13th Seminar *Computer Modeling in Microwave Engineering & Applications*, Thun, Switzerland, March 7-8, 2011

Microwave Dielectric Spectroscopy in the Supercritical and Near Critical Regions

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Abstract - The aim of this work was to develop a device capable of performing direct measurements of complex permittivity on high pressure and high temperature liquids (alcohols and water) up to supercritical conditions. The design utilises a coaxial line terminated at the end by a metal cavity that contains the sample. The monitoring of the reflection of the microwave signal from the sample combined with mode matching analysis is used to measure the complex permittivity of water and various alcohol samples and permittivity values for various liquids at supercritical pressures and temperatures. It has been observed that there is a large variation both in the real and imaginary parts of the complex permittivity with temperature, which is related to the change of the relaxation time of the molecules. For example, in the case of alcohols at 2.45 GHz the imaginary part of permittivity displays large variations between the low temperature and the supercritical region.

Introduction

The evaluation of complex permittivity is very important for understanding the molecular orientation and structure of materials, and also for establishing the various processing parameters of a material with the use of microwave energy. The importance of accurate permittivity measurements is well established within the scientific community, and is of increasing importance in the areas of green and MW chemistry. For this purpose advanced techniques have been developed [1, 2] over the last years. However, under extreme experimental conditions involving high temperatures and pressures the measurement of complex permittivity is highly challenging, and the techniques available to date are limited [3, 4]. In the field of supercritical fluid chemistry, the importance of the determination of the relative permittivity ε^* has been appreciated for a long time [5], and a plethora of scientists used dielectric measurements in their research [6-11].

The only techniques reported in the literature which are capable of measuring the dielectric properties of fluids at supercritical conditions are those developed in [3] and [4]. Okada *et al.* [3] utilised a cell based on a transmission line device. In their design, a cell was created by two quartz windows within a platinum coaxial line. $\varepsilon'(0)$ is evaluated by applying a pulse signal and measuring the time that it takes to propagate through the sample. In order to evaluate ε' at different frequencies, a broadband signal is transmitted through the cell and the S-parameter matrix is extracted; a curve fitting exercise is then conducted, with the relaxation time τ and the infinite permittivity ε_∞ as the adjustable parameters, in order for the permittivity to be calculated indirectly at different frequencies and temperatures. Lee *et al*. [4] have taken a more direct approach in measuring the complex permittivity of carbon dioxide and methanol mixtures at supercritical conditions. An open ended technique using a 2.2 mm coaxial probe was utilised. However, from this work it is not clear if this technique is suitable for supercritical or near critical pure liquids which require high pressures and temperatures i.e. alcohols.

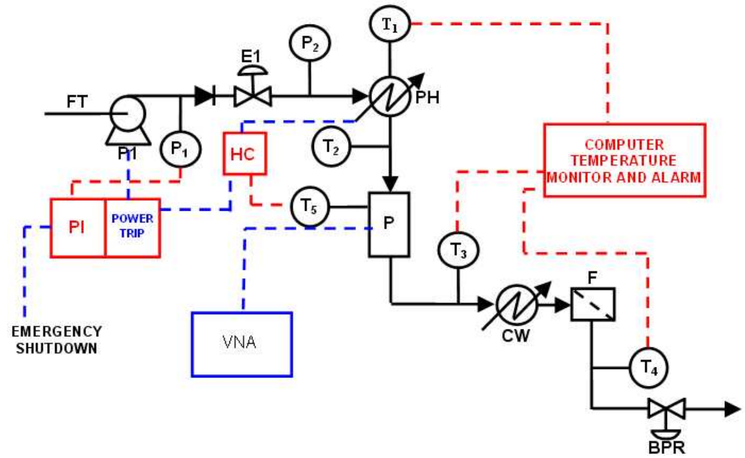


Fig.1. Basic flow diagram of the high pressure/temperature dielectric measurement apparatus. Key: **FT** – test chemical feed, **P1** – Gilson HPLC pump, **P1/PI** – electronic pressure transducer, **P2** – mechanical pressure indicator, **PH** – pre-heater, **P** – coaxial probe, **CW** – water cooling, **F** – 0.5μm Filter, **BPR** – Tescom back pressure regulator, **E1** – emergency relief valve, **HC** – Eurotherm PID temperature controller, **T_1 – T_5** – K-type thermocouples (internal to process stream). All temperatures are monitored using a Pico TC08 data logger.

