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Physico-Chemical Properties of *N,N*-Di(2-hydroxyethyl)alkylamines

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Abstract—In view of potential application of *N*-alkyl derivatives of diethanolamine $RN(CH_2CH_2OH)_2$ (R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, and $C_{14}H_{29}$) as surfactants, we have studied their physico-chemical properties, constructed the surface tension isotherms at the liquid–gas interphase boundary in the cases of water and aqueous hydrochloric acid, and estimated critical micelle concentrations as well as surface activity of the studied compounds.

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Etoxylated amines are known as nonionic surfactants; however, in acidic medium they are protonated and thus can act as cationic surfactants [1]. Potential applications of *N*-alkyl derivatives of diethanolamine [*N,N*-di(2-hydroxyethyl)alkylamines **I**] include cationic surfactants as component of latex paints [2]; synergists of biocides in diesel oil, masout, jet fuel [3], paints, and adhesive coatings [4]; dispersants enhancing stain removing action of fabric bleaching agents [5]; antistatic agents [6]; pH regulators, resin solubilizers [4]; corrosion inhibitors [4, 7]; hydrolysis inhibitors for phosphites and phosphonites [8]; slurry traps [9]; and others. Certain physico-chemical properties of compounds **I** have been reported [10–12]; however, their systematic studies have been lacking to the very best of our knowledge. Studies of changes of physico-chemical properties in the series of surfactant homologues would aid in development of their practical applications. Recently, we have carried out similar investigation of *N*-alkyl derivatives of 2-aminoethanol [13].

N-Alkyldiethanolamines $RN(CH_2CH_2OH)_2$ (R = C_8H_{17}, $C_{10}H_{21}$, or $C_{12}H_{25}$) are transparent yellowish viscous fluids, compound **I** with R = $C_{14}H_{29}$ is white crystalline solid (Table 1). ^1H NMR data of the studied compounds are collected in Table 2. IR spectra of compounds **I** contained the following absorption bands (cm^{-1}): 3364–3348 (O–H), 2924 (C–H), 2854 (C–H), 1464–1460 (C–H), 1369–1368 (O–H), and 1045–1041 (C–O). The observed spectral features coincided well with the reference data [14, 15].

Table 1 shows the data on compounds **I** solubility as well: they were found to be poorly soluble in water and moderately soluble in aqueous HCl. Solubility in the both media decreased with increasing the alkyl chain length; however, the solubility decrease was less steep in the case of aqueous HCl. As the studied compounds could form micelles in the solutions, accurate determination of the actual solubility was complicated due to absence of macrophase separation. Nevertheless, the obtained solubility values provided reasonable estimate for the concentration range suitable for further surface tension studies.

According to thermal analysis results, compounds **I** were stable up to 200°C. At 200–325°C all the studied samples were decomposed, the process being accompanied with significant mass loss.

Compounds **I** were more basic than the parent diethanolamine (pK_a 8.78 ± 0.03) [16]. The compounds basicity was slightly decreasing with increasing the alkyl chain length; the determined pK_a values are given in Table 1.

Chemical stability of compounds **I** was reflected in their resistance towards hydrolysis, most likely giving the corresponding primary amine and ethylene glycol.

Table 1. Physico-chemical parameters of $RN(CH_2CH_2OH)_2$

R	bp, °C	n_D	Solubility, mol/L		pK_a (n = 6–8, P 0.95)
			in water	in 0.1 mol/L HCl	
C_8H_{17}	168–170 (5 mm Hg) {128–133 (0.5 mm Hg) [11]}	1.4620	9.2×10^{-3}	1.6×10^{-1}	8.49 ± 0.05
$C_{10}H_{21}$	183–185 (5 mm Hg) {203–204 (12 mm Hg) [10]}	1.4635	4.8×10^{-3}	1.4×10^{-1}	8.48 ± 0.05
$C_{12}H_{25}$	190–192 (4 mm Hg) {193–195 (3 mm Hg) [12]}	1.4655	1.8×10^{-3}	1.2×10^{-1}	8.45 ± 0.05
$C_{14}H_{29}$	27–28[a] (hexane–ethyl acetate)	–	6.6×10^{-4}	9.4×10^{-2}	8.33 ± 0.05

[a] Melting point.

