

## Kinetic Study of Complex Formation of Silver (I) with Ortho-Aminobenzoic acid in Micellar and Microemulsion Phases

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- (Ag<sup>+</sup>)

micellar ) (OABA)

(L2 microemulsion) (solutions

cetyltrimethyl- sodium dioctylsulfosuccinate (AOT)

.sodium dodecyl sulfate (SDS) ammonium bromide (CTAB)

460

OABA Ag<sup>+</sup>

(k<sub>obs</sub>)

CTAB SDS AOT

k<sub>obs</sub> OABA Ag<sup>+</sup>

.CTAB SDS AOT

OABA Ag<sup>+</sup>

(ΔH<sup>\*</sup>, ΔS<sup>\*</sup>, ΔG<sup>\*</sup>)

(oil)

(co-surfactants)

.CTAB SDS

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## Abstract

Kinetic study concerning the complex formation of silver ion ( $\text{Ag}^+$ ) with Ortho-aminobenzoic acid(OABA) was conducted. The reaction kinetics was studied in aqueous, micellar solutions and L2 microemulsion media of different surfactants. Sodium dioctylsulfosuccinate (AOT), cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were the studied surfactants. Spectrophotometric study follow up at 460 nm was used.

The results show that the reaction is first-order with respect to  $\text{Ag}^+$  and OABA in all cases. Generally; values of the observed rate constants ( $k_{\text{obs}}$ ) were increasing with increasing of surfactant concentration in micellar media. AOT media was mainly more promotional than each of SDS and CTAB. A pseudo-phase kinetic model was applied and association constants of  $\text{Ag}^+$  and OABA with surfactant micelles were calculated. Values of  $k_{\text{obs}}$  for the reaction rates in microemulsion phases have been reported. AOT L2 microemulsion system has been found as the most promotional system among all the other studied systems. Association constants of  $\text{Ag}^+$  and OABA with surfactant layer in microemulsion were calculated and tabulated. The reaction rate was increasing by increasing temperature in aqueous, micellar and microemulsion phases. The activation parameters  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  have also been obtained. The reaction rate in different microemulsion media is affected by oil nature (n-heptane > n-hexane > n-pentane). Co-surfactants nature (n-butanol, n-pentanol and n-hexanol) has a very slight effect on  $k_{\text{obs}}$  values in the case of CTAB or SDS microemulsion.

**Keywords:** Complexion, kinetics,  $\text{Ag}^+$ , OABA, micelles, microemulsion.

### 1. Introduction:

Micelles are known to provide different microenvironments for different parts of the reactant molecules; i.e., a non-polar hydrophobic core can provide binding energy for similar groups while the outer shell interacts with the reactant's polar groups. These properties of micelles play an important role in influencing the rates of reactions(Akram et al. 2013, 2014).

Microemulsions have been used as chemical reactors because of their special interfacial properties allowing an intimate contact, at nanoscale

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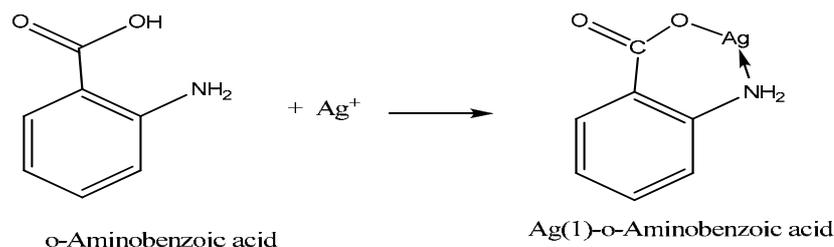
level, of hydrophilic and hydrophobic domains. The dynamic character of these nano-reactors is one of the most important features, which has to be taken into account for a comprehensive understanding of chemical reactions carried out in these media (Lo'pez-Quintela et al. 2004).

Ortho-aminobenzoic acid(OABA)is consequently amphoteric fluorescent molecule that has been used in internally quenched fluorescent peptides, which are employed for continuous protease assays. It is sometimes mentioned as vitamin L1 and has a sweetish taste (Brown. 1968, Turchiello et al. 1998).

A lot of phenolic compounds as 1-nitroso-2-naphthol and o-aminobenzoic acid have been developed as reagents for the spectrophotometric determination of several metal cations. However, most of them have several disadvantages: the reagents themselves often have absorption band in visible region because of their conjugation structures, and they often form colored complexes with these metal cations (Nunez et al 1986, Rioux et al. 1986, Yohannes et al. 1995). Several studies describe the complexation reaction of phenolic derivative compounds with metal cations to be used as reagents for the quantitative and qualitative analysis of these cations (Mukherjee and Ansuman 2002, Abd El Wahed et al.2001, Fernandes et al. 1997).

