

Dielectric properties of electrolytic solutions

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MS received 4 June 1998; revised 21 August 1998

Abstract. The variation in dielectric properties of water with the addition of ionic salts have been measured using automated frequency domain experimental microwave *C*-band. The dielectric properties, that is dielectric constant (ϵ') and dielectric loss (ϵ'') of two electrolyte solutions for various concentrations have been measured at 5-GHz frequency at room temperature. It has been observed that for concentration between 0.2 to 1.0 mole the dielectric constant of water is smaller and some larger than that of pure water and dielectric loss increases with increasing concentration of these salts. It has been also observed that the variation in dielectric loss is different, though the ionic concentration of the two salts are equal.

Keywords. Dielectric properties; electrolyte solutions; frequency domain microwave *C*-band set-up.

PACS Nos 77.22; 77.80

1. Introduction

The authors have investigated the dielectric properties of pure water with the addition of ionic salts at 5-GHz frequency at room temperature. The ionic salts are calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and calcium chloride (CaCl_2) having an equal ionic concentration. Investigation of dielectric properties serve important properties of the solution such as activity and conductivity. It is also a very useful parameter in ascertaining the shape and size of the molecule. The basic problem of the electrolyte solution concerns interaction between ions as well as ions and solvent molecules [1].

The static dielectric constant of electrolytes originally proved difficult to measure. The Debye–Hückel theory of electrolytes [2] had some fifty years ago predicted a rise in static dielectric constant above that of pure water, proportional to the square root of the concentration or molarity. Debye and Falkenhagen [3, 4] showed that the relaxation of the ionic atmosphere would give rise to both an elevation of the conductivity and a relaxation of the dielectric constant. But whereas the enhancement of the conductivity was verified experimentally by Sack [5] and others, the ionic atmosphere dielectric relaxation has not been substantiated in experiment, since the loss angles of the electrolytes are so great and the electrode effects so marked that the required accuracy is not available. The early literature of electrolytes of Sack [5] is studied with widely divergent reported results;

some dilute solution measurements showed that the permittivity to be smaller than that of pure water and some larger. The reason is the conductivity σ ($\text{ohms}^{-1} \text{cm}^{-1}$) may be regarded as contributing to the dielectric loss, the contribution being inversely proportional to the frequency [6].

2. Theory

An alternating electric field of appropriate frequency gives rise to dielectric dispersion; the characteristic orientation motion of the dipoles results in the frequency variation of the dielectric constant and the appearance of the 'dielectric loss' over a broad band of frequencies. When the direction of the field changes sufficiently fast, the molecular force impeding the dipole orientation dominates, and the dipoles become unable to flow the charges; at these frequencies the orientation of the permanent dipoles no longer contributes to the dielectric constant. Moreover, in a certain frequency band a phase lag between the field and the dipole orientation develops, and energy is drawn from the electric source by the material, and is dissipated as heat. This phenomenon is described by a complex representation of dielectric constant, ϵ^* given as

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

The imaginary part ϵ'' , is known as dielectric loss and the real part ϵ' is constant of the medium that measures the efficiency of transfer of electric charge and it is called as dielectric constant of the medium [6, 9].

The dielectric loss is a parameter which describes the motion of the electric charge i.e. a conduction phenomena. Certain dielectrics are found to display conduction which arise not only from the effect of polarization on the displacement current, but actual charge transport, i.e. ionic conduction in electrolytes. Such conduction would normally be described by a volume conductivity and the effect of it would be to add an additional term to the dielectric loss [6]. The expressions used for evaluating ϵ' and ϵ'' are;

$$\epsilon' = \lambda_0^2 \left[\frac{1}{\lambda_c^2} + \frac{\beta_1^2 - \alpha_1^2}{4\pi^2} \right] \quad (2)$$

and

$$\epsilon'' = \frac{\lambda_0^2 \alpha_1 \beta_1}{2\pi^2} \quad (3)$$

where λ_c is the cutoff wavelength given by $\lambda_c = 2 \times a$, a is the border side of the rectangular waveguide [10].

3. Experimental

The experimental procedure adopted for the determination of dielectric constant and loss of electrolyte solutions is that of Roberts and Von Hippel [7] and fixed frequency method of Gopal Krishana [8]. However the dielectric constant and dielectric loss and errors in ϵ' and ϵ'' are computed by using least square fitting technique of Sobhanadri [11] and later suitably modified by the authors.

