

ORIGINAL ARTICLE

Kinetics of hydrolysis of organophosphate soman by cationic surfactant Resamin AE

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Received 20th August 2009.

Published online 15th January 2010.

Summary

This experiment tested the reactivity of the cationic surfactant Resamin AE [N-(2-hydroxyethyl)-N-(2-hydroxy-4-oxa(C14÷22-alkyl))-N,N-dimethylammonium chloride] with organophosphonate soman. It was confirmed that soman is incorporated in the micelle of Resamin AE and that the hydroxyl group of Resamin AE supports the hydrolysis of this organophosphonate. A further increase in reactivity was achieved by the addition of hydrogen peroxide into the reaction mixture. In contrast, if the concentration of neutral salts was increased, a decrease in the velocity of the hydrolysis was obtained. The hydrolytic efficacy of Resamin AE was also compared with that of hexadecyldimethyl-(2-hydroxyethyl)-ammonium bromide. Resamin AE appeared to be a more efficacious hydrolytic agent than other similar compounds due to its advantageous chemical structure.

Key words: cationic surfactants; micellar catalysis; soman; decontamination; Resamin AE

INTRODUCTION

Decontamination of chemical warfare agents (CWA) is a very important process which would be necessary if CWA were spread accidentally or intentionally (Cabal et al. 2004, 2007, Waysbort et al. 2009). For the last 50 years or so, attention has been paid to the development of novel means of decontamination, especially to nucleophiles able to act through the hydrolytic reaction of surfactants with carboxylic or

phosphate esters. The structure of promising surfactants able to support a hydrolytic reaction has been identified and further modified (Cabal et al. 2003, Kuča et al. 2004). Mostly, however, simple cationic surfactants have been used because of their ability to concentrate anions with the properties of nucleophile on their micellar surface (Ouarti et al. 2000, Tiwari et al. 2009a), and surfactants carrying reactive nucleophile directly in their structure have been prepared to improve the reactive properties of micelles (Kotoučová et al. 2001, Kivala et al. 2006).

The hydrolytic efficacy of many compounds containing the hydroxyl group, the oxime group or cupric chelate has been tested (Bunton et al. 1983, Scrimin et al. 1996, Cibulka et al. 1999, Cabal et al. 2007, Tiwari et al. 2009a, b). Surfactants bearing an imidazol group have also been tested, but they were synthesized only for the purposes mentioned above and their usage does not range beyond the laboratory level (Simanenko et al. 2004). Compounds with a similar structure can also be found among surfactants

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produced on an industrial scale mainly as disinfectants or softeners of fabrics (Kuča et al. 2005, 2007).

When novel hydrolytically active surfactants are designed there is a need to consider their spatial arrangement; that of the detergent should be considered in relation to the substrate, which should be broken down, and in relation to its location in the micelle.

Resamin AE belongs to the group of quaternary detergents which have a hydroxyl group, and its structure (Fig. 1) is unusual due to the location of the hydroxyl groups. This spatial arrangement of Resamin AE could be the great advantage of this detergent. The first group is placed in the main and the second in the adjacent alkyl chain. Based on this setup, the first hydroxyl is located in the water phase and the second hydroxyl group is located under the surface of the micelles.

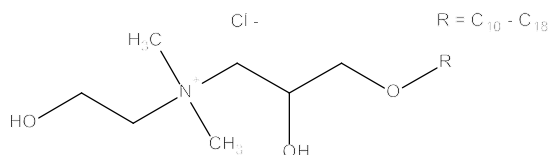


Fig. 1. Structure of Resamin AE.

In this paper, we describe the reactivity of the surfactant Resamin AE with the nerve agent soman with the aim of characterizing the influence regulating its reactivity in relation to its possible further use in actual decontamination mixtures of the foam or emulsion type.

