.45 |
| 1:2 | 0.06498 | 6.2498 | 3.1955 | 1.0947 | 2.6883 | 20.71 | 20.20 | 20.35 |
| 1:1 | 0.0598 | 6.2708 | 3.2109 | 1.1017 | 2.6967 | 21.04 | 22.21 | 21.78 |
| 2:1 | 0.05461 | 6.2491 | 3.2243 | 1.0937 | 2.6888 | 20.74 | 20.34 | 20.54 |
| 3:1 | 0.05202 | 6.2547 | 3.2355 | 1.1003 | 2.6976 | 20.32 | 21.24 | 20.26 |

Dielectric constants and optical frequency had uncertainties ε' = ±0.0005, ε∞ = ±0.0002

The relevance of relaxing period increases with increasing amides chain length of basicity and acidity nature of phenolic compounds, according to a table. The static dielectric constant, dielectric constant at optical frequency, dielectric constant, and dielectric loss at microwave frequency all the values increases as mixture concentration increases at 1:1 complexes. As a result, connection between the phenol group’s positive hydrogen and the carbon molecule in Benzene is feasible. The possibility of hydrogen bonding in the benzene molecule might lead to a greater relaxation time. As the 4-fluorophenol chain length increases, the number of additional τ0 values increases. It shows that τ0 is also affected by viscosity. As a result, it is τ0 frequency and viscosity dependent, as well as the chain length of the proton donor molecules (4-fluorophenol) and the same result will be found for hexanamide system[46] was seen in tables 3 and 4.

Our consequences of τ Higasi show that it reduces with increasing amide complex. This may be seen from the perspective of reverberation structures, which help to modify the stable base of electron-deficient amides. The unoccupied turn of C=O and N—H in Formamide and acetamide should happen limited because of this reverberation structure changes equally completed by means of Basha et al.[47]. As the ratio of the electron-deficient amide was decreased gradually, the hydrogen bonded complexes stabilised by splitting in resonance form. This mechanism is aided by the solvent action of benzene, which has a higher Hydrogen bonding capacity with phenols than the amides’ own identity Hydrogen bonding capability. The amides carbonyl oxygen functions as a hydrogen bond acceptor, while the amides NH group acts as a hydrogen bond donor. The contact between the carbonyl oxygen and the OH group of phenols as well as the interaction between the NH group of amides and the oxygen of phenol is the main hydrogen bonding interaction. However, hydrogen bonding between the CH group and the carbonyl oxygen or phenols oxygen are also crucial for the complexes overall stability. Enanthamide is a more efficient proton donor than Valeramide, and it is more soluble in benzene because of resonance in benzene ring. This is why Enanthamide has a longer relaxation time in benzene than Valeramide at the same concentration. Amides basicity is determined by the substituent linked to the carbonyl group. When the benzene group bonds with the carbonyl group, the resonance is extended. As a result, the lone pairs of N are accessible for protonation. As a result, benzamide is more basic than acetamide, and likewise our results too same.

H-bonding in pyridine/phenol and quinoline/phenol structures now various conformations were investigated by Saxena et al.[49]. They found that tertiary mixtures have a significantly longer relaxation time.
than all of the polarity substances throughout the neutral solution. Furthermore, if the complexes are tight, the distributed parameters are larger, and the two relaxation periods are well separated, one reflecting the complex’s overall rotation and another indicating the rotations of several of the connecting polarized intermolecular forces. In the current research, the relaxation period for concentrated samples of p-cresol, p-chlorophenol, 2, 4-dichlorophenol, and p-nitrophenol ranged from 4.5 to 34 ps. The relaxation times in amide/phenol systems are slightly longer because there are so many phenols present. This finding is consistent with Tucker et al [50] previous research. The findings also suggest that the structural interaction among amides and phenolic compounds peaks at 1:1 mol% and thereafter falls at other mol%. As a consequence, we may deduce that the 1:1 complex is prevalent in amide/phenol complexes. In complex structures, the relaxation time rises as the sharpness of the proton donor rises, but due to steric effects and the stabilization of complex compounds, the $\tau_0$ values of amides of 4-fluorophenol systems are greater than the other phenols complexes, as shown in figure 4.

