THE ABSORPTION SPECTRA OF SODIUM m-BENZENEDISULFONATE IN NICKEL SULFATE SOLUTIONS

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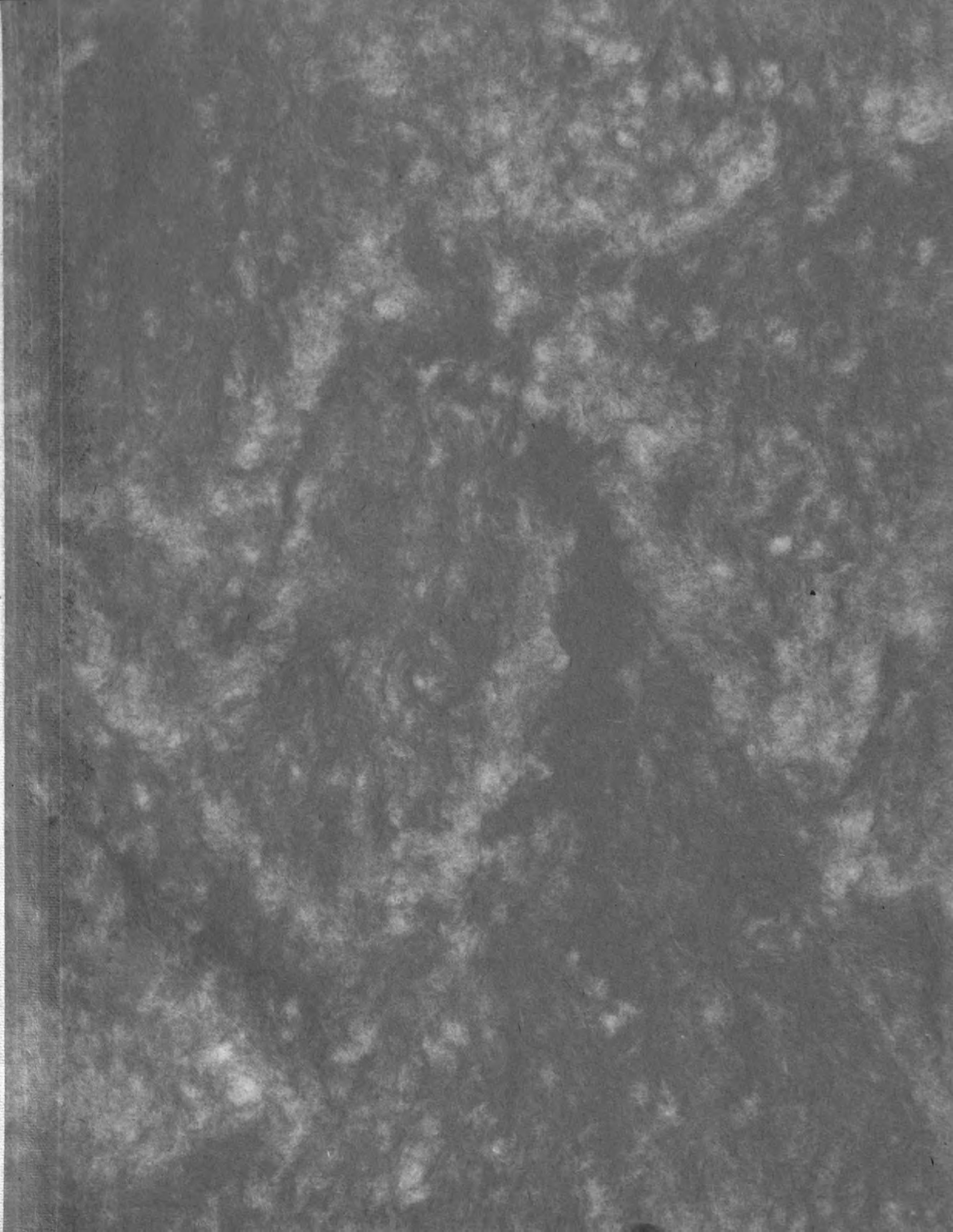

THE ABSORPTION SPECTRA OF SODIUM m-BENZENEDISULFONATE IN NICKEL SULFATE SOLUTIONS

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APPRECIATION

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Introduction

The application of spectrophometry to the quantitative determination of constituents by means of absorption spectrum has been recognized since 1873 by Vierordt (1).

