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Soft nanosystems based on hydroxypiperidinium surfactants as adjuvants and micellar catalysts

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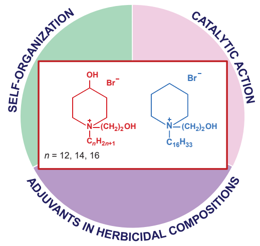
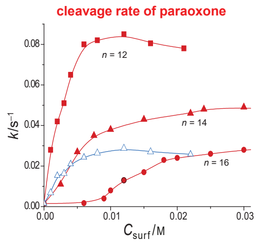
Quantitative parameters characterizing aggregation behaviour and wetting effect of 1-(2-hydroxyethyl)-piperidinium surfactants have been obtained. Their ability to act as adjuvants in herbicidal compositions based on clopyralid has been revealed. The kinetics of alkaline hydrolysis of paraoxon and armine, organophosphorus ecotoxicants, in the surfactant solutions has been explored and it has demonstrated more than 100-fold micellar rate enhancement.



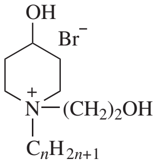


Keywords: hydroxypiperidinium salts, piperidinium salts, surfactants, aggregation, wetting, micellar catalysis, alkaline hydrolysis.

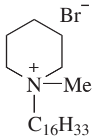
Compositions based on surfactants are widely used in various fields of technology and medicine as ‘soft’ systems with controlled behaviour. There are several basic properties of surfactants that determine their practical application: surface activity, ability to form nanosized aggregates, solubilization and wetting effects, ability to overcome biological barriers,[1–5] *etc*. Design of amphiphilic molecules and functionalization of their structure by the introduction of substituents allow one to involve various mechanisms of self-association and binding of guest compounds and to establish the structure–property relationships. This is the way that provides a high applied potential of surfactant-based systems and the foundation for solving various nanotechnological problems. These are in agreement with the modern trends in the fabrication of multifunctional compositions with high biotechnological potential.[1,6]

In the present work, a systematic study of 1-alkyl-1-(2-hydroxyethyl)piperidinium bromides was carried out, whose functional behavior depends not only on hydrophobic and electrostatic forces, but also on the ability of these compounds to participate in the formation of hydrogen bonds. The properties of a number of new surfactants with two hydroxy groups in the molecule and with a variable hydrophobic tail length (series **1a–c**) have been investigated. Their aggregation behavior, wetting effect, ability to act as adjuvants in herbicidal compositions based on clopyralid, as well as their catalytic effect in the processes of decomposition of organophosphorus ecotoxicants were studied. The properties of these surfactants were compared with the behavior of known 1-hexadecyl-1-methylpiperidinium bromide **2** and 1-hexadecyl-1-(2-hydroxyethyl)piperidinium bromide **3**. For the synthesis of new compounds **1a–c**, see Online Supplementary Materials.

Surface tension measurements were performed by the ring detachment method using KRUSS 6 tensiometer. UV-VIS spectra of the herbicide solutions were recorded using Specord 250 Plus spectrophotometers. The wetting ability of surfactant solutions was assessed by determining the spreading area of the drop on the test surface. Treatment of the leaves with herbicide solution and determination of clopyralid content in them was previously described.[7]



a $n = 12$
b $n = 14$
c $n = 16$
1a–c



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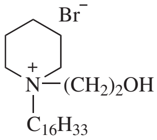

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The critical micelle concentration (CMC) is the most important characteristic of surfactant solutions, which makes it possible to establish the concentration limits of their functional activity. CMC values determined by tensiometry (see Online Supplementary Materials, Figure S1) are 11, 4.0 and 1.0 mM for compounds **1a–c**, respectively. They are in agreement with the StauffClevens equation, which relates the CMC values and the length of the hydrophobic surfactant tail (n): $\log(\text{CMC}) = 1.19 - 0.26n$ ($R = 0.984$). However, the values of the intercept and the slope for compounds **1a–c** are somewhat different than those typical for trimethylammonium or methylpiperidinium surfactants, for which the free term is in the range from 1.5 to 1.9, and the slope is ~ 0.3.[8,9] Probably, the presence of a hydroxy group introduces the specificity of the interaction of 4-hydroxypiperidinium surfactants with water dipoles in comparison with non-functionalized analogues.

