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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Oxyethyl Hydrazides as Potential Flotation Agents

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Abstract—Physicochemical (acid-base, solubility, stability against oxidation and hydrolysis) and surface-active (wetting angles, surface tension, foaming) properties of *N*'-oxyethyl hydrazides of aliphatic carboxylic acids were studied. The data obtained are analyzed in terms of the main requirements imposed on flotation agents.

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Flotation processes are widely used in hydrometallurgy and mining industry [1]. This necessitates development of new floating agents with improved technological properties, which should satisfy a number of requirements [2]. Aliphatic acid hydrazides are bidentate ligands and form flotoactive precipitates of complexes with nonferrous metal ions [3]. Introduction of oxyethyl substituents at the β-atom of nitrogen in hydrazides can impart additional properties, collect

ing and surface-active, to the compounds obtained.

The aim of this study was to examine properties of *N*'-(2-oxyethyl)hydrazides of aliphatic acids, necessary for assessing the possibility of using these reagents in flotation processes, and to analyze their flotation activity with model Cu(II) solutions.

EXPERIMENTAL

N',*N*'-Di-(2-oxyethyl)hydrazides of hexanoic, octanoic, and undecanoic acids and *N*'-2-oxyethyl)hydrazide of octanoic acid were synthesized at the laboratory of organic complexing reagents, Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences. The individual nature and purity of the reagents was confirmed by IR and ^{1}H NMR spectroscopies and elemental analysis.

The optical density of solutions was measured with an SF-2000 spectrophotometer, and the pH values, with an I-160M pH-meter with glass and silver chloride electrodes. Voltammograms in alkaline solutions were measured with a PU-01 polarograph on a dropping mercury electrode at potentials in the range from –2.41 to –0.11 V at a potential sweep rate of 3 mV s^{-1}. A silver chloride electrode served as reference, and platinum as auxiliary electrode. In other cases, polarization curves were measured on a rotating disc electrode at potentials of 0–1.07 V and a potential sweep rate of 5 mV s^{-1}. The solubility was determined gravimetrically [4]. pK_{a1} and pK_{a2} were calculated by the formulas [5]:

$$pK_{a1} = pH + \log\frac{A_{HL} - A}{A - A_{HL+}}, \quad (1)$$

$$pK_{a2} = pH + \log\frac{A_{L^-} - A}{A - A_{HL}}, \quad (2)$$

where pK_{a1} and pK_{a2} are negative logarithms of the acid dissociation constants of H_2L^+ and HL, respectively; A_{HL}, $A_{HL}+$, and A_{L^-}, optical densities of solutions containing neutral, protonated, and deprotonated forms of the reagents, respectively; and A, optical density of the solution at a certain pH value.

The stability against hydrolysis was determined by the extraction method [6]. The surface tension at the water–air interface was studied by stalagmometry; the foaming kinetics and the wetting angles were analyzed using standard techniques [7]. To examine the ionic flotation, ethanol solutions of collecting agents were introduced

Table 1. Solubility of $RC(O)NHN(C_2H_4OH)_2$ in some solvents

Compound	R	Solubility, g l^{-1} (M)				
		H_2O	EtOH	chloroform	1 M HCl	toluene
I	C_5H_{11}	15.0 (6.9×10^{-2})	29.4 (1.3×10^{-1})	25.7 (1.2×10^{-1})	14.6 (6.8×10^{-2})	3.5 (1.6×10^{-2})
II	C_7H_{15}	5.9 (2.3×10^{-2})	16.3 (6.1×10^{-2})	12.4 (5.2×10^{-2})	3.7 (1.5×10^{-2})	4.0 (1.6×10^{-2})
III	$C_{10}H_{21}$	3.0 (1.0×10^{-2})	39.9 (1.4×10^{-1})	23.9 (8.3×10^{-2})	4.0 (1.4×10^{-2})	4.3 (1.5×10^{-2})

