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Spontaneous Oscillation of pH and Electrical Potential in an Oil–Water System

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Abstract: Sustained, regular oscillations of pH and electrical potential appear in a system consisting of a solution of 1.25 mM picric acid in 2-nitropropane and an aqueous solution of 5 mM hexadecyltrimethylammonium bromide (CTAB). These oscillations, which have a constant period (0.5–2 min) and continue for 1–2 h, can be explained by a simple model involving ion-pair formation between the cationic detergent and picrate and formation of inverted micelles in the oil phase. Computer simulation with appropriate parameters in kinetic equations based on this model reproduced the observed rhythmic oscillation well.

Various biological systems exhibit periodic phenomena, e.g., oscillation of cells of nerve and muscle tissue, oscillation in mitochondria, and biological clocks. These phenomena have recently received much attention as "dissipative" effects in nonequilibrium systems.[1-3] Oscillatory phenomena have also been found in artificial membrane systems,[4-7] the oscillatory variables being the electrical potential of the membrane and/or the hydrostatic pressure between the compartments on the two sides of the membrane. The present paper reports rhythmic electrochemical oscillations appearing in a system consisting of oil and water phases, which is much simpler than model membrane systems.

Experimental Section

All reagents were commercial products. Picric acid was dried in vacuo. The organic solvents 2-nitropropane and 1-nitropropane were purified by distillation. Measurements were made after bringing 2 mL of the aqueous phase, a solution of hexadecyltrimethylammonium bromide (CTAB), in contact with an upper phase of 1.5 mL of the organic solvent containing picric acid in a test tube (13 mm in diameter). Experiments were usually carried out without stirring and the temperature was kept at 18 °C during measurements. The pH of the aqueous phase and the electrical potential between the organic and aqueous phases were measured with Hitachi-Horiba F-7 pH/mV meters. The pH was monitored with an Ingold combination glass electrode (3-mm diameter, catalog No. 6030-02). When necessary, separate type glass and reference electrodes were used to monitor the pH. Essentially the same results have been obtained with the combination electrode and separate type electrodes. Usually the combination glass electrode was placed about 5 mm from the interface. The amplitude of the observed pH oscillation depended on the position of the glass electrode, and was less when the glass electrode was far from the interface. The electrical potential was monitored with two bright platinum probes (wire) situated on either side of the interface, and about 3–5 mm from it.

Results

Figure 1 shows the whole profile of the change of pH in the aqueous phase after contact of the organic and aqueous phases with and without continuous stirring. The absence of oscillation when the system was stirred continuously suggests that the oscillation is strictly associated with the interface structure between the organic and aqueous phases.

Figure 2 shows the oscillations of pH in the aqueous phase and of electrical potential between the two phases in a system of a solution of picric acid in 2-nitropropane and an aqueous solution of hexadecyltrimethylammonium bromide (CTAB). This experiment was carried out without stirring. Oscillations started 1–2 h after the organic and aqueous phases came in contact, and continued for 1–2 h. The oscillations of pH and electrical potential showed a constant period (0.5–2 min) and constant amplitude, and as seen in Figure 2, they were synchronized.

Similar oscillations were obtained when CTAB was replaced by other cationic detergents, such as dodecyltrimethylammonium bromide or 1-laurylpyrydinium chloride. Periodic oscillations were also observed when 1-nitropropane was used as the organic solvent instead of 2-nitropropane.

Oscillations were observed only when the concentration of CTAB was above 2 mM. But in the presence of 2.5% v/v ethanol, periodic oscillations occurred even when the concentration of CTAB was as low as 1.5 mM. The aqueous phase did not turn yellow after contact with the organic phase, indicating that picric acid does not dissolve in the bulk aqueous phase when the latter contains CTAB.

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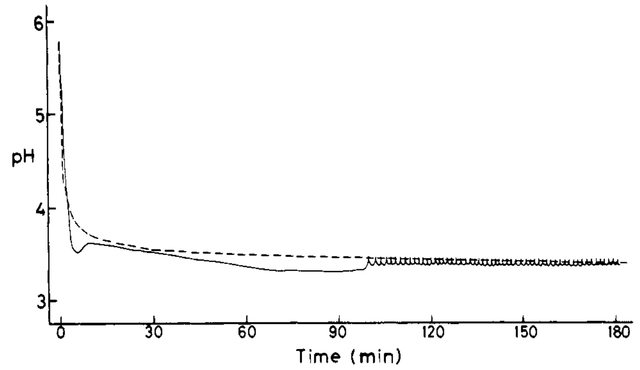

Figure 1. pH variation after contact of the two phases. Solid line, without stirring; dotted line, with stirring.

