Adsorption Potential of Activated Carbon in Some Acidic and Alkaline Media

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ABSTRAK

Satu elektrod telah diperbuat daripada karbon yang telah diaktifkan. Perubahan pada keupayaan permukaannya terdapat apabila ia direndamkan dalam larutan-larutan mengandungi HCl dan hidroksida dan karbonat bagi Na^+, K^+ dan NH_4^+. Perubahan-perubahan ini telah disabitkan sebagai kesan kepekatan Cl^- dan OH^- ke atas kuasa penjerapan pelbagai kumpulan berfungsi di atas permukaan karbon yang telah diaktifkan.

ABSTRACT

An electrode was constructed using activated carbon. Changes in its surface potential were observed when it was dipped into solutions containing HCl and hydroxide and carbonate of Na^+, K^+ and NH_4^+. These changes have been attributed to the effect of concentration of Cl^- and OH^- ions upon the adsorptive strength of various functional groups on the surface of activated carbon.

INTRODUCTION

Almost every kind of activated carbon contains combined oxygen and hydrogen on its surface forming a variety of complexes (Puri & Bansel 1964). Even though a complete list of these complexes (or functional groups as they are commonly called) is not yet available, some, such as carboxyl, carbonyl, phenol, lactone and hydroxyl, are said to have been definitely identified (Boehm 1966). A summary of the reactions carried out for group identification has also been published (Donnet 1968).

In addition, activated carbon samples prepared by different methods show different characteristics in the reaction with acids and bases (Epstein *et al.* 1971). These differences reflect the nature and the abundance of the functional groups on the surface of carbon. The acidic groups such as carboxyl, for example, ionize to release hydrogen ions into solution (Puri 1966) while the basic groups, such as oxides with a pyrone-type structure, adsorb hydrogen ions from solution (Boehm & Voll 1970). In either case, the reaction of the functional groups with water results in the formation of immobile charged species on the surface of carbon with their conjugates staying alongside them in the solution. Such an arrangement of charges would give rise to an electrical double layer. The magnitude of the potential of this double layer would depend on the degree of ionization and adsorption as well as the surface concentration of each type.

Measurement of this potential would be difficult, if not impossible. However, its variation as a result of changes in the degree of ionization and adsorption could be investigated. This can be done by bringing opposite sides of a piece of activated carbon into contact with two different solutions. Under such conditions it is expected that an electrical double layer would be developed at each side and that they would differ in magnitude depending on the nature and

concentration of the ionic species in the solutions. The nett potential developed can be measured using electrical circuitry similar to that used in pH measurements with a glass electrode. This paper is intended to illustrate such a measurement on activated carbon prepared in our laboratory.

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 1×10^{-6}S) and show very little increase in conductivity upon adsorption of water and simple ions (Badri *et al.* 1984). Fairly flat pieces were ground with fine sand paper into discs of about 6 mm diameter and 2 mm thickness. Two discs were washed, dried and used for the contruction of a carbon electrode as previously described (Badri & Crouse 1989).

An Ag/AgCl electrode (Shoemaker & Garland 1962) was used as a reference. It was inserted into a glass tube containing 1M HCl and having a sliver of Whatman Qualitative 3 filter paper as a porous junction. The paper was soaked with Araldite epoxy resin and dried before use so that the leak of the acid through the junction into the test solutions would be minimal (Ramli *et al.* 1989). The test solutions were HCl and hydroxides and carbonates of Na^+, K^+ and NH_4^+ of various concentrations. They were kept in small, covered polyethylene bottles and were equilibrated at $25.0 \pm 0.2°C$.

The potential developed when the carbon and the reference electrodes were dipped into a test solution was measured using a Hewlett-Packard 3476 A Multimeter. The meter reading was recorded when a constant value was registered. After such measurement, both electrodes were rinsed with distilled water and gently dried with soft tissue paper before being dipped into a solution of different concentration. In addition, the carbon electrode was washed continuously for 24 hours with distilled water dripping from a 10 litre container at a rate of about 3 drops per minute before being used again for measurement with a test solution containing a different base.

