JOURNAL OF APPLIED ELECTROCHEMISTRY 23 (1993) 56–59

Isolation and purification of iminodiacetic acid from its sodium salt by electrodialysis

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Received 24 February 1992; revised 28 April 1992

Iminodiacetic acid (IDA) is a key intermediate for the synthesis of glyphosate, a broad-spectrum herbicide. In the main current synthetic methods IDA is obtained as its sodium or potassium salts. The recovery of IDA in high yield and purity is not an easy task if current procedures are used. Both problems can be overcome by using electrodialysis. Thus, IDA with a purity higher than 99.2% was obtained. Faradaic and material yields were 90.5% and 99.9%, respectively.

1. Introduction

Iminodiacetic acid (IDA) is a key intermediate for the synthesis of glyphosate, a broad-spectrum herbicide. There are two major methods for synthesizing IDA: by catalytic oxidation of diethanol amide [1–6] and via hydrocyanic acid [7–9]. In both processes the product obtained in the synthetic step is either the sodium or the potassium salts of IDA. Converting these salts into IDA is carried out by neutralization and crystallization. The degree of recovery in this procedure is a maximum of 85%. Consequently, an important fraction of the IDA is lost in the waste stream, giving rise to a penalty from both economic and environmental standpoints. Part of the IDA dissolved in the waste stream is recovered by passing the stream through several columns filled with ion exchange resins, but this procedure is cumbersome due to the high volumes to treat and to the number of recycles necessary to maintain the performance of the resins at a high level. Electrodialysis provides a method for overcoming these problems. The use of electrodialysis for obtaining table salt is a well known process and its application to the purification of organic acids is becoming more popular [10–14].

Several electrodialysis procedures for isolating and purifying organic acids and aminoacids have been reported. For instance, in [15] an electrodialysis cell of 3 compartments is described. The central compartment is fed with a solution of the organic salt. Both the cathode and anode compartments are separated from the central compartment by means of cation exchange membranes. When a potential difference between the electrodes is applied, both the hydrogen ions of the anolyte solution and the cations (sodium or potassium) of the central compartment migrate towards the cathode, while the anions remain in their initial compartments since they cannot pass through the cation exchange membranes. In theory, a solution of pure acid in the central compartment is produced. However, in practice, this is extremely difficult to achieve, due to the difference in transport numbers of the hydrogen ions and of the cations of the organic salt. The result is that the solution of the organic acid is always contaminated with its corresponding salt. Therefore, the isolation of a high purity product is difficult. To overcome this problem in [16] a cell of four compartments is used. The compartments are separated by three cation exchange membranes. In this case, the solution containing the salt of the organic acid is fed by the two central compartments. The salt solution initially treated in the intermediate compartment located adjacent to the cathode compartment is further treated by passing into the intermediate compartment located adjacent to the anode compartment and thereafter removing the same as the final acid product. This method of operation reduces the loss of hydrogen ions into the cathode compartment resulting in an increased current efficiency. The product purity is also improved, but it is not possible to obtain a high purity product.

An important improvement can be achieved by using an electrodialysis stack of four compartments formed by alternating anion and cation exchange membranes (Fig. 1) [17, 18]. Thus, in one of the compartments there is always a solution of the pure organic acid. With this type of assembly it is possible to obtain a high purity compound, consuming an inorganic acid (for instance, sulphuric acid) as a source of hydrogen ions, and producing a solution of pure inorganic salt (for instance, sodium sulphate) as by-product, which in some cases could give rise to environmental problems.

Further improvement may be achieved by using bipolar membrane technology [19] recently developed at industrial scale by AQUATECH Systems. With this technology, using a three compartment cell, the production of an aqueous solution of an inorganic salt is avoided. Instead, a solution of sodium hydroxide or potassium hydroxide is produced which can almost

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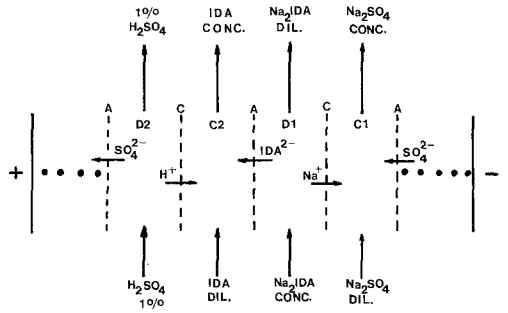


Fig. 1. Scheme of the electrodialysis cell stack. C, cation exchange membrane; A, anion exchange membrane.

always be recycled to the production process (usually in the synthetic step). In addition, no inorganic acid is needed as source of hydrogen ions. The advantages from both economic and environmental standpoints are obvious.

