THE ASSAY OF POTASSIUM p-PHENOLSULFONATE, ITS pH RANGE, AND ITS ULTRAVIOLET ABSORPTION SPECTRUM

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ABSTRACT

Potassium p-phenolsulfonate is a good buffer for the pH range of 8.4 to 9.2 and for spectrophotometric studies of metacresolsulfonphthalein and thymolsulfonphthalein. Its useful pH range lies between those for borates and secondary phosphates and therefore fills an important gap. The purified product is not commercially available and quantitative tests for indicating its purity have not been reported. It was found that a pure product may be obtained after only three recrystallizations. A quantitative method of analysis by bromometric titration was developed. Two molecules of bromine react quantitatively with 1 molecule of p-phenolsulfonate in molar hydrochloric acid at 0° C within 5 minutes.

Ultraviolet absorption spectra were obtained and showed differences between the primary and the secondary salt. The spectrophotometric data indicate that the sulfonate group is almost completely ionized in dilute solutions.

CONTENTS

I. INTRODUCTION

In spectrophotometric studies of indicators it is sometimes necessary to use buffers to stabilize the solutions which cover the pH and colorimetric transformation ranges. It is especially important that the compounds used as buffers and the indicators do not react or have overlapping absorption bands. The phenolsulfonates and some of their halogenated derivatives have been suggested [1] as components of a stable buffer system over a wide pH range.

Highly purified phenolsulfonates are not available commercially. However, some of the compounds can be easily recrystallized from water and hence can be purified in the laboratory. After preliminary investigations of the potassium, sodium, calcium, and zinc salts of p-phenolsulfonic acid and of several salts of halogenated derivatives, potassium p-phenolsulfonate was chosen for more detailed study. The fact that it is anhydrous makes it more desirable than the sodium salt. The latter crystallizes with 2 molecules of water, which can be removed by drying but are taken up again at room temperature at

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[1] S. F. Acree, R. R. Mellon, B. M. Avery, and E. A. Slagle, A stable single buffer solution pH 1 to 12. J. Infectious Diseases **29,** 7 to 10 (1921).

humidities as low as 40 and 50 percent. Two samples of the recrystal-
lized potassium salt lost 0.02 and 0.03 percent in weight when heated
at 110° C for 24 hours and regained about the same amount over a
period of 10 days, during which they were exposed from time to time in
air of 40- to 50-percent humidity. Bromometric assay, by the proce-
dure described later, showed no change in purity of the samples
heated at 110° C for 24 hours. The same was true of a 10^{-2} molar
solution which stood on the laboratory bench for 2 months. After
heating at about 167° C for 20 hours, however, three samples lost 0.30
to 0.36 percent in weight and were found to contain sulfate. Bromo-
metric analysis showed these samples to be 99.7 percent pure.

There apparently is no oxidation-reduction or other adverse reaction
with the sulfonphthalein indicator series, as indicated by spectropho-
tometric curves, using 10^{-2} molar potassium p-phenolsulfonate
buffers with metacresolsulfonphthalein and thymolsulfonphthalein.

II. PURIFICATION OF POTASSIUM p-PHENOLSULFONATE

The p-phenolsulfonate received from the manufacturer was a pink-
ish-white crystalline powder with a distinct phenolic odor. Impurities
were removed before the first crystallization by treating a hot solution
for about 10 minutes with an activated carbon. To remove all the
carbon, the solution was filtered several times while hot. Each re-
crystallization was made by adding just enough hot water (about 80°
to 90° C) to dissolve the crystals. The solution was then cooled to
about 10° C, and the crystals were filtered with suction but not allowed
to dry between recrystallizations. A yield of about 40 percent for
each recrystallization was obtained. The first mother liquor was
pinkish and contained a small amount of sulfate. The subsequent
mother liquors were colorless and sulfate tests were negative.