RESULTS

The results of the potential measurement on the test solutions using the carbon electrode are given in Table 1 and are plotted as a function of -log concentration, pC, in *Figs.* 1, 2 and 3. *Fig.*1 shows the relations for HCl, NaOH and Na_2CO_3; *Fig.*2 for HCl, KOH and K_2CO_3 and *Fig.*3 for HCl, NH_4OH and $(NH_4)_2CO_3$. The values obtained for HCl are shown in each figure for ease of comparison only.

TABLE 1

Surface potential of carbon electrode

Solution	mV							
at pC =	0	1	2	3	4	5	6	7
HCl	106	164	218	269	312	323	310	323
NaOH	77	101	137	245	287	325	307	333
Na_2CO_3	102	124	138	180	276	314	330	314
KOH	54	87	130	173	293	322	310	301
K_2CO_3	110	133	151	178	252	325	347	329
NH_4OH	64	98	140	234	292	330	324	312
$(NH_4)_2CO_3$	117	146	188	235	270	303	313	305

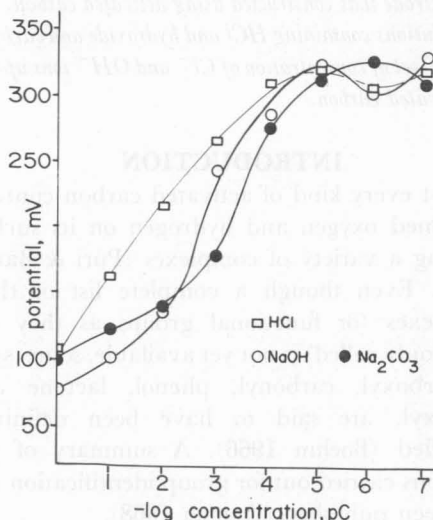*Fig. 1: Surface Potential of Carbon Electrode in HCl, NaOH and Na_2CO_3*

In each case, it was found that the potential increased with increasing pC reaching a maximum at about $pC \approx 5$. Between $pC \approx 5$ and $pC \approx 7$, the potential decreased slowly except for solutions of HCl and NaOH. For these two, a minimum was observed at $pC \approx 6$.
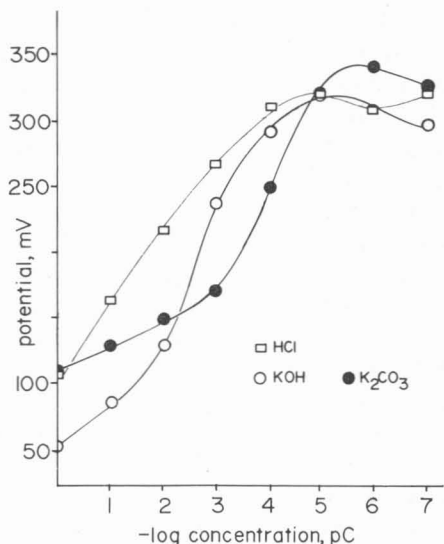
Fig. 2: Surface Potential of Carbon Electrode in HCl, KOH and K_2CO_3

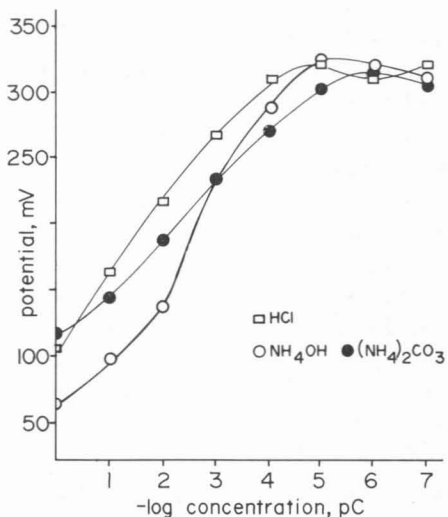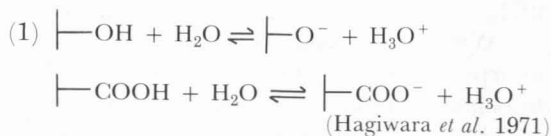*Fig. 3: Surface Potential of Carbon Electrode in HCl, NH_4OH and $(NH_4)_2CO_3$*

At high concentrations (pC=0 to 2), the potential found for the hydroxides were lower than those found for the carbonates. For the more dilute solutions, however, the opposite was found true. At pC≈5 the potentials approached approximately the same value.

