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Characterization of Corrosive Lithium-Bromide/Water Solutions up to 6 GHz Using a Low Cost SMA Connector

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Abstract— In this paper, we present the results of complex permittivity extraction up to 6 GHz from eight aqueous lithium bromide (LiBr/water) solutions. These solutions, known for their high corrosivity, were measured across LiBr mass concentrations ranging from 1% to 54% and for conductivities up to 14 S/m. They are widely used in thermochemical compressors installed in absorption machines, which are primarily employed to generate cooling from a heat source. Thermochemical compressors are more efficient than conventional compressors enabling a significant reduction in the energy consumption of absorption machines. The applications of these machines are numerous, including cooling systems in vehicles and buildings, as well as energy recovery in chemical industries. To characterize the aqueous lithium bromide (LiBr/water) solutions, microwave measurements were conducted using a low-cost SMA connector, which acted as an open-circuit coaxial probe and was brought into contact with the liquids to be characterized. From the reflection coefficient measurements, we validated the complex permittivity extraction using reference liquids (ethanol and methanol). Subsequently, we extracted the complex permittivity of LiBr/water solutions and analyzed its variation as a function of LiBr mass concentration. Results show that the complex permittivity exhibits significant variation (with the real part decreasing and imaginary part increasing) for aqueous solutions with a LiBr mass concentration between 1% and 30%. For higher concentrations, the evolution of complex permittivity become less pronounced, with an inversion in the direction of variation observed for LiBr mass concentrations above 40%.

Keywords—material characterization, low-cost sensor, corrosive liquid, permittivity extraction

I. INTRODUCTION

Absorption machines are primarily used to generate cooling from a hot source (around 100 °C) and, in some cases, from an intermediate source (at approximately room

temperature). The water–lithium bromide pair in a binary mixture, LiBr/H₂O, remains the thermochemical pair that provides the best performance for these machines [1]. In other words, the water-lithium bromide solution is a refrigerant-rich mixture where lithium-bromide is used for its drying and hygroscopic properties as shown in Fig. 1 for a cooling absorption machine diagram.

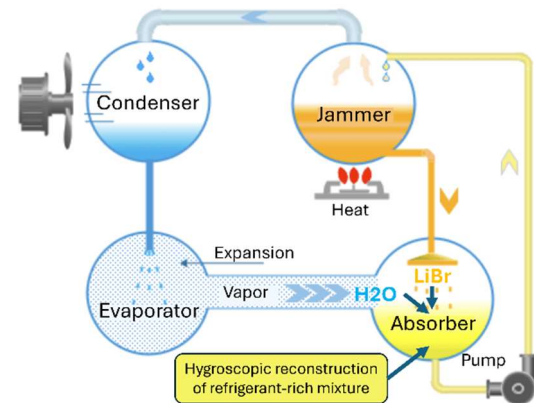


Fig. 1. Absorption machine diagram [2]

In the current energy context, where research is increasingly focused on the recovery of waste heat, the use of this type of machine is becoming increasingly relevant. Optimizing these machines requires accurate knowledge of the temperature and concentration distributions of these LiBr/water solutions.

To our knowledge, LiBr/water solutions have not yet been characterized in the microwave spectrum for the purpose of extracting their permittivity. The challenge is compounded by the extreme corrosivity of these solutions, requiring the use of

specific test cells that are safe for the operator and constructed from suitable materials. The corrosive nature of LiBr excludes the use of certain metals and polymers. Significant work has been done to measure the permittivity of various solutions composed of salt since it is a well know absorbent and dehydrator (also called desiccant for the habit to use it in bags like silica gel). In the literature we have found studies of salt solutions such as seawater [3,4], pure NaCl solutions [5-7], or other specific liquids [8]. These studies have demonstrated a strong correlation between the complex permittivity of a liquid and the temperature–concentration link.

