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Ultramicroelectrode Voltammetry in a Drop of Solution: A New Approach to the Measurement of Adsorption Isotherms at the Solid-Liquid Interface

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A new approach to the determination of adsorption isotherms at the solid-liquid interface is proposed, employing an ultramicroelectrode (UME) to monitor amperometrically the concentration of adsorbate in a small volume of solution (3.5–20 μL) deposited on a macroscopic adsorbent. The technique both allows for the use of well-characterized surfaces (single crystals when available) and provides the high ratio of adsorbent surface area to solution volume required for accurate measurements. The application of the method is demonstrated using the adsorption and ion exchange of H^+ on the {010} surface of the mineral albite ($\text{NaAlSi}_3\text{O}_8$). By judicious selection of the chemical pretreatment of this surface, it is possible to measure the isotherm for H^+ adsorption and estimate the number of protonation and exchange sites. Additional experiments, comparing the adsorption of methylene blue cation on various graphite surfaces, provide an illustration of how the chemical nature of the adsorbent affects the extent of adsorption.

INTRODUCTION

The measurement of the extent to which a solute is adsorbed at the interface between a solid and a liquid is of fundamental importance in a number of areas of chemistry (1–3), including geochemistry (4–7), analytical chemistry (8), and electrochemistry (9), and in industrial applications (10). A common approach to determining adsorption isotherms is to measure the change in the concentration of the solute, in a solution in contact with the solid under study, as a function of various (initial) solute concentrations and ascribe the measured difference to the extent of adsorption of the solute species. In general, this strategy requires a high ratio of adsorbent surface area to solution volume to ensure that the changes in solution composition are sufficiently large to be measured with good precision and accuracy by the chosen analytical method.

Traditionally, this requirement has been met by carrying out experiments with large volumes of solution containing suspensions of high surface area material (1, 2). However, this

approach makes it difficult to reproducibly prepare and characterize the surface of adsorbents with the desired degree of control. In this respect, adsorption studies at the solid-liquid interface currently lag behind those at the gas-solid interface (11), where a number of methods for preparing well-defined surfaces (generally through the use of single crystals) and characterizing them are available (12). Given this current state of affairs, we have been motivated to develop a new approach for measuring adsorption isotherms at the solid-liquid interface which allows the use of well-characterized surfaces (single crystals when available), while retaining the high surface area/solution volume ratio required for analytical sensitivity.

The methodology proposed in this paper is useful for measuring the adsorption characteristics of any electroactive solute. The general concept is to use an ultramicroelectrode (UME) to monitor amperometrically the concentration of solute in a small drop of solution (3.5–20 μL in the present study) deposited on the surface of interest (typically covering an area of 0.05–0.3 cm^2). The concentration of solute in the drop (once the adsorption process has attained equilibrium), C_d^* , is determined directly from the measured diffusion-limited current, i_d , at the UME (13, 14):

$$i_d = 4nFDaC_d^* \quad (1)$$

where n is the number of electrons transferred per redox event, F is the Faraday constant, D is the diffusion coefficient of the solute, and a is the radius of the UME. The concentration of solute in the absence of adsorption, C_s^* , can similarly be determined, for example, by utilizing a comparatively large volume of solution. The difference in limiting currents can be used to calculate the concentration of material adsorbed at the interface (mol cm^{-2}):

$$\Gamma_{\text{ad}} = (V/A)(i_s - i_d)/(4nFDa) \quad (2)$$

where i_s is the current measured in the absence of adsorption, V is the volume of the drop, and A is the substrate surface area which it covers. A similar approach has been used in electrochemical thin-layer cells (TLC) for studying adsorption on electrodes (15). The method proposed here has the advantage of being applicable to a wide range of sample surfaces, including insulators, of small size, without the need to construct a TLC for each. Although UMEs have previously been utilized in small-volume environments, for example, in trace

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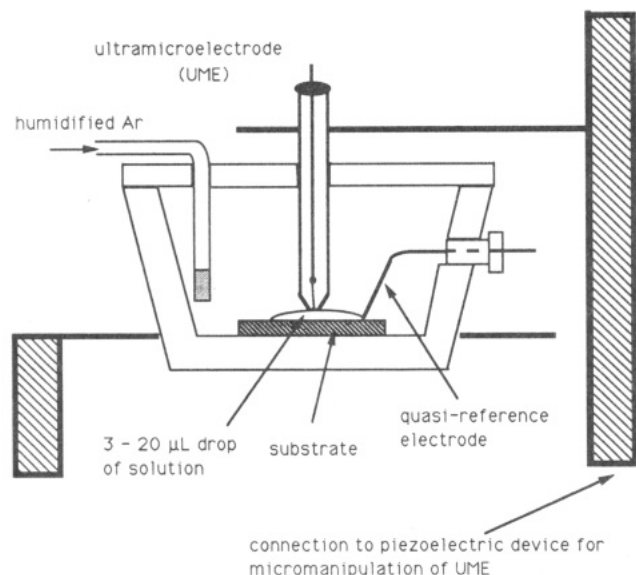


Figure 1. Schematic of the experimental apparatus for adsorption studies via UME voltammetry in a drop of solution.

analysis (16, 17) and *in vivo* studies (18, 19), we are unaware of previous work concerning surface studies like those proposed here.