MATERIAL AND METHODS

Chemicals

The chemicals used in this study were purchased as follows: sodium hydroxide (Dr. Jan Kulich, Hradec Králové, Czech Republic), potassium chloride (Lachema, Brno, Czech Republic), hydrogen peroxide (Peroxides, Sokolov, Czech Republic), propan-2-ol (Merck, Darmstadt, Germany), Resamin AE – 30% water solution (Chemotex, Děčín, Czech Republic). Soman was obtained from the Military Repair Facility VOZ 072 Zemianske Kostolany (Slovak Republic).

Equipment used

For all experiments the following pieces of equipment were used: automatic titrator Radiometer RTS 822 (Radiometer, Copenhagen, Denmark), thermostat UI

(VEB Prüfgeräte Werk, Medingen, Germany) and a device for measurement of the surface tension by the ring method which was constructed at the Military Medical Academy Hradec Králové.

Determination of kinetic parameters of the reactions of soman in the micellar environment

The kinetics of hydrolytic reactions of soman was monitored by an automatic titrator in pH-stat mode. The consumption of 0.01 M NaOH necessary for a constant pH of the hydrolytic reaction producing hydrogenfluoridic acid and methylphosphonic acid rising from the cleavage of soman was recorded. The reaction was usually monitored at constant pH 9 and temperature $25\text{ }^{\circ}\text{C} \pm 0.1\text{ }^{\circ}\text{C}$. 20 ml of a solution containing all the required substances except soman was poured into the titration vessel of the pH stat. After the stabilization of the temperature and pH, a reaction was started by adding 0.1 ml of 0.05 M soman solution. The reaction was monitored for seven halftimes or longer.

Determination of critical micelle concentration of surfactants

The determination was carried out by the Du Noüy ring method under conditions determined in the OECD manual (OECD 1981). Solutions of the surfactants were placed in a crystallisation cup with a volume of 100 ml and diameter 75 mm. A ring with a diameter of 33 mm was used for the measurement.

Math processing of raw experimental data

The calculation of rate constant

Data on the consumption of the titration solution over time were transferred from the plotter of the pH-stat to the MS Excel program. The observed rate constant was calculated by the procedure described by Guggenheim (1926) using a modification introduced by Zajíček and Rádl (1979). This procedure is based on acceptance of the following equation:

$$A_{t+\Delta t} = A_t \cdot \exp(k_{\text{obs}} \cdot \Delta t) + A_n \cdot (1 - \exp(-k_{\text{obs}} \cdot \Delta t)) \quad (1)$$

where:

$A_{t+\Delta t}$ = consumption of titration solution at time $t+\Delta t$

A_t = consumption of titration solution at time t

\exp = base of natural logarithm

k_{obs} = observed rate constant

Δt = time distance between two successive measurements

A_n = consumption of titration solution in infinite time

This relationship is a linear equation with slope $\exp(k_{\text{obs}} \cdot \Delta t)$ and intersection $A_n \cdot (1 - \exp(-k_{\text{obs}} \cdot \Delta t))$.

Data obtained from one measurement (10 min) were arranged in two columns of MS Excel so that the second column was shifted one row up. This shift presents one value Δt . Data prepared in such a way were displayed in an XY Scatter chart. A trend line was interlaid through the displayed points with a printout of the coefficients regression equation. The slope obtained was used for the calculation of the rate constant k_{obs} from the term $\exp(k_{\text{obs}} \cdot \Delta t)$.

