J. Chem. Eng. Data 1989, 34, 265-268

Therefore, it was not possible to correlate data with isotherms of established theories such as Langmuir, Freundlich, Brunauer, Emmett, and Teller. However, the following linear relationship, which has been proposed by Li and Deckwer (*8*), can be used to describe the experimental results (see Figure 4):

$$n_v = K \ln (1 + bP) \qquad (2)$$

Here n_v is the adsorbed gas volume (reduced to 273 K and 101.3 kPa) in centimeters per gram of activated carbon and K and b are temperature-dependent constants. In this case, they were found to be $K = 5.02$ cm/g and $b = 2.72 \times 10^{-2}$ kPa^{-1} for 298 K. Li and Deckwer (*8*) have examined various other activated carbons of different sources. They found that although eq 2 was valid in each case the values for K and b differed considerably, showing the adsorption capacity of activated carbon depended also on the source and the method of preparation, which affects, of course, the surface area.

The results here show that the slurried porous materials, such as alumina and activated carbon, adsorb dissolved carbon dioxide appreciably. The effect is more pronounced for the activated carbon, which is to be expected—to some extent—due to its nonpolar and hydrophobic nature and its large surface area. These results indicate that although the dissolved carbon dioxide competes with water for adsorption on alumina or activated carbon, the equilibrium adsorption is significant to the extent that the total amount of carbon dioxide in the slurry is increased considerably. It is further noted that the presence of $NaNO_3$ in the solution does not alter the trend in the adsorption capacities.

Registry No. CO_2, 124-38-9; Al_2O_3, 1344-28-1; C, 7440-44-0.

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Determination of the Diffusion Coefficients of Catecholamines by Potential Step Chronoamperometry

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The diffusion coefficients for a number of catecholamines and a related compound have been determined at 20 °C by use of potential step chronoamperometry at a planar platinum electrode. All of the compounds behaved well with no sign of polymerization or filming. The diffusion coefficients were in the region of 0.6×10^{-5} cm^2 s^{-1}, which is typical for molecules of this size. The results had a ±6% average coefficient of variation.

Introduction

The use of electrochemical techniques for the detection and analysis of catecholamines both in physiological systems and with chromatography has seen a great increase in activity (*1*, *2*). A need for accurately determined diffusion coefficients of these compounds exists both for calibration of electrochemical instruments and for the study of their transport in biological systems. We therefore have measured the diffusion coefficients of a group of catecholamines and a related compound using potential step chronoamperometry at a platinum button electrode.

Potential step chronoamperometry at a planar electrode is a well-established standard method for the determination of both electrode areas and diffusion coefficients of electrochemically active compounds. This method has been reviewed in *Treatise in Analytical Chemistry* (*3*) and is covered in many electrochemistry texts (*2*, *4*, *5*). An especially helpful treatment on this topic is given in a monograph by R. N. Adams (*6*).

Experimental Section

The chronoamperometry and cyclic voltammetry experiments were carried out with a Princeton Applied Research Model 362 scanning potentiostat and a Linear strip-chart recorder. The working electrode was an unshielded Beckman platinum button electrode with a geometric area of 0.24 cm^2. The platinum buttom electrode was held such that the electrode surface was horizontal. The reference electrode was a Corning saturated calomel electrode. The auxiliary electrode was a 20-cm spiral coil of 24 gauge platinum wire. The cell container employed was a standard Princeton Applied Research conical voltammetry cell. A potassium nitrate salt bridge was employed between the reference electrode and the test solutions.

The following chemicals were from Sigma Chemical Co.: (±)-arterenol (norepinephrine), L-dihydroxyphenylalanine (DOPA), L-β-dihydroxyphenylalanine methyl ester (methyl-DOPA), (−)-epinephrine, 3-hydroxytyramine hydrochloride (dopamine), and (±)-isoproterenol hydrochloride. The 3,4-dihydroxyhydrocinnamic acid, (−)-3,4-dihydroxynorephedrine, and (−)-3-(3,4-dihydroxyphenyl)-2-methyl-L-alanine were from Aldrich Chemical Co. The potassium ferrocyanide, potassium chloride, potassium dichromate, potassium nitrate, and sulfuric acid were analytical reagent grade from Mallinckrodt. The catecholamine solutions were prepared fresh daily with deionized water from a Barnstead Bantam demineralizer (S-27781) which was fed distilled water.

