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Experiments
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A NOVEL APPROACH FOR KINETIC STUDY OF ALKALINE HYDROLYSIS OF ETHYL ACETATE

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Abstract. We present an innovative electromotive force (EMF) measurement technique to study the kinetic behavior during alkaline hydrolysis of ethyl acetate. The explicit feature of this research is the application of green chemistry ideas that are inherent in the experiment. Using the new approach, we find that the kinetic behavior of the reaction under study follows second order with an estimated rate constant value at 25°C to be 2.45×10^{-3} cm^{-3} min^{-1}. This value is in excellent agreement with the conventional end-point neutralization titration method discussed previously in the literature. The novel EMF measurement technique is simple, fast, accurate and eco-friendly. Keeping in view of long-term sustainability of the ecosystem, we feel that there is an urgent need to switch over from conventional laboratory practices to green chemistry approaches. Further, the method discussed here may prove to be extremely useful for teachers, researchers and students who wish to carry out kinetic study of other systems.

Keywords: kinetic study; emf measurement; eco-friendly

Introduction

During the past two decades there has been growing concern to carry out conventional laboratory experiments in chemistry using fresh and novel approaches. Outcome of such efforts can be seen in a number of publications where the researchers across the globe are engaged in executing micro scale experiments using alternate approaches (Roesky et al., 2009; Mohamed et al., 2012; Skinner, 1997; Hofstein &Mamlok-Naaman, 2007; Das Sharma & Dhanamma, 2009). Application of green chemistry through design of innovative approaches is one of the primary goals of all these studies. In addition, such initiatives also provide opportunities to develop bright working plan for each experiment, which in itself is a challenging task. Our attempt in this direction during the past ten years yielded a number of significant contributions (Das Sharma & Dhanamma, 2009; Das Sharma, 2009; 2013; Das Sharma & Karuna, 2014; Das Sharma et al., 2016) and we realized that such efforts naturally attract scientific inquisitiveness in the minds of many researchers and students. The underlying experimental innovation allows them to discover critical processes that need to be considered while performing an experiment using a new approach.

Here we carry forward our endeavor on green chemistry research program, where the main aim is to work for continuous evolution of simplified methods by adopting environment friendly approaches. Therefore, in this communication, we present an alternative approach to estimate the rate constant, k, for alkaline hydrolysis of ethyl acetate. This is one of the most common reactions in chemistry and to our knowledge this experiment is conducted in many universities across the globe as a routine laboratory exercise [Mulcahy, 2011). The hydrolysis of ester occurs according to the equation

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH \tag{1}$$

As the reaction (1) progresses, reaction kinetics is conventionally studied by measuring the concentration of hydroxide ions employing end-point titration method at different time intervals (Khosla et al., 2001). Reaction (1) follows second order kinetics and at a particular temperature the rate law is represented by

$$\text{Rate} = k\,[CH_3COOC_2H_5]^1\,[NaOH]^1 \tag{2}$$

with overall order 1+1=2.

The alternative approach proposed here is based on the concept of measurements of electromotive force (EMF), which is generated in response to the changes in pH values. The rate constant value obtained from our newly adopted EMF measurement method is also compared with that of conventional end point titration method (Khosla et al., 2001). The results are discussed with a special emphasis on the novel attitude and approach to green chemistry besides highlighting the advantages of the proposed method.

Rate law and its relation to measurements of electromotive forces

Before describing the experimental procedure, it is necessary to introduce the rate law as well as the underlying principle pertaining to the newly adopted unconventional EMF measurement method. As stated above, the kinetic of reaction (1) is conventionally studied by determining the concentrations of the reactant NaOH at regular interval of time. The integrated rate law for second order reaction with equal concentration of both the reactants is given by

$$k=x/at(a-x) \tag{3}$$

where “a” represents initial concentrations of the reactants, viz., ester or NaOH, “x” corresponds to concentration of product formed or concentration of reactant converted to product at time t, and (a–x) denotes concentration of left over reactant at time t.

