

Conductometric Studies of Simple Electrolytes and Micellar Solutions

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A new technique was developed to measure the conductance of a conductive type of cell. A theoretical model was designed. Similar to spectroscopy in IR/UV-vis, the frequency of the input signal was swept from a few hertz to 1 MHz and the conductance of the whole cell was measured. The developed theoretical model was in good agreement with the experimental results. Change of conductance with concentration between simple electrolytes such as HCl solution with micellar solution was compared. The concentration limits of HCl as low as 45 μM was measured. Critical micellar concentrations of two types of micelles, sodium salt of dodecyl sulfate and 1-cetylpyridinium chloride monohydrate were measured. It was shown that a voltage divider circuit can be used for conductometric titrations.

Key Words: Conductometry, Oscillometry, Micellar solution, Electrolytes, Titration.

INTRODUCTION

Oscillometric measurements using capacitive cell or condenser-type cell was discussed in detail¹. In this type of cell, solution to be analyzed is placed between external, parallel metal sheet electrodes. Since the solution is insulated from the metal plates by the walls of the container, the measurements and characterization methods can only be performed at high frequencies. For these purposes, the electrodeless cells were used for high frequency titrations and an extensive study of high frequency titrations and their applications was conducted². In addition, oscillometric measurements were used to characterize the structural properties of solutions³⁻⁵.

In an experimental attempt to verify the Debye-Falkenhagen effects, a capacitor cell was used⁶. Using this cell, detailed theoretical and experimental investigation of Debye-Falkenhagen effect by means of modern network analyzer was studied⁷. Consequently, the overall circuit response of this type of cell, which was studied incompletely² or misunderstood^{5,6}, was clarified.

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In another work, the conductive types of cells, in which the electrodes are in contact with electrolytes, were studied⁸. Using network analyzer, the measurements were performed at the frequency range of tens of MHz and conductometry of conductive type cell was carried out. The present work is a further study of a conductive type of cell from low to high frequencies.

In order to measure accurately the conductance as a function of frequency, Wheatstone bridge is used². However, Wheatstone bridge should be balanced at each measurement point. In this work, by adopting a theoretical model to measurement results, a voltage dividing technique is developed. Using this method, automated conductometry measurements of concentrations as low as 45 μM were carried out.

In the following sections, conductometry of conductive type cell from a few hertz to 1 MHz signal frequency range is studied. The equivalent model for the conductive type cell and the equation of conductance are explained in theory part, experimental procedure and the measurement setup are presented in experimental section, followed by a discussion of the measurement results in results and discussion and finally a conclusion is drawn.

Theory: An equivalent circuit for cells of conductive type is given in Fig. 1. The capacitor (C_{DL}) is due to the double-layer capacitance and inductor (L_{wire}) is mainly due to the wirings. The parasitic capacitor that forms between the parallel plate electrodes is modeled by C_{SOL} . The dielectric of this capacitor is the solution material. The voltage-dividing resistor is shown by R_{VD} , while R_{SOL} is the resistance of the solution. Typical values of double-layer capacitance (C_{DL}) are several orders of magnitude larger than the solution capacitance (C_{SOL}). Thus, the impedance of the parasitic capacitor (C_{SOL}) was ignored.

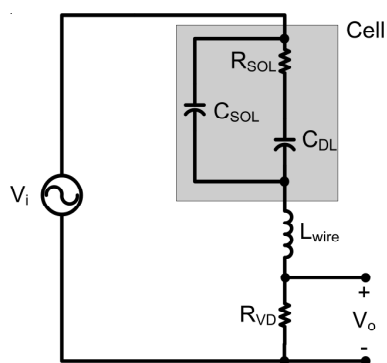


Fig. 1. Circuit model of a voltage divider

Thus, the ratio of output potential to input potential of the circuit model shown in Fig. 1 is computed as:

$$\frac{V_o}{V_i} = \frac{R_{\text{VD}}}{R_{\text{SOL}} + R_{\text{VD}} + \frac{1}{j\omega \cdot C_{\text{DL}}} + j\omega \cdot L_{\text{wire}}} \quad (1)$$

