Influence of the Polarity of the Medium on the Alkaline Hydrolysis of n-Butyl Acetate in Hydroalcoholic Mixtures

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The kinetics of the alkaline hydrolysis of n-butyl acetate have been studied in water and in hydroalcoholic mixtures. The rate constants, activation energies, frequency factors, entropies, Gibbs free energies and enthalpies of activation have been determined. The radii of the activated complexes have been calculated and related to their degree of solvation. A possible reaction mechanism is formulated.

Introduction

In previous papers the hydrolytic behaviour of a series of simple esters in alkaline medium has been studied [1–3]. In the present work we investigate the kinetics and thermodynamics of the alkaline hydrolysis of n-butyl acetate in water and hydroalcoholic mixtures. Our aim is to determine the influence of the polarity of the medium on the kinetic-thermodynamic data and to establish the nature and size of the activated complex.

Experimental

A conductometric method was used for determining the kinetic data since the nature of the ionic species in the reaction medium is modified during the process.

$$\mathrm{CH_3-COOCH_2-CH_2-CH_2-CH_3+Na^+OH^-} \rightarrow \mathrm{CH_3-COO^-Na^+ + CH_3-CH_2-CH_2-CH_2OH} \,. \quad (1)$$

An increase in the concentration of acetate ions, $\mathrm{CH_3-COO^-}$, together with a simultaneous decrease of $\mathrm{OH^-}$ ions causes the electric conductivity of the reacting system to decrease with time. The Kolrausch law can correctly be applied here since the concentrations of ester and alkali are sufficiently low. This gives:

$$x = \frac{(\chi_0-\chi)\cdot 10^3}{\Lambda_{\mathrm{OH^-}} - \Lambda_{\mathrm{CH_3-COO^-}}} \;(\text{Eq. g/l}) \qquad (2)$$

where χ_0 and χ are the specific conductivities at the beginning of the experiment and after a certain time and $\Lambda_{\mathrm{OH^-}}$ and $\Lambda_{\mathrm{CH_3-COO^-}}$ are the equivalent conductivities.

A Model RC 16 BZU Beckman conductometer, with conductivity cell constants $k = 0.1$, was used for the experiment.

The reagents used were: anhydrous sodium acetate, p. a. from Merck; n-butyl acetate, p. a. from B.D.H.; 0.1 M sodium hydroxide, p. a. "Titrisol" from Merck and absolute ethyl alcohol from Merck.

Model NB/DS-1269 Colora ultrathermostats with a thermal constancy of 0.05 °C were used. The working temperatures were 20, 25, 30, 40 and 50 °C.

The reaction media were: water, 80% water – 20% ethanol, 70% water – 30% ethanol, 50% water – 50% ethanol. These percentages refer to volume.

Calculation of the Kinetic-thermodynamic Parameters

The rate constants were found by means of the equation for 2nd order reactions:

$$k = \frac{1}{t\,(a-b)} \ln \frac{b\,(a-x)}{a\,(b-x)} \,. \qquad (3)$$

The activation energies E and frequency factors A were calculated using the Arrhenius equation with the values of k obtained at various temperatures:

$$k_i = A \cdot e^{-E/RT_i} \,. \qquad (4)$$

The free enthalpies ΔG^{++}, entropies ΔS^{++} and enthalpies ΔH^{++} were calculated using the theory of absolute reaction rates [4] and the appropriate thermodynamic relations:

$$k = k_{\mathrm{B}}\, T/h \cdot e^{-\Delta G^{++}/RT} \,, \qquad (5)$$

$$\Delta H^{++} = E - R\,T \,, \qquad (6)$$

$$\Delta S^{++} = (\Delta H^{++} - \Delta G^{++})/T \,. \qquad (7)$$

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The kinetic-thermodynamic values were adjusted by the least squares method, using a 9100 Hewlett Packard computer. The standard deviation of these values is $\leq 1\%$.

