

# Dynamic instability at liquid/vapor interface far from equilibrium

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## Abstract

Attempt has been made to elucidate the mechanism of electric potential oscillations at oil–aqueous solution interface involving adsorption at oil–vapor interface on a semi-theoretical basis. The mechanism stipulates adsorption of ammonia, amines and pheromones at the liquid–vapor interface followed by transfer of ions through membrane–aqueous solution interface and subsequent interaction of ammonium (amine) ions and carbocations from pheromones with diffusing halide ions from the bulk. Relationship of the above mechanism with sensing mechanism of smell by olfactory nerves has also been pointed out.

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## 1. Introduction

Interfacial instability is a common phenomenon since in most cases the events occurring at the interface are in the region far from equilibrium [1,2]. A typical example is Marangoni instability [3–6]. Electric potential oscillations have been observed in biphasic systems [7,8]. Self-induced oscillations in similar systems have also been observed [9]. Theoretical efforts have also been made to understand the mechanism in some cases [10,11].

There is considerable interest in the above phenomena from the angle of electro-physiology. The neuronal action involving sense of smell depends on the generation of self-excited electric potential [12,13]. Hence a deeper study from fundamental angle is likely to be of considerable use for medicinal or physiological purposes.

## 2. Mechanism of Yoshikawa oscillator

Recent studies on electrical potential oscillations across a liquid membrane consisting of an oil layer, 90% oleic acid and

10% 1-propanol, containing tetraphenyl phosphonium chloride (TPPC), between aqueous solutions of 0.5 M NaCl and KCl in two different compartments have been reported by Yoshikawa and Matsubara [7]. TPPC is a cationic lipophilic salt, which can act as a surfactant. When oil-phase is exposed to vapor, following are the important observations:

- (i) On exposure to amine vapor, the electrical potential usually remained constant for 5–20 min and then changed abruptly, accompanied with spontaneous, temporal movement of the organic phase.
- (ii) System showed periodic changes of electrical potential of the order of 10–20 mV.
- (iii) Time period is of the order of a few minutes.
- (iv) On exposure to amine vapor, initially upward deflection occurs indicating that the KCl solution becomes negative with respect to NaCl solution.
- (v) Electric potential oscillations did not occur when the concentration of ammonia was below a critical value.

However, their studies are limited to qualitative study of oscillations using different types of amines only indicating that the phenomenon is general.

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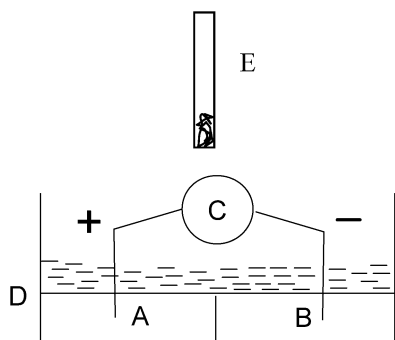


Fig. 1. Schematic diagram of Yoshikawa oscillator: A = 0.5 M NaCl, B = 0.5 M KCl, C = millivoltmeter, D = liquid membrane (4.5 mm), E = cotton-soaked solution of olfactory agent in a tube.

A schematic diagram of their experimental set-up is shown in Fig. 1. The phenomenon is interesting from the view-point of olfactory transduction. But so far no satisfactory mechanism for generation of such self-excited oscillations has been proposed.

A simple mechanism can be postulated as follows. The system contains two interfaces: oil/air( $\text{NH}_3$ ) and oil/aqueous phase. Along first interface ammonia interacts with oleic acid to form ammonium oleate. At the second interface, ammonium oleate interacts with TPPC. Ammonium ion interacts with  $\text{Cl}^-$  of TPPC and gets transferred to the aqueous phase.  $\text{NH}_4^+$  ions combine with  $\text{Cl}^-$  to produce  $\text{NH}_4\text{Cl}$ , the ionization constant of which is much less than that of KCl or NaCl. The formation of  $\text{NH}_4\text{Cl}$  takes place earlier in the compartment having KCl due to higher diffusion coefficient [14a] of KCl (1.466) in comparison with NaCl (1.17). Hence the KCl compartment is negative. It has been suggested that concentration difference between sodium and potassium ions is essential for the excitability of biological membranes [12].

