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Preparation of Polyvinyl Alcohol from Local Raw Material

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Abstract

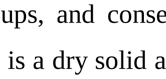
Polyvinyl alcohol, (PVA) was prepared using polyvinyl acetate emulsion (manufactured by Al-Jihad factory, That-Al-Sawary Company) as a local raw material. In this investigation, polyvinyl acetate emulsion was converted to solid form by coagulation the polymer from its emulsion using sodium sulphate salt as coagulant aid, then alcoholyzed the solid polyvinyl acetate in methanol using sodium hydroxide as catalyst, polyvinyl alcohol produced by this method is a dry, white to yellow powder.

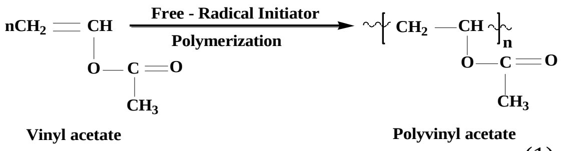
Three affecting variables on the degree of hydrolysis of PVA were studied, these variable are Catalyst to polymer weight ratio in the range of 0.01 – 0.06, reaction time in the range of 20 – 90 min, and reaction temperature in the range of 25 – 50 oC. The effect of degree of hydrolysis of PVA produced on its properties such as water solubility and degree of polymerization were studied also.

Finally the alcoholysis reaction kinetics were studied to determine the reaction constants such as initial rate constant and degree of autocatalytic effect of the alcoholysis reaction. It was found that the degree of hydrolysis of formed polyvinyl alcohol increase with increasing of variables catalyst concentration, reaction time and reaction temperature, furthermore, the water solubility of PVA increase with increasing degree of hydrolysis up to about 87 % after this value the solubility is decrease, also the degree of polymerization of PVA decrease with increasing of degree of hydrolysis up to about 89 %.

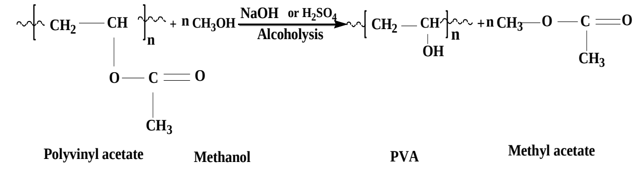
Keywords**:** polyvinyl alcohol, alcoholysis reaction, polyvinyl acetate emulsion, coagulation.

Introduction

Polyvinyl alcohol, (PVA) is a polyhydroxy polymer,  $\sim\!\!\left[CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}\right]_n\!\!\sim$, containing significant number of OH-groups, and consequently a water soluble synthetic resin. It is a dry solid and available in granular or powder form, white to yellow in color. PVA is readily obtainable from hydrolysis of polyvinyl acetate or other polyvinyl esters by replacement of acetate groups by hydroxyl groups in the polymer chain, using either base or acid catalyst [1]:



(1)



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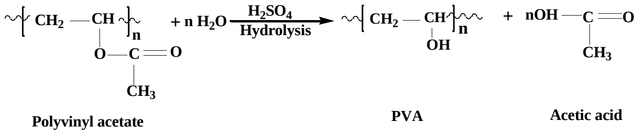


(3)

The theoretical monomer, vinyl alcohol evidently does not exist in free state, whenever, it rearranges to give its tautomer, acetaldehyde [2]:

$$\mathrm{CH2{:}CHOH} \rightleftharpoons \mathrm{CH3{:}CHO} \qquad (4)$$

Discovery of polyvinyl alcohol was credited to German scientists, W. O. Herrman and Haehnel in 1924 [3] and the polymer was commercially introduced into United State in 1939 [4].

PVA is manufactured commercially by several methods; alkaline hydrolysis is usually used as an industrial scale. Sodium hydroxide and sodium methoxide are the most important catalyst for alcoholysis with present of alcohol such as methanol or ethanol. Other alkaline catalyst may be employed in alcoholysis reaction for example potassium hydroxide, guanidine carbonate, sodium methyl carbonate and sodium ethoxide [2].