where, ω is the angular frequency of the input voltage source. After the necessary transformations, the amplitude and the phase angle are obtained:

$$A(\omega) = \left[\frac{R_{VD}^2}{(R_{SOL} + R_{VD})^2 + \left(\omega L_{wire} - \frac{1}{\omega C_{DL}} \right)^2} \right]^{1/2} \quad (2)$$

$$\varphi(\omega) = -\tan^{-1} \left\{ \frac{1}{R_{VD} + R_{SOL}} \left(\omega L_{wire} - \frac{1}{\omega C_{DL}} \right) \right\} \quad (3)$$

The graph of eqn. 2 as frequency varies from 10 Hz to 1 MHz is plotted in a semilog scale in Fig. 2. Typical values of $R_{SOL} = R_{VD} = 1 \text{ k}\Omega$, $C_{DL} = 1 \text{ }\mu\text{F}$ and $L_{wire} = 1 \text{ mH}$ are chosen. The peak occurs at the resonant frequency (f_r), which is defined as:

$$f_r = \frac{1}{2\pi\sqrt{L_{wire} \times C_{DL}}} \quad (4)$$

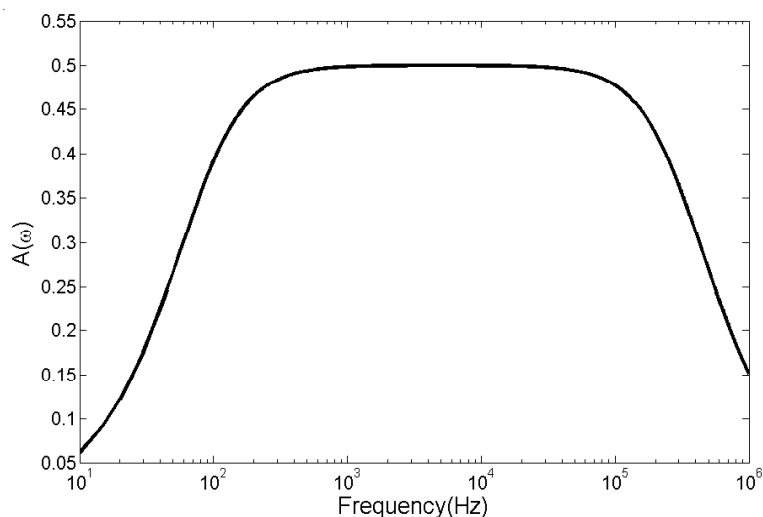


Fig. 2. Amplitude response *versus* frequency

For the above typical values, the resonant frequency is computed as $f_r = 5 \text{ kHz}$. As seen from the graph of $A(\omega)$ in Fig. 2, a flat region in the vicinity of the resonant frequency is observed. At the peak, where the resonance occurs, the reactance of the inductor (L_{wire}) and capacitor (C_{DL}) cancel each other. Thus, $A(\omega)$ is further simplified as:

$$A(\omega_r) = \frac{R_{VD}}{R_{SOL} + R_{VD}} \quad (5)$$

where, $\omega_r = 2\pi f_r$. Using eqn. 5, the solution resistance (R_{SOL}), or alternatively, the conductance of the solution (g_{SOL}), is written as:

$$g_{SOL} = \frac{1}{R_{VD}} \cdot \frac{A(\omega_r)}{1 - A(\omega_r)} \quad (6)$$

Therefore, by measuring the ratio of output voltage (V_o) to input voltage (V_i) at the resonant frequency, the conductance of the solution using eqn. 6 is computed. By increasing concentration, the conductance of electrolyte increases and consequently, the peak increases in Fig. 2.

