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Synthesis and Physicochemical Properties of 1-(2-Alkylamidoethyl)-2-alkyl-2-imidazolines Based on α,α'-Branched Carboxylic Acids

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Abstract—Condensation of diethylenetriamine with lauric, 2-ethylhexanoic, and α,α'-branched $C_{10,12}$-carboxylic acids results in 1-(2-alkylamidoethyl)-2-alkyl-2-imidazolines. A stability of the synthesized compounds relative to the acid and alkaline hydrolysis was studied. Their protonation constants were determined. The effect of the structure of the alkyl substituents on the distribution of the substance between the organic and aqueous phases was examined. The principal possibility of extracting Zn(II), Fe(III), Cu(II), Co(II), Mn(II) chlorides from hydrochloric acid solutions was shown. A mixture of 1-(2-alkylamidoethyl)-2-alkyl-2-imidazolines based on the α,α'-branched carboxylic acids was suggested as a potential extractant of the metal salts from hydrochloric acid and chloride solutions.

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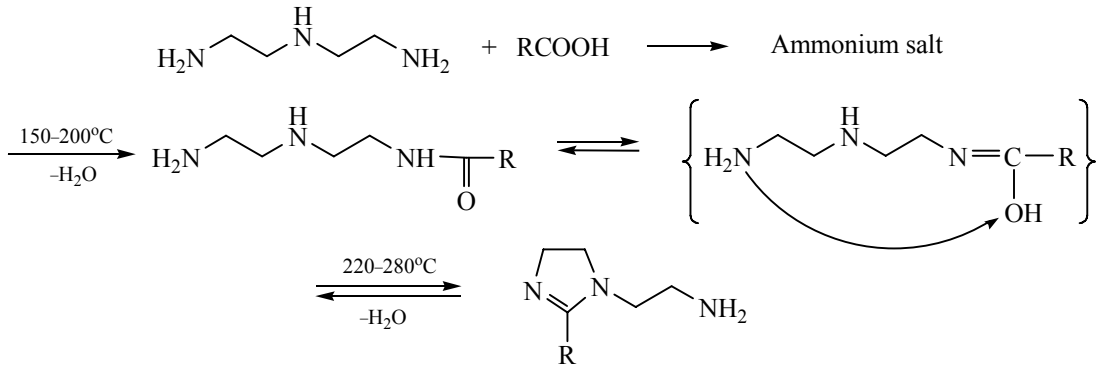
1,2-Disubstituted imidazolines has been used to produce the cationic and ampholytic surfactants since over 50 years. As a rule, non-toxic, biodegradable, disubstituted imidazolines have a relatively high thermal stability, emulsifying and wetting properties, and are used in a wide variety of industries [1]. However the extraction properties of the disubstituted imidazolines were not studied.

In the literature a large number of preparative methods for the synthesis of disubstituted imidazolines is described [2]. Apparently, the most promising method is the condensation of carboxylic acids or their esters with the amine components (Scheme 1).

High pressure makes it possible to carry out the reaction at 250–350°C, and the low pressur, at 200–280°. Raising the temperature to 300°C is undesirable, since along with the imidazolines formation their thermal degradation and polymerization of the by-products proceed. Using the catalysts (aluminum chloride, ascorbic acid) it is possible to increase the product yield, but in this case there are difficulties in the isolation of the disubstituted imidazolines from the

Scheme 1.



