Chemical Kinetic Study Using Sequential Injection Systems Incorporating Lab-at-Valve with a Longer (30 mm) Path Z-Cell

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Abstract

Simple sequential injection systems incorporating Lab-at-Valve (LAV) with a longer (30 mm) path Z-cell spectrophotometric measurement are proposed for chemical kinetic investigation. The Z-cell serves as a reaction reactor as well as a detection cell. Performances of such the systems are demonstrated by 3 model chemistries, namely, (1) iodide and persulfate (2) Griess reaction for nitrite and (3) the molybdenum blue reactions.

Keywords Chemical kinetics, Sequential injection, Lab-at-Valve, Iodide, Nitrite, Griess reaction, Molybdenum blue

1. Introduction

Kinetic study of reactions plays important roles in chemistry. Flow based analysis offers advantages for kinetic study. The stopped-flow injection proposed by Ruzicka and Hansen with simple instrumentation for kinetic study could be performed by flowing the sample zone and stop at a desired point, generally at the detection flow cell, for signal obtaining. Manual and semi-automatic kinetic studies based on such the concept have been reported [1-4]. Sequential injection (SI) analysis has been also proposed for this area as it provides higher degrees of automation and miniaturizability [5]. The kinetic studies by using SI methods have also been proposed [6-8].

In this work, we propose simple SI-LAV systems with a longer (30mm) path Z-cell spectrophotometric measurement for chemical kinetic investigation. Three model chemical systems were chosen for demonstration: (1) iodide-persulfate reaction, (2) Griess reaction and (3) molybdenum blue reaction.

2. Experimental

2.1. Reagents

All solutions were prepared using analytical grade reagent. De-ionized (DI) water (Millipore, USA) was used throughout the experiments except otherwise stated.

2.1.1 The iodide reaction

Potassium iodide stock solution (0.1 M, 100 mL) was prepared by dissolving 1.66 g KI (BDH, England) in water. A stock solution of 0.1 M 100 mL ammonium persulfate (Sigma-Aldrich, USA) was prepared by dissolving $(NH_4)_2S_2O_8$ 2.28 g. Standardization of the stock solutions were made. These solutions were further diluted for use in the experiments. Reagents were daily prepared.

2.1.2 Griess reaction

Sodium nitrite (0.5 M, 100 mL) stock solution was prepared by dissolving $NaNO_2$ (Baker, USA) 3.45 g in water. Sulfanilamide (Fluka, Switzerland) solution (0.25% w/v) was prepared in 5% v/v orthophosphoric acid. 0.1% w/v N (1-naphthyl) ethylenediamine dihydrochloride, NED, (BDH, England) solution was prepared in water. The reagents were protected from light by covering bottles with aluminum foil.

2.1.3 Phosphate reaction

An ascorbic acid solution (1.2% w/v, 50 mL) was freshly prepared by dissolving 0.6 g L-ascorbic acid (Carlo Erba, Rodeno, France) in 0.1 M sulfuric acid. The prepared solution was kept in bottle covered with aluminum foil to prevent it from light. A standard phosphate (0.01 M, 100 mL) was prepared as a stock solution by using disodium hydrogen phosphate dihydrate (Fluka, Switzerland) 0.177 g in milli-Q water. Molybedate solution (0.8% w/v, 50 mL) was a solution of ammonium molybdate tetrahydrate (Sigma-Aldrich, USA) 0.4 g dissolved in Milli-Q water.

2.2 SI-LAV

2.2.1 The set-up

SI systems consist of a flow propelling system via a syringe pump (FIAlab instrument, USA) with 2.5 mL syringe barrel and a 10-port selection valve (Valco instruments Co. Inc., USA). The system was automatically controlled by via a computer with labVIEW [TM] (National Instruments, USA) based software.

