

Scientific paper



**ANALYTICAL APPLICATION OF THE REACTION SYSTEM
METHYLENE BLUE B-K₂S₂O₈ FOR THE SPECTROPHOTOMETRIC KINETIC
DETERMINATION OF SILVER IN CITRIC BUFFER MEDIA**

Sofija M. Rančić¹, Snežana D. Nikolić-Mandić², Aleksandar Lj. Bojić^{1*}

¹Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Serbia

²Faculty of Chemistry, University of Belgrade, Belgrade, Serbia

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*Corresponding author: Aleksandar Lj. Bojić

Postal address: Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Visegradska 33, 18 000 Niš, Serbia

E-mail address: bojica@gmail.com

phone: +381 63 106 40 16, fax: +381 18 533 014

Abstract

A new, simple, rapid, sensitive and selective spectrophotometric kinetic method for Ag(I) traces determination at room temperature was elaborated in this paper. It is based on catalytic effect of silver ions upon the oxidation of methylene blue B (MBB) by $K_2S_2O_8$ (PPS) in citric buffer (BUF) solution. The method was confirmed by determination of Ag(I) in PbO. The obtained results were compared to those obtained by ICP-OES method and good agreement of results was found.

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Introduction

The silver traces determination is present in analytical practice for a long time. At the first time silver was determined in the photographic materials and solutions for black and white films, silver-plating solutions and effluents. Recently, silver has also been analyzed in ayurvedic and other drugs and medicines, chemical substances, natural and waste water samples, electronics, flow-solders, white metals, ores, alloys, biological samples, etc. [1,3,4] The toxico-kinetic of silver is very complex: its ability to form organometallic compounds and chelate complexes with influence on the metabolic processes in living organisms is subject of investigations in biology and environmental studies.

There are different methods for Ag(I) determination, like atomic absorption spectrometry (AAS) [1,2], capillary zone electrophoresis (CZE) [3], fluorimetric [4], high performance liquid chromatography (HPLC) [5], kinetic [16-19], flow injection analysis (FIA) [20], spectrophotometric [21-28], photometric, etc. Silver was also determined using PVC-membrane electrodes based on 18-crown-6 and dibenzo-18-crown-6 ethers [29].

Kinetic methods for Ag(I) determination with spectrophotometric detection, are mainly based on catalytic effect of silver ions upon the reaction rate of oxidation of different reductors by $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ [6-15]. So, silver was determined as a catalyst of kongo red oxidation in the presence of 1,10 phenantroline as an activator [6], and oxidation of BAPDAB in the presence of 2,2 dipyridyl as an activator [7], oxidation of pyrocatechol-1-aldehyde-2-pyridyl hidrazone [8], pyridoxal nicotinyl hydrazone [9], fuchsine [10], SPADNS [11], 7-(antipyrinylazo)-8-hydroxyquinoline [12], indigo carmine, etc. Silver was also determined as the catalyst of chromotropic acid oxidation by bromate, in the range $2-10 \mu\text{g cm}^{-3}$ [16]. There are only a few kinetic methods for silver determination based on its inhibitory effect. One of the most interesting is the reaction of oxidation of arsenite by Ce(IV), which is catalyzed by iodide ions [17]. As the inhibitor of this reaction, Ag(I) was determined in silicate rocks.

Kinetic methods were also published for silver determination in ores and alloys [18], sulfide minerals molybdenite and sphalerite and some other natural materials [19].

FIA method with spectrophotometric detection was published in 2011. for silver determination in silver plating solutions [20]. One of many spectrophotometric methods is the method for silver determination in 2500 soil samples of agricultural areas subjected to cloud seeding in Greece [25]. Also, flotation-spectrophotometric method was developed for silver detection in semiconductors in the process of crystal growth [28].

The main goal of our investigation was to develop new, easy to performance, sensitive kinetic method for silver determination at room temperature, using common and available chemicals. In addition, we wanted to check the method on the real sample in order to discover its possibilities for further applications.

Experimental

Apparatus

Spectrophotometric measurements were performed on UV-VIS spectrophotometer Shimadzu UV- VIS 1650 PC (Shimadzu, Japan). ICP-OES measurements were performed on ICP-OES, model ICAP 65000 Duo (Thermo Scientific, UK). The cylindrical cells were thermostated at $20.00\pm 0.02^{\circ}\text{C}$ using thermocirculating bath (Julabo MP-5A). The pH measurements were performed using a Hach H260G pH-meter with a non-glass pH probe PH77SS (Hach, USA).

