



Kinetic Study of Esterification Reaction

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Abstract

The Esterification kinetics of acetic acid with ethanol in the presence of sulfuric acid as a homogenous catalyst was studied with isothermal batch experiments at 50-60°C and at a different molar ratio of ethanol to acetic acid [EtOH/Ac]. Investigation of kinetics of the reaction indicated that the low of [EtOH/Ac] molar ratio is favored for esterification reaction, this is due to the reaction is catalyzed by acid. The maximum conversion, approximately 80% was obtained at 60°C for molar ratio of 10 EtOH/Ac. It was found that increasing temperature of the reaction, increases the rate constant and conversion at a certain mole ratio, that is due to the esterification is exothermic. Activity coefficients were calculated using UNIFAC program. Results showed deviation in activation energy in the non-ideal system of about 20% this is due to the polarities of water and ethanol compared to the non-polar ethyl acetate this dissimilarity leading to strong non-ideal behavior. The homogenous reaction has been described with simple power-law model. The chemical equilibrium combustion calculated from the kinetic model in agreement with the measured chemical equilibrium.

Keywords: Esterification, ethyl acetate, acetic acid, kinetics, non-ideal systems

1. Introduction

Esters are important classes of chemicals have many applications in a variety of areas such as solvents, plasticizers, pharmaceuticals and intermediate for many industries (Kirk and Othmer 1980, Yadav and Metha, 1994).

Esters are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing water that is formed (Hangx et al. 2001). The limiting conversion of the reactants is determined by the equilibrium. The equilibrium constant of esterification reactions have values ~1~10, which implies that considerable amounts of reactants exist in the equilibrium mixture. This problem is in practices surmounted by continuous removal all the product – especially water – from the reaction mixture through distillation. Tang et al. (2003) studied the process which contains sulfuric acid as catalyst (homogenous reaction) using a reactive distillation column with an overhead decanter and stripping column. High pure EtAC product was

obtained and all the outlet streams met product and environmental specification (Majid et al. 2008). The reaction rate is enhanced with added catalyst. Homogeneous and heterogeneous acids act catalytically in the esterification, because the limiting step in the reaction mechanism is the protonation of the carboxylic acid (Neil, 2004). This reaction is reversible, forming ester in the forward reaction and hydrolysis of ester occurs in the backward reaction. Efficient homogenous catalysts are mineral acids, such as H₂SO₄, HCl, HI and strong organic acids. The equilibrium composition is a weak function of temperature.

A common method of operating equilibrium limited reactions is to use an excess of one reactant in order to increase the conversion of the limiting reactant (Ismail et al. 2001, Maris and Jurgen, 2006).

This reaction shows a strong non ideal behavior due to presence of water and ethyl alcohol which is highly polar compared to the non polar methyl acetate. This dissimilarity leads to a strong non ideal behavior.

The situation concerning reactions in solutions or in non-perfect gases is much more complicated, here the true equilibrium constant has to be

expressed in terms of activities – or alternatively concentrations multiplied by activity coefficients (Denbigh and Turner, 1984). The main differences in the different chemical equilibria calculation is the type of physical model assume the models based on Maurer (1986a) treat the vapour phase as an ideal gas whereas most other model include vapour non-ideality terms such as vapour fugacity coefficients.

The esterification of Ac with EtOH has been widely studied, mainly because of its industrial uses (Mazoti et al. 1997, Ismail et al. 2001, Calvar el al. 2007) all investigated published either covered only a limited temperature range, covered a large excess of acid used at the different catalyst loaded and at a low conversion.

Pöpken et al. (2000) developed rate based model that contains activity coefficients from experimental data for acetic acid esterification with methanol. This is said to give a slight improvement on the kinetic model that uses mole fractions. Activity coefficients are used in the rate expressions for the system.

When reaction system reaches equilibrium the constraint is: $\sum_{i=1} r_i \mu_i = 0$

The chemical equilibrium constant is related to standard Gibbs free energy change of and can be further expressed by: $Ka = \prod_i (x_i \gamma_i)^{r_i} = \prod_i a_i^{r_i}$

Assuming that the reaction is only in the liquid phase. The chemical equilibrium constants have been determined experimentally as slight functions of temperature (Neil, 2004).

