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Physicochemical Properties of 1,2-Diacylhydrazines Based on α-Branched Tertiary Carboxylic Acids Versatic

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Abstract—New 1,2-diacylhydrazines based on higher α-branched tertiary carboxylic acids Versatic-10 were prepared. Taking into consideration the possible application of these reagents in the processes of heterophase separation of nonferrous metal ions the physicochemical properties of the reagents were examined: the solubility, the stability against hydrolysis, thermal stability. The values of the constants of acid dissociation pK_{a1} and pK_{a2} and the protonation constant pK_{prot} were determined.

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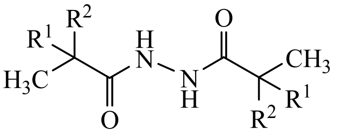
Symmetric 1,2-diacylhydrazines are tetradentate chelate-forming reagents, and they are suggested for the use in concentration nonferrous metals from solutions by precipitation and ionic flotation [1]. Physicochemical properties of 1,2-diacylhydrazines were investigated in [2], and they were shown to be well soluble in polar solvents (e.g., in alcohols) and practically insoluble in hydrocarbons which limits their application in extraction processes.

It was presumable that the reagents of the general formula **I** obtained from the higher α-branched carboxylic acids Versatic would significantly improve the physicochemical characteristics of obtained reagents (in particular, the compatability with organic solvents) due to branching of the alkyl chains and unique properties of the initial acids.



I

Here R^1, R^2 are Alk, and the sum of the carbon atoms of R^1 and R^2 is on the average 6–8.

Initial acids Versatic-10 were prepared as a narrow fraction obtained by the distillation of the mixture of technical grade acids; on the average Versatic-10 contains overall 10 carbon atoms.

Compounds of the general formula **I** were synthesized for the first time. Their IR spectra contain the absorption bands of amide group: stretching vibrations of free NH group at 3008 and 3168 cm^{-1}, amide I at 1649 cm^{-1}, amide II at 1484 cm^{-1}, amide III at 1219 cm^{-1}.

With respect to chromatography the acid Versatic-10 (Fig. 1, curve *1*) and compounds **I** (Fig. 1, curve *2*) differ by the retention times. The group of peaks of acid **I** possesses significantly longer retention time that the group of peaks of the initial acid in keeping with nearly twice greater molecular weight of acid **I**. More compact location of the peaks of acid **I** may be ascribed to the "averaging" of properties owing to cross-acylation of initial homologs in Versatic-10.

The average mass spectrum of a sample of Versatic-10 with the retention time 5.90–6.42 min is very similar to the mass spectrum of neodecanoic acid (NIST08). The peak at *m*/*z* 172.1 corresponds to the molecular ion of compound of the general formula $C_9H_{19}CO_2H$. The subgroups of peaks in the chromatogram at 5.90–6.15, 6.20–6.35, and 6.35–6.42 min are distinguished by the intensities of the signals at *m*/*z* 87, 88, 102, 130, and other which is connected apparently with variation in the length of hydrocarbon chains of the branches of the acids comprising the mixture Versatic-10.

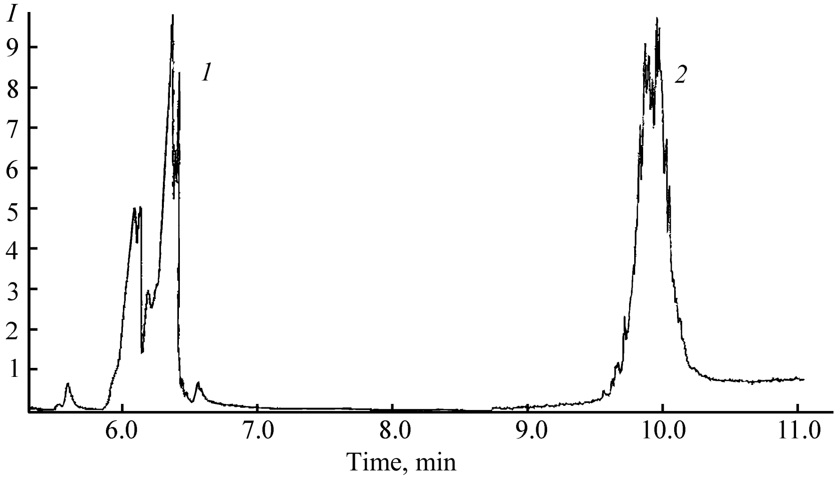


Fig. 1. Chromatograms of samples of acids Versatic-10 (*1*) and compounds **I** (*2*).

