Analysis of the Experimental Data of Acid Hydrolysis in Micelle Assemblies Using Kinetic Model

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Abstract : Acid Hydrolysis of carboxylate ester with hydroxamate ions in micellar media has been discussed in our last research works. In this paper, we used all the obtained kinetic experimental data for correlation and explanation by modeling techniques. We know the different types of modeling techniques available and used in the current times. Michael menten one site total binding constant and one site fite Ki models apply for the explanation of kinetics data. The models were given a good explanation and correlation of these types of kinetic data.

Keywords : Kinetic, Models, Hydrolysis, Michael-Menten.

Introduction

In recent time modeling techniques is one in every of the foremost necessary correlations and clarification techniques within the analysis field. The study of the dynamics of reactions is that the space of chemical mechanics, specifically the study of the factors that confirm the reaction rates which square measure accountable for the institution of chemical equilibria in reversible reactions. The most aim of chemical mechanics is thus twofold:

– Determinative the final pathway, the reaction network, the reaction mechanisms, and therefore the numerous intermediates, and

– Etymologizing quantitative rate equations (with their rate parameters) that predict the speed of reaction as an operation of the native conditions (temperature, pressure, section state, composition, ionic strength, pH, solvent, catalysts, etc.).

The formulation of the reaction mechanism used for the kinetic modeling is usually subject to discussion and will be supported all accessible physical measurements, along side surface science knowledge, chemical data, and kinetic experiments (preferably off from equilibrium). Hence, chemical mechanics has to mix data noninheritable through varied different disciplines, like analytical chemistry (composition), chemical science (reaction types), chemical science (structure of matter), classical physical science (equilibrium), applied math physical science and quantum physics (rate theories), qualitative analysis and procedure chemistry (reaction intermediates), and arithmetic (parameter estimation and method simulation), among others. By predicting the rates of the assorted reaction pathways, chemical mechanics permits the prediction of production rates and selectivity's, and is thus a necessary tool within the modeling and style of chemical reactors [1]. Hence, chemical mechanics is one in every of the pillars of the chemical engineering discipline. Chemical mechanics employed by the various modeling techniques, in 1913, German chemist Leonor Michaelis associated Canadian Dr. Maud Leonora Menten investigated the mechanics of an protein reaction, within which associate disaccharidase catalyzedthe chemical reaction of saccharose into aldohexose and fruit sugar. The planned model was tow step reaction mechanisms within which the primary step was at quasi-equilibrium, and developed the corresponding rate equation. With in the past decade many varieties of modeling techniques like multi-step collision model, Michaelis-menten model, Eyring equation, Lumped Kinetic Models etc. planned by the researchers. In gift investigation we tend to used michaeis – menten protein mechanics model apply for rationalization of the straight forward kinetic reaction and correlate with protein mechanics. For the reason of binding constant we tend to used one site fite binding constant model and one site fite Ki model.

Experimental

Kinetic data were obtained by our published research work in the field of kinetic study. We used kinetic data in our last published research paper on the hydrolysis of carboxylate ester with hydroxamate ions in micellar media. These obtained kinetic data were correlated and explained by the different modeling techniques. We used the michaelis –menten and one site fite binding constant model and one site fite Ki model. The michaelis –menten model was given by the german biochemist for the investigation of an enzymatic reaction. In the current paper, we correlate the simple surfactant-based catalyzed reaction with enzyme kinetics reaction to used enzyme kinetic models for surfactant catalyzed reaction. Binding constant was determined by the user of one site fite binding constant model and one site fit Ki model. We used our kinetics data as a raw material for the different model. All the raw data was put in a prescribed kinetics model for the better explanation and correlation of the resultant data. In this method, we used graph paid prism software for the analysis of data by different modeling techniques. The data were obtained by the acid hydrolysis and alkaline hydrolysis of carboxylate ester in micellar media.

