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Physicochemical Properties and Complexing Ability of *N*-(2-Ethylhexanoyl)-*N*'-sulfonylhydrazines

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Abstract—The effect of substituent at the sulfonyl group on the physicochemical properties and complexing ability of the sulfonyl derivatives of 2-ethylhexanoic acid hydrazide of the general formula $C_4H_9CH(C_2H_5)C(O)\cdot NHNHSO_2C_6H_5R$ [R = H, CH_3, NO_2, $NHC(O)CH_3$, Cl] with respect to Cu(II), Co(II), and Ni(II) ions was studied.

Keywords: acylsulfonylhydrazines, physicochemical properties, complex formation, non-ferrous metals

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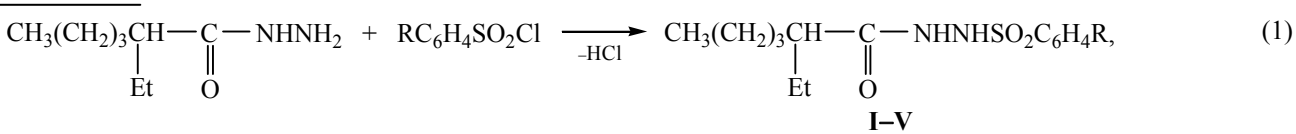
The interest to acyl derivatives of sulfonylhydrazides is connected with a wide spectrum of their application: surfactants, antioxidants, curing agents, a basis of power supply sources in electronic engineering, fungicides, drugs [1–3].

Much less attention was paid in the literature to their complexing properties with respect to nonferrous metals. At the same time, the presence of the hydrazide group makes it possible to consider these compounds as promising chelating ligands. For example, *N*'-sulfonylhydrazides of benzylic acid are known and suggested [4] for extraction-photometric determination of osmium; *N*-acyl-*N*'-(tosyl)- and *N*-acyl-*N*'-(mesyl)-hydrazines, which have more simple and synthetically accessible structure of the acyl radical, were investigated as potential flotation reagents of nonferrous metals [5]. The effect of the length of alkyl radicals of the acyl group of *N*-acyl-*N*'-tosyl(mesyl)hydrazines on the physicochemical and complexing properties was established [5, 6]. It was shown that considering the combined properties the most promising reagent for ionic flotation of nonferrous metals was *N*-2-ethylhexanoyl-*N*'-(tosyl)hydrazine [6].

The present work consists in the synthesis of *N*-(2-ethylhexanoyl)-*N*'-sulfonylhydrazines (**I–V**) (H_2L) as well as in the investigation of their physicochemical properties and the processes of complex formation with ions Cu(II), Co(II), Ni(II) in ammonia solutions in order to assess the possibility of their use in the processes on concentration of nonferrous metals. *N*-(2-Ethylhexanoyl)-*N*'-sulfonylhydrazines **I–V** were synthesized along Eq. (1)



(1)

I–V

R = H (**I**), CH_3 (**II**), NO_2 (**III**), $NHC(O)CH_3$ (**IV**), Cl (**V**).

Compounds **I–V** are white crystals; principal characteristics are presented in Table 1. They are practically insoluble in water, poorly soluble in hexane and toluene, moderately soluble in chloroform and ethanol, readily soluble in 0.1 M KOH (Table 2). Hence, *N*-(2-ethylhexanoyl)-*N*'-sulfonylhydrazines can

Table 1. Principal characteristics of compounds **I–V**

Comp. no.	mp, °C	ν, cm^{-1}				
		NHCO	$NHSO_2$	amide I	amide II	SO_2
I	106–108	3247	3210	1651	1536	1333, 1172
II	107–108	3320	3240	1669	1538	1380, 1135
III	117–119	3237	3203	1643	1529[a]	1311,[a] 1169
IV	207–209	3280, 3320	3180	1670, 1665	1535	1330, 1170
V	93–97	3335	3335	1663	1528	1345, 1160

[a] Overlapped with stretching vibrations of aromatic nitro group.

