Interface-controlled electric potential oscillations in salt water/density oscillator

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Detailed studies have been undertaken to understand the mechanism of development of electric potential oscillations in salt water/density oscillator. For this purpose, four types of systems, viz., (i) non-polar/non-polar liquid systems, (ii) polar-polar liquid systems, (iii) aqueous solution of non-electrolyte systems and (iv) aqueous solution of electrolyte water systems have been chosen. In case of (i) electric potential oscillations are not observed. On the contrary, for other cases both oscillatory upward and downward flow along with electric potential oscillations are observed. Experimental results show that both oscillatory flow and electric potential oscillations are in phase. Further, for all the systems except (i), electric potential increases during upward flow, while it decreases during downward flow thus confirming the streaming potential hypothesis suggested by Srivastava and coworkers. Density gradient and viscosity essentially control the oscillatory flow. In the case of aqueous glycerol-water system, both oscillatory flow and electric potential oscillations stop when the concentration of glycerol solution and consequently its viscosity is too high showing thereby that the two types of oscillations are interrelated.

Exotic phenomena such as oscillations, bistability and chaos in reacting systems have been investigated extensively during recent years. Similar phenomena have also been observed in some membrane processes.

The salt water oscillator, also called density oscillator, is an interesting example of an oscillatory system maintained quite far from equilibrium. If a vessel with capillary filled with solution of electrolyte is immersed in an outer vessel filled with water, upward and downward flow of liquid occurs through the capillary, which is reflected by oscillatory movement of liquid level in the inner vessel. When the electrodes in the two chambers are connected to a voltage measuring device, oscillations in electric potentials are observed. This type of hydrodynamic instability is different from Benard instability or Taylor instability which have been the subject of intense investigation earlier.

The origin of electric potential oscillations appeared to be baffling in the beginning, and it was felt that “it may involve interesting principles of Physical Chemistry”. Srivastava and coworkers suggested that streaming potential might be responsible for the generation of electric potentials in salt-water oscillator. Evidence for the same is provided by the following observations:

1. Amplitude of oscillations in different aqueous solutions of electrolyte/water systems follows the following order: aluminium chloride > barium chloride > sodium chloride, depending on the order of magnitude of zeta potential developed in each case.

2. Time period increases with decreasing diameter of capillaries since these would offer more resistance to the flow of liquids and hence longer time is required for the displacement of the mobile phase of this double layer.

3. Neutralization of electrical oscillation during circular flow when experiments with two capillaries are performed.

In spite of the above developments, further tests of streaming potential hypothesis are needed. In particular, more information about the interrelationship of oscillatory upward and downward flow and electric potential oscillations would be desirable.

Accordingly, in order to have a deeper understanding of the phenomena involved and to test the streaming potential hypothesis, experiments have been performed.
(i) to record change in the relative magnitudes of potential when the inner electrode in Fig.1 is positive. One would expect lower magnitude during downward flow in contrast with higher magnitude during upward flow, in case streaming potential hypothesis is valid.

(ii) to test whether oscillatory flow and electric potential oscillations are interrelated, and

(iii) to investigate the role of viscosity in controlling oscillatory flow and electric potential oscillations.

For this purpose, following type of systems were chosen for detailed study:

(a) Non-polar (non-electrolyte) liquid-liquid systems, e.g., CS$_2$-hexane and benzene-toluene

(b) Polar-polar liquid systems, e.g., D$_2$O - H$_2$O, glycerol - water

(c) Aqueous solution of non-electrolyte-water system, e.g., urea-water and glucose-water system

(d) Aqueous solution of electrolyte-water systems

In case (a), development of diffusion potential or streaming potential is not possible whereas this is possible in the case (d). Further, in cases (b) and (c), only streaming potential can develop since zeta potential at the glass-liquid interface can exist.

