The Standard Electrode Potential of AgClO₂/Ag and Electrochemical Determination of The Solubility Product of [Ag⁺][ClO₂⁻]

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Abstract

The standard electrode potential of AgClO₂/Ag and the solubility product of [Ag⁺][ClO₂⁻] were determined from the electrode potential measurements of the AgClO₂/Ag and AgCl/Ag electrodes. The standard electrode potential of AgClO₂/Ag was +0.267 V vs. standard hydrogen electrode (SHE) at 22°C. The solubility product of [Ag⁺][ClO₂⁻] in aqueous solution was calculated from the difference between the standard electrode potentials of AgClO₂/Ag and AgCl/Ag. It was found that log K sp = log[Ag⁺][ClO₂⁻] = −9.09 (in mol dm⁻³)². The solubility product was one order as large as that of log[Ag⁺][CI⁻] = −10.09.

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1. Introduction

Chlorine dioxide (ClO₂) is an effective disinfecting agent, which can be used in the gaseous state and as an aqueous solution. It has some characteristics superior to those of chlorine gas and sodium hypochlorite. For example, it can be used as a disinfecting agent against various microorganisms, as an inactivating agent against viruses, for odor elimination, for its adverse effect on carcinogens, etc. It is currently used as a disinfecting agent for food products such as large blocks of meat and as an inactivating agent against the avian influenza virus. However, it is not yet legally sanctioned in Japan as a disinfecting agent for food products.

Chlorine dioxide seems to be gaining acceptance for widespread usage. However, most of the chemical properties of chlorine dioxide have not yet been determined, and few reports exist in literatures. The authors wish to further develop the practical use of chlorine dioxide; as a disinfecting agent and for odor elimination. As the first step to achieve this, it is essential to accumulate fundamental chemical data regarding chlorine dioxide and its related compounds.

This paper deals with the electrochemical determination of the solubility product [Ag⁺][ClO₂⁻] in aqueous solutions. The electrochemical data of AgClO₂ are also necessary to develop a chemical ClO₂ gas-sensor. The AgClO₂/Ag electrode is used as a reference electrode in the gas-sensor. Only one paper, published in 1936 by Larimer et al., reported the molal heat capacity and the solubility product of NaClO₂ raw-reagent using a potentiostat equipped with an input impedance of 10¹² Ω. The Nernst equation was used to account for the effect of the co-existing NaCl in the NaClO₂ raw-reagent and NaCl might have an adverse effect on the potential measurement of AgClO₂/Ag, because the electrode potential measured might be ascribed to AgClO₂/Ag and not to AgCl/Ag. This issue was resolved by the experimental comparison of AgClO₂/Ag with AgCl/Ag. A silver rod of 2 mm diameter was purchased from Sanwa Metal Industry, Co. Ltd.

2. Experimental

2.1 Reagents

Practical grade sodium chlorite (NaClO₂ raw-reagent), Kanto Kagaku Co. Ltd., was used as a source of ClO₂⁻. The nominal assay of this reagent was 79%, and the analytical assay of this batch was 84.3% (including 0.5% water by weight) as reported by the manufacturer. The rest of the reagent was sodium chloride, whose content was about 15% by weight (20% by mol ratio). Sodium hypochlorite (NaClO) was another assumable impurity and the content was less than 1 ppm according to the semi-quantitative analysis using N,N-Diethyl-1,4-phenylenediamine. The co-existing NaCl might have an adverse effect on the potential measurement of AgClO₂/Ag, because the electrode potential measured might be ascribed to AgClO₂/Ag and not to AgCl/Ag. This issue was resolved by the experimental comparison of AgClO₂/Ag with AgCl/Ag. A silver rod of 2 mm diameter was purchased from Sanwa Metal Industry, Co. Ltd.

