UDC 547.435+661.74

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«Green» chemistry methods in synthesis of flotation agents

A review of the authors' own works devoted to the development of «green» methods of chemistry in the synthesis of various derivatives of monoethanolamine and diethanolamine, which are potential surface active substances and flotation agents, is made up. It is shown that the application of the «green» chemistry principles, for example, implication of 5 molar % an organic phase transfer catalyst — tetrabutylammonium iodide in alkylation reactions makes it possible to significantly increase (in two to three times) the yields of target substances N-alkylated derivatives of diethanolamine and monoethanolamine with a tenfold reduction in the duration of reactions and a lowering of the process temperature, which leads to a significant reduction in energy and labor costs. Synthesis of target flotation agents, for example, O-2-((dimethoxyphosphoryl)-(2-hydroxyethyl)amino)ethylxanthate and sodium 2-dimethoxyphosphoryloxyethyl carbamate by the atom-economic method — four-component reaction of the one-reactor interaction with a reduction in the number of stages from two to one also contributes to an increase in the total yield of target substances by 2–3 times.

Keywords: surface active substances, flotation agents, «green» chemistry, monoethanolamine and diethanolamine alkyl and dialkoxyphosphoryl derivatives, xanthate, carbamate.

Introduction

It is known, «green» chemistry means chemistry that efficiently processes raw materials (preferably renewable), excludes drains, avoids the use of toxic and harmful reagents and solvents in the production of chemical products and their application [1–3]. Acquiring new positions in technology development, «green» chemistry in the 21st century has become a truly new way of thinking, a new philosophy, a new language that allows us to look at chemistry not only from utilitarian positions (production of products that have demand), but above all with humanitar positions [2]. It should be emphasized that «green» chemistry and ecology are not the same thing. On the contrary, the final goal of «green» chemistry is to negate the efforts of ecologists to remove those harmful emissions that are the main problem of almost all chemical (and not only chemical) industries. If ecologists try to neutralize the consequences created by chemistry, then the task of «green» chemistry is to provide such production in which harmful consequences are generally absent or minimized. The basic principles of «green» chemistry were formulated at the beginning of the 21st century by Paul Anastas, one of the leaders of the US Environmental Protection Agency [3].

The current state of the technology of mineral processing makes it possible to ensure a fairly high degree of complex utilization of raw materials [4]. However, the further solution of the interrelated problems of more rational use of natural resources, ecology, energy and production management requires technologies for processing and enriching the mineral and other types of raw materials of a qualitatively new level [5]. Successful solution of the above problems is impossible without further improvement of the theory of enrichment processes, including selective opening and separation of minerals, separation of components of organic and inorganic substances from water [6]. The creation of new and modification of traditional flotation agents will allow increasing the extraction of target components from ores of nonferrous, noble and rare metals. In addition, from the economic point of view, the principle of creating new flotation agents should be the availability of starting reagents, which are easily obtained from petroleum hydrocarbons. In this regard, the problem of developing an efficient technology for the enrichment of polymetallic ores and the creation of highly effective, original and affordable flotation agents continues to be very actual [7].

It is known that the main groups of reagents used in the flotation of polymetallic sulphide ores are sulfhydryl anionic collectors — alkylxanthates, dithiocarbamates [5, 8] and dialkyldithiophosphates. Their collective ability largely depends on the structure and location of the hydrocarbon radical. This dependence has been studied in detail in a number of papers, from which it can be seen that a relatively small change in the structure of the collector molecule (for example, the elongation or isomerization of the hydrocarbon radical) leads to a significant change in the collection ability of the reagent [9−13].

The study of the properties of modified alkyl xanthates and dialkyl dithiophosphates is especially interesting, because a very limited number of publications are devoted to the study of the flotation properties of reagents of this kind, both in domestic and foreign literature.