Several complexes of silver (I) with different ligands have been synthesized and characterized. Applications of these complexes have been studied [Fernandes et al. 1997, Wu. G et al. 1991). Many silver (I) complexes are of biological significance and have shown great potential as chemical disinfectants. (Yohannes et al. 1995, Perreault et al 1992). No studies on the complexation reaction of silver ion ( $Ag^+$ ) and o-aminobenzoic acid neither in micellar solutions nor in microemulsion systems are known. The objective of the present work is to conduct a systematic kinetic study in each of aqueous and micellar solutions. AOT, CTAB and SDS were used as the surfactants. The reaction was also studied in different L2-microemulsion phases: (AOT/ n-heptane/ water), (CTAB/ n-pentanol/ n-heptane/ water) and (SDS/n-pentanol/ n-heptane / water) at different temperatures. The influence of changing oil (n-pentane, n-hexane, n-heptane) and changing of co-surfactant (n-butanol, n-pentanol, n-hexanol) was included in this study.

The reaction of  $Ag^+$  with OABA to form silver(I)-o-amino-benzoic acid a complex can be written as equations(1)and(2)(El-Aila 2007, Proskurnin et al. 2003, Yohannes et al. 1995).



## 2. Experimental:

### 2.1 Materials and methods:

Sodiumdioctylsulfosuccinate (AOT), cetyltrimethylammonium bromide (CTAB) were purchased from Across Organics (Fairlawn, NJ, USA). Sodium dodecyl sulfate (SDS), AgNO<sub>3</sub> and NaOH were obtained from Fluka Chemical Co. (Buchs, Switzerland), o-amino-benzoic acid (OABA) heptane, hexane, pentane, butanol, pentanol and hexanol were obtained from Merck and were used as received. Double-distilled water was used throughout the experiments.

Proper volume of the required concentration of (AgNO<sub>3</sub>) from a freshly prepared stock solution was introduced in one glass tube (tube A). A reagent mixture of a suitable volume OABA or a suitable volume of OABA + surfactant (AOT, SDS or CTAB) in a second tube was prepared. The required volume of NaOH was added to tube B to give the required total volume of reaction mixtures which is identical in all experiments (10.0 mL).

Samples for kinetic study of inverse micellar microemulsion (L2) were prepared such that, suitable volume of (AgNO<sub>3</sub>) was prepared in a glass tube (A). The other components mixture of surfactant (AOT, SDS or CTAB) + proper volume of oil (heptane) + proper volume of co-surfactant in each case of SDS and CTAB microemulsion. The proper volume of the required concentration of OABA was added and mixed well by vortex in the test tube B. The total volume of the contents of A and B in all cases is 10.0 mL. Before mixing by vortex, both tubes A and B were thermostated separately for at least 20 minutes at 25°C. The contents of tube B were added to the

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contents of tube A. The reaction time was followed using a stop watch starting immediately on mixing. All runs employed a relatively large excess of  $\text{Ag}^+$  over OABA concentration in order to obtain pseudo first order rate conditions. The same procedure was employed to study the effects of OABA and  $\text{Ag}^+$  concentration. Surfactant type, surfactant concentration, co-surfactant nature (butanol, pentanol and hexanol), oil (pentane, hexane and heptane), water/surfactant molar ratio (W), oil/surfactant molar ratio (Z) and the influence of temperature were studied.

### 2.2 Kinetics and instruments:

The rates of the reaction between OABA and  $\text{Ag}^+$  in aqueous, micellar and microemulsion systems were studied spectrophotometrically by monitoring the absorption of a complex (silver-o-amino benzoic acid) as a function of time at 460nm (Yohannes et al, 1995) at  $25.0\text{ }^\circ\text{C} \pm 1.0\text{ }^\circ\text{C}$  using a Shimadzu-1601 UV-VIS spectrophotometer. It was noticed that the absorbance is higher in microemulsion as (AOT > SDA > CTAB) than micellar (AOT > SDA > CTAB) than in aqueous medium with no shift in  $\lambda_{\text{max}}$  (460 nm), i.e., the wave length of maximum absorbance remains the same in both aqueous, micellar and microemulsion media. The pseudo first order rate constants ( $k_{\text{obs}}$ ) were calculated up to (80 %) completion by using equation (3) with average correlation factor of (0.98).

$$\ln[A_\infty - A_o / A_\infty - A_t] = k_{\text{obs}}t \quad (3)$$

Where:  $A_\infty$  = absorbance at infinite time,  $A_o$  := absorbance at zero time,  $A_t$  = absorbance at time (t).

The pH values of the solutions were adjusted using a microprocessor combined pH-meter and thermometer, model pH 211 by Hanna instruments.

The values of critical micellar concentration(CMC)of different surfactants were measured conductometrically by carrying out series of measurements for increasing surfactant concentrations at  $25^\circ\text{C}$ . The employed instrument was Hanna conductometer using a dip-type cell made of platinum black with an accuracy of about  $\pm 0.03$ . CMC values were obtained from the points showing discontinuity in the plots of the measured specific conductivity vs. surfactant concentration(Zourab et al. 2003, Sanchez et al. 1997, Rodrigues et al. 1998).The obtained values were in the vicinity of 0.68, 0.88, 6.5 mM, for AOT, CTAB, and SDS respectively, in

agreement with the literature value of 0.70, 0.9, and 6.8 Mm in water at 25°C for previous surfactants respectively(Fendler J.H. and Fendler E.J. 1975).

### 3. Results and discussion:

The observed rate constant in the studied aqueous system of complex formation of  $Ag^+$  with OABA was found to be increasing with increasing of the pH values up to 8.0. It was not changing in the range of 8-12. The pH range(8 to12)is expected to cover the pH range of the micellar and microemulsion systems under study.

