Electrosorption of *n*-Alcohols on Graphite Particles

The loading of organic molecules adsorbed on high surface area carbon materials can be influenced by the potential of the surface. This phenomenon can form the basis for carbon regeneration and for separation processes. A theoretical treatment demonstrates that adsorption loading becomes more sensitive to potential change when the double layer capacitance of the interface and the size of the organic species are increased. An experimental method was developed to estimate isotherm parameters. The technique was demonstrated on model adsorbates, pentanol and heptanol. The values of the measured isotherm parameters ($B = 3.4-9.1\ V^{-2}$: $E_{max} = 0.36-0.5$ V vs. Hg/Hg_2SO_4) are in the range of expected values based on literature values for similar systems. Although only 5% of activated carbon surface area was shown to be electrochemically accessible, it still has ten times the area available for electrosorption as compared to the graphite, thus making it attractive for industrial application.

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Introduction

The potential dependent adsorption of organic compounds on electrode surfaces has been the subject of many investigations. Several noteworthy reviews are available (Gileadi, 1967; Damaskin and Kazarinov, 1980; Butler, 1929; Delahay, 1965; Damaksin et al., 1971; Horanyi, 1980). The potential dependent adsorption of organic compounds on mercury was initially examined by Gouy (1903, 1906, 1916, 1917) and Frumkin (1926). Gouy qualitatively examined the effect of the addition of an organic substance on the electrocapillary curve of mercury in a solution of sodium sulfate and found that the amount of adsorbed organic substance was greatest when the electric field at the mercury interface was small and diminished as the field increased positively or negatively. Frumkin later quantified the effect. Bockris and Reddy (1970) gave a comprehensive description of organic adsorption at electrified interfaces. Using a water flip-flop model they were able to show that the noncharge transfer adsorption of aliphatic molecules is directly related to the adsorption ability or desorbability of water molecules on the electrified interface. The predominant part of the work of adsorption of these organic molecules consisted of replacing water molecules. The greatest organic adsorption would occur at the potential where the adsorption of water molecules was a minimum, near or at the potential of maximum adsorption. In all this work by Frumkin and Bockris it was assumed that there was no charge transfer in the adsorption of the organic molecules.

It is reasonable to expect that the potential dependency of organic adsorption on high surface materials such as activated carbon could result in large swings in adsorption loading with potential. By exploiting the potential dependent loading characteristic, a separation process somewhat similar to pressure swing parametric pumping becomes possible. Also, potential driven desorption could become a method for regenerating adsorption beds.

The electroadsorption capacity of carbon electrodes, because of their high surface area and porosity, has been recognized by several researchers (Garten and Weiss, 1957; Johnson and Newman, 1971; Eisinger and Alkire, 1980; Alkire and Eisinger, 1983; Oren et al., 1984; McGuire et al., 1985). Not many data for the potential dependent adsorption of uncharged species or organic molecules on moderate to high surface area adsorbent materials such as carbon have been presented in the literature. Eisinger and Alkire (1980) studied the electrosorption of β-naphthol on graphite; their data showed that the adsorption equilibrium constant could be modified by a factor of six by potential variation. Alkire and Eisinger (1983) presented a one-dimensional mathematical model to describe the electrosorption

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of uncharged compounds in a flow through porous electrode. They also presented potential dependent adsorption data of β-naphthol on glassy carbon and were able to show that the adsorption capacity of the loaded glassy carbon could be restored by periodic application of a desorbing potential. McGuire et al. (1985) studied the phenol-water system on activated carbon and demonstrated a potential dependent isotherm. They showed that carbon regeneration can be enhanced modestly by application of cathodic polarization.

The design of a separation or regeneration process requires a detailed dynamic analysis of charge and mass flow (Alkire and Eisinger, 1983). Also, an understanding of the thermodynamic equilibrium and surface area accessibility characteristics of the packed bed must be known. This paper addresses these latter points. An equilibrium model for correlating potential dependent adsorption loading of neutral organic compounds on a bed of carbon particles is developed. An experimental technique is described that allows one to obtain isotherm parameters for this type of system. Calculations and experiments were demonstrated on a homologous series of aliphatic alcohols. This model system was chosen for simplicity and because of the readily available data base of their physical properties.

Theory

Isotherm and capacitance relationships

The change in the differential or double layer capacitance of an electrode as a result of the potential dependent adsorption of an organic species can be expressed as (Parsons, 1963; Delahay, 1965):

$$C - C_b = RT\left[\Gamma \frac{\partial^2 \ln K}{\partial E^2} + \left(\frac{\partial \Gamma}{\partial \ln K}\right)_\mu \left(\frac{\partial \ln K}{\partial E}\right)^2\right] \qquad (1)$$

The above expression is derived using the first and second laws of thermodynamics written for an electrode-electrolyte interface with the adsorption process assumed to be reversible and the electrode assumed to be ideally polarizable; that is, the current supplied to the electrode surface is assumed to go into charging the double layer. In order to explicitly express Eq. 1 in terms of organic surface coverage Γ, the dependence of the surface coverage on the equilibrium constant K and its dependence on potential E must be determined.

The adsorption equilibrium constant can be related to the free energy of adsorption by

$$K = e^{-\Delta G^o/RT} \qquad (2)$$

In the case of adsorption at an electrode-solution interface, there are basically three types of interactions that determine the free energy of adsorption: electrode-adsorbate, electrode-solvent, and adsorbate-solvent interactions. There have been theories in the literature that have been proposed to account for these interactions in the open circuit case. Such theoretical approaches include the Polanyi theory (Maines, 1980) and the net adsorption energy theory (McGuire and Suffet, 1980).