PVA can be also made by an acidolysis process, this can involve both alcoholysis reaction (ester interchange) when working in an anhydrous system with present of alcohol, and a hydrolysis reaction when a polyvinyl acetate emulsions or of finely divided water suspensions are used as the starting material, usually sulfuric acid, hydrochloric acid or any other strong mineral acid is employed as the acid catalyst, this process is used industrially only to a very limited extent [2].

A number of other methods for the manufacture of PVA have been used , these employ starting materials other than polyvinyl acetate ,often the polyvinyl alcohol made by these methods have specific properties such as tacticity , better cold-water solubility and steroregularity [5].

PVA is one of very few high molecular weight commercial polymers that are water soluble, the basic properties of PVA such as water solubility depend on the degree of replacement of acetate groups by hydroxyl groups (***degree of hydrolysis***) and the degree of polymerization.

The most common commercial grades classified by the percentage hydrolysis and degree of polymerization; therefore, there are three important commercially available grades of PVA distinguished by the mole percent residual acetate groups in the polymer chain as follows [5]:

1. Fully hydrolyzed (1 – 2 mol% acetate groups)
2. Intermediate hydrolyzed (3 – 7 mol% acetate groups)
3. Partially hydrolyzed (10 – 15 mol% acetate groups)

PVA with other degree of hydrolysis are also produced, but collectively they have a much smaller market share than any of the three principal grades.

In term of the degree of polymerization (based on the viscosity at 20 oC of 4% aqueous solution of PVA), there are four general molecular weight ranges(5):

1. Low viscosity grade (5 –7 cp)
2. Intermediate viscosity grade (13 – 16 cp)
3. Medium viscosity grade (28 – 32 cp)
4. High viscosity grade (55 – 65 cp)

These grades of polyvinyl alcohol lend to variety of applications. The principle applications are in textile industry for warp sizing, as emulsifier agent in vinyl acetate emulsion polymerization systems, as a component in aqueous adhesives, for the production of polyvinyl acetyls, e.g., polyvinyl butyral for safety glass. Significant volumes are also used in such diverse application as joint cements for building construction, water-soluble film for hospital laundry bags, emulsifiers in cosmetics, temporary protective films to prevent scratching of high polished surfaces, soil binding to control erosion, paper coating, and in smaller amounts as the binder for phosphorescent pigments and dyes in television tubes and in other optical applications such as polarization lenses [2].

Experimental Work

Materials

1. Commercial polyvinyl acetate emulsion, manufactured by Al-Jihad factory, from That–Al–Sawary Company, Baghdad, was used as starting material.
2. Commercial grade (Hopkin & Williams) of 99.5% pure methanol was used as alcoholysis medium.
3. Analytical reagent grade sodium hydroxide was used as alkaline catalyst.
4. Commercial grade sodium sulphate (BDH Chemicals Ltd) was used as coagulant agent.
5. Analytical grade (Hopkin & Williams) methyl acetate was used as precipitation agent for polyvinyl alcohol.

Experimental procedure

Coagulation process of polyvinyl acetate emulsion

Polyvinyl acetate was coagulated from its emulsion by using solution of sodium sulfate in the presence of methanol solvent and water, according to the following recipe:

Materials	Weight parts
Polyvinyl acetate emulsion	100
Sodium sulfate salt	100
Water	250
Methanol	25 – 50
Sulfuric acid	1 – 2

In one–liter flask, 200 gm of polyvinyl acetate emulsion (53% by weight solid content) was stirred with 50 gm methanol, and it was overlaid with aqueous solution of sodium sulfate salt (consists of 200 gm Na2SO4 and 500 gm water) and 2 gram sulfuric acid.

The mixture was stirred for 20 minutes at a temperature in the range of 30–50oC. After settling time of about 30 min. at room temperature, the polyvinyl acetate was coagulated and three layers were present as shown in Fig. (1), the top or the first layer is emulsifiers (soaps), the intermediate layer is liquid phase (water, dissolved salt, and methanol), and the bottom layer is precipitated polymer.

