

Kinetics and Mechanism of Oxidation of Indigo Carmine with Potassium Bromate: Effect of CTAB and SDS Micelles

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Abstract

The oxidation of indigo carmine with potassium bromate both in absence and presence of SDS, CTAB micelles is investigated. The kinetic runs were carried out in mercuric acetate which scavenges the bromate-bromide reaction. The pseudo first order rate constants are under the condition $[IC] < [BrO_3^-]$. The reaction shows first order kinetics with indigo carmine, H⁺ ion and Bromate ion. The reaction rate is increased with increase in the [SDS] and [CTAB]. The effect of micelles on reaction rate is explained by Berezin treatment and the binding constant of reacting substances with micelles is determined.

Keywords: Potassium bromate; Indigo carmine (IC); Sodium dodecyl sulphate (SDS); Cetyl trimethyl ammonium bromide (CTAB)

Introduction

Textile industries are one of the chief sources for release of waste water containing unused dyes. On the basis of functional group and structure, dyes were classified as anionic, neutral and cationic [1]. Indigo carmine with chemical name 5, 5¹ indigo disulphonic acid sodium salt is an oldest anionic dye which belongs to the class of indigoids which are extensively used in dyeing cotton clothes (blue jeans). The primary component of the dye is indigotin synthesized from the extract of *indigofera tinctoria* [2]. In aqueous solutions, the dye possess intense blue colour which is because of cross conjugation or H-chromophore attached at double bond [3]. In the structure of this dye, there are two NH donor and two CO acceptor groups attached to the double bonded carbon atoms [4]. The dye shows its role as an indicator in quantitative analysis [5,6] and in drug synthesis [7]. The dye has appreciable toxicity and show adverse effects when comes in contact with eyes, skin and also effects reproductive, developmental and neuronal systems [8]. Certain methods were in force in decolorization of this dye like adsorption [9], Nano degradation using TiO₂ as catalyst [10], photo catalytic methods using visible and UV light [11], advanced oxidation processes [12-16] and chemical oxidation [17,18]. Jonnalgadda et al. [19] investigated the oxidation of indigo carmine with bromate in

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aqueous sulphuric acid at high concentration and reported a competitive mechanism. The present authors carried out the kinetic study in low [acid] in presence of CTAB and SDS micelles.

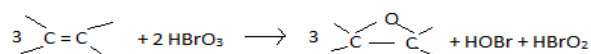
Experimental

Preparation of solutions

The solutions of indigo carmine, potassium bromate, sulphuric acid and sodium sulphate were prepared from the samples procured from E-Merck-India Pvt. Ltd., Mumbai, of AR grade quality. SDS (AG, Fluka) and CTAB (Sigma Aldrich) is prepared as per the literature and the cmc is determined [20,21]. The solutions are standardized as per the procedure available in the literature.

Stoichiometry

The stoichiometry of the reaction is determined by mole ratio method. The reaction between IC and Bromate is carried out by fixing the [IC] and varying the $[\text{BrO}_3^{1-}]$ in the range of $(1.0 \text{ to } 9.0) \times 10^{-5} \text{ moldm}^{-3}$ in aqueous sulphuric acid and in presence of mercuric acetate. The reaction stoichiometry is determined from the plot of absorbance vs. mole ratio which is found to be 3:2 (i.e., 3 moles of Indigo carmine reacts with 2 moles of Bromate ion). The stoichiometric equation is presented as:



Product analysis

Indigo carmine solution ($1.0 \times 10^{-5} \text{ moldm}^{-3}$) was mixed with an equivalent amount of bromate ($1.0 \times 10^{-5} \text{ moldm}^{-3}$) in 0.1 moldm^{-3} sulphuric acid and in presence of mercuric acetate. After the discharge of the blue colour, a yellow coloured solid was obtained as product. The product is identified as Isatin-5-monosulphonic acid by carrying out the spot test prescribed by Feigl [21]. The test consists in heating the product in a micro test tube with a drop of alcoholic solution of 4-NitroPhenyl Hydrazine for 5 minutes. After cooling the solution a drop of 10% sodium hydroxide and a drop of 1% magnesium nitrate were added. The formation of blue colour precipitate confirmed the product as Isatin-5-monosulphonic acid.

