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Carbamate-bearing surfactants as effective adjuvants promoted the penetration of the herbicide into the plant

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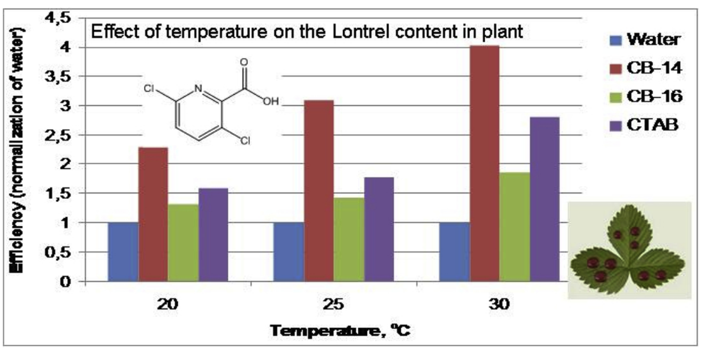
GRAPHICAL ABSTRACT



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ABSTRACT

Novel pesticide loaded formulations were developed through amphiphile self-assembly strategy, allowing of concentrating the herbicide Lontrel in salad leaves. The structure-activity correlations were analyzed in terms of Lontrel amount taken up by plants and wetting ability of formulations. Key factors responsible for the efficacy of herbicide compositions are the structure and concentration of surfactants, time of treatment, wetting effect, and temperature. The leader position was demonstrated by the biodegradable carbamate-bearing surfactants *N*-[2-((butylcarbamoyl)oxy)ethyl]-*N*,*N*-dimethylalkylammonium bromides (CB-n) resulting in a threefold increase in the Lontrel content in plant within the concentration of 0.1–0.2 wt %. An increase in temperature may significantly enhance the penetration ability of the herbicide through biological barriers of plant; in this case, CB-14 analog exhibited highest transport properties compared to other test surfactants, providing the largest response to the temperature change.

1. Introduction

Weed and pest management is decisive for the increase in the yield and quality of agricultural production. Development of chemistry gives a wide variety of pesticides to farm workers, which is continuously added by new types of herbicides, fungicides, insecticides, growth regulators, and others. Herbicides represent the most widely used pesticides. Their employment for weed management increases the yield and cost effectiveness and allows soil treatment without its wetting, which leads to the increase in the productivity and profit of farm industry [1–3]. However, many herbicides exert

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toxic effect when they are brought at soil and water reservoirs, which may cause undesirable consequences for insects, animals, and people [4–9]. For this reason, on the one hand, the use of herbicides should be strictly standardized and controlled; on the other hand, the compositions containing adjuvant substances, which enhance the effect of herbicide and decrease the consumption dose of the preparation, should be designed. Adjuvants improve wetting of the plant surface, provide a longer retention of the preparation on leaves, and increase the penetration ability of preparation. Surfactants are known to be very effective as solubilizers and nanocarriers for a variety of biologically active molecules including pesticide [10–13] and therefore are often used as adjuvants [14–20]: they do not change the characteristics of water, decrease the consumption of preparations and thus increase sustainability of herbicides. Nonionoic surfactants, which include ethoxylated alcohols, alkyl phenols, and trisiloxanes, are most often used. These surfactants are nontoxic, represent good dispersing agents, possess high solubilizing effect, stable under normal conditions, low-toxic, and are miscible with any herbicides [21–24]. Cationic surfactants in herbicide compositions are used less frequently due to their toxicity; however, they are used in agriculture due to their high surface activity, low critical micelle concentration (CMC), and a significant solubilizing capacity [23,25].

