Technical Article

Spectrophotometric Determination of Sulfamic Acid in Metal Sulfamate Bath Effluents

by B.Deepa, K.S.Nagaraja[1] and N.Balasubramanian*

A proposed spectrophotometric method for the determination of sulfamic acid involves acid hydrolysis of sulfamic acid to form ammonium sulfate. The formed ammonium sulfate is determined based on the Berthelot reaction using salicylic acid, sodium hypochlorite and sodium nitroprusside. The γ_{max} for the indophenol dye formed is 648 nm and the calculated molar absorptivity is 1.9×10^4 L/mol-cm. Beer's law is obeyed in the concentration range of 0 to 70 µg and the relative standard deviation is 2% for n = 10 at 50 µg levels of sulfamic acid. The method was applied to determine sulfamic acid in the effluents of nickel and lead sulfamate electroplating baths. The results obtained were validated by recovery studies of added sulfamic acid.

Sulfamic acid has a unique combination of properties that makes it particularly well suited for scale removal and chemical cleaning operations. Metal sulfamates are employed in electroplating baths. Sulfamic acid also finds application in the electropolishing of zinc, molybdenum and cadmium and as a non-selective herbicide. It is used in the dyeing industry to destroy excess nitrite in diazotization processes.[1]

Besides being reactive, sulfamic acid and its salts are corrosive to the eyes, skin and respiratory tract. Inhalation may cause pulmonary edema, which can be delayed for several hours, and there is a risk of death in serious cases.[2] The exposure limit of sulfamic acid, according to the American Conference of Governmental Industrial Hygiene (ACGIH), was found to be 10 mg/m^3. The Occupational Safety and Health Administration (OSHA) sets the limit at 15 mg/m^3 (total) and at 5 mg/m^3 (resp). Hence the determination of residual amounts of sulfamic acid in the effluents of sulfamate baths is essential.

There are reports available in the literature for the determination of sulfamic acid by techniques as varied as gravimetry,[3] gasometry,[4,5] and titrimetry.[6] An extensive literature survey indicated the absence of spectrophotometric methods for the determination of sulfamic acid.

In this study, a simple spectrophotometric method has been developed based on the acid hydrolysis of sulfamic acid to form ammonium ions. The ammonium ion formed was determined with indophenol dye after reaction with salicylic acid, sodium hypochlorite and sodium nitroprusside. The response of the proposed method in the presence of potential interferents was evaluated. In order to demonstrate the applicability of the proposed method, the sulfamic acid contents in the effluents of nickel and lead sulfamate baths were evaluated. The results were established by recovery studies of added sulfamic acid.

Experimental

All absorbance measurements were made using a scanning spectrophotometer** with 1-cm glass cells.

Reagents

All chemicals used were analytical grade reagents, and the working solutions were made up as follows.

Nuts & Bolts: What This Paper Means to You

Besides being used in low-stress nickel processes, sulfamic acid finds use in scale removal, chemical cleaning and electropolishing. However, sulfamic acid and its salts are corrosive to the eyes, skin and respiratory tract. Thus, the determination of residual amounts in the effluents of sulfamate baths is essential. This work involves the development of a spectrophotometric analysis to do that.

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** *Elico Scanning Mini Spec SL 177, Elico Ltd., Hyderabad, India.*

Standard Sulfamic acid solution (10ppm). 0.1000g of sulfamic acid was dissolved in 1000 mL of distilled water to give a stock solution with a sulfamic acid concentration of 100 ppm, which was diluted to obtain a 10 ppm solution.

Salicylic acid (35%). 35 g of salicylic acid was dissolved in 100 mL of 2.5N sodium hydroxide solution.

Sodium hypochlorite solution. A 3% solution was prepared by diluting 5% sodium hypochlorite solution on the day of use.

Sodium nitroprusside (0.24%). 0.24g of sodium nitroprusside was dissolved and diluted to 100 mL.

Hydrochloric acid. 4N HCl was prepared by diluting concentrated hydrochloric acid (specific gravity 1.19).