«Green» synthesis of alkyl diethanolamine derivatives

As a result of our previous studies, high flotation activity and the selectivity of the action of a number of alkyl diethanolamine derivatives as additional collectors in flotation enrichment of sulfide polymetallic ores have been established. The disodium salt of N-octyl-N,N-bis(2-xanthateethyl)amine [14] and 2-[N-heptyl-N-(2-hydroxyethyl)amino]ethylxanthate sodium [15] significantly improve the quality of copper-lead concentrate at the processing of copper-lead-zinc-pyrite ore. N,N-Di(2-hydroxyethyl)aminononane [16] shows a high collecting activity in the flotation of lead-zinc-silver-containing ore, significantly increasing the extraction of lead, zinc and silver into the collective concentrate.

These reagents-collectors are obtained from commercially available diethanolamine in two stages via intermediate N-alkylldi(2-hydroxyethyl)amines.

In order to increase the yields of intermediate N-alkyldi(2-hydroxyethyl)amines in the preparation of compounds having flotation activity, an alkylation reaction of diethanolamine (DEA) with alkyl C_4-C_7 bromides (AB) was carried out. Previously, the alkylation reaction of DEA was usually carried out by heating (50–60 °C) in a water-alcohol medium for 3 days in the presence of a stoichiometric amount of potash [17]. At the same time, the yields of C_4-C_7 alkylated DEA derivatives ranged from 42 to 72 %.

Using one of the principles of «green» chemistry: «Catalytic systems and processes (as selective as possible) are better in all cases than stoichiometric ones» [2, 3] alkylation of DEA in the presence of an organic phase transfer catalyst — tetrabutylammonium iodide was carried out. As a result of the reactions of alkylation of DEA at room temperature for 2 hours in an aqueous alcohol medium and a molar ratio of DEA:AB:K_2CO_3: n-Bu_4NI = 1:1:1:0.1 reagents, 81 % of N-butyl-N,N-di(2-hydroxyethyl)amine, 87 % of N-pentyl-N,N-di(2-hydroxyethyl)amine, 87 % of N-hexyl-N,N-di(2-hydroxyethyl)amine, 92 % of N-heptyl-N,N-di(2-hydroxyethyl)amine were obtained (Fig. 1).

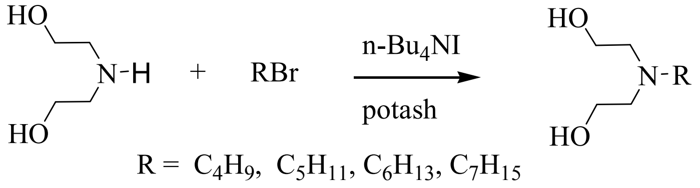

Figure 1. Synthesis of N-alkyl-N, N-diethanolamines

Based on the results obtained, it can be concluded that the alkylation reaction of DEA in accordance with the principles of «green» chemistry makes it possible to obtain N-alkyldi(2-hydroxyethyl)amines selectively and in a high yield, with a significant reduction in the reaction time and a 30 ºC decrease in the process temperature, it leads to a reduction in energy and labor costs. At the same time, the yield of the target alkylaminoglycols almost doubles increases [18].

Application of the principles of «green» chemistry in the synthesis of sodium O-2-((dimethoxyphosphoryl)(2-hydroxyethyl)amino)ethylxanthate

In continuation of our research to obtain new diethanolamine-based surfactants, we performed a diethanolamine phosphorylation reaction by dialkyl phosphites, as shown in the diagram in Figure 2.