The objective of the present work was therefore to quantify the variation in permittivity of different LiBr/water solutions as a function of their mass concentration over a frequency range from a few 100 MHz to 6 GHz, and to set up a characterization technique adapted to the constraints due to the high corrosiveness of LiBr. The ultimate goal is to determine whether permittivity variations at a specific frequency or over a particular frequency range, could be sufficient, to develop a sensor for measuring LiBr concentration and/or temperature. This sensor would need to be sensitive to LiBr/water solutions with LiBr mass concentrations varying between 35 and 60%, and temperatures ranging from 25 to 45 °C, corresponding to the concentrations and operating temperatures of absorption machines.

This paper presents the conductivity measurements of LiBr/water solutions, the theoretical permittivity of some reference liquids, the principle of microwave measurement, and the complex permittivity extraction technique used. The results obtained are then presented and discussed, followed by a conclusion.

II. CONDUCTIVITY MEASUREMENT

To cover all possible concentrations without crystallization at room temperature (LiBr mass concentration below 60%), eight solutions of LiBr/water at different concentrations were prepared. The concentration of each solution was measured with a pycnometer, and their conductivities were measured with a Consort K916 conductivity meter. The conductivities of distilled water, methanol, and ethanol, as reference liquids, were also measured and presented in Table 1.

TABLE I. PARAMETERS OF REFERENCE LIQUIDS

	Distilled water	Ethanol 99.5 %	Methanol 99.8 %
$\epsilon_{m,s}$	87.85	28.56	37.90
$\epsilon_{m,\infty}$	6.22	4.67	5.97
$\alpha_s [10^{-3}/^\circ\text{C}]$	-4.57	-6.34	-5.94
$\alpha_\infty [10^{-3}/^\circ\text{C}]$	-5.79	-1.40	-2.76
$\tau_0 [\text{fs}]$	5.88	14.8	89.1
$E_A [\text{kJ/mol}]$	18.02	23.11	15.72
$\sigma [\mu\text{S/cm}]$	1	1.76	2.2

Fig. 2 details the conductivity measurements of the LiBr/water solutions at 25 °C as a function of their measured concentration. The decrease in conductivity observed at high LiBr concentrations (over 35% by mass) has been previously reported by various research teams [9,10].

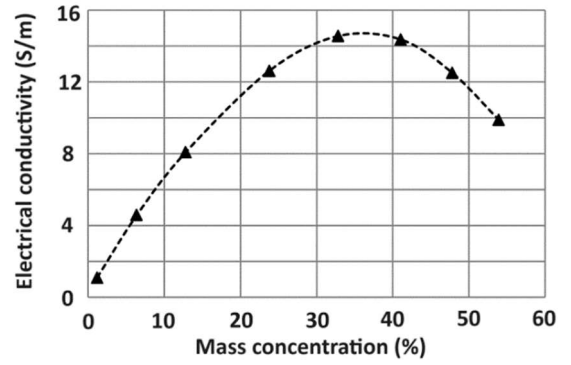


Fig. 2. Conductivity measurements of LiBr/water solutions at 25 °C as a function of their LiBr mass concentrations.

Permittivity of reference liquids: Liquids with precisely known permittivity are often used as reference and to calibrate experimental procedures. For our study we selected distilled water, methanol, and ethanol as reference liquids. Their complex relative permittivity is defined by equation (1) from the Cole–Cole model [11], with the different parameters given in Table 1 (derived from the work of Wagner et al. [12]) and the measured conductivities:

$$\epsilon_r^*(\omega, T) = \frac{\epsilon_S - \epsilon_\infty}{1 + j\omega\tau_0} e^{\frac{E_A}{RT}} + \epsilon_\infty + \frac{\sigma_i}{j\omega\epsilon_0} \quad (1)$$

Where T is the temperature (in K), ϵ_r^* is the complex relative permittivity of the medium, $\epsilon_S = \epsilon_{m,s} \cdot e^{\alpha_s T}$ is the static relative permittivity, $\epsilon_\infty = \epsilon_{m,\infty} \cdot e^{\alpha_\infty T}$ is the high-frequency limiting relative permittivity (T' is the temperature in °C), ϵ_0 is the vacuum permittivity (in F/m), ω is the angular frequency (in rad/s), σ_i is the ionic conductivity (in S/m), R is the perfect gas constant (in J/(mol.K)), E_A is the activation energy (in J/mol), and τ_0 is the relaxation time (in s). $\epsilon_{m,s}$, $\epsilon_{m,\infty}$, α_s and α_∞ are empirical parameters detailed in Table I.