However, several problems of minor importance related to bipolar membrane technology remain unsolved and prevent the generalized use of the technology, which is likely to be of major importance in the near future in the minimization of the environmental impact of many chemical processes.

In this paper, the use of an electrodialysis cell stack, formed by alternating anion and cation exchange membranes, for the isolation and purification of IDA from an aqueous solution of its sodium salt is reported.

A pilot plant was continuously run for 1007 h. Faradaic and material yields were 90.5% and 99.9%, respectively, and the IDA purity was higher than 99.2%. The process is under patent [5, 6, 17, 18]. To our knowledge, the results obtained are the best reported in the literature for the isolation and purification of IDA.

2. Experimental details

2.1. *Electrodialysis cell stack and operation procedure*

The electrodialysis was carried out in a TS-5-12-D electrodialyzer supplied by Eurodia (France). The electrodialysis cell stack was designed by Tokuyama Soda. Basically, the cell stack was formed by 12 cells of four compartments. A scheme of the basic assembly is shown in Fig. 1. Each cell was defined by two anion exchange membranes (Neosepta AM-1 from Tokuyama Soda) and two cation exchange membranes (Neosepta CM-1). The intermembrane gap was 0.85 mm. The effective area was 0.05 m^2 per cell. The effective total area was 0.6 m^2 and the total area was 2.4 m^2. Pt/Ti was used as anode and 316 stainless steel as cathode. Power was supplied by a 25 A, 75 V rectifier. Solutions were contained in 5 × 40 dm^3 polypropylene tanks and were recirculated through their respective compartments by means of magnetic pumps (Iwaki MD 55 R5) to provide flow rates of 350 $dm^3 h^{-1}$ (linear velocity 7 cm s^{-1}). Temperature was 39 °C. The electrode rinse solution was an aqueous solution of sodium sulphate 5% w/w. IDA sodium salt was synthesized in a pilot plant following the method described in [5, 6]. Its purity was 97%. All the streams were filtered through 10 μm polypropylene filters before entering the cell stack. The current density was 250 A m^{-2}. Demineralized water was used to prepare all solutions.

The pilot plant was continuously operated by shifts (8 h/shift) for 1007 h. Only one man per shift was needed.

The general procedure of operation was as follows. In compartment D2, the sulphuric acid concentration was constant and equal to 1%. It was controlled by monitoring the pH of the solution (0.8–1.0) and adding concentrated (96%) sulphuric acid from time to time in order to maintain the desired pH value. Likewise, about 0.75 $dm^3 m^{-2} h^{-1}$ of water was added to compensate the water loss associated with migration of ions to compartments C1 and C2.

In compartment C2, the initial IDA concentration ranged between 25 and 28 g dm^{-3}. When the concentration of IDA reached a value between 40 to 45 g dm^{-3}, about 35 dm^3 of solution was sent to a crystallizer where IDA was precipitated at 5 °C. After filtering the solution, IDA was dried at 80 °C and the filtrate was reintroduced to the electrodialysis stack. The cycle was continuously repeated until the pilot plant was halted.

About 0.93 $dm^3 m^{-2} h^{-1}$ of filtrate were sent to an evaporator in order to maintain the volume of the tank constant, since an increase was continuously produced due to water migration from compartments D2 and D1.

IDA concentration was monitored by measuring the conductivity of the solution and by HPLC.

In compartment D1, the initial IDA sodium salt concentration was 120 g dm^{-3} (density 1.1 g cm^{-3}). When the density of the solution dropped to 1.03 (salt concentration about 50 g dm^{-3}), 95% of the solution was sent to a 80 dm^3 polypropylene tank where more sodium salt was dissolved and its initial concentration restored. Fresh sodium salt solution from another 80 dm^3 tank was fed to the electrodialyzer and this cyclic operation was repeated until the pilot plant was stopped (1007 h). Loss of water by migration to adjacent compartments was 1.7 $dm^3 m^{-2} h^{-1}$.

