TECHNICAL NOTE

Preparation of pyrazine 2,3-dicarboxylic acid from its potassium salt by electrodialysis

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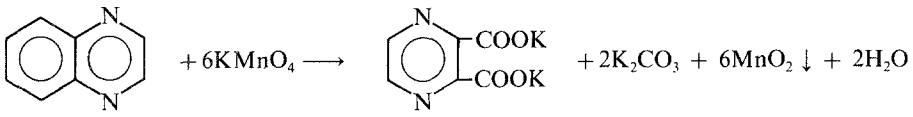
Received 9 June 1988; revised 14 July 1988

1. Introduction

2-Amido-pyrazine (AP) is a well-known antitubercular drug [1]. Pyrazine 2,3-dicarboxylic acid is an important intermediate in the preparation of AP. Its preparation involves the oxidation of quinoxaline by potassium permanganate to yield pyrazine 2,3-dicarboxylic acid (PDA). The reaction conditions are such that the diacid produced is present as potassium salt along with potassium carbonate.



Quinoxaline — Di-potassium salt of PDA (PDA–K)

One of the methods of recovery of PDA from the product mixture is acidification of the filtrate with hydrochloric acid after the removal of manganous dioxide. Subsequently, the liberated PDA, which has a high solubility in water, is selectively extracted [2].

Yet another procedure [3] is the acidification of the filtrate with acetic acid followed by basification with ammonium hydroxide. The resulting solution is treated with barium chloride to precipitate PDA as barium salt. The barium salt is then treated with a stoichiometric quantity of sulphuric acid to liberate PDA. Further, the precipitated barium sulphate is filtered off, and the filtrate is evaporated to obtain PDA. The above-mentioned methods are cumbersome and they involve many steps before PDA is obtained in the pure form.

The use of electrodialysis in the pharmaceutical and food industry for the separation of salts, acids and bases from aqueous solutions is of recent origin [4]. Electrodialysis is also used in the purification of organic acids [5–10]. In the present work, we describe the use of electrodialysis for the preparation of PDA from an aqueous solution containing the potassium salt of PDA and potassium carbonate.

2. Experimental details

The electrodialysis was carried out in a suitably modified Electrosyn Cell (Electrocell AB, Sweden) made of polyvinylidene fluoride (PVDF) frames with six compartments using cation exchange membranes (Nafion 324, 423 and 901 Du Pont, USA) and anion exchange membrane (DSV, Asahi Glass Co. Ltd, Japan) (Fig. 1). Lead dioxide coated over lead was used as anode and nickel was used as cathode. The area of the membranes used was 0.04 m^2.Power required for electrodialysis was drawn from a Transformer–Rectifier unit (Ruttonsha International Rectifier Ltd, India). The current density was varied from 375 to 750 A m^{-2}.

Sodium hydroxide solution was circulated in compartment 1 (Fig. 1). Sulphuric acid at the same con-

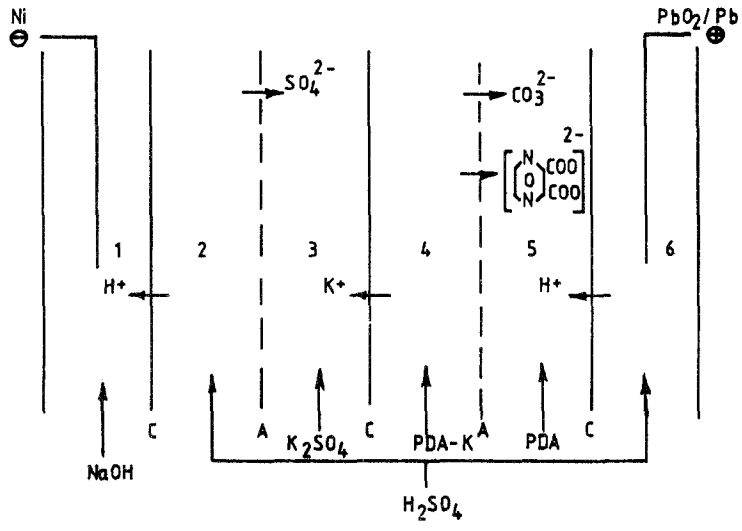


Fig. 1. Electrodialysis cell stack with various flow streams. C, cation exchange membrane; A, anion exchange membrane.

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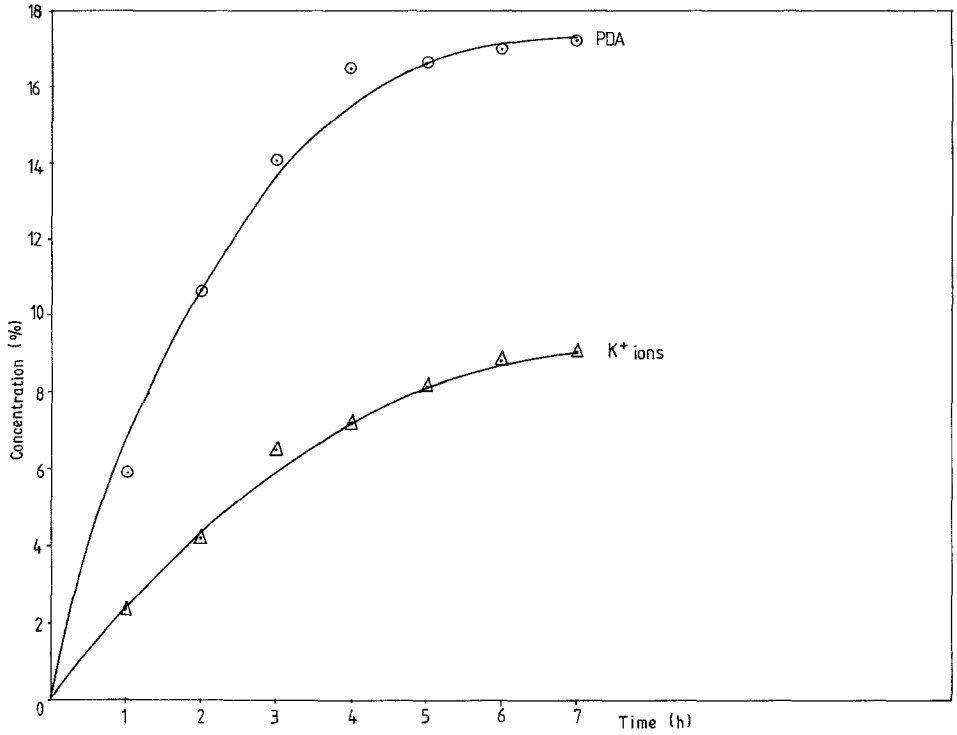