Two adsorption systems are described in this paper: (i) H^+ on the {010} surface of the mineral albite ($NaAlSi_3O_8$) and (ii) the methylene blue cation (MB^+) on both highly oriented pyrolytic graphite (HOPG) and polycrystalline pyrolytic graphite. The first system was chosen since the surface acidity of solids is an important subgroup within the general area of solid-liquid interfacial adsorption which, hitherto, has been studied predominantly via potentiometric acid-base titrations on powders (4, 5, 20, 21). Additionally, the acid-base characteristics of albite powders have been previously characterized, and this material is an important model system in the study of water-rock reactions (22). The system is also of interest in that Na^+/H^+ ion exchange can occur, in addition to protonation/deprotonation reactions of surface hydroxyl groups (22, 23). The experiments reported in this paper show that it is possible to measure the isotherm for the protonation reaction, determine the number of protonation sites on the surface, and estimate the thickness of the surface layer in which Na^+/H^+ ion-exchange occurs. The second system was considered because MB^+ adsorption is widely employed as a general method for determining the surface areas of powders (1, 24, 25), including graphitic materials (26-28). With the methodology proposed in this paper, it is possible to compare adsorption on basal plane vs edge plane HOPG and investigate the effects of various surface pretreatments of pyrolytic graphite on the adsorption of MB^+ .

EXPERIMENTAL SECTION

Apparatus. A schematic diagram of the experimental apparatus is shown in Figure 1. A Pt-disk UME, with an effective radius of 12.3 μm (29), was employed as the working electrode in all experiments. This was fabricated by sealing Pt wire (25 μm nominal diameter) in a glass tube (1 mm i.d.; 3 mm o.d.), as previously described (30). After the electrode surface was polished to 0.25 μm , with a succession of finer diamond pastes (Buehler Ltd., Lakebluff, IL), the glass surrounding the disk was fashioned into a cone by subsequent polishing until the radius of the glass insulating sheath was around 10 times the size of the electrode itself. Either a 100- μm -diameter Pt wire (H^+ /albite experiments) or a 250- μm -diameter Ag wire (MB^+ /graphite, MB^+ /Plexiglas, and ferricyanide/Plexiglas experiments) was used as a quasi-reference electrode (QRE) to complete a two-electrode arrangement. In the latter case, the wire was coated with "Nail Protector" (Pavion Ltd., NY) and then cut so as to expose a small disk. These

procedures ensured that the electrode areas in contact with the drop of solution were small in comparison to the substrate area, thus minimizing the extent of adsorption of the solute on these surfaces. Control experiments, reported below, demonstrated that extraneous adsorption of this nature was negligible with the setup described.

The electrochemical cell, containing the two electrodes, was fabricated from Teflon and had a maximum volume of around 2 cm^3 . It was equipped with a lid containing a gas line to enable experiments to be conducted under a humidified argon atmosphere. The solid substrate was secured flat on the base of the cell, and the QRE was mounted through the side of the cell, so that it just made contact with the substrate. The Pt UME was mounted on the z-piezoelectric inchworm (Burleigh Instruments, Fischer, NY) of a conventional scanning electrochemical microscope (30), which was used to manipulate its position. The apparatus was shielded with a Faraday cage. The equipment for current-potential measurements was as previously described (29). Drop areas were determined with an RF Inter-Science (New York) Macroscope 25, 8 \times 30 monocular (0.1-mm resolution).

Materials. Amelia albite crystals were obtained from Ward's Natural Science Establishment (Rochester, NY). The majority of crystals were tabular with the {010} faces prominent and were cleaved in this plane and polished with a succession of diamond lapping compounds down to 0.25 μm , followed initially by vigorous rinsing with a jet of Milli-Q reagent water (Millipore Corp.) and then either Ar-purged Milli-Q water (pH approximately 7) or 0.1 M sodium hydroxide for several min, depending upon the nature of the experiment (see below).

HOPG samples were kindly provided by Dr. Arthur W. Moore of Union Carbide Corp., Parma, OH. For studies on the basal plane, cleavage with commercial adhesive tape was executed immediately prior to the adsorption experiments. Owing to reports of the retention of certain polishing materials by edge plane graphite (31), this surface was simply pretreated by polishing on a Nylon cloth (Buehler Ltd.). Experiments involving commercial pyrolytic graphite, composed of microcrystallites, used a 1/2-in. disk which was polished to a finish of 15 μm and rinsed with either water or ethanol followed by water. For some experiments the surface was further treated by exposure to an oxygen/natural gas flame for several seconds.

Hydrochloric acid solutions of various concentrations in the range 4×10^{-5} - 10^{-3} M were prepared using 0.1 M volumetric standard solution (Aldrich) and Milli-Q water (Millipore Corp.). Either 0.1 M potassium chloride ("ultrapure", Alfa Products, Danvers, MA) or 1.0 M sodium chloride (Baker Analyzed) was employed as the supporting electrolyte. MB^+ solutions (10^{-5} - 10^{-3} M) contained buffer/supporting electrolyte of 0.2 M KH_2PO_4 adjusted to pH 7.5 with KOH, and potassium ferricyanide solutions (2×10^{-3} M) contained 0.1 M KCl. Sodium hydroxide solution (approximately 0.1 M) was prepared from Baker Analyzed reagent.

