Changes in Surface Potential of Activated Carbon Due to Adsorption of Ions

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ABSTRAK

Pembinaan satu elektrod karbon dan sukatan ke atas pertukaran keupayaan di permukaan yang diakibatkan daripada penjerapan ion dibincangkan sebagai fungsi kepada penjerapan dan pengionan kumpulan-kumpulan berfungsi di permukaan karbon.

ABSTRACT

The construction of a carbon electrode and the measurement of the changes in the potential that developed on its surface as a result of adsorption of ions are discussed as a function of the cation adsorption and ionization of the functional groups on the surface of carbon.

INTRODUCTION

It has been proposed that activated carbon possesses many kinds of organic functional groups lined up along the wall of the pores (Hassler 1974). These functional groups react with water to produce hydrogen ions which can act as additional charge carriers in carbon under an applied voltage (Badri *et al.* 1984). As a result of the reaction, the walls of the pores would be lined with the negatively charged conjugates of the acids. Since these conjugates are immobile, the hydrogen ions would remain in their vicinity in the pores thereby establishing a charged double layer.

Activated carbon is also known for its ability to adsorb cations. When cation adsorption takes place, these adsorbed species will be fixed at the active centres on the walls of the pores leaving the anions lined up alongside them in the solution. Thus another charged double layer of opposite polarity to the one described above will be formed.

It was found possible to vary the degrees of ionization and adsorption by changing the concentration of the H^+ on the solution side of the pores (Badri and Crouse 1987). These changes were reflected in the changes in the potential developed across the double layer. In this paper the effect of the adsorption of some other cations will be described.

MATERIALS AND METHODS

All reagents were of analytical grade unless otherwise specified.

Large pieces of activated carbon were prepared by a method described earlier (British Patent 1984). Samples thus prepared have very low electrical conductivity, of the order of 1 x 10^{-6} (ohm - cm)$^{-1}$ (Badri *et al.* 1987). Fairly flat pieces were chosen and were ground with fine sand paper into discs of about 6 mm diameter and 1.5 mm thickness. These discs were refluxed in 1 M HCl for about one week then continously washed with distilled water in a Soxhlet apparatus for another week. After drying in an oven at 110°C for 12 hours, two discs were glued together with silver-loaded epoxy resin and then sealed in glass tubing of appropriate diameter with Araldite epoxy resin. After drying at room temperature, the glass tube was filled

with ~0.5 ml 1M HCl. An Ag/AgCl electrode (prepared according to Shoemaker and Garland) was inserted into the tube. This assembly is henceforth referred to as the carbon electrode. For the present experiments, three such electrodes were used.

Solutions of a number of chlorides of various concentrations were prepared. These were kept in small, covered polyethylene bottles and were equilibrated at $25 \pm 0.2°C$. The potential of the double layer which developed when the carbon electrode was dipped into the prepared solution was measured against a Coleman calomel electrode using a dc microvoltmeter. The voltmeter reading was recorded when a constant value was registered. After each measurement, both electrodes were rinsed with distilled water and gently dried with soft tissue paper before proceeding to a solution of different concentration. In addition, the carbon electrodes were also soaked in distilled water for 16 hours before being used again for measurements with a test solution containing a different cation.

RESULTS

The potentials of the double layer measured are given in Table 1 and are plotted as a function of -log concentration, pC, in *Figs 1 to 4*.

Fig. 1 shows this relationship for the values obtained from Electrode 1 in HCl and NaCl solutions. Reproducibility was good with an average uncertainity of $\pm$ 4mV.

The rate of change of the potential in the whole range of pC from 0 to 7 was found to be not linear. To simplify discussion, each of the curves given in *Fig. 1* is separated into two regions. Region 1 refers to that for pC range from 0 to 3 (or 4) where the rate of change was high and almost linear except for a slight shoulder at pC ~1. Region 2 refers to that for higher pC range where the rate of change was lower and in which maxima and minima were interspersed.

