



A Simple Stopped-flow System for Kinetic Study of Arsenate-molybdenum Blue Reaction

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ABSTRACT

A low-cost stopped-flow spectrophotometric system was fabricated in the laboratory for a kinetic study on the reaction of molybdenum blue with arsenate. The influence of the concentration of the reagents on the rate of reaction has been studied. Arsenate and reagent solutions were flowed to mix together in-line, and the mixed zone was stopped at a flow cell where the absorbance at 880 nm was continuously recorded. The initial slope of the stopped-flow profile was evaluated as an initial rate of the reaction, and then the order of reaction and rate law equation were derived. The following reaction rate equation: $\text{Rate} = k[\text{As(V)}]^2 [\text{Mo}]^3 [\text{PAT}]^1 [\text{AA}]^1 [\text{H}_2\text{SO}_4]^{-7}$ was obtained. This kinetic data could be used to suggest on the influencing of reactants to the reaction rate. The proposed system provided reproducible and accurate kinetic profile, convenient and fast operation, and low chemical consumption. The developed method is a suitable platform for the kinetic study of the reaction.

Keywords: arsenate, molybdenum blue, stopped flow injection, kinetic study, initial rate

1. INTRODUCTION

Molybdenum blue is represented by a partially reduced molybdenum oxide hydroxide compound[1]. It is produced under acidic condition by the reduction of aqueous MoO_4^{2-} . By utilizing sophisticated synthesis methods, it is possible to get monodisperse and crystalline samples, for instance, ring-shaped, supramolecular clusters [1-2]. Molybdenum blue shows a deep blue color, usually used to perform selective dye of samples for quantitative determination.

The molybdenum blue chemistry has been widely applied for phosphate, arsenate, and silicate determinations, which are based on the reaction with molybdate and antimonyl ions whereby a yellow heteropolyacid is formed [3-11]. This complex can be reduced to intensely colored molybdenum blue species, the absorbance of which is measured at 630, 700, or 880 nm. This absorbance is directly related to the concentration of the analyte. Although the molybdenum blue

method can be used to determine phosphate, arsenate and silicate that presented in samples, the corresponding heteropolyacid compounds are isomorphous, and they cannot be distinguished from each other. In most of the case, silicate levels are low in freshwater and drinking water, so phosphate is the main interference in arsenic determination [12].

The molybdenum blue method is well-established for determining inorganic arsenate in solution, and it has been broadly used. However, arsenate determination by this method has the disadvantage of requiring around 1 hour for color development of the arsenate-molybdate complex, it also reacts in the same way as phosphate but this color development is much slower [11]. Therefore, many efforts have been devoted to developing a highly sensitive method for arsenic determination. The factors that regulate the reaction rates have been investigated, such as the individual concentrations of molybdate, antimony, ascorbic acid, and sulfuric acid. The reaction is complicated and probably involves the formation of a mixture of two isomeric arsenoantimonylmolybdate in proportions, which depend on the acidity in the final solution. For

this reason, the effects on the reaction rate of change in the reactant concentrations have been studied by several investigators [3-12].

Several reaction rate procedures based on an experimental study of the mechanism of the molybdenum blue reaction in the determination of phosphate have been studied to investigate the order of the reaction and the experimental rate law, as shown in Table 1. Initial reaction rates are obtained graphically from the slopes of the absorbance vs. time curves. This induction period was usually quite short, about 5-20 seconds, which the assumption made in the theoretical treatment that the solution concentration is the same as the initial concentration. Reaction orders are obtained graphically from the slopes of a plot between the logarithm of initial rate vs. logarithm of initial concentration. The obtained experimental rate law is consistent with that predicted by a mechanism involving equilibrium to form molybdophosphoric acid and subsequent reduction of the complex to molybdenum blue.

In the present report, the result of kinetic stopped-flow studies of the formation of arsenomolybdate in ammonium molybdate (Mo), potassium antimonyl tartrate (PAT), sulfuric acid

Table 1. Experimental rate law from spectrophotometric measurement on the phosphate molybdenum blue method.

