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J. H. Strohl[a]; K. Sexton[a]
[a] DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY, MORGANTOWN, WEST VIRGINIA

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Potential-Controlled Adsorption at Chemically Modified Graphite

J. H. STROHL and K. SEXTON

DEPARTMENT OF CHEMISTRY
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA 26506

Abstract

The use of some chemically modified graphites for separation is described. Chemically bonded sulfonic acid groups can apparently be added by the use of fuming sulfuric acid.

INTRODUCTION

Potential dependent adsorption of compounds at an electrode surface is a fairly commonly observed process and has been studied by a variety of techniques. The use of this process for separation and removal has only recently been studied. Packed bed electrodes which have a large surface area and efficient solution contact have made the study of this process practical.

The reasons for studying this process are:

(1) Any new method may have application to the separation of mixtures that are presently difficult.

(2) It may be capable of rapid batch removal of single components.

(3) It is a rapidly reversible process since only the potential has to be changed, making the process suitable for regenerative removal and separation systems.

Potential controlled adsorption has been applied to the separation of mixtures of dyes (*1*), to the separation of mixtures of quinones, and to the concentration of dilute solutions of quinones (*2*).

EQUIPMENT

The cells necessary for these experiments are relatively simple to construct and maintain. The essential parts are:

(1) A packed electrode bed of small enough particle size that efficient, rapid contact can be achieved. The sample solutions are passed through this bed.

(2) Some sort of a porous barrier which has a relatively high solution conductivity. This barrier serves to prevent gross mixing of the sample solution with counter electrode solution but allows for ionic conduction.

(3) A counter-reference electrode compartment which is necessary for the control of the potential of the packed electrode bed.

The cell should have relatively uniform, low-resistance paths between electrodes to minimize potential inhomogenieties on the packed electrode bed. Relatively low currents are required for potential controlled adsorption experiments and therefore relatively low potential (*IR*) gradients are produced so that cell design is not as critical as for high current applications. Many cell designs have been published that appear to be suitable for this application, although most were not used for potential controlled adsorption experiments. The most recent design (*3*) used a silver packed bed electrode and gives reference to other suitable designs.

Since these experiments are performed at essentially constant potential and the currents are low, any standard potentiostat circuit may be used (even manual). A pump is convenient for the control of flow rate although gravity flow has been used successfully. Some type of detection system is necessary for the observation of amounts; the type would be determined by the nature of the compounds being studied.

ELECTRODE MATERIALS

The electrode materials or adsorbents must be conducting, relatively unreactive in the potential range to be used, and available in a form suitable for a packed bed. Many metals and some forms of carbon are suitable. In addition, modified forms such as conductors with adsorbed or chemically bonded surface layers may have interesting separation properties.

At present a relatively nonporous graphite is the only adsorbent that has been extensively studied (*1*, *2*). It appears to have a high affinity for aromatic compounds and very low affinity for metal ions. The capacity of this adsorbent for most quinones is in the range of 1 to 5 μmoles/g of graphite (105 to 147 μ size). Other, more porous graphites and conducting carbons would probably be useful as adsorbents and might have higher capacities. Platinum and perhaps mercury-coated platinum would be useful. There have been numerous observations of potential controlled adsorption at these surfaces although they have not been used for separations. Other less noble metals may be useful in specific cases, but would probably not be as generally useful.

The modified forms appear to be potentially useful in the area of selective removal by tailoring the surface layer to suit the problem. A recent report by Lane and Hubbard (*4*) serves as an excellent example. They adsorbed 3-allylsalicylic acid on a platinum electrode in a thin-layer cell and observed the accumulation of ferric ion at the adsorbed layer, apparently by chelation. When the potential of the electrode was changed to a more positive value, the accumulation of ferric ion was negligible. From a simple calculation based on surface area and the amount of 3-allylsalicylic acid adsorbed per unit area, a bed of 40 μ platinum particles should have a capacity of about 0.1 to 1 μmole of ferric ion per cubic centimeter of packing material. This would compare favorably with the capacities exhibited by graphite and should have much more selective properties. The adsorption of other olefins with similar selective properties is also described and should have utility for other separations.

Two recent studies in this laboratory on modified graphite surfaces indicate that graphite is also suitable for the production of selective adsorbents for potential controlled adsorption. Adsorption of the sodium salts of 2-naphthalenesulfonic acid and 2,7-naphthalenedisulfonic acid on graphite produces a material with ion-exchange properties. These can be converted to the acid form and then the ion-exchange capacity can be determined by passing a sodium chloride solution through and determining the liberated hydrogen ion by titration. These materials exhibit exchange capacities of about 2 μmoles/cc of graphite, which is in reasonable agreement with the known adsorption capacities for the sulfonic acids.

The second study was the production of a surface which is apparently composed of chemically bonded sulfonic acid groups. Graphite treated with fuming sulfuric acid (30% SO_3) produces a material which has an exchange capacity of 200 μmoles/cc initially and decreases to about 80 μmoles/cc after 20 days as determined by the hydrogen ion liberated by sodium chloride. Preliminary experiments with ferric ion in hydrochloric and in perchloric acid media indicate that it can be adsorbed at some potentials and desorbed at other potentials. For example, in 0.05 *M* perchloric acid the retention volume for ferric ion at +0.48 V (vs SCE) is over twice the retention volume at +0.71 V.

MODES OF USE

Potential-controlled adsorption at graphite has been applied to two types of problems; concentrating dilute samples and the single stage separation of mixtures. It has not been applied to a chromatographic separation although this should be possible for systems with rapid adsorption kinetics.

The concentrating of dilute samples is accomplished by applying a potential at which the compound of interest is adsorbed, passing a large volume of a dilute solution through the packed bed electrode, and then changing the potential so that the accumulated compound is released to a small volume of solution. Concentrating factors of as high as 50 have been achieved. Attempts to concentrate samples further are limited by less than quantitative recovery, apparently due to migration of sample through the bed. If solution conditions are chosen so that the extent of adsorption is higher, then the desorption step may become more difficult. This mode is very similar to the plating-stripping technique for concentrating metals.

The single stage separation of mixtures is based on differences in the potential-adsorption properties for different components of the mixture. For example, consider a two-component mixture. If a potential exists such that one component is adsorbed and the other is not, mixtures of the two can be separated because one component would be held on the packed bed electrode while the other component passed through. More complex mixtures would require a potential such that all but one component is adsorbed, a second potential such that all but two components are adsorbed, etc. However, due to the migration effect, those separations would probably be less than quantitative.

The application of modified electrode surfaces to the above types of problems might lead to improvements in concentrating factors and degree of separation because of much greater specificity. The general method appears to have application to regenerative removal systems for specific materials because of the ease and low cost of the regeneration step. A general example would be the removal of a specific pollutant from mine drainage or an industrial discharge.

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