Protonation of 1,2-disubstituted imidazolines and other products of condensation of 2-ethylhexanoic acid with diethylenetriamine and triethylenetetramine

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The protonation constants for the products of condensation of 2-ethylhexanoic acid with diethylenetriamine or triethylenetetramine were determined by potentiometric titration. The sequence of protonation of the nitrogen atoms in the imidazoline ring was found from the UV, IR, and ^{13}C NMR spectra.

Key words: disubstituted imidazolines, protonation sequence, potentiometric titration, protonation constants.

1,2-Disubstituted imidazolines are widely used for the production of cation-active and ampholytic surfactants. In recent decades they have also been used for the synthesis of insecticides and medicines.[1] Previously[2] we synthesized the products of condensation of 2-ethylhexanoic acid (2-EHA) with diethylenetriamine (DETA), which are highly efficient copper tinning and sealing additives.[3] In this work, we prepared similar derivatives of triethylenetetramine (TETA). Some of them are efficient extractants of iridium from hydrochloric acid solutions.[4] Therefore, it is necessary to study the complex formation of these compounds with d-metals and, first, to study their protonation. The protonation constants are necessary for the calculation of complex formation constants. In addition, an analogy between the protonation of "hard" (according to Pearson) nitrogen-containing ligands and their complex formation with "hard" or "medium" metal ions exists.[5,6] The question as to in which sequence the N atoms of the synthesized compounds are protonated arose during the study.

This work is aimed at determining the basicity and the order of protonation of the N atoms in the compounds under study and the stepwise protonation constants in water, as well as at estimating the protonation constants in 95% ethanol.

Experimental

All synthesized products (**1**—**8**, Table 1) were prepared by the condensation of anhydrous DETA or TETA with 2-EHA at a molar ratio of 1 : (0.7—2) in a nitrogen atmosphere at 200—300 °C. The purity of the compounds was monitored by GLC[7] on a Chrom-5 instrument (carrier gas He, column 1.2 m × 3 mm with 15% SE-30 on Chromaton N-AW). Samples containing at least 99% of the main substance were used. Electronic spectra were recorded on Specord UV—Vis and Specord M-40 spectrophotometers in the 50500—28000 cm^{-1} region, and IR spectra were recorded on a Specord M-80 spectrophotometer in thin films. ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer (solvent $CDCl_3$ using Me_4Si as internal standard and solvent D_2O using sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) as external standard).

Potentiometric studies were carried out on an OR-211/1 pH-meter with a modified glass electrode using a known procedure[8] in water or 40% aqueous ethanol for water-insoluble compounds (against the supporting electrolyte 1 *M* KCl) and also in 95% and 85% aqueous ethanol (supporting electrolyte 1 *M* LiCl). The concentrations of ethanol and supporting electrolyte in the titrant and titrated solution were the same. The concentrations of HCl and studied polyamines were preliminarily determined by potentiometric titration. The temperature of the cell was 24±0.1 °C. A linear relation $E = f(\mathrm{pH})$ was observed for the whole working pH region (1.5—12.0). The protonation constants were calculated from the results of four titrations (40—80 experimental points, polyamine concentration 0.01—0.03 mol L^{-1}, HCl concentration 0.01—0.02 mol L^{-1}). The preliminary studies showed that 95% ethanol is the most appropriate solvent in our case because in an aqueous medium the complex formation of the majority of synthesized compounds with metals is impeded by hydrolysis. The plot of the glass electrode potential *vs.* activity of hydrogen ions obeys[9] the Nernst equation if the alcohol content does not exceed 90%. Nevertheless, the relative activity of hydrogen pa_H can be measured even in anhydrous ethanol. However, the pa_H value includes the effect of the medium corresponding to a change in the free energy of a proton on going from aqueous to water-ethanol media, reaching high values at high ethanol concentrations. To experimentally determine pa_H, it has previously[9] been proposed to introduce the tabulated correction δ to the numerical pH values obtained on a pH-meter:

$$pa_H = pH_{exp} - \delta. \quad (1)$$

The δ value is constant for a medium with a specified composition and includes the residual diffusion potential E_D and a correction for the medium effect $\log_m \gamma_H$:

$$\delta = E_D - \lg_m \gamma_H. \quad (2)$$

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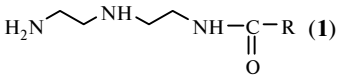
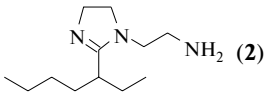
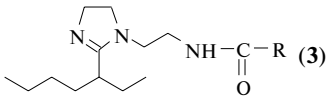
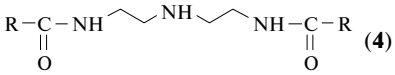
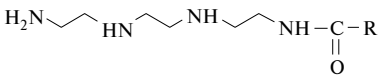
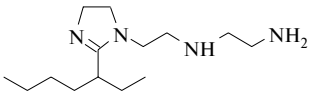
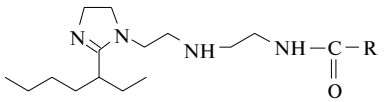
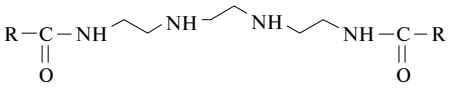
Table 1. Characteristics of synthesized compounds

Compound*	B.p./°C (*p*/Torr)	Solvent	UV spectrum (EtOH), λ/nm (log ε)	IR spectrum (film), ν/cm^{-1} (assignment)
 (**1**)	190—192 (2—3)	Water, EtOH, $CHCl_3$, CCl_4	204 (3.60)	1644, 1552 (—NHC=O)
 (**2**)	140—142 (2—3)	Water, EtOH, $CHCl_3$, CCl_4 hexane	202 (3.20); 232.5 (3.78)	1610 (C=N); 998 (C—N of ring)
 (**3**)	210—213 (1—2)	EtOH, $CHCl_4$, hexane	201 (3.67); 234 (3.83)	1644, 1610, 1552, 1000
 (**4**)	251—254 (2—3)	EtOH, $CHCl_3$, CCl_4	205 (3.57)	1644, 1552
 (**5**)	228—230 (2—3)	Water, EtOH, $CHCl_3$, CCl_4	205 (3.58)	1644, 1552
 (**6**)	182—185 (2)	Water, EtOH, $CHCl_3$, CCl_4, hexane	204 (3.28); 236 (3.80)	1604, 996
 (**7**)	245—248 (1—2)	EtOH, $CHCl_3$, CCl_4	202 (3.78); 232 (3.79)	1644, 1604, 1552, 1000
 (**8**)	290—295 (2)	EtOH, $CHCl_3$, CCl_4	206 (3.61)	1640, 1548

* R = .

The values of the constant δ for water-methanol and water-ethanol media found by independent authors[10—12] demonstrated a good coincidence and were tabulated.[9] In our case, to refine δ, the electrode was additionally calibrated by buffer aqueous-ethanolic solutions.[13]

Results and Discussion

The sequence of protonation of the N atoms in amides and diamides (**1**, **4**, **5**, **8**) is doubtless. However, the presence of the imidazoline ring in the compounds required additional study of the basicity of the N atoms. The basicity of the N atoms, as other factors, is defined by accessibility of its lone electron pair (LEP) to form a bond with the H^+ ion. The basicity of the sp^2-hybridized N atom is reduced because on going from the sp^3- to sp^2-orbitals the degree of participation of the p-orbital in hybridization decreases and that of the s-orbital increases.[14] At the same time, if in the imidazoline cycle the LEP of the tertiary N atom can be conjugated with the double bond, its basicity substantially decreases as compared to that of the imine N atom.[15] Nevertheless, in the synthesis of ampholytic surfactants based on 1,2-disubstituted imidazolines the latter are alkylated at the tertiary N atom of the ring.[1]

The sequence of protonation of the N atoms of the imidazoline ring was determined for both imidazolines and amidoimidazolines because the replacement of the high-basicity N atom of the primary amino group by the much lower-basicity N atom of the amide group can result in substantial redistribution of the electron density on the N atoms in the ring. The protonated forms of

compounds **2** (**2-1H**$^+$, **2-2H**$^+$) and **3** (**3-1H**$^+$, **3-2H**$^+$) were isolated by the results of pH-metric titration and characterized in detail by UV, IR, and ^{13}C NMR spectroscopy.