We demonstrate that the kinetic study of the reaction can also be performed potentiometrically through measurement of EMF. The basic premise of the EMF method is that the electromotive force (EMF) generated in a galvanic cell consisting of a reference electrode and a suitable indicator electrode in response to pH changes can be measured. In the present study, quinhydrone indicator electrode and saturated calomel electrode as the reference have been used. The quinhydrone electrode consists of acid solution saturated with quinhydrone and a platinum (Pt) electrode is dipped in the solution. A redox electrode has been constructed and therefore the following reduction reaction occurs at the indicator electrode

$$Q + 2H^{+} 2e \rightleftarrows H_2Q \tag{4}$$

From Nernst equation, the potential of this electrode can be written as

$$E_{QH} = E^{0}_{QH} - \frac{RT}{2F}\, 2.303 \log \frac{[H_2Q]}{[Q][H^{+}]^{2}} \tag{5}$$

where E^0_{QH} represents the standard electrode potential, R is the universal gas constant. T is the room temperature in Kelvin and F = 1 Faraday (~96500 Coulomb).

Since quinhydrone (QH) is a equimolar mixture of quinine and hydroquinone, $[H_2Q] = [Q]$, then Eq. (5) can be written as

$$E_{QH} = E^{0}_{QH} + \frac{RT}{F}\, 2.303 \log [H^{+}] \tag{6}$$

At room temperature of ~25°C, the above equation reduces to

$$E_{QH} = E^{0}_{QH} + 0.059 \log [H^{+}] \tag{7}$$

The cell construction can typically be represented as

$$\overset{\ominus}{\mathrm{Hg}},\ Hg_2Cl_2\,(\mathrm{solid}),\ KCl\,(\mathrm{sat.\ sol^{n}.}) \,\|\, H^{+}\,(\mathrm{sol^{n}.})\ Q.\ H_2Q \,\|\, \overset{\oplus}{\mathrm{Pt}}$$

The EMF of the cell is give by

EMF = Reduction potential of cathode (E_{QH}) – Reduction potential of anode (E_{SCE}) (8)

Substituting Eq. (7) in Eq. (8),

$$EMF = E^{0}_{QH} + 0.059 \log [H^{+}] - E_{SCE} \tag{8}$$

Since E^0_{QH} and E_{SCE} are both constants at a particular temperature, EMF depends on $[H^+]$

Thus as the reaction progresses based on $[H^+]$, the change in the voltage or millivoltage value at each time interval can be estimated.

Experimental

Analar grade chemicals were used for this work. The stock solutions of NaOH, HCl and ethyl acetate were prepared using double distilled water. Stock solutions of HCl and NaOH were standardized against standard sodium carbonate and oxalic acid solutions, respectively. In this study we conducted two experiments. The first one was based on traditional indicator-based end point titration method and the second one was conducted on the basis of EMF measurements. These procedures are described below.

Indicator-based end point titration method

The following steps were carried out: (i) 80 cm^3 of water and 10 cm^3 M/4 ethyl acetate were taken in a reagent bottle; (ii) 10 cm^3 of M/4 NaOH solution was pipetted out and poured in the reagent bottle and the time of half discharge was noted down; (iii) 10 cm^3 of reaction mixture from the reagent bottle was immediately pipetted out and poured in a conical flask containing 40 cm^3 of M/40 ice-cold HCl; (iv) the solution was titrated against M/40 NaOH solution using phenolphthalein indicator. Steps (iii) and (iv) were repeated by pipetting out 10 cm^3 of reaction mixture in the reagent bottle at a regular interval of 10 minutes. The titre values obtained in the experiment corresponds to the concentration of unreacted HCl at the chosen time intervals.

Since 40 cm^3 of M/40 HCl was taken in the conical flask, (40–first titre value) in cm^3 corresponds to the initial concentration “a” of the reactant NaOH or ester (Eq. (3)). Likewise, (40–other titre values) obtained at every ten minute interval yield the left over reactant at time intervals 10, 20, 30, etc. These values therefore represent (a–x). The rate constant k was estimated using Eq. (3).

