An Experimental Investigation of Ionic Vibration Potential Sensing in Electrolytes

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Abstract

Passing of an ultrasonic wave through an ionic solution results in distortion in electric balances between anion and cation ions, generating Ionic Vibration Potential (IVP) signals in solution for various electrolytes. In previous work, methods of Colloid Vibration Potential (CVP) imaging for characterization of nano-particle suspensions have been reported. This paper reports the further work on effect of IVP for various 1-1, 1-2 and 1-3 electrolytes, including NaCl, KCl, RbCl, CsCl, MnCl2, CuCl2, FeCl2 and FeCl3. Transition metals were chosen to understand the effect of different valences but also to understand how IVP signals change due to the closeness of atomic weight of these metals. Concentration and electrical conductivity effects were also measured. Group 1 chlorides were used to compare non-invasive imaging results with invasive imaging results from previous work. Two different valences of iron were used to investigate the effect of the number of anions on signal amplitude.

Keywords: ultrasound; ionic vibration potential (IVP); electric charge; valence; anion; atomic weight

1. Introduction

Ionic Vibration Potential (IVP) imaging is an electro-acoustic measurement method originating from the potential difference between two separate points of a homogeneous electrolyte due to ultrasound waves. Many features and behaviors of ions can be determined by this method. The ultrasonic wave causes dynamic reaction of ions in

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electrolytes which is different for each ion due to effective mass and charge differences among anions and cations. Solutions containing a balance of anions and cations are overall neutral. When a pressure wave is applied to such a solution, it results in a disruption of the balance. Consequently, an electric dipole will be formed resulting in an electric field. This electric field is known as IVP for electrolytic solutions and CVP (Colloidal Vibration Potential) for colloidal solutions. In general, it can be said that ultrasonic waves cause ions or particles acceleration and this acceleration changes the electrical neutrality around the ions (anions and cations) or particles and counter-ions (formation of dipoles) which produces an electrical current in electrolytes [1]. Non-invasive imaging method is used in medical science for a wide range of applications for example kidney stone imaging by ultrasonography which is based on pulse and echo technique and is applicable for structural organs [2]. The current research is based on non-invasive sensing to explain and address the electro-acoustic measurements on non-structural solutions like electrolytes. The reported method, which is based on vibration potential, has a potential to be employed for non-structural imaging in medical science.

1.1. The IVP Theory

For the first time, application of ultrasound in electrolytes was introduced by Debye (1933) to determine how a pressure wave can form dipoles and how they can change solution potential via oscillations of ions [4-6]. Debye had concluded that due to the small masses of ions, the dynamic reaction can be taken as negligible in relation to the friction among the ions. However, Debye also mentioned that the ions have different masses in solution in which they may show different potentials and acceleration when a sound wave passes through the solution. So, a dynamic potential due to changes in ion acceleration will be created. This potential in the electrolyte solution can be measured known as the Ionic Vibration Potential (IVP) [4], [6].

Debye had considered the second law of Newton to present his model:

$$e_jX - \rho(v_j - v_0) = m_j \frac{dv_j}{dt}$$  \hspace{1cm} (1)

The first term indicates the electric force due to charges that arise in the solution. Because of the velocity gradient of ions and solvent (liquid), the frictional force is introduced as the second term. In the equation, $e_j$ and $X$ are electrical charge and the electric field strength, respectively. $v_j$ and $v_0$ represent the velocity of ion (jth ion) and solvent velocity respectively. $m_j$ is the mass of jth ion in the solution.

Later, the equation was extended to achieve an approximation for the IVP [8]:

$$\phi = \frac{a_0g m_H}{\epsilon} \sum p_j \frac{z_j^2 M_j}{\rho_j} \frac{4 \pi \lambda / \omega D}{\left[1 + (4 \pi \lambda / \omega D)^2 \right]^{1/2}} \exp(\omega t - \sigma x - \Delta)$$  \hspace{1cm} (2)