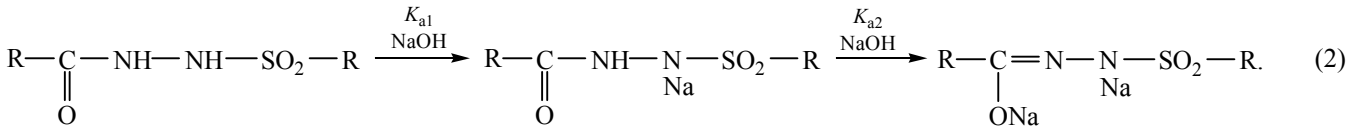
Table 2. Solubility (20°C) and the pK_a and pK_{a2} values of compounds **I–V**[a]

Comp. no.	Solubility, mol/L (g/L)					pK_{a1}	pK_{a2}
	EtOH	0.1 M KOH	toluene	chloroform	hexane		
I	6.17×10^{-1} (184)	6.03×10^{-2} (18.0)	2.86×10^{-2} (8.53)	6.33×10^{-1} (189)	3.35×10^{-4} (0.10)	9.40±0.13	13.45±0.18
II	4.00×10^{-1} (125)	9.50×10^{-2} (29.6)	–	1.00 (312)	4.50×10^{-4} (0.14)	9.20±0.14	14.43±0.38
III	1.89×10^{-1} (65.0)	8.12×10^{-2} (27.9)	5.82×10^{-4} (0.20)	1.65×10^{-1} (56.7)	1.75×10^{-3} (0.60)	7.59±0.05	–
IV	5.62×10^{-2} (20.0)	6.25×10^{-2} (22.2)	5.63×10^{-4} (0.20)	1.57×10^{-2} (5.60)	8.44×10^{-4} (0.30)	9.56±0.15	14.24±0.29
V	7.88×10^{-1} (262)	3.50×10^{-2} (11.7)	3.68×10^{-2} (12.3)	8.77×10^{-1} (292)	1.20×10^{-3} (0.40)	8.76±0.05	–

[a] $n = 5$, $P = 0.95$. Conditions of determination: $c_{\mathbf{I}} = 6 \times 10^{-5}$ mol/L, λ = 210 nm; $c_{\mathbf{II}} = 4 \times 10^{-5}$ mol/L; $c_{\mathbf{III}} = 6 \times 10^{-5}$ mol/L, λ = 220 nm; $c_{\mathbf{IV}} = 4 \times 10^{-5}$ mol/L, λ = 262 nm (pK_a) and λ = 225 nm (pK_{a2}); $c_{\mathbf{V}} = 4 \times 10^{-5}$ mol/L, λ = 220 nm.

be used as collecting agents in the processes of ionic flotation in the form of ethanol or alkali solutions.

Acylsulfonylhydrazines act as dibasic acids characterized by the dissociation constants K_{a1} and K_{a2} [Eq. (2)] [6]. The spectrophotometrically determined values of pK_{a1} and pK_{a2} are given in Table 2. As follows from the table, they are weak two-basic acids dissociating in two steps depending on the pH of the solution. For compounds **III** and **V** the values of pK_{a2} were not determined; apparently, the second dissociation step occurs only in very concentrated alkali.



(2)

The pK_{a1} values linearly correlate with the Hammett σ-constants according to Eq. (3):

$$pK_a = 9.44 - 2.33\sigma_{para},\ r = 0.986. \quad (3)$$

Complexation of the obtained sulfonylhydrazines with Cu(II), Co(II), and Ni(II) ions was studied by the method of precipitation sedimentation since the formed precipitates are insoluble in water and poorly soluble in conventional solvents. The time required for sedimentation of complexes was 10 min.

The dependence of degree of sedimentation of Cu(II), Co(II), Ni(II) ions is shown by the example of *N*-(2-ethylhexanoyl)-*N*'-benzenesulfonylhydrazine in Fig. 1. Other reagents of the series demonstrated similar dependencies. The maximum degree of

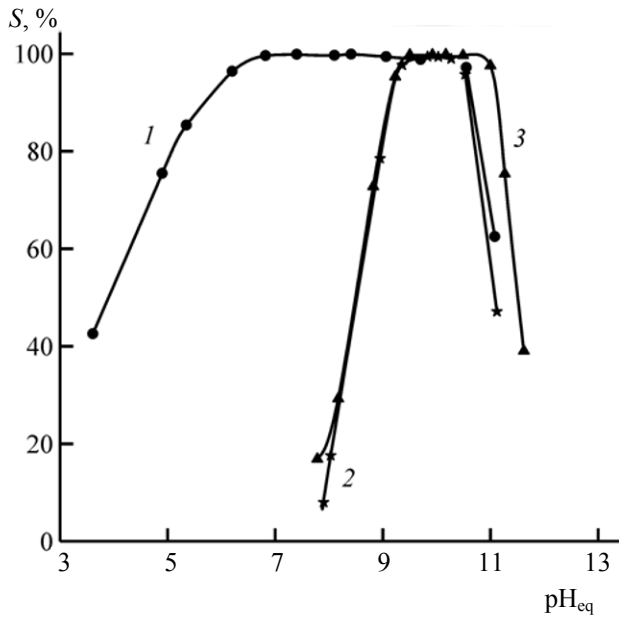


Fig. 1. Dependence of the degree of precipitation of metal ions (*S*, %) with *N*-(2-ethylhexanoyl)-*N*'-benzenesulfonylhydrazine (**I**) on pH_{eq} of the solution. $c^{init}_{M(II)}$, mg/L: (*1*) 64.3 [Cu(II)]; (*2*) 50.0 [Ni(II)]; (*3*) 48.5 [Co(II)]; [M(II)] : [I] = 1 : 2; pH was controlled by addition of NH_4OH solution.