Table 2. Spectrophotometrically found values of pK_{a1} and pK_{a2} for $RC(O)NHN(C_2H_4OH)_2$ and reagent **IV** [$C_7H_{15}C(O)NHNHC_2H_4OH$] ($P = 0.95$, $n = 5$, aqueous-Degree of hydrolysis, %, at indicated heating duration, min)

Compound	R	pK_{a1}	pK_{a2}
I	C_5C_{11}	2.50 ± 0.04	12.04 ± 0.05
II	C_7H_{15}	3.86 ± 0.05	–
III	$C_{10}H_{21}$	4.41 ± 0.04	–
IV	Reagent	2.32 ± 0.03	13.42 ± 0.06

into a $CuSO_4$ solution, and the mixture was thoroughly agitated for 1 min. The pH values were adjusted with a 0.1 M NH_3 solution. The volume of the solutions under study was 250 ml, and the flotation time, 10 min. Experiments were performed at a temperature of 20 ± 2°C. The flotation installation was described in [8]. In the course of flotation, Cu(II) complexes with collecting agents passed across the liquid–air interface and were removed from the solution. Samples of a purified solution were taken with a sampling device and the residual content of Cu(II) in the samples was determined on an AAS-30 atomic-absorption spectrometer [9].

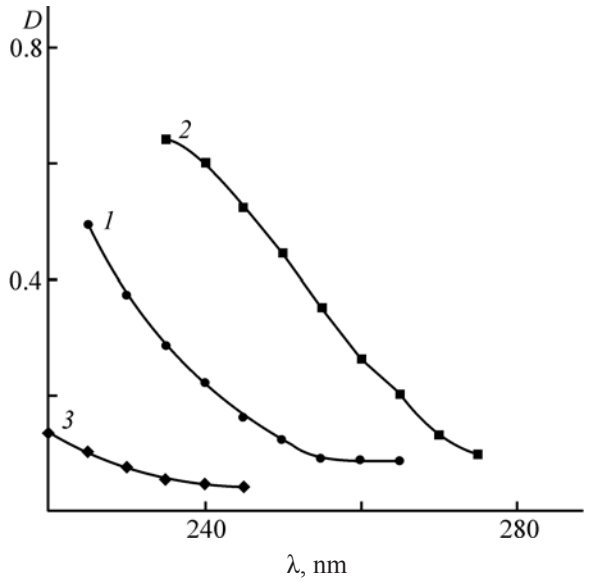

Fig. 1. Absorption spectra of a solution of *N*',*N*'-di(2-oxyethyl)hydrazide of hexanoic acid (**I**) in relation to the type of the medium. $c = 4 \times 10^{-4}$ M; $l = 1$ cm; the same for Fig. 2. (*D*) Optical density and (λ) wavelength. pH: (*1*) 5.5, (*2*) 14.0, and (*3*) 1.0.

Four reagents were studied: three compounds of the *N*',*N*'-di(2-oxyethyl)hydrazide series with a general formula $RCONHN(C_2H_4OH)_2$ (DEHA), where R is C_5H_{11} (**I**), C_7H_{15} (**II**), and $C_{10}H_{21}$ (**III**), and *N*'-(2-oxyethyl)hydrazide of octanoic acid $C_7H_{15}CONHNHC_2H_4OH$ (**IV**). Compounds **I**–**III** are white tarry substances, and (**IV**) is a white crystalline substance with mp 78–79°C.

It follows from the data in Table 1 that the reagents under study are well soluble in ethanol and chloroform, and moderately soluble in water and 1 M HCl solution. Consequently, to apply these compounds as collecting agents in flotation, it is advisable to use, e.g., their aqueous solutions or hydrochloric emulsions.

Figure 1 shows UV spectra of solutions of compound **I** at various pH values. It can be seen that, as indicated by the type of light absorption, the forms of the reagent in neutral (curve *1*), alkaline (curve *2*), and acid (curve *3*) media strongly differ. This shows that acid-base equilibria exist in the solutions:

$$H_2L^+ \overset{K_{a1}}{\leftrightarrows} HL \overset{K_{a2}}{\leftrightarrows} L^-. \quad (3)$$

The basicity of HL compounds is characterized by dissociation constants K_{a1} of conjugated acids H_2L^+, and the acidity, by constants K_{a2} of dissociation of neutral HL molecules to give L^- anion.

