Study the Experimental Data of Hydrolysis Reaction of Carboxylate Ester with nucleophile in Cationic Microemulsion Media Using Kinetic Models

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Abstract

We analyze the obtained experimental data of Ester hydrolysis test and it's processing to obtain the kinetic parameter by specific modeling techniques. The compare alongside was denominated twisting nonlinear measure and consists in the conformable to graph plot of a dataset of kinetic parameter Vmax and Km from the Michaelis-Menten equation. The data were putted in simple kinetic models like Michaelis-Menten, one site fit ki, and one site total binding constant gave the kinetic parameters Kcat, Vmax, Km, logKi, Ki, Bmax, Kd and NS. The calculations are presented by specific better statistics mist with the using of the software graph paid prism. The rate matters were related by spin-off ten point's kinetic parameter datasheet. The obtained kinetic parameters supported the experimental figure during the reaction and result. The development kinetic parameter is to support the result that the cationic surfactant CPC is more reactive than CTAB.

Key words: Kinetic, Surfactant, CTAB, CPC, Michaelis-Menten.

Abbreviations:

PNPA - P-Nitrophenyl acetate

SHA - Salicylhydroxamic acid

CPC - Cetylpyridinium chloride

CTAB – Cetyl trimethyl ammonium bromide

Bmax - Maximum specific binding

Kd - Equilibrium binding constant

NS – Non specific binding

Vmax – Maximum velocity

Kcat – Turnover number

Km – Michaelis menten constant

Log Ki – Molecular equilibrium dissociation constant

Ki – Equalibrium dissociation constant

1. Introduction

Kinetic modeling is a technique that is very useful in relation to chemical reaction and properties. The processes involved are mainly chemical and physical reactions. Such changes proceed at a reaction rate and with certain kinetics. As per our early research the reaction of carboxylate ester with hydroxamate ion in cationic microemullsion environment obtained experimental facts. The microemulsions are thermodynamically stable, clear reaction medium. A microemulsion is a single optically isotropic and thermodynamically stable liquid solution [1]. The microemulsions are basically two class oil in water and water in oil but we used the oil in water are as a reaction medium [2-5]. The term microemulsion was first coined by the professor schulman from Columbia university along with his coverker in 1959 [6]. However, the definition of ME was given by Danielsson and Lindman in the year 1981[7] as "the transparent, homogenous optically isotropic solution which acquires thermodynamic stability."[8, 9] The droplet size of ME ranges from 10 to 100 nm [10]. The microemulsion solution enhances the permeability and solubility of substance and provide well reaction medium [11]. Recent year's microemulsion medium was used for the

chemical and electrochemical studies of nano-partical in different field [12-16]. The conventional method of pesticides formation replaced by water based microemulsion formulation method [17]. In drug delivery system microemulsion medium play vital role in pharmaceutical industries [18-23]. We use microemulsions as a reaction medium for the hydrolysis reaction of carboxylate ester with hydroxamic acid in specific conditions. The hydrolysis of P-Nitrophenyl acetate with hydroxamate ions recently interest of studied [24, 25].The obtained experimental data was explained by the Appling of different kinetic models in this paper. The Kinetic modeling allows us to explain these changes and their rates quantitatively. Subsequently, the kinetic modeling techniques apply as an important and powerful tool for the explanation of reaction mechanism. The considerate of the basic mechanisms is fundamental for excellence modeling and quality control. The kinetic study was required for the knowledge of basic concept in reaction. The thermodynamic study useful for the explanation of the reaction pathway and energy and entropy vary in reaction. It's only given the knowledge of force in reaction. Due to thermodynamic cannot explain the reaction rate during reaction time. This is only discuses by the kinetics. The reaction take place with certain speed at time is known as reaction rate. The chemical kinetics was first established Arrhenius and van't Hoff on the nineteenth century. In the twentieth century Ball, Stumbo [26-27] and Bigelow pioneered kinetic principles in food processing.

Also, the measurement of kinetic parameter in specific condition was very difficult. However, a simplified kinetic model useful in studying chemical processes could be used like Michael-Menten, one site fit binding and one sit binding models. In current age the study of microemulsion is important due to the advantage and broad application in different area [28-29]. Wide reviews on the physicochemical and electrochemical characterization of microemulsions

are obtainable [30-33], but the kinetic modeling technique was never being applied for the correlation and explanation of experimental data. So for in this paper we are applying simple kinetic models for the correlation and explanation of our previous published experimental data in microemulsion media.