The platinum button working electrode was cleaned by placing it in a stirred solution of sulfuric acid saturated with

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potassium dichromate for 5 min; the electrode was then thoroughly washed with deionized water and air-dried. The electrode cleaning was carried out before each decay experiment. The electrode was washed thoroughly with deionized water when it was transferred from the ferrocyanide solution to the catecholamine solution. The electrochemical cell was kept within the range of 20 ± 1 °C by use of warm- and cold-water baths available in the lab. The temperature was measured with a calibrated mercury thermometer (Ertco) with 0.2 °C divisions, which had been calibrated. The potential was stepped from 0 to 0.750 V (relative to SCE) for the chronoamperometry of the catecholamines. All the catecholamines were at 1.00×10^{-3} M in 0.1 M sulfuric acid. The ferrocyanide solutions were at 4.00×10^{-3} M in 0.1 M KCl solution. The potential was stepped from 0 to 0.500 V (SCE) for chronoamperometry of the ferrocyanide solution. A cyclic voltammogram for 0 to 0.750 V (SCE) was recorded before and after each chronoamperometry experiment.

Data Analysis

In all the experiments the first step was to determine the active electrode area by using chronoamperometry in a standard ferrocyanide solution. Then the same electrode was immediately used to determine the diffusion coefficient of one of the catecholamines by using chronoamperometry. A typical experimental current time response of 1.00 mM L-DOPA solution to a potential step is shown in Figure 1a. This recording of an L-DOPA solution is typical of all the experiments carried out. Current measurements from 5 to 15 s after the potential step were used for the calculations discussed below.

Two methods were used to analyze the chronoamperometry data. The first method employed was to fit the current–time data to the Cottrell equation (eq 1) using an i vs $t^{-1/2}$ plot.

$$it^{1/2} = \frac{nFAD^{1/2}C_0}{\pi^{1/2}} \qquad (1)$$

The variables are defined in the Glossary. The slope of this plot is the best fit value of $it^{1/2}$. This method was compared with the use of eq 2 proposed by Lingane and co-workers (*7*) for

$$it^{1/2} = \frac{nFAD^{1/2}C_0}{\pi^{1/2}}\left[1 + b\left[\frac{Dt}{R^2}\right]^{1/2}\right] \qquad (2)$$

correction of edge effects when using an unshielded electrode. Depending on the time interval studied and the electrode dimensions, Soos and Lingane (*7*) have shown that nonlinear diffusion from the edge can cause significant errors with the Cottrell equation method. The variable R is the electrode radius and b is an empirical fit parameter; the other variables are described in the Glossary. In this second method a plot of $it^{1/2}$ vs $t^{1/2}$ is generated and the intercept at $t = 0$ is the best fit value of $it^{1/2}$. At $t = 0$ the second term in eq 2 vanishes, and the equation assumes the form of the Cottrell equation.

A linear regression program was used to fit the current–time data both to the Cottrell equation and to the Lingane correction for edge effects. An example of both the Cottrell plot and the edge correction plot are shown in Figure 1b and Figure 1c, respectively, for the L-DOPA data presented in Figure 1a.

The platinum working electrode area was determined with chronoamperometry in a standard ferrocyanide solution. In this situation the unknown area is the only unknown term in the Cottrell equation. The ferrocyanide diffusion coefficient used was the value of von Stackelberg et al. (*8*). The electrode area was calculated by substituting the best fit values of $it^{1/2}$ into the Cottrell equation.

The same electrode was then immediately used to determine the diffusion coefficient of one of the catecholamines. The current decay was analyzed in similar fashion as described above. In this situation the diffusion coefficient is the only unknown term in the Cottrell equation. The values of $it^{1/2}$ determined by both methods were then substituted in the Cottrell equation and the diffusion coefficient was calculated. The working electrode area was measured electrochemically before each catecholamine experiment.

