

BPC 01039

## CHEMORECEPTION OF SUGARS BY AN EXCITABLE LIQUID MEMBRANE

Kenichi YOSHIKAWA, Teruyuki OMOCHI and Yasuhiro MATSUBARA

*Department of Chemistry, College of General Education, University of Tokushima, Tokushima 770, Japan*

Received 5th September 1985

Revised manuscript received 26th October 1985

Accepted 5th November 1985

*Key words: Oscillation; Self-excitation; Chemical sensing; Far-from-equilibrium*

Studies were made on electrical oscillations across a liquid membrane consisting of an oil layer, nitrobenzene containing picric acid, between two aqueous layers. This system showed sustained rhythmic oscillations of electrical potential of 200–300 mV with intervals in the order of 1 min. It was found that the histogram of frequency of oscillations was characteristic depending on the structures of the sugars. The histograms of glucose, fructose, galactose and sorbose showed a single maximum whereas those of sorbitol and mannitol showed double maxima.

### 1. Introduction

The physico-chemical mechanisms of taste and olfaction are not yet clear enough in spite of several studies over many years, perhaps because of the difficulty of investigating sensory organs at the molecular level [1–4]. Investigations mimicking the manner of sensing in biological systems are awaited.

Recently the present authors found [5] that a simple liquid membrane showed characteristic responses to alcohols in a similar manner to biological chemoreceptive membrane. The liquid membrane consisted of an oil layer, nitrobenzene containing picric acid, between two aqueous layers: that on the left containing cetyltrimethylammonium bromide (CTAB) plus alcohol at various concentrations and that on the right containing sucrose. This system showed sustained rhythmic oscillations of electrical potential of 200–400 mV with an interval in the order of 1 min. It was found that the frequency of oscillations increased with increasing concentration of alcohol and that the critical concentration of alcohols needed to induce oscillations decreased with increase in their

hydrophobicity, i.e., increase in their alkyl-chain length. From the results of this study, it was suggested that the response to alcohols in the liquid membrane resembled that of biological chemoreceptive membranes. As an extension of this work, we studied the manner of response to various sugars in the liquid membrane. This article describes the result of this study, showing that the response to sugars is clearly characteristic of their chemical structures.

### 2. Materials and methods

Experiments were performed in an apparatus with a U-shaped glass tube (12 mm inner diameter) as shown in fig. 1. A solution (4 ml) of 1.5 mM picric acid in nitrobenzene was placed in the base of the U-cell. Aqueous solutions (10 ml each) were introduced simultaneously into the arms of the U-cell above the organic phase without stirring. All measurements were carried out at 25°C. The voltage across the liquid membrane was measured with a Hitachi-Horiba F-7 pH/mV meter connected by two salt bridges to two Ag/AgCl elec-

trodes. All reagents were commercial products of analytical grade. Before use, nitrobenzene was purified by distillation and picric acid was dried in vacuo.

### 3. Results

Fig. 2 shows the oscillation of voltage across a liquid membrane, consisting of an oil layer, nitrobenzene containing 1.5 mM picric acid, between two aqueous phases, 5 mM CTAB plus 1.5 M ethanol on the left and 0.1 M sugar on the right. The oscillations started 30–40 min after the organic phase came into contact with the two aqueous solutions and continued for 1–2 h. The amplitude of the oscillations was between 200 and 300 mV and remained nearly constant during the oscillatory period. No oscillations were observed in the absence of sugar.

In order to clarify the difference in the manner of the oscillations. Fig. 3 shows histograms of the frequency of the oscillations. Here  $n$  is the number of the oscillations and  $f$  ( $s^{-1}$ ) is the inverse of the period ( $s$ ) between the pulses. For each histogram the result of three experimental runs was given. First, let us compare the histograms of monosaccharides. The histograms of glucose, fructose, galactose and sorbose are similar to each other,

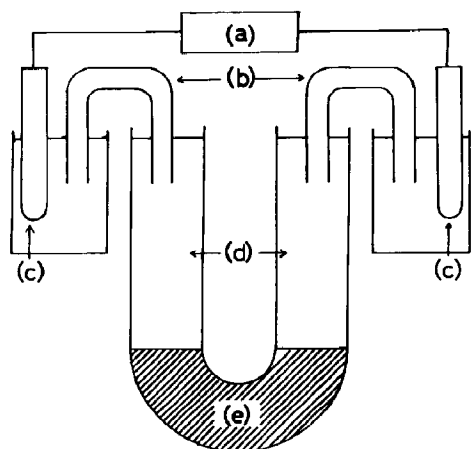


Fig. 1. Experimental apparatus: (a) millivolt meter, (b) salt bridge, (c) Ag/AgCl electrode, (d) aqueous layer, (e) organic layer.

showing only one maximum. It should be noted that the chemical composition of these four sugars is the same ( $C_6H_{12}O_6$ ) whereas the histograms of sorbitol and mannitol, having the chemical formula  $C_6H_{14}O_6$ , show double maxima of the frequency. A similar trend, i.e., double maxima of the frequency, has been encountered for the histo-