Further, experiments were performed to record the relative changes in the magnitude of electric potential during upward and downward flow. Simultaneous measurements of the time period for oscillatory flow and electric potential oscillations have been made for glucose-water system, in order to understand whether oscillations are synchronous. Glycerol-water system has been studied for a wide range of concentrations in order to study the effect of viscosity on electric potential oscillations. Experiments have been performed for a larger number of systems to record whether electric potential increases/decreases during upward/downward flow.

Materials and Methods

Glucose (A.R., C.D.H.), benzene (Sarabhai Chemicals), hexane (E.Merck), carbon disulphide (S.D. Fine Chemicals Ltd.), H$_2$SO$_4$ (A.R., E.Merck), HCl (L.R., ARC Industries), urea (Spectrochem), glycerol (L.R., Qualigens Chemicals), toluene (A.R., Ranbaxy), HNO$_3$ (L.R., E. Merck) and sucrose (A.R., Sisco Research Laboratories) were used as such. Heavy water was procured from Varian. Distilled water/deionized water was used in all experiments. The density and viscosity ratio of components was noted from standard literature$^{11}$.

Electrodes

Initially, a Pt-electrode in conjunction with a calomel electrode was used for the investigations. Subsequently, both the electrodes used were Pt-electrodes, which were cleaned with cone. HNO$_3$, cone. HCl and washed several times with distilled water. The asymmetry potential was determined before use.

Experimental set-up

The apparatus used for the present investigation is shown in Fig.1. It consists of an outer vessel A and a chamber B (radius b = 1.5 cm) kept inside the former. Chamber B had a capillary tube (length d = 4.5 cm, with radius a = 0.05 cm). Chamber A contained liquid of lower density while chamber B contained liquid of higher density. The latter was closed with a rubber stopper through which a glass tube containing electrode $P_1$ was inserted. Another electrode $P_2$ was kept in the fluid in the outer vessel. The inner chamber had a side-tube having a stop-cock for initiating the flow.

Electric potential oscillations could be recorded by connecting the two electrodes to an electronic recorder (Digital Electronics Ltd., Bombay) as well as a digital voltmeter (DVM with input impedance $-10^6$ ohm) in parallel. The heights of the liquid column in the inner chamber and outer chamber were measured with a cathetometer, which could read correctly to ±0.001 cm.

Fig. 1—Schematic diagram of the experimental set up [A = outer vessel; B = inner vessel; C = glass joint; D = capillary; E = stop cock].
Monitoring of electric potential oscillations

Experiments were performed with a Pt electrode in the inner container and a Pt or calomel electrode in the outer vessel. The set-up was kept in an air-thermostat, the temperature of which could be maintained constant with an accuracy of ±0.1°C. The electrode in the inner chamber was kept close to the upper end of the capillary and connected to the positive terminal of recorder/DVM. The actual potential at the maxima and minima during oscillations was estimated by DVM. Further, potential differences estimated by DVM and the electronic recorder were found to be mutually consistent. For the systems involving water as one component, both distilled water as well as 0.001 M KCl solution in deionized water were used. The trend of the results was similar.

Monitoring of oscillatory flow

Oscillations in the position (x) of liquid in the inner chamber were visually observed using the experimental set-up. For this purpose, amplitude (peak to peak) \( \Delta x = x_{\text{max}} - x_{\text{min}} \) where \( x_{\text{max}} \) and \( x_{\text{min}} \) are maximum and minimum values of x, was measured. The time period was also noted with the help of a stop watch which could read correct to ±1 sec.

Relationship between electric potential oscillations and oscillatory fluid flow

Visual observations were made initially. The direction of the fluid flow and the movement of the needle of the recorder were simultaneously observed. For studying the phenomena quantitatively, the time periods of the electric potential oscillations and oscillatory flow were measured using the same set-up (Fig. 1), a cathetometer and the recorder.

