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Dissociation of Ethoxy Methyl Carbenium Hexachloroantimonate in Methylene Chloride Solution. I. Measurement of the Specific Conductivity and Dielectric Constant

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ABSTRACT

The problems of measuring the specific conductivity of very low conductivity organic solutions are explored. A simple ac system using readily available components is described, and its limitations are examined. The low-frequency dielectric constant can also be determined with reasonable accuracy.

INTRODUCTION

The degree of dissociation of a number of stable carbenium ion salts has been determined by a number of authors [1-4] using electrical conductivity measurement.

This method can give useful information regarding the initiation step in carbenium ion polymerization. However, as pointed out, for example by Bawn et al. [1], this is not necessarily related to the dissociation of the actual growing chain ends. As part of a study of the polymerization of ethyl vinyl ether with trityl hexachlorantimonate [2-4], a model of the propagating species has been studied. This is ethoxy methyl carbenium hexachloroantimonate,

$CH_3CH_2-O-\overset{+}{C}HCH_3-SbCl_6^-$

The measurement of the specific conductivity of very low conductivity organic solutions such as ethoxy methyl carbenium hexachloroantimonate is not, however as simple as might at first be thought, and has been examined in more detail in this paper.

THEORETICAL

The measurement of electrical conductivity in liquids can be complicated because of electrode polarization effects and the presence of potential barriers at the electrode-liquid interfaces [5]. These problems become more prevalent as the conductivity of the liquid decreases, and can be especially difficult to overcome if a dc measurement is attempted.

For low-conductivity liquids, an ac measurement technique is more desirable, since it greatly alleviates contact problems in the experiment. However, another problem presents itself with the ac technique, which must be taken into account if accurate measurements are to be expected. This problem is the effect on the conductivity measurement due to the capacitive reactance of the test cell construction and the electrode geometry. Thus, the experiment must be carried out at a frequency which is low enough that the capacitance of the cell has no appreciable effect on the measurement. Usually commercial conductivity instruments utilize only one or two test frequencies [2-4]. Caution must be used with this type of instrument in measuring the conductivity of liquids, and usually the manufacturer will give the minimum conductance for which the instrument is useful. However, this minimum conductance is not rigid and depends on the capacitance of the test cell for the liquid.