Technique

Fig. 1 shows the flow diagram of the high pressure and temperature experimental apparatus developed for measuring complex permittivity. This equipment can be used to measure the dielectric properties of various test chemicals under a variety of test conditions including those in the supercritical region. The apparatus consists of a Gilson HPLC piston pump (PI), a TESCOM back pressure regulator (BPR) under manual control and the measurement cell (P). The stream temperature is maintained using a specifically designed 2.3 kW heating coil, which is under PID control via the temperature of the measurement cell. The measurement cell consists of a standard 50 Ω 7 mm coaxial line with a 3 mm inner connector, made of high pressure and temperature resistant stainless steel. A sapphire bead 15.23 mm in diameter with a thickness of 10 mm is used as a high pressure window. The sapphire bead sits on a GRAFLEX™ flange which, together with a KALRETZ™ O-ring, forms a high pressure seal. The inner conductor passes through the sapphire bead and stops at the same level with its upper surface forming an open ended coaxial line. The open ended coaxial line terminates with a stainless steel cylindrical cavity 22.22 mm in diameter and 22.23 mm high which contains the measurement sample. An Agilent 8753ES Vector Network Analyzer (VNA) with a frequency range 30 kHz-6GHz is connected to the coaxial and is used to transmit and receive a signal from the cell. The pressure and the temperature of the system are constantly monitored with the use of a pressure transducer and K-type thermocouples. The entire apparatus is surrounded by LEXAN™ high impact resistant plastic and includes several other safety systems such as a high pressure system power trip and a spring loaded emergency relief valve. At the beginning of a complex permittivity measurement session, the open ended coaxial line is calibrated with the use of three different configurations, which correspond to three different calibration standards: an open line, a short-circuited line and a line terminated with a reference liquid of known dielectric response inside the cylindrical cavity.