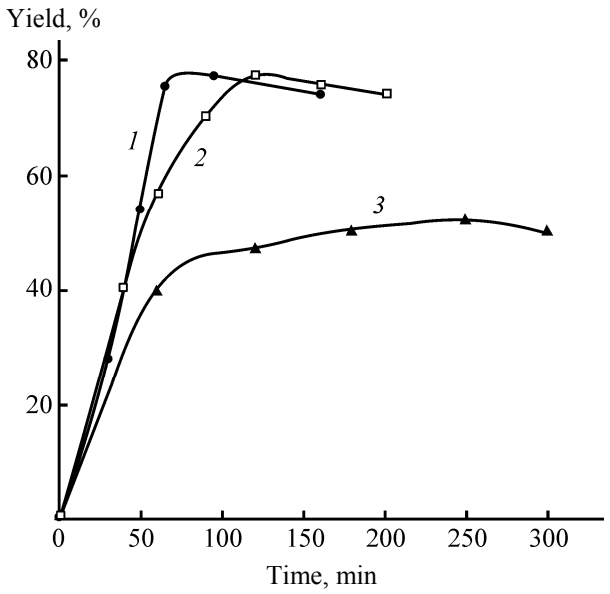


Fig. 1. Cyclization of diethylenetriamine acylated with caprylic acid at 190°C (*1*), 2-ethylhexanoic acid at 270°C (*2*), a fraction of the α,α'-branched acid at 270°C (*3*). The reaction volume is 20 ml.

reaction mixture.To intensify the process the synthesis is carried out in the solvents (higher alcohols, aromatic hydrocarbons, etc.), followed by azeotropic distillation of water and the solvent.

Earlier we synthesized imidazoline **I** on the basis of 2-ethylhexanoic acid. It is virtually insoluble in water and shows an ability to extract a number of metal salts from the ammonium and weakly acidic chloride solutions [3]. However, its solubility in water increases as an acidity of the aqueous phase increases, significantly reducing its application scope. To increase the hydrophobicity of compound **I** it would be appropriate to introduce the alkyl substituents with a greater number of the carbon atoms into the imidazoline ring. For example, the α,α'-branched $C_{\geq 10}$-carboxylic acids can be used for this purpose.

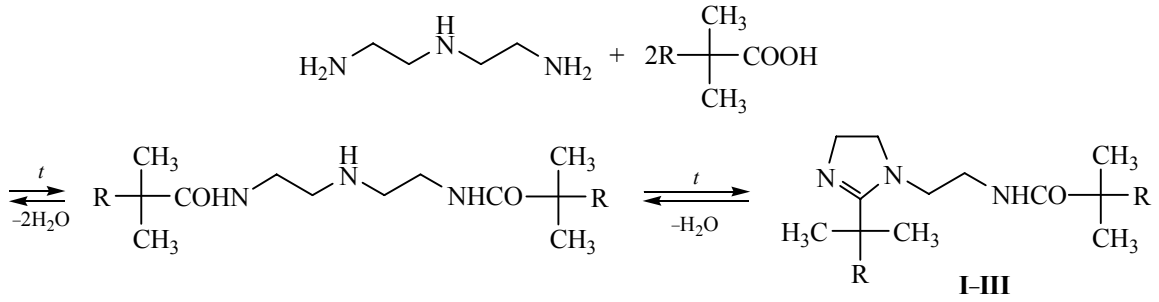
The aim of this work is developing a synthesis method of 1-(2-alkylamidoethyl)-2-alkyl-2-imidazolines with the α,α'-branched substituents ($\geq C_{10}$) in a relatively high yield, the identification of the synthesized compounds, and evaluation of the possibility of their use in a liquid extraction as the extracting agents for the metal ions.

As follows from Scheme 1, the initial products of the condensation of diethylenetriamine with carboxylic acids are mono- or diamides, which cyclize into the corresponding imidazolines at higher temperatures. It was previously shown that the cyclization of amides of the linear acid into the imidazolines proceeds at 160–190°C [4], and the cyclization of 2-ethylhexanoic acid amide occurs at 280–300°C [5]. The reaction time should be increased 1.5–2 times. As an example, Fig. 1 shows the curves of the cyclization of diethylenetriamine acylated with caprylic, 2-ethylhexanoic, and α,α'-branched acids. The presence of a branched alkyl substituent causes the steric hindrance in the condensation of the α,α'-branched acids compared with 2-ethylhexanoic acid, and moreover, with the linear acids used in the industry. Some influence has a positive inductive effect (+*I*) of the α,α'-branched alkyl substituents, which hampers the carboxylic acid ionization. As expected, the cyclization of amide acylated with the α,α'-acids occurs inefficiently (Fig. 1, curve *3*). As a rule, an increase in the temperature and time of the synthesis causes the tarring of products. The isolation of the target compounds is a complex problem, since the target material and its precursor are a mixture of the high-boiling homologs. The attempts to carry out this synthesis under the reduced pressure (8–10 mm Hg, 200–240°C, 3–4 h) or in an *n*-decanol medium failed. However, carrying out the synthesis in the presence of octyl alcohol gave good results: the yield of a homologues mixture of **I** was 80–90% (Fig. 2). It should be noted that this synthesis method is very simple, and the presence of small amounts of *n*-octanol in the final product does not interfere, since *n*-octanol is a part of the diluent on using a mixture of imidazolines **I** as an extractant.

