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Diffusion Coefficients of Phenolic Aromatics by Chronocoulometry at the Glassy Carbon Electrode

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The diffusion coefficients of a number of phenolic aromatic compounds have been determined by potential step chronocoulometry employing the base-activated glassy carbon electrode. We have found that the background for base-activated glassy carbon electrode is significantly lower than for platinum. The background from carbon is reproducible and can be accurately subtracted from the sample signal in individual experiments. The diffusion coefficients determined at 25 °C were at expected values around 7×10^{-6} $cm^2 \cdot s^{-1}$ with a coefficient of variation below ±1%.

Introduction

Catecholamines and related substances are important biologically active compounds, and their physical properties are of significant interest. Specifically diffusion coefficients are necessary to predict the mobility of these compounds in solution. Also, accurate values of diffusion coefficients are necessary for the electrochemical analysis of these bioactive compounds. This note presents the diffusion coefficients of a number of catechols and related compounds determined using potential step chronocoulometry employing glassy carbon electrodes.

Potential step chronocoulometry has become an important method for the electrochemical determination of diffusion coefficients, electrode area, and adsorbed reactants (Anson et al., 1966, 1967; Christie et al., 1967; Dana et al., 1993). With the advent of digital instrumentation chronocoulometry has become widely available in the laboratory. The use of microcomputers allows for rapid data acquisition in the time frame where the Cottrell equation is obeyed, and these instruments also allow for signal averaging, background correction, and data analysis in real time.

We have employed glassy carbon electrochemically activated in strong base as the working electrode for these experiments. Our previous studies have shown that this method of activation yields an electrode with low background and a reversible response for catechols (Anjo et al., 1989). We present a comparison of the response of this glassy carbon electrode with the more commonly used platinum electrode. As will be presented, we have found the glassy carbon electrode to be far superior to the platinum electrode under the conditions employed in these determinations.

Experimental Section

Materials. The carbon electrodes were prepared from Atomergic Chemetals 3 mm diameter glassy carbon rods (v-25 grade). The glassy carbon was sealed in 6.35 mm (o.d.) glass tubing using epoxy cement. The end of the electrode was ground flat using carborundum papers going stepwise from 100 to 600 grit. The electrode was thoroughly washed with deionized water. The end of the electrode was then polished on polishing mats (Buehler) using a series of alumina polishes, 1, 0.3, and 0.05 μm; a separate mat was used for each polish. The electrode was thoroughly washed and sonicated for 5 min between each polishing step.

The platinum electrode was a BAS platinum button electrode (1.5 mm diameter). The electrode was polished with alumina in the same manner as the carbon electrodes. The platinum electrode was also base activated in the same manner as the carbon electrodes. All chronoamperometry experiments for the platinum electrode used the same conditions as with the carbon electrodes.

All experiments were carried out in a double-jacketed beaker attached to a water bath with a temperature control of 25 ± 1 °C. The counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (PARC). All salts, acids, and bases were analytical grade. The water used was from an ion exchange (Barnstead) system fed from house-distilled water. The source of the compounds used is listed in the data table.

Instrumentation. The chronocoulometry was carried out using an EG&G Princeton Applied Research Model 362 scanning potentiostat; the potentiostat was controlled using an MS-DOS-based microcomputer with a MetraByte DAS-8 interface. The interface had a 12 bit D/A, a 12 bit A/D, and an integral clock counter. We have written our own custom software for the chronoamperometry experiment and chronocoulometry calculations; the main program was written in MicroSoft Quick Basic 4 with assembly language subroutines for data acquisition. The program controlled the potential step, recorded the chronoamperometry data, subtracted the background from the experiment, and calculated the chronocoulogram.

Electrode Preparation. Each electrode was electrochemically activated prior to the chronoamperometry experiments using a procedure we have previously published (Anjo et al., 1989). The electrodes were polished with 0.3 and 0.05 μm polish with the method used above; the electrodes were washed and sonicated after each polishing step. Electrodes were activated at 1.2 V (SCE) for 5 min in 1.0 M sodium hydroxide. Each electrode was then thoroughly washed with deionized water and immediately used in the chronoamperometry experiments. Each electrode was polished and activated prior to each series of chronoamperometry steps; the electrode was used for a single area determination in ferrocyanide and for a single diffusion coefficient and was then reactivated.

Cyclic Voltammetry Procedures. Each compound was initially evaluated using cyclic voltammetry (CV); the formal electrode potentials determined by CV were used to set the potential limits for the chronoamperometry experiments. The CV experiments were recorded with the compounds at 1.00 mM in 0.10 M sulfuric acid using base-activated carbon electrodes. The formal electrode potential, $E^{\circ\prime}$, was the midpoint between the anodic and cathodic CV peaks.