Effect of the Dielectric Constant of the Medium and Determination of the Radius of the Activated Complex

There are several equations which relate the rate constant k of a process with the dielectric constant of the medium and the temperature. These equations are based on the Debye-Hückel theories for reactions between ions. Kirkwood[5] extends the treatment to the case in which one or both reacting molecules are dipoles. Scatchard[6], Born[7], Laidler-Eyring[8] and Amis[9] propose similar equations for ion-ion, ion-dipole and dipole-dipole reactions. In our particular case (ion-dipole), an appropriate equation is that of Amis:

$$\ln k_{\mathrm{D}} = \ln k_{\infty} + \frac{Z e \mu}{k_{\mathrm{B}} T D r_{\ddagger}^{2}} \tag{8}$$

where k_D is the rate constant at a dielectric constant D, k_∞ the rate constant corresponding to infinite dielectric constant, k_{B} Boltzmann's constant, T the absolute temperature, Ze the charge of the ion, μ the dipole moment of the ester, and $r_{\ddagger}$ the radius of the activated complex.

This expression predicts a linear relation between $\ln k$ and $1/D$. The corresponding graph should give a straight line whose slope would permit the determination of the radius of the activated complex for given values of the dielectric constant and the temperature.

An empirical equation of Elsemongy[10] relates the rate constant k with D at constant temperature:

$$\ln k_{\mathrm{D}} = \ln k_1 + a(D-1) \tag{9}$$

where k_1 is the rate constant for $D=1$ and a is a specific constant. Here a linear relation between $\ln k$ and D is to be expected.

A linear relation is predicted between $\ln k$ and $(D-1)/(2D+1)$ when the Laidler-Eyring equation[8] for a dipole-dipole reaction is applied:

$$\ln k_D = \ln k_\infty - \frac{1}{k_{\mathrm{B}} T} \cdot \frac{D-1}{2D+1} \left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right) \tag{10}$$

where r and μ are the radii and dipole moments of the species indicated.

Results and Graphs

Table 1 gives the values of the rate constants at different temperatures for various reaction media of the alkaline hydrolysis of n-butyl acetate. In Table 2, the thermodynamic parameters as a function of the polarity of the medium are shown. Figures 1, 3 and 4 represent the hydrolytic progress of n-butyl acetate in 50% water – 50% ethanol, 80% water – 20% ethanol and 70% water – 30% ethanol, respectively. In Fig. 2 the Arrhenius lines of the hydrolysis in pure water (——) and in 50% water – 50% ethanol (-----) are given. In Figs. 5, 6 and 7 the variation of $\log k$ vs. D, $1/D$ and $(D-1)/(2D+1)$ is given, and in Fig. 8 the activation energy as a function of the percentage of ethanol in the reaction medium is shown.

Table 1. k (l.mole^{-1} min^{-1}).

Reaction medium	20 °C	25 °C	30 °C	40 °C	50 °C
Water	4.90	6.46	8.36	13.45	19.86
80% water – 20% EtOH	3.41	—	4.54	7.62	—
70% water – 30% EtOH	2.49	—	3.56	5.62	—
50% water – 50% EtOH	0.98	1.23	1.52	2.35	3.48

Discussion

The activation energy E varies according to the percentage of alcohol in the mixture. It is lowest for

Table 2

Reaction medium	$\log A$ l.mole^{-1} h^{-1}	E kcal/mole	ΔH^{++} kcal/mole	ΔG^{++} kcal/mole	ΔS^{++} cal °K/mole
Water	8.97	8.71	8.10	19.07	−35.81
80% water – 20% EtOH	7.70	7.25	6.64	19.39	−41.61
70% water – 30% EtOH	7.64	7.34	6.74	19.56	−41.87
50% water – 50% EtOH	7.64	7.87	7.27	20.09	−41.89

approximately 20% alcohol by volume (Figure 8). For this minimum value of the activation energy the entropy values are very negative which indicates the formation of a highly ordered or structured activated complex due to its high degree of solvation. It can be observed that there is a compensation effect between ΔH^{++} and $T\,\Delta S^{++}$; very similar values for the free activation enthalpy ΔG^{++} are found in all the media investigated.