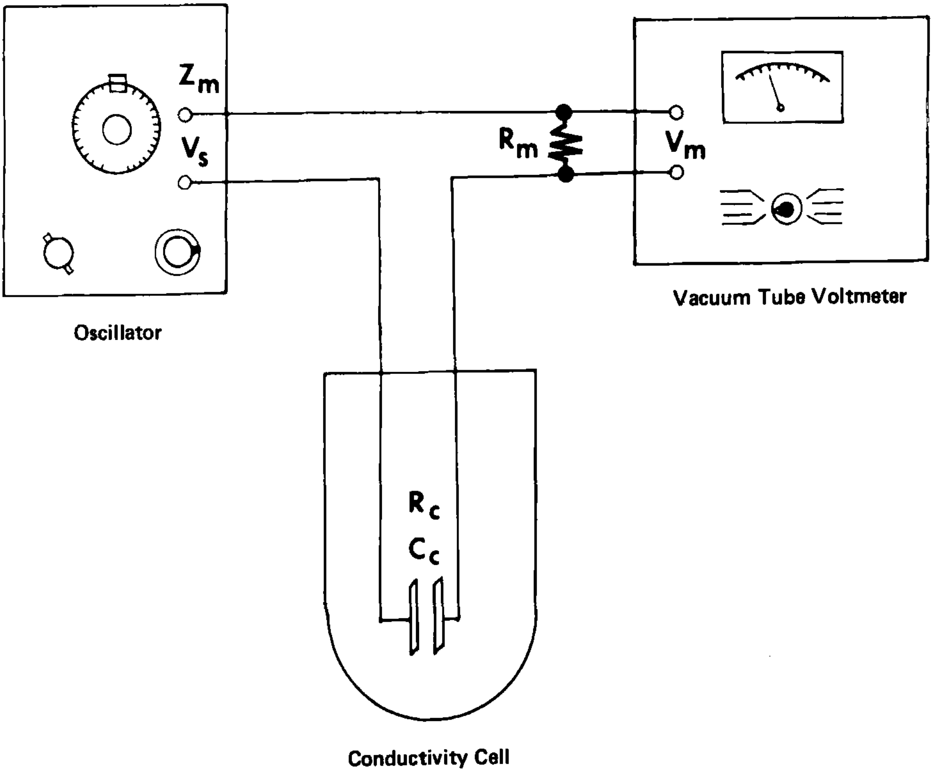

FIG. 1. Schematic of experimental apparatus.

In the experiments reported in this paper, a simple system was constructed for the study of low conductivity liquids. This system uses inexpensive electronic instruments which can be calibrated and has been found to give accurate and reproducible results. Also, by using frequency as a variable in the experiment, the low-frequency dielectric constant of the liquid can be determined with reasonable accuracy.

Figure 1 shows a schematic of the measurement apparatus used in these experiments, along with a simple electrical equivalent circuit. In this figure, R_c and C_c are the resistance and shunt capacitance of the cell, and R_m is the sampling resistor used to measure the current in the network. The ac signal source was calibrated for both frequency and voltage, and the vacuum tube voltmeter was also calibrated across the anticipated frequency range. In the experiment, the quantities V_s and V_m are measured root-mean-square (rms) values at a given frequency, and the quantity Z_m is calculated from:

$$Z_m = (V_s/V_m)R_m \tag{1}$$

Here Z_m is the magnitude of the ratio of V_s and $I = V_m/R_m$. From the equivalent circuit in Fig. 1 the quantity Z_m can be calculated in phasor notation in the following manner. Thus

$$\tilde{Z}_m = \tilde{V}_s/\tilde{I} = R_m + \tilde{Z}_c \tag{2}$$

where

$$\tilde{Z}_c = R_c/(1 + j\,\omega R_c C_c) \qquad j = \sqrt{-1} \tag{3}$$

is the ac impedance of the cell. At low frequencies $(\omega R_c C_c \ll 1)$ $\tilde{Z}_c \approx R_c$. Now from Eq. (2) $\tilde{Z}_m$ can be written as

$$\tilde{Z}_m = [R_c/(1 + j\omega R_c C_c)]\ [1 + (R_m/R_c)\ (1 + j\omega R_c C_c)] \tag{4}$$

or

$$\tilde{Z}_m = \frac{R_c}{1 + j\omega R_c C_c}\ (1 + \frac{R_m}{R_c})\ [1 + j\omega(\frac{R_m R_c}{R_m + R_c})C_c] \tag{5}$$

From this equation the conditions for obtaining the magnitude of the impedence $\tilde{Z}_c$ from the measured quantities given in Eq. (1) can be established. These are

$$R_m \ll R_c \tag{6}$$

$$\omega R_m C_c \ll 1 \tag{7}$$

If these conditions are satisfied even for all frequencies below that required to satisfy (7) $\tilde{Z}_m \approx \tilde{Z}_c$, or

$$Z_m = | Z_c | = R_c/\sqrt{(1 + \omega R_c C_c)2} \tag{8}$$

now, from this equation at low frequencies such that $\omega R_c C_c \ll 1$, then

$$Z_m = R_c \tag{9}$$

which is the desired measurement. Also, for frequencies in the range [where Eqs. (6) and (7) are also satisfied],

$$1/R_c C_c \ll \omega \ll 1/R_m C_c \tag{10}$$

Eq. (8) becomes

$$Z_m = 1/\omega C_c \tag{11}$$

Now, the cell capacitance can be written as

$$C_c = C_w + C_p \tag{12}$$

where C_w is the wiring capacitance and C_p is the parallel plate capacitance of the test cell electrode configuration. Hence, for a parallel plate electrode structure

$$C_p = \epsilon_r \epsilon_o A_p / L_p \tag{13}$$

where ϵ_o is the permittivity of free space (8.85 pf/m), ϵ_r is the dielectric constant, A_p is the electrode area, and L_p is the spacing between electrodes. If the measurement is performed such that conditions (6), (7), and (10) are satisfied then the slope of Z_m versus log ω in this frequency range from Eq. (11) yields C_c. If the wiring capacitance is known and the cell constant (L_p/A_p) accurately determined, then the dielectric constant can be obtained from the measurement.

