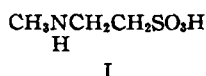


Polarographic Analysis of Some Sulfonic Acids

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Sulfonic acids gave fine polarographic waves. Alkyl sulfonic acids have a half-wave potential of -1.6 v., while the half-wave potential of aromatic sulfonic acids can vary with substituents.

DURING THE investigation of the antimicrobial factor in the giant milkweed bug, *N*-methyltaurine (I) was isolated and identified (1). The authors concluded that since the spot test for sulfonic acids involves the reduction to sulfite (2), the polarographic reduction should also occur.



Using a rapid-dropping mercury electrode, *N*-methyltaurine gave a fine wave and a half-wave potential of -1.6 v. Camphor-10-sulfonic acid and methane sulfonic acid also gave the same half-wave potential. These values neglect internal resistance within the cell.

Polarographic reductions of sulfonic acids have not been reported previously, although the reduction of sulfonic esters, amides, and acid chlorides have been observed (3). Zuman reported a correlation of half-wave potentials and Hammett sigma values for a large number of aromatic sulfonic acid derivatives. Some correlation appears to exist for aromatic sulfonic acids (Table I). Benzene sulfonic acid and *p*-toluenesulfonic acids exhibit half-wave potentials at -1.6 v., *p*-acetamidobenzene sulfonic acid, somewhat more negative, and *p*-nitrobenzenesulfonic acid exhibited a half-wave potential at -1.5 v. Irregular behavior was observed in polarograms of *ortho*-, *meta*-, and *para*-aminobenzenesulfonic acids. These three compounds all exhibited half-wave potentials of -1.6 v. Zuman (3) had reported that groups capable of mesomeric effects (e.g., *p*-hydroxy, *p*-amino) generally did not fit his plots of half-wave potentials versus Hammett sigma values. He did not attempt to explain this observation.

TABLE I.—HALF-WAVE POTENTIALS OF SULFONIC ACIDS

Compd.	Half-wave Potential, v.
<i>N</i> -Methyltaurine	-1.6
Camphor-10-sulfonic acid	-1.6
Benzenesulfonic acid	-1.6
<i>p</i> -Toluenesulfonic acid	-1.6
<i>p</i> -Nitrobenzenesulfonic acid	-1.5
<i>p</i> -Acetamidobenzenesulfonic acid	> -1.6
<i>p</i> -Aminobenzenesulfonic acid	-1.6
<i>m</i> -Aminobenzenesulfonic acid	-1.6
<i>o</i> -Aminobenzenesulfonic acid	-1.6

If the amino group existed as the ammonium cation in the aromatic sulfonic acids, the half-wave potential should have been less negative, since the cation would withdraw electrons from the ring and in turn make the sulfur more positive. If the amino group were present in the free form, the *para* and the *ortho* isomers could have participated in resonance stabilization involving the sulfur which should have made the half-wave potential more negative. Since neither of these possibilities appeared to occur, it might be attractive to postulate the removal of the amino group prior to reduction of the sulfonic acid to account for the identical half-wave potentials.

EXPERIMENTAL

To 1 ml. of 10^{-3} *M* sulfonic acid solution was added 9 ml. of 10^{-1} *M* tetramethylammonium iodide solution. In those cases where 10^{-3} *M* solutions could not be formed, a saturated solution was employed.

The solution was deoxygenated using nitrogen gas and the polarograms run within 30 minutes of mixing. A Metrohm polarograph equipped with a rapid-dropping mercury electrode was used versus an Ag, AgCl, anode.

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