

SHORT COMMUNICATION

EFFECTS OF SOLVENT AND CONCENTRATION OF SUPPORTING ELECTROLYTE ON ELECTROCHEMICAL MEASUREMENTS: DETECTION OF CATECHOL

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Abstract: Effect of electrolyte concentration and solvent composition on electrochemical measurements of catechol are reported. In cyclic voltammetric and amperometric experiments, anhydrous lithium chloride was used as the electrolyte; 98% acetonitrile and distilled water were used in mixed solvent systems. The maximum peak current was obtained at $0.075 \text{ mol dm}^{-3}$ LiCl concentration in experiments conducted in aqueous catechol solutions. In amperometric studies, in mixed water/acetonitrile solvent systems, the peak current for catechol reduction/oxidation was higher in solutions with a higher acetonitrile concentration.

Key words: Catechol, electrochemical detection.

INTRODUCTION

The addition of nonelectroactive ions (supporting electrolyte) to the electrochemical cell decreases the contribution of migration to mass transfer of electroactive species. The detailed study of the effect of supporting electrolyte (electrolyte) on the limiting current shows that the migration component of the total current is negligible when the electrolyte concentration is as high as 0.1 mol dm^{-3} .^{1,2} Therefore, in most electrochemical measurements, electrolyte solutions of 0.1 mol dm^{-3} are used without any prior optimization.³⁻⁶

Liquid chromatography in conjunction with electrochemistry (LCEC) has been a popular analytical tool for detection of electroactive organic and inorganic substances at low concentrations.⁷⁻¹¹ Traditional chromatographic separations with nonelectrochemical detectors are performed in the absence of any electrolyte or ionic species. On the other hand, classical electrochemical detection procedures are conducted in electrolyte solutions with concentrations of 0.1 mol dm^{-3} or higher. Thus, it is appropriate to have a compromise between the two conditions of liquid chromatography and electrochemistry in order to achieve efficient electrochemical detection after liquid chromatographic separation. However, many LCEC procedures still use high electrolyte concentrations.^{9,10}

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The nature and the composition of the solvent system also play a major role in liquid chromatographic separations, and hence in electrochemical detection of liquid chromatographic eluents.^{12,13} However, classical electrochemical experiments are usually conducted either in aqueous or in nonaqueous solvents, and only a few reports have appeared on the use of mixed solvent systems in electrochemical studies.^{14,15} Nevertheless, it is of great significance to study the effect of mixed solvent systems on electrochemical measurements as such systems are very common in liquid chromatographic separations. In the present study, we report the effect of electrolyte concentration and solvent composition on electrochemical measurements of catechol solutions. Catechol was specifically selected because procedures have already been established for detection of catechol and its derivatives in aqueous medium.¹⁶⁻¹⁹ Cyclic voltammetric experiments were first conducted at different electrolyte concentrations and solvent compositions as it is an effective and versatile electroanalytical technique. Amperometric experiments were also conducted in order to search for suitable experimental conditions for LCEC experiments.

METHODS AND MATERIALS

Materials: Anhydrous lithium chloride (Vickers Laboratories) and catechol (BDH Chemicals) were used as the supporting electrolyte and the analyte, respectively. Acetonitrile (98%) was purchased from Park Scientific Ltd., and used without any purification. All aqueous solutions were prepared from freshly distilled water. Appropriate proportions of acetonitrile and distilled water were used to prepare mixed solvent systems of desired electrolyte concentration.

Instrumentation: A home-made saturated calomel electrode, a glassy carbon disk (Bioanalytical Systems) and a platinum gauze were used as reference, working and counter electrodes, respectively. All potentials are reported with respect to the saturated calomel electrode (SCE). Cyclic voltammograms were obtained with an Oxford Instruments potentiostat and recorded on a Yew Instruments Model 3022 X-Y recorder. Amperograms were also obtained using the same instrument and recorded on the same recorder with the time mode. The volume of the electrolyte solution in the cell was always 50 cm³, and all experiments were conducted at ambient temperature.