Two SI manifolds, namely, A and B (Fig 1(A) and 1(B)) were set: Manifold A having the Z-cell at port # 5 of the 10 port selection valve while manifold B having the Z-cell at the center of the selection valve. The home made Z-cell was made of acrylic piece (Fig 1(C)) drilled for a channel (2 mm ID) having 90 μL. It was wrapped to be opaque with black tape. This Z-cell would serve as a reaction reactor as well as a detection cell.

Different angles (0, 45 and 90 degrees) of the Z-cell aligning

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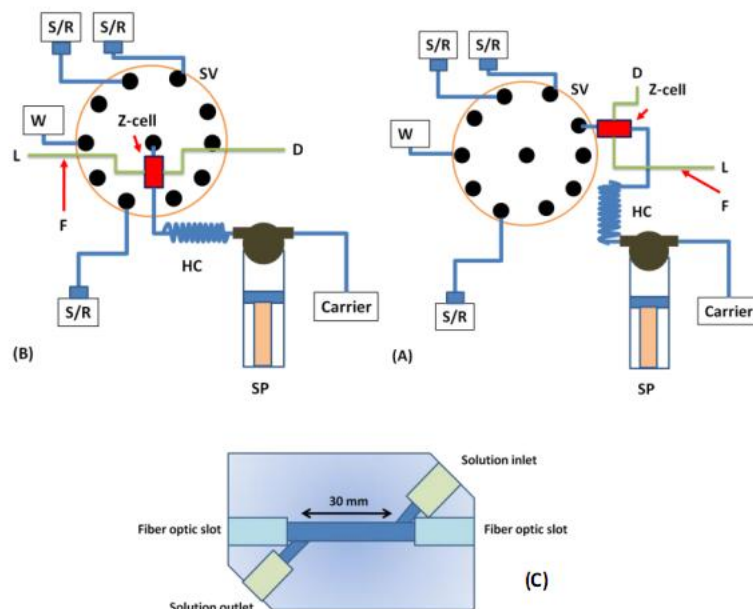E-mail: kate@chiangmai.ac.th, kgrudpan@gmail.com

Fig. 1 Illustration of the two SI manifolds (A and B) for investigations of kinetics using 30 mm light path homemade Z-cell (C) situated at either the port position # 5 (A) or the center (B) of the 10 port selection valve. SP: syringe pump; HC: holding coil; S/R: sample/reagent; F: fiber optics; D: detection unit (USB 2000); L: light source (tungsten lamp)
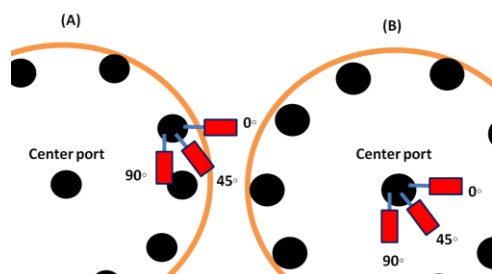

Fig. 2 Illustrating the aligning in different angles (0, 45 and 90 degrees) of the z-cell (A) and (B) for the manifolds in Fig 1, respectively.

with respect to the inlet line (horizontal line) (Fig 2) were also made.

The detection system was equipped with a fiber-optic UV–VIS diode array detector USB 2000 (Ocean Optics Inc., USA), 30 mm light path home-made Z- flow cell (depicted in Figure 1C) and UV-VIS (tungsten-halogen) light source (LS-1-LL, Ocean Optics Inc., USA). Detection software was operated by using FIAlab® for Windows version 5.0. Teflon tubes (0.30" ID, Upchurch Scientific Inc., USA) were used for making solution flow lines and holding coils.