EXPERIMENTAL

Methylene chloride was purified by the method described by Rooney [8, 9] until it had a specific conductance lower than 10^{-9} ohm^{-1} cm^{-1} [10].

Conductivity Cell

The design was based on Plesch's [10] description. The cell was calibrated with aqueous 0.01 N KCl solution at 0°C, having a specific conductivity [11] of 7.736×10^{-4} ohm^{-1} cm^{-1}. The cell constant was 2.37×10^{-2} cm^{-1}.

Oscillator

A HP-200 CD wide-range (5-500 Hz) oscillator was used. It had been calibrated by a Monsanto Model 101 A Electronic Counter.

Vacuum Tube Voltmeter

A HP Model 400C voltmeter was used.

RESULTS AND DISCUSSION

In order to test the measurement technique, several experiments were performed. First of all, a precision resistance of 1.54×10^{7} ohm was placed in parallel with the test cell filled with air. Figure 2

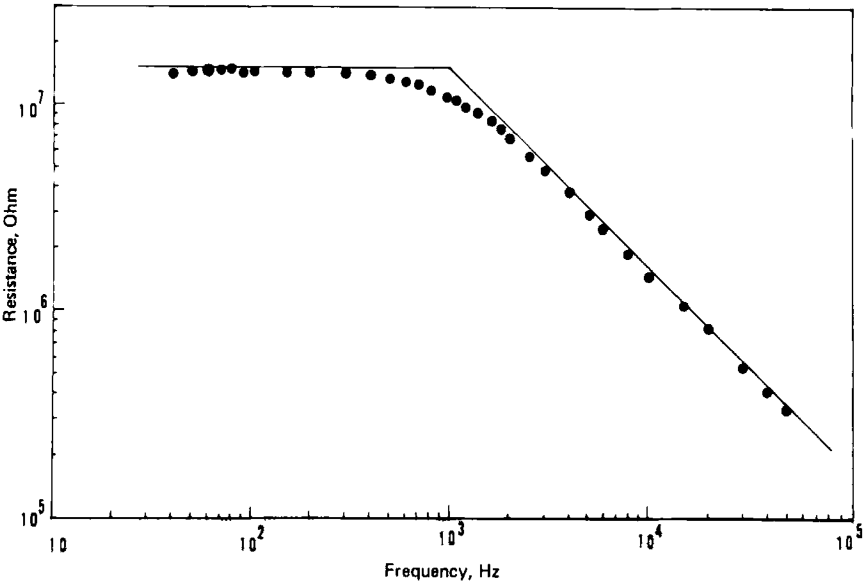

FIG. 2. Effect of frequency on the resistance of a standard resistance; 25°C. Standard resistor: $R = 1.54 \times 10^7$ ohms.

shows the results of this experiment. The resistance measured at low frequencies was 15×10^6 ohm by this technique, within the experimental error of reading the instruments. Other techniques were used to measure the resistance, giving numbers which were all in excellent agreement. In addition, the wiring capacitance was measured by this technique and by others, and the results were well within experimental error. These results are shown in Fig. 2.

Methylene chloride is the most commonly used solvent for conductivity studies on partly dissociated ionic systems used as models for cationic polymerization. This solvent must be very drastically purified (see experimental part), and one of the purity criteria is the specific conductivity should be as low as 10^{-9} ohm^{-1} cm^{-1} [10].

