

## Application of Self-Oscillation of the Electrical Potential across the Water-Oil-Water Liquid Membrane to Quantitative Analysis of Aluminum Nitrate

Toshifumi Yoshidome,\* Toshifumi Higashi, and Satsuo Kamata

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University,  
1-21-40 Korimoto, Kagoshima 890-0065

(Received January 31, 2000; CL-000101)

Self-oscillation of an electrical potential across a water-oil-water liquid membrane was measured in the presence of metal nitrate in one of the aqueous phases. Oscillation mode changed particularly in the case of metal ion with the electric charge of  $3+$ , and the magnitude of the change monotonously increased in frequency with the concentration of  $\text{Al}(\text{NO}_3)_3$ .

Self-oscillation of an electrical potential at an oil-water interface was first observed by Dupeyrat et al.,<sup>1</sup> and was expanded to a water-oil-water system by Yoshikawa et al.<sup>2</sup> This three-phases system has been studied on mechanism<sup>2,3</sup> of the oscillation, and was applied to the method to analyze various substances such as tastes,<sup>4</sup> drugs,<sup>5</sup> and metal ion.<sup>6</sup> Since metal salt in an aqueous solution is simpler in structure than tastes and drugs, analysis of metal salt is more difficult than analyses of tastes and drugs by the use of this three-phases system. In the previous paper,<sup>6</sup> the analysis of metal ion in the aqueous phase was carried out by the use of a ligand in the organic phase, which likely forms complex with the metal ion around the water-oil interface. This method is useful for selective detection of some metal ions, but a particular ligand is necessary for each metal ion. In the present paper, this three-phases system was applied to the analysis of metal ion without any ligand. Some metal nitrates were taken up, and the self-oscillation modes were measured in the presence of one of nitrates in the aqueous phase. The mode changed depending on the electric charge of metal ion: the larger the charge was, the larger the magnitude of the change was, which was first observed in this experiment. Concentration dependence of the oscillation mode was studied in the case of  $\text{Al}^{3+}$  as an example of metal ion with the large electric charge. The experimental set-up<sup>6</sup> used enabled these small differences in oscillation mode to be detected.

The experimental set-up used is the same as that reported before.<sup>6</sup> 3.0 mL of nitrobenzene solution of 1.5 mM picric acid was first placed in the cell to form the organic phase. Two aqueous solutions were placed on the organic phase to form W1 and W2 phases. The W1 phase contained 10 mM hexadecyl trimethyl ammonium bromide as a surface active substance and 0.5 M 2-butanol. The W2 phase contained metal nitrate in case of need. Nitrates of  $\text{Al}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  were used.

Figure 1 shows typical oscillations of the electrical potential between the two aqueous phases in the absence (a) and presence (b) of 1 mM  $\text{Al}(\text{NO}_3)_3$  in the W2 phase. The oscillation mode in the absence of  $\text{Al}(\text{NO}_3)_3$  (a) is characterized as follows. The electrical potential slightly fluctuated around  $-300$  mV for the first 22 min. Next sharp pulses of about 160-mV amplitude appeared at regular time intervals up to 45 min, and continued at longer and irregular time intervals up to 54 min. The potential subsequently approached 0 mV gradually after the pulses disappeared. In the presence of 1 mM  $\text{Al}(\text{NO}_3)_3$  in the W2 phase, the oscillation mode largely changed: the inductive and oscillatory periods became longer, and the frequency of the oscillation became lower. Amplitudes of the pulses also fluctuated like a sine wave. Since the sine wave changed in mode in the presence of 1 mM  $\text{Al}(\text{NO}_3)_3$ , that may be applicable to the analyses of metal nitrates.

The oscillation modes were measured similarly in the presence of one of the other metal nitrates in the W2 phase at the concentration of 1 mM. Figure 2 shows the time courses of the frequency of the oscillation for the regular oscillatory period. The time courses were reproducible to about  $\pm 5\%$  in oscillato-

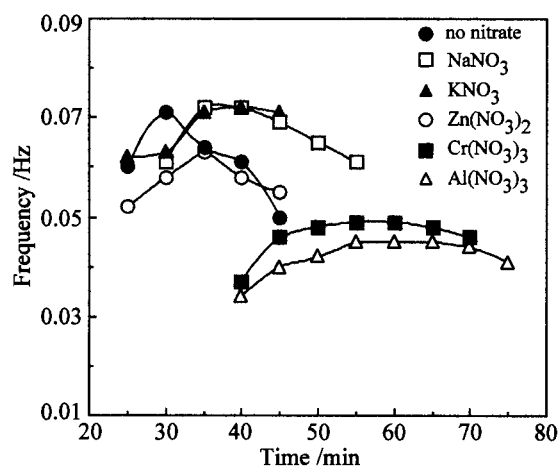


Figure 2. Time courses of the frequency of oscillation for a regular oscillatory period for various 1 mM metal nitrates.

