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Reaction of Chloramine-B with Cr(III), Al(III) and Fe(III) Solutions-A Conductometric and pH Study

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Chloramine-B, the sodium salt of N-chlorobenzenesulphonamide produces a while turbidity with $CrCl_3$, $AlCl_3$ and $FeCl_3$ in aqueous solution. Conductometric and pH titrations have been carried out and the results are discussed. The turbidity has been identified as dichloramine-B through UV, IR, ^1H and ^{13}C nmr spectral studies. The breaks in the conductance graphs also substantiate the formation of the free acid RNHCl, where R is $C_6H_5SO_2$.

INTRODUCTION

Sodium salt of N-chlorobenzenesulphonamide or chloramine-B (CAB) has received considerable attention as an oxidimetric[1] and analytical reagent[2]. Subhashini *et al*[3] have studied the kinetics of chlorine isotope exchange between CAB and chloride ion using ion-exchange separation and tracer technique. The protonation constant of CAB at pH < 3.3 by an ion-exchange method has been studied by Subhashini *et al*[4]. The conductometric study of the interaction of CAB with silver nitrate, mercuric chloride, zirconium and thorium ion solutions have been reported[5]. Conductometric and pH titrations between aqueous solutions of CAB and HCl has been studied by Yathirajan *et al*[1]. The conductometric and pH behaviour of chloramine-T, bromamine-T and bromamine-B with metal ions have been reported.[6–10] Although the oxidation mechanisms of many chloraminometric reactions have been kinetically investigated, the information available in literature about the conductance and pH behaviour of CAB is scanty.

The present work describes a study on the interaction of CAB with chromium(III), aluminium(III) and iron(III) solutions. Conductometric and pH titrations have been carried out and the resulting curves have been explained and discussed. The product formed in these reactions has been analysed through UV, infrared, ^1H and ^{13}C NMR spectroscopy.

EXPERIMENTAL

A direct reading conductivity meter 304 (systronics) and a digital pH meter, Model LI-120 (Elico) were used for conductance and pH measurements (T = 25 ± 0.1°C) respectively. A dip type conductivity cell with a cell constant = 1.0 cm^{-1}, was used. A JASCO, Model UVIDEC-610 UV-VIS spectrophotometer with 1.0 cm matched quartz cells was used to record the UV spectra. IR spectra (KBr disc) were recorded on a Carl-Zeiss UR 10 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX 400 MHz NMR spectrometer, using $D_2O/CDCl_3$ (TMS as internal reference) with chemical shifts expressed in δ.

Triply distilled water (Sp. cond. $< 1 \times 10^{-6}$ ohm^{-1} cm^{-1}) was used for preparing all the solutions.

Chromic chloride $CrCl_3 \cdot 6H_2O$ (BDH AR), aluminium chloride $AlCl_3 \cdot 6H_2O$ (BDH AR) and ferric chloride $FeCl_3 \cdot 6H_2O$ (Merck, recrystallized from water) were used. Chromic chloride solutions were standardized by iodometry, where as ferric chloride solutions from dichrometry. Aluminium ion solutions were filtered to remove traces of aluminium hydroxide and were standardized by using EDTA.

CAB was prepared[11] by passing pure chlorine gas through benzenesulphonamide (Aldrich, USA) dissolved in NaOH solution (4M) over a period of 1 h at 70°C. The mass obtained was filtered, dried and recrystallized from water at 50°C. The purity of the compound was checked by estimating the amount of active chlorine present in the compound[12]. CAB solutions were standardized by iodometry. CAB was further characterised by its UV, IR, ^1H and ^{13}C NMR spectra.

Procedure

The initial conductance of a known volume of the metal ion solution of known concentration was measured. To this solution was added a solution of CAB (5 to 10 times stronger) from a microburette in small volumes. In the initial stages, a white turbidity was formed which dissolved on stirring the solution. Conductance of the solution was recorded after the disappearance of turbidity. The precipitate formed on further addition of CAB was allowed to settle wherever possible, before the conductance of the solution was measured. Conductance of the solution with each addition of CAB solution was calculated after applying the volume correction[13]. The end point was obtained graphically by plotting the conductance of the solution against the volume of CAB added. Reverse titrations were carried out in the same manner.