Ref.	Spectrophotometric procedure	Rate law
13	Batch	$\frac{d[\text{Blue}]}{dt} = \frac{k[\text{PO}_4^{3-}][\text{Mo(VI)}]^6[\text{Ascorbic acid}]}{[\text{H}^+]^{10}}$
14	Batch	$\frac{d[\text{Blue}]}{dt} = \frac{k[\text{PO}_4^{3-}][\text{Mo(VI)}]^6}{\{[\text{H}^+]^{10} / [\text{Ascorbic acid}]\} + 1}$
15	Batch	$\frac{d[\text{Blue}]}{dt} = \frac{k[\text{PO}_4^{3-}][\text{Bi}^{3+}][\text{Mo(VI)}]^9}{\{k'[\text{H}^+]^9 / [\text{Ascorbic acid}]\} + 1}$
16	Stopped-flow	$\frac{d[12\text{-MPA}]}{dt} = \frac{k[\text{PO}_4^{3-}][\text{Mo(VI)}]}{k[\text{H}^+]^8 / [\text{Mo(VI)}]^5 + k[\text{H}^+]^4 / [\text{Mo(VI)}]^4 + k[\text{H}^+]^2 + 1}$
17	Stopped-flow	$\frac{d[12\text{-MPA}]}{dt} = \frac{k[\text{PO}_4^{3-}][\text{Mo(VI)}]}{[\text{H}^+]}$

(H_2SO_4), arsenate (As(V)), and ascorbic acid (AA) to rate of reaction are presented. The influence of all reactant concentrations to the rate of reaction has been studied by varying the initial concentration of one reactant while keeping the others constant. In addition, the reaction order and experimental rate law for the reactions can be derived from the experimental data. The proposed stopped-flow method exhibited various advantages for kinetic study of the reaction such as fast, low chemical consumption, precise timing control, real-time monitoring of the reaction product, and more convenient operation.

2. MATERIAL AND METHODS

2.1 Reagents

All the reagent and standard solutions were prepared by using de-ionized water purified by a Milli-Q filtration system (Millipore, Japan). A stock standard solution of arsenate 1000 mg/L As(V) was prepared by dissolving 0.4164 g of sodium arsenate $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and adjusting the volume to 100 mL with de-ionized water. The working standard solutions of As(V) were daily prepared by diluting the stock standard solution with water. Acidic molybdate solution

was prepared by dissolving 2.50 g of ammonium molybdate with water, and 10 mL of 98% v/v sulfuric acid was added before adjusting the final volume to 500 mL. The solution was added by potassium antimonyl tartrate solution (2%w/v) and kept in a polyethylene bottle to prevent the introduction of silica. The ascorbic acid solution was freshly prepared before use by dissolving 0.50 g of ascorbic acid and adjusting the volume to 100 mL with water, and it was kept in an amber glass bottle.

2.2 Apparatus

The stopped-flow spectrophotometric system was fabricated in the laboratory as shown in Figure 1. It consisted of 2 line manifold, a peristaltic pump, two 3-way solenoid valves, a stopped-flow controller, a mixing coil, a spectrophotometer, and a personal computer. The reaction involved the formation of arsenomolybdate, which was then reduced by ascorbic acid to form molybdenum blue. Arsenate and acidic molybdate reagent solution that consisted of ammonium molybdate, potassium antimonyl tartrate, sulfuric acid, and ascorbic acid were propelled by a peristaltic pump and flowed to mix together in the mixing

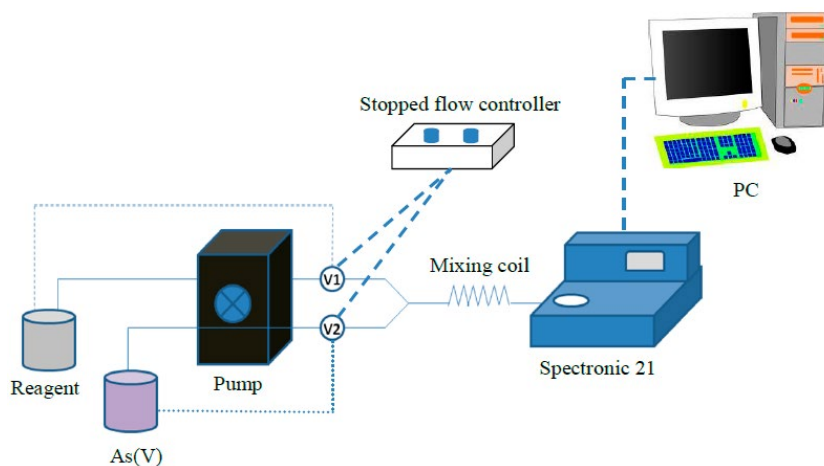


Figure 1. A stopped-flow spectrophotometric system.

