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OSCILLATIONS OF ELECTRICAL POTENTIAL DIFFERENCES ACROSS THE INTERFACE IN PHASE-TRANSFER CATALYTIC SYSTEMS

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Oscillations of electrical potential differences across the liquid–liquid interface in phase-transfer catalyst systems are reported. The occurrence of the oscillations is consistent with the Starks' shuttling mechanism.

INTRODUCTION

In a phase-transfer catalyst system where the two reactants are located in two different phases, the phase-transfer catalyst (PTC) serves as a vehicle to bring one reactant into the same phase as the second so that the reaction between them which otherwise is inhibited takes place. The classical diagram of a phase-transfer catalytic cycle, first given by Starks,[1] is shown below:

$$\begin{array}{ccccl} Q^+Nu^- + R{-}X & \rightarrow & R{-}Nu + Q^+X^- & & \text{Organic phase} \\ \uparrow\downarrow & & \uparrow\downarrow & & \text{Interface} \\ Q^+Nu^- + M^+{-}X^- & \rightleftharpoons & M^+Nu^- + Q^+X^- & & \text{Aqueous phase} \end{array} \qquad (1)$$

where Q represents a quaternary ion, Nu the nucleophile, MX the salt of the cation M with anion X and R an organic radical.

The reaction cycle (1) implies that if one inserts in the two phases two electrodes capable of sensing the ions, one should observe oscillations of electrical potential difference across the electrodes. In fact, electrical potential oscillations across liquid–liquid interfaces, where a surfactant was added to one of the phases, have been documented.[2–4] The overall mechanism, which involves a dynamic equilibrium between micelles in the aqueous phase, reversed micelles in the non-aqueous phase and a monolayer at the interface, has been proposed by Yoshikawa and Matsubara[2] for such electrical potential oscillations.

Although phase-transfer catalysts need not be effective surfactants prone to forming micelles,[5,6] they always have both hydrophilic and hydrophobic domains in their structures and therefore aggregation of PTC molecules in both aqueous and non-aqueous phases, similar to that proposed by Yoshikawa and Matsubara,[2] cannot be ruled out. Should this be so, one may suspect the existence of electrical potential oscillations in PTC systems also.

Prompted by these ideas, electrical potential oscillations in three PTC systems listed in Table 1 were monitored. The PTC systems chosen are similar to those reported previously[7,8] except for some minor modifications.

Table 1. PTC systems chosen for monitoring electrical potential oscillations[a]

System	Description
1	$\frac{\text{(acidic aqueous KMnO}_4\text{) (0·01 M)}}{\text{Aliquat 336 + benzyl alcohol (30 ml)}}$ Interface
2	$\frac{\text{Benzene (25 ml) + benzyl alcohol + TBAC(0·07 M)}}{\text{acidic aqueous KMnO}_4\text{ (0·01 M)}}$ Interface
3	$\frac{\text{Aliquat 336 + chlorooctane (30 ml)}}{\text{Aqueous KCN (0·1 M)}}$ Interface

[a] Volume of each phase ≈ 30 ml. In systems 1 and 3 a few drops of Aliquat 336 were used

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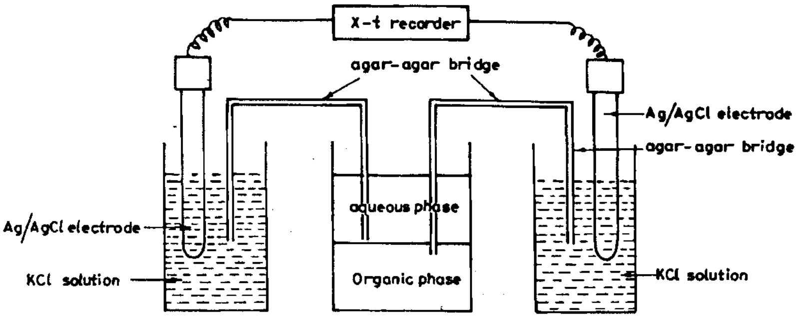

Figure 1. Experimental set-up for monitoring electrical potential oscillations

EXPERIMENTAL

Materials. Aliquat 336 and tetrabutylammonium chloride (TBAC), which were used as phase-transfer catalysts, were obtained from Aldrich (Milwaukee, WI, USA) and Fluka (Buchs, Switzerland), respectively. Benzene and benzyl alcohol (extra-pure quality) were obtained from S.D. Fine Chemicals (India) and 1-chlorooctane from Merck (Darmstadt, Germany). All other chemicals were of analytical-reagent grade. Deionized water distilled twice in an all-Pyrex glass still was used for preparing aqueous solutions.

Methods. The experimental set-up is depicted schematically in Figure 1. The volume of both organic and aqueous phase was 30 mL in all three systems presently studied. The phase-transfer catalysts were dissolved in the organic phase in all three systems (Table 1). In systems 1 and 2 the $KMnO_4$ solution was made acidic by adding one drop of concentrated hydrochloric acid. To monitor electrical potential oscillations, the sensing electrodes (Ag/AgCL electrodes obtained from Elico, Hyderabad, India) were placed as close to the interface as possible and connected to an x–t recorder (Omniscribe Series 5000, Digital Electronics, Bombay, India). While monitoring electrical potential oscillations, no stirring was applied.

All experiments were carried out at constant temperature using an air thermostat set at 30 ± 0·1 °C.