Reagents and Chemicals

Analytical grade reagents, provided by Merck, Germany, unless indicated otherwise and ultrapure water ($18.2\text{ M}\Omega$) (water purification system Thermo Fisher Scientific Smart2Pure Standard) were utilized for solutions preparation. Adequate polyethylene vessels were used for storage of the solutions. Citric buffer solutions were prepared by mixing $\text{NaC}_6\text{H}_5\text{O}_7$ and

NaOH or HCl solution (0.1 mol dm^{-3}) according the rule and their pH values were checked using a pH-meter. A stock Ag(I) solution ($1 \cdot 10^{-3} \text{ g cm}^{-3}$) was prepared by dissolving the exactly measured dry AgNO_3 in deionised water. The concentration of the stock solution was checked by complexometric determination. The methylene blue B solution was prepared by dissolving the exactly measured substance in deionised water. All the polyethylene containers and the glassware were washed by diluted hydrochloric acid (1:1), solution of potassium hydroxide in ethanol and then repeatedly well rinsed by tap, distilled and deionised water. All concentrations described here are the initial concentrations in the reaction mixture at time zero after mixing. Each kinetic result is the average of five determinations

Procedure

In order to obtain good mechanical and thermal stability, the instruments were run for ten minutes before the first measurement. Selected volumes of reactants and deionized water were poured separately in the reaction mixture vessel with four compartments (Budarin vessel) up to a predetermined total volume of 10 cm^3 . The solution of Ag(I) was measured into one leg of the Budarin vessel for catalytic reaction and the same volume of deionized water was measured for non-catalytic reaction. After thermostating for ten minutes, the reagents were mixed and simultaneously the stopwatch was turned on. To properly rinsed spectrophotometer cell with a path length of 10 cm, the solution was immediately added and absorbance was measured every 15 seconds, starting from the 45th second of reaction, up to ten minutes of the reaction. Spectrophotometric measurements were performed at the wave length of 662.4 nm, and at working temperature of $20 \pm 0.02^\circ\text{C}$.

The reaction was tested by examination the influence of each component of the reaction mixture upon the reaction rate of catalytic and non-catalytic reaction. The concentration of

each component was changing consecutively, while the concentrations of other components, as well as the working temperature, were kept constant.

Results and discussion

While the reaction proceeds, the initial blue color of the solution fades and a colorless reaction product is formed. Neither the exact mechanism of reaction nor the chemical nature of the products was of major interest in the investigation. The spectrophotometric measurements were performed at the wavelength of absorption maximum of methylene blue B (662.4 nm) in citric buffer media (Fig. 1). The logarithm of absorbance-time curves is linear during the first five to ten minutes of reaction for different Ag(I) concentrations, so all kinetic results were treated by the integral variant of the tangent method [30]. The rate of reaction was obtained using the slope of the kinetic curves of the absorbance-time plot.

Fig. 1.

Hence, the influence of the pH value of the selected citric buffer solutions on the rate of both the catalytic and non-catalytic reaction was examined in the pH interval of about 5 to about 6 (Fig. 2). The value of 5.2 was selected as the most appropriate one, because it provides very well difference of reaction rates of the catalytic and non-catalytic reaction and good reproducibility of absorbance measurements in the absorbance area of the least error for spectrophotometric measurements, for both reactions. The same principles were used for optimal conditions selection in all further investigations. The citric buffer pH 5.2 was used in subsequent examinations.

Fig. 2.

The rate of the non-catalytic reaction shows first order dependence on the buffer concentration, while the catalytic reaction rate shows complex dependence (Fig. 3) within the range of $2.6 \cdot 10^{-3}$ to $9.2 \cdot 10^{-3}$ mol dm⁻³, and a concentration of $7.9 \cdot 10^{-3}$ mol dm⁻³ was selected as the optimal concentration of citric buffer for further measurements.

Fig. 3.

The dependence of the rate of the catalytic and non-catalytic reaction on the reductor concentration was monitored within the concentration range of about $1.5 \cdot 10^{-6}$ to about $6.0 \cdot 10^{-6}$ mol dm⁻³ MBB. Within this interval, both the catalytic and non-catalytic reaction rate shows a complex dependence of the MBB concentration (Fig. 4). As optimal, a concentration of $4.5 \cdot 10^{-6}$ mol dm⁻³ MBB was selected.

Fig. 4.