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Chronoamperometry–Chronocoulometry Methods. A series of potential steps from 0.1 to 0.7 V at intervals of 0.1 V were applied to each compound. It was found that a step of 0.5 V was sufficient for diffusion control of the current for all the compounds studied. To allow comparison of the results between the experiments, the same potential step width was applied with all the compounds. The potential step employed with chronoamperometry experiments below was from 0.15 V below $E^{\circ\prime}$ to 0.35 V above the formal potential for the compounds employed. The chronoamperometry experiment was recorded as follows: 500 current values were recorded immediately before the potential step to obtain an accurate zero current line for the data. Then following the potential step, 1000 current values were measured. All the current measurements both before and after the potential step were made at 20 ms intervals. Failure to accurately set zero on the current scale can lead to serious nonlinear errors in the calculated chronoamperometry and chronocoulometry plots. All solutions were purged with high-purity nitrogen prior to electrochemical measurements; a blanket of nitrogen was then kept over the solutions during all measurements.

The chronoamperometry measurement of electrode area and the diffusion coefficient was as follows. The background current transient of the electrode was recorded in 0.1 M KCl, the electrolyte for the ferrocyanide; this background transient was signal averaged for 25 potential steps. The solution in the beaker was then replaced with the ferrocyanide solution, while keeping the electrode and solutions under a blanket of nitrogen. The time between the background measurements and measurements on the ferrocyanide solution was 1 min. Then the response to the potential step in 4.00 mM potassium ferrocyanide was recorded. The background was subtracted from the faradaic signal, and the current was integrated with respect to time. A chronocoulogram plot known as an Anson plot, charge versus the square root of time, was constructed, and the slope was determined using linear regression. Only background-corrected chronocoulograms with correlation coefficients exceeding 0.999 were retained for the calculations. The electrode area was determined from the slope of the chronocoulogram using the diffusion coefficient of ferrocyanide from Stackelberg et al. (1953). The area chronoamperometry was repeated a minimum of 10 times for each activated electrode. The chronocoulogram equation is listed below:

$$Q = 2nFAD_0^{1/2}C_0t^{1/2}/\pi^{1/2}$$

In the equation Q is the charge in coulombs, n is the electron number, F is the Faraday constant, A is the electrode area in cm^2, D_o is the diffusion coefficient in cm^2·s^{-1}, C_o is the concentration in mol·cm^{-3}, and t is time in seconds.

The same electrode was then placed in 0.1 M sulfuric acid, which was the background electrolyte for all the catechol and hydroquinone compounds studied. The potential step was applied, and the chronoampermetry background was recorded; this was signal averaged for 25 potential steps. The electrode was then placed in the test compound solution, and the same potential step was applied while recording the current. The test compound was at 1.00 mM in 0.10 M sulfuric acid. As above, the background was subtracted from the signal and the response was integrated as a function of time. An Anson plot of charge versus the square root of time was constructed, and the slope was determined using linear regression. Only background-corrected chronocoulograms with correlation coefficients exceeding 0.999 were retained for the calculations. The diffusion coefficient was calculated using the previously determined area and the slope of the chronocoulogram. The diffusion chronoamperometry experiment was repeated at least 10 times per activated electrode.

The whole series, backgrounds, areas, and diffusion coefficients were repeated with at least 3 different electrodes per new compound for more than 80 individual experiments. Dopamine, a compound we have previously studied (Nowinski and Anjo, 1989) was run for over 50 individual chronocoulograms in this study.

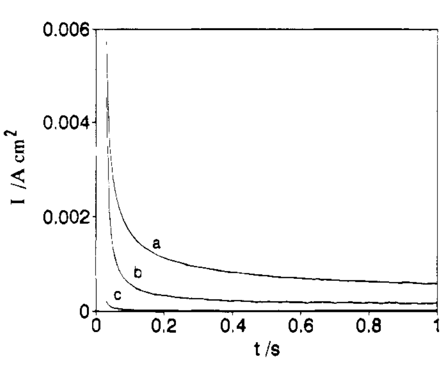

Figure 1. Potential step background current comparison: (a) response of 1.0 mM dopamine solution with a base-activated glassy carbon electrode; (b) background signal from a platinum electrode in 0.1 M sulfuric acid; (c) background signal from a base-activated glassy carbon electrode in 0.1 M sulfuric acid. All traces normalized for electrode area.

Background Comparison Procedure. For the comparison of background signals the background was recorded in 0.10 M sulfuric acid. Both base-activated platinum and base-activated carbon electrodes were employed for the background comparison. For these experiments the chronoamperometry results were recorded in the background electrolyte. The background signals were then compared.

