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ORIGINAL ARTICLE

Kinetics of decompositition of organophosphate Fenitrothion by decontaminating foam-making blends

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Summary
The hydrolytic efficacy of foam-making blends on the basis of cationic and nonionic surfactants and hydrogen peroxide was tested against the organophosphate Fenitrothion. The length of alkyl chains in both classes of surfactants and their mutual ratios are not parameters which significantly influenced the reactivity of blends. On the other hand, an increase in the hydrogen peroxide concentration induced a significant increase in the velocity of hydrolysis of Fenitrothion.

Keywords: Foams – decontamination – organophosphate – cationic surfactants

INTRODUCTION

Decontamination is the basic means of personal protection and recovery of the use of equipment after contamination by chemical warfare agents (Patočka 2004). At the present time, increasing the efficacy and availability of the means of decontamination is motivated by the threat of terroristic misuse of chemical warfare agents (Kotinský 2002).

Decontamination solutions used previously have been replaced by gels, emulsions and foams, which have better rheologic properties (Töpfer 2006). For example, foams are exploited mainly in the large–scale decontamination of vehicles. Experiments were carried out to exploit foams for the primary decontamination of persons contaminated by chemical warfare agents. The efficacy of such procedures has already been evaluated in *in vivo* experiments in our department (Cabal et al. 2003).

These experiments were carried out to find the appropriate structure of surfactants for the preparation of foams with good rheological properties and with high reactivity to the organophosphates. Foam based on dodecyldimethylbenzylammonium chloride and ethoxylated alcohols C13-C16 with ten ethyleneoxide units seemed to be the most efficacious (Cabal et al. 2003).

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The aim of the study was to evaluate the influence of the alkyl lengths of both kinds of surfactants (cationic and nonionic) and the degree of ethoxylation of nonionic surfactant, on the reactivity of selected foam-making blends with the appropriate rheologic properties. The results obtained could be used for optimization of the composition of foam-making blends and for further investigation.

MATERIAL AND METHODS

Equipment used

The following equipment was used for the experiments discussed in this study: Spectrophotometer doublebeam SPECORD M42 (Carl Zeiss, Jena, Germany), Quartz flow cuvette (path length 1 cm, Hellma GmbH, Muellheim, Germany), Stirrer MT2 (Laboratorní přístroje, n.p., Prague, Czech Republic), Peristaltic pump model 315 (ZALIMP, Warszawa, Poland).

Chemicals

All chemicals used in this work were purchased from appropriate providers: hydrogen peroxide (Lachema, Brno, Czech Republic), sodium hydroxide (Dr. Jan Kulich, Hradec Králové, Czech Republic), Fenitrothion (Sumitomo Chemical Co. Ltd., Tokyo, Japan). Nonionic surfactants with structure of ethoxylated alcohols (C12E10, C12E20, C13E10, C16E10, C16E20) were purchased from Sigma–Aldrich (Prague, Czech Republic). Cationic surfactants with structure of alkyldimethylbenzylammonium bromide were synthesized earlier in our department (Kuča et al. 2004). Their identity and purity were confirmed by NMR spectroscopy and HPLC (Kuča et al. 2005).

Preparation of stock solution of surfactants (100 ml)

Calculated amounts of surfactants were dissolved in 30 ml of distilled water and then the solution obtained was poured into a volumetric flask. 60 ml of a 5% solution of sodium peroxide was added to the flask and the flask was filled with water to 100 ml.

Used device setup

After adding Fenitrothion, a flow cuvette setup was used, instead of the standard device setup, in order to achieve homogeneity of the reaction blend. The measurement of the kinetics of hydrolysis of Fenitrothion was carried out with the help of a closed circle setup containing the cuvette, peristaltic pump and reaction vessel.

The reaction vessel was placed on the top of the stirrer and filled with 25 ml of the surfactants solution. Then the peristaltic pump and stirrer were started and the solution mixed and circulated through the device. 0.2 ml of 5% hydrogen peroxide and after 20 seconds, 0.15 ml of the 0.02 M solution of Fenitrothion in isopropanol were added to the circulated solution. Then, the absorption of the reaction blend was monitored by the spectrophotometer for 10 minutes at 400 nm. A flow cuvette filled with distilled water was used as blank.

Measurement of the decomposition kinetics of Fenitrothion

The reaction of Fenitrothion with hydrogenperoxidic anion was monitored in the above mentioned device setup. The presence of 3-methyl-4-nitrophenol as a result of this reaction, was followed. 3-methyl-4-nitrophenol in alkaline media creates a yellow colored nitrophenoxide anion with absorption maxima at 400 nm. This decomposition reaction proceeded under pseudofirst order reaction conditions. Changes in absorption induced by increased nitrophenoxide anion were monitored by the spectrophotometer and noted in six second periods.