This paper describes an application of the spectrophotometer to the quantitative determination of sodium m-benzenedisulfonate in nickel sulfate solutions. Data are given showing that small quantities of sodium m-benzenedisulfonate in nickel sulfate solution have a distinct and characteristic absorption spectra in the ultra violet region with maximum absorption at 2680 A° and 2750 A°, with absorption extending from about 2350 A° to 2900 A°. Taking advantage of these two maximum absorption points, and employing the extinction coefficients, one is able to compute quantitatively the concentration of sodium m-benzenedisulfonate. With carefully controlled working conditions, the extinction coefficient was found to be reproducable with a high degree of accuracy.

Sodium m-benzenedisulfonate is used for a brightener in nickel plating solutions, and when an estimation of concentration is desired, the usual method of determination is by a gravimetric analysis as barium sulfate, which is

long and involves considerable time and work. The advantage of the spectrophotometric method is that it is rapid and convenient.

The procedure for this method of analysis is based upon the principal that the percentage transmittancy of light at a certain wave length is a function of the concentration of the desired substance in the solution. In recent years such a method of measuring a constituent spectrophotometrically has been applied by Mehlig to the determination of manganese in steel (2), iron in ores (3); to copper (4); to vitamins and hormones by Morton (5); and also to dyestuffs, by Brode (6) and Holmes (7).

Apparatus and Reagents

The transmittancy measurements were made by the Bausch and Lomb medium quartz spectrograph No. 746, having a dispersion varying from 7 A. per mm. at 3500 A. to 21 A. per mm. at 3500 A., and a rotating sector to regulate the percentage of incident light. Tungsten steel electrodes, sharpened at the arc end to a wedge shape, and setting the electrode gap at 3.4 mm., excited by a 450 volt alternating current provided an ample source of spectra. The tungsten steel gave a satisfactory source for absorption work, yielding many lines at all parts of the working spectrum, plus considerable continuous. Zeiss quartz cells, having a volume of approximately 5 ml. and length of 1 cm. were employed throughout the experiment. The photographic plates used were Eastman "33" commercial, and were developed with fresh D-1 tray developer for five minutes at a temperature of 18 degrees. The chemicals used were C. P. grade nickel sulfate hexahydrate and sodium m-benzenedisulfonate. Water solutions of these salts were prepared during the course of the investigation at the concentrations desired.

Procedure

In the development of the method, samples of sodium m-benzenedisulfonate were accurately weighed out and dissolved in a measured volume of 30% nickel sulfate water solution. After the solution and the solvent cells have been filled (for preparation see below), they are filled with the respective solution, placed on the spectrograph, and the absorption spectra at various shutter readings recorded on the photographic plate. After development, the plates are washed one-half hour in running water, dried at room temperature, and the absorption indicated on the plate by means of ink dots at the points where "iso-density reversals" occur. The resulting curve may be graphed, or, in the determination of an unknown sample, the curve inspected for evaluation of the concentration. Concentrations of salts are expressed as percent solution throughout the experiment.

It was found that the windows of these cells must be meticulously clean and free from any adhering thin layer of foreign material. Before this precaution was observed, considerable variation was found in the results. It is not advisable to use the ordinary organic solvents in cleaning these cells, as they dissolve the cement which holds the cell together. It was found necessary to clean the cells by an initial rinsing with tap water to remove the salts, then several careful rinsings with distilled water, and a

third rinsing with redistilled water. This is followed by a thorough swabbing of the inside and outside surfaces with a swab made by wrapping a sheet of lense paper around the end of a nickel spatula, and then a final rinsing with redistilled water. As long as one is able to see reflections from the surfaces when held up against daylight, the cell requires further cleansing.

Method and Discussion

In the development of the method for the quantitative determination of sodium m-benzenedisulfonate, over fifty solutions of varying known concentrations were prepared, spectrograms made, and the absorption curves plotted. In order to evaluate the E values for the desired wave lengths for use in subsequent work, these curves were inspected and the E maxima and minima established. The maximum at 2680 A° is the point of greatest absorption, E is 19.0, see Fig. I. It is a narrow, though distinct and well defined band. The second E maximum at 2750 A° is 15.6. This point, however, is not as sharply defined, though readable. When making a reading of the peaks of the curves, coordinating concentrations with percentage transmittancy, it was found that certain portions give results of greater accuracy than others. Care was exercised to read all absorption maxima in the same relative position, and as near the tip as possible. From the data in Table I, Beer's law holds for solutions of concentrations under 0.5%.