Table 2. ^1H NMR spectroscopy data (δ, ppm) of $RN(CH_2CH_2OH)_2$

R	OH (s)	$\underline{CH_2}OH$ (t)	$\underline{CH_2}CH_2OH$ (t)	$R\underline{CH_2}N$ (t)	$R\underline{CH_2}CH_2N$ (m)	CCH_2C (m)	CH_3 (t)
C_6H_{13}	3.79	3.59	2.63	2.50	1.40–1.47	1.24–1.31	0.88
C_8H_{17}	3.17	3.60	2.64	2.51	1.42–1.48	1.24–1.30	0.87
$C_{10}H_{21}$	3.80	3.59	2.63	2.50	1.41–1.47	1.23–1.30	0.87
$C_{12}H_{25}$	4.09	3.59	2.62	2.50	1.42–1.49	1.22–1.28	0.87
$C_{14}H_{29}$	2.80	3.61	2.66	2.53	1.43–1.48	1.21–1.27	0.87
$C_{16}H_{33}$	3.18	3.62	2.76	2.60	1.44–1.49	1.22–1.30	0.87

$$RN(CH_2CH_2OH)_2{\cdot}HCl + 2HOH \xrightarrow{[H^+]} RNH_2{\cdot}HCl + 2HOCH_2CH_2OH.$$

The compounds chemical stability was estimated by TLC using *N*-dodecyldiethanolamine as representative example. The most suitable solvent was 1 : 2 mixture of chloroform and methanol, R_f values of the studied compound and the hydrolysis product (dodecylammonium hydrochloride) being of 0.87 and 0.18, respectively. At 20°C, *N*-dodecyldiethanolamine was stable over at least 1 day; at 60°C it was hydrolyzed after 3 h. The compound resistance towards hydrolysis was sufficiently high in view of their potential flotation agent and surfactant applications.

One of the key surfactant properties is its ability to decrease the interfacial surface tension; the surface activity of compounds **I** was determined in neutral and acidic (0.1 mol/L HCl) media.

Figure 1a shows isotherms of surface tension of compounds **I** (R = $C_{12}H_{25}$ and $C_{14}H_{29}$) in water and in aqueous HCl; the plots in the cases of other compounds **I** were similar. At low concentration of the studied compounds, σ was sharply decreasing with the concentration; in more concentrated solutions, surface tension decrease was less steep. The curves shape was due to decreasing of number of surfactant-free adsorption centers. At far higher concentration of the surfactant, micelle formation was evident [17].

The above-described results revealed that the studied compounds were surfactants of moderate surface activity: the lowest σ values were of 27–48 mJ/m^2 (water) and 36–41 mJ/m^2 (0.1 mol/L HCl) (Table 3).

The critical micelle concentration CMC is known as certain measure of surfactant molecular solubility: further addition of the surfactant portions will not change its concentration at the interphase boundary, influencing only the molecules micellar organization in the solution.

In the series of compounds **I**, minimal surface tension values decreased and micelle formation ability was enhanced with increasing the alkyl chain length (Table 3). In the case of R = $C_{14}H_{29}$, σ_{min} could not be reached due to limited solubility.