In compartment C1, the initial sodium sulphate concentration was 3.5% w/w (density 1.03 g cm^{-3}). When the solution density was 1.11–1.15, the tank was discharged leaving a volume of 10 dm^3. Then, 30 dm^3 of water were added in such a way that the sodium sulphate concentration was restored to its initial value. The cycle was repeated throughout the duration of the pilot plant run.

A fraction of the ions coming from compartment D2 migrated as bisulphate ions. In fact, the pH of compartment C1 was 2 at the end of every cycle. Taking into account this pH value, the discharged solution was composed of 80% w/w of sodium sulphate and 20% of sodium bisulphate.

2.2. *Analysis*

IDA was analysed by HPLC at 195 nm using a Perkin–Elmer Chromatograph model 3B, equipped with a UV detector. Eluent was composed of a solution of monopotassium phosphate 0.084% w/w in methanol (4%): water (96%). Its pH was adjusted to 2.5 with phosphoric acid. The flow rate was 2.3 $cm^3 min^{-1}$. The column was a spherisorb SAX 10 (5 μm).

The concentration of sodium in compartments D2 and C2 was monitored by flame photometry (Perkin Elmer 5100 PC). The concentration of sulphate ions in compartments C2 and D1 was monitored by liquid chromatography (Perkin Elmer model series 4) using a thermic conductivity detector (Ionic Chromatograph Metrohm 690).

The column was an ionic exchange column PRP-X 100. The eluent was a solution of phthalic acid 2 mM (adjusted to pH 5) in methanol (20%): water (80%). The flow rate was 2 $cm^3 min^{-1}$.

3. Results

To determine the feasibility of an electrodialysis process two questions have to be answered. First (a) What is the impurity level in the different compartments? Such contamination is due to ions coming from adjacent compartments, since the permselectivity of the membranes is not 100%. Secondly (b) What is the ageing rate of the membranes? The answer to this question is the key to the economic feasibility of the process.

To answer the first question it is sufficient to monitor the concentration of the different species in each compartment. To answer the second, the variation of both the faradaic yield and cell stack voltage with operation time has to be monitored.

3.1. *Impurity levels*

IDA is the only impurity possible in compartment C1. Its concentration was always lower than 0.1% w/w.

Sodium and sulphate ions are the two possible impurities in compartment C2. The variation of their respective concentrations against time is given in Fig. 2. Both increase slowly in such a way that IDA purity is not affected.

IDA and sodium ions are the only possible impurities in compartment D2. The concentration of the latter was constant and equal to 0.25% w/w. There is no possibility that an accumulation of sodium is produced because sodium would migrate easily to compartment C2 through the cation exchange membrane.

With respect to IDA, in preliminary tests carried out before starting the continuous operation of the pilot plant, a sulphuric acid concentration of 10% w/w was tested in compartment D2. The IDA concentration in this compartment reached values of 8% w/w because taking into account the pH of the adjacent compartment C2, about 30% of IDA in this last compartment was in its electrically neutral form,

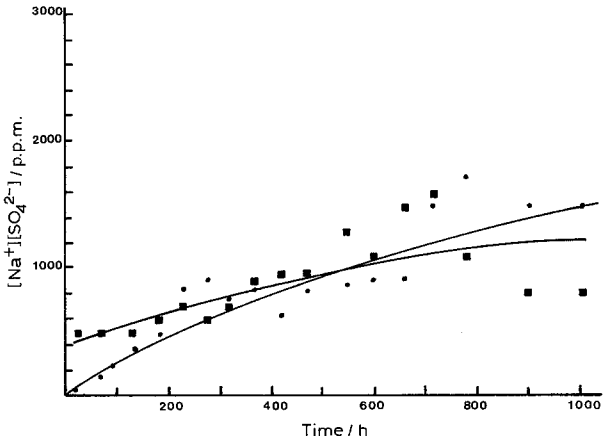
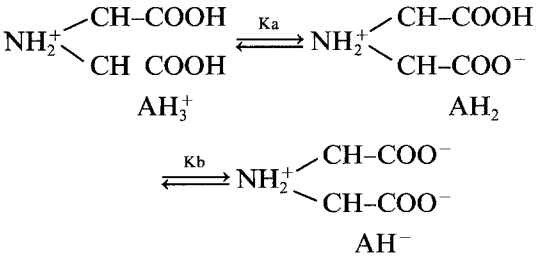


Fig. 2. Compartment C2. Variation of sulphate and sodium concentrations as a function of time. (■) Sulphate ion, and (●) sodium ion.