Procedure. The cell, containing the sample, was purged with humidified Ar for about 15 min prior to the addition of the analyte solution, which had likewise been purged with Ar. A drop of solution was deposited on the surface of the substrate using either a 5-40- μL Finnpiptette (Helsinki, Finland) for 10- and 20- μL drops or a Hamilton 5- μL (7000 Series) syringe (for smaller volumes) inserted through a small entrance in the cell lid. The position of the drop was such that it just contacted the QRE. The substrate area covered by the drop depended upon the nature of the surface pretreatment (see below) but was typically around 0.05 cm^2 (3.5- μL drop), 0.15 cm^2 (10- μL drop), or 0.3 cm^2 (20- μL drop).

The UME (which was polished with 0.05- μm alumina and vigorously rinsed prior to each run) was lowered, first manually and then with the piezoelectric device, until it contacted the drop. Neither this process nor the withdrawal of the electrode after the experiment appeared to distort the drop area. Additionally, test measurements of the area before and after this procedure showed no measurable change. Given the typical drop volumes and areas defined above, the UME was sufficiently distant from the substrate that diffusion to the UME was not hindered by the presence of the substrate (32).

Following the deposition of the drop, sufficient time must be allowed for the adsorption process to attain equilibrium. Since the rate of adsorption of H^+ on albite is essentially diffusion-

Table I. Data for Control Experiments To Test for Extraneous Adsorption of H⁺ and MB⁺

analyte	C _s */M	i _s /nA	i _d /nA	V/μL	A/cm ²
H ⁺	4.95 × 10 ⁻⁴	20.3	20.1	20	0.177
H ⁺	2.20 × 10 ⁻⁴	9.0	8.9	20	0.181
H ⁺	9.90 × 10 ⁻⁵	4.0	4.1	20	0.189
MB ⁺	1.37 × 10 ⁻⁵	0.108	0.106	3.5	0.062

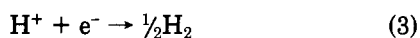
controlled under the conditions of these experiments (33), only several minutes are required for this situation to prevail and for the concentration of the solute in the drop to become uniform (considering the substrate/drop/Ar "sandwich" approximately as a thin-layer cell) (34). This was confirmed experimentally by the fact that, after this period of time, the magnitude of the measured diffusion-limited current showed no detectable change upon subsequent remeasurement. Similarly, studies on powdered material suggest that the adsorption of MB⁺ on graphite is fairly rapid (time scale of min) (35). In these experiments the diffusion-limited current was recorded as a function of time (generally over a period of around 30 min) until a constant value was obtained.

After the voltammogram was recorded for the electrolysis of the analyte, the electrode was withdrawn and the drop area measured. The cell was then filled with a comparatively large volume of the same solution (ca. 1 mL), and the diffusion-limiting current was recorded to determine the analyte concentration in the absence of interfacial adsorption.

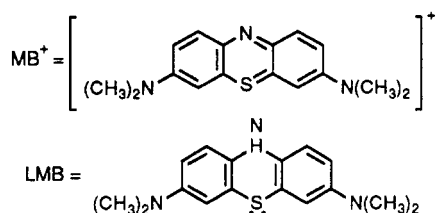
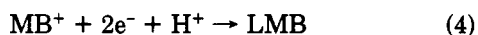
RESULTS AND DISCUSSION

Control Experiments. Initial control experiments were conducted (i) to check that extraneous adsorption of analyte, of the nature described above, was negligible with the experimental setup proposed and (ii) to determine whether evaporation of solvent from the drop was significant over the time scale of a typical experiment.

With reference to the first point, experiments were conducted on drops of the two analyte solutions (with concentrations typical of the range used in the adsorption studies reported below) deposited on a Plexiglas substrate. This was considered unlikely to adsorb either of the analytes of interest (and is confirmed experimentally below). Results of these experiments, for the two species, are given in Table I. For the H⁺ system, the UME reaction is



which had a measured half-wave potential of around -0.8 V vs PtQRE. The reduction of MB⁺, under the defined conditions, proceeds according to (36, 37):



The half-wave potential for this process was around -0.3 V vs AgQRE. Although an adsorption prewave is observed at both mercury (36, 38, 39) and platinum (37) macroelectrodes, this was not discernable at the UME with the scan rates employed (typically between 1 and 5 mV/s, with the lower limit preferred at the lowest [MB⁺], ca. 10⁻⁵ M). This is due to the small UME area and high diffusional flux of MB⁺ with the concentrations employed. For both analyte systems, the close agreement between the diffusion-limited currents measured in the drop of solution, *i_d*, and in a larger volume (ca. 1 mL), *i_s*, suggested little extraneous adsorption, thereby

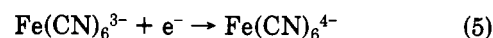
Table II. Time Dependence of the Diffusion-Limited Current for the Reduction of MB⁺ (6.78 × 10⁻⁵ M Methylene Blue) in a 20-μL Drop on a Plexiglas Substrate

t/min	i/pA	t/min	i/pA
4	428	12	430
6	420	14	425
8	415	31	440
10	415		

confirming the validity of the proposed experimental procedure in this regard.

