

DIELECTRIC SPECTRAL STUDY IN LOW FREQUENCY OF I_E WATER AND SOME OTHER SOLVENTS

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Spectra of dielectric constant ϵ and dissipation factor D of I_E water, distilled water; acid and base solutions; polar solvents: (methyl alcohol, methyl formate); non-polar solvents (CCl_4 and dimethyl benzene) were studied.

1. Introduction

As stated in our previous papers^{1,2}, I_E water contains stable water cluster. These clusters consist of highly ordered water molecules with their electric dipole lining up. It is well known that, dielectric constant ϵ is an important parameter reflecting the dipole property of materials. In the recent years, dielectric spectral methods are used in colloidal and aqueous solutions chiefly to gain information about chemical and physical properties of solutes and its interaction between the solute and solvent (3-6). I_E water is created by very low concentration of initiator, but contains many stable water clusters with a strong electric dipole moments. These stable water clusters are called I_E clusters. Dielectric spectroscopy studies may help us to understand the structural characteristics of I_E clusters. An experimental device was used to measure the complex dielectric constant. Some interesting results have been obtained.

2. Principle and Experimental Set-up

In principle, dielectric constant measurement of a medium is obtained by comparing the capacitance C_0 in air and capacitance C_i , with the medium of a condenser. The ratio $\varepsilon = C_i / C_0$ is the dielectric constant. If the medium inside the gap of condenser is acted upon by an alternating voltage $V = V_0 e^{j\omega t}$ with angular frequency $\omega = 2\pi f$, the charge of the condenser is equal to $Q = C_i V$ and the charging current is:

$$I_c = \frac{dQ}{dt} = I_0 \exp[j(\omega t - \pi/2)] \quad (1)$$

which leads the voltage in phase by 90° . The material, which fills in the condenser, normally possesses conductivity, and the stray current component $I_1 = V / R_i$, I_1 is in phase with the applied voltage V . Thus, the full current passing through the condenser is equal to:

$$I = I_1 + I_c = \frac{V}{R_i} + C_i \frac{dV}{dt} \quad (2)$$

where V and I are voltage and current of the condenser with the medium. They have a phase difference with each other and could be expressed as a complex variable. The dielectric constant, which is determined by I and V , is also complex:

$$\text{Re } \varepsilon - j \text{Im } \varepsilon \quad (3)$$

$$\varepsilon = |\varepsilon| = (\text{Re } \varepsilon^2 - \text{Im } \varepsilon^2)^{1/2}; D = \tan \Delta = \text{Im } \varepsilon / \text{Re } \varepsilon \quad (4)$$

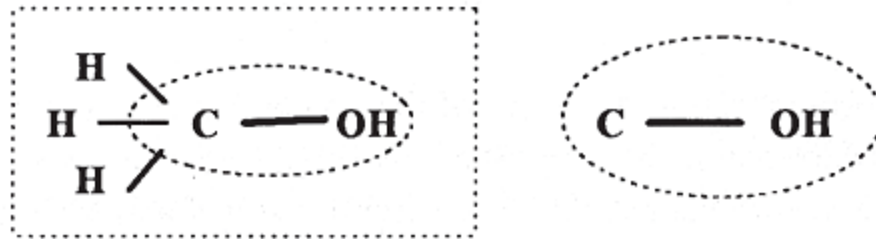
where ε is dielectric constant. The ratio $\text{Im } \varepsilon / \text{Re } \varepsilon$ is equal to the ratio of stray current to charging current. It is called the dissipation factor D of medium. Its value is equal to the tangent of loss angle Δ . The angle in question is that on the complex plane between the vectors of full and the charging currents.

In dielectric spectroscopy, ε_i and D are measured as a function of scanning frequency. Therefore, we have:

$$\varepsilon_i(\omega) = \frac{C_i(\omega)}{C_0(\omega)}; \frac{(in\ medium)}{(in\ air)}, \quad D_i(\omega) = \frac{R_i}{1/\omega C_i} = \omega C_i R_i \quad (5)$$

Generally, ϵ reflects the capacitance variation of a liquid medium compared with a dry air medium. This variation is created by permanent and induced dipole moments of liquids inside the condenser. Stray current, which is measured by is due to either the line up, or migration of dipole clusters in testing liquid between the gap of condenser. In the case of very thin solution, a variation in R_i , causes a variation in D_i . However, $\epsilon_i(\omega)$ mainly relates to the dielectric property of medium molecules, and $D_i(\omega)$ relates to the movement of dipole cluster in testing liquid. Obviously, these are related to the mechanical characteristics of clusters and the viscosity of solvent. A peak of $\epsilon_i(\omega)$ in a certain frequency means a resonance in the creation of the induced dipole moment. The peak of $D_i(\omega)$ gives significant information on the mass, the size of clusters and rheological properties of testing liquid.

