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Physicochemical Properties of Benzoic Acid *N,N*-dialkylhydrazides

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Abstract—Benzoic acid *N,N*-dialkylhydrazides of the general formula $C_6H_5C(O)NHNR_2$, R = C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, were obtained,. Their solubility, acid-base properties, stability against hydrolysis, distribution between organic and water phases were studied.

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In [1, 2] benzoic acid *N,N*-dialkylhydrazides were shown to be promising extraction agents of copper(II) from ammonia media. However they were not systematically explored: Some properties important for practical use were not studied, influence of hydrocarbon radical length was not revealed. This work is devoted to the study of some physicochemical properties of benzoic acid *N,N*-dibutyl- (**I**), dihexyl- (**II**), dioctyl- (**III**), and didodecylhydrazides (**IV**).

The explored compounds are white crystalline substances. They are insoluble in water, but well soluble in isopentyl alcohol and aromatic hydrocarbons (Table 1). The solubility passes through a maximum (compound **II**). The presence of a maximum is due to the increase in hydrophobicity of compounds at the elongation of the hydrocarbon radical, but at further growing of hydrocarbon chain the solubility decreases because of stronger intermolecular interaction. The solubility of no less than 0.05–0.1 mol l^{-1} is necessary for the use of reagents in extraction processes. By this characteristic all of the compounds studied are applicable except for compound **IV**. The data obtained are quite unlike the benzylhydrazide solubility, which is well soluble in water and virtually insoluble in aromatic hydrocarbons [3]. Thus, introducing two alkyl radicals into the benzylhydrazide molecule increases hydrophobicity of compounds obtained and improves their compatibility with organic solvents that permits their application to the extraction processes and leads to the decrease in the water phase losses.

Acid–base properties of these compounds were examined by spectrophotometric method [4]. The UV spectra of neutral, acidic and basic solutions of compound **I** are shown in Fig. 1. The spectra are different indicating that in these solutions various forms of reagent are in acid-base equilibrium characterized by pK_{a1} and pK_{a2} values.

$$H_2L^+ \underset{}{\overset{-H^+,\ pK_{a1}}{\rightleftharpoons}} HL \overset{-H^+,\ pK_{a2}}{\rightleftharpoons} L^-. \qquad (1)$$

Here HL is *N,N*-dialkylhydrazide molecule, H_2L^+ and L^- are its protonated and deprotonated forms respectively. The spectra of other compounds are similar.

The dependence of optical density of the reagent solutions on the medium acidity was determined for pK_{a1} and pK_{a2} calculation. The acidity was controlled by addition of HCl solutions or saturated water-alcohol solution of KOH. Measurements were accomplished in the water–alcohol solutions at the wavelengths where

Table 1. Solubility of *N,N*-dialkylhydrazides at 20±1°C

Comp. no.	Solubility, g l^{-1}				
	water	hexane	*i*-AmOH	toluene	*p*-xylene
I	0.26	0.08	35.24	51.08	–
II[a]	0.2	1.9	177.8	51.90	48.60
III	insol.	1.8	96.18	39.90	27.39
IV	insol.	1.12	14.66	17.04	11.80

[a] Data are taken from [1].

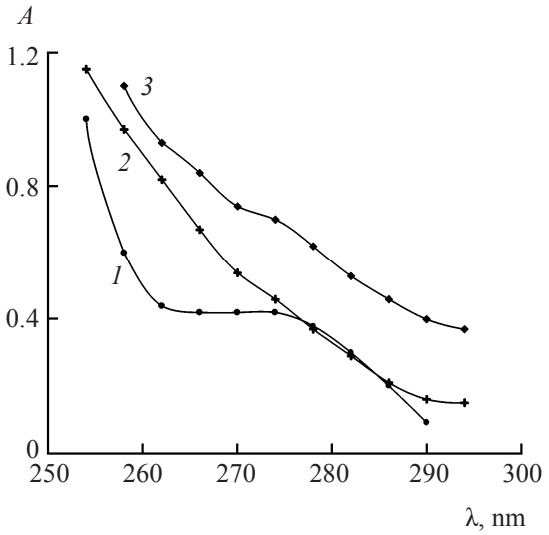

Fig. 1. Electron absorption spectra of compound **I** solution in the mixture water–EtOH (1:3), $C_I = 5\times10^{-4}$ mol l^{-1}, l = 1 cm. (*1*) pH = 1.97; (*2*) pH = 6.60; and (*3*) 3.15 mol l^{-1} of KOH.