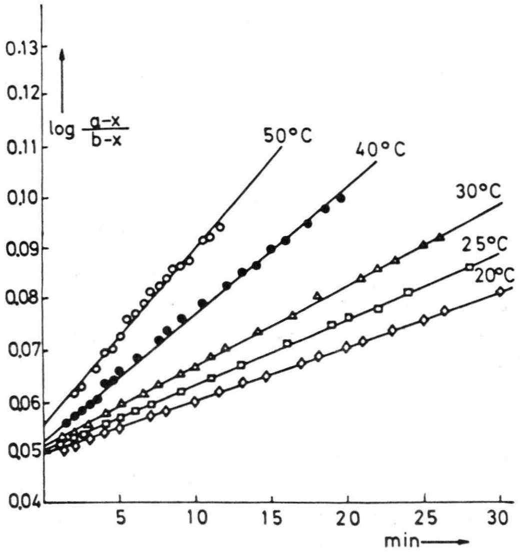


Fig.-1-Hydrolysis of n-butyl acetate in water-ethanol 50:50

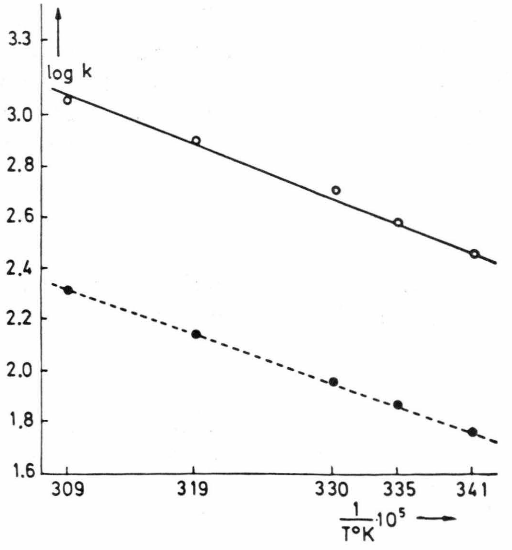


Fig.-2-Arrhenius straight lines of the hydrolysis in pure water (—) and in water-ethanol 50:50 (- - -)