The average mass spectrum of the group of peaks of the compound **I** sample corresponds to the formula $C_9H_{19}CONHNHCOC_9H_{19}$ ($C_{20}H_{40}N_2O_2$). In the mass spectrum the molecular ion peak is present at *m*/*z* 340, and also characteristic fragment peaks appear: 270 $[M-C_5H_{10}]^+$, 155 $[C_9H_{19}CO]^+$, 127 $[C_9H_{19}]^+$, 71 $[C_5H_{11}]^+$, and others. The spectra of unresolved peaks of all group at 9.7–10.2 min are similar as seen from the chromatograms.

The solubility data [(g l^{-1})/M] are given below. They show that acid **I** like the previously obtained 1,2-diacylhydrazines of *n*-aliphatic acids [2] are sparingly soluble in water, acid, alkali, and ammonia, but very well soluble in hydrocarbon solvent, kerosene, whereas the 1,2-diacylhydrazines are practically insoluble in, e.g., hexane.

H_2O	0.1 M HCl	1 M HCl	0.1 M NH_4OH	1 M KOH	Kerosene
$0.18/5.2\times10^{-4}$	$0.22/6.3\times10^{-4}$	$0.16/4.6\times10^{-4}$	$0.28/8.1\times10^{-4}$	$0.31/9.0\times10^{-4}$	1201/3.47

The character of light absorption in the region 220–270 nm of the neutral molecule of compound **I** in water-alcohol medium is distinguished from the ionized forms in the alkaline and strong acidic environment (Fig. 2) indicating the involvement of compound **I** into acid-base equilibria.

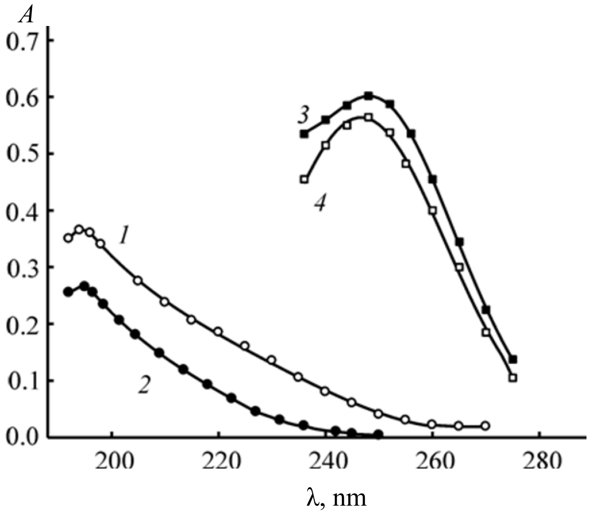


Fig. 2. Electronic spectra of acids **I** in water-alcohol (1:1) solution depending on the character of the environment (c_I 4×10^{-5} M). (*1*) pH 6.5; (*2*) c_{HCl} 6 M; (*3*) c_{KOH} 0.5 M; (*4*) c_{KOH} 3.4 M.

Compounds of the overall formula **I** behave as weak dicarboxylic acids. The estimation of their pK_{a1} and pK_{a2} was performed by the study of the dependence of the optical density (*A*) on the pH value of the water-alcohol solutions at 250 nm, for the evaluation of pK_{prot} the dependence of the optical density on HCl concentration at 240 nm was investigated. On the curve $A = f(pH)$ in alkaline media two bends were observed: the first in the region of pH 11.5–12.5, corresponding to the first step of the dissociation of acid **I**, and at pH 12–13 corresponding to the second step of the dissociation.

In the region of the HCl concentrations 3–4 M a bend was observed corresponding to the protonation of acid **I** (Fig. 3) which in keeping with the quantum-chemical calculations analogously to 1,2-diacylhydrazines occurs apparently at the oxygen atom [2]. The following constants were found for acid **I** by the method [3]: pK_{a1} 11.71±0.06 and pK_{a2} 12.82±0.05, pK_{prot} −1.23±0.01.