Procedure — developing the calibration graph

Add 4 mL of 4N HCl to a 10 mL sample containing 0 to 70 μg of sulfamic acid in a 100-mL beaker and dilute to 40 mL with distilled water. Heat the solution on a hot plate until the volume of the solution is reduced to 10 mL. Cool the solution to room temperature and add 2 mL of 35% salicylic acid, 4 mL of 4N sodium hydroxide, 1 mL of 0.12% sodium nitroprusside and 1 mL of 3% sodium hypochlorite. Mix well and transfer the solution to a 25-mL calibrated flask. Wash the beaker with 3 mL of water and transfer the washing to the flask. Dilute to 25 mL with water. Measure the absorbance at 648 nm using a 1-cm glass cell against a reagent blank. Plot the absorbance versus the amount of sulfamic acid to obtain a calibration graph.

Results and discussion

With acid hydrolysis, sulfamic acid yields ammonium ions.[7] The ammonium ions formed were determined based on the formation of indophenol dye. The quantitative conversion of sulfamic acid to ammonium salt was established by spectrophotometric measurement of the absorbance of the indophenol dye formed. The absorbance values compared well with the direct color development using an equivalent concentration of ammonium sulfate as a standard. The results indicated the quantitative hydrolysis of sulfamic acid under experimental conditions. The conditions were optimized for the formation of indophenol dye. The optimized concentrations of salicylic acid, sodium nitroprusside, sodium hypochlorite were incorporated into the working procedure. The ammonium ions, on reaction with salicylic acid and sodium hypochlorite under alkaline conditions, forms the indophenol dye (Fig. 1) in the presence of sodium nitroprusside as a catalyst.[8]

The proposed method was useful for the determination of sulfamic acid in the concentration range of 0 to 70 μg in an overall volume of 10 mL. The molar absorptivity of the colored system was calculated to be 1.9×10^4 L/mol-cm and the developed color remained stable for 24 hr. The calibration graph was a straight line with a positive slope. The equation of the line was:

$$Y = 0.0081X,$$

where Y is the absorbance and X (μg) is the concentration of sulfamic acid. The relative standard deviation was 2% at the 50-μg level of sulfamic acid (n = 10) and the correlation coefficient was 0.9999.

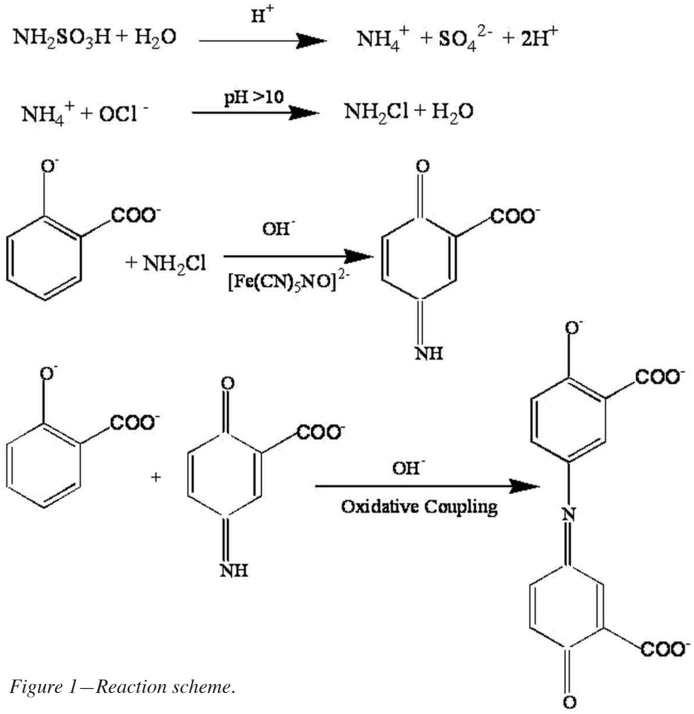

Figure 1—Reaction scheme.

Effect of interfering species on the sulfamic acid determination

The interference effects of common anions and cations, which may coexist with sulfamic acid, were studied. Any deviation in the absorbance of ±0.01 to that obtained in the absence of other interfering ions was taken as sign of interference. Varying concentrations of interfering species were introduced into 50 μg of sulfamic acid and the recovery of sulfamic acid was established following the procedure described to derive the calibration graph. Tolerance limits of various ions studied in the sulfamic acid determination are summarized in Table 1.

