Chemistry International 8(4) (2022) 136-143

International Scientific Organization
http://iscientific.org/
Chemistry International
www.bosaljournals.com/chemint/

Kinetic study of factor affecting the reaction of cyanide and picrate ions in the presence of micellar catalyst

Abdo S. Albadani, Mohammed Hassan* and Fathi A. Obayed

Chemistry Department, Faculty of Science, Ibb University, Ibb, P. O. Box: 70270, Yemen
*Corresponding author's E. mail: m-hassan@ibbuinv.edu.ye

ARTICLE INFO

Article type:
Research article
Article history:
Received September 2022
Accepted October 2022
October 2022 Issue
Keywords:
Picrate and cyanide ion
Activation energy
Micellar effect

ABSTRACT

In the present investigation, various factors (KOH concentration, resorcinol, temperature and reaction time) that affect the rate of the reaction between cyanide and picrate ions in the alkaline medium were evaluated in the presence of micellar catalyst. The reaction was found to be of zero-order with respect to cyanide ion and first order with respect to picrate ion which confirmed that the mechanism of the reaction is of SN1 type. The reaction was found to be thermally activated with relatively high activation energy. Addition of surfactant, TX-100, to the reaction mixture was found to enhance rate of the reaction as far as its concentration remains below its CMC, the behavior was modeled successfully using Berezin's Model.

Capsule Summary: The effect of KOH concentration, resorcinol, temperature and reaction time in the presence micellar catalyst was studied on the reaction between cyanide and picrate ions in the alkaline medium. The reaction was zero-order and first order with respect to cyanide and picrate ions, respectively.

Cite This Article As: A. S. Albadani, M. Hassan and F. A. Obayed. Kinetic study of factor affecting the reaction of cyanide and picrate ions in the presence of micellar catalyst. Chemistry International 8(4) (2022) 136-143.
https://doi.org/10.5281/zenodo.7192379

INTRODUCTION

Cyanide is a fast acting; potentially deadly chemical that can exist as both a gas and as a crystalline salt. Both forms can be lethal in high enough concentrations. Cyanide compounds occur naturally as part of sugars or other naturally occurring compounds in certain plant-derived foods, including almonds, millet sprouts, lima beans, soy, spinach, bamboo shoots, sorghum, and cassava roots (Newhouse and Chiu, 2010). Cyanide is also found in air and water with concentrations reached 190 ng/m^3 in the former and 160 ug/L in the latter (Tucker et al., 2008).

Cyanides in environmental media are normally collected in sodium or potassium hydroxide and measured by spectrometry (Haque and Bradbury, 2003; Drochioiu et al., 2011; Cacace et al., 2007), ion chromatography (Koch, 1983), potentiometry (Yari and Sepahvand, 2011), voltammetry (LaFuente et al., 2000; Anh and Sharp, 2000) and flow injection (Shondorf and Engelhardt, 1989). Surveying literature revealed that spectrometric methods are the mostly used for the determination of cyanide in environmental samples and particularly those which depends on the reaction of cyanide with picric acid. In major works that adopted this method, the Beer-Lambert law was found to be obeyed in the range 0.1-5 ppm. Several attempts have been made to improve this method as to increase its precision or its range of detection. In some cases, this method is adopted with addition of resorcinol that results in shifting the maximum wavelength (λ_{max}) toward higher values (Drochioiu et al., 2008) or by employing varied conditions of concentrations of reactants, temperature and other additives

(Migue et al., 2000; Drochioiu et al., 2003). Although the stoichiometry of the reaction and the colored complex have been identified, no attempt was made to study the detailed kinetics of the reaction as to clarify the dependence relationship between the various conditions that control the rate of the reaction and thereby enabling manipulation of these conditions to suggest the optimal ones that can be used in the analysis of cyanide ion. This was the motivation behind this work that was devoted to study kinetics of the reaction between picrate and cyanide ion and investigate the influence of various variables affecting the rate of the reaction.

MATERIAL AND METHODS

Chemical and reagents

Picric acid with purity of 98% was brought from Aldrich, UK, resorcinol (>99%) was from Merck, Germany, potassium cyanide with Analar Grade purity was from BDH, UK, potassium hydroxide with Analar grade was from Fisher, UK and sodium carbonate of 99.5% purity was from HiMedia, India. Stoke solutions of (0.002 mol/L) picric acid, (0.002 mol/L) resorcinol was prepared in doubly distilled water. A stoke solution of potassium cyanide (0.0002 mol/L) was prepared by dissolving the appropriate amount of the salt in 0.01 mol/L of potassium hydroxide, and a fresh solution was always being used through a one-day experiments.