Kinetic procedure

The reaction was followed spectrophotometrically at known intervals of time using "Systronics 106 visible spectrophotometer". The course of the reaction was followed at a wavelength of 610 nm in presence of SDS micelles and at 570 nm in presence of CTAB micelles till the completion of 90% reaction [22]. All the kinetic runs were carried out in a temperature controlled water bath ($\pm 0.1^\circ\text{C}$). The kinetic runs were carried out under pseudo first order conditions $[\text{BrO}_3^{1-}] \gg [\text{IC}]$ in presence of mercuric acetate ($1.0 \times 10^{-3} \text{ moldm}^{-3}$) which scavenges bromide in the reaction. The pseudo first order rate constants are determined from the slopes of the linear plots drawn between $\log(\text{absorbance})$ vs. time. The kinetic runs were carried out in duplicate and rate constants found to agree within $\pm 5\%$.

Results and Discussion

The kinetic results are summarized as follows:

- 1) The reaction obeys first order kinetics with indigo carmine in presence of SDS and CTAB micelles. The rate data is presented in TABLE 1.

- 2) The reaction obeys first order kinetics with respect to $[H^+]$ ion in absence and presence of SDS micelles. This is evident from the linear plots of k_1 and $[H^+]$ ion passing through origin. (FIG. 1). In presence of CTAB micelles, the reaction rate is inhibited by $[H^+]$. (TABLE 2).
- 3) The reaction shows first order kinetics with respect to $[BrO_3^{1-}]$ ion both in absence and presence of SDS, CTAB micelles. Plots drawn between $[BrO_3^{1-}]$ and k_1 are linear passing through origin. (FIG. 2). The kinetic data is presented in TABLE 3.
- 4) The reaction rate is increased by 232 times with increase in the $[CTAB]$ and by 15 times with increase in the $[SDS]$ and limiting value is reached (FIG. 3).

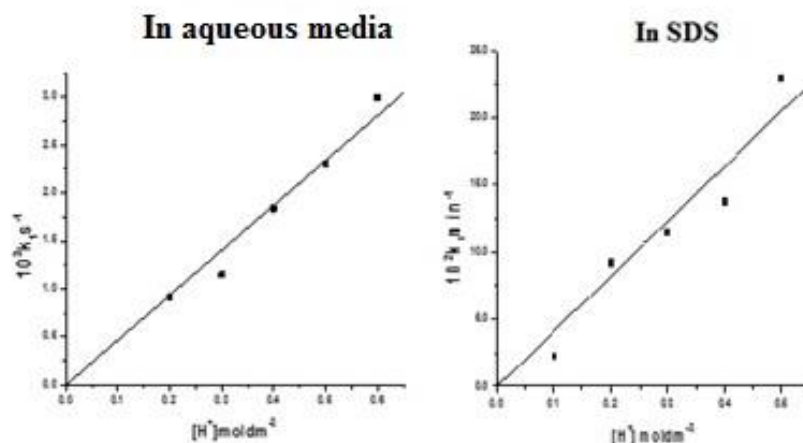


FIG. 1. Effect of varying H^+ ion concentration on rate.

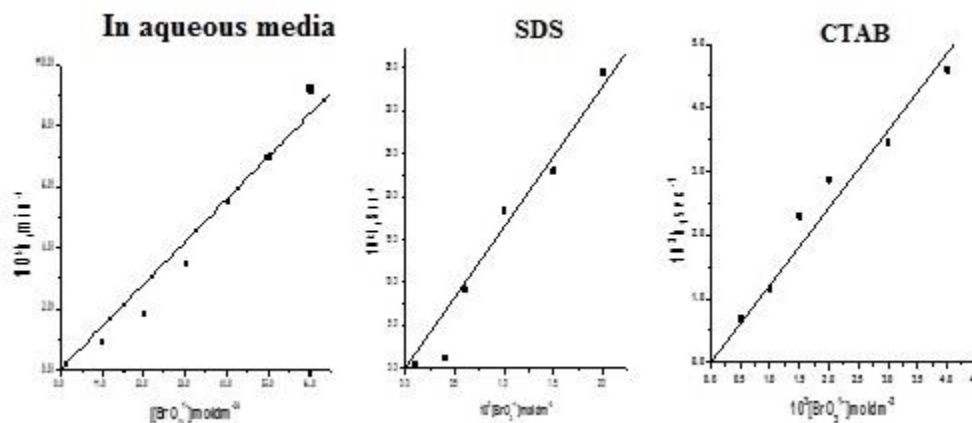


FIG. 2. Effect of varying bromate ion concentration on rate.