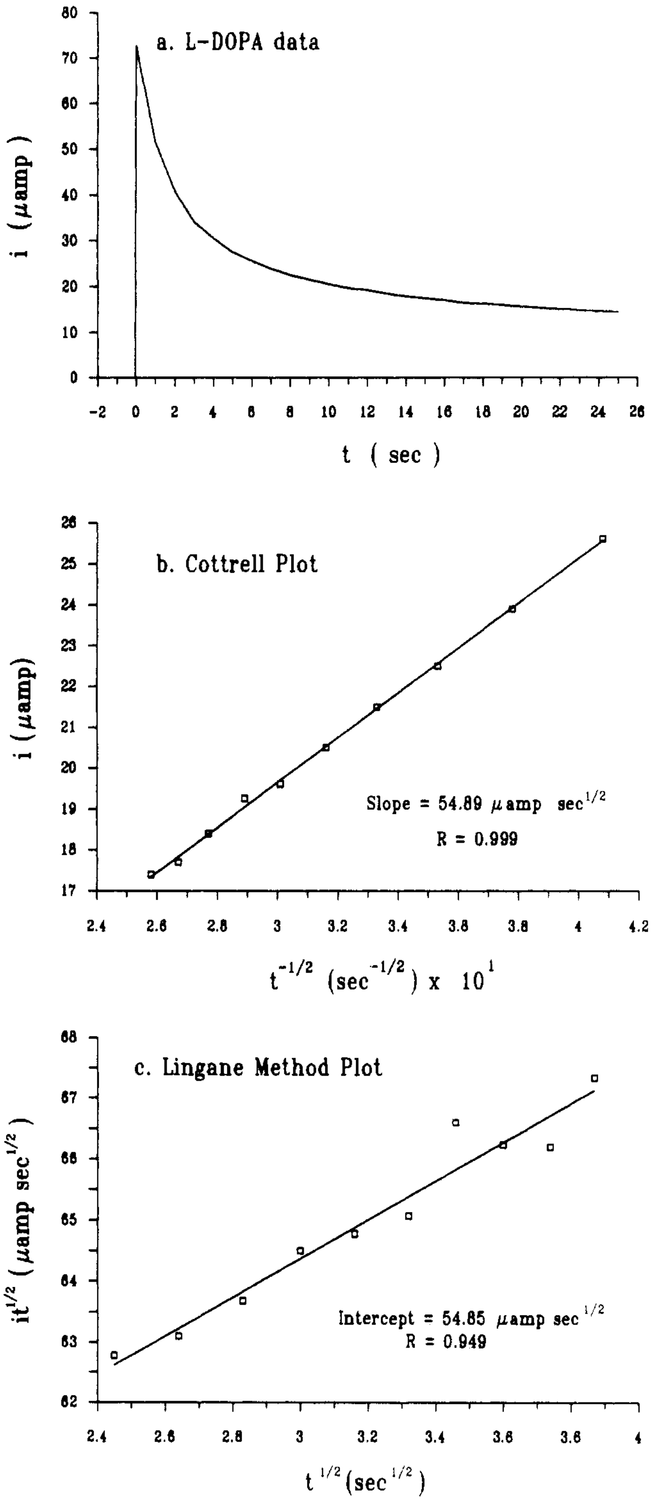
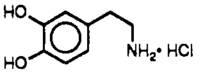
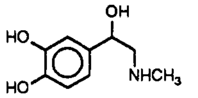
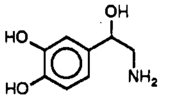
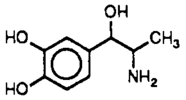
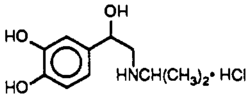
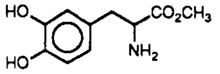
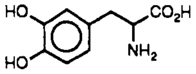
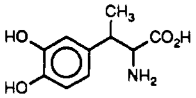
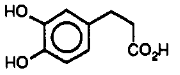


Figure 1. (a) Experimental current decay of 1.00 mM L-DOPA in 0.10 M sulfuric acid following a potential step from 0.0 to 0.75 V (SCE). (b) The Cottrell plot of the data shown in (a). (c) The Lingane edge correction plot of the data from (a).