The observed rate constant( $k_{obs}$ ),is a composite of parameters. It contains contributions from the equilibrium complex formation step and the electron transfer step. Under the condition of  $[Ag^+] \gg [OABA]$  the observed values were found to fit Equation (4) (Proskurnin et al. 2003, El-Aila 2007)

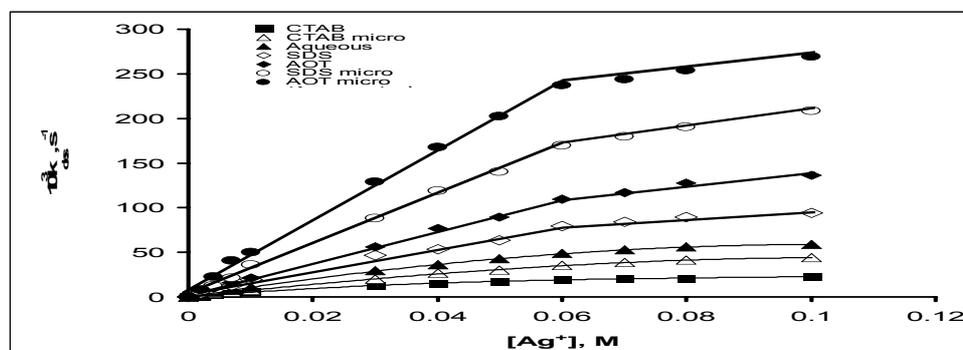
$$k_{obs} = \left[ \frac{k_{et} K_{IP} [Ag^+]}{1 + K_{IP} [Ag^+]} \right] \quad (4)$$

Where  $K_{IP}$  is the complex formation constant and  $k_{et}$  is the electron transfer rate constants. On the basis of Equation 4 and in the presence of high  $Ag^+$  concentration, one would expect saturation behavior, that is, the possibility of reaching a plateau in which  $k_{obs}$  is independent of  $Ag^+$  concentration and, therefore, equal to  $k_{et}$ . Data summarized in Table 1 show variation of  $k_{obs}$  with reactants concentration. The  $k_{obs}$  values at different OABA concentrations( $1 \times 10^{-3}$  to  $9 \times 10^{-3}$ )M were found to be approximately the same, indicating that the reaction is first order with respect to OABA. The dependence of  $k_{obs}$  on  $Ag^+$  concentration is also shown graphically in Figure 1. The results show a linear dependency on  $Ag^+$  concentration in aqueous and in presence of 0.002 M CTAB up to 0.06 M, indicating a first-order behavior.  $k_{obs}$  is independent of  $[Ag^+]$  at higher concentrations than 0.06 M. Micellar surface is saturated with  $Ag^+$  molecules above 0.06 M.

From reciprocal of equation(4),the plot of  $1/k_{obs}$  against  $1/[Ag^+]$  gave a straight line with a slope =  $[(1/K_{IP}) \times (1/k_{et})]$  and intercept =  $(1/k_{et})$ . The  $K_{IP}$  and  $k_{et}$  values have been obtained from the slope and the intercept, the results are depicted in table 2. Values of  $K_{IP}$  are consistent with greater destabilization of initial state of reactants than of ion /ligands complex ( $Ag^+/OABA$ ) as the reactivity sequence  $AOT_{micro} > SDS_{micro} > AOT > SDS > aqueous > CTAB_{micro} > CTAB$ . The same sequence was shown for  $k_{et}$  values

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tension state goes to product through electron transfer of amino group to silver ion (El-Aila 2007, - Rodrigues et al. 1996, Salem et al. 2002).



**Figure 1.** Effect of  $[Ag^+]$  on  $k_{obs}$  for  $Ag^+/OABA$  complex formation in either of aqueous, 0.02 M surfactant micellar solution and (AOT 18% / heptane(64%)/ aqueous ( $Ag^+ + OABA$ ) 18%) microemulsion, CTAB 20% / pentanol(18%)/ heptane(46%)/aqueous ( $Ag^+ + OABA$ ) 18%) microemulsion, SDS (18%) / pentanol (18%) / heptane(46%) / aqueous ( $Ag^+ + OABA$ ) 18%) microemulsion) at 25°C and (pH = 9.0).

**Table 1.** Effect of changing  $[Ag^+]$  and  $[OABA]$  on  $k_{obs}$  for  $Ag^+/OABA$  complex formation in either of :aqueous, 0.02 M surfactant micellar solution and [AOT18%/heptane(64%)/aqueous( $Ag^+ + OABA$ )18%]microemulsion, [CTAB 18%/pentanol(18%)/heptane(46%)/aqueous( $Ag^+ + OABA$ )18%]microemulsion, [SDS(18%)/pentanol(18%)/heptane(46%)/( $Ag^+ + OABA$ ) 18%] microemulsion) at 25°C and pH = 9.0 .