Result and Discussion

We used our published experimental kinetics data as a raw material for correlation and explanation by the different kinetic models. The published experimental work on the acid hydrolysis of carboxylate ester with hydroxamic acid in micellar media resultant data mention below [2-3]experimental run give the pseudo-first-order rate constants are summarized in (Table - 01). Kinetics rate data for this illustrated reaction protocol show the rate of hydrolysis increase in acidity increase up to 3.5 M HCl and further ascends acidity to decrease the reaction rate. In obtained data represent the reactivity of SHA was more than AHA in the same condition and both nucleophile higher rates at 3.5 M HCl above this concentration the rate was decreasing [4]. We are applied kinetics model michaelis –menten Kcat, one site fite total binding and one site fit Ki for the determination explanation and correlation of obtained data. The obtained kinetic data were put in kinetic modeling software graph paid prism followed the given equation (1, 2, 3and 4) for the analysis of resultant data (Table -2). The Bmax and Kd of highest (7.0 and 5.1) for the SHA in CTAB compare to other resultant data of Bmax and Kd was support the result of SHA was more than AHA (Fig: 4.1). Michaelis – menten Kcat model resultant data was used for the analysis reactivity of surfactant and nucleophile in a given reaction. The data of Kcat and Km was highest (2.57 and 0.004) for the SHA in CTAB compare to other resultant data of Kcat and Km (Fig: 4.2 & 4.3). The Kcat/Km value was five-time more than other resultant data support the result of SHA was more than AHA.

$$Y = Vmax*X/(Km + X) \tag{1}$$

$$Y = Et*kcat*X/(Km + X) \tag{2}$$

$$Y=Bmax*X/ (Kd+X) + NS*X + Background \tag{3}$$

$$logEC50=log (10\text{^}logKi*(1+RadioligandNM/HotKdNM)) \tag{4}$$

$$Y=Bottom + (Top-Bottom)/ (1+10\text{^}(X-LogEC50))$$

Table: 01 – Kinetics data for the Effect of acidic medium for the hydrolysis of carboxylate ester with nucleophiles (AHA & SHA) in different surfactants.

S.N.	HCl (mol dm^{-3})	pH	$10^5 \, k_{obs} \, (s^{-1})$					
			AHA			SHA		
			CTAB	SLS	Brij 35	CTAB	SLS	Brij 35
1	0.1	1.0	1.81	1.78	1.60	2.41	2.01	1.82
2	0.2	.70	1.90	1.80	1.70	2.46	2.08	1.88
3	0.3	.55	2.10	2.02	1.98	2.55	2.11	1.91
4	0.4	.45	2.30	2.09	2.01	2.61	2.15	2.06
6	0.5	.30	2.36	2.12	2.09	2.66	2.21	2.9
7	0.8	.15	2.45	2.18	2.16	2.70	2.32	2.10
8	1.0	.00	-	-	-	-	-	-
9	3.5	.00	2.47	2.19	2.18.	2.75	2.36	2.19
10	5.5	.00	1.98	1.87	1.84	2.13	2.01	1.94

Reaction condition [PNPA] = (1.6×10^{-4}M), [Nu] = (1.6×10^{-3}M), [Surfactant] = (1.0×10^{-3}M), [Temp] = 27°C.