Two separate lots of potassium p-phenolsulfonate were recrystal-
lized four and six times, respectively. Some material from each
recrystallization was reserved for experimentation and dried for 2
hours in a vacuum oven at 2-mm pressure and 60° C. Analyses of
the recrystallized product by micromethods for hydrogen, carbon, and
sulfur, made by K. D. Fleischer of this Bureau, gave the following
results: Found: C, 34.02, 34.03; H, 2.40, 2.57; S, 14.92, 15.04. Theo-
retical: C, 33.95; H, 2.37; S, 15.10.

III. BROMOMETRIC ASSAY OF POTASSIUM p-PHENOLSULFONATE

Previous work on furfural and related compounds [2] showed that
under controlled conditions of acidity and temperature the reaction
of bromine with some organic compounds can be used as a method for
their quantitative determination. Preliminary experiments indicated
that the reaction of bromine with phenolsulfonate gives slightly high
results at room temperature. However, using essentially the method
previously reported for furfural, it was found that at 0° C 2 molecules
of bromine react within 5 to 10 minutes with 1 molecule of p-phe-
nolsulfonate in normal hydrochloric acid to form 2,6-dibromophenol-
4-sulfonate and 2 molecules of hydrobromic acid. The reagents used
and experimental procedure are given below.

[2] Elizabeth E. Hughes and S. F. Acree, *Quantitative determination of furfural at 0° C with bromine*, Ind
Eng. Chem. **6**, 123 (1934); *Volumetric estimation of 5-bromo-2-furoic acid with bromine*, Ind. Eng. Chem. **6**, 292
(1934).

1. REAGENTS

Potassium bromate was recrystallized three times from water, and 5.567 g was used to make a solution approximately 0.2 *N*, which contained 50 g of potassium bromide in 1 kg of water. The bromate-bromide solution was used on a weight basis to standardize in normal hydrochloric acid through iodine the 0.1 *N* thiosulfate solution used for the titrations. The weighed amount of the bromate-bromide delivered by a special 25-ml pipet with curved tip was reproducible within 0.05 percent. A solution of potassium iodide, about 10 percent by weight, was prepared freshly before use. Hydrochloric acid was used to make the reacting solution about normal in acidity. The potassium bromide, potassium iodide, and hydrochloric acid conformed to specifications of the American Chemical Society.[3] As an additional check, the thiosulfate was standardized against potassium dichromate, recrystallized twice, using the same procedure described below. The two methods of standardization agreed within 0.1 percent.

2. EXPERIMENTAL PROCEDURE

Specially designed titration flasks, described previously (see footnote 2), were fitted with two side-arms for the bromate and iodide solutions, respectively. By means of pipets with curved tips, 25 ml of the 0.2 *N* bromate-bromide solution was placed in one side-arm and 10 ml of the potassium iodide solution in the other. A known amount of phenolsulfonate was transferred to the body of the flask and diluted to about 200 ml. The solution was made normal in acidity by the addition of hydrochloric acid, using extreme care that the fumes did not reach the bromate in the side-arm. Blanks of the reagents were prepared in a similar manner, substituting water for the phenolsulfonate. Each flask was closed with a ground-glass stopper and placed in an icebox to attain a temperature of $0°$ to $2°$ C.

The reaction was started by tilting the flask so that the bromate-bromide solution ran into the body of the flask, and the contents were gently swirled to mix the liberated bromine with the phenolsulfonate without disturbing the potassium iodide solution in the other side-arm. A stop watch was used to time the reaction, which was stopped by the addition of the potassium iodide. The contents were thoroughly shaken to absorb any bromine vapors, and the iodine equivalent to the residual bromine was titrated with 0.1 *N* thiosulfate, using starch as an indicator. At $0°$ C the discharge of the blue color at the end point was very definite, but it was found that the titration must be made as rapidly as possible. The blue color returns after several minutes, and consequently error may be introduced if the titration is prolonged. Experiments over a period of several hours, in which the blue color was discharged with thiosulfate as soon as it returned, showed that this error was of the order of 0.01 ml per minute at low temperatures and twice this amount at room temperatures.

