

Ionic Strength Effect on the Rate of Reduction of Hexacyanoferrate(III) by Ascorbic Acid

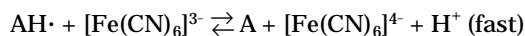
A Flow Injection Kinetic Experiment

Joaquim A. Nóbrega and Fábio R. P. Rocha

Department of Chemistry, Federal University of São Carlos, Caixa Postal 676, 13.560-270, São Carlos, SP, Brazil

Flow systems have been mainly used for quantitative determination of analytes in solution and are chiefly employed to increase precision and analytical frequency. This view was focused in some previous educational papers (1–3). However, flow injection analysis (FIA) can also be applied in fast experiments to determine physical chemistry parameters such as diffusion coefficients (4, 5), viscosity (6, 7), and complexing capacity of ligands (8, 9). Other less usual FIA systems have also been proposed to determine reaction stoichiometries (10) and investigate temperature effects on dispersion (11).

The aim of this work was to use a flow injection apparatus to evaluate the effect of ionic strength on the rate of reduction of hexacyanoferrate(III) by ascorbic acid. A mechanism was proposed (12) for this reaction that involves formation of an intermediate ascorbate anion (AH⁻) by ionization of ascorbic acid (AH₂). The ascorbate anion transfers one electron to hexacyanoferrate(III) in a slow step that is followed by a fast step in which the ascorbate free radical (AH[•]) transfers one electron to hexacyanoferrate(III) to generate dehydroascorbic acid (A):



The rate-determining step of this second-order reaction involves the collision between two anionic species. Thus, it is influenced by the ionic strength of the medium, which causes an alteration of ionic atmosphere and changes the charge densities around anions.

The kinetics of the reduction of hexacyanoferrate(III) can be followed spectrophotometrically. When dissolved in aqueous medium, this compound generates a yellow solution. Ascorbic acid and reaction products are colorless. This study was previously made using a manual spectrophotometric procedure (13). That experiment was conducted in a medium containing 10⁻² M nitric acid to decrease the reaction rate and to make practicable the manual procedure, since the rate constant is inversely proportional to the acid concentration (14).

In the flow diagram designed to carry out this study, flow is stopped by commutation when the center of the sample zone reaches the flow cell, and the gradual decrease in signal, related to the redox reaction, is recorded as a function of time. A direct examination of this record allows determination of the half-time (*t*_{1/2}), and this parameter is used to calculate the rate constant and to estimate the charge product of the two reacting species.

The proposed experiment can be completed in a 4-hour laboratory class. All reagents are nontoxic. Obtaining kinetic data without clock experiments is more compatible with the modern instrumentation that students will find in laboratories.

Treatment of Data

For a second-order reaction, if the initial amounts of reagents (*C*₀) are equal and the half-time (*t*_{1/2}) is known, the rate constant (*k*) at the ionic strength *I* can be calculated by the following expression:

$$k = 1/t_{1/2} C_0 \quad (1)$$

After obtaining the rate constant, the Brønsted–Bjerrum equation (2), based on the limiting law of Debye–Hückel, can be used to estimate the rate constant at infinite dilution (*k*₀) and the value of *z*_A*z*_B, where *z*_A and *z*_B are the charges of the ions involved in the rate-determining step.

$$\log k = \log k_0 + 1.02 z_A z_B I^{1/2} \quad (2)$$

For more concentrated solutions, *k*₀ and *z*_A*z*_B can be estimated by combining the Brønsted–Bjerrum and the extended law of Debye–Hückel to obtain the expression

$$\log k = \log k_0 + 1.02 z_A z_B [I^{1/2} / (1 + I^{1/2})] \quad (3)$$

Experimental Procedure

Apparatus

A peristaltic pump with at least 3 channels is required. Polyethylene tubing (0.8 mm i.d.) and propulsion tubes (Technicom) with different internal diameters were used to set up the system shown in the diagram (Fig. 1). The spectrophotometer must be equipped with a flow cell with a reduced dead volume and must be connected to a potentiometer recorder. The stopped-flow condition was obtained by commutation using a sliding bar injector (15). This is a homemade device consisting of two fixed lateral bars and a movable central bar that is moved back and forth for sample injection and stopped flow.