where, $\Delta = \arctan(\omega D / 4 \pi \lambda)$

In equation (2), $\omega$ and $a_0$ are the angular frequency of the ultrasonic waves and the velocity amplitude, $g$ represents the wave velocity which is propagated through the solution, $\sigma$ is the same as $\omega / g$, $\lambda$ is called the specific conductance of the solution (for this term, the ion interactions are so small and therefore ignored), $D$ is introduced as the dielectric constant of the solvent (water), $m_H$ is the hydrogen atom mass which is equal to $1.67 \times 10^{-24}$ g, $\epsilon$ is indicative of the fundamental electric charge that is equal to $4.8 \times 10^{-10}$ e.s.u, and $p_1$, $p_2$, ..., $p_i$, ..., $p_n$ are indicative of the relative numbers per unit volume of the various types of ion valences which are $z_1$, $z_2$, ..., $z_i$, ..., $z_n$, $M_1$, $M_2$, ..., $M_i$, ..., $M_n$ and $\rho_1$, $\rho_2$, ..., $\rho_i$, ..., $\rho_n$ are the ionic weights in terms of gram and frictional coefficient, respectively.
Bugosh et al. [1947] [7] derived a new concept - Ionic Vibration Current (IVC). The basis of that theory is a system with \((2N+1)\) equations which can determine the behaviors of the electro-diffusion effects, whenever a mechanical pressure wave passes through an electrolyte of \(N\) electrolyte components. For a wave propagating into an electrolyte in the \(x\) direction, the sum of all forces applying on the ion in the electrolyte should be equal with acceleration of ions multiplied with their masses [7]:

\[
e_j X - \rho_j \left( v_j - v_0 \right) - e_j \left\{ \frac{e_j e_2 q K X}{\left( 3 D k T \right) \left[ 1 + \sqrt{q (1 + j w \Theta)^2} \right]} \right\} - \frac{e_j X K \rho_j}{6 \pi \eta_0} \frac{\partial n_j}{\partial x} + \frac{V_j \sigma_0}{n} = \frac{m_j}{\partial t} \frac{\partial v_0}{\partial t}
\]

Hermans [5], based on his experiments, concluded that the relaxation, diffusion, electrophoretic terms in equation 3 have negligible effects and can be ignored. He expressed the equation which represents the IVC:

\[
\text{IVP} = \frac{c_m}{U_m} \left[ \frac{t \ ' W^+}{z^+} - \frac{t \ ' W^-}{z^-} \right] \sqrt{1 + \frac{\omega^2}{\omega_{MW}^2}}
\]

where, \(U_m\) known as amplitude of oscillation velocity, \(z^\pm\) parameters represent the valances of the cation and anion, \(N_A\) is Avogadro number, \(cm\) is the speed of sound in the electrolyte, \(t \ ' \) represent the number of transport of anion and cation, \(W^\pm\) are the anion and cation molar masses and \(\omega_{MW}\) represents the Maxwell-Wagner frequency.

Later O’Brien (1988) [9] suggested a new method for measuring the potential of particles within colloidal suspensions. He derived equation (5) to find the electric field which is produced due to the pressure gradient arising from wave propagation within the solution [9].

\[
E = \frac{\phi \Delta \rho \mu_e}{\rho_m K^*} \nabla P
\]

where \(\phi\) is the volume fraction of the colloidal particles in the fluid, \(\rho\) is the density of solution, \(\mu_e\) is the electrophoretic mobility of the particles, \(K^*\) is the conductivity of the suspension, \(\Delta \rho\) is indicant of the density difference between particle and liquid.

2. Material and Methods

2.1. Materials

Vanadium chloride (VCl₃) 98%, manganese chloride (MnCl₂) 99.0%, iron (II and III) chloride (FeCl₂ and FeCl₃) 99% and 98%, and copper chloride (CuCl₂) 99% were purchased from Sigma-Aldrich. Alkali metals including sodium chloride (NaCl) 99.5%, potassium chloride (KCl) 99.0%, rubidium chloride (RbCl) 99.8% and Cesium chloride (CsCl) were purchased from Sigma-Aldrich.
2.2. Methodology

A novel method for ex-situ IVP imaging was carried out where there was no physical contact between electrodes and sample. The block diagram and the picture of the experimental system are indicated in Figures 1 and 2.