The amount of bromine consumed by the phenolsulfonate is determined from the difference between the amounts of standard thiosulfate solution used in titrating the blank and the solution containing the phenolsulfonate. The figures in table 1 for "percent reaction" are calculated on the assumption that in the desired reaction 1 mole of the phenolsulfonate consumes 2 moles of bromine.

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[3] ACS Analytical Reagents. (American Chemical Society, Washington, D. C., March 1941).

Table 1.—*Reaction of potassium p-phenolsulfonate with bromine at 0° C in normal hydrochloric acid*

Time allowed for reaction	0.1698 g of potassium p-phenolsulfonate		0.2124 g of potassium p-phenolsulfonate	
	Milliequivalents of bromine consumed	Percentage of reaction	Milliequivalents of bromine consumed	Percentage of reaction
Minutes				
2	----------	----------	{ 3.937	98.4
			{ 3.922	98.0
5	3.195	99.9	4.001	100.0
10	{ 3.199	100.0	4.006	100.1
	{ 3.200	100.0	4.002	100.0
15	3.199	100.0	{ 4.004	100.0
			{ 4.009	100.1
20	{ 3.205	100.1	----------	----------
	{ 3.207	100.2	----------	----------
30	3.210	100.2	----------	----------
120	3.256	101.8	4.025	100.6
180	----------	----------	4.038	100.9

The values in table 1 show the variation with time in the consumption of bromine at 0° C by two concentrations of phenolsulfonate. In all cases there were approximately 5.0 milliequivalents of bromine available, requiring 50 ml of 0.1 N thiosulfate for titration of the blank. For the above amounts of phenolsulfonate, the excess bromine required about 18 and 10 ml of thiosulfate, respectively. The table indicates that the reaction of 1 molecule of phenolsulfonate with 2 molecules of bromine is complete after about 5 minutes, and little additional reaction is noted until after 30 minutes. The figures for percentage of reaction show that the method is accurate to about 0.1 percent. A difference of 0.02 ml in thiosulfate titration, representing in the above instances less than 0.1 percent, is possible due to the difference in time taken to add the 50 ml for titration of the blank and that taken to add the smaller volume in the titration of the sample.

The values in table 2 show the analyses of the original material and the recrystallized fractions.

Table 2.—*Brommetric assay of samples of potassium p-phenolsulfonate subjected to a series of recrystallizations*

	First lot	Second lot
	Percent	*Percent*
Original material_____	92.8	92.7
Recrystallization I_____	98.4	99.6
Recrystallization II_____	99.7	100.0
Recrystallization III_____	100.0	100.1
Recrystallization IV_____	100.0	100.0
Recrystallization V_____	_____	100.1
Recrystallization VI_____	_____	100.1

IV. SPECTRAL ABSORPTION IN THE ULTRAVIOLET BY POTASSIUM p-PHENOLSULFONATE

In the spectrophotometric studies of indicators stabilized with 10^{-2} molar phenolsulfonate buffer, it was found that ultraviolet absorption spectra could not be obtained below 280 mμ, owing to the absorption bands of the buffer itself. A study therefore was made of the buffer without the indicator. Repeated dilutions of the phenol-

sulfonate solutions were made and their transmittancy values measured until the main absorption bands were located. The series of spectral transmittancy values given in figure 1 represent concentrations of the phenolsulfonate in water from 10^{-2} molar (curve A) to 10^{-5} molar (curve I). The main absorption band, whose peak is at 230 mμ, is not sharply defined except in the more dilute solutions (curves E through I). The transmittancy curves show bands similar to those of indicators.