Adsorption–desorption kinetics in the present case is quite complicated. Observation (1) is related with initial adsorption of  $\text{NH}_3$ , which affects the surface tension after sometime influencing the movement of the organic phase, governed by Gibbs adsorption equation [15], provided local equilibrium is assumed,

$$\gamma^{2'} = (1/2.303RT)(d\gamma/d\ln C)T, \quad (1)$$

where  $T$  = temperature;  $\gamma^{2'}$  = surface excess of solute;  $\gamma$  = surface tension and  $C$  = concentration of  $\text{NH}_3$  in oil phase. It may be noted that for quantitative explanation, the above equation has to be modified in order to account for the diffusion process in vapor and state of non-equilibrium.

The electrical potential difference would arise on account of difference in  $[\text{Cl}^-]$  in the two compartments, which would be controlled by the influx of  $\text{NH}_3$  in the form of  $\text{NH}_4^+$  ion and subsequent interaction at the aqueous/liquid membrane interface particularly in compartment B. Hence, there is larger concentration of  $\text{Cl}^-$  in compartment A as compared to that in compartment B. Consequently, compartment B (containing KCl) becomes negative while compartment A becomes positive. The positive current one Faraday of electricity will move from left to right which would result in the transfer of t + g-ion of cations from left to right (A–B) and transfer of  $\text{Cl}^-$  in the

opposite direction. Noting that there are different electrolytes in different compartments, the liquid–junction potential or diffusion potential  $\Delta\phi$  would be given by

$$\Delta\phi = RT/F \ln \Lambda_2/\Lambda_1, \quad (2)$$

where  $R$  = gas constant;  $F$  = Faraday;  $\Lambda_2$  and  $\Lambda_1$  are the equivalent conductance of NaCl and KCl solutions, respectively [14b]. The ratio of the conductance would be proportional to  $C_1/C_2$  where  $C_1$  and  $C_2$  are the concentrations of  $\text{Cl}^-$  prevailing in the two compartments A and B, respectively.

As discussed above,  $\Delta C = C_1 - C_2$  and  $[\text{NH}_4^+]$  in compartment B would vary with time.  $\Delta C$  will vary with time in the following manner,

$$(\Delta C)/dt = -k_1\Delta C + k_2[\text{NH}_4^+]. \quad (3)$$

The first term on the left-hand side occurs on account of diffusion of  $\text{Cl}^-$  from compartment A to compartment B and  $k_1$  is a constant, which would be related to diffusion coefficient and surface area. The second term is related to interaction of  $\text{Cl}^-$  and  $\text{NH}_4^+$  ion.  $k_2$  is a constant which depends on extent of  $\text{NH}_3$  (amine) adsorption. It may be noted that  $[\text{Cl}^-]$  would be depleted with increase in  $[\text{NH}_4^+]$  and consequently  $\Delta C$  would increase.

Since  $[\text{NH}_4^+]$  would decrease when  $\Delta C$  decreases and its increase would be related to its influx from organic phase/aqueous solution interface, we can write

$$d[\text{NH}_4^+]/dt = -k_3\Delta C + k_4[\text{NH}_4^+], \quad (4)$$

where  $k_3$  and  $k_4$  are constants.  $k_4$  will depend on extent of ammonia/amine adsorption.

Putting,  $(\Delta C) = (\Delta C)_0 e^{\lambda t}$  and  $(\Delta\Phi)_0 e^{\lambda t}$  where  $(\Delta C)_0$  and  $(\Delta\Phi)_0$  are constants.