The pH titrations of both direct and reverse were carried out in a similar fashion.

RESULTS AND DISCUSSION

Conductometric titrationof Cr^{3+} ion with CAB

The conductometric titrations of chromic chloride solutions (0.01013 and 0.00215 M) with CAB (0.09752 and 0.1600 M) have been performed and a typical graph is shown in Figure 1. Aliquots ranging from 20 to 50 mL have been employed. It is seen from the figures that the conductance of chromic chloride solution decreases initially with the addition of CAB. The first break noticed corresponds to the point at which the precipitate becomes insoluble beyond which the conductance slowly increases. A second break however is observed at 1:2 molar ratio with respect to chromic ion and CAB. There is a steep increase in conductance beyond this point.

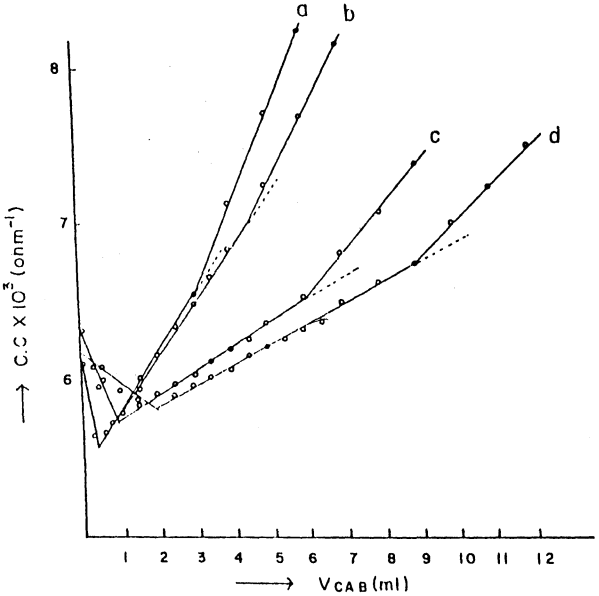

Fig. 1 Conductance graph for the titration of 20, 30, 40 and 50 mL of chromic chloride (0.0215 M) against chloramine-B (0.160 M)

The reverse titrations of CAB (0.009502 and 0.01600 M) with chromic chloride (0.09474 and 0.2150 M) are carried out and shown in Figure 2. It is seen

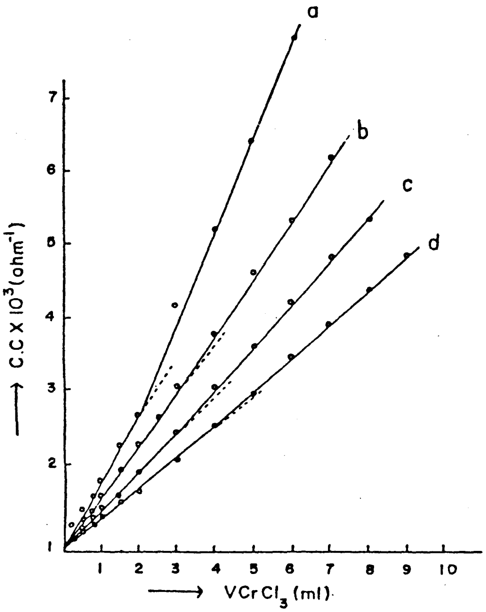

Fig. 2 Conductance graph for the titration of 20, 30, 40 and 50 mL of chloramine-B (0.009502 M) against chromic chloride (0.09474 M)

that the conductance of CAB solution gradually increases and a faint break is found at 2:1 molar ratio with respect to CAB and chromic ion. The conductance rapidly increases beyond this point.