Table 1
Effect of interfering species on the determination of sulfamic acid (NH_2SO_3H = 50 µg)

Species	Amount(s) tolerated, μg
Carbonate, Phosphate, Borate, Oxalate, Tartrate, Citrate	1000
Chloride, Bromide, Iodide, Fluoride, Nitrate	1000
Ethanol, Formaldehyde	1000
Mg(II), Sn(II), Sr(II), Ba(II), Ca(II), Pb(II), Mn(II), Cd(II), Co(II), Ni(II) Cu(II), Fe(II), Hg(II) Zn(II)	1000
NH_2 $NH_{2.}$ H_2SO_4	1000*

*As hydrazine.

Applications

Metal sulfamates are employed in electroplating baths. As effluent samples were not readily available samples were prepared by dilution of synthetic nickel and lead sulfamate bath solutions and prepared, following the procedure recommended by Lowenheim.[9] The compositions of the plating baths are given in Table 2. The raw wastewater streams from electroplating baths contain nickel[10] in the concentration range of 0.019 to 2954 mg/L and lead in the concentration range of 0.663 to 25.39 mg/L. The bath solutions were diluted to obtain a nickel concentration of 3000 mg/L and a lead concentration of 30 mg/L. The resulting solutions were suitably diluted to contain no more than 70 μg of sulfamic acid in a sample volume of 10 mL. For analytical purposes, 5-mL aliquots of suitably diluted synthetic lead and nickel sulfamate bath effluents were taken and the overall volume was adjusted to 10 mL using distilled water. The procedure was followed as described previously. The results obtained are given in Table 3. Because of the non-availability of the spectrophotometric method for comparison, the results obtained were validated by standard addition and recovery studies of added sulfamic acid. The observed results compare well.

Conclusion

A new and simple spectrophotometric method is proposed for the determination of sulfamic acid in the concentration range of 0 to 70 μg of sulfamic acid. The molar absorptivity is 1.9×10^4 L/mol-cm and the correlation coefficient was found to be 0.9999. The relative standard deviation was 2% for n = 10 at 50-μg levels of sulfamic acid. The application of the proposed method demonstrated the utility of the method for the determination of sulfamic acid in plating effluents.

Table 2
Composition of nickel and lead sulfamate electroplating solutions

Solution	Composition, g/L (oz/gal)		
Nickel sulfamate solution			
A	Nickel sulfamate Boric acid	450 30.0	(60.1) (4.0)
B	Nickel sulfamate Boric acid Nickel chloride	450 30.0 6.0	(40.0) (4.0) (0.8)
Lead sulfamate solution			
A	Lead sulfamate (as Lead metal) Free sulfamic acid	104 54.0 50.0	(13.9) (7.2) (6.7)
B	Lead sulfamate (as Lead metal) Free sulfamic acid	154 80.0 100	(20.6) (10.7) (13.4)

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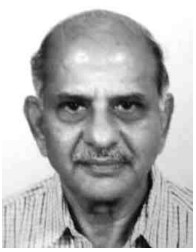

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Table 3
Determination of sulfamic acid in nickel and lead sulfamate solution effluents (Dilution Method); Ni concentration, 3000 mg/L; Pb concentration, 30 mg/L. The sample volume was 5 mL in all cases

Solution	Sample dilution, D	NH_2SO_3H added, μg	NH_2SO_3H present, μg	% Recovery of NH_2SO_3H added	NH_2SO_3H Concentration[b], (mg/L)[a]
Nickel sulfamate solution					
A	1000	---	49.56	---	9916
		10	59.51	99.5	
		---	49.60	---	
		10	59.52	99.2	
		---	49.57	---	
		10	60.17	100.6	
			49.58[a]		
B	1000	---	49.57	---	9914
		10	59.56	99.9	
		---	49.59	---	
		10	59.55	99.6	
		---	49.55	---	
		10	59.44	98.9	
			49.57[a]		
Lead sulfamate solution					
A	10	---	27.94	---	55.88
		20	47.78	99.2	
		---	27.95	---	
		20	47.22	98.6	
		---	27.94	---	
		20	47.86	99.6	
			27.94[a]		
B	10	---	32.80	---	65.62
		20	52.82	100.1	
		---	32.82	---	
		20	52.70	99.4	
		---	32.81	---	
		20	52.74	99.7	
			32.81[a]		

[a] Average of three values.

[b] Concentration of NH_2SO_3H (mg/L) $= \dfrac{\text{Amt. of } NH_2SO_3H(\mu g)}{\text{Sample Volume (mL)}} \times$ Dilution Factor