III. HIGH FREQUENCY CHARACTERIZATION TECHNIQUE

To characterize the different liquids in the microwave domain, we used a coaxial probe in open circuit configuration lightly soaked at the surface of the liquid under test. Microwave measurements of the reflection coefficient (S_{11}) were performed using a Keysight P9372A vector network analyzer (VNA). The measurement system (VNA + semi-rigid coaxial cable) was calibrated automatically using an electronic kit. As shown in Fig. 3, the reference plane for the measurement (identified by S_{11}) is located at the output of the male connector of the semi-rigid coaxial cable with a characteristic impedance of 50Ω.

The coaxial probe, which was soaked in the liquid under test consisted of a female SMA-type connector, usually mounted on the edge of a Würth Elektronik PCB (ref. 60312202114514) and repurposed from its original function. This connector was chosen for its low cost and its resistance to corrosive LiBr/water solutions. However, it was modified by removing all its pins to create a flat surface in contact with the liquid. It is at this contact interface that the liquid is characterized by the measurement of the reflection coefficient, noted S_{11} in Fig. 3. It is then important to not immerse the probe entirely as it would change the interface behavior.

IV. COMPLEX PERMITTIVITY EXTRACTION METHOD

The permittivity extraction method we employed was developed by Lacrevez et al. [13] using two reference media

(air and distilled water). To adapt this method to our test configuration, it was necessary to de-embed the SMA connector (probe) to place the measurement reference at the probe–liquid interface. To achieve this, we determined the propagation exponent of the SMA connector. Thus, we measured the propagation exponent of an SMA-female to SMA-female adapter from the same manufacturer and assumed to have the same electrical characteristics as the SMA probe connector ($\alpha \approx 0$ Np/m and $\beta = 28.9$ rad/m at 1 GHz). The extraction of the complex permittivity was then performed using the S_{11} parameters (Fig. 3).

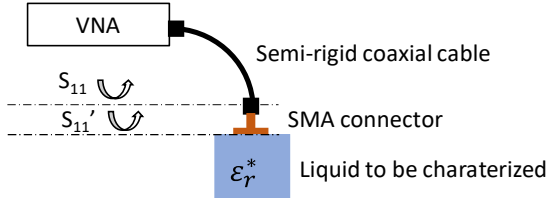


Fig. 3. Principle of LiBr/water solutions characterization.

