

HYDROLYSIS OF BUTYL ACETATE

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Hydrolysis of butyl acetate leads to great losses of the solvent at the RAS Kiviter dephenolization plant. The rate of the acid hydrolysis for butyl acetate is studied by alkalimetric titration of acetic acid formed in two-phase systems. The rate of the alkaline hydrolysis is studied by pH-rate profiles in one-phase aqueous solutions and by the concentration of the acetate anions revealed in two-phase pH-buffered systems. The temperature dependencies for the rate constants and for the pH value, providing the minimum hydrolysis, are described.

Introduction

Butyl acetate (BA) is a widely applied organic solvent for liquid-liquid extraction of organic compounds from water solutions. Hydrolysis of BA during an extraction leads to great losses of the solvent, resulting in the contamination of the aqueous phase by acetic acid formed and in the instability of the organic phase due to the butyl alcohol formed. The same trouble occurs at the dephenolization plant at the RAS Kiviter oil shale processing facility, Kohtla-Järve. In our recent study [1], dealing with the improvement of the dephenolization plant's operation, it was found that BA hydrolyses most intensively in the steam stripping columns where the temperature of water is the highest. The temperature dependence for the BA hydrolysis is not clear, despite the fact that the kinetics of the reaction has been studied from the beginning of the century. For example, in the reference book [2], the rate constant value for the acid hydrolysis (k_{ac}) of BA is reported only at a temperature of 25 °C, and that for the alkaline hydrolysis (k_{al}) only within the temperature range of 0-45 °C. In the handbook [3], the Arrhenius constants in Equation (10) for the alkaline hydrolysis of BA are given

without any temperature indication. Moreover, the published values for k_{al} are not in good agreement.

Our study [1] gives the k_{ac} values for BA within the temperature range of 20-100 °C.

The aim of this paper is to describe the coinfluence of the temperature and the catalysts', H_3O^+ and OH^- , concentrations on the hydrolysis rate of BA. For that purpose the value of k_{al} within the range of 40-100 °C was determined and the study of acid hydrolysis [1] was detailed for BA.

The total hydrolysis of BA in water solutions is proved to be of a second order kinetic reaction, depending on the ester concentration $[BA]$ and the catalyst ion concentration $[H^+]$ or $[OH^-]$

$$d[BA] / dt = -k_{ac}[BA][H^+] \quad (1)$$

or

$$d[BA] / dt = -k_{al}[BA][OH^-] \quad (2)$$

Experimental

Reagents

Pure grade BA was applied. The reagent was purified by double extraction with distilled water directly before the experiments. The aqueous solutions of catalysts were prepared by mixing the 0.100 M standard solutions of NaOH or HCl and water in the required proportions. The pH-buffered aqueous phase was prepared adding the 50 % solution of KOH to the 1 or 3 M solutions of H_3PO_4 or to the 1 M solution of H_3BO_3 up to the value of pH demanded.

Hydrolysis

In the two-phased systems a typical run of the acid and alkaline hydrolysis was conducted as follows. Flasks with BA and 200 ml of an aqueous solution of HCl or a pH-buffer, were thermostated at a required temperature. Then a known amount of BA was poured on top of the aqueous solution. Agitation was started. 20 ml of samples was withdrawn periodically, cooled immediately in an ice-bath to stop the hydrolysis, and titrated.

When k_{al} was studied in the one-phase systems, 100 ml of 0.005 or 0.010 M of NaOH was maintained at the desired temperature. Then 0.100 or 0.200 ml of BA was injected. The concentration of OH^- was tested by monitoring pH values. At that, the readings of pH-meter (pH^*) were standardised by the initial concentration of NaOH. So, the influence of the activity coefficient for OH^- (γ_{OH^-}) was eliminated.

