CHEMISTRY LETTERS, pp. 1833-1836, 1990.

A Convenient Apparatus for the Study of the Electric Pulse Generation in the Liquid Membrane System. Critical Behaviour of the Voltage Generation

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A new experimental set-up consisting of a hollow glass tube inserted into the organic phase of an aqueous-organic-aqueous system in a beaker exhibited reproducible electric pulses. Changes in the electric pulses are brought about by changing the separation distance between the two aqueous phases as well as the concentration of CTAB and the picric acid.

The oscillating membrane system is one of the best known models for the taste and olfactory detecting organs.[1-4] Among them, the liquid membrane system, developed by K. Yoshikawa et al.,[5,6] generates electric pulses whose periodicity is affected by co-existing compounds such as alcohols[7] and sugars.[8] However, this 'Yoshikawa system' was, as they point out, highly sensitive to the experimental conditions.[5] The U-tube normally used in the experiment (Fig. 1a) seemed to be responsible for the low reproducibility since the interface between the aqueous and nitrobenzene phases was at the bent part of the U-tube, as shown in Fig. 1a.[5] In this paper, we report a new experimental set-up shown in Fig. 1b capable of observing the electric pulses with relatively high reproducibility and stability.

In the new experimental set-up, a hollow tube fixed to a Z-stage is inserted into a nitrobenzene solution of picric acid (**B**) stored in a beaker. The tube is used to separate the two aqueous phases (**A**) and (**C**), which contains CTAB and glucose respectively. As the tube is raised, the distance separating the two aqueous phases decreases, while the area and shape of the aqueous-nitrobenzene interfaces is kept constant, thus ensuring a reproducibile interface. However, the voltage across the two aqueous phases (**A**) and (**C**) is found to increase, when the inner tube is raised, and at a certain threshold voltage, suddenly begins to generate electric pulses. The size of the tube diameter, on the other hand, had no effect on the voltage from 8 to 14 mm.

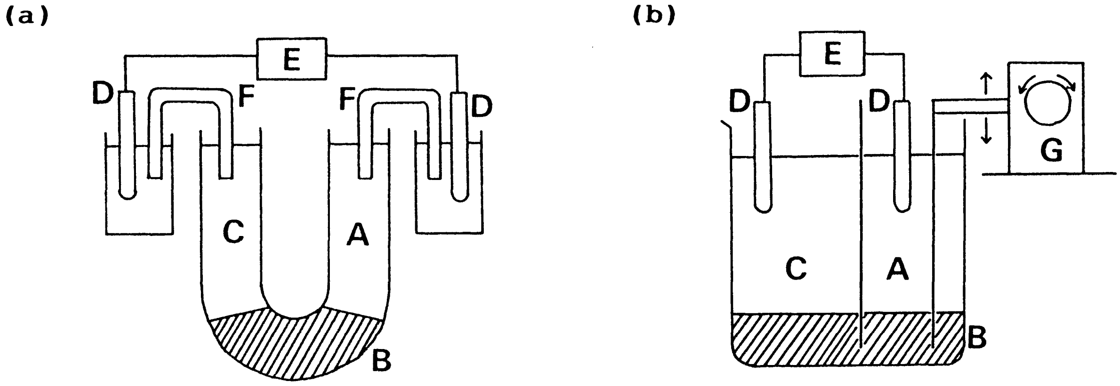

Fig. 1. The experimental set-up (**a**) Conventional, (**b**) This paper. **A:**CTAB aqueous solution, **B:**Picric acid nitrobenzene solution, **C:**Glucose aqueous solution, **D:**Ag/AgCl Electrode, **E:**Potentiometer, **F:**Salt Bridge, **G:**Z-Stage.

In Fig. 2 is shown the dependence of the generated voltage as a function of the distance of the tube inserted into the nitrobenzene solution. The (**A**) phase is CTAB 5 mmol·dm^{-3} aqueous solution, the (**B**) phase is picric acid 1.5 mmol·dm^{-3} nitrobenzene solution, and the (**C**) phase is glucose 0.1 mmol·dm^{-3} aqueous solution. As the tube, immersed in the nitrobenzene solution is raised, the distance between the two aqueous phases decreases and the generated voltage increases. Few little bumps, probably due to the wetting of the inserted tube, are also observed. It should be remembered that neither the size nor the shape of the interface is changed as the tube is raised but only the distance between the two aqueous phases is changed. Thus the generated voltage can be expressed by a monotonously decreasing function of the distance between the two interfaces. The electric pulses, however, are always observed, when the generated voltage exceeds 200 mV. In the conventional experimental set-up, the distance between the two aqueous phases is highly sensitive to the experimental conditions and procedures, and in some cases, the voltage does not exceed the threshold voltage, resulting in a constant base line with no electric pulses.

This observation strongly suggests that the voltage generated between two aqueous phases is the driving force for the formation of the electric pulses. Forced oscillation studies also support this suggestion.[9] When a voltage is applied externally between two aqueous phases, the system begins to generate current pulses. It is also shown that the application of the voltage critically accelerates the ion transfer through the aqueous-nitrobenzene phase.[10] Therefore, it can be said that a voltage generation of ca. 200 mV is needed for the formation of the periodic electric pulses, and that the new set-up, capable of changing the inter-interface distance and thus the voltage generated, provides more flexibility in variation of other relevant parameters.