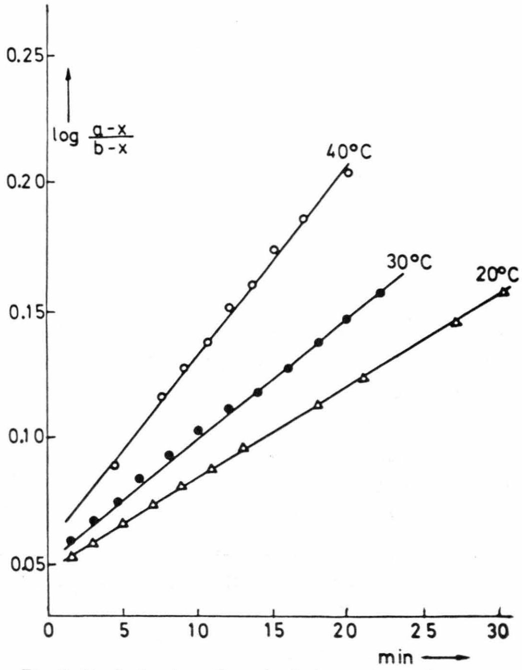


Fig.-3-Hydrolysis of n-butyl acetate in water-ethanol 80:20

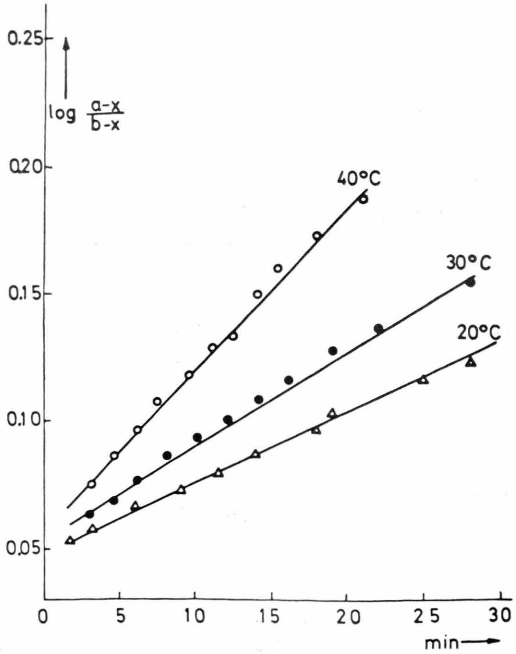


Fig.-4-Hydrolysis of n-butyl acetate in water-ethanol 70:30

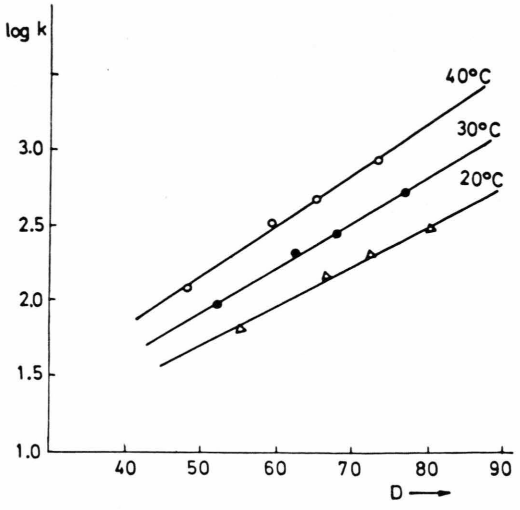


Fig.-5-Variation of log k with D

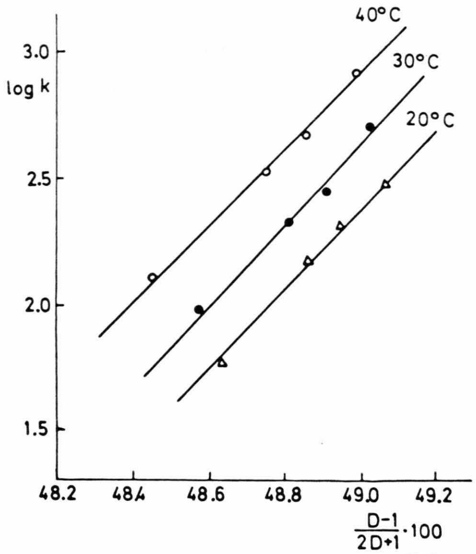


Fig.-7-Variation of log k with $\frac{D-1}{2D+1}$

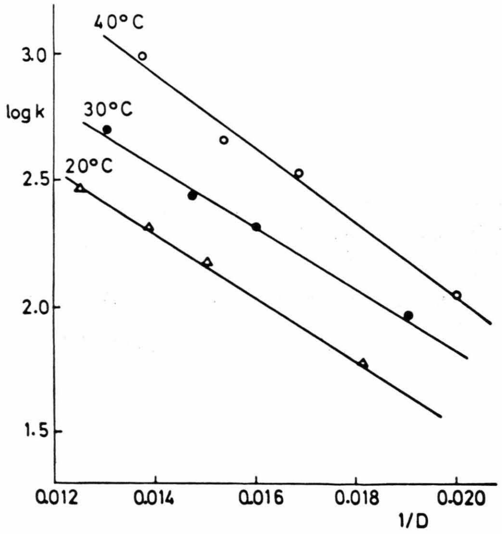


Fig.-6-Variation of log k with 1/D

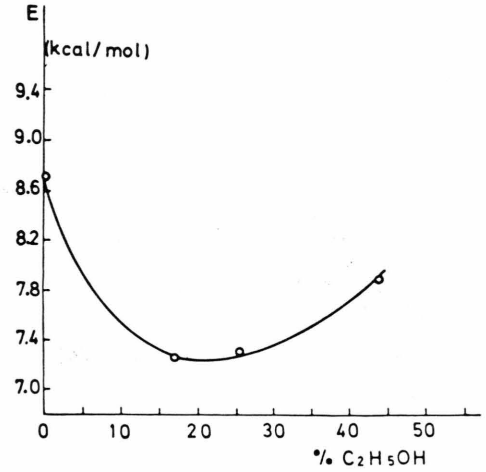


Fig.-8- Activation energy as function of the porcentage of ethanol in the reaction medium.

Any of the equations of Elsemongy, Laidler-Eyring and Amis can correctly be applied in the range of dielectric constants which we have used (40...80).

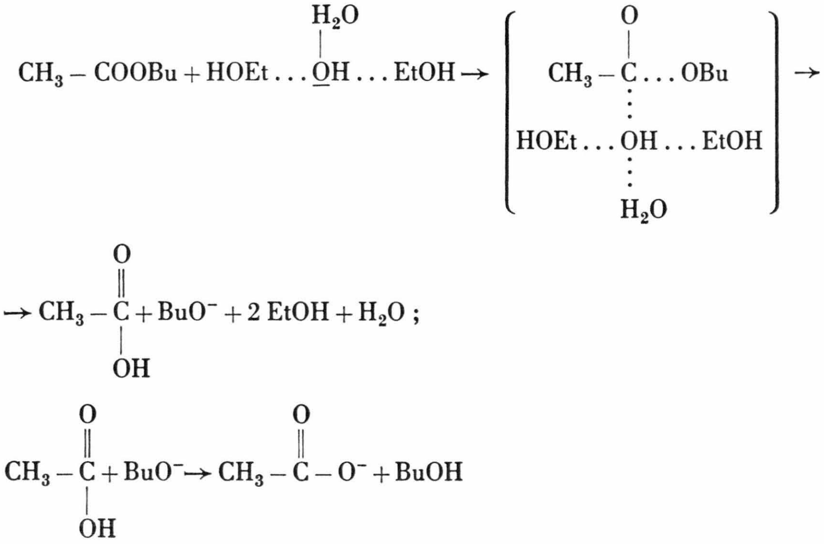
The variation of the rate constant with the polarity of the medium can basically be attributed to the different degree of solvation of the activated complex, which can be estimated from the value of its radius. It is found that, as the radius decreases, the degree of solvation increases. Similarly, when the temperature increases, the radius of the activated complex becomes larger due to a decrease in the degree of solvation (see Table 3).