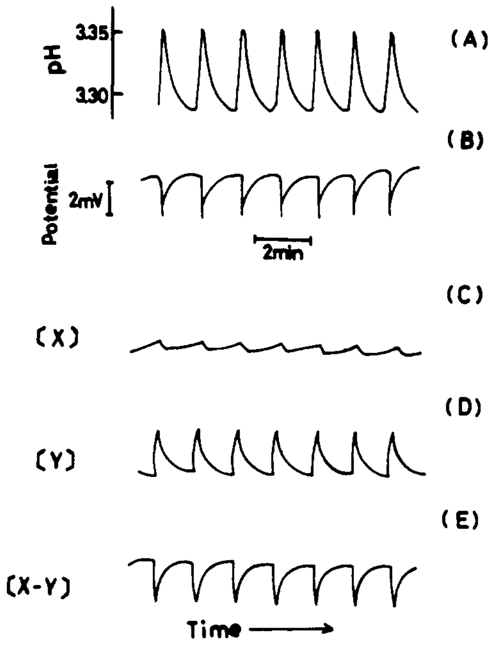

Figure 2. Temporal oscillations of (A) pH in the aqueous phase and (B) electrical potential between the aqueous and organic phases and (C, D, and E) the results of computer simulation. x and y denote concentration of picrate anion (A^-) and hexadecyltrimethylammonium ion (CTA^+) near the interface, respectively, and $[x - y]$ is thus the difference between the concentrations of A^- and CTA^+.

Discussion

Dupeyrat and Nakache[8,9] observed quasiperiodic variations of a relaxation type in the interface tension and the electrical potential of a system of solutions of hexadecyltrimethylammonium chloride in water and picric acid in nitroethane or nitrobenzene. We observed rhythmic oscillation in similar experimental conditions to theirs except that 2-nitropropane was used as the organic solvent. We also found that movement of the interface was considerably reduced by using 2-nitropropane as the organic solvent instead of nitroethane. It is noteworthy that the specific gravity (20 °C with reference to water at 20 °C) of nitroethane is 1.052 and that of 2-nitropropane is 0.992, the latter being close to unity. This difference in specific gravities of the two organic solvents, as well as differences in viscosity and interfacial tension, may explain the discrepancy between our experimental results and those of Dupeyrat and Nakache. They proposed a mechanism[8,9] involving ion-pair complexes between CTA^+ and picrate anion to explain the interfacial movement that they observed. On the basis of a theoretical consideration, however, Sanfeld et al. claimed[10] that no interfacial motion could occur by the mechanism proposed by Dupeyrat and Nakache.

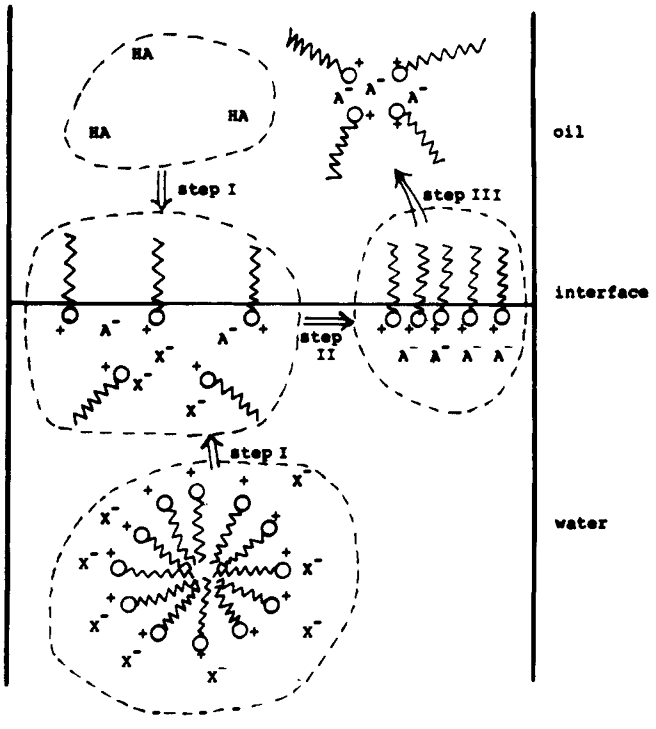

Figure 3. Schematic representation of the mechanism of the oscillation (see text).

We propose the mechanism shown in Figure 3.

Step I: Hexadecyltrimethylammonium cations (CTA^+), which are mainly present as micells in the aqueous phase, move toward the interface and become situated in a manner such that the hydrophilic ammonium group and the alkyl chain are orientated to the aqueous and organic phases, respectively. Simultaneously the molecules of picric acid move toward the interface and dissolve in the aqueous phase, increasing the concentration of picrate anion (A^-) near the interface.

Step II: The concentrations of CTA^+ and picrate anion (A^-) increase gradually, and CTA^+ ions form a monolayer structure on the interface. In steps I and II, the driving force is dominated by the hydrophobic interactions between detergent and picrate.

Step III: When the concentration of CTA^+ reaches a critical value, CTA^+ ions suddenly transfer the organic phase accompanied with the formation of inverted micells ("co-operative" movement of CTA^+ ions). In this step an additional driving force arises from the formation of micells in the oil phase. When the concentration of CTA^+ decreases to a lower critical value, the system again does back to step I. As steps I and II are considered to proceed simultaneously, this model can be regarded as a two-step pump (between steps I and II and step III).

