Formal Oxidation-Reduction Potencials Of Peroxymonosulfuric Acid In Water Solutions And Ni(II) – Dimethylhlioxym System

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Abstract – The value of formal potential in peroxymonosulfate/sulfate system has been found. The influence of medium acidity, concentration of sulfate-ions and general concentration of peroxymonosulfate–sulfate on the value of formal potential was investigated. The difference between standard and formal potentials in peroxymonosulfate/sulfate system in water solutions was approximately equivalent to 0.5 V. The oxidation reaction of dimethylhlioxym with peroxymonosulfuric acid in the presence of nickel (II) ions was studied. The research has shown the possibility of kinetic determining the Ni(II) ions.

Key words – potentiometry, formal potential, Caro's acid, dimethylhlioxym, peroxymonosulfate.

I. Introduction

Nowadays there are many types of oxidants in chemistry. They are widely used in spectrophotometric and kinetic methods of analysis.

Peroxymonosulfuric acid, or as it is called, Caro's acid, belongs to a number of strong oxidants (E^0 + 1.81 V) [1-2]. It is stronger oxidant than hydrogen peroxide and persulfate-ion, that is proved by potentials of the following compounds.

However, despite the quite high potential, and, consequently, strong oxidizing properties, Caro's acid is widely used in industry. It should be noted that there is much less literature data about Caro's acid than about other peroxyacids.

Since the standard potential in real systems could not be reliably determined, the goal of this work is to determine the formal potential of peroxymonosulfuric acid with the option to use it in kinetic and catalytic methods of analysis.

II. Experimental

Potentiometric studies were performed on a potentiometer EV – 74 with argentum chloride electrode and a platinum indicative electrode. Acidity of the solution was controlled by pH-meter (150M) with argentum chloride electrode and a glass indicative electrode using diluted solutions of NaOH and HNO_3.

All analytical researches were connected with peroxymonosulfuric acid, (H_2SO_5), which is a liquid at room temperature. It was prepared by grinding of potassium persulfate with concentrated sulfuric acid, and with further neutralization by potassium carbonate to 3-4 pH [3-5].

Before proceeding to the experiments connected with the determination of peroxymonosulfuric acid's formal potential we performed some preliminary experiments [6-7], and they are:

- Changed turbidimetry and conductivity methods of finding the concentration of sulfate ions;
- modified well known photometric method of finding the ions concentration of titanium at a constant concentration of peroxide in the method of finding the concentration of peroxide at constant ion concentration of titanium (IV);
- carried iodometry standardization of Caro's acid

$$SO_5^{2-} + 2H^* + 2I^- \Leftrightarrow SO_4^{2-} + I_2 + H_2O \quad (1)$$

$$2S_2O_3^{2-} + I_2 \Leftrightarrow S_4O_6^{2-} + 2I^- \quad (2)$$

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \Leftrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad (3)$$

III. Results and Dicussion

According to the Nernst equation the oxidation-reduction potencial of peroxymonosulfuric acid depends on the concentration of peroxymonosulfate- and sulfate-ions and the acidity of the solution [8-9].

$$E = E^0 + \frac{0{,}059}{2}\lg\frac{[HSO_5^-]*[H^+]^2}{[SO_4^{2-}]} \quad (4)$$

Obviously, to calculate the potential E the concentrations of all components of this ratio should be known. The concentration of peroksymonosulfate ions is known from the standardization. The concentration of sulfate ions in the solution is found using the turbidimetry and conductivity titrations using Ba^{2+} ion. Therefore, the ratio $[HSO_5^-]$ / $[SO_4^{2-}]$ = 0,065 was found.

The formal potential of peroxymonosulfuric acid was measured at various acidity, using nitric acid solution and sodium hydroxide (Fig. 1).

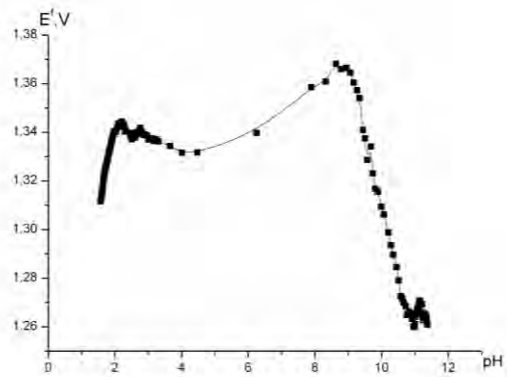

Fig. 1 The dependence of the formal potential of peroxymonosulfuric acid from the acidity of the solution; $C(H_2SO_5)$ = 0.0565 M, $C(K_2SO_4)$ = 0.3100 M

Potentiometric determination of the formal potential of peroxymonosulfuric acid was carried out using the pH-meter and the potentiometer. The pH-meter gauged the acidity and the potentiometer gauged a difference between indicator electrode and reference electrode.