Dilution of the phenolsulfonate with water immediately introduces the question of dissociation. At any wavelength the molar absorp-
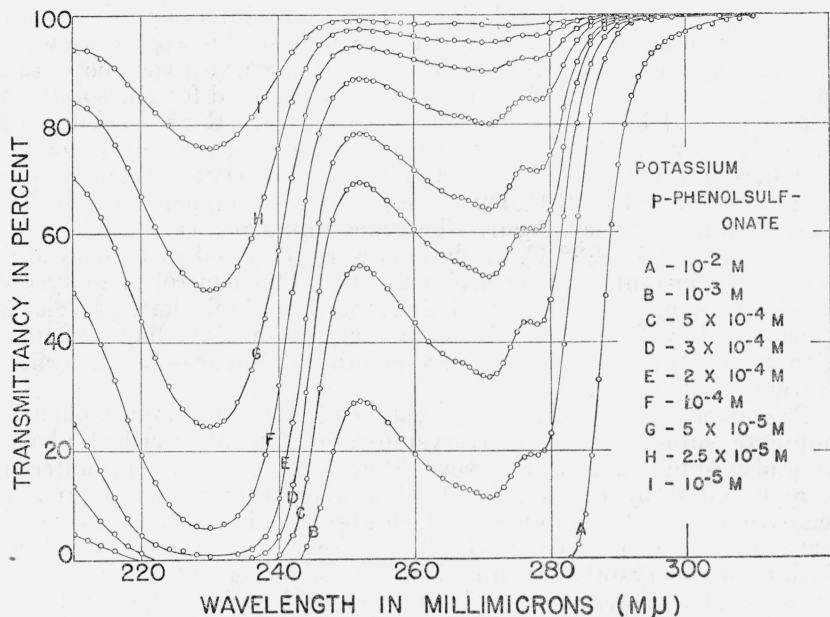
FIGURE 1.—*Ultraviolet spectra of several concentrations of purified potassium p-phenolsulfonate.*

tion index is determined by dividing the index $(-\log_{10}$ transmittancy) for that solution by the concentration multiplied by the depth of the solution (cell length in centimeters) through which the light beam passes, according to Beer's law. If the molar absorption indices do not agree well within experimental error for several wavelengths, then dissociation, association, or some chemical change is suspected. For this purpose the absorption indices of solutions of phenolsulfonate 10^{-4}, 2×10^{-4}, and 3×10^{-4} molar in water were first compared. Additional solutions of the same concentrations were made in 10^{-1} molar hydrochloric acid. These data agreed well within experimental error for practically the entire absorption curve, except on the steep portions of the bands where the errors are large, showing that the sulfonate group is completely ionized and the phenolic group non-ionized in all the above solutions. As an additional check, a 10^{-4} molar solution in the 5-cm cells was compared with a solution in the 1- and 2-cm cells. The agreement was well within experimental error.

The spectrophotometric data were obtained by use of a Beckman quartz photoelectric spectrophotometer.[4] It was improved by the

replacement of the cell compartment [5] by a small light-tight box with a slide for holding two 38-mm (i. d.) cylindrical metal cell holders in which Pyrex cylinders of 1-, 2-, and 5-cm lengths could be fitted with quartz end plates to hold the solutions. One cell was filled with the solution under investigation. The solvent, or 100-percent cell, contained the same components of the solution except the compound under investigation. The cells were placed alternately in the light beam for the transmittancy measurements. They were calibrated each day at the beginning and end of the test by filling both cells with distilled water, using the solvent cell for 100-percent transmission and reading the value for the solution cell at 10-mμ intervals from about 210 to 400 mμ. The quartz end plates used in this work were well-matched and gave a satisfactory calibration curve over the entire spectral range. The transmittancy values obtained for the solutions were corrected by use of the calibration curve. Reproducibility of transmittancy values for a given concentration of solution prepared at different times was usually within ± 0.2 percent, except at the lowest wavelengths (210 to 230 mμ), where discrepancies of ± 0.5 percent transmittancy occur. The measurements were made in a room kept at 25° $\pm 2°$ C. Solutions were prepared in a room also kept at a constant temperature of 25° C. This control of temperature is important in spectrophotometric studies of solutions, especially when the pH value of the solution and ionization of the buffer change with temperature, and cause corresponding differences in the transmittancy of the solution.