EMF measurement method

The experimental set up for EMF measurement method is shown in Fig. 1. Different steps were carried out in this method: (a) EMF was measured by making the indicator electrode with 20 cm^3 M/40 HCl saturated with quinhydrone, (b) 40 cm^3 of water and 5 cm^3 M/4 ethyl acetate were taken in a reagent bottle, (c) 5 cm^3 of M/4 NaOH solution was pipetted out and poured in the reagent bottle and the time of half discharge was noted down, (d) 5 cm^3 of reaction mixture from the reagent bottle was immediately pipetted out and poured in the beaker containing 20 cm^3 M/40 HCl saturated with quinhydrone and the EMF was noted down. The difference of this EMF value and the EMF recorded in step (a) with 20 cm^3 HCl solution saturated with quinhydrone corresponds to the initial concentration (in millivolt) of reactant “a”.

The above step (i.e., step d) was repeated after every ten minutes interval with continuous stirring with the help of a magnetic stirrer to obtain EMF values at each interval, and thus (a-x) values at 10, 20, 30, minute intervals were estimated. The rate constant k was estimated using Eq. (3).

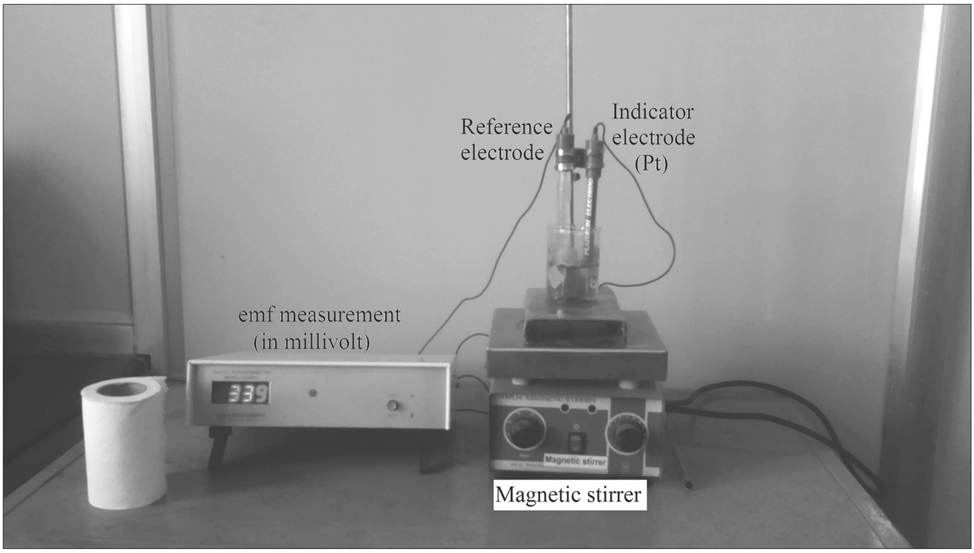

Figure 1. The experimental device

Results and discussion

The data obtained from the experimental runs related to both conventional titration as well as potentiometric approaches are presented in Tables 1 and 2 respectively. The rate constant values calculated for individual runs for both the experiments are remarkably close to each other (Tables 1 and 2). While the average rate constant value estimated from individual runs of conventional titration method is centered on (2.68±0.23) × 10^{-3} cm^{-3} min^{-1} at 25°C (Table 1), those from EMF method yields an average of (2.44±0.08) × 10^{-3} cm^{-3} min^{-1} (Table 2). Therefore, the average values obtained from both the methods are in close agreement with each other. In other words, our data suggest that within the limits of experimental error, they overlap with each other. Further, it can be noted that the standard deviation associated with EMF method is characterized by less scatter, indicating that this method is more precise compared to the conventional method.