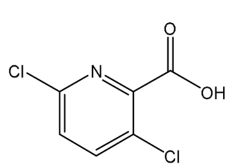
The penetrating power of herbicides, which determines their performance, depends to a significant extent on anatomical and morphological structure of plant; however, in this case, physicochemical properties of active ingredients, the presence and nature of adjuvants, and external conditions play an important role [26,27]. Cuticle (the layer of fatty substances and wax) is the main barrier, which restricts penetration of herbicide into plant and, consequently, determines its activity. It complicates wetting of leaves and caulis by aqueous solutions of chemicals [28–30]. The types of plants possessing thick cuticle are more resistant to most herbicides dissolved in water rather than those in which cuticle is thin or absent, which determines high resistance of some plants to a number of preparations. Resistance of weed, which is defined by pubescence or the presence of a thick cuticle layer, can be decreased by adding surfactants, which can dissolve fatty and wax substances, thereby provides higher spreading of the solutions on the leaf surface and increases the permeability of the latter [21,31–33]. However, dissolution of waxes on a cultivated plant may lead to disturbance of its hydrological balance, which requires preliminary assessment of possible risks related to herbicide compositions.

At present, there is no sufficient semi-empirical or integrated model, which can predict quantitatively the effect of a particular surfactant on the properties and performance of herbicide. Therefore, optimization of the nature of surfactant and its concentration is an essential problem, which is solved at each individual case. The aim of this work was to improve liquid preparative forms of herbicides and improve their physicochemical properties and operational characteristics using surfactants.

In this work, we focused on a Lontrel target systemic herbicide, whose active ingredient is clopyralid, whose structure is close to vitamins, which quickly decompose in soil. Lontrel is target herbicide, which completely destructs malignant offset weeds (thistles and sow thistles) and effectively suppresses ambrosia, persicaria, chamomile, dandelion, and some other weeds; in this case, it does not affect lawn grass or strawberry leaves [33–35].

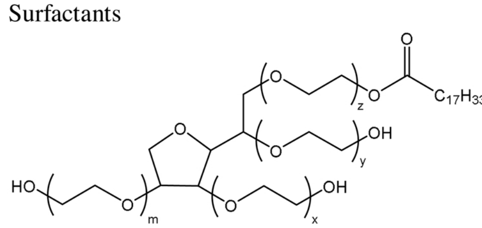
The work considered following stages, namely, development of the methods for the control of the Lontrel content in plant; determination of the effect of various surfactants on the penetration ability of preparation; optimization of the time of contact of plant and the preparation; revealing the factors, which affect the effectiveness of penetration of the preparation into plant (change of the wetting ability of herbicide composition and exposure of temperature and UV radiation). Nonionic surfactants (Tween 80, Pluronc F127) and polyethylene glycols with various molecular masses, which are widely used due to their low toxicity, were tested as adjuvants. The choice of cationic carbamate-bearing surfactants is caused by the fact that they have low aggregation threshold and high solubilization capacity, they fulfill the criterion of biodegradability and are related to moderately toxic compounds [36,37]. In addition, the discovered high antimicrobial effect of these surfactants with respect to *Staphylococcus aureus*, *Escherichia coli*, *Bacillus cereus*, *Trichophyton mentagrophytes*, and *Candida albicans* [36] would result in the increase in the effectiveness of the herbicide composition due to the ability to inhibit undesirable effect of mentioned pathogenic fungi and bacteria on plant. Cetyltrimethylammonium bromide (CTAB) is a known standard for cationic surfactants in colloidal chemistry; for this reason, some experiments were performed with it in spite of its toxicity. In addition, dicationic surfactant 1,6-hexalyden-bis-(dimethylammonium) dibromide, (16-6-16) which is capable of micelle formation and solubiliszation action at a very low concentration was tested. Structural formulas of the compounds are given below.

Herbicide

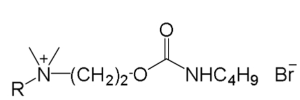


Clopyralid

Surfactants

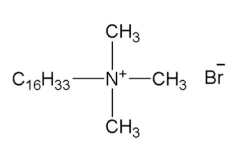


Tween 80 (m+x+y+z = 20)

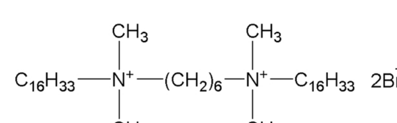


CB-n

R = $C_{12}H_{25}$ (CB-12), $C_{14}H_{29}$ (CB-14), $C_{16}H_{33}$ (CB-16)