Kinetics study

The kinetic measurements were performed using pseudo-order method. The concentration of picric acid was kept as 10fold over that of cyanide ion. The principal experiment was carried out in 0.01M KOH. The ionic strength of the reaction mixture was fixed by the presence of 0.1 mol/L of sodium carbonate. The absorbance of the mixture at 550 nm then followed at constant temperature at subsequent time intervals. The order of the reaction with respect to other reactants was estimated by carrying out several experimental runs in which the concentration of one reactant fixed and varying the concentrations of the others. The activation parameters of the reaction were evaluated by carrying out several experimental runs at different temperatures while fixing other conditions. Micellar catalysis was also tested in separate runs in which a specific concentration of non-ionic surfactant TX-100 was added to the reaction mixture. Each experimental run was always repeated three times and the mean of absorbance values was used in the plots and calculations that followed.

RESULTS AND DISCUSSION

Effect of reaction time

The relationship between the absorbance of the colored complex and time was investigated to obtain the integrated rate law that fit the data. The plots of absorbance of the reaction mixture against time are shown in Figure 1 at different initial concentration of cyanide ion and fixed concentrations of other components. These plots appear to be linear with intercepts close to zero, indicating that the order of reaction with respect to cyanide ion is zero. The pseudo- zero order rate constants were calculated by fitting the data to straight lines using regression method, the slopes of the lines equal the pseudo-zero order rate constants. These constants at various concentration of cyanide ion are presented in Table 1. These values show unexpected increase with raising the concentration of cyanide ion, and this can be explained either by the deviation from pseudo-order conditions or presence of another interfering path of the reaction. The latter, is related to mechanism of the reaction and the nature of the solvent used and the effect of which can be studied in the future study.

Order of the reaction with respect to picric acid

Figure 2 shows the plots of absorbance and time at various concentrations of picric acid and fixed concentrations of other components. When k_{obs} values, that were calculated from fitting the plots to straight lines (Table 1), were plotted versus the concentration of picric acid (Figure 3), they showed points that tend toward linearity with intercept close to zero, indicating that the reaction is of first-order with respect to picrate ion.

Effect of KOH concentration

The purpose of presence of KOH in the solution of cyanide ion is to prevent the formation of hydrogen cyanide (HCN) gas that may evolve out from the solution and eventually alter the concentration of cyanide ion. The presence of KOH, however, alters the properties of the reaction medium and finally affects the reaction rate. The values of k_{obs} of the reaction that were calculated from the plots of absorbance and time at various concentrations of KOH and fixing other conditions are presented in Table 1. Plotting these values against the concentration of KOH did not produce straight line that indicates that the order of the reaction with respect to KOH is not first order. However, when the reciprocals of k_{obs} were plotted against the corresponding reciprocals of concentrations (Figure 4), they gave a straight line (r = 0.818), with positive intercept which indicates that the rate dependence on the concentration of KOH is of the type ($a+b$) [KOH] (Babatunde et al., 2008).

Effect of resorcinol

It was reported by Drochioiu et al. (2008) that the presence of resorcinol in reaction mixture of picrate and cyanide ion could enhance the absorbance of the product and shift λ_{max} toward higher wavelength. Moreover, it has been suggested that the resorcinol participate in the reaction to form a newly product that is responsible for this absorbance. To investigate the role of resorcinol further, dependence of the observed rate constant has been investigated at various concentrations of resorcinol with other conditions kept fixed. Figure 5 shows the nature of this relation where the k_{obs} values were plotted against the concentration of resorcinol. The observed rate constant decreases slightly with raising the concentration of resorcinol which contradicts the results and suggests that resorcinol does not lead to the formation to a species distinguished from that produced in absence of resorcinol and the role of resorcinol is limited to act as a solvent.