The measure of reaction rate of component A (acetic acid) in a constant- volume isothermal system, ignoring the backward reaction for a large excess of one reactant (Xu and Chuang, 1996, Popken et al. 2004,) and ignoring all the side reactions, is calculated as follows:

The esterification reaction is first written as;



Where A=Acetic acid, B=Ethyl alcohol, C= ethyl acetate and, D=Water

For the above reaction:

$$-r_A = \frac{\partial C_A}{\partial t} = \frac{\partial C_B}{\partial t} = k C_A C_B \gamma_A \gamma_B \quad \dots(1)$$

Where; γ_A and γ_B are activity coefficients.

Eq. 1 may be written in terms of X_A :

$$-r_A = C_{A0} \frac{\partial X_A}{\partial t} = k(C_{A0} - C_{A0} X_A) (C_{B0} - C_{A0} X_A) \gamma_A \gamma_B \quad \dots(2)$$

Let $M = \frac{C_{B0}}{C_{A0}}$ be the initial molar ratio of reactants,

$$-r_A = K C_{A0}^2 (1 - X_A)(M - X_A) \gamma_A \gamma_B \quad \dots(3)$$

By separation and rearranging;

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0} k \gamma_A \gamma_B \int_0^t dt \quad \dots(4)$$

γ_A and γ_B are considered constants for changes in their numeric values are negligible. The final result is:

$$\begin{aligned} \ln \frac{1 - X_B}{1 - X_A} &= \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \\ &= \ln \frac{C_B}{M C_A} = C_{A0} (M - 1) k \gamma_A \gamma_B t \quad M \neq 1 \quad \dots(5) \end{aligned}$$

And for ideal system, equation 5 may be written as (Levenspiel 1999);

$$\begin{aligned} \ln \frac{1 - X_B}{1 - X_A} &= \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \\ \ln \frac{C_B}{M C_A} &= C_{A0} (M - 1) k t \quad M \neq 1 \quad \dots(6) \end{aligned}$$

Where γ_A and $\gamma_B = 1$

The above mentioned kinetics (for ideal system) has been studied previously by (Ismail et al. 2001) which that did not taken into account the activity coefficient of the compounds in the mixture.

In this work, the esterifications of Ac with EtOH catalyzed homogenously have been investigated. Several experiment have been carried out to analyzed the influence of temperature, initial reactant molar ratio (excess of EtOH used) because there is a limited work in literature about this ratio, all literatures deal with studying the excess ratio of Ac acid used and taking in account the non- ideality at the liquid mixture, activity were used instead of mole fraction. The activity coefficients were calculated by UNIFAC equation, at a constant catalyst loading.

2. Experimental Work

Materials

Acetic acid and sulfuric acid were used of analytical grade (99.6% GCC) and (Schwefelsaure 99%) respectively, while commercial ethyl alcohol 95% was used.

Experimental Procedure

The experimental assembly consisted of 500 ml volumetric flask which serves as batch reactor fitted with along reflex condenser to prevent any loss of products, the reaction mixture was magnetically stirred. The reaction vessel was kept in stirred constant temperature.

Experiments was carried out at temperature between (50-60)°C, when temperature increases up to 60°C, the rate of hydrolysis reaction is higher than the esterification reaction (Liu and Tan,2001) and at different molar ratio of ethanol to acetic acid [10:1], [30:1] and [50:1] and at a constant catalyst loading [only one drop of sulfuric acid] till the pH of initial sample be 1.4,2.73 and 3.2 for M equal to 10.30 and 50 respectively. The volume of the reaction mixture remained constant at (300) ml during all experiments.

Acetic acid and catalyst were charge into reaction vessel after desired temperature was reached. Ethyl alcohol preheated to the same temperature was quickly poured into the reactor, this time account for the start of the reaction. Samples were taken every 10 mints by a syringe to measure the pH of solution.

The experimental setup is shown in Fig .1.