Fig: 4.1, 4.2, 4.3 - Graph for kinetic data of acid hydrolysis of carboxylate ester with nucleophile in different surfactant
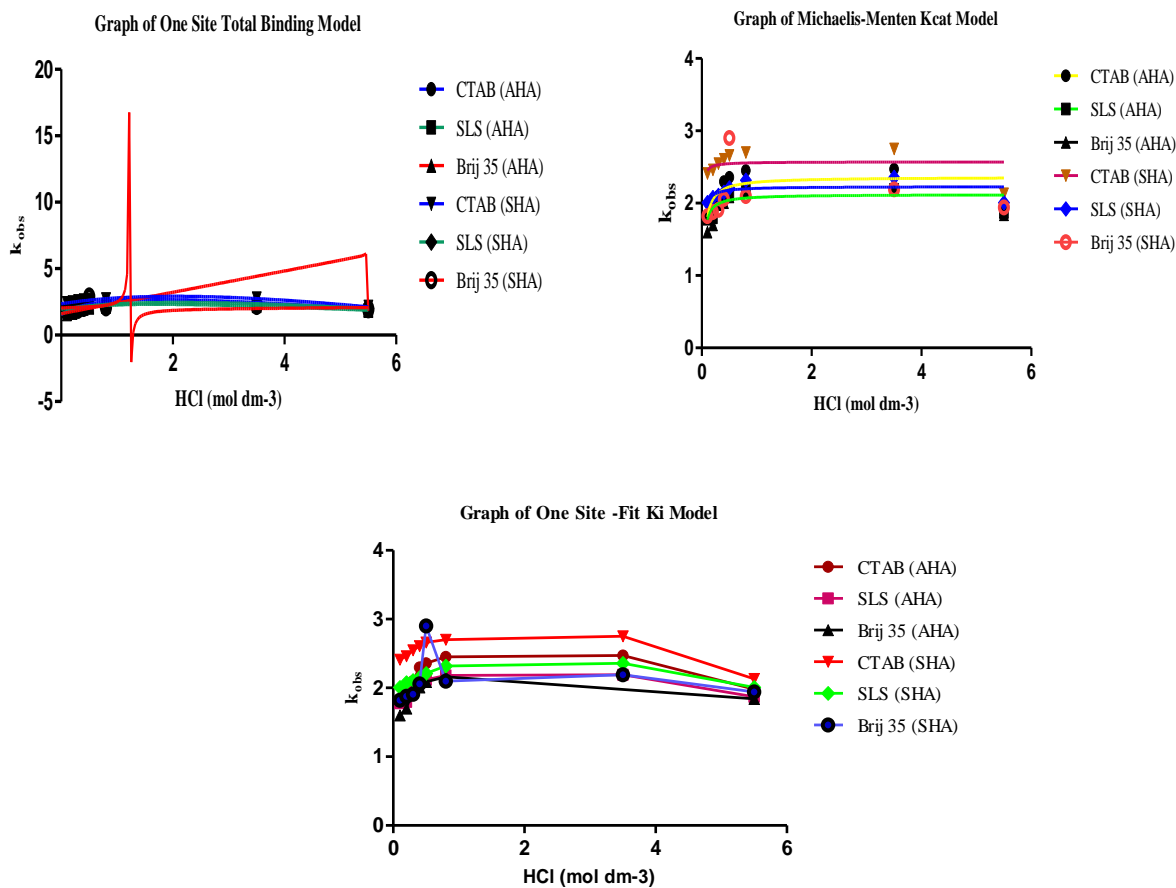
Table: 02- Kinetic parameters obtained for the acid hydrolysis of carboxylate ester with nucleophile in different surfactants.

Kinetic parameter	$10^5 \, k_{obs} \, (s^{-1})$					
	AHA			SHA		
	CTAB	SLS	Brij 35	CTAB	SLS	Brij 35
Bmax	2.436	1.506	0.0007773	7.022	2.775	-0.09510
Kd	0.8156	0.7487	-5.499	5.175	2.751	-1.226
NS	-0.3062	-0.1907	0.8020	-0.6994	-0.3244	0.02811
R^2	0.9540	0.9205	0.9336	0.9819	0.9955	0.3172
logKi	-	-	-	-	-	-
Ki	-	-	-	-	-	-
Kcat	2.360	2.121	-	2.572	2.230	-
Km	0.03060	0.01961	-	0.004924	0.01150	-
Vmax	2.360	2.121	-	2.572	2.230	-
Kcat/Km	786	1116	-	6430	1939	-

