The 7th World Congress on Particle Technology (WCPT7)

An Experimental Investigation of Ionic Vibration Potential Sensing in Electrolytes

Mohammad Hosseini, Lucy Bramson and Mi Wang*

Institute of Particle Science and Engineering, School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK

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, $MnCl_2$, $CuCl_2$, $FeCl_2$ and $FeCl_3$. 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.

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

* Corresponding author.
  E-mail address: m.wang@leeds.ac.uk

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:

$$e_j X - \rho(v_j - v_0) = m_j \frac{dv_j}{dt} \tag{1}$$

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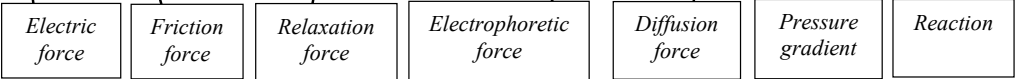
Later, the equation was extended to achieve an approximation for the IVP [8]:

$$\phi = \frac{a_0 g m_H \sum p_j z_j M_j / \rho_j}{\varepsilon \sum p_j z_j^2 / \rho_j} \cdot \frac{4\pi\lambda / \omega D}{\left[1 + (4\pi\lambda / \omega D)^2\right]^{\frac{1}{2}}} \exp i\left(\omega t - \sigma x - \Delta\right) \tag{2}$$

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

In equation (2), ω 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, σ is the same as ω/g, λ 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 1.67×10^{-24} g, ε is indicant of the fundamental electric charge that is equal to 4.8×10^{-10} e.s.u, and p_1, p_2, ...,p_j,...,p_n are indicant of the relative numbers per unit volume of the various types of ion valences which are z_1, z_2, ...,z_j, ..., z_n. M_1, M_2, ...,M_j, ..., M_n and ρ_1, ρ_2, ..., ρ_j, ..., ρ_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 (IVI). 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]:

$$e_j X - \rho_j\left(v_j - v_0\right) - e_j\left\{ \frac{|e_1 e_2| qKX}{(3DkT)\left[1 + \sqrt{q(1+iw\Theta)^{1/2}}\right]} \right\} - \frac{e_j XK\rho_j}{6\pi\eta_0} - \frac{kT}{n_j}\frac{\partial n_j}{\partial x} + V_j s_0 \frac{dv_0}{dt} = m_j \frac{dv_0}{dt} \tag{3}$$

| Electric force | Friction force | Relaxation force | Electrophoretic force | Diffusion force | Pressure gradient | Reaction |

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 IVP:

$$\frac{\text{IVP}}{U_m} = \frac{c_m}{N_A e}\left[\frac{t^+ W^+}{z^+} - \frac{t^- W^-}{z^-}\right]\frac{1}{\left[\frac{\omega^2}{\omega_{MW}^2} + 1\right]^{1/2}} \tag{4}$$

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, $t^\pm$ represent the number of transport of anion and cation, $W^\pm$ are the anion and cation molar masses and ω_{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].

$$E = \frac{\varphi \Delta\rho_m \mu_E}{\rho_m K^*}\nabla P \tag{5}$$

where φ is the volume fraction of the colloidal particles in the fluid, ρ is the density of solution, μ_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 (VCl_3) 98%, manganese chloride ($MnCl_2$) 99.0%, iron (II and III) chloride ($FeCl_2$ and $FeCl_3$) 99% and 98%, and copper chloride ($CuCl_2$) 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.
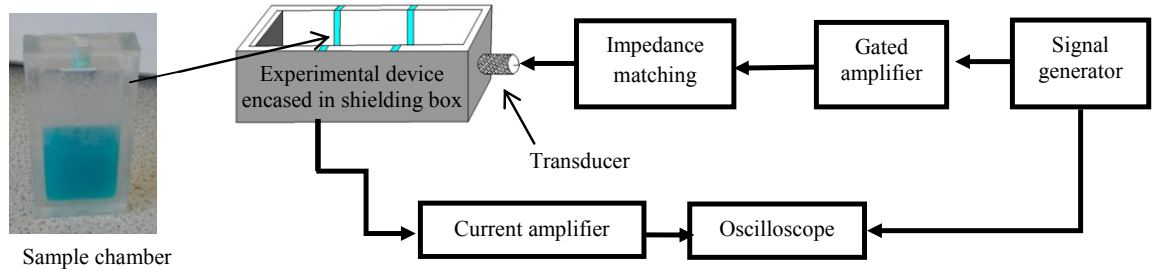