The theoretical approach taken here is based on the solvophobic theory of adsorption. This theory was originally developed to explain differences in reaction rates and equilibria due to solvent effects (Haliocioglu, 1968). This theory was extended to explain adsorption in high-pressure liquid chromatography systems by Horvath and Melander (1976) and Melander and Horvath (1980). The extended theory also was applied to adsorption in activated carbon water purification systems by Altshuler and Belfort (1983), Belfort et al., (1984), and Miller (1980). In the theory, expressions for the electrostatic interaction between nonionic molecules and solvent, and between ionic molecules and solvent have been developed. It can be shown that

$$\Delta G^o = \Delta G^o_c + \Delta\Delta G^o_{es} \qquad (3)$$

where ΔG^o_c represents nonelectrostatic contributions and $\Delta\Delta G^o_{es}$ represents the electrostatic contributions to the free energy of adsorption. In the absence of the application of potential, the electrostatic contribution to the free energy of adsorption is often small (Belfort et al., 1984). However, in the situation where a potential or charge is applied on the surface, the electrostatic contribution can become quite significant. Bockris et al. (1963) developed a theoretical model of an elementary type for the free energy of electrostatic interactions for the competition for adsorption sites between water and organic molecules on the adsorbing surface. In the model, attention was focused on the role of the surface water molecule dipoles. A strong electric field aligns the dipoles of water rigidly on the surface. When the net charge on the surface is zero or approximately zero, water molecule attraction to the surface is minimized. In this situation, the neutral organic molecules obtain their maximum adsorption.

The theory developed can be expressed as

$$\Delta\Delta G^o_{es} = Nn\mu\bar{X} \tanh \frac{\mu\bar{X}}{kT} \qquad (4)$$

where n is the number of water molecules displaced by the organic molecule, μ is the dipole moment of water, and $\bar{X}$ is the electric field through the center of the water dipoles. In this expression, lateral interactions among surface adsorbed water molecules have been neglected. Utilizing Gauss's law ($\bar{X} = 4\pi q_m/\epsilon$), Eq. 4 can be expressed as

$$\frac{\Delta\Delta G^o_{es}}{RT} = \frac{n\mu}{kT\epsilon\epsilon_0} q_m \tanh\left(\frac{\mu q_m}{\epsilon\epsilon_0 kT}\right) \qquad (5)$$

The charge on the electrode surface, q_m, can be related to the potential by utilizing a simple capacitor model (Delahay, 1965) giving

$$q_m = C^i (E - E_{\max}) \qquad (6)$$

where $E_{\max}$ is the potential of maximum adsorption and C^i is the integral capacitance, assumed to be constant, and defined by

$$C^i = \frac{1}{E - E_{\max}} \int_{E_{\max}}^{E} C\, dE$$

It is the differential capacitance, C, that is often described by molecular models. A recent review of the models for the differential capacity has been presented by Damaskin and Kazarinov (1980).

Substituting Eq. 6 into Eq. 5 gives

$$\frac{\Delta\Delta G^o_{es}}{RT} = B^{1/2} n^{1/2} (E - E_{\max}) \tanh\left[\frac{B^{1/2}(E - E_{\max})}{n^{1/2}}\right] \qquad (7)$$

where $B = n(\mu C^i/kT\epsilon\epsilon_0)^2$.

Assuming $B^{1/2}(E - E_{\max})/n^{1/2}$ is small, the hyperbolic tangent can be approximated by a linear relation using a Taylor series to give

$$\frac{\Delta\Delta G^o_{es}}{RT} = B(E - E_{\max})^2 \tag{8}$$

Hence, given Eqs. 2, 3, and 8,

$$K = K_{\max} e^{-B(E - E_{\max})^2} \tag{9}$$

where $K_{\max} = e^{-\Delta G_c/RT}$.

Substituting Eq. 9 into Eq. 1 yields

$$C - C_b = BRT\left[-2\Gamma + 4B(E - E_{\max})^2 \left(\frac{\partial \Gamma}{\partial \ln K}\right)_\mu\right] \tag{10}$$

If operating at the potential of maximum adsorption, $E_{\max}$, Eq. 10 reduces to

$$(C - C_b)_{\max} = -2BRT\Gamma_{\max} \tag{11}$$

where $\Gamma_{\max}$ is the surface coverage at $E = E_{\max}$.

In order to estimate the dependence of Γ on K in Eq. 10, isotherm models must be utilized. Parsons (1963) derived expressions for the Henry's law, Langmuir, and Temkin isotherm models. Another isotherm that can be used is the modified Langmuir isotherm, which takes into account the number of solvent molecules that are displaced by organic molecules when these molecules are adsorbed on the surface. This isotherm was derived by Bockris and Swinkels (1964) and was used by Eisinger and Alkire (1980) to correlate electrosorption data of β-naphthol on graphite. It is written as

$$\left[\frac{\theta}{(1 - \theta)^n}\right]\left\{\frac{[\theta + n(1 - \theta)]^{n-1}}{n^n}\right\} = KC_s \tag{12}$$

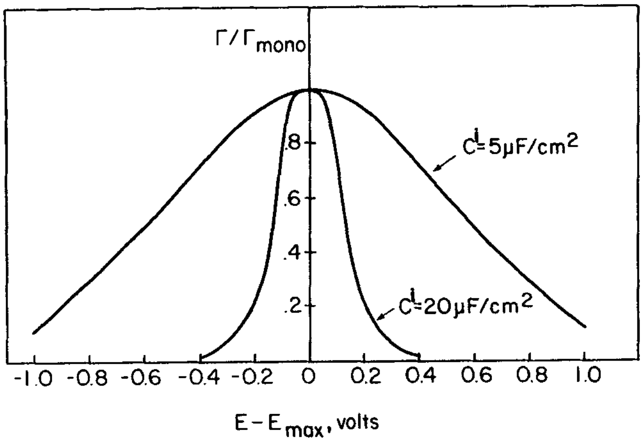

Figure 1. Surface coverage dependency on potential with capacitance as parameter, using properties of ethanol.