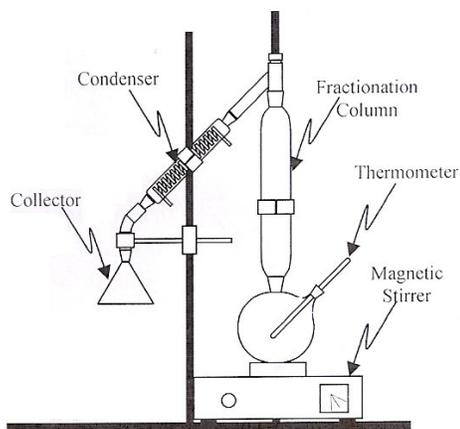


Fig.1. Schematic Diagram of the Experimental Setup.

3. Results and Discussion

Calculation of Rate Constant

Investigation of the kinetics of the system is made by plotting $\ln((M-XA)/(M(1-XA)))$ vs. time, which gave a straight line as shown in Figures (2-4). By referring to equations 5 and 6, the slope of the line in the aforementioned figures equals to $[C_{Ao}(M-1)k]$ in the case of ideal behavior of the system, while for non-ideal system the slope will equal to $[C_{Ao}(M-1)k \gamma_A \gamma_B]$. Since the data points fitted the plot of $\ln((M-XA)/(M(1-XA)))$ vs. time well, and equation 5 & 6 are quite satisfied therefore the reaction is first order with respect to both acetic and ethyl alcohol. Activity coefficients which are function of mole fractions and temperature are calculated using UNIFAC program. These values are given in Table (1). By examining these values it can be seen that the variation in these coefficients during the reaction are quite small, therefore these were considered as constants and the average values were calculated to obtain the rate constant for the non-ideal case. Values of the rate constants are listed in Table (2).

Effect of Temperature

It was found that increasing the temperature of the reaction, increases the rate constant and conversion at a certain mole ratio of reactants that is due to the esterification reaction is exothermic; therefore the increasing the temperature increase the rate of reaction. This observation is well agreed with investigation reported by (Robert et al.1997 and Ismail et al. 2001). For example; the increase in temperature gave an increase in rate constant and conversion from 0.0812 and 70.9% at 50°C to 0.105 and 80% at 60 °C at molar ratio of 10: 1 EtOH/Ac. Fig. 5 shows the increase of conversion during reaction at molar ratio of 10 EtOH/Ac.

Effect of EtOH/Ac

It was also found that the highest values of conversion were obtained at the lowest studied molar ratio of EtOH/Ac, shown in Fig.5 That is due to the reaction is catalyzed by an acid, therefore the use of excess ethanol (M=30 and 50) decreases the conversion. This result is in agreement with the work of (Calvar et al.2007 and Ismail et al. 2001).

It is also concluded that the molar ratio of EtOH/Ac has an effect on the rate constant and

conversion. The rate constant at 60°C was 0.374 at M=30 and 0.105 at M=10 while conversion was

59.5 % and 80% respectively, therefore an optimization must be made for both cases.

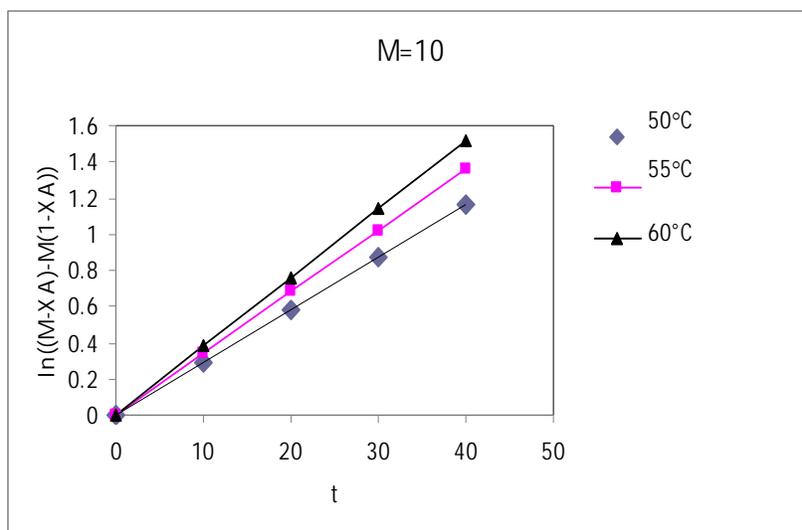


Fig.2. A Plot of $\ln((M-XA)/(M(1-XA)))$ vs. Time in 10 EtOH/Ac at Various Temperatures.