Conductometric titration of Al^{3+} ion with chloramine-B

Figure 3 shows the results of titration of different aliquots of aluminium chloride (0.01836 and 0.02526 M) with CAB (0.1093 and 0.2663 M). The conductance shows a slight decrease initially upon the addition of CAB to aluminium chloride solutions, which corresponds to the solubility of the precipitate. The conductance thereafter increases steadily and a faint and strong break corresponding to 1:1 and 1:2 molar ratio with respect to aluminium ion and CAB are observed.

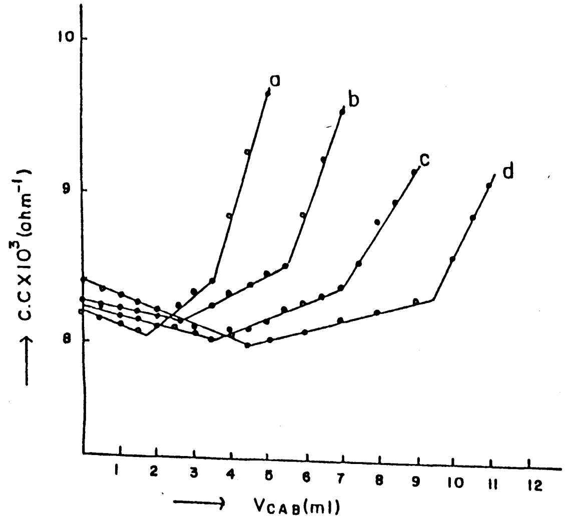

Fig. 3 Conductance graph for the titration of 20, 30, 40 and 50 mL of aluminium chloride (0.02526 M) against chloramine-B (0.2663 M)

The results of the reverse titration of CAB (0.01093 and 0.02663 M) with aluminium chloride solution (0.1121 and 0.2642 M) are shown in Figure 4. The conductance gradually increases with the addition of aluminium chloride to CAB solution up to a point of inflection equivalent to 2:1 molar ratio with respect to CAB and aluminium ion. Thereafter, the conductance increases rapidly.

Conductometric titration of ferric chloride with chloramine-B

The results of titration of different aliquots of ferric chloride (0.01378 and 0.02394 M) with CAB (0.1058 and 0.2152 M) and those of the reverse titrations of CAB (0.01105 and 0.02091 M) and ferric chloride (0.1261 and 0.2169 M) are shown in Figures 5 and 6. In the direct titration of ferric ion with CAB in the burette, the conductance initially decreases to give a break at 1:1 molar ratio followed by an increase and a decrease giving two points of inflection corresponding to 1:2 and 1:3 molar ratio with respect to ferric ion and CAB, beyond which

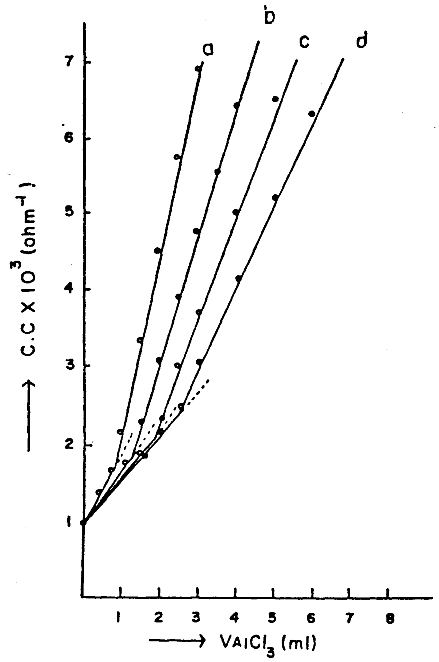

Fig. 4 Conductance graph for the titration of 20, 30, 40 and 50 mL of chloramine-B (0.01093 M) against aluminium chloride (0.1121 M)

the conductance increases. In the reverse titration, the conductance increases systematically show in two breaks at approximately 1:1 and 2:1 with respect to CAB and ferric chloride.