CTAB



16-6-16

2. Experimental

2.1. Materials

Commercial target Lontrel herbicide with the content of clopyralid active ingredient of 300 g/L (Avgust, Russia) was used for this study. Commercial specimens of nonionic and cationic surfactants were chosen as adjuvants, namely, Tween 80, Pluronc F 127, cetyltrimethylammonium bromide (CTAB); polyethylene glycols with the molecular mass of 1000 and 10,000 (Sigma Aldrich), as well as laboratory specimens of surfactants containing carbamate fragment: *N*-[2-((butylcarbamoyl)oxy)ethyl]-*N*,*N*-dimethyldodecaneammonium bromide (CB-12), *N*-[2-((butylcarbamoyl)oxy)ethyl]-*N*,*N*-dimethyltetradecaneammonium bromide (CB-14), *N*-[2-((butylcarbamoyl)oxy) ethyl]-*N*,*N*-dimethylhexadecaneammonium bromide (CB-16) synthesized according to the procedure from [36]. Dicationic surfactant 16-6-16 synthesized through reaction of cetylbromide with *N*,*N*'-tetramethyl hexamethylenediamine, in analogy with ref. [38,39].The solutions were prepared using bidistilled water purified on a Direct – Q5 UV instrument (pH 6.8–7, χ = 2–3 μS cm^{-1}). The experiments were carried out on fresh *Lactuca sativa* dubachek, *Ficus benjamina*, and strawberry (Fragária) leaves.

2.2. Treatment of salad leaves with herbicide solution

An aqueous solution of Lontrel with initial concentration of 3 g/L (that is, 100-fold dilution), as well as herbicide compositions based on surfactant, where the surfactant content was varied from 0.1 to 1 %, were prepared for the experiments. The salad leaf with the mass of 2 g was added to 40 mL aqueous solution of herbicide and surfactant and maintained for various time intervals from 10 min to 2 h.

2.3. Determination of Lontrel content in leaves after extraction

To determine the Lontrel content in leaves, they were taken from herbicide solutions, washed with bidistilled water, and dried using filter paper. Then, the leaves were added to 50 mL of phosphate buffer solution and maintained for 24 h taking the aliquots for spectrophotometric measurements after particular time periods. The absorbance (D) of the solutions at 280 nm was measured using a Specord 250 Plus spectrophotometer (Germany) and the dependence, which reflected its change with time, was plotted. End of the process was determined by reaching plateau of this dependence. The Lontrel content in the plant was evaluated on the basis of calibration graphs assuming possible dilutions. The experiment was repeated at least three times to obtain reliable results.

2.4. Spreading area of the drop of herbicide solution with and without surfactant

The wetting ability of herbicide solution with and without surfactant was assessed by determining the spreading area of the drop on glass preliminarily degreased with ethanol or on the upper surface of freshly cut leaves of the plants with various cuticle thickness such as *Ficus benjamina*, strawberry. A water-soluble rhodamine dye was added to herbicide compositions for a better visualization of the determination. A drop (0.06 mL) of the test herbicide solution was added to the surface of glass or leaf during experiment using a dosator (Eppendorf, Germany); and, then, the spreading area of the drop was determined. The experiment was repeated at least five times to obtain reliable data.

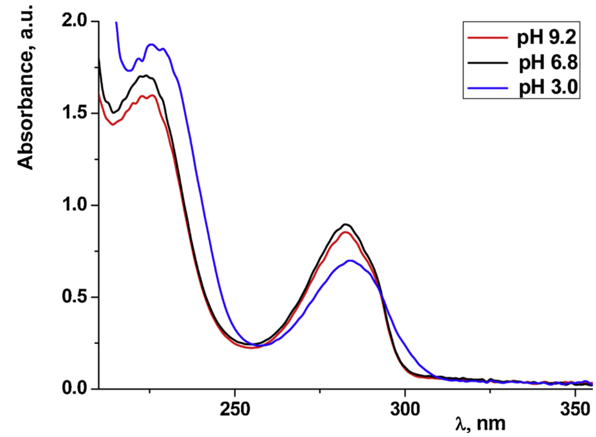


Fig. 1. Spectra of aqueous solutions of Lontrel recorded in water at various pH (concentration of active ingredient is 0.12 mM and the absorption layer thickness is 1 cm).