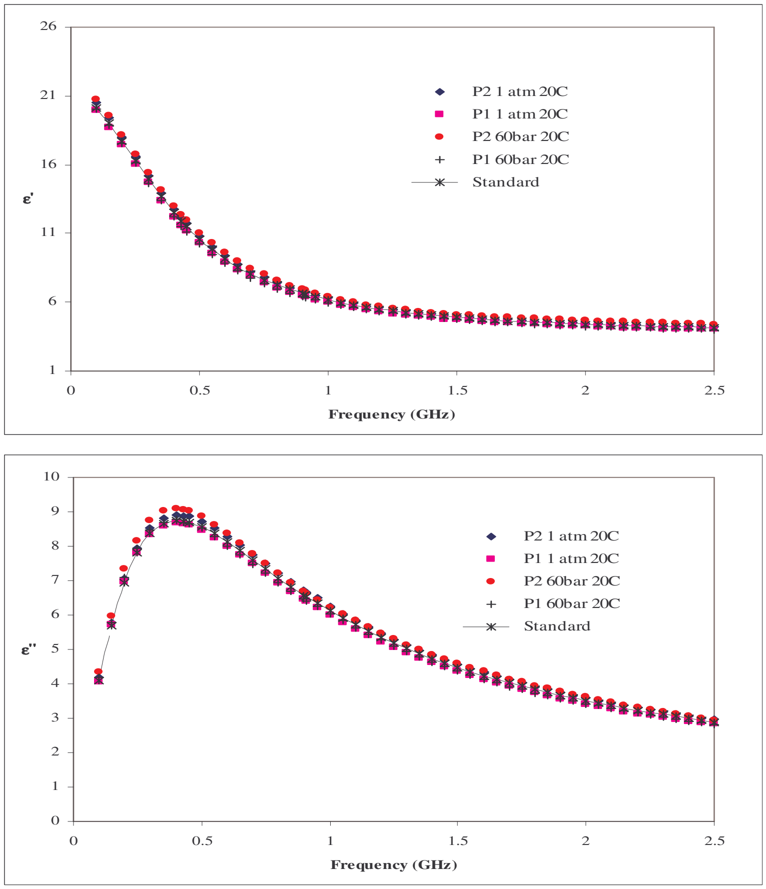


Fig. 2. Variation in the real and imaginary part of the complex permittivity versus frequency for n-Propanol for different pressures at 20 °C. The broken line is the standard value accepted by NPL at 20 °C and ambient pressure.

Fig. 2 shows two measurements of complex permittivity versus frequency of *n*-propanol at ambient and high pressure at 20 °C, together with the values of *n*-propanol accepted as standard by the National Physical Laboratory, UK (NPL) for this liquid at this temperature. These measurements are used to check the validity of the calibration. The liquid sample is pumped with the use of the HPLC piston pump into the system. The pressure of the system is adjusted to desirable levels with the use of the back pressure regulator. The temperature of the system is set manually and is controlled automatically by the PID controller via the measurement of the temperature inside the measurement cell. The amplitude and the phase of the reflection coefficient Γ are obtained with the use of the VNA and fed into a computer program, which utilises a modal analysis technique to calculate the real and imaginary part of the complex permittivity.

Results

Fig. 3 shows the values of the real and imaginary parts of complex permittivity versus temperature for ethanol, methanol and *n*-propanol. The imaginary part of permittivity for Methanol decreases with increasing temperature where the imaginary part for Ethanol and *n*-propanol displays a more complicated trend. The real part of permittivity for all three samples