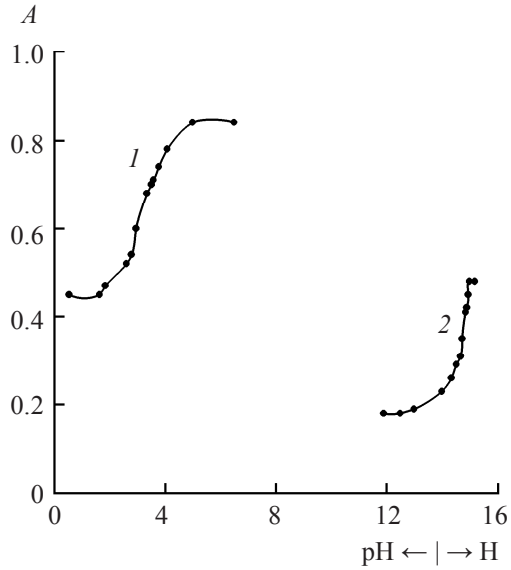

Fig. 2. The dependence of optical density (*A*) on pH for compound **I** in water:EtOH (1:3) medium, $C_I = 5\times10^{-4}$ mol l^{-1}, l = 1 cm. (*1*) λ = 262 nm, and (*2*) λ = 286 nm.

the difference in optical density of two reagent forms was maximal. The reagent concentrations are (4–5)× 10^{-4} mol l^{-1} and l = 1 cm. It is seen from Fig. 2 that the process of proton elimination from the protonated molecule begins at pH~2 and completes at pH ~5; deprotonation of neutral molecule begins at pH~13 and completes at 4.5–5 mol l^{-1} of KOH (while working with concentrated solutions of alkali we use Hammett function for the calculation). Therefore there are protonated (pH < 2), neutral (pH 5–13) and deprotonated (C_{KOH} > 5 mol l^{-1}) forms of compound **I**. Analogous results were obtained for the other compounds.

The values of pK_{a2} and pK_{a2} were calculated by formulas (2) and (3).

$$pK_{a1} = pH + \log\frac{A_{HL} - A}{A - A_{H_2L^+}}, \quad (2)$$

$$pK_{a2} = pH + \log\frac{A_{L^-} - A}{A - A_{HL}}. \quad (3)$$

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

For the benzoic acid *N,N*-dialkylhydrazides the following pK_{a1} values were obtained: 3.24±0.02 (diethylhydrazide) [2]; 3.16±0.02 (compound **I**); 2.83± 0.04 (compound **II**) [1]; 2.66±0.05 (compound **III**); 2.63±0.04 (compound **IV**), for all of the found values R = 0.95, n = 5; pK_{a2} values: 14.94±0.04 (benzoic acid dethylhydrazide) [2]; 14.6±0.2 (compound **I**); 14.6±0.2 (compound **I**); R = 0.95, n = 9 and 6, respectively. In the series of benzoic acid *N,N*-dialkylhydrazides the basic properties characterized by pK_{a1} become weaker as the hydrocarbon radical length is increased, whereas the acidic properties characterized by pK_{a2} almost do not change. For benzylhydrazide pK_{a1} equals 3.27 and pK_{a2} is 12.2 [3]. Thus, N,N-alkylation of benzylhydrazide reduces negligibly the basic properties of compounds obtained and decreases substantially their acidic properties. The decrease in acidic properties is caused by a positive inductive effect of alkyl substituents that makes difficult to eliminate a proton from the neutral molecule. The basic properties weakening is probably associated with steric hindrances growing as the hydrocarbon radical length increases, which imparts the proton addition to the neutral molecule of the reagent.

Chemical stability of hydrazides in acid and alkali is characterized by hydrolysis index, which in turn determines their suitability as extraction reagents. Presumably, the hydrolysis of *N,N*-dialkylhydrazides would proceed similarly to that of the unsubstituted hydrazides [5].

Hydrolysis was carried out by refluxing a solution of reagents in 0.5 M H_2SO_4 and 1M NaOH for 2 h.