Table 1 Steps in the study of Griess reaction using SI manifold A (F = flow rate, V = volume, P = port number)

Step	Actions	F (μL/L)	V (μL)	P
1	Aspirate water to syringe barrel	100	1000	-
2	Aspirate sulfanilamide to holding coil	30	30	9
3	Dispense to detector	30	30	5
4	Aspirate NaNO$_2$ to holding coil	30	30	3
5	Dispense to detector	30	30	5
6	Aspirate NED to holding coil	30	50	4
7	Dispense to detector	30	50	5
8	Stop flow 60 s	0	0	-
9	Dispense all	100	1000	5

Table 2 Steps in the study of Griess reaction using SI manifold B (F = flow rate, V = volume, P = port number)

Step	Actions	F (μL/L)	V (μL)	P
1	Aspirate water to syringe barrel	100	1000	-
2	Aspirate sulfanilamide to holding coil	30	30	9
3	Aspirate NaNO$_2$ to holding coil	30	30	3
4	Aspirate NED to holding coil	30	50	4
5	Stop flow 60 s	0	0	-
6	Dispense all to waste	100	1110	1

2.2.2 System Operation

Iodide reaction: The SI system was set up as aforementioned, carrier was DI water, and the UV-VIS detector was set for monitoring at a wavelength of 355 nm [9], the maximum absorption wavelength of I$_3^-$. *In manifold A*, the operation was started with aspiration of DI water (1000 μL) into syringe barrel with flow rate of 100 μL/sec. Then persulfate solution (30 μL) was aspirated with a flow rate of 100 μL/sec into holding coil. The solution (30 μL) was flowed to Z-cell with

flow rate of 30 μL/sec. KI solution (30 μL) was aspirated with flow rate of 30 μL/sec into holding coil. Then the solution (40 μL, KI + water) in the holding coil was flowed with flow rate of 100 μL/sec into the Z-flow cell and then stop for 90 s for signal monitoring. Finally, solution was drained to waste until syringe was empty. *In manifold B*, DI water, 1000 μL, was aspirated into syringe barrel with flow rate of 100 μL/sec. The solution of persulfate was aspirated into holding coil, through Z-cell, with volume of 30 μL, 100 μL/sec. After that, KI solution volume of 40 μL was aspirated through Z-cell. Stop flow signal was monitored for 90 s and then flush all solution to waste. It should be noted that a higher flow rate of aspiration would promote efficient mixing of the reactants but too high flow rate would result in less precision in volume of solution to be aspirated.

Griess reaction: The SI operation steps were described as Tables 1-2, for the manifolds A and B respectively. The detection wavelength was set at 550 nm.

Molybdenum blue reactions: In this work, we also demonstrated the effects of flow cell and inlet angle to the kinetic profile of the reaction. The experiments were carried on using both the manifolds A and B of which flow cell arranged as aforementioned. The SI operation steps were performed similar to that of the Griess reaction in Tables 1-2. Wavelength of monitoring was set at 660 nm.

3. Results and discussion

3.1 The iodide reaction

The reaction of iodide and persulfate, or well-known as clock reaction, is basic reaction for study of kinetics (eq.1) [10].

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-} \qquad (1)$$
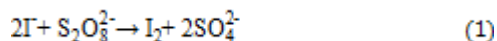
when "k" is referred to a rate constant, "α" as rate order with respect to iodide and "β" as rate order with respect to persulfate. The rate of reaction would be described as equation (2).

$$\text{Rate of reaction (R)} = \frac{d[I_2]}{dt} = k[I^-]^\alpha [S_2O_8^{2-}]^\beta \qquad (2)$$

Generally, we can assume that iodine would react with iodide rapidly (3) and would form triiodide ion which could be monitored for absorbance at a wavelength of 350 nm.