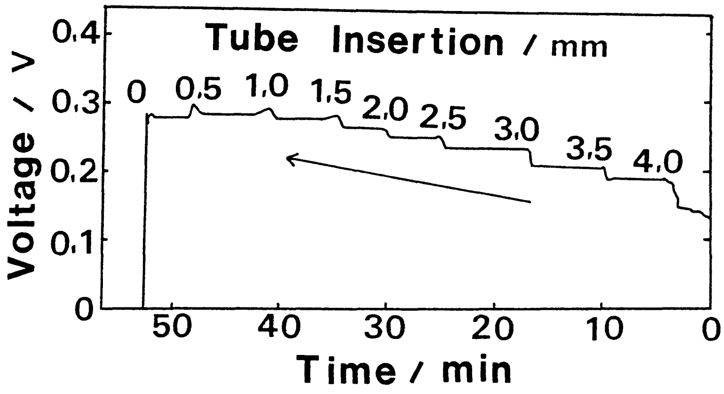

Fig. 2. Voltage generated as a function of the depth of the tube inserted to the nitrobenzene phase.

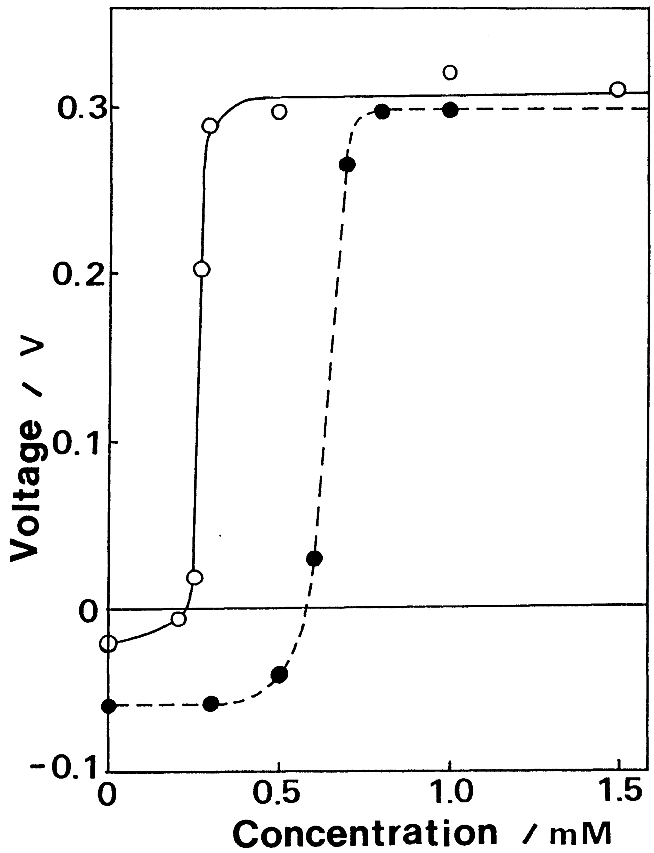

Fig. 3. Picric acid concentration dependence of the voltage generated with CTAB concentration of 5 $mmol \cdot dm^{-3}$ (—o—) and 10 $mmol \cdot dm^{-3}$ (--●--).

With this experimental set-up, the effect of the alcohols added and that of the picric acid concentration was investigated. The **(A)**, **(B)**, and **(C)** phases are the same as that in Fig. 2 except for the presence of 0.5

mol·dm^{-3} of alcohol species in the **(A)** phase. The frequency of the electric pulses was observed to be proportional to the alkyl chain length of the alcohol. This dependency accords with that observed with the U-tube system,[7] and also confirms that the phenomena observed in the new set-up are the same phenomena as observed in the conventional U-tube system. In Fig. 3, on the other hand, is shown the picric acid concentration dependence of the voltage generated for CTAB concentrations of 5.0 and 10.0 mmol·dm^{-3}. The voltage between the two aqueous phases drastically increases to ca. 300 mV at a critical picric acid concentration, which also is nearly proportionally to the concentration of CTAB.

This phenomenon strongly suggests the formation of an ion pair between the CTA cation and the picrate anion, as postulated by K. Yoshikawa et al.[5] The generation of voltage in aqueous-nitrobenzene-aqueous system occurs by adsorption of the ions at the interface, and has a critical dependence on the ion concentration.[11] The increase in the picric acid concentration up to the CTA cation concentration increases the ion pair formation that cancels the voltage. Thus, dissociation of the picric acid above the critical concentration is responsible for the generated voltage, and the periodic electric pulses are observed above the critical picric acid concentration. More detailed kinetics investigations are needed to clarify the exact mechanism, but by using the new experimental set-up, one is capable of performing new systematic experiments which were difficult to do before with the conventional experimental set-up.

The present work was partly supported by a Grant-in-Aid for Scientific Research No. 63750752 from the Ministry of Education, Science and Culture.

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(Received July 10, 1990)