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Ecology

Comparative Assessment of the Ecological Characteristics of Auxiliary Organic Compounds in the Composition of Foaming Agents Used for Fire Fighting

Maya Gurbanova[*], Valentyna Loboichenko[**], Nataliia Leonova[§], Victor Strelets[**], Roman Shevchenko[**]

[*]*Academy of Ministry of Emergency Situations of the Azerbaijan Republic, Baku, Azerbaijan Republic*
[**] *National University of Civil Defence of Ukraine, Kharkiv, Ukraine*
[§]*Chemical Metrology Department, Kharkiv National University Named by V.N. Karazin, Kharkiv, Ukraine*

(Presented by Academy Member Vladimer Tsitsishvili)

The paper considers the impact on the environment and living organisms of a number of organic additives in foaming agents used for extinguishing the fires of different classes. The ecological characteristics of the most common organic components used as auxilieries in fire fighting mixtures have been calculated. The Quantitative Structure Property Relationships method was used to evaluate the environmental parameters of the 6 most common auxiliary components of foaming agents. 2D descriptors were used in the Quantitative Structure Property Relationships model to obtain the following values: 96-hour 50% lethal concentration for Fathead minnow (Pimephales promelas), 48-hour 50% lethal concentration for Daphnia magna, 50% growth inhibition concentration Tetrahymena pyriformis and Bioaccumulation factor. Thus, the least environmentally hazardous organic compounds used as additives in foaming agents are considered to be carboxymethylcellulose, acetic acid and glycols. Given the negative effects on humans and the environment, additives in fire fighting foams such as ethylene glycol, propylene glycol and carboxymethylcellulose are recommended as the most environmentally safe for humans and the environment. *© 2020 Bull. Georg. Natl. Acad. Sci.*

Ecological characteristic, auxiliary organic compound, calculation method, foaming agent

The deterioration of the environment that we are observing today is largely due to anthropogenic activity. In turn, this forces us to study more closely the influence of various components of this impact. One of the elements affecting the environment is natural and man-made emergencies [1], and, in particular, fires. Fire extinguishing agents, used for extinguishing the fires, also have an additional negative effect on the biotic and abiotic components of ecosystems [2].

The most optimal option of leveling the negative effect on humans [3] and the environment [4-6] is to prevent fires. There is also research and development of environmentally friendly

innovative approaches for extinguishing the fires, such as the use of gelsystems [7], methods [8] and devices [9,10] based on acoustic waves, high speed impulse liquid jets [11], early response sensors [12].

But today they are used as fire extinguishing compounds water, foams, aerosols and powders [13], that have different environmental characteristics [14]. At the same time, water and foams are the most frequently used for extinguishing fires of various classes.

The water as a universal natural solvent has minimal negative impact on the environment. Although it can act as a mean of transporting the products of anthropogenic activity to various natural sources and the soil [15, 16]. The impact of foaming agents on natural objects is not so clear. On the one hand, foaming agents are effective means in fighting fires of class A and B [17], and on the other hand, they have a negative impact on the environment [18, 19].

Foaming agents can contain both inorganic and organic components. The latter is a mandatory element of foaming agents as basic substance [20] and as auxiliary, giving them specific characteristics.

The growing interest of the world community in the environmental characteristics of chemical compounds used in various fields of activity [21, 22] has led to the restriction of using the number of fire extinguishing compounds, for example, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride [23] and to the search for more environmentally friendly products and new ones.

When studying the ecological properties of organic components of foaming agents for fire fighting, including their impact on the environment, there is a complication due to several factors: a huge number of synthetic compounds; the necessary time to research and full funding; the complexity of the structure of organic molecules and a number of other features. The above mentioned significantly complicates the qualified and reliable experiment to be done. In these conditions, the use of approaches related to calculated characteristics, in particular, the methods of Quantitative Structure Activity Relationships (QSARs) [24, 25], seems more attractive. These methods allow to predict the properties of chemicals based on their chemical structure and evaluate them by calculation. At the same time, there is significant time- saving and money-saving which has ensured the widespread use of these approaches in various fields (chemistry, ecology, pharmacy, medicine, etc.).

QSAR modeling is based on chemical descriptors. It is known that various methods of QSARs take into account the dimensions of the description of the structure of molecules or the way of representing descriptors. Today, there are many different types of descriptor data that reflect different levels of representation of the chemical structure [20, 26].