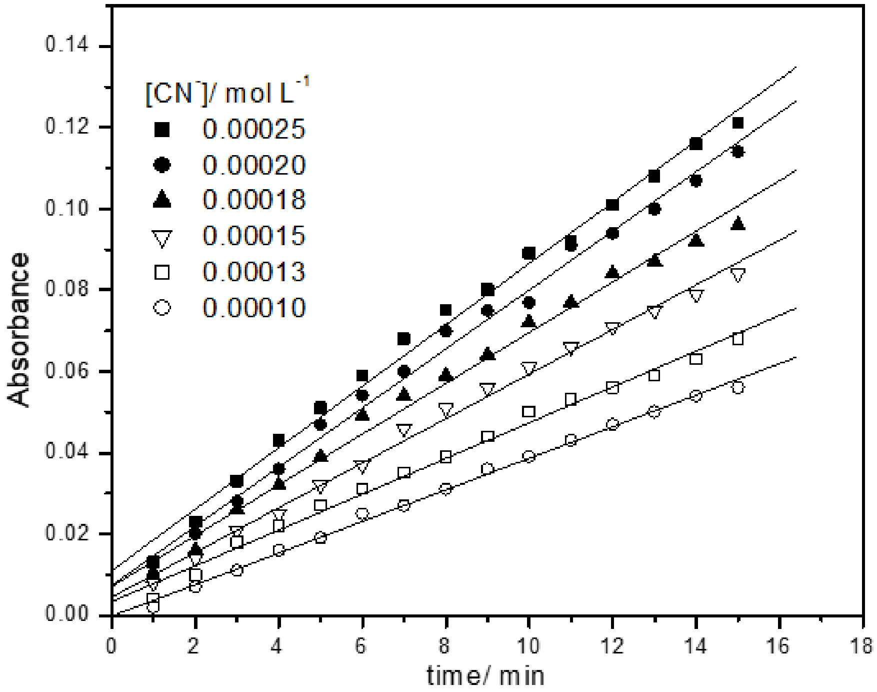


Fig. 1: Absorbance of the reaction mixture vs. time at 540 nm, varied cyanide ion concentration and fixing other concentrations at 297K

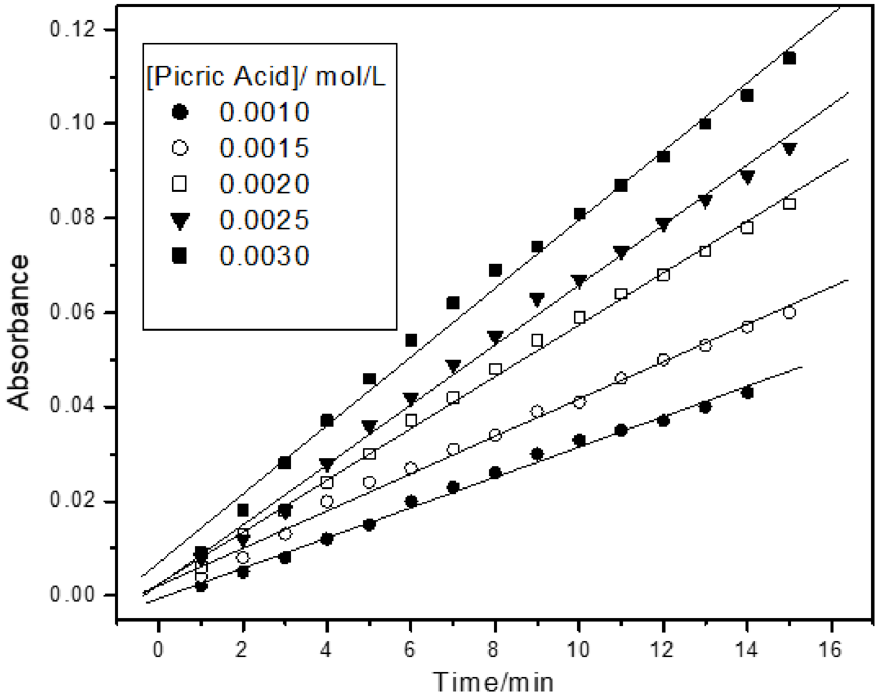


Fig. 2. Absorbance of the reaction mixture vs. time at 540 nm, varying picrate ion concentration and fixing other concentrations at 297K.