The emulsifiers' layer was removed mechanically and the polymer was filtered from the liquid phase, the resultant filtrate is recycled for treating another batch of emulsion.

The polymer was then washed several times with water and filtered after each time. The resulting polymer consists of 75-80 % polymer and 20-25% water.

Preparation of polyvinyl alcohol (Alcoholysis process)

Preparation of polyvinyl alcohol was carried out in a stainless-steel jacketed reactor with a total capacity of 1.4 liter which was heated to the required temperature by hot water circulation in the jacket of the reactor, the reactor was equipped with variable speed stirrer, reflux condenser to prevent losses of vapor from the reactor during the hydrolysis reaction, thermometer, and thermostat. The laboratory experimental unit is shown in Fig. (2).

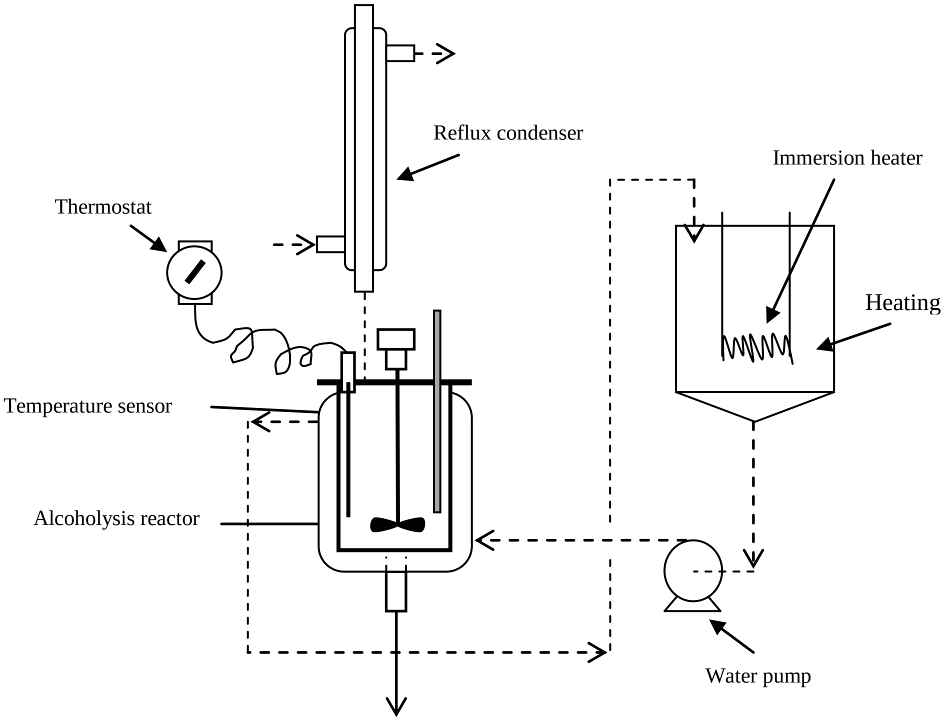


Fig. 2 Alcoholysis process unit

200g of pretreated solid polyvinyl acetate (containing about 20% water) was dissolved at the desired temperature in 400gm of methanol by stirring in the reactor, after it reached the same temperature with the jacket; the desired amount of sodium hydroxide catalyst solution in methanol was added to the reactor. The sodium hydroxide solution was prepared separately by dissolving the desired amount of sodium hydroxide catalyst in 80g of methanol, therefore the concentration of polyvinyl acetate in the total reaction mixture being in the range of 15 – 30 % by weight and the methanol to water weight ratio in the reaction mixture was about (90 methanol:10 water).

The reaction mixture thickened after 10 min. and the gel that formed was comminuted by raising the speed of the stirrer. The sample was removed periodically, from the reactor and immediately, the sodium hydroxide which still present in the sample, has been neutralized by strong hydrochloric acid, then polyvinyl alcohol formed in the sample was precipitated in methyl acetate by agitation at about 25° C. Each polyvinyl alcohol sample was very effectively isolated from the liquid phase by suction filtration on a textile filter under vacuum operation and then dried.