For the reaction protocol surfactant concentration (1.0×10-3 M) HCl = 0.1 M, temp 27°C and variation of nucleophilic concentration (1.5 to 7.0Mm), the resultant data summarized in (Table: 03). The reaction rate was increased with increasing the concentration of nucleophile. We observed that the kobs' value for the reaction of PNPA increases with the increasing concentration SHA and AHA in the presence and absence of cationic surfactant. We observed that the kobs' value for the reaction of PNPA increases with the increasing concentration SHA and AHA in the presence and absence of cationic surfactant. Kinetic rate data Effect of surfactant for the hydrolysis of carboxylate ester (PNPA) by Nucleophiles with various concentrations of different surfactants at 27°C and 40°C.

The kinetic rate data of substrate (PNPA) at various concentrations of cationic, anionic and nonionic surfactants are summarized in (Table: 05). Resultant data represent that cationic, anionic and nonionic surfactants play a significant role in the hydrolysis of PNPA with both nucleophiles. For the resultant data of the kinetic study, the reactivity order of the surfactant is CTAB>SLS> Brij-35. The binding constant optimized on the basis of the binding models with the help of prism graph pad software. We use the michaelis –menten Kcat [9-10], one site total binding [5-7] and one site fit Ki [8] model equation (1, 2, 3 and 4) are mentioned above. The experiential data were treated with equations (1, 2, 3 and 4) to determine the value of Kd, Ki, Bmax, Kcat, Km, and Kcat/Km with different conditions were summaries in (Table – 4 and 6). The summarised data Kd (4542), Ki (19680), Kcat (4.7) and Kcat/Km (52) were supporting evidence for the nucleophile SHA more reactive than AHA in presence and absence of surfactants, and nucleophile is more reactive in the presence of surfactant. The kinetic modeling data and graph (Fig: 4.4, 4.5, 4.6) support the resultant data that the CTAB is more reactive then both the surfactant in SHA. The represented data Kd, Ki, Kcat and Kcat/Km was support as evidence proof for the temperature effect on the reaction media as a plotted graph (Fig: 4.7, 4.8, 4.9).

Table 03 – Effect of nucleophile for the hydrolysis of carboxylate ester with nucleophiles in presence and absence of surfactants.

S.N.	Nu. mM	$10^5 \, k_{obs} \, (s^{-1})$			
		NIL		SURFCANT (CTAB)	
		AHA	SHA	AHA	SHA
1	1.5	0.24	0.75	2.10	3.21
2	3.0	0.30	0.98	2.5	3.30
3	4.5	0.45	1.0	2.8	3.85
4	5.0	0.65	1.25	3.0	4.10
5	6.5	0.78	1.55	3.10	4.21
6	7.0	0.98	2.30	3.22	4.45

Reaction condition [PNPA] = (1.6×10⁻⁴M), [Surfactant] = (1.0×10⁻³M), [Temp] = 27°C.