To calculate pK_{a1} and pK_{a2}, dependences of the optical density *D* on pH_{eq} were examined for the example of solutions of reagent **I** at 225 nm in an acid medium (Fig. 2a) and at 250 nm in an alkaline medium (Fig. 2b).

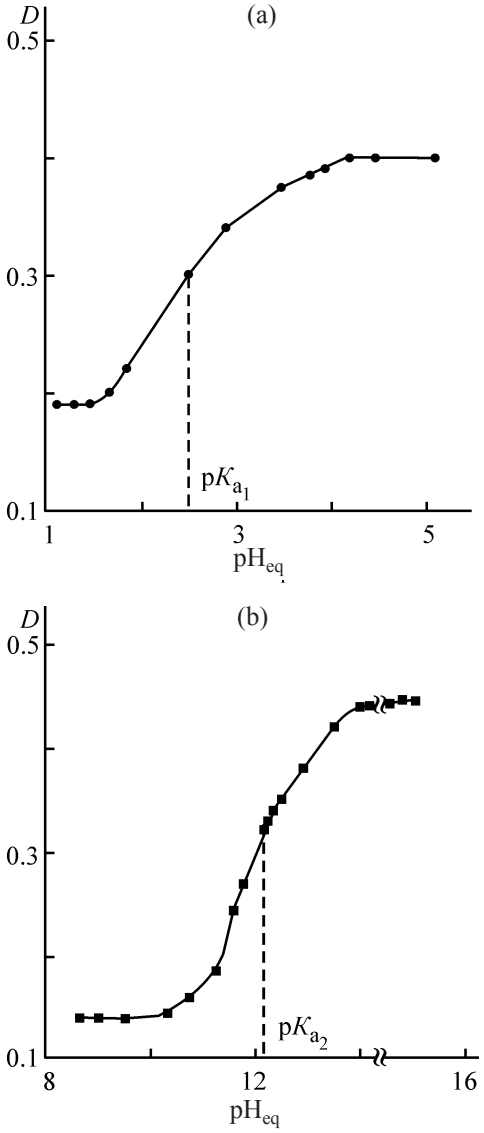

Fig. 2. Optical density D of a solution of *N*',*N*'-di(2-oxyethyl)-hydrazide of hexanoic acid (**I**) vs. the pH of the medium and values of the Hammett function (H_). λ (nm): (a) 225 and (b) 250.

The results obtained are listed in Table 2. For compounds **II** and **III**, pK_{a2} could not be calculated because of the small difference in absorption between the neutral and deprotonated forms. As can be seen in Table 2, the compounds are amphoteric and behave as weak acids and bases; the basic properties in the DEHA series become more pronounced as the length of the alkyl radical grows. Compound **IV** has lower basicity and acidity, compared with the DEHA series.

By analogy with unsubstituted hydrazides [10], hydrolysis of *N*',*N*'-di-(2-oxyethyl)hydrazides probably occurs as follows:

$$RCONHN(C_2H_4OH)_2 \overset{OH^-}{\rightleftharpoons} RCC^- + NH_2N(C_2H_4OH), \quad (4)$$

$$RCONHN(C_2H_4OH)_2 \overset{H_3^+O}{\rightleftharpoons} RCCOH + NH_3^+N(C_2H_4OH)_2, \quad (5)$$

This yields the corresponding carboxylic acid (or its salt). The degree of hydrolysis was calculated from the amount of the acid or its salt formed (Table 3). It can be seen that DEHA are moderately stable against hydrolysis in 1 M KOH or HCl solutions: in 3 h, 26–35% of DEHA is hydrolyzed in a 1 M KOH solution (compound **IV** is less stable under similar conditions: it decomposes by 63% in 3 h); in a 1 M HCl solution, the degree of hydrolysis in the DEHA series is 19–29%.