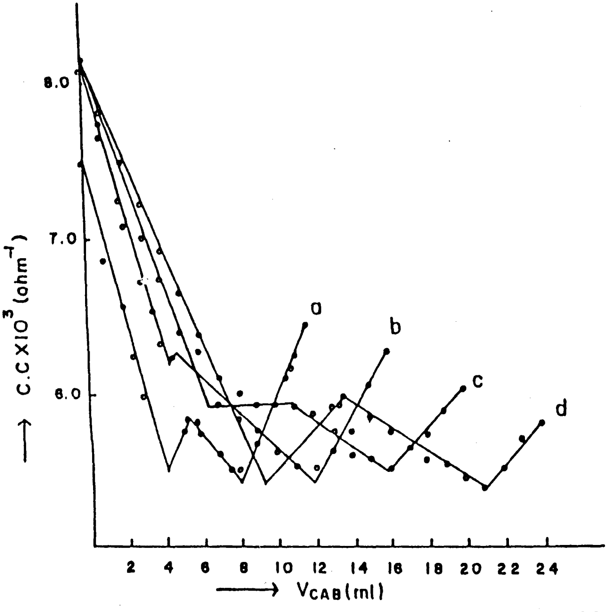

Fig. 5 Conductance graph for the titration of 20, 30 40 and 50 mL of ferric chloride (0.01378 M) against chloramine-B (0.1058 M)

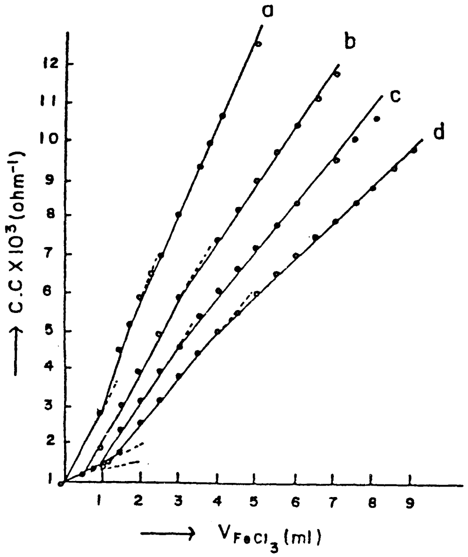

Fig. 6 Conductance graph for the titration of 20, 30, 40 and 50 mL of chloramine-B (0.01105 M) against ferric chloride (0.1261 M)

pH titrations of metal ion solutions with chloramine-B

pH titrations of CAB and Cr^{3+}, Al^{3+} and Fe^{3+} were carried out and a typical graph for Cr^{3+} is shown in Figure 7. In the reverse titrations {20 or 30 mL of CAB (0.009502 M) and $CrCl_3$ (0.09474 M)}, the pH of CAB solution rapidly decreases in the initial stages upon the addition of metal ion solutions, up to a small point of inflection corresponding to the appearance of the precipitate. Thereafter, there is a further decrease in the pH of the solution followed by a horizontal section probably corresponding to a region of supersaturation with the precipitate. In the direct titration {20 or 30 mL of $CrCl_3$ (0.01013 M) and CAB (0.09752 M)}, with the addition of CAB to metal ion solutions, pH of the solution slowly increases reaching a saturation at higher volumes of the titrant.

Conductometric titrations between neutralised metal ion solutions and chloramine-B

Known volumes of the metal ion solutions were carefully neutralised to pH 6.8 by adding 0.1 M sodium hydroxide solution and the neutralised solutions were conductometrically titrated against standard CAB solution. These results are shown in a typical graph for Cr^{3+} in Figure 8. It was observed that, no precipitation took place under these conditions and the conductance of the neutralised metal ion solution increased almost linearly without any break.