Fig: 4.4, 4.5, 4.6- Graph modeling data for acid hydrolysis of carboxylate ester with nucleophile in presence and absence of surfactant.
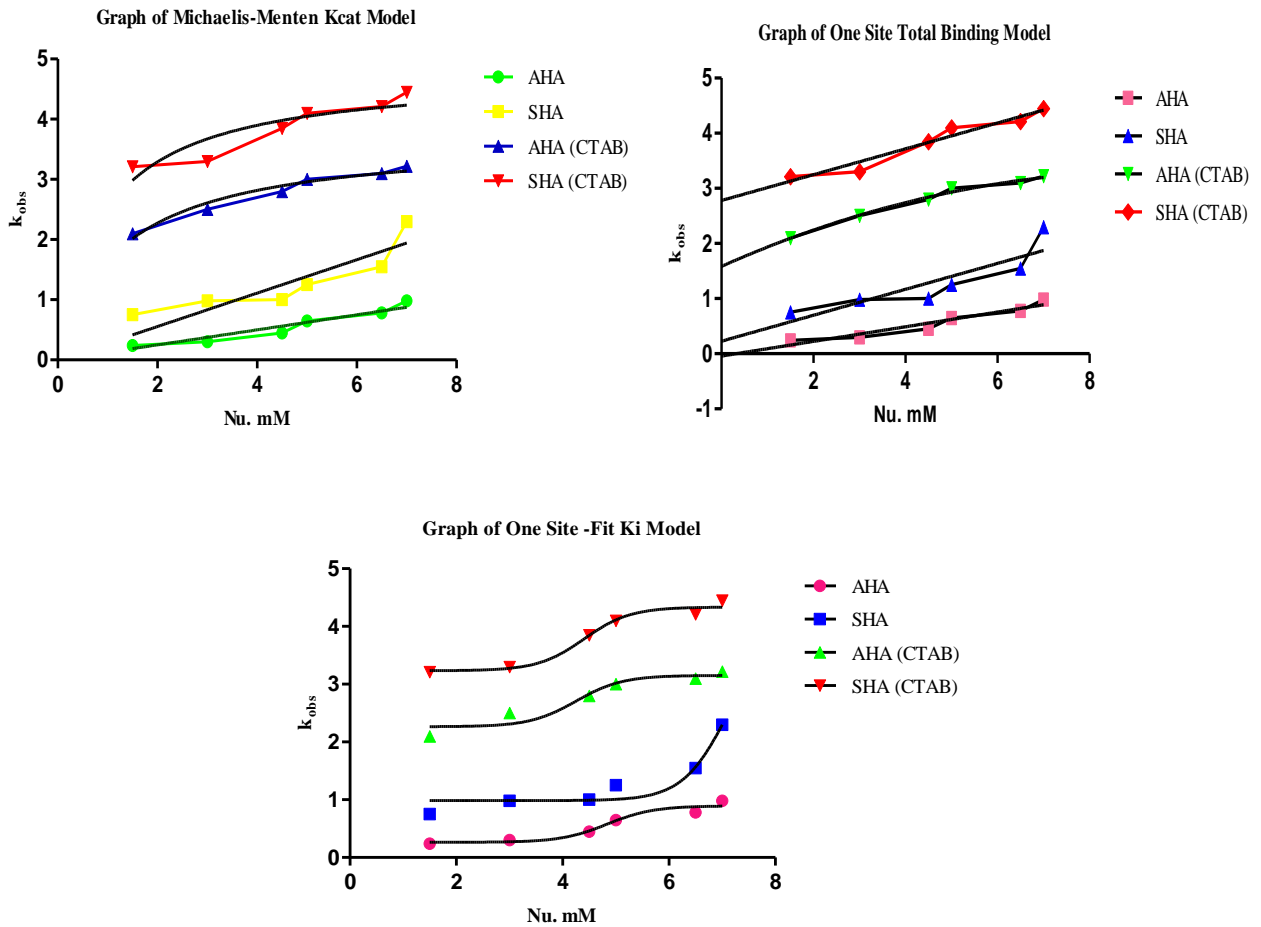

Graph of Michaelis-Menten Kcat Model

Graph of One Site Total Binding Model

Graph of One Site -Fit Ki Model

Table: 04 - Kinetic parameters obtained for the hydrolysis of carboxylate ester with with nucleophile in presence and absence of surfactant.

Kinetic parameter	$10^5 \, k_{obs} \, (s^{-1})$			
	NIL		SURFCANT (CTAB)	
	AHA	SHA	AHA	SHA
Bmax	0.5966	1.028	289.8	17.70
Kd	5327	7839	116.4	4542
NS	0.1326	0.2349	-2.117	0.2305
R^2	0.9520	0.9266	0.9193	0.9772
logKi	4.808	6.762	3.841	4.294
Ki	64251	5.783e+006	6929	19680
Kcat	7.985e+022	2.828e+024	3.700	4.779
Km	6.389e+023	1.019e+025	1.255	0.9047
Vmax	7.985e+022	2.828e+024	3.700	4.779
Kcat/Km	12.5	28	30	52

Table: 05- Kinetics data for the hydrolysis of carboxylate ester with nucleophile in various concentrations of surfactants.