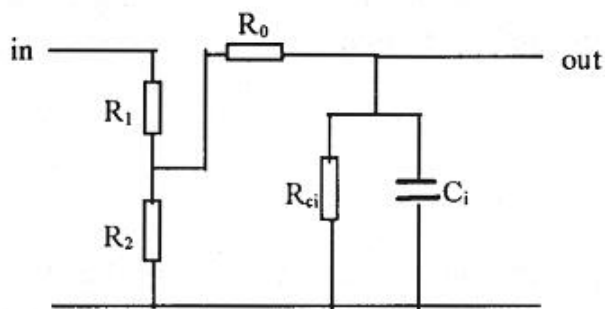
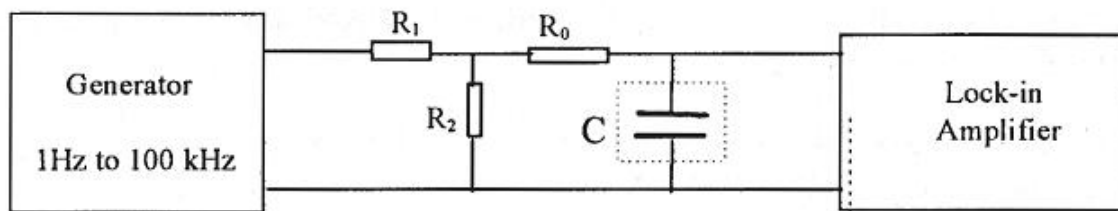
For example, a methanol molecule CH_3OH can be separated into two groups: OH, a polar group and CH_3 , a non-polar group. Under the action of an applied alternative electric field, the OH group will have induced dipole moment resonance. Certainly, in this condition, the whole methanol molecule is in motion. This motion will consume energy, the reading is dissipation (Figure 1).



$D \propto$ whole molecular movement $\epsilon \propto$ induced dipole moment resonance

Figure 1: Dielectric constant and Dissipation

So far many authors have indicated that ϵ which measured at low frequency and high frequency are different. Frequency spectral methods have been extensively used in dielectric materials research in the last ten years. A commercial frequency scanning instrument, an Impedance Analyzer, is widely used for this purpose. Usually, this instrument is suitable for low dissipation medium studies. In the case of a high dissipation medium, it is difficult, to match the impedance with the built-in circuit. Figure 2 shows the set up of the equipment.



Equivalent circuit

Figure 2 Experimental set-up and equivalent circuit

Condenser C is a pair of aluminum planes with diameter of 60 mm. It is put into a plastic chamber where the testing liquid fills the whole chamber. The condenser in the measuring circuit is equivalent to C_i in parallel with R_{ci} . To match the impedance of various kind of samples, a variable resistance R_0 and voltage divider is put inside the circuit. A sinusoidal current from divider through R_0 , feeds to the testing condenser. V_{ci} , and ϕ_{ci} are read by a lock-in amplifier. The V_0 and ϕ_0 of input signals are measured by the lock-in amplifier as well. According to the alternating circuit analysis, we can easily calculate the R_{ci} , and C_i , and then calculate ϵ , and D , for each medium by using special software. The scanning sinusoidal current is provided by a numerically synthetic oscillator from 1 Hz to 100 kHz.

3. Experimental Results and Discussion

Several classes of solutions are studied. They are:

- (1) Water: Ordinary water and I_E water.
- (2) Polar organic solvent: Methanol CH_3OH , and CH_3OH are dissolved in water at ratios of 5:1 and 1:50.
- (3) Non-polar organic solvent: CCl_4 , an entirely non-polar solvent. Dimethyl benzene $[C_6H_4(CH_3)_2]$, which has an induced dipole moment.
- (4) Strong polar organic solvent: Methyl formate $[HCOOCH_3]$ has high solubility. We prepared the solutions at the ratios of 1:50, 1:200 and 1:2500 with water and measurements are then taken.
- (5) Ionic solution: Similarly, a suitable amount of NaOH is added into water until a pH=12 is

achieved. They are acidic solutions and alkaline solutions respectively. These are real ionic solutions.