At last, the influence of the concentration of the oxidant was tested (Fig. 5). Inside the investigated concentration range of K₂S₂O₈ of about $6.0 \cdot 10^{-2}$ to about $14.0 \cdot 10^{-2}$ mol dm⁻³, the catalytic reaction rate exhibited a complex dependence, while the non-catalytic reaction showed first order dependence on oxidant concentration. PPS concentration of $12.6 \cdot 10^{-2}$ mol dm⁻³ was selected as the adequate for further work.

Fig. 5.

Hence, the optimal conditions were found to be: pH 5.2, $c_{\text{BUF}} = 7.9 \cdot 10^{-3}$ mol dm⁻³, $c_{\text{MBB}} = 4.5 \cdot 10^{-6}$ mol dm⁻³, $c_{\text{PPS}} = 12.6 \cdot 10^{-2}$ mol dm⁻³.

Under the optimal conditions, the dependence of catalytic reaction rate on the Ag(I) concentration was observed at three temperatures: 20 ± 0.02 , 23 ± 0.02 and $25\pm 0.02^\circ\text{C}$. The linear dependence of calibration curves falls within the range of 0.4 to $2.1\ \mu\text{g cm}^{-3}$ Ag(I).

The adequate equations of calibration curves for $20\pm 0.02^\circ\text{C}$ (Eq. 1), $23\pm 0.02^\circ\text{C}$ (Eq. 2), and $25\pm 0.02^\circ\text{C}$ (Eq. 3), were calculated as follows:

$$\text{Slope} = (0.00726\pm 0.00001)\cdot c + (0.02892\pm 0.00010) \quad (1)$$

$$\text{Slope} = (0.01183\pm 0.00003)\cdot c + (0.03491\pm 0.00012) \quad (2)$$

$$\text{Slope} = (0.01502\pm 0.00002)\cdot c + (0.03811\pm 0.00013) \quad (3)$$

where: c is Ag(I) concentration in $\mu\text{g cm}^{-3}$.

The accuracy and precision of the method were checked for three different Ag(I) concentrations within the range of the calibration curve. Five repeated measurements were performed for each concentration. Satisfactory results were obtained. For Ag(I) concentrations of $0.5\ \mu\text{g cm}^{-3}$, $1.0\ \mu\text{g cm}^{-3}$, and $2.0\ \mu\text{g cm}^{-3}$, RSD values were found to be 3.2%, 2.4%, and 1.3%, respectively.

The selectivity of the method was established by interference studies: selected ions were separately added in the reaction mixture. The tolerance limit was estimated as the concentration of the added ion that gives up to a 3% relative error in the determination of cobalt and tin. Cations were added as chlorides or nitrates and anions were added as sodium or potassium salts. Each ion was added in six known concentration ratios (0.01:1, 0.1:1, 1:1, 10:1, 100:1 and 1000:1) against the constant Ag(I) concentration of $1.05\ \mu\text{g cm}^{-3}$. The measurements were performed at $20\pm 0.02^\circ\text{C}$, and about 30 most frequently used cations and anions were tested (Na^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Pd^{2+} , Ni^{2+} , Co^{2+} , Hg^{2+} , Sn^{2+} , Bi^{3+} , Fe^{3+} , Al^{3+} , As^{3+} , Sb^{3+} , Au^{3+} , acetates, tartarates, oxalates, molybdates, wolframates, Br^- ,

I⁻, Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻). The results presented in Table 1. reveal that proposed methods for silver determination have a very good selectivity.

Table 1.

Only the presence of Ni²⁺ and Co²⁺ in the ratio 1:1 and Cu²⁺ and molybdates in the ratio 10:1, interferes with the determination of silver. The presence of Zn²⁺, in the ratio 10:1, inhibits and Au³⁺, in the ratio 1:1, catalyzes the determination of silver by proposed method. The ions that interfere determination of silver can be easily removed by standard analytical methods like masking, precipitation, etc., depending of different samples nature.

By application of spectrophotometric technique, at the wavelength of 662.4 nm, a limit of quantification (LQ) of 83 ng cm⁻³ Ag(I),^{was} reached, and the limit of detection (LD) of 24 ng cm⁻³ Ag(I), was obtained. LQ was defined as the ratio signal:noise = 10:1 and LD was defined as signal 3:1 against the blank.

The method was successfully applied to Ag(I) determination in PbO (Merck, Germany). Solution containing a known quantity of silver was analyzed by application of both the presented kinetic method and ICP-OES method. As presented in Table 2, there is a good agreement of results.

Table 2.