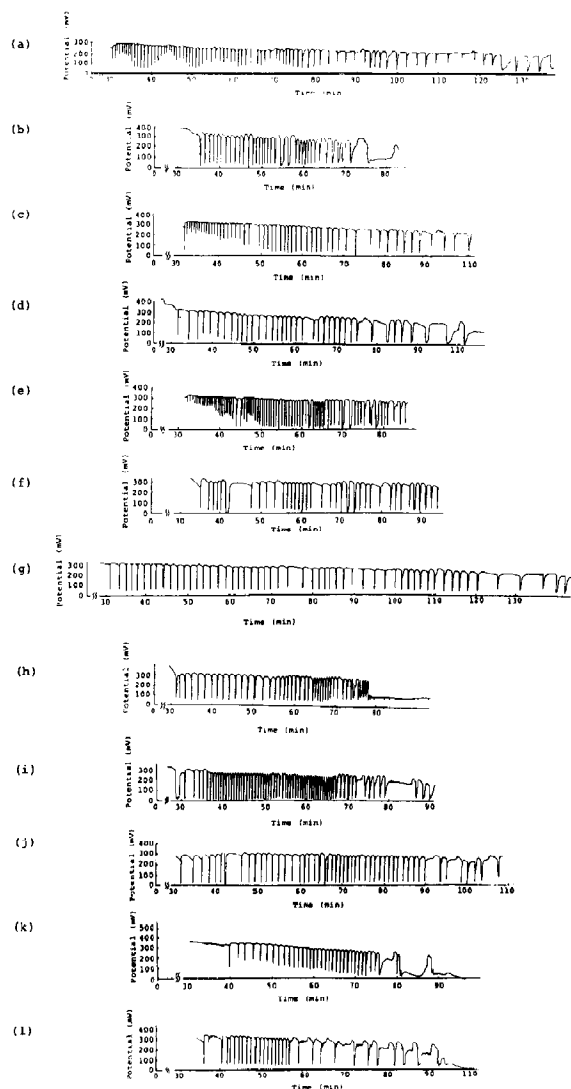


Fig. 2. Oscillation of the electronic potential across the organic phase: (a) D-glucose, (b) D-fructose, (c) D-galactose, (d) L-sorbose, (e) D-sorbitol, (f) D-mannitol, (g) D-ribose, (h) L-arabinose, (i) D-xylose, (j) D-sucrose, (k) D-maltose; (l) glycine.

gram of ribose, arabinose and xylose, with the formula  $C_5H_{10}O_5$ . This result suggests that the liquid membrane studied here is able to distinguish sugars differing in their chemical compositions based on information on the pattern of the oscillation. Such a characteristic feature of the histogram (monophasic or biphasic) has been well reproduced for each experimental run.

The histograms of disaccharides, sucrose and maltose show a single maximum, having slightly broader distributions of  $\log f$  than those of glucose, fructose, galactose and sorbose. It is also

noted that the pattern of the histogram of glycine, a sweet tasting substance, is markedly different from those of the sugars.

#### 4. Discussion

In section 3 we demonstrated that the manner of the oscillations depended markedly on the chemical structure of the sugars added to the aqueous phase in the liquid membrane. In connection with this, it is interesting to note that the