Processing of the raw experimental data

Data dealing with changes in absorption dependent on time were transferred from the spectrophotometer to MS Excel (Microsoft Corporation, Redmond, USA). The constant rate was calculated by the procedure described by Guggenheim (Guggenheim 1926) with the usage of modification introduced by Zajíček and Rádl (1979). The procedure used is based on acceptance of following equation:

$$A_{t+\Delta t} = A_t * \exp(k_{obs}*\Delta t) + A_n*(1-\exp(-k_{obs}*\Delta t)),$$

where:

$A_{t+\Delta t}$ = absorption at time t+Δt
A_t = absorption at time t
exp = base of natural logarithm
k_{obs} = observed rate constant
Δt = time distance between two successive measurements
A_n = absorption at infinite time

This relationship is a linear equation with slope $\exp(k_{obs}*\Delta t)$ and intersection $A_n*(1-\exp(-k_{obs}*\Delta t))$. Data from ten minutes measurement were put in two columns of MS Excel so that second column was shifted about one row up. This shift presents one value Δt. Data prepared in such way were displayed in an XY scatter chart. A trends line with print-out of the coefficients regression equation was interlayed through the displayed points. The slope thus obtained was used for the calculation of the rate constant k_{obs} from the term $\exp(k_{obs}*\Delta t)$. Rate constants were recalculated on halftime of reaction.

RESULTS

All results obtained in this study are shown in Table 1. From the results, it is clear that the lowest halflife of the decomposition reaction was obtained for mixture no 15. The highest halflife was reached for mixture no 5. This means that the highest velocity of the Fenitrothion cleavage can be expected for a mixture of the 8% solution of cationic surfactant having a C14 alkylating chain, together with the 2% solution of nonionic surfactant having a C12 alkylating chain.

Table 1. **Dependence of halflife of hydrolysis of Fenitrothion on the composition of surfactant foam-making blends**

Blend no.	Mixture composition	Halflife [Min]
1	CB10-8% + C12E10-2%	1.18
2	CB10-2% + C12E10-8%	2.65
3	CB10-2% + C12E20-8%	2.22
4	CB10-2% + C16E10-8%	3.57
5	CB10-2% + C13E10-8%	4.13
6	CB10-8% + C16E10-2%	1.36
7	CB10-5% + C13E10-5%	1.78
8	CB10-2% + C16E20-8%	2.67
9	CB10-5% + C16E20-5%	1.43
10	CB10-8% + C16E20-2%	1.28
11	CB12-5% + C13E10-5%	1.78
12	CB10-8% + C18E10-2%	1.26
13	CB12-5% + C16E20-5%	1.29
14	CB14-2% + C12E20-8%	2.19
15	CB14-8% + C12E20-2%	1.06
16	CB16-5% + C12E20-5%	1.14
17	CB14-5% + C18E20-5%	1.21
18	CB16-5% + C16E20-5%	1.13

CBx – cationic surfactant with structure of benzalkonia, x indicates number of carbons in lipophilic radical
CxEy – nonionic surfactant with structure of ethoxylated linear alcohol, x indicates number of carbons in lipophilic radical, y indicates a degree of ethoxylation of alcohol

DISCUSSION

In previous experiments, it was found that an increase of concentration of nonionic tenside significantly decreases the velocity of hydrolysis of the substrate. This effect started after the overrun of critical micelle concentration (Cabal et al. 2003). The experiment described in this study verified this fact. The nonionic surfactants used and their mutual ratios with cationic surfactants caused a change in velocity to only one order of magnitude. This result corresponded with ratios used of concentrations of surfactants. The ratio of surfactants 8:2 (cationic: nonionic) and 5:5 (cationic:nonionic) provided almost the same results, while the ratio 2:8 (cationic:nonionic) reaction was slower, as described in the previous study (Cabal et al. 2003). Changes in the structure of the surfactants had a still smaller influence on velocity of reactions than the change of ratios of surfactants.

As shown in the results, an increase in the length of the alkyl in the benzalkonium structure induced a slight increase in velocity. The influence of the length of the alkyl of nonionic surfactants induced a slight increase in cleavage for compounds with an alkyl chain from 13 to 16 carbons. The increase in the grade of ethoxylation caused an increase in velocity in all cases. The velocity of reaction in the tested group of foam-making blends is a relatively constant parameter, which is not influenced by the quantity or quality of the surfactants used. It was observed in these and previous experiments that considerably higher changes in velocity can be induced by changes in the concentration of hydrogen peroxide (Cabal 1995).

Although a 0.04% concentration of hydrogen peroxide was used in this study, a real decontamination requires a much higher concentration of hydrogen peroxide: up to 3% .

Based on the fact, that the velocity of reaction is increased linearly by the concentration of hydrogen peroxide (Cabal et al. 2003), it is possible to expect an increase in the velocity by up to two or three orders of magnitude. Our results clearly demonstrate that change in the composition of blends (for instance due to improved rheologic properties) does not cause any significant change in the velocity of the reaction (if the change is within test limits).

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