Fig. 1. The block diagram of the experiment system along with sample chamber.
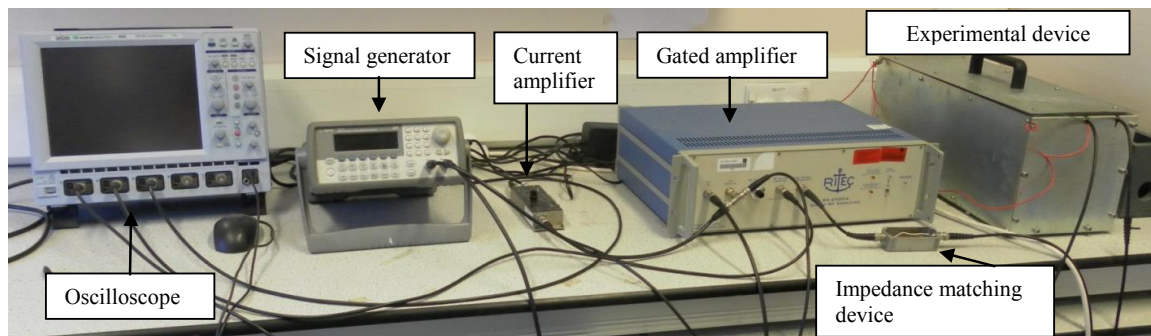

Fig. 2. The layout of experiment equipment.

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.
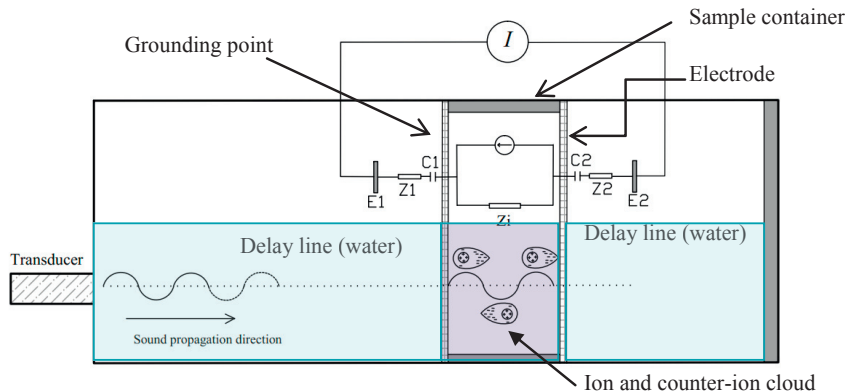

Fig. 3. The evice and circuit diagram of the experiment system.

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.
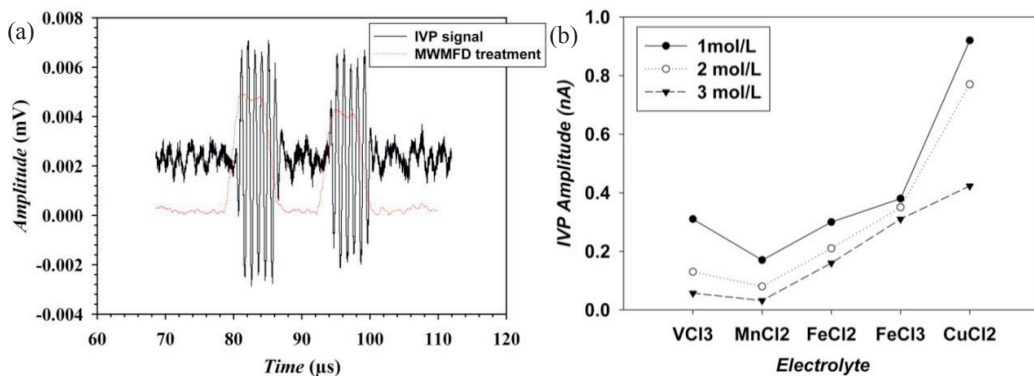