$\Delta G^o_c/RT = -3.96$ kJ/mol; $n = 1$; $\epsilon = 6$; $T = 298$ K; $C_s = 10$ ppm
$B = 1.98\ \text{V}^{-2}(C^i = 5\ \mu\text{F/cm}^2)$; $B = 7.9\ \text{V}^{-2}(C^i = 20\ \mu\text{F/cm}^2)$

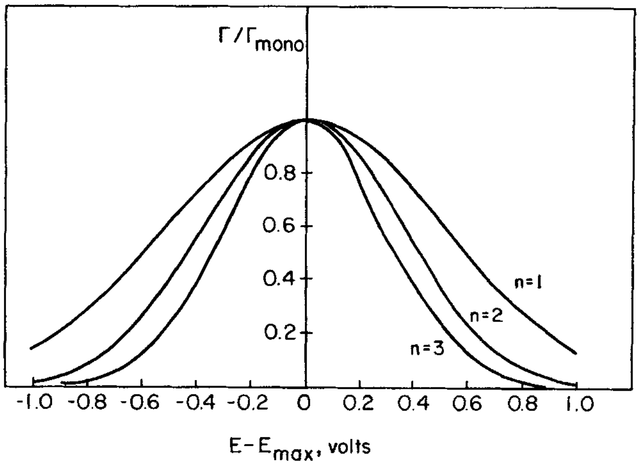

Figure 2. Surface coverage dependency on potential with number of displaced water molecules as parameter, using properties of ethanol.

$\Delta G^o_c/RT = -3.96$ kJ/mol; $C^i = 5\ \mu\text{F/cm}^2$; $\epsilon = 6$; $T = 298$ K; $C_s = 10$ ppm

Substitution of this expression into Eq. 10 yields

$$C - C_b = 2BRT\left(-\Gamma + 2B(E - E_{\max})^2 \cdot \frac{\Gamma_{\text{mono}}(KC_s n^n)^{1/n-1}}{\dfrac{n}{(1 - \theta)^2}\left\{\left[\dfrac{\theta}{1 - \theta}\right]^{1/n-1} + \left[\dfrac{\theta}{(1 - \theta)}\right]^{2-n/n-1}\right\}}\right) \tag{13}$$

where $\theta = \Gamma/\Gamma_{\text{mono}}$, the fractional surface coverage, and Γ_{mono} is the monolayer surface coverage.

Figures 1 and 2 show the potential sensitivity of the surface coverage for the modified Langmuir isotherm with the integral capacitance of the surface and the number of solvent molecules displaced from the surface as parameters. ΔG^o_c shown in these figures was calculated using the solvophobic theory with data in the literature (Belfort et al., 1984) for ethanol. The figures show that the potential sensitivity, $[\partial(\theta)/\partial(E - E_{\max})]$, increases with the number of solvent molecules, n, displaced and the integral capacitance of the surface, but diminishes as the surface coverage, $\Gamma/\Gamma_{\text{mono}}$, approaches zero or unity. Since n increases with organic adsorbate molecular size, these results show that the potential sensitivity of the organic surface coverage will be enhanced by an increase in the molecular weight of the organic adsorbate. If a process is to be designed for the separation of linear aliphatic organic molecules from their aqueous mixtures, from the results obtained above, the following conditions would favor the separation: a high molecular weight organic compound, intermediate values of organic surface coverage on the electrode surface, and a large interfacial double layer capacitance of the adsorbing surface.

Figure 3 shows the differential capacitance change with potential for the larger molecule of 2,3 dimethyl 2-butanol using the modified Langmuir isotherm ($n = 3$) and Langmuir isotherm ($n = 1$) at 10 ppm. The corresponding change in surface coverage is shown in Figure 4. Both Figures 3 and 4 show that as

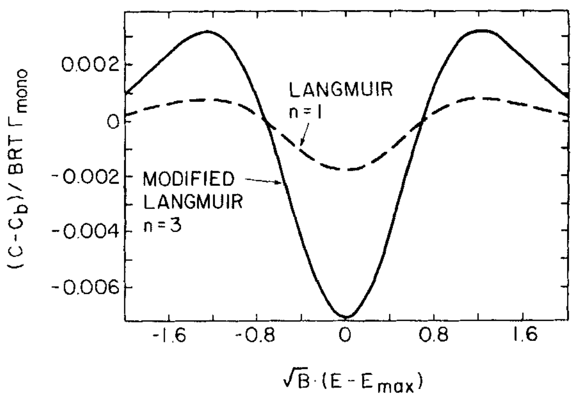

Figure 3. Differential capacitance change with potential for Langmuir and modified Langmuir isotherms for 2,3 dimethyl 2-butanol at 10 ppm.