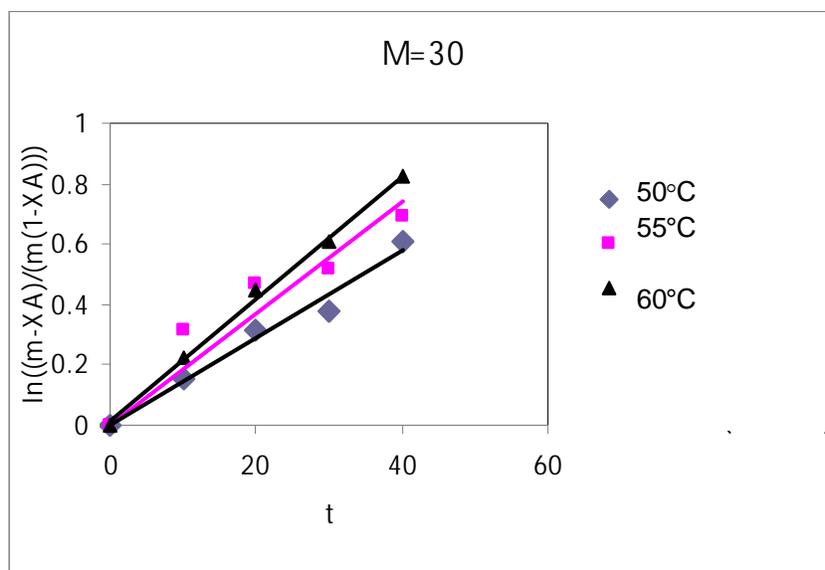


Fig.3. A Plot of $\ln((m-XA)/(m(1-XA)))$ vs. Time in 30 EtOH/Ac at Various Temperatures.

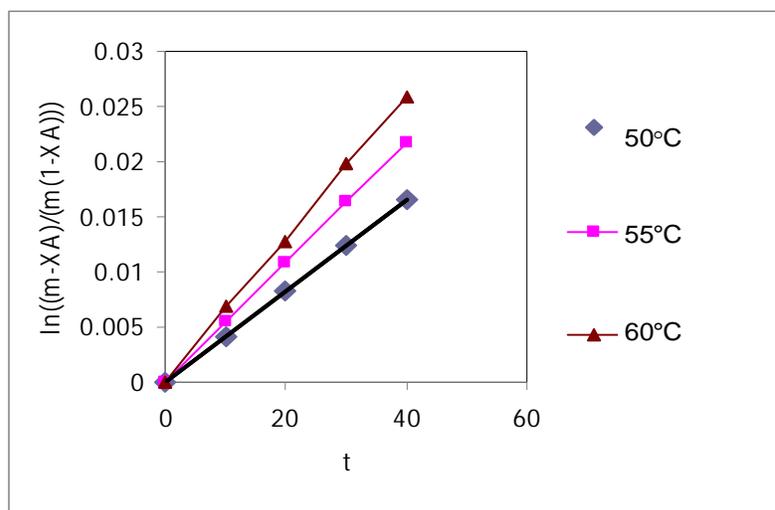


Fig.4. A Plot of $\ln((M-XA)/(M(1-XA)))$ vs. Time in 50 EtOH/Ac at Various Temperatures.

Table 1,
Values of Activity Coefficients.

M=10						
50°C		55°C		60°C		
t min	γ_A	γ_B	γ_A	γ_B	γ_A	γ_B
0	1.872	1.0088	1.875	1.0088	1.848	1.0108
10	1.880	1.0084	1.955	1.0045	1.945	1.0049
20	1.914	1.0067	2.034	1.002	2.023	1.002
30	2.086	1.0009	2.084	1.00001	2.08	1.001
40	2.129	1.0008	2.163	1.0002	2.117	1.0005
Ave.	1.945	1.0008	2.01	1.0027	2.003	1.0025
M=30						
50°C		55°C		60°C		
t min	γ_A	γ_B	γ_A	γ_B	γ_A	γ_B
0	2.104	1.0001	2.081	1.001	2.059	1.001
10	2.127	1.0008	2.12	1.0006	2.085	1.0007
20	2.145	1.0006	2.135	1.0004	2.11	1.0004
30	2.150	1.0005	2.139	1.0003	2.123	1.0003
40	2.174	1.0003	2.154	1.0002	2.139	1.0002
Ave.	2.14	1.0007	2.126	1.0002	2.103	1.0005
M=50						
50°C		55°C		60°C		
t min	γ_A	γ_B	γ_A	γ_B	γ_A	γ_B
0	2.162	1.00004	2.137	1.00004	2.113	1.00004
10	2.162	1.00004	2.137	1.00004	2.113	1.00004
20	2.162	1.00004	2.137	1.00004	2.113	1.00004
30	2.163	1.00004	2.138	1.00004	2.114	1.00004
40	2.163	1.00004	2.138	1.00004	2.114	1.00004
Ave.	2.162	1.0004	2.137	1.0004	2.113	1.0004