In order to further investigate the impact of the solution parasitic capacitance (C_{SOL}) on the frequency response of the cell, circuit of Fig. 1 was simulated by a typical capacitor value of 1 nF ($C_{SOL} = 1$ nF). Fig. 3 shows the results obtained for three different values of the solution resistances. As suggested by eqn. 5, Y-axis was scaled by the proportionality factor $(1 + R_{SOL}/R_{VD})$. Thus, all the three curves have identical values at the resonant frequency. However, with the increasing value of solution resistance (R_{SOL}), as depicted in Fig. 3, a high frequency overshoot in the output characteristic showed up. This is an indication of signal by passing through the parasitic solution capacitance (C_{SOL}) rather than the series connection of the solution resistance (R_{SOL}) and the double-layer capacitance (C_{DL}). On the other hand, the flat region in the vicinity of the resonant frequency is unchanged comparing with Fig. 2. Therefore, as the value of the solution resistance varies, the value of $A(\omega) \times (1 + R_{SOL}/R_{VD})$ is constant at the resonant frequency. This verifies eqn. 5 and consequently, eqn. 6 as a method of measuring the conductance of a solution.

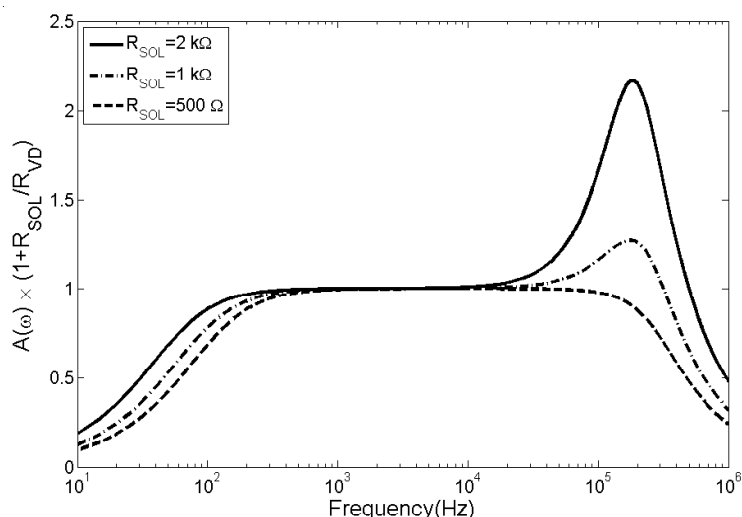


Fig. 3. Amplitude response *versus* frequency as the solution resistance increases

EXPERIMENTAL

In the previous work, high frequency conductometry of capacitive cells were considered⁷. However, in present work, a frequency response of a few hertz to 1 MHz range for conductive type of cell is studied. In conventional conductometry, usually a Wheatstone bridge is used to measure conductance of a solution. In the proposed technique, a voltage divider is used rather than Wheatstone bridge. As a result, automated conductometry is carried out.

As a signal source, a function generator which could supply sine wave signals with frequencies of a few hertz to 1 MHz was used. Signal amplitudes were measured using a conventional two-channel oscilloscope. The function generator output was connected to channel A, while the voltage across the voltage-dividing resistor was measured through channel B. The measurement bandwidth of combination of oscilloscope and probes was chosen to be well above the operating frequency of the whole circuit. Non-porous platinum electrodes with the area of 1 cm^2 were used. A 50 mL pipette was employed for doing the titrations. Experiments were done at $25 \text{ }^\circ\text{C}$.

Sodium hydroxide pellets were used for preparing hydroxide solutions. Analytical grade hydrochloric acid was employed for preparing various concentrations of hydrochloric acid. Two concentrations of 12 and 1.2 mM HCl were used. Dodecyl sulfate sodium salt (SDS) and 1-cetylpyridinium chloride monohydrate (CPC) were used to prepare micellar solutions. Merck was the supplier.