$\Delta G_c^\circ/RT = -6.22$ kJ/mol; $T = 298$ K; $C_s = 10$ ppm

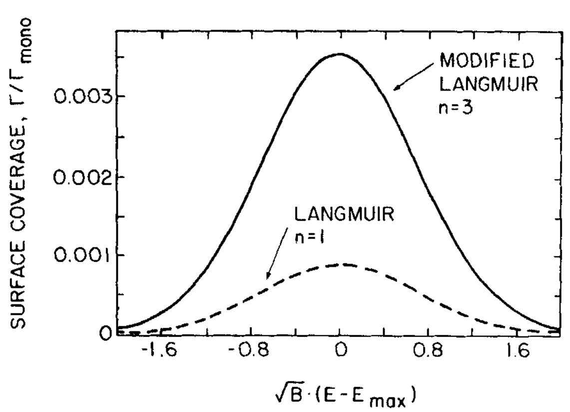

Figure 4. Change in surface coverage with potential for Langmuir and modified Langmuir isotherms for 2,3 dimethyl 2-butanol at 10 ppm.

$\Delta G_c^\circ/RT = -6.22$ kJ/mol; $T = 298$ K; $C_s = 10$ ppm

$E - E_{max} \rightarrow \pm\infty$, the modified Langmuir isotherm approaches the Langmuir isotherm.

Approximation of the Henry's law isotherm model

There is no simple and direct way of utilizing differential capacitance equations such as Eq. 13 to fit experimental data because of the complexity of the equations involved (Parsons, 1963). In order to identify the isotherm corresponding to the differential capacitance data, Parsons showed that only values of the differential capacity obtained at $E = E_{max}$ were of real use if an accurate determination of such an isotherm was required. In the case of activated carbon and multicrystalline graphite, the E_{max} will strongly depend on the form and history of the material, and values are not readily available in the literature.

It is possible to correlate experimental data to theory by utilizing the approximation represented by the Henry's law isotherm. For adsorption on highly porous activated carbon, the isotherm has been frequently used to model adsorption data at very low concentrations of organic adsorbate (Mattson and Mark, 1971; Belfort et al., 1983). The differential capacitance equation for this isotherm can be obtained by substituting the Henry's law equation ($\Gamma = \Gamma_{mono}KC_s$) into Eq. 10 and obtaining:

$$C - C_b = 2BRT\Gamma_{max}e^{-B(E-E_{max})^2}[-1 + 2B(E - E_{max})^2] \quad (14)$$

where $\Gamma_{max} = \Gamma_{mono}K_{max}C_s$.

By retaining only the first term of the Taylor series expansion of $\ln(1 - 2B(E - E_{max})^2)$, Eq. 14 becomes

$$\ln(-(C - C_b)) = -3BE^2 + 6BE_{max}E + \text{const.}(B, E_{max}, \Gamma_{max}, R, T) \quad (15)$$

Limitations of the approximation

Utilization of the Henry's law isotherm limits the concentration range of the organic adsorbate to low concentrations. The isotherm has been shown to fit data in which the amount of adsorption and concentration of the organic adsorbate are low.

The assumption, $B(E - E_{max})^2 \ll 1$, is implied when retaining only the first term of the Taylor series expansion in obtaining Eq. 15. A similar, but less restrictive assumption was incorporated in arriving at Eq. 8. This assumption limits the usefulness of Eq. 15 to a potential range that depends on the values of B and E_{max}. Otherwise, a nonlinear regression of Eq. 14 must be employed.

Theoretical basis for experimental determination of isotherm parameters

For porous electrodes such as a packed bed of activated carbon or graphite particles, all the BET surface area might not be accessible to potential dependent adsorption because of the high degree of microporosity that usually exists within the porous electrode matrix. Tiedemann and Newman (1975) developed a transient method that could be used to estimate the double layer (differential) capacity and also the electrochemically active surface area of a porous electrode. This method was used here to experimentally measure the parameters for the equilibrium model. In the method, the product of the specific surface area and the double layer capacity, aC, is determined from the current response to a potential step perturbation applied at the surface of the porous electrode. The current transient response to the potential step can be expressed as:

$$\frac{i(t)\sqrt{\pi T'}L}{\Delta V k_e} = 2\sqrt{\pi T'}\sum_{n=1}^{\infty}\frac{\exp(-\alpha_n^2 T')}{1 + \rho + \alpha_n^2\rho^2} \quad (16)$$

Tiedemann and Newman outlined a step by step procedure for evaluating the double layer capacitance, aC, from the transient current response given by Eq. 16. This quantity represents the electrochemically accessible surface area of the carbon bed with a representing the electrochemically active surface per volume of carbon bed.

If this accessible surface area a is incorporated into Eq. 15, the equation becomes:

$$\ln[-a(C - C_b)] = -3BE^2 + 6BE_{max}E + \text{const.}(B, E_{max}, \Gamma_{max}, a, R, T) \quad (17)$$

By experimentally obtaining values of aC and aC_b at different potentials, values of B and E_{max} can be estimated using Eq. 17 with regression. From Eq. 11, values of the surface coverage per unit volume, $a\Gamma_{max}$, can be estimated after obtaining B and E_{max}.

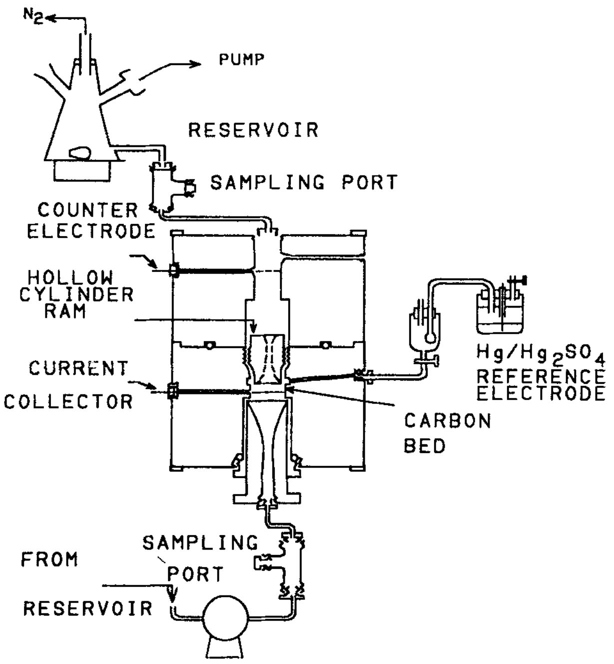

Figure 5. Experimental cell.