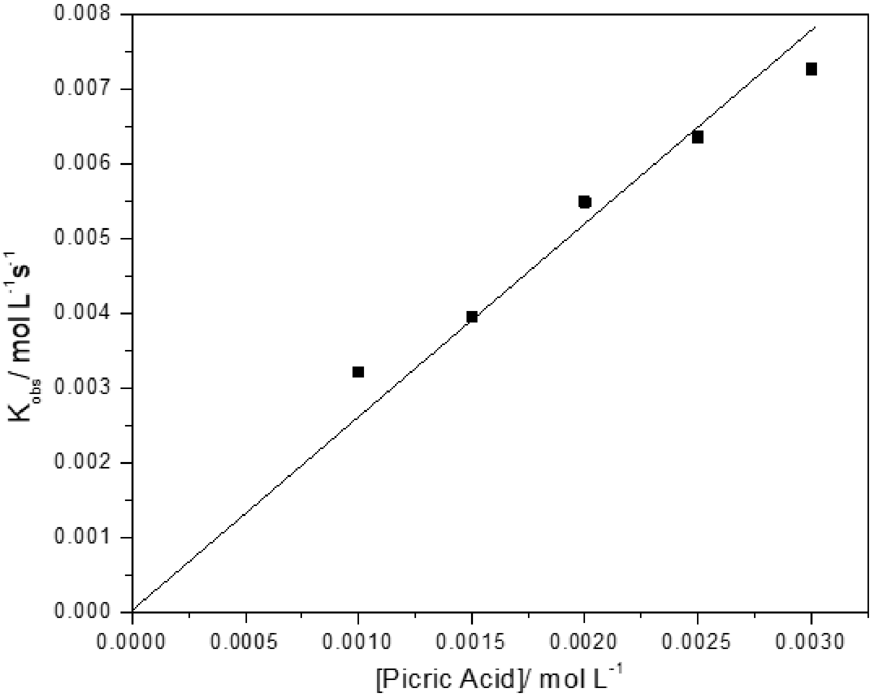


Fig. 3: Observed rate constant vs. concentration of picric acid at 297K and fixing other concentrations

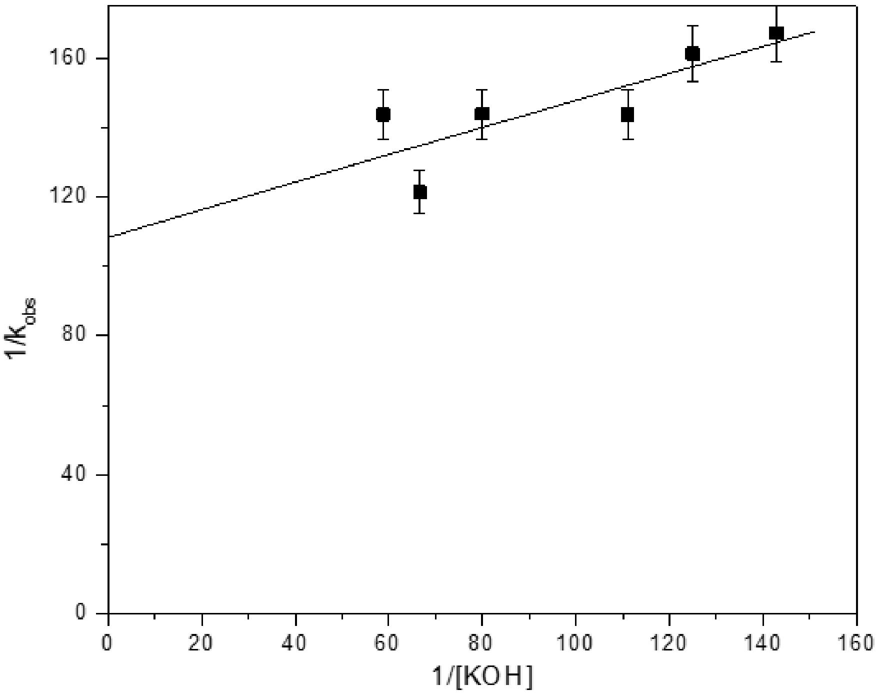


Fig. 4. Reciprocals of observed rate constants vs. KOH concentration at 297K and fixing other conditions

Effect of temperature

The k_{obs} values of the reaction at various several temperatures over the range 296K to 348K, and fixing other conditions are shown in Table 1. These values show that the rate of reaction is relatively sensitive to temperature, and the rate constant almost triplicates when the temperature was increased by 10K.

The quantitative relationship between the observed rate constant and the temperature of the reaction was investigated by applying Arrhenius equation. Figure 6 represents this relation in which the natural logarithm of

k_{obs} values were plotted versus the inverse of reaction temperatures and shows that points of the plot occurred in a linear mode with (r > 0.999). The activation energy of the reaction was evaluated from the slope of straight line and found to be -62.883 kJmol^{-1}. Other activation parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ at 296K were also calculated and found to be 60.310, -82.312 and 24.425 kJmol^{-1}. The activation energy is relatively high that reflects that the reaction is sensitive to temperature. The value of activation enthalpy is fairly high, which indicates that the transition complex is highly solvated (Manhas et al., 2007). The negative value of activation entropy indicates that the transition state complex is more compact than either of those of the two reactants (Tripathi and Upadhyay, 2014).