$$I^- + I_2 \rightarrow I_3^- \qquad (3)$$
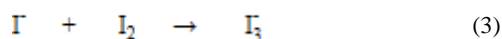
When ε is molar absorptivity of compounds (I_3^-) and b is path length of light through sample, the absorbance, A, from triiodide ion would relate to rate of reaction as:

$$R = \frac{d[\frac{A}{\varepsilon b}]}{dt} = \frac{d[I_3]}{dt} = k[I^-]^\alpha [S_2O_8^{2-}]^\beta \qquad (4)$$

$$\ln R = \ln\frac{d[\frac{A}{\varepsilon b}]}{dt} = \ln K + \alpha \ln[I^-] + \beta \ln[S_2O_8^{2-}] \qquad (5)$$

$$\ln\frac{d[\frac{A}{\varepsilon b}]}{dt} = K' + \alpha \ln[I^-] \qquad (6)$$

when $\quad K' = \ln K + \beta \ln[S_2O_8^{2-}]$

The terms of molar absorptivity and path length could be considered as constant. So, if the concentration of persulfate was kept constant by having it in enough excess concentration. Using equation (6), rate order with respect to iodide (α) could be determined via a plot of ln (slope of the triiodide absorbance against time (dA/dt)) and ln (concentration of iodide $[I^-]$).

Similarly, rate order with respect to persulfate could be estimated by fixing concentration of iodide (excess of it).

The detection point of solution in flow cell was investigated to obtain reliability of absorbance signals. The experimental measurement for a detectable position was performed by variation of volume injected into flow cell. In order to obtain good signals, it was found that, zones of persulfate solution and KI solution should be merged and transferred immediately into flow cell. The merging point has to be occurred at the middle of flow cell. Although, experimental calculation of void volume from a port, in manifold A, (or center port in manifold B) to the light path way should be 50 μL but it was found that a volume of 40 μL of KI solution yielded better profile than that of 50 μL. This might be the effect due to zone dispersion of the two solutions when they flowed into channel (Z-cell).
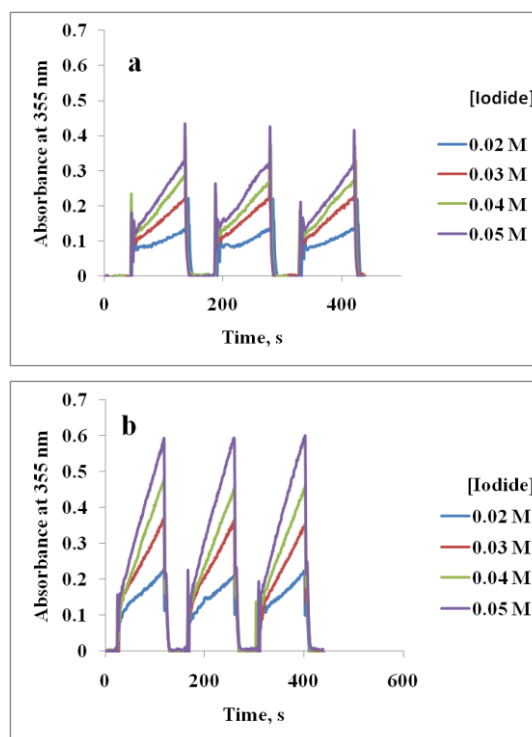

Fig. 3 SIgram profiles due to triiodide by SI manifold A (a) and manifold B (b). The kinetics of the reaction in different concentrations of iodide, at concentration of 0.1 M ammonium persulfate, was evaluated from the signal profiles.

The signal profiles of triiodide collected from the experiments performed using the manifolds A and B are presented in Fig 3. The rate of reactions, slope at initial 20 s