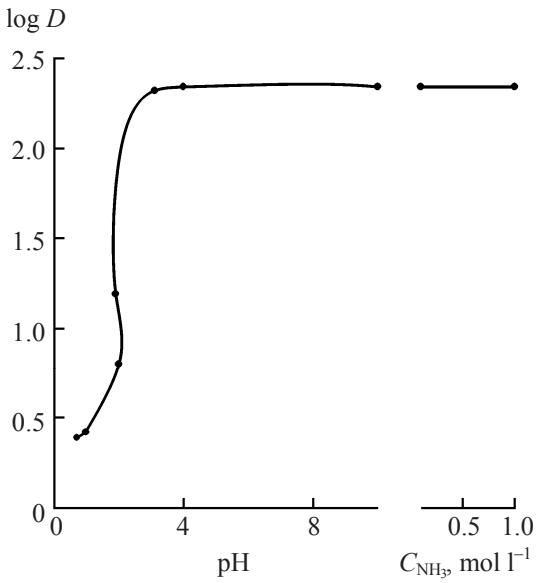

Fig. 3. Dependence of logarithm of distribution coefficient (log *D*) of compound **I** between organic and water phases on medium acidity, C_I = 0.05 mol l^{-1} (*p*-xylene), I = 0.2 (KCl). $V_{o.ph.}$:$V_{w.ph.}$ 1:1, stirring for 3 min.

$$\mathrm{PhCONHNR_2} \xrightarrow{\mathrm{H_3O^+}} \mathrm{PhCOOH + NH_3^+NR_2} \qquad (4)$$
$$\mathrm{PhCONHNR_2} \xrightarrow{\mathrm{OH^-}} \mathrm{PhCOO^- + NH_2NR_2}$$

The amount of nonhydrolyzed reagent was determined by the extraction-photometry method we had de-veloped. The extent of hydrolysis was calculated by formula (5).

$$h = \frac{m_1 - m_2}{m_1} \times 100\%. \qquad (5)$$

Here m_1 is mass, g, of the taken hydrazide sample, m_2 is the hydrazide mass, g, determined after hydrolysis.

In H_2SO_4 the hydrolysis index of compound **I** equals to 6.0%; of compound **II,** to 5.3%; of compound **III,** to 1.1%. In NaOH it equals to 6.6, 4.0, and 2.6%, respectively. Evidently, the hydrolysis index decreases as the alkyl radical chain elongates that can be due to the increased steric hindrances.

Table 2. Values of logarithm of distribution coefficient (log *D*) of *N,N*-dialkylhydrazides, V_o:V_w = 1:1, stirring 3–5 min, I = 0.2 (KCl)

Comp. no.	log D_{av}			*M*
	pH ~4	NH_3, 0.1 M	H_2SO_4, 0.5 M	
I	2.34	2.34	0.47	248
II	2.58	2.58	1.93	304
III	2.58	2.63	2.60	360

An important characteristic of reagents used in liquid extraction is their distribution between organic and water phases. Dependence of logarithm of distribution coefficient (log *D*) of **I** on pH and ammonia concentration is presented in Fig. 3.

From this figure it is obvious that at pH ≥ 3 the values of log *D* remain constant due to the presence of neutral reagent form in this region. When pH is decreased, values log *D* are also decreased that is caused by protonation of the reagent. The obtained data on *N,N*-dialkylhydrazides distribution are given in Table 2. By these data, log *D* increases as the molecular mass, i. e. hydrophobicity, increases.

EXPERIMENTAL

The ^{1}H NMR spectra were registered on a MERCURY-plus300 spectrometer (300 MHz) in $CDCl_3$ relative to internal HMDS. The IR spectra were obtained on an IFS 66/S Fourier-spectrometer (Bruker, Germany) from mulls in mineral oil. The UV spectra were taken on an SF-26 spectrophotometer. Values of pH were measured on an I-160M ionometer with a glass and silver chloride electrodes. Optical density was measured on a KFK-3-01 photocolorimeter. Conductometric titration was accomplished on a OK-102/1 conductometer. Elemental analysis was carried out on a CHNS-932 LECO Corporation analyser. Thin-layer chromatography was fperformed on a Silufol plates in *m*-xylene–BuOH system (2:1) using phosphomolybdenum acid as a detecting agent. We used our own extraction-photometry method to determine reagents content in the water phase on studying hydrolysis and reagents distribution between water and organic phases. This method is based on an ability of *N,N*-dialkylhydrazide to form colored complexes with copper(II) ions in ammonia medium when extracted with *p*-xylene.