Jonnalagadda et al. [19] reported the oxidation of indigo carmine with bromate in aqueous sulphuric acid at high concentration in the range of (1.5 to 3.0) mol dm^{-3} . They reported consecutive – competitive mechanism and reported the rate expression assuming the active oxidizing species as HOBr.

$$-\frac{d[IC]}{dt} = k_1[H^+]^2[IC][BrO_3^{1-}]$$

The present authors employed a different approach in the kinetic study of this reaction. It is known that when the reaction is carried out in presence of mercuric acetate under the condition $[\text{Hg}(\text{CH}_3\text{COO})_2] \gg [\text{indigo carmine}]$ the mercuric ion Hg^{+2} forms a complex with Br^{-1} thus scavenging it and now only BrO_3^{-1} oxidise IC. Since $[\text{BrO}_3^{-1}] \gg [\text{IC}]$, the Br^{-1} concentration found in the reaction is equivalent to Indigo carmine and almost all the bromide will be bound by Hg^{+2} as a complex.

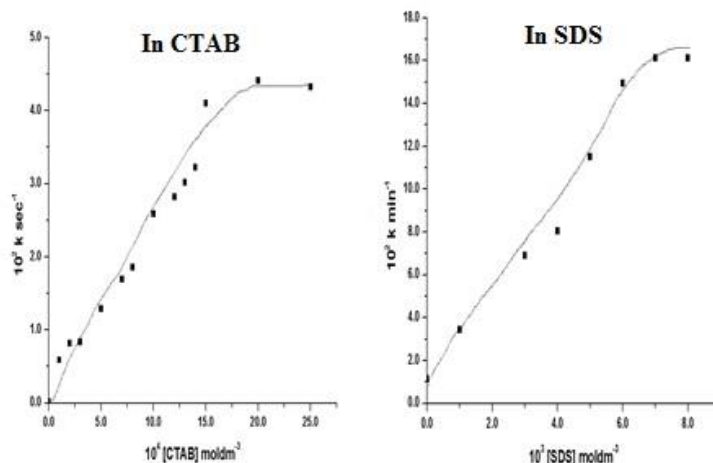


FIG. 3. Plot between k_1 vs. $[\text{CTAB}]$, $[\text{SDS}]$.

The present author found that in presence of no auto catalysis is present, presumably due to elimination of $\text{BrO}_3^{-1} - \text{Br}^{-1}$ reaction forming Br_2 . Plot of $\log(\text{absorbance})$ vs. time is a good straight line even up to 95% of the reaction with no sign of auto catalysis or auto inhibition showing clear first order kinetics with respect to Indigo carmine. The reaction obeys first order kinetics with respect to BrO_3^{-1} and H^+ ion. The second order path in H^+ ion is absent because the author employed much lower H^+ ion concentration than Jonnalagadda et al. [19]. The $[\text{H}^+]$ ion catalysis can be explained as due to the formation of more reactive species HBrO_3 by interaction with BrO_3^{-1} in a pre-equilibrium which interacts with indigo carmine in the subsequent rate determining step.



The protonated BrO_3^{-1} i.e, HBrO_3 is more effective oxidizing species than the negatively charged BrO_3^{-1} ion. The rate equation for the rate determining step (2) will be,

$$K = \frac{[\text{HBrO}_3]}{[\text{H}^+][\text{BrO}_3^{-1}]} \quad (3)$$

$$\text{Rate} = k [\text{HBrO}_3] [\text{IC}] \quad (4)$$

$$\text{Hence Rate} = kK[\text{H}^+][\text{IC}][\text{BrO}_3^{-1}] \quad (5)$$

The rate law explains the first order kinetics with respect to $[\text{H}^+]$, IC and BrO_3^{-1} .