coil by a ratio of 1:1 volume per volume. Then, the mixed zone was stopped at a flow cell where the absorbance at 880 nm was continuously measured. A flow rate of each line was set at 0.8 mL per minute and a mixing coil length was 100 cm. Under these conditions, the precise time to stop the flow while the reaction mixture presented in the flow cell of a spectrophotometer could be achieved. By using a 3-way confluence point and the mixing coil, the arsenate and the acidic molybdate reagent were effectively mixed. The time for the mixed solution to flow from the 3-way confluence point to the flow cell is 7 s, which is very short comparing to the stopped-flow time to monitor the kinetic of the reaction. So, the flow conditions did not affect the rate of chemical reaction. The home-made stopped-flow controller was built and programmed the operation step for electronically control of solenoid valves (V1 and V2), so the accurate time data of the kinetic profile could be obtained. The initial slope of the stopped-flow profile was evaluated as an initial rate of reaction, and then the order of reaction and the rate equation were examined.

The absorbance of the reactant was continuously measured at 880 nm with a spectrometer (Spectronic 21, Bausch & Lomb, USA) and it was proportional to the concentration of molybdenum blue. The wavelength of 880 nm was selected because it provided the highest sensitivity (maximum absorption wavelength). Data were collected with a Chart software (eDAQ) in a series of adjacent blocks and converted the data to plot a graph between potential signal versus time. The ratio of the voltage output signal to the absorbance was 500 mV per absorbance unit. Therefore, in this study, the rate of reaction is the slope of the potential signal at the initial period. The sampling rate of the data collection system is 4 sampling points per second (sampling interval time of 0.25 s). This is fast enough to follow the rate of the chemical reaction. For a faster reaction, the higher sampling rate can be set, but with the need of high memory to store the data.

2.3 Kinetic Measurement

The influence of initial concentration of the reactants such as ammonium molybdate (Mo), potassium antimonyl tartrate (PAT), sulfuric acid (H_2SO_4), arsenate (As(V)), and ascorbic acid (AA) to rate of reaction has been studied by varying the initial concentration of one reactant, e.g., arsenate, while keeping the others constant. The initial rate was obtained from the initial slope of the recorded profile of absorbance vs. time. Arsenate and reagent solution was flowed to mix together in-line and the mixed zone was stopped at a flow cell where the absorbance at 880 nm was continuously recorded. The stopped-flow F1gram was obtained from the experiment for examining the initial rate of each reaction condition as shown in Figure 2. Then, the order of the reaction and rate equation were derived as followed:

The experimental rate law:

$$\text{rate} = k [\text{Mo}]^m [\text{H}_2\text{SO}_4]^n [\text{As(V)}]^o [\text{PAT}]^p [\text{AA}]^q \quad (1)$$

When

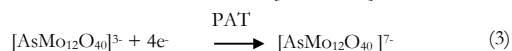
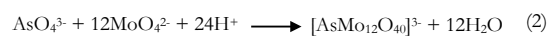
rate = rate of molybdenum blue formation

k = rate constant

m, n, o, p and q = order of reaction of each reactant

3. RESULTS AND DISCUSSION

The kinetic study of molybdenum blue method is based on spectrophotometric observation of the reaction of the arsenate (AsO_4^{3-}) or As(V) with ammonium molybdate to form a yellow heteropoly arsenomolybdate complex. The complex is then reduced to the intense colored arsenomolybdenum blue or molybdenum blue as a function of time. The acceleration of reduction reaction can be achieved by the use of a catalyst (e.g., potassium antimonyl tartrate), the stoichiometry of the reaction is as follow [18]:



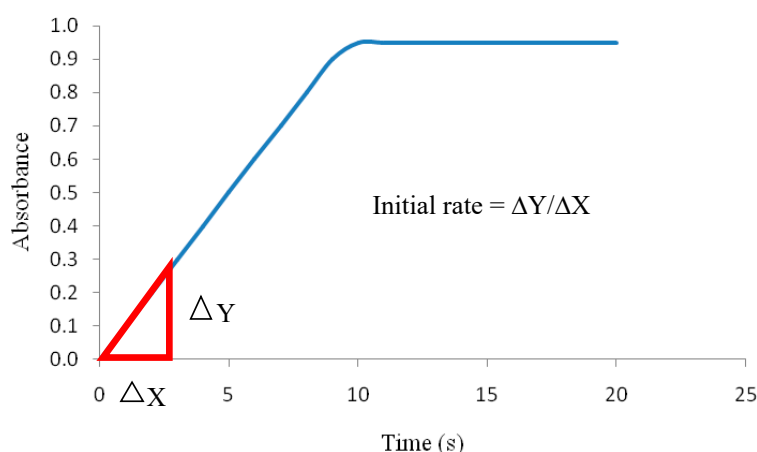


Figure 2. The F1gram profile plotting between the absorbance and the reaction time, and how to examine the initial rate.

It should be noted that at low pH the majority of arsenate is in the form of H_3AsO_4 . The kinetic profile is obtained from the absorbance-time plot that proportional to the production of the colored complex against time. The instantaneous rate of reaction is the slope of the signal at the initial period, and the order of reaction, rate law and rate constant can be derived from the acquired data. Therefore, the influences of the initial concentration of the reactants such as ammonium molybdate (Mo), potassium antimonyl tartrate (PAT), sulfuric acid (H_2SO_4), arsenate (As(V)), and ascorbic acid (AA) to rate of reaction have been studied.

3.1 Effect of Ammonium Molybdate to the Order of Reaction

The kinetic profile of molybdenum blue formation at four levels ammonium molybdate concentrations (from 0.4 mM to 8.1 mM) was carried out while concentration of other reactants were fixed as excess as follows: 0.75 M H_2SO_4 , 0.59 mM PAT, 110 mM AA and 13.3×10^{-3} mM As(V). The product formation is directly related to the concentration of molybdate in the solution; the effect of molybdate concentrations was examined from 0.4 mM to 8.1 mM as shown in

Figure 3. It was observed that molybdenum blue formation did not occur when the molybdate concentration lower than 2.0 mM, no change in the absorbance could be noticed. On the other hand, self-reduction of the molybdate ion had occurred, causing high absorbance baseline when molybdate concentration higher than 8.1 mM. Therefore, at 4.0 and 8.1 mM molybdate that the rate of the reaction could be measured, doubling the molybdate concentration increased the initial rate by six times. The experimental reaction order data are summarized in Table 2, and the reaction was found to be a third order with respect to molybdate.

3.2 Effect of Sulfuric Acid on the Order of Reaction

Sulfuric acid concentrations between 0.50 and 2.0 M were examined, but detailed experiments were carried out for only the range of 0.75-1.00 M. The experimental reaction order data are summarized in Table 3. The reaction was found to be inverse seventh order in sulfuric acid. At the lowest concentration mentioned, self-reduction of the molybdate ion had occurred (in the absence of As(V) and reducing agent) causing a high background signal and at 2.0 M, the time

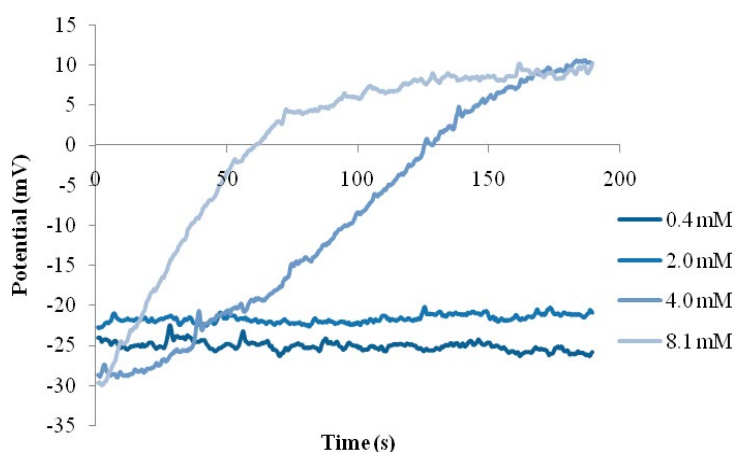


Figure 3. Effect of molybdate concentration on molybdenum blue formation.

Table 2. Initial rate of molybdenum blue formation at various molybdate concentrations.