Similar potential-concentration relationships were also found for other salts, *Figs. 2 to 4*. The first set of values, *Fig. 2(A)*, was obtained from Electrode 2 with solutions of HCl, NaCl, KCl and LiCl when measurements were done in that order. The potentials obtained for KCl and LiCl solutions in repeat measurements

after the first set was completed are shown in *Fig. 2(B)* to illustrate the possible error that might be introduced in a potential measurement if inadequate desorption of adsorbed species had not taken place. Curve 1 was obtained immediately after the first set while Curves 2 were obtained after soaking Electrode 2 in distilled water for approximately 12 hours. Electrode 2 was soaked in HCl (6M) for 3 days and then in distilled water for three days in an attempt to restore it. The results which are shown in *Fig. 3* seem to indicate some improvement. However, the original characteristics of Electrode 2 were not fully restored. The linearity of the rate in the pC range of 0 to 1 was lost and the potential measured for 1M solution was found to have increased from the original value of ~15mV to ~40mV. Data obtained for the chloride of $Ca^{2+}(aq)$ are also included in *Fig. 3* for comparison.

The potentials obtained from Electrode 3 for the solutions of doubly- and triply -charged cations are given in *Fig. 4*. The values obtained for KCl solutions are included for the purpose of comparison. The magnitude of charge present on the cations does not appear to affect the potential characteristics of the double layer.

DISCUSSION

Activated carbon is known to have a variety of active centres which are either basic or acidic. The acidic groups such as carboxylic and phenolic may dissociate in water to give H^+ depending on the pH of the solution. The basic groups can be carbonyl, ether, quinone, benzpyrene and so on. Both groups are responsible for the adsorptive character of activated carbon.

In these experiments, the opposite surfaces of the carbon discs were in contact with solutions of different concentrations. Since the concentration of the HCl solution that was in contact with the internal surface of the disc was kept constant, the potential gradient developed across the charged double layers due to ionization of the functional groups and adsorption of H+ would remain constant as well. Thus changes in the potential observed as the external surface of the disc was dipped into the test solutions must be due to the changes in the potential gradient across the charged double layer of the external surface alone.

TABLE 1
Double layer potential* of activated carbon

Electrode	Solution	$-\log$ Concentration, pC							
		0	1	2	3	4	5	6	7
1	HCl	20	57	87	113	103	110	129	110
	HCl	20	57	83	109	107	111	120	128
	NaCl	49	69	84	101	120	122	132	110
	NaCl	43	62	79	97	119	120	135	100
2	HCl	− 18	40	76	102	94	102	117	100
(1st set)	NaCl	− 17	19	55	88	120	113	118	103
	KCl	− 9	27	67	101	110	123	120	110
	LiCl	− 15	20	61	93	120	131	138	89
	KCl (Curve 1)	61	69	87	100	96	100	86	94
	KCl (Curve 2)	51	67	90	113	122	128	130	119
	LiCl	67	70	90	106	122	123	129	118
(2nd set)	NaCl	40	65	90	108	122	122	118	111
	NH_4Cl	58	65	86	103	119	117	127	123
	KCl	51	67	90	113	122	128	130	119
	$CaCl_2$	44	65	90	108	121	118	139	120
	LiCl	67	70	90	106	122	123	129	115
3	KCl	− 27	23	56	73	69	74	76	75
	$AlCl_3$	− 42	− 1	39	72	82	74	75	70
	MgC_2	− 42	0	39	68	72	75	76	64
	$CaCl_2$	− 42	− 2	35	63	78	75	76	67

* All potentials are expressed in mV.

With respect to this, one might suggest that the changes in the potential were due to the ohmic drop across the electrode as the solution filled the pores. We have discounted this theory because according to our previous work (Badri *et al.* 1985) the conductivity of activated carbon soaked in HCl followed the Onsager equation in the pH range of 1.6 to 6.7 whereas the present results do not.