Electrode preparation: Surface of the glassy carbon electrode (GCE) was cleaned by polishing with an alumina slurry and rinsing thoroughly with distilled water prior to each experiment. Such electrodes gave reproducible results and more sophisticated cleaning procedures were not required.

Cyclic voltammetric studies: Cyclic voltammograms were obtained at bare GCE with and without the analyte (5×10^{-3} mol dm⁻³ catechol) in aqueous LiCl electrolyte solutions with concentrations varying from 0.001 mol dm⁻³ to

0.100 mol dm⁻³. To improve reproducibility of voltammetric results, all cyclic voltammograms of the catechol solution at bare GCE in aqueous LiCl solutions were recorded after completion of the first two cycles. Therefore, the oxidized form of catechol (quinone) is present at the initial potential of +1.10 V. A scan rate of 200 mV s⁻¹ was used for all voltammetric measurements. Electrolyte solutions (0.1 mol dm⁻³ LiCl) in acetonitrile/water mixtures of compositions varying from 95:05 to 00:100 (% v:v) were used to study solvent effects.

Amperometric studies: All amperometric experiments in aqueous medium were conducted at bare GCE in LiCl solutions at a constant potential of +0.25 V. This potential is barely sufficient for the reduction of catechol and more negative potentials were not applied to minimize interferences. A potential of +0.05 V was applied when mixed solvent systems were used. This potential corresponds to the anodic peak of catechol in most mixed acetonitrile/water solvent systems as observed in Figure 4. Each measurement was obtained by injecting a 2.00 cm³ aliquot of 5.0x10⁻² mol dm⁻³ catechol stock solution to 50 cm³ of the electrolyte solution in the cell. Sequential additions of the analyte were not attempted to prevent electrode fouling in the presence of catechol. Therefore, the electrode surface was cleaned after each amperometric response.

RESULTS

Concentration effects

Cyclic voltammetry of bare glassy carbon electrodes in aqueous electrolyte solutions between the potential limits of +1.10 V and -0.90 V shows a gradual decrease in the background current with the decrease in the concentration of the electrolyte. This variation is due to the decrease in solution conductivity with decreasing electrolyte concentration.

Cyclic voltammograms of 5x10⁻³ mol dm⁻³ catechol at bare glassy carbon electrode in aqueous 0.1 mol dm⁻³ LiCl solution show two reduction peaks at +0.12 V (A) and -0.08 V (C), and two oxidation peaks at +0.64 V (B) and +0.035 V (D) (Figure 1a). Similar electrochemical behaviour has already been observed for catechol and its derivatives.¹⁹ Cyclic voltammetric studies conducted in aqueous lithium chloride solutions of concentrations varying from 0.001 mol dm⁻³ to 0.075 mol dm⁻³ show a gradual increase in the anodic and cathodic peak currents (Figure 2). However, the peak currents in 0.100 mol dm⁻³ electrolyte solution, which is the typical electrolyte concentration of most electrochemical studies, are smaller than that in 0.075 mol dm⁻³ electrolyte concentration, as expected. Additionally, increase in peak broadening and peak separation (ΔE_p) are observed when the concentration of the electrolyte is decreased (Figure 3, Table 1). Nevertheless, the ratio i_{pc}/i_{pa} is a constant at all concentrations showing similar variations of anodic and cathodic peak currents with electrolyte concentration (Table 1).

Table 1: Variation of Cyclic Voltammetric Peak Current and Peak Separation between A and B (ΔE_p) of 5×10^{-3} mol dm $^{-3}$ Catechol with Electrolyte Concentration (C).

C (mol dm $^{-3}$)	i_{pc} (μ A)	i_{pa} (μ A)	i_{pc}/i_{pa}	ΔE_p (V)
0.100	58.75	96.25	0.61	0.52
0.075	70.00	111.25	0.63	0.56
0.050	63.75	106.25	0.60	0.60
0.025	55.00	88.75	0.62	0.65
0.010	45.00	75.00	0.60	0.85

