

## **FLOW MICROCALORIMETRY APPLIED TO THE STUDY OF CHEMICAL STABILITY OF ORGANIC COMPOUNDS\***

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This work reports on the possibility of using the LKB 2277 thermal activity monitor to study the influence of anionic, cationic and neutral surfactants on the stability of a series of a *n*-alkyl acetates.

Thermodynamic parameters as well as rate constants could be calculated.

Two conclusions can be drawn: 1. The stability of esters increases with increasing concentrations of surfactants. 2. The stability of esters in the presence of surfactants increases with the chain length of the esters; the contribution of a CH<sub>2</sub> group to a higher stability of the esters in the presence of surfactants seems to be constant.

Surfactants dispersed in water provide complex environments in which poorly soluble organic compounds can be solubilized. Such a complex environment can have a tremendous effect on chemical reaction processes. The aim of this research is to elucidate the dependence of the rate constants for basic hydrolysis of a series of aliphatic acetic acid esters on the concentration of neutral, anionic and cationic surfactants and to show that flow microcalorimetry is a suitable technique in stability studies.

### **Materials and methods**

**Chemicals.** Acetic acid esters, cetyltrimethylammoniumbromide (CTAB), sodium laurylsulphate (NaLS) and cetomacrogol 1000 (C1000) of pure analytical grade were used without any further purification.

The critical micellar concentrations (cmc) of CTAB, NaLS and C1000 were respectively 0.5 mM, 6.5 mM and 0.05 mM [1].

**Microcalorimetry.** The LKB 2277 Thermal Activity Monitor [2] was used in its flow through mode. All hydrolyses have been carried out under pseudo first order conditions (pH 12). The reaction was initiated outside the calorimeter in a thermostated bath (298 K ± 0.01) and the reacting solution

\* To the memory of Prof. Dr. A. Hulshoff

was pumped into the flow-through cell [3]. The initial concentration of the esters was 1 mM. For first order reactions the following equation between the thermal output  $P$  and the rate constant have been demonstrated and verified [3, 4].

$$P = k C h \nu \exp(-kt) \quad (1)$$

where  $k$  is the rate constant,  $C$  is the initial concentration of the reactant,  $h$  is the enthalpy of the reaction,  $\nu$  is the volume of the microcalorimetric cell,  $t$  is the time elapsed after the reaction was initiated. The rate constant values were obtained by least square analysis of the calorimetric signal according to Eq. (1). They were accurate within about 1%.

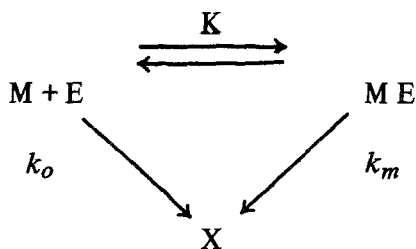
### Results and discussion

The effect of varying surfactant concentrations on the rate of hydrolysis of various acetic acid esters was determined. As an example, the results of the hydrolysis of propyl and heptyl acetate in the presence of C1000 are shown in Table 1. The decrease in rate of hydrolysis with increasing concentrations of surfactant is apparent. This decrease is clearly more pronounced with heptyl acetate. Such a behaviour was found with each of the three surfactants used. Both the surfactant concentration and the chain length of the ester contribute to a higher stability of the esters.

**Table 1** Observed rate constants for basic hydrolysis (pH 12) of propyl and heptyl acetate and the influence of various concentrations of C1000 (indicated by [C])

[C], mM	Propylacetate $k_{\text{obs}} \cdot 10^3 \text{ s}^{-1}$	Heptylacetate $k_{\text{obs}} \cdot 10^3 \text{ s}^{-1}$
0.00	1.63	1.63
5.25	1.58	0.42
9.18	1.55	0.25
13.12	1.42	0.22
26.25	1.30	0.20
52.5	1.08	0.17

This influence of the surfactant of the kinetics of hydrolysis of esters has been treated in terms of Micelle (M) – Ester (E) complex formation and hydrolysis in the aqueous and micellar phase.



where  $K$  is the association constant for micelle substrate interaction,  $k_o$  and  $k_m$  are the hydrolysis rate constants respectively in the bulk and the micellar phase. Such an assumption leads to the following equation [5]:

$$1/(k_o - k_{obs}) = 1/(k_o - k_m) + 1/(k_o - k_m)K[M] \tag{2}$$

In this equation  $k_{obs}$  is the overall measured hydrolysis rate constant and  $[M]$  the concentration of the micelles, given by  $[M] = ([C] - cmc)/N$ , assuming a constant  $cmc$  over the range of surfactant concentrations used; where  $[C]$  is the total surfactant concentration,  $cmc$  is the critical micellar concentration of the surfactant under experimental conditions and  $N$  is the aggregation number.