Results and Discussion

The cyclic voltammograms and the current decays indicated that the compounds behaved reproducibly in acidic media during

Table I. Diffusion Coefficients of Catecholamines and a Related Compound at 20 °C

compound[a]	D, × 10^5 cm^2 s^{-1} this work[b]	reported value	ref
 3,4-dihydroxyphenylethylamine hydrochloride {dopamine hydrochloride}	0.669 ± 6% (n = 11)	0.60	*11*
 (R)-(−)-dihydroxy-α-(methyaminomethyl)benzyl alcohol {(R)-(−)-epinephrine}	0.611 ± 6% (n = 11)	0.51	*11*
 (±)-α-(aminomethyl)-3,4-dihydroxybenzyl alcohol {(±)-norepinephrine}	0.621 ± 7% (n = 10)	0.55	*11*
 (−)-α-(1-aminoethyl)-3,4-dihydroxybenzyl alcohol {(−)-3,4-dihydroxynorephedrine}	0.664 ± 5% (n = 8)		
 (±)-1-(3′,4′-dihydroxyphenyl)-2-isopropylaminoethanol hydrochloride {(±)-isoproterenol hydrochloride}	0.669 ± 7% (n = 10)		
 L-β-3,4-dihydroxyphenylalanine methyl ester	0.695 ± 6% (n = 8)		
 L-3,4-dihydroxyphenylalanine {L-DOPA}	0.550 ± 7% (n = 10)		
 (−)-3-(3,4-dihydroxyphenyl)-2-methyl-L-alanine	0.735 ± 5% (n = 9)		
 3,4-dihydroxyhydrocinnamic acid	0.693 ± 6% (n = 11)		

[a] Formal compound names are followed by common names in braces. [b] Uncertainties are expressed as coefficients of variation.

the experiments. Lane and Hubbard (*9*) have shown that electrode filming is severe for catecholamines in physiological pH solution when analyzed with a platinum electrode, but Fike and Curran (*10*) found that no significant filming problems occurred in acidic media. The cyclic voltammograms before and after each chronoamperometry experiment were identical within experimental limits; there was no indication of filming, which usually decreases current and shifts peak potentials. There was also no significant change in the electrochemical electrode area throughout the experiments, which indicated that the chronocoulometry and the cleaning steps had no deleterious effect on the electrode surface.

The method used to determine the catecholamine diffusion coefficients was to first carry out a chronoamperometry experiment with the platinum electrode in ferrocyanide solution. The ferrocyanide data were used to determine the electrode area which was then employed in the calculation of the diffusion coefficient.

Interestingly, for all compounds tested both the calculations using the Cottrell equation method and those using the edge correction method gave the same value for the diffusion coefficient to three significant figures. These methods did not have identical fits; the correlation coefficient for the Cottrell method always exceeded 0.999 while the coefficient seldom exceeded 0.99 for the edge effect correction. These data indicate that for the short time intervals chosen edge diffusion was a negligible component in the total current using electrodes of the dimensions employed.

The diffusion coefficients we have determined are listed in Table I along with results from another reference for comparison. Our results are somewhat higher in value than the results of Gerhardt and Adams (*11*) although this may be due to major differences in experimental conditions. Gerhardt and Adams employed flow injection peak dispersion at unspecified catecholamine concentrations in a physiological pH phosphate buffer. We employed 0.1 M sulfuric acid with the catecholamines at 1.00 mM concentration. Our results are quite comparable with the diffusion coefficients determined by Sharma and Kalia (*12*) for molecules of similar size in 0.1 M sulfuric acid. Typical results of Sharma and Kalia are 2,6-dimethoxyphenol ($D = 0.727 \times 10^{-5}$ cm^2 s^{-1}), *o*-ethoxyphenol ($D = 0.718 \times 10^{-5}$ cm^2 s^{-1}), and *p*-phenetidine ($D = 0.661 \times 10^{-5}$ cm^2 s^{-1}).