The synthesized reagent **I** is a thick yellow-brown liquid, insoluble in water, readily soluble in alcohols, aromatic hydrocarbons, chloroform (~3 M), and saturated hydrocarbons (~ 0.75 M).

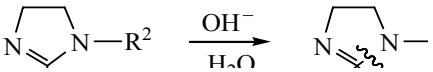
The resulting mixture **I** was identified by an intensive absorption band in the ultraviolet and infrared regions belonging to the >C=N fragment (see the table). The IR spectra of the disubstituted imidazolines also contain the intensive amide I and II bands. In the ^{13}C NMR spectra there are characteristic signals of the sp^2-hybridized carbon atoms of the imidazoline ring and amide groups. For comparison, the table also contains the spectral data of the imidazolines **II** and **III** previously studied by us [5] with the α-branched and linear substituent, respectively, in the second position of the imidazoline ring. The presence of ethyl group in the α-position of the alkyl substituent leads to a certain shifting the spectral parameters (**III**, **II**), without changing their

Scheme 2.

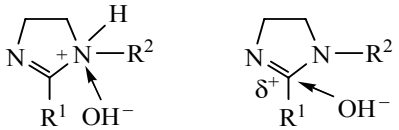


I–III

nature. The introduction of two methyl groups into the α-position of the alkyl substituent (**III**, **I**) has a little effect on the spectral parameters of amidoethylimidazolines. The most significant differences are observed in the absorption frequencies of imine and amide bands: they are 12 [ν(C=N)], 25 [ν(NHCO)], and 24 cm^{-1} [δ(NHCO)], respectively.



An important characteristic of the extractants is their resistance to the acid and alkaline hydrolysis. For comparison with [6], alkylimidazolines hydrolysis was performed at 60°C.



The limiting stage of the hydrolysis is the nucleophilic attack on the imidazoline molecule by the hydroxide ions [7].

The presence of a positive charge on the nitrogen atom prevents hydrolysis, since in this case there is no partial positive charge on the carbon atom.

For this reason, the imidazolines solutions are stable in acidic media, and the imidazoline ring opening occurs under rigid conditions (10–12 M H_2SO_4, 100°C) [8]. Evidently, under our experimental conditions (2.5 M H_2SO_4, 60°C) a conversion of amidoethylimidazolines was not observed.

At the alkaline hydrolysis of imidazolines the bulky substituent α-positioned relative to the reaction center interferes with the hydroxide ions addition, decelerating the amidoethylimidazoline hydrolysis. The rate of hydrolysis of compound **III** is about 5 times higher than that of the rest of imidazolines. Since the reagent **I** is only moderately stable in alkaline media, the best use of it is for the extraction of metals from acidic solutions.

Comp. no.	$k_{ef}\cdot10^5$	log K
I	1.5±0.1	10.87±0.05
II	1.1±0.1	10.65±0.05
III	6.0±0.5	10.75±0.05

Imidazolines are basic compounds. Determination of the step protonation constants of amidoethylimidazolines indicate that the presence of the α- or α, α'-branching in a second position of the imidazoline ring has virtually no effect on the basic nitrogen atom in the molecule.

Spectral parameters of imidazolines **I–III**

Comp. no.	UV spectrum (isopropanol), λ, nm (log ε)	IR spectrum (film), ν, cm^{-1}	^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm
I	202 (3.77) ($n \rightarrow \sigma^*$-transitions in the ring and amide group), 229 (3.79) ($\pi \rightarrow \pi^*$, C=N)	3346 (NHCO), 1643 (C=O), 1595 (C=N), 1527 [δ(NH)], 998 (C–N)	171.56 (C=N), 177.93 (NHCO)
II	201 (3.67) ($n \rightarrow \sigma^*$) 234 (3.83) ($\pi \rightarrow \pi^*$)	3304 (NHCO), 1644 (C=O), 1605 (C=N), 1552 [δ(NH)], 1000 (C–N)	170.43 (C=N), 176.11 (NHCO)
III	201 (3.70) ($n \rightarrow \sigma^*$) 228 (3.79) ($\pi \rightarrow \pi^*$)	3321 (NHCO), 1640 (C=O), 1607 (C=N), 1551 [δ(NH)], 1000 (C–N)	167.7 (C=N), 173.9 (NHCO)