2. Experiment

2.1 Material:

As per our research work, we used many required chemicals PNPA (p-Nitrophenyl acetate), SHA (Salicylhydroxamic acid), CTAB (Cetyl trimethyl ammonium bromide), CPC (Cetylpyridinium chloride), n-Butanol, n-Hexane for the preparation and chemical reaction of microemulsion [34-35].

2.2 Preparation of stock solution:

Stock solution was prepared by mixing the appropriate amount of reagents with double distilled water. The substrate stock solution was prepared by mixing the appropriate amount of PNPA with double distilled water by the help of magnetic stirrer. Microemulsion stock solution was prepared mixing the surfactant with double distilled water and added co-surfactant and oil phase with the help of magnetic stirrer, finally clear thermodynamically stable solution appear. The nucleophile stock solution prepared by mixing the appropriate amount of SHA with double distilled water and shack vigorously. The evaluation of thermodynamic stable microemulsion formation by following methods:

2.21 Visual observations: visual observation of the microemulsion formation done to check the parameter such as transparency and phase separation etc.

2.22 Measurement of pH: The pH   of the microemulsion is an important parameter as change in the pH may result in the instability of microemulsion. The pH of the microemulsions was determined by the calibrated pH meter.

2.23 Electric conductivity: Electric conductivity of microemulsion was determined by nano particle size 100. The calibrated conductivity meter was used for the conductivity measurement.

2.3 Detection Method:

Spectrophotometric detection method used for the determination of reaction rate. We detect the λmax at 400nm with the help of uv-vis-spectrophotometer and calculate the reaction rate for the reaction according to our previously research work [35]. The experimental data (Table: 01) was obtained by the reaction of substrate PNPA with a nucleophile (SHA) in a specific microemulsion medium by spectrophotometric methods. In reaction medium the concentration of reactant $[PNPA] = 1.0 \times 10^{-4}M$, nucleophile $[SHA] = 1.0 \times 10^{-3}$ and maintain the pH = 7.7 on reaction using phosphate buffer and temperature 27 °C.

2.4 Data analysis method:

We use this obtained data for the correlation and explanation by the kinetic models (Michael-Menten, one site fit ki, and one site total binding) with the help of software graph paid prism. The modeling techniques were used for the more explanation and correlation of given experimental data (Table: 01).

Table 01: Represented the experimental data of reaction of carboxyate ester in cationic microemulsion media.

ME	W_0	Rate Constant			
		CTAB		CPC	
		$10^3 k_{obs}(s^{-1})$	$K_2(M^{-1} S^{-1})$	$10^3 k_{obs}(s^{-1})$	$K_2(M^{-1} S^{-1})$
1	5	1.01	1.95	3.24	5.32
2	6	1.25	3.05	3.78	5.53
3	7	1.68	3.65	4.21	6.04
4	8	2.04	4.04	4.48	6.43
5	9	2.23	5.62	5.09	6.99
6	10	2.3	6.08	5.39	7.27
7	11.6	2.39	7.39	5.93	7.88
8	12.6	3.74	7.91	6.16	8.21
9	13.6	4.9	8.23	6.59	9.87
10	15.1	5.16	9.95	6.97	10.5

3. Result and Discussion

The observed investigational facts were second-hand to conclude the kinetic parameter by using the kinetic model Michaelis–Menten Kcat [31-32], one site total binding constant [36-38] and one site fit Ki [39]. In accordance with Michaelis–Menten, Km Michaelis-Menten constant, Kcat turnover number, binding constant given in Kd equilibrium binding constant and Ki equilibrium dissociation constant. The practical truth was treated with equations (1, 2, 3 and 4) to determine the value of Kcat, Km, Vmax, Bmax, Kd, and Ki, in (Table: 02). The Km, Kcat, Kcat/Km