Conclusions

The proposed kinetic method for the determination of Ag(I) shows a very good selectivity and provides rapid and easy performance at room temperature, by using available equipment and

cheap chemical substances. The obtained results are precise and reproducible. The RSD value was found to be in the range 1.3-3.2% for the investigated concentration range of Ag(I).

On the grounds of the obtained results, the new spectrophotometric kinetic method is recommendable for the determination of Ag(I) in chemical substances of high grade purity, and potentially also in different samples from industrial processes and environment. The results suggest that it could also be a good basis for further investigations, not only in the area of kinetic methods development, but also in the area of noble metals determination.

Acknowledgements

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Izvod

ANALITIČKA PRIMENA REAKCIONOG SISTEMA METILEN PLAVO B-K₂S₂O₈ ZA SPEKTROFOTOMETRIJSKO KINETIČKO ODREĐIVANJE SREBRA U CITRATNOM PUFERU

Sofija M. Rančić¹, Snežana D. Nikolić-Mandić², Aleksandar Lj. Bojic^{1*}

¹Departman za Hemiju, Prirodno-matematički fakultet, Univerzitet u Nišu, Srbija

²Hemijski fakultet, Univerzitet u Beogradu, Beograd, Srbija

(Naučni rad)

Predložena kinetička metoda za određivanje Ag(I) pokazuje vrlo dobru selektivnost i lako se i brzo izvodi na sobnoj temperaturi. Uz korišćenje dostupne opreme i jeftinih supstanci, ostvaruju se precizni i reproduktivni rezultati. Spektrofotometrijskim merenjem, na talasnoj dužini od 662.4 nm, postignuta je granica kvantifikacije (LQ) od 83 ng cm⁻³ Ag(I), kao i granica detekcije (LD) od 24 ng cm⁻³ Ag(I). LQ je definisana kao odnos signal:šum = 10:1 and LD kao signal 3:1 u odnosu na slepu probu. RSD vrednosti se nalaze u rasponu od 1.3-3.2% za ispitivanu oblast koncentracija Ag(I). Na osnovu dobijenih rezultata se može zaključiti, da je nova spektrofotometrijsko kinetička metoda pogodna za određivanje Ag(I) u hemijskim supstancama visoke čistoće, a potencijalno i u drugim uzorcima iz proizvodnih procesa i životne sredine. Takođe, rezultati ispitivanja ukazuju na to da ona može da bude dobra osnova, ne samo za dalja istraživanja u oblasti razvoja kinetičkih metoda analize, već i u oblasti razvoja novih metoda za određivanje plemenitih metala.

Keywords: Ag(I) determination, catalyst, kinetic spectrophotometric method

Ključne reči: određivanje Ag(I), katalizator, kinetičko spektrofotometrijska metoda

Table captions

Table 1. Selected results of interference studies for silver determination

Initial conditions: pH 5.2; MBB $4.5 \cdot 10^{-6}$ mol dm⁻³; BUF $7.9 \cdot 10^{-3}$ mol dm⁻³; PPS $12.6 \cdot 10^{-2}$ mol dm⁻³; Ag(I) $1.05 \mu\text{g cm}^{-3}$; $20 \pm 0.02^\circ\text{C}$.

Table 2. Ag(I) determination in PbO

Initial conditions: pH 5.2; MBB $4.5 \cdot 10^{-6}$ mol dm⁻³; BUF $7.9 \cdot 10^{-3}$ mol dm⁻³; PPS $12.6 \cdot 10^{-2}$ mol dm⁻³; $20 \pm 0.02^\circ\text{C}$.

Naslovi tabela

Tabela 1. Izabrani rezultati ispitivanja uticaja stranih jona pri određivanju srebra

Početni uslovi: pH 5.2; MBB $4.5 \cdot 10^{-6}$ mol dm⁻³; BUF $7.9 \cdot 10^{-3}$ mol dm⁻³; PPS $12.6 \cdot 10^{-2}$ mol dm⁻³; $1.05 \mu\text{g cm}^{-3}$ Ag(I); $20 \pm 0.02^\circ\text{C}$.

Tabela 2. Određivanje Ag(I) u PbO

Početni uslovi: pH 5.2; MBB $4.5 \cdot 10^{-6}$ mol dm⁻³; BUF $7.9 \cdot 10^{-3}$ mol dm⁻³; PPS $12.6 \cdot 10^{-2}$ mol dm⁻³; $20 \pm 0.02^\circ\text{C}$.

Figure captions

Fig. 1. Absorption spectra of MBB in citric buffer. Initial conditions: MBB $7.15 \cdot 10^{-6}$ mol dm⁻³; $20 \pm 0.02^\circ\text{C}$; pH: A 1.0, B 7.0.