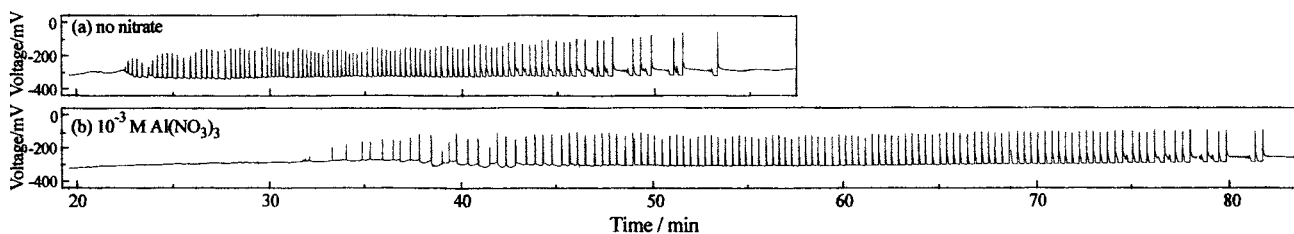


Figure 1. Typical oscillations of the electrical potential between the two aqueous phases in the absence (a) and presence (b) of 1 mM  $\text{Al}(\text{NO}_3)_3$  in the W2 phase.

ry period, to about  $\pm 4\%$  in frequency, and to about  $\pm 10\%$  in inductive period on repeated runs. In the absence of any metal nitrate in the W2 phase ( $\bullet$ ), the frequency was 0.059 Hz at the time of 25 min, suddenly increased to reach maximum of 0.071 Hz at 30 min next, and decreased to 0.048 Hz at 45 min. In the case of  $\text{Na}^+$  ( $\square$ ), the frequency was 0.061 Hz at 30 min, suddenly increased to reach maximum of 0.072 Hz at 37 min next, and decreased to 0.061 Hz at 55 min. In the case of  $\text{K}^+$  ( $\blacktriangle$ ), the time course of the frequency was very close to that in the case of  $\text{Na}^+$  though the inductive and oscillatory periods were a little shorter. Thus, the oscillation in the presence of nitrate of metal ion with the charge of 1+ was in frequency close to that in the absence of any metal nitrate. In the case of  $\text{Zn}^{2+}$  ( $\circ$ ), the time course of the frequency resembled that in the case of  $\text{K}^+$ , but the frequency was lower for the entire oscillatory period by 0.005 to 0.015 Hz. Since the addition of  $\text{Zn}(\text{NO}_3)_2$  into the W1 phase did not affect the oscillation mode very much,<sup>6</sup> the presence of metal nitrate in the W2 phase is thought to affect the oscillation mode more largely than that in the W1 phase. In the case of  $\text{Cr}^{3+}$  ( $\blacksquare$ ), the frequency became further lower, and the inductive and oscillatory periods became further longer: the frequency was 0.036 Hz at 40 min, gradually increased to reach maximum of 0.049 Hz at 55 min next, and gradually decreased to 0.046 Hz at 70 min. In the case of  $\text{Al}^{3+}$  ( $\triangle$ ), the time course of the frequency resembled that in the case of  $\text{Cr}^{3+}$  though the frequency was lower by 0.003 to 0.006 Hz for the entire oscillatory period. Thus, the characteristics of the oscillation mode strongly depended on the electric charge of metal ion: the larger the charge was, the lower the frequency was, and the longer the inductive and oscillatory periods were. This charge dependence of the oscillation mode, which was first observed in this experiment, is thought to be ascribed in part to the structures of these metal ions accompanied by  $\text{NO}_3^-$  ions and/or the picric anions around the interface: the metal ion with the charge of 3+ can be surrounded by more  $\text{NO}_3^-$  ions and/or picric anions than the metal ion with 1+ can. The frequency observed in the case of  $\text{Al}^{3+}$  was a little lower than that in the case of  $\text{Cr}^{3+}$ , which may show a small difference in structure between these metal nitrates in the aqueous solution. Since the metal ion with the charge of 3+ particularly affected the oscillation mode, quantitative analyses of  $\text{Al}(\text{NO}_3)_3$