Fig. 2. Change in concentration of potassium ions in compartment 3 and PDA in compartment 5 with time.

centration was circulated through compartments 2 and 6. An aqueous solution containing the potassium salt of PDA and potassium carbonate was circulated in compartment 4. Initially, only de-ionized water was circulated in compartments 3 and 5. The solution stream required for compartment 4 was prepared from quinoxaline using potassium permanganate [2]. In the initial stage of the electrodialysis, there was only a small current flow because of the low conductivity. However, after 15 min there was enough migration of ions to compartments 3 and 5 to allow the desired flow of current. Flow rate (recycle flow) of all the streams was maintained at $1.5\,l\,h^{-1}$.

The concentration of potassium ion in compartments 3 and 4 was followed by means of flame photometry (Systronics, India, Model No. 121). The concentration of PDA in compartment 5 was followed using a UV–visible spectrophotometer (Bausch & Lomb, USA, Spectronic 2000) at 275 nm.

3. Results and discussion

During the course of electrodialysis, potassium sulphate is produced in compartment 3 as a result of migration of potassium ions from compartment 4 and sulphate ions from compartment 2. Further, the solution in compartment 3 turns acidic because of the migration of the hydrogen ions through the anion exchange membrane separating compartments 2 and 3. Such acidification is advantageous in view of the higher solubility of potassium bisulphate compared to potassium sulphate in water. Also it avoids the blockage of the membrane by potassium sulphate. Both carboxylate anion and carbonate anion migrate simultaneously from compartment 4 to compartment 5. Here, they combine with the hydrogen ions which migrate from compartment 6 and form PDA and carbonic acid. Continuous evolution of carbon dioxide is also observed in compartment 5.

The changes in concentrations and volumes of electrolytes in various compartments for a typical case are given in Table 1. It can be seen that the decrease in sulphuric acid concentration in compartments 2 and 6 can be stoichiometrically accounted for by the formation of PDA in compartment 5 and the formation of potassium bisulphate in compartment 3 along with the

Table 1. Change in concentration and volume of electrolytes in various compartments

Compartment No.	*Electrolyte*	*Concentration (%)*		*Volume (ml)*	
		Initial	*Final*	*Initial*	*Final*
1	NaOH	4.9	3.8	1000	800
2 and 6	H_2SO_4	19.14	8.33	2500	1750
3	K_2SO_4	–	9.0*	1000	1500
4	PDA–K + K_2CO_3	16.4*	4.25*	1000	460
5	PDA	–	17.3	350	500

* As potassium ion.

Table 2. Specific power consumption of the product (PDA) for various current densities

Sl No.	*Current density* ($A m^{-2}$)	*Power* ($kWh kg^{-1}$)
1	375.0	4.74
2	500.0	3.10
3	750.0	4.51

evolution of carbon dioxide in compartment 5. A small decrease in sodium hydroxide concentration ($\approx 1\%$) in compartment 1 may be due to the inevitable neutralization across the membrane.

The volume changes in compartments 3 and 4 are caused by the water of hydration of potassium ions. In compartment 5, the liberation of carbon dioxide causes an increase in volume. The decrease in volume of the sulphuric acid stream in compartments 2 and 6 is due to the transportation of hydrogen ions with water of hydration from compartment 6 to 5.

It is also observed that the final concentration of PDA in aqueous solution in compartment 5 can be changed by varying the volume of water circulated. In the present set of experiments a maximum concentration ($\approx 17\%$) of PDA in the aqueous stream in compartment 5 was obtained.

The transportation of potassium, carboxylate and carbonate ions from compartment 4 was considered to be complete when a drop in current occurred. This was confirmed by the constancy of concentration of potassium ions in stream 3 and PDA in stream 5 as illustrated in Fig. 2.

Further, on average, 97% of the potassium ions were observed to have migrated from the PDA–K stream into the potassium sulphate stream. The rest of the potassium ions was found in the PDA–K stream. Neutralization of the stream from compartment 3 with potassium hydroxide resulted in the precipitation of potassium sulphate.

The specific power consumption values obtained for various current densities are given in Table 2. The optimum current density was found to be $500 A m^{-2}$.

4. Conclusions

Compared to the methods reported earlier, the present method involving electrodialysis gives PDA from its potassium salt directly without involving acidification, filtration, extraction, etc. In addition, the aqueous solution containing PDA may be obtained in a concentrated form at a good yield (95%). The product (PDA) obtained was also of high purity since the acid formation is due to the migration of carboxylate and carbonate ions leaving the other impurities in the PDA–K stream.

Acknowledgements

The authors are grateful to SPIC management for permission to publish this work. Thanks are also due to Dr R. M. Krishnan for his keen interest and constant encouragement.

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