The surface activity of surfactants allows them to be used as adjuvants upon the fabrication of herbicidal compositions, since it improves the wetting of the treated surface, promotes the penetration of the active substance into the plant, and thereby increases the effectiveness of the applied agrochemicals.[10–12] A measure to assess the wetting effect of the surfactant solution may be the spread area of the droplet (S) on the test surface. The ratio of S values for the water drop in the presence of surfactant

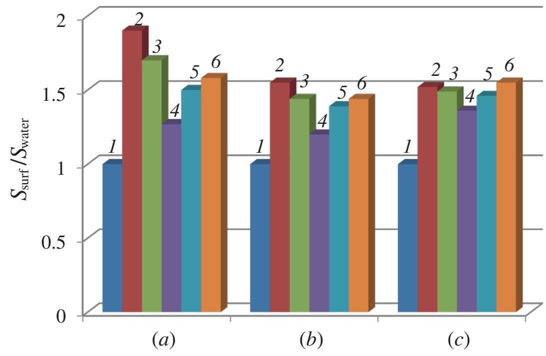


Figure 1 The spread area of drops of 0.1% surfactant solution (25 °C) on the surface of (*a*) glass, (*b*) parafilm, (*c*) dandelion leaf: (*1*) water, (*2*) with **2**, (*3*) with **3**, (*4*) with **1a**, (*5*) with **1b**, and (*6*) with **1c**.

and without it is one of the indicators of the surfactant effectiveness. The results obtained essentially depend not only on the properties and concentration of surfactants, but also on the properties of the surface itself. So, when the solution spreads on the surface of the leaf, its structure will play an important role, including hairiness and surface roughness, the presence of hydrophobic plant waxes on the outer tissue of the plant, the thickness of the cuticle, *etc*. The difficulty of conducting experiments on plants is due to the irregularity of the surface of the leaf and its insufficient area for applying a statistically acceptable number of drops. We tested the wetting effect of piperidinium surfactants on various substrates: glass, 'parafilm' imitating wax leaf cuticle, and on common dandelion leaves. The data presented in Figure 1 make it possible to conclude that addition of 0.1% of tested surfactants to water provides improvement of surface wetting by 30–80%. There is an increase in the efficiency of surfactant as the length of its hydrophobic tail increases, while the presence of hydroxy groups has little effect on their wetting.

Another factor determining the effectiveness of the surfactants as adjuvants is their ability to transport growth regulators into a plant. The present work has focused on the systemic herbicide clopiralids. Spectrophotometric method (*cf*. ref. 7) was used for determination of clopyralid in common dandelion leaves and in lettuce leaves after their two-hour contact with herbicide solutions with addition of 0.1% piperidinium surfactants, the results having been compared with those for pure water (Figure 2). Note that when working with dandelion, the interfering effect of the components extracted from the leaf simultaneously with the herbicide having absorption in the same area as clopyralid should be taken into account. There were no interfering influences with salad leaves.

Regardless of the type of plants, the addition of surfactant improves the penetration of clopyralid into the leaves by 40–70%. The presence of hydroxy groups in the surfactant structure has little effect on their transport properties. Compound **1a** exhibits somewhat greater efficacy. By analogy with current ideas about the penetration of surfactant into bacterial cells,[13] it can be assumed that in this case the best geometric correspondence between transport channels in plant membranes and the structure of surfactant is observed.

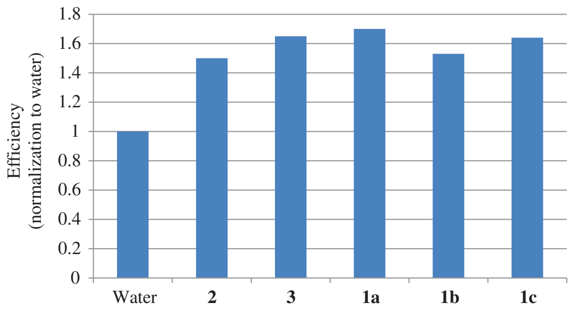
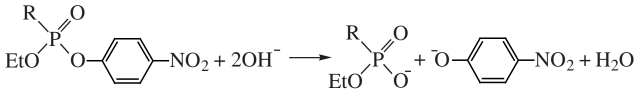


Figure 2 Increased herbicide content in lettuce leaf when used in a composition with 0.1% piperidinium surfactants added as compared to water (the error of experiments was < 5%.)