3. Results and discussion

3.1. Development of the procedure of analytical control of Lontrel content in solutions

The demand to determine the Lontrel content in plant initiated the development of the procedure of a quantitative control of this herbicide in solutions. For these purposes, optical spectroscopy was used. Determination of the content of this preparation using this method is possible due to the fact that UV spectrum of its active ingredient, clopyralid, is characterized by intense absorption in the range of 220 – 250 nm, as well as the band with the maximum of 280 nm, which was chosen as analytical signal. At first stage, the studies were carried out in water and solutions of various surfactants to plot calibration dependences. It was determined that change of pH and the presence of surfactants affect insignificantly the absorption of preparation. A slight difference of absorption in acidic range is related to the fact that Lontrel partially exists in protonated formed under these conditions (pK_a 2.3 [40]). The most intrinsic spectra and calibration plots are given as examples in Figs. 1, S1–S3. In order to evaluate the concentration of Lontrel in plant, it was extracted from the treated plant into water and determined the herbicide content in solution spectrophotometrically.

3.2. Optimization of the time of contact of herbicide with plant leaves

At first stage of this work, we optimized the time of contact of water of water-micelle solution of Lontrel with freshly cut salad leaves (*Lactuca sativa* dubachek). The concentration of surfactant in solutions at this series of experiments was three times as large as CMC value. The

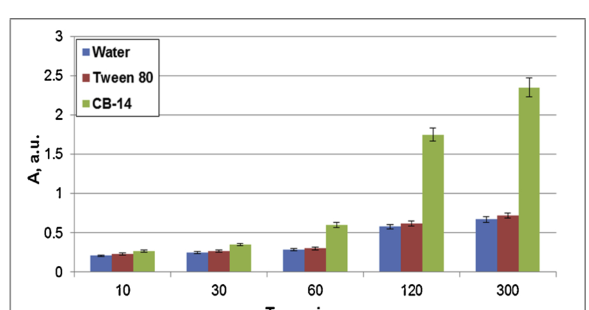


Fig. 2. Effect of the time of contact of salad leaves and Lontrel solutions on the absorbance of the specimens obtained during the extraction of herbicide from plant (the cuvette is 1 cm; the concentration of surfactant is three times as large as CMC value: C_{CB-14} = 1.20 mM, $C_{Tween80}$ = 0.15 mM).

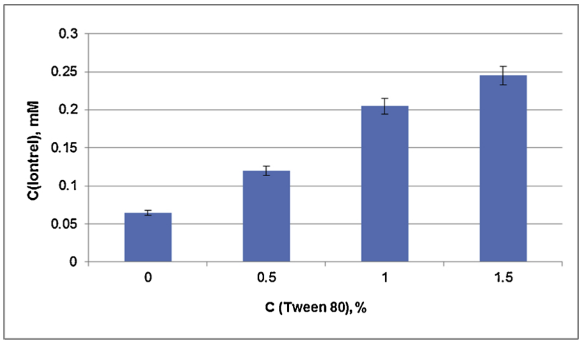


Fig. 3. Concentration of Lontrel accumulated in salad leaves depending on the concentration of Tween 80 in herbicide composition.

time of contact was varied from 10 min to 24 h. After that, the herbicide content accumulated in the plant was measured after a particular time interval. The data in Fig. 2 illustrate the principles, which are general both for water and solutions of various surfactants. It follows from them that after 10 min the plant absorbs Lontrel; however, this amount is insignificant and is determined in experiment with a large error. With an increase in the time of contact, the Lontrel content increases. However, too long time of contact (more than 5 h) results in a large difference in *in vitro* experimental conditions and treatment of plants with herbicides under real conditions. In addition, leaf gets soaked upon long-term exposure in water and loses its integrity. As a result, we chose 2 h as the optimal time of contact for the studies. The resulting data are reproduced well and allow us to compare the results in water and micellar solutions.

