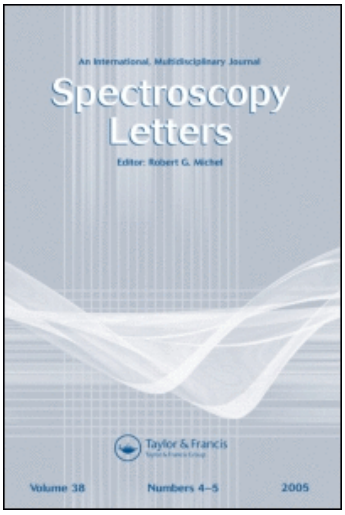

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SULPHONATION OF MONOHYDROXYBENZENE AND DETERMINATION OF THE ACIDITY CONSTANTS OF 2-MONOSULPHOHYDROXYBENZENE

Key words: hydroxybenzene, sulphuric acid, sulphonation, Na-salt of sulphonated hydroxybenzene, UV/VIS spectroscopy, acidity constants.

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Abstract

2-monosulphohydroxybenzene is spontaneously formed as a white deposit in a 3mol/dm^3 solution of monohydroxybenzene in 96% sulphuric acid after nine days at 298K. The composition of this compound was determined by using Rast's method as well as AAS, IR and UV/VIS spectroscopy. Determination of acidity constants of 2-monosulphohydroxybenzene was done by using pH-metric and spectrophotometric titration.

Introduction

Literature data show that sulphonation occurs after dissolution and fast protonation in solutions of hydroxybenzenes and their derivates[1-8] in sulphuric acid. After dissolution of monohydroxybenzene in 96% sulphuric acid o-product is built at the room temperature. Acidity constant of monohydroxybenzene is $Ka=1.3x10^{-10}$ [9]. There are no data in the literature on acidity constants of sulphonated monohydroxybenzene.

Experimental

In the experiments the following were used: monohydroxybenzene, 96% H_2SO_4, camphor, NaOH, NaCl, HCl, KNO_3, KBr and ethanol (96%), all p.a. as well as ion exchange resin. pH measurements were performed using pH-meter JENCO 6071. Solutions were thermostated by a thermostat (±0.1K). UV/VIS spectra were obtained using a Perkin-Elmer Lambda 15 Spectrophotometer with a 1cm quartz cell. IR spectra were recorded on a Perkin-Elmer IR spectrophotometer, model 983, using the KBr pellet technique. Natrium was determined by AAS method on a Perkin-Elmer-1100 spectrophotometer, model MHS-10.

Results and discussion

Preparation of sulphonated product. A $25cm^3$ of $3mol/dm^3$ solution of monohydroxybenzene in 96% H_2SO_4 was prepared. A solid product of

sulphonated monohydroxybenzene was formed after nine days at 298K. The product was separated by filtration and dissolved in saturated NaCl solution to obtain Na-salt. After drying in an desiccator with $CaCl_2$, recrystallization from ethanol was performed in order to eliminate NaCl (the product was dissolved in water and by adding ethanol the crystals occurr again). The Na-salt of sulphonated monohydroxybenzene is a white crystalline substance, soluble in water.

Characterization of sulphonated product. UV/VIS absorption spectra of monohydroxybenzene and Na-salt of sulphonated monohydroxybenzene (NaSPh) are given at Figure 1.

At spectra of product maximums undergo a bathochromic shift (Table 1) and a new maximum at 202.8 nm has occurred. On the basis of literature data[10] it can be concluded that hydroxybenzene was sulphonated.

The molecular mass of Na-salt of sulphonated hydroxybenzene was determined by using Rast's method[11]. Experimentally determined and calculated values for molecular mass (the calculated value is for Na-salt of monosulphonated hydroxybenzene) are 199g/mol and 196g/mol respectively. Relative determination error is δ=2%.

It was found that the Na-salt of sulphonated hydroxybenzene contains 11.85% Na. Calculated value for Na content of Na-salt of monosulphonated hydroxybenzene is 11.73%. According to this data the determined molecular mass formula of the resulting product is $C_6H_5SO_3Na$.