Analysis

The concentration of BA in the aqueous phase was determined on a gas-liquid chromatograph "Chrom 5". Activity of H_3O^+ was measured at the desired temperature on a pH-meter "pH-268". The concentration of CH_3COOH formed in the acidic solutions was titrated with the CO_2 -free 0.1 M alkali solution. The concentration of CH_3COO^- formed in the alkaline solutions was determined as acetic acid. The latter was distilled from the samples acidified with H_3PO_4 . Before the distillation these samples were evaporated at pH 6-8 to a half of the volume to remove the dissolved BA.

Data Processing

Acid Hydrolysis

The study of the acid hydrolysis of BA following Equation (1) was simplified by applying two-phase systems of BA and an aqueous solution.

It was proved experimentally that the amount of acetic acid formed was independent of the ratio of the phases' volumes and of the impeller speed. Therefore, the hydrolysis of BA in the organic phase and in the interface can be neglected. Moreover, under the acidic conditions, the aqueous phase has to be saturated with BA. Therefore, in the Equation (1) the concentration of BA can be replaced with its solubility $[BA]_s$.

The value of the dissociation constant for acetic acid ($K_a = 1.74 \times 10^{-5}$ mol/l) permits neglect of a slight increase of the H_3O^+ concentration coming from the dissociation of acetic acid formed at hydrolysis under the studied conditions. Therefore, the value of $[H^+]$ in Equation (1) can be replaced with the concentration of the acidic catalyst applied.

When $[BA]_s$ and $[H^+]$ are constant and $d[BA] = d[CH_3COOH]$ an integration of Equation (1) gives a linear plot of the acetic acid concentration against time

$$[CH_3COOH] = k t \quad (3)$$

where

$$k = k_{ac}[BA]_s[H^+] \quad (4)$$

Alkaline Hydrolysis

The simple model above is not suitable when the alkaline hydrolysis of BA is studied. The concentration of the alkaline catalyst, unlike the acidic catalyst, decreases during the hydrolysis due to the reaction of the OH^- anions with releasing acetic acid. Besides, the concentration of BA

in the aqueous phase is lower than $[BA]_s$ due to the higher rate of the hydrolysis under alkaline conditions. Therefore, k_{al} for BA was studied in the following systems:

- two-phase pH-buffered system
- diluted aqueous solution without any organic layer and buffer

In the two-phase systems strong pH-buffers ($I = 1-3$ M) were added to avoid the exhaustion of the OH^- ions by acetic acid formed.

An equation with three variables on time was deduced to compute the value of k_{al} in the pH-buffered solutions. This equation bases on the minimum squared difference between the sums of hydrolyzed BA calculated by Equation (2) for intervals $t_n - t_{n-1}$ and the tested concentrations of the acetic anions:

$$\sum_{n=1}^p \left\{ 0.25 k_{al} \sum_{n=1}^n ([BA]_n + [BA]_{n-1}) ([OH^-]_n + [OH^-]_{n-1}) \times (t_n - t_{n-1}) - [CH_3COO^-]_n \right\}^2 = \min \quad (5)$$

where n - turn number of the sample withdrawn, $1 \leq n \leq p$

p - total number of samples

The concentrations of BA, OH^- and CH_3COO^- in time had to be tested for the above-described approach.

In the second system, dealing with the one-phase alkaline solutions of BA, any decrease of BA and alkali are equimolar with the quantity of acetate anion formed:

$$[BA]_0 - [BA] = [OH^-]_0 - [OH^-] = [CH_3COO^-] \quad (6)$$

Therefore, Equation (2) can be rearranged as

$$d[OH^-] / \{ ([BA]_0 - [OH^-]_0 + [OH^-]) [OH^-] \}^{-1} = k_{al} dt \quad (7)$$

A linear relationship between a function Y and time t

$$Y = k_{al} t \quad (8)$$

where

$$Y = ([OH^-]_0 - [BA]_0)^{-1} \ln \{ [OH^-]_0 [BA]_0^{-1} [OH^-]^{-1} ([BA]_0 - [OH^-]_0 + [OH^-]) \} \quad (9)$$

was deduced by integration of Equation (7) in boundary conditions from $[OH^-] = [OH^-]_0$ up to $[OH^-] = [OH^-]$ and from $t = 0$ up to $t = t$.