To test the second point, voltammograms were recorded at various times for the reduction of MB⁺ (6.78 × 10⁻⁵ M) in a 20-μL drop of solution, following deposition on the Plexiglas substrate (A = 0.188 cm²). As in the experiments reported above, these measurements were made under a humidified Ar atmosphere. The results, shown in Table II, indicated that evaporation was negligible over a period of about 30 min, as evidenced by the essentially constant value of *i_d* (and thus, from eq 1, C_d*).

Additional experiments, of a similar nature, were conducted on the reduction of ferricyanide (ca. 2 mM):



in a 20-μL drop deposited on the Plexiglas substrate (A = 0.212 cm²). These measurements were conducted in the absence of a humidified Ar atmosphere, and the tip electrode was held at a potential (ca. 0.0 V vs AgQRE) such that the electrode reaction, eq 5, was diffusion-controlled for the duration of the measurement of *i_d*. Even without a humidified atmosphere the limiting current was observed to increase by only 5% over a period of 30 min, again suggesting that evaporation is not a problem. Although some of the experiments reported below were conducted with volumes smaller than 20 μL, the measured ratio of A/V was not appreciably larger than for the above control experiments, and thus complications arising from evaporation in smaller drops during the course of an experiment were also anticipated to be negligible.

One of the advantages of the proposed technique is that electrolysis of the analyte during the measurement of the diffusion-limited current does not significantly perturb its concentration, due to the low ratio of UME area to drop volume. It follows from eq 1 and the rate of depletion of solute in the drop, $V(dC_d^*/dt) = -i_d/nF$, that if the UME potential is held at a value at which the electrolysis current is diffusion-limited, the time dependence of *i_d* is given by

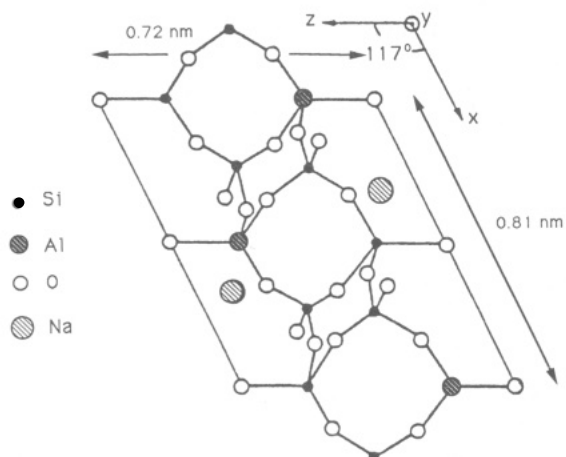
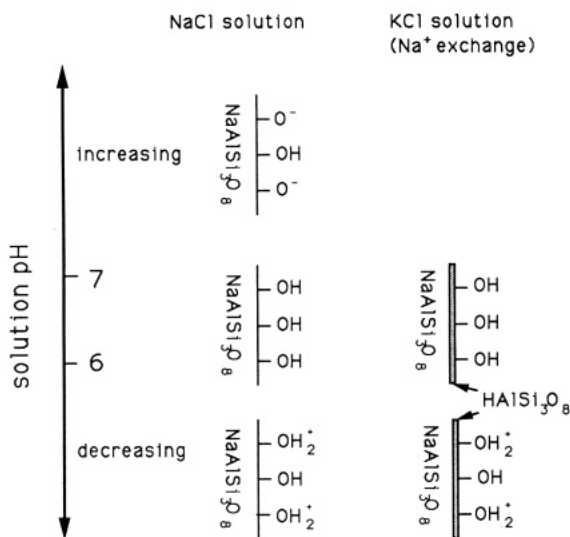
$$i_d(t) = i_d(t=0) \exp(-4aDt/V) \quad (6)$$

Thus for typical values of $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $a = 12.5 \text{ μm}$, and $V = 20 \text{ μL}$, a time of over 5 h is required for *i_d* to fall to 95% of its initial value. Even for H⁺, with a much larger diffusion coefficient ($8.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), an electrolysis time in excess of 40 min is necessary to decrease *i_d* by this degree.

Application to Protonation, Deprotonation, and Ion-Exchange Processes on an Albite {010} Surface. Albite is a naturally-occurring aluminosilicate with a {010} surface structure shown in Figure 2 (40-43). The oxygens on the surface can undergo proton-exchange reactions. In addition, under some conditions, Na⁺, which serves as a counterion, can be exchanged by H⁺. The proton-exchange reactions which occur in aqueous solution, as deduced from experiments on powdered material (22), are illustrated in Figure 3. These can be summarized as follows: (i) at pH < 6, protonation of surface hydroxyl groups; (ii) at pH > 7, deprotonation of surface hydroxyl groups (or equivalently adsorption of OH⁻ ions), (iii) in the absence of Na⁺ in solution, complete and rapid (less than 1 min under typical conditions for powder experiments) (22) exchange of H⁺ for Na⁺.