3.3. Effect of various surfactants on the Lontrel uptake by salad leaves

Due to the fact that the ability of surfactant to transport herbicide into plant mainly depends on its nature and structure, we compared the effectiveness of a series of amphiphilic compounds with respect to Lontrel. The herbicide content in salad leaves after a 2-h contact of plant and surfactant solution was determined and these data were compared to those for water. A major part of experiments with nontoxic nonionic substances was carried out at their content of 1 wt % in solution. The observed effect from their administration corresponded to 1.3, 1.6, 1.9, and 3.1 times in the case of Pluronic F127, PEG 1000, PEG 10,000, and Tween 80, respectively. That is, all tested nonionic polyoxyethylated compounds allow one to increase the herbicide content in plant as compared to water. This can presumably be caused by the high content of hydrated ethylene oxide fragments in test compounds; their penetration into cuticle membranes results in the increase in water content in transport limiting barrier and, consequently, can increase permeability even more [41,42]. Polyethylene glycol with a larger molecular mass exhibits slightly better characteristics than its low-molecular counterpart presumably due to the increase in the number of oxyethyl groups. However, Tween-80 is the most effective; its employment as adjuvant provides a three-fold increase in the Lontrel content in salad leaves as compared to water, which is caused by the high ethylene oxide content in surfactant molecule. It should also be noted that the performance of surfactant as adjuvant increases with an increase in its content in solution as illustrated by Tween 80 (Fig.3).

Cationic surfactants, more toxic that nonionic amphiphiles, were tested as adjuvants at the concentration, which is three times as large as CMC value, which corresponded to 0.1–0.2 wt %. In this concentration range, micelles exist in spherical shape in solutions, which are characterized by high solubilization properties [43]. Carbamate-bearing surfactants, CB-14 and CB -16, as well as CTAB, which is conventionally used in colloidal chemistry as a reference compound, were used. In addition, dicationic surfactant 16-6-16, capable of micelle formation at a very low concentration (CMC 4 10^{-5} M), was tested [38]. Their effect can be compared based on the data in Fig. 4, which reflect the extent of the increase in the Lontrel content in plant with a transition from water to micellar solutions. All tested cationic surfactants are significantly more effective than Tween 80, which was used at the concentration of 3 CMC. This can be rationalized by the fact that Lontrel exists in anionic form at neutral pH in solutions, which provides strong binding with cationic surfactants due to electrostatic interactions. Dicationic surfactant exhibits stronger effect than CTAB presumably due to the fact that 16-6-16 has a higher surface potential than its monocationic counterpart.

In the case of the surfactants CB-n additional binding of herbicides due to hydrogen bonds, whose formation is intrinsic for the compounds containing carbamate fragment, is possible. CB-14 is the most effective among tested cationic surfactants, which is 0.16 % at the concentration of 3 CMC, which allows almost a three-fold increase in the Lontrel content in plant. It should be emphasized that again, CB-14 demonstrated the leader behavior in the cases when pesticide compositions were prepared with the similar quantity of surfactant used. Fig. S4 shows transport properties of the surfactant (0.2 % solution).

Recommending CB-14 for further tests, it should be noted that this compound is significantly less toxic than many other cationic surfactants: LD_{50} (mice, intraperitoneal administration) is 95 mg/kg, the class of moderately toxic surfactants [36]. In addition, CB-14 exhibits high bactericidal and fungicidal properties, which gives additional opportunities for the increase in the effectiveness of the herbicide composition [36].

3.4. Effect of temperature on the absorption ability of herbicide

The action of herbicides mainly depends on environmental

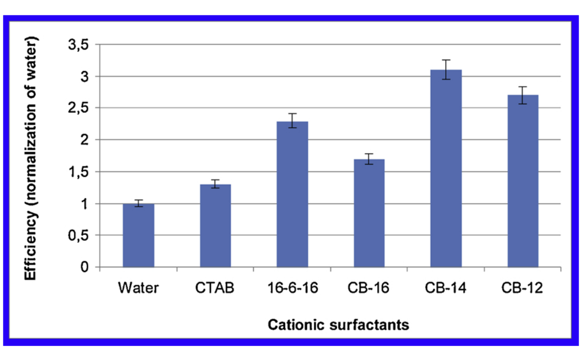


Fig. 4. An increase in the herbicide content in salad leaf when using in the composition with surfactant as compared to water (time of exposure is 2 h; C_{surf} = 3 CMC).