The slope of Y tallies with the k_{al} value.

At this approach only the pH-rate profile had to be obtained under prescribed initial concentrations of alkali and BA.

Temperature Dependence

The temperature dependence of any rate constant follows the Arrhenius equation:

$$k = A \exp[-E / (RT)] \quad (10)$$

where T - temperature, K

E - activation energy

A - constant

R - universal gas constant

It is simple to estimate the Arrhenius constants A and E by means of the factors a and b in the rectilinear plot of $\ln k$ versus T^{-1}

$$\ln k = a + bT^{-1} \quad (11)$$

as

$$A = e^a \quad (12)$$

and

$$E = -bR \quad (13)$$

Coinfluence of pH and Temperature

The total hydrolysis reaction is the slowest at the pH value where

$$\frac{d}{d[H^+]} (k_{ac}[BA][H^+] + k_{al}[BA][OH^-]) = 0 \quad (14)$$

In diluted water solutions

$$[OH^-] = K_W [H^+]^{-1} \quad (15)$$

Therefore Equation (14) gives

$$k_{ac} = k_{al} K_W [H^+]^{-2} \quad (16)$$

Logarithming Equation (16) and replacing

$$\lg K_W = a_W + b_W T^{-1} \quad (17)$$

$$\lg k_{ac} = \lg A_{ac} - E_{ac}(RT)^{-1} \lg e \quad (18)$$

and

$$\lg k_{al} = \lg A_{al} - E_{al}(RT)^{-1} \lg e \quad (19)$$

result the optimum pH value for extraction which is described by the following equation:

$$pH_{opt} = 0.5 \left\{ \lg(A_{ac}A_{al}^{-1}) - a_W + [(E_{al} - E_{ac})R^{-1} \lg e - b_W]T^{-1} \right\} \quad (20)$$

Results and Discussion

Acid Hydrolysis

The experimental results obtained in the study [1] and detailed in Table 1 confirm the suitability of the model applied when the acid hydrolysis was studied.

Table 1. Rate Constants for Acid Hydrolysis of Butyl Acetate

Concentration $\times 10^3$, mol l ⁻¹			Time, min	Rate constant $\times 10^3$, l mol ⁻¹ s ⁻¹	
BA	HCl	CH ₃ COOH		k_{ac}	$\bar{k}_{ac} \pm \sigma_n$
$T = 313\text{ K}$					
37.0	5	0.27	60	0.42	0.44 ± 0.02
		0.56	120	0.42	
		0.91	180	0.45	
		1.22	240	0.47	
	10	0.55	60	0.42	
		1.10	120	0.42	
		1.68	180	0.42	
		2.28	240	0.43	
	20	1.2	60	0.45	
		2.4	120	0.45	
		3.9	180	0.48	
		5.2	240	0.48	
$T = 339\text{ K}$					
41.8	5	3.2	60	4.25	3.85 ± 0.18
		5.8	120	3.85	
		8.9	180	3.95	
		11.9	240	3.95	
		14.8	300	3.93	
		17.8	360	3.95	
	10	5.9	60	3.92	
		11.3	120	3.75	
		16.9	180	3.75	
		22.4	240	4.25	
		27.8	300	3.70	
		33.5	360	3.78	
	20	11.3	60	3.75	
		22.6	120	3.75	
		34.0	180	3.77	
		43.8	240	3.63	
		54.4	300	3.65	
		66.0	360	3.65	

Table 1. Rate Constants for Acid Hydrolysis of Butyl Acetate (end)