$[Ag^+]$ , M	$[OABA]$ , M	$10^3 k_{obs}, s^{-1}$						
		CTAB	CTAB micro	Aqueous	SDS	AOT	SDS micro	AOT micro
0.000	0.006	0	0	0	0	0	0	0
0.002	0.006	0.85	1.7	2.1	4.1	5.7	5.7	8.0
0.004	0.006	2.55	3.7	5.1	6.8	10.3	12.8	29.2
0.007	0.006	3.49	5.4	7.3	12.9	16	21.6	47.8
0.010	0.006	6.20	7.4	10.7	19.4	21.5	40.8	58.4
0.030	0.006	12.77	20	29.4	47.1	55.8	98.3	145.4
0.040	0.006	15.09	26.5	35.8	53.2	76.7	118.8	180
0.050	0.006	17.34	30.3	42.6	63.3	89.7	140.4	204.1
0.060	0.006	19.71	35.3	49	70.1	98.1	155.4	229.2
0.070	0.006	20.62	38.5	52.7	78.5	108.4	166.4	237.7

0.080	0.006	21.0	41.3	55.8	82.8	117.2	173.5	254
0.100	0.006	22.81	44.1	59	84.2	127.5	179.4	269.5
0.100	0.001	13.1	27.4	41.8	62.7	86.8	141.6	212.1
0.100	0.003	11.1	29.4	39.2	58.1	86.2	144.3	219.3
0.100	0.005	19.2	34.9	48.6	69.8	97.6	155.4	224.5
0.100	0.006	19.71	35.3	49	70.1	98.1	155.4	229.2
0.100	0.007	23.5	38.5	54.2	73.8	98.5	156.5	229.8
0.100	0.008	24.8	41.8	58.1	75	101.2	160.6	230.2
0.100	0.009	25.5	43.7	59.4	76.5	116.2	165.8	231

### 3.1 Micellar catalysis:

The complex formation rate has been studied in three different types of micellar solutions: AOT, SDS and CTAB. According to data depicted in Figure 1; the reaction was catalyzed with AOT more than with SDS and was inhibited with CTAB, i.e.,  $rate_{AOT} > rate_{SDS} > rate_{aqueous} > rate_{CTAB}$ . The relation between  $k_{obs}$  and surfactant concentration is shown in Figure 2.

It is expected that the rate should be higher in the negative charge of AOT and SDS micelles due to the columbic attraction between the positive charge of ammonium group in OABA and  $Ag^+$  ion with the anionic micelles (Pal et al. 1997, 1998). The micelle behaves as a bridge to minimize the distance between OABA and  $Ag^+$  to form the complex. Also the OABA molecule will be attracted strongly to the doubly hydrophobic chains of AOT surfactant through hydrophobic attraction (Vander Waal's force) more than the singly hydrophobic chains of SDS. This trend makes the reaction rate in AOT micelle greater than in SDS micelle. (Pal et al. 1997, 1998, Bunton et al. 1999). In positively charged CTAB micelle, the  $Ag^+$  ion will be repelled and be away from interaction with OABA molecule to form the complex; this behavior makes the reaction rate slower than in aqueous media.

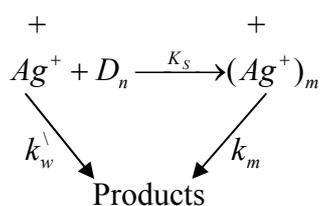
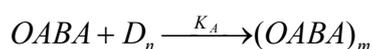
**Table 2. Values of complex constants for  $Ag^+$ / OABA complex formation in either of aqueous, 0.02 M surfactant micellar solution and [AOT 18% /heptane(64%)/aqueous ( $Ag^+$ +OABA)18%]microemulsion,[CTAB18%/pentanol(18%)/heptane(46%)/aqueous ( $Ag^+$ +OABA)18%]microemulsion,[SDS(18%/pentanol(18%)/heptane(46%)/( $Ag^+$ +OABA) 18%] microemulsion) at 25°C and pH = 9.0**

Complex constants	CTAB	CTAB micro	AQ	SDS	AOT	SDS micro	AOT Micro
$K_{IP}, M^{-1}$	0.083	0.125	0.210	0.23	0.27	0.720	1.130
$k_{et}, s^{-1}$	0.043	0.106	0.210	0.37	0.60	2.50	5.95

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### 3.2 Application of pseudo-phase:

In this model, the micelle phase is uniformly distributed among the aqueous phase. Thus, the reaction may occur in both phases, according to Scheme 1:



Scheme 1

Subscripts  $w$  and  $m$  denote the aqueous and micellar pseudo-phases, respectively;  $K_A$  ( $M^{-1}$ ) is the association constant of  $Ag^+$  ions to surfactant micelles;  $K_s$  ( $M^{-1}$ ) is the association constant of OABA molecules to surfactant micelles;  $[D_n(M)]$  is the micellized surfactant whose concentration is given by  $[D_n] = [\text{surfactant}]_T - \text{CMC}$ ;  $k_w$  ( $M^{-1}s^{-1}$ ) and  $k_m$  ( $M^{-1}s^{-1}$ ) are the second rate constants in the aqueous and micellar pseudo-phases, respectively.  $k_w$  is written as molar concentration and  $k_m$  is written as molar ratio ( $[Ag^+]_m/[D_n]$ ). The association constant of  $Ag^+$  ions to surfactant micelles,  $K_A$  was determined independently by following the spectrophotometric method. (Bunton et al., 1998, Romsted, 1977) To rationalize the kinetic data, the following equation (5) based on the pseudo-phase model is considered:

$$k_{obs} = \frac{k_w + k_m K_s K_A [D_n] [Ag^+]_T}{(1 + K_s [D_n])(1 + K_A [D_n])} \quad (5)$$