Table 2,
Values of rate Constant at Various Temperatures and EtOH/AC Ratio.

Temp °C	k_{ideal}	k_{real}	Conversion%
50	0.0832	0.043	70.9
55	0.095	0.047	76
60	0.105	0.052	80
M=30			
50	0.2595	0.121	46
55	0.333	0.157	51
60	0.374	0.178	59.5
M=50			
50	0.012	0.0055	1.7
55	0.0163	0.0076	2.2
60	0.0194	0.0092	2.6

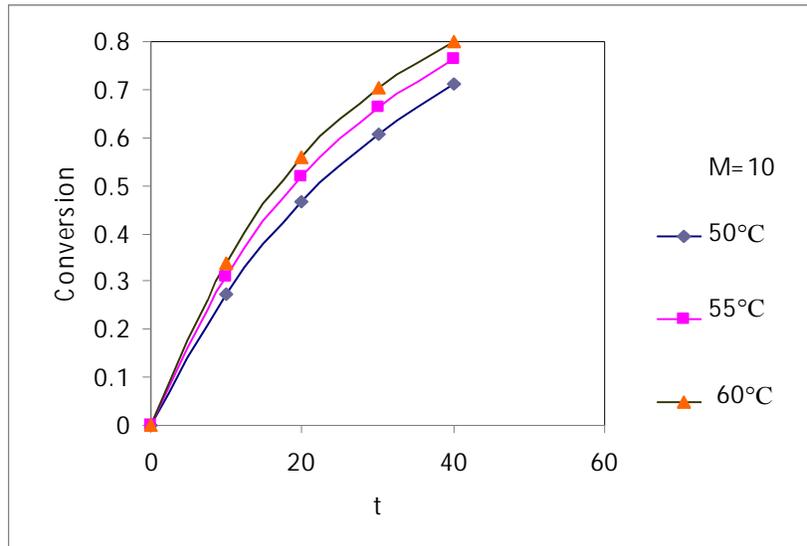


Fig.5. Conversion of Acetic Acid vs. Time for Various Temperatures and M=10.

Apparent Activation Energy Measurement

The temperature dependency of reactions is determined by calculating activation energy at the temperature level of the reaction.

From Arrhenius' law ($k=k_0e^{-E/RT}$), a plot of $\ln(k)$ vs. $(1/T)$ gives a straight line with slope E (activation energy) and intercept of k_0 (frequency factor) as shown in Figures (6-8). Comparison of the values on the assumption of ideal and non-ideal behavior of the system is made on the same

graph. Values of the activation energy and the frequency factor at each molar ratio studied are given in Table (3).

In most esterification reactions, the equilibrium constant is a weak function of the temperature because of the small value of heat of reaction. The same behavior was observed in the reaction of lactic acid with ethanol (Patricia et al. 2007).

The high value of activation energy confirms that there is no mass transport limitation (V.Ragaini et al.2007).

