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Preliminary studies on the electrolytic reduction of nitrobenzene to aniline

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The reduction of nitrobenzene by an electrolytic method is fairly simple and it does not require the complicated equipment needed in the vapour phase reduction method. On account of the simplicity of operation, an attempt is being made to work out a suitable electrolytic method for this tonnage of chemical and study its economics as compared to other known methods of production. In this paper, the results obtained in the preliminary experiments using the rotating electrode technique are discussed. It is found that it is necessary to add certain 'hydrogen carriers' to catalyse the reduction. Without the addition of such carriers, complete reduction is not possible. Various conditions such as current density, depolarizer ratio, temperature and concentration of the hydrogen carrier have been studied. An attempt is made to work out the material balance for the nitrobenzene employed.

Introduction

During 1968, aniline production was 120 000 tons in the U.S. (estimated total plant capacities 180 000 tons), 70–90 000 tons in Western Europe and 25 000 tons in Japan. During the 10 year period 1958–68, U.S. demand growth rate has been 7% per annum and is forecast at 6% per annum to 1973 [1].

Aniline is largely used in the preparation of dyes of various classes, either directly or after conversion into numerous other intermediates. A considerable amount of aniline is needed for the production of aniline black [2]. Aniline is also an important starting material in the production of pharmaceutical products like atoxyl and salvarsan [3]. Aniline derivatives are used in large quantities nowadays in rubber industries. It is also used in the manufacture of germicides, paints, varnishes and explosives. Aniline sulphate is used as a starting material for the manufacture of sulphanilic acid [4]. Aniline is also used to extract bromine from sea water [5].

Aniline can be prepared by the Bechamp method in which nitrobenzene is reduced to aniline by iron and hydrochloric acid. The reported yield is about 91% of the theoretical amount [6].

In another method, a catalyst, say ferrous chloride, and sodium chloride or sodium acid sulphate is used instead of HCl and the reported yield is about 98% of the theoretical amount [7].

In the above methods, if the acid concentration is below the optimum, phenyl hydroxylamine will undergo para transformation to p-aminophenol and if the acid concentration is above the optimum, too much of the iron will go into solution and then when the reaction mixture is made alkaline a voluminous precipitate of iron hydroxide will be formed.

Aniline is also obtained by reducing nitrobenzene in the vapour phase with a nickel catalyst. Brown and Henke obtained a 95% yield of aniline from nitrobenzene [8].

Though this method is better than the other methods for the continuous conversion of reactants to finished amine, minimum operating labour requirements, low steam and power costs by utilizing the heat in vapours leaving the catalytic chamber and absence of industrial waste problems such as iron oxide, it is not without any drawback. With a constant rate of flow of nitro-

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benzene, the yields drop off with too much or too little hydrogen. This fluctuation has been ascribed to over- or under-reduction. Since nickel is such an active catalyst for this purpose, reduction of the aniline to cyclohexane and ammonia is known to take place. Separation of aniline from nitrobenzene and formation of water as co-product affecting the catalysts are also some of the problems.

Aniline is also obtained from chlorobenzene and ammonia. The reduction is carried out at very high pressure (up to 340 atmospheres and temperatures (340°C) forming aniline and ammonium chloride [9, 10].

In another method, phenol and ammonia are passed over alumina at a pressure of 10 atmospheres and at a temperature of 450–480°C. Oxides of thorium, titanium, tungsten, molybdenum and vanadium have also been described as catalysts [11].

Reduction with alkali and metal sulphides such as iron and manganese, hydrogen sulphide, ferrous sulphate, and alkali sodium hydrosulphite [12] has also been reported for the production of amines from nitro compounds. Paraffinic and cycloparaffinic hydrocarbons, hydrogen in the presence of platinum oxide or metal sulphides or palladium have also been used.