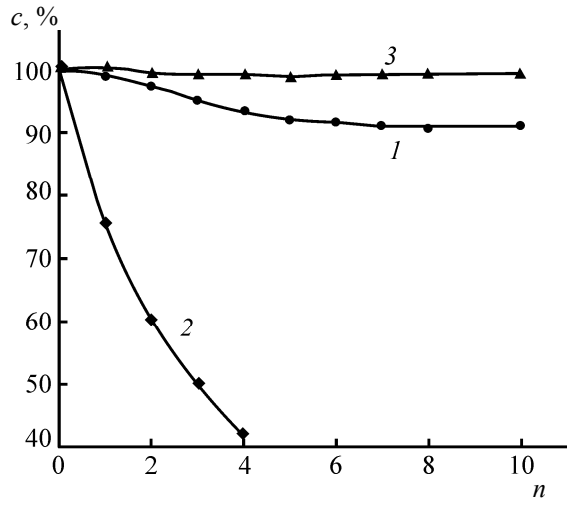


Fig. 2. Distribution of imidazolines **I–III** between the organic phase and hydrochloric acid solution: **I** – 5 M HCl (*1*), **II** – 1 M HCl (*2*), **III** – 5 M HCl (*3*). The initial reagents concentration in organic phase is 0.1 M. (corresponds to 100% on a vertical axis), diluent is 15% octanol solution in toluene. *c* (%) is the reagent concentration in the organic phase, *n* is a number of the contacts of the organic phase with an HCl solution.

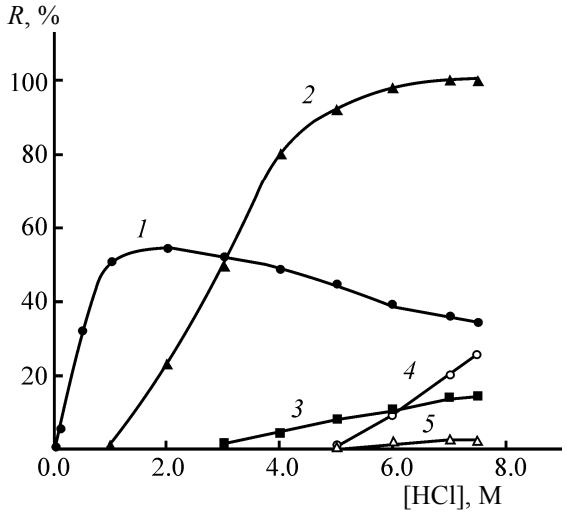


Fig. 3. Dependence between the extraction degree of the non-ferrous metals with imidazolines and hydrochloric acid concentration in the aqueous phase: (*1*) Zn(II); (*2*) Fe(III), (*3*) Cu(II); (*4*) Co(II); (*5*) Mn(II). The imidazoline concentration equals 0.07 M, diluent is 15% octanol solution in toluene, the initial concentrations of the metal ions in the aqueous phase are 0.04 M.