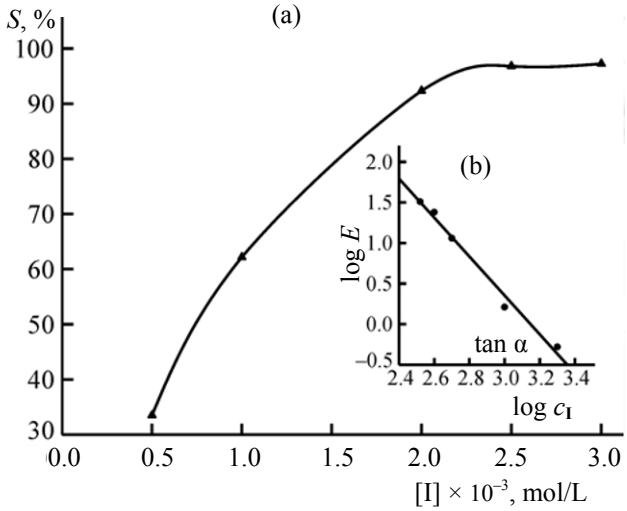


Fig. 2. Dependence of the degree of extraction of Cu(II) (*S*, %) on concentration of *N*-(2-ethylhexanoyl)-*N*'-benzenesulfonylhydrazine (a) and treatment by the method of shift of equilibrium (b). [I] = [Cu] = 1×10^{-3} mol/L; ammonia medium, pH = 9.9.

precipitation was for Cu(II) 99.9% (c_{res} = 0.068 mg/L) at pH = 6.5–10.0; Co(II), 99.9% (c_{res} = 0.067 mg/L) at pH = 9.5–11.0; Ni(II), 99.5% (c_{res} = 0.27 mg/L) at pH = 9.3–10.0.

Figure 2 shows the dependence of the degree of extraction of Cu(II) ions on the amount of the reagent and the processing of the curve of saturation by the method of equilibrium shift in the coordinates log ε–log c_R [where e is the sorption ratio; $e = S_i/(1 - S_i)$; S_i is the degree of precipitation]. The slope α is equal to 2.43 suggesting the formation of complex [Cu] : [I] = 1 : 2 in ammonia solutions during precipitation. This ratio was also proved by the method of isomolar series (Fig. 3) and conductometric titration (Fig. 4).

Complexes of Cu(II), Co(II), Ni(II) of [M(II)] : $[H_2L]$ = 1 : 2 composition are crystalline compounds of green, pink and blue-green color, respectively.

The IR spectra of the ligand and complexes were analyzed to determine the structure of the synthesized compounds (Tables 1, 3). In the spectra of the reagents, two absorption bands are observed related to stretching vibrations of the NH bonds; the spectra of complexes Cu(II) and Co(II) contain one band, which proves the structure of the ligand in the ionized by the first step form (HL^-). The second NH absorption band in Ni(II) complex at 3373 cm^{-1} corresponds to vibrations of NH_3 molecules in compliance with the results of the elemental analysis. The ratio of integral intensities in the ^1H NMR spectra for the signals of aliphatic and aromatic protons and the NH signals at 9.98 and 10.07 ppm in the molecule of the reagent is

