

# Conductometric Studies Of Kinetics Of Ionic Reaction Between $\text{Ag}^+$ And $\text{Cl}^-$ In Aqueous Solution

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**Abstract:** In the present report, conductometric studies on the kinetic of formation of AgCl by ionic reaction between  $\text{Ag}^+$  and  $\text{Cl}^-$  in aqueous solution have been presented. The order of the mentioned reaction was determined by a new conductometric approach using half-life method. The obtained result showed that the reaction follows a second-order kinetics. The second-order rate constant of the reaction was obtained conductometrically using different initial concentrations of the reactants in the range of 2.5-5.0 mM. The average value of the rate constant was obtained as  $20.648 \text{ L mol}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ .

**Index Terms:** Ionic reaction; Conductometric method; Order of reaction; Rate constant of reaction

## 1 INTRODUCTION

The reaction of silver ( $\text{Ag}^+$ ) and chloride ( $\text{Cl}^-$ ) ions takes place in aqueous solution and produces neutral AgCl. AgCl has many practical importance. For example, AgCl is used in preparing Ag/AgCl/ $\text{Cl}^-$  reference electrode which is extensively used by the researchers in the field of electrochemistry. Ag/AgCl is a very stable and highly efficient photocatalytic materials. Modification by cocatalyst and nanonization of Ag/AgCl photocatalyst were done via a facile reduction-reoxidation route by using graphene oxide as the cocatalyst modifier to enhance its performance by P. Wang et al. [1,2]. X. Yana et al. [3] described photocatalytic behavior of Ag@AgCl-RGO composite with both special electronic state structure of graphene and excellent visible light catalytic performance of Ag@AgCl. Phase composition of the photocatalyst were characterized using X-ray diffraction. Scanning electron microscope and UV-visible absorption spectra were used to characterize the surface morphology and spectroscopic properties. Conductometric method for monitoring ionic reactions is very important and has received considerable scientific interest. For examples, the complexation reactions between 3,5-diiodo-8-hydroxy quinoline and  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  were studied in dimethylformamide (DMF)-ethanol binary solvent systems at different temperatures using conductometric method by A. Nezhadali et al. [4]. M. Rosés et al. [5] determined the limiting molar conductances and dissociation constants of perchloric, hydrochloric, picric and benzoic acids as well as their tetrabutylammonium salts conductometrically in propan-2-ol/water mixtures in wide composition range at  $25^\circ\text{C}$ . S. Sharma et al. [6] studied the kinetics of base-catalyzed hydrolysis of ethyl acrylate in ethanol-water (10–50% v/v) binary systems at the temperature range of  $30\text{--}45^\circ\text{C}$  using conductometric method.

The method involved the conversion of trace quantity of extremely poor conducting boric acid present in the sample to a relatively better conducting complex boronmannitol using mannitol. A gravimetric and complexometric titration method based on conductometric technique was described for the quantitative determination of brilliant green in water by R. Kakhki et al. [7]. The equilibrium constants and the thermodynamic parameters for the complex formation of  $\beta$ -cyclodextrin with brilliant green (BG) and precipitation of silver nitrate with BG were determined by conductance measurements in water by them. The complexation reactions of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Y}^{3+}$  and  $\text{ZrO}^{2+}$  with the macrocyclic ligand, 4'-nitrobenz-15-crown-5 (4'-NB15C5), in acetonitrile (AN), methanol and AN-MeOH binary mixtures was studied at various temperatures using the conductometric method by M. Esmaelpourfarkhani et al. [8]. The potentialities of conductometric titration were investigated for the study of protolytically active groups using organosilicas with immobilized acid groups of different types by V. N. Zaitsev et al. [9]. It was shown by them that conductometry is a promising method for estimating the energetic heterogeneity of the immobilized layer and the concentration of functional groups on the surface of organosilicas. N-acetyl-cysteine present in pharmaceuticals containing known quantities of the drug was conductometrically titrated in aqueous solution with copper(II) sulphate using a conductometric cell coupled to an autotitrator by B.C. Janegitz et al. [10]. Conductometric titration of fluoxetine hydrochloride in pharmaceutical products using silver nitrate as titrant was described by E. R. Sartori et al. [11]. Formation of AgCl by the reaction of  $\text{Ag}^+$  and  $\text{Cl}^-$  is a well-known ionic reaction but monitoring of kinetics of such an ionic reaction is complex and time consuming. Kinetics of formation of precipitates of cerium oxalate and silver chloride was studied by M.N. Parveen [12] using turbidity measurements. Generally it is more convenient to study kinetics of ionic reactions using conductometric technique as often changes of other physical parameters, like turbidity, color etc may not be achieved. The advantage of this method is that it avoids the use of many chemicals and time consuming tedious procedures. Conductometric technique could be a very convenient technique for studying AgCl formation and other ionic reaction, as the conductance of the solution under investigation either increases or decreases with the progress of reaction. To the best of our knowledge, conductometric technique has not been employed for investigating the kinetics