Experimental Details

A diagram of the experimental cell used in evaluating the double layer capacity, aC, is shown in Figure 5. The cell has an internal cell diameter of 1 cm and is constructed of clear plastic. The cell consists of two parts, with the upper part holding the counterelectrode and the bottom part holding the current collector, the carbon bed, and the reference electrode. The current collector and counterelectrode are made of platinum mesh screen spot-welded to a platinum wire lead. The carbon bed and the platinum mesh screen current collector are sandwiched between a pair of fritted glass discs that are protected by several glass microfiber filters. The carbon bed thickness can be varied (0.2 to 0.5 cm) by adjusting the length of a hollow cylinder ram that sits on top of the bed. An opening in the ram and a circular ring within the cell wall ensures that there is contact between solutions in the reference electrode chamber and the working electrode compartment. The composition of the solution used in this work was 0.002 M H_3PO_4/0.01 M $NaH_2PO_4 \cdot 2H_2O$ at pH 2.7, and 0.01 M $NaH_2PO_4 \cdot 2H_2O$/0.02 M K_2HPO_4 at pH 6.5, with 1.0 M Na_2SO_4 as the supporting electrolyte. All solutions were made with deionized distilled water. The reference electrode used was Hg/Hg_2SO_4 in 1 M H_2SO_4 (+0.4 vs. Standard Calomel Electrode).

The carbon materials used in the experiments were Witcarb activated carbon Grade 950 (Witco Chemical, NY, NY) and polycrystalline graphite KS-15 (Lonza Inc., Fairlawn, NJ). The surface areas of the activated carbon and graphite particles measured by BET were respectively 1,010 and 15 m²/g. The bulk densities were 0.36 and 0.12 g/cm³, respectively, for activated carbon and graphite. The specific surface areas of the carbon electrodes calculated based on these densities were 3.64×10^6 cm^{-1} for activated carbon and 1.82×10^4 cm^{-1} for graphite. The ash and moisture contents of the activated carbon and graphite were 1% and less than 0.15%, respectively. The size of the activated carbon particles was $-50 + 100$ mesh, while the particle size of the graphite was less than 32 μm. Prior to being used in the experiments the carbon electrodes were washed and rinsed in deionized, distilled water, dried at 110°C in a vacuum oven overnight, and then stored in a desiccator. The amount of carbon used in each experiment was between 0.1 and 0.25 g.

The cell used in the experiments was connected to a flow loop with a solution capacity of 100 mL which consisted of a reservoir, a peristaltic pump, and a pair of sampling ports for monitoring the concentration of the organic adsorbate. The latter was measured using an FID gas chromatograph. The electrolytic solution was deoxygenated in the reservoir prior to recirculation and was stirred constantly by a magnetic stir bar during recirculation. Prior to applying the potential step perturbation, the carbon bed was polarized at a set potential until the current decayed to a low value (values in the range of 10 μA for graphite and 100 μA for activated carbon). The potential step perturbation was then applied and the current response was recorded. The residual current was not more than 10% of the peak current. Faradaic reactions of an organic adsorbate in a potential electrosorption process become significant if operating in the potential regions where oxidation or reduction of the organic adsorbate can occur. In the case of low porosity graphite surfaces, the oxidation of the alcohols has been reported to take place at potentials ~1.3 V (vs. Hg/Hg_2SO_4) while the reduction has been reported to take place at potentials ~ −1.2 V (vs. Hg/Hg_2SO_4) (Blurton, 1973).

Further details of the experiments and data analysis are reported elsewhere (Zabasajja, 1987).

Results

Figures 6 and 7 respectively show the typical current response to potential step perturbations obtained with Witcarb activated carbon Grade 950 and polycrystalline graphite KS-15 acting as the working electrodes in the absence of any alcohol in solution. In the figures, it is shown that the rate of charge and discharge of the activated carbon was slower than that of graphite. This result is due to the high degree of microporosity of the activated carbon. Pore size distribution data of the activated carbon and graphite electrodes using a mercury intrusion method, showed that most of the surface area of the activated carbon was concentrated in pores in the micropore range (5–20 Å). In the case of graphite, however, more than 60% of the surface area was found to be in pores greater than 60 Å. The graphite was found

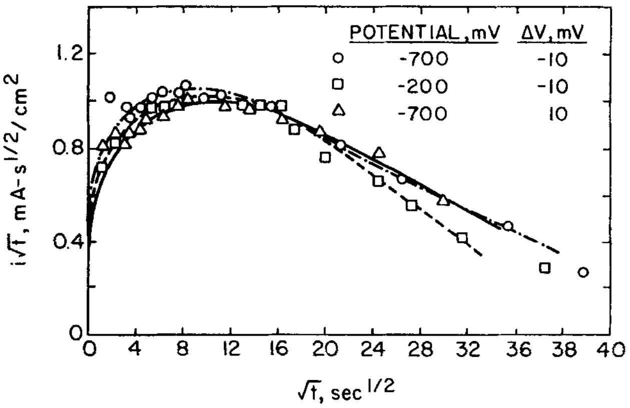

Figure 6. Typical current response obtained for activated carbon.