4a,**b**
a R = Et
b R = OEt

Scheme 1

Another important aspect of the application of cationic surfactants is their use as micellar catalysts that are able to affect the rate and mechanism of a number of practically significant chemical transformations[14–17] and, in particular, markedly accelerate hydrolytic processes. Their catalytic action is widely employed in decomposition of organophosphorus ecotoxicants and neurotoxins.[18–20]

To identify the peculiarities of the effect of the structure of hexadecyl piperidinium surfactants on the rate of nucleophilic substitution in phosphorus acid esters, the kinetics of alkaline hydrolysis of ethyl (4-nitrophenyl) ethylphosphonate (armine, **4a**) and diethyl (4-nitrophenyl) phosphate (paraoxone, **4b**) were studied (Scheme 1).

It should be noted that both esters in the absence of additives undergo hydrolysis slowly even in highly alkaline media; and therefore, they are often used as model substrates upon the development and testing of catalytic systems for the prevention and treatment of organophosphorus poisoning.[21]

Hydrolysis of phosphorus acid esters was carried out at a temperature of 25 °C in 0.01 M NaOH with varying the surfactant concentration in the solution from 0 to 0.05 M. The process was spectrophotometrically monitored by control of changing the absorption intensity at 400 nm (maximum absorption of 4-nitrophenolate ion, Specord 250 Plus). Figure 3 shows the concentration relationship of the observed rate constant of armine **4a** and paraoxone **4b** cleavage in piperidinium surfactant solutions. It follows that hydroxy-containing surfactants exhibit substantially greater activity than their unsubstituted analogues with respect to both esters. The catalytic action is enhanced by increasing the number of OH groups in the molecule, as well as by elongation of the chain of the hydrophobic tail. The highest effect is observed for compound **1c** at a concentration of 0.05 M: 70-fold and 120-fold accelerations of the process are observed for armine **4a** and paraoxone **4b**, respectively. It should be noted that in highly alkaline media, compounds containing the hydroxyethyl moiety at the quaternary nitrogen atom are capable of conversion into zwitterion form (pK 12.4–12.6),[22] which also acts as a nucleophile and interacts with the substrates, which would contribute to increasing the observed process rate. The second hydroxy substituent introduced into the *para*-position of the piperidinium cycle is not capable of cleavage of the proton

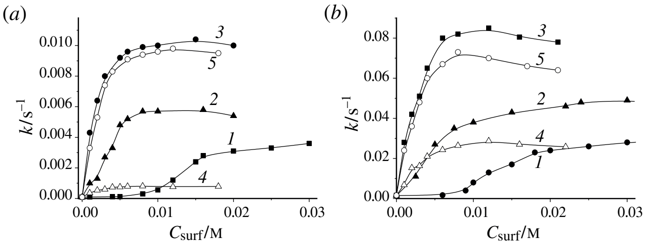


Figure 3 Dependence of the observed rate constant of hydrolytic cleavage of (*a*) armine **4a** and (*b*) paraoxone **4b** on concentration of piperidinium surfactants (0.01 M NaOH, 25 °C): (*1*) **1a**, (*2*) **1b**, (*3*) **1c**, (*4*) **2**, and (*5*) **3**.

under the reaction conditions. Therefore, it does not generate an additional nucleophilic center, and the transition from mono- to dihydroxy-substituted surfactants is accompanied by only a minor effect. At the same time, compounds **1b**,**c** which are similarly capable of generating a reactive form, not only exhibit their effect at substantially higher concentrations than their hexadecyl analogue, but also provide a significantly lower catalytic effect. This allows us to say that the factors of micellar catalysis are mainly responsible for changes in the cleavage rate of the esters studied. In the case of hydroxypiperidinium surfactants, the rate acceleration is due to both various types of interactions (hydrophobic, electrostatic, specific) that provide solubilization of the organophosphorus substrate, and concentration of hydroxide ions at the micelle surface. The transition to higher homologues often results in an increase in catalytic action of cationic surfactants, which can be explained by enhancement of solubilization activity toward hydrophobic solutes and increase in surface potential responsible for the binding of negatively charged nucleophiles.

In conclusion, the piperidinium surfactants studied can be effectively used as adjuvants to improve the wetting of the plant surface and the transport of the herbicide into it, as well as catalysts capable of more than 100-fold accelerating the cleavage of organophosphorus ecotoxicants. The length of the hydrocarbon tail of a surfactant plays a significant role in the first case, while in the second, key factor is the functionalization of the head by introducing hydroxyl substituents.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.014.

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