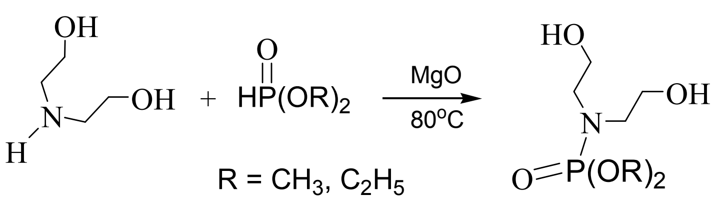

Figure 2. Scheme of phosphorylation of diethanolamine by dialkyl phosphites

The diethanolamine phosphorylation reaction was carried out by reacting diethanolamine with a dialkyl phosphite in a benzene medium in the presence of magnesium oxide at a temperature of 80 ºC. As a result, dialkyl bis (2-hydroxyethyl) phosphoramidates were obtained in the yields of 67 % and 65 %, respectively. The composition of the obtained phosphoramidates was confirmed on the basis of elemental analysis data, and the structure was confirmed on the basis of IR and NMR data of ^{1}H and ^{13}C, ^{31}P spectra [19]. In the IR spectra of synthesized phosphoramidates, intense bands of characteristic stretching vibrations of P=O and P–O–C bonds in the region 1196, 1162 cm^{-1} are observed, confirming the presence of a phosphorus-containing radical in the molecule of the obtained compounds. The presence in the spectra of intense absorption bands in the region of 3267±3387 cm^{-1} confirms the presence of hydroxyl groups in the structure of phosphoramidates. In the PMR spectrum of dimethyl-bis(2-hydroxyethyl)phosphoramidate in D_2O the protons of the OCH_3 substituents are observed as a doublet at 3.20 and 3.23 ppm, the protons of NCH_2 groups are resonated at 2.80–2.92 ppm, protons of OCH_2 groups at 3.48 ppm, protons of OH groups at 4.70 ppm in the form of a broadened singlet, which also confirms the reaction of the amine group.

In the PMR spectrum of diethyl-bis(2-hydroxyethyl)phosphoramidate in DMSO-d_6, the protons of ethyl substituents manifest themselves as two groups of signals: a triplet at 1.15 ppm with J = 7.3 Hz and two quartets at 3.85 ppm and 3.87 ppm with the same SSIC, the protons of NCH_2 groups are resonated at 2.95 and 2.98 ppm in the form of two triplets with SSIC 6.1 Hz, protons of CH_2OH groups at 3.41 ppm in the form of a triplet with J = 6.3 Hz, protons of OH groups at 4.70 ppm in the form of a broadened singlet.

The two-dimensional COSY spectrum of dimethyl-bis(2-hydroxyethyl)phosphoramidate, shown in a Figure 3, made it possible to establish the homonuclear interactions of H-H through three bonds and unambiguously confirm the structure of the obtained phosphamidate.