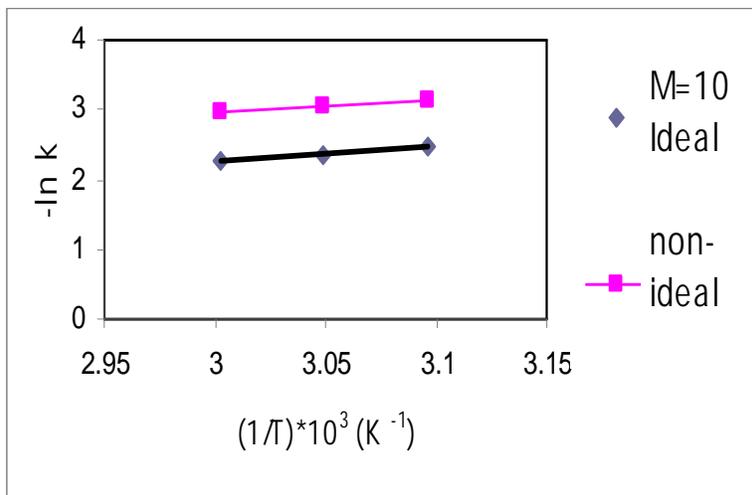


Fig.6. Comparison Plot of ln k vs. (1/T) for Ideal and Non –Ideal System at M=10.

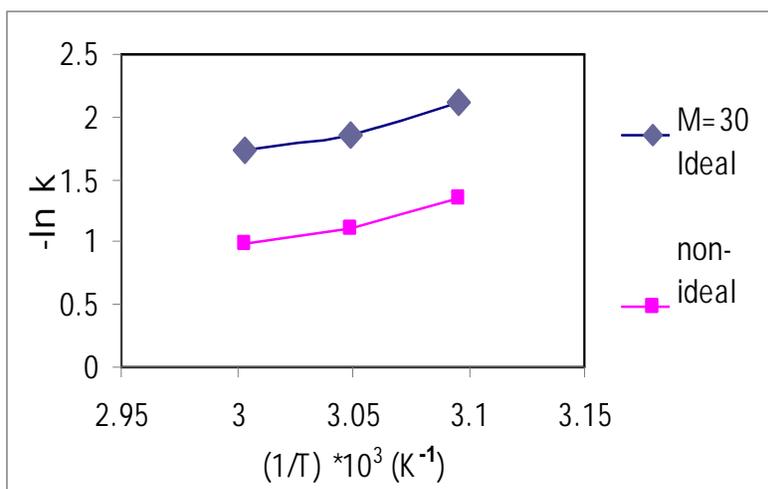


Fig.7. Comparison Plot of ln k vs. (1/T) for Ideal and Non –Ideal System at M=30.

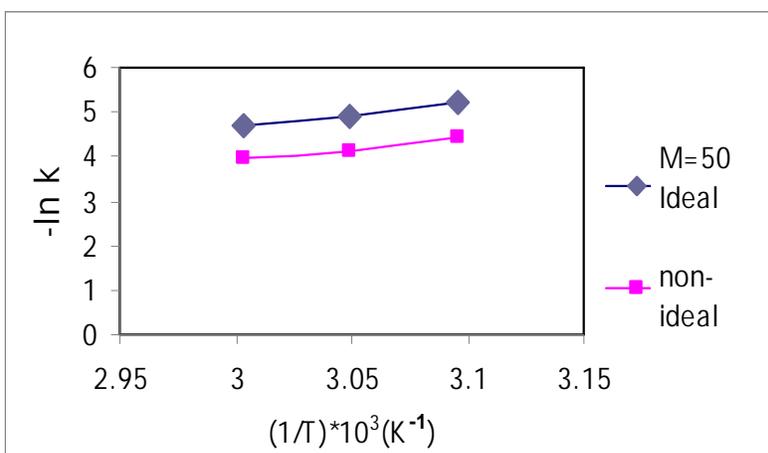


Fig.8. Comparison Plot of ln k vs. (1/T) for Ideal and Non –Ideal System at M=50.

**Table 3,
The Activation Energy and Frequency Factor.**

EtOH/Ac	k_0	E_{ideal} (J/mol)	$E_{non-ideal}$ (J/mol)	% E_a
10	195	20823	16988	18.4
30	52313	32743	34576	-5.6
50	110747	56632	46061	18.6

Effect of Molar Ratio on the Activation Energy

By examining this table (3), it is found that the apparent activation energy decreases with increasing molar ratio, therefore the lowest value of activation energy is found at $M=10$. This can be explained by the fact that the acidity of the liquid phase mixture at this molar ratio is higher comparing to the other ratios, and by referring to the fact that the esterification reaction toward ethyl acetate is preferentially carried out in an acidic media, it can be concluded that the activation energy will be lower.