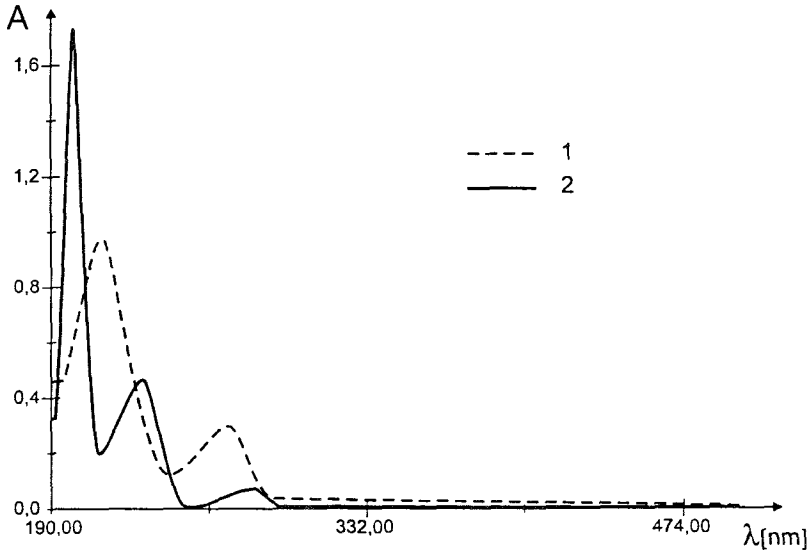

Figure 1. **UV/VIS spectra of monohydroxybenzene (1) and NaSPh (2); $C_1=C_2=1x10^{-4}$mol/dm^3; I=0,1; pH=3,5; T=298±0,1K**

*Table 1.***Band position and intensities of UV/VIS spectra of monohydroxybenzene and NaSPh**

	λ_{max}[nm]	A
phenol	217.0	0.966
	269.6	0.296
NaSPh	231.8	0.437
	279.4	0.083
	202.8	1.730

Band positions of IR spectra of hydroxybenzene and sulphonated product (Fig 2) are given in Table 2. In the spectra of product new bands within the range of 1250-1140cm^{-1} (band at 1222cm^{-1}) appeared. Bands in this range are from S-O vibrations and therefore are proof for presence of one or more sulpho groups in the product[12]. From the same spectra we can also observe the band at 743cm^{-1} which can point on monosubstitution of hydroxybenzene in the ortho position[12].

On the basis of the literature data as well as those presented in these results it can be concluded that the sulphonated product is o-monosulphohydroxybenzene (SPh).

Determination of SPh dissociation constant. Using cationic ion-excange resin in the H^+ form, the Na salt of SPh was transformed into an acid by passing an aliquot of the product, which was dissolved in 5cm^3 of deionizated water, through a column of resin. The procedure was repeated until total substitution of Na^+ by H^+ ions occurred (to the constant pH value).

Titration of 10 cm^3 of SPh solution, with a concentration of 0.0200mol/dm^3, was completed with 0.1mol/dm^3 of standard NaOH solution at a temperature of 298K. pH value was measured 15 sec after adding aliquots of NaOH solution. The titration curve is shown in Fig 3.

By using the following equation[13]:

$$\log K = \log \frac{a \cdot C_L - [H^+] + [OH^-]}{(1-a) \cdot C_L + [H^+] - [OH^-]} + pH \qquad (1)$$