Reagents and Solutions

The experiments were conducted at four ionic strengths: 2.0 × 10⁻², 5.0 × 10⁻², 1.0 × 10⁻¹, and 2.0 × 10⁻¹ M, adjusted with sodium nitrate solutions. Nitrate solutions in these same ionic strengths were employed as carrier in the flow system. Solutions containing 10⁻³ M ascorbic acid and different concentrations of sodium nitrate to adjust the ionic strength were also prepared. To maintain the ionic strength constant, 10⁻³ M potassium hexacyanoferrate(III) solutions were prepared in media containing 1.4 × 10⁻², 4.4 × 10⁻², 9.4 × 10⁻², and 1.9 × 10⁻¹ M sodium nitrate. This took into account the dissociation of potassium hexacyanoferrate(III). All solutions were prepared in distilled deionized water.

Procedure

The students assemble the stopped-flow apparatus based on commutation as depicted in Figure 1. In this system, the hexacyanoferrate(III) is injected as a sample in the

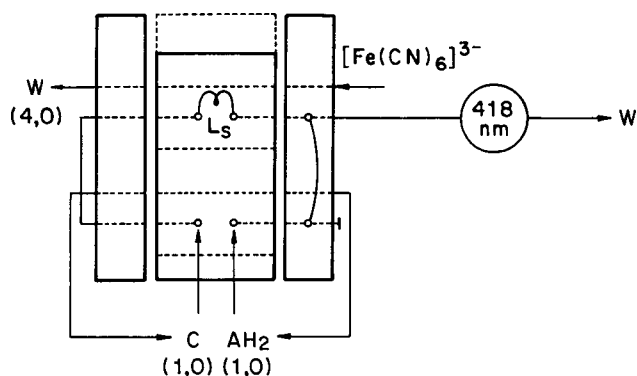


Figure 1. Flow diagram for evaluation of the ionic strength effect on the rate of redox reaction. The position depicted represents the injection state. Dashed lines represent the position of the sliding bar after commutation. The numbers between parentheses indicate the flow rate (mL min^{-1}). W indicates waste and L_s is the sample loop.

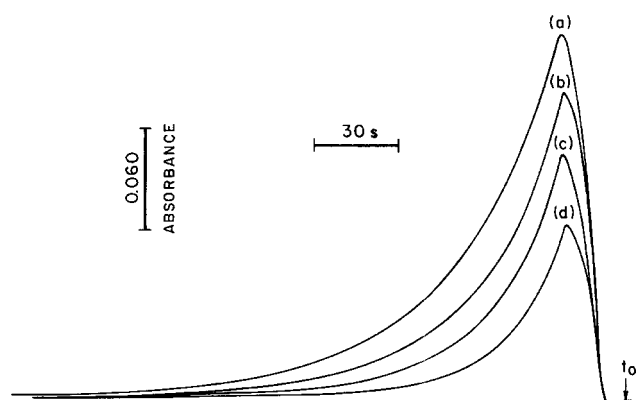


Figure 2. Variation of absorbance signals with time at various ionic strengths: (a) 2.0×10^{-2} , (b) 5.0×10^{-2} , (c) 1.0×10^{-1} , and (d) 2.0×10^{-1} M; t_0 indicates injection time.

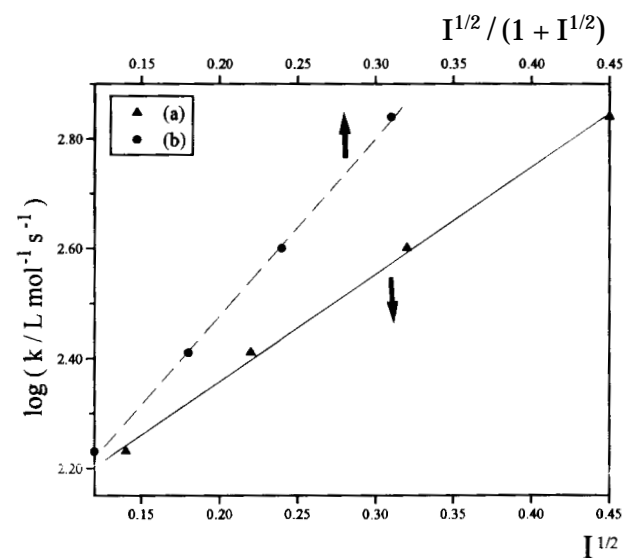


Figure 3. Effect of ionic strength on rate of reaction: (a) limiting law of Debye-Hückel, and (b) extended law of Debye-Hückel.