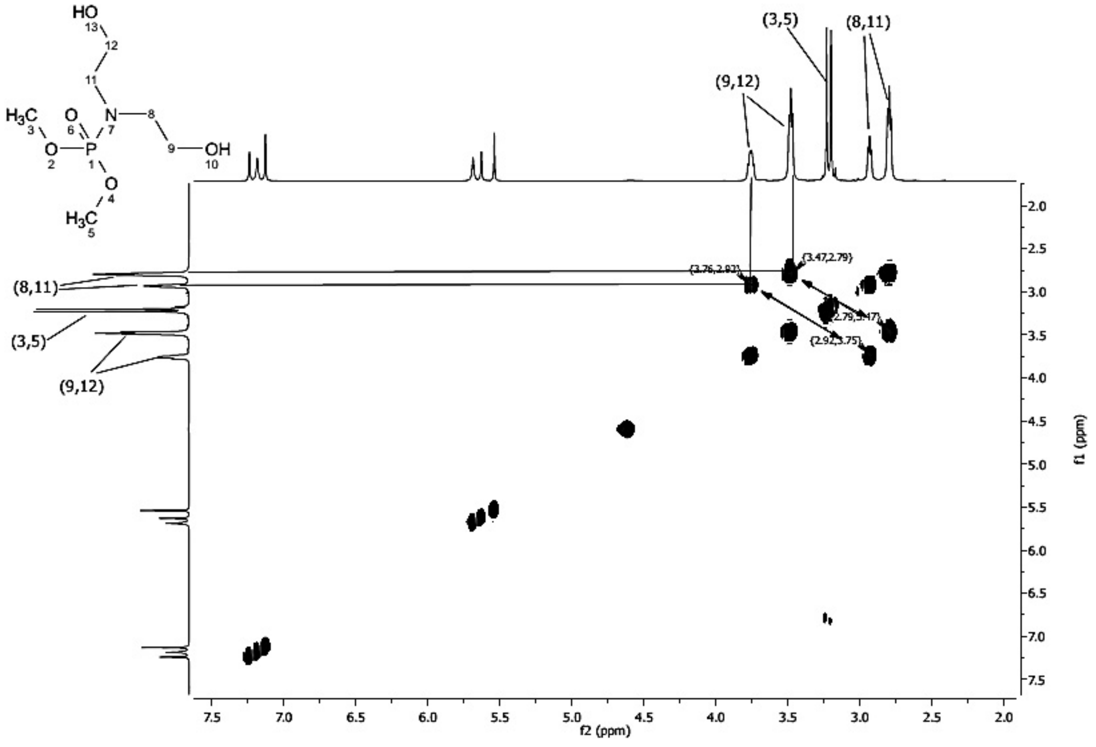

Figure 3. The two-dimensional COSY spectrum of dimethyl bis(2-hydroxyethyl)phosphamidate in D_2O

In the ^{13}C NMR spectrum of dimethyl-bis(2-hydroxyethyl)phosphoramidate, resonance signals in the region of 50.61 ppm corresponding to the OCH_3 groups, 57.44 and 59.82 ppm corresponding to the CH_2OH groups and the signals in the 39.87 and 41.05 ppm which belong to the groups CH_2N are observed. In the ^{13}C NMR spectrum of diethyl-bis(2-hydroxyethyl)phosphoramidate resonance signals are observed in the 16.4 ppm region corresponding to the $OCH_2\underline{CH_3}$ groups, at 60.28 ppm. $-O\underline{CH_2}CH_3$ groups and signals in the region of 49.28 ppm belong to the CH_2N groups, the signals at 61.78 ppm. — to CH_2OH groups.

In the ^{31}P spectrum of dimethyl-bis(2-hydroxyethyl)phosphoramidate, only one signal is observed in the region of 8.86 ppm, and in the ^{31}P spectrum of diethyl-bis(2-hydroxyethyl)phosphoramidate — one signal in the region of 11.17 ppm corresponding to the dialkoxyphosphamide group is observed.

Further conversion of dimethyl bis(2-hydroxyethyl)phosphamidate to sodium xanthate was carried out by reacting phosphamidate (FA) with carbon disulphide and sodium hydroxide at room temperature and the molar ratio of FA:CS_2:NaOH = 1:1:1 reagents in an alcohol medium, as shown in Figure 4. Sodium O-2-((dimethoxyphosphoryl)(2-hydroxyethyl)amino)ethylxanthate was obtained in a yield of 28 %, m.p. 78 °C. Since the yield of dimethyl-bis(2-hydroxyethyl)phosphamidate in the first stage was 67 %, the total yield of xanthate in two stages is 19 %.

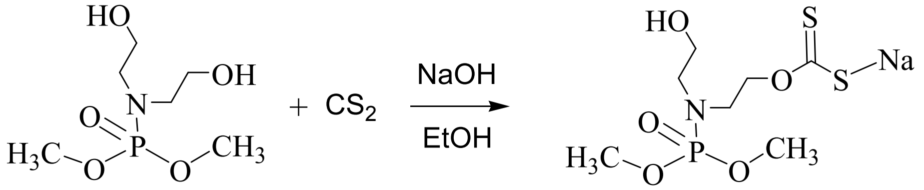

Figure 4. Scheme of dimethyl-bis(2-hydroxyethyl)phosphamidate reaction with carbon disulphide and sodium hydroxide

Since the development of «green» methods for the synthesis of diethanolamine derivatives is one of the goals of our studies, we studied a one-reactor method for carrying out a four-component reaction of diethanolamine, dimethyl phosphite, carbon disulfide and sodium hydroxide, as the reduction in the number of stages of obtaining the target substance corresponds to a number of principles of «green» chemistry, and namely, principle 2, which reads: «*The synthesis strategy must be chosen in such a way that all materials used in the synthesis process are maximized were included in the product*», and also to principle 5, which reads: «*The use of auxiliary substances (solvents, extractants, etc.) should be minimized whenever possible*» [2, 3].