Eq. 2 becomes:

$$1/(k_o - k_{obs}) = 1/(k_o - k_m) + N/K(k_o - k_m)([C] - cmc) \tag{3}$$

Typical plots of Eq. (3) are shown in Fig. 1a, b and c, for the hydrolysis of a series of esters in the presence of respectively C1000, CTAB and NaLS. As can be seen from this figure, Eq. (3) holds for the hydrolysis of acetates in the presence of all types of surfactants studied. Some  $K/N$  values are given in Table 2;  $K/N$  values increase with increasing lipophilic character (chain length) of the ester. This dependence of  $K/N$  on the chain length can be formulated as follows.

If  $k_m \ll k_o$  Eq. 2 can easily be rearranged to:

$$1/k_{obs} - 1/k_o = K[M]/k_o \text{ or to:}$$

$$\ln((t_{0.5})_{obs} - (t_{0.5})_o) = \ln[M] \ln 2/k_o + \ln K \tag{4}$$

in which  $(t_{0.5})_{obs}$  and  $(t_{0.5})_o$  are the half-lives of the esters respectively

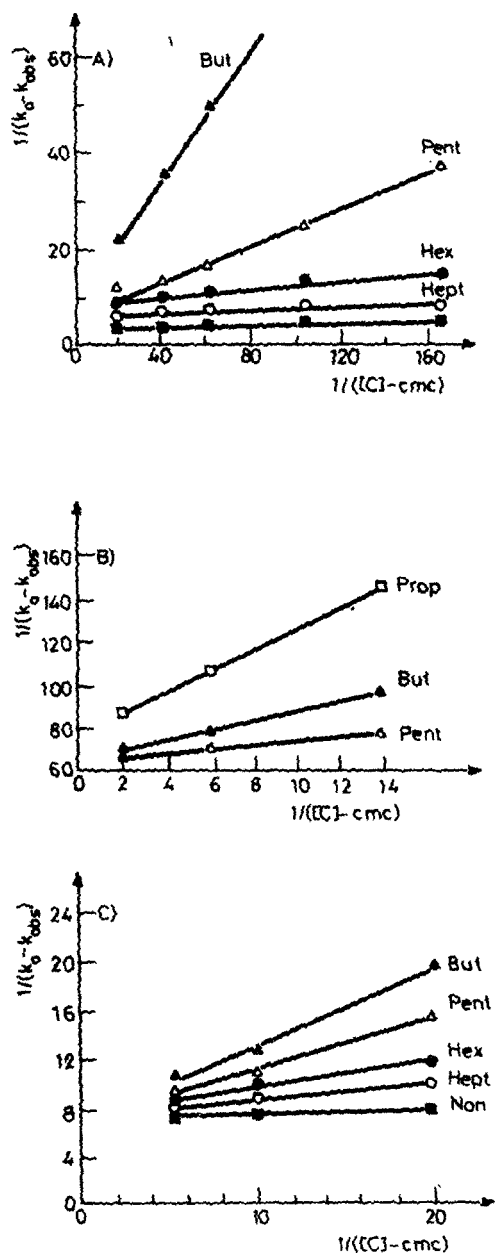


Fig. 1 Plots of  $1/k_o - k_{obs}$  against  $1/([C] - cmc)$  for some acetates in the presence of various concentrations of CTAB (A), NaLS (B) and C1000 (C).