DISCUSSION

Several mechanisms have been proposed to explain the acidic and basic characteristics of activated carbon which are manifested by the phenomena of adsorption and desorption of H^+ when it comes into contact with water. The simplest among these is the dissociation of the acidic groups (hydroxyl and carboxylic):

$$(1) \quad |\!\!-OH + H_2O \rightleftharpoons |\!\!-O^- + H_3O^+$$

$$|\!\!-COOH + H_2O \rightleftharpoons |\!\!-COO^- + H_3O^+$$

(Hagiwara *et al.* 1971)

It has been suggested that H^+ might also be released through hydrolysis of some other groups as given below:

(2)

(Boehm *et al.* 1964)

(3)

or $)CO_2 + H_2O \rightleftharpoons)CO_3^{2-} + 2H^+$, (Puri 1970)
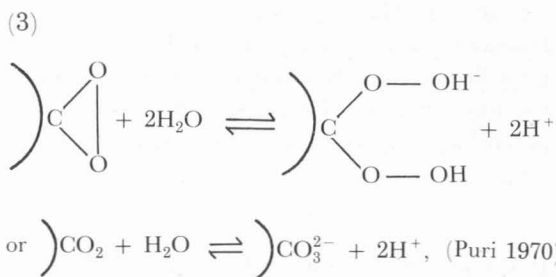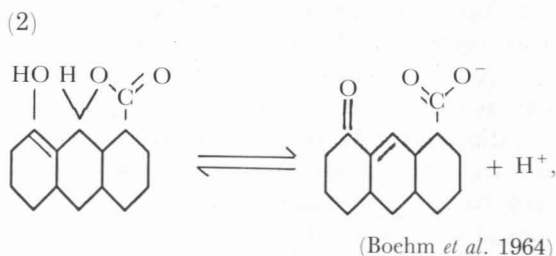
On the other hand, some of the basic functional groups can adsorb H^+ possibly through reactions such as (4) dan (5):

(4)

(Boehm & Voll. 1970)

(5)

(Garten & Weiss. 1957)
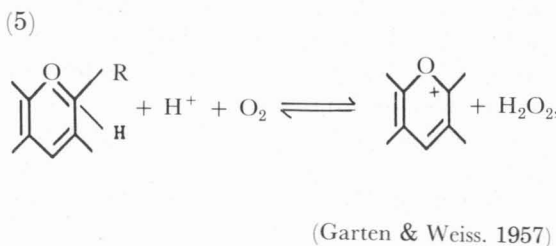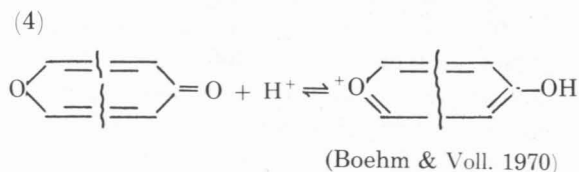
or any other reaction involving electron-rich groups such as lactone, quinone, ester, ether, *etc.*, that may be present on the surface of activated carbon (Hassler 1974 and Mattson & Mark 1971).

When the solution contains an acid, adsorption of H^+ would be more favorable than dissociation. Hence the double layer formed would have positive charges residing on the surface of the carbon (this we arbitrarily call the α-type double layer). This α-type was probably the type formed on the internal surface of the carbon electrode. The magnitude of the potential developed, α_i, remained constant since the concentration of HCl was unchanged.