In Figure 3a, variation of dissipation D vs. frequency of the applied AC field is shown for both ordinary water and I_E water. There is a gradual increase in D that begins from 100 Hz and has a peak at 3 kHz in water sample. In the D spectrum of I_E water, there is the same gradual increase in values from 100 Hz onward. At the peak position of 3 kHz, the reading is 2.5 times higher than that of ordinary water. In addition, at the lower and higher frequency side of the 3 kHz peak, in this' spectrum, there are two additional shoulders, respectively. We plot the difference of dissipation between I_E and H_2O ($\Delta D = D_{I_E} - D_w$) vs. frequency (Figure 3b) and we processed this difference of spectrum with a spectral analysis software. Three individual bands at 800 Hz, 3.6 kHz and 11 kHz are found. The peak at 3.6 kHz can be considered as a small frequency shift of the peak at 3 kHz, in water spectrum. Peaks at 800 Hz and 11 kHz can be attributed to I_E water alone. The spectra of the dielectric constant ϵ for distilled water and I_E water are shown in Figure 3c. In the frequency range of less than 150 Hz, the dielectric constants of I_E water is higher than that of DI water, however the dielectric constant ϵ of I_E is lower than that of DI water when the range is greater than 150 Hz. We plot the difference of dielectric constant between I_E and DI water ($\Delta\epsilon = \epsilon_{I_E} - \epsilon_w$) as a function of frequency (Figure 3d). Four peaks at 10 Hz, 70 Hz, -300 Hz and 1 kHz appear in plus or minus direction. Comparing these with Figure 3c, we observe two peaks (70 Hz and 300 Hz) appearing simultaneously in both samples. The I_E water peak height at 70 Hz is higher than that of H_2O , while at 300 Hz, the reverse happens. It seems that structures reflected by these two peaks exist in both samples in varying amounts. Peaks of 10 Hz and 1 kHz are characteristic of additional structures that exist in I_E water only.