The first-order constant at the micellar interface,  $k_m$  ( $s^{-1}$ ) and the binding constant of OABA molecules to surfactant micelles,  $K_s$ , were obtained by fitting equation 5 to the experimental values of  $k_w$ ,  $K_A$ , CMC, and  $D_n$  and depicted in Table 3. Thus, the second order in the micellar pseudo-phase can be written with the concentration as a local molarity ( $k_m$ ) according to equation (6):

$$k_m = k_m' V_m \quad (6)$$

Where  $V_m$  is the molar volume of the reaction region at the micellar surface. Its value is approximately  $0.14 \text{ M}^{-1}$  (Vega et al., 2004). This result supports the suggestion that bimolecular reactions occur predominantly in the stern layer, therefore; the rate constant value in the micellar pseudo-phase is greater than its value in the aqueous pseudo-phase (Tascioglu, 1996).

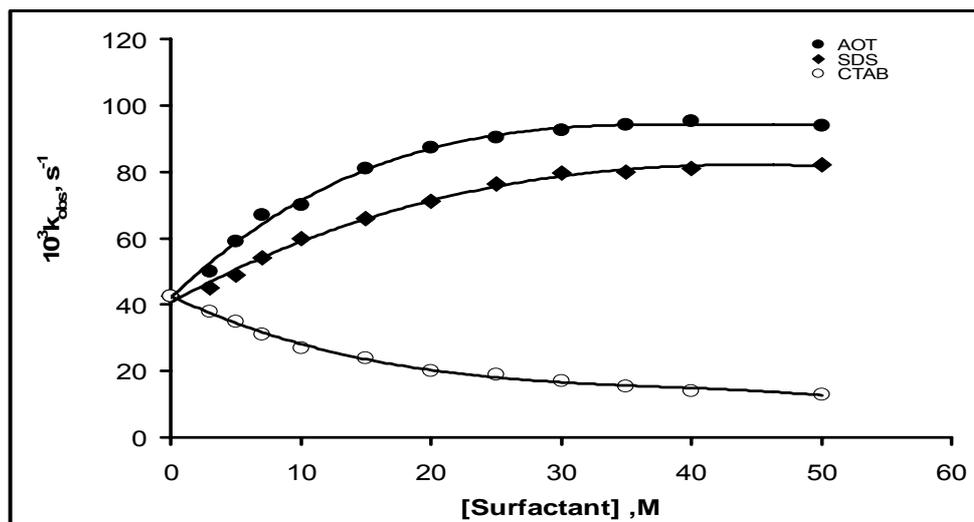


Figure 2. Effect of [surfactant] on  $k_{obs}$  for  $Ag^+/OABA$  reaction at  $25^\circ C$ .  $0.06 \text{ M } [Ag^+]$ ,  $0.006 \text{ M } [OABA]$ , and  $(pH = 9.00)$ .

Table 3. Kinetic Results for the reaction of  $Ag^+/OABA$  in  $0.02 \text{ M}$  micellar solution at  $25.0^\circ C$ ,  $[Ag^+] = 0.06 \text{ M}$ ,  $[OABA] = 0.006 \text{ M}$  and  $pH = 9.0$ .

Kinetic constants	AOT	CTAB	SDS
$k_m^{\setminus}, s^{-1}$	11.6	2.26	8.54
$k_m, M^{-1} s^{-1}$	1.63	0.32	1.18
$K_s, M^{-1}$	166	144	157
$10^2 k_w^{\setminus}, M^{-1} s^{-1}$	81.6	81.6	81.6
$K_A, M^{-1}$	122	12	118
$10^3 CMC, M^{-1}$	0.68	0.88	6.5

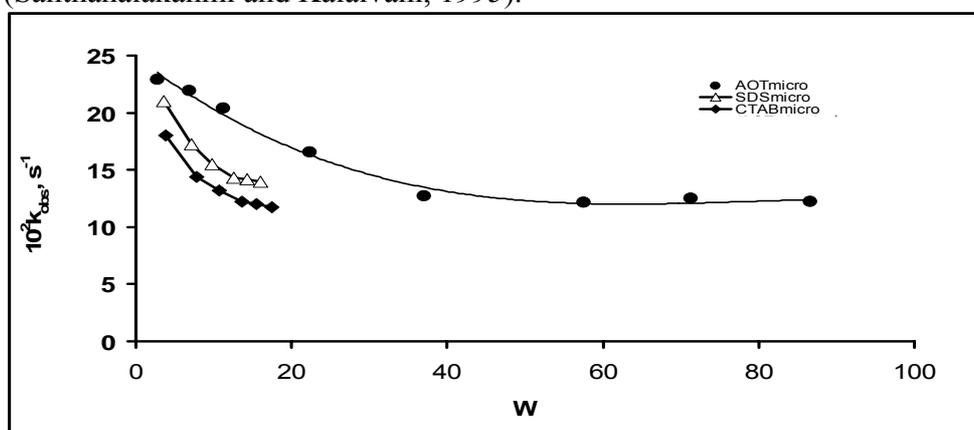
### 3.3 Inverse Micellar Microemulsion Catalysis:

The reaction kinetics was studied in L2 microemulsion. The reaction is expected to depend mainly on both factors: W (molar ratio of water/surfactant) and Z (molar ratio of oil/surfactant). Comparing with the

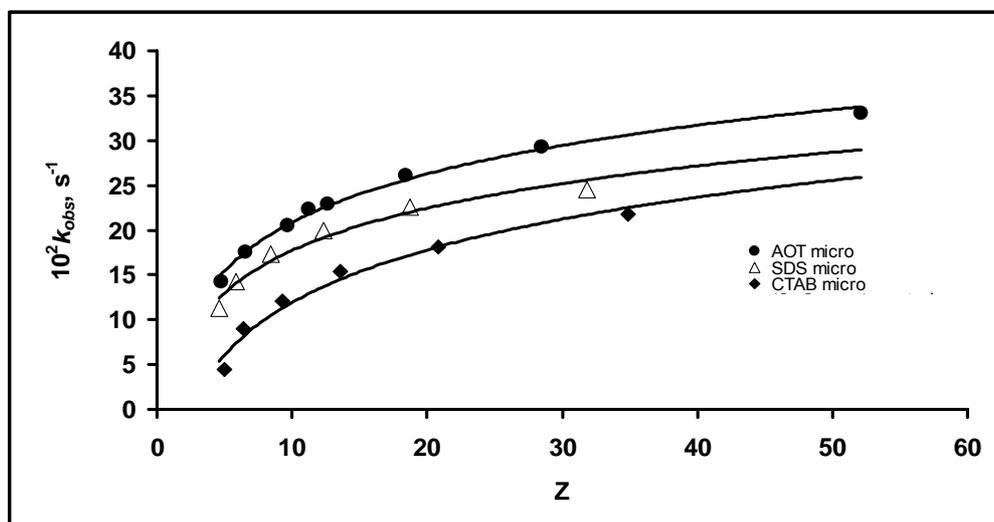
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other observed values in aqueous and normal micellar systems it has been found that  $k_{obs}$  was the highest in AOT/heptane/water system among the others according to the experimental results depicted in Figure 1. While fixing the value of  $Z$ ,  $k_{obs}$  value decreases as  $W$  increases as shown in Figure 3. This behavior may be due to the change in the droplet size. The droplet size is increasing by increasing  $W$ , which decreases the concentration of the reactants in the micellar bulk, and that is supposed to decrease the reaction rate.

Increasing  $Z$  values at constant  $W$  was also studied. It follows from the results shown in Figure 4 that the reaction rate was increasing by increasing  $Z$ . Increasing  $Z$  is mainly accompanied by decreasing of the surface area due to decreasing of the number of micro droplets. This trend makes a decrease in droplets number per unit volume of the solution which may lower the rate. In this study, the increase in the values of  $k_{obs}$  with increasing  $Z$ , means also increasing concentrations of the substrates in the aqueous phase inside the micelles within the micro droplets (Sanchez et al. 1997, Verma and Ghosh, 2010, 2013). The solubilization of oil mainly occurs at hydrophobic micellar wall, resulting in oil-swollen micelles. This causes an excess of interfacial area created during microemulsification. This effect increases the interfacial association of both substrates in the stern layer. Also interdroplet interaction assesses the association of the reactants with micelles (Santhanalakahmi and Kalaivani, 1995).



**Figure 3.** Effect of changing  $W$  on  $k_{obs}$  value in: [AOT/ heptane/ aq.( $Ag^+$ +OABA)], [CTAB/ heptane/pentanol/aq.( $Ag^+$ +OABA)], [SDS/ heptane /pentanol/ aq.( $Ag^+$ +OABA)] at 25 °C and  $Z=5.91, 6.42, 5.89$  for AOT, CTAB and SDS microemulsion respectively.  $[Ag^+]=0.06$  M,  $[OABA]=0.006$  M.



**Figure 4.** Effect of changing oil/surfactant mole ratio ( $Z$ ) on  $k_{obs}$  values of [AOT/ heptane/ aq. ( $Ag^+$  + OABA)], [CTAB/heptane/pentanol /aq. ( $Ag^+$  + OABA)], [SDS/ heptane / pentanol /aq. ( $Ag^+$ +OABA)] microemulsion at 25 °C, and  $W = 24.65, 17.44, 16.0$  for AOT, CTAB, SDS respectively.  $[Ag^+] = 0.06$  M,  $[OABA] = 0.006$  M.

To rationalize the kinetic data, equation (7) is considered: (Sanchez et al., 1997, Rodrigues et al., 1998, Vega et al., 2004).

$$k_{obs} = \frac{k_w' + k_M K_S' K_A' [1/W] [Ag^+]}{(1 + K_S' [1/W]) (1 + K_A' [1/W])} \quad (7)$$

where  $K_A'$  ( $M^{-1}$ ) is the association constant of ( $Ag^+$ ),  $K_S'$  ( $M^{-1}$ ) is the association constant of (OABA) and  $k_M$  ( $M^{-1}s^{-1}$ ) is the second order rate constant in inverse micellar microemulsion phase and  $k_w'$  ( $M^{-1}s^{-1}$ ) is the second order rate constant in water.