Eq. (3) shown above can be rewritten as $1/(a–x) = kt + 1/a$. Therefore, a plot between $1/(a–x)$ and t would represent a linear relationship, where the slope of the line corresponds to the rate constant and the intercept on the y-axis would indicate 1/a. In order to examine what kind of relationship is observed from the data obtained in the present study, we plotted 1/(a–x) values with respect to time pertaining to both the experiments (Fig. 2). It is interesting to note that excellent linear relationships are observed for both the experiments, with high correlation coefficients of 0.991 and 0.996 (Fig.2). While the rate constant value for conventional titration approach comes out to be 2.23×10^{-3} cm^{-3} min^{-1} with 1/a= 0.086 cm^{-3} (Fig. 2a), the EMF method yields a rate constant value of 2.9×10^{-3} mv^{-1} min^{-1} with 1/a= 0.083 mv^{-1}. From the graph plotted in Fig 2(a), the initial concentration a=11.63 cm^3 can be compared with that of the measured value of 13 cm^3 (Table 1). Likewise, from Fig. 2(b) the initial concentration comes out to be 12.04 mv as against measured value of 12 mv (Table 2). Thus the initial concentration derived from Fig. 2(b) is significantly close to the measured value, once again establishing the fact that the EMF method is more precise than the conventional titration method. Furthermore, Eq. (3) itself represents straight line relationship of the form $y=m_1x$. Therefore, when x/a(a–x) values are plotted as a function of time, we expect a straight line relationship passing through the origin. It is noteworthy that such a linear correlation is indeed observed from our data (Fig. 3). The correlation coefficients are extremely high 0.969 (Fig. 3a) and 0.996 (Fig. 3b). This linear relationship clearly indicates that the reaction conditions represent second order, where the concentrations of both the reactants are equal (at least within ≈ 1%). The slopes of the straight lines represent the rate constant values, which in the present study have been found to be 2.53×10^{-3} cm^{-3} min^{-1} (Fig. 3a) and 2.45×10^{-3} cm^{-3} min^{-1} (Fig. 3b). In this context it is pertinent to mention that in a recent study on the determination of reaction rate and rate constant of the hydrolysis of ethyl acetate with sodium hydroxide at 28°C, Ikhazuangbe & Oni adopted the conventional titration method and reported a rate constant value of 3.0×10^{-3} cm^{-3} min^{-1}, which is slightly higher than the values obtained by us. The marginally high rate constant value obtained by them may be attributed to slight elevation in experimental temperature (Ikhazuangbe & Oni, 2015). Taken together, all these observations provide authenticity to our newly adopted EMF measurement method described in this study.

There are several advantages that emerge from the newly adopted EMF measurement method. Firstly, the experimental setup is neat and the procedure is simple. Secondly, it gives better estimates of initial concentration as shown graphically through Fig. 2 (a and b). Thirdly, the amount of chemicals needed to perform the new experiment is far less compared to the conventional method. Fourthly, the experiment is devoid of any titration to be performed within a stipulated time, thereby making the method trouble-free. Finally, the method also uses less number of breakable glass apparatus.

Table 1. Results obtained from conventional indicator-based end point titration method: temperature 25˚C; V_0 = 27 cm^3; a = (40–27) cm^3 = 13 cm^3

Sl. No.	Time interval (min)	Volume of NaOH (V_t, cm^3)	(a – x) = (40– V_t) cm^3	x = a–(a– x) cm^3	1/(a–x) cm^{-3}	x/a(a–x) cm^{-3}	Rate constant, k = x/at(a– x) cm^{-3}min^{-1}
1	0	27	–	–	–	–	–
2	10	30.6	9.4	3.6	0.1064	0.02946	0.00295
3	20	32.4	7.6	5.4	0.1316	0.05466	0.00273
4	30	33.6	6.4	6.6	0.1563	0.07933	0.00264
5	40	34.2	5.8	7.2	0.1724	0.09549	0.00239