The UV spectrum of sample **2** contains two absorption bands at 49000 cm^{-1} (logε ~2.7) and 42500 cm^{-1} (logε ~3.8). The short-wave band is due to the n→σ*-transition in the NH_2 group, and the higher-intensity long-wave band is attributed to the π→π*-transition of the C=N bond in the heterocycle.[2] The short-wave band disappears upon acidification due to the protonation of the amino group, and the long-wave band does not change noticeably. However, it has previously[16] been found that the involvement of the LEP of the N atom of the C=N group in protonation irreversibly changes the UV spectrum of pyrrolines: the not very intense π→π*-band (λ_{max} ≈ 220—222 nm, logε ~2.3—3.0, EtOH) is replaced by intense absorption in the region of the "tail" of the short-wave band.

When sample **2** is dissolved in 1 *M* HCl, the ~1.5-fold increase in the intensity of the π→π*-band in the UV spectrum indicates, most likely, the protonation of the imine N atom of the ring. Analysis of the distribution curves of the protonated forms of compound **2** (Fig. 1) suggests that this reaction occurs to a noticeable extent at pH < 2.

The IR spectra of **2-1H**$^+$ and **2-2H**$^+$ are virtually the same and mainly differ by the structure of the bands: the bands in the spectrum of **2-2H**$^+$ are narrower and, hence, the spectral data presented in Table 2 concern both compounds.

When compound **2** is protonated, the bands characterizing the primary amino group (3272, 852 cm^{-1}) disappear from the IR spectrum to exhibit new bands attributed to the appearance of the NH_3^+ group (3000, 1588, 1520 cm^{-1}). The band ν(C—N) shifts upfield by 30 cm^{-1}, which is accompanied by the disappearance of its multiplet structure. The imine band ν(C=N) ~1600 cm^{-1} remains unchanged.

The application of ^{13}C NMR spectroscopy makes it possible to monitor a gradual change in signals upon imidazoline protonation during titration with HCl (Table 3). This method is free of inevitable errors related to the isolation of intermediate products from the solution (IR spectra) and those that appear due to the dilution of the working solution (UV spectra).

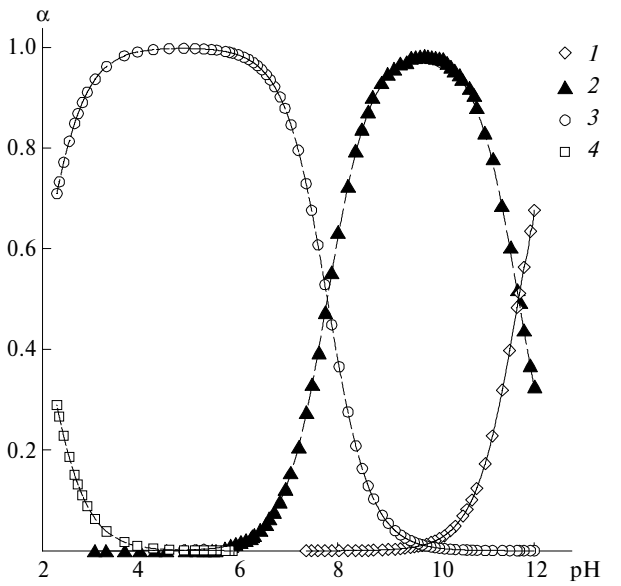


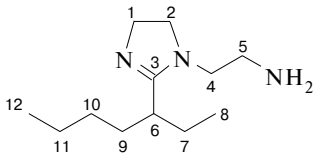
Fig. 1. Fraction distribution (α) of the protonated forms of compound **2** in the **2**—HCl—H_2O system as a function of pH: [L] (*1*), $[LH]^+$ (*2*), $[LH_2]^{2+}$ (*3*), and $[LH_3]^{3+}$ (*4*).