data of each signal profiles, was simply determined by varying iodide concentrations, 0.02-0.05 M, with fixing concentration of persulfate at 0.1 M. The order of the reaction respect to iodide was estimated by plotting a graph using the equation (6) and illustrated in Fig 4. It was found that the data obtained using the manifold B yielded better signals for evaluation than that of the manifold A. Rate orders with respect to iodide were evaluate to be 1.39 and 1.09 by using SI manifold A and B, respectively. The order value obtained from the manifold B is closer to theoretical value (1st order). It can be observed that using the manifold A, linearity of graph is unacceptable. This could be due to the effect in term of sensitivity which less than that of manifold B. For the manifold A, the mixture was traveled in line, tubing, much more than using manifold B. Dispersion phenomena could reduce the flux of product and disturb sensitivity of detection method.
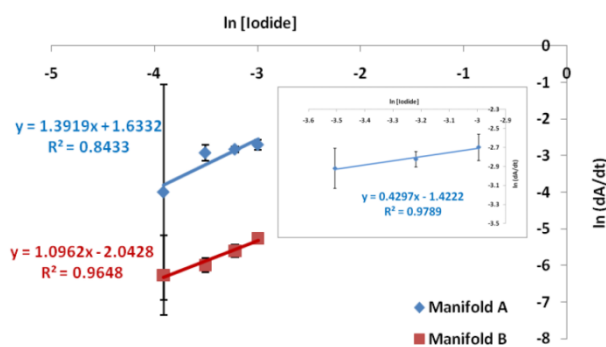

Fig. 4 Relation between ln(dA/dt) and ln[Iodide] for calculation rate order of iodide. Insert picture is data selected from SI manifold A without 0.02 M Iodide.

The order of persulfate was also evaluated similarly. The concentration of iodide was kept at constant concentration, 0.1 M, and concentrations of persulfate were investigated at 0.01-0.05 M. The values obtained from the experiment are presented in Table 1

Table 1 Kinetic data of iodide reaction obtained from the proposed SI-LAV system

	Manifold A		Manifold B	
	Rate order	Linearity	Rate order	Linearity
Iodide	1.39 (0.43)*	0.8433 (0.9789)*	1.09	0.9648
Persulfate	1.32	0.9827	1.18	0.9918

Note * In blanket, values using 3 point data.

3.2 Griess reaction

Griess reaction is the well-known for determination of nitrite. The reactions involve sulfanilic acid and 1-napthylamine, Griess reagent, to react with nitrite. This reaction generates a red solution which is produced from diazotization and azo coupling reactions [11]. The reaction has been modified to be generally basic methods. In this work,

sulfanilamide and N-(1-napthyl)ethylenediamine dihydrochloride (NED) were used to react with nitrite, the reactions could be expressed as Fig 5;
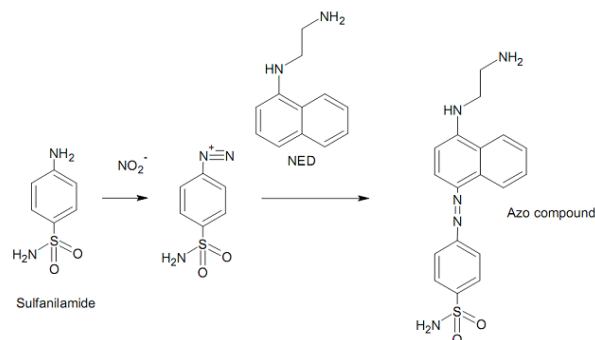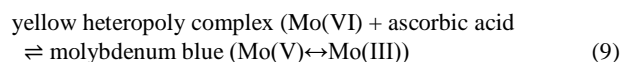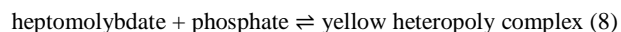

Fig. 5 Griess reaction for nitrite analysis [10]

Concentrations of reagents were set at 0.25% w/v sulfanilamide in 5% v/v phosphoric acid and 0.1% w/v NED. Nitrite solutions were: 0.02, 0.04, 0.06 and 0.08 M. The SI signal profiles were investigated for evaluation of the kinetic data. Performances for both the manifolds were found to be similar to that of iodide reaction. Using manifold B provided higher sensitivity of signal than manifold A. For the kinetic data, with considering the equation for calculate kinetic data:

$$\ln\frac{d[\frac{A}{\varepsilon b}]}{dt} = K' + \alpha \ln[NO_2^-] \qquad (7)$$

It was observed that the data obtained from the manifold B seem to be more reliable as the deviation and linearity of plot are much better (Table 2).