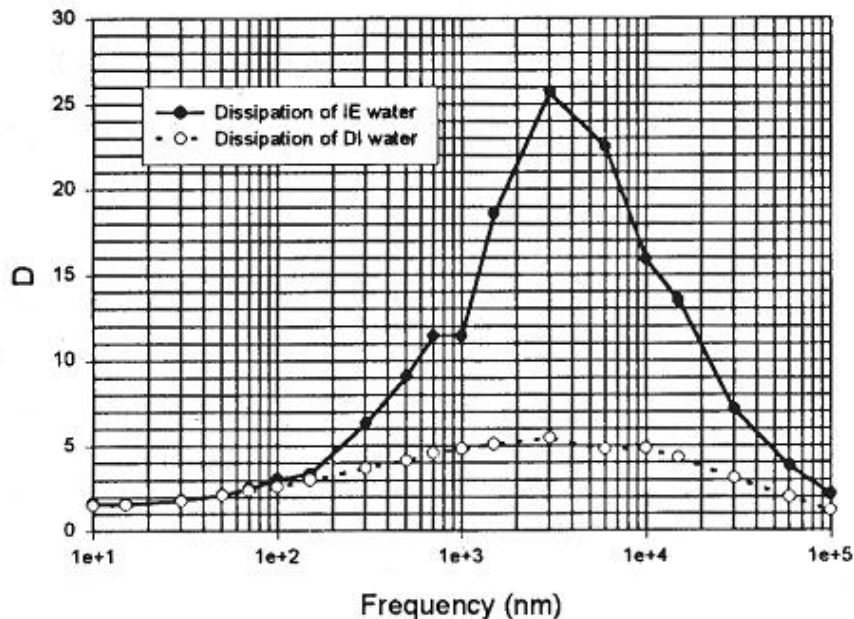


Figure 3a. Dissipated D spectra of I_E and distilled water

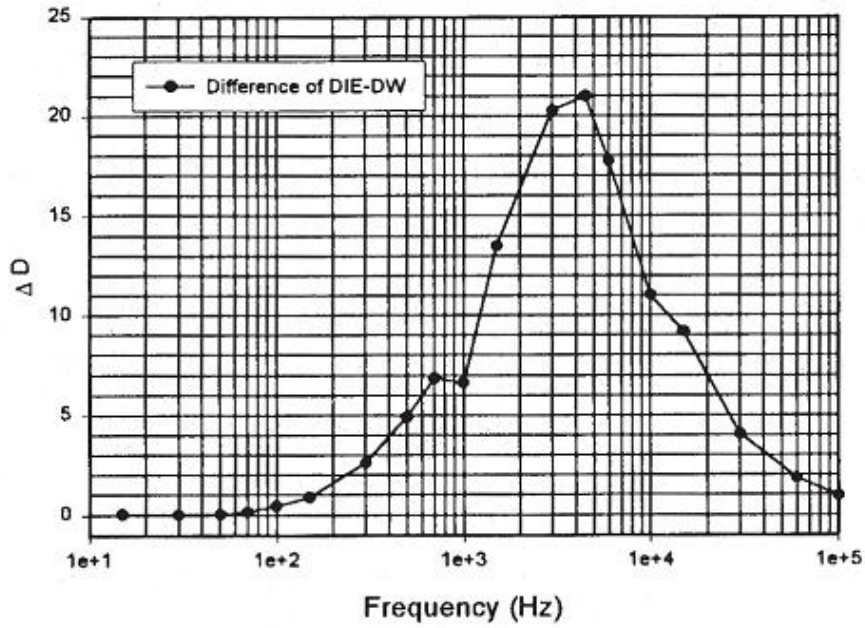


Figure 3b. Difference of dissipation ΔD spectra between I_E and distilled water

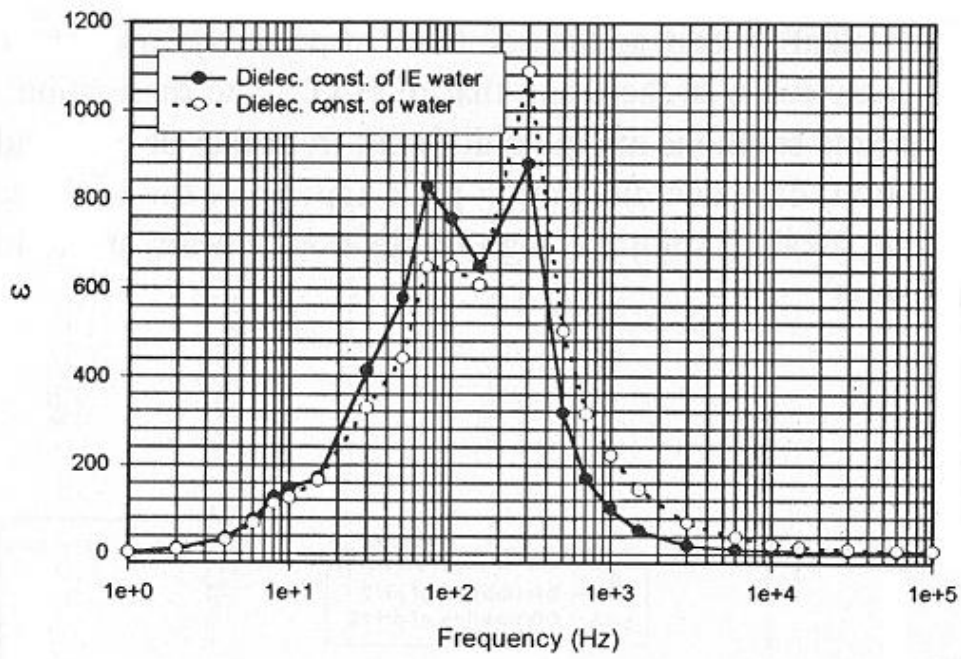


Figure 3c Dielectric constant spectra of I_E and DI water

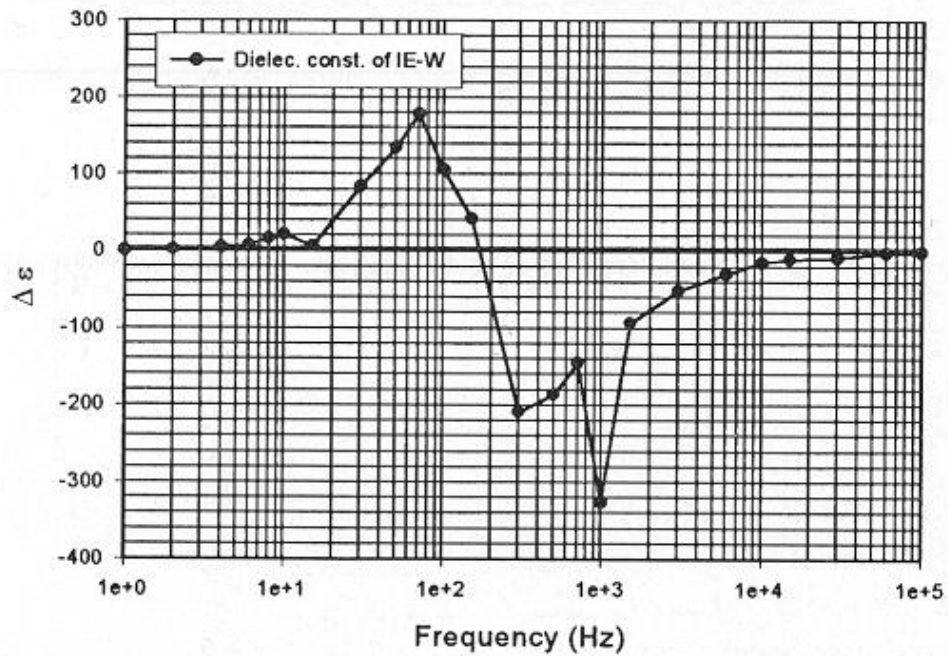


Figure 3d Difference of dielectric constant $\Delta\epsilon$ spectra between I_E and DI water

The dissipation D and dielectric constant ϵ spectra of acidic and alkaline solutions are shown in Figures 4a and 4b. The peak values at 300 Hz are 3×10^5 and 7×10^4 for alkaline and acidic solution, respectively, and are three hundred times and seventy times higher than that of H_2O . The dissipation D spectra for alkaline and acidic solutions are quite different from that of H_2O and I_E water. In an acidic solution, only one dissipation peak appears at the low frequency region (≤ 2 Hz). In an alkaline solution, high dissipation appears at the high frequency region (≥ 60 kHz).

