Non-electrolyte analogues of salt-water oscillator—Studies with quinine-water system

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Electrical potential oscillations in quinine solution/water system in a salt-water oscillator type of setup have been studied. The data support the point of view that these oscillations are streaming potential oscillations. Bistable nature of the system has been demonstrated.

More than twenty years ago Martin discovered a curious phenomenon that rhythmic oscillations of water flow are generated when a vertically oriented hypodermic syringe, with the plunger removed, is filled with salt solution and partially submerged in a beaker filled with pure water. Yoshikawa et al. demonstrated that this device which they called by the name of salt-water oscillator can be usefully utilised to demonstrate and study non-linear characteristics such as limit cycles, bifurcation of the oscillatory flow, entrainment among the oscillators etc.

More curious than the up and down flow of the liquids was the observation of oscillating electrical potential differences between electrodes inserted in the inner tube and the outer vessel. In an earlier study from this laboratory it was demonstrated that these electrical potential oscillations are oscillating streaming potentials.

In the present communication we present data on quinine solution-water system, i.e., aqueous solution of quinine (hydrochloride) in the inner tube and water in the outer vessel which further substantiates the point of view that the oscillations of electrical potential differences in the salt-water type of oscillator are oscillations of streaming potential. Bistable nature of the system has also been demonstrated.

Materials and Methods

Quinine (hydrochloride) used in these studies was obtained from G.S. Chemicals, Bombay. Distilled water, distilled twice in an all-pyrex glass still, was used for preparing solutions. All the experiments were performed at constant temperature using an air thermostat set at 20 ± 0.2°C.

The experimental setup and the procedures used in the present studies were the same as described previously. A schematic diagram of the setup is reproduced in Fig. 1. To monitor the electrical potential oscillations the rubber membrane C was ruptured and the potential difference across the electrodes was recorded using an x-t recorder (Digital Electronics, model Omniscribe series-5000).

Bistability studies were conducted using the all-glass cell described earlier which is reproduced in Fig. 2 for ready reference. The data on volume flux \( J_v \) induced by various pressure differences \( \Delta P \) in the presence of a constant density difference between the liquids in the inner tube B and in the outer vessel A were obtained by applying known pressure to the inner tube and noting the rate

![Fig. 1—Schematic representation of the oscillator: A, outer vessel; B, inner tube; C, side tube](image-url)
of movement of the liquid meniscus in the capillary $L_1L_2$. The solutions in the inner tube and the outer vessel were exchanged with fresh samples after each run to ensure the condition of a constant density difference.

**Results and Discussion**

At first sight, one is likely to suspect that the oscillation of electrical potential differences in the salt-water oscillator may be due to changes in the local concentrations of the electrolyte in the vicinity of the electrodes as the liquids move up and down. It was also suggested that these oscillations could be due to changes in junction potentials generated at the interface between dilute and concentrated salt solutions. In our earlier publications it was shown that neither of these suggestions are experimentally substantiated. We proposed another explanation for the occurrence of the electrical potential oscillations based on the formation of an electrical double layer in the capillary (Fig. 1). When the denser liquid flows down the capillary it carries along with it the mobile phase of the double layer causing charge separation. Similarly, when the liquid moves upwards in the capillary, the mobile phase of the double layer is again carried along. The direction of the charge separation when the liquid moves upwards in the capillary would be opposite to that when the liquid moves downwards, hence, producing oscillations. This implies that the electrical potential oscillation in the salt-water oscillator is not a preserve of electrolytes; even nonelectrolytes capable of forming electrical double layer should show the effect in the salt-water oscillator type of setup (Fig. 1).

The present data, obtained when quinine (hydrochloride) was taken in the inner tube and water in the outer vessel (Fig. 3), support this implication. This observation is in conformity with earlier data on several other nonelectrolytes. Nonpolar nonelectrolytic systems not capable of forming electrical double layer, e.g., benzene in inner tube B and cyclohexane in the outer vessel A (Fig. 1) did not show any oscillations of electrical potential difference although one could see with naked eye the up and down movement of the liquids in the capillary. It is necessary to clarify that oscillations in electrical potential difference are a consequence of the up and down movement of the liquids in the capillary which is caused by the imbalance of hydrostatic pressure due to difference in densities of the liquids in the inner tube and in the outer vessel (Fig. 1).

As pointed out by Meares and Page the basic ingredients which made the oscillations possible are, at least, two independent transport processes driven by two different forces which oppose each other. Such oscillatory systems should be at least bistable. The oscillatory behaviour consists of repeated transitions between the two stationary states. This implies that if the balance point marked by the condition of no net flux falls on either of the stable stationary states no oscillations should be observed. However if the state of no net flux falls in between the stable stationary states which is a region of fragile stability oscillations should be observed. In the present system the two driving forces are: (i) the pressure difference due to liquids of unequal densities in tube B and vessel A.
The amplitude of electrical potential oscillations in the present study shows a decrease with decrease in concentration of quinine (hydrochloride) and at concentrations equal to or lower than 0.05 mol dm$^{-3}$ no oscillations are observed; at such lower concentrations even the up and down movement of the liquids ceased. This observation is consistent with the data on bistability of the present system. The data obtained on volume flux $J_v$ induced by a pressure difference $\Delta P$ in the presence of a constant density difference are plotted in Figs. 4 and 5. The data in Fig. 4 are for the case when the inner tube (Fig. 2) was filled with 0.10 mol dm$^{-3}$ solution of quinine (hydrochloride) at which oscillations were observed and those in Fig. 5 are for the case when the inner tube B (Fig. 2) was filled 0.05 mol dm$^{-3}$ solution of quinine (hydrochloride), the concentration at which no oscillations were observed. The portions AB and CD in Fig. 4 represent the two stable steady states. Similarly, portions A'B' and C'D' in Fig. 5 represent the two stable steady states. The portions shown by the dotted lines in both Figs 4 and 5 represent the region of fragile stability, not accessible to experimental determinations.

It can be seen that the state of no net flux ($J_v = 0$) in Fig. 4 lies in the region of fragile stability whereas in Fig. 5 it lies on one of the stable steady states. This explains why oscillations are not observed at 0.05 mol dm$^{-3}$ concentration and below.

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References