Experimental acidic strength order: 4-bromophenol > 4-iodophenol > 4-chlorophenol > 4-fluorophenol. The $+R$ effect of FF on 4-fluorophenol is considerable but weaker than the $-I$ effect. Because of the stronger, the electron pair on the 2p2p orbitals of FF may rapidly delocalize with the benzene ring, making the $+R +R$ effect strong. As a result, it improves the electron density on the carbon near the $\text{–OH} \text{–OH}$ group to such an extent that it reduces its capacity to transfer protons, resulting in a significant drop in acidity. The $+R$ effect is reduced for 4-chlorophenol because it is considerably weaker, and so the $-I$ $-I$ effect becomes more significant. As a result, it becomes more difficult to remove hydrogen atoms from the $\text{–OH} \text{–OH}$ group, lowering its acidity. Because 4-bromophenol and 4-iodophenol are substantially less electronegative, there is no strong hydrogen bonding, and the $+R$ effect is ineffective due to its weakness. Only the $-I$ effect fails in favour of acidity for these two compounds. As a result, 4-bromophenol has a higher acidity than 4-iodophenol. The transfer of an electron.
concentrations. The positive result indicates endothermic interaction between the system mixtures. The negative values of become positive. This might imply that the molecules have cooperative orientations as a result of steric forces. The activated system tends to restore the activated system back to the normal state. In this case the changes in entropy for the process, the activated system becomes more unstable than the regular system, and the system translates motion of molecules. The system environment is more cooperative for the molecular reorientation process, the activated system environment is less ordered than for a normal system and the entropy change is negative. In the same way, if the system environment is cooperative for a certain process, the activated system becomes more stable than the typical system, and the environment tends to restore the activated system back to the normal state. In this case the changes in entropy for the process become positive. This might imply that the molecules have cooperative orientations as a result of steric forces.

For all the studied systems, the molar enthalpy, free energy of activation (ΔH and ΔF) values is positive at all concentrations. The positive result indicates endothermic interaction between the system’s amides-phenols mixtures. The negative values of ΔS indicate a decrease in entropy-the system becomes less random (The system environment is more cooperative for the molecular reorientation process) and A positive value of ΔS indicates an increase in entropy-the system becomes more random (The activated system environment is less ordered than for a normal system) [54, 55]. The similar result was found in the dielectric study of nitrobenzene and 2-butanol mixtures [56]. It is also evident that ΔHfl > ΔHvec for all the systems under investigation. This may be explained by the fact that the dielectric relaxation process includes the rotation of the molecules involved, whereas viscous flow involves both rotation and translational motion of the molecules [57].

According to Smyth [58], the relaxation period of a proton donor rises as the acceptor capacity of the solute system increases. The relaxation period of a proton acceptor must equally increase in amount of the donor solute proton donor potential. Our findings contributed to the idea for this investigation.

5. Conclusion

The complex permittivity of amides with halogenated phenols binary mixtures was investigated at microwave frequency in the temperature range of 298K to 323K. Enanthamide and Valeramide hydrogen bonded

| ΔF | ΔH | ΔS | ΔF | ΔH | ΔS |
|----|----|----|----|----|----|
| 33.93 | 34.69 | 29.97 | 30.47 | 1.094 | 0.818 |
| 32.67 | 34.52 | 30.09 | 30.59 | −0.813 | −0.765 |
| 31.81 | 34.32 | 30.21 | 30.71 | −0.678 | −0.513 |
| 31.12 | 34.11 | 30.39 | 30.88 | −0.561 | −0.499 |
complexes with halogenated phenols (4-bromophenol, 4-chlorophenol, 4-iodophenol, and 4-fluorophenol) were found in benzene. At 1:1 molar ratios of amides to halogenated phenols, the values of average relaxation time $\tau(1)$ total dielectric relaxation $\tau(2)$ and mean relaxation time $\tau(0)$ were found to be maxima. According to the findings of this study, the proton donating capacity of phenols and the proton accepting ability of amides vary linearly with the alkyl chain length of both phenols and amides and have a significant impact on the dielectric properties of the above-mentioned systems studied. As the donating ability of the solute environment improves, so does the relaxation time of the proton acceptor. The increasing relaxation time reveals information about the dipole orientation between the interacting molecules. From the above outcome it may be understood that, the ability of amides to accept proton is decreasing in order: Enanthamide $<$ Valeramide. Thermodynamic properties like molar enthalpy of activation ($\Delta H^\circ$), free energy of activation ($\Delta F^\circ$) and entropy of activation ($\Delta S^\circ$) for our system are discussed.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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