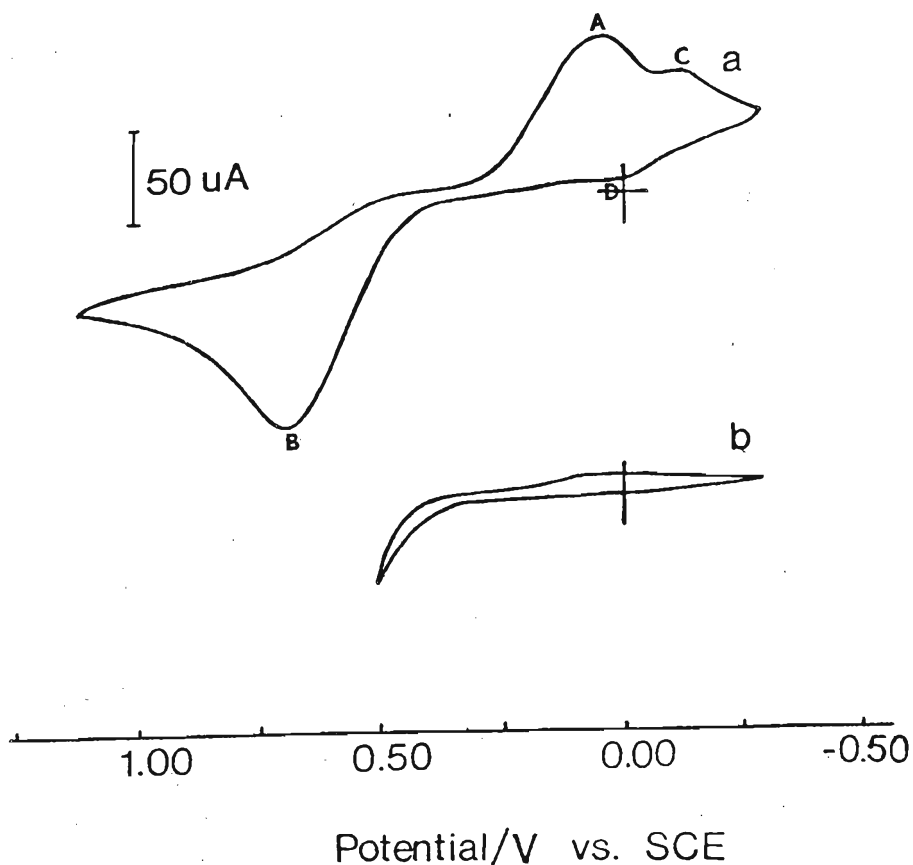


Figure 1: Cyclic voltammograms at bare glassy carbon electrode of 5×10^{-3} mol dm $^{-3}$ catechol in aqueous 0.1 mol dm $^{-3}$ LiCl. Scan rate, 200 mV s $^{-1}$. (a) from +1.10 V to -0.30 V (b) from +0.50 V to -0.30 V.

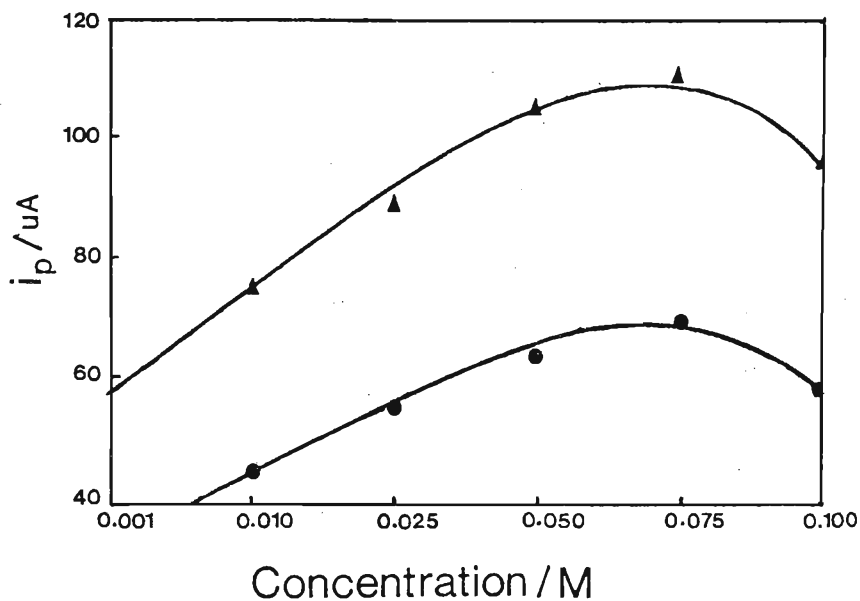


Figure 2: Electrolyte concentration dependence of cyclic voltammetric peak currents (i_p) of 5×10^{-3} mol dm^{-3} catechol in aqueous LiCl solutions. (●) cathodic peak current and (▲) anodic peak current.

