Detection of Zinc(II) Ion by Using Self-Oscillation of the Electrical Potential across the Water-Oil-Water Liquid Membrane

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Oscillation of an electrical potential across a water-oil-water liquid membrane was measured in the presence of metal ion in one of the aqueous phases and a ligand in the organic phase, which likely forms a complex with Zn^{2+}. By use of the formation of the complex around the interface, Zn^{2+} was detected through the measurement of the oscillation mode.

Oscillation of an electrical potential at an oil-water interface, which was first observed by Dupeyrat et al.,[1] was expanded to a water-oil-water system by Yoshikawa et al.[2] Lots of studies of this three-phases system have been reported on the mechanism[2,3] of the oscillation and on the application of the oscillation to the method to analyze various substances such as tastes[4] or drugs.[5] The application to the method to analyze any metal ion in water, however, has never reported yet. The analysis of the metal ion seems to be difficult simply by the addition of the metal ion into the aqueous phase. In the presence of a ligand in the organic phase, some kinds of metal ions in one of the aqueous phases form complexes with the ligand around the water-oil interface, which will affect the oscillation mode. Thus, the use of the formation of the complex may enable to analyze the metal ion through the measurement of some changes in the oscillation mode. In the present paper, we measured the oscillation of the electrical potential across the water-oil-water liquid membrane in the presence of Tetra-n-butyl thiuram disulfide (TBTDS) as the ligand in the organic phase. The oscillation modes were compared between the presence and the absence of some metal ions in one of the aqueous phases. Zn^{2+} which likely forms the complex with TBTDS was detected through the measurement of the frequency of the oscillation for the first time.

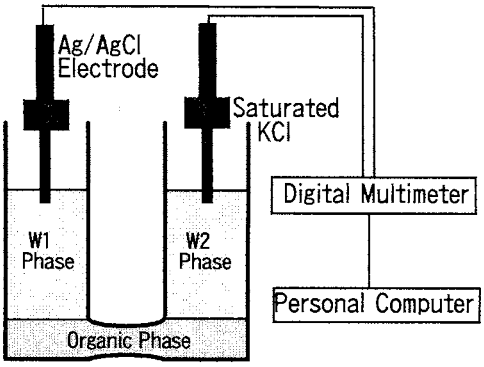

Figure 1. Experimental set-up used. W1, W2; aqueous phase.

The experimental set-up used is shown in Figure 1. 3.2 ml of nitrobenzene solution of picric acid with the concentration of 1.5 mM was first placed in the cell to form the organic phase. The surface of the solution was reached just the top surface of the lateral glass tube connecting the two vertical glass tubes. Two aqueous solutions were placed on the organic phase to form W1 and W2 phase. The W1 phase contained 10 mM hexadecyl trimethyl ammonium bromide as a surface active substance, 0.5 M 2-butanol, and 1 mM metal ion in case of need. Zn^{2+} ($Zn(NO_3)_2$) or Ca^{2+} ($Ca(NO_3)_2$) was used as the metal ion. The W2 phase was only water. TBTDS was added into the organic phase at the concentration of 1 mM in case of need. The experiments were carried out at the temperature of 17 ± 0.2 ℃. The electrical potential between the two aqueous phases was measured through a pair of Ag/AgCl electrodes by a digital multimeter and recorded with a personal computer. The W1 phase was connected with the positive terminal of the digital multimeter; the W2 phase, to the negative terminal.

Figure 2 shows the typical oscillation of the electrical potential between the two aqueous phases in the presence of 1 mM Zn^{2+} in the W1 phase and 1 mM TBTDS in the organic phase. The voltage is shown between 40 and −400 mV. The