Readings of the absorption maxima were most suitable at a certain transmittancy range. The optimum working range for log I_0/I values was found to be between 1.20 and 0.80 (sector settings from 6 to 15). A concentration suitable for this transmittancy range is obtained by dilution of the sample. Knowing the optimum range for the light transmittancy values, and the E value at 2680 A°, we may

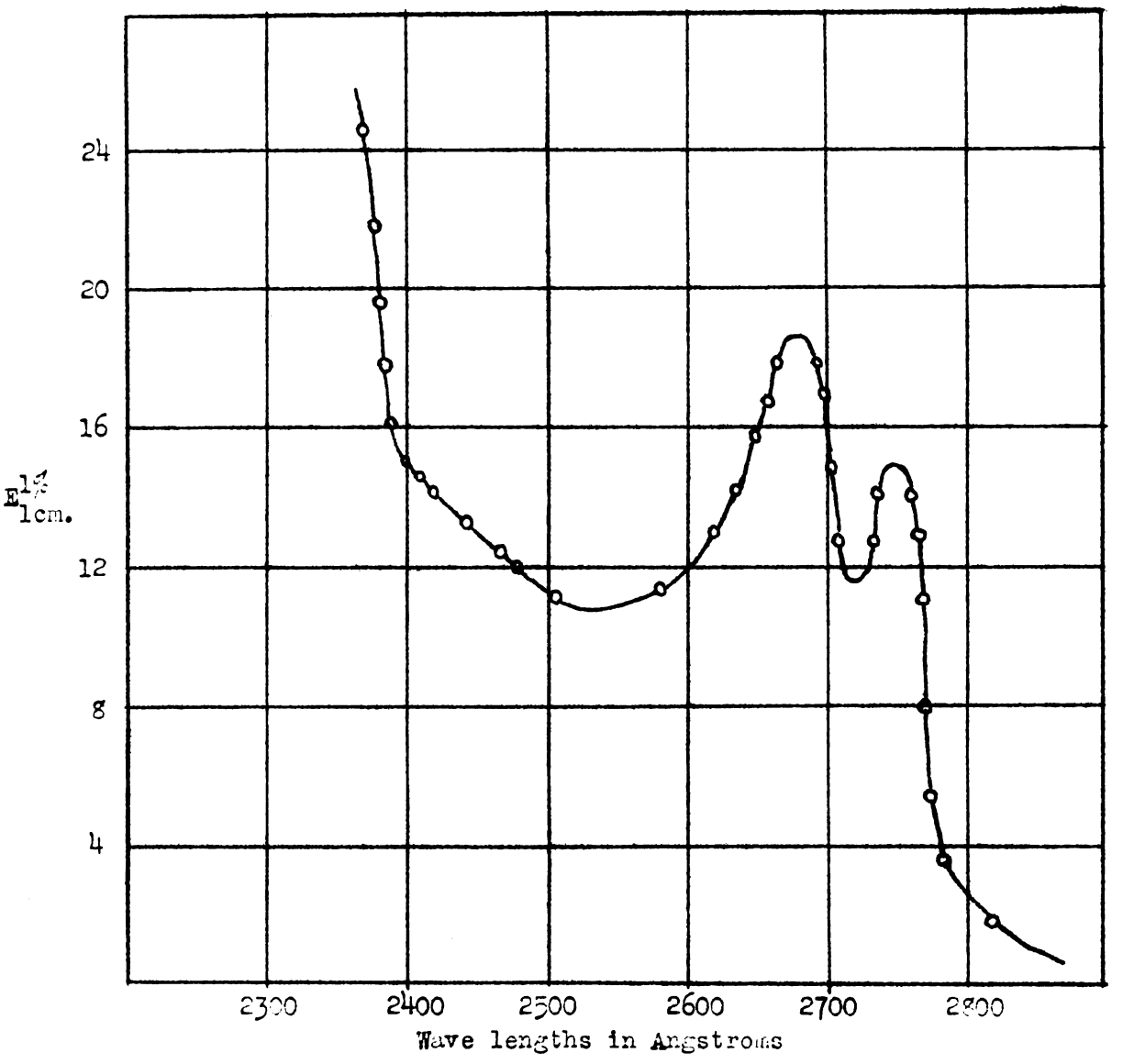

Fig. I Absorption Curve of
Sodium m-benzenedisulfonate in Nickel Sulfate Solution

Table I
Comparison of E values for different percentage concentrations of Sodium m-benzenedisulfonate (Beer's Law)