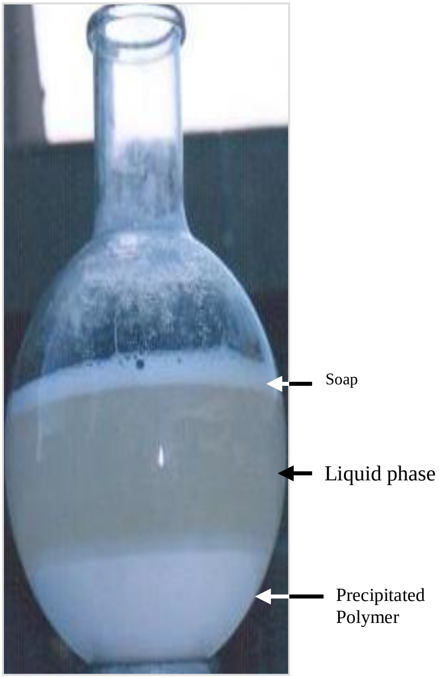


Figure (1) Representation of Polyvinyl acetate Coagulation

Experiments setup

In this work, two set of experiments are considered, the first set at 25° C and the second set at 50° C. In each set of experiments, the two variables, catalyst ratio and reaction time were studied. The catalyst ratio was varied among (0.01, 0.0266, 0.0433, and 0.06 weight of cat. / weight of Polyvinyl acetate), and the reaction time was varied among (20, 43.3, 66.6, and 90 min.).

Analysis and Testing of PVA(6)

Volatile Content

Volatile content is the percentage weight loss of polyvinyl alcohol on drying at 105oC to constant weight. Accurately weighting about 5 gm of the sample was placed into a weighting bottle, dry it at 105 °C to constant weight; allowed it to cool in a desicator and weighting the sample again. The volatile content was calculated to two decimal places from the formula:

$$R_v = \frac{\text{S - W}}{\text{S}} \times 100\% \tag{5}$$

And the pure component of polyvinyl alcohol can be calculated from:

$$P = 100 - Rv \tag{6}$$

The values taken are the average of two determinations.

Degree of Hydrolysis

Accurately weighting about 3 gm of sample and 100 ml of water were placed into a stoppard conical flask; and the sample was dissolved by heating then cooled at room temperature. 25 ml of 0.1 N NaOH solution was added to the solution and kept at room temperature for at least 2 hr. Then 25 ml of 0.1 N sulfuric acid was added and excess acid was titrated with 0.1 N NaOH using phenolphthalein as an indicator, until a pale pink color was persisted in the solution. The volume of solution consumed in this titration was [a] ml.

The percentage weight of residual acetic acid radical, based on the pure component as well as the mole percent hydrolysis was calculated to two decimal places from the following formula:

$$\text{A} = \frac{0.6 \times (\text{a})\,\text{F}}{\text{S} \times \text{P}} \text{ percent} \tag{7}$$

$$\text{B} = \frac{44.05\ \text{A}}{60.06 - 0.1601\ \text{A}} \text{ mole percent} \tag{8}$$

$$\text{X} = 100 - \text{B mole percent} \tag{9}$$

Average degree of polymerization (PA) & molecular weight.

About 10gm of sample was weighted into a stoppered conical flask and 200 ml of methanol was added, followed by 3 ml of 12.5 N sodium hydroxide (with samples of not less than 97 mole % hydrolysis) or 10 ml of 12.5 N sodium hydroxide (with samples of less than 97 mole % hydrolysis). After stirring the solution was heated for 1 hr in a water path at 40oC, to hydrolyze the polymer completely.

The solution was then washed thoroughly with methanol to remove the sodium hydroxide and sodium acetate. The solution was then transferred to a watch glass and dried to remove the methanol. 1gm of the dried sample was weighed, and dissolved, with heating in 100 ml of water. Then cooled at room temperature, and filtered carefully. 10 ml of the filtered solution was placed in a capillary viscometer (Cannon Fenske No. 100) and the time of flow of solution was measured at 30±0.1 °C. The same capillary viscometer was used to measure the time of flow of water at the same temperature.

