

## Salt-water oscillator and its non-electrolyte analogues

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**Abstract** - Electrical potential oscillations in the recently reported salt-water oscillator (refs. 1,2) and its non-electrolyte analogues have been critically examined. It turns out that these oscillations are oscillating streaming potentials. Taking a clue from these studies it has been possible to design a non-electrolyte (urea) analogue of Teorell membrane oscillator and demonstrate oscillating electrical potential differences across the membrane. Bistable nature of these systems which represents a far equilibrium situation has been studied.

### INTRODUCTION

A salt-water oscillator was designed by Yoshikawa et al (ref. 1) with purely didactic intentions of bringing home some of the concepts of non-linear dynamics in a far from equilibrium region. This simple system was shown (ref. 2) to exhibit various non-linear characteristics such as limit cycle, bifurcations, entrainment among the oscillators etc. This simple device consists of an open glass tube with a capillary at one end. The glass tube and the capillary are filled with the aqueous solution of sodium chloride and hung in another glass vessel containing water such that the liquid in the inner tube and in outer vessel stand at the same level. Due to density difference the salt solution begins to flow downwards through the capillary which terminates after some time and then begins the upward flow of water from the outer vessel to the inner tube through the capillary. After some time the upward flow also terminates and the downward flow again sets in and so on.

More curious than the up and down flow of the liquids was the observation that the electrical potential difference across the electrodes inserted in the inner and the outer tubes also showed oscillations. Noyes (ref. 3) suggested that these electrical potential oscillations could be due to variations in the liquid-liquid junction potential; the variations may arise because the interface between the denser liquid and the lighter liquid may alternately become concave or convex.

Prompted, by these suggestions we investigated (refs. 4,5) the phenomenon more closely and concluded that these electrical potential oscillations are not due to variations in liquid-liquid junction potentials but due to oscillating streaming potentials. Our studies also revealed that a non-electrolyte analogue of Teorell membrane oscillator should, in principle, be possible. In fact we did succeed in designing one with aqueous urea solutions in place of electrolytes (ref. 6).

A consolidated account of these efforts is presented in this lecture.

### EXPERIMENTAL

The experimental setup used for monitoring the electrical potential oscillations was the same as described by Yoshikawa et al (Fig.1 of ref.1). The denser liquid (electrolyte/non-electrolyte) was filled in the inner tube and the lighter one in the outer vessel such that the level of the liquids in the inner tube and that in the outer vessel was the same. Electrical potential oscillations were monitored across the sensing electrodes inserted in the inner tube and the outer vessel connected to a x-t recorder. To obtain the data on volume flux  $J_v$  induced by pressure difference  $\Delta P$  in the presence of a constant density difference, required to demonstrate the bistable nature of the system, the glass cell described in our earlier publication (Fig.2 of ref.4) was used. To maintain the condition of constant density difference, the denser liquid in the inner tube B and the lighter liquid in the outer vessel A were replaced by fresh samples after each run. The details of the procedure were the same as described in the earlier publication (ref.4).

Bistable nature and the trans-membrane electrical potential oscillations in the non-electrolyte analogue of the Teorell type membrane oscillator were studied using the glass cell depicted in Fig.1 which has been well labelled to make it self explanatory. To demonstrate bistability, data on volume flux  $J_v$  induced by various pressure differences  $\Delta P$  in the presence of a constant current driven through the membrane, were obtained. To demonstrate oscillations of the trans-membrane electrical potential difference, the horizontal capillary  $L'_1 L'_2$  and the pressure head (Fig.1) were replaced by vertical tubes which were filled with water and aqueous urea such that a known pressure difference was created across the membrane initially. A known constant current was then passed through the membrane and the trans-membrane potential across the sensing calomel electrodes monitored with time using a x-t recorder. In these experiments the polarities of the electrodes  $E_1$  and  $E_2$  were made such that the electro-osmotic flow opposed the pressure driven flow.

All chemicals used in these studies were of 'AnalaR' grade. All experiments were carried out at constant temperature using a thermostat set at  $30 \pm 0.1^\circ\text{C}$ .