$\lambda$  is also a constant. Making appropriate substitutions in Eqs. (3) and (4) and using normal mode analysis [16], we get,

$$\lambda[\Delta C]_0 = -k_1[\Delta C]_0 + k_2[\text{NH}_4^+]_0, \quad (5)$$

$$\lambda[\text{NH}_4^+]_0 = -k_3[\Delta C]_0 + k_4[\text{NH}_4^+]_0. \quad (6)$$

On solving the above equations we get,

$$\lambda = \alpha + i\omega = -\{(k_4 - k_1) \pm \sqrt{(k_4 - k_1)^2 - 4(k_2k_3 - k_1k_4)}\}/2, \quad (7)$$

where  $\alpha = -(k_4 - k_1)/2$  and  $\omega$  is the frequency. It follows that oscillations would occur when,

$$4(k_2k_3 - k_1k_2) > (k_4 - k_1)^2. \quad (8)$$

$k_4$  would have a lower magnitude as compared to  $k_2$  and  $k_3$ , which are related to ionic reaction. Consequently, transfer of  $\text{NH}_4^+$  from organic liquid/aqueous phase interface would be a slower process. Hence Eq. (8) would be satisfied in the present case. It is obvious that if  $\Delta C$  oscillates, there would be oscillations in electric potential.  $k_4$  would be dependent on the extent of  $\text{NH}_3$  adsorption.

The mechanism and kinetics of adsorption in this case is quite complex in view of the fact that two interfaces, viz., vapor/organic liquid and organic liquid/aqueous solution are

involved. Kinetics of adsorption in such type of complicated systems have been investigated recently involving kinetics at fluid–fluid interface, non-ionic surfactant solutions and surfactant mixtures [17]. In the present case we take only a simplistic view by considering Langmuir adsorption isotherm [15], and assuming that in each compartment, the interface is in equilibrium between a sublayer in the oil phase near the interface and the interface of the aqueous phase both in compartment A and B following Ward and Todai [17b]

$$\theta = k_a P / (k_d + k_a P) = bP / (1 + bP), \quad \text{where } b = k_a / k_d, \quad (9)$$

where  $\theta$  = fraction of surface area covered by the adsorbed molecules,  $k_a$  is the rate constant of adsorption and  $k_d$  is the rate constant of desorption and  $P$  is the partial pressure. When  $bP$  is much less than 1,

$$\theta = bP. \quad (10)$$

It may be noted that  $P$  would depend on the concentration of  $\text{NH}_3$ /amine in the vapor phase and also on the distance of the cotton soaked solution in the glass tube from the interface.

The amplitude would depend on  $\Delta\phi$  given by Eq. (2). The larger the ratio of the concentration difference in the two compartments, the larger the magnitude of amplitude. Greater diffusivity of KCl would decide the polarity of the particular compartment. Consequently, the greater the amine concentration, the greater the value of the amplitude. In the same fashion, the nearer the cotton plug, the greater the amplitude as is found experimentally by Srivastava and co-workers [8].

The above relations cannot be checked in view of lack of experimental data. However, recent data reported by Srivastava et al. in the next section can be used for semi-quantitative test.

### 3. Oscillator with different surfactant in two compartments (Srivastava's oscillator)

Srivastava and coworkers [8] using a similar type of experimental set-up and using a membrane, which is bipolar in nature, have observed similar type of oscillations on exposure to amines and pheromones (*cis*-8-dodecyl acetate and *trans*-10-dodecyl acetate). For this purpose a cationic surfactant was used in compartment A and an anionic surfactant in compartment B. In the oil phase 2,2'-bipyridine was added to reduce the impedance for diminishing the external noise [8].

In their set-up, A = aqueous solution (1 ml) of sodium lauryl sulfate containing 0.1 M NaCl; B = aqueous solution (2 ml) of cetylpyridinium chloride (CPCl) containing 0.1 M KCl.