Concentration $\times 10^3$, mol l ⁻¹			Time, min	Rate constant $\times 10^3$, l mol ⁻¹ s ⁻¹	
BA	HCl	CH ₃ COOH		k_{ac}	$\bar{k}_{ac} \pm \sigma_n$
$T = 348\text{ K}$					
43.5	5	5.16	60	6.58	6.59 ± 0.19
		10.6	120	6.77	
		16.2	180	6.98	
		21.4	240	6.83	
		26.5	300	6.77	
		31.9	360	6.78	
	10	10.0	60	6.38	
		20.6	120	6.58	
		31.8	180	6.77	
		41.3	240	6.60	
		51.0	300	6.52	
		62.1	360	6.62	
	20	19.9	60	6.35	
		40.4	120	6.45	
		61.5	180	6.55	
		80.6	240	6.43	
		100	300	6.38	
		120	360	6.38	
$T = 353\text{ K}$					
44.4	5	7.2	60	9.02	8.66 ± 0.44
		13.9	120	8.70	
		22.2	180	9.27	
		29.8	240	9.32	
	10	13.1	60	8.20	
		27.2	120	8.52	
		43.2	180	9.02	
		66.5	240	8.73	
	20	25.2	60	7.88	
		51.6	120	8.07	
		81.6	180	8.52	
		110.7	240	8.65	
$T = 364.5\text{ K}$					
46.4	5	7.1	30	11.97	15.4 ± 1.9
		14.6	60	12.32	
		30.3	120	12.77	
		46.6	180	13.08	
		62.6	240	13.20	
	10	13.8	30	16.52	
		27.6	60	16.52	
		57.0	120	17.07	
		84.5	180	16.87	
		116.0	240	17.37	
	20	51.0	60	16.52	
		103.6	120	16.52	
		155	180	17.07	
		209	240	15.63	

The k_{ac} values calculated by Equation (4) are independent of the time and the catalyst concentration at any temperature. The relationship (11) is linear for all the values of k_{ac} , except those at 91.5 °C. Obviously, in the latter case the real concentration of BA is lower than $[BA]_s$, due to the formation of an azeotropic mixture boiling at 90.2 °C and consisting 71.3 mass% of BA and 28.7 mass% of water.

All the k_{ac} values depicted in Table 1, omitting those at 91.5 °C, were included when characteristics for the temperature dependence of the acid hydrolysis was computed. The constants for Equation (11) with standard error for $\ln k_{ac}$ estimates $s = 0.074$ and correlation coefficient $r = 0.9986$ are as follows

$$\begin{aligned}a_{ac} &= 19.52 (\pm 0.87) \\b_{ac} &= -8539 (\pm 320)\end{aligned}$$

The constants in the Arrhenius Equation (10) calculated from a and b are

$$\begin{aligned}A_{ac} &= 3.0 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1} \\E_{ac} &= 70.96 \text{ kJ mol}^{-1}\end{aligned}$$

The only published value dealing with the acid hydrolysis of BA, except those in our paper [1], is $\lg k_{ac} = -3.96$ at 25 °C in [2]. The data for A_{ac} and E_{ac} found in this study give at 25 °C a coinciding value, $\lg k_{ac} = -3.97$.

Alkaline Hydrolysis

One can see from Tables 2 and 3 that the rate constants at the same temperature for the alkaline hydrolysis are 100-400 times higher than those for the acid hydrolysis.

Due to the reasons described above, the simple two-phase model, proven to be excellent for the acid hydrolysis, turned out to be biased for the alkaline hydrolysis.

Calculation of a value of k_{al} by the more complicated Equation (5) requires computation of the relationship between concentrations of BA, CH_3COO^- and OH^- tested in time for a variety of samples. At that, the following difficulties occurred.

The estimated concentrations of BA in the aqueous phase $[BA]$ varied unsystematically 10-20 %. Probably, at the high rate of hydrolysis, $[BA]$ is limited by the dissolution rate of BA in water. The latter depends on temperature and varies accidentally due to the uncontrolled change of the interphase area. Therefore, the mean concentration of BA had to be applied for every catalyst-temperature condition studied.

As described above, a double distillation procedure is required to separate the pH-buffer when the CH_3COO^- concentration is tested. This procedure can lead to losses of CH_3COO^- .