It should be noted that all the measurements in this work were made at 20 °C. Therefore the results should be slightly lower than the results presented by other workers in the field who have used 25 °C. Note, the 2% per degree correction mentioned by Gerhardt and Adams (*11*) which was originally from a work by Meites (*13*) is actually for the polarographic diffusion current. This diffusion current correction has a number of temperature-dependent terms in addition to the diffusion coefficient such as changes in the properties of mercury with temperatures. Meites indicates that the variation in a diffusion coefficient due to temperature is 0.4% per degree, which is in agreement with the diffusion coefficient correction commonly used for biomolecules (*14*). This would indicate that our results are approximately 2% lower than values obtained at 25 °C.

The precision of the repetitive results had an average coefficient of variation of ±6%. This is consistent with the precision limits of Gerhardt and Adams (*11*) and with Sharma and Kalia (*12*).

Glossary

i	current, A
t	time, s
n	electron number of the half-reaction
F	the Faraday constant, 96 485 C/equiv
A	electrode area, cm^2
D	diffusion coefficient, cm^2 s^{-1}
C_0	bulk solution concentration, mol/cm^3

Registry No. L-DOPA, 59-92-7; dopamine hydrochloride, 62-31-7; (±)-norepinephrine, 138-65-8; (–)-3,4-dihydroxynorepinephrine, 829-74-3; (±)-isoproterenol hydrochloride, 949-36-0; L-β-3,4-dihydroxyphenylalanine methyl ester, 7101-51-1; (–)-3-(3,4-dihydroxyphenol)-2-methyl-L-alanine, 555-30-6; 3,4-dihydroxyhydrocinnamic acid, 1078-61-1; (*R*)-(–)-epinephrine, 51-43-4.

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Effect of Acetamide on the Viscosities of Several Aqueous Electrolyte Solutions at Different Temperatures

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The relative viscosities of NaCl, NaI, KCl, KBr, and CsI solutions in water–acetamide mixtures have been measured at 298.15, 313.15, 333.15, 348.15 and 358.15 K. From these data the values of *A* and *B* coefficients of the Jones–Dole equation have been estimated. The values of ionic *B* coefficient for alkali-metal and halide ions were calculated. Ionic viscosity *B* coefficient values have been analyzed on the basis of structural contributions.

The variation of viscosity with temperature and solvent composition has been employed by many workers (*1*) to study the ion–solvent interaction in both aqueous and nonaqueous solutions. The *B* coefficient in water shows strong temperature dependence (*2–5*) which can be attributed to ion–solvent interactions, which should decrease at higher temperature where the water structure itself is diminished (*6*). Such interactions also should decrease with increasing ionic size. In the present paper an attempt has been made to deal with the ion–solvent interaction of alkali-metal and halide ions in water–acetamide mixtures of varying compositions to see the effect of size and nature of ion, temperature, and water–acetamide hydrogen bonding on the *B* coefficient of the viscosity.

Experimental Section

The methods of purification of acetamide and salts were described previously (*7*). The mixed solvents and all solutions used for investigations were made by weighing. The viscosity measurements were made in an Ubbelohde-type suspended level viscometer and carried out in a constant-temperature bath controlled to within 0.01 K. The procedure of viscosity measurements was the same as described earlier (*8*). The total uncertainty of viscosity was (3–6) × 10^{-4} mPa·s. The density of solutions were determined by the magnetic float densimeter with the precision 1 × 10^{-5} g cm^{-3}. All measurements were made at a series of concentration covering the range 0.005–0.2 mol dm^{-3} in water and three mixtures containing 5.10, 11.55, and 23.36 mol % acetamide in water at 298.15, 313.15, 333.15, 348.15, and 358.15 K.

Results

The relative viscosity of a solution containing electrolyte was obtained from the flow times of the electrolyte solution and

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