

## AN ELECTROCHEMICAL METHOD FOR SINGLE AND SIMULTANEOUS DETERMINATION OF GEOMETRIC ISOMERS MESACONIC AND CITRACONIC ACID

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**Abstract:** The electrochemical behaviour of the isomer couple citraconic-mesaconic acid was studied in aqueous solution of square-wave and cyclic voltammetry in order to develop a method for their single and simultaneous quantification. The proposed method is fast, simple and can be explored for routine analysis of both compounds as single compounds, or simultaneously as well. The effect of interfering compounds is briefly discussed.

**Key words:** citraconic acid, mesaconic acid, determination square-wave voltammetry, electrochemical method

### 1. INTRODUCTION

Geometric isomerism is a common phenomenon producing very often opposite biological effects on the components which differ only in the space orientation of the functional group(s). A lot of efforts have been spent in recent years on developing analytical methods for quantitative simultaneous determination of geometrical isomers [1–7]. We have recently shown that square-wave voltammetry (SWV) can be explored as an effective tool for quantitative single and simultaneous determination of geometric isomers (dicarboxylic acids) with one double bond [8–9]. Choosing the appropriate experimental conditions, a simultaneous determination of *cis*- and *trans*-aconitic acid [8] as well as fumaric and maleic acid [9] has been easily achieved. Moreover, the last method was successfully applied for the determination of fumaric acid in 10 kinds of wine [9]. In this paper, the electrochemical behaviour of the isomer couple citraconic

and mesaconic acids in aqueous media is briefly elaborated and fast and simple methods for their single and simultaneous determination are proposed.

Citraconic and mesaconic acid (*cis* and *trans* 2-methyl-2-butenedioic acid, respectively) (see Fig. 1) are members of the group of unsaturated dicarboxylic acids with one double bond. Citraconic acid is widely used as a raw material for link of proton transfer across liquid membranes for synthesis of acyl phosphates and adenosine triphosphate [10], as well as for preparing amphiphilic polyelectrolytes containing carbazoyl chromophores [11]. On the other hand, mesaconic acid has been successfully used as a competitive inhibitor of fumarate reduction in a method for purification of some flavocytochromes [12]. Moreover, Asano et al [13] employed mesaconic acid as a raw agent for synthesis of 3-substituted (S)-aspartic acid derivatives. To the best of our knowledge, the electrochemical properties of both acids are not presented in the literature.

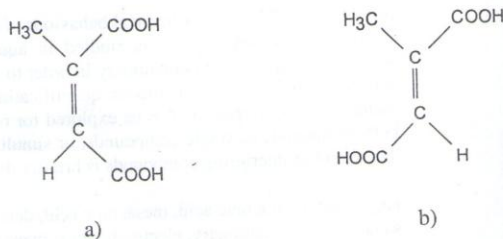


Fig. 1. Molecular formulas of citraconic a) and mesaconic b) acids

## 2. EXPERIMENTAL

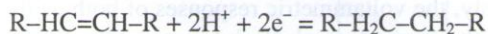
Citraconic and mesaconic acid were products of Merck with a purity of 99.9 %. All the chemicals used were of p.a. purity and products of Fluka. The water used was twice distilled. The stock solutions of both acids were prepared by dissolving appropriate amounts in redistilled water. Britton-Robinson buffer were used for adjusting the pH of the solutions. All voltammograms were recorded using the Princeton Applied Research Model 384 B polarographic system, connected with a SMDE Model 303 A. Pure nitrogen was used to purge the solutions 8 minutes before the first measurement and 30 seconds before each measurement. For each condition, three voltammograms were recorded and average values were presented. The working electrode was a mercury drop with surface area of 0.0149 cm<sup>2</sup>, the reference was Ag/AgCl (sat. KCl), while Pt wire

served as a counter electrode. All experiments were performed at room temperature.

### 3. RESULTS AND DISCUSSION

Because of the similarities in electrochemical behaviour of citraconic and mesaconic acid, the discussion of both acids will be presented simultaneously.

The presence of two carboxyl groups with a strong negative inductive effect makes feasible the reduction of the double bond of both unsaturated acids in the potential region available. In neutral and acidic media, the reduction of both acids is a diffusion controlled irreversible process followed by simultaneous protonation and can be represent by the general scheme, common for all members of unsaturated dicarboxylic acids with one double bond [8, 9].



The relevant parameters of the square-wave voltammetric responses of both acids in different supporting electrolytes are given in Tables 1a and 1b.

Table 1a

*Supporting electrolytes tested for citraconic acid.*

*Experimental conditions: frequency  $f = 120$  Hz, amplitude  $E_{sw} = 20$  mV, scan increment  $dE = 4$  mV, and  $c(\text{citraconic acid}) = 1 \cdot 10^{-4}$  mol/L*

Supporting electrolyte	$E_p/\text{V}$	$I_p/\mu\text{A}$	$\Delta E_{p/2}/\text{mV}$
0.1 mol/L $\text{KNO}_3$ buffered to pH = 4.2	-1.226	4.260	100
0.1 mol/L $\text{Na}_2\text{SO}_4$ buffered to pH = 4.4	-1.236	1.980	100
<b>0.1 mol/L HCl</b>	<b>-0.750</b>	<b>5.890</b>	<b>100</b>
1 mol/L acetic acid	-0.848	3.110	100
0.1 mol/L ammonia buffer pH = 7.60	-1.644	3.345	105

Table 1b

*Supporting electrolytes tested for mesaconic acid.*  
*Experimental conditions: frequency  $f = 120$  Hz, amplitude  $E_{sw} = 20$  mV,*  
*scan increment  $dE = 4$  mV, and  $c(\text{mesaconic acid}) = 1 \cdot 10^{-4}$  mol/L*

Supporting electrolyte	$E_p/V$	$I_p/\mu A$	$\Delta E_{p/2}/mV$
0.1 mol/L $KNO_3$ buffered to pH = 4.2	-1.304	0.789	110
0.1 mol/L $Na_2SO_4$ buffered to pH = 4.4	-1.320	0.585	150
<b>0.1 mol/L HCl</b>	<b>-0.840</b>	<b>1.524</b>	<b>120</b>
1 mol/L acetic acid	-0.944	1.246	170
0.1 mol/L ammonia buffer with pH = 7.40	-1.708	2.224	140

Obviously, the voltammetric responses of both acids are sensitive to the type and pH of the supporting electrolyte, as expected for processes in which protonation occurs. Increasing the pH of the supporting electrolyte solutions causes a shift of the peak potentials ( $E_p$ ) of the square-wave voltammetric responses in negative direction and a decrease of the peak current ( $I_p$ ). The decrease of the peak current with an increase of pH occurs due to the lowering of the concentration of the undissociated forms of unsaturated acids as a consequence of their first dissociation step and conversion into mono-dissociated form. In the pH regions roughly between 4.7 and 6.2 two peaks appeared as a result of the reduction of both electroactive forms (undissociated and mono-dissociated) of acids presented in the solutions. Above a pH of 7, in the region where only double dissociated forms of acid exist again one peak appears at very negative potentials. This is a common behaviour of such compounds and a detailed explanation can be found in our previous papers [8, 9].

For a quantitative determination of single compounds, the most convenient conditions were found to be in 0.1 mol/L HCl. The representative square-wave and cyclic voltammetric responses of citraconic acid are shown in Figs. 2a and 2b, respectively.

Being dependent on the proton concentration, peak potentials of the SW voltammetric responses of both acids shift towards negative direction with a slope of about -60 mV per decade of increase of the proton concentration in an aqueous solution (shown in Fig. 3 for both acids).