Table 1. Experimental Data at Various Ionic Strengths^a

I (M)	A_o	$t_{1/2}$ (s)	k ($\text{M}^{-1} \text{s}^{-1}$)
2.0×10^{-2}	0.216	25.2	1.72×10^2
5.0×10^{-2}	0.182	20.4	2.58×10^2
1.0×10^{-1}	0.142	16.8	3.97×10^2
2.0×10^{-1}	0.102	13.2	6.89×10^2

^a I , ionic strength; A_o , maximum absorbance signal; $t_{1/2}$, half-time; k , rate constant. Measurements were made at 25°C .

sodium nitrate carrier (C), and the ascorbic acid (AH_2) is introduced by confluence immediately after the injection point. To decrease the residence time, the system is designed without a reactor before the flow cell. Solutions introduced by the sample loop (L_s , 50 cm) reach the flow cell by confluence 6 s after commutation. Measurements are made at 418 nm at room temperature. When the absorbance signal attains its maximum value, the injector is again commuted to stop the sample zone in the flow cell. The carrier and ascorbic acid recycle while the sample loop is filled. During this step, the signal is registered, indicating the occurrence of the redox reaction during the measurement time. After each experiment, all solutions can be changed to obtain data in another ionic strength. Substituting all solutions by a hexacyanoferrate(III) solution of known concentration, the absorbance signal obtained can be used to calculate the amount of reagents at peak maximum, since Beer's law is obeyed.

Results and Discussion

The decrease in absorbance with time for solutions with different ionic strengths is shown in Figure 2. The half-time for each condition was graphically determined considering the time after the peak in which the absorbance signal is 50% of the maximum. Table 1 shows the half-time and maximum absorbance in all experimental conditions evaluated.

For each ionic strength, the rate constant can be estimated employing the half-time and the concentration at maximum absorbance. However, eq 1 can be used only when the initial concentrations of reactants are similar (I^0). This condition is attained with the experimental conditions proposed because the residence time is very short and the dispersion of the injected hexacyanoferrate(III) is limited. Additionally, the concentration of each reactant in the bottles and the flow rates are equal. From the data in Table 1 it can be observed that higher rate constants are attained at higher ionic strengths. This can be related to alterations of ionic atmosphere and changes in the charge densities around anions involved in the rate-determining step. The formation of a single highly charged ionic complex from two less highly charged ions is favored by a high ionic strength because the new ion has a denser ionic atmosphere (17).

Using rate constant data at different ionic strengths, a graph was obtained employing the Brønsted-Bjerrum equation, based on the limiting law of Debye-Hückel (Fig. 3a). The rate constant at infinite dilution (k_o) is $89.1 \text{ M}^{-1} \text{ s}^{-1}$ and the product of charges $Z_A Z_B$ is 2.0. Considering the extended law of Debye-Hückel (Fig. 3b), k_o is $75.8 \text{ M}^{-1} \text{ s}^{-1}$ and $Z_A Z_B$ is 3.2. This value is close to the expected value of 3.0 considering the proposed mechanism, which involves a collision between a monovalent and a trivalent anion in the rate-de-

termining step. The value determined using the limiting law is not so accurate because this law is valid only for diluted solutions with ionic strengths lower than 10^{-2} M.

The rate constants at infinite dilution experimentally determined by the flow injection experiment are higher than those measured by Watkins and Olson (13) because they conducted their experiments in 10^{-2} M nitric acid medium.

Conclusions

The result obtained for Z_{AZ_B} by using flow experiments is an indication that approximations made are acceptable and flow systems can be used to obtain correct kinetic data. The experimental determination of Z_{AZ_B} is relevant to indicate if a proposed mechanism is valid. This experiment can be useful to demonstrate for students that flow systems should not only be seen as an instrumental tool to obtain analytical data, but also as a powerful process for management of solutions and to obtain physical chemistry data.

Acknowledgment

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