

Relative Analysis of Dielectric Behaviour of CsCl and LiCl using Time Domain Reflectometry Technique

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ABSTRACT

Complex dielectric permittivity spectra, in the frequency range 10 MHz to 20 GHz are reported for aqueous Cesium chloride (CsCl) & Lithium chloride (LiCl) solutions at 25°C using time domain reflectometry technique. The static dielectric constant, relaxation time and conductivity have been determined using nonlinear least squares fit method. The TDR technique is based on the study of the change in shape of a fast rising voltage step which is propagated through coaxial line section filled with the material under study. The voltage pulse, registered by fast sampling scope, is then compared with that reflected from the sample cell. Fourier transformation of both the pulses gives the Frequency dependent complex dielectric permittivity.

Keywords : Dielectric Permittivity, Time Domain Reflectometry, Electrolyte Solution

I. INTRODUCTION

All the alkali metal chlorides are highly soluble in water, producing strong electrolyte solutions. Strong electrolytes are solutions which are highly dissociated into ions at all concentrations and contain both ions and neutral molecules. The process of ionization is influenced by the nature of the solute and the solvent, the ionic size, and the solute solvent interaction. The dielectric constant of the solvent plays a dominant role in the ionization process. A large dielectric constant leads to a small electrostatic force between ions and increases the electrolyte conductivity. The TDR technique is based on the study of the change in

shape of a fast rising voltage step which is propagated through coaxial line section filled with the material under study. The voltage pulse, registered by fast sampling scope, is then compared with that reflected from the sample cell. Fourier transformation of both the pulses gives the frequency dependent complex dielectric permittivity.

The study of electrolyte solutions has contributed to our understanding of matter on the molecular scale [1-4]. Electrolyte solutions form a particular series in which the cation size varies systematically and as such, they have also been widely employed to test theories of electrolyte solutions. Yan Zhen et al [5] have

studied ion size effects on the dynamic and static dielectric properties of aqueous alkali solutions using dielectric spectroscopy technique at frequencies between 45 MHz and 20 GHz. The behavior of the static dielectric constant and dielectric relaxation time of the solutions were studied as functions of ion size and concentration. For moderate concentrations, both static dielectric constant and dielectric relaxation time were found to decrease linearly with solution conductivity. Recently, Ting Chen et. al [6] have reported results of a dielectric relaxation study of the aqueous solutions of KCl and CsCl at 25°C using vector network analyzer. It reveals that the impact of the solute on water structure, reflected in a decrease in the bulk water relaxation time with rising electrolyte concentration, decreases in the sequence NaCl > KCl > CsCl and appears to be proportional to the surface charge density of the cation. The interactions of K⁺ and Cs⁺ with their hydration shells are too weak to cause irrotational bonding of H₂O molecules. In the present paper, the dielectric relaxation of cesium chloride & Lithium chloride in water solutions have been investigated using time domain reflectometry from 10 MHz to 20 GHz.

Experimental

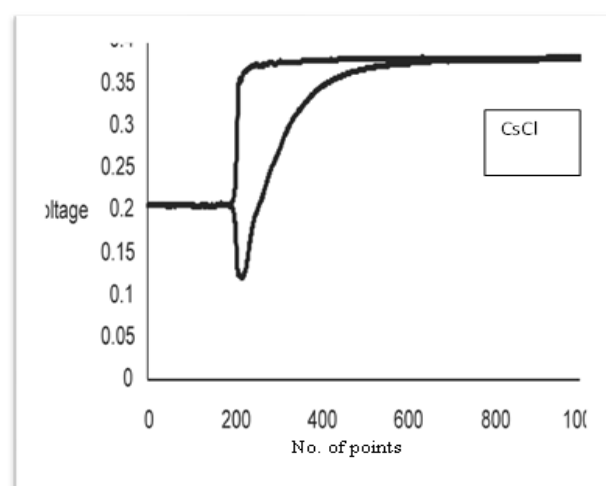
The Cesium chloride (CsCl) and Lithium chloride (LiCl) was obtained from s. d. Fine Chemical Limited. Double glass distilled and deionized water is used for preparation of Cesium chloride-water mixture and Lithium Chloride-water mixture.