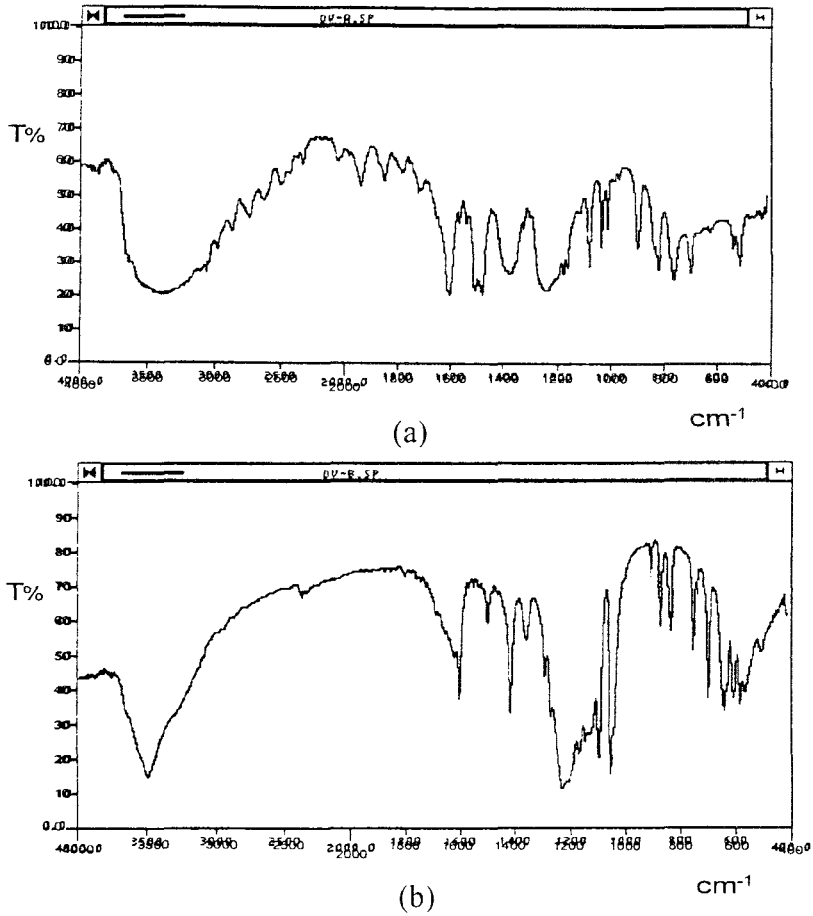

Figure 2. **IR spectra of monohydroxybenzene and NaSPh**

Table 2. **Band position and intensities of IR spectra of monohydroxybenzene and NaSPh**

	υ,cm^{-1}							
phenol	3852	3750	3626	3351	3048	2961	2851	2726
	2618	2482	2322	2052	1934	1844	1780	1715
	1596	1557	1530	1500	1472	1373	1316	1235
	1169	1153	1071	1025	1000	888	811	754
	691	619	531	508	424	410		
NaSPh	3949	3930	3903	9884	3871	3853	3838	3819
	3801	3768	3749	3735	3724	3689	3469	2358
	2323	1868	1845	1792	1772	1773	1716	1683
	1646	1610	1595	1559	1542	1521	1507	1494
	1457	1409	1351	1285	1263	1222	1158	1136
	1086	1042	898	864	832	824	743	730
	689	630						

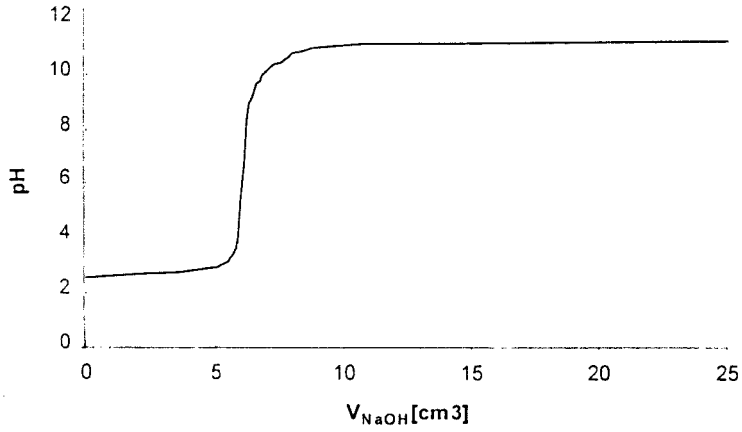

Figure 3. **Titration curve of SPh with standard NaOH solution; C_{SPh}=0.0200mol/dm^3; C_{NaOH}=0.1mol/dm^3; T=298±0.1K**

the protonation constant (a value inversely proportional to the dissociation constant) was calculated. Points from the titration curve given in Figure 3, which were used for the calculations are given in Table 3.

The determination was completed for different values of *a* (from a=0.1 to a=0.9). The concentration of OH^- ions was neglected because pH<9 and $C_L>10^{-3}$. The calculation was done by using the concentration of H^+ ions obtained by previously measurement of their activity. Since the solutions used were diluted, the values of the activity factor, as well as their change in the vicinity of the half-neutralization point, were lower than the dissociation constant determination error. Therefore, no correction of H^+ concentration was done.