Table 2. IR spectra of compound **2** and its protonated forms

ν/cm^{-1}	Characteristics	Assignment
	Compound 2	
3272	m, br	ν(NH_2)
1600	s, brn	ν(C=N), δ(NH)
1248	m, multiplet of complex structure	ν(C—N, prim. N, tert. N)
1000	m, narr	ν(C—N, tert. N)
852	w, br	δ(NH_2)
	H$^+$-Forms	
3176, 3000	br	ν(NH_3^+)
1600	s	ν(C=N)
1588, 1520	s, narr	δ(NH), δ(NH_3^+)
1276	s, narr	ν(C—N)
1044, 966	w, narr	
744, 708	w	

Note. The following abbreviations were used: s, m, and w are strong, medium, and weak bands, respectively; br is broad, brn is broadened, narr is narrow, prim. and tert. are primary and tertiary N atoms, respectively.

Table 3. Data of ^{13}C NMR spectroscopy for the protonation of compound **2** (D_2O, external standard DSS)



δ	Assignment	Change in signals at different protonation degrees of the N atom*			
		$\Delta_1 = \delta_0 - \delta$		$\Delta_2 = \Delta_1 - \delta$	
		$n \approx 0.5$	$n \approx 1$	$n \approx 1.5$	$n \approx 2$
51.916	C(1)	0.15	0.2	0.1	0.2
50.891	C(2)	0.45	0.55	1.8	5
175.214	C(3)**	−0.4	−0.45	−0.2	−0.5
50.566	C(4)	0.9	2.1	1.9	4.5
41.379	C(5)	0.3	0.5	0.9	1.6
40.368	C(6)	0.1	0.15	0.4	1.8

* The protonation degree was characterized by the parameter *n* (the number of protonated N atoms).

** The signal from C(3) exhibits a downfield shift upon protonation.

As was expected, the protonation of the amine group results in the upfield shift of the α- and β-signals from the methylene groups by 0.5 and 2.1 ppm, respectively (the upfield shifts of the signals of the C atoms in the α-, β-, and γ-positions for the protonation of linear amines are[17] 2.5—3, 6, and 0.2 ppm, respectively, and for cyclic amines they are[18] 0.7, 5.5, and 1.2 ppm, respectively). The upfield shift (0.5 ppm) of the methylene group in the δ-position to the amino group is stipulated, most likely, by the redistribution of electron density on the tertiary N atom due to an increase in the induction effect ($-I$) of the NH_3^+ group and a possible field effect. The shift is somewhat lower than that expected from the published data, most likely because compound **2** diluted in water exists as a mixture of the main compound (85—90%) and its protonated form (10—15%) (see Fig. 1). Thus, we initially detect an already partially shifted signal from the C(5) atom.

The further protonation of sample **2** results in an insignificant downfield shift (~0.5 ppm) of the sp^2-hybridized C atom of the imine fragment, and the signal from the α-methylene group of the imine fragment remains almost nonshifted (~0.2 ppm). Since the downfield shift of the immonium C atom for the salt formation of imines is[19] 5—27 ppm, we may assume that the second stage of protonation involvess the tertiary N atom: the α-methylene group of the ring at the tertiary N atom (C(2)) exhibits an upfield shift by 5 ppm, whereas the signals from the C(3), C(4) atoms in the α-position and that from the C(5) atom in the β-position are shifted by 0.5, 4.5, and 1.6 ppm, respectively, and the signal of the C(3) atom exhibits a downfield shift.

Based on the data obtained, we may assume that in imidazoline the primary N atom of the amino group is first protonated, then the tertiary N atom in the imidazoline ring is protonated, and finally, the imine N atom undergoes protonation.