Table 2. Rate Constants for Alkaline Hydrolysis of Butyl Acetate in the Two-Phase pH-Buffered Sytem

Buffer	Time, min	pH	Concentration ×10 ³ , mol l ⁻¹		Rate constant ×10 ³ , l mol ⁻¹ s ⁻¹	
			CH ₃ COO ⁻	BA	k _{al} [*]	$\overline{k}_{al}^* \pm \sigma_n$
T = 313 K						
1 M H ₃ BO ₃ + KOH	0	10.0	-	20.83	0.288	0.30 ± 0.08
	30	9.96	3.1			
	60	9.93	5.8			
	90	9.90	9.4			
	120	9.90	10.2			
	160	9.90	12.0			
	180	9.91	13.4			
	210	9.91	15.9			
1 M H ₃ PO ₄ + KOH	0	11.00	-	7.37	0.408	
	31	11.00	11.9			
	46	10.95	18.3			
	61	10.87	23.9			
	76	10.84	29.0			
	91	10.83	34.1			
	106	10.74	37.9			
	121	10.55	41.0			
3 M KOH + H ₃ PO ₄	0	11.92	-	2.66	0.212	
	30	11.90	19.3			
	60	11.93	36.7			
	90	11.91	55.4			
	125	11.93	72.9			
	180	11.36	116			
	240	11.25	138			
	300	11.16	145			
T = 353 K						
1 M H ₃ BO ₃ + KOH	0	9.57	-	20.8	2.48	2.24 ± 0.40
	20	9.56	43.1			
	42	9.50	72.0			
	60	9.31	99.4			
	80	9.17	127			
	100	9.02	190			
	120	9.02	207			
	1 M H ₃ PO ₄ + KOH	0	10.66			
15		10.58	137			
30		10.10	160			
45		10.05	188			
60		9.89	214			
75		9.79	223			
100		9.03	239			
3 M KOH + H ₃ PO ₄	0	11.25	-	3.57	2.01	
	10	11.25	131			
	20	10.82	214			
	30	10.66	288			
	40	10.56	333			
	50	10.44	367			

Table 3. Rate Constants for Alkaline Hydrolysis of Butyl Acetate

[BA] ₀ , mol l ⁻¹ ;	0.0143												0.007																							
	0.0107			0.0097			0.005			0.010			0.00498		0.00500																					
[OH ⁻] ₀ , mol l ⁻¹ ;																																				
Temperature, °C :	20						40						50						60						70						80					
Time, min	pH ^(*)		Y ⁽²⁾	pH [*]		Y	pH [*]		Y	pH [*]		Y	pH [*]		Y	pH [*]		Y	pH [*]		Y	pH [*]		Y	pH [*]		Y	pH [*]		Y						
2.5	12.11	13.89		11.40	20.69	10.72	41.9	10.73	58.4	10.27	125.7	9.51	157.6	9.93	162.1																					
5	12.05	25.51		11.30	41.26	10.50	85.7	10.45	138.8	9.95	241.1	8.92	296.8	9.71	300.5																					
7.5	12.00	36.07		11.20	64.68	10.25	139.9	10.24	214.1	9.70	347.9			9.50	461.0																					
10	11.93	52.24		11.10	90.97	10.04	187.9	10.06	287.4	9.50	440.6			9.36	581.4																					
12.5	11.90	59.69		11.00	120.1			9.91	353.5	9.31	533.0			9.24	691.8																					
15	11.82	81.12		10.90	152.0			9.79	409.0	9.17	603.0			9.12	807.9																					
20	11.74	104.9																																		
25	11.68	124.2																																		
30	11.62	144.9																																		
40	11.51	186.2																																		
50	11.40	231.7																																		
60	11.25	299.9																																		
<i>K_w</i> × 10 ¹⁴ 3)	0.69			2.95		5.50		9.55		15.8				25.1																						
<i>r_Y</i>	0.996			0.989		0.997		0.998		0.988				0.993																						
<i>k_{rel}</i> ± <i>σ_n</i> , l mol ⁻¹ s ⁻¹	0.081 ± 0.001			0.159 ± 0.004		0.308 ± 0.005		0.465 ± 0.005		0.710 ± 0.017				0.940 ± 0.015																						

¹⁾ *pH*^{*} = -lg *a_{H⁺}* *γ_{OH⁻}*⁻.