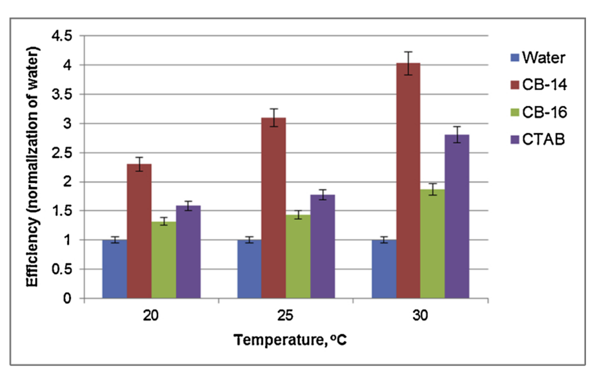
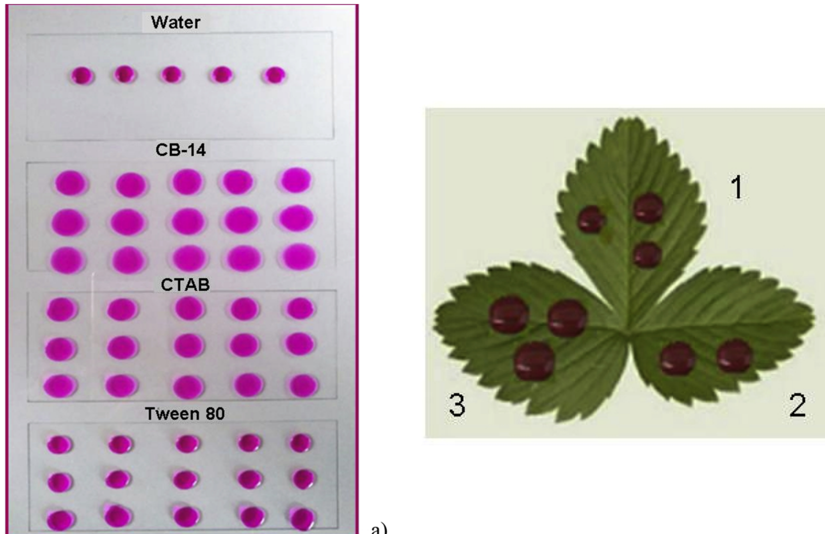


Fig. 5. Effect of temperature on the Lontrel content in plant (normalization of data by water).



a) b)

Fig. 6. The drop area of herbicide without and with surfactants: a) on a glass; b) on a strawberry leaf (1-water, 2-Tween 80, 3-CB-14).

Table 1
Increase in the contact area of the drop of herbicide solution containing surfactant[a,b] as compared to aqueous solution on various surfaces.

System	C_{surf}, mM[a]	C_{surf}, %[a]	Glass	*Ficus benjamina* leaf	Fragária leaf
Water	–	–	1	1	1
Tween 80	0.15	0.02	1.41	2.98	1.26
	0.30	0.04	1.67	3.47	1.58
	0.45	0.06	1.85	3.99	1.95
CTAB	0.9	0.035	1.92	3.30	
	1.8	0.07	2.09	3.64	
	2.7	0.105	2.16	4.37	
CB-14	1.0	0.05	2.81	4.37	1.89
	2.0	0.10	3.13	4.76	2.30
	3.0	0.15	3.54	5.16	2.95

[a] The studied concentrations of surfactant correspond to the CMC value or exceed it by two and three times.
[b] The contact area of the herbicide solution drop containing 0.2 % (wt) of the surfactant on the glass as compared to aqueous solution is 1.8, 4.0, 3.3 and 2.4 for CB-16, CB-14, CB-12 and Tween 80, respectively.

conditions, such as temperature, humidity, illumination intensity, and others [27,29,44]. At this stage of work, we studied the effect of temperature on the penetration ability of Lontrel into plant. *In vitro* experiment was carried out under the temperature conditions, which reproduce more probable temperature conditions in the summer period of plant growth. The data compared the change in the herbicide content in plant, when using its aqueous and micellar solution in the range of $20-30\,^{\circ}C$ are given in Fig. 5.