The ultraviolet transmittancy values of the potassium p-phenolsulfonate subjected to the recrystallization steps described above were also obtained and are given in figure 2. The original material is represented by curve A. The first recrystallization apparently removes most of the impurities which absorb light[6] between 250 and 300 mμ, as shown by curve B, whereas the third, fourth, fifth, and sixth crops of crystals give practically the same transmittancy values, curve C. The material successively recrystallized from the first lot of phenolsulfonate showed a systematic change in the transmittancy values, as in the bromine analyses (given in table 2 but not shown in fig. 2).

Studies of a number of buffers have shown them to be highly resonant and chromophoric in the ultraviolet, and also that their absorption index bands are altered greatly by pH changes, just as in the case of indicators in the visible, ultraviolet, and infrared regions. Some measurements therefore were made of the ultraviolet absorption of solutions of the secondary p-phenolsulfonate salt, which is formed when alkali is added to a solution of the primary salt. The spectrophotometric curves shown in figure 3 represent the p-phenolsulfonate, 5×10^{-5} molar, in 10^{-1} molar hydrochloric acid (curve A) and the same concentration in 10^{-3} molar sodium hydroxide (curve D). The two intermediate curves, B and C, were obtained by using dilute borax–boric-acid buffers of pH 8.4 and 9.0, which do not have absorption bands in this region. In these dilute solutions there may have been some error due to the absorption of carbon dioxide during the
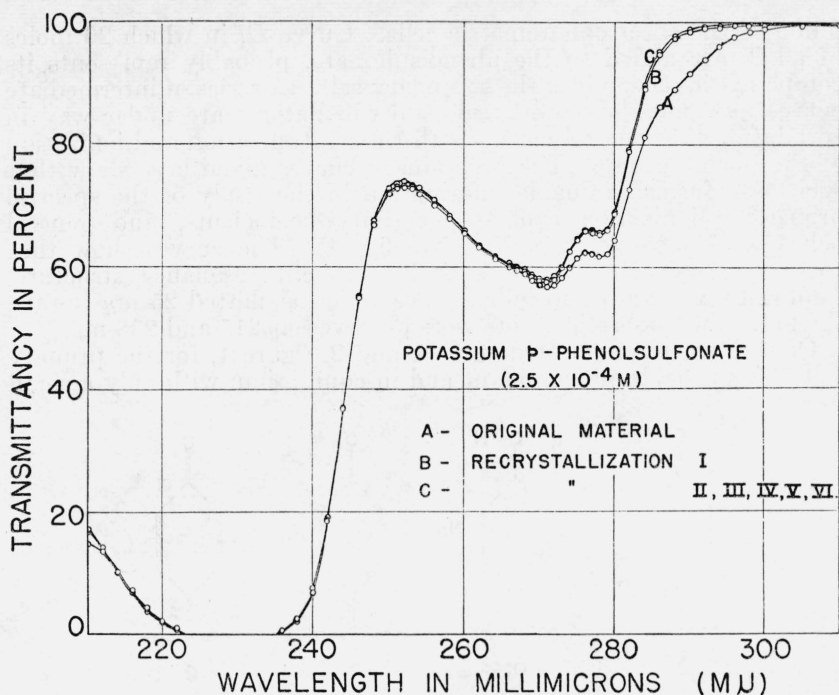
FIGURE 2.—*Ultraviolet spectra of impure and recrystallized potassium p-phenolsulfonate.*
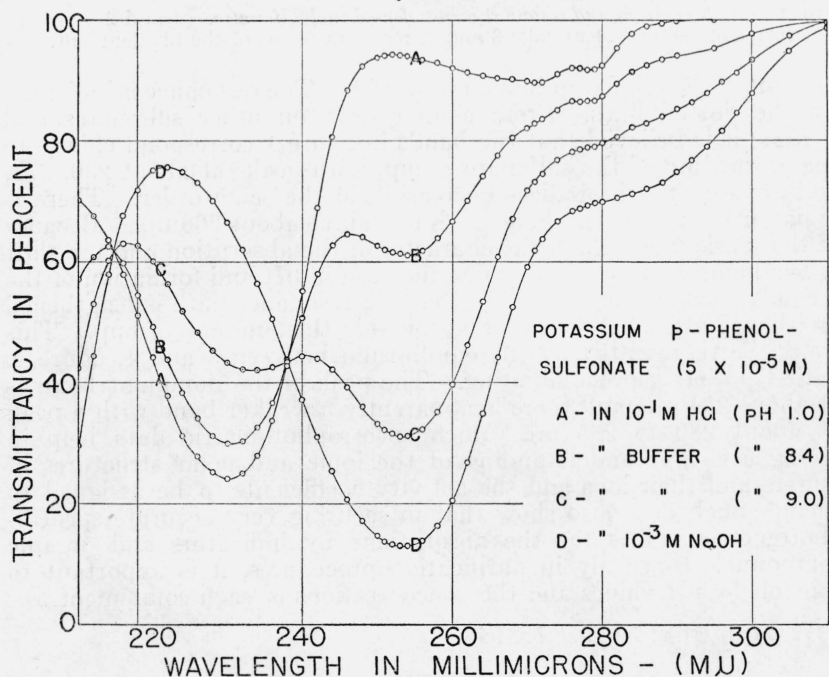