On the basis of this model, the following kinetic equations are proposed where x and y are the concentrations of A^- and CTA^+, respectively, near the interface.

(i) $y_{\min} \rightarrow y \rightarrow y_{\max}$ (when y is increasing, steps I and II)

$$dx/dt = \alpha(y - x) \tag{1}$$

$$dy/dt = c - \beta(y - x) \tag{2}$$

(ii) $y_{\max} \rightarrow y \rightarrow y_{\min}$ (when y is decreasing, step III).

$$dx/dt = \alpha(y - x) - \gamma y^n/(\theta + y^n) \tag{3}$$

$$dy/dt = c - \beta(y - x) - \delta y^n/(\theta + y^n) \tag{4}$$

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These equations shows that the kinetics of x and y effect each other, i.e., the concentrations of CTA^+ and A^- near the interface are mutually dependent. Equations 1 and 2 represent the kinetics of diffusion of picric acid from the bulk organic phase and of diffusion of CTAB from the bulk aqueous phase toward the interface, respectively. The last term in eq 3 and 4 implies the "co-operative" behavior between CTA^+ ions in step III (Hill approximation).[11] The parameters chosen tentatively for computation in Figure 2 are $y_{\min} = 0.4$, $y_{\max} = 0.8$, $\alpha = 0.3$, $\beta = 2$, $c = 0.25$, $\gamma = 2$, $\delta = 30$, $\theta = 2$, and $n = 3$. (Numerical calculations were carried out with use of a Runge-Kutta approximation on a NEC PC-8800 microcomputer.)

In spite of the simplicity of our model, the simulated results reproduce the experimental trend well, as shown in Figure 2. The difference in concentrations of CTA^+ and A^- near the interface may correlate with the electrical potential between the two phases. Indeed the calculated variation of $[x - y]$ corresponds well to that of the electrical potential. The pH value of the aqueous phase may depend on several complicated factors, such as the concentrations of CTA^+ and Br^- and also the concentration and shape of the micells of CTA^+. Accordingly, explanation of the variation of pH is more complicated and difficult than that of variation of the electrical potential. However, it is interesting that the manner of the calculated change of $[y]$ is quite similar to that of pH, as shown in Figure 2.

Our model is too simple to allow discussion of experimental trend quantitatively, but the correspondence of experimental and calculated results suggests its validity. Further experimental and theoretical studies on the oscillatory phenomena are in progress in our laboratory.[12]

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Registry No. CTAB, 57-09-0; picric acid, 88-89-1; 1-nitropropane, 108-03-2; 2-nitropropane, 79-46-9.

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Matrix Isolation Studies of Nucleic Acid Constituents. 1. Infrared Spectra of Uracil Monomers

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Abstract: Results of infrared studies of uracil and its N_1,N_3-dideuterated homologue isolated in argon and nitrogen matrices are presented and discussed in terms of normal modes predicted by quantum-mechanical calculations. The effects on the spectrum of N-deuteration and of the interaction between the isolated molecule and the matrix are discussed. The quantum-mechanical calculations are used to make a reasonably reliable first assignment of absorption bands to all the normal modes for the matrix-isolated uracil molecule. The wavenumbers and relative intensities for the absorption bands for the isolated molecule are related to those reported previously for uracil in the solid phase but differ significantly from them.

Introduction

For a proper interpretation of the vibrational spectra of nucleic acids in biophysical research, it is essential first to obtain, and then to understand, the spectra for the isolated noninteracting molecules. By studying the spectral changes which occur from the isolated molecule to molecules placed in more and more strongly interacting environments, one may hope to interpret the vibrational spectrum and also to obtain information about the interacting environment of such molecules in truly biological conditions. Although the vibrational spectra of uracils have been extensively investigated in solutions and in the solid state (e.g., ref 1 and 2), the analyses are complicated by intermolecular hydrogen bonding and/or interactions with polar solvents, or by the low solubility in nonpolar solvents. In the vapor phase[3-5] rotational broadening of the bands complicates the analyses of the spectra of the monomeric species.

Matrix isolation spectroscopy provides a unique method for study of vibrational spectra of monomeric molecules under conditions where interaction between molecules, and their rotational motions, are minimized.[6-8] This procedure results in drastic sharpening of the absorption bands, so that bands which overlap in the spectra of the vapor, solution, or solid may often be readily resolved in the spectrum of the matrix. Although some secondary effects may result from the matrix, the infrared spectra of species isolated in rare gas matrices correspond closely to the pure vibrational spectra for molecules in the gas phase. Hence, these results are preferred for comparison with theoretically predicted vibrational spectra.

In a continuation of studies[5] on 2(4)-dioxopyrimidines using matrix isolation infrared spectroscopy, we report here the infrared spectra of uracil and its N_1,N_3-dideuterated homologue. We present the infrared spectrum for the isolated uracil molecule dilute in an argon matrix and its modification in a nitrogen matrix. The

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