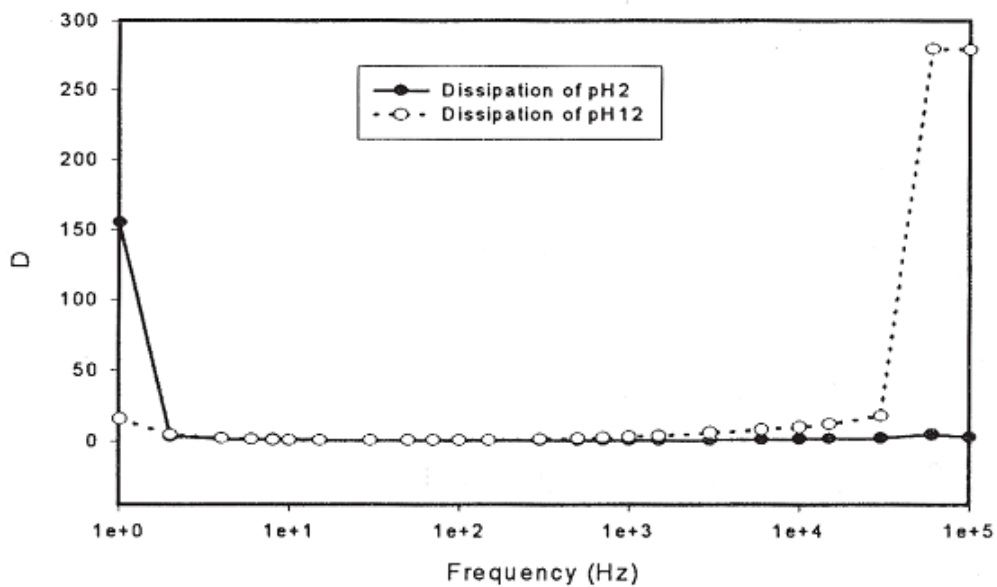


Figure 4a. Dissipation spectra of acidic (HC) and alkaline (NaOH) solutions

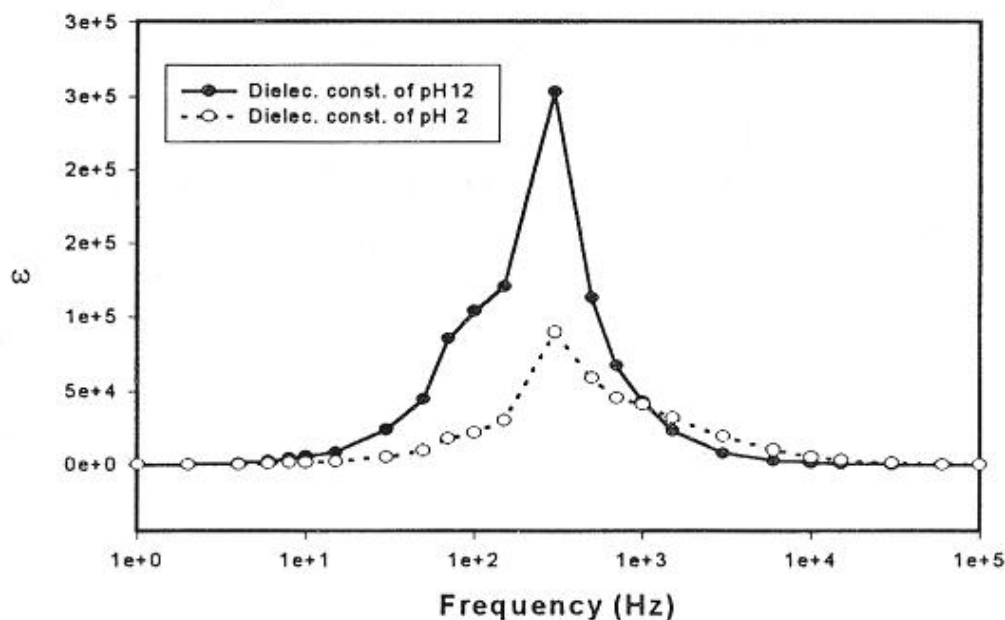


Figure 4b. Dielectric constant spectra of acidic (HCl) alkaline (NaOH) solution

For further understanding of the characteristics of the peaks, in Figure 4b several kinds of polar and non-polar organic solvents and ionic solutions are studied. The position and values of different peaks for different solutions are tabulated in Table 1 and 2.