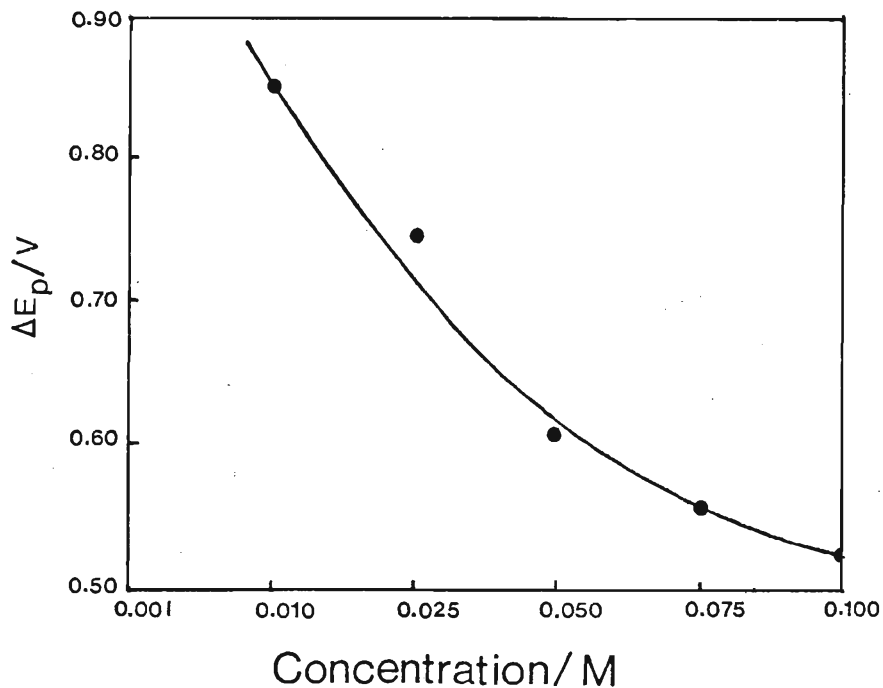


Figure 3: Electrolyte concentration dependence of peak separation (ΔE_p) of 5×10^{-3} mol dm^{-3} catechol in aqueous LiCl solutions.