3.2 The molybdenum blue reaction

The reaction used for phosphorus determination, as phosphate, was observed for kinetic information. The phosphate ion would react with ammonium molybdate in acid medium to generate phosphomolybdic acid. Reduction of the product with ascorbic acid, and antimony potassium tartrate used as a catalytic agent, would produce blue complex. Spectrophotometric monitoring at 660 nm absorption wavelength could be applied for tracing the reaction behavior. The reactions for molybdenum blue may be described as [4]:

heptomolybdate + phosphate ⇌ yellow heteropoly complex (8)

yellow heteropoly complex (Mo(VI)) + ascorbic acid
⇌ molybdenum blue (Mo(V)↔Mo(III)) (9)

When (8) is considered as a faster reaction than (9). The reaction was investigated by SI-LAV using manifolds A and B. Herein, we design to study the effect of angle between a flow cell and the solution inlet line. The reagents were: ascorbic acid solution,1.2% w/v ; molybedate solution, 0.8% w/v ; phosphate concentrations (2.10 x 10^{-5} - 8.42 x 10^{-5} M). Kinetic data could be calculated similarly to that of the iodide and nitrite reaction, as aforementioned. The SI gram profiles are illustrated in Figure 6 and kinetic information is presented in Table 3.

Table 2 Kinetic data of Griess reaction (Nitrite) obtained from SI-LAV system

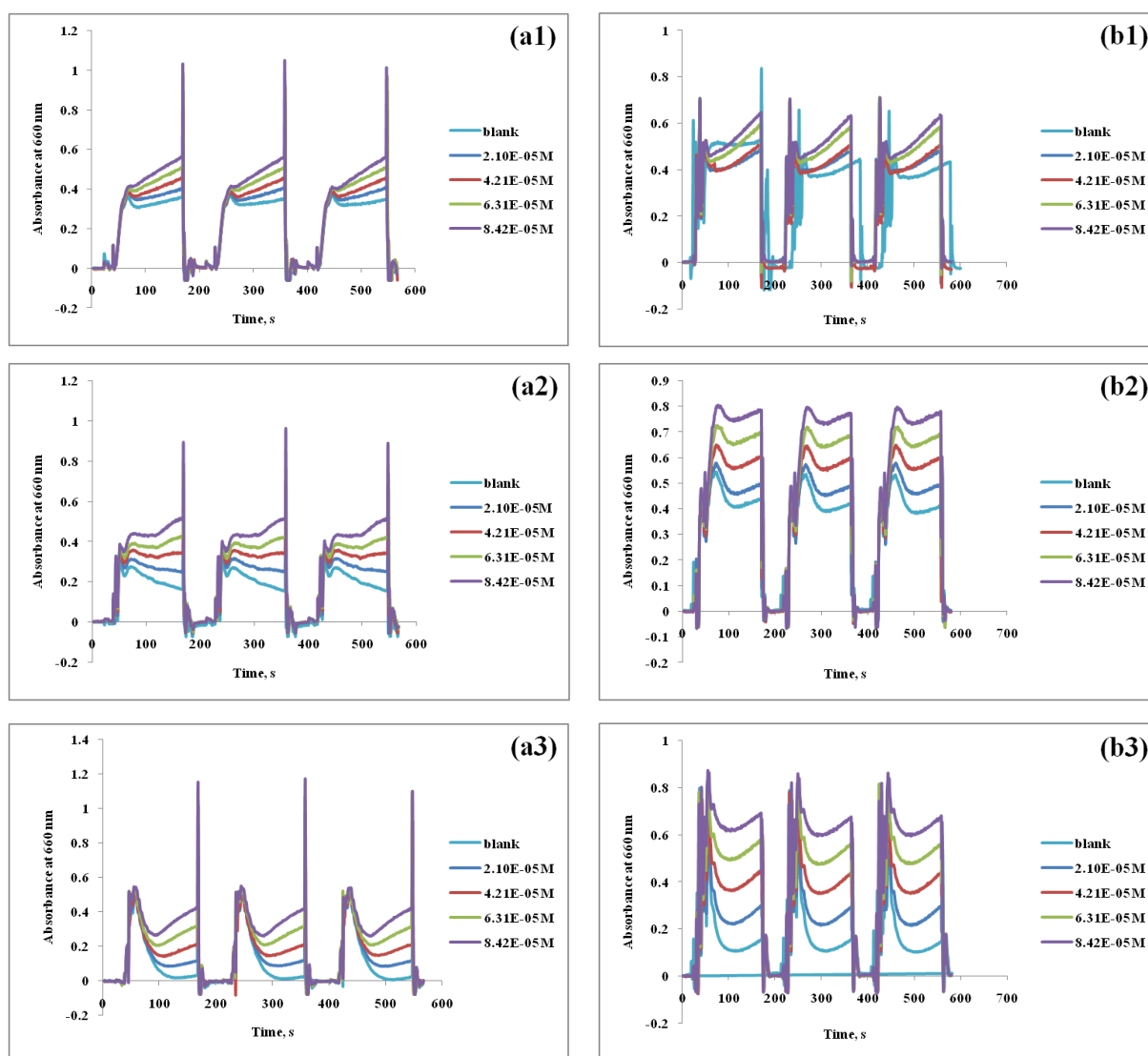| [Nitrite] M	ln[Nitrite]	Manifold A			Manifold B		
		dA/dt	ln(dA/dt)	sd	dA/dt	ln(dA/dt)	sd
0.02	-3.91202	0.0003	-8.11	0.54	0.0014	-6.57	0.13
0.04	-3.21888	0.0005	-7.60	1.11	0.0025	-5.99	0.23
0.06	-2.81341	0.001	-6.90	0.34	0.0035	-5.65	0.33
0.08	-2.52573	0.0022	-6.11	0.14	0.0045	-5.40	0.43
Rate order with respect to nitrite		1.37 $R^2 = 0.9166$			0.84 $R^2 = 0.9999$		