As the surface of the disc comes into contact with a solution, adsorption occurs at the basic active centres, since these electron-rich groups would share the electron clouds with the adsorbed species. As a result of this, a shift of the electron cloud from the graphite rings of the carbon crystallite to the surface would occur. Taking the carbonyl as an example, the reaction could be written as:

(solid) (surface) (solution)   (solid) (surface)   (solution)

$$\rangle C = O + M^+ X^- \rightarrow \rangle C = {}^+OM + X^-$$
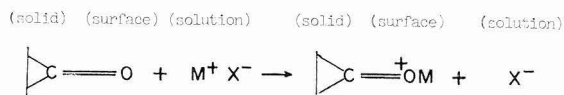
Since the adsorbed ions were immobilized, their negatively charged conjugates, X', would be lined up along the surface but on the solution side of the pores. An array of these opposing charges would give rise to an electrical double layer on each of the opposite surfaces of the disc. We denote the respectve potentials as α_i for the internal surface and α_e for the external surface.

The acidic functional groups on the surface could also undergo ionization when the pores are flooded with the solutions. Taking the phenolic group as an example, the ionization reaction of these acidic groups could be written as

(solid) (surface) (solution)   (solid) (surface) (solution)

$$\rangle C - OH + aq \rightarrow \rangle C - O^- + H^+(aq)$$
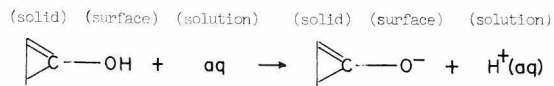
It is assumed that most of these acidic groups were weakly ionized and their population was relatively small compared to the total number of adsorption sites. However, when
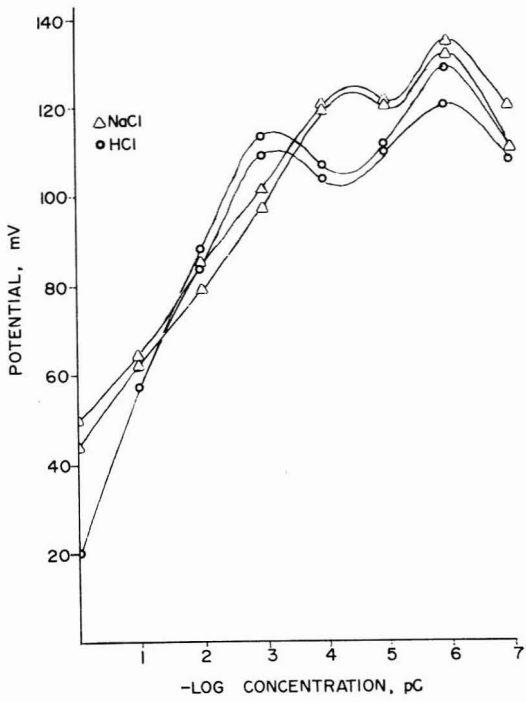
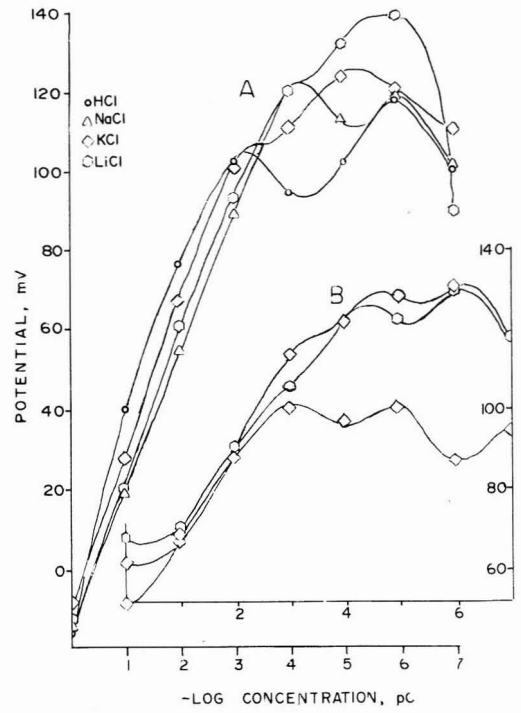Fig. 1. *Double layer potential of activated carbon Electrode 1 in HCl and NaCl solutions*