Today the most frequently applied methods are 2D and 3D QSAR. 2D representation allows you to define 2D molecular descriptors in 2D QSAR methods. With the main advantage, these QSAR parameters are quite easy in use, containing simple and useful information about the molecular structure. Furthermore, they can be calculated by avoiding structure optimization. Also, they are invariant to molecular rotation. In 3D QSAR methods, they emphasize the methods by using lattice-based descriptors and surface-based descriptors. The disadvantages of this group of methods, are significant amounts of data that characterize the volumetric structure of a molecule and, ultimately, the can create additional informational interference that complicate the true relationships between the structure and properties of the substance.

2D QSAR methods include the General Unrestricted Structure-Activity Relationships (GUSAR) application. GUSAR allows to evaluate the following environmental characteristics of

compounds: 96-hour 50% lethal concentration (LC_{50}) for Fathead minnow (Pimephales promelas), 48-hour 50% lethal concentration (LC_{50}) for Daphnia magna, 50% growth inhibition concentration (IGC_{50} 50% Inhibition Growth Concentration) Tetrahymena pyriformis and Bioaccumulation factor – Log10 (BCF). In addition, GUSAR allows in silico prediction of LD_{50} values for rats with four types of applying (oral, intravenous, intraperitoneal, subcutaneous, inhalation).

The aim of the paper is a comparative analysis of the environmental characteristics of auxiliary organic components of foaming agents which are used for firefighting by applying QSAR approaches.

Results and Discussion

GUSAR is based on the use of 2D descriptors. 2D QSAR methods are the search for dependencies based on 2D characteristics of the structure without taking into account the spatial structure of molecules. GUSAR uses three randomly selected parameters to generate different 2D QSAR models based on QNA descriptors: changing the coefficient before the connectivity matrix, calculating QNA descriptors for all atoms or for atoms in a molecule with two or more immediate neighbors, and changing the parameters of Chebyshev polynomials. The average similarity of the three nearest neighbors is used to estimate the applicability domain of the model.

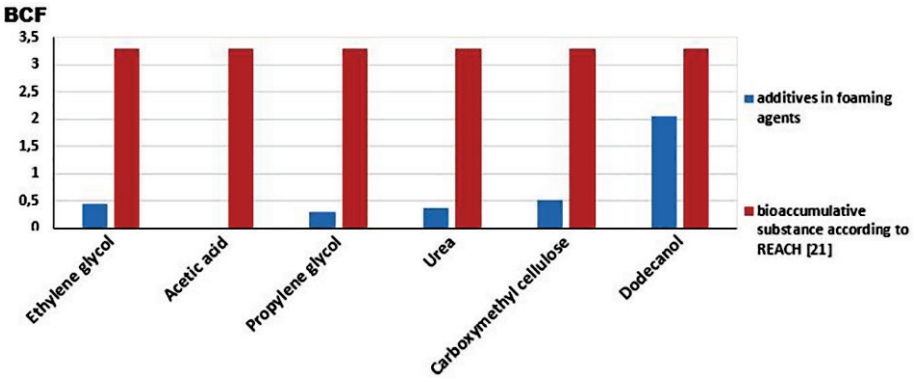

Fig. 1. Values of calculated BCF foaming additives and value of bioaccumulative criterion according to REACH [21].

Materials and Methods

In order to obtain the ecological characteristics of the components of foaming agents for fire firefighting, the GUSAR application has been used [20, 27, 28] in the framework of the applicating Quantitative Structure Activity Relationships methods. The analysis was performed using databases of the European Chemicals Agency [29] and PubChem [30]. These databases contain information on various properties of the known organic and inorganic compounds, including their 2D and 3D structural formulas.

The analysis shows that acetic acid [31], fatty alcohol (C12–C14), carboxymethylcellulose, ethylene glycol, propylene glycol, urea and a number of other substances can be introduced into the foaming agents as additives [20, 32].

Their environmental characteristics can also be determined using the GUSAR application based on appropriate structural 2D formulas of the considered additives.

The presence of structural 2D formulas allowed to obtain data on the values of BCF, LC_{50} for Daphnia magna, Fathead minnow and Tetrahymena pyriformi, which are presented in Table 1.