Results

Electric potential oscillations

Results on typical electric potential oscillations for (i) glycerol-water, (ii) \( \text{D}_2\text{O}-\text{H}_2\text{O} \), (iii) urea-water, (iv) glucose-water, (v) sucrose-water, (vi) HCl-water and (vii) H_2SO_4-water are recorded in Figs 2-6. When Pt-calomel electrodes are used, in the case of glycerol-water system, periodic oscillations are observed after cessation of relaxation oscillations. After a certain stage, sinusoidal oscillations also ceased and onset of convection is observed. In the case of Pt-calomel electrodes life-time is found to be much shorter as compared to that when Pt-Pt electrodes are used. Experimental results on concentration dependence of electric potential oscillations on glycerol-water system, lead to following conclusions:

[a] Oscillations are observed only in the concentration range 0.68-13.6 mol dm\(^{-3}\). Below the lower limit and upper limit, no oscillations are observed.

[b] Time period does not significantly depend on glycerol concentration.

[c] The amplitude decreases with increase in the concentration of glycerol.

Fig. 2—Electric potential oscillations (Pt-Pt) for glycerol-water system (a) 0.68 mol dm\(^{-3}\) glycerol; (b) 1.4 mol dm\(^{-3}\) glycerol; (c) 2.7 mol dm\(^{-3}\) glycerol; and (d) 6.8 mol dm\(^{-3}\) glycerol; ABC represents downward flow and CDE represents upward flow; Temperature = 30 ± 1°C.

Fig. 3—Electric potential oscillations (Pt-Calomel) for glycerol-water system (a) 1.4 mol dm\(^{-3}\) glycerol; (b) 4.1 mol dm\(^{-3}\) glycerol; (c) 5.5 mol dm\(^{-3}\) glycerol; (d) 6.8 mol dm\(^{-3}\) glycerol; ABC represents downward flow and CDE represents upward flow; Temperature = 28 ± 1°C.
glycerol concentration when Pt-Pt electrodes are used as compared to the case when Pt-calomel electrodes are used (Figs 3 and 5).

Oscillatory flow

For the typical case of one molar glucose solution, the peak-to-peak amplitude of oscillations in $\Delta h$ is found to be equal to 0.250 ± 0.002 cm.

Electric potential oscillations and oscillatory flow

In order to study the relationship between oscillatory fluid flow and electric potential oscillations, detailed studies for oscillatory flow and electric potential oscillations for one molar aqueous glucose-water system were made using the technique described in the experimental section. The time-period for electric potential oscillations was found to be 105 ± 3 s. The corresponding time-period for the simultaneously recorded oscillatory flow was found to be 98 ± 4s.

Discussion

Experimental results obtained in the present investigation show:

[i] Oscillations are not produced in the case of non-polar-non-polar liquid systems, as observed by earlier workers.

[ii] Oscillations are observed in polar-polar liquid systems as well as aqueous solutions of electrolytes-water systems, confirming the earlier observations.

[iii] The electrode in the inner chamber is found to be less positive or more negative during upward flow whereas during downward flow, the same is found to be more positive or more negative (Figs 2-6).

The origin of electric potentials in the system under discussion can be qualitatively understood in terms of thermodynamics of irreversible processes in the linear range. During oscillations, there would be three types of flow, viz., flow of fluid, flow of solute and current. If we take a simplistic view, the phenomenological relations for the system would be given by,

$$J_v = L_{11} \Delta P + L_{12} \Delta \phi + L_{13} \Delta \mu$$  \hspace{1cm} (1)
$$I = L_{21} \Delta P + L_{22} \Delta \phi + L_{23} \Delta \mu$$  \hspace{1cm} (2)
$$J_s = L_{31} \Delta P + L_{32} \Delta \phi + L_{33} \Delta \mu$$  \hspace{1cm} (3)

where $\Delta P$ is the pressure difference between the fluid in the outer and inner chambers. When $\Delta P$ is positive, the flow occurs in the upward direction, while on the other hand when $\Delta P$ is negative, the same occurs in the downward direction. $\Delta \mu$ is the difference in chemical potential of the solute across conc. solution/dil. solution interface. $\Delta \phi$ is the potential difference across conc. solution/dil. solution interface. $J_v$, $I$ and $J_s$ are the volume flow, electric current and solute flow respectively. $L_{ij}$ ($i, j = 1, 2, 3$) are called phenomenological coefficients.