The extent and stability of reactants association with micelle/microemulsion interface are reflected from association constants ( $K_A'$  and  $K_S'$ ). ( $K_S' > K_A'$ ) in microemulsion in a trend which is greater than in micellar trend ( $K_A, K_S$ ), that causes higher solubilization of reactants which gives the interface higher extent of fluidity and higher substrate association (Santhanalakahmi and Kalaivani, 1995).

The experimental values of ( $k_w', K_A', k_M$  and  $K_S'$ ) were depicted in Table

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4. The obtained values of  $k_M$  are larger than that of  $k_W$ . This fact can be explained by taking into account that  $k_M$  corresponds to the rate constant of the process which takes place in the interface of the microemulsion. The interface behaves as a concentrated electrolyte solution (Rodrigues et al., 1998, Nadia et al., 2005).

Incorporation of the substrate into the micellar pseudo phase explains the increase in  $K_M$  observed at higher surfactant concentrations.  $K_M$  increases with surfactant concentration probably as a result of the distribution of the substrate between the micelles and the external solvent (Verma and Ghosh 2010, 2013). The catalytic activities are dependent on the water pool size of the micelles, i.e. on the  $W$  parameter consequently the optimal sized of micelles allow the achievement of complex formation (Verma and Ghosh, 2010, 2013). The values of the  $K_M$  in AOT > SDS > CTAB indicate that  $Ag^+$  and OABA are tightly bound and form the complex.

**Table 4. Kinetic Results for  $Ag^+$ / OABA reaction [AOT/ heptane/ aq. ( $Ag^+$ + OABA)], [CTAB/heptane/pentanol/ aq. ( $Ag^+$ + OABA)], [SDS/ heptane /pentanol/ aq. ( $Ag^+$ + OABA)] microemulsions at 25 °C and (pH = 9.0).**

kinetic constants	AOT	CTAB	SDS
$k_M, M^{-1}s^{-1}$	3.83	0.60	2.60
$K_S, M^{-1}$	188	171	176
$10^2 k_W, M^{-1}s^{-1}$	81.6	81.6	81.6
$K_A, M^{-1}$	140	22	134

### 3.4 Dependence of the reaction rate on temperature:

The complex formation of  $Ag^+$  with OABA in aqueous, micellar solutions and microemulsion media was carried out in the range of (20–50°C). The values of  $k_{obs}$  increased with increasing the process temperature. The activation thermodynamic parameters  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  were determined by the plot of ( $\ln k_{obs}$ ) vs. (1/T) according to the Eyring equation: (Verma and Ghosh, 2010, 2013, El-Aila, 2012, 2013). The values of  $\Delta S^*$ ,  $\Delta H^*$  and  $\Delta G^*$  were obtained using a nonlinear squares technique and are summarized in Table 5. (Verma and Ghosh, 2010, 2013, El-Aila, 2012, 2013).

These results indicated that the values of  $\Delta H^*$  and  $\Delta G^*$  increased in the order of: CTAB<sub>aq.</sub> > CTAB<sub>micro</sub> > aqueous > SDS<sub>aq.</sub> > AOT<sub>aq.</sub> > SDS<sub>micro</sub> > AOT<sub>micro</sub> which also accompanied by less negative  $\Delta S^*$  values. This

signifies that the micellar surface is friendly environment for the present reaction. Since the reactants have electrostatic attraction forces (columbic) and hydrophobic interactions(vander Waal's force)in micellar and also microemulsion media. Attraction forces are thought to have positive effects on the stabilization of the transition state. The microemulsion media lower  $\Delta H^*$  and  $\Delta G^*$  with a substantial negative  $\Delta S^*$  more than micellar more than aqueous. This lowering cannot be attributed to a dramatic change in the reaction pathway. But mainly to more convenient environment for the reactants.

Entropic and enthalpic factors control the association of the  $Ag^+$  and OABA at the micellar interface. The entropic factor played a major role in the reaction, which was more effective for anionic surfactants. Positive charges of reactants ( $Ag^+$  and OABA) were pushed into the aqueous phase, leading to a greater association in the micellar phase. This leads to a decrease in the transition state entropy (negative  $\Delta S^*$ ). In cationic surfactant case, the positive charges of reactants were repelled and pushed out of the aqueous phase, leading to lowering the association in the micellar phase. The other factor was enthalpic, where the association of OABA with the double chain AOT surfactant through hydrophobic van der Vaals interaction is greater than SDS and CTAB surfactants. This made it possible to lower the enthalpy of the transition state,  $\Delta H^*$  of the reaction.