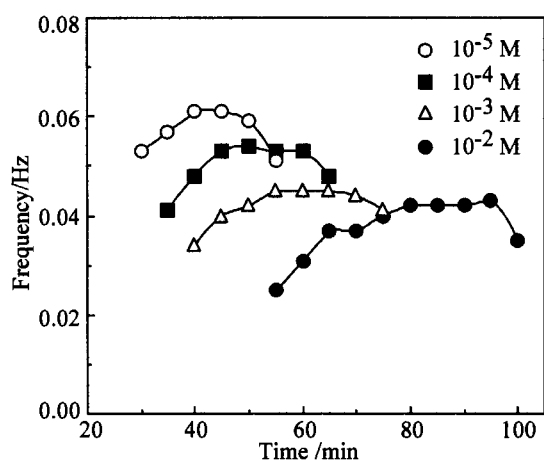


Figure 3. Time courses of the frequency of oscillation for a regular oscillatory period in the presence of  $\text{Al}(\text{NO}_3)_3$  with the concentration of  $10^{-5}$ - $10^{-2}$  M.

were carried out as an example. Figure 3 shows the time courses of the frequency of the oscillation observed in the presence of  $\text{Al}(\text{NO}_3)_3$  with the concentration of  $10^{-5}$ - $10^{-2}$  M for the regular oscillatory period. The oscillation mode strongly depended on the concentration of  $\text{Al}(\text{NO}_3)_3$  as expected: the higher the concentration was, the lower the frequency was, and the longer the inductive and oscillatory periods were. Figure 4 shows a plot of the frequency for the regular oscillatory period against the concentrations of  $\text{Al}(\text{NO}_3)_3$ . The datum adopted for Figure 4 corresponds to the middle point on each time course of the frequency in Figure 3 because the frequency was most stable and most reproducible at about the time of the middle point on the time course. The frequency decreased monotonously with the concentration of  $\text{Al}(\text{NO}_3)_3$  though the frequency change was saturated in magnitude at  $10^{-2}$  M due to the high concentration of  $\text{Al}(\text{NO}_3)_3$ . Thus, the concentration of  $\text{Al}(\text{NO}_3)_3$  was able to be known through the frequency of the oscillation.

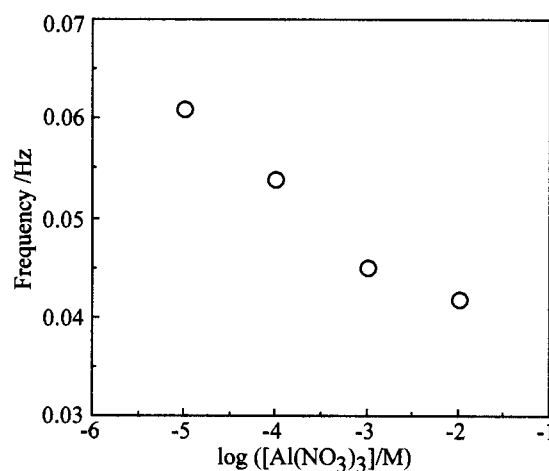


Figure 4. Plot of the frequency for the regular oscillatory period against the concentration of  $\text{Al}(\text{NO}_3)_3$  in the W2 phase.

Metal nitrates in the aqueous solution do not differ in structure from one another as much as substances such as drugs and tastes differ, but the oscillation mode of the electrical potential was found to change depending on the charge of metal ion, and further quantitative analysis was possible through the change of the frequency in the case of nitrate of metal ion with the charge of 3+.

The authors thank to Dr. K. Maeda and Dr. S. Kihara of Kyoto Institute of Technology for their encouragement.

#### References

- 1 M. Dupeyrat and E. Nakache, *Bioelectrochem. Bioenerg.*, **5**, 134 (1978).
- 2 K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.*, **105**, 5967 (1983).
- 3 H. Yoshihisa, K. Miyamura, and Y. Gohshi, *Chem. Lett.*, **1997**, 1031; K. Arai, F. Kusu, and K. Takamura, *Denki Kagaku*, **1997**, 452.
- 4 K. Yoshikawa, T. Omochi, and Y. Matsubara, *Biophys. Chem.*, **23**, 211 (1986).
- 5 K. Arai, S. Fukuyama, F. Kusu, and K. Takamura, *Bioelectrochem. Bioenerg.*, **33**, 159 (1994).
- 6 T. Yoshidome, T. Higashi, M. Mitsushio, and S. Kamata, *Chem. Lett.*, **1998**, 855.