![Fig. 4 Electric potential oscillations (Pt-Pt) for D$_2$O-H$_2$O system](image1)

![Fig. 5 Electric potential oscillations (Pt-Pt) for system](image2)
From equation (2), it follows that when $I = 0$ (i.e. stationary state) and considering the time derivative,
\[
(\Delta \phi)_{t=0} = -\frac{L_{21}}{L_{22}} \cdot \Delta \mu - \frac{L_{23}}{L_{22}} \cdot \Delta \mu
\]  
... (4)

From equation (4), it follows that there can be the following two sources of electric potentials:

[i] Streaming potential

[ii] Diffusion or liquid junction potential

Between the two, streaming potential plays a major role, since there is no likelihood of existence of liquid junction potential in non-electrolyte systems. Glass is negatively charged and the formation of electrical double layer does occur when polar liquids or aqueous solutions of electrolytes are in contact with glass capillary. Thus, when flow occurs, positive charges in the mobile part of double layer move along the direction of flow giving rise to development of streaming potential in view of the fact that glass is negatively charged. Based on the usual concept of Helmholtz Double Layer theory, the streaming potential is related to the pressure difference according to the equation (5),
\[
(\Delta \phi)_s = \frac{\varepsilon \xi}{4\pi \eta \chi} \Delta P
\]  
... (5)

for the steady state. In the far from equilibrium situation preventing in the present case, it is not easy to estimate the variation of streaming potential with varying $\Delta P$. In addition, $\varepsilon$ (dielectric constant), $\xi$ (zeta potential), $\eta$ (coefficient of viscosity) and $\chi$ (conductance) are the functions of composition. Streaming potential hypothesis is supported by the fact that such oscillations are not observed in systems where the possibility of existence of double layer does not exit such as CS$_2$ - hexane or cyclohexane - CCl$_4$. If the streaming potential hypothesis holds good, then during upward flow, the observed potential would be higher while the same would be lower during downward flow due to the movement of positive charges along the direction of flow. Results recorded in the Figs 2-6 support the above inference, thereby confirming the validity of streaming potential hypothesis.

There is a distinct possibility of existence of liquid junction potential at the interface of the two components at least in the case of electrolytes. Liquid junction potential is given by

![Fig. 6—Electric potential oscillations (Pt-Pt) for system (a) 1.5 mol dm$^{-3}$ HCl-water; (b) 1.5 mol dm$^{-3}$ H$_2$SO$_4$-water; ABC represents downward flow and CDE represents upward flow; Temperature = 32 ± 1°C.](image-url)
where \( E_t = \text{liquid junction potential} \); \( t_+ \) = transport number of anion; \( t_- \) = transport number of cation; \( R \) = gas constant; \( T \) = temperature (K); \((a_+)\) activity of anion in dilute solution; \((a_-)\) activity of anion in concentrated solution; \((a_+)\) activity of cation in dilute solution; \((a_-)\) activity of cation in concentrated solution; \( F \) = Faraday; \( z_+ \) = valency of cation; \( z_- \) = valency of anion.

When \( I = 0 \), then since the ratio of the activity of ions at the upper end of the capillary would be different from that at the lower end, oscillation in the electric potentials due to liquid junction potential is expected. But it is not easy to make a quantitative estimate since the system is far from equilibrium. Its contribution does not seem to be significant in view of the following observations.