Calculation of limit values of rate constant of hydrolysis of soman by surfactant

Rate constants of the hydrolysis of soman by surfactants were calculated by means of the Menger and Portnoy equation (1967). This equation was set up so as to include the data from the premicellar region of the surfactant concentration in the calculation:

$$k_{\text{Ct}} = k_0 + \frac{(((-k_0 + k_{\text{max}}) \cdot K/N \cdot ((10^{\text{Ct}}) - \text{CMC})) / (1 + K/N \cdot ((10^{\text{Ct}}) - \text{CMC}))^2)^{0,5} + ((-k_0 + k_{\text{max}}) \cdot K/N \cdot ((10^{\text{Ct}}) - \text{CMC})) / (1 + K/N \cdot ((10^{\text{Ct}}) - \text{CMC})))}{2} \quad (2)$$

where:

k_{Ct} = first order rate constant for molar concentration of surfactant Ct

k_0 = first order rate constant of hydrolysis in premicellar region of surfactant concentration

k_{max} = limit rate constant for $\text{Ct} = \infty$

K/N = fraction of association constant of substrate and aggregation number of surfactant

Ct = logarithm of molar concentration of surfactant

CMC = critical micelle concentration of surfactant

Calculation of critical micelle concentrations – measuring by the ring method

The data on the dependence of the surface tension on the concentration of surfactant were processed by a program for nonlinear regression using the Syzskowski equation in semilogarithmic expression (Syzskowski 1908). The equation was set up so as to include in the calculation the data from the region where the surface tension was not dependent on the concentration of the surfactant:

$$U_{\text{Ct}} = U_{\text{min}} + \frac{(((((U_{\text{max}} - U_{\text{min}}) - A \cdot \text{LOG}(1 + B \cdot (10^{\text{Ct}})))^2)^{0,5} + ((U_{\text{max}} - U_{\text{min}}) - A \cdot \text{LOG}(1 + B \cdot (10^{\text{Ct}}))))}{2} \quad (3)$$

where:

U_{Ct} = surface tension by concentration of surfactant Ct

U_{min} = minimal attainable surface tension

U_{max} = surface tension of solvent

A = constants defining kind of surfactant

B = constant defining position of surfactant in

homologous sequence by magnitude of hydrophobic alkyl

Ct = logarithm of molar concentration of surfactants

The values of constants obtained from equation (3) were introduced in another equation (4) to obtain the logarithm of critical micelle concentration

$$\text{LOG}(\text{CMC}) = \text{LOG}((10^{(U_{\text{max}} - U_{\text{min}})/A} - 1)/B) \quad (4)$$

RESULTS AND DISCUSSION

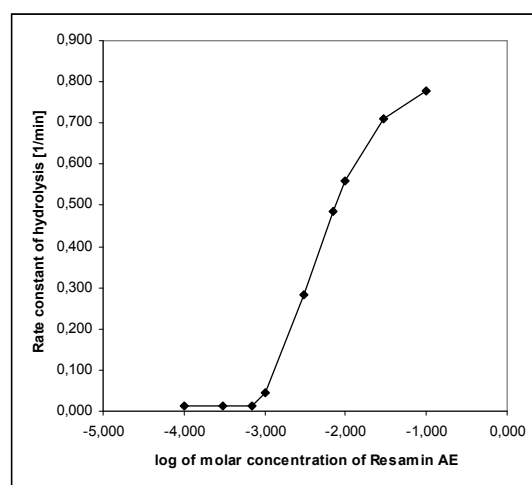


Fig. 2. Dependence of the rate of hydrolysis of soman on the concentration of Resamin AE (pH9, I = 0.01M KCl, t = 25 °C).

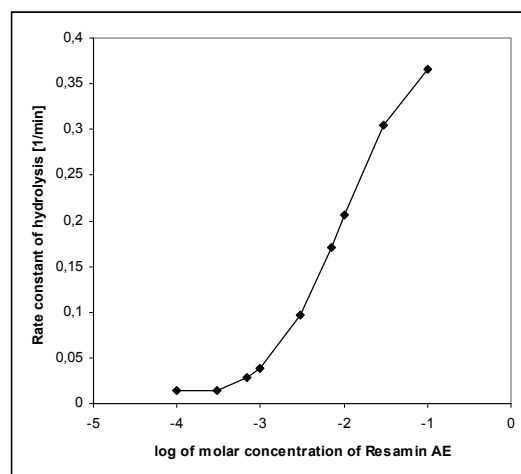


Fig. 3. Dependence of the rate of hydrolysis of soman on the concentration of N-(2-hydroxyethyl)-hexadecyldimethylammonium bromide (C16OH1) (pH9, I = 0.01M KCl, t = 25 °C).