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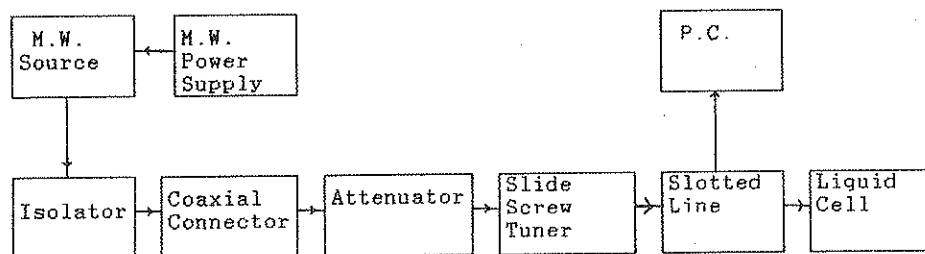


Figure 1. Block diagram of experimental set-up of microwave C-band.

The C-band microwave bench set-up consists of a low power microwave source varactor tuned oscillator (VTO), isolator, tuner, attenuator, slotted line, and liquid dielectric cell. The measurements of microwave power in the slot line is done by using a detector fixed into a tunable probe mounted on the slot line. This detecting device is quite useful and reliable. Its performance is quite limited and time consumable due to manually operated mechanical system for moving the tunable probe along the slotted line. Reading and writing data for more than 200 plunger positions and corresponding micrometer reading from one set of observation, makes the experimental observation more tedious.

These shortcomings in the present system are overcome by modifying the existing C-band microwave bench set-up. The block diagram of modified experimental set-up is shown in figure 1. The system modification mainly incorporates addition of the modified mechanical assembly and the PC add-on card. This modification leads to the automation of the bench. The automated microwave bench has been used for measurement of dielectric properties in liquids.

3.1 Mechanical modification

The mechanical modifications consist of modification in slot line and modification in liquid dielectric cell.

3.1.1 *Modification in slot line:* In the existing slot line of the microwave bench set-up the detector produces DC current output in the waveguide generated by the microwave source. The detector fixed into the probe is sitting onto a mount attached to a 'rack and pinion' arrangement so that the probe can be moved on the slot line in forward and reverse directions by rotating the knob in clockwise/anticlockwise directions correspondingly. Its displacement can be measured on a scale fixed the slot line having vernier arrangement.

The mechanical modification is made by using box nut and lead screw instead of the rack and pinion system. The lead screw passes through the box nut coupled to the probe mount, is fixed between the two supports holding the slot line piece of waveguide. A 1 : 1 set of gears is fitted on the lead screw near its FAR end and shaft of the stepper motor, so that the stepper motor can control position of the probe on the slot line.

Two electrical limit switches are fixed at the two ends of the slot line. On operating limit switch at HOME position, the motor takes detector to 'start position' after removing backlash in the box nut. By operating the motor through the PC interfacing in 'auto

mode' the detector starts moving from HOME to FAR position and reads the current at every 1 mm position along its traverse. Its position and current at that instant are displayed on the monitor. On traversing more than 100 steps of 1 mm the probe reaches to FAR position where it stops automatically by operating the limit switch at that end.

3.1.2 *Modification in liquid dielectric cell:* A suitable mechanical coupling for moving the plunger in the liquid column in liquid dielectric cell, with the help of stepper motor was developed and used for the automated operation of the liquid cell used for measurement of dielectric properties of liquids.

The coupling assembly consists of a circular disc A of 6 cm diameter in which four polished spokes are fixed symmetrically. The disc A is fixed on the shaft of stepper motor mount at the top of the fabricated stand. Another similar disc B, of the same diameter (6 cm) is fixed on the head of the micrometer screw to which the plunger of the liquid dielectric cell is connected. The four spokes fixed on disc A pass through the corresponding slightly oversized holes on disc B. Thus when the stepper motor rotates, the disc A, fixed on its shaft also rotates, and this rotational motion is transferred to disc B through the spokes. The holes on disc B being slightly oversized than the diameter of the spokes and the surface of the spokes being polished, the advancement of disc B fixed on the micrometer head, along the axis, takes place with minimum loss of mechanical energy.

In the experiment, the liquid dielectric cell is connected to the other end of the microwave bench set-up with zero position of the plunger. The microwave source used in this experimental frequency domain technique is Avantek varactor tuned oscillator (VTO 8490). Firstly, energizing the microwave source the probe on the slotted line was moved along the slot line for perfect standing wave pattern, figure 2, then the probe was fixed at the first minima nearest to the liquid dielectric cell. The liquid under test was filled into the liquid dielectric cell and the plunger of the liquid cell was moved by a fixed amount of 0.25 mm automatically with the help of stepper motor with suitable software. The

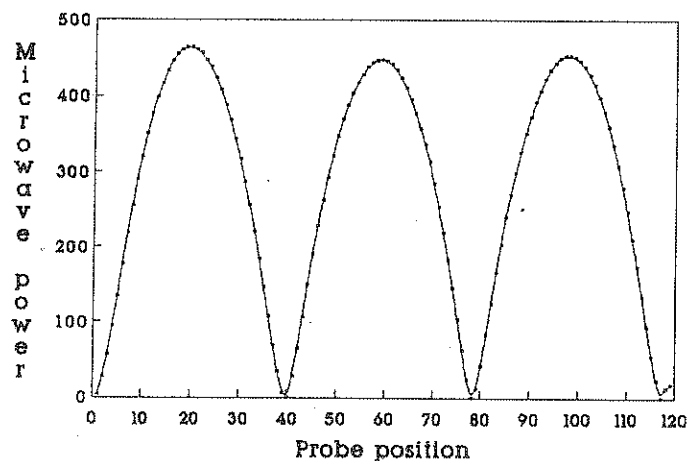


Figure 2. Standing wave pattern of empty dielectric cell or perfect standing wave pattern.