Micellar catalysis

The k_{obs} values of the reaction in the presence of different concentrations of non-ionic surfactant, Triton X-100 (TX-100), were calculated from the slopes of the plots of the

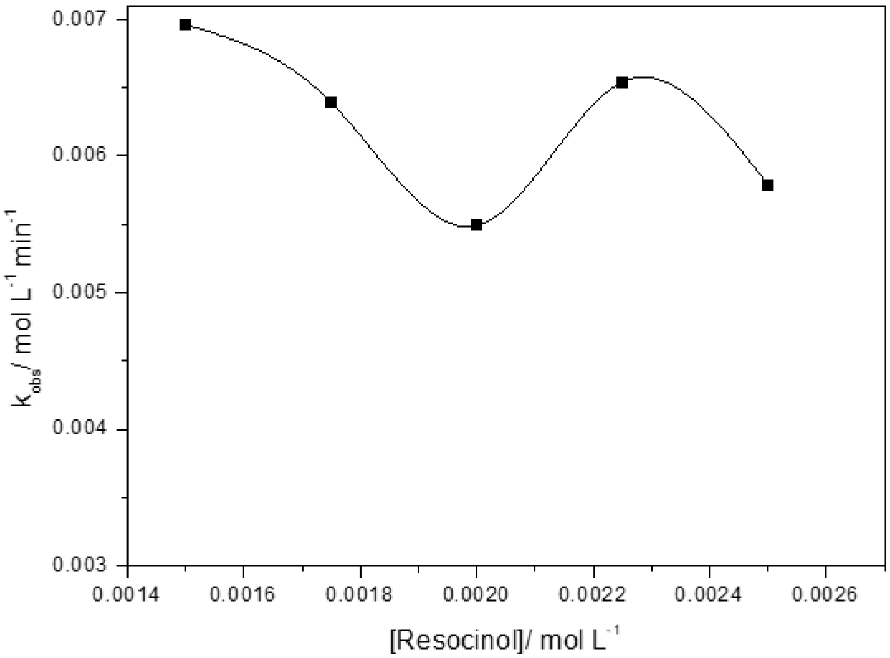


Fig. 5: Observed rate constant vs. resorcinol concentration at 297K and fixing other conditions.

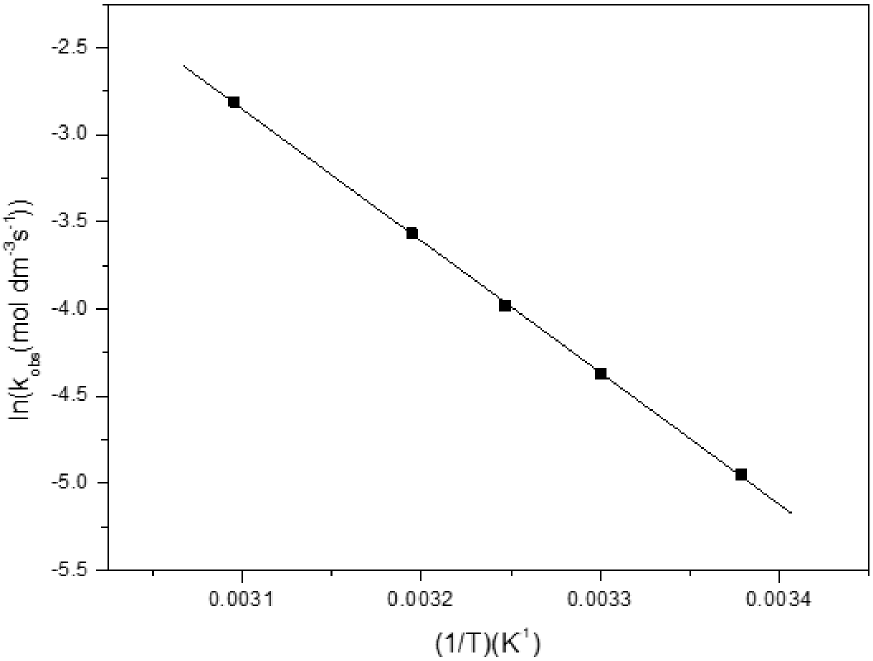


Fig. 6. logarithm of observed rate constant vs. reciprocal of temperature and fixing other conditions.

absorbance against time at constant temperature and initial concentrations of other components in the reactions mixture and tabulated in Table 1. When these values were plotted versus the concentration of TX-100 in (Figure 7), they showed gradual increase with raising the concentration of TX-100, reached a maximum at concentration of TX-100 close to its measured CMC (0.00023 mol/L), after which started to diminish with continue raising the concentration of surfactant.