calculated data evidence and support for the observed result. Binding constant model parameters Bmax, Ki and Kd value prove the result that CPC is more reactive than CTAB in microemulsion media. Maximum specific binding Bmax value (9.596), equilibrium binding constant Kd (12.99), and turnover number (16.15) of CPC was higher than CTAB represented in the table and graphical representation of all models (Fig: 01, 02 and 03). The maximum specific binding value represents the higher specific binding properties of CPC and the equilibrium binding constant value indicate the overall binding value of CPC is higher than CTAB. The graphical representation of (Fig.-1) indicate graph of michaelis-menten Kcat model represent the triangle spot line of CPC is higher than other line. On the next graphical representation (Fig.-2) graph of one site fit ki model indicate the triangle spot line of CPC higher than other line and (Fig.-3) represent graph of one site total binding model indicate the higher value of CPC than other. So the all graphical representation indicates the CPC was more reactive than CTAB, and it is evidence and supports of our research data.

$$Y = Vmax*X/(Km + X) \qquad\qquad (1)$$

$$Y = Et*kcat*X/(Km + X) \qquad\qquad (2)$$

$$Y=Bmax*X/ (Kd+X) + NS*X + Background \qquad (3)$$

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

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

Table 02: Represented the kinetic parameter obtained by experimental data of reaction of carboxyate ester in cationic microemulsion media

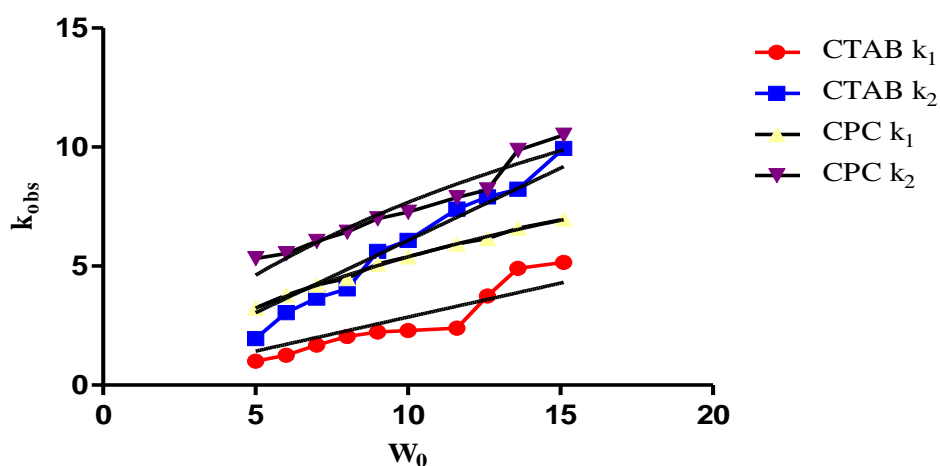| Kinetic Parameter	Rate Constant			
	CTAB		CPC	
	$10^3 k_{obs}(s^{-1})$	$K_2(M^{-1} S^{-1})$	$10^3 k_{obs}(s^{-1})$	$K_2(M^{-1} S^{-1})$
B_{max}	5.556e+007	6.031	9.596	90.95
K_d	7.990e+012	1.642	12.99	-3.446e+008
NS	0.4055	0.6767	0.1217	0.5046
R^2	0.9236	0.8661	0.8703	0.8388
logKi	12.11	9.167	9.071	10.71
Ki	1.277e+012	1.468e+009	1.177e+009	5.153e+010
K_{cat}	-	3.779e+014	16.15	22.59
K_m	-	6.219e+014	19.99	19.44
V_{max}	-	3.779e+014	16.15	22.59
K_{cat}/K_m	-	5.9	8.0	11.6