The complex permittivity of CsCl in water solutions was studied using Time Domain Reflectometry (TDR) [7-10]. The Hewlett Packard HP 54750A sampling oscilloscope along with HP54754A TDR plug in module has been used for the TDR setup. A 200 mV step voltage pulse with 40 ps rise time was propagated through a coaxial 50 ohms line. The sample was placed in a SMA cell of 3.5 mm outer diameter and 1.35 mm effective pin length. Sampling oscilloscope monitored the reflected pulse with $R_x(t)$ and without

sample $R_1(t)$. A typical example of these recorded pulses is shown in Figure 1. The reflected pulses were digitized with 1024 sampling points in the time window of 5ns. The subtraction and addition of these pulses are done in the memory of the oscilloscope. The subtracted pulse $p(t) = [R_1(t) - R_x(t)]$ and added pulse $q(t) = [R_1(t) + R_x(t)]$ are transferred to the computer for further analysis. The subtracted and added pulses are time dependent. Therefore it is necessary in this technique to convert time dependent data into frequency dependent data by means of Fourier Transformation. The processing of the data was carried out to yield complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency of 10 MHz to 20 GHz, which is obtained as follows [15-18].

$$\rho^*(\omega) = \frac{c}{j\omega d} \frac{p(\omega)}{q(\omega)}$$

Where, $p(\omega)$ and $q(\omega)$ are Fourier transformation of $p(t)$ and $q(t)$ pulses. c is the velocity of light, ω is the angular frequency and d is effective pin length. The complex permittivity spectra were obtained from reflection coefficient spectra by applying the least squares fit method as described in our earlier publications [11-14].



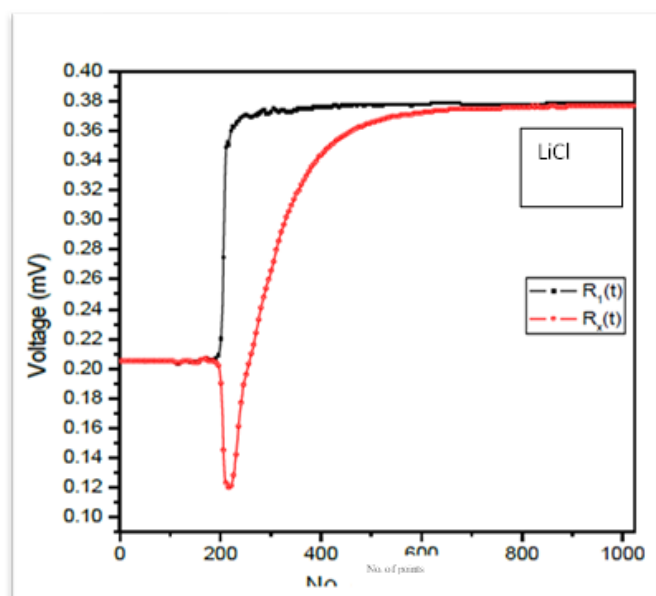


Figure 1: Typical recorded pulses without sample R1 (t) and with sample Rx (t) CsCl & LiCl

II. RESULT AND DISCUSSION

The values of static dielectric constant (ϵ_0) and relaxation time (τ) has been determined by fitting the

complex permittivity $\epsilon^*(\omega)$ spectra with the Havriliak-Negami expression [16].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} - j \frac{\sigma}{\omega \epsilon_v} \quad (1)$$

where ϵ_0 is the static dielectric constant, ϵ_∞ is the permittivity at high frequency, τ is the relaxation time, σ is the dc conductivity of the solution, which is essentially due to free ions, and $\epsilon_v = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum. For the systems studied here, the values of α and β are found to be 0 and 1 respectively within experimental error. As the frequency range of dielectric study in present work is from 10 MHz to 20 GHz, the value of ϵ_∞ is just a fitting parameter. In the fitting procedure, ϵ_∞ is not fitted and assumed to be 3.0. The resulting values of dielectric relaxation parameters for LiCl & CsCl water mixture and at different concentrations are listed in Table 1.