Procedure of extraction-photometry determination of *N,N*-dialkylhydrazides. Into a separating funnel (50 ml) were placed 25 ml of water phase containing 1 ml of 10% copper(II) salt and a calculated volume of ammonia to its concentration 0.1–1 mol l^{-1} in the final volume. To this mixture was added a sample of reagent or its water solution aliquot, or solution in *p*-xylene, and 10 ml of pure *p*-xylene. This

mixture was stirred for 3–5 min. Then the extract was filtered through cotton wool, diluted with *p*-xylene to 25 ml and photometrically measured depending on *N,N*-dialkylhydrazide content at λ 330 (determination interval 0–0.03 mmol) or 460 nm (determination interval 0.03–0.5 mmol) in optical cell with l = 1 cm. Reagent content was determined using the calibration plot. The relative error of measurements did not exceed 5%.

Reagents syntheses were carried out similar to procedure [2].

Compound I. Yield 59%, mp 98.5–99°C (EtOH–H_2O 2:1), R_f 0.73. IR spectrum, ν, cm^{-1}: 3250 (NH); 1660 (amide **I**); 1550 (amide **II**). ^1H NMR spectrum, δ, ppm: 0.83 t (6H, CH_3, J 7 Hz), 1.22–1.36 m (4H, CH_3CH_2), 1.43–1.53 m (4H, NCH_2CH_2), 2.75 t (4H, NCH_2, J 6.9 Hz), 6.75 s (1H, NH), 7.30–7.45 m (3H, Ph), 7.67 d (2H, Ph, J 6.9 Hz). The base compound content determined by conductometric titration [6] is 98%. Found, %: C 72.41; H 9.34; N 11.04. $C_{15}H_{24}N_2O$. Calculated, %: C 72.58; H 9.68; N 11.29.

Compound II. Yield 62%, mp 77–78°C [1]. IR spectrum, ν, cm^{-1}: 3240 (NH); 1652 (amide **I**); 1538 (amide **II**). ^1H NMR spectrum, δ, ppm: 0.86 t (6H, CH_3, J 6.8 Hz), 1.24–1.37 m [12H, $CH_3(CH_2)_3$], 1.52–1.61 m (4H, NCH_2CH_2), 2.82 t (4H, NCH_2, J 7.6 Hz), 6.60 s (1H, NH), 7.36–7.52 m (3H, Ph), 7.73 d (2H, Ph, J 6.9 Hz). The base compound content: 99%. Found, %: C 74.59; H 10.22; N 9.17. $C_{19}H_{32}N_2O$. Calculated, %: C 75.00; H 10.53; N 9.21.

Compound III. Yield 64%, mp 87.5–88°C (acetone–H_2O, 4.5:1). R_f 0.73. IR spectrum, ν, cm^{-1}: 3224 (NH); 1652 (amide **I**); 1544 (amide **II**). ^1H NMR spectrum, δ, ppm: 0.80 t (6H, CH_3, J 6.9 Hz), 1.18 br.s [20H, $CH_3(CH_2)_5$], 1.45–1.56 m (4H, NCH_2CH_2), 2.75 t (4H, NCH_2, J 7.8 Hz), 6.62 s (1H, NH), 7.3–7.46 m (3H, Ph), 7.66 d (1H, Ph, J 8.4 Hz), 7.67 d (1H, Ph, J 7.8 Hz). The base compound content: 99%. Found, %: C 76.50; H 11.04; N 7.74. $C_{23}H_{40}N_2O$. Calculated, %: C 76.67; H 11.11; N 7.78.

Compound IV. Yield 54%, mp 69–71°C (acetone). R_f 0.73. IR spectrum, ν, cm^{-1}: 3228 (NH); 1652 (amide **I**); 1544 (amide **II**). ^1H NMR spectrum, δ, ppm: 0.80 t (6H, CH_3, J 6.9 Hz), 1.18 br. s [28H, $CH_3(CH_2)_7$], 1.44–1.56 m (4H, NCH_2CH_2), 2.75 t (4H, NCH_2, J 7.5 Hz), 6.51 s (1H, NH), 7.30–7.46 m (3H, Ph), 7.66 d (1H, Ph, J 8.4 Hz), 7.67 d (1H, Ph, J 7.8 Hz). The base compound content: 98%. Found, %: C 77.38; H 11.21; N 6.67. $C_{27}H_{48}N_2O$. Calculated, %: C 77.88; H 11.54; N 6.73.

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