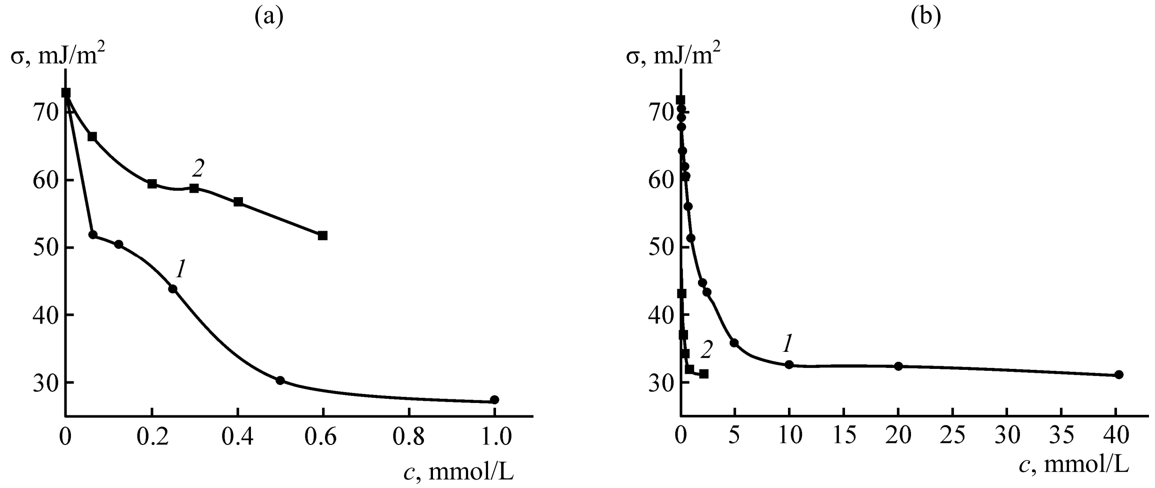

Fig. 1. Isotherms of surface tension (σ) of $RN(CH_2CH_2OH)_2$ (a) in water and (b) in 0.1 mol/L HCl. R = (*1*) $C_{12}H_{25}$ and (*2*) $C_{14}H_{29}$.

Surface activity *G* is another important surfactant parameter. It is known that in the homologous series of surfactants *G* increases with the alkyl chain length [18]. The *G* values calculated for the studied compounds **I** are given in Table 3. *G* increased with the alkyl chain length, the exception being R = $C_{14}H_{29}$; that was likely due to insufficient solubility of the compound in water (Table 1) not allowing for saturation of adsorption layer.

Generally, the surfactant activity is enhanced in the presence of strong electrolyte [18]. In the case of studied compounds **I**, decrease (in any) of the minimal surface tension was not significant; however, the critical micelle concentration was increased and the surface activity was decreased in acidic medium (Table 3). That was due to protonation of the compounds amino group: CMC of cationic surfactants is generally higher than that of the nonionic surfactants [19]. Another reason for the described trend could be the broader range of spherical micelles existence in acidic medium as compared to neutral aqueous solutions [18].

The experimental surface tension isotherms were recalculated into the adsorption isotherms following the Gibbs equation. Contrary to the expectations, the calculated isotherms did not follow the classical shape of Langmuir isotherm [20], and maxima were observed in the plots [Fig. 2 displays the curves in the case of $C_8H_{17}N(CH_2CH_2OH)_2$, the representative example]. Similar adsorption behavior of surfactants was discussed in [21].

Table 3. Medium effect on surface activity of $RN(CH_2CH_2OH)_2$ at room temperature

R	Minimal surface tension σ_{min}, mJ/m² (*c*, mmol/L)		Critical micelle concentration CMC, mmol/L		Surface activity *G*, mJ m mol^{-1}	
	in water	in 0.1 mol/L HCl	in water	in 0.1 mol/L HCl	in water	in 0.1 mol/L HCl
C_8H_{17}	48	41	0.40	1.00	32	2
	(0.9)	(20.0)	0.80	5.00		
$C_{10}H_{21}$	34	38	0.30	2.5	132	4
	(0.6)	(18.0)	0.68	18		
$C_{12}H_{25}$	30	36	0.06	0.86	338	19
	(0.5)	(10.0)	0.46	4.00		
$C_{14}H_{29}$	52	36	0.18	0.28	108	127
	(0.6)	(0.6)	–	–		