Table 1

| C(M) | ϵ_s | | τ (ps) | | σ (mho/m) | |
|------|--------------|-----------|-------------|----------|------------------|------------|
| | CsCl | LiCl | CsCl | LiCl | CsCl | LiCl |
| 0.05 | 77.8 (61) | 78.0 (22) | 7.7 (22) | 8.4 (44) | 0.5 (55) | 0.137 (9) |
| 0.10 | 76.4 (78) | 77.6 (53) | 7.2 (19) | 8.2 (23) | 2.4 (43) | 0.213 (16) |
| 0.50 | 74.5 (67) | 77.3 (48) | 6.9 (20) | 7.8 (28) | 7.6 (49) | 0.297 (24) |
| 1.00 | 71.0 (89) | 76.9 (47) | 6.7 (34) | 7.7 (34) | 13.6 (59) | 0.385 (33) |
| 1.50 | 69.8 (93) | 75.7 (59) | 6.3 (35) | 7.5 (18) | 15.4 (61) | 0.598 (52) |

Table 1. Dielectric relaxation parameters for CsCl & LiCl in aqueous solution. Numbers in parenthesis denote uncertainties in the last significant digit as obtained by least squares method. e.g. 77.8(61) means 77.8 ± 6.1 .

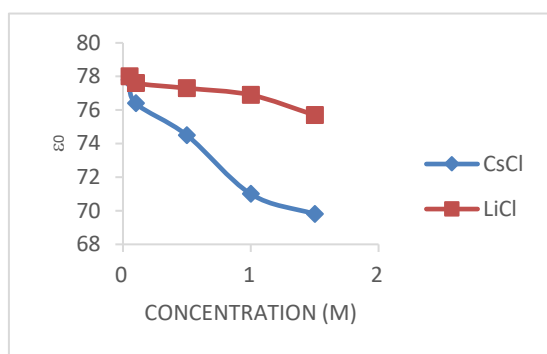


Figure 2: Static permittivity of the solution with Concentration (M) in CsCl vs LiCl.

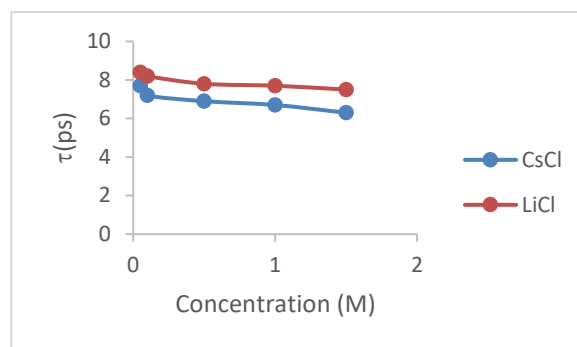


Figure 3: Relaxation time of the solution Concentration (M) in CsCl vs LiCl.

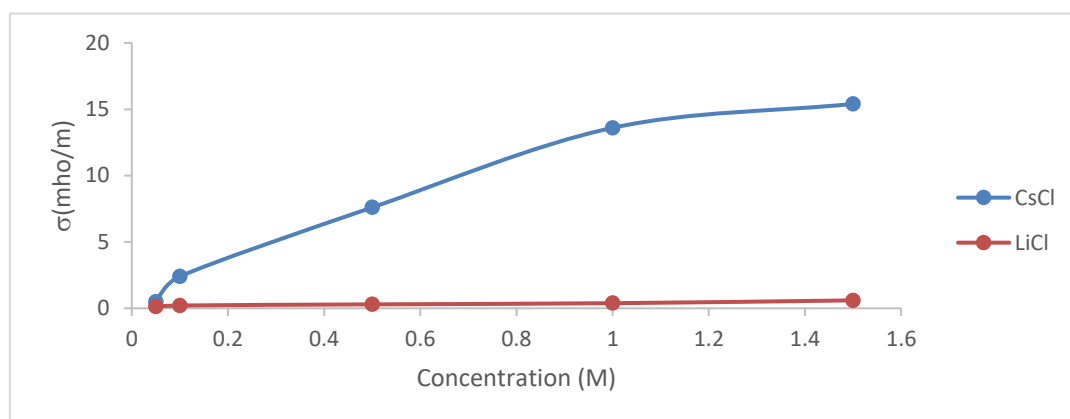


Figure 4: Static permittivity of the solution with Concentration (M) in CsCl vs LiCl.

III. CONCLUSION

The dielectric relaxation parameters for aqueous CsCl & LiCl have been studied at various concentrations using Time Domain Reflectometry. The static dielectric constant, relaxation time and d. c. conductivity have been determined. The dielectric data reveal the formation of a solvation sheath of bound water molecules around the ions. As a consequence the ion-water interaction is progressively weaker, with fewer water molecules bounded by Coulomb forces.

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