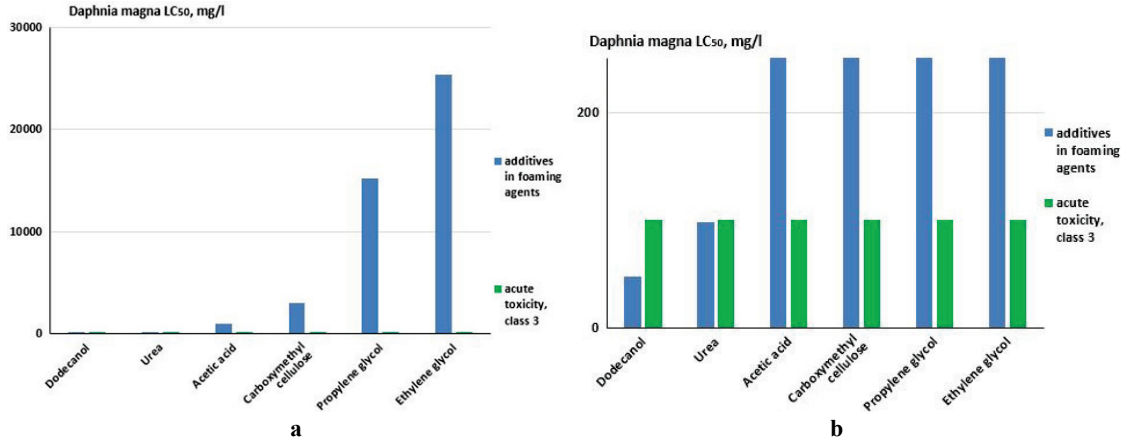

Fig. 2. Values of LC_{50} (mg/l) on the effect of additives in foaming agents on Daphnia magna: a) general view of the data, b) enlarged part of Fig. 2 a).

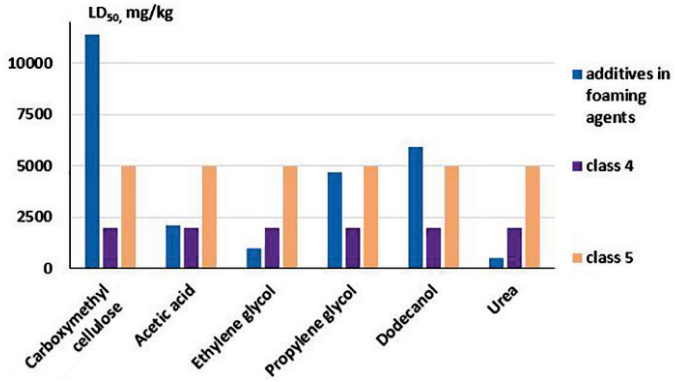

Fig. 3. Values of LD_{50} (mg/kg) on the effect of additives in foaming agents on a person by oral going into the body.

By comparing the obtained BCF values with the bioaccumulation criterion regulated by Regulation (EC) No 1907/2006 Of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) [21] the analysis of the results, given in Table 1, allowed concluding (Fig. 1) that these compounds do not belong to the bioaccumulative. The highest value of the bioaccumulation parameter from the presented compounds is characteristic of dodecanol (substance №5 in Table 1).

Calculation of the LC_{50} criterion (mg/l) for crustacean species Daphnia magna using the data in Table 1 and its comparison with the criteria of acute toxicity of Globally Harmonized System of Classification and Labelling of Chemicals (GHS) [24] showed (Fig. 2) that only dodecanol and urea have acute toxicity of hazard class 3. Other additives do not have a toxic effect on living organisms.

Comparison of the obtained data on acute toxicity to rats (Table 2) on exposure to humans by oral way into the body according to GHS (part 3. Dangers to human health) [24] show (Fig. 3) that most of compounds belong to 4 and hazard class 5, and carboxymethylcellulose and dodecanol have no toxic effects. Urea and ethylene glycol have the most negative effect on human health when being taken orally.

In addition, the dermal (skin) effect on the body of the studied additives was noted (Fig. 4). The analysis of the obtained results shows that urea and acetic acid belong to the 2nd and 3rd classes of acute toxicity, respectively, while the dangerous for the aquatic environment dodecanol is not toxic to humans at all.