Hydrolysis equilibria in Cr^{3+}, Al^{3+} and Fe^{3+} ion solutions

The hydrolysis equilibria present in aqueous solutions of chromic chloride,

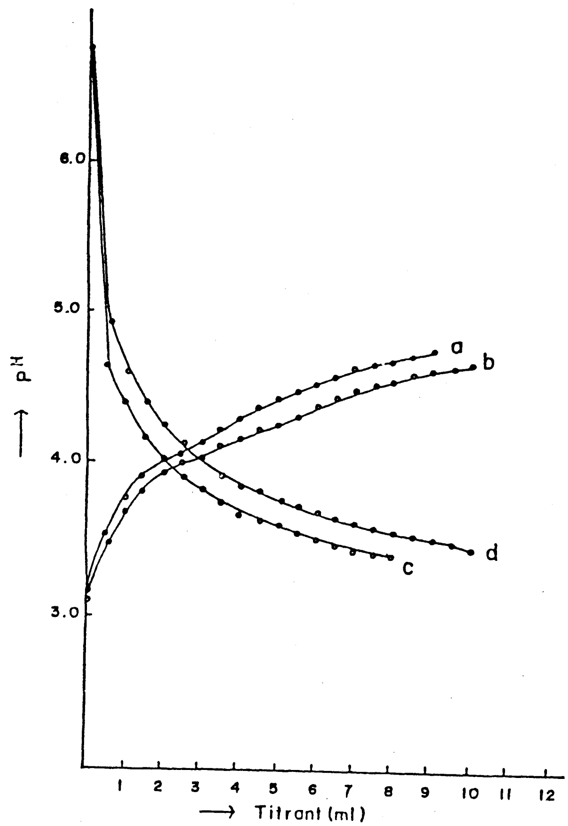

Fig. 7 pH titration curves for the titration of Cr^{3+} ion solution and chloramine-B

aluminium chloride and ferric chloride have been studied[14–18]. For chromic chloride[19] the equilibria are give as:

$$2ClCr^{2+} + H_2O \overset{K_1}{\rightleftharpoons} [ClCrOH^+]_2 + 2H^+ \quad (i)$$

$$2Cl^- + 2H_2O + 2Cr^{3+} \overset{K_2}{\rightleftharpoons} [ClCrOH^+]_2 + 2H^+ \quad (ii)$$

Here $K_1 = 10^{-6}$ and $K_2 = 4 \times 10^{-2}$. It is likely that step (ii) is important during the hydrolysis of $CrCl_3$.

For aluminium chloride, the three step equilibra[20] are represented as:

$$[ClAl^{2+}]_2 + 2Cl^- + 2H_2O \overset{K_1}{\rightleftharpoons} (Cl_2AlOH)_2 + 2H^+ \quad (iii)$$

$$[ClAl^{2+}]_2 + 2H_2O \overset{K_2}{\rightleftharpoons} [ClAlOH^+]_2 + 2H^+ \quad (iv)$$

$$Cl^- + Al^{3+} + H_2O \overset{K_3}{\rightleftharpoons} ClAlOH^+ + H^+ \quad (v)$$

where $K_1 = 7 \times 10^{-9}$, $K_2 = 3.2 \times 10^{-11}$ and $K_3 = 8 \times 10^{-3}$

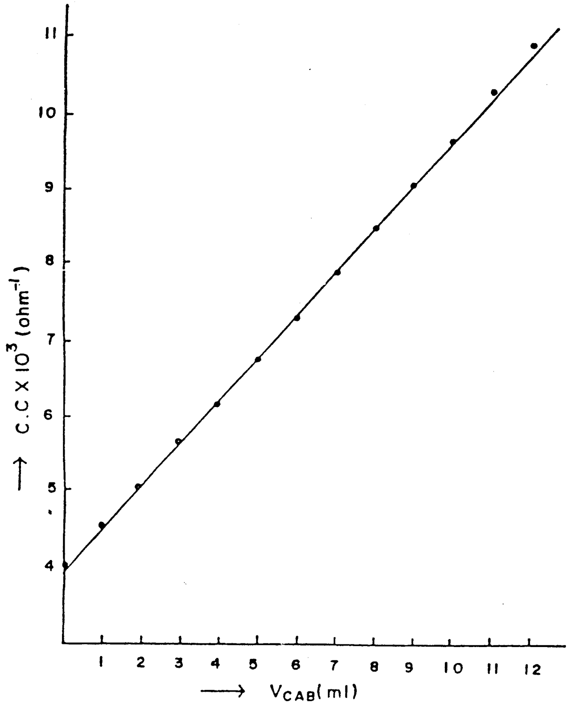

Fig. 8 Conductance graph for the titration of neutralised chromic chloride (0.0215 M) against chloramine-B (0.1600 M)