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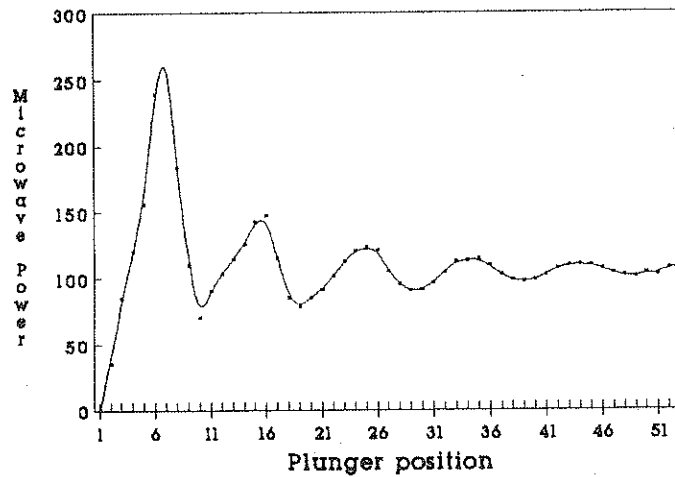


Figure 3. Standing wave pattern of pure water.

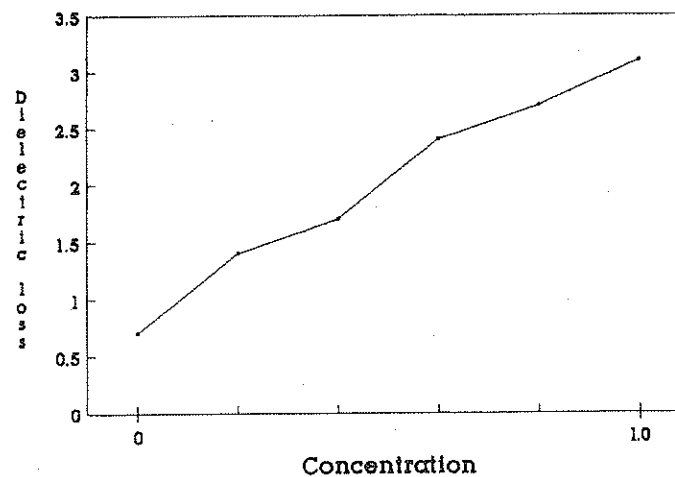


Figure 4. Variation of dielectric loss of water with increasing concentration of calcium nitrate solution.

number of points and the corresponding microwave current (power) display on the monitor of the PC can be saved in the memory. This saved data file of experimental observations can be used as it is in the source programme to calculate dielectric constant and dielectric loss and error in dielectric constant and loss. The standing wave pattern of pure water is shown in figure 3. The variation in dielectric loss of water with increasing concentration of calcium nitrate and calcium chloride solutions are shown in figures 4 and 5.

3.2 The PC add-on card

This specially prepared hardware of the system mainly consists of three parts as follows:

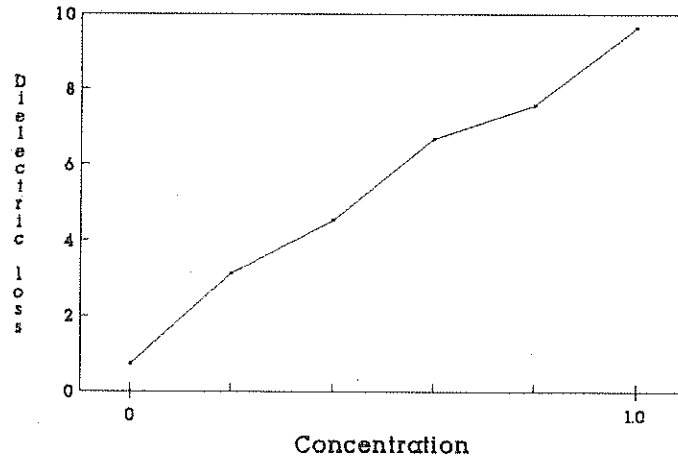


Figure 5. Variation of dielectric loss of water with increasing concentration of calcium chloride solution.

