

Physical and Chemical Properties of *N*-(2-Hydroxyethyl)alkylamines

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Abstract—Physical and chemical properties of *N*-(2-hydroxyethyl)alkylamines were studied, isotherms of a surface tension of homologous series of these compounds on a liquid–gas interface in water and hydrochloric acid were obtained.

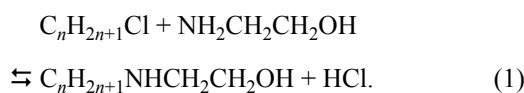
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It is known that *N*-(2-hydroxyethyl) alkylamines (HEA) are nonionic surfactants [1]; *N*-(2-hydroxyethyl) alkylamines with radicals C₅N₁₁–C₈H₁₇ were suggested as precipitants for waste water treatment from ions of Cu(II) [2]. The presence of amine and hydroxyethyl groups in these compounds opens up prospects for their use as complexing agents, including surfactant properties. However, information on their physical and chemical properties is necessary for practical application of HEA. In the literature there are only fragmentary data on the properties of some of the lower representatives of this series [2].

The aim of this work was to study the physical and chemical properties in a HEA series to assess the possibility of using them in the separation and concentration of metals or as a surfactant.

EXPERIMENTAL

N-(2-Hydroxyethyl) alkylamines of RNHCH₂CH₂OH formula, where R = C₈H₁₇–C₁₆H₃₃ was prepared by a reaction of monoethanolamine with primary chloroalkanes according to technique described in [2]:



The products were purified gradually by washing with

hexane and 2–3 fold recrystallization from a hexane–ethyl acetate mixture (1 : 1). In the case of the reagent with R = C₈H₁₇ cleaning was performed by a vacuum distillation. Identity and purity of compounds were confirmed by IR and ¹H NMR spectroscopy and elemental analysis. An amount of the main substance in the samples was not less than 96%, it was determined by the potentiometric titration in an I160M ionomer equipped with glass and silver chloride electrodes. We dissolved a weighted portion of the sample (0.1 g) in 20 ml of ethanol, then we added 16 ml of distilled water and 4 ml of 1 M KCl solution and titrated with 0.1 M aqueous solution of HCl. Calculation of HEA content (%) was conducted by the following formula

$$c = \frac{V_{HCl} N_{HCl}}{M m_{\text{sample}}} \times 100, \quad (2)$$

where V_{HCl} is a volume of hydrochloric solution treated for titrating (ml); N_{HCl} , a concentration of the working solution of HCl (M); M , molecular weight of the appropriate HEA.

Computation of pK_a values of the compounds with the aid of potentiometric measurements was conducted by the following equation [3]

$$pK_a = \log \frac{\alpha_{c_L} - [H^+] + [OH^-]}{(1 - \alpha_{c_L}) + [H^+] - [OH^-]} + pH, \quad (3)$$

where α is neutralization degree of HEA (a fraction of a unit) c_L is HEA concentration in the weighted sample (M), $[H^+]$ and $[OH^-]$ are concentration of the ions in the computation point in a titration curve (M).

Solubility was determined by gravimetric method [4], thermal stability was studied on a Q-1500D MOM company derivatograph (Hungary) in air at a temperature of 20–600°C at a heating rate of 10 deg min⁻¹. ¹H NMR spectra were recorded on a MERCURY plus 300 spectrometer in CDCl₃, the IR spectra, by Fourier IFS 66 spectrometer (Bruker, Germany): suspension in vaseline oil, glass of KBr, a resolution of 1 cm⁻¹, 100 scans. Elemental analysis was performed on a CHNS-932 analyzer (LECO Co., USA).

To study the stability to acid hydrolysis the weighted samples containing 5×10^{-2} mol of reagent were thermostatically controlled to within 1 day in 0.1 M HCl solution at 20 and 60°C. Monitoring the hydrolysis was carried out at regular time intervals by TLC on Silufol plated in a chloroform–methanol system (1 : 2), the developing was performed by a 3% solution of chloranil in toluene

with heating the plate to 70°C. The surface tension at the interface of aqueous solution of HEA–air, HEA solution in 0.1 M HCl–air was measured by stalagmometr [5]. The critical micelle concentration (CMC) was determined graphically by the points of inflection on the plot of surface tension dependence on the concentration of reagents.