Several models were proposed to interpret the catalytic effect of surfactants, widely known as micellar catalysis, such as Menger and Portnoy's model, Sepulveda model, Berezin model and Piszkiewicz Co-operativity model (Upadhyay, 2006). The most applicable model for the data of this work is Berezin model. The model assumes that the observed rate constant k_{obs} for the reaction under investigation may be made of two parts, i.e., k_w and k_m, which are due to partition of reactants in the aqueous

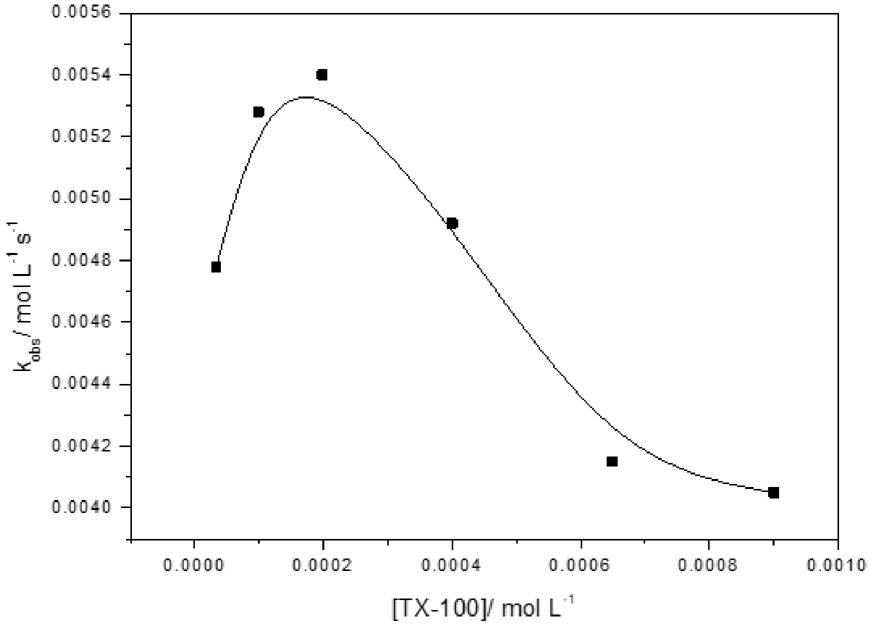


Fig. 7: Observed rate constant vs. concentration of TX-100 at 297K and fixing other conditions.

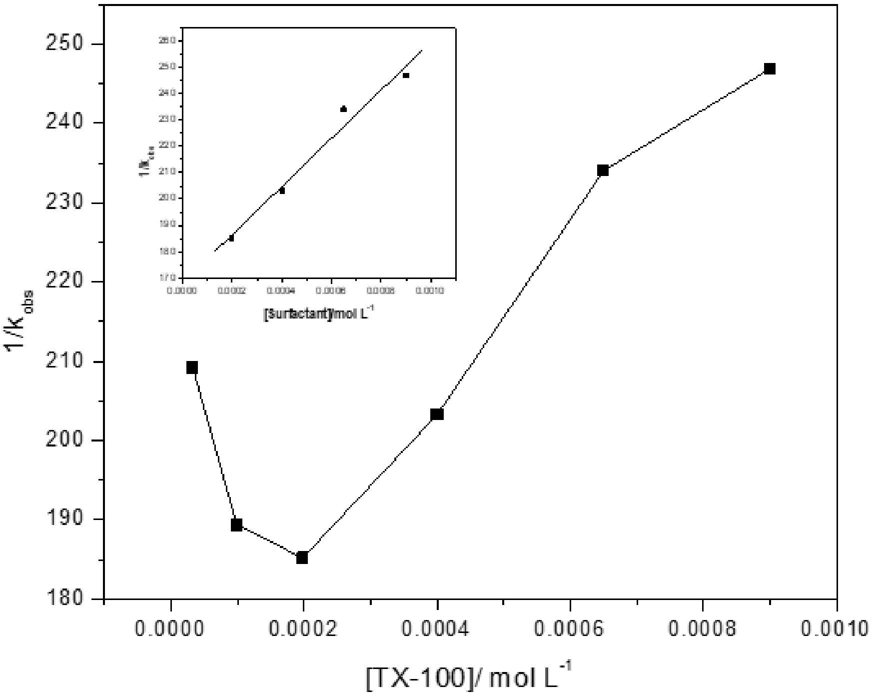
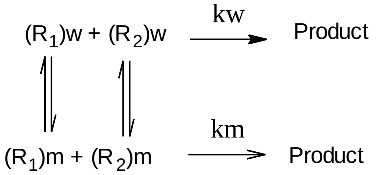