Some previous studies like, Popken et al.(2000), used acetic acid itself as the catalyst; therefore they used lower ratios of EtOH/Ac so as to obtain the required acidic media for the reaction therefore the activation energy in the ideal case was about 6% higher than the highest value in this study.

Comparison of Ideal and Non-Ideal Behavior of the System

The values of the activation energy were examined from non-ideal behavior point of view. It was found that there is some deviation of less than 20% for the values calculated on the assumption of non-ideal behavior. Table (3) summarizes the kinetic parameter values. Although the rate constants in both cases were found to deviate appreciably but the activation have the same trend. It is concluded that the assumption of ideal behavior of the system is valid, because the activation energy ($E_{non-ideal}$) is found lower than those of ideal system (E_{ideal}) therefore the ideal behavior is a reasonable assumption for a kinetic consideration.

The same behavior was observed in the reaction of acetic acid with ethanol catalyzed both heterogeneously by Amberlyst 15 and homogeneously by acetic acid, using acetic acid an excess reactant combustion (Calvar et al.2007).

They studied the non-ideal behavior of systems for homogeneous acetic acid catalyzed system. They compare the UNIFAC and ASOG methods. Values of activation energy in this study agree well with the results obtained by the aforementioned authors. Hangx et al. (2001) also studied the reaction kinetics for this system on the assumption of ideal behavior and their results fall in the range of this study.

4. Conclusions

The reaction kinetics of esterification of Ac with EtOH catalyzed homogeneously has been determined. The resultant kinetic model fitted the experiment data well, therefore the reaction is first order with respect to both Ac and EtOH.

The rate constant and conversion increases with increasing the temperature of the reaction at a certain mole ratio of reactants. This leads to the esterification reaction is exothermic.

The use of an excess EtOH decreases the conversion because the reaction is catalyzed by an acid. A maximum final conversion of 10 EtOH /Ac molar ratio was obtained. The present investigation also showed that the lowest activation energy was found to be 16988 J.mol^{-1} at molar ratio 10 EtOH /Ac for non-ideal system.

Activation energy based with UNIFAC activity coefficient estimation for non ideal system matches these of the ideal case with deviation of 20% less.

Nomenclature

a	Activity.
E_a	Absolute error = $ABS ((E_{ideal}-E_{non-ideal})/E_{ideal})*100$.
Ac	Acetic Acid.
C	Concentration of acetic acid mol/lit
E	Activation energy.
EtOH	Ethyl alcohol.
k	rate constant lit/mol.min.
k_0	Frequency factor.
M	Molar ratio of ethyl alcohol to acetic acid.
-r	Rate of reaction = mol/lit.min
UNIFAC	UNIversal functional group activity. coefficient.
X	Conversion.

Greek

- γ Activity coefficient.
 μ Chemical potential.
 ν Stoichiometric coefficient in reaction.

Subscript

- A acetic acid.
 B Ethyl alcohol.
 i component with the system.