Table 1. Comparison of the parameters of the hydrolysis of soman by Resamin AE and surfactant C16OH1.

		Resamin AE	C16OH1
k_o	1/min	0.014	0.014
k_{max}	1/min	0.81	0.40
K/N	L/mol	237	103
CMC	mol/L	8.30E-04	3.40E-04

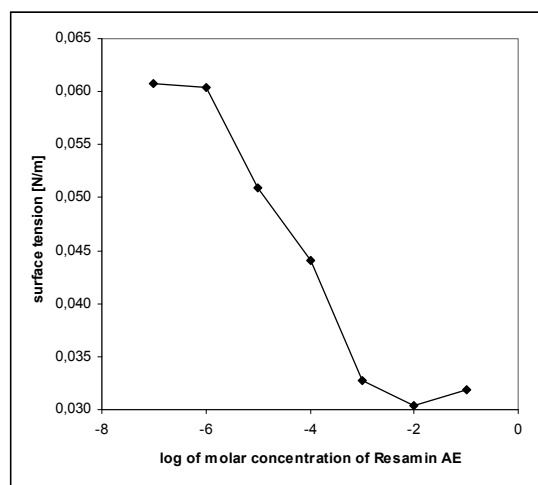


Fig. 4. Dependence of surface tension on the concentration of Resamin AE measured by the ring method.

Table 2. Calculated parameters of the Szyszkowski equation for Resamin AE.

Parameter		
A	—	0.012
B	—	300 000
CMC	mol/L	0.0015

Table 3. Dependence of the rate of hydrolysis of soman by Resamin AE on pH ($t = 25\text{ }^{\circ}\text{C}$, $C_{tenz} = 0.01\text{M}$, $I = 0.01\text{M KCl}$).

pH	k_{obs} (1/min)
8	0.084
9	0.593
10	1.900

Table 4. Influence of ionic strength on the rate of hydrolysis of soman by Resamin AE ($t = 25\text{ }^{\circ}\text{C}$, $C_{tenz} = 0.01\text{M}$, pH9).

C_{KCl} mol/L	k_{obs} 1/min
0.000	1.090
0.001	0.866
0.010	0.638
0.100	0.277
0.500	0.109

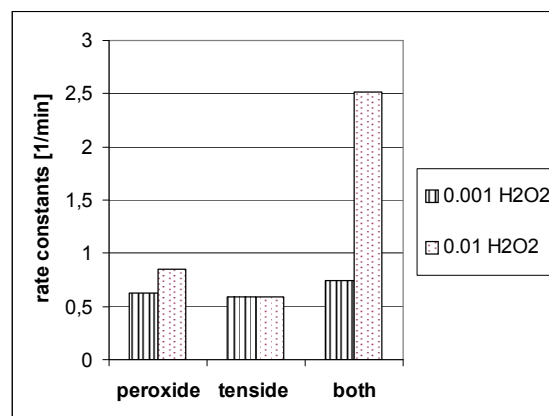


Fig. 5. Influence of hydrogen peroxide on rate of hydrolysis of soman by Resamin AE ($t = 25\text{ }^{\circ}\text{C}$, $C_{tenz} = 0.01\text{M}$, pH9, $I = 0.01\text{ M KCl}$).

The dependence of the rate constant of soman hydrolysis on the concentration of the surfactant is characterized by a typical shape, with a short plateau of premicellar concentration and subsequent progressive phase up to the maximal rate constant (Fig. 2). Therefore, this dependence can be described by a Menger-Portnoy equation. The parameters calculated are shown in Table 1.