The electrochemical reduction of nitrobenzene to aniline has been studied by various workers and the results will be briefly reviewed. Elbs and Silbermann [13] have studied the reduction under stationary electrode conditions using a zinc electrode in the presence of a zinc salt. The yields obtained by them were 80–90%. Similar results were obtained with a platinum electrode by Elbs [14]. Snowden [15] studied the reduction with an iron cathode in the presence of ferrous chloride at 100°C. It was observed that iron dissolution increased at low current densities. A yield of 95% aniline was obtained. The use of lead and nickel as cathodes in an hydrochloric acid medium was studied by Otin [16]. There was dissolution of the metal at the lower current density ranges but an overall yield of 92–94% was reported. Similarly Reich [17] has obtained a yield of 96% at a lead cathode. Antropov and Vagramyan [18] have studied the effect of pH on electrochemical hydrogenation at low currents (10^{-5}–10^{-3} A). They have also studied the reduction at a mercury cathode but reported larger quantities of p-aminophenol, as compared to aniline.

So far the studies have been confined to stationary electrodes only. The studies carried out by Wilson and Udupa [19] on the reduction of nitro compounds using rotating cathodes have shown that the current efficiency is increased to a great extent over that for a stationary cathode for the same current density. This was further developed to commercial scale cells by Udupa, Subramanian and Pathy [20] who have emphasized in detail the advantages of the rotating cathode over the stationary cathode in the design of high amperage cells.

The usual conditions for the reduction of nitro compounds to aniline were studied [21–26], namely using a copper cathode in dilute sulphuric acid. But it was noted that under the best conditions, the yields of aniline were quite low (less than 50%) and it was not possible to improve the yields further.

It is reported that certain ions like titanium, vanadium, chromium, iron and cerium by virtue of their two valency states can catalyse the electrolytic reduction of organic compounds. For example, the higher valency state of the carrier e.g. Ti^{++++} is reduced at the cathode to the lower state Ti^{+++}. The latter, being a powerful reducing agent, reacts with the substance present in the solution and while doing so is reoxidized to its original state [27].

In view of the good demand for aniline for the dye industries and other industries as mentioned earlier, the electrolytic reduction of nitrobenzene was studied in order to work out a suitable process for industrial exploitation.

The influence of different factors on the yields of aniline were studied and some of the preliminary results are reported.

Experimental

A glass beaker of 1200 cm^3 capacity with a lead cover having holes for the rotating cathode, porous pot, condenser and thermometer was used. A ceramic porous pot with a lead electrode served as the anode chamber. The condenser with suction minimized the loss due to carry over with water vapour. The cathode was cylindrical and was made of copper. It was 8·5 cm high and 2·6 cm in diameter, the total area being 0·80 dm^2. The cell was kept in a water bath which was used to adjust the temperature.

The supporting electrolyte was dilute sulphuric acid (10% vol/vol) with an addition of copper sulphate, about 0·1% by weight of catholyte. Various hydrogen carriers such as titanium, vanadium, chromium, iron or cerium ions are added to the catholyte before adding the depolarizer. The reduction was continued till, according to theory, all the nitrobenzene had been reduced. The solution is steam distilled to remove any unreduced nitrobenzene. It is cooled and neutralized with ammonium bicarbonate to liberate the free base aniline which is then recovered by steam distillation. The steam distilled water containing aniline is treated with sodium chloride when part of the aniline gets salted out. After separating aniline, the dissolved aniline in water is extracted with benzene. The aniline content is estimated by the bromination method [28].

Results and discussion

Studies were made to obtain the optimum current density, depolarizer ratio, temperature and concentration of hydrogen carrier to obtain the maximum yield.

The effect of current density was studied under the following conditions; the results are tabulated in Table 1.

It is noted according to the table that increasing the current density decreases the yield of aniline and increases the yield of p-aminophenol. The higher current density favours the formation of the intermediate phenyl hydroxylamine which immediately undergoes transformation to p-aminophenol. While in the low current density range, the reduction of phenyl hydroxylamine is favoured over its transformation to p-aminophenol.

The effect of depolarizer ratio was studied by keeping the conditions the same as in Table 1. The results are given in Table 2.

The higher the quantity of nitrobenzene, the greater the formation of p-aminophenol at the same current density. It is, therefore, necessary to have a lower concentration of nitrobenzene in order to have higher yields of aniline.