A four-component reaction of a single-reactor reaction of diethanolamine, dimethyl phosphite, carbon disulfide and sodium hydroxide, taken in a molar ratio of 1:1:1:1, was carried out in a ethyl alcohol medium at room temperature, as shown in the diagram in Figure 5. After appropriate treatment of the reaction mixture, sodium O-2-((dimethoxyphosphoryl)(2-hydroxyethyl)amino)ethylxanthate was isolated in a yield of 65 %, m.p. 78 °C.

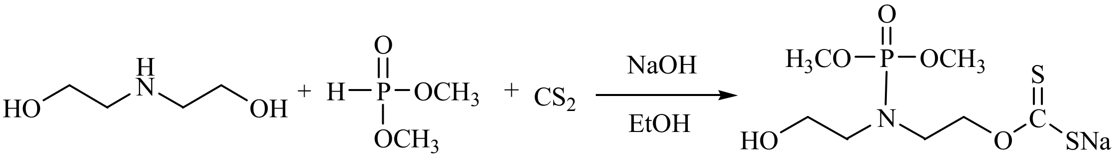

Figure 5. Scheme of a four-component reaction of a single-reactor interaction of diethanolamine, dimethylphosphite, carbon disulfide and sodium hydroxide

The structure of the synthesized samples of O-2-((dimethoxyphosphoryl)(2-hydroxyethyl)amino)ethyl xanthogenate was established on the basis of the IR and ^{1}H NMR spectra analysis [19]. In the IR spectra of both xanthate samples in the region of 2847 ± 2952 cm^{-1}, absorption bands characteristic for valence vibrations of CH_2 and CH_3 groups of saturated hydrocarbons are observed. A wide strong OH band absorption band is manifested in the 3300 cm^{-1} region. The absorption band of medium intensity in the region of 1201 cm^{-1} is attributed to the stretching vibrations of the P=O group. Strong bands of stretching vibrations of P–O–C bonds are observed in the region of 1050 cm^{-1}. The presence of the C=S group is confirmed by the presence of very strong absorption bands in the spectrum at 1063 and 1070 cm^{-1}, weak bands in the 781 and 575 cm^{-1} regions correspond to vibrations of the C–S bond.

As a result of our studies, we have established that both the sequential reactions of diethanolamine phosphorylation and the interaction of the dimethylbis(2-hydroxyethyl)phosphoramidate formed with the carbon disulphide and the four-component reaction of the one-reactor interaction of diethanolamine, dimethylphosphite, carbon disulfide and sodium hydroxide form sodium O-2-((dimethoxyphosphoryl)-(2-hydroxyethyl)amino)ethyl xanthate. The coincidence of the physicochemical characteristics of both xanthate samples confirms that in both cases the same substance was obtained.

Consequently, the practical application of the principles of «green» chemistry leads to the synthesis of the desired compound: sodium O-2-((dimethoxyphosphoryl)(2-hydroxyethyl)amino)ethylxanthate by the atom economical method — with a reduction in the number of stages from two to one, and increase of the total yield of the target substance more than three times (from 19 to 65 %).

The «green» method of monoethanolamine N-alkylation

Continuing the search for highly effective flotation agents among amino alcohol derivatives, we investigated the «green» methods for the alkylation of monoethanolamine (MEA) in order to increase the yield of target products while reducing energy and labor costs [20]. Previously, the alkylation reaction of MEA was carried out by the usual method of amine reaction with alkyl bromide in the presence of potassium acetate in anhydrous alcohol at 50–55 ºC [21]. As a result of prolonged heating (20–30 h), corresponding N-monosubstituted MEA derivatives with the yields of 27–42 % and N,N-disubstituted derivatives of MEA with the yields of 7–10 % are formed. Obviously, the use of the conventional alkylation process gives a rather low yield of the target amino alcohols with a total reaction time of 3–5 days. Therefore, a search for a more economical method of synthesis was carried out.