²⁾ *Y* is calculated by Equation (8).

³⁾ Taken from [4].

The values for activity coefficients, γ_{OH^-} are unknown under the conditions studied. So, the activity of OH^- anions, α_{OH^-} found from pH readings, had to be applied instead of OH^- concentration when Equation (5) is computed. Since $\alpha_{OH^-} = [OH^-] \gamma_{OH^-}$ the computed rate constant $k_{al}^* = k_{al} \gamma_{OH^-}$.

The results obtained when the one-phase aqueous solutions were studied (Table 3) should give the real values for k_{al} .

Introducing the k_{al} values from Table 3 into Equation (11) gives the following constants for the temperature dependence with standard error for $\ln k_{ac}$ estimates $s = 0.11$ and correlation coefficient $r = 0.994$

$$a_{al} = 12.46 (\pm 0.76)$$

$$b_{al} = -4415 (\pm 247)$$

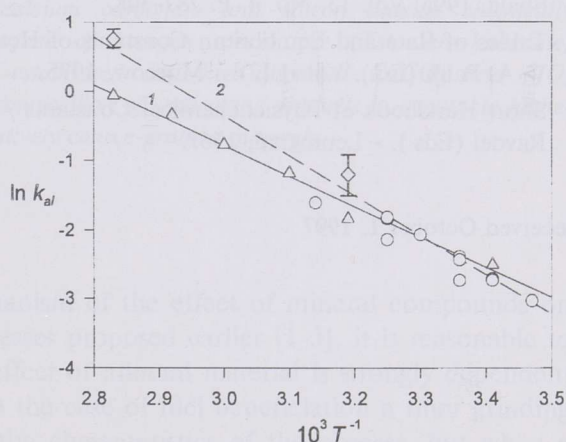
The constants in the Arrhenius Equation (10), calculated from a_{al} and b_{al} are

$$A_{al} = 2.58 \cdot 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$$

$$E_{al} = 36.7 \text{ kJ mol}^{-1}$$

The $\ln k_{al}$ values obtained in this work and those published in [2] and [3] are compared in Figure. The fact that the values of k_{al}^* , found for the solutions with high ionic strength, overcome the values of k_{al} found for solutions without pH buffers applied, suggests that γ_{OH^-} must be higher than 1 when the buffers are added.

Plot of $\ln k_{al}$ versus T^{-1} : 1 - calculated by A and E from this work; 2 - calculated by A and E from [3]; Δ - experimental results in one-phase systems (Table 3); $\diamond$ - experimental results for k_{al}^* in two-phase pH-buffered systems; (Table 2); $\circ$ - values reported in [2]



Coinfluence of pH and Temperature

The following regression constants for the temperature dependence of the water ion product, Equation (16), were calculated, taking the values for K_W within the range 0-100 °C from the handbook [3]

$$a_W = -4.96 (\pm 0.16)$$

$$b_W = -2690 (\pm 0)$$

When the estimated values of A_{ac} , E_{ac} , A_{al} , E_{al} , a_W and b_W are replaced in Equation (20), the optimum value for pH providing the minimum hydrolysis of BA follows the simple temperature dependence

$$pH_{opt} = 4.01 + 450 T^{-1} \quad (21)$$

The results obtained confirm a conclusion in the paper [1]: the pH value of the water phase should not be greater than 5.5. Otherwise, the faster alkaline hydrolysis begins to dominate and, thus BA breaks down rapidly. Besides, it is remarkable that the values for pH_{opt} do not increase with an increase of temperature, while the ratio of k_{ac} and k_{al} values decreases ($E_{al} < E_{ac}$). For example, at 311 °C ($p \geq 1.6$ at) when $k_{ac} = k_{al}$, the minimum hydrolysis of BA occurs already at pH 4.76. The temperature dependence of pH_{opt} , opposite to that of the rate constants, results from the substantial growth of the water dissociation when the temperature increases.

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