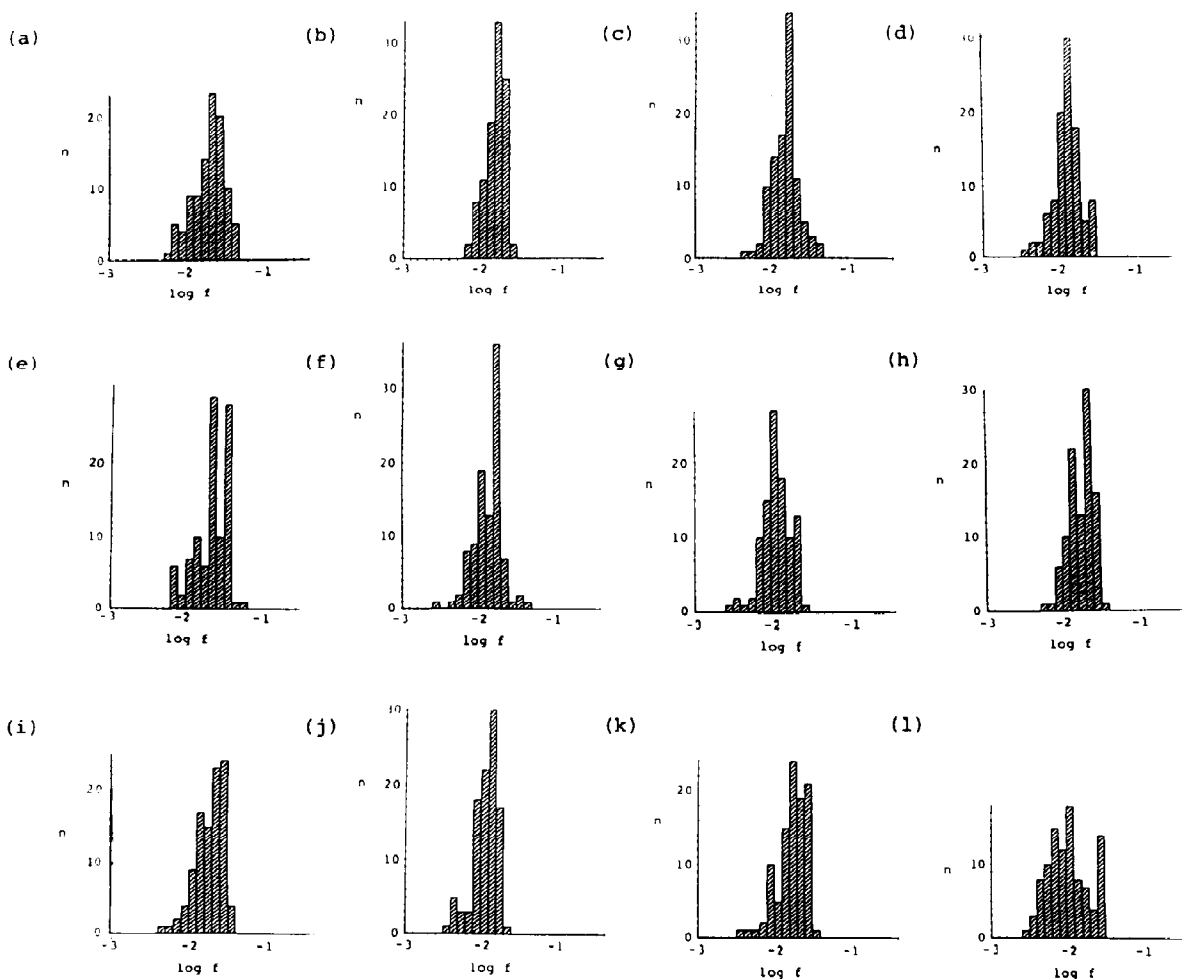


Fig. 3. Histogram of the logarithm of frequency of oscillation: (a) D-glucose, (b) D-fructose, (c) D-galactose, (d) L-sorbose, (e) D-sorbitol, (f) D-mannitol, (g) D-ribose, (h) L-arabinose, (i) D-xylose, (j) D-sucrose, (k) D-maltose, (l) glycine.

temporal discharge pattern or the interspike interval histogram in taste neurons changes markedly with different kinds of stimulus [6].

Next let us discuss such an experimental trend in relation to the mechanism of oscillation. Previously, we proposed [5,7] a mechanism of successive formation and abrupt destruction of the monolayer structure to explain the oscillations occurring in the liquid membrane. At the first stage when the organic phase is in contact with the two aqueous phases, hexadecyltrimethylammonium cations ( $\text{CTA}^+$ ), which are mainly present as micelles in the aqueous phase, move toward the interface where they become situated. Simultaneously, molecules of picric acid move toward the interface and dissolve in the aqueous phase. Thus the concentrations of  $\text{CTA}^+$  and picrate anion increase gradually, and  $\text{CTA}^+$  tends to form a monolayer structure at the interface. When the concentration of  $\text{CTA}^+$  at the interface reaches a critical value,  $\text{CTA}^+$  is abruptly transferred to the organic phase with formation of inverted micelles, thus producing the first pulse of the potential. When the concentration of  $\text{CTA}^+$  on the interface decreases to a lower critical value, accumulation of  $\text{CTA}^+$  on the interface begins again with gradual formation of a monolayer structure. Then, when the concentration of  $\text{CTA}^+$  increases to an upper critical value, abrupt transfer of  $\text{CTA}^+$  to the organic phase occurs. Such processes may occur repeatedly.

Sugars probably affect the structure of the monolayer of  $\text{CTA}^+$  on the interface. They may also influence the rates of migration of  $\text{CTA}^+$  from the aqueous phase to the interface and from

the interface to the organic phase. These effects of sugars may induce a change in the manner of the oscillations.

Recently we have succeeded in simulating the oscillation between a oil and water interface, using a set of nonlinear kinetic equations. Details of this theoretical study will be published elsewhere [8]. Although this study is preliminary, it indicates the possibility of developing a new type of chemical sensor capable of distinguishing chemical substances on the basis of information on the pattern of the oscillation.

### Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research to K.Y. from the Ministry of Education, Science and Culture of Japan.

### References

- 1 L.M. Beidler, in: *Handbook of Sensory Physiology IV, Chemical Senses 2, Taste*, (Springer-Verlag, Berlin, 1971), pp. 200.
- 2 N. Akaike and M. Sato, *Comp. Biochem. Physiol.* 55A (1976) 383.
- 3 K. Kurihara, N. Kamo and Y. Kobatake, *Adv. Biophys.* 10 (1978) 27.
- 4 J.A. De Simone and S. Price, *Biophys. J.* 16 (1976) 869.
- 5 K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.* 106 (1984) 4423.
- 6 T. Nagai and K. Ueda, *J. Neurophysiol.* 45 (1981) 574.
- 7 K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.* 105 (1983) 5967.
- 8 K. Toko, K. Yoshikawa, M. Tsukiji, M. Nosaka and K. Yamafuji, *Biophys. Chem.* 22 (1985) 151.