Procedure: The apparatus was assembled as shown in Fig. 4. A $1 \text{ k}\Omega$ resistor was connected in series to the conductive cell. This resistor and the electrolytic cell together, were considered a voltage divider. Sine wave signals were applied across both the resistor and the electrolytic cell. Frequency of the function generator was swept from a few hertz to 1 MHz. Oscilloscope was used to measure the voltage across the $1 \text{ k}\Omega$ resistor connected to channel B. Function generator output was connected to channel A. The ratio of signal amplitude on channel B to the signal on

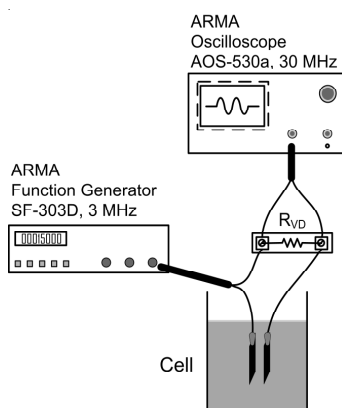


Fig. 4. Instrument and measurement setup

channel A, were computed. If the current is low as in the case of pure water, the measured potential across 1 k Ω resistor is low. On the other hand, for more concentrated solutions, the current is high and consequently, the measured potential across the resistor is high.

In order to measure the conductance, several solutions with different concentrations were prepared and the amplitude response $[A(\omega)]$ was computed. The best fitted curves to the measured data points, in a least-square sense, were depicted and the resonant frequency was identified. Thus, the amplitudes at the resonant frequency $[A(\omega_r)]$ and the corresponding solution conductances (g_{SOL}) were computed.

RESULTS AND DISCUSSION

Figs. 5 and 6 depict the conductances *versus* frequencies for hydrochloric acid at various concentrations. Semilog plots are used. Fig. 5 illustrates the data for HCl

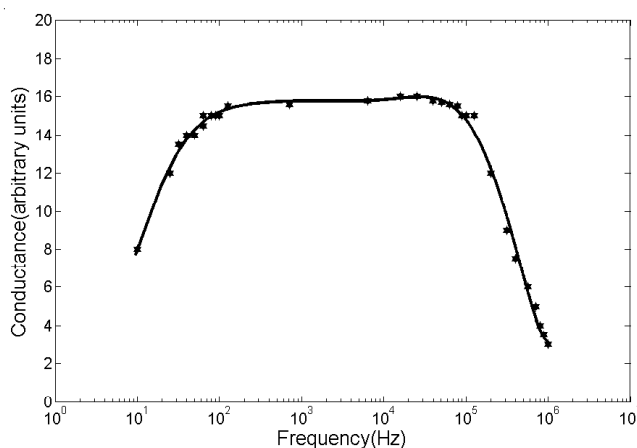


Fig. 5. Conductance of 10 Hz to 1 MHz of 12 mM HCl solution

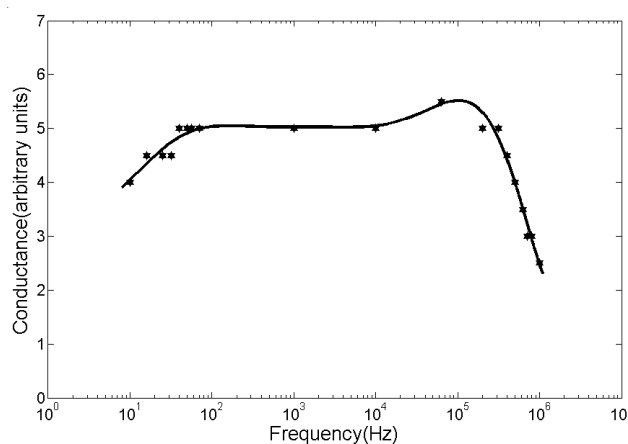


Fig. 6. Conductance of 10 Hz to 1 MHz of 1.2 mM HCl solution

by weight 12 mM. There is a very good agreement between the experimental Fig. 5 and the theoretical Fig. 2. Three regions are observed in Fig. 5, the increasing region is due to the impedance of the double-layer capacitor, the flat region is due to the conductance of the solution and the decreasing region represents impedance due to the inductance of the wiring. The signal by passing through the solution parasitic capacitor (C_{SOL}) of the dilute solution, starts to appear as an overshoot in Fig. 6, which is similar to the conductance of water in Fig. 7. Fig. 8 depicts the conductance of HCl solutions at various concentrations. Semilog plot is used for this demonstration. Conductances initially increase with concentration linearly and then a flat region appears. The range of concentrations of HCl in Fig. 8 is from 45 μ M to 12 M. This suggests sensitivity of the technique in measuring concentrations as low as 45 μ M HCl.