20 ml of the same filtrate was taken separately onto an evaporating dish of known weight and evaporated to dryness. The residue was further dried at 105 ∓ 2oC to constant weight, and the concentration (in g/L) was determined. The average degree of polymerization was calculated from the formula:

$$\log \bar{P}_A = 1.613 \log \frac{10^4}{8.29}\left(\frac{2.303}{C_v} \log \frac{t_1}{t_o}\right) \qquad (10)$$

Where: $\left(\frac{2.303}{C_v} \log \frac{t_1}{t_o}\right)$ = limiting viscosity (g-1 l-1)

And the average molecular weight of polyvinyl alcohol was calculated from:

Average Molecular Weight of PVA = PA × 44 (11)

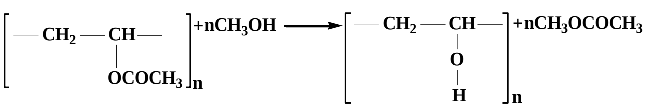
Solubility in water [5]

The water solubility of PVA was calculated after 30 min. at 40° C by dissolving 4 parts by weight of PVA in 96 parts of water.

Results and Discussion

When polyvinyl acetate is alcoholyzed with sodium hydroxide as basic catalyst in methanol, a mixed polymer, or hydrolyzed polyvinyl acetate, is formed which contain both hydroxyl and acetyl groups. As a ratio of hydroxyl to acetyl groups increases, the solvent – solute relationship in the reaction mixture is changed, i.e. the alcoholyzed acetate become increasingly water – susceptible, passing through a stage at which it is swollen and somewhat water – solubility.

The essential over-all reaction may be represented in terms of the simple monomeric units, as follows:



$$\left[-CH_2-\underset{\underset{OCOCH_3}{|}}{CH}-\right]_n + nCH_3OH \longrightarrow \left[-CH_2-\underset{\underset{\underset{H}{|}}{O}}{\underset{|}{CH}}-\right]_n + nCH_3OCOCH_3$$

(12)

The results of typical alcoholysis experiments of polyvinyl acetate to polyvinyl alcohol are tabulated in Table (1).

Table (1) Results of degree of hydrolysis (X) of PVA of alcoholysis reaction experiments of polyvinyl acetate to polyvinyl alcohol using sodium hydroxide as alkaline catalyst

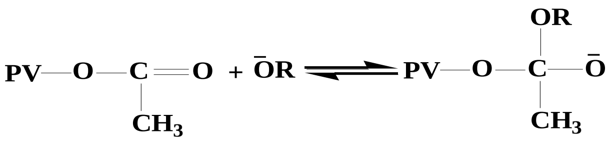
Temp.(°C)	Time (min.)	Catalyst Ratio			
		0.01	0.02667	0.04334	0.06
25	20	56.6	58.34	65	73
	43.3	59	60.5	67	75.99
	66.6	67.71	76	82	87.9
	90	78.77	89.65	97.5	98.31
50	20	59	63	69.5	75.55
	43.3	61.99	68.8	72	79.46
	66.6	65.12	77.74	83.83	90
	90	79	90.69	97.25	99

Effect of catalyst ratio

Results of the study of the effect of catalyst ratio on the degree of hydrolysis of polyvinyl alcohol at different reaction time and at temperature of 25oC and 50oC respectively are shown in Fig.s (3) and (4). It is clear, from these Fig.s that the degree of hydrolysis of PVA increases with increasing of catalyst ratio at constant time, [i.e. the time required to reach desired degree of hydrolysis decreases with increasing of catalyst concentration].

For example, increasing the catalyst ratio from 0.01 to 0.02667 at 25oC and 90 min. causes an increase in degree of hydrolysis from 78.77% to 89.65%.