As can be seen from the above data, the log *K* values corresponding to the protonation of the tertiary N atom of the ring are close. Even in a weak acid media the imidazolines **I–III** exist completely in the salt form, which is more soluble in water in comparison with the neutral imidazoline. To estimate the solubility of the extractants in acidic solutions we studied the distribution of alkylimidazolines between the organic and aqueous phases, depending on the number of the contacts of the organic phase with hydrochloric acid (Fig. 2). The presence of alkyl substituents with a greater number of carbon atoms in the imidazoline ring reduces the transition of compound **I** in the aqueous phase at the contact with 5 M hydrochloric acid solution. The initial part of a curve *1* is apparently caused by the presence of some amount of the low-molecular homologues in the sample **I**. A solubility of the imidazolines salts reduces sharply as the number of the carbon atoms in the alkyl substituents increases: $C_7 >> C_9 > C_{11}$ (Fig. 2). An ability of the imidazolines to emulsify, when the aqueous phase was acidified, depends on the branching of the alkyl substituents. For the reagent **I** the phase separation time is 1–2 min in the entire investigated range of acidity (0.1–7 M HCl), for compound **II** it is 10–30 min (when in contact with a 1 M HCl solution). In the case of compound **III** the complete phase separation occurs within 1–8 h (when in contact with a 1.5 M HCl solution). In contact with the sulfuric acid solutions an extraction system based on the reagent **III** is not separated completely even within 1 day. Consequently, the imidazolines based on the α,α'-branched carboxylic acids are better solvated in the studied systems.

In acidic media ethylamidoimidazolines exist in a salt form. They extract the anionic forms of the metals by the anion exchange mechanism. In the pH range of 0.1–5.0 M. HCl solution for compound **I** we obtained the following extraction series: Zn(II) > Fe(III) > Cu(II) > Co(II)> Mn(II) (Fig. 3). All the metals are quantitatively reextracted with the diluted sulfuric acid (0.05–0.1 M.) in 1 step, while the reextraction time is 1–2 min, and the complete phase separation is achieved in 2–5 min.

Using the acylated ethyleneamines as an an example of the ethylamidoimidazolines precursors, we have shown earlier [9] that neither the length nor the branching of alkyl substituents do not have a clear effect on the extraction properties of the reactants. Differences in the efficiency of the metal salts extraction by this class of the agents were due to the different removal of the extractants with the aqueous phase and the absence of the third phase in the extraction system. Apparently, this is also true for imidazolines.

The alkylimidazolines with the linear alkyl substituents are probably inappropriate to be applied in the metals extraction, since compared with the reagent **I** compound **III** has a number of drawbacks: it is less soluble in alcohols, aromatic hydrocarbons, chloroform (0.3–0.5 mM), and practically insoluble in the saturated hydrocarbons (~10–3 M), it has a lower hydrolytic stability in the basic media and a high emulsifying capacity in the acidic media.

Probably, for these reasons the industrial imidazolines based on the coconut or tallow oil acids were not considered as the potential extractants of the metals.

Thus, 1-(2-alkylamidoethyl)-2-alkyl-2-imidazolines based on the α,α'-branched carboxylic acids are offered by us as a new class of the extractants of the metal salts and acids from the hydrochloric acid and chloride solutions. The synthesis of imidazolines is simple. The starting reactants, ethyleneamines and α,α'-branched synthetic carboxylic acids (versatic acid) are produced on an industrial scale. Amidoethylimidazolines are well soluble in organic solvents and insoluble in water; they do not practically pass into the aqueous phase with increasing acidity in the presence of octyl alcohol and do not tend to form emulsions; they quickly stratify the extraction system and are resistant to the hydrolysis in an acidic media. The non-ferrous metals are quantitatively reextracted with the dilute sulfuric acid.

EXPERIMENTAL

For the synthesis of imidazolines we used the previously distilled diethylenetriamine [59–60°C (2 mm Hg)], 2-ethylhexanoic acid [117°C (12 mm Hg)], and a fraction of the α,α'-branched synthetic fatty $C_{10,12}$-carboxylic acids [140–160°C (8 mm Hg), *M* 191]. Lauric acid of chemical garde was used without purification.

The reagent **I** was prepared by the cyclization of diethylenetriamine acylated with a fraction of the α,α'-branched $C_{10,12}$-carboxylic acids [10] in the presence of *n*-octanol. Compounds **II**, **III** were synthesized by a known method [5].

All amidoethylimidazolines were isolated by a vacuum distillation. The molecular weight was determined by measuring the condensation heat [11] in the concentration range of 0.02–0.1 M using ethanol as a solvent and dihexylsulfoxide as a reference. The relative error of this method is 2–5%.

The electronic spectra were recorded on a Specord M40 spectrophotometer. The IR spectra (film) were taken on a Specord M80 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer ($CDCl_3$, Me_4Si). The potentiometric studies were performed on a OP-211/1 pH-meter using a combined glass electrode in 60% aqueous isopropanol (supporting electrolyte 0.5 M $NaClO_4$).

