Soviet-era science, translated into English

Corresponding Member of the Academy of Sciences of the USSR I. P. ALIMARIN and D. I. KUZNETSOV

1960

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196001.88417

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

structural formulas of *o*-hydroxybenzenesulfinic acid (I) and salicylic acid (II)

Figure 1: structural formulas of *o*-hydroxybenzenesulfinic acid (I) and salicylic acid (II)

Fig. 1. Absorption curves of aqueous solutions of *o*-hydroxybenzenesulfinic acid and salicylic acid

Figure 2: Fig. 1. Absorption curves of aqueous solutions of *o*-hydroxybenzenesulfinic acid and salicylic acid

Abstract

Full Text

Corresponding Member of the Academy of Sciences of the USSR I. P. ALIMARIN and D. I. KUZNETSOV

o-HYDROXYBENZENESULFINIC ACID—A NEW ANALYTICAL REAGENT AND STRUCTURAL ANALOG OF SALICYLIC ACID

Sulfinic acids may be regarded as analogs of carboxylic acids. The analytical use of aromatic sulfinic acids is in a number of cases more advantageous than the use of aromatic carboxylic acids: sulfinic acids dissolve better in water, precipitate certain metals from a more acidic medium, and possess a more selective action ([1–4]).

It was of interest to synthesize and study the analytical behavior of *o*-hydroxybenzenesulfinic acid (I)—a structural analog of salicylic acid (II).

The acid, obtained by us for the first time, consists of colorless prismatic crystals readily soluble in water. Recrystallized from ether, they had m.p. 71°. The analysis performed showed that the percentage sulfur content in this compound corresponds to the theoretical content.

Absorption spectra of this acid were recorded (see Fig. 1, in which only two selected curves I are presented for comparison with the absorption curve II) at various pH values, and on the basis of the obtained absorption curves K'_{OH} was determined—the apparent dissociation constant of the OH group of this reagent. In solution the sulfinic group dissociates, apparently completely, since the concentration of hydrogen ions, measured with a glass electrode in a precisely prepared 0.01 M solution of *o*-hydroxybenzenesulfinic acid, was $1.38 \cdot 10^{-2}$ g-ion H^+, i.e., pH 1.86; therefore the method of isosbestic points used for determining K'_{OH} is not applicable for determining the dissociation constant of the $\mathrm{SO_2H}$ group.

Fig. 1. Absorption curves of aqueous solutions of *o*-hydroxybenzenesulfinic acid and salicylic acid: *a*—nonionized form I (at pH 6); *b*—ionized form I (at pH 11.98); *v*—nonionized form II (at pH 6, with the plotted value $\varepsilon_{\mathrm{II}}$ increased 10-fold)

The determination of K'_{OH} by this method (^{5,6}) was carried out by solving two equations:

$$D = D_0\left(1 + \frac{K'_{\mathrm{OH}}}{[\mathrm{H}^+]}\right) \quad \text{and} \quad K'_{\mathrm{OH}} = \frac{D - D_0}{D_1 - D}[\mathrm{H}^+],$$

where D_1, D_0, and D are the optical densities of solutions containing, respectively, molecules of this acid with the OH group ionized, nonionized, and a mixture of molecules in the ionized and nonionized forms; $[\mathrm{H}^+]$—

the molar concentration of hydrogen ions in a solution containing a mixture of molecules in the above-mentioned forms. The mean value of K'_{OH} was calculated from 5 values obtained from the transformed equation:

$$K'_{\mathrm{OH}} = \frac{D - D_0}{D_0}\,[\mathrm{H}^+].$$

The data obtained are presented in Table 1.

Table 1

pH	H^+	D	D_0	K'_{OH}	$K'_{\mathrm{OH,\,mean}}$
8.34	$4.57 \cdot 10^{-9}$	0.075	0.0125	$2.29 \cdot 10^{-8}$	$7.15 \cdot 10^{-9}$ $(pK'_{\mathrm{OH}} =$ $= 8.15)$
9.15	$7.08 \cdot 10^{-10}$	0.125	0.0125	$6.37 \cdot 10^{-9}$	
9.55	$2.82 \cdot 10^{-10}$	0.150	0.0125	$3.10 \cdot 10^{-9}$	
9.65	$2.24 \cdot 10^{-10}$	0.165	0.0125	$2.93 \cdot 10^{-9}$	
10.38	$4.17 \cdot 10^{-11}$	0.200	0.0125	$6.26 \cdot 10^{-10}$	

For the reagent obtained, by analogy with II, one should have expected the formation of characteristic compounds with a number of metals and, in particular, with Fe^{3+}.

The light-absorption curves of complexes of *o*-hydroxybenzenesulfinic acid with Fe^{3+} were recorded (see Fig. 2). It is evident from Fig. 2 that the first violet complex ($\lambda_{\max} = 523$–527 mμ) exists over a broad pH interval, 1.9-7.53 (the pH region below 1.9 was not studied); the strongly absorbing second complex ($\lambda_{\max} = 336$–$337, 345$ mμ) exists in the narrow pH interval 8.34-8.71 and is in equilibrium with the third complex ($\lambda_{\max} = 406$–410 mμ), which forms in the pH interval 8.34-9.02. At pH values above 9, turbidity of the solution is observed, associated with decomposition of the complex and formation of $\mathrm{Fe(OH)}_3$.