Increasing the catalyst concentration leads to a lowering the activation energy required to bring the anion of the alcohol (RO-) up to the carbonyl carbon atom of the acetate group in the first step of alcoholysis reaction as shown in equation (13).



$$PV-O-\underset{\underset{CH_3}{|}}{C}=O + \bar{O}R \rightleftharpoons PV-O-\overset{\overset{OR}{|}}{\underset{\underset{CH_3}{|}}{C}}-\bar{O}$$

(13)

Effect of Reaction time

Fig.s (5) and (6) and table (1) show the effect of reaction time on the degree of hydrolysis of PVA at different catalyst ratio and at temperatures of 25oC and 50oC respectively. The rate of degree of hydrolysis of PVA increase with increasing of reaction time. As reaction time increase, the number of hydroxyl groups increase in the polymer chain, and rate of the alcoholysis reaction increase continuously because of the autocatalytic effect of these functional groups as explained by Sakurada [7] and L. M. Minsk [8].

It is clear from each curve in Fig.s (5) and (6), that the slopes at selected points of X (degree of hydrolysis), increase with increasing the reaction time, this mean that the rate of reaction increase as shown in table (2).

Effect of Alcoholysis Reaction on the Degree of Polymerization of PVA

Fig. (7) shows the effect of alcoholysis reaction on the degree of polymerization of PVA. The reaction conditions are: Temperature = 25° C, Catalyst ratio=0.06. It is clear from this Fig. that a noticeable decrease of the degree of polymerization of formed PVA with increasing of degree of hydrolysis up to degree of hydrolysis of 75%, followed by slightly decrease up to 89%.

Decreasing of degree of polymerization of PVA during the alcoholysis reaction may be attributed to that the alcoholysis reaction causes some degradation of the original polyvinyl acetate , this effect is probably due to fission of chain branching through the methyl unit of the acetoxy group in the polymer chain [5].

Effect of Degree of Hydrolysis on the Water Solubility of PVA

Fig. (8) shows the effect of degree of hydrolysis on the water solubility of PVA, it is shown from this Fig. that the water solubility of PVA is very affected by the degree of hydrolysis at constant temperature. The solubility of PVA in water increase with increasing of degree of hydrolysis (i.e. number of hydroxyl groups in polymer chain) at constant temperature up to about 87% (partially hydrolyzed), after this value the solubility of PVA decreases. Fully hydrolyzed PVA has low water solubility because of the high number of hydrogen bonding between the intra – and intramolecular hydroxyl group which is greatly impeding the PVA solubility in water. The residual acetate groups in partly hydrolyzed PVA are essentially hydrophobic and weaken the intra – and intramolecular hydrogen bonding of adjoining hydroxyl groups. And this, increases the solubility of PVA, as explained by Martin K. Lindemann [5].

Kinetics Study

The kinetics of alcoholysis reaction of polyvinyl acetate in methanol using sodium hydroxide as alkaline catalyst was studied. The aim of this study is to find the initial rate constant, K_o and degree of autocatalytic effect, m (which means the degree of acceleration during the hydrolysis reaction) at different catalyst concentration and at temperature of 25 and 50° C respectively, and to determine the effect of catalyst ratio used in the initial reaction mixture and temperature on the K_o and m.

The initial rate constant, (K_o) and degree of autocatalytic effect, m can be calculated at different catalyst ratio by fitting the data in Table (1) as a linear equation using equations bellow:

$$dx/dt = Ko[(1+mx)(1-x)] \qquad (14)$$

$$dx/dt\,[1/(1-x)] = Ko+Komx \qquad (15)$$

$$\text{Where } K = K_o+K_omX \qquad (16)$$

From each plot of (x) verses (t), the slope of each curve is obtained at suitably selected (x). These slopes represent the values of (dx/dt), straight lines can be obtained by plotting of (dx/dt[1/(1-x)]) versus (x) at different catalyst ratio and at temperature of 25 and 50° C respectively according to equation (15).

The data of these figures are shown in table (2), where the slope is (K_om) and the intercept is (K_o), therefore the results of K_o and m can be obtained as tabulated in Table (3).