Plate number	Conc. of disulfonate	Conc. of $NiSO_4$	$E^{1\%}_{1cm.}$ 2680	$E^{1\%}_{1cm.}$ 2750
599	0.20 %	30.0 %	no inflection	
554	0.0637	2.4	16.0	15.7
621	0.055	30.0	13.6	16.1
548	0.055	30.0	13.4	16.2
631	0.040	30.0	20.6	17.7
637	0.035	30.0	20.3	19.6
553	0.025	0.95	15.2	14.4

Table II
Analysis of unknown samples of Sodium m-benzenedisulfonate in Nickel sulfate solution

Plate number	Solution in solvent cell	% present in solution	% found spectroscopically
631	H_2O	0.040%	0.040%
637	H_2O	0.035	0.038
639	H_2O	0.055	0.057
630	$NiSO_4$	0.040	0.038
638	$NiSO_4$	0.035	0.035
640	$NiSO_4$	0.055	0.060

calculate the percent concentration of solution which will give the desired absorption. This was found to be around a 0.05% solution of sodium m-benzenedisulfonate in 30% nickel sulfate. For concentrations higher than 0.05% it was necessary to dilute the sample to approximately that value. By having the solution at this optimum concentration range the sector readings can be properly set, resulting, ultimately, in obtaining the E maximum points in the desired optimum transmittancy range, thus enabling the results to be read with greater accuracy, and offering simplicity in computation of the concentrations.

Since Beer's law holds for solutions of sodium m-benzenedisulfonate (Table I), the concentration in a given sample can be calculated from the fundamental Lambert-Beer equation.

$$I = I_0 \, 10^{-ecd}$$

in which I is the intensity of transmitted light.

I_0 the intensity of incident light (100%).

c the concentration of absorbing substance in moles per liter.

d the length of cell in centimeters.

e the molecular extinction coefficient.

Employing the percentage concentration instead of molar concentrations the following equation is obtained:

$$E^{1\%}_{1cm.} = \log \frac{I_0}{I} \times \frac{1}{cd}$$

or

$$E^{1\%}_{1cm.} = \frac{1}{c} \times \frac{\log I_0/I}{\% \text{ conc.}}$$

Where $E^{1\%}_{1cm.}$ = extinction coefficient, used on the basis of a one centimeter cell and one percent solution. The transmittancy I_0/I can be read directly as shutter readings, and if the extinction coefficient is known, c can be calculated. Solving for c from the above equation,

$$c = \frac{\log I_0/I}{E^{1\%}_{1cm.}}$$

An example will illustrate the method of calculation of an unknown. Using Plate No.670, the transmission of solution (I), at 2670A° was 17.5%; transmission of solvent (I_0) is 100%; E value is 19.0; cell length is 1 cm.; and c is unknown. The Lambert-Beer formula solved for c gives:

$$c = \frac{\log 100/17.5}{E^{1\%}_{1cm.}} = \frac{.757}{19} = 0.039\%$$

The results of the analysis of unknown samples of sodium m-benzenedisulfonate are shown in Table II. Attention should be called to the fact that the results, in order to be accurately interpreted, must be considered in the light of the facts revealed in Table III. The conditions upon which results are dependent are the following: (1) solutions in solution cell; (2) solvents in solvent cell; and (3) concentration of nickel sulfate in the solvent. Deviations from a standard set of working conditions will obviously produce varying results, even with the same or an identical sample. Table V indicates that a mixture of nickel sulfate and disulfonate in solution does not deteriorate upon standing together.

Table III

Comparison of E values for Sodium m-benzenedisulfonate when cells contain either nickel sulfate or water

Solution number	Plate number	$E^{1\%}$ 2660 1cm.	$E^{1\%}$ 2750 1cm.
(Both cells contain nickel sulfate 30%)			
1.	620	19.4	15.8
2.	621	17.6	14.1
3.	629	17.6	15.8
4.	630	18.9	15.05
5.	638	19.4	-
6.	640	19.3	16.4
	Mean	18.0	15.83
	Maximum range	4.2 %	8.5%
	Max. deviation	2.1 %	4.1%
(Both cells contain water)			
1.	611	15.5	14.0
2.	613	15.8	13.1
3.	614	16.3	14.7
4.	615	15.9	14.0
5.	616	15.6	13.3
	Mean	15.8	13.9
	Maximum range	5.4 %	11.5%
	Max. deviation	3.2 %	5.0%
(Solvent cell contains water; solution cell 30% nickel sulfate)			
1.	622	19.4	17.8
2.	628	20.5	17.1
3.	631	20.6	17.7
4.	637	20.3	-
5.	639	20.2	18.0
	Mean	20.2	17.9
	Maximum range	6.0 %	10.3%
	Max. deviation	4.0 %	5.5%