The acid properties of compounds **I** are only slightly different from those of unbranched 1,2-diacylhydrazines, e.g., from 1,2-dipentanoylhydrazine with pK_{a1} 11.21±0.04, and pK_{a2} 12.50±0.30 [2]. Formerly studied 1,2-diacylhydrazines are sensitive to hydrolysis: in 1 M KOH at 60°C within 4 h nearly half of the initial 1,2-dipentanoylhydrazine is hydrolyzed [2].

Compounds **I** turned out to be stable against hydrolysis evidently due to steric factors [4]. According to GC-MS data compounds **I** remained intact after 4 h boiling in 1 M KOH solution and 2 M H_2SO_4 solution. On the chromatograms of the samples taken from the reaction mixtures every hour no peaks appear of the possible hydrolysis products. Besides the comparison of the optical density of initial samples of compound **I** and the samples after hydrolysis showed that the optical density changed insignificantly and was within the limits of the experimental error: The increase in the optical density by 6% after 4 h of boiling should be attributed to the partial evaporation of the solution. Hence the presence in the molecules of compounds I of branched alkyl radicals significantly increases the stability of the reagent against hydrolysis as compared with 1,2-diacylhydrazines [2].

The stability of compounds **I** toward heating was evaluated by thermogravimetric analysis. The thermal decomposition of compounds **I** starts at $T > 160°C$ and proceeds in the temperature range 160–280°C. The most intensive mass loss is observed in the range 175–280°C with an exothermic effect at 260°C and the mass loss of 90%.

The distribution of compounds **I** between the water and organic phase was estimated by the equilibrium concentrations in these phases obtained by multiple washing of the extractant with water solutions of H_2SO_4 and NH_4OH at the phases ratio $V_o:V_w = 1:5$. The following values of the logarithms of the distribution factors were obtained: in 0.5 M H_2SO_4 (pH 0.4) log $D = 4.0$, in NH_4OH solution (pH 9.2) log $D = 4.2$.

The log D values of compounds **I** and consequently the carry-over with the water phase for these media is comparable with the characteristics required of industrial extractants (log $D > 3.0$–3.5).

Therefore the data on the physicochemical properties indicate that compounds **I** in contrast to 1,2-diacylhydrazines can be regarded as potential extractants with a high resistence to the hydrolysis, and also permit forcasting the areas of existence and character of complexing with ions of nonferrous metals.

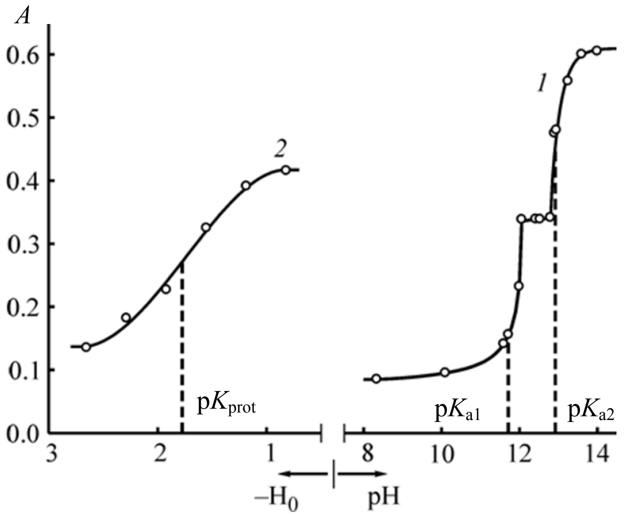


Fig. 3. The dependence of the optical density of water-alcohol solution of acids **I** on the character of the environment. (*1*) solutions of KOH, λ 250 nm, *l* 1 cm, c_I 4×10^{-5} M; (*2*) solutions of HCl, λ 240 nm, *l* 1 cm, c_I 5×10^{-4} M.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrophotometer IFS 66/S (Bruker). Optical density was measured on a spectrophotometer SF-2000. For measuring pH were used ionometers I-160M equipped with a glass and a silver chloride electrodes. Melting points were determined on a device of PTP type. GC-MS spectra were registered on an instrument Agilent Technologies 6890N/5975B, column HP-5ms (30 m×0.25 mm, 0.25 μm), carrier gas helium, electron impact ionization (70 eV). The thermogravimetric anlysis was carried out on a derivatograph Paulik–Paulik–Erdey model Q-1500D at the programmed heating at a rate 2.5 deg/min from room temperature to 1000°C in air using platinum microcrucible. The solubility of compounds was determined gravimetrically [5]. The solubility in 1 M solution of KOH was measured by optical density of solutions at λ 210 nm, cell thickness 1 cm. The acid concentration was estimated using a graduation curve. The solubility in kerosene was evaluated from the change in the refraction index n_d depending on the acid content in the solution.