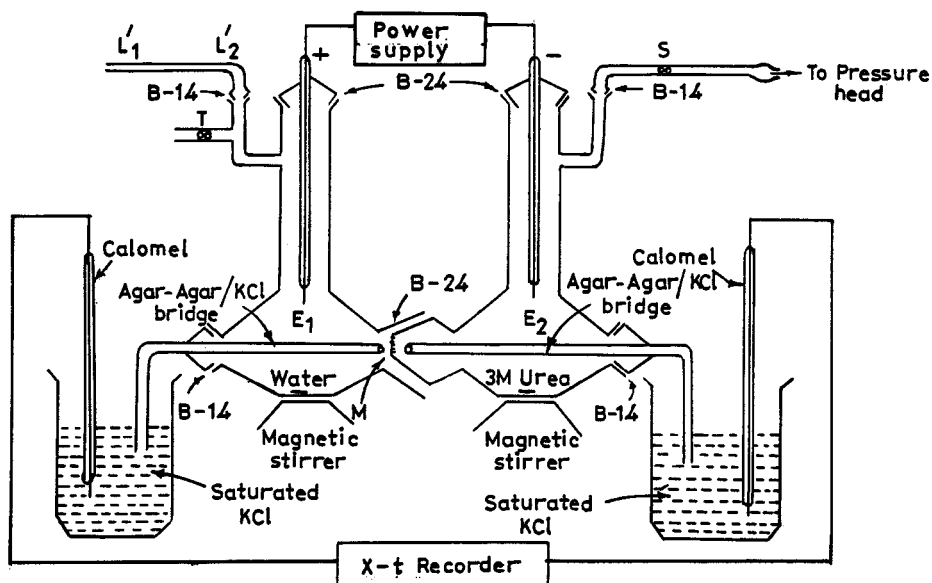


Fig.1. Schematic representation of the Teorell type membrane oscillator using urea solution.  $E_1$  and  $E_2$  bright platinum electrodes,  $L'_1 L'_2$  capillary, M Sartorius cellulose acetate microfiltration membrane (Cat.No.11107), S, T stop cocks.

## RESULTS AND DISCUSSION

To demonstrate that the electrical potential oscillations in the salt water oscillator (ref.1) are not due to variation in the liquid-liquid junction potentials, we experimented with such electrolytes whose cationic and anionic transport numbers are very close to each other e.g. Potassium chloride and nitrate, ammonium chloride and nitrate and observed electrical potential oscillations of substantial amplitudes. A typical trace in one particular case of potassium chloride vis-a-vis sodium chloride is shown in Fig.2. Having ruled out the possibility of junction potential as a cause of these oscillations we mooted another proposal invoking streaming potentials due to the formation of an electrical double layer in the capillary. Due to imbalance of hydrostatic pressure when the denser liquid flows from the inner tube to the outer vessel it carries alongwith it the mobile phase of the double layer causing charge separation. Similarly when the liquid flows from the outer vessel to the inner tube the mobile phase of the double layer is again carried along. Directions of the charge separation in the upward movement of the liquid will be opposite to that in the downward movement and hence oscillations.

Since non-electrolyte systems are best suited for substantiating the streaming potential hypothesis, we experimented with the following systems: (i) Formamide in the inner tube and water in the outer vessel (ii) ethylene glycol in the inner tube and water in the outer, (iii) water in the inner tube and acetonitrile in the outer (iv) water in the inner tube and dimethyl formamide in the outer (v) water in the inner tube and acetone in the outer, (vi) aqueous urea in the inner tube and water in the outer and (vii) benzene in the inner tube and cyclohexane in the outer. All systems except system (vii) where also one could see the up and down movement of liquids, showed oscillations of electrical potential differences. A typical trace in one particular case of system (vi) is shown in Fig.2. The observation that system (vii) showed no electrical potential oscillations is quite expected because both benzene and cyclohexane being non-polar would not form electrical double layer in the capillary whereas all other components e.g. water, acetonitrile, formamide etc. will.

Amplitudes of the electrical potential oscillation showed a decrease with the decrease in concentration, e.g. in case of system (vi) no oscillations were observed when the concentration of urea solution in the inner tube was equal to or lower than 0.25M. Rationale for this observation can be had from bistability studies.