Fig. 8. Reciprocal of observed rate constant vs. TX-100 concentration at 297K and fixing other conditions.

phase and micellar pseudo-phase, respectively are as follows;



The apparent rate constant is given by the Eq. 1.

$$k_{obs} = \frac{k_w + k_m k_S k_R C}{(1+k_S C)(1+k_R C)} \qquad (1)$$

Where, K_S and K_R are the binding constants for the substrate and the reactant, respectively and C the concentration of surfactant. Assuming $k_w << k_m K_S K_R C$, k_w can be neglected compared to the second term in the numerator of the equation and on rearranging, we get Eq. 2.

$$\frac{1}{k_{obs}} = \frac{1}{k_m k_S k_R C} + \frac{k_S + k_R}{k_m k_S k_R} + \frac{C}{k_m} \qquad (2)$$

According to this equation, the plot of $1/k_{obs}$ as a function of C would show a minimum and the plot beyond C_{min} would be linear with a positive slope and positive intercept. However, at the optimum surfactant concentration corresponding to the maximum in the plot of k_{obs} against concentration of surfactant, the following relationship is obtained (Eq. 3).

$$C_{opt} = (K_S K_R)^{-1/2} \qquad (3)$$

Hence, the value of k_m could be obtained from the slope of the linear plot and those of K_S and K_R from the ratio of slope and intercept ($\frac{k_S k_R}{k_S + k_R}$) and the value of C_{opt} (Panigrahi and Mishra, 1993).

Table 1: Observed rate constants at 297K and various concentrations of picric acid, KCN, KOH, resorcinol and TX-100.

[Picric acid] (mol/L)	[KCN] (mol/L)	10^3[KOH] (mol/L)	[Resorcinol] (mol/L)	10^3[TX-100] (mol/L)	k_{obs} x10^{-4} (min^{-1})
0.0010	0.00020	0.0100	0.0010	0	0.0032
0.0015	0.00020	0.0100	0.0010	0	0.0040
0.0020	0.00020	0.0100	0.0010	0	0.0055
0.0025	0.00020	0.0100	0.0010	0	0.0064
0.0020	0.00020	0.0100	0.0010	0	0.0073
0.0020	0.00010	0.0100	0.0010	0	0.00389
0.0020	0.00013	0.0100	0.0010	0	0.0044
0.0020	0.00015	0.0100	0.0010	0	0.00549
0.0020	0.00018	0.0100	0.0010	0	0.00624
0.0020	0.00020	0.0100	0.0010	0	0.00727
0.0020	0.00025	0.0100	0.0010	0	0.00756
0.0020	0.00020	0.0070	0.0010	0	0.00598
0.0020	0.00020	0.0080	0.0010	0	0.0062
0.0020	0.00020	0.0090	0.0010	0	0.00696
0.0020	0.00020	0.0100	0.0010	0	0.00549
0.0020	0.00020	0.0125	0.0010	0	0.00695
0.0020	0.00020	0.0125	0.0010	0	0.00478
0.0020	0.00020	0.0125	0.0010	0	0.00528
0.0020	0.00020	0.0125	0.0010	0	0.0054
0.0020	0.00020	0.0125	0.0010	0	0.00492
0.0020	0.00020	0.0125	0.0010	0	0.00415
0.0020	0.00020	0.0125	0.0010	0	0.00405
0.0020	0.00020	0.010	0.0010	0.0015	0.00696
0.0020	0.00020	0.010	0.0010	0.00175	0.00639
0.0020	0.00020	0.010	0.0010	0.00200	0.00549
0.0020	0.00020	0.010	0.0010	0.00225	0.00654

Plot of $1/k_{obs}$ versus concentration of TX-100 for the current reaction at the specified experimental conditions, is shown in Figure 8 and its inset. As expected by the model, the curve goes to minimum and the points beyond C_{min} was fitted successfully to straight line (r= 0.987), with slope of 91475.983 and intercept of 168.220. The calculated values of k_m, K_S and K_R were found to be 1.09 x 10^5 mol $L^{-1}s$-1 5.35 × 10^2 mol^{-1} L and 3.48 × 10^4 mol^{-1} L, respectively.

CONCLUSIONS

The results of the work confirmed that the reaction between cyanide and picrate ions is of nucleophilic substitution type and the major product results via SN1 mechanism, where only picrate ion participates in the slow step of the reaction. Hence, the concentration of picrate ion could be one the factors that can be adjusted to enhance the absorbance of the coloured product and raising the sensitivity and detection limit when the reaction is used for quantitative analysis of cyanide ion. Moreover, the reaction was found to be thermally activated indicating that raising the temperature and time of heating can also enhance the absorbance of the coloured product.