V. RESULTS

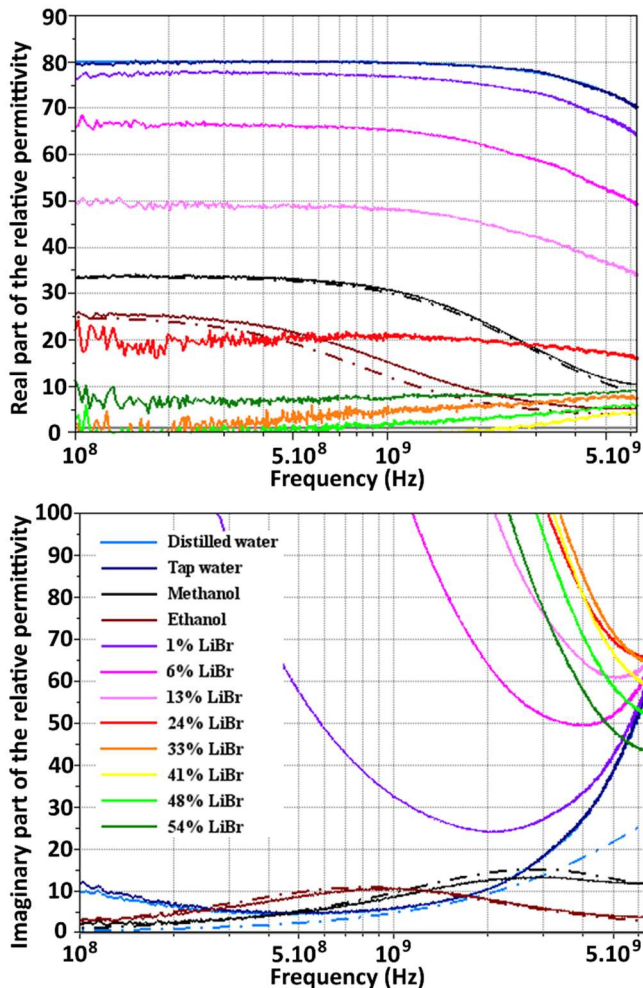


Fig. 4. Extraction of the complex relative permittivity of reference liquids and different LiBr/water solutions.

The complex relative permittivity of reference liquids and LiBr/water solutions is shown in Fig. 4 for frequencies up to 6 GHz. The solid line represents the measurement results from the permittivity extraction method, and the dashed line represents the theoretical results from equation (1) using the

parameters in Table 1. The curves for air and distilled water whose equations were used in the permittivity extraction method, cannot be used to validate the experimental results. However, the curves of ethanol and methanol validate the permittivity extraction method we used. Indeed, we note that the theoretical and practical curves for ethanol and methanol are very similar, from 100 MHz to 6 GHz, validating the relative complex permittivity extraction method in this frequency range using this low cost SMA connector to characterized low-loss liquids.

Regarding the extraction curves for the permittivity of LiBr/water solutions, both the real part and the imaginary part of the relative permittivity depend strongly on the LiBr mass concentration. For concentrations between 1% and 33% by mass, the real part of the relative permittivity decreases rapidly, while the loss tangent increases. This variation is less significant for concentrations over 33% by mass, with an inversion in the direction of variation for concentrations over 30-40% by mass. This inversion phenomena, for which we currently have no explanation, mirrors what we observed in the conductivity curve in Fig. 2, where the slope inverts for LiBr mass concentration greater than 35%.

We also note that for higher concentrations, which have high conductivity, the real part of relative permittivity becomes negative, contrary to all theoretical models. We believe that the very high conductivities, which affect the imaginary part of the permittivity have an impact on the extraction of the real part of the permittivity, leading to a decrease in its value.

The curves of the imaginary part of the permittivity seem in very good agreement with the conductivity measurements (Fig 2). Indeed, according to equation (1), the imaginary part of the permittivity depends strongly on the conductivity at low frequencies. The higher the conductivity, the more it shifts towards higher frequencies, as observed in the curves. Moreover, we observe that the curve of the imaginary part of the permittivity at a LiBr mass concentration of 54% is close to the one at 13%, which is consistent with the conductivity measurements of Fig. 2.

VI. DISCUSSION

To our knowledge, measurements of LiBr/water solutions permittivity have not been reported, highlighting the originality of the results presented in this paper. Despite the lack of comparable data and chemical study which reveal the limits of this work, these first results appear consistent and encouraging. Then, it would be relevant to complete the study with: (1) the characterization of high-loss known liquids, and (2) a chemical study to understand the inversion phenomena observed at LiBr concentrations higher than 35%.

VII. CONCLUSION

A complex permittivity extraction method using a low cost SMA connector was validated between 100 MHz and 6 GHz by characterizing two known reference liquids (ethanol and methanol). The method was then applied to characterize corrosive LiBr/water solutions with LiBr mass concentrations ranging from 1% to 54%. Despite the complexity of characterizing high-loss liquids, we were able to obtain permittivity results that appear consistent for the imaginary part. For the real part, the extraction curves appear to be underestimated for high LiBr mass concentrations

associated with very high conductivities. But the variation of the overall curves seems to be consistent.

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