1. Control mother board.
2. Precision of 13-bit analog to digital convector (ADC).
3. Low cost stepper motor controller.

The daughter boards consist of ADC and stepper controller circuitry are fixed on the main control mother board which is fully IBM PC compatible. The ADC converts the analog current from the probe into digital form for PC based instrumentation. The stepper motor facilities for full step/half step rotation in clockwise/anticlockwise direction is provided by suitable software. PC controlled rotation of the stepper motor rotates the lead screw through 1 : 1 gear coupling which causes the advancement of the probe along the slot line in forward or reverse direction, generating ultimately motion of the detector in the slot line of the microwave bench set-up. The system control software is written in quick basic and hardware development routines like moving stepper motor and reading data from ADC is written in 8088 assembly language. After executing the programme file the main menu appears on the screen.

The solutions of the increasing concentration were accurately made by mixing appropriate volumes of pure water and ionic salts solutions. The values of ϵ' were found to be accurate up to $\pm 2\%$ and of ϵ'' up to $\pm 5\%$.

4. Chemicals

The chemicals used were of purest available quality and obtained from BDH, England. The standard procedures for preparation of 1 mole solution and for further dilution were used before using them for experimental purpose.

5. Results and discussion

The dielectric properties data, i.e. the value of dielectric constant and dielectric loss for calcium nitrate solution are reported in table 1, and calcium chloride solution in table 2.

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Table 1. Dielectric study of pure water with increasing concentration of calcium nitrate.

Salt	Concentration mole/litre (Q)	EPS (ϵ')	DELEPS ($\Delta\epsilon'$) per cent	EPSP (ϵ'')	DELEPSP ($\Delta\epsilon''$) per cent
Ca(NO ₃) ₂	0.0	80.8	±0.5	0.7	±0.4
	0.2	80.0	±0.4	1.4	±0.4
	0.4	79.8	±0.6	1.7	±0.7
	0.6	80.0	±0.4	2.4	±0.6
	0.8	81.1	±0.5	2.7	±0.8
	1.0	80.9	±0.7	3.1	±1.1

Table 2. Dielectric study of pure water with increasing concentration of calcium chloride..

Salt	Concentration mole/litre (Q)	EPS (ϵ')	DELEPS ($\Delta\epsilon'$) per cent	EPSP (ϵ'')	DELEPSP ($\Delta\epsilon''$) per cent
CaCl ₂	0.0	80.8	±0.5	0.7	±0.4
	0.2	80.7	±0.4	3.1	±0.7
	0.4	81.5	±0.9	4.2	±1.5
	0.6	83.5	±1.8	6.6	±1.4
	0.8	85.5	±3.5	7.5	±3.9
	1.0	84.0	±1.7	9.6	±3.0

The errors in dielectric constant (Δ EPS) and dielectric loss (Δ EPSP) for calcium nitrate are given in table 1, and calcium chloride in table 2.

From tables 1 and 2 it is observed that for concentrations between 0.2 and 1.0 mole the dielectric constant of water is smaller and some larger than that of pure water. The variation in dielectric constant with concentration observed for the above electrolyte solutions is found to be in accordance with the earlier investigation of Sack [5], Debye-Huckel [2]. Similar behaviour of dielectric constant has been reported by Mehrotra *et al* [12].

From tables 1 and 2 it is also observed that the dielectric loss of water increases with increasing concentration of calcium nitrate and calcium chloride solutions. This behaviour is similar to Ca(NO₃)₂ · 4H₂O in aqueous solution of urea [12], and dielectric relaxation study of primary alcohol-water mixtures using TDR technique [13].

According to Sack [5] and Debye-Huckel [2] as described in Hasted [6], the dielectric loss is high in KHz and MHz frequency and low in GHz frequency and in microwave region the dielectric loss of pure water is less than unity. As reported in tables 1 and 2 zero concentration is nothing but the pure water and its loss in microwave frequency (5-GHz) region is 0.7 (less than unity). This is in agreement with the earlier statement of Debye-Huckel [2] and Sack [5].

It has been also observed from tables 1 and 2 that, the variation in dielectric loss is different for the two ionic salts. It is because of the difference in the ionic size of these ions. The ionic size of NO₃⁻ ion is bigger than that of Cl⁻, therefore the mobility of NO₃⁻ is slower than that of Cl⁻ showing less conductivity in NO₃⁻ and more conductivity in

Cl^- . This shows a large variation in dielectric loss of calcium chloride than that of calcium nitrate solution though ionic concentration in the respective solutions of the same concentrations are equal i.e. (Ca^{++} and 2NO_3^-) and (Ca^{++} and 2Cl^-).

Acknowledgements

The authors are thankful to the Indian Space Research Organization (ISRO) for providing experimental set-up of C-band microwave bench under the RESPOND project. They are also thankful to S C Mehrotra, Department of Computer Science and P B Patil and G S Raju, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for discussion.

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