Fig 01: Graph of Michaelis-Menten Kcat Model for reaction of carboxylate ester in cationic microemulsion media.
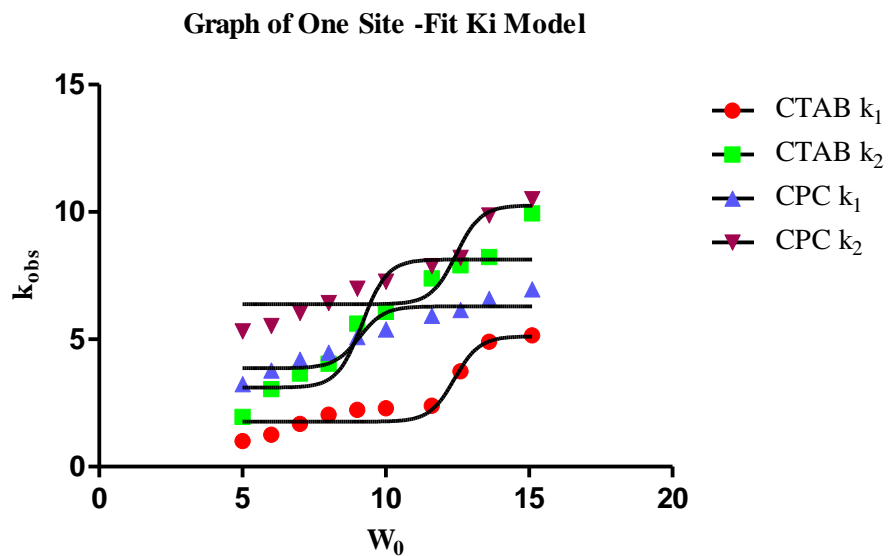
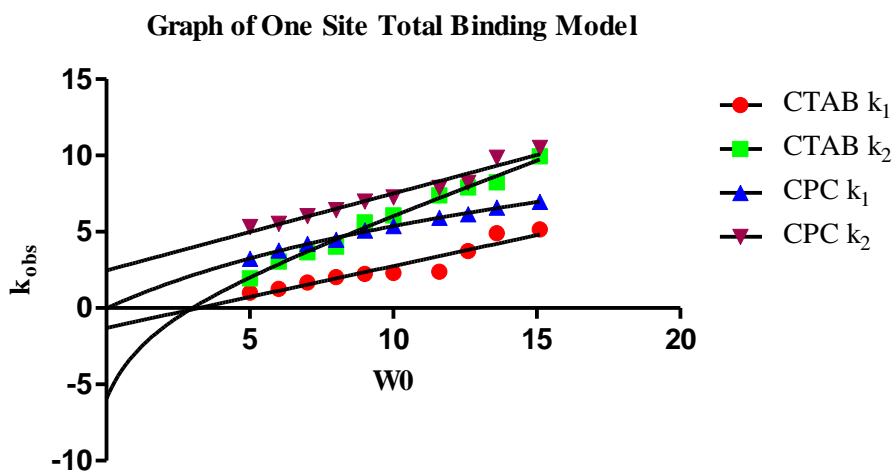Fig 02: Graph of One site-fit Ki Model for reaction of carboxylate ester in cationic microemulsion media.

Fig 03: Graph of One site total binding Model for reaction of carboxylate ester in cationic microemulsion media.

4. Conclusion

The obtained kinetic parameter was support and evidence for the published experimental work. According to experimental data, the water content (W_0) was an important factor that determines the reaction rate. The nucleophilic reactivity in the cationic microemulsion media substrate molecule located into a hydrophobic droplet and anionic nucleophile reside in water content. The result represents that the cationic microemulsion CPC is more reactive than CTAB. Michaelis menten constant (Km), Molecular equilibrium dissociation constant (logKi) and equalibrium dissociation constant (Ki) represent the dissociation of substrate is fast in hydrolysis reaction in cationic microemulsion CPC compare to CTAB. The Kinetic parameter value of Maximum specific binding (B_{max}) was higher in cationic microemulsion CPC represents the more binding nature compare to CTAB. The obtained parameter Equilibrium binding constant (K_d) and Non specific binding (NS) support the our experimental data that the cationic microemulsion CPC more reactive than CTAB. The Maximum velocity (V_{max}) and Turnover number (K_{cat}) show the higher reaction velocity of reaction in cationic microemulsion CPC than CTAB. All the mathematical calculated data indicate the hydrolysis reaction of PNPA with hydroxamite ion in cationic microemulsion system accelerates the reaction compare to other medium and the cationic microemulison with CPC is more favorable than CTAB. The concluded data will be useful for the decomposition of pesticides and use for development of new environmental protection methodology in future aspects.

We would like to acknowledge providing the modeling software support of Prof. Dr. K. K. Ghose and their scholar, Pt. R.S.U. Raipur, C.G., India, and heartily acknowledge to prof. Dr. S. Sar, bit, durg, c.g. for valuable guideline.

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