Average value of k = 0.00268 = 2.68 × 10^{-3} cm-3min^{-1}
Rate constant, 'k' obtained from slope of Fig. 2a = 2.23 × 10^{-3} cm^{-}3min^{-1}
Initial concentration, 'a' obtained from intercept of concentration axis of Fig. 2a= 11.63 cm^{-3}
Rate constant, 'k' obtained from slope of Fig. 2b = 2.9 × 10^{-3} mv^{-1} min^{-1}
Initial concentration, 'a' obtained from intercept of concentration axis of Fig. 2b= 12.04 cm^{-3}

Table 2. Results obtained from emf measurement method: temperature 25˚C; measured value of EMF for 20 ml HCl solution = 340 mv; a = (340–328) mv = 12 mv = 13 cm^3 (Table 1)

Sl. No.	Time interval (min)	EMF (mv)	(a–x) (mv)	x = a–(a–x) (mv)	1/(a–x) (mv^{-1})	x/a(a–x) (mv^{-1})	x/a(a–x) (cm^{-3})	k = x/at(a– x) cm-^{3}min^{-1}
1	0	328	–	–	–	–	–	–
2	10	332	9	3	0.1111	0.02564	0.023669	0.00237
3	20	334	7	5	0.1429	0.05495	0.050718	0.00254
4	30	335	6	6	0.1667	0.07692	0.071006	0.00237
5	40	336	5	7	0.2000	0.10769	0.099408	0.00249

Average value of k = 0.00244 = 2.44 × 10^{-3} cm^{-3}min^{-1}
Rate constant, 'k' obtained from slope of Fig. 3a = 2.53 × 10^{-3} cm^{-}3min^{-1}
Rate constant, 'k' obtained from slope of Fig. 3b = 2.45 × 10^{-}3 cm^{-3}min^{-1}

Conclusion

Precise determination of rate constant of 2.45 × 10^{-3} cm^{-3} min^{-1} for alkaline hydrolysis of ethyl acetate at 25°C was carried out using novel EMF measurement technique. Based on the results obtained in this study we feel that the method will be extremely useful for researchers and students who wish to carry out kinetic study in any other system where the potential of the indicator electrode is a function of pH. As a note of concern we would also like to point out that depending upon the reaction chosen, it is quite possible that minor changes or innovations in the experimental set up or procedure may be required.

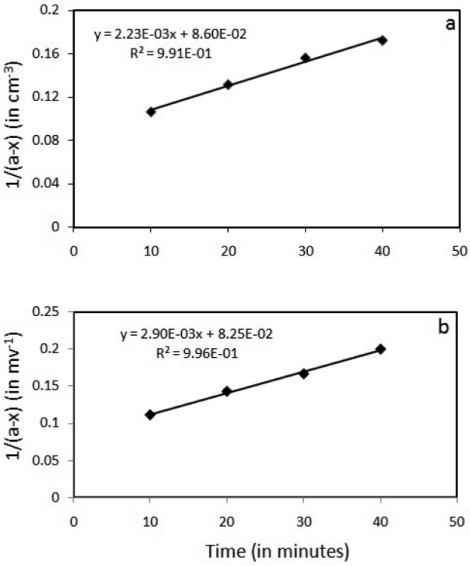

Figure 2. Experimental results

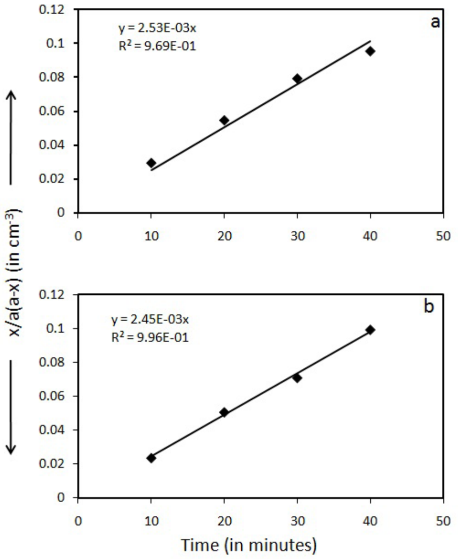

Figure 3. Experimental results

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