$L = 0.5$ cm; $\Delta V = 10$ mV; area = 1 cm²; $aC_b = 7.6 - 8.5$ F/cm³; $T = 23$°C; pH = 2.7

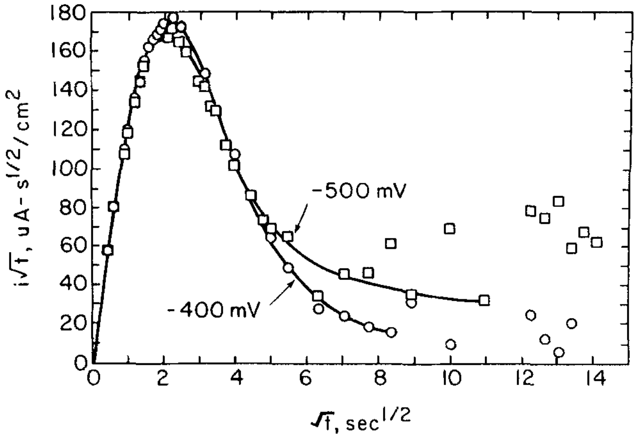

Figure 7. Typical current response obtained for graphite.

$L = 0.5$ cm; $\Delta V = 3$ mV; area = 1 cm^2; $aC_b = 0.17 - 0.25$ F/cm^3; $T = 23$°C; pH = 2.7

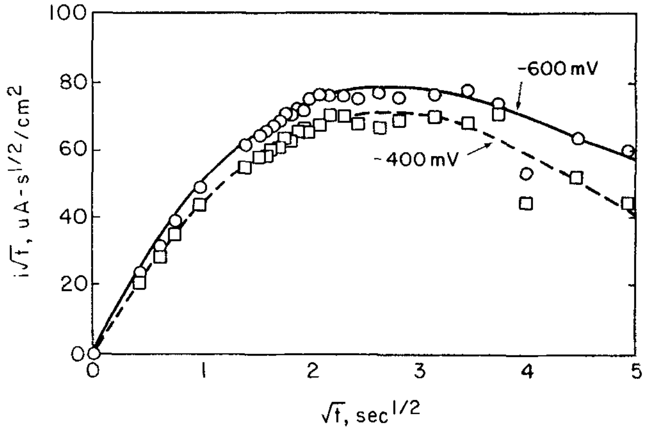

Figure 8. Current response obtained for graphite with bulk solution concentration of 16.3 ppm heptanol.

$L = 0.22$ cm; $\Delta V = 3$ mV; area = 1 cm^2; pH = 6.5

to be relatively free of any microporosity. From the electrochemical measurement, values of aC between 6 and 12 F/cm^3 were obtained for activated carbon. The double layer capacitance for carbon surfaces such as activated carbon with surface functional groups, has been reported to be at least 50 μF/cm^2 by Randin (1981). Using this differential capacitance value to calculate the electrochemically accessible surface area, a, gives values from 0.120×10^6 to 0.24×10^6 cm^{-1} for activated carbon. These values are low compared to the BET data (3.64×10^6 cm^{-1}) and indicate that only a small fraction of the surface area is electrochemically accessible. In the case of graphite, however, values of aC between 0.17 and 0.25 F/cm^3 were experimentally obtained. Double layer capacitance values between 10 and 12 μF/cm^2 have been reported for carbon and graphite electrodes having BET surface areas between 1.12 and 91 m^2/g (Oren et al., 1984). Using a value of 12 μF/cm^2 for the capacitance of the graphite, values of $a = 1.42 \times 10^4$ to 2.08×10^4 cm^{-1} are obtained. These values are similar to the BET specific surface area of the graphite ($a = 1.82 \times 10^4$ cm^{-1}) and indicate that most of the surface area of the graphite is electrochemically accessible.

Even though the percent of total area accessible for adsorption on activated carbon is lower than on graphite, overall more adsorption area and larger capacitance are still available for the activated carbon. Consequently, activated carbon shows promise for industrial applications of electrosorption. Further experiments were performed only with graphite to avoid any complicating issues of interpretation that might arise because of micropores. The potential range for these studies was selected to include the potential of zero charge for graphite, E_{pzc}, which has been shown by Randin (1981) to vary from −400 to −600 mV (vs. Hg/Hg$_2$SO$_4$). Assuming initially that $E_{max} = -400$ mV, the potential range between −100 and −700 mV was selected for the adsorption experiments.

Figure 8 shows a typical current response obtained for graphite at potentials of −400 and −600 mV in the presence of heptanol at a bulk solution concentration of 16.3 ppm and pH 6.5. Table 1 reports the values of $a(C - C_b)$ obtained for various applied potentials. The error involved in determining the values of $a(C - C_b)$ was ±20%. The largest contribution to this error came from estimating the bed thickness, L, which was one of the experimental parameters used in calculating aC. The other major source of error is estimating the maximum in the current response plot, which is needed to find the double layer capacity using the Tiedemann and Newman (1975) method. Table 2 reports estimates of B and the potential of maximum adsorption, E_{max}, obtained from regressing the capacitance data for heptanol according to Eq. 17. The ± variations shown in the table represent the standard deviation of the parameters obtained from the regression of the capacitance data.