Table IV
Comparison of E values of different concentrations of Nickel sulfate in solution

Plate number	Conc. of $NiSO_4$	Conc. of disulfonate	$E^{1\%}_{1cm.}$ 2680	$E^{1\%}_{1cm.}$ 2750
553	0.95%	0.025%	15.2	14.4
554	2.40	0.063	16.0	15.7
548	30.0	0.05	18.4	16.2
620	30.0	0.055	19.4	15.8

Table V
Effect of time on E values for Sodium m-benzenedisulfonate

Plate number	Conc. of disulfonate	Time after mixing	$E^{1\%}_{1cm.}$ 2680	$E^{1\%}_{1cm.}$ 2750
620	0.055% in H_2O	15 min.	18.6	16.1
621	0.055 in $NiSO_4$	15 "	19.4	17.8
614	0.055 in H_2O	24 hrs.	16.3	14.7
615	0.055 in H_2O	24 "	15.9	14.0
616	0.055 in H_2O	6 da.	19.4	15.8
622	0.055 in $NiSO_4$	8 "	20.5	17.1
623	0.055 in $NiSO_4$	8 "	17.6	19.0
639	0.055 in $NiSO_4$	14 "	20.2	19.0
640	0.055 in $NiSO_4$	14 "	19.3	16.4

The nickel sulfate solution has practically no absorption in the ultra violet (8), (9), and see Fig. II. On the other hand, sodium m-benzenedisulfonate has no absorption in the visible spectrum. This fact is remarkable, making this method for the determination of the disulfonate possible with no interference nor overlaping of the nickel sulfate and the sodium m-benzenedisulfonate absorption bands. The disulfonate band extends from 2350 A° to 2800 A° at 18 degrees, which the nickel sulfate band is from 3400 A° to about 4700A°

Jones and Strong (8) in their studies on nickel sulfate solutions indicate that the violet band for nickel sulfate extends from 3700 A. to 4350 A.. However, the data obtained with the instrument used by the writer, shows a wider band, namely, from about 3400 A. to 4700 A., see Fig. I[1]. Jones and Strong also show that the nickel sulfate absorption is independent of the temperature. Extensive studies made by Müller (9) on inorganic solutions indicate there are no deviations from Beer's law for nickel sulfate solutions.

In plating baths benzenedisulfonic acid is frequently used as a brightener instead of the sodium salt, Ghosh and Bisvas (10) have tested this acid and found the acid has the same absorption as the sodium salt. Also in the investigation of Wright (11), the same result is confirmed. Boric acid, which is added to a plating bath as a buffer,