![Block diagram of the experiment system along with sample chamber.](image1)

**Fig. 1.** The block diagram of the experiment system along with sample chamber.

![Layout of experiment equipment.](image2)

**Fig. 2.** The layout of experiment equipment.

Within the experiment, several equipment were employed which can be divided into two streams, an input and output. The input involves equipment necessary for producing the ultrasonic wave including a signal generator, gated amplifier, impedance matching box and transducer. The output contains equipment for monitoring the response signal either as a current or voltage attached to an oscilloscope. The signal generator was set up for generating burst sinusoidal signals (Agilent 33250A) with a period of 50 ms, 6 cycles and 1 MHz frequency which are amplified to 1000 volts by the gated amplifier (RITEC-GA 2500A). The amplified signals are passed through the impedance matching resistor before being sent to the transducer. The transducer (Sonatest SLIM 1-25, 1MHz, 25mm diameter) converts the generated electrical waves to ultrasonic mechanical waves which are applied into the solution. The current amplifier (FEMTO-DHPCA-100) amplifies the ultra-weak signal generated as IVP signal with a gain of $10^4$ V/A, and monitored on the oscilloscope (Lecroy Wavesurfer 454). The apparatus system includes an experimental device which is used to contain the experimental materials, delay line solution and electrodes during the test. This box has 33 cm length, 7.5 cm width and 13.5 cm height. Two slots for installing the sample chamber with the testing medium are embedded within the device. A Perspex sample chamber for containing the testing samples was used and both sides covered with cling film. The thickness of the cling film is much less than the ultrasound wave length therefore the wave passes through the chamber easily without delay by assuming that the interface effect is negligible. This sample chamber is shown in Figure 1.
The sketch of the experimental device along with the sample container and electrodes is shown in Figure 3. A circuit diagram is applied for measuring current within experiment shown schematically in Figure 3. The water that is functioned as a delay line is employed as electrical impedance and polyethylene (cling) film is used as a coupling capacitance. Therefore, E1 and E2 represent electrical potentials, and Z1, Z2 and C1, C2 are shown as electrical impedances and coupling capacitances of the plastic film respectively.

3. Results and Discussion

The signal is detected and analyzed using the experiment system. A program code with the name Moving Window Match Filter Demodulation (MWMFD) was employed to demodulate the alternating signals. A typical IVP signal generated in copper chloride (3 M) solution is shown in Figure 4(a), which is much smaller that the CVP signal reported for nano-particle suspension [10]. Figure 4(b) indicates the IVP amplitudes obtained as a function of electrolyte type tested.

Concentration and atomic weight effect: According to Figure 4(b), the IVP amplitude for all components decreased with increasing of electrolyte concentration. Moreover, except for MnCl2, it can be concluded that increasing of atomic weight can result in larger response amplitudes. This is very true for 2 and 3 M concentrations.
Valence effect: Although the atomic weight of manganese (54) is larger than vanadium (50.9), its IVP amplitude is smaller than vanadium. This is due to the affinity of ions and counter ions which result in strong bonds. Furthermore, valence effect has a dominant effect on. Higher valence of ions requires more anions to keep the solution neutral, thus larger electron clouds are needed to ensure neutrality. Therefore, large IVP will be formed when the valence is increased. To understand effect of valence better, iron (II and III) chloride were tested. In this condition, the atomic mass of metal ion in both cases was constant. According to Figure 4(b), it was observed that FeCl$_3$ had a larger amplitude comparing to FeCl$_2$. The same trend was noted at all concentrations. Consequently, it can be said that the number of anions within the solution had a great effect on the IVP amplitude. This phenomenon can be explained according to mathematical theories proposed previously. According to equation (4), IVP has an inverse relation to valence ($z^+$) and a direct relation to the number of transport of anion and cation ($t^\pm$). Based on these solutions, W has a greater effect on IVP signal. For example for each molecule of FeCl$_2$ and FeCl$_3$ in the solution except for $z^+$, $\text{FeCl}_2$ and $\text{FeCl}_3$, all other factors are the same, therefore:

\[
IVP = K \left[ \frac{i^W z^+ - t^W z^-}{z^+} \right]
\]