**Table 5. Activation parameters for  $Ag^+$ /OABA complex formation in either of aqueous, 0.02 M micellar solution and [AOT 18% / heptane (64%)/aq.( $Ag^+$ / OABA) 20%], [CTAB 18% /pentanol (18%)/ heptane (46 aq.( $Ag^+$ /OABA)18%)], [SDS 18% /pentanol (18%)/ heptane (46 aq.( $Ag^+$ / OABA) 18%)] micro emulsions, [ $Ag^+$ ] = 0.06 M, [OABA] = 0.006 M.**

Reaction medium	activation parameters		
	$\Delta H^*$ ,kJmol <sup>-1</sup>	- $\Delta S^*$ , Jmol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^*$ , kJmol <sup>-1</sup>
AOT micro	13.23	212.0	76.4
SDS micro	15.50	208.8	77.4
AOT	19.18	200.2	78.8
SDS	20.5	198.1	79.5
Aqueous	22.6	194.7	80.7
CTAB micro	26.4	184.7	81.4
CTAB	30.6	175.5	82.9

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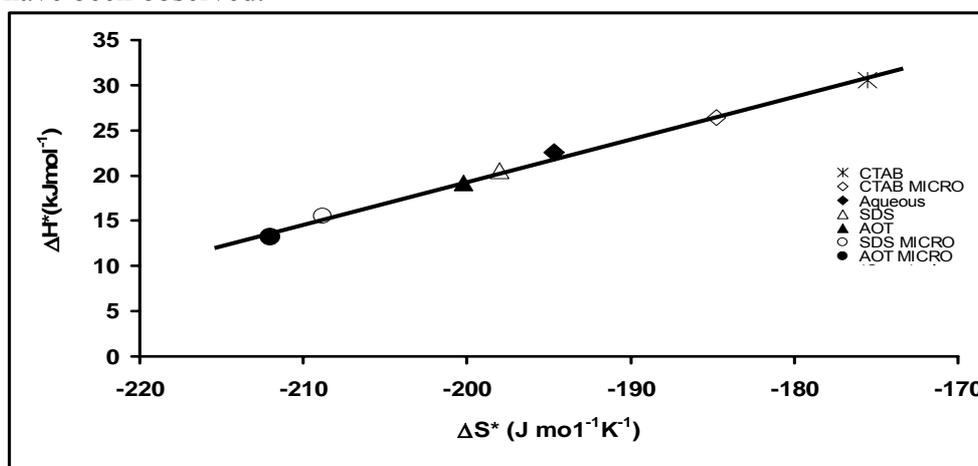
The plot of  $\Delta H^*$  vs.  $\Delta S^*$  of an isokinetic relationship ( $\Delta H^* = C + B\Delta S^*$ ), where  $B$  and  $C$  are slope and intercept for the reaction were fairly linear, as shown in Figure 5. This linearity indicates that the kinetics of the reaction followed the same reaction mechanism in all the studied phases (Bunton et al., 1998, Verma and Ghosh, 2010, 2013, El-Aila, 2012, 2013, Cai et al., 1995, Zourab et al., 2005).

### 3.5 Effect of variation of oil and co-surfactant in microemulsion media:

Variation of oil in the constituent of microemulsion media showed an increase in the value of  $k_{obs}$  in the order of heptane > hexane > pentane in the three microemulsion systems. The results are shown in Table 6.

Generally higher solubilization causes interfaces with higher extent of fluidity and lowers the extent of counter ion of surfactants binding and higher substrate ( $\text{Ag}^+$  and OABA) association with surfactant (Santhanalakahmi and Kalaivani, 1995). Also the oil facilitated the interaction of reactants with surfactant in microemulsion interface.

Variation of co-surfactant type (butanol, pentanol, hexanol) in CTAB and SDS In microemulsion media: a slight detectable change in  $k_{obs}$  value have been observed.



**Figure 5.** Isokinetic relationship  $\Delta H^*$  vs.  $\Delta S^*$  for  $\text{Ag}^+$ / OABA complex formation in either of aqueous 0.02 M surfactant micellar solution and [AOT 18% / heptane (64%)/ aq.( $\text{Ag}^+$ + OABA)18%], CTAB 20% / pentanol (18%)/ heptane (46%)/ aq.( $\text{Ag}^+$ + OABA)18%) SDS 18% / pentanol (20%)/ heptane (46%)/ aq. ( $\text{Ag}^+$ + OABA)18%) microemulsions] at different temperatures and pH = 9.0 [ $\text{Ag}^+$ ] = 0.06 M, [OABA] = 0.006 M.

**Table 6. Variation of  $k_{obs}$  value with oil for  $Ag^+$ /OABA reaction in: [(AOT 18% / oil (64%)/ aqueous (aq.  $Ag^+$  + OABA) 18%)], [CTAB 18% / pentanol (18%)/ oil(46%)/ (aq.  $Ag^+$  + OABA) 18%], [SDS 18% / pentanol (18%)/ oil(46%)/ (aq.  $Ag^+$  + OABA) 18%] at 25°C. [ $Ag^+$ ] = 0.06 M, [OABA] = 0.006 M.**

oil	$10^3 k_{obs}, s^{-1}$		
	AOT micro	CTAB micro	SDS micro
Heptanes	229.2	35.3	155.4
Hexane	190.7	29.2	132.1
Pentane	169.2	24.1	112.4

### Conclusion:

From this study, it has been found that inverse microemulsion systems can be more promotional media than micellar or aqueous media for the complex formation of silver ion( $Ag^+$ )with *Ortho*-aminobenzoic acid (OABA).This is favored for faster quantitative investigation of silver ion by OABA.

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