A similar double layer was developed on the external surface of the carbon electrode when it was dipped into HCl test solutions. Its magnitude, α_e, was in the opposite direction to α_i and changed with changing concentrations. At the same time, ionization of the acidic groups might have also taken place leading to the development of another type of double layer, β_e, whose field direction was, however, parallel to α_i. Such a double layer is most likely to develop at lower concentrations of the test solution. Thus at any instant, the nett potential measured, p, could be expressed as:

$$p = \alpha_i - \alpha_e + \beta_e$$

It is clear that as the concentration of the test solution was lowered, α_e became smaller and β_e became larger leading to an overall increase in p as observed. [The contribution of β_e to the nett potential was small because of two reasons. Firstly, the surface concentration of the acidic groups is small (Puri & Bansel 1964, and Barton *et al.* 1972) and secondly, the degree of dissociation of these acids did not reach 100% due to the fact that they are weak acids, and more important still, the hydrogen ions released were confined to the vicinity of their conjugates.]

It has been found that carbon has a low intrinsic ion-exchange property for simple ions such as Cl^- (Tsuchida & Muir 1986). The active site for Cl^- adsorption is not known but positive centres developed through equations (4) and (5) were the most probable ones. The effect of Cl^- adsorption was to lower α_e but as the concentration of HCl was lowered, and hence more acidic groups dissociated, the residual

negative charge thus produced on the carbon surface would, through resonance or induction, neutralize these positive centres. Under such a condition, carbon would begin to desorb Cl^-. Desorption of Cl^- increased α_e and this was perhaps the reason for the decrease in p as observed for HCl at pC between 5 and 6.

The increase in p with dilution for the other test solutions can be similarly explained. Hydroxides and carbonates can neutralise the acidic groups on the surface of carbon (Boehm *et al.* 1964). Such neutralization reactions would produce negative charges on the surface of carbon which then could be delocalized through resonance or induction to the entire graphite ring system (Given & Hill 1969). Besides neutralizing the positive centres as described above, this process could also further enhance the ability of the electron-rich centres to adsorb cations. Potassium ions, for example, were thought to be adsorbed on the phenolic groups at $pH > 11$ (Tsuchida & Muir 1986). As the alkalis became more dilute, less neutralization occurred, leading to less adsorption and hence p increased.

Hydroxide ions influence adsorption in a manner similar to chloride ions. That is, at a higher concentration, the adsorption of OH^- would contribute to the increase in the potential by neutralizing the positive centres on carbon surface. At lower concentration of the alkalis, this effect was less important and the ionization of the acidic groups through reactions (1) to (3) became more extensive helping to desorb OH^-. The combined effect would be to lower p as observed at $pC \approx 5$ and higher.

Assuming complete dissociation of the hydroxides and carbonates used in these experiments, the concentration of the cation in a carbonate solution is expected to be twice that of the corresponding hydroxide. However, hydroxides are stronger bases than their corresponding carbonates. Therefore, they were able to neutralize weaker acidic groups as well (Boehm *et al.* 1964) leading to a greater degree of delocalization of charges which enhanced cation adsorption. This was probably the reason for lower p for the hydroxides compared to the carbonates on the high concentration side of *Figs. 1, 2* and *3*.

To a first approximation, it can be shown that at low pC the concentration of OH^- in the

alkali metal hydroxide is greater than that in the corresponding carbonate solutions. The reverse is true for solutions with high pC. The change-over point occurs at pC between 3 and 4. Thus as discussed above, neutralization of the acidic functional groups would be more extensive in dilute carbonate solutions as compared to the corresponding hydroxides. Consequently, adsorption of cations was greater, leading to lower p for the carbonates compared to the hydroxides in this concentration region, *Figs. 1* and *2*. This was probably also true for the case of ammonia, *Fig. 3*. The slight variation observed was probably due to the multiple equilibria that can take place in ammonium carbonate solutions.

CONCLUSION

In summary it can be said that the electron-rich centres were the active sites for cation adsorption on the carbon surface. The activity of these centres could be enhanced either by the development of negative charges on the acidic functional groups or the adsorption of anions that could neutralize positive charges developed as a result of manifestation of basic character by carbon. The development of negative centres could either be due to ionization of the acidic functional groups at low concentration of the electrolytes or, more markedly, through the ionization of these groups by bases.

ACKNOWLEDGEMENT

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