Step (v) seems to be predominant, but the break at 1:2 with respect to aluminium chloride and CAB indicate that at least two protons could have been released in the hydrolysis equilibria. Investigations[19] have revealed that the hydrolysis equilibria in the case of aluminium chloride are very complex. Aveston[21] and others[22] suggest that the hydrolysis equations (iii) to (v) are too simple and that the main species present in aluminium chloride solutions are the ions, $[Al_2(OH)_2]^{4+}$ and $[Al_{13}(OH)_{32}]^{7+}$. The former species is found to be important and it is formed as follows:

$$2Al^{3+} + 2H_2O \overset{K_4}{\rightleftharpoons} [Al_2(OH)_2]^{4+} + 2H^+ \qquad \text{(vi)}$$

$$K_4 = 8.511 \times 10^{-8}.$$

Investigations[19] have revealed that hydrolysis of Fe^{3+} ion involves more complex equilibria which can be shown as follows:

$$[Fe(H_2O)_6]^{3+} \overset{K_1}{\rightleftharpoons} [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad \text{(vii)}$$

$$[Fe(H_2O)_5(OH)]^{2+} \overset{K_1}{\rightleftharpoons} [Fe(H_2O)_4(OH)_2] + H^+ \qquad \text{(viii)}$$

$$[2Fe(H_2O)_6]^{3+} \overset{K_3}{\rightleftharpoons} [Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+} + 2H^+ \qquad \text{(ix)}$$

$K_1 = 8.913 \times 10^{-4}$, $K_2 = 5.495 \times 10^{-4}$ and $K_3 = 1.23 \times 10^{-3}$.

The three steps are found to be equally important and these reactions could possibly account for the three breaks observed in the conductance graphs.

Conductometric and pH titrations of CAB with HCl indicate the possible equilibria[1] in acidified CAB solutions.

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad (x)$$

$$2RNHCl \rightleftharpoons RNH_2 + RNCl_2 \qquad (xi)$$

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl \qquad (xii)$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \qquad (xiii)$$

Where $R = C_6H_5SO_2$.

Zilberg[23] has shown that acidification of CAB with HCl, acetic acid or H_2SO_4 gives DCB and RNH_2. Mogilevskii[24] and co-workers have reported the presence of HOCl in acidified CAB solutions. Further, pH measurements on aqueous solutions of CAB showed that a 0.05 M CAB solution has a pH of 7.7 at 25°C. From this, the ionization constant (K_a) of RNHCl is found to be 2.4×10^{-3}.

It is likely that the precipitate obtained in the conductometric titrations is dichloramine-B, which is slightly soluble in water (0.125 g/lit. at 30°C), but it is fairly soluble in glacial acetic acid (175.2 g/lit. at 30°C) and other common organic solvents. The breaks obtained at 1 : 1 molar ratio probably indicates the formation of RNHCl. The breaks found at 2 : 1 and 3 : 1 molar ratios with respect to CAB solution could just indicate the availability of the number of protons in the solutions for reacting with CAB, as shown below:

$$n\,RNCl^- + nH^+ \rightleftharpoons n\,RNHCl \qquad (xiv)$$

where n = 2 or 3.

The initial decrease in conductance of metal ion solutions when CAB is taken in the burette could be attributed to the removal of H^+ from the solution and solubility of the precipitate in the metal salt solution, while the increase noted after the breaks is due to the addition of excess of titrant.