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$$Pt|\ HSO_4^-, H^+, SO_4^{2-} \| Cl^- | AgCl, Ag \quad (5)$$

$$Ag, AgCl | HCl(0.1M) \| (glass) | HSO_5^-, H^+, SO_4^{2-} \quad (6)$$

It can be seen that the value of the formal potential maintains a relatively steady value (1,34-1,37) in the pH range of 2-9. At pH greater than 9 a sharp decrease of the formal potential was observed, which we suppose is due to the destruction of the peroxymonosulfuric acid. The slightly reduced value of the formal potential in the pH range of 4-6 coincides with the simultaneous existence of two forms of acid in the solution, leading to the presence of multiple equilibrium on a platinum electrode.

The dependence of the formal potential of the peroxymonosulfuric acid from acidity of the solution can be described by the following equations:

$$\Delta E = E_{Pt/HSO_5^-, H^+, SO_4^{2-}} - E_{Ag, AgCl/Cl^- 9нас)} =$$

$$= E^f + \frac{0,059}{2} \lg \frac{[HSO_5^-] * [H^+]^2}{[SO_4^{2-}]} - E_{Ag, AgCl/Cl^- (нас)} \quad (7)$$

$$E^f = \Delta E + E_{Ag, AgCl/Cl^- (нас)} + 0,059\, pH -$$

$$- \frac{0,059}{2} \lg [HSO_5^-] + \frac{0,059}{2} \lg [SO_4^{2-}] \quad (8)$$

The results showed that the value of the formal potential depends on the concentration of peroxymonosulfuric acid to the value of 10^{-3} mol/L. The subsequent increase of the concentration of acid has little effect on the value of the formal potential. The concentration of sulfate ions does not affect on the formal potential of the peroxymonosulfuric acid.

Adding of the peroxymonosulfuric acid to Ni(II)-dimethylhlioxym solution leads to the oxidation reaction product and changes its spectrophotometric characteristics. Literature data on chemical reactions in this system are rather contradictory. There is an evidence indicating the oxidation of dimethylhlioxym in the complex, others argue that Ni (II) ions are oxidized.

Potentiometric titration curve of peroxymonosulfuric acid with nickel ions in ammonia buffer solution indicates the red/ox reactions, evidenced by a jump on the curve. We assume that in the solution are the following reactions:

$$SO_5^{2-} + 2H^+ + 2e^- \rightarrow SO_4^{2-} + 2H_2O$$

$$Ni^{2+} - e^- \rightarrow Ni^{3+}$$

Known value of the peroxymonosulfuric acid oxidation formal potential allows to calculate the formal potential oxidation of Ni (II) ions. The calculated value of the potential is 120 mV . It can be assumed that the assumption is true, as the potential value is correlated with the known potential electrode of the pair Co(II) / Co(III).

Titration of the mixture of nickel ions, peroxymonosulfuric acid and dimethylhlioxym leads to a linear decrease in system capacity. So this dependence indicates a flow of indicator substances which is the peroxymonosulfate. Studies have shown the possibility of kinetic determination of the Ni(II) ions.

Conclusion

Potentiometric method has confirmed resistance of Caro's acid in aqueous solutions within pH 2-9 range. The dependence between the red/ox potential and pH in these ranges of medium acidity obeys to the Nernst law. It was studied that the formal potential of Caro's acid/sulfate depends on the total concentration of components, not only on their ratio. Using potentiometric method the formal potential of peroxymonosulfuric acid was found, and it is 1.35 V. It was found out that the difference between standard and formal potentials in the peroxymonosulfate/sulfate system in aqueous solutions is about 0.5 V, which provides good conditions for the use of Caro's acid in kinetic and catalytic methods of analysis. The formal potential value of Ni (II) ions oxidation reactions were calculated by peroxymonosulfuric acid. The results indicate the promising application of peroxymonosulfuric acid in analysis.

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