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of the mentioned reaction between  $\text{Ag}^+$  and  $\text{Cl}^-$  forming  $\text{AgCl}$ . In the present report, we present the measurements of conductance of reaction mixture containing  $\text{Ag}^+$  and  $\text{Cl}^-$  in aqueous solution at 25 °C. The data were then utilized in determining the order and rate constant of the reaction using a new approach.

## 2 EXPERIMENTAL

### 2.1 Procedure

The reaction of  $\text{Ag}^+$  and  $\text{Cl}^-$  was carried out in a glass vessel in which the conductometer cell was immersed. The glass vessel and the cell were thoroughly washed with water to remove any abrasive materials, especially ionic species, which have very profound effect on the conductance. The reaction was carried out at 25 °C temperature. The reaction vessel with the cell was placed in a hot water bath that can control the temperature within  $\pm 1$  °C.  $\text{Ag}^+$  solution was taken in the reaction vessel and that of  $\text{Cl}^-$  was taken in a test tube. Both the reaction vessel and the test tube were placed in the hot water bath until the desired temperature was achieved. After achieving the temperature at 25 °C, the  $\text{Cl}^-$  solution was poured into the reaction vessel in which the cell was previously placed. The conductance of the reaction mixture was recorded within possible shortest time following the mixing of the reactants. The time of the reaction was measured by a digital stop-watch.  $\text{AgNO}_3$  and  $\text{KCl}$  solutions were prepared by dissolving aliquot amounts of them in double-distilled water. The conductometer was calibrated each time prior to measurements using 0.01 M  $\text{KCl}$  solution that has specific conductance equal to  $1408 \mu\text{S cm}^{-1}$  at 25 °C. Potassium chloride ( $\text{KCl}$ ) (Merck, Germany) and silver nitrate ( $\text{AgNO}_3$ ) (Merck, Germany) were purchased and used as received.  $\text{KCl}$  and  $\text{AgNO}_3$  solutions of same concentrations of 5, 7 and 10 mM were prepared.  $20 \text{ cm}^3$  of each of  $\text{AgNO}_3$  and  $\text{KCl}$  solutions were mixed in the reaction vessel. Therefore, the final concentrations in the different reaction mixture were  $[\text{Ag}^+] = [\text{Cl}^-] = 2.5$  (R1), 3.5 (R2) and 5.0 (R3) mM.