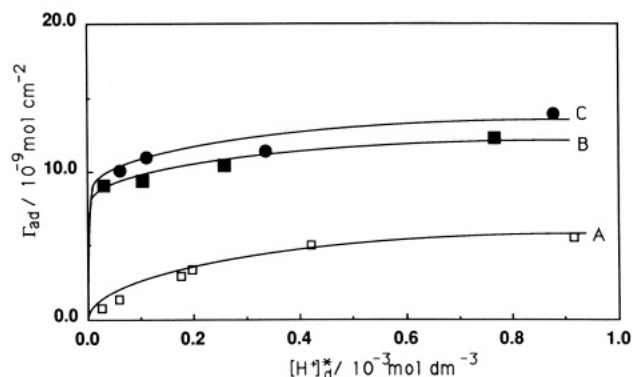
Table III. Data for the Reduction of H⁺ (0.1 M KCl Supporting Electrolyte) in Drops Deposited on Albite Pretreated with Ar-Purged Water

C_s^*/M	i_s/nA	C_d^*/M	i_d/nA	$V/\mu L$	A/cm^2	$10^9 \Gamma_{ad}/mol\ cm^{-2}$
3.97×10^{-5}	1.60	2.73×10^{-5}	1.10	20	0.332	0.75
7.93×10^{-5}	3.20	5.95×10^{-5}	2.40	20	0.289	1.4
2.18×10^{-4}	8.8	1.76×10^{-4}	7.1	20	0.283	3.0
2.43×10^{-4}	9.8	1.98×10^{-4}	8.0	10	0.130	3.4
5.06×10^{-4}	20.4	4.21×10^{-4}	17.0	20	0.335	5.0
1.00×10^{-3}	40.4	9.17×10^{-4}	37.0	20	0.305	5.5

**Figure 2.** Schematic projection of the albite structure on the {010} surface.**Figure 3.** Summary of the H⁺ adsorption and ion-exchange reactions which occur on the surface of albite.

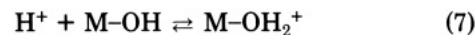
Albite also undergoes dissolution under the conditions of the experiments reported here, but at an extremely low rate (10^{-15} – 10^{-16} mol cm⁻² s⁻¹) (22, 23, 44) so that the material is effectively insoluble on the time scale of the experiments.

Thus, at pH 6–7 the surface hydroxyl groups are expected to be predominantly in the $\geq M-OH$ state, where M = Al or Si. The protonation of these groups to $\geq M-OH_2^+$ was investigated by pretreating the albite surface with Milli-Q reagent water which had been purged overnight with Ar, so as to remove CO₂ and thus raise the pH into the desired range. The surface was rinsed for several min to ensure sufficient time for complete exchange of H⁺ for surface Na⁺ and formation of surface $\geq M-OH$ species. Voltammetric data obtained in drops of HCl solution (0.1 M KCl as supporting electrolyte) of various concentrations deposited on this surface are summarized in Table III, along with corresponding data

**Figure 4.** Surface concentration of adsorbed H⁺ on albite as a function of solution H⁺ concentration for (A) H₂O pretreatment, 0.1 M KCl supporting electrolyte, (B) 0.1 M NaOH pretreatment, 1.0 M NaCl supporting electrolyte, (C) 0.1 M NaOH pretreatment, 0.1 M KCl supporting electrolyte.

measured in larger volumes of these solutions. The measured diffusion-limited currents for the two situations, i_d and i_s , were used to deduce the corresponding concentrations, C_d^* and C_s^* , via eq 1 with $D = 8.5 \times 10^{-5}$ cm² s⁻¹. (The value of the latter parameter was determined from UME voltammetry with known concentrations of HCl [9.90×10^{-4} , 4.95×10^{-4} , and 1.98×10^{-4} M]). In all cases, i_d was found to be significantly lower than i_s , implying that the concentration of H⁺ was lower in the drop following deposition on the albite surface. Taking this loss of material from the drop to adsorption on albite, we obtain the values of Γ_{ad} shown in Table III, deduced by applying eq 2. The corresponding isotherm (Γ_{ad} vs C_d^*) is shown in Figure 4, curve A.

The adsorption process, under the conditions of these experiments, can be written as



for which the equilibrium constant (written in terms of concentrations rather than activities) is

$$K_a = [M-OH_2^+]/[M-OH][H^+]_d^* \quad (8)$$

$$= \Gamma_{ad}/(\Gamma^\infty - \Gamma_{ad})[H^+]_d^* \quad (9)$$

It follows that

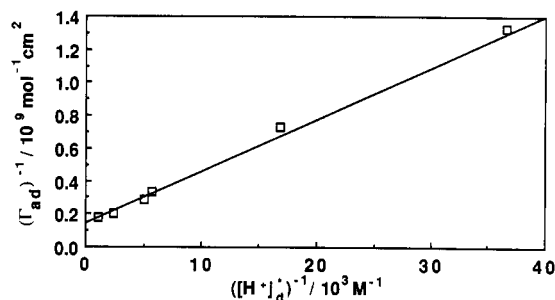
$$(\Gamma_{ad})^{-1} = (\Gamma^\infty)^{-1} + ([H^+]_d^* K_a \Gamma^\infty)^{-1} \quad (10)$$

In eqs 8–10, $[H^+]_d^*$ is the concentration in the drop of solution, $[i]$ is the surface concentration (mol cm⁻²) of the species i (i.e., M–OH or M–OH₂⁺), and Γ^∞ is the maximum density of M–OH sites available for protonation.