Fig. 6 SI grams obtained from molybdenum blue reaction. The profiles are operated on different angles; for manifold A: (a1) 0, (a2) 45, (a3) 90 degrees and for manifold B (b1) 0, (b2) 45, (b3) 90 degrees.

Table 3 Kinetic data of phosphomolybdate (phosphate) obtained from SI-LAV system using different angles of detection.

Phosphate (M)	ln[Phosphate]	ln(dA/dt)					
		SI-LAV manifold A			SI-LAV manifold B		
		0°	45°	90°	0°	45°	90°
2.10×10^{-5}	-10.76	-7.601	nd	-7.824	-7.824	-7.264	-7.601
4.21×10^{-5}	-10.07	-7.013	-8.112	-6.908	-7.264	-7.131	-7.131
6.31×10^{-5}	-9.66	-6.645	-7.131	-6.266	-6.725	-7.264	-7.419
8.42×10^{-5}	-9.38	-6.320	-6.502	-5.952	-6.725	-7.131	-7.601
Rate orders with respect to phosphate		0.912	2.328	1.373	0.979	0.06	0.007
Linearity (R^2)		0.9967	0.9992	0.9977	0.9807	0.2218	0.0004

It could be noticed that the manifold B, which worked well for the iodide and nitrite systems, resulted in unsatisfied profiles for phosphate and data extracted from the profiles were complicated. However, the manifold A presented satisfied information in angles of 0 and 90 degrees. This could be due to that, for manifold A, there were more steps of aspiration and flow than that of manifold B. So, ascorbic acid and molybdate have much more time to react to each other before dealing with phosphate, as previously investigated [4]. Further investigation to support the explanation will be made.

Acknowledgments

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