The test reagents (Table 1) were white crystalline substance (except reagent with R = C₈H₁₇, which was a liquid). NMR spectra of compounds obtained are presented in Table 2. For compounds **III** and **IV** (Table 2) values of proton chemical shifts of OH- and NH-groups coincide. The IR spectra of these reagents have absorption bands of medium intensity in the regions of 3290 and 3280 cm⁻¹ [$\nu(NH)$] and 3150 and 3120 cm⁻¹ [$\nu(OH)$], respectively.

Data on the solubility of reagents (Table 1) demonstrate that the compounds are of poor solubility in water, of moderate one in aqueous solutions of HCl, and of good solubility in ethanol; their use is preferably in the form of hydrochloride salts. With increasing length of hydrocarbon radical the solubility of reagents markedly

Table 1. Melting points and solubility of compounds RNHCH₂CH₂OH at T = 20°C

Compd. no.	R	mp, °C	Solubility, M		
			water	0.1 M HCl	EtOH
I	C ₈ H ₁₇	125–126/4 Hg mm ^a	3.0×10^{-3}	1.2×10^{-1}	>0.9
II	C ₁₀ H ₂₁	28–29	2.0×10^{-3}	1.3×10^{-1}	>0.8
III	C ₁₂ H ₂₅	44–45	3.9×10^{-4}	1.1×10^{-1}	>0.7
IV	C ₁₄ H ₂₉	54–55	3.9×10^{-4}	1.1×10^{-3}	>0.4
V	C ₁₆ H ₃₃	58–59	2.8×10^{-4}	9.1×10^{-4}	>0.1

* bp is noted here.

Table 2. ¹H NMR spectroscopy data of compounds RNHCH₂CH₂OH

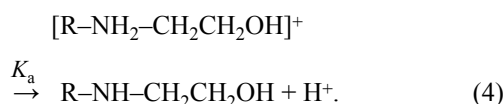
Compd. no.	R	δ , ^a ppm							
		OH(s)	<u>CH</u> ₂ OH(t)	<u>CH</u> ₂ CH ₂ OH(t)	<u>RCH</u> ₂ N(t)	NH(s)	<u>RCH</u> ₂ CH ₂ N(m)	CCH ₂ C(m)	CH ₃ (t)
I	C ₈ H ₁₇	3.10	3.64	2.73	2.60	1.95	1.48	1.26	0.87
II	C ₁₀ H ₂₁	3.16	3.65	2.77	2.61	2.00	1.49	1.25	0.87
III	C ₁₂ H ₂₅	2.34	3.64	2.76	2.63	2.39	1.48	1.25	0.87
IV	C ₁₄ H ₂₉	2.28	3.63	2.76	2.60	2.28	1.48	1.25	0.87
V	C ₁₆ H ₃₃	3.18	3.62	2.76	2.60	1.78	1.47	1.25	0.87

^a (s) singlet, (t) triplet, (m) multiplet.

reduced (except reagent **II** in 0.1 M HCl, where there is a maximum solubility). The choice of these solvents was made from practical considerations: application of HEA to the flotation of metals.

Based on data of the thermal analysis we established that up to 140°C the compounds are stable. In the temperature range 140–275°C there is thermal decomposition of all the samples accompanied by a considerable loss of weight.

Like the aliphatic amines, the compounds under study have the basic properties due to an capability of lone pair of electrons of the nitrogen atom to attach a proton. Basicity of HEA can be characterized by the values of acid dissociation constants K_a of conjugated acids:



Results of the computations of $\text{p}K_a$ of the conjugated acids $\text{RNHCH}_2\text{CH}_2\text{OH}$ series, calculated according to data of the potentiometric, show that the constant values are practically independent of the length of the HEA radical; in comparison with monoethanolamine [6] the basicity of the compounds under study changes slightly.

Chemical stability of HEA is determined by their resistance to hydrolysis, which will most likely be occur with the formation of the primary amine (A) and ethylene glycol. The chemical stability was assessed by thin layer chromatography (TLC) on the example of *N*-(2-hydroxyethyl) dodecylamine. The most suitable was chloroform–methanol solvent system (1 : 2), for which values of the relative speed of movement R_f of the reagent under study and a hydrolysis product (dodecylamine) were 0.45 and 0.60, respectively. Found that the reagent is chemically stable to within a 1 day in 0.1 M HCl solution at 20°C. At 60°C after 45 min in the chromatogram were revealed two spots corresponding to the initial reagents and dodecylamine; after 1 h incubation reagent was completely hydrolyzed: only one spot of dodecylamine was revealed.