Analysis of the data in Table III and Figure 4A, in terms of eq 10, is shown in Figure 5 as a plot of $(\Gamma_{ad})^{-1}$ vs $([H^+]_d^*)^{-1}$. This yields $K_a = 4.3 \times 10^3$ M⁻¹ and $\Gamma^\infty = 7.1 \times 10^{-9}$ mol cm⁻². The former value is around half that determined from powder experiments (22), although neither the nature nor the concentration of the supporting electrolyte (if any) was reported in the powder studies, making a direct comparison of the two

Table IV. Data for the Reduction of H⁺ in 10- μ L Drops Deposited on Albite Pretreated with 0.1 M NaOH

supporting electrolyte	C _s [*] /M	i _s /nA	C _d [*] /M	i _d /nA	A/cm ²	10 ⁹ Γ _{ad} /mol cm ⁻²
KCl	2.43 × 10 ⁻⁴	9.8	6.20 × 10 ⁻⁵	2.50	0.180	10.1
KCl	3.32 × 10 ⁻⁴	13.0	1.12 × 10 ⁻⁴	4.50	0.200	11.0
KCl	5.06 × 10 ⁻⁴	20.4	3.35 × 10 ⁻⁴	13.5	0.150	11.4
KCl	1.12 × 10 ⁻³	45.3	8.80 × 10 ⁻⁴	35.5	0.172	13.9
NaCl	1.93 × 10 ⁻⁴	7.8	2.97 × 10 ⁻⁵	1.20	0.182	9.0
NaCl	2.53 × 10 ⁻⁴	10.2	1.04 × 10 ⁻⁴	4.20	0.158	9.4
NaCl	4.21 × 10 ⁻⁴	17.0	2.58 × 10 ⁻⁴	10.4	0.158	10.4
NaCl	9.66 × 10 ⁻⁴	39.0	7.68 × 10 ⁻⁴	31.0	0.161	12.3

Figure 5. Analysis of the H⁺ adsorption data, for albite pretreated with Ar-purged water, in terms of eq 10.

values difficult. The measured value of Γ^∞ suggests a surface roughness factor of around 3, for the crystal surface used in this work, if a comparison with the results of experiments on powdered material ($\Gamma^\infty \approx 2.5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) (22) is valid. The larger value obtained in this work is not unreasonable given the surface preparation of the crystal described above. A roughness factor of 3, with the measured value of Γ^∞ , implies about one H⁺ per surface "MO₄" tetrahedron on the basis of the geometry of the {010} surface (Figure 2 and refs 41–43). Note, however, that a porous, protonated layer forms on the surface of feldspars during dissolution (45–47). Although the majority of such measurements relate to conditions of prolonged dissolution, where an extensive layer (up to 1000 Å) (45) can be formed, it may be that a thin hydrated layer, only a few angstroms thick, forms under the conditions of the experiments reported here, thereby giving a larger value for Γ^∞ than predicted simply from the geometry of the surface.

When the adsorption data are analyzed in terms of the simple model outlined above, it is assumed that surface charge effects due to adsorption of H⁺ are insignificant. This appears to be reasonable, given the fit of the data to eq 10. Data obtained on powdered material have also been shown to comply to this model (22). The absence of surface charge effects would also be compatible with the formation of a hydrated surface layer and the electrostatic adsorption of oppositely charged ions (e.g., Cl⁻) at protonated sites within it, serving to maintain overall surface electroneutrality. X-ray photoelectron spectroscopy on the surface of albite, hydrothermally altered in chloride solutions, provides evidence for this process (48).

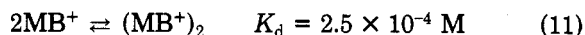
Confirmation of the density of protonation sites, Γ^∞ , was obtained by pretreating the albite surface with 0.1 M NaOH, which should serve to deprotonate $\geq \text{M-OH}$ sites to a surface concentration approaching the saturation value (22). This treatment does not, however, induce the ion exchange of H⁺ for surface Na⁺ (23). Subsequent exposure of the surface to a drop of HCl solution, with 1.0 M NaCl as the supporting electrolyte to suppress the exchange of surface Na⁺ for H⁺ (23), then leads to the protonation of M-O⁻ sites (formed during the surface pretreatment) and, if the pH is sufficiently low, further protonation of the resulting M-OH entities. Data for these experiments are summarized in Table IV, and the corresponding isotherm is shown in Figure 4B. The large

difference (about $6 \times 10^{-9} \text{ mol cm}^{-2}$) in Γ_{ad} between this case and the one described above can be assigned to the density of $\geq \text{M-O}^-$ sites, $N_{\text{M-O}^-}$. The similarity between the values $N_{\text{M-O}^-}$ and Γ^∞ suggests that an equal number of M-OH sites are available for both protonation and deprotonation.

Given the above information, the surface density of Na⁺ ions involved in the exchange process could be determined, by difference, by conducting voltammetric measurements in drops of HCl with KCl as the supporting electrolyte, following pretreatment of the crystal with 0.1 M NaOH. Data for these experiments are given in Table IV and Figure 4C. With KCl as supporting electrolyte, ion exchange is not suppressed, and thus the concentration of H⁺ adsorbed by the crystal is a measure of the density of exchange sites N_{Na^+} and $N_{\text{M-O}^-}$, and the (partial) protonation of the resulting M-OH groups. From the results of these experiments and the data presented above, a value of around $10^{-9} \text{ mol cm}^{-2}$ is indicated for N_{Na^+} . Assuming the surface roughness factor deduced above, this corresponds to between 1 and 2 monolayers of Na⁺ involved in the exchange process.