In order to optimize the conditions for the interaction of MEA with alkyl halides and increase the yield of N-alkylation products, the reaction was carried out in various solvents — alcohol, acetone, dioxane, tetrahydrofuran, benzene. It has been experimentally established that 90 % alcohol is the most suitable solvent. In fact, the solubility of the initial reagent — MEA in alcohol is greatest. While in other polar solvents such as sulfuric ether, ethyl acetate, dioxane, tetrahydrofuran, MEA is practically insoluble, or dissolves poorly at room temperature, which consequently affects the yield of the final product.

Among the tested binding agents of hydrogen bromide, which was released in the reaction, — NaOH, KOH, sodium and potassium acetate, potash, the best yields of alkylated ethanolamines were obtained by using potash. Based on the analysis of scientific chemical literature on the application of «green» chemistry methods, it has been shown that one of the main principles of «green» chemistry is the use of catalysts in order to shorten the time of synthesis, reduce energy costs and increase the selectivity of reactions for rational use of initial reagents and reduce the costs of target products [1–3].

Since the MEA alkylation reaction is carried out in a two-phase liquid-solid system, an organic catalyst for the interfacial transfer the tetrabutylammonium iodide was used. With the addition of five mole percent catalyst, the alkylation process is significantly accelerated, and the reaction ends after two hours at room temperature. As a result of the reaction, monosubstituted N-alkyl-N-ethanolamines in the yields of 72–81 % and disubstituted N,N-dialkyl ethanolamines in the yields of 7–19 % were obtained under the conditions obtained (Fig. 6). The composition of the obtained compounds was confirmed on the basis of elemental analysis data, and the structure was based on IR and NMR data of ^{1}H and ^{13}C spectroscopy [20].

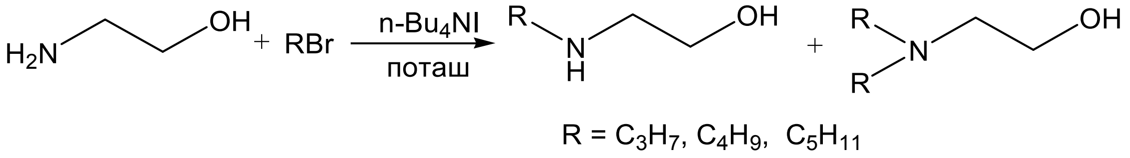

Figure 6. Synthesis of C_3–C_5 alkylated derivatives of MEA in «green» conditions

Thus, using the principles of «green» chemistry, carrying out the alkylation reaction of MEA in aqueous alcohol under organocatalysis conditions makes it possible to obtain N-alkylated derivatives of MEA selectively and in high yield, with an almost doubling of the yield of the target substances and a reduction in the reaction time by a factor of ten.

«Green» chemistry in the synthesis of sodium dimethoxyphosphoryloxyethyl carbamate

With the aim of developing new highly effective flotation reagents-collectors, we investigated the reaction of phosphorylation of MEA [22]. In the study of various reaction conditions, the best conversion of the initial MEA was achieved by phosphorylation with dimethyl phosphite (DMF) at 80 ºC in benzene using magnesium oxide as the catalyst and a molar ratio of reagents MEA:DMF:MgO = 1:1:1. As a result of the reaction, 2-aminoethyldimethylphosphate (ADMP) was obtained in a yield of 65 % (Fig. 7). 2-Aminoethyldimethylphosphate is an oil, that is highly soluble in water.