Figure 1 shows the isotherms of the surface tension of the solutions of HEA with $\text{R}=\text{C}_8\text{H}_{17}$ (curve 1), $\text{C}_{12}\text{H}_{25}$ (curve 2), and $\text{C}_{14}\text{H}_{29}$ (curve 3). The isotherms of the reagents with $\text{R}=\text{C}_{10}\text{H}_{21}$, $\text{C}_{16}\text{H}_{33}$ were analogous. In the region of the HEA small concentrations a value of σ decreases sharply and then a decrease in the surface tension slows upon the concentration growth. A descending

portion of the curve reflects a gradual filling of the surface layer by the surfactant molecules thereby the adsorption attains the limiting value, the further input of the surfactant leads to the micelle formation in a bulk of the solution and does not effect on the surface tension of the solution. The further growth in the surfactant concentration causes a transition from spherical micelles formed in the solutions at the small surfactant concentrations to asymmetric ones, aspheric, that affects the state of the surface layer [7]. These changes result in the shape of the following portion of the isotherm where a further gradual decrease in the surface tension occurs.

The results are evidence that HEA series belongs to a class of the strong surfactant since minimal values of the surface tension σ_{min} of compounds with $\text{R}=\text{C}_8\text{H}_{17}$, $\text{C}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}$ are 25–45 mJ m^{-2} in water, of compounds with $\text{R}=\text{C}_8\text{H}_{17}$, $\text{C}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}$, $\text{C}_{14}\text{H}_{29}$ in 0.1 M HCl, 30–35 mJ m^{-2} (Table 3). The slight decrease in the surface tension by compounds with $\text{R}=\text{C}_{14}\text{H}_{29}$ in water ($\sigma_{\text{min}}=63 \text{ mJ m}^{-2}$) and with $\text{R}=\text{C}_{16}\text{H}_{33}$ in water and in 0.1 M HCl

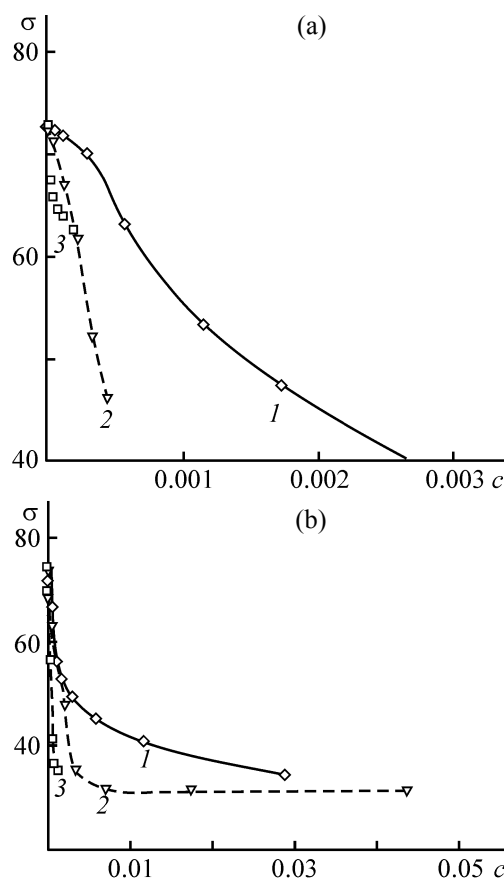


Fig. 1. The isotherms of the surface tension σ (mJ m^{-2}) of compounds $\text{RNHCH}_2\text{CH}_2\text{OH}$ (a) in water and (b) in 0.1 M HCl. (c) Concentration, M. R: (1) C_8H_{17} , (2) $\text{C}_{12}\text{H}_{25}$, (3) $\text{C}_{14}\text{H}_{29}$.

Table 3. Minimal value of the surface tension in water and in 0.1 M HCl compounds RNHCH₂CH₂OH, critical micelle concentration (CMC) and surface activity *G* at *T* = 20°C

Compd. no.	R	σ_{\min} , mJ m ⁻² (<i>c</i> _{reagent} , M)		KKM, M		<i>G</i> , kg m ³ s ⁻² mol ⁻¹	
		water	0.1 M HCl	water	0.1 M HCl	water	0.1 M HCl
I	C ₈ H ₁₇	40 (2.65)	35(28.8)	1	2	0.033	0.020
II	C ₁₀ H ₂₁	24 (1.58)	28(24.8)	0.68	5.5	0.072	0.008
III	C ₁₂ H ₂₅	46(0.44)	32(6.97)	0.32	4	0.084	0.011
IV	C ₁₄ H ₂₉	63 (0.20)	36(1.12)	0.025	0.43	0.400	0.088
V	C ₁₆ H ₃₃	63(0.14)	70 (0.175)	0.024	0.032	0.417	0.125

(σ_{\min} 63 and 70 mJ m⁻², respectively) is influenced by their small solubility in water (Table 1). With increasing the length of the radical increases the ability of micelle reagents. The most promising surfactant of this series based on a complex of the physical and chemical properties is *N*-(2-hydroxyethyl)dodecylamine.