SovietRxiv

Fig. 2. Light-absorption curves of solutions of the Fe^{3+} complex with I at different pH values (shown by solid lines). 1—pH 1.9-7.53; 2—pH 8.34; 3—pH 8.57; 4—pH 8.71; 5—pH 9.02. Iron concentration = $2.04 \cdot 10^{-4}$ mole/liter; cuvettes = 1.00 cm; concentration of I = 0.04%. (The light-absorption curve of the reagent is shown by a dashed line.)

Figure 3: Fig. 2. Light-absorption curves of solutions of the Fe^{3+} complex with I at different pH values (shown by solid lines). 1—pH 1.9-7.53; 2—pH 8.34; 3 —pH 8.57; 4—pH 8.71; 5—pH 9.02. Iron concentration = $2.04 \cdot 10^{-4}$ mole/liter; cuvettes = 1.00 cm; concentration of I = 0.04%. (The light-absorption curve of the reagent is shown by a dashed line.)

Fig. 2. Light-absorption curves of solutions of the Fe^{3+} complex with I at different pH values (shown by solid lines). 1—pH 1.9-7.53; 2—pH 8.34; 3—pH 8.57; 4—pH 8.71; 5—pH 9.02. Iron concentration = $2.04 \cdot 10^{-4}$ mole/liter; cuvettes = 1.00 cm; concentration of I = 0.04%. (The light-absorption curve of the reagent is shown by a dashed line.)

Using the Ostromyslensky-Job method, we established that at pH 1.9 the molar ratio of reagent and Fe^{3+} for the violet complex is 1 : 1 (the measurement was carried out at 500 mμ and 415 mμ). At pH 6 and above, the components of the buffer mixture interfere, and the molar ratio could not be established owing to the formation of acetate complexes of iron under these conditions. Foley and Anderson (7) similarly note the impossibility of determining by this method the ratio of moles of Fe^{3+} and sulfosalicylic acid in complex compounds in alkaline buffer solutions. Taking into account that at pH 1.9 dissociation of the OH group should be completely suppressed, while the sulfinic group, on the contrary, under these conditions is fully ionized and reactive, we believe that the composition of the violet complex can probably be expressed by the formula:

[structural formula shown in the source] [structural formula shown in the source] [structural formula s

Comparing the data on the spectrophotometric study of the complexes of *o*-hydroxybenzenesulfinic acid and salicylic (or sulfosalicylic) acid (8–11) with Fe^{3+} (see Table 2), one can find an analogy in the behavior of these acids: they form three complex compounds with Fe^{3+}, and

Table 2

SovietRxiv

Fig. 3. Curve of the dependence of D of a solution of the complex UO_2^{2+} with I on pH. Uranium concentration $1.68 \cdot 10^{-4}$ mol/l

Figure 4: Fig. 3. Curve of the dependence of D of a solution of the complex UO_2^{2+} with I on pH. Uranium concentration $1.68 \cdot 10^{-4}$ mol/l

Acids	Sequential number of the complex	pH interval of existence of the complex	λ_{max}	ε_{max}	Sensitivity, γ in 1 ml
o-Hydroxybenzenesulfinic	1	1.9—7.53	523—527	1440	0.4
o-Hydroxybenzenesulfinic	2	8.34—8.71	336—337,345	6960	0.08
o-Hydroxybenzenesulfinic	3	8.34—9.02	406—410	1620	0.35
Sulfosalicylic	1	0.7—2.0	497	1800*	0.3*
Sulfosalicylic	2	4.8—5.8	464	4300*	0.13*
Sulfosalicylic	3	above 8	427	5750*	0.1*

* Calculated by us from literature data (8).

the absorption maxima of the 1st and 3rd complexes almost coincide; there is the same reagent : Fe^{3+} ratio in the first violet complex; the sensitivity of the reaction is of the same order.

The stability of the violet complex (I) with Fe^{3+} (several days), as well as obedience to the laws of light absorption even in the range of fairly low concentrations, 0.18—0.9 γ Fe^{3+} in 1 ml, makes it possible to use this reagent for the quantitative determination of iron.

o-Hydroxybenzenesulfinic acid forms soluble complexes with some other metals, mainly in alkaline medium, including colored ones: orange-red with the uranyl ion, brown with cobalt, yellow-brown with nickel, emerald-green with copper. It seemed of interest to examine the reaction of U(VI) with this reagent. We obtained a curve of the dependence of the optical density of a solution of the uranium complex with I on the pH of the solution (Fig. 3), on which there are two clearly expressed maxima. The assumption that two complex compounds of U(VI) with *o*-hydroxybenzenesulfinic acid exist in weakly acidic (pH 6.56) and weakly alkaline (pH 8.71) media was confirmed when the absorption curves of solutions of the complexes at these pH values were obtained (the maximum of the absorption curve of the 1st complex is located at 326 mμ, and of the second at 362 mμ).