Table 4. IR spectra of compound **3** and its protonated forms

ν/cm^{-1}	Characteristics	Assignment
	Compound 3	
3288	s, narr	ν(amide NH)
3080	w	ν(C=O) overtone
1648	s, narr	Amide band I
1600	s, narr	ν(C=N)
1552	s, narr	Amide band II
1290, 1268, 1244, 1220	m, multiplet of complex structure	ν(C—N, sec. N, tert. N)
1000	m, narr	ν(C—N of ring)
	H^+-Forms	
3288	s, narr	ν(NH amide)
3080	w	ν(C=O) overtone
1645	s, narr	Amide band I
1600	s, narr	ν(C=N)
1552	s, narr	Amide band II
1296	m, brn	Amide band III

Note. For designations, see Table 2.

Amidoimidazoline **3** contains the N atom of the amide group instead of the basic N atom of the primary amino group. Therefore, the tertiary N atom of the imidazoline ring is protonated first. This is confirmed in the IR spectra (Table 4) by the disappearance of the narrow characteristic band at ~1000 cm^{-1} attributed to stretching vibrations $\nu(C—N_{tert})$ in the ring and the degeneration of the multiplet band of stretching vibrations of the secondary and tertiary N atoms into the broadened band that characterizes the amide group.

Then protonation occurs at the imide N atom, but neither UV nor IR spectra exhibit a shift of the imine band; however, its intensity increases significantly.

Table 5. Protonation constants of compounds **1**—**8** at 24 °C

Compound	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
DETA	9.9	8.9	5.0	—
	(10.0)	(9.1)	(5.0)	—
	[10.15]	[9.3]	[5.0]	—
DETA[a]	[10.101]	[9.386]	[4.889]	—
DETA[b]	—	[9.38]	[5.21]	—
1	9.3	6.7	2.6	—
	(9.4)	(6.1)	(2.1)	—
	[9.60]	[6.0]	[2.0]	—
2	10.4	8.0	2.1	—
	[11.70]	[7.8]	[1.9]	—
3	9.9	2.8	2.0	—
	(10.2)	(2.6)	(1.9)	—
	[10.65]	[2.8]	[1.5]	—
4	8.3	2.3	—	—
	[8.00]	[2.6]	—	—
5	9.8	8.7	5.2	2.6
	(9.8)	(8.9)	(5.3)	(2.5)
	[10.05]	[8.5]	[5.6]	[2.5]
6	10.5	9.7	8.2	—
	[11.80]	[9.4]	[7.2]	—
7	9.7	6.8	2.0	—
	(10.0)	(6.6)	(2.5)	—
	[10.40]	[6.6]	[2.4]	—
8	9.0	6.3	2.6	—
	(8.6)	(6.0)	(2.3)	—
	[8.75]	[5.7]	[2.5]	—

[a] See Ref. 22.
[b] Water, 1 *M* NaCl (see Ref. 23).
Note. The equilibrium constants correspond to the following reactions:

$$L + H^+ \overset{K_1}{\rightleftharpoons} LH^+, \qquad LH^+ + H^+ \overset{K_2}{\rightleftharpoons} LH_2^{2+},$$

$$LH_2^{2+} + H^+ \overset{K_3}{\rightleftharpoons} LH_3^{3+}, \qquad LH_3^{3+} + H^+ \overset{K_4}{\rightleftharpoons} LH_4^{4+}.$$

The $\log K$ values were determined in 95% EtOH, 1 *M* LiCl (presented without parentheses); 85% EtOH, 1 *M* LiCl (indicated in parentheses); and in the system water, 1 *M* KCl/40% EtOH, 1 *M* KCl (indicated in brackets). Values obtained with the following errors are presented: $\log K_1 \pm 0.05$; $\log K_2 \pm 0.1$; $\log K_3 \pm 0.3$ (for DETA, $\log K_3 \pm 0.15$); $\log K_4 \pm 0.4$ (for aqueous solutions); $\log K_1 \pm 0.1$; $\log K_2 \pm 0.2$; $\log K_3 \pm 0.4$; $\log K_4 \pm 0.5$ (for ethanol solutions).