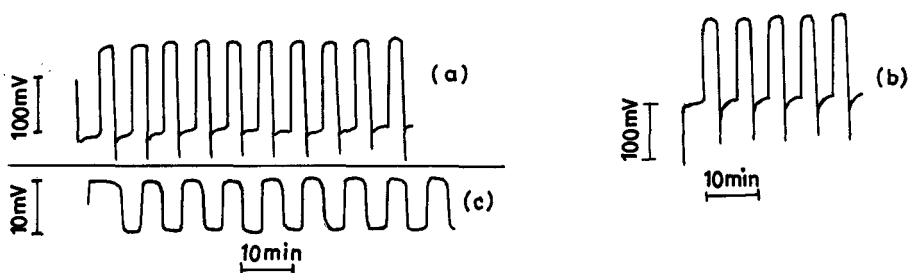


Fig.2. Traces of the electrical potential differences: (curve a) data using 1M KCl in the inner tube, and water in the outer vessel and bright platinum electrodes: (curve b) data using 1M NaCl in the inner tube and water in the outer and bright platinum electrodes: (curve c) data using 3M urea in the inner tube and water in the outer, and bright platinum electrodes.

Bistability studies were conducted on system (vi). Prima facie two steady states are possible; one in which the capillary is filled with urea solution and the other in which it is filled with water. The  $J_v$  versus  $\Delta P$  plots in the presence of constant density difference in the case (i) when inner tube contained 3M urea solution and (ii) when it contained 0.1M urea solution are shown respectively in Figs. 3a and 3b. The straight line portions represent the stable steady states and the portion shown by dotted lines is the region of fragile stability inaccessible to experimental determinations. It can be seen that in Fig. 3a the state of no net volume flux ( $J_v = 0$ ) lies in the unstable region where even the slightest fluctuation would lead the system switching over to one of the stable states and hence oscillations. In Fig. 3b, however, the state of no net flux ( $J_v = 0$ ) lies on the stable segment and hence no oscillations should be expected in this case.

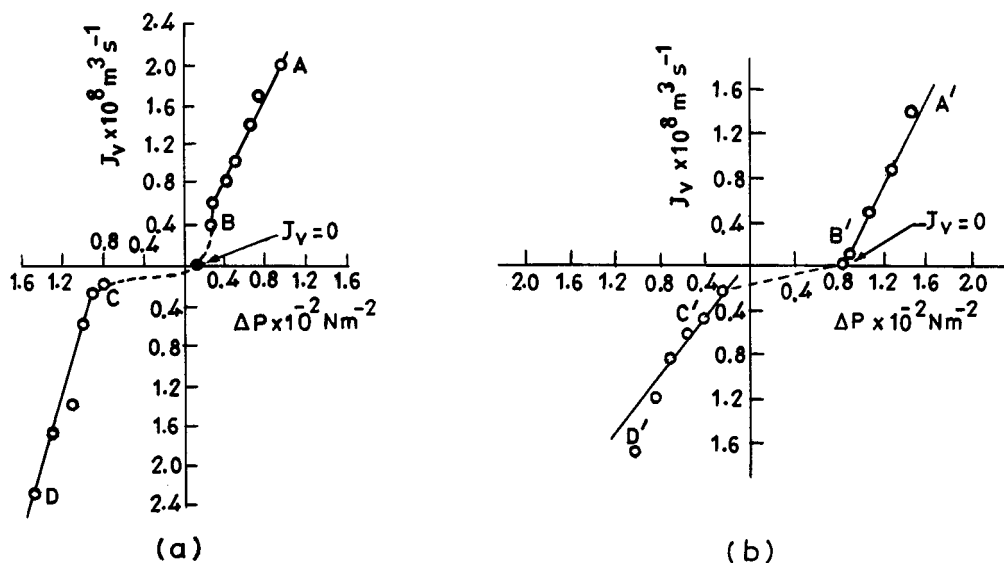


Fig. 3. Plot of volume flow ( $J_v$ ) against pressure difference  $\Delta P$  in the presence of constant density difference: (a) 3M urea in the inner tube and water in the outer vessel; (b) 0.1M urea in the inner tube and water in the outer vessel. AB, CD, A'B', C'D' represent the stable steady states.