### 2.2 Methodology

The relation between half-life and initial concentration of reactant can be expressed by Eq. (1):

$$n = \frac{\ln(t_1/t_2)}{\ln(a_2/a_1)} + 1 \quad (1)$$

where  $n$  is the order of the reaction,  $t_1$  and  $t_2$  are the half-lives of the reaction corresponding to the initial concentrations equal to  $a_1$  and  $a_2$ , respectively. Although Eq. (1) is derived for half-life of reaction but it can be used for the completion of any fraction of the reaction with two different initial concentrations. The rate constant of a second-order reaction can be expressed by the Eq. (2):

$$k = \frac{1}{t} \frac{x}{a(a-x)} \quad (2)$$

Where the symbols have their usual meanings. The terms  $x$  and 'a' can be expressed in conductance ( $\kappa$ ). The conductance

of the reacting solution is proportional to the remaining concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$ . Therefore,  $x \propto (\kappa_0 - \kappa_t)$  and  $a \propto (\kappa_0 - \kappa_t)$  and hence  $(a-x) \propto (\kappa_t - \kappa_\infty)$ . Therefore, Eq. (3) can be achieved by rearrangement of Eq. (2):

$$\kappa_t = \frac{1}{ak} \left( \frac{\kappa_0 - \kappa_t}{t} \right) + \kappa_\infty \quad (3)$$

The value of second-order rate constant can thus be calculated from the slope  $(1/ak)$  of a linear plot of  $\kappa_t$  vs.  $((\kappa_0 - \kappa_t)/t)$ .