AH_2 (see Scheme 1), and therefore diffusion to compartment D2 occurred. To overcome this problem, the sulphuric acid concentration in D2 was adjusted to about 1% w/w so that the pH of the solution ranged from 0.8 to 1.0. Thus, at this pH all the IDA was in its protonated form, AH_3^+, and could back migrate to compartment C2 through the cation exchange membrane.

pKa = pKb = 2.98



Scheme 1

Then, 1% w/w sulphuric acid solution was chosen for piloting the process in order to minimize the IDA content in compartment D2. The variation of IDA concentration with time can be seen in Fig. 3. The peak values were due to deterioration of the pH probe. Changing the probe, the IDA concentration decreased sharply at values lower than 1% w/w, allowing a recovery of isolated IDA of 99.9%.

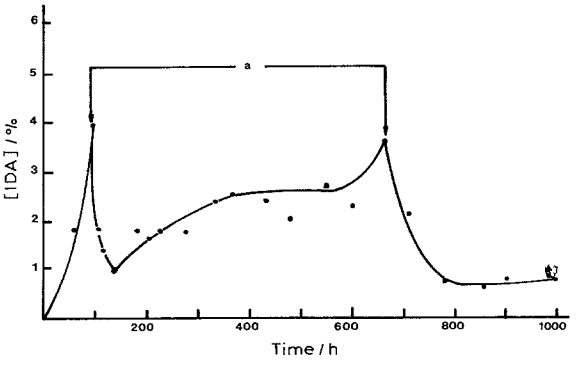


Fig. 3. Compartment D2. Variation of IDA concentration as a function of operation time. pH 0.8–1.0. a: Change of pH probe.

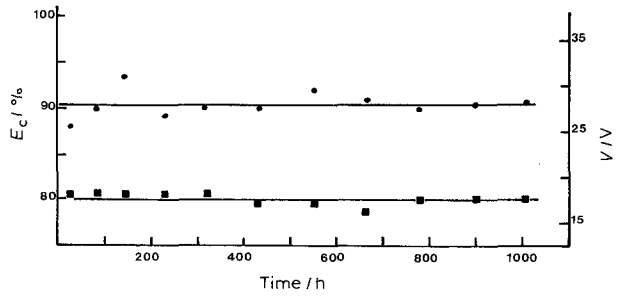


Fig. 4. Variation of the current efficiency (E_c) and mean cell voltage (V) through the operation time. (●) E_c and (■) V.

3.2. *Current efficiency and mean cell voltage variation*

The variation of both parameters is given in Fig. 4. As can be seen, they were constant throughout the operation time, showing that no evident ageing of membranes was produced.

After 1007 working hours, 339 kg of IDA were isolated. The final results are given in Table 1. The analytical results in Table 2 are the average of 28 samples isolated at different times of operation. To our knowledge, the IDA quality obtained by this method is the best available.

4. Conclusions

Compared to the methods reported earlier, electrodialysis provides a superior alternative from both economic and environmental points of view. Present results show clearly the industrial feasibility of this procedure. The purity of the product offers another advantage for adopting electrodialysis as the best procedure to isolate and purify IDA.

Acknowledgements

The authors are grateful to Ercros I&D management for permission to publish this work. Thanks are also due to Messrs J. M. Garrido F., J. M. Alfarco R., F. López A. and J. Muñoz M. for their help in the running of the pilot plant. HPLC measurements were made by L. C. Qintero and Dr D. Rosales. Flame photometry measurements were carried out by A. Cantalejo V.

Table 1. Recovery of IDA by electrodialysis. Final results.

Working hours	1007 h
Current efficiency	90.5%
IDA recovery	99.9%
Mean voltage	17.5 V
Specific productivity	0.56 kg h^{-1} m^{-2}
Power consumption	0.65 kWh kg^{-1}
Mass balance	100%

Table 2. IDA purity obtained by electrodialysis

HPLC	99.2 + 0.14% (28 samples. Statistical analysis for a confidence interval of 95%
Elemental analysis	99.9%. Calc: C: 36.09, H: 5.30, N: 10.52 Obs: C: 36.04, H: 5.30, N: 10.57
Sulphates	less than 0.05%
Water	less than 0.05%
Sodium	less than 0.03%
Ash	less than 0.05%
Glycine	non detected
NTA	less than 0.01%

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