Experiment	Mo (mM)	H ₂ SO ₄ (M)	As(V) (mM)	PAT (mM)	AA (mM)	Initial rate (mV/Sec)
1	0.4	0.75	13x10 ⁻³	0.59	110	N.D.
2	2.0	0.75	13x10 ⁻³	0.59	110	N.D.
3	4.0	0.75	13x10 ⁻³	0.59	110	3.00
4	8.1	0.75	13x10 ⁻³	0.59	110	19.37

Table 3. Initial rate of molybdenum blue formation at various sulfuric acid concentrations.

Experiment	Mo (mM)	H ₂ SO ₄ (M)	As(V) (mM)	PAT (mM)	AA (mM)	Initial rate (mV/Sec)
1	4.0	0.50	13x10 ⁻³	0.59	110	N.D.
2	4.0	0.75	13x10 ⁻³	0.59	110	0.66
3	4.0	1.0	13x10 ⁻³	0.59	110	0.09
4	4.0	2.0	13x10 ⁻³	0.59	110	N.D.

for color formation was too long. The kinetic profile of molybdenum blue formation at various sulfuric acid concentrations while concentrations of other reactants were kept constant is illustrated in Figure 4.

3.5 Effect of Ascorbic acid Concentration on the Order of Reaction

The concentration of the reductant also affects the reduction rate, while the formation of the heteropoly complex was very rapid, the reduction to form a heteropoly blue was slow. The

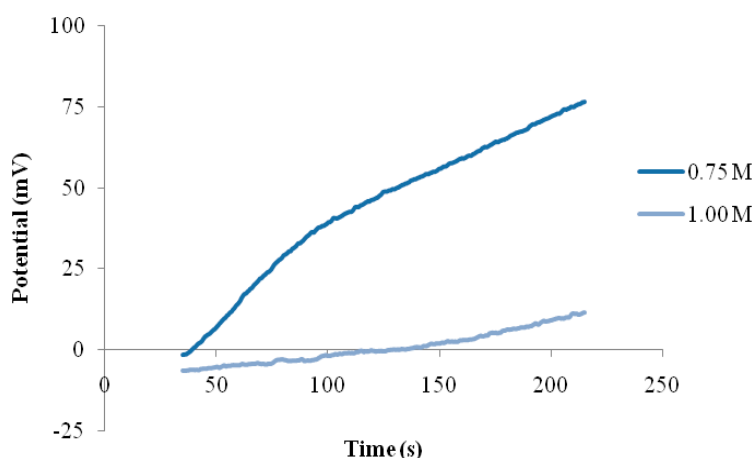


Figure 4. Effect of sulfuric acid concentration on molybdenum blue formation.

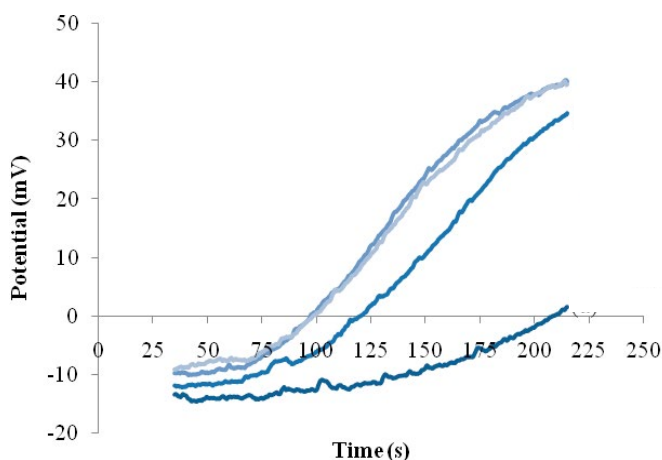


Figure 5. Effect of ascorbic acid concentration on molybdenum blue formation.