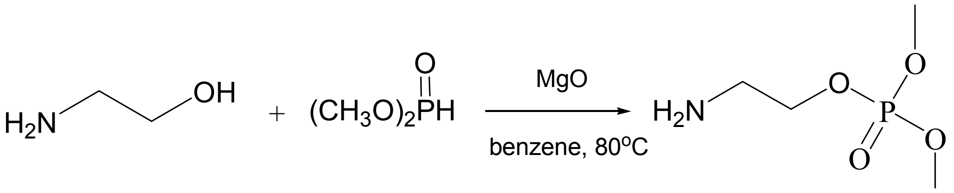

Figure 7. Phosphorylation of MEA by dimethyl phosphite

The composition and individuality of synthesized 2-aminoethyldimethylphosphate are confirmed by thin-layer chromatography and physicochemical characteristics. The structure of the compound was established on the basis of an analysis of the IR and NMR spectra of ^{1}H and ^{13}C, ^{31}P [22]. In the IR spectrum of the synthesized phosphate, given in a Table, there is an absorption band of the characteristic vibrations of the NH_2 group at 3440 cm^{-1}, in the region of 1190 cm^{-1} a characteristic band of the P=O group is observed, in the 1070 cm^{-1} the absorption band of P–O–C. In the ^{31}P 2-aminoethyldimethyl phosphate spectrum, only one signal is observed in the 6.72 ppm region corresponding to the phosphate group.

In order to obtain new surfactants, we investigated the reaction of 2-aminoethyldimethylphosphate with carbon disulfide. The reaction was carried out in the presence of an equimolar amount of sodium hydroxide in an ethyl alcohol medium at room temperature, as shown in Figure 8. The reaction yielded a crystalline product in 48 % yield, which is sodium 2-dimethoxyphosphoryloxyethylcarbamate (DMPC-1). At the same time, its total yield with respect to the initial MEA is 31 %.

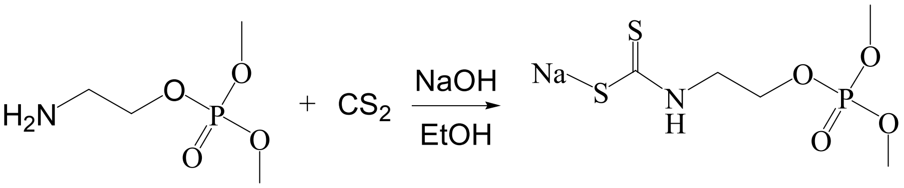

Figure 8. Interaction of 2-aminoethyldimethylphosphate with carbon disulfide

The structure and individuality of the synthesized compound — sodium 2-dimethoxyphosphoryloxyethylcarbamate — are confirmed by the data of physicochemical methods, IR and PMR spectroscopy [22], presented in Table.

In order to develop a «green» method for the synthesis of sodium 2-dimethoxyphosphoryloxyethylcarbamate, we carried out a four-component reaction of monoethanolamine, dimethylphosphite, carbon disulfide and sodium hydroxide, due to the fact that the reduction in the number of stages of obtaining the target substance corresponds to a number of principles of «green» chemistry [2, 3].

The four-component reaction of single-reactor method of MEA, DMF, carbon disulfide and sodium hydroxide in a molar ratio of 1:1:1:1 interaction was carried out in an ethyl alcohol medium at room temperature, as shown in the scheme in Figure 9. After the appropriate treatment of the reaction mixture, 2-dimethoxyphosphoryloxyethylcarbamate (DMFC-2) in 78 % yield.