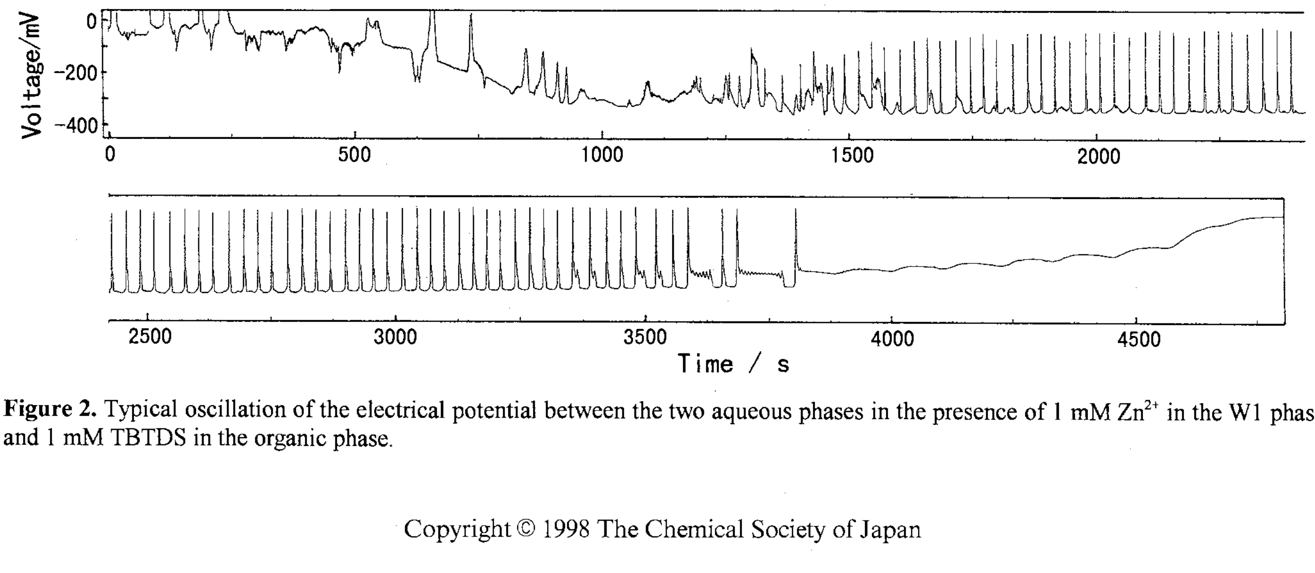

Figure 2. Typical oscillation of the electrical potential between the two aqueous phases in the presence of 1 mM Zn^{2+} in the W1 phase and 1 mM TBTDS in the organic phase.

electrical potential fluctuated between 100 and −320 mV for the first 1300 s. Next sharp pulses of about 300-mV amplitude appeared at regular time intervals of about 31 s up to 3400 s and continued at longer and irregular time intervals up to 3700 s. The potential subsequently approached 0 mV gradually. The pulses are attributed to the transfer of H^+ of picric acid in the organic phase across the interface.[6] The amplitude and shape of one of the pulses were not absolutely exact because the response of the instruments used was not so quick as to follow the variation in the potential so rapidly. In other cases of various contents of each phase also the voltage fluctuated at the beginning, next oscillated regularly, and approached 0 mV although the frequency of the oscillation and the oscillatory period changed.

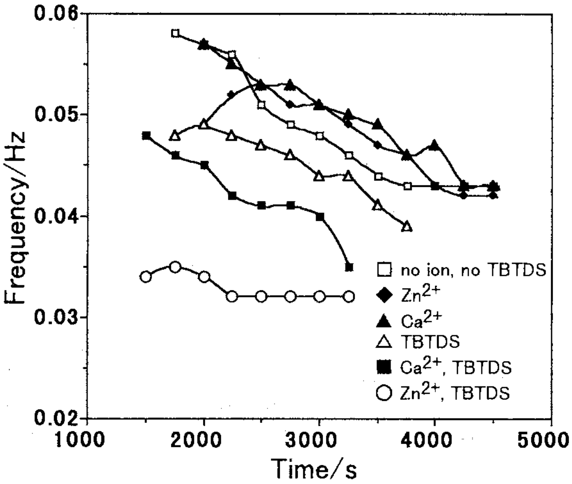

Figure 3. Time courses of the frequency of the oscillation of the electrical potential for the regular oscillatory period in the cases of various contents of each phase.

Figure 3 shows the time courses of the frequency of the oscillation for the regular oscillatory period in the cases of various contents of each phase. In the absence of any metal ion and TBTDS (□), the frequency was 0.058 Hz at the time of 1600 s, followed by decreasing gradually to 0.043 Hz at 4500 s. The frequencies at each time were reproducible to ± 5% on repeated runs. The addition of 1 mM Zn^{2+} (◆) or 1 mM Ca^{2+} (▲) into the W1 phase little changed the time course (□) of the frequency obtained in the absence of the metal ion. This means that any metal ion with the concentration of 1 mM was not able to be detected simply by the addition of the metal ion alone. When 1 mM TBTDS which likely forms the complex with Zn^{2+} was further added into the organic phase of the system containing Zn^{2+} in the W1 phase (○), the time course of the frequency changed greatly: the frequencies became smaller by 0.014-0.023 Hz and the oscillatory period became shorter. These changes were not only due to the presence of TBTDS for reasons mentioned below. In the absence of Zn^{2+} but the presence of TBTDS (△), the frequencies at each time were close to those (□) obtained in the absence of both TBTDS and Zn^{2+} up to 3700 s. Thus, TBTDS and Zn^{2+} form the complex around the W1-oil interface, which affects the oscillation mode. This was supported experimentally by use of Ca^{2+} which little forms any complex with TBTDS as mentioned below. In the presence of 1 mM Ca^{2+} in the W1 phase instead of Zn^{2+} (■), the frequencies were larger than those (○) obtained in the presence of Zn^{2+} by 0.008-0.015 Hz and were consequently close to those (△) obtained in the presence of only TBTDS. Thus, Zn^{2+} was distinguished from Ca^{2+} by the difference in the frequency of the oscillation. The Zn^{2+}-concentration dependence of the oscillation mode was studied: the frequency at the time of 3000 s was 0.03 Hz for 10 mM, 0.032 Hz for 1 mM, 0.041 Hz for 0.1 mM, 0.043 Hz for 0.01 mM, and 0.044 Hz in the absence of Zn^{2+}. Thus, the detection limit of this method for Zn^{2+} was about 0.01 mM.

The oscillation of the electrical potential was proved to be applicable to the method to detect Zn^{2+}. The oscillation observed in the water-oil-water system contains lots of valuable information for analyses of substances: the frequency, the oscillatory period, the induction period, and the amplitude and shape of the pulse. The analyses of drugs were carried out by use of the amplitude, the oscillatory period, and the induction period.[5] These characteristics of the oscillation are expected to be useful for analyses of the metal ion.

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