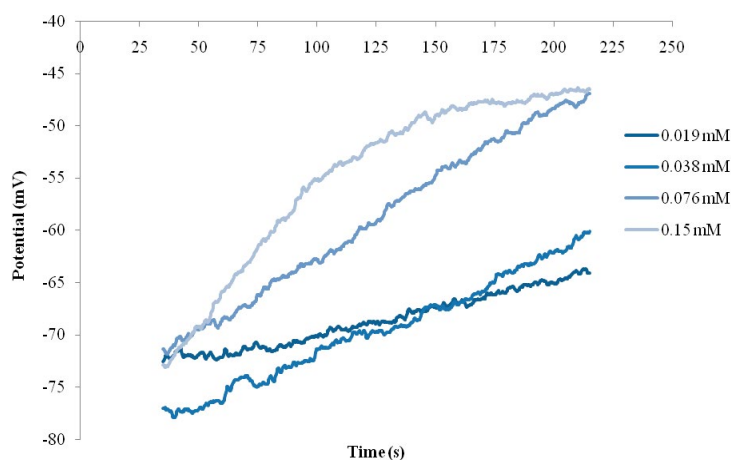
reaction time required for completion depends on the conditions employed [19]. Stannous chloride, hydrazine, and ascorbic acid have been used as reducing agents in the molybdenum blue method [3,20-22], but stannous chloride and hydrazine show a slower reduction rate [23]. To help clarify the overall reaction scheme, the kinetics of the formation of the heteropoly blue resulting from the reduction by ascorbic acid was investigated by varying ascorbic acid concentrations.

The effect of ascorbic acid concentration on the molybdate reduction was studied at four

different levels between 5.5 and 110 mM. When 5.5 mM of ascorbic acid was used, the initial rate could not be observed, the absorbances of the product were increased slowly. On the other hand, the higher concentrations of ascorbic acid produced a greater initial rate. However, no difference in the absorbance could be noticed until the concentration higher than 55 mM as shown in Figure 5. The experimental reaction order data are summarized in Table 4. For ascorbic acid in the range of 5.5 – 110 mM, the reaction was found to be the first order.

Table 4. Initial rate of molybdenum blue formation at various ascorbic acid concentrations.

Experiment	Mo (mM)	H ₂ SO ₄ (M)	As(V) (mM)	PAT (mM)	AA (mM)	Initial rate (mV/Sec)
1	4.0	0.75	13×10^{-3}	0.59	5.5	N.D.
2	4.0	0.75	13×10^{-3}	0.59	28	0.03
3	4.0	0.75	13×10^{-3}	0.59	55	0.05
4	4.0	0.75	13×10^{-3}	0.59	110	0.05

**Figure 6.** Effect of potassium antimonyl tartrate concentration on molybdenum blue formation.

3.6 Effect of Potassium Antimonyl Tartrate Concentration on the Order of Reaction

Potassium antimonyl tartrate (PAT) has a significant effect on the color development of the complex. The addition of antimonyl tartrate to the mixed reagent can significantly accelerate the reduction of molybdate [3,24]. The effect of antimonyl tartrate concentrations between 0.019 and 0.15 mM on the initial rate of the reaction was examined. These studied concentrations quite lower than the excess concentration that is using in the determined method to demonstrate the role of PAT. It was found that increasing the concentration of antimonyl tartrate significantly improved the rate of color development. From Figure 6, the initial rate was obtained and summarized in Table 5. The reaction order was

found to be first order with respect to potassium antimonyl tartrate.

3.7 Effect of As(V) Concentration on the Order of Reaction

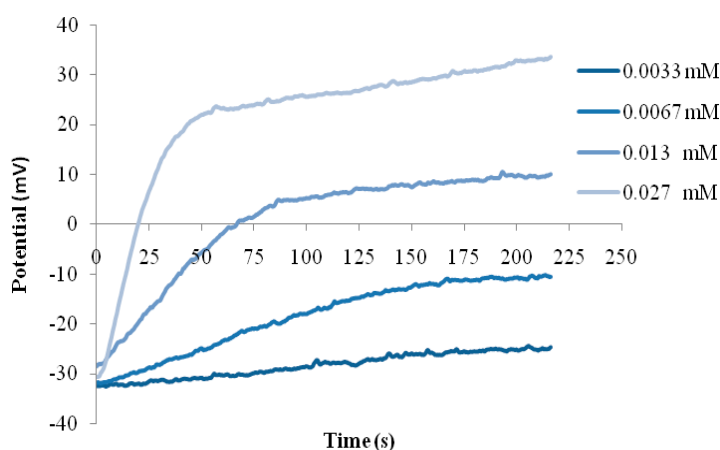
The kinetics of the formation of arsenomolybdenum blue from As(V) were investigated in the range 3.34×10^{-3} to 26.69×10^{-3} mM. The faster initial rate of molybdenum blue formation could be obtained if the concentration of As(V) was increased as shown in Figure 7, and the experimental rate data are summarized in Table 6.