The standard deviations due to regression to estimate the parameter values B and E_{max} are reported in Table 2. In many cases the values are substantial and therefore the interpretation of B and E_{max} must be approached carefully. In principle, the standard deviation could be reduced by reducing the error in the measurement of $a(C - C_b)$, obtaining more data as a function of potential, and ensuring that the data are in the range of validity of Eq. 17.

For accurate use of Eq. 17 it must be confirmed that the values of $B(E - E_{max})^2 \ll 1$. In these experiments the magnitude of $B(E - E_{max})^2$ is not small at the limits of the applied potential range as required by Eq. 15; nevertheless, reasonable values of B and E_{max} are extracted from the data. The experimental data obtained in this work also were used in the direct nonlinear regression of Eq. 14. The resulting estimates are reported in Table 2. The values of B from the nonlinear regression are of the same order of magnitude as given by the regression of Eq. 17.

Table 1. Values of Double Layer Capacity Obtained at 16.3 ppm Heptanol, pH 6.5, 23°C

Potential mV	$a(C - C_b)$ F/cm^3
−200	−0.025
−300	−0.027
−400	−0.168
−500	−0.159
−550	−0.073
−600	−0.081
−650	−0.121

Table 2. Parameters for Electrosorption of Hepatanol on Graphite, pH 2.7 and 6.5, 23°C

	Regress. of Eq. 17		Regress. of Eq. 14	
Conc. ppm	B V^{-2}	E_{max} V	B V^{-2}	E_{max} V
		pH = 2.7		
4.6	6.6 ± 2.2	−0.50 ± 0.15	4.3 ± 1.5	−0.50 ± 0.04
7.8	7.2 ± 1.9	−0.40 ± 0.11	4.1 ± 1.1	−0.42 ± 0.03
12.0	5.1 ± 0.83	−0.42 ± 0.07	3.4 ± 0.4	−0.42 ± 0.01
21.0	6.1 ± 2.0	−0.36 ± 0.13	3.6 ± 0.7	−0.38 ± 0.02
		pH = 6.5		
4.1	7.2 ± 1.1	−0.47 ± 0.1	4.9 ± 1.5	−0.41 ± 0.04
9.8	8.3 ± 2.7	−0.45 ± 0.13	6.9 ± 2.0	−0.46 ± 0.02
16.3	8.3 ± 5.3	−0.47 ± 0.2	9.1 ± 3.6	−0.47 ± 0.03

Table 4. Values of $a\Gamma_{max}$ and Γ_{max} for Heptanol and Pentanol Adsorption on Graphite, pH 2.7, 23°C

Conc. ppm	$a\Gamma_{max}$ molecules/cm^3 × 10^{-18}	Γ_{max} cm^{-1} × 10^{-14}
Heptanol		
4.6	1.41	0.775
7.8	1.08	0.590
12.0	2.31	1.27
21.0	2.45	1.35
Pentanol		
5.5	0.44	0.240
9.3	0.50	0.280
20.3	0.62	0.340

BET specific surface area of graphite, $a = 1.82 \times 10^4 cm^{-1}$ Γ_{mono} (heptanol) = 2.2×10^{14} molecules/cm^2 calc. Γ_{mono} (pentanol) = 2.6×10^{14} molecules/cm^2 calc.

However, in most cases the values of the nonlinear regression are somewhat smaller. The values for E_{max} are nearly equivalent for both methods of data regression.

The values of B in Table 2 are of the same order of magnitude as reported for amyl alcohol adsorption on mercury surfaces (Parsons, 1963). Since $B = n(\mu C^i/kT\epsilon\epsilon_0)^2$, values of the dielectric constant, ϵ, were estimated. In the estimations, $n = 4$, the dipole moment for water, $\mu = 6.14 \times 10^{-28}$ C/cm, and the integral capacitance, $C^i = 12\ \mu F/cm^2$, are assumed. Values of the dielectric constant calculated with the results of the nonlinear regression are shown in Table 3 and vary between 13 and 22. These values appear to be reasonable since the range of values of ϵ in aqueous solvent varies between 6 and 78 across the double layer (Bockris et al., 1963). Since the adsorption phenomenon is occurring close to the surface, the measured dielectric constant is expected to be nearer the lower value.

The values of E_{max} reported in Table 2 are within the range of values given for the potential of zero charge for graphite. The values measured at pH 2.7 appear to vary more with concentration than those values measured at pH 6.5. This was probably due to increased nonspecific adsorption of protons at pH 2.7, which could interfere with the adsorption of the organic molecules. Protons and other cations have been shown to affect the location of the potential of maximum adsorption, E_{max}, on surfaces such as mercury (Delahay, 1965).

Table 4 shows values of $a\Gamma_{max}$ and Γ_{max} obtained experimentally for heptanol ($n = 4$) and pentanol ($n = 3$) at pH 2.7. In principle, these values can be estimated from Eq. 11. However, the values reported here were obtained directly by nonlinear regression of Eq. 14. The value of a was assumed to be a constant and was estimated from BET data. In Table 4, experimental values of Γ_{max} can be compared to estimated monolayer coverages based on molar volumes of the organic molecules (234.6 and 179.65 Å^3 per molecule for heptanol and pentanol, respectively (Belfort et al., 1984). These values were calculated to be 2.2×10^{14} molecule/cm^2 for heptanol and 2.6×10^{14} molecule/cm^2 for pentanol.

The experimental values of Γ_{max} for pentanol are less than heptanol and both are less than calculated monolayer coverages. This suggests that heptanol is more strongly adsorbing than pentanol. This result is also consistent with adsorption data of aliphatic organic compounds on mercury surfaces, which show that the adsorption of organic compounds is generally dependent on the size of organic species, increasing with increasing length of the hydrocarbon chain of the organic molecule (Schiffrin, 1970). The fact that Γ_{max} is not substantially smaller than Γ_{mono} in these experiments, especially for heptanol, implies that a Langmuir isotherm may be more appropriate for these systems.