S.N.	Surf. mM	$10^5 k_{obs}$ (s⁻¹)											
		AHA						SHA					
		CTAB		SLS		Brij-35		CTAB		SLS		Brij-35	
		27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C
1	0.0	0.25	0.50	0.25	0.50	0.25	0.50	0.78	1.0	0.78	1.0	0.78	1.0
2	1.0	1.81	3.21	1.98	3.09	1.60	3.01	2.41	4.99	2.01	4.02	1.82	3.98
3	2.0	2.48	4.50	2.31	4.36	2.11	4.22	4.11	8.23	3.84	7.32	3.59	7.20
4	3.0	3.58	6.89	3.32	6.60	2.78	5.11	5.01	9.98	4.64	9.50	4.21	8.40
5	10	2.41	4.85	2.11	4.24	1.99	2.01	4.21	8.44	4.10	8.10	4.00	8.10
6	20							3.79	6.97	3.34	6.60	3.01	6.10

Reaction condition [PNPA] = (1.6×10^{-4}M), [Nu] = (1.6×10^{-3}M), [Temp] = 27°C& 40°C.

Fig: 4.7, 4.8, 4.9 Graph of modeling data for the acid hydrolysis of the carboxylate ester with nucleophile in various concentration of surfactant
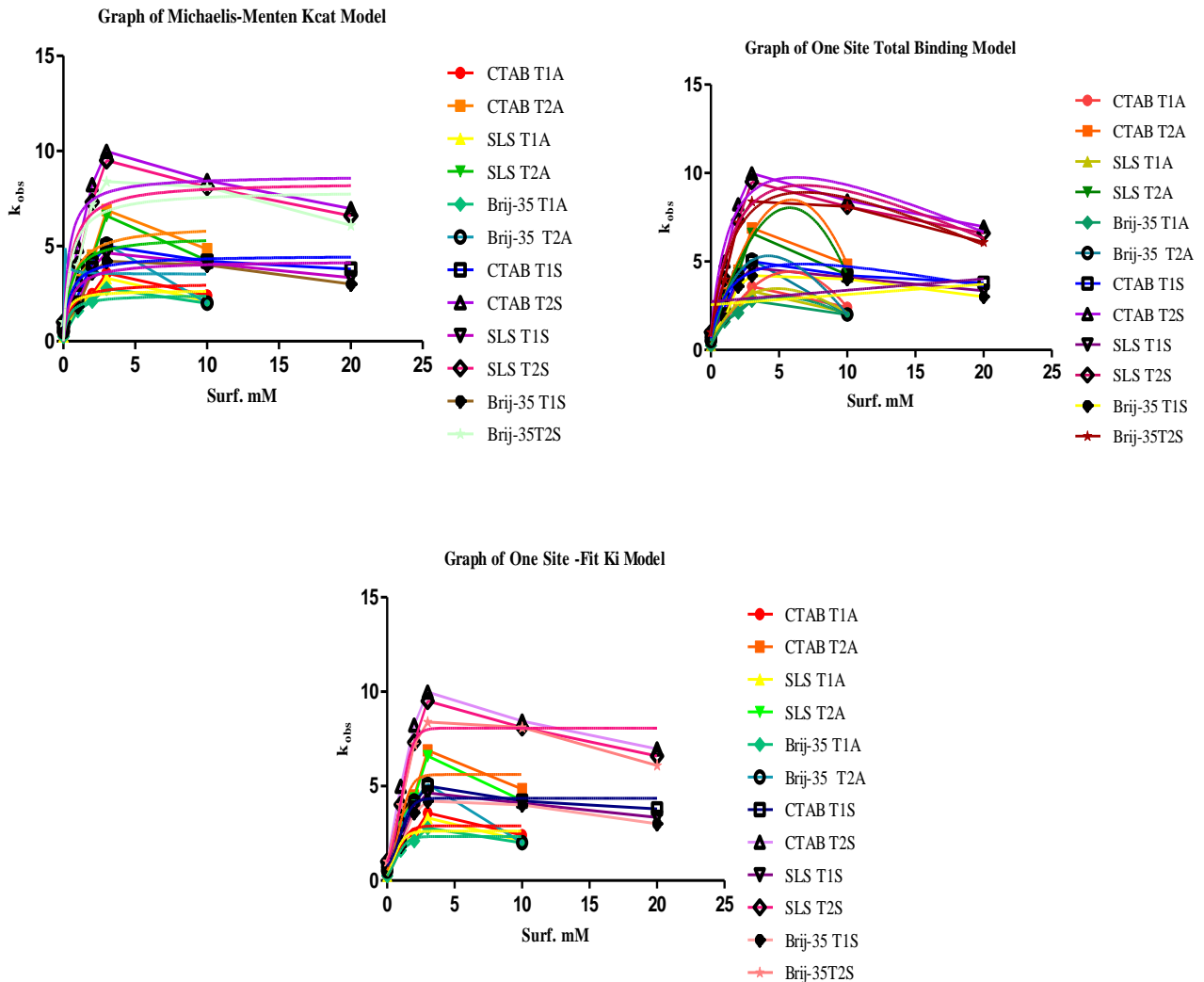
Table: 06 Kinetic parameters obtained for the acid hydrolysis of the carboxylate ester with nucleophile in various concentration of surfactant.