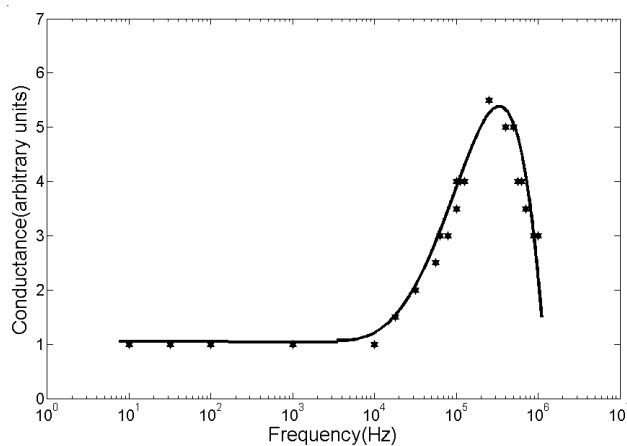


Fig. 7. Conductance of 10 Hz to 1 MHz of water

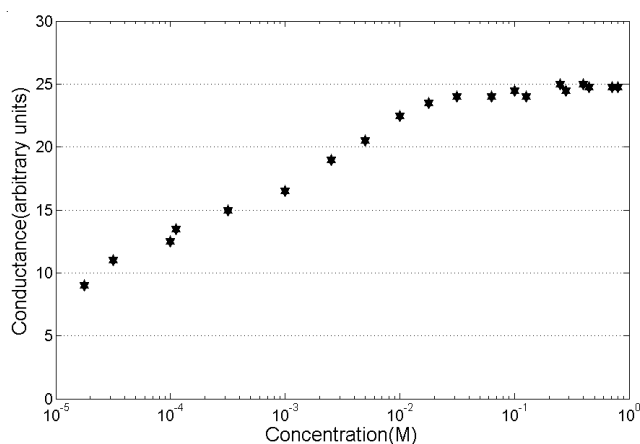


Fig. 8. Conductance of HCl solutions *versus* concentration

Conductometry of micellar solutions using conductivity probe was reported in the previous literature⁹. In order to investigate the functionality of the developed technique, conductometry of the micellar solutions were carried out. Figs. 9 and 10 show the measurements of conductance *versus* concentration for SDS and CPC