The effect of temperature on the yields of aniline sulphate is given in Table 3.

Higher temperatures favour the p-aminophenol transformation and therefore the yields of aniline are reduced. It is advisable to employ lower temperatures for the reduction to aniline.

The effect of the addition of the hydrogen ion carrier titanous sulphate is given in Table 4.

It is evident from these tables (1 to 4) that higher current densities, higher temperatures, higher depolarizer ratios and lower concentra-

Conditions followed in Table 1

Volume of catholyte taken	500 ml
Concentration of catholyte	10% vol/vol
Volume of anolyte taken	150 ml
Concentration of anolyte	10% vol/vol
Weight of $CuSO_45H_2O$ added to catholyte	0·5 g
Weight to titanous sulphate added	4·3 g as TiO_2
Temperature	45–55°C
Weight of nitrobenzene added	120 g
Area of the cathode	0·8 dm^2

Table 1

Study No.	Current (A)	Current density (A/dm^2)	Nitrobenzene recovered (g)	Nitrobenzene recovered (%)	Aniline recovered (g)	Aniline recovered (%)	Aniline estimated (g)	Aniline estimated (%)	Wt. of nitrobenzene converted to p-aminophenol (g)
1	20	25	—	—	79·8	87·8	81·3	89·5	12·6
2	24	30	—	—	74·6	82·2	75·2	82·8	20·6
3	28	35	—	—	76·0	83·7	77·1	84·9	18·1
4	32	40	—	—	53·6	59·0	55·4	61·0	46·8

Table 2

Conditions same as Table 1—Current density 25 A/dm²

Study No.	*Nitrobenzene taken (g)*	*Nitrobenzene recovered (g)*	*(%)*	*Aniline recovered (g)*	*(%)*	*Aniline estimated (g)*	*(%)*	*Wt. of nitrobenzene converted to p-aminophenol (g)*
1	240	11·6	4·9	141	81·3	143·3	82·6	39·7
2	180	8	4·4	102·2	78·6	104·5	80·4	33·7
3	120	—	—	79·8	87·8	81·3	89·5	12·6

Table 3

Conditions same as Table 1—Current density 25 A/dm²

Study No.	*Temperature (°C)*	*Aniline recovered (g)*	*(%)*	*Aniline estimated (g)*	*(%)*	*Wt. of nitrobenzene converted to p-aminophenol (g)*
1	45–50	78·8	86·7	80	88·1	14·3
2	50–55	76·2	83·9	80	88·1	14·3
3	55–60	—	—	78	85·9	16·9

Table 4

Conditions same as in Table 1—Current density 25 A/dm²

Study No.	*Volume of titanous sulphate taken (ml)*	*Weight of titanium as TiO_2 (g)*	*Aniline recovered (g)*	*(%)*	*Aniline estimated (g)*	*(%)*	*Nitrobenzene converted to p-aminophenol (%)*
1	5	0·43	50·1	57·2	51·1	56·3	52·4
2	10	0·86	40·9	45	41·9	46·2	64·6
3	30	2·58	56·7	62·4	59·5	65·5	41·4
4	40	3·44	64·4	70·9	66·0	72·7	32·8
5	50	4·30	79·8	87·8	81·3	89·5	12·6
6	60	5·16	82·8	91·2	84	92·5	9·0
7	80	6·88	79·1	87·2	81·3	89·6	12·5

Increasing the concentration of titanous sulphate increases the yield of aniline, and reduces the formation of p-aminophenol. This is so because the catalytic effect of the titanous sulphate favours the reduction of the intermediate phenyl hydroxylamine formed rather than its transformation to p-aminophenol. There is, however, an optimum limit to the concentration of the titanous sulphate depending upon the stability of the titanous sulphate under the concentration of the acid employed. It is necessary to maintain the free acid concentration at the desired level in order to avoid the hydrolysis of the titanous sulphate as TiO_2.

tions of the hydrogen carriers do not favour good yields. Further work is in progress on the material balance for nitrobenzene and the recovery of aniline as sulphate and also on the possibility of further recycling of the electrolyte.

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