Teorell type oscillator. Teorell membrane oscillator (ref. 7, 8) is defacto a salt-water oscillator and its non-electrolyte analogue should be possible in principle. We experimented with aqueous urea (3M) instead of electrolytes in the Teorell type setup (Fig. 1). As pointed out by Meares and Page (ref. 9) the basic ingredients which make oscillations possible are at least two opposing independent flows driven by different forces. In the Teorell oscillator electro-osmotic flow and the pressure driven flows oppose each other. This condition was realized in our experiments also by suitably adjusting the polarities of the electrodes  $E_1$  and  $E_2$  (Fig. 1) and the direction of  $\Delta P$  across the membrane.

The other requirements for the occurrence of oscillations is that the system should be at least bistable and that the balance point (e.g.  $J_v = 0$ ) should lie in the region of fragile stability. In view of this requirement bistability studies were conducted and the data are plotted in Figs. 4a and 4b. It can be seen from these figures that when  $I = 0.1 \text{ mA}$  the state of no net flux ( $J_v = 0$ ) falls on the segment representing the stable steady state whereas for  $I = 0.2 \text{ mA}$  it falls in the unstable region represented by the dotted line.

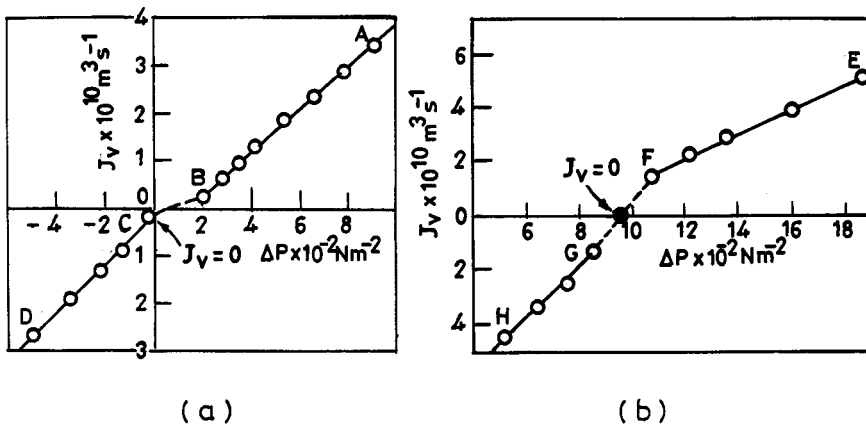


Fig.4. Plot of volume flux ( $J_v$ ) against pressure differences ( $\Delta P$ ) in the presence of: (a) constant current 0.1mA and using 3M aqueous urea (b) constant current 0.2mA and using 3M aqueous urea. AB,CD,A'B' and C'D' represent the stable steady states.

Therefore, no oscillations should be expected when  $I = 0.1\text{mA}$  whereas when  $I = 0.2\text{mA}$  one may look for oscillations. In fact we did observe oscillations when the current  $I = 0.2\text{mA}$  was driven through the membrane (Fig.5). To monitor oscillations  $\Delta P$  corresponding to some value of  $J_v$  in the unstable region, shown by dotted lines in Fig.4b,

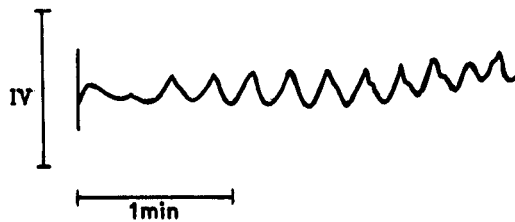


Fig.5. A typical trace of transmembrane potential with time ( $I=0.2\text{mA}$ ). Initially applied  $\Delta P$  across the membrane = 22.15cm of urea solution column.

was imposed across the membrane initially. The transmembrane potential (Fig.5) on a prior grounds should be the algebraic sum of the ohmic potential and the streaming potential. Because the pores of the membrane get alternately filled with water and urea solutions, the solutions of differing conductivities the potential drop across the membrane would vary with time. Streaming potentials arise because the pressure driven volume flow carries along with it the mobile phase of the double layer formed inside the pores of the membrane, causing charge separation.

Thus, the oscillations observed in the Teorell oscillator are not the preserve of electrolytic systems; non-electrolytes also can show oscillations. The only requirement appears to be that the non-electrolyte solutions should be capable of forming electrical double layer inside the pores of the membrane otherwise the opposing electro-osmotic flow would be absent.

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