2.2 Apparatus

The electrode potential was measured using an Ag reference electrode dipped in a solution including 0.100 and 0.140 mol dm⁻³ NaCl through a low-resistance membrane (0.006 ohm dm², Yuasa UMICRON Y-9201 T) with a low electric resistance. The electrode potential of AgClO₂/Ag was measured at various concentrations of NaClO₂ raw-reagent using a potentiostat equipped with an input impedance of 10¹² Ω. The Nernst equation was used to account for the result by correcting the activity coefficient. The liquid junction potential which ascribed to the membrane was ignored because of the low electric resistance and low ionic-selectivity. All measurements were carried out at 22°C.

3. Results and Discussion

3.1 Standard electrode potential of AgCl/Ag

The Nernst plot of AgCl/Ag was measured beforehand to reveal the effect of the co-existing NaCl in the NaClO₂ raw-reagent and to verify the adequacy of the operating equipment (Fig. 1, (c)).
The following equation was indicated by the practical molar concentration rather than the theoretically desirable activity.

\[
E(\text{AgCl/Ag}) = E(\text{AgCl/Ag: } [\text{Cl}^-] = 0.100) - 2.303 \frac{RT}{F} \log([\text{Cl}^-])
\]

The observed Nernst plot (the slope was 0.057 V) was corrected by introducing the concentration dependence of the activity coefficient. The average activity coefficients of NaCl were 0.875 for 0.02 mol dm\(^{-3}\) (log 0.02 = −1.70, log[0.875 × 0.02] = −1.176) and 0.730 for 0.2 mol dm\(^{-3}\) (log 0.2 = 0.700, log[0.730 × 0.2] = −0.840). The corrected Nernst slope was 0.062 which is a little larger than that of the theoretical slope 0.059 V for the one-electron transfer reaction, AgCl + e\(^-\) = Ag + Cl\(^-\). The corrected Nernst slope was consistent with the theory within the limits of the experimental error. The standard electrode potential of AgCl/Ag was determined by extrapolating the Nernst plot to 1 mol dm\(^{-3}\). It was +0.267 V vs. SHE (standard hydrogen electrode).

### 3.2 Effect of NaCl on the electrode potential of AgClO\(_2\)/Ag

The co-existing NaCl in the NaClO\(_2\) raw-reagent could obstruct the potential measurement of AgClO\(_2\)/Ag if the potential were more positive than that of AgCl/Ag. The electrode potential of AgCl/Ag was calculated to reveal the problem assuming that the solution included a similar amount of NaCl to that of co-existing NaCl in the NaClO\(_2\) raw-reagent. The resulting curve is shown in Fig. 1(b). The curve appeared between the potential of AgClO\(_2\)/Ag prepared by the NaClO\(_2\) raw-reagent (line (a)) and the potential of AgCl/Ag prepared by the high purity NaCl solution (line (c)). Generally speaking, the finding suggested that the measurement of AgClO\(_2\)/Ag was impossible in the solution including significant amount of NaCl. This problem could be solved in the present study as follows.

First, the Ag electrode was dipped in 0.1 mol dm\(^{-3}\) NaClO\(_2\) raw-reagent solution for 1 h. The color of the electrode surface changed into black rapidly due to the deposition of AgClO\(_2\) (Fig. 2). The oxidation of Ag to Ag\(^+\) must occur to form AgClO\(_2\). The oxidation of Ag could be ascribed to the oxidation by the dissolved oxygen.

The second was somewhat preposterous. If the solution were prepared by the nominal composition of 80% NaClO\(_2\) raw-reagent, it must include 0.08 mol dm\(^{-3}\) NaClO\(_2\) and 0.02 mol dm\(^{-3}\) NaCl in the case of 0.1 mol dm\(^{-3}\) NaClO\(_2\) raw-reagent such as in Fig. 1. Thus the measured electrode potential must be determined by AgCl/Ag in the solution including 0.02 mol dm\(^{-3}\) NaCl, i.e. line (b). Actually, however, the electrode potential of Ag measured in a high-purity NaCl solution (line (c)) shifted to a more positive curve (toward line (a)) upon further addition of the NaClO\(_2\) raw-reagent, which included 20% NaCl. The shifted potential was independent of the further addition of Cl\(^-\) (about 0.1 mol dm\(^{-3}\) NaCl). If the electrode potential were determined by AgCl/Ag, the potential should shift to a more negative, toward line (c). The present observation suggested that the electrode potential measured using NaClO\(_2\) raw-reagent which included NaCl could be ascribed to that of AgClO\(_2\)/Ag and not to AgCl/Ag.