Table 1. Ecological characteristics of the studied additives for foaming agents

№	Substance	Molar mass	Activity	Predicted value	Applicability area
1	$C_6H_{12}O_6$ Carboxymethyl cellulose	240	Bioaccumulation factor log10 (BCF)	0.528	In AD
			Daphnia magna LC_{50} -log10 (mol/l)	1.906	In AD
			Fathead Minnow LC_{50} log10 (mmol/l)	0.040	In AD
			Tetrahymena pyriformis IGC_{50} -log10 (mol/l)	-1.561	In AD
2	CH_3COOH Acetic acid	60	Bioaccumulation factor log10 (BCF)	-0.292	In AD
			Daphnia magna LC_{50} -log10 (mol/l)	1.822	In AD
			Fathead Minnow LC_{50} log10 (mmol/l)	1.350	In AD
			Tetrahymena pyriformis IGC_{50} -log10 (mol/l)	-1.694	In AD
3	$C_2H_4(OH)_2$ Ethylene glycol	62	Bioaccumulation factor log10 (BCF)	0.440	In AD
			Daphnia magna LC_{50} -log10 (mol/l)	0.388	In AD
			Fathead Minnow LC_{50} log10 (mmol/l)	1.845	In AD
			Tetrahymena pyriformis IGC_{50} -log10 (mol/l)	-2.532	In AD
4	$CH_2(OH)CH(OH)CH_3$ Propylene glycol	76	Bioaccumulation factor log10 (BCF)	0.299	In AD
			Daphnia magna LC_{50} -log10 (mol/l)	0.700	In AD
			Fathead Minnow LC_{50} log10 (mmol/l)	1.462	In AD
			Tetrahymena pyriformis IGC_{50} -log10 (mol/l)	-2.300	In AD
5	$CH_3(CH_2)_{10}CH_2OH$ Dodecanol	186	Bioaccumulation factor log10 (BCF)	2.047	In AD
			Daphnia magna LC_{50} -log10 (mol/l)	3.591	In AD
			Fathead Minnow LC_{50} log10 (mmol/l)	-2.284	In AD
			Tetrahymena pyriformis IGC_{50} -log10 (mol/l)	1.712	In AD
6	NH_2CONH_2 Urea	60	Bioaccumulation factor log10 (BCF)	0.367	In AD
			Daphnia magna LC_{50} -log10 (mol/l)	2.788	In AD
			Fathead Minnow LC_{50} log10 (mmol/l)	0.841	In AD
			Tetrahymena pyriformis IGC_{50} -log10 (mol/l)	-1.416	In AD

Table 2. Acute toxicity to rats

№	Substance	Rat IP LD_{50} (mg/kg)	Rat IV LD_{50} (mg/kg)	Rat Oral LD_{50} (mg/kg)	Rat SC LD_{50} (mg/kg)
1	$C_6H_{12}O_6$ Carboxymethyl cellulose	931.300 in AD	1837.000 in AD	1,143E4 in AD	2256.000 in AD
2	CH_3COOH Acetic acid	198.300 in AD	565.900 in AD	958,200 in AD	203.100 in AD
3	$C_2H_4(OH)_2$ Ethylene glycol	1410.000 in AD	3125.000 in AD	2111,000 in AD	1379.000out of AD
4	$_2(OH)CH(OH)CH_3$ Propylene glycol	2826.000 out of AD	2654.000 in AD	4674,000 in AD	3499.000in AD
5	$CH_3(CH_2)_{10}CH_2OH$ Dodecanol	3107.000 in AD	604.700 in AD	5944,000 in AD	7364.000 in AD
6	NH_2CONH_2 Urea	48.500 in AD	92.550 in AD	483,700 in AD	75.160 in AD

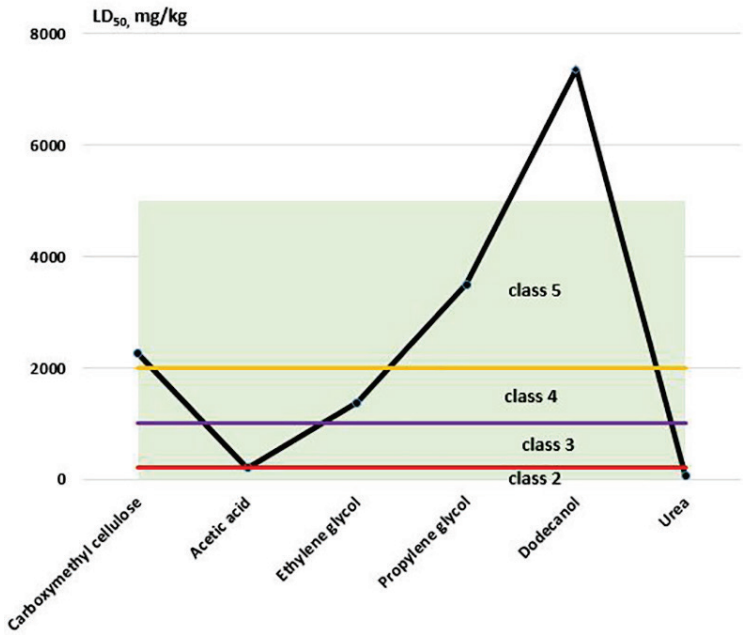

Fig. 4. LD_{50} values (mg/kg) on the effect of additives in foaming agents on a person with dermal effects on the body.