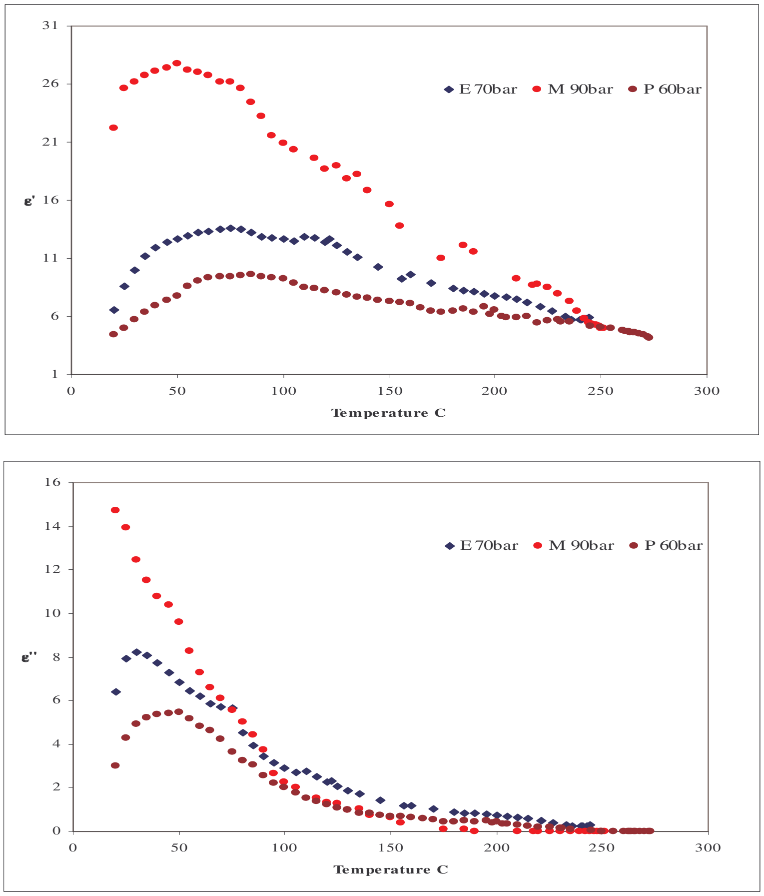


Fig. 3. Variation of the real and imaginary part of complex permittivity versus temperature for Ethanol, Methanol, and n-Propanol. The pressure of the Methanol sample is 90 bar, the pressure of the Ethanol is 70 bar and n-Propanol is 60 bar. The frequency is 2.45 GHz.

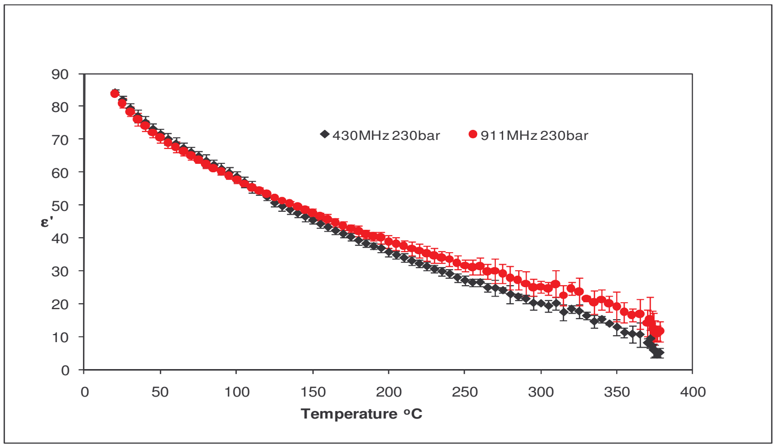
exhibits an initial increase and then decreases with temperature. It is generally accepted that polar liquids follow a Debye-like response versus frequency and it is known that the relaxation time of such systems under high pressure varies with temperature [3]. Fig. 4 shows the variation of the complex permittivity in water. Both the real and imaginary parts of the permittivity are decreasing with temperature, and the decrease in the imaginary part of the permittivity becomes more rapid as the temperature increases.

Conclusion

The variation of the dielectric properties of alcohols and water at high pressures versus temperature is considerably different than for these materials at ambient pressure and temperature. These differences are attributed to the effect that the high pressure has on the phase and the density of the alcohols.

Acknowledgments

The authors would like to thank EPSRC (grant reference EP/D012996/1) for funding this project.



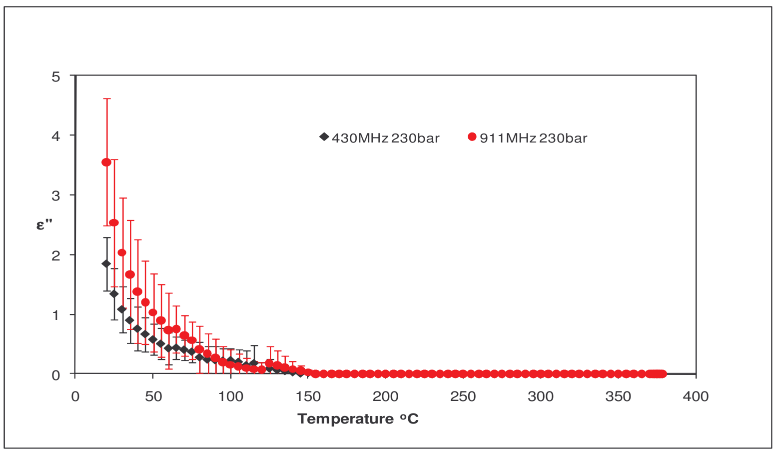


Fig.4. Variation of the real and imaginary part of complex permittivity versus temperature for water. The pressure is 230 bar. The frequencies are 430 MHz and 911 MHz.

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