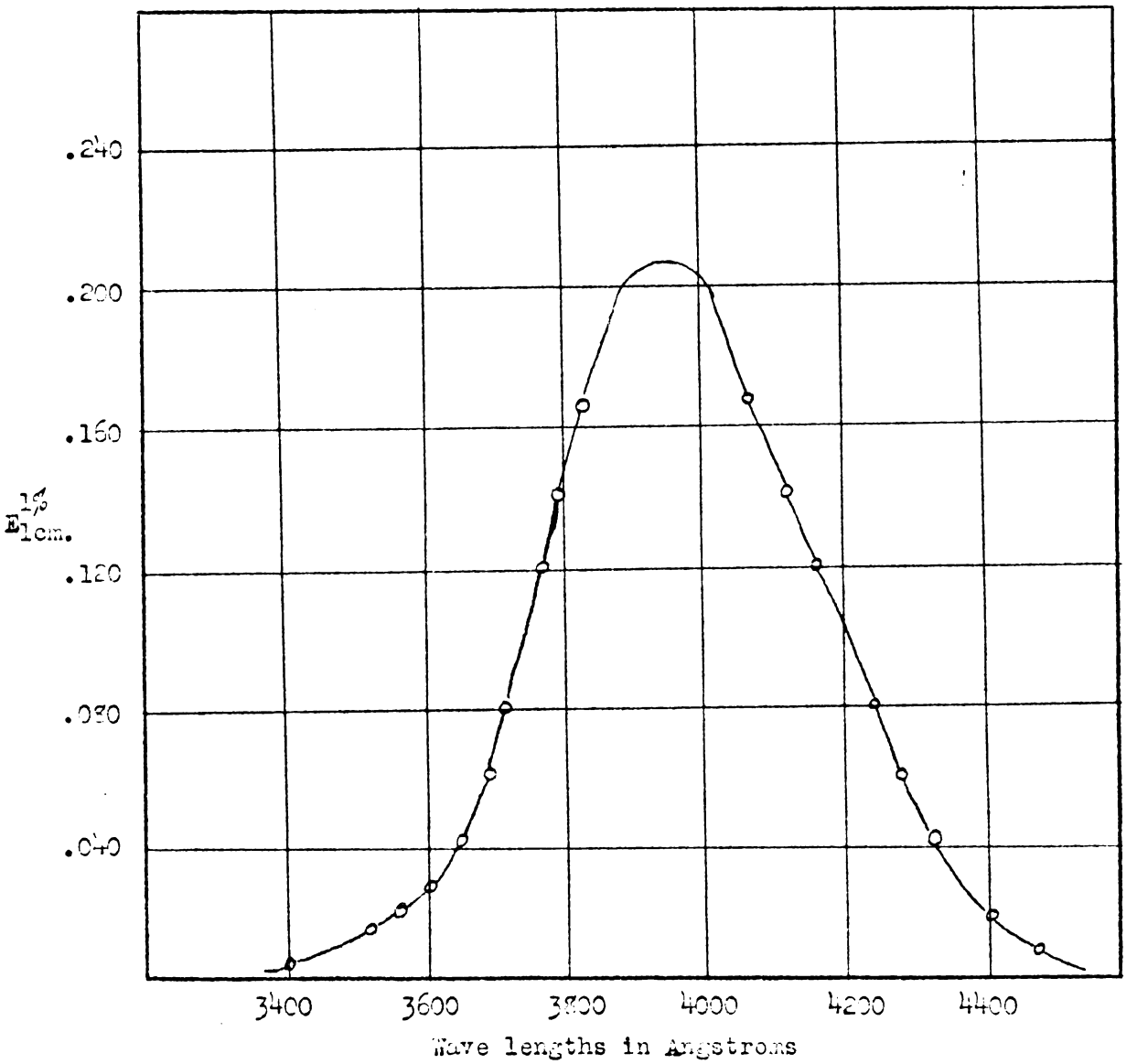

Fig. II. Absorption Curve of Nickel Sulfate Solution

has no absorption in the region where the disulfonate absorption appears.

An interesting observation was the comparison of the difference between the absorption curves for sodium monobenzenesulfonate and sodium m-benzenedisulfonate. The formmer has three maxima and three minima, while the latter has only two maxima and two minima. Incidently, the curve of the sodium mono-benzenesulfonate is very similar to the absorption curve of benzene, which has seven maxima and seven minima (12). Apparently as more sulfonate groups are attached to a benzene molecule, a greater difference in the in the identity of the curve is obvious.

By inspection of Table III it is evident that the E value for sodium m-benzenedisulfonate depends on the solvent and solution. When both cells contain nickel sulfate (30%) solution, the E value is 19.0. When the solvent cell contains 30% nickel sulfate and the solution cell, water, the E value increases from 19.0 to 20.2, making an increase of 1.2 units, or 6.3% difference, a significant amount. It appears from this that the presence of nickel sulfate adds to the size of the E value. Since an increase of 1.2 units in E value is due to absorption by nickel sulfate, and a decrease of 3.2 units in the absence of nickel sulfate, the difference of 2.0 units is evidently due to the presence of nickel sulfate; 2.0 units would make a increase

of 10.5%. This data seems to indicate that the deviations are not due to absorption by nickel sulfate, but rather to a combination--sodium m-benzenedisulfonate and nickel sulfate. However, errors in the result of an analysis can be entirely overcome by using constant working conditions. Likewise, varying concentrations of nickel sulfate influences the E value as seen from the data in Table IV. This variation of E values with concentration, however, does not appear for sodium m-benzenedisulfonate Table I.

It is recommended that a set of conditions, especially of solvent and solute, be decided upon before an analysis is made, or comparison of results contemplated. These conditions, summarized in Tables I and III, have been worked out to give satisfactory results.

Summary and Conclusion

Spectrophotometric data for the quantitative determination of sodium m-benzenedisulfonate in nickel sulfate solution have been presented. Although the technique must be standardized for each series of determinations and carried out with care, it is obviously a more expedient method than the usual gravimetric method used for determining the disulfonate content of nickel plating baths. The results indicate that the spectrophotometric method involving the use of the extinction coefficient can be satisfactorily applied to the determination of sodium m-benzenedisulfonate, and other sulfonates used for bright nickel plating. The average percentage error from six determinations is about 5%.

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