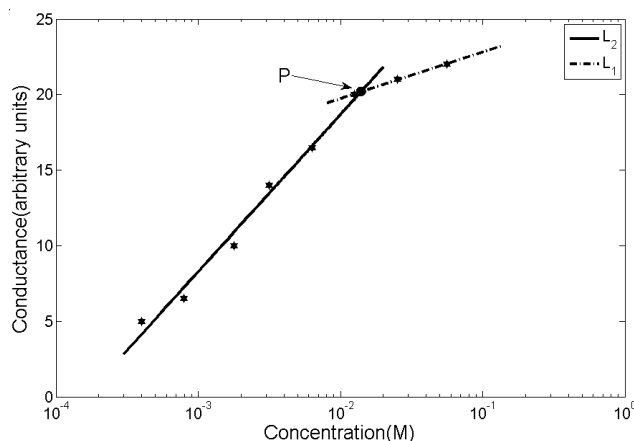


Fig. 9. Conductance of SDS solutions *versus* concentration

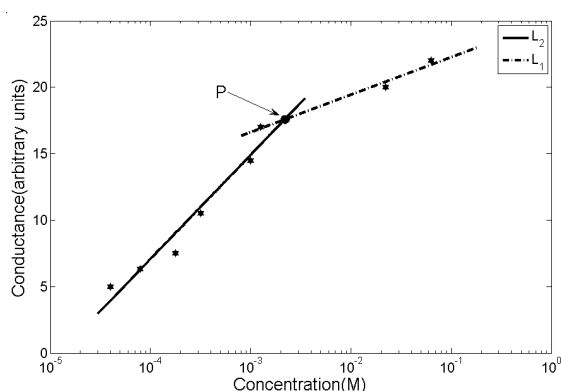


Fig. 10. Conductance of CPC solutions *versus* concentration

solutions, respectively. In both plots, two regions of conductance are observed. The first region is the part with greater slope and the second region is the part with smaller slope. The smaller slope region is due to the formation of micelles. The intersection point between smaller slope region and greater slope region in both groups of data is the critical micellar concentration (CMC). In order to determine the CMCs for both SDS and CPC solutions, the least square analysis was used^{10,11}. Using this method, straight lines were passed through the last three data points in conductivity diagrams of SDS and CPC solutions. Other straight lines were passed through the first five data points. The equations obtained for these straight lines for SDS and CPC solutions are shown in Table-1. For simplicity, variable X is defined

as the logarithm of the concentration. The coordinates of the intersection points are $X_p = -1.84, Y_p = 20.03$ and $X_p = -2.4, Y_p = 18.2$ for SDS and CPC solutions, respectively. Thus, the critical micellar concentration (CMC) for SDS solution is computed as 14.5 mM. The extracted value of CMC for CPC solution is 4 mM.

TABLE-1
CRITICAL MICELLAR CONCENTRATION
CALCULATION FOR SDS AND CPC SOLUTIONS

	Equations of lines: L_1 and L_2	Coordinates of intersection point (P)	CMC (M)	Comment
SDS	$L_1: Y = 3.2X + 25.9$ $L_2: Y = 10.3X + 39$	$X_p = -1.84$ $Y_p = 20.03$	0.0145	X is defined as $\log [C(M)]$
CPC	$L_1: Y = 2.8X + 24.8$ $L_2: Y = 6.6X + 34$	$X_p = -2.4$ $Y_p = 18.2$	0.0040	

In addition to measuring conductance by this technique, this conductive type of cell, combined with a voltage divider can be used for titrations. Fig. 11 shows the results of titration of 22 mM NaOH with 0.1 M HCl. As can be seen, this titration curve is V-shape. The minimum of the curve and its corresponding coordinate on the X-axis is the equivalent point.

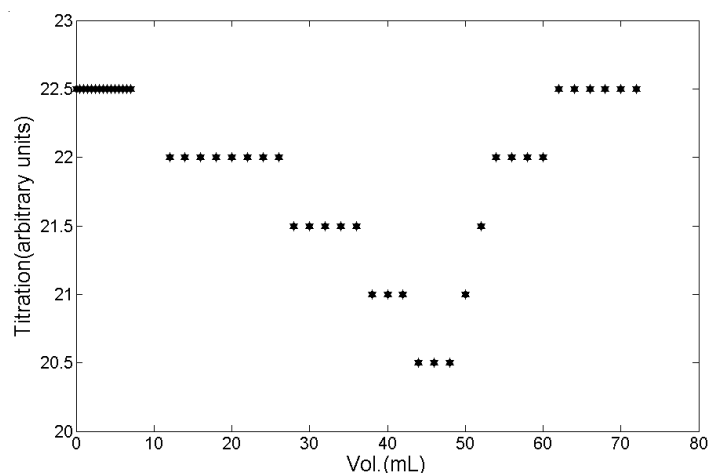


Fig. 11. Titration of 22 mM NaOH with 0.1 M HCl

Conclusion

A new technique for conductometry of simple electrolytes and micellar solutions was developed. Good agreement between experimental measurements and theoretical model was observed. It was shown that this technique can be used for conductometric titration. The automated technique proposed in this article constitutes an efficient method for detailed observation of the conductances of simple electrolytes and micellar solutions.

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