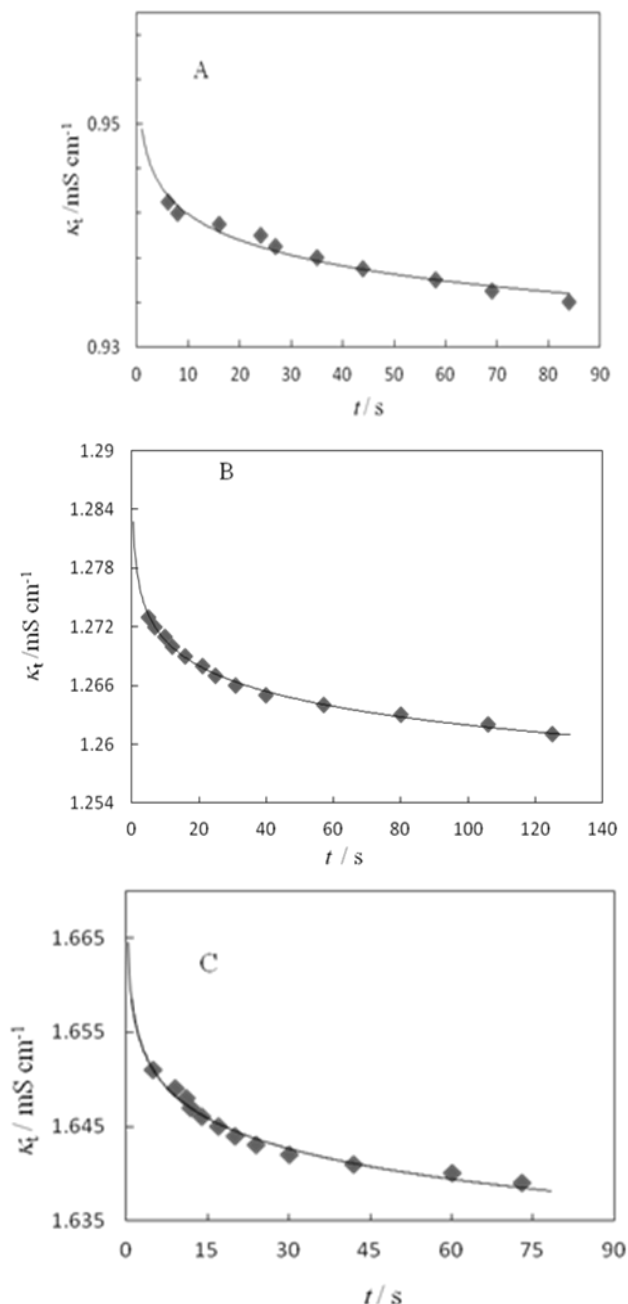
## 3 RESULTS AND DISCUSSION

### 3.1 Determination of time-dependence conductance curves

Firstly, the conductance of the reacting mixture (R1) having  $[\text{Ag}^+] = [\text{Cl}^-] = 2.5$  mM was measured using conductometer. The obtained values of conductance were plotted against time of the measurement and the result is shown in Fig. 1(A). The curve shows that the value of conductance of the solution decays exponentially with time, that is, it decays rapidly at lower times but attains a level off trend at higher times. The decay of conductance is attributed to the consumption of the uni-positive and negative  $\text{Ag}^+$  and  $\text{Cl}^-$ , respectively and the formation of neutral  $\text{AgCl}$ . Similarly to the reaction mixture R1, the conductance of R2 and R3 mixtures were also recorded, plotted against time and the corresponding results are presented in Fig. 1(B) and (C). Similar to reaction mixture R1, the obtained curves also show the similar trend of decaying rapidly at lower experimental times and attaining a level off trend at higher times. The value of solubility product constant of  $\text{AgCl}$  is  $1.8 \times 10^{-10}$  at 25 °C. The product of concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  used in the experiment exceeds the value of solubility product constant. Therefore, the decrease in conductance in the present experiment is obviously attributed to the precipitation reaction of  $\text{Ag}^+$  and  $\text{Cl}^-$  forming  $\text{AgCl}$ . Each of the curves in Fig. 1 was extrapolated to y-axis and the initial conductance ( $\kappa_0$ ) of each of the solutions was determined from the intercept ( $t=0$ ). The obtained values of  $\kappa_0$  are summarized in Table 1.

**TABLE 1**  
Summarization of the values of  $\kappa_0$  for the reaction mixtures R1, R2 and R3 at 25 °C

Reaction mixture	R1	R2	R3
$\kappa_0 / \text{mS cm}^{-1}$	0.9496	1.2793	1.6585



**Fig. 1.** Curves of conductance ( $\kappa_t$ ) vs. experimental time ( $t$ ) for different reaction mixtures: (A)  $[Ag^+] = [Cl^-] = 2.5$  (R1), (B) 3.5 (R2) and (C) 5.0 (R3) mM. The data were obtained at 25 °C for the reaction of  $Ag^+$  and  $Cl^-$  in aqueous solution.

### 3.2 Determination of order of the reaction between $Ag^+$ and $Cl^-$

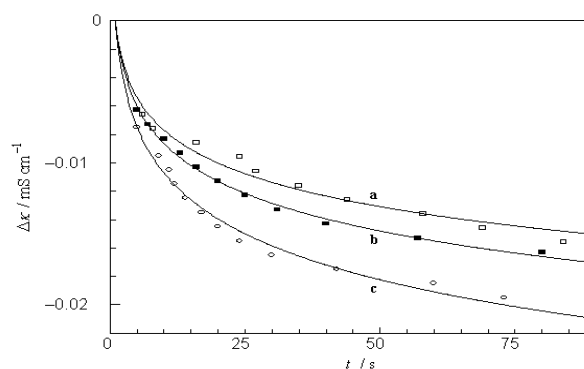
The Eq.(1) is generally used for half-life of reaction. But versatility of this equation is that it can be applied to the time required for completion of any specified fraction of the reaction for two different initial concentrations.. In the present article, the new approach to use Eq. (1) for the determination of order of the ionic reaction between  $Ag^+$  and  $Cl^-$  is

attempted considering completion of any equal fraction of the reaction. An equal decrease of conductance ( $\Delta\kappa$ ) is considered as an indicator of completion of same fraction of the reaction with different initial concentrations. For this purpose, the values of  $\Delta\kappa$  were derived from the curves (A-C) in Fig. 1 at different times and the values are summarized in Table 2.