1,2-Diacylhydrazines of α-branched tertiary carboxylic acids were prepared by the reaction of these acids chlorides with hydrazine hydrate at the molar ratio 1:1.5 at cooling with ice bath. The compounds were purified by recrystallization from a mixture EtOH–water (2:1). Yield 70%, white powder, mp 75–80°C. Found, %: C 69.71; H 11.60; N 8.57. $C_{20}H_{40}N_2O_2$. Calculated, %: C 70.54; H 11.84; N 8.23. *M* 340. The content of the main substance determined by conductometric titration by procedure [6] attained 98%.

The values of pK_{a1}, pK_{a2} (at 250 nm) and pK_{prot} (at 240 nm) were calculated by the following formulas [3].

$$pK_{\text{prot}} = H_0 + \log\,[(A_{\text{H3L}}+ - A)/(A - A_{\text{H2L}})],$$

$$pK_{\text{a1}} = \text{pH} + \log\,[(A_{\text{HL}}- - A)/(A - A_{\text{H2L}})],$$

$$pK_{\text{a2}} = \text{pH} + \log\,[(A_{\text{L}}2- - A)/(A - A_{\text{HL}}-)].$$

Here pK_{prot}, pK_{a1}, and pK_{a2} are negative logarithms of constants of protonation and acid dissociation of 1,2-diacylhydrazines in the first and second step respectively; A_{H2L}, $A_{\text{H3L}}+$, $A_{\text{HL}}-$, $A_{\text{L}}2-$ are optical densities of solutions containing neutral, protonated, and ionized in the first and second steps forms of acid **I** respectively, *A* is the optical density at a definite pH value, H_0 is Hammett's function depending on the molar HCl concentration [7].

For investigation of the distribution of acid **I** between organic and water phases 5 ml of its 0.1 M solution in kerosene and 25 ml of water solution of definite pH were placed in a separatory funnel of 50 ml capacity, and the funnel was shaken for 5 min. The mixture was left standing for 30 min to achieve the phase separation, then a sample of 0.5 ml was taken from the organic layer, diluted 200 times by kerosene and placed in a separatory funnel with 10 ml of water phase containing 0.5 ml of copper sulfate solution of concn. 0.01 M and ammonia to pH 10.7. The funnel was shaken for 5 min. The extract was filtered through a cotton wool and subjected to photometry at λ 465 nm in a cell of 1 cm on a spectrophotometer SF-2000. The content of reagent **I** in the sample was determined from the calibration curve corresponding to the range 0.01–0.5 mmol (λ 465 nm) analogously to method [8]. The distribution factors (*D*) of compounds **I** averaged over 2–3 measurements were calculated by the following formula:

$$D = [c_0 - \sum_{n=1}^{n} c_n\cdot(V_{\text{w}}/V_{\text{o}})]/c_n.$$

Here *D* is the distribution factor after the *n*th washing; c_0 is the initial concentration of acid **I** in the organic phase, M; c_n is the concentration of compounds **I** in the water phase after the *n*th washing, M; V_o, V_w are the volumes of organic and water phases, ml, respectively.

Hydrolysis test of acid I. *a.* A sample of acid **I** (0.04 mmol) was boiled at reflux for 4 h in 20 ml of 2M H_2SO_4 solution or in 20 ml of 1M KOH solution. On cooling 20 ml of EtOH was added and the solution was subjected to optical density measurement on a spectrophotometer SF-2000 in a quartz cell 1 cm thick. The extent of hydrolysis was estimated by the comparison of the absorption character and of the optical density at λ 200 and 247 nm of initial samples of the acid and the samples subjected to hydrolysis.

b. A weighed sample of acid **I** (0.1 g) was dissolved in 10 ml of octane and the solution was boiled at reflux for 4 h either with 20 ml of 2M H_2SO_4 solution or with 20 ml of 1M KOH solution. After every hour samples of 0.5 ml of the organic layer were taken and on cooling were subjected to GC-MS analysis with subsequent comparison.

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