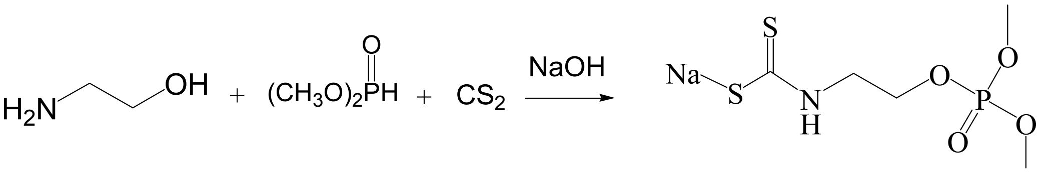

Figure 9. The single-reactor method of four-component reaction of MEA, DMF, carbon disulfide and sodium hydroxide

As can be seen from the data in Table, the infrared spectra and nuclear magnetic resonance spectra of ^{1}H and ^{13}C of the sample of sodium 2-dimethoxyphosphoryloxyethyl carbamate (DMPC-2) obtained in the four-component reaction coincide with the spectra of the sample obtained in the reaction of 2-aminoethyldimethylphosphate with carbon disulfide DMPC-1.

Table

Physico-chemical characteristics of synthesized MEA derivatives

MEA derivatives	A yield %	R_f	PMR spectra data, δ, ppm			IR spectra data, ν, sm^{-1}		
			CH_2NH_2 (CH_2NH)	OCH_3	OCH_2	P=O	P-O-C	NH_2(NH)
ADMP	65	0.17	2.95	3.24–3.27	3.58	1190	1070	3440
DMPC-1	48	0.28	(4.50)	3.26–3.28	3.62	1163	1050	(3414)
DMPC-2	78	0.29	(4.50)	3.27–3.31	3.62	1200	1053	(3425)

Thus, we have established that as a result of sequential reactions of phosphorylation of monoethanolamine and subsequent reaction of the 2-aminoethyldimethylphosphate formed with carbon disulphide and the four-component reaction of monoethanolamine, dimethyl phosphite, carbon disulfide and sodium hydroxide, a sodium 2-dimethoxyphosphoryloxyethyl carbamate is formed. In the latter case, its total yield increases in 2.5 times. Consequently, the application of the principles of «green» chemistry makes it possible to carry out the synthesis by an atom-economic method with a reduction in the number of stages from two to one and a significant increase in the yield of the target substance.

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Флотореагенттер синтезіндегі «жасыл» химия әдістері

Мақалада потенциалды беттік белсенді заттар және флотореагенттер болып табылатын моноэтаноламин мен диэтаноламиннің әртүрлі туындыларының синтезіне «жасыл» химия әдістерін жасауға арналған авторлардың өз жұмыстарына шолу жүргізілген. Онда «жасыл» химия принциптерін қолданғанда мақсатталған өнімнің шығымдары біршама (екі-үш есеге) жоғарылайтыны және процесті жүргізу температурасы мен реакция жүргізу ұзақтығы он есе төмендеуі біршама энергетикалық және еңбек шығындардың қысқаруына әкелген. Атомэкономды әдіспен мақсатталған флотореагенттердің синтезі — саты саны екіден бірге дейін қысқартып, сонымен қатар мақсатталған заттың жалпы шығымын 2-3 есеге дейін жоғарылатуға қабілеттілігін көрсеткен.

Кілт сөздер: беттік белсенді заттар, флотореагенттер, «жасыл» химия, моноэтаноламин және диэтаноламиндердің алкилді және диалкоксифосфорил туындылары, ксантогенат, карбамат.

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«Зеленые» методы химии в синтезе флотореагентов

В статье проведен обзор собственных работ авторов, посвященных разработке «зеленых» методов химии в синтезе разнообразных производных моноэтаноламина и диэтаноламина, являющихся потенциальными поверхностно-активными веществами и флотореагентами. Показано, что применение принципов «зеленой» химии позволяет значительно (в два-три раза) повысить выходы целевых веществ при десятикратном сокращении продолжительности проведения реакций и снижении температуры проведения процессов, что приводит к значительному сокращению энергетических и трудовых затрат. Синтез целевых флотореагентов атомэкономным методом — с сокращением числа стадий от двух до одной также способствует повышению общего выхода целевых веществ в 2-3 раза.

Ключевые слова: поверхностно-активные вещества, флотореагенты, «зеленая» химия, алкильные и диалкоксифосфорильные производные моноэтаноламина и диэтаноламина, ксантогенат, карбамат.

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