FIGURE 3.—*Ultraviolet spectra which represent the transformation of potassium p-phenolsulfonate from the primary to the secondary salt.*

filling of the spectrophotometric cells.   Curve *D*, in which 20 moles of alkali are added to the phenolsulfonate, probably represents its complete conversion into the secondary salt.   A series of intermediate curves has since been obtained, and calculations are under way in correlating the spectral curves with the neutralization and ionization of the phenol group.   The preliminary curves given here show that such data furnish valuable information in the study of the spectral properties, ionization constant, activity coefficients, and general behavior of such polar buffers (see fig. 4).   The curves show that the secondary salt has an entirely different resonance structure, leading to an absorption index curve which is shifted 25 mμ toward the red.   Two isobestic points were observed at 215 and 238 mμ.

Of the two resonant structures 1 and 2, figure 4, for the primary salt, 2 is probably predominant and in equilibrium with only a small
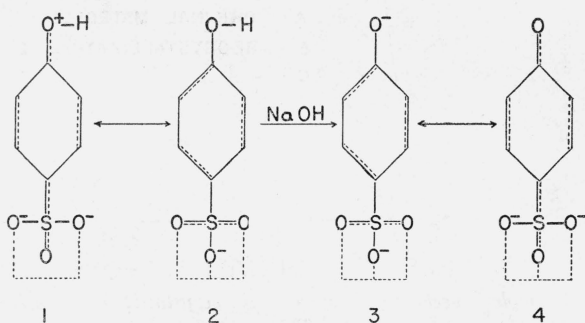

FIGURE 4.—*Structural and resonant forms of p-phenolsulfonates.*   1 and 2, resonant forms of the univalent salt; 3 and 4, resonant forms of the bivalent salt.

amount of the dipolar quinoidal form of 1.   The resonance is indicated by the dotted lines.   From similar data on other sulfonates and buffers, it is believed that the bands in figure 1 correspond chiefly to the absorption of the sulfonate group, with peaks at about 230, 271, and 278 mμ and the indices decreasing in the same order.   There is apparently also a weak band with a peak at about 266 mμ.   Because of the marked change in the character of the absorption and the shift of the band toward the red upon increase in pH and formation of the secondary salt, it seems likely that the resonance path is lengthened and hence extended considerably outside the sulfonate group.   This would be represented by the equilibrium between 3 and 4, figure 4, with 4 probably predominating.   The peak of the dominant band is at about 254 mμ, and there is apparently a weaker band with a peak at about 280 to 285 mμ.   Such spectrophotometric data help in giving a clearer understanding of the ionic and polar structures of buffers and their ions and the activity coefficients to be assigned to them.   Such data also show that in securing very accurate spectrophotometric values for the absorptions by indicators and organic compounds, especially in purification procedures, it is important to control the pH values and the concentrations of each component.

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