The potentials of oxidation half-waves, $E_{1/2}$, are listed in Table 4. It can be seen that, on passing from alkaline to acid media, $E_{1/2}$ increases from negative values of –0.19….–0.22 V to positive values of +1.28–1.11 V. This points to an increase in the stability of the reagents against oxidation. No dependence of $E_{1/2}$ on the length of the alkyl radical in the DEHA series was observed. The data on the chemical stability (Tables 3, 4) satisfy the requirements to flotation agents [2].

The wetting angle is one of the most important characteristics of surfactants. Figure 3 shows as an example the wetting isotherm for compound **III**, which has the form typical of collecting agents [11]. The presence of the compounds studied in a concentration of 2×10^{-5} M causes an abrupt increase in the wetting angle from 50° in the background solution to 90°. No effect of the reagent

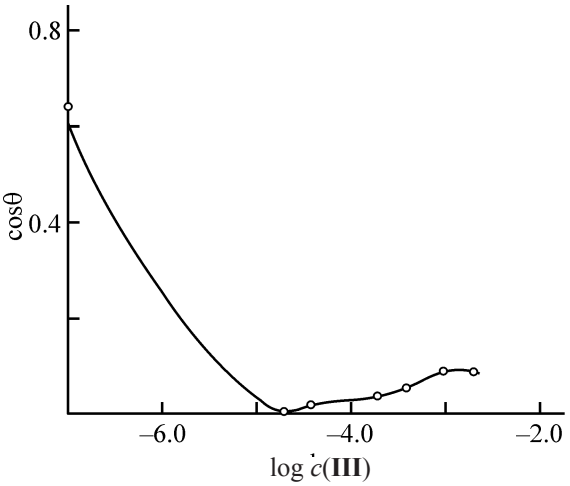

Fig. 3. Wetting isotherm at pH 5.5 for *N*',*N*'-di(2-oxyethyl)-hydrazide of undecanoic acid (**III**).

Table 3. Degree of hydrolysis of $RC(O)NHN(C_2H_4OH)_2$ in relation to the radical length and of reagent **IV** $[C_7H_{15}C(O)NHNHC_2H_4OH]$. c_{KOH} = 1 M, c_{HCl} = 1 M; T = 60 ± 1°C

Compound	R	Degree of hydrolysis, %, at indicated heating duration, min							
		30		60		120		180	
		KOH	HC1	KOH	HC1	KOH	HC1	KOH	HC1
I	C_5H_{11}	4	6	11	23	20	27	26	29
II	C_7H_{15}	6	7	10	15	22	21	31	23
III	$C_{10}H_{21}$	9	9	12	10	26	15	37	19
IV	Reagent	4	–	24	–	42	–	63	–

Table 4. Potentials $E_{1/2}$ of oxidation half-waves for $RC(O)NHN(C_2H_4OH)_2$ and reagent **IV** $[C_7H_{15}C(O)NHNHC_2H_4OH]$ ($c_{DEHA} = 1 \times 10^{-3}$ M)

Compound	$E_{1/2}$, V			
	R	1 M H_2SO_4	pH 3.9	1 M NaOH
I	C_5H_{11}	+0.64 +1.21	+0.92	–0.22
II	C_7H_{15}	+0.62 +1.19	+0.92	–0.20
III	$C_{10}H_{21}$	+0.68 +1.28	+0.97	–0.22
IV	Reagent	+0.50 +1.11	+0.89	–0.19

concentrations or pH of the medium on the wetting angles was observed.

The surface activity of all the compounds, except reagent **III**, in a neutral medium in water–ethanol solutions is low; values of the surface tension σ decrease by 2–3%, compared with those in background solutions, which is probably due to the insufficient length of the hydrocarbon radical. In the case of **III**, σ_{min} is about 21 mN m^{-1}. Compound **III** exhibits a rather high surface activity (G = 19.5 mN mol m^{-2}). Because the reagents are fully protonated in aqueous solutions at pH < 2, the surface activity of the compounds was studied in an acid medium (pH 1.6). The surface-tension isotherms of compounds **I**–**III** are shown in Fig. 4. As the hydrocarbon radical becomes longer, the surface activity increases. The values of G were 38.0, 50.0, and 108.5 mN mol m^{-2} for the DEHA series (**I**, **II**, and **III**, respectively) and 38.0 mN mol m^{-2} for **IV**. The surface-tension isotherms were used to estimate the critical micelle concentrations (CMC) to be 8×10^{-3}, 7×10^{-3}, 3×10^{-4}, and 3×10^{-4} M for reagents **I**, **II**, **III**, and **IV**, respectively.