**Table 2** Calculated values of  $k_m$  and  $K/N$  for some acetates under the influence of CTAB, NaLS, and C1000.

Esters and Surfactants	$k_m, s^{-1}$	$K/N$
Propyl		
CTAB	*	0.75
NaLS	$2 \cdot 10^{-4}$	16
C1000	$0.7 \cdot 10^{-4}$	8.7
Butyl		
CTAB	$2.3 \cdot 10^{-4}$	12
NaLS	$0.4 \cdot 10^{-4}$	35
C1000	*	31
Pentyl		
CTAB	*	*
NaLS	$1.9 \cdot 10^{-4}$	17
	$1.5 \cdot 10^{-4}$	101
Heptyl		
CTAB	$1.6 \cdot 10^{-4}$	34
NaLS	*	*
C1000	$1.5 \cdot 10^{-4}$	1600

\* not determined

in the presence and the absence of surfactant.  $\ln K$  is known to be dependent on the chain length of the ester [6] as follows:

$\ln K = a + bn$ , where  $n$  is the number of  $\text{CH}_2$  groups of the ester:  $a$  and  $b$  are constants,  $b$  represents the group contribution of a  $\text{CH}_2$  to the complexation of the ester to the micelle.

Egn. (4) then becomes:

$$\ln[(t_{0.5})_{\text{obs}} - (t_{0.5})_o] = c + bn \quad (5)$$

where  $c = a + \ln\left[\frac{[M]}{k_o} \ln 2\right]$

Since  $k_o$  was found to be constant for all the esters studied ( $k_o = 1.6 \cdot 10^{-3} \text{ s}^{-1}$ ) under the prevailing experimental conditions, Eq. (5) can be used to compare the hydrolysis of a series of esters at the same  $[M]$ .

As an example of Eqn. (5) Fig. 2 shows a plot of  $\ln[(t_{0.5})_{\text{obs}} - (t_{0.5})_o]$  against the chain length of the esters for three various concentrations of C1000. As the model predicts there is a reasonable linearity between  $\ln[(t_{0.5})_{\text{obs}} - (t_{0.5})_o]$  and the chain length, with a slope independent of the concentration of C1000. The contribution of a  $\text{CH}_2$  group of the alkyl chain

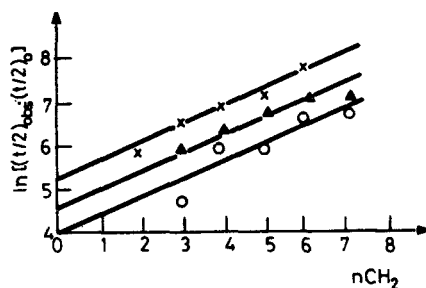


Fig. 2 Plots of  $\ln[(t_{0.5})_{obs} - (t_{0.5})_0]$  against the alkyl acetates chain length in the presence of various concentrations of C1000 (x-x = 200 mM; ▲ - ▲ = 100 mM; o-o = 50 mM)

of the ester to the higher stability of esters in the presence of C1000 seems to be constant. This has also been found with CTAB and NaLS.

## Conclusions

These results demonstrate that flow microcalorimetry can be successfully used as an analytical tool to study stability problems.

Since this technique relies only on heat exchange it can be sometimes a unique tool for complex mixture where other techniques fail.

## References

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**Zusammenfassung** – Das Kalorimeter LKB 2277 kann verwendet werden, um den Einfluss kationischer, anionischer und neutraler Tenside auf die Stabilität einer Serie von n-Alkylacetaten zu untersuchen. Thermodynamische Parameter und Geschwindigkeitskonstanten werden berechnet. Folgende Schlussfolgerungen werden gezogen: 1. Die Stabilität der Ester steigt mit zunehmender Tensidkonzentration. 2. In Gegenwart von Tensiden steigt die Stabilität mit zunehmender Kettenlänge des Esters, der Beitrag einer CH<sub>2</sub>-Gruppe zur steigenden Stabilität des Esters scheint konstant zu sein.

**РЕЗЮМЕ** — Приведены результаты возможного использования термического монитора ЛКБ 2277 для изучения влияния катионных, анионных и нейтральных поверхностно-активных веществ на устойчивость ряда *n*-алкилацетатов. Вычислены термодинамические параметры и константы скорости. Найдено, что устойчивость сложных эфиров увеличивается с увеличением их длины и концентрации поверхностно-активных веществ. Установлен постоянный вклад  $\text{CH}_2$  групп в более высокую устойчивость эфиров в присутствии поверхностно-активных веществ.