In the homologous series of surfactant the surface activity is largely dependent on the number of carbon atoms in the chain and increases with a growth of the length of the hydrocarbon radical [7]. The surface activity *G* can be determined by the equation [7]

$$G = \lim_{c \rightarrow 0} \left(-\frac{d\sigma}{dc} \right) = RT\delta \exp\left(\frac{W_0 + n\Delta W}{RT}\right),$$

where δ is an adsorption layer thickness, m; W_0 , an adsorption work of polar groups, J mol⁻¹; *n*, a number of methylene group; ΔW , the contribution of one methylene link in the adsorption work (J mol⁻¹), *R*, universal gas constant, J mol⁻¹ K⁻¹; *T*, temperature, K.

Computed values are listed in Table 3.

From equation (5) implies that for the homologous series a dependence in the coordinates $\ln c_{\Delta\sigma} - n$ should be linear with slope $\tan \alpha = \Delta WR^{-1}T^{-1}$, where $c_{\Delta\sigma}$, the surfactant concentration causing a reduction in the surface tension on the magnitude of $\Delta\sigma$; ΔW , a growth rate of the adsorption potential: the contribution of a CH₂ link to the work of adsorption. The obtained isotherms of the surface tension allow calculation of this characteristic for the homologous series of HEA. The calculation was performed at $\sigma_x = 70$ mJ m⁻². The value of the surface tension lies

on the linear portion of the isotherm of surface tension for all the studied homologues and meets the condition $c_{\text{reagent}} > 0$. Dependence $\ln c_{\Delta\sigma} - n$ is shown in Fig. 2.

The calculated value of ΔW was in the water and in 0.1 m HCl 1.28 and 0.645 kJ mol⁻¹, respectively, and that is below the theoretical value (~ 2.7 kJ mol⁻¹) for the aqueous medium [8]. Such a deviation may be due to the large number of carbon atoms in the radical ($n = 8-16$, whereas ΔW_{theor} corresponds to $n = 3-6$) and to the presence of two heteroatoms causing an increase in the lateral cohesive interaction of surface molecules of HEA. For the same reason too low values of ΔW compared with the theoretical ones were observed, for example, for a series of 1,1-dimethyl-1-alkylhydrazinium chlorides [9].

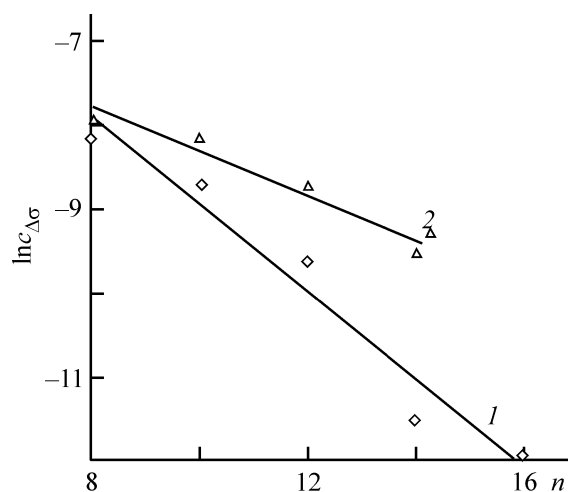


Fig. 2. Effect of the radical length in the surface activity of compounds RNHCH₂CH₂OH in (1) water and (2) in 0.1 M HCl. ($c_{\Delta\sigma}$) the reagent concentration, M, (*n*) a number of the methylene groups in alkyl radical.

CONCLUSIONS

(1) We established that *N*-(2-hydroxyethyl)alkylamines are poor soluble in water, moderately soluble in aqueous solutions of HCl, and readily soluble in ethanol.

(2) The compounds under study possess the basic properties which are slightly dependent on the length of alkyl radical. The reagents are stable to hydrolysis in 0.1 M HCl at 20°C at least to within 24 h.

(3) Reagents belong to the strong surfactants whose the surfactant activity and micelle forming capability grow upon an increase in the number of carbon atoms in the radical.

(4) Based on the complex of the properties: solubility and surfactant activity, *N*-(2-hydroxyethyl)dodecylamine is the most promising surfactant.

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