Fig. 2. Dependence of the reaction rate on pH. Initial conditions: MBB $4.5 \cdot 10^{-6}$ mol dm⁻³; PPS $7.9 \cdot 10^{-2}$ mol dm⁻³; $9.2 \cdot 10^{-3}$ mol dm⁻³ BUF; $2.1 \mu\text{g cm}^{-3}$ Ag(I); $20 \pm 0.02^\circ\text{C}$; A-catalytic reaction, B-non-catalytic reaction.

Fig. 3. Dependence of the reaction rate on the BUF concentration. Initial conditions: MBB $4.5 \cdot 10^{-6}$ mol dm⁻³; PPS $7.9 \cdot 10^{-2}$ mol dm⁻³; pH 5.2; Ag(I) $2.1 \mu\text{g cm}^{-3}$; $20 \pm 0.02^\circ\text{C}$; A-catalytic reaction, B-non-catalytic reaction.

Fig. 4. Dependence of the reaction rate on the MBB concentration. Initial conditions: PPS $7.9 \cdot 10^{-2} \text{ mol dm}^{-3}$; pH 5.2; BUF $7.9 \cdot 10^{-3} \text{ mol dm}^{-3}$; Ag(I) $2.1 \mu\text{g cm}^{-3}$; $20 \pm 0.02^\circ\text{C}$; A-catalytic reaction, B-non-catalytic reaction.

Fig. 5. Dependence of the reaction rate on the PPS concentration. Initial conditions: MBB $4.5 \cdot 10^{-6} \text{ mol dm}^{-3}$; pH 5.2; BUF $7.9 \cdot 10^{-3} \text{ mol dm}^{-3}$; Ag(I) $2.1 \mu\text{g cm}^{-3}$; $20 \pm 0.02^\circ\text{C}$; A-catalytic reaction, B-non-catalytic reaction.

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Table1.

Added ion	Ion ratio:Ag(I)	Silver determination
Ni(II)	1	interferes
Co(II)	1	interferes
Cu(II)	10	interferes
Molybdate	10	interferes
Zn(II)	10	inhibits
Au(III)	1	catalyses

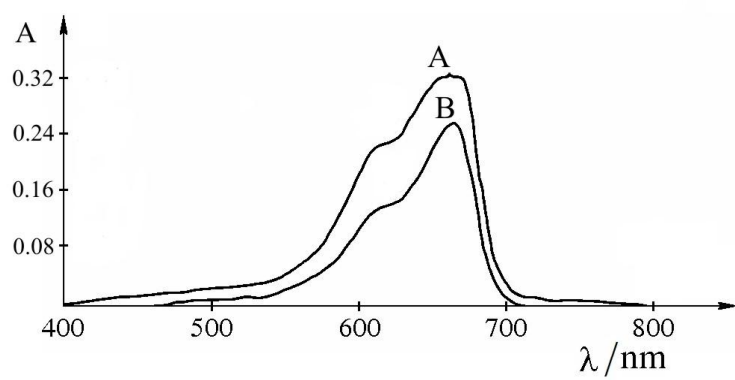
Table 2.

Kinetic determination ^a g cm ⁻³ · 10 ⁻⁷	Recovery %	Determination by ICP-OES ^a g cm ⁻³ · 10 ⁻⁷	Recovery %
5.38±0.05	97.8	5.48±0.02	99.6

^aThe mean value of five measurements±2SD

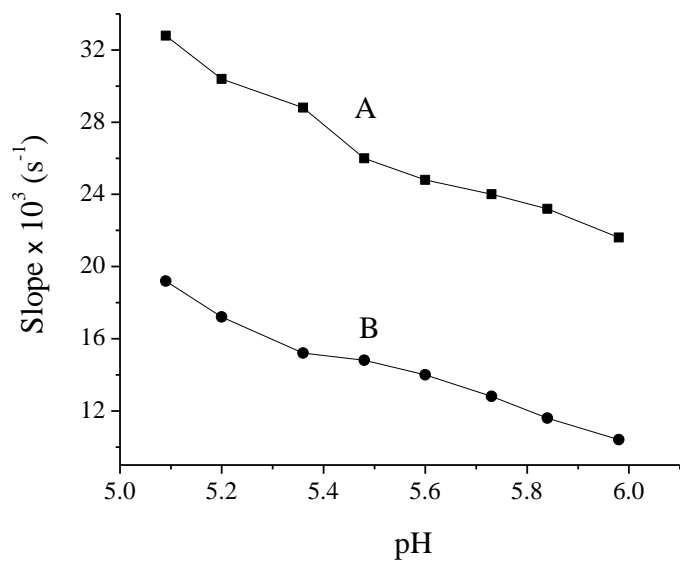
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Fig. 1.