5. References

- [1] Calver N., Gonzales B., Dominguez A.,2007; "Esterification of acetic with ethanol Reaction kinetics and operation in a packed bed reactive distillation column", chem. Eng. and Processing, 46, 1317-1323.
- [2] Denbigh and Turner, 1984; "Chemical reactor theory", An Introduction, Cambridge University Press.3rd.
- [3] Hangx G., Kwant G., Maessen H., Markusse P., and Urseanu I., 2001, "Reaction Kinetics of the esterification acid towards ethyl acetate", Technical report on the European Commission (INTINT) Deliverable 22.
- [4] Ismail Kirbaslar, Baris Baykal and Umur Dramur,2001,"esterification of acetic acid with ethanol catalyzed by an acidic ion-exchange resin", Turk J Engin environment sci 25,569-577.
- [5] Kirk R.E. and D.F. Othmer, 1980 ; Encyclopedia of chem. Tech. 9,Wiley and Sons. Inc. New York.
- [6] Levenspiel O., 1999; " Chemical reaction engineering" 3rd ed.,John Wiley & Sons.
- [7] Liu W.T., C.S.Tan, 2001," Liquid phase esterification", Ind.Eng.Chem. Res., 40,3281-3286.
- [8] Majid S. Radhaa, Khalid A.Sukkar, Jamal M.Ali, Zaidoon,Shakoor, Niran. 2008,"Hydrodynamics, mass and heat transfer in reactive distillation", Al-Khwarizmi, Eng.Journal ,Vol.4 ,No.2, 10-18.
- [9] Maris Teresa Sanz, Jurgen Gmehling, 2006. "Esterification of acetic acid with isopropanol coupled with pervaporation part 1 (Kinetics and pervaporation studies)", Chem. Eng. Journal, 123,1-8.
- [10] Maurer G.,1986,"Vapor-liquid and chemical equilibrium of formaldehyde and water containing multicomponent mixture", ALCHE journal ,Vol.32, No. 6, 932-948.
- [11] Mazotti, M., Neri, B., Gelosa, D., Kruglov, A. and Morbidelli, M., 1997, "Kinetics of liquid-phase esterification catalyzed by acidic resins", Ind. Eng. Chem. Res., 36, 3-10.
- [12] Neil E. Small, 2004; "Using activity for reaction kinetics" Chem. Eng.5 Engineering Analysis Project.
- [13] Patricia D.,Maria T.S., Sagrario B.2007,"Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion exchange resin catalyst", Chem. Eng. Journal,126, 111-118.
- [14] Popken T., Gotze L., and Gmehling, 2000, "reaction kinetics and chemical Equilibrium of homogeneously and heterogeneously catalyzed acetic acid esterification", Ind. Eng. Chem. Res., 39, 2601-2611.
- [15] Robert Ronnbach Tapio Salmi, Antt V., Heikki H.Juha,Anna S. and Esko T.,1997 "development of kinetic model for the esterification in presence of homogeneous acid catalyst", chemical engineering science vol 52, No 19, P 3369-3381.
- [16] Roennback,R;Salmi,T., Vuori, Haario, H.,Lehtonen,Sundqvist,1997, "Development of kinetic model for the esterification in the presence of homogeneous acid catalyst", Chem. Eng. Sci.,52, 3364.
- [17] Tang, Y.T.,Huang,H.P., and Chain ,I.L.,2003, "Design of a complete EtAC reactive distillation system" , J. Chem. Eng. Japan, 36,1352-1363.
- [18] V.Ragaini,C.L.Bianchi, C.Pirola, 2007, "Kinetic of esterification of diluted acetic acid with 2-ethyl-1-hexanol", Chem.Eng.Journal, 131,257- 262.
- [19] Xu,Z.P., Chuang,K.T., 1996, "kinetics of acetic acid esterification over ion exchange catalyst" ,Can.J.chem Eng. 74,493.
- [20] Yadav, G.D. and Metha, P.H. 1994, "Heterogeneous catalysis in esterification reaction", In.Eng. Chem. Res .33, 2198-2208.

دراسة حركية تفاعل الاسترة

ندى سعدون احمد زكي مها هادي الحسني حيدر عبد الكريم الجندي

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الخلاصة

تمت دراسة حركية تفاعل استرة حامض الخليك والكحول الايثيلي باستعمال حامض الكبريتيك كعامل مساعد في مفاعل ذو الدفعات. اجري التفاعل في درجات حرارة مختلفة تتراوح بين 50-60م عند نسب مولية مختلفة للكحول الى حامض الخليك. فقد وجد انه كلما قلت نسبة الكحول الى حامض الخليك يزداد التحول وذلك بسبب ان التفاعل حامضي ولقد تم الحصول على تحول 80% بدرجة حرارة 60م ونسبة مولية 10 كحول ايثيلي/ حامض الخليك. لقد لوحظ ان زيادة درجة الحرارة تؤدي الى زيادة ثابت التفاعل والتحول عند نسبة معينة من الايثانول وحامض الخليك وهذا لكون التفاعل باعث للحرارة. تمت الدراسة من زاوية النظام الغير مثالي. تم حساب معامل الفعالية باستعمال برنامج (UNIFAC). اوضحت النتائج وجود انحراف في طاقة التنشيط للنظام الغير مثالي بمقدار 20% تقريبا. تم الحصول على اعلى تحول تقريبا 80% باستعمال نسبة مولية 10 ايثانول/ حامض الخليك وهذا سببه كون الماء والكحول الايثيلي مواد ذات قطبية عالية مقارنة بالاستر الناتج وهذا الاختلاف يؤدي الى السلوك الغير مثالي.