Fig. 2. *Adsorption potential of activated carbon Electrode 2.* (A) *1st set of readings* (B) *2nd set of readings*
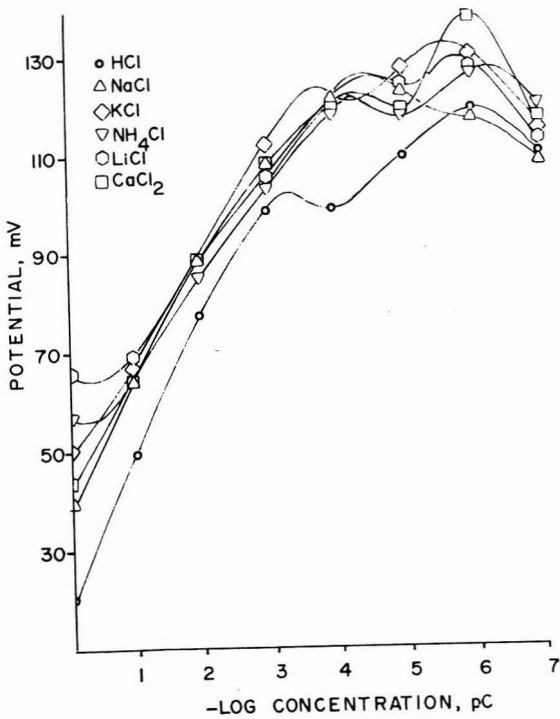

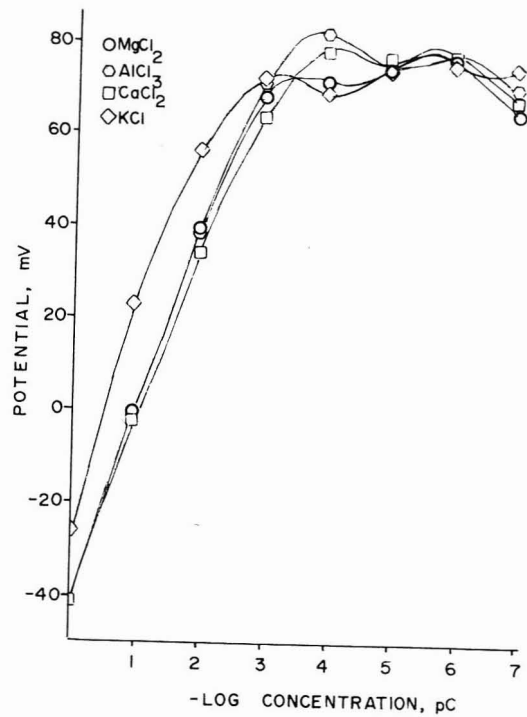Fig. 3. *Adsorption potential of activated carbon Electrode 2 after partial regeneration of active sites*


Fig. 4. *Adsorption potential of activated carbon Electrode 3 in solutions of doubly-and triply-charged cations*

ionization took place, an array of negatively charged conjugates would line up the surface of the pores with protons staying near them on the solution side. This situation would also give rise to an electrical double layer but the potential gradient, β, across the layers would be small and opposite to that discussed above for the adsorption.

However, such ionization of the acidic groups might further increase the activity of other electron-rich groups at least by induction if not by outright transfer of the electron cloud through the graphite rings of the carbon crystallite. In this way the less active groups such as peroxides or etheral oxygen which may be present on different rings of the same graphite layer would be transformed into more active sites and hence increase the adsorptive capacity of the surface. An example of such a mechanism could be given as follows:


I
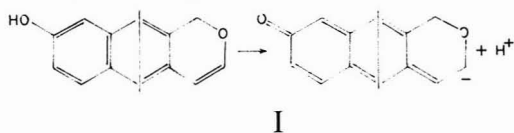
A strong acid, such as HCl, at a concentration of 1M, would supress the ionization of the acidic groups. Thus, being weak and relatively small in number, the acidic groups would contribute very little to the development of the potential at the internal surface of the disc. Hence, the potential gradient at the internal surface of the disc could be safely assumed to be due to adsorption, α_i. However, at the external surface of the disc this would be true only at low pC, and therefore, the potential gradient was determined by both α_e and β_e, the potential due to the ionization, β_e being very small compared to α_e. Thus the net potential, V, that was measured was the sum of α_i, α_e and β_e:

$$V = \alpha_i - (\alpha_a - \beta_e)$$

In region 1, where the concentrations of the cations were large, extensive adsorption occured resulting in a large α_e and small V. At lower concentrations of the cation, V increased because α_e decreased. The trend continued until a maximum was reached at pC = ~3 or 4 where the effect of the reversal potential due to ionization took place. It is assumed that at these pCs, some of the acidic groups began to ionize.

On ionization, the activity of other electron-rich functional groups was enhanced according to I above, thus increasing the adsorption. This resulted in greater α_e which in turn reduced V.

The subsequent increase in V could perhaps be explained as the direct result of completion of ionization of these weak acids. Once ionization was complete, there would be no more less-active sites to be promoted according to Scheme I and therefore a decrease in the concentration of the action would decrease α_e, and hence V would increase again. The subsequent increase of V in region 2 could also be due to the dissociation of a protonated pyrone type structure which was formed according to scheme II (Parentich and Kinsella, 1984).


II
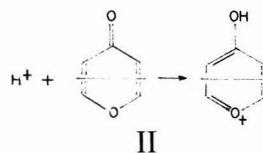
The protonated species contribute to α_e, whereas the unprotonated species is neutral. As the concentration was reduced, dissociation of the protonated species took place hence reducing α_e.

Similarly, if a benzpyrene group which is found in many natural products is present (Tsuchida and Muir 1986), the surface of activated carbon would also have species such as III.

III
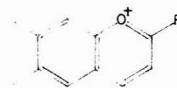
which contribute to the development of α_e. At lower concentration of acids, the charged species would revert to its neutral form according to scheme IV

IV
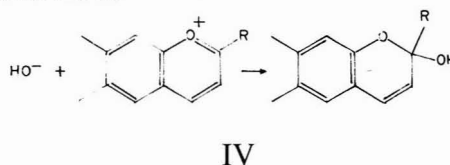
and at the same time reduce α_e to increase V.

The fact that there were three minima in a V-pC curve (including the shoulder in Region 1) might indicate that there were at least three acidic groups, each comprising members hav-

ing similar ionization constants. The identification of these species may be determined only through further experiments.

There seems to be very little difference in the effect of adsorption of various cations on the adsorption potential of the carbon surface. Adsorption of cations carrying higher charges would be expected to suppress the activity of the adjacent sites more than singly-charged cations. If this did not occur, equal number of Ca^{2+} adsorbed, for example, would decrease V by 2-fold over that due to the adsorption of K^+. But the fact that at pC = O, V was just slightly smaller for the doubly-charged cations indicates that the number of occupied sites was only fractionally greater that one-half of the total sites occupied by the singly-charged cations.

After adsorption, the characteristics of the carbon electrode could be reestablished simply by soaking it in distilled water except for the case where the adsorbed cation was Li^+. Li^+ was more strongly adsorbed compared to other cations including Al^{3+}. This is probably due to its ability to enter the micropores of the activated carbon. This further substantiates the conclusion that the magnitude of the charge on a cation did not play a main role in determining the strength of the bond formed at the adsorption sites. It is interesting to note, however, that a surface contaminated with some preadsorbed species gave higher values of V, *Fig. 2*. It seems that pre-adsorption did not shift the entire ordinate of *Fig. 2* towards a higher value but affected only the adsorption side of the V-pC curve, i.e. Region I. This could only mean that, if the solution were to contain various cations, these cations would compete for the same adsorption sites.

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