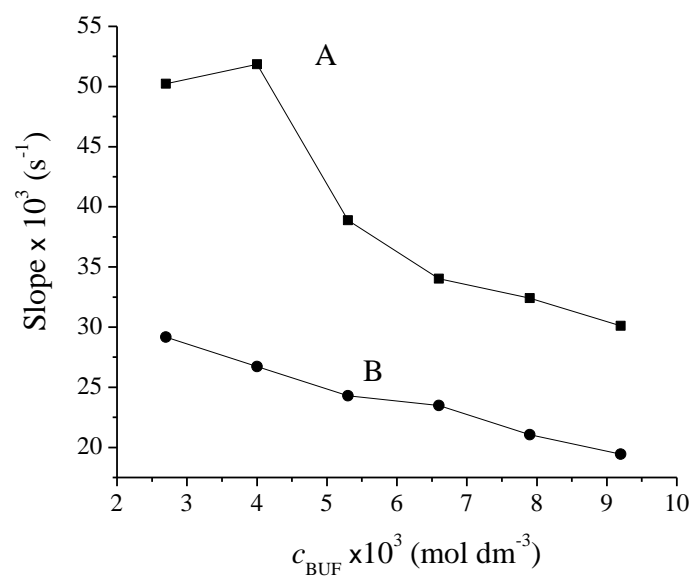
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Fig. 2.



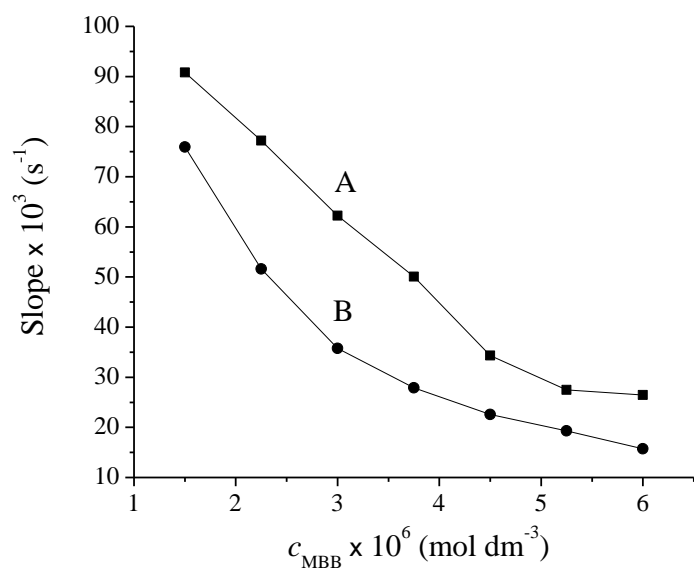
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Fig. 3.



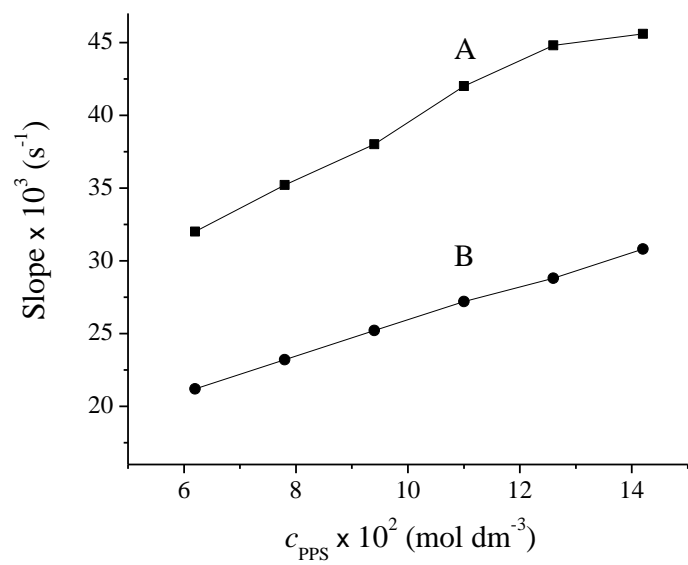
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Fig. 4.



PAPER ACCEPTED

Fig. 5.



PAPER ACCEPTED