A sample of purified methylene chloride (see experimental part) having very low conductivity and known dielectric constant was studied. The results of this experiment are shown in Fig. 3.

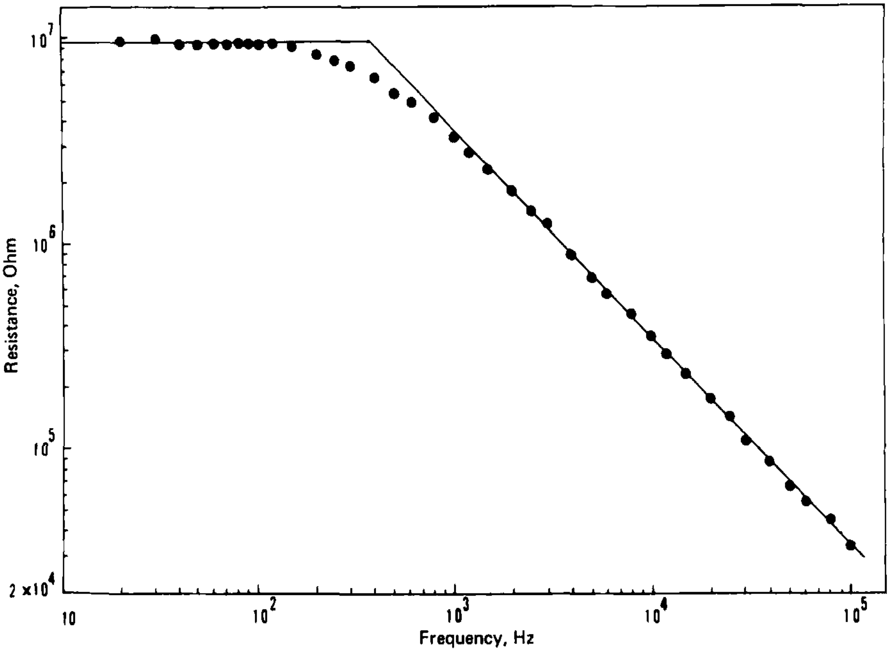

FIG. 3. Effect of frequency on the resistance of methylene chloride.

CONCLUSION

It appears that the simple technique used here is a useful one for studying conductivity and for measuring dielectric constant of liquids especially in the case of very low conductivity liquids. An example of the method of calculation is given in the Appendix. This technique was used to investigate the dissociation of the system α-chloroethyl ethyl ether-$SbCl_5$, used as a model of the cationic polymerization of the ethyl vinyl ether initiated by $(Ph)_3C^+SbCl_6^-$, these results will be described in Part II. A more accurate experimental arrangement is planned for the future to enhance the precision with which these measurements can be made.

APPENDIX: EXAMPLE OF CALCULATION OF DIELECTRIC CONSTANT

Cell constant measured = $(L_p/A_p) = 2.37 \times 10^{-2}\ \mathrm{cm}^{-1}$

Empty cell:

$$\epsilon_o = 8.85\ \mathrm{pf/m}$$

$$C_p = \epsilon_o\,(A_p/L_p) = 3.73\ \mathrm{pf}$$

Empty cell with wire:

$$C_c = 10.8\ \mathrm{pf}$$

$$C_w = C_c - C_p = 7.07\ \mathrm{pf}$$

Filled with CH_2Cl_2, at 0°C:

$$R_{CH_2Cl_2} = 9.67 \times 10^6\ \mathrm{ohm}$$

$$f = 375\ \mathrm{Hz}$$

$$C_c' = \frac{1}{2\pi R_{CH_2Cl_2} \cdot f} = 43.9\ \mathrm{pf}$$

$$C_p' = C_c' - C_w = 43.9 - 7.07 = 36.83\ \mathrm{pf}$$

Dielectric constant of CH_2Cl_2 (at 0°C)

$$\epsilon_r = \frac{36.83}{3.73} \approx 9.87$$

The value reported in the literature [7] is 9.92.

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