As the average value of the two titrations and nine values for each titration provided the following result:

$$\log K_{SPh}=2.52\pm0.15$$

The sulpho group is much stronger than the hydroxyl group. Therefore, value of the acidity constant of the sulpho group of SPh is presented. Changes in the curve caused by the hydroxyl group can not be noticed.

Spectrophotometric titration[13] was done for the Na-salt of SPh (NaSPh) and is given in Figure 4 while band positions and intensities of absorbance is given in Table 4.

At low pH values (pH=2.31) only acid form of NaSPh is present in solution and three maximums can be noticed: at 206.6nm, 232nm, and 279.6nm.

Table 3. **Points from titration curve given in Figure 3, which were used for calculation of the SPh dissociation constant; C_{SPh}=0.0200mol/dm^3; C_{NaOH}=0.1mol/dm^3; T=298±0.1K**

a	V_{NaOH}[ml]	pH
0.1	0.60	2.60
0.2	11.2	2.65
0.3	11.8	2.70
0.4	12.4	2.72
0.5	13.0	2.75
0.6	13.6	2.80
0.7	14.2	2.87
0.8	14.8	2.95
0.9	15.4	3.10

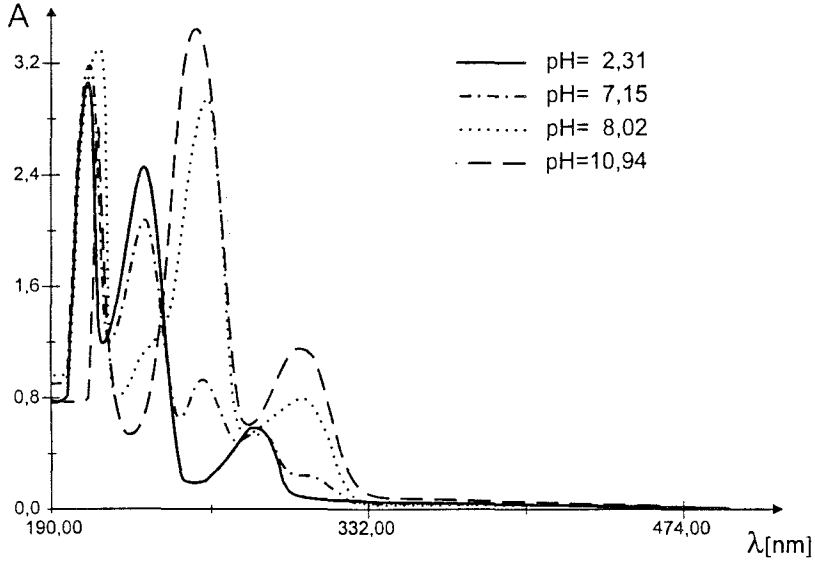

Figure 4. **Absorption spectra of NaSPh solution on different pH values; C_{NaSPh}=5x10^{-4}mol/dm^3; I=0.1, T=298±0.1K**

Table 4. **Band positions and intensities of absorbance for absorption spectra of NaSPh given in Figure 4; C_{NaSPh}=5x10^{-4}mol/dm^3; I=0.1, T=298±0.1K**

NaSPh		
pH	λ_{max}[nm]	A
	212.6	2.710
10,94	258.0	3.402
	302.4	1.138
	211.0	3.307
8,02	257.0	2.948
	301.8	0.785
	207.4	3.195
7,15	232.2	2.087
	258.4	0.932
	280.0	0.537
	206.6	3.004
2,31	232.0	2.452
	279.6	0.583

With increased pH value (pH=7.15) both acid and base form are present in solution. The intensity of previous showen maximums is lower and new maximums occurred: at 258.4nm and 302nm. At pH value of pH=10.94 only the base form is present in solution. The maximum at 280nm doesn't exist and the absorbance is higher for the maximum at 258nm and 302nm. The isobestic value for NaSPh is at 240nm.

For Figure 5, spectra of the hydroxybenzene water solution at different pH values are given while band positions and intensity of absorbances are given in Table 5. A bathochromic shift of the maximum at 252.8nm with an increased pH value of the solution can be noticed.