Fig. 4. (a) A typical IVP signal generated from $CuCl_2$ (3M) together with MWMFD results in red and (b) Concentration and atomic mass effect of ions on IVP amplitude

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 $MnCl_2$, 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 ($z^{\pm}$) 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 $z^{\pm}$, 爐煥nd熄$^{\pm}$, all other factors are the same, therefore:

$$IVP = K\left[\frac{t^{+}W^{+}}{z^{+}} - \frac{t^{-}W^{-}}{z^{-}}\right] \quad (6)$$

Therefore, the theoretical ratio will be:
$$\begin{cases} IVP_{FeCl3} = K\left[\dfrac{1 \times 55.8}{3} - \dfrac{3 \times 35.4}{-1}\right] = 124.8 K \\ IVP_{FeCl2} = K\left[\dfrac{1 \times 55.8}{2} - \dfrac{2 \times 35.4}{-1}\right] = 98.7 K \end{cases} \rightarrow \frac{IVP_{FeCl3}}{IVP_{FeCl2}} = 1.26$$

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.
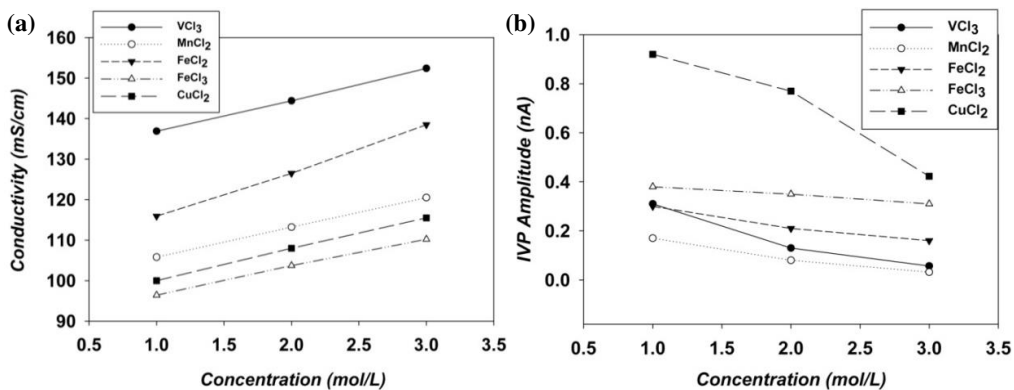
Fig. 5. The concentration effect on conductivity (a); and IVP amplitude (b) of electrolytes

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 $CsCl?$ $RbCl > KCl > NaCl$.
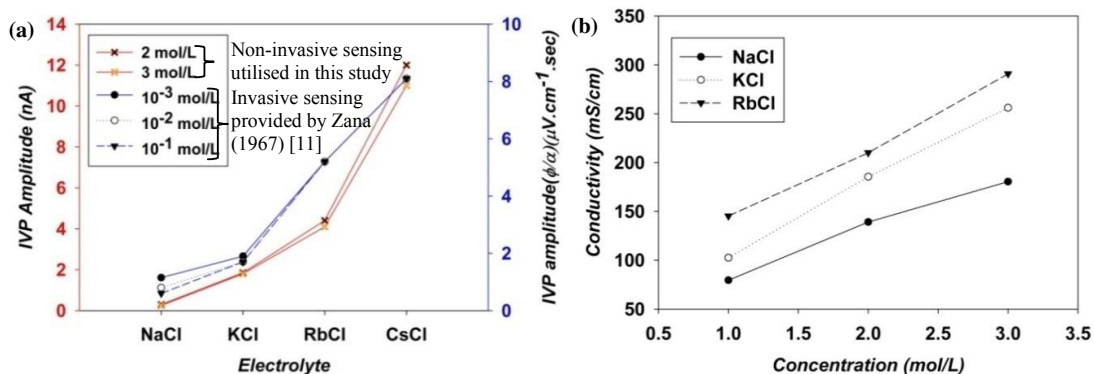

Fig. 6. (a) Concentration and atomic mass effect of ions on IVP amplitude; (b) Concentration effect on conductivity.