Results

Figure 1 is a comparison of the background signal between base-activated carbon and platinum working electrodes used in our chronoamperometry studies. Trace a is the faradaic response from 1.0 mM dopamine in 0.1 M sulfuric acid for comparison; trace a was with a base-activated carbon electrode normalized for area and background corrected. Trace b is the normalized result for a platinum electrode under the conditions described below. Trace c is the background current recorded with a base-activated glassy carbon electrode; the current was normalized for the electrode area. The potential step was from 0.3 to 0.8 V (SCE) in 0.1 M sulfuric acid. Both Adams (1969) and Sawyer and Roberts (1974) indicate that platinum electrodes have a surface faradaic reaction in the voltage window for catechols. Clearly, the base-activated glassy carbon electrode has a significantly lower background current in the voltage range employed for catechols.

The reproducibility of the background transient from individual base-activated glassy carbon electrodes was excellent; for each experiment the background 25 pulse signal average experiment was repeated at least twice and was used only if the traces were superimposible. The background traces between different experiments and between different treatments of the same electrode were variable; the background trace of one experiment was never used to correct data from a different experiment.

A typical chronocoulometry experiment is shown in Figure 2; this experiment is for 1.0 mM dopamine (4-(2-aminoethyl)-1,2-benzenediol) in 0.1 M sulfuric acid. Trace a is the raw data of current vs time. Trace b is an Anson plot chronocoulogram using the same data; the plot is Q vs $t^{1/2}$. The slope was calculated, and the diffusion coefficient was determined from the slope. The area of the electrode had been previously determined. The result of 58 repetitions was a diffusion coefficient of $6.978 \times 10^{-6} \pm$ cm^2·s^{-10} with a coefficient for variation (COV) of 0.89%. This COV is significantly lower than the 6% ($n = 11$) value from our previous published result with dopamine using a platinum electrode (Nowinski and Anjo, 1989). The lower

Table 1. Diffusion Coefficients of Phenolic Aromatics

compound[a]	$E^{\circ\prime}$(SCE)/V	$10^6D/(\mathrm{cm^2 \cdot s^{-1}})$					
		this work	COV[b]	n	reported value	ref
2,5-dihydroxy-1,4-benzenediacetic acid, Aldrich [5488-16-4]	0.306	5.83	0.36	88		
2,5-dihydroxy-1,4-benzenedisulfonic acid, dipotassium salt, Aldrich [15763-57-2]	0.464	6.90	0.62	85		
2,5-dihydroxy-*N*-(2-hydroxyethyl)benzamide, Aldrich [61959-53-7]	0.426	7.20	0.40	88		
2,5-dihydroxyphenylacetic acid {homogentisic acid}, Aldrich [451-13-8]	0.338	7.24	0.39	84		
3,4-dihydroxybenzylaminehydrobromide, Aldrich [16290-26-9]	0.496	7.78	0.33	89		
3,4-dihydroxycinnamic acid {caffeic acid}, Aldrich [331-39-5]	0.484	7.12	0.42	89		
L-3,4-dihydroxyphenylalaninehydroxamic acid, Research Organics	0.474	6.92	0.65	88		
3,4-dihydroxyphenylacetic acid, Aldrich [102-32-9]	0.455	8.91	0.92	146	5.9	c
β-(3,4-dihydroxyphenyl)propionic acid ethyl ester, Pfaltz and Bauer	0.428	6.18	0.74	87		
4-(2-aminoethyl)-1,2-benzenediol hydrochloride {dopamine hydrochloride}, Aldrich [62-31-7]	0.455	6.98	0.89	58	6.0 6.69	c d

[a] Formal compound names are followed by common names in braces, the manufacturer, and the CAS registry number in brackets. [b] Uncertainties are expressed as coefficients of variation. [c] Gerhard and Adams (1982). [d] Nowinski and Anjo (1989).