As follows from these data, an increase in temperature by 10 °C increases the penetration of herbicide into salad leaf by 1.2–2 times. In this case, CB-14 displays the highest response on the temperature change, which exhibits highest transport characteristics as compared to other test surfactants. Growth of permeability can be related to the change of the viscosity of leaf cuticle. In addition, one would anticipate that the sensitivity of salad leaf to Lontrel grows with an increase in temperature due to the faster absorption of herbicide and displacement in plants.

3.5. Wetting ability of herbicide with and without various surfactants

Effective wetting of leaf is an essential factor, which is responsible for the penetration of herbicide into the cuticle of leaves and increases its biological effect. Surfactants provide good contact of the leaf surface with the herbicide solution due to the decrease in the surface tension a interface and a decrease in contact angle. These characteristics depend both on the characteristics of surface and the characteristics and concentration of the surfactant. Wetting of the plant surface depends on its roughness and hierarchical structure in leaves, as well as the presence of hydrophobic plant waxes, which cover the external tissue of plant with a thin layer. The spreading area of drop (S) on test surface is a parameter, which can evaluate the effectiveness of wetting. We evaluated D for the drop of aqueous solutions of surfactant deposited onto the glass plate or the leaf surface of the plants, which differ by the cuticle thickness, namely, *Ficus benjamina*, strawberry, and linden tree. The drop volume was constant in all cases and corresponded to 0.06 mL. Hydrophilic rhodamine dye was added to the solution for a better visualization of the determination. Some results are given in Figs. 6(a,b), S5, S6 and Table 1.

It should be noted that the principles of the behavior of drop on glass were the same as on the leaf surface. One example is that the drop of aqueous solution of Lontrel was almost spherical and its contact area with the glass surface was 56.8, while that on the ficus leaf corresponded to 95 mm^2. The thinner the cuticle, the higher is the spreading of drop.

The consequence of spreading of drop and an increase in S values in the presence of surfactant is that the preparation was absorbed by leaves at the first stage of contact of the herbicide and plant faster than without it (Fig. 6b). Surfactants, which are known membranotropic agents, may further provide the penetration of herbicide through the cell barriers inside plant.

4. Conclusions

Thus, in this work, a supramolecular strategy has been applied for the development of surfactant based nanoformulations enhancing the efficacy of herbicide Lontrel compared to unformulated preparation. For this purpose, surfactant compositions and procedures used were optimized by varying the type and concentration of surfactant, time of treatment, pH and temperature of sample preparation and monitoring the Lontrel amount taken up by plants and wetting ability of formulations. The most beneficial results were obtained for series of biodegradable carbamate-bearing surfactants *N*-[2-((butylcarbamoyl)oxy) ethyl]-*N*,*N*-dimethylalkylammonium bromides (CB-n). They provide a threefold increase in the Lontrel content in plant within the concentration range of 0.1–0.2 wt %. Temperature factor was revealed to play a positive role: an increase in temperature by 10 deg increases the Lontrel uptake by the plant by 1.2–2 times; in this case, CB-14 exhibits the highest response to the temperature change.

Authors contribution

Alla B. Mirgorodskaya - planning methodology to reach the conclusion, wrote the paper.

Rushana A. Kushnazarova - performed experiments, analyzed data.

Svetlana S. Lukashenko - performed the synthesis of surfactants.

Eugeny N. Nikitin - performed the experiments with plants.

Kirill O. Sinyashin - constructing an idea for research.

Liliya M. Nesterova - participated in the discussion of the results.

Lucia Ya. Zakharova - taking responsibility in logical interpretation and presentation of the results, co-wrote the paper.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2019.124252.

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