The peak at 300 Hz appears in all kinds of aqueous solutions (Table 1). ϵ values of acidic or alkaline solutions are in the order of 10^5 , and are about 10^3 for H_2O or I_E water. Polar solvents such as CH_3OH , $HCOOCH_3$ are about tens in value, but once those molecules bond with water, their ϵ immediately rise to 10^3 . The rise in value indicates the increase of dipole strength due to the ordering of H_2O molecules, which are attracted and aligned around a polar site of the original molecule. Non-polar organic solvents such as CCl_4 and dimethyl benzene $C_6H_4(CH_3)_2$ have ϵ values are less than ten.

The dielectric constants ϵ of various solutions are plotted in Figure 5a. The curves could be classified into three groups: non-polar solutions (lower part), polar solutions, where molecules have permanent electric dipole polar (middle) and ionic solutions (upper). The dielectric constant ϵ of ionic solutions are ten to hundreds of times larger than those of polar solutions. The situation is quite similar to results by J.P. Hansen *et al*, 1998, where the pH measurements reflect ions in solution created hundreds mV between two testing electrodes. The corresponding measurements in dipole solutions have tens mV dipole potential between electrodes. These phenomena are consistent with the universal knowledge of physicists and chemists that dipole effects are always 2 to 3 orders lower than that of monopole (ionic) effects.

The dissipation D values of various peaks of solutions are found in Table 2. The peak at 3 kHz appears in following solutions: H_2O and I_E water, CH_3OH with or without water and $HCOOCH_3$ with or without water. The peak at 3 kHz does not appear in non-aqueous methyl alcohol or methyl formate solutions. As the concentration of methyl formate in water goes down the dissipation value goes up and approaches that of I_E water. This peak also does not appear in acidic, alkaline solution and non-polar solvent, such as CCl_4 and dimethyl benzene. Summing up

above evidence, we suggest that this peak belongs to water cluster. Another peak of I_E water at 700 to 800 Hz also appears in CH_3OH , which are greatly enhanced in an aqueous solution.

Dissipation factors of various solutions are plotted together in Figure 5b. In the range of 10 Hz to 10 kHz, acidic and alkaline solutions have very low dissipation, and a very high ϵ (Figures 4 and 5). It is well known, that electrolytes have high dielectric constants and low dissipation. Accordingly, high capacitance (electrolytic) condensers, are widely used in low frequency electronic devices. Conversely, CCl_4 and dimethyl benzene have extremely high dissipation, but very low ϵ at the range of 30 Hz to 500 Hz. Perhaps in these solutions, molecules are grouped together and have a resonance absorption at above the frequency range.

Table 1. Peak values of ϵ in I_E water and other solvents

Frequency	8 Hz	10 Hz	70 Hz	100 Hz	300 Hz	500 Hz	1 kHz	3 kHz	10 kHz	60 kHz
H ₂ O			648		1089					
I_E water		148	828		880					
HCl in water pH = 2					8.9×10^4					
NaOH in water pH = 12				1.1×10^5	2.5×10^5					
CH ₃ OH	2.80		472.5		489.7	404.6	219.3			
H ₂ O + CH ₃ OH 1:5	79.7		70.8		55.4	24.37	14.2			
CH ₃ OH + H ₂ O 1:50	315		878		1294	607	280			
HCOOCH ₃		2.0	2.54		5.67				1.77	
HCOOCH ₃ in water 1:50		1456	1.7×10^4	1.8×10^4	3.8×10^4				692.4	
HCOOCH ₃ in water 1:2500		785	2323	2020	2647		457.7	135.9	41.1	32.0
HCOOCH ₃ in water 1:25000		320	614	525	619		115.5	36.9	16.9	11.5
C ₆ H ₄ (CH ₃) ₂					2.01					
CCl ₄					2.98					

Table 2. Peak values of D in I_E water and other solvents

Frequency	1 Hz	8 Hz	70 Hz	150 Hz	300 Hz	700 Hz	1 kHz	3 kHz	10 kHz	60 kHz
H ₂ O								5.49		
I _E water						11.46		25.74	15.9	
HCl in water pH = 2	155.2									
NaOH in water pH = 12										279.7
CH ₃ OH						5.29		5.85		
H ₂ O + CH ₃ OH 1:5						4.12		5.07		
CH ₃ OH + H ₂ O 1:50						86.82		47.42		
HCOOCH ₃		40.4	130.7		131.3					
HCOOCH ₃ in water 1:50								2.48		
HCOOCH ₃ in water 1:2500								10.76		
HCOOCH ₃ in water 1:25000								19.62		
C ₆ H ₄ (CH ₃) ₂			50 Hz 512.8	513	256					
CCl ₄		42.7	50 Hz 170.8		170.7					