SovietRxiv

Fig. 3. Curve of the dependence of D of a solution of the complex UO_2^{2+} with I on pH. Uranium concentration $1.68 \cdot 10^{-4}$ mol/l.

The sensitivity of the reaction of our reagent with uranium at pH 8.71 in borate buffer is 1.4 γ U in 1 ml. Obedience to the laws of light absorption exists even in the concentration range 2—50 γ U in 1 ml, which can be used for the quantitative determination of uranium. The sensitivity of the sulfosalicylate reaction is equal to 7γU in 1 ml (12).

Finally, it should be noted that the presence of the sulfinic group in the molecule of the reagent described causes the formation of insoluble precipitates with Ti, Zr, Th, U(IV), Sc, Bi, and some other metals. Of particular interest is the behavior of the yellow-orange precipitate of *o*-hydroxybenzenesulfinic acid with Ti: it is not extracted by organic solvents, but dissolves in those that mix with water and contain an alcoholic group. The precipitates of the other listed cations do not possess this property.

possess. The light-absorption curve of a solution of the Ti complex with (I) at pH 1-2 in a mixture with ethyl or isopropyl alcohol at a ratio of 1 : 1 (optimal reaction conditions) has a maximum at $\lambda = 329$–330 mμ ($\varepsilon_{\text{max}} = 1160$). The sensitivity of this reaction (0.4 γ Ti in 1 ml), its obedience to the laws of light absorption over the concentration interval 3.5–50 γ Ti in 1 ml, and its stability with time (12 h) make it possible to use this reaction for the quantitative determination of Ti. It is of interest to say a few words about the compound of Ti with this organic substance in 96% H_2SO_4. It is known that under these conditions salicylic acid with Ti gives a red coloration. We have established that such a reaction is characteristic of all phenols and compounds with an enol grouping, including β-naphthol, 8-hydroxyquinoline, etc. (which may be used as a qualitative reaction for the enol group). *o*-Hydroxybenzenesulfinic acid in 96% H_2SO_4 itself becomes blue (a qualitative reaction for the sulfinic group), but in the presence of Ti changes the coloration to red.

Discussing the results obtained and comparing the properties of *o*-hydroxybenzenesulfinic and salicylic acids, as well as their behavior toward metal cations, one can draw certain conclusions that are of theoretical interest. The new organic compound retains almost all the chemical properties characteristic of II, but, unlike salicylic acid, reacts with a number of metals in a more acidic medium, which is its analytical advantage. Analogous precipitates with salicylic acid are formed in acidic medium, but are immediately decomposed with precipitation of the free acid. A special property of the sulfinic group —to exist in two tautomeric forms (13)—increases the dissociation constant of this acid and at the same time ensures the formation of compounds in acidic medium. In its physical properties, *o*-hydroxybenzenesulfinic acid differs rather sharply from salicylic acid: its melting point is approximately half that of the latter; it is more soluble in water; it fluoresces barely perceptibly; it sublimes less readily (only in vacuum); the sulfinic group of this acid dissociates completely, pK' of its OH group is 8.15, whereas pK' of the carboxyl group of salicylic acid is 3 and pK' of the OH group is 13.4 (11). The similarity of the chemical properties of these acids emphasizes the real analogy in their structure, while the differences in their physical properties can be explained by the ability of the sulfinic group to exist in two equilibrium forms with tetravalent and hexavalent sulfur atoms.

Moscow State University
named after M. V. Lomonosov

Received
19 X 1959

CITED LITERATURE

1. G. J. Henning, Chem. weekbl., **51**, 519 (1955).
2. J. Thomas, J. Chem. Soc., **95**, 342 (1909).
3. I. P. Alimarin, S. S. Alikberov, Zav. lab., **24**, 804 (1958).
4. T. R. Forrest, D. E. Ryan, Canad. J. Chem., **36**, 1674 (1958).
5. W. Stenström, N. Goldsmith, J. Phys. Chem., **30**, 1683 (1926).
6. C. V. Banks, A. B. Carlson, Anal. Chim. Acta, **7**, 292 (1952).
7. R. T. Foley, R. C. Anderson, J. Am. Chem. Soc., **72**, 5609 (1950).
8. L. Vareille, Bull. Soc. chim. France, **22**, 873 (1955).
9. L. Vareille, Bull. Soc. chim. France, **22**, 1494 (1955).
10. A. K. Babko, ZhOKh, **16**, 968 (1946).
11. P. Romain, J. C. Colleter, Bull. Soc. chim. France, **25**, 867 (1958).
12. *Analytical Chemistry of Uranium and Thorium*, Moscow, 1956, p. 159.
13. J. Howben, Th. Weyl, *Methoden der organischen Chemie*, **9**, Stuttgart, 1955, p. 289.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.