Figures (9) and (10) show the effect of catalyst ratio on the initial rate constant and degree of autocatalytic effect respectively, it is clear from figure (9) that the initial rate constant, K_o increase with increasing the catalyst concentration, but the degree of autocatalytic effect (m) decrease with increasing of catalyst concentration. The rate constant (K) of the hydrolysis reaction after a degree of hydrolysis (X) can be calculated from equation (16), it is clear from figures (11) and (12) that the rate constant of the hydrolysis reaction increase with increasing degree of hydrolysis (i.e. the rate of hydrolysis reaction increases continuously), and the relationship between K and X is linear because the autocatalytic effect of this reaction.

Table (2) Results of dx/dt [1/ (1-x)] verses X at different Cat. Ratio and temperature

Temp. (°C)	Cat. Ratio	X	dx/dt [1/ (1-x)]
25	0.01	60	0.66675
		66	1.18617
		70	1.558467
		76	2.5
	0.0266	60	0.673
		70	1.8334
		80	3.5105
		86	5.2628
	0.0433	66	0.5392
		70	1.2766
		80	3.125
		90	8.182
	0.06	74	0.7692
		80	1.81
		90	5
		96	14.795
50	0.01	60	0.375
		64	1.13056
		70	1.556
		76	2.334
	0.0266	64	0.463
		70	1.1853
		80	2.3684
		86	4.2093
	0.0433	70	0.476
		76	1.231
		84	3.125
		90	6.48
	0.06	76	0.726
		84	2.138
		90	4.2
		96	12

Table (3) Results of initial rate constant and degree of autocatalytic – effect

Temp. (°C)	Cat. Ratio	K_o	m
25	0.01	4.675	0.019
	0.0266	7.926	0.0179
	0.0433	11.654	0.01587
	0.06	19.434	0.01389
50	0.01	6.376	0.01788
	0.0266	7.149	0.01664
	0.0433	13.09	0.01466
	0.06	18.001	0.01356

Conclusions

1. A dry and solid powder form polyvinyl alcohol can not be obtained from polyvinyl acetate emulsion directly, because the water present in the emulsion solublies the formed PVA and the product still in aqueous solution state. It can be claimed from the literature that if polyvinyl acetate is available in emulsion state, the hydrolysis process is carried out in aqueous media using strong acid catalyst such as sulfuric acid, the reaction needs long time and dark color, unsuitable for many uses PVA is obtained.
2. Polyvinyl acetate emulsion can be treated to convert the emulsion to solid state by coagulation the polymer from its aqueous emulsion using sodium sulphate salt as coagulant agent. The final treated polymer contains about 20% by weight water.
3. Solid polyvinyl acetate was alcoholyzed easily in methanol using sodium hydroxide as alkaline catalyst, the parent polyvinyl acetate containing a small amount of water, and the final weight ratio of methanol – water in the reaction mixture is about (90 methanol : 10 water). Polyvinyl alcohol produced in this method is dry solid, white to yellow powder.
4. In the alcoholysis process, three variables of catalyst concentration, reaction time and reaction temperature are affecting the degree of hydrolysis of polyvinyl alcohol in the order:

   Catalyst ratio > Reaction time > Reaction temperature

   a. Degree of hydrolysis of PVA increase rapidly with increasing the catalyst concentration at constant reaction time and temperature.
   b. Degree of hydrolysis PVA increase continuously with reaction time because of the autocatalytic effect of the alcoholysis reaction.
   c. Degree of hydrolysis of PVA increase slightly with increasing of reaction temperature. The change of alcoholysis reaction rate with temperature follows the Arrhenius temperature dependence equation.
5. At constant temperature the water solubility of product PVA increase with increasing of degree of hydrolysis up to 87 %, after this value the solubility of PVA is decrease.
6. The degree of polymerization of formed PVA decrease slightly with increasing of degree of hydrolysis, after a degree of hydrolysis about 89 %, the degree of polymerization is almost constant.

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