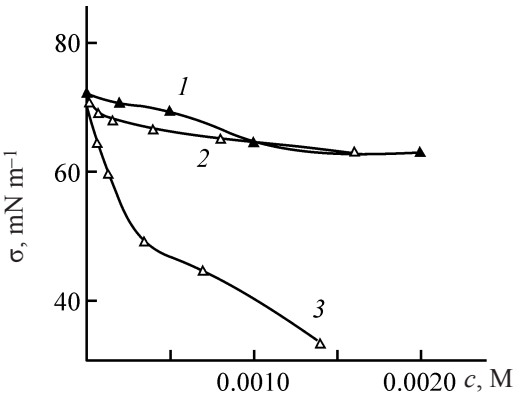

Fig. 4. Isotherms of the surface tension σ of compounds **I–III** (*1–3*, respectively) at pH 1.6. (*c*) DEHA concentration.

The surface tensions and wetting angles were used to calculate by the Jung equation [7] the work of adhesion in neutral and acid media (Table 5). A decrease in the pH of the medium makes the interphase interaction stronger, which will probably favor a more effective flotation activity of reagents **I**–**III** in acid media, compared with a neutral medium.

As expected in accordance with the wetting-angle and surface-tension data, reagents **I** and **II** cannot form stable foams because of the insufficient length of the hydrocarbon radical. Compound **III** gives stable foams with a lifetime exceeding 4 h at pH 1.6; at higher pH values, only wet low-stability foams are formed. It is known that stable foams can be formed at concentrations exceeding the CMC; for reagent **III**, this value is 4×10^{-4} M. At lower concentrations, when the content of the surfactant is insufficient for a monomolecular stabilizing layer to be formed, the lifetime of the foam does not exceed 30 s (Fig. 5). Compound **IV** has a low CMC value (4×10^{-4} M) and can form foams, but their stability will

Table 5. Effect of the pH value of aqueous solutions of $RC(O)NHN(C_2H_4OH)_2$ on the work of adhesion, W_a

Compound	R	c, g l^{-1} (M)	W_a, mN m^{-1}, at indicated pH	
			5.5	1.6
I	C_5H_{11}	$0.436(2 \times 10^{-3})$	26	66
		$0.218(10^{-3})$	26	69
II	C_7H_{15}	$0.487(2 \times 10^{-3})$	25	66
		$0.246(10^{-3})$	26	65
III	$C_{10}H_{21}$	$0.576(2 \times 10^{-3})$	19	67
		$0.057(2 \times 10^{-4})$	30	55

be low because of the insufficiently high surface activity (σ_{min} is 64 mN m^{-1}, compared with 72 mN m^{-1} for the background solution); presumably, additional foam stabilizers should be introduced in flotation processes with reagent **IV**.

It was shown in [13] that the compounds under study can be used in flotation of copper-molybdenum sulfide ores. In fact, principles of the mineral flotation are used for separation of solution components in ionic flotation. Therefore, it was of interest to study reagents suggested for flotation of minerals as collecting agents for recovery of nonferrous metals by ionic flotation. Despite that compounds of the DEHA series exhibit surface activity in an acid medium, which makes these compounds potential flotation agents for recovery of metal anions, e.g., MoO_4^{2-} and CrO_4^{2-}, the key factor governing the collecting activity of reagents is formation of hydrophobic precipitates of complexes, which are formed at alkaline pH values in the case of nonferrous metal ions.