3.8 Experimental Rate Law

The initial rate of formation of molybdenum blue was measured as a function of molybdate,

Table 5. Initial rate of molybdenum blue formation at various potassium antimony tartrate concentrations.

Experiment	Mo (mM)	H ₂ SO ₄ (M)	As(V) (mM)	PAT (mM)	AA (mM)	Initial rate (mV/Sec)
1	4.0	0.75	13x10 ⁻³	0.019	110	0.01
2	4.0	0.75	13x10 ⁻³	0.038	110	0.10
3	4.0	0.75	13x10 ⁻³	0.076	110	0.16
4	4.0	0.75	13x10 ⁻³	0.15	110	0.28

**Figure 7.** Effect of As(V) concentration on molybdenum blue formation.**Table 6.** Initial rate of molybdenum blue formation at various As(V) concentrations.

Experiment	Mo (mM)	H ₂ SO ₄ (M)	As(V) (mM)	PAT (mM)	AA (mM)	Initial rate (mV/sec)
1	8.1	0.75	3.3x10 ⁻³	0.59	110	0.64
2	8.1	0.75	6.6x10 ⁻³	0.59	110	5.78
3	8.1	0.75	13x10 ⁻³	0.59	110	19.37
4	8.1	0.75	27x10 ⁻³	0.59	110	75.08

arsenate, reducing agent (ascorbic acid) and sulfuric acid concentrations. The experimental reaction order data are summarized in Table 7. The concentration range of 3.3×10^{-3} – 27×10^{-3} M As(V) was employed in order to fit over concentration that found in a natural water sample, the reaction

was found to be reverse seventh order in H₂SO₄, the third order in molybdate, the first order in potassium antimonyl tartrate and the first order in ascorbic acid.

Therefore, the experimental rate law is proposed to be:

Table 7. The experimental reaction order data.

	Mo (mM)	H ₂ SO ₄ (M)	As(V) (mM)	PAT (mM)	AA (mM)	Order
Mo	0.4 - 8.1	0.75	13x10 ⁻³	0.59	110	3
H ₂ SO ₄	4.0	0.50 - 2.0	13x10 ⁻³	0.59	110	-7
As(V)	8.1	0.75	(3.3- 27) x10 ⁻³	0.59	110	2
PAT	4.0	0.75	13x10 ⁻³	(19 -151) x10 ⁻³	110	1
AA	4.0	0.75	13x10 ⁻³	0.59	5.5 -110	1

$$\text{Rate} = \frac{k [\text{Mo}]^3 [\text{As(V)}]^2 [\text{PAT}] [\text{AA}]}{[\text{H}_2\text{SO}_4]^7} \quad (4)$$

The experimental rate law equation suggested that the formation of the molybdenum blue was based on the concentrations of various reagents significantly to predict for a faster determination method such as a decreasing the concentration of sulfuric acid is very important to increase the rate of formation of molybdenum blue that can be applied to develop a spectrophotometric method for determination As(V) at very low concentration. However, too low acid concentration may cause self-reduction of molybdenum complex, resulting in the increase of background signal [18].

4. CONCLUSIONS

In this work, we developed a simple stopped-flow spectrophotometric system for studying the kinetic of molybdenum blue reaction with As(V). The reaction orders with respect to ammonium molybdate (Mo), potassium antimonyl tartrate (PAT), sulfuric acid (H₂SO₄), arsenate (As(V)), and ascorbic acid (AA) were examined. The rate measurements were carried out by determining the slope of the recorded absorbance *vs.* time curve in a stopped-flow system. The initial slope of the stopped-flow profile was evaluated as an initial rate of reaction, and then the order of reaction and rate equation were derived.

Considering the rate law, the order of acid

concentration is very high, suggesting that the acid concentration dramatically affected the reaction rate. Molybdate concentration also played an important role in the sensitivity of the reaction for the determination of arsenate. Besides, a suitable [H₂SO₄] / [Mo] ratio give a plateau background in which color formation is complete, but the self-reduction of molybdate ion does not occur. The kinetic information about the influence of various reagents on the formation of molybdenum blue product should be useful for improving the sensitivity of arsenate determination. Moreover, the proposed stopped-flow method provided convenient and fast operation, low chemical consumption, and it is a closed system that is suitable for the strong odor or toxic compound, therefore it should be a suitable platform for the kinetic study of other interesting reactions too.

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