Thus, the least dangerous additives for foaming agents for the environment are carboxymethylcellulose, acetic acid and glycols. Due to the negative impact on humans and the environment, additives such as ethylene glycol, propylene glycol and carboxymethylcellulose are recommended as the most environmentally safe for humans and the environment.

Conclusions

Estimation of ecological characteristics of organic components of foaming agents on the basis of the results received by the 2D QSAR method in the GUSAR application allows considering interrelation of structure and properties of the organic chemicals used for fire fighting.

The QSAR-based analysis showed that carboxymethylcellulose, acetic acid, and glycols were among the least hazardous organic additives for the environment.

The introduction of additives in foaming agents used in fire extinguishing, such as ethylene glycol, propylene glycol and carboxymethylcellulose, are recommended as the most safely for humans and the environment.

ეკოლოგია

ხანძარსაწინააღმდეგო მოქმედებებისას გამოყენებული ქაფის შემადგენლობის დამატებითი ორგანული ნაერთების ეკოლოგიური თვისებების შედარებითი შეფასება

მ. გურბანოვა*, ვ. ლობოიჩენკო**, ნ. ლეონოვა§, ვ. სტრელეცი**, რ. შევჩენკო**

*აზერბაიჯანის რესპუბლიკის საგანგებო სიტუაციათა სამინისტროს აკადემია, ბაქო, აზერბაიჯანი
**უკრაინის სამოქალაქო დაცვის ეროვნული უნივერსიტეტი, ხარკოვი, უკრაინა
§ვ. ნ. კარაზინის სახ. ხარკოვის ეროვნული უნივერსიტეტი, ხარკოვი, უკრაინა

(წარმოდგენილია აკადემიის წევრის ვ. ციციშვილის მიერ)

ნაშრომში განხილულია გარემოს და ცოცხალ ორგანიზმებზე გარკვეული რაოდენობის ორგანული დანამატების ზემოქმედება სხვადასხვა კატეგორიის ხანძრების ჩასაქრობად გამოსაყენებელ ქაფის შემადგენლობაში. გამოკვლეულ იქნა ხანძარსაწინააღმდეგო საშუალებებში დანამატების სახით ყველაზე ფართოდ გამოყენებული ორგანული კომპონენტების ეკოლოგიური მახასიათებლები. ქაფწარმომქმნელი ნივთიერებების ყველაზე ფართოდ გავრცელებული 6 დამატებითი კომპონენტის გარემოს დაცვითი პარამეტრების შესაფასებლად გამოყენებულ იქნა რაოდენობრივი სტრუქტურის თვისებების კავშირის (QSPR) მეთოდი. გამოყენებული იყო 2D დესკრიპტორები რაოდენობრივი სტრუქტურის თვისებების კავშირის მოდელში შემდეგი შეფასების მისაღებად: 96-საათიანი, 50% სასიკვდილო კონცენტრაცია სქელშუბლა თევზისთვის (Pimephales promelas), 48-საათიანი 50% სასიკვდილო კონცენტრაცია დიდი დაფნიასთვის (Daphnia magna), 50% ზრდის შეფერხების კონცენტრაცია Tetrahimena pyriformis და ბიოაკუმულაციის ფაქტორი. ამრიგად, გარემოსთვის ყველაზე ნაკლებად სახიფათოა ხანძარსაწინააღმდეგო საშუალებებში ორგანული ნარევების სახით გამოყენებული შემდეგი დანამატები: კარბოქსიმეთილცელულოზა, ძმარმჟავა და გლიკოლები. ადამიანებსა და გარემოზე უარყოფითი ზემოქმედების თვალსაზრისით, ხანძარსაწინააღმდეგო ქაფებში გამოყენებული დანამატები, როგორიცაა ეთილენგლიკოლი, პროპილენგლიკოლი და კარბოქსიმეთილცელულოზა მიჩნეულია, როგორც ყველაზე უსაფრთხო ადამიანებისა და გარემოსთვის.

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