1. Oscillations are observed in KCl-water system for which the magnitude of liquid-junction potential is much smaller since transport numbers of potassium ion and chloride ion are close to each other.
2. The amplitude of oscillations does not depend on the position of the electrodes in the inner chamber with respect to the mouth of the capillary. Nevertheless, when aqueous solutions of electrolytes are involved, its contribution, if at all, would be superimposed on this magnitude of the streaming potential.

If streaming potential is responsible for major contribution to the observed potential changes, then obviously electric potential oscillations would be triggered by the upward and downward flow of the fluid through the capillary. This is supported by the fact that oscillatory flow (time period = 98 ± 4 s) are synchronous as is confirmed by experiments with one molar glucose solution reported in the present contribution to the observed potential changes, then electric potential oscillations would be observed although upward and downward oscillatory flow is observed. Oscillatory flow is governed by density difference. In case of benzene-toluene system, even oscillatory flow is not observed since the density difference between the two components is too small.

It was thought of interest to examine the effect of viscosity on oscillatory flow in view of the possibility of existence of the following force-balance equation.

Force due to = Viscous force (B)+Force due to acceleration(A)+Buoyancy(D)

During upward flow, forces A, C and D will act in the upward direction while force B will act in the downward direction. On the other hand, during downward flow, forces A and C will act in the downward direction while forces B and D will act in the upward direction. Hence, it is obvious that viscosity would play a major role in controlling oscillations. Experimental results on peak-to-peak amplitude during oscillatory flow in glycerol-water system (ratio of viscosity of glycerol and water = 950) confirm this conjecture. At higher [glycerol], oscillations die down. There is an upper limit of [glycerol], above which electric potential oscillations and oscillatory flow are not observed. Similarly, there is a lower limit of [glycerol], below which both types of oscillations do not occur. Thus, there are two bifurcation points and [glycerol] acts as the bifurcation parameter. Beyond the upper limit, the viscosity of glycerol solution is quite high and oscillations cease presumably on this account.

Following Yoshikawa et al., the above terms can be expressed as follows:

\[
(A) = \pi b^2 \rho_s \left( \frac{d^2 x}{dt^2} \right)^2
\]

where \( \rho_s \) is the density of solution

\[
(B) = 8 \eta \left( \frac{dx}{dt} \right) \left( \pi b^2 \rho_s \right) \left( \frac{h}{a^2} \right)
\]

\[
(C) = \pi a^2 \rho_s \left( gh \right) - \pi a^2 \rho_s \left( h^2 \right)
\]

where \( \rho_s \) is density of solvent, and \( h \) is the height of liquid from orifice of capillary.

\[
(D) = \pi a^2 \rho_s \left( \rho - \rho_o \right) g
\]

On substituting the values of various terms in the force-balance equation, one obtains

\[
\left( \frac{d^2 x}{d t^2} \right) = - \left( 8h/a^2 \right) \frac{dx}{dt} - \left( \rho / \rho_o \right) \left( a^2 g / b^2 d \right) x + \left( a^2 gh / b^2 d \right) \left( \rho_s / \rho_o \right) g
\]

The experimental results reported in the present communication lead to following conclusions:

(i) The electric potential oscillations start when oscillatory flow starts. Further, such oscillations cease when the oscillatory flow stops.
(ii) Electric potential oscillations and oscillatory flow are found to be in phase.

(iii) Electric potential oscillations are not observed in nonpolar-nonpolar systems although oscillatory flow may be observed in systems where density difference is large.

(iv) During upward flow, the potential has an increasing magnitude while during downward flow, it has decreasing magnitude in all cases.

The above findings strongly support the streaming potential hypothesis of Srivastava and co-workers that electric potential oscillations are primarily due to streaming of fluid through the capillary. However, in the case of aqueous solutions of electrolytes, diffusion may make some contribution. It may be noted that experimental estimates of individual contributions of streaming potential and diffusion potential to the overall potential are not easy. So is the case with the theoretical evaluation of these on account of the far from equilibrium nature of the phenomenon where giant fluctuations in a free diffusion process can occur

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