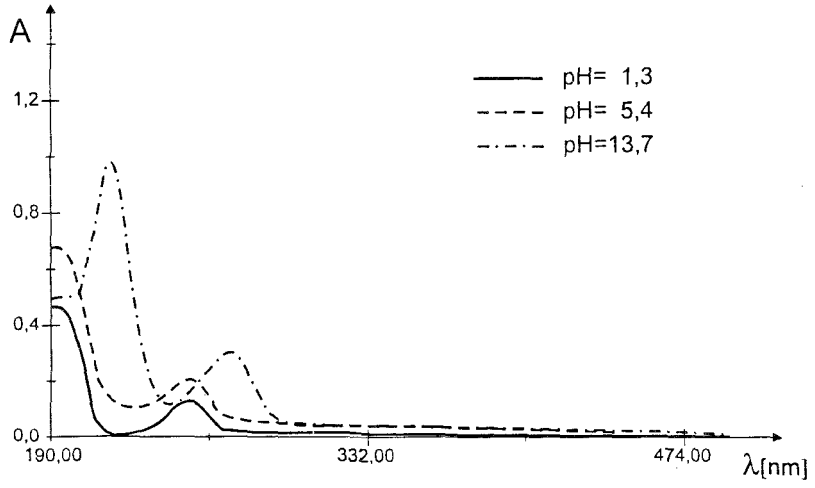

Figure 5. **Absorption spectra of hydroxybenzene water solution on different pH values C_{Ph}=2x10^{-4}mol/dm^3 , I=0.1, T=298±0.1K**

Table 5. **Band position and intensity of absorbance for absorption spectra of the hydroxybenzene water solution at different pH values given in Figure 5; C_{Ph}=2x10^{-4}mol/dm^3, I=0.1, T=298±0.1K**

pH	λ_{max}	A
1,31	194,0	0,464
	252,8	0,124
5,40	194,0	0,681
	252,4	0,206
13,78	217,0	0,966
	269,6	0,296

A similar spectral intensity shift is noticed in spectra of NaSPh, so it can be concluded that with the changing the pH in solution the following equilibria can be presented for both hydroxybenzene and NaSPh solutions:

According to the work presented the acidity constant of the hydroxyl group of SPh can be calculated by using the spectrophotometric method[13] and determined values are given in Table 6. During the calculations following equation was used[13]:

$$\log K = \log \frac{A_L - A}{A - A_{HL}} + pH \qquad (2)$$

pH values were revised by using the equation:

$$a = f \cdot c \qquad (3)$$

The ionic strength value during the titration was always I=0.1 so the activity coefficient value[14] was $f_{H^+} = 0.76$.

The value for log K can also be calculated from graph A=f(pH) which is given in Figure 6. According to the literature data[15] $pH_{1/2}$=logK. The logK value

Table 6. **Values for SPh acidity constant calculated by using spectrophotometric method; I=0.1, T=298±0.1K**

λ[nm]	logK	$logK_{sr}$	Δ_K
250	7.61	7.58	0.03
260	7.53		0.05
300	7.60		0.02

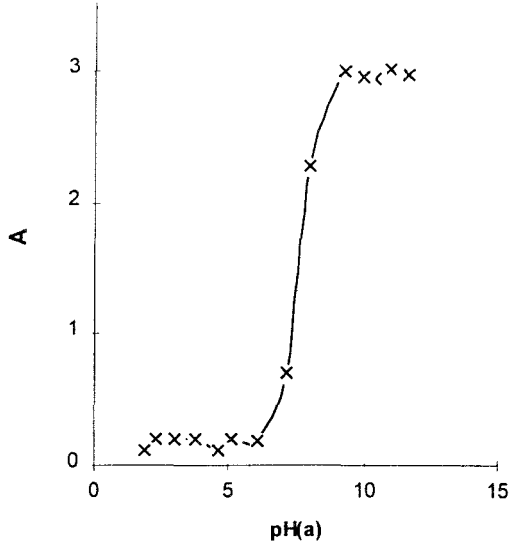

Figure 6. **The dependence of the absorbance of the NaSPh solution on the pH value; C_{NaSPh} =5x10^{-4}mol/dm^3; I=0,1; λ =250nm**

obtained from this graph is:

$$\log K_{NaSPh} = 7.6$$

It can be noticed that agreement with values given in Table 6 is excellent.

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