The reagent **I** is probably a mixture of four homologues: 1-(2-dimethylheptylamidoethyl)-2-(1,1-dimethylheptyl)-2-imidazoline, 1-(2- dimethylheptyl-amidoethyl)-2-(1,1-dimethylnonyl)-2-imidazoline, 1-(2-dimethylnonylamidoethyl)-2-(1,1-dimethylheptyl)-2-imidazoline and 1-(2-dimethylnonylamidoethyl)-2-(1,1-dimethylnonyl)-2-imidazoline.

Reagent I. To a mixture of 13.3 g of diethylenetriamine acylated with a fraction of the α,α'-branched $C_{10,12}$-carboxylic acids was added 10.0 g of *n*-octanol. The reaction mixture was heated at 200–205°C for 1 h in a nitrogen atmosphere. Then octanol was distilled for 3–4 h with a gradual increase in temperature in the reactor up to 240–260°C and the cooled in a nitrogen stream to room temperature. Yield 10.6 g (83%), bp 220–240°C (2 mm Hg), *M* 414 (calculated 431). ^1H NMR spectrum, δ, ppm: 0.75–0.9 m (6H, $CH_2C\underline{H}_3$), 1.1–1.15 m [12H, $(C(C\underline{H}_3)_2]$, 1.15–1.25 m (CH_2), 1.4–1.5 m [4H, $(CH_3)_2CC\underline{H}_2$], 3.25 t (2H, CH_2N, *J* 9.5 Hz), 3.3–3.4 m (4H, CH_2N, $C\underline{H}_2NHCO$), 3.62 t (2H, $CH_2N{=}C$, *J* 9.6 Hz), 5.9 br. s (1H, NHCO).

1-(2-Ethylpentylamidoethyl)-2-(1-ethylpentyl)-2-imidazoline (II) and 1-(2-undecylamidoethyl)-2-undecyl-2-imidazoline (III) (general procedure)**.** To 0.02 mol of diethylenetriamine was added 0.039 mol of 2-ethylhexanoic or lauric acid. The mixture was kept for 1 h at 100±10°C, at 210±20°C for 1.5 h and then at 280±10°C for 1.2 h in a nitrogen atmosphere under stirring and removal of the water vapor released. The resulting compound was cooled under nitrogen to room temperature. Compound **II**. Yield 4.7 g (72%), bp 210–213°C (7 mm Hg), *M* 330 (calculated 337.4). Compound **III**. Yield 6.6 g (75%), bp 250–252°C (5 mm Hg), *M* 454 (calculated 449.76).

Hydrolysis of imidazolines. Into a thermostated reactor (60.0±0.2°C) was placed 10 ml of 0.1 M of a imidazolines solution in octanol, 10 ml of 10% sulfuric acid, and 10 ml of 0.1 M. sodium hydroxide solution. The mixture was kept under stirring for the required time. The imidazoline content in the mixture was

determined by the UV spectroscopy using the intensive $\pi\rightarrow\pi^*$-absorption band at 228–234 nm corresponding to the transition of the C=N bond in the heterocycle.

The extraction procedure. We used toluene of analytical grade as a diluent and *n*-octanol of analytical grade as a modifier. The equal volumes (5.10 ml) of the organic and aqueous phases were stirred at 20.0±1.0°C in the temperature-controlled separating funnels. The extractant concentration was

0.07 M, the working concentration of the metal ions equals 0.04 M, the concentration of hydrochloric acid was varied from 0.05 to 7.5 M. The extraction equilibrium in the system was achieved in 45–60 s, so the time for the practical phase contact was 5 min.

The amidoethylimidazoline distribution between the organic and aqueous phases was studied by the above extraction method. A certain amount of the extractant with the precisely known concentration of imidazoline (~0.1 M) contacted with an equal volume of a hydrochloric acid solution. The aqueous phase was separated, and a part of the organic phase was collected. The concentration of imidazoline was determined by the UV spectroscopy and pH-titration using 0.1 M NaOH solution in 60% aqueous isopropanol as a titrant. Then the cycle was repeated.

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