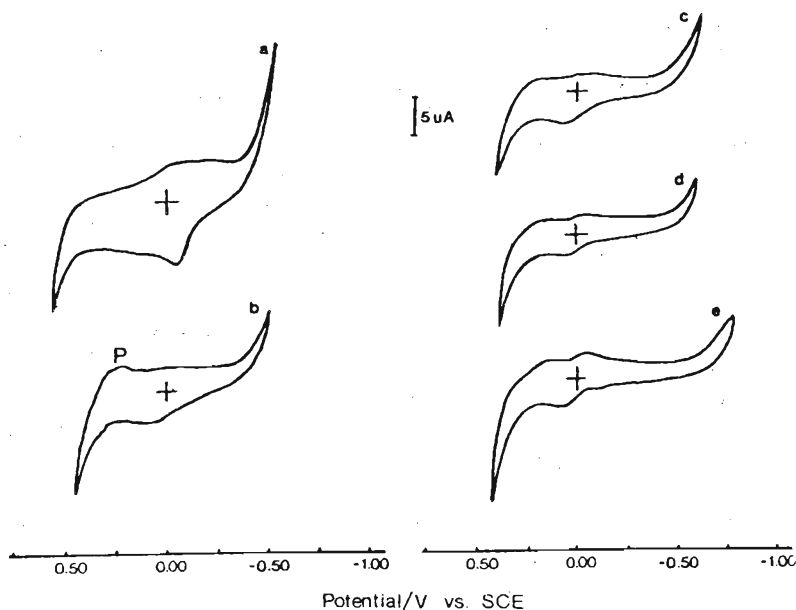


Figure 4: Cyclic voltammograms at bare glassy carbon electrode of 5×10^{-3} mol dm^{-3} catechol in 0.1 mol dm^{-3} LiCl dissolved in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ mixed solvent systems with compositions (a) 05:95 (b) 20:80 (c) 40:60 (d) 60:40 (e) 80:20. Current scale in (a) has been increased by a factor of two.

Solvent effects

Cyclic voltammetric studies of catechol in the water/acetonitrile mixed solvent system with compositions varying from 100% H_2O to 5% H_2O and 95% CH_3CN in 0.1 mol dm^{-3} LiCl electrolyte shows that the oxidation and the reduction peaks appear at all compositions. However, there is no systematic variation between peak current or peak separation with solvent composition (Table 2).

Table 2: Variation of Cyclic Voltammetric Peak Current and Peak Separation (ΔE_p) of 5×10^{-3} mol dm^{-3} Catechol with Solvent Composition ($\text{H}_2\text{O}:\text{CH}_3\text{CN}$ v/v) in 0.1 mol dm^{-3} LiCl Solutions.

Composition	i_{pc} (A)	i_{pa} (μA)	i_{pc}/i_{pa}	ΔE_p (V)
05:95	0.62	4.00	0.16	0.14
20:80	0.50	1.75	0.28	0.12
40:60	0.50	1.75	0.28	0.11
60:40	0.75	2.00	0.38	0.08
80:20	1.25	2.75	0.45	0.10

Amperometric results

Amperometric results obtained at a constant potential of +0.25 V in aqueous LiCl solutions of different concentrations also show a similar trend between current and electrolyte concentration as observed in voltammetric experiments (Figure 5). However, similar experiments conducted in mixed solvent systems at a potential of +0.05 V showed only a slight increase in current when the composition of the electrolyte solution was changed from aqueous to nonaqueous systems.