A comparison of the parameters of Resamin AE and C16OH1 (Fig. 3) shows that the rate of reaction with Resamin AE is double that of C16OH1. This difference is probably caused by the better structural disposition of Resamin AE for the soman hydrolysis.

The calculated values of critical micellar concentrations (Table 1) have the same magnitude of order and, therefore, they do not influence the reactivity of surfactants. Parameter K/N is a fraction of the association constant of the substrate and aggregation number of the surfactant. Constant K

describes the affinity of the substrate to the micellar phase and constant *N* describes how many molecules of the surfactant are needed to create one micelle. The instrumentation used in this study does not make it possible to determine these parameters separately.

With regard to the similarity of the structure of both surfactants, it is possible that the difference in the values of *K/N* is caused by the difference in the affinity of the substrate to the micelles of both surfactants. The critical micellar concentration of Resamin AE was also measured by the ring method in distilled water only, and is only twice higher than the CMC in a solution with pH9 and ionic strength 0.01 M KCl. It is evident that the changes of solution properties have no influence on the aggregation ability of Resamin AE.

On the other hand, a change of pH is an essential parameter remarkably changing the rate of hydrolytic reaction. The values of p*K*_a of both hydroxyl groups in Resamin AE were predicted with the help of the program p*K*_aDB (ACDlab, USA). The value of p*K*_a for the hydroxyl group localized on the 2-hydroxyethyl group of the surfactant was 12.7 and for the hydroxyl group localized on the hydrophobic alkyl of the surfactant it was 11.9. The values of p*K*_a do not explain the strong dependence of rate constants on pH in the range of pH 8–10. The results of the kinetic measurements give us evidence for considerably lower (9–10) values of p*K*_a. This discrepancy can be caused by the properties of the Stern layer of micelles, where the acidobasic properties of the reaction environment are strongly changed. Unfortunately, our program is not able to take this fact into account.

The next parameter tested was the influence of the electrolytes on the rate of hydrolysis where the concentration of KCl was found to be especially important. This influence can be described by the equation: $k_{\text{obs}} = 0.29 \cdot \log \text{CKCl} + 0.016$. The phenomenon described – the so called “salt effect” – has been demonstrated also by other authors (Zakharova et al. 1993).

The last measurement was focused on the influence of other nucleophiles in the reaction, where hydrogen peroxide was used. It is known that the micelles of cationic surfactants are able to concentrate negatively charged ions on their surface. If ions are nucleophilically active, it is possible, that this higher concentration influences the rate of hydrolysis. This hypothesis was confirmed by the results as presented in Fig. 5.

In conclusion, the data obtained in this study confirmed that Resamin AE may be an effective component of blends designed for the decontamination of organophosphorus warfare agents.

ACKNOWLEDGEMENT

This work was also supported by Czech Ministry of Defence project No. OVUOFVZ200803.

REFERENCES

- Bunton C A, De Buzzaccarini F, Hamed FH: Nucleophilic aromatic substitution in microemulsions of a hydroxyethyl surfactant. *J Org Chem* 48:2461–2465, 1983.
- Cabal J, Kassa J, Severa J: A comparison of the decontamination efficacy of foam-making blends based on cationic and nonionic tensides against organophosphorus compounds determined *in vitro* and *in vivo*. *Hum Exp Toxicol* 22:507–514, 2003.
- Cabal J, Kuča K, Mičová J: Kinetics of decomposition of organophosphate Fenitrothion by decontaminating foam-making blends. *J Appl Biomed* 5:167–170, 2007.
- Cabal J, Kuča K, Ševelová L, Dohnal V: Cyclodextrines as functional agents for decontamination of the skin contaminated by nerve agents. *Acta Medica (Hradec Králové)* 47:115–118, 2004.
- Cibulka R, Hampl F, Martinů T, Mazáč J, Totevová S, Liška F: Metal ion chelates of lipophilic alkyl diazinyl ketoximes as hydrolytic catalysts. *Collect Czech Chem Commun* 64:1159–1179, 1999.
- Guggenheim EA: On the determination of the velocity constant of a unimolecular reaction. *Phil Mag* 2:538–543, 1926.
- Kivala M, Cibulka R, Hampl F: Cleavage of 4-nitrophenyl diphenyl phosphate by isomeric quaternary pyridinium ketoximes – How can structure and lipophilicity of functional surfactants influence their reactivity in micelles and microemulsions? *Coll Czech Chem Commun* 71:1642–1658, 2006.
- Kotoučová H, Cibulka R, Hampl F, Liška F: Amphiphilic quaternary pyridinium ketoximes as functional hydrolytic micellar catalysts – does the nucleophilic function position influence their reactivity? *J Mol Catal A – Chem* 174:59–62, 2001.
- Kuča K, Kivala M, Dohnal V: General method for the quaternization of N, N-dimethyl benzylamines with long chain n-alkylbromides. *J Appl Biomed* 2:195–198, 2004.
- Kuča K, Dohnal V, Bielavská M, Cabal J: Determination of benzalkonium bromide homologues in disinfection products using