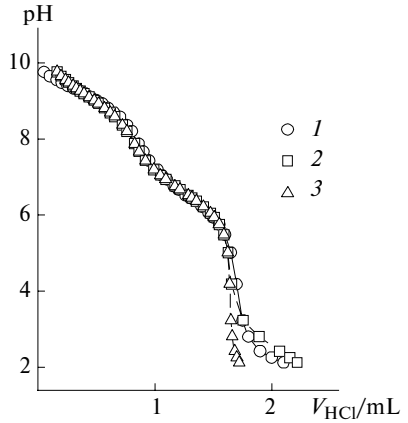


Fig. 2. Curves of pH-metric titration for the **1**—HCl—EtOH system at $C_L = C_{HCl} = 0.015$ mol L^{-1}: *1*, theoretical curve; *2*, experimental points; and *3*, curve calculated neglecting the third-step protonation.

Thus, the primary N atom of the amino group is protonated first in imidazolines, and in amidoimidazolines it is the tertiary N atom of the imidazoline ring. The amide group can be protonated completely only in concentrated HCl. This results in the entire disappearance of the band at 201 nm in the UV spectrum. This band characterizes the n→σ*-transitions in the ring and amide group. In the IR spectrum the amide band II (1552 cm^{-1}) shifts toward higher frequencies and is almost completely disguised by the intense band assigned to the vibrations over the C=N bond.

Analyzing the function $d(\log K)/d(pH)$, which characterizes the possibility and accuracy of determination of stepped protonation constants by pH-metric titration, the authors pointed out[20,21] that

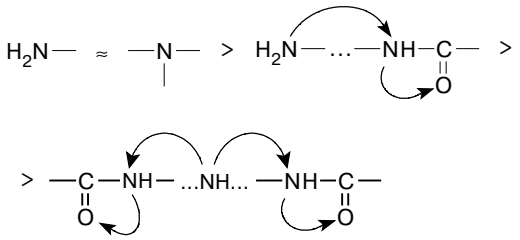
(1) unreliable results are obtained in the intervals $\log K < 3$ and $\log K > 11$;

(2) at $\log K \approx -\log C_L$ the error in pH measurement results in an almost threefold higher error in the protonation constant.

Taking into account the above data, we can doubt the expediency of presenting the values of $\log K_3 \approx 1.5$—3 in Table 5, which characterize the protonation of the amide group or imine N atom in the imidazoline ring. However, the theoretical curves calculated from the $\log K_3$ values obtained by us coincide, as a whole, with the experimental values (Fig. 2). To decrease the error, the $\log K_3$ values for the compounds containing the amide group (**1**, **3**, **4**, **7**, and **8**) were additionally refined at $C_L \approx 0.1$ mol L^{-1}.

Despite the error introduced by the increasing medium effect at high ethanol concentrations, the constants determined in ethanol (see Table 5) correctly reflect the basicity of the synthesized ligands. For example, the highest $\log K_1$ values are found for the compounds in which the NH_2 group is protonated first (**2**, **6**, and DETA as the model compound). The $\log K_1$ values corresponding to the protonation of the tertiary N atom

Scheme 1



of the imidazoline ring (**3** and **7**) are close. Somewhat lower $\log K_1$ values characterize the protonation of the primary amino group in aminoamides (**1** and **5**). It is most likely that here the basicity of the primary N atom of the NH_2 group decreases due to the redistribution of the electron density in the chain stipulated by the (−*I*)-effect of the C=O group. The insertion of the second amide group still decreases the electron density at the secondary N atom and hinders its protonation (**4** and **8**). As compared to ethanol, water exhibits a weak differentiating effect: for compounds with the imidazoline cycle (**2**, **3**, **6**, and **7**) $\Delta = \log K_1$ (water) − $\log K_1$ (ethanol) ≈ 0.7—1.3; for other compounds this value is ≤0.5. Nevertheless, the basicity series obtained in ethanol for the synthesized compounds (Scheme 1) is also valid in water.

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