

## Potentiometric Determination of Arylsulfonic Acids

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Methods for the determination of benzenesulfonic acid and its salts have been published by Thomas<sup>1</sup>, Krishna and Singh<sup>2</sup>, Ackerman<sup>3</sup>, Faerman and Simkina<sup>4</sup>, and Alimarin and Kusnetsov<sup>5</sup>. Dale Nogare<sup>6</sup>, reviewing known analytical methods, stated that attempts to determine various aromatic sulfonic acids failed: they gave only 80–90 % of the theoretical value. Alimarin and Sotnikov<sup>7</sup> stated that ceric sulfate in acid solution oxidizes the benzenesulfonic acid, the reaction products being dibenzenedisulfone, benzenesulfonic acid and an equivalent amount of cerous sulfate. No ceric benzenesulfinate was obtained. Forrest and Ryan<sup>8</sup> titrated benzenesulfonic acid with ceric sulfate. The endpoint of the titration, indicated by Ferroin, occurred at a molecular ratio of 1.8 Ce<sup>4+</sup> to 1.0 benzenesulfonic acid. Dibenzenedisulfone was identified as a reaction product. Alimarin and Kusnetsov<sup>5</sup> attempted to use ceric sulfate for the determination of sulfonic acid but found that the reagent did not react stoichiometrically, the mole ratio being 1.1–1.2.

The aim of the present study has been to investigate the conditions under which ceric sulfate can be used as an analytical tool in the determination of arylsulfonic acids.

Ceric sulfate was chosen because of the stability of its solutions and the simple change of oxidation number from 4 to 3.

*Experimental and results.* The sodium and ammonium salts of *p*-toluenesulfonic acid were used as primary test substances. The acid itself is less suitable, being easily disproportionated and only slightly soluble in water.

The sodium salt was prepared from *p*-toluenesulfonyl chloride by reduction with zinc<sup>9</sup>. The salt is obtained as the dihydrate, the tetrahydrate was obtained by recrystallization from a saturated solution.

The ammonium salt was prepared in the following way. A cold saturated solution of the sodium salt was treated with ether, which removed traces of disulfides and mercaptans. The aqueous phase was filtered

and the clear filtrate was acidified with 1:1 hydrochloric acid whilst being stirred and cooled. The precipitated *p*-toluenesulfonic acid was collected by suction on a Büchner funnel. The precipitate was washed with small portions of cold water which removed the very soluble *p*-toluenesulfonic acid. Without delay, the *p*-toluenesulfonic acid was dissolved in a small excess of ammonia and the clear solution was carefully evaporated on an infra-red heater to a volume small enough for cooling to initiate crystallization. Only the first crop of crystals of ammonium *p*-toluenesulfinate was collected; this was dried to constant weight at room temperature.

After drying for 2 h at 100°C the sodium salt decreased in weight by 27.6 %, which corresponds to the loss of four molecules of water of hydration. The dried salt gave a completely clear solution. The loss of weight for the ammonium salt was only 4.6 % and its solution in water was opaque, indicating that a disproportionation had taken place.

Surprisingly, the water of hydration could also be determined with the Karl-Fischer reagent (K-F stabilized, Pharmacia, Uppsala). The titration of the sodium *p*-toluenesulfinate in pre-titrated methanol gave the same figures for the water content as did the drying method. The titration of the ammonium salt indicated a water content of 10.2 % in good agreement with the theoretical value of 10.47 corresponding to one mole of hydration water. The ammonium salts of benzene and 2-naphthalenesulfinate also crystallize with one mole of water. The calcium *p*-toluenesulfinate crystallizes with four moles of water.

An approximately 0.1 N ceric sulfate solution (F. Smith, reagent grade) in 1.5 N sulfuric acid, was prepared and filtered. This solution was then carefully standardized against As<sub>2</sub>O<sub>3</sub> with osmic acid as catalyst and Ferroin as indicator. The titer was checked every 8th day, but practically no change was observed. The titration was carried out potentiometrically with a Metrohm Potentiograph. The titrant was delivered from a 20 ml syringe buret synchronously driven by the recording unit. The solution to be titrated was stirred with a magnetic stirrer. A combined Pt-calomel electrode gave steady and reproducible readings. The end point was also very distinct at high dilution, and the very steep potential break indicated that the reaction was practically irreversible (Fig. 1). Of course, a simpler poten-

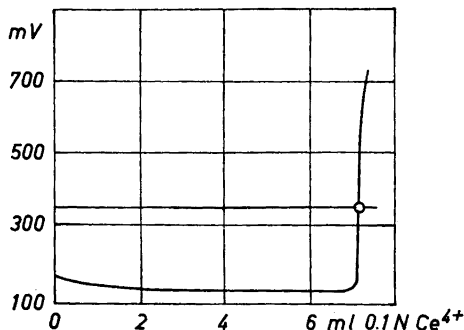


Fig. 1. Titration of 50 ml 0.01 N *p*-toluenesulfonic acid with 0.1 N Ce(IV) sulfate.

tiometer and a common buret may be used. The end of the titration was marked by a potential jump amounting to about 200 mV after the addition of only one drop.

Series of concentrations of *p*-toluenesulfonic acid ranging from  $10^{-4}$  to  $10^{-1}$  M were prepared by diluting aliquot portions of a 0.1 M standard solution to a volume of 100 ml. Prior to the dilution the solutions were acidified with 5 ml of 1 N sulfuric acid. In some experiments greater amounts of sulfuric acid up to 10 N were used, but the greater concentration of acid seemed to have no effect on the result of the titration.

In Fig. 2 the mole ratio,  $\text{Ce}^{4+}/\text{RSO}_3^-$ , obtained by the titration, is plotted as

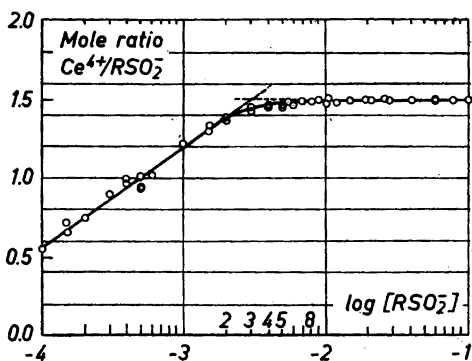
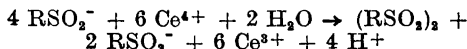


Fig. 2. The dependence of the  $\text{Ce}^{4+}/\text{RSO}_3^-$  mole ratio at the end point on the concentration of the solution to be titrated.

ordinate *versus* the concentration of the titrated solution in logarithmic units as abscissa. Within the limits of experimental error, this ratio is 1.5 in the concentration range above  $5 \times 10^{-3}$  M. At lower concentrations the mole ratio gradually decreases. For the range from  $5 \times 10^{-3}$  to  $1 \times 10^{-1}$  M, the overall reaction may be summed up as follows



Some gravimetric experiments were performed to verify the stoichiometry of the reaction. The precipitated disulfone was collected by suction in a porcelain filter crucible, dried at  $100^\circ\text{C}$  for 2 h and weighed. The recovery was only 80–85 % of the theoretical value, possibly because of the solubility of the ditolyldisulfone.

Within the concentration limits indicated above, the following equation may be used in the calculation:

$$\frac{\text{ml of titrant} \times \text{normality}}{1000 \times 1.5} = \frac{\text{g of sample} \times \text{per cent purity}}{\text{mole-weight} \times 100}$$

For salts with divalent or tetravalent cations the factor 1.5 has to be replaced by 3.0 or 4.5.

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