Effect of CTAB

The author investigated the micellar effect of CTAB on oxidation of Indigo carmine by BrO_3^{1-} in aqueous sulphuric acid medium and in presence of excess mercuric acetate which scavenges Br^{1-} and eliminates the auto catalysis – complication. The author found that CTAB micelle exerts more catalytic effect than SDS. The reaction exhibits first order kinetics in BrO_3^{1-} and Indigo carmine and H^+ ion inhibited the reaction. The H^+ ion inhibition is due to BrO_3^{1-} is preferred by CTAB to HBrO_3 , the former being the active oxidizing species for the reaction in the CTAB micelles.

The positive CTAB micelles interact with both BrO_3^{1-} and indigo carmine which are bound by these micelles. The micellar catalysis did not conform to the bimolecular pattern of Berezin's where in the rate initially increases with increase in the [CTAB] for greater than critical micellar concentration (cmc) but shows limiting at higher value of [CTAB]. The author found that rate-[CTAB] profile has a plateau with no maximum. Therefore, the Berezin rate law will be:

$$k = \frac{k_w + \bar{k}_m K_A K_B C}{(1 + K_A C)(1 + K_B C)} \quad (6)$$

Where $C=[\text{CTAB}]$ -critical micellar concentration of CTAB ($9.2 \times 10^{-4} \text{ mol dm}^{-3}$)

K_A and K_B represents the binding constants of bromate ion and Indigo carmine respectively.

Since HBrO_3 is hydrophilic, it may not be strongly bound CTAB and $K_A C \cong 1$ (where A represents bromate ion) and can be neglected. The equation now reduces to,

$$k = \frac{k_w + \bar{k}_m K_A K_B C}{(1 + K_B C)} \quad (7)$$

This equation 7 explains the binding pattern of plot of k vs. C .

As the value of k_w in the above equation is found to very small in comparison with k , it can be neglected. The equation further reduces to,

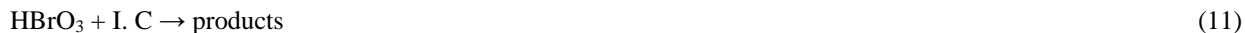
$$k = \frac{\bar{k}_m K_A K_B C}{1 + K_B C} \quad (8)$$

$$\frac{1}{k} = \frac{1}{\bar{k}_m K_A K_B C} + \frac{1}{\bar{k}_m K_A} \quad (9)$$

The author found that the plot of $1/k$ vs. $1/C$, where $C=[\text{CTAB}]$ -cmc, is linear with positive intercept (FIG. 4). From the value of slope and intercept obtained the value of K_B (binding constant of Indigo carmine with CTAB micelles) and \bar{k}_m have been determined and found to be $2307.0 \pm 115.35 \text{ dm}^3 \text{ mol}^{-1}$ and $6.66 \times 10^{-2} \text{ sec}^{-1}$.

Effect of SDS

In the presence of SDS micelles the reaction obeys first order kinetics with respect to bromate ion, H^+ ion and Indigo carmine and the hydrogen ion catalysis can be explained by assuming that HBrO_3 but not BrO_3^{1-} as the active oxidizing species in the presence of SDS involving the following rate-determining steps:



The Berezin equation can be written:

$$k = \frac{k_w + \bar{k}_m K_A K_B C}{(1 + K_A C)(1 + K_B C)} \quad (12)$$

Where K_A and K_B are binding constants of Bromate ion and Indigo carmine respectively,

The rate- [Surfactant] profile shows a limiting behaviour at higher SDS concentration. It is easy to explain this behaviour because $HBrO_3$ being hydrophilic will have a low value of binding constant (K_A) and $(1 + K_A C) \cong 1$.

Then the Berezin equation undergoes modification to,

$$k = \frac{k_w + \bar{k}_m K_A K_B C}{(1 + K_B C)} \quad (13)$$

Since the uncatalyzed component is small compared to micellar component, k_w can be neglected. Then the equation 16 reduces to,

$$\frac{1}{k} = \frac{1}{\bar{k}_m K_A K_B C} + \frac{1}{\bar{k}_m K_A} \quad (14)$$

The plot of $1/k$ vs. $1/C$ is linear with a positive intercept (FIG. 5) and from the slope and intercept of the plot, K_B (Binding constant of Indigo carmine with SDS) and $\bar{k}_m K_A$ has been found to be $78.2 \pm 3.91 \text{ dm}^3 \text{ mol}^{-1}$ and $4.86 \times 10^{-3} \text{ min}^{-1}$.