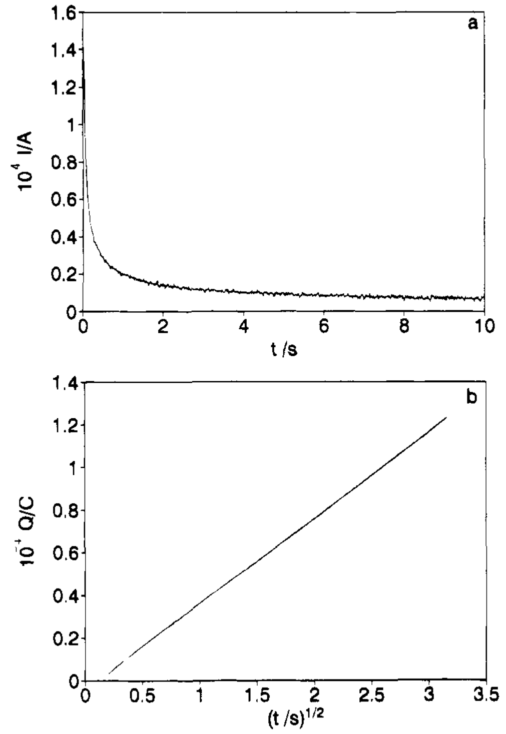

Figure 2. Chronocoulometry experiment: (a) raw chronoamperometry data for a base-activated glassy carbon electrode in 1.0 mM dopamine; (b) calculated chronocoulogram for the data recorded in (a).

value of COV was not due to the greater number of repetitions, which would cause only a 2.3-fold reduction; the improved COV was due to a real improvement in the precision when employing both carbon electrodes and the chronocoulometry method.

Please note that the intercept of Figure 2b is clearly below zero. This is an artifact of the data-recording method employed. We set the current sensitivity at a level for maximum precision in the slope of the chronocoulogram. Because the sensitivity was high, the first 100 ms of the experiment was outside the range of the current-recording digitizer. The initial current maximum does not contain irreplaceable diffusion information, and clipping it does not affect the slope of the chronocoulogram.

Table 1 lists the results for the experiments carried out. The $E^{\circ\prime}$ values for the catechols studied were determined by cyclic voltammetry; no anomalies in the $E^{\circ\prime}$ were observed for the compounds studied. The redox reactions for the catechols studied by cyclic voltammetry were all reversible or quasi-reversible with the base-activated carbon electrode (ΔE_p were all below 40 mV). We have employed an electron number, n, of 2 for all the compounds studied; this is based on the cyclic voltammetry peak separation. Table 1 presents the diffusion coefficients of the 10 compounds including dopamine. Also presented is the COV for each compound, and the results of other determinations of the diffusion coefficients when available.

Conclusion

We have determined the diffusion coefficients of a number of phenolic aromatic compounds using potential step chronocoulometry at the base-activated glassy carbon electrode. This method yields diffusion coefficients of higher precision than our previous work with chronoamperometry employing platinum electrodes. Our results are somewhat higher in value than the results of Gerhard and Adams (1982), but this may be due to the major differences in experimental conditions; Gerhard and Adams used flow injection analysis peak dispersion at an unspecified catecholamine concentration in a physiological pH phosphate buffer. Our results are comparable with the diffusion coefficients determined electrochemically by Sharma and Kalia (1977) for molecules of similar size in 0.1 M sulfuric acid. Typical results of Sharma and Kalia are as follows: for 2,6-dimethoxyphenol, $D = 0.727 \times 10^{-5}$ cm²·s⁻¹; *o*-ethoxyphenol ($D = 0.718 \times 10^{-5}$ cm²·s⁻¹; *p*-phenetidine, $D = 0.661 \times 10^{-5}$ cm²·s⁻¹. The values of the diffusion coefficients compare well with our previous results and with the results of diffusion experiments in a similar electrolyte done by Sharma and Kalia.

In our previous manual chronoamperometry experiments (Nowinski and Anjo, 1989), the background from platinum had decayed to a negligible value when the data were analyzed; the diffusion coefficients determined from the linear region of both the Cottrell plots and the Lingane plots were not corrupted by the background signal. Chronoamperometry experiments recorded with high-speed digitizers have significant background signal in the early data points. If the data are integrated to a chronocoulogram without subtraction of the background, the background error of the initial points is summed into all the data points. We have also found that failing to accurately set the current scale to zero leads to serious errors in the Anson plots. Either the failure to properly zero the current or failure to subtract the background corrupts all the points of a chronocoulogram in a nonlinear manner.

The background signal from glassy carbon is a complex mixture of double layer charging, surface redox reactions, and roughness effects. Hance and Kuwana (1987), Freund and Brajter-Toth (1991), and Sucheta and Rusling (1991) have shown that uncorrected chronocoulograms recorded with carbon electrodes show significant anomalies due to the background signal. Although we have found the background current from base-activated glassy carbon is significantly lower than the background from platinum in the same voltage region, the carbon background must be carefully subtracted from each individual faradaic experiment for accurate determinations of diffusion coefficients.

The precision of the repetitive results had an average COV of ±0.57%. This precision value is an order of magnitude lower than our previous results (Nowinski and Anjo, 1989) employing chronoamperometry at the platinum electrode.

The registry numbers in this paper were supplied by the author.

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