It must be the so-called Bac2 mechanism which is involved in the hydrolysis in hydroalcoholic mix-

°C	(Å) $r_{\ddagger}$
20	0.88
30	0.89
40	0.93

Table 3. Radii of the activated complex in the alkaline hydrolysis of the n-butyl acetate.

tures, as can be deduced from the very negative entropy values and from the reaction order of the process. It is possible that the nucleophilic attack on the ester is made by the OH^- ion solvated with molecules of water and alcohol. One formulation of the process could be, for example, the following:



$$\mathrm{CH_3 - COOBu + HOEt\ldots \overset{\overset{\displaystyle H_2O}{|}}{\underline{O}}H\ldots EtOH} \rightarrow \left[\begin{array}{c} \mathrm{O} \\ | \\ \mathrm{CH_3 - C\ldots OBu} \\ \vdots \\ \mathrm{HOEt\ldots OH\ldots EtOH} \\ \vdots \\ \mathrm{H_2O} \end{array}\right] \rightarrow$$

$$\rightarrow \mathrm{CH_3 - \underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + BuO^- + 2\,EtOH + H_2O}\ ;$$

$$\mathrm{CH_3 - \underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + BuO^- \rightarrow CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - O^- + BuOH}$$

or:

$$\mathrm{BuO^- + H_2O \rightarrow BuOH + OH^-}\,.$$

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