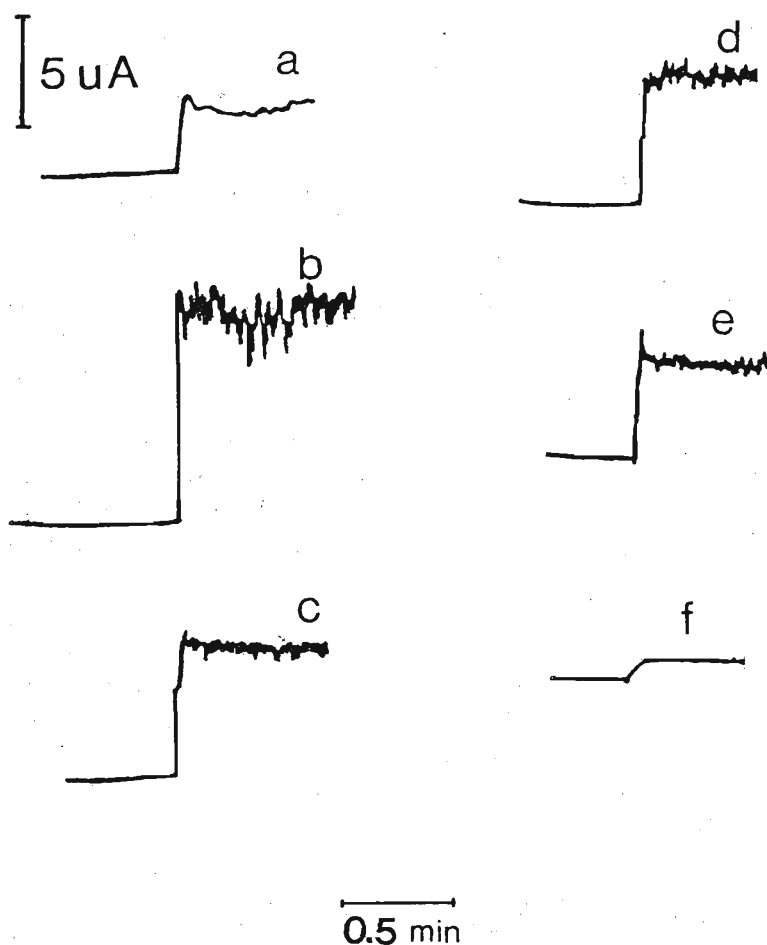


Figure 5: Amperometric responses of bare glassy carbon electrode with a 2 cm^3 injection of $5 \times 10^{-2} \text{ mol dm}^{-3}$ catechol. Concentration of LiCl electrolyte concentration, (a) 0.100 (b) 0.075 (c) 0.050 (d) 0.025 (e) 0.010 (f) 0.001 mol dm^{-3} .

DISCUSSION

The peaks A and B which are separated by 0.520 V were selected for investigation of the effect of electrolyte concentration on the voltammetric behaviour as this couple of peaks is more intense and sharper compared to the other couple (C and D). The disappearance of the peaks A and B within the potential range of +0.5 V and -0.3 V (Figure 1b) indicates that peaks A and C (also B and D) are coupled to each other. However, the full potential range indicated in figure 1a was used to investigate peak currents and separations of the couple A and B.

The decrease in the current at 0.100 mol dm⁻³ electrolyte concentration can be explained by considering the migration component of the total current which has a significant contribution at low concentrations (Figure 2). However, at a concentration as low as 0.001 mol dm⁻³ LiCl, voltammograms do not provide any meaningful information, and no detectable peaks are observed.

As a result of the iR drop, where i is the current going through the cell and R is the uncompensated resistance, the applied voltage is changed from the desired value, E , to $E - iR$. This results in lowering peak heights with increasing peak separations, and such a behaviour is similar to that expected for a slow electron transfer process.²⁰ Furthermore, deviation of ΔE_p from the standard value, 0.059 V, indicates that the electron transfer process has deviated from reversibility (Figure 3, Table 1). The deviation of i_{pc}/i_{pa} from unity is indicative of complicated electrode kinetics of the electrode process. Such complications are due to slow rate of charge transfer and coupled chemical reactions which are very common among organic substances even at high electrolyte concentrations.^{8, 20} These kinetics complications become enhanced at low electrolyte concentrations where potential differences are created across the Outer Helmholtz Plane (OHP) and solution, giving a potential drop through the diffuse layer (1).

The smaller peak separation in H₂O:CH₃CN mixed solvent systems (Figure 4) indicates that the electrode process involves a faster electron transfer than that in pure aqueous systems. Electrochemical reactions of organic substances may be faster in organic solvents due to common chemical and physical properties. However, the observed peak broadening in mixed solvent systems may be due to higher uncompensated resistance of the medium.

Additionally, a pre-peak (P) is seen in these voltammograms which is probably a result of an adsorbed oxidized product of catechol. This pre-peak may restrict the electron transfer of the cathodic process which results in a smaller cathodic peak current. Higher cathodic peak currents observed at solvent compositions of 60:40 and 80:20 H₂O:CH₃CN are probably due to the decrease in uncompensated resistance in the solution as the amount of water is increased (Figure 4d, 4e). However, the reason for such a high peak current in 5:95

H₂O:CH₃CN system is yet to be understood. Furthermore, the ratio i_{pc}/i_{pa} increases with increasing the amount of water in the solvent composition, and deviates from unity in all cases. This is most likely due to complicated electrode kinetics of catechol electrochemistry in water/acetonitrile mixed solvent systems. Both voltammetric and amperometric experiments conducted in aqueous catechol solutions indicate that the maximum peak current is obtained at 0.075 mol dm⁻³ LiCl electrolyte concentration. Amperometric studies conducted in mixed water/acetonitrile solvent system show that the peak current for catechol reduction/oxidation is higher in solutions having a higher acetonitrile content. Such experiments demonstrate the importance of performing voltammetric and amperometric experiments prior to chromatographic separation in order to optimize electrolyte concentration and solvent composition for electrochemical detection of liquid chromatographic eluents.

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