Various reasons could be thought of as the very few effect of Cl\(^-\) on the electrode potential of AgClO\(_2\)/Ag. For example, the precipitation of AgClO\(_2\) occurred faster than the precipitation of AgCl. Secondly, the activity coefficient of AgCl decreased largely due to the dissolution in AgClO\(_2\) to form solid-solution. If the eutectic-mixture of AgClO\(_2\) and AgCl were formed, the electrode potential of AgCl/Ag must have a superiority over AgClO\(_2\)/Ag. Further experimental studies were desired to discuss more precisely on this electrode system.

### 3.3 Determination of the standard electrode potential of AgClO\(_2\)/Ag and the solubility product of [Ag\(^+\)][ClO\(_2\)^{-}] in aqueous solution

The electrode potential of AgClO\(_2\)/Ag was measured assuming that the raw-reagent included 80 mol% NaClO\(_2\) and included no NaCl. Nernst plot of AgClO\(_2\)/Ag at various concentrations of NaClO\(_2\) (ClO\(_2\)^{-}) is shown in Fig. 1, line (a). From several runs of the potential measurement, the averaged standard electrode potential of AgClO\(_2\)/Ag was determined as +0.0009 ± 0.002 V vs. AgCl/Ag ([Cl\(^-\)] = 0.140 mol dm\(^{-3}\)). The Nernst slope was 0.059 ± 0.003 V. The slope became 0.063 V after the activity-coefficient correction. The value was consistent with the one-electron transfer reaction, AgClO\(_2\) + e\(^-\) = Ag + ClO\(_2\)^{-}. The standard electrode potential could be calculated by extrapolating the Nernst plot to [ClO\(_2\)^{-}] = 1 mol dm\(^{-3}\) according to the following equation in mol concentration. Then the standard electrode potential \(E^o(\text{AgClO}_2/\text{Ag})\) was corrected using the average activity-coefficient of the monovalent ion salts. The activity-coefficient correction was −6 mV and the corrected value was +0.267 V vs. SHE.

\[
E(\text{AgClO}_2/\text{Ag}) = E^o(\text{AgClO}_2/\text{Ag}) + E(\text{AgCl/Ag: } [\text{Cl}^-] = 0.140) - 2.303 \frac{RT}{F} \log([\text{ClO}_2^-]) \quad \text{vs. SHE}
\]

The solubility product of [Ag\(^+\)][ClO\(_2\)^{-}] was calculated from the difference between the standard electrode potential of Ag\(^+\)/Ag (+0.799 V vs. SHE) and that observed for AgClO\(_2\)/Ag (+0.267 V vs. SHE) according to the following well known equation for the one-electron transfer reaction.
\[ \Delta E^\circ = E^\circ(\text{Ag}^+/\text{Ag}) - E^\circ(\text{AgClO}_2/\text{Ag}) \]
\[ = -2.303 \ (RT/F) \log K_{sp} \]

The calculated value was \( \log K_{sp} = \log[\text{Ag}^+][\text{ClO}_2^-] = -9.09 \). Thus the solubility product was \([\text{Ag}^+][\text{ClO}_2^-] = 8.13 \times 10^{-10} \) (in \( \text{mol dm}^{-3} \))\(^2\), which was 10 times as large as that of \([\text{Ag}^+][\text{Cl}^-] = 0.813 \times 10^{-10} \) calculated from the present experimental data in Fig. 1. The standard electrode potential of \( \text{Ag}^+/\text{Ag} \), +0.799 V vs. SHE in the literature, was used for the above calculation. The value was about 6 order smaller than that reported previously.\(^1\) The yellow precipitate reported previously\(^1\) and the black precipitate in this study must be a different chemical species. According to the previous study,\(^2\) the yellow precipitate changed into black and the former must be meta-stable and a precursor species of the latter. The large difference in the solubility product must be ascribed to the different chemical species.

References