RESULTS AND DISCUSSION

Traces of the variation of the electrical potential differences across the interfaces with time in the three PTC systems given in Table 1 are shown in Figure 2. The oscillations commenced after 90–120 min. These oscillations can be viewed as further evidence in favour of the shuttling mechanism given by Starks [equation (1)]. The pH of the organic layer in both systems 1 and 2 showed a decrease during the experiment, indicating the formation of benzoic acid in the organic layer. After 180 min the pH of the organic layer in system 1 changed from 5·4 to 4·4 and in system 2 from 6·65 to 5·25.

A mechanism leading to the oscillations in electrical potential differences observed in this study can be proposed along the lines of Yoshikawa and Matsubara,[2] who invoked 'cooperativity' in the process of diffusion through the interface as a necessary condition to induce oscillations; to realize cooperativity they used surfactant molecules. Let us take the case of electrical potential oscillations and the oscillation of pH observed by them[2] across the interface in a system consisting of a solution of picric acid in 2-nitropropane and an aqueous solution of hexadecyltrimethylammonium bromide (CTAB). The mechanism proposed by them, which is depicted schematically in Figure 3, consisted of three steps:

1. Cations of CTAB which are present as micelles in the aqueous phase move towards the interface and

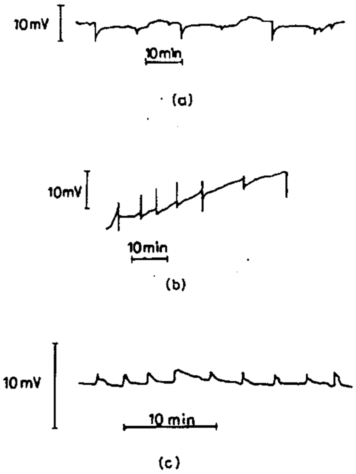

Figure 2. Traces of electrical potential oscillations across the interface in systems (a) 1, (b) 2 and (c) 3

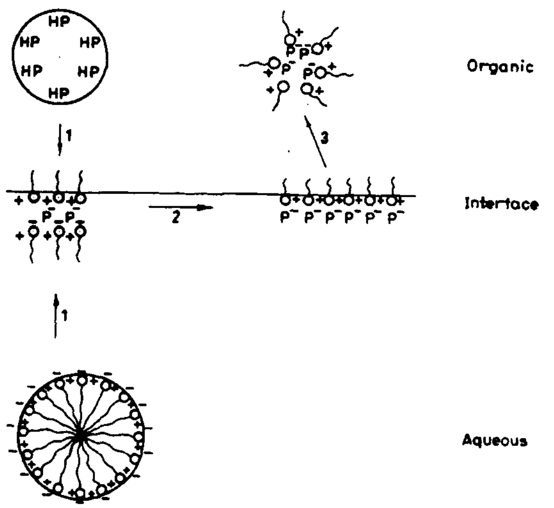

Figure 3. Schematic representation of the mechanism of oscillations in biphasic systems[2]

acquire an orientation such that hydrophilic groups are oriented towards the aqueous phase and the hydrophobic chain is oriented towards the organic phase. Simultaneously, picric acid (HP) molecules move towards the interface and dissolve in the aqueous phase, thus increasing the concentration of picrate ion (P^-) near the interface.

2. The concentrations of the CTAB cation and the picrate anion (P^-) increase gradually, leading to the formation of a monolayer structure at the interface (Figure 3).

In steps (1) and (2) the hydrophobic interaction between the detergent and the picrate is the main driving force.

3. On reaching a critical value of the concentration, the CTAB cations are suddenly transferred to the organic phase where they form inverted micelles (Figure 3); cooperative movement of CTAB cations. In this step an additional driving force arises from the formation of micelles in the organic phase.

When the concentration of CTAB cation decreases to a lower critical value, the system reverts back to step (1).

A mechanism similar to that postulated above by Yoshikawa and Matsubara[2] can be extended to the systems studied in this work (Table 1). Although phase-transfer catalysts need not be effective surfactants prone to forming micelles,[5,6] aggregation of PTC molecules in both aqueous and non-aqueous media cannot be ruled out owing to the presence of both hydrophilic and hydrophobic domains in their structures. One can therefore extend the mechanism proposed by Yoshikawa and Matsubara[2] (Figure 3) to the present systems (Table 1) by replacing micelles with submicellar aggregates. The counterpart of the picrate ion (Figure 3) in systems 1 and 2, for example, would be the MnO_4^- ion.

We should emphasize that although electrical potential oscillations in a biphasic system where surfactant molecules have been used in one of the phases have been demonstrated earlier by Yoshikawa and co-workers,[2,9] this is the first report of electrical potential oscillations in PTC systems.

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REFERENCES

1. C. M. Starks, *J. Am. Chem. Soc.* **93**, 195–199 (1971).
2. K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.* **105**, 5967–5969 (1983).
3. K. Yoshikawa, M. Shoji, S. Nakata and S. Maeda, *Langmuir* **4**, 759–762 (1988).
4. K. Yoshikawa and Y. Matsubara, *Biophys. Chem.* **17**, 183–185 (1983).
5. J. H. Fendler, *Membrane Mimetic Chemistry*. Wiley, New York (1982).
6. W. P. Weber and G. W. Gokel, *Phase Transfer Catalysis in Organic Synthesis*. Springer, Berlin (1977).
7. A. W. Herriott and D. Picker, *Tetrahedron Lett.* **16**, 1511–1514 (1974).
8. C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.* **95**, 3613–3617 (1973).
9. K. Yoshikawa, S. Maeda and H. Kawakami, *Ferroelectrics* **86**, 281–298 (1988), and references cited therein.