To demonstrate the reversibility of the capacitance data, double layer capacitance measurements were performed at potentials of −470 and −240 mV for heptanol. Table 5 reports the values of aC experimentally obtained at these potentials. It appears that the values of the double layer capacity measured are indeed reversible between the two potentials.

Conclusions

The change in the capacitance of the surface has been used to characterize the potential dependent adsorption of linear aliphatic alcohols on graphite and activated carbon. Parametric studies with the modified Langmuir isotherm showed that when the capacitance of the surface is increased, the potential sensitivity of the surface coverage also increases. It was further

Table 3. Values of Dielectric Constant ϵ Calculated from Experimental Values of B in Table 2

pH = 2.7		pH = 6.5	
Conc. ppm	ϵ ↓	Conc. ppm	ϵ ↓
4.6	19.5	4.1	18.3
7.8	20.0	9.8	15.4
12.0	22.0	16.3	13.4
21.0	21.3	—	—

$n = 4$; $C^i = 12\ \mu F/cm^2$; $\mu = 6.14 \times 10^{-28}$C/cm

Table 5. Reversibility of Values of aC for Electrosorption of Heptanol on Graphite, pH 6.5, 23°C

Initial Conc. = 8 ppm	
Potential mV	aC F/cm^3
−240	0.106
−470	0.190
−240	0.095
−470	0.201
−240	0.102

shown that this potential sensitivity increases as the molecular weight and molecular volume of the organic adsorbate increases but decreases as the surface coverage of the organic approaches unity or zero. Transient capacitance measurements were performed to demonstrate the change in the capacitance due to organic adsorption. The test systems were pentanol or heptanol adsorbed on a carbon or graphite surface.

Potential dependent isotherm parameters B, E_{max}, and $a\Gamma_{max}$ were obtained from these measurements. The values of the parameters that were obtained were consistent with literature values. Estimates of the dielectric constant calculated from the parameter B agreed with expected values of the solvent water near a surface. The electrochemically active surface area of the graphite and activated carbon were also estimated from the capacitance measurements. It was shown that for graphite, all of its surface area was electrochemically accessible while for activated carbon only a small fraction of its surface area was electrochemically accessible. Overall, activated carbon still provides more surface area available for electrosorption. Furthermore, it was shown that heptanol surface coverage is greater than that of pentanol, as expected, since adsorption is dependent on the size of the organic species, increasing with organic adsorbate molecular size.

These measurements clearly demonstrate that it is possible to control the amount of organic material that is adsorbed or desorbed from an electroadsorptive material such as carbon by application of a surface potential. The theory and experimental technique is readily extendable to other nonreacting adsorbing systems. Further work needs to be done, however, to more accurately and rigorously determine potential dependent isotherms for the adsorption of organic solutes on porous carbon. An accurate determination of these isotherms will aid in further understanding the electrosorption of neutral organic molecules on porous carbon and could lead to the development of processes for separating these organic materials from their aqueous mixtures using electrosorption.

Acknowledgment

Support provided by the National Science Foundation through NSF Grant No. CBT-8696069 and NSF (PYI) Award No. CPE-8696073 for this work is gratefully acknowledged. The comments and discussions of William Brian Arbuckle were of considerable help to us.

Notation

a = specific interfacial area, cm^2/cm^3
B = constant for electrostatic interaction defined as $n(\mu/kT\epsilon\epsilon_o)^2$
C = differential or double layer capacitance, F/cm^2
C_b = differential capacitance in the absence of the organic, F/cm^2
C^i = integral capacitance, F/cm^2
C_s = bulk solution concentration, ppm
E = electrode potential, V
E_{max} = potential of maximum adsorption, V
ΔG^o = free energy of adsorption, J/mol
ΔG^o_c = free energy of adsorption due to chemical effect without electrostatic contribution, J/mol
$\Delta\Delta G^o_{es}$ = free energy of adsorption due to electrostatic effects, J/mol
i = current, A
k_e = effective conductivity of solution in porous matrix, $\Omega^{-1} \cdot cm^{-1}$
k = Boltzmann's constant, 1.38×10^{-23} J/K
K = equilibrium isotherm constant
L = one-half the bed or pore length, cm
n = number of water molecules displaced by organic on surface
N = Avogadro's number, 6.023×10^{23} molecules/cm^2
q_m = charge on electrode, C/cm^2
R = universal gas constant
R_e = effective resistance of solution in porous electrode
R_{ref} = resistance of solution between reference electrode and porous electrode
t = time, s
T = temperature, K
T' = dimensionless time, $k_e t/aCL^2$
$\underline{V}$ = potential, V
$\overline{X}$ = electric field, $J/C \cdot cm$

Greek letters

α_n = positive roots of $\alpha \tan \alpha = 1/\rho$
ϵ = solvent dielectric constant
ϵ_o = permittivity constant, $8.854 \times 10^{-12}\ C^2/N \cdot m^2$
Γ = surface coverage, molecules/cm^2
Γ_{max} = surface coverage at E_{max}, molecules/cm^2
Γ_{mono} = monolayer surface coverage, molecules/cm^2
ρ = resistance ratio of porous electrode, R_{ref}/R_e
θ = fractional surface coverage, Γ/Γ_{mono}
μ = dipole moment, C/cm

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Manuscript received Aug. 31, 1988, and revision received Dec. 29, 1988.