Kinetic parameter	$10^5\ k_{obs}\ (s^{-1})$											
	AHA						SHA					
	CTAB		SLS		Brij-35		CTAB		SLS		Brij-35	
	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C
Bmax	1758	8292	16.29	7886	13.48	27.11	6.476	13.90	-233800	14.47	-33430	14.17
Kd	113.6	184.4	6.150	181.3	6.135	5.804	1.630	1.546	2.913e+009	2.024	2.236e+008	2.201
NS	-14.01	-42.22	-0.8273	-40.85	-0.6633	-1.566	-0.1518	-0.3525	0.06434	-0.3776	0.05844	-0.3815
R^2	3.58	6.89	3.32	6.60	2.78	5.11	5.01	9.98	4.64	9.50	4.21	8.40
logKi	2.41	4.85	2.11	4.24	1.99	2.01	4.21	8.44	4.10	8.10	4.00	8.10
Ki							3.79	6.97	3.34	6.60	3.01	6.10
Kcat	3.070	6.128	2.673	5.538	2.449	3.522	4.517	8.721	4.223	8.381	-	7.924
Km	0.4310	0.5878	0.2151	0.4693	0.3397	-0.03771	0.4322	0.3520	0.4947	0.4991	-	0.4814
Vmax	3.070	6.128	2.673	5.538	2.449	3.522	4.517	8.721	4.223	8.381	-	7.924
Kcat/Km	71	105	127	119	73	106	104	249	86	169	-	165

Conclusion

Kinetic model Michael Menten Kcat, one site binding constant and one site fit Ki model support correlation and evidence for the explanation of our published kinetics results. As per resultant data, acid-catalyzed hydrolysis of carboxylate ester, decrease in rates at higher acidity, due to the water activity & decreasing the pH. The experimental data shows that the SHA has higher catalytic activity compared with AHA in acidic micellar media. In this study, we report, that raising the concentration of nucleophile increase the reaction rate in the presence and absence of surfactant. In the presence of a surfactant reaction rate higher than the absence of surfactant on both nucleophiles. The models support and evidence for the all resultant data, that the Michael Menten Kcat represent the evidence for the above resultant data. One site binding constant and one site fit Ki model support the explanation of resultant data of acid hydrolysis.

Acknowledgement

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