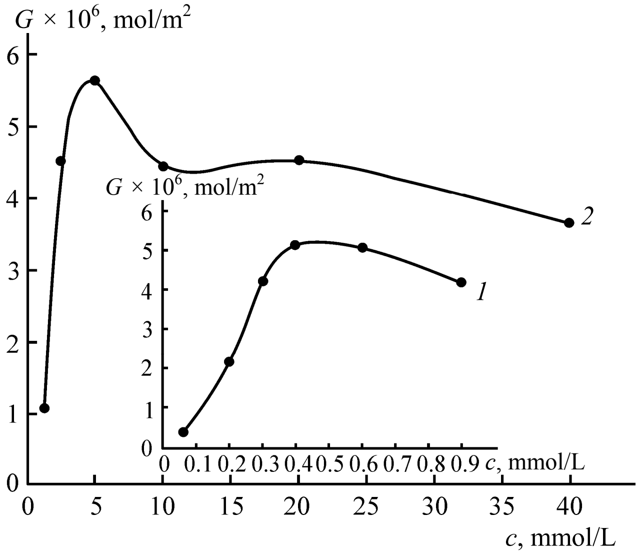

Fig. 2. Isotherm of $C_8H_{17}N(CH_2CH_2OH)_2$ adsorption at the water–air interphase boundary (*1*) and at 0.1 mol/L HCl–air interphase boundary (*2*).

At lower concentrations, the surfactant adsorption at the liquid surface occurred due to hydrogen bonding. With increasing concentration, interaction of the alkyl tails of the surface-adsorbed surfactant molecules with micelles in solution was possible. Likely, that was the reason for appearance of the maxima in adsorption isotherms. Adsorption reached the limit at sufficiently high surfactant concentration, when no further growth of micelles in the solution was possible.

EXPERIMENTAL

Compounds **I** were prepared from diethanolamine and the corresponding primary alkyl halogenides as described in [22]. Liquid products were purified by vacuum distillation. Solid compound **I** (R = $C_{14}H_{29}$) was purified by the reaction mixture washing with hexane followed by repeated recrystallization (two or three times) from hexane–ethyl acetate 2 : 1 mixture.

Purity and identity of the products was confirmed by IR, ^{1}H NMR, and elemental analysis data. ^{1}H NMR spectra were recorded using the MERCURY plus 300 spectrometer ($CDCl_3$ solution). IR spectra were recorded using the IFS 66 Bruker spectrometer (Vaseline oil suspension, KBr window, 100 scans at 1 cm^{-1}). Elemental analysis was performed using the CHNS−932 analyzer (LECO Corporation).

Content of the main component in the samples (>98%) was determined by potentiomentric titration using the I–160M ionomer with glass and silver chloride electrodes. In particular, the 0.1000 g specimen was dissolved in 4 mL of KCl solution (1 mol/L) and titrated with 0.1 mol/L aqueous HC1. Content of *N*-alkyldiethanolamines and their pK_a values were calculated as described in [13].

Compounds solubility was determined by gravimetry [23]. Their thermal stability was estimated using the Q−1500D Paulig–Paulig–Erdei derivatograph (in air, at 20–600°C and 10 deg/min).

The compounds resistance towards acid hydrolysis was studied by incubation of the 5×10^{-2} mol specimen during 1 day at 20 and 60°C. The reaction mixture was regularly sampled and analyzed by TLC (Silufol plates, 1 : 2 chloroform–methanol, development with 3% chloranil in toluene at 70°C, visual inspection with the reference sample).

Surface tension at the interphase boundary between the compounds solution (either in water or in 0.1 mol/L HCl) and air was measured with stalagmometer [20]. Critical micelle concentration was determined graphically as the kink of surface tension plot as function of concentration.

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