REFERENCES

Alonso-Amelot, M.E., Oliveros, A., 2000. A method for the practical quantification and kinetic evaluation of cyanogenesis in plant material. application to Pteridium aquilinum and Passiflora capsularis, Phytochemical Analysis 11, 309–316.

Anh, N.B.H., Sharp, M., 2000. Determination of cyanide by cathodic stripping voltammetry at a rotating silver disk electrode. Analytica Chimica Acta 405, 145-152.

Babatunde, O.A., 2008. A study of the kinetics and mechanism of oxidation of L-ascorbic acid by permanganate ion in acidic medium, World Journal of Chemistry 3, 27-31.

Cacace, D., Ashbaugh, H., Kouri, N., Bledsoe, S., Lancaster, S., Chalk, S., 2007. Spectrophotometric determination of aqueous cyanide using a revised phenolphthalin method, Analytica Chimica Acta 589, 137–141.

Drochioiu, G., Arsene, C., Murariu, M., Oniscu, C., 2008. Analysis of cyanogens with resorcinol and picrate, Food and Chemical Toxicology 46, 3540–3545.

Drochioiu, G., Arsene, C., Murariu, M., Oniscu, C.,2008. Analysis of cyanogens with resorcinol and picrate, Food and Chemical Toxicology 46, 3540–3545.

Drochioiu, G., Oniscu, C., Sunel, V., Popa, K., Cucia, C., Cozma, D., 2003. Cyanide assay based on its novel reaction with resorcinol and picric acid, The European Journal of Mineral Processing and Environmental Protection 3, 291-296.

Drochioiu, G., Sandu, I., Gradinaru, R., Zbancioc, G., Mangalagiu, I., 2011. Ninhydrin-based forensic investigations: II. Cyanide Analytical Toxicology, International Journal of Criminal Investigation 1, 213-226.

González LaFuente, J.M., Fernández Martínez, E., Vicente Pérez, J.A., Fernández Fernández, S., Miranda Ordieres, A.J., Sánchez Uría, J.E., Fernández Sánchez, M.L., Sanz-Medel, A., 2000. Differential-pulse voltammetric determination of low μgl^{-1} cyanide levels using EDTA, Cu(II) and a hanging mercury drop electrode. Analytica Chimica Acta 410, 135-142.

Haque, M.R., Bradbury, J.H., 2002. Total cyanide determination of plants and foods using the picrate and acid hydrolysis methods, Food Chemistry 77, 107–114.

Koch, W.F., 1983. The determination of trace levels of cyanide by ion chromatography with electrochemical detection, Journal of Research of the National Bureau of Standards 88, 157-161.

Manhas, M.S., Mohammed, F., Khan, Z., 2007. A kinetic study of oxidation of β-cyclodextrin by permanganate in aqueous media, Colloids and Surfaces A 295, 165–171.

Newhouse, K., Chiu, N., 2010. Toxicological review of hydrogen cyanide and cyanide salts. US Environmental Protection Agency: Washington, DC, USA, 153.

Panigrahi, G.P., Mishra, S.K., 1993. Micellar catalysis: effect of lauryl sulphate in the oxidation of lactic acid by chromic acid, Journal of Molecular Catalysis 81, 349-362.

Shondorf, G., Engelhardt, H., 1989. determination of cyanide in waste water by flow injection analysis, Fresenius Z Anal Chem 333, 718-719.

Tripathi, R., Upadhyay, S.K., 2014. Inhibitory Effect of {Surfactant- MnO^{-4}} Aggregation in $KMnO_4$ Oxidation of Proline and Methionine: A Kinetic Study, Journal of the Korean Chemical Society 58, 351-358.

Tucker, P., Curry, V., Doyle, J., Fowler, B., Gehle, K., Hall, S., Hatcher, M., Jenkins, K., Jolly, R., Roberts, D., 2008. Agency for Toxic Substances and Disease Registry Case Studies in Environmental Medicine (CSEM) Cadmium Toxicity. US Department of Health Human Services Agency for Toxic Substances, Disease Registry Division of Toxicology, Environmental Medicine, Educational Services Branch, Atlanta, 10-18.

Upadhyay, S.K., Chemical Kinetics and Reaction Dynamics, Springer, New Yor, NY, 2006, pp 161-165.

Yari, A., Sepahvand, R., 2011. Highly sensitive carbon paste electrode with silver-filled carbon nanotubes as a sensing element for determination of free cyanide ion in aqueous solutions, Microchim Acta 174, 321–327.