The possibility of recovery of Cu(II) ions ($c_{Cu(II)}$ = 7.132 mg l^{-1}) from difficultly purifiable ammonia solutions by ionic flotation. Di-(2-oxyethyl)hydrazides with R = C_5H_{11}, C_7H_{15}, $C_4H_9CH(C_2H_5)$, $C_{10}H_{21}$, and $C_{14}H_{29}$ were studied as collecting agents. All the reagents exhibited a strong complex-forming capacity at pH 7–9, which provides a high degree of recovery of Cu(II) ions. The maximum degree of recovery (99.0%, residual Cu(II) concentration 0.07 mg l^{-1}) was reached at pH 9.0, flotation time of 10 min, and [Cu(II)] : [reagent] = 1 : 1 with *N*',*N*'-di(2-oxyethyl)hydrazide of pentadecanoic acid. The compound exhibits a high surface activity, which enables its use in flotation processes without introduction of additional foam-forming agents. The possibility of deep single-stage purification of ammonia solutions to remove Cu(II) is an advantage of these reagents over the known flotation agents, e.g., carboxylates [2].

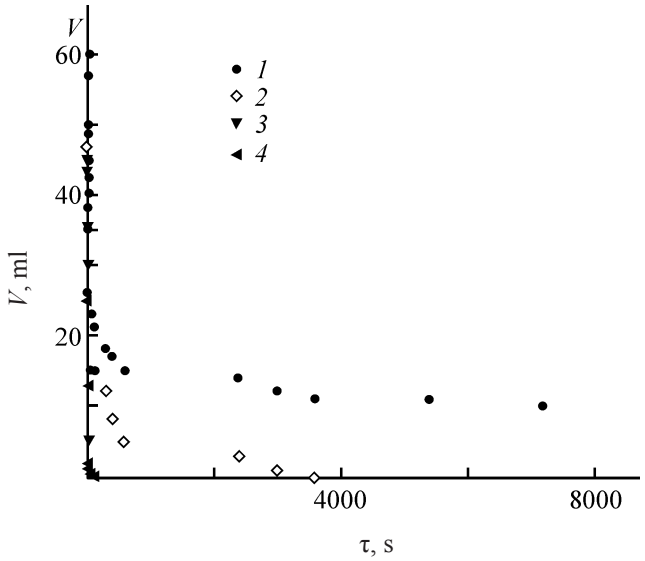

Fig. 5. Foam stability vs. the concentration of solutions *N*',*N*'-di(2-oxyethyl)hydrazide of undecanoic acid (**III**) at pH 1.6. (*V*) Volume and (τ) time. Concentration of compound **III** (M): (*1*) 0.002, (*2*) 0.001, (*3*) 0.0005, and (*4*) 0.0001.

CONCLUSIONS

(1) *N*',*N*'-Di-(2-oxyethyl)hydrazides and *N*'-2-oxyethyl hydrazide of octanoic acid are amphoteric; the basic properties in the series of *N*',*N*'-di-(2-oxyethyl)hydrazides become more pronounced as the length of the alkyl radical increases. *N*',*N*'-Di-(2-oxyethyl)hydrazides are moderately stable against hydrolysis in 1 M KOH and HCl solutions. On passing from alkaline to acid media, the reagents become more stable against oxidation.

(2) The surface activity of the compounds studied, except *N*',*N*'-di-(2-oxyethyl)hydrazide of undecanoic acid, is low. The surface tension at pH 1.6 substantially exceeds that in a neutral medium; the effect of the reagent concentration and the pH of the medium on the wetting angles is insignificant. Values of the work of adhesion in neutral and acid media show that a decrease in pH makes the interphase interaction stronger.

(3) The compounds studied, except *N*',*N*'-di-(2-oxyethyl)hydrazide of undecanoic acid, do not give stable foams.

(4) According to the results of a study of the ionic flotation of Cu(II) from ammonia solutions, the optimal choice is the reagent with a radical R = $C_{14}H_{29}$, which provides the deepest purification of solutions to remove Cu(II) ions in a single stage without introduction of additional foam-forming agents.

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