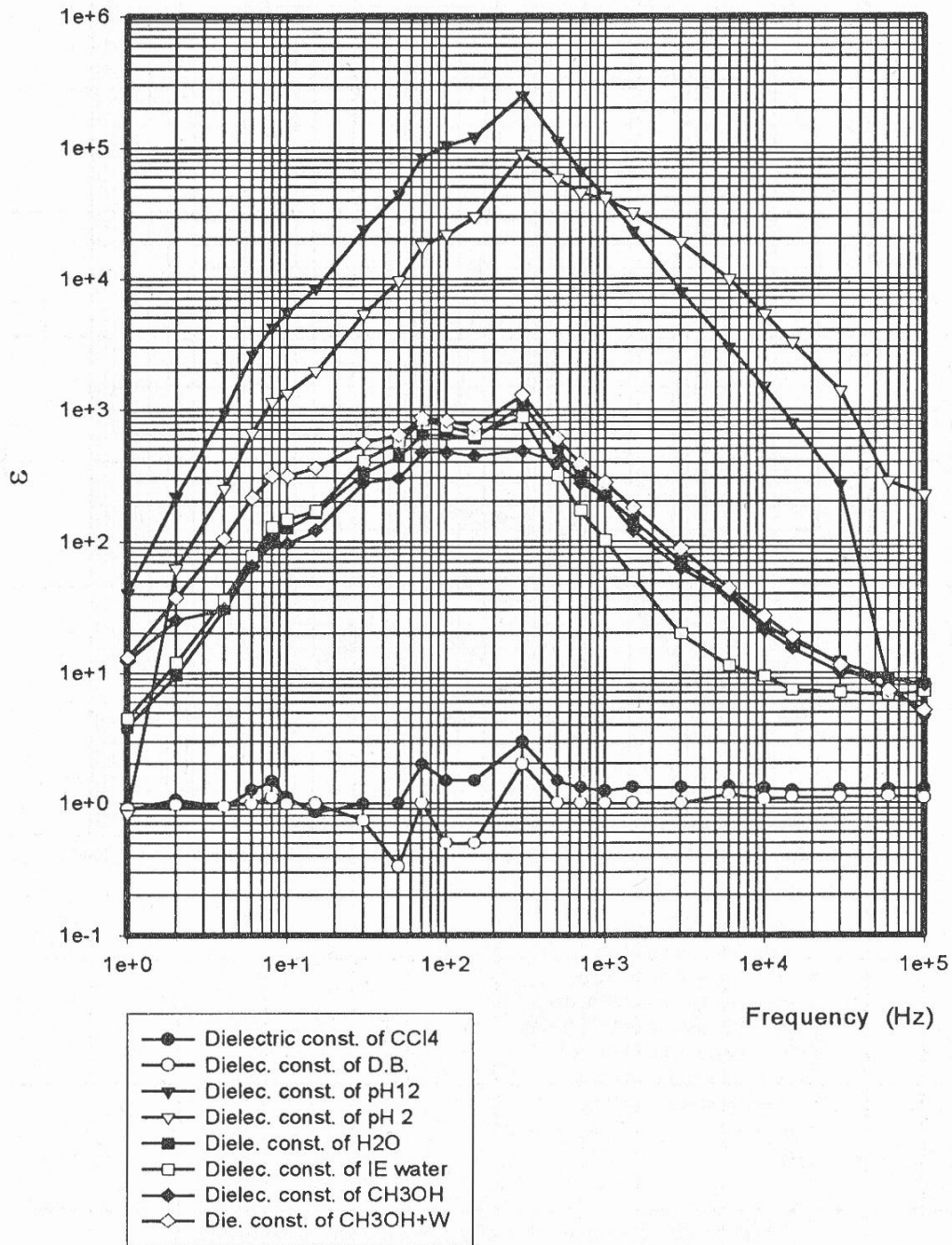


Figure 5a. ϵ spectra of I_E water and some other solutions

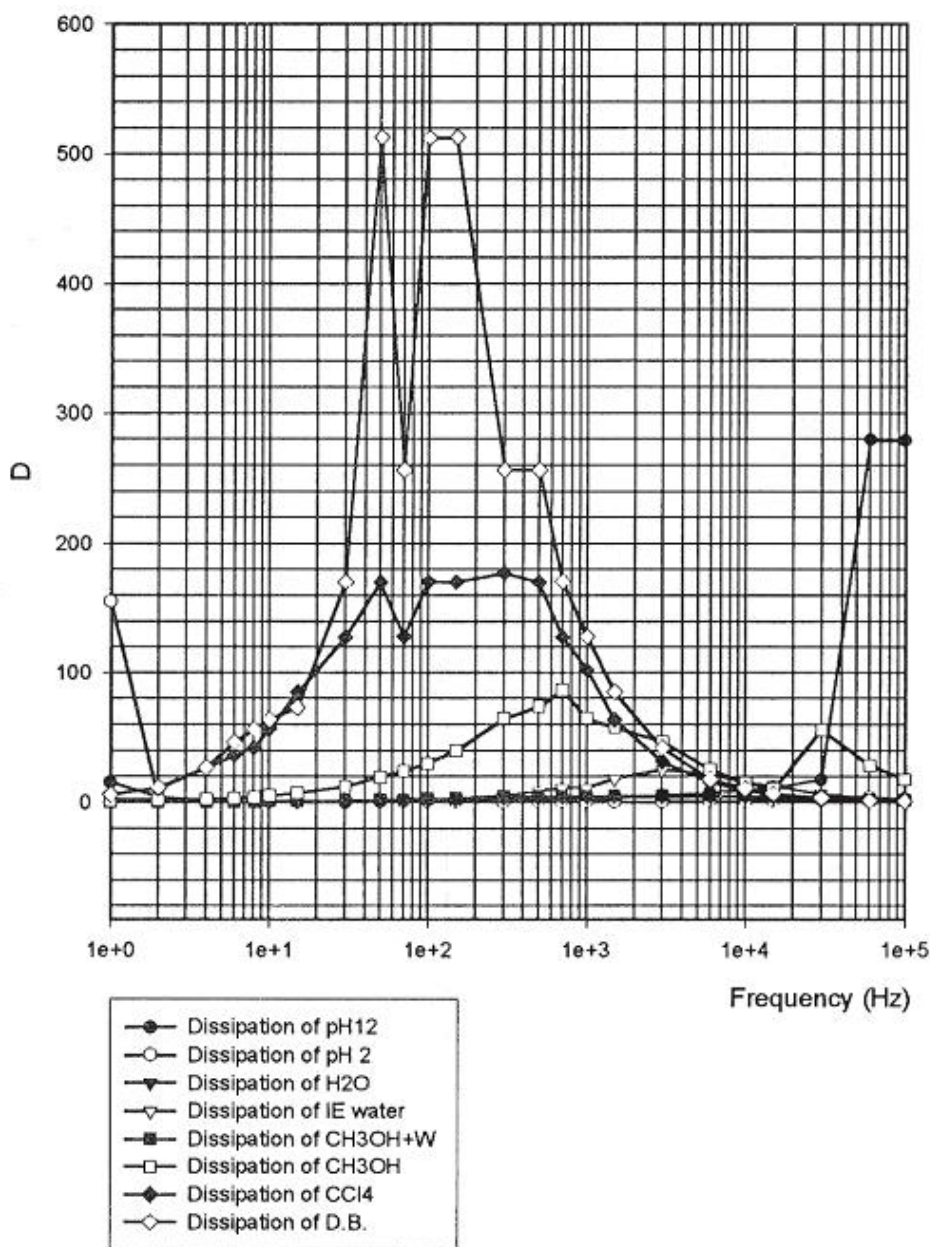


Figure 5b. Dissipation spectra of all kind of solutions

Electric dipole moment of CH_3OH in gas phase is 1.77 debyes, which is slightly lower than that of H_2O (1.85 debyes), however, they would have similar dielectric constant ϵ values. In general, small amounts of CH_3OH added into H_2O have the effect of increasing the ϵ value; whereas addition of a small amount of H_2O in CH_3OH decreases the ϵ value. The ϵ at 300 Hz of CH_3OH is 489.7 (Table 1). When it is diluted with water at the ratio of 1:50, ϵ increases to 1294 by a factor of 2.6. The value is nearly that of H_2O ($\epsilon_{300} = 1089$). However, if one fifth of H_2O is put into CH_3OH , the ϵ value decreases to 55.4. For methyl formate (HCOOCH_3), the ϵ is 5.67, and when diluted with water at a ratio of 1:50, the ϵ increases to 3.8×10^4 by a factor of 6.7×10^3 .

These results indicate the bonding ability of water with methyl formate (COO= group), which is much higher than that of methyl alcohol (OH group).

4. Summary

- (1) Dielectric spectra provide a reasonable picture to classify the ionic, polar and non-polar solution. ϵ_E water belongs to polar solutions where molecules have permanent electric dipole moments.
- (2) Variation of a value of some organic solvents between itself and its aqueous solution provide valuable information on aqueous affinity.

Under the action of low frequency electro-magnetic fields, each solution has some resonant dissipation peaks. These peaks probably reflect characteristic structures of the molecular cluster in the solution.

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