In the reverse titrations, with CAB in the beaker, initial increase in conductance of the solution is due to the addition of metal ions, although $RNCl^-$ ions are removed from the solution by the added H^+ ions according to the equation:

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad (x)$$

The steep increase observed after the breaks is due to the addition of excess titrant.

pH titrations curves of CAB obtained by taking Cr^{3+}, Al^{3+} and Fe^{3+} ions in the burette (reverse titration) are similar and are indentical with the titration curves of CAB and HCl. From the pH data obtained, it was found that the conductance breaks generally occurred between pH 3 and 4 in both direct and reverse titrations.

The precipitation generally continued until a pH of 5.2 in direct titrations and a pH of 2.5 in reverse titrations. The pH titration curves resemble the normal acid-base titration curves and are similar with the work of Morris *et al*[25], Rangaswamy *et al*[7] and Yathirajan *et al*[1].

Attempts to check the mass balance for these reactions were unsuccessful as dichloramine-B formed was initially soluble in the metal ion solutions. However, the quantitative estimation of any of these metal ions is possible if the molarity of CAB is known or vice versa.

Further, when carefully neutralised solutions of Cr^{3+}, Al^{3+} and Fe^{3+} ions with NaOH were titrated against CAB, no precipitation was observed and the conductance increases continously without a break indicate that H^+ ion seems to play a prominent role in these precipitation reactions.

In the present investigations, the disproportionation reaction (xi) appears to be fastest at pH = 4 and thereafter the rate decreases. This could as well account for the decrease in the amount of precipitation after pH = 4. It is probable that RNHCl formed around pH = 3 disappears above this pH by reaction (xi), giving rise to DCB and RNH_2. Similar observations were made by Higuchi *et al*[26].

Identification of the product through spectral data

The precipitate formed during the above experiments was suspected to be DCB. The precipitate was filtered, washed with water, shaken with dilute H_2SO_4, filtered and dried. Respective metal ions could be detected in the filtrate indicating the adsorption of metal hydroxides on the surface of the precipitate during the later stages of titration. The active chlorine content in DCB was found to be 31.0% (theoretical 31.4%). DCB melted at 74°C (theoretical 74°C). DCB was further characterized by UV. IR, ^{1}H, ^{13}N MRC spectral studies, the details of which are given below. The spectra of DCB prepared by the method of Yathirajan *et al*[27] and the spectra of DCB obtained from the above reactions were similar.

UV spectrum of DCB: Found to be characteristic of benzenoid absorption with a$\lambda_{max}^{(H_2O)}$ of 212.0 nm and can be probably attributed to π–π^* transition. It may be noted that benzenesulphonamide (RNH_2) absorbs in this region[28].

IR spectrum (KBr disc) of DCB: SO_2 sym. stretch-1180 cm^{-1}, SO_2 asymm. stretch-1340 cm^{-1}, N-Cl stretch-538, 563 and 580 cm^{-1}.

^{1}H NMR spectrum of DCB

($CDCl_3$) δ 7.70 (t, 2H, Ar-H) ppm
δ 7.86 (t, 1H, Ar-H) ppm
δ 8.12 (d, 2H, Ar-H) ppm

^{13}C NMR spectrum of DCB

($CDCl_3$) δ 131.402 (d, 2, 6-C) ppm
δ 129.186 (d, 3, 5-C) ppm
δ 136.031 (d, 4-C) ppm
δ 128.70 (s, 1-C) ppm

Conclusion

It may be concluded that aqueous chloramine-B reacts with chromic chloride, aluminium chloride and ferric chloride solutions to produce dichloramine-B, which is substantiated by conductometric and pH titrations and also through spectral data. An experimental proof for the formation of free acid, N-chlorobenzenesulphonamide (RNHCl) in these reactions is demonstrated.

It may be pointed out that no chromic, aluminium or ferric salt of the free acid RNHCl, similar to silver and mercuric salts can be prepared even by the addition of excess reagents. However, the results are significant, for the conductance breaks can be taken as positive evidence for the formation of the free acid RNHCl.

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