Therefore, the theoretical ratio will be:

\[
\begin{align*}
IVP_{\text{FeCl}_3} &= K \left[ \frac{1 \times 55.8}{3} - \frac{3 \times 35.4}{-1} \right] = 124.8K \\
IVP_{\text{FeCl}_2} &= K \left[ \frac{1 \times 55.8}{3} - \frac{2 \times 35.4}{-1} \right] = 98.7K
\end{align*}
\]

\[
\text{IVP}_{\text{FeCl}_3} = 1.26
\]

Experimentally, for a 1 M solution, a ratio of 1.266 was found agreeing well with the theoretical value of 1.26 for a 1 M solution. For a 3 M solution, 1.66 was determined to be the ratio. It can be seen that FeCl$_3$ results in larger IVP signals. Consequently, it can be concluded that valence has an important effect on IVP amplitude which should be considered.

According to Figure 4(b), MnCl$_2$, FeCl$_2$ and CuCl$_2$ have the same valences; therefore atomic weight will be the main and important factor. Thus, it can be observed that IVP amplitude increases with increasing atomic weight. The same effect is noted for VCl$_3$ and FeCl$_3$. FeCl$_3$ has a larger mass than VCl$_3$; therefore IVP measured for FeCl$_3$ is as expected, i.e. larger than VCl$_3$.

Electric conductivity effect: As shown in equation (5), conductivity has inverse proportionality effect on IVP amplitude ($E \propto 1/K$). Therefore, conductivity of all electrolytes was measured and plotted in Figure 5(a). It is clear that conductivity increases linearly with increasing of concentration. Also, Figure 5(b) indicates how the IVP amplitude is changing with changing concentration. Finally what can be understood from the figures is that IVP amplitude is decreased when conductivity is increasing.

![Fig. 5. The concentration effect on conductivity (a) and IVP amplitude (b) of electrolytes](image)
Furthermore, this experimental method was applied for electrolytes in group 1 of the periodic table and results were compared with outcomes provided by Zana in 1967 [11]; both results are plotted in Figure 6(a). As shown in Figure 6(a), concentration has little effect on amplitude in both experiments for this group of electrolyte. However, increasing concentration provides increased conductivity as shown in Figure 6(b) in solutions and according to equation (5) conductivity has an inverse proportionality to IVP amplitude. But since concentration has little affect on the IVP amplitude as shown in Figure 6(a), it can be said that the conductivity also has little effect on the IVP amplitude, therefore some other factor must be changing the amplitude. This other factor is the atomic weight. Increasing atomic weight results in increasing of IVP amplitude. For instance, in 2 M solution, the mass of Cs$^+$ (32.9) > Rb$^+$ (5.47) > K (39.1) > Na (22.99), therefore amplitude of CsCl > RbCl > KCl > NaCl.

As shown in Figure 7, IVP amplitude was increased with increasing of atomic mass of metal ions in group 1 and transition metals; however, valance affect and conductivity of solution are important factors and they should to be considered in intensity of amplitude.

Fig. 6. (a) Concentration and atomic mass effect of ions on IVP amplitude; (b) Concentration effect on conductivity.

Fig. 7. Atomic mass effect on IVP amplitude for variety of 1 M electrolytes with different valences.
4. CONCLUSION

A wide range of electrolytes were utilized to investigate the effect on IVP signals using non-invasive measurement techniques. IVP imaging was applied for electrolytes successfully; however amplitude was much smaller than colloidal (nanoparticle) solutions. The atomic weight range of ions was 30 to 200 pm. Signal generated had a direct relation to atomic mass of metal ions; the heavier the metal ion, the larger the IVP signal. Number of anions had a great effect on the amplitude and it can be seen that metal ions with higher valence can produce greater IVP signal. This evidence is indicated for FeCl$_3$ and FeCl$_2$. FeCl$_3$ results in a larger amplitude than FeCl$_2$ due to the greater number of anions in solution for FeCl$_3$. Therefore, spatially, the electron cloud is bigger. In addition, it was found that although manganese (MnCl$_2$) has a higher atomic weight than vanadium (VCl$_3$), the amplitude was smaller than VCl$_3$ due to their different valence. It was found that increasing concentration reduced the IVP amplitude. The electrical conductivity shown an important factor which has an inverse proportionality with IVP signals.

References