**TABLE 2**

Summarization of the derived values of  $\Delta\kappa$  for reaction mixtures R1, R2 and R3. The values were derived from the curves in Fig. 1 (A-C)

2.5 mM (R1)		3.0 mM (R2)		5.0mM (R3)	
t / s	$\Delta\kappa$ / mS cm <sup>-1</sup>	t / s	$\Delta\kappa$ / mS cm <sup>-1</sup>	t / s	$\Delta\kappa$ / mS cm <sup>-1</sup>
6.0	-0.0066	5.0	-0.0063	5.0	-0.0075
8.0	-0.0076	7.0	-0.0073	9.0	-0.0095
16.0	-0.0086	10.0	-0.0083	11.0	-0.0105
24.0	-0.0096	13.0	-0.0093	12.0	-0.0115
27.0	-0.0106	16.0	-0.0103	14.0	-0.0125
35.0	-0.0116	20.0	-0.0113	20.0	-0.0145
44.0	-0.0126	25.0	-0.0123	24.0	-0.0155
58.0	-0.0136	40.0	-0.0143	30.0	-0.0165
69.0	-0.0146	57.0	-0.0153	60.0	-0.0185
84.0	-0.0156	80.0	-0.0163	73.0	-0.0195



**Fig. 2.** Plots of  $\Delta\kappa$  vs.  $t$  for different reaction mixtures: (a) 2.5 (R1), (b) 3.0 (R2) and (c) 5.0 (R3) mM.

The obtained values of  $\Delta\kappa$  were plotted as a function of time and the results are presented in Fig. 2. The times required corresponding to  $\Delta\kappa$  equal to  $-0.010$ ,  $-0.115$  and  $-0.125$  mS  $cm^{-1}$  for reaction mixtures R1, R2 and R3 were derived from Fig. 2 and summarized in Table 3.

**TABLE 3**

Summarization of times required to decrease the conductance by different amount for different initial concentrations. The data were derived from Fig. 2

$\Delta\kappa$ / mS cm <sup>-1</sup>	a / mM	t / s	n	n (average)
-0.100	2.5	8.5	2.5	2.2
	3.0	14.0	1.9	
	5.0	19.5	2.2	
-0.115	2.5	12.0	2.3	2.2
	3.0	19.0	2.1	
	5.0	28.8	2.2	
-0.125	2.5	15.5	2.6	2.3
	3.0	27.0	2.1	
	5.0	41.0	2.4	

The order of the reaction was calculated by putting the values of 't' and 'a' in Eq. 1 for each pair of reaction mixture (R1, R2), (R2, R3), (R1, R3). The average value of order was calculated as 2.2, which can approximately be considered as 2. The reaction between  $\text{Ag}^+$  and  $\text{Cl}^-$  forming  $\text{AgCl}$  in aqueous solution was thus found to follow a second-order kinetics. The obtained order is reasonable as being the reactants ionic, the rate of the reaction is expected to depend on both of  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$ . The present article therefore, describes a new conductometric approach of determination of order which can largely be employed to many ionic reactions.

### 3.3 Determination of rate constant of reaction between $\text{Ag}^+$ and $\text{Cl}^-$

The second-order rate constant of the reaction was calculated using Eq. (2) modified for equal initial concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  and replacing concentration with conductance ( $\kappa_t$ ). The values of  $((\kappa_0 - \kappa_t)/t)$  were calculated at different times for the reaction mixtures R1, R3 and R3 using  $\kappa_0$  (summarized in Table 1) and  $\kappa_t$  (From Fig.1) The values of  $\kappa_t$  of the reaction mixtures were plotted against the calculated values of  $((\kappa_0 - \kappa_t)/t)$  and the results are shown in Fig. 3. The values nicely fall on their respective straight lines. The regression equations of the linear plots corresponding to reaction mixtures R1, R2, R3 are presented by Eqs. (4)-(6), respectively:

$$\kappa_t = 19.249((\kappa_0 - \kappa_t)/t) + 0.931 \quad (4)$$

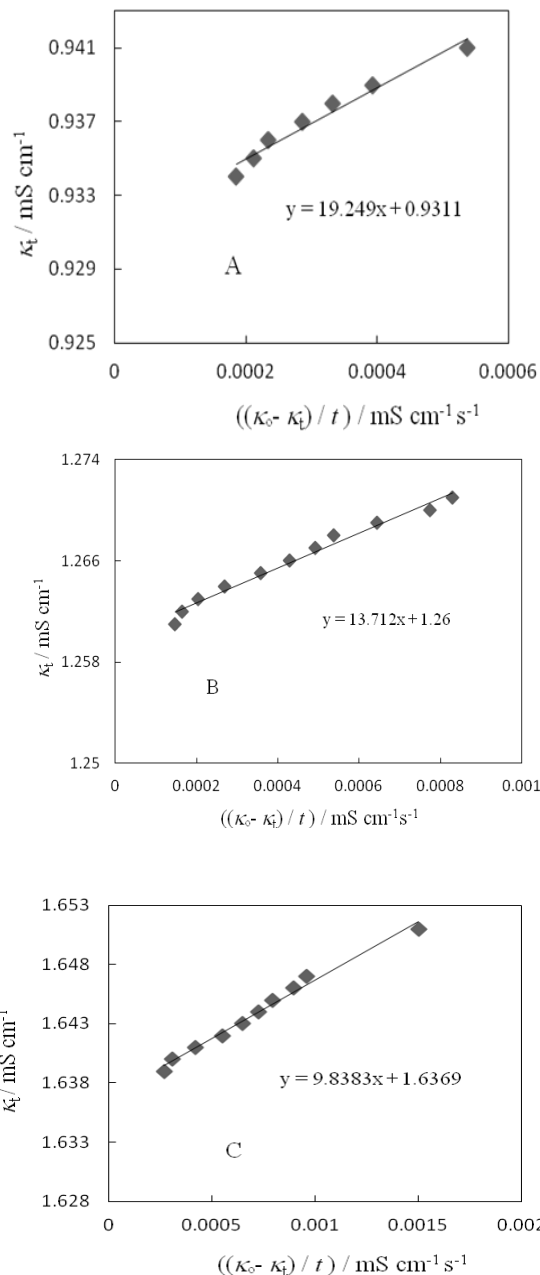
$$\kappa_t = 13.711((\kappa_0 - \kappa_t)/t) + 1.260 \quad (5)$$

$$\kappa_t = 9.838((\kappa_0 - \kappa_t)/t) + 1.637 \quad (6)$$

From the slopes ( $1/\alpha k$ ) of the straight lines as presented by the regression Eqs. (4)-(6), the rate constants were calculated as 20.780, 20.836 and 20.329  $\text{L mol}^{-1} \text{s}^{-1}$ . The obtained values are well consistent within an error of 0.3-2.4%.

## 4 CONCLUSIONS

The ionic reaction between  $\text{Ag}^+$  and  $\text{Cl}^-$  forming  $\text{AgCl}$  in aqueous solution was studied using conductometric method. The conductances of the reaction mixture corresponding to zero time were obtained as 0.9496, 1.2793 and 1.6585  $\text{mS cm}^{-1}$  from the intercept of the  $\kappa_t$  vs. t plots for different reaction mixtures. The times required for the decrease of conductance ( $\Delta\kappa$ ) to the same extent for all the reaction mixtures were obtained at several values of  $\Delta\kappa$ . The order of the reaction was then calculated as ca. 2.0 using the obtained time. A new conductometric approach for determination of order of ionic reaction was achieved. A modified second-order rate expression was developed in terms of conductance and the rate constants of the reaction were calculated as 20.780, 20.836 and 20.329  $\text{L mol}^{-1} \text{s}^{-1}$  from the values of slopes of the  $\kappa_t$  vs.  $((\kappa_0 - \kappa_t)/t)$  linear plots for different concentrations. The values were well-consistent within the experimental errors. The present article demonstrate a very important new approach of determination of order that can widely be employed for other ionic reactions.



**Fig. 3.** Linear plots of  $\kappa_t$  vs.  $((\kappa_0 - \kappa_t)/t)$  for different reaction mixtures: (A) 2.5 (R1), (B) 3.5 (R2) and (C) 5.0 (R3) mM. The data were derived from Fig. 1.

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