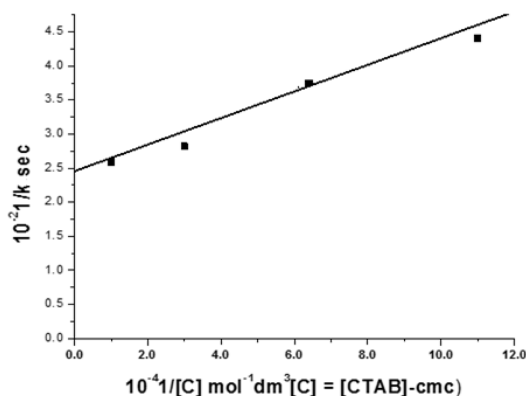


FIG. 4. CTAB effect (plot between $1/k$ vs. $1/[C]$).

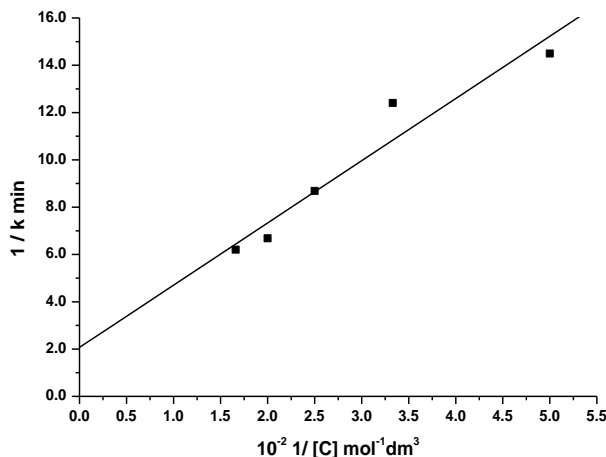


FIG. 5. SDS effect (plot between 1/k vs. 1/[C]).

TABLE 1. Effect of varying concentration of indigo carmine.

$[\text{BrO}_3^-]=1.0 \times 10^{-3} \text{ moldm}^{-3}$, $[\text{H}^+]=0.1 \text{ moldm}^{-3}$, $[\text{SDS}]=7.0 \times 10^{-3} \text{ moldm}^{-3}$, $[\text{Hg}(\text{OAc})_2]=1.0 \times 10^{-3} \text{ moldm}^{-3}$,
 $[\text{BrO}_3^-]=1.0 \times 10^{-3} \text{ moldm}^{-3}$, $[\text{H}^+]=0.05 \text{ moldm}^{-3}$, $[\text{CTAB}]=5.0 \times 10^{-4} \text{ moldm}^{-3}$, $[\text{Hg}(\text{OAc})_2]=1.0 \times 10^{-3} \text{ moldm}^{-3}$.

In SDS

$10^5[\text{IC}] \text{ moldm}^{-3}$	$10^3 k_1 \text{ sec}^{-1}$
0.5	1.15
1.0	1.15
1.5	1.15
2.0	1.15
3.0	1.15

In CTAB

$10^5[\text{IC}] \text{ moldm}^{-3}$	$10^3 k_1 \text{ sec}^{-1}$
1.65	1.34
2.48	1.35
3.30	1.27
4.13	1.26
4.96	1.22

TABLE 2. Effect of varying H^+ ion concentration.

In aqueous media $[\text{IC}]=2.0 \times 10^{-5} \text{ moldm}^{-3}$, $[\text{BrO}_3^-]=1.0 \times 10^{-2} \text{ moldm}^{-3}$, $\mu=0.8 \text{ moldm}^{-3}$, $[\text{Hg}(\text{OAc})_2]=1.0 \times 10^{-3} \text{ moldm}^{-3}$,
In CTAB: $[\text{IC}]=1.0 \times 10^{-5} \text{ moldm}^{-3}$, $[\text{BrO}_3^-]=1.0 \times 10^{-2} \text{ moldm}^{-3}$, $[\text{Hg}^{+2}]=1.0 \times 10^{-3} \text{ moldm}^{-3}$, $[\text{CTAB}]=1.0 \times 10^{-3} \text{ moldm}^{-3}$,
 $\mu=0.8 \text{ moldm}^{-3}$,
In SDS: $[\text{IC}]=3.0 \times 10^{-5} \text{ moldm}^{-3}$, $[\text{Bromate}]=1.0 \times 10^{-2} \text{ moldm}^{-3}$, $[\text{SDS}]=7.0 \times 10^{-3} \text{ moldm}^{-3}$, $\mu=0.8 \text{ moldm}^{-3}$, $[\text{Hg}^{+2}]=1.0 \times 10^{-3} \text{ moldm}^{-3}$.