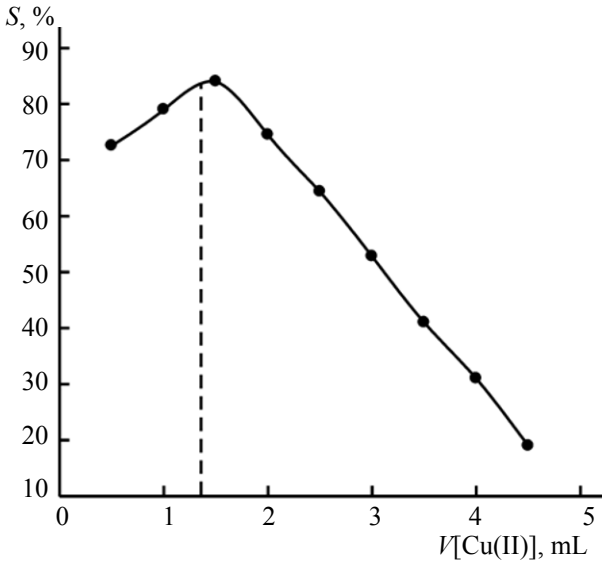


Fig. 3. Determination of the ratio of the components in complex [Cu(II)] : [reagent] by the method of isomolar series. $c^{init}_{Cu(II)} = c^{init}_{reagent} = 1 \times 10^{-2}$ mol/L; ammonia medium, pH = 9.9.

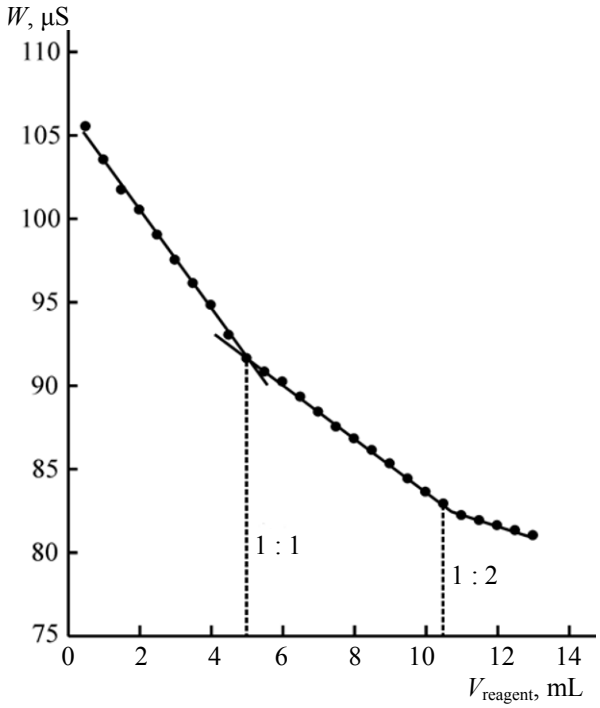


Fig. 4. Variation of electroconductivity of ammonia solution (W) of Ni(II) on the amount of the added solution of *N*-(2-ethylhexanoyl)-*N*'-benzenesulfonylhydrazine. $c^{init}_{Ni(II)} = c_{reagent} = 1 \times 10^{-3}$ mol/L; $V_{Ni(II)} = 5$ mL, $V_0 = 70$ mL (EtOH : H_2O = 1 : 2), ammonia medium, pH = 10.6.

2 : 20; in complex of [Co(II)] : [HL^-] = 1 : 2 composition it is 2 : 38, which also is indicative of form HL^-.

The C=O stretching vibrations band in complexes M(II) is shifted by 50–116 cm^{-1} to low frequencies relative to that in the ligand, which is indicative of coordination of the ligand to the metal via the carbonyl oxygen atom. In complexes of Co(II) and Ni(II) the absorption bands at 3489 and 3480 cm^{-1}, respectively, are caused by the presence of water [8]. The presence of crystallization water in complexes of Ni(II) and Co(II) is confirmed by the data of thermal analysis. The DTA curve of the Ni(II) complex shows the endothermic effect in the range 104–143°C with the minimum at 125°C, which can be assigned to the loss of crystallization water (mass loss of 3.02% corresponds to the theoretically calculated content of water (2.62%) in the suggested complex). For the complex of Co(II), the loss of mass at 130°C is 4.82%, also in good agreement with the theoretically calculated value of 5.23%.

The data of elemental, thermal analysis, and IR spectroscopy of the studied complexes are most close to the calculated values for the compounds $Cu(HL)_2$, $Co(HL)_2 \cdot 2H_2O$, $[Ni(NH_3)(HL)_2] \cdot H_2O$ in agreement with the earlier obtained data for other series of acylsulfonylhydrazines [6].

The solubility of the complexes is essential for evaluation of the possibility of using the reagents in the processes of ionic flotation. The values of solubility product (SP) for complexes were calculated as was described [9] but without taking into account the ionic states of the metals above the precipitate (Table 4). The experimentally obtained degrees of precipitation and calculated by the procedure [10] equilibrium constants prove the completeness of the complexation reaction (Table 4).