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.
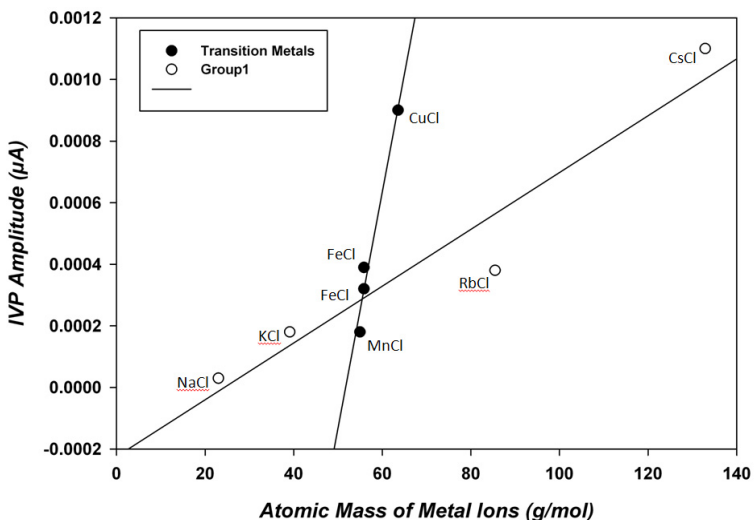

Fig. 7. Atomic mass effect on IVP amplitude for variety of 1 M electrolytes with different valences.

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

[1] Dukhin, A.S. and Goetz, P.J., 2002, Ultrasound for characterizing colloids: Particle sizing, zeta potential, rheology, 1st ed., Elsevier, Boston.
[2] Duck, F.A., Baker, A.C. and Starritt, H.C., 1998, Ultrasound in medicine, Institute of Physics Pub., Bristol, Philadelphia, Pa.
[3] O'Brien, R.W. and White, L.R., 1978, "Electrophoretic mobility of a spherical colloidal particle", Journal of the Chemical Society, Faraday Transactions 2, Vol. 74, p. 1607.
[4] Debye, P., 1933, "A Method for the Determination of the Mass of Electrolytic Ions", Journal of Chemical Physics, Vol. 1 No. 1, p. 13.
[5] Hermans, J., 1938, "Charged colloid particles in an ultrasonic field", Philosophical Magazine Series 7, Vol. 25 No. 168, pp. 426–438.
[6] Ohshima, H., 2005, "Colloid Vibration Potential and Ion Vibration Potential in a Dilute Suspension of Spherical Colloidal Particles", Langmuir, Vol. 21 No. 26, pp. 12100–12108.
[7] Bugosh, J., Yeager, E. and Hovorka, F., 1947, "The Application of Ultrasonic Waves to the Study of Electrolytic Solutions I. A Modification of Debye's Equation for the Determination of the Masses of Electrolytic Ions by means of Ultrasonic Waves", Journal of Chemical Physics, Vol. 15 No. 8, pp. 592–597.
[8] Yeager, E., Bugosh, J., Hovorka, F. and McCarthy, J., 1949, "The Application of Ultrasonic Waves to the Study of Electrolytic Solutions II. The Detection of the Debye Effect", Journal of Chemical Physics, Vol. 17 No. 4, pp. 411–415.
[9] O'Brien, R.W., 1988, "Electro-acoustic effects in a dilute suspension of spherical particles", Journal of Fluid Mechanics, No. 190, pp. 71–86.
[10] Guan, P., Wang, M., Schlaberg, H.I., Iqbal Khan, J. and Speirs, V., 2011, "Towards a-scan imaging via Ultrasonic Vibration Potential measurements", Nuclear Engineering and Design, Vol. 241 No. 6, pp. 1994–1997.
[11] Zana, R. and Yeager, E., 1967, "Ultrasonic vibration potentials and their use in the determination of ionic partial molal volumes. The Journal of Physical Chemistry, Vol. 71 No. 3, pp. 521–536.