$[\text{H}^+] \text{ moldm}^{-3}$	$10^3 k_1 \text{ sec}^{-1}$ In aqueous media	$[\text{H}^+] \text{ moldm}^{-3}$	$10^2 k_1 \text{ sec}^{-1}$ In CTAB	$[\text{H}^+] \text{ moldm}^{-3}$	$10^2 k_1 \text{ min}^{-1}$ In SDS
0.2	0.92	0.3	4.03	0.1	2.30
0.3	1.15	0.4	3.45	0.2	9.21
0.4	1.84	0.5	2.76	0.3	11.5
0.5	2.30	0.7	2.30	0.4	13.8
0.6	3.0	0.8	1.84	0.5	23.0

TABLE 3. Effect of varying bromate ion concentration on rate.

In aqueous media: $[IC]=2.0 \times 10^{-5} \text{ moldm}^{-3}$, $[H^+]=0.2 \text{ moldm}^{-3}$, $\mu=0.8 \text{ moldm}^{-3}$, $[Hg(OAc)_2]=1.0 \times 10^{-3} \text{ moldm}^{-3}$

In CTAB: $[IC]=2.0 \times 10^{-5} \text{ moldm}^{-3}$, $[acid]=0.2 \text{ moldm}^{-3}$, $[CTAB]=1.0 \times 10^{-3} \text{ moldm}^{-3}$, $[Hg^{+2}]=1.0 \times 10^{-3} \text{ moldm}^{-3}$

In SDS: $[IC]=1.0 \times 10^{-5} \text{ moldm}^{-3}$, $[H^+]=0.1 \text{ moldm}^{-3}$, $[SDS]=5.0 \times 10^{-3} \text{ moldm}^{-3}$, $[Hg^{+2}]=1.0 \times 10^{-3} \text{ moldm}^{-3}$.

$[BrO_3^{1-}]10^2$ moldm^{-3}	$10^3 k_1 \text{ min}^{-1}$ In aqueous media	$[BrO_3^{1-}]10^3$ moldm^{-3}	$10^3 k_1 \text{ sec}^{-1}$ In CTAB	$[BrO_3^{1-}]10^2$ moldm^{-3}	$10^2 k_1 \text{ sec}^{-1}$ In SDS
1.0	0.92	0.5	0.69	0.1	0.46
2.0	1.84	1.0	1.15	0.4	1.15
3.0	3.45	1.5	2.30	0.6	9.21
4.0	5.5	2.0	2.87	1.0	18.4
5.0	7.0	3.0	3.45	1.5	23.03
6.0	9.2	4.0	4.60	2.0	34.5

TABLE 4. Micellar effects.

CTAB effect: $[IC]=4.0 \times 10^{-5} \text{ moldm}^{-3}$, $[KBrO_3]=1.0 \times 10^{-2} \text{ moldm}^{-3}$, $[H^+]=0.2 \text{ moldm}^{-3}$, $[Hg(OAc)_2]=1.0 \times 10^{-3} \text{ moldm}^{-3}$

SDS effect, $[IC]=3.0 \times 10^{-5} \text{ moldm}^{-3}$, $[BrO_3^-]=1.0 \times 10^{-2} \text{ moldm}^{-3}$, $[H^+]=0.2 \text{ moldm}^{-3}$, $[Hg^{+2}]=1.0 \times 10^{-3} \text{ moldm}^{-3}$.

$10^4 [CTAB]$ moldm^{-3}	$10^2 k \text{ sec}^{-1}$
0.0	0.019
1.0	0.59
2.0	0.82
3.0	0.83
5.0	1.29
7.0	1.69
8.0	1.86
10.0	2.59
12.0	2.82
15.0	4.10
20.0	4.41

$10^3 [SDS] \text{ moldm}^{-3}$	$10^2 k \text{ min}^{-1}$
0.0	1.15
1.0	3.45
3.0	6.90
4.0	8.06
5.0	11.51
6.0	14.96
7.0	16.12
8.0	16.12

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