Some of their important observations are as follows:

- (i) Time period of oscillations as well as amplitude increase with increase in [amine].
- (ii) Time period as well as amplitude increase with decrease in the distance of cotton-soaked tube.
- (iii) When few drops (0.5 ml) of ammonia solution were directly added to the oil phase, the electric potential oscillations were observed almost instantaneously.

The mechanism of the above modified oscillator is similar to that as outlined in the earlier section. The cationic surfactant in B would favor preferable transfer of  $\text{Cl}^-$  in KCl compartment. The above observations support Eq. (8). Taking into account the chemical nature of the surfactants, negative and positive nature of the interfaces in the each compartment can be visualized. Obviously A would be positive while B would be negative as pointed out earlier.

The  $[\text{NH}_4^+]$  in the aqueous phase can also be expected to depend on the partition coefficient between non-aqueous and aqueous phase separated by the specific surfactant. Such studies on partition coefficient in surfactant solutions are very few. Partition coefficient of pentanol in NaDS has been investigated recently [18]. However, this is not relevant in the present case on account of the state of non-equilibrium.

Oscillations are also observed [8], when methylamine, dimethylamine and trimethylamine, which are more basic in character, are used. Similar effects are also produced when pheromones are used in place of amines, which generate corresponding carbocations [19].

The observed oscillations in both the type of oscillators appear to be non-periodic, sometimes chaotic and noisy. This is probably due to random adsorption of amine and pheromone vapors. However, periodicity increases in case of methylamine, and pheromones.

Thus, the interfacial instability in the above oscillators occurs on account of adsorption at the vapor–liquid interface followed by transport of ammonia across in the form of ammonium ion at the oil–water interface. The latter is controlled by the nature of the surfactant (cationic or anionic). Diffusion of  $\text{K}^+/\text{Na}^+$  from the bulk of the aqueous phase to interface influences the relative concentrations of  $[\text{Cl}^-]$  in the two chambers which ultimately generates oscillations.

A simplified mechanism of oscillatory phenomena at liquid–liquid and liquid–vapor has been elaborated in the present communication. However, more detailed investigation is warranted to take into account the adsorption–desorption kinetics in both the compartments since the phenomena is occurring in a region far away from equilibrium.

### 4. Sensing mechanism of smell

Generation of sense of smell by olfactory nerves is a complex phenomenon [20–23]. Although theories of sense excitation have been suggested by physiologists, but these are quite complex. The simplest theory suggests that the molecules of odorant proteins open up to become ion-channels, allowing mainly large number of positively charged sodium ions to flow to the interior of olfactory cell and depolarize it. The second theory postulates the odorant binding protein to become an activated adenylate cyclase, which in turn catalyzes the formation of cyclic adenosine monophosphate (cAMP). Subsequently cAMP acts on other proteins to open up ion-channels. The essential steps in sensing smell are the following:

- (i) Self-excitation of electrode potential by external sense stimulant.

- (ii) Depolarization of nerve cell.
- (iii) Generation of active potential.
- (iv) Nerve transmission.
- (v) Decoding of sensation by:
  - (a) Intensity of potential.
  - (b) Frequency.
  - (c) Number of active fibers.
  - (d) Nature of oscillation: Periodic, bioperiodic, triperiodic, sequential, intermittency, deterministic chaos, random noise.

A much simpler mechanism based on the self-excitation of potentials discussed in this paper in relation to generation of sense of smell by olfactory nerves can be postulated as follows,

In the case of amines and pheromones, one may speculate that periodic adsorption of amines and pheromones and subsequent interaction of  $\text{NH}_4^+$  ions and carbocations with  $\text{Cl}^-$  would lead to depletion of  $[\text{Cl}^-]$ . This would result in migration of  $\text{Cl}^-$  to the surface of the nerve cell leading to depolarization followed by development of action potential. The stimulus would travel through the resulting polarized cell. However, further experiments are needed for confirming the proposed mechanism.

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