Application to the Adsorption of MB⁺ on Graphite Surfaces. The main aim of these studies was to compare the adsorption characteristics of MB⁺ on different graphite surfaces, rather than to deduce isotherms, since MB⁺ adsorption, on a variety of substrates, is generally irreversible (49).

Studies of the adsorption of MB⁺ from solution are complicated by the fact that, for the solution concentrations of interest, dimer formation must be considered (50):



Since the kinetics (50) of dimerization and dissociation are extremely rapid (on the time scale of UME voltammetric measurements), it is reasonable to assume that when MB⁺ is reduced at an UME, reaction 11 will be at equilibrium throughout the diffusion layer. For the case where both the forward and reverse chemical processes are first order, it is generally accepted that the diffusion process can be treated in terms of the total concentration of material and an effective diffusion coefficient, D_{eff} , written as the mole fraction sum of the individual diffusion coefficients (51–53). For the dimerization process, eq 11, it is readily established that a similar expression holds:

$$D_{\text{eff}} = D_{\text{M}}X_{\text{M}} + D_{\text{D}}X_{\text{D}} \quad (12)$$

$$X_{\text{M}} = [\text{MB}^+]/([\text{MB}^+] + 2[(\text{MB}^+)_2]) \quad (13)$$

$$X_{\text{D}} = [2(\text{MB}^+)_2]/([\text{MB}^+] + 2[(\text{MB}^+)_2]) \quad (14)$$

D_{M} and D_{D} are diffusion coefficients of the monomer and dimer, respectively. Thus, eq 1 will describe the diffusion-limited current for MB⁺ reduction at an UME, with D_{eff} replacing D and the concentration term relating to the quantity of methylene blue added to solution (i.e., $[\text{MB}^+] + 2[(\text{MB}^+)_2]$).

To test the validity of the above approximation and deduce the diffusion coefficients for the two species, preliminary UME voltammetric measurements were conducted at several methylene blue concentrations (Table V). A plot of the resulting

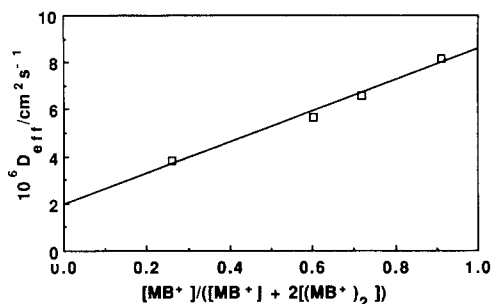


Figure 6. Analysis of the experimentally determined effective diffusion coefficient, D_{eff} , for MB^+ as a function of methylene blue concentration (eq 12).

Table V. Diffusion-Limited Currents (and D_{eff}) for MB^+ Reduction as a Function of Methylene Blue Concentration

[methylene blue] ^a /M	$[\text{MB}^+]^b/\text{M}$	$[(\text{MB}^+)_2]^b/\text{M}$	i/nA	$10^6 D_{\text{eff}}/\text{cm}^2 \text{ s}^{-1}$
1.37×10^{-3}	3.56×10^{-4}	5.07×10^{-4}	5.05	3.82
1.37×10^{-4}	8.25×10^{-5}	2.72×10^{-5}	0.75	5.67
6.78×10^{-5}	4.88×10^{-5}	9.51×10^{-6}	0.430	6.57
1.37×10^{-5}	1.25×10^{-5}	6.21×10^{-7}	0.108	8.17

^a[methylene blue] denotes the concentration added to solution. ^b $[\text{MB}^+]$ and $[(\text{MB}^+)_2]$ were calculated using eq 11.

values of D_{eff} versus X_M is shown in Figure 6, from which it is deduced that $D_M = 8.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (D_{eff} at $X_M = 1$) and $D_D = 1.96 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (D_{eff} at $X_M = 0$). The former value is in reasonable agreement with a previous report of $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (54); the value for D_D is about twice that previously determined (54).

Due to the large molecular area of adsorbed MB^+ (reports range from about 60 to 200 \AA^2 , depending upon the orientation of the adsorbed molecule on the surface and other factors) (27, 49) and thus the consequent low predicted surface concentrations, adsorption experiments were carried out with low concentrations of methylene blue in the solution drops (ca. 1×10^{-5} – 7×10^{-5} M) so that the relative concentration change, as a result of adsorption, could be accurately detected with the proposed method. Results obtained using cleaved basal and polished edge plane (see Experimental Section for polishing procedure) HOPG as the adsorbents are summarized in Table VI. With 1.37×10^{-5} M methylene blue in solution, there is no detectable decrease in the concentration upon exposure of a 3.5- μL drop to basal plane graphite (during a period of around 25 min), as evidenced by the equal magnitude of the currents measured in the drop and in a larger volume of solution (ca. 1 mL). Given the resolution to which the currents could be measured for this case (to within 2 pA), this translates into a maximum surface coverage of around $10^{-11} \text{ mol cm}^{-2}$ (or about 10% of one monolayer, assuming "flat" adsorption of MB^+ monomer (molecular area = 130 \AA^2)) (38). In contrast, voltammetric measurements of $[\text{MB}^+]$ showed a large decrease upon exposure of a drop to edge plane graphite;

the magnitude of the current decrease corresponded to a surface coverage of ca. $2.6 \times 10^{-10} \text{ mol cm}^{-2}$, or the equivalent of two compact monolayers of "flat" molecules (based on the geometric area of the adsorbent).