- high-performance liquid chromatography. *Anal Lett* 38:673–682, 2005.
- Kuča K, Musilek K, Hanušová P, Hrabínová M, Marek J, Stodůlka S, Jun D: Preparation of the benzalkonium salts differing in the length of the side alkylating chain. *Molecules* 12:2341–2347, 2007.
- Menger FM, Portnoy CE: On the chemistry of reactions proceeding inside molecular aggregates. *J Am Chem Soc* 89:4698–4703, 1967.
- OECD Guidelines for the Testing of Chemicals, Test No. 115: Surface Tension of Aqueous Solutions. OECD, Paris 1981.
- Ouari N, Marques A, Blagoeva I, Ruasse MF: Optimization of micellar catalysis of nucleophilic substitutions in buffered cetyltrimethylammonium salt solutions. 1. Buffers for the 9–10 pH range. *Langmuir* 16:2157–2163, 2000.
- Scrimin P, Ghirlanda G, Tecilla P: Comparative reactivities of phosphate ester cleavage by metallomicelles. *Langmuir* 12:6235–6241, 1996.
- Simanenko YS, Karpichev EA, Prokop'eva TM: Functional detergents containing an imidazole ring and typical fragments of alpha-nucleophiles underlying micellar systems for cleavage of esters of phosphorus acid. *Russ J Org Chem* 40:206–218, 2004.
- Szyszkowski B: Experimentelle Studien der Fiber Kapillaren Eigenschaften der Wasserigen Losungen von Fettsauren. *Z Phys Chem* 64:385–415, 1908.
- Tiwari S, Kolay S, Ghosh KK, Kuča K, Marek J: Kinetic study of the reactions of p-nitrophenyl acetate and p-nitrophenyl benzoate with oximate nucleophiles. *Int J Chem Kinet* 41:57–64, 2009a.
- Tiwari S, Ghosh KK, Marek J, Kuča K: Comparative study of nucleophilic efficacy of pralidoxime towards phosphorus, sulphur and thiophosphorus based esters. *React Kinet Catal Lett* 2009b, In press.
- Waysbort D, McGarvey DJ, Creasy WR, Morrissey KM, Hendrickson DM, Durst HD: A decontamination system for chemical weapons agents using a liquid solution on a solid sorbent. *J Hazard Mater* 161:1114–1121, 2009.
- Zajíček M, Rádl Z: Katalytický vliv kationaktivního tenzidu na hydrolýzu fosfonátu (In Czech). In *Sborník výzkumného ústavu 070*, Brno 1979, pp. 115–129.
- Zakharova LY, Fedorov SB, Kudryavtseva LA, Bel'skii VE, Ivanov BE: The effect of electrolytes on the reaction rates and acid-base equilibria in ionic micelles. *Russ Chem Bull* 42:1329–1333, 1993.