The effect of the substituent in the sulfonyl group in the series of the obtained sulfonylhydrazines on the degree of extraction of Cu(II) (Table 5) is satisfactorily described by the linear dependence of the –log SP values of compounds **I, III, IV, V** on the Hammett σ-constants. For the Cu(II) ions the correlation is expressed by Eq. (4).

$$-\log SP = 20.01 - 0.69\sigma_{para},\ r = 0.950. \quad (4)$$

Therefore, high solubility in alkali solutions, stability to alkaline hydrolysis, low solubility of complexes with nonferrous metals in water meet the requirements imposed on potential collecting agents for ionic flotation. On the basis of all properties, the optimal reagent from the studied series is *N*-(2-ethylhexanoyl)-*N*'-benzolsulfonylhydrazine.

Table 3. Parameters of IR spectra of *N*-(2-ethylhexanoyl)-*N*'-(benzenesulfonyl)hydrazine (**I**) and its complexes with Cu(II), Co(II), and Ni(II) (ν, cm^{-1}, suspension in mineral oil)

Compound	N–H	C=O	SO_2	O–H (H_2O)
I	3209, 3247	1654	1332, 1171	–
[Cu(II)] : [I] = 1 : 2	3356	1538	1322, 1141	–
[Co(II)] : [I] = 1 : 2	3260	1604	1339, 1136	3489
[Ni(II)] : [I] = 1 : 2	3262, 3373 (NH_3)	1602	1340, 1140	3480

Table 4. Values of –log SE of complexes formed by M(II) ions with *N*-(2-ethylhexanoyl)-*N'*-benzene-sulfonylhydrazine (H_2L) in ammonia media[a]

Compound	pH_{eq}	*S*, %	$[M]_{eq}^{res}$, mol/L	$[HL^-]$, mol/L	$K([Me(NH_3)_4]^{2+})$	–log SE	K_{eq}
$Cu(HL)_2$	8.41	99.89	1.07×10^{-6}	2.25×10^{-7}	9.33×10^{-13}	19.27	1.72×10^{7}
$[Co(HL)_2]\cdot 2H_2O$	10.17	99.86	1.14×10^{-6}	1.65×10^{-5}	8.51×10^{-6}	15.51	2.74×10^{10}
$[Ni(NH_3)(HL)_2]\cdot H_2O$	9.83	99.46	4.61×10^{-6}	2.90×10^{-5}	3.40×10^{-8}	16.51	1.10×10^{9}

[a] $[M(II)] = 1.0 \times 10^{-3}$ mol/L; $[H_2L] = 2.0 \times 10^{-3}$ mol/L.

Table 5. Values of –log SP of complexes of compounds **I–V** with Cu(II) ions in ammonia media[a]

Comp. no.	S_i, %	$[Cu]_{eq}^{res}$ mol/L × 10^6	pH_{eq}	$[[HL^-]$, mol/L	–log SE	K_{eq}
I	99.89	1.07	8.4	2.25×10^{-7}	19.27	1.72×10^{7}
II	99.90	6.80	9.0	1.26×10^{-6}	16.97	8.64×10^{4}
III	99.82	1.82	7.5	1.22×10^{-6}	17.95	6.91×10^{5}
IV	99.91	0.92	9.1	6.09×10^{-7}	18.47	2.74×10^{6}
V	99.80	2.02	7.6	2.59×10^{-7}	18.87	6.91×10^{6}

[a] $[Cu] = 10^{-3}$ mol/L; $[H_2L] = 2.0 \times 10^{-3}$ mol/L.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrometer IFS-66 (Bruker), ^{1}H NMR spectra were registered on a Bruker Avance III HD spectrometer, 400 MHz, in DMCO-d_6. UV spectra were taken on an SF-2000 spectrophotometer (OKB Spektr). pH values were measured on an ANION 4100 ionomer with combined electrode ESK-10603/7. Elemental analysis was performed on an CHNS-932 analyzer (LECO Corporation). The conductometric titration was carried out on a SEVEN MULTI S70-K conductometer (Mettler). Metal content was determined on iCE 3500 atomic absorption spectrophotometer with flame atomization (Thermo Scientific, США). Thermal analysis was performed on a synchronous thermoanalyzer STA 449 C Jupiter and quadruple mass spectrometer QMS 403 C Aeolos (Netzsch).

The solubility of compounds in alcohol, toluene, and chloroform was measured by the method of refractometry [11], in hexane, by gravimetry [12], in 0.1 M KOH solution, spectrophotometrically [12]. First and second ionization constants of sulfonylhydrazines were determined spectrophotometrically [13]. The complexation of sulfonylhydrazines with ions of nonferrous metals M(II) was studied by the method of sedimentation as decribed in [9]. The preparative isolation of complexes and their analysis was performed as described in [9].

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