Although the cleaved basal plane of graphite is atomically flat over large areas (55, 56), with only a small percentage of other features (56), while the polished surface probably has a higher "roughness factor" (57), it is unlikely that the drastic difference in the behavior of basal and edge plane graphite toward MB^+ adsorption can be explained in terms of a difference in the true areas of the two surfaces alone. A more important factor may be the difference in the chemical nature of these two surfaces: the basal plane is hydrophobic (31, 58), with a very low concentration of surface-bound oxygen (O/C = 0.02) (31), while the polished edge plane has a very high concentration of various carbon-oxygen species (31, 58). The latter surface is more likely to adsorb a cation such as MB^+ . These results clearly have important implications for surface area determinations via MB^+ adsorption, in that MB^+ may only "see" certain (hydrophilic) sites on a heterogeneous surface.

As a final example of MB^+ adsorption on graphite, experiments were conducted with a commercial sample of polycrystalline pyrolytic graphite. For all experiments, the sample was polished to 15 μm with diamond paste and then subjected to the various treatments defined in Table VI. Although polishing increases the surface concentration of carbon-oxygen moieties (31), polished samples rinsed with either water or ethanol followed by water showed no tendency to adsorb MB^+ for the duration of experimental runs of 30 min (within the accuracy of the measurement; the upper limits deduced for Γ_{ad} in Table VI were based on the experimental accuracy—ca. ± 5 pA for this case). However, brief exposure of the sample to an oxygen/natural gas flame, following polishing, produced a surface with a strong affinity toward the adsorption of MB^+ . The effect of the latter treatment may be to desorb polishing materials from the graphite surface, which were not removed by simple rinsing, and produce a heavily oxidized, or otherwise modified, surface, thereby promoting MB^+ adsorption. For example, anodic oxidation of HOPG basal plane is known to break up the surface and lead to better performance as an electrode (55, 56).

CONCLUSIONS

This study has demonstrated that the equilibrium adsorption characteristics of electroactive adsorbates on well-defined surfaces can be made through UME voltammetric measurements of the adsorbate concentration in a small drop of solution deposited on the solid of interest. The determination of trace adsorption requires a high ratio of drop area/volume which, in turn, is governed by the drop volume employed and the wettability of the surface by the solvent. With the two-electrode probe approach described in this paper, the minimum practical volume which could be utilized was found to be about 3.5 μL . With this volume, it was possible to measure the adsorption of small surface concen-

Table VI. Adsorption Data for MB^+ on Various Graphite Surfaces

surface	pretreatment	$10^5 [\text{MB}]^a/\text{M}$	i_d/pA	i_s/pA	A/cm^2	$V/\mu\text{L}$	$\Gamma_{\text{ad}}/\text{mol cm}^{-2}$
basal plane HOPG	cleaved	1.37	108	108	0.070	3.5	$<10^{-11}$
edge plane HOPG	polished on Nylon cloth	1.37	110	40	0.115	3.5	2.6×10^{-10}
polycrystalline pyrolytic graphite	polished to 15 μm , rinsed with water	6.78	430	430	0.177	20	$<10^{-10}$
polycrystalline pyrolytic graphite	polished to 15 μm , rinsed with ethanol and then water	6.78	420	430	0.196	20	$<10^{-10}$
polycrystalline pyrolytic graphite	as above, then exposure to oxygen/natural gas flame for several seconds	6.78	320	420	0.212	20	1.2×10^{-9}

^aMB denotes the concentration of methylene blue added to solution, i.e., $[\text{MB}^+] + 2[(\text{MB}^+)_2]$.

trations, as evidenced by the results of the adsorption of MB⁺ on edge plane graphite, where the adsorption of only 2.6×10^{-10} mol cm⁻² of MB⁺ caused a decrease in the UME current by over 50% (at low methylene blue solution concentrations). Smaller drop volumes could undoubtedly be utilized, but this would probably require the fabrication of a single probe to carry both electrodes.

An approach similar to that proposed for adsorption could also be employed to measure quantities of material desorbed from a surface upon application of a solution drop. In this case it should be possible to measure very small surface coverages, since the problem is simply one of measuring absolute concentrations of trace material in solution, rather than a small concentration change. The use of an UME allows the routine determination of solution concentrations down to the micromolar level via steady-state voltammetry (14), and other forms of electrochemical detection would permit detection down to the nanomolar range (16, 17).

The general methodology proposed here is not limited to the study of electroactive adsorbates alone. Alternative types of microsensors, such as ion-selective microelectrodes (59), could also be used to measure analyte drop concentrations, significantly diversifying the range of adsorbates open to study.

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Registry No. MB, 61-73-4; H⁺, 12408-02-5; albite, 12244-10-9; graphite, 7782-42-5.

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