# The Effects of Sorbed Alkali Metal Ions on the Conductance of Activated Carbon

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## ABSTRAK

*Kadar kenaikan kekonduksian karbon yang diaktifkan didapati lebih rendah apabila di-benamkan dalam larutan NaCl yang kepekatan garamnya ditambah. Kejadian ini telah disabit-kan sebagai bertambahnya kelikatan larutan yang menahan aliran ke segenap liang kepada tahap yang dicapai oleh air tulen. Nilai kekonduksian akhir pun lebih rendah juga. Kesan yang berlawanan didapati bagi larutan HCl. Pengukuran dalam larutan Li$^+$ dan K$^+$ membayangkan kelincahan ion-ion ini memainkan peranan penting dalam penentuan kerendahan kekonduksian itu.*

## ABSTRACT

*The rate of increase of the conductance of activated carbon immersed in NaCl solutions was found to be lower when the concentration of the salt was increased. This was probably due to the increase in the viscosity of the solutions which prevented the filling of the pores to the same extent as in the case of pure water. In addition, the final conductance of the sample was also lowered. The opposite effect was however observed in HCl solution. Measurements in the presence of Li$^+$ and K$^+$ suggested that the mobility of the ions determined the final value.*

## INTRODUCTION

The presence of pores of different sizes in activated carbon makes it an excellent adsorbent for many chemical species both in the gaseous state and in solution. This adsorbing power has been attributed mainly to its ability to form bonds of varying strength with the adsorbates. There are numerous active sites on the walls of the pores where bonding can occur through the participation of the unsaturated orbitals of the carbon atoms. Besides these neutral centres, there are also present various organic functional groups such as phenolic and carboxylic (Hassler, 1984) that can attract the adsorbate strongly.

When a piece of activated carbon is immersed in water, the filling of its internal cavities would be expected to be governed by the rate at which the water flows in through the pores that are open to the bulk aqueous medium. As water seeps into the pores, the various functional groups are ionized, giving hydrogen ions. It has been suggested that these ions were responsible for the increase in the conductance of the carbon (Badri *et al.*, 1984) because on formation they would stay in the vicinity of the negatively charged functional groups in the pores and thus act as the charge carriers. As more pores were filled, the conductance would increase as a result of the greater number of hydrogen ions formed.

The change in conductance of the activated carbon due to the sorption of water has been

found to increase with time according to the equation:

$$\left(\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o}\right)^2 = \frac{\delta\tau}{\eta}\, ct$$

where $\sigma_o$, $\sigma_f$ and $\sigma$ are the initial conductance, the final conductance and the conductance of the sample at time t respectively, $\delta$ and $\eta$ are the surface tension and viscosity of water, c is a constant related to the size and shape of the conductor and r is the average radius of the pores.

For a given piece of activated carbon, the conductance depends on the rate at which the water flows into the pores. Since flow rate is determined by surface tension and viscosity, it can be varied by addition of solutes. Higher surface tension and lower viscosity of the aqueous medium would result in an increase in the rate of flow. This paper describes the effect of some monovalent cations in solution upon the conductance of activated carbon.

## MATERIALS AND METHODS

A piece of activated carbon conductor was prepared and assembled as previously described (Badri *et al.*, 1984). Solutions of alkali metal chlorides, LiCl, NaCl and KCl, of $1.00 \times 10^{-4}$M were prepared from recrystallized reagents (Hopkin and Williams GPR) in distilled water. Solutions of NaCl of concentrations $5.00 \times 10^{-5}$M, $2.50 \times 10^{-5}$M and $1.00 \times 10^{-5}$M were prepared by dilution. HCl solutions of various pH were prepared by diluting the A.R. grade supplied by Berk Spenser Acid Ltd of London. pH measurements were done using a TOA HM 7A pH meter.

The conductor assembly was placed in a test tube and allowed to equilibrate at the temperature of the bath. The conductance of the dry conductor was measured using an Autobalance Universal Bridge B642. When a constant value was obtained, the salt solution was quickly poured in, completely immersing the conductor. The conductance was immediately measured, $\sigma_o$, and it was then followed to the end of the experi-

ment. The level of solution in the test tube was kept constant by dropwise addition of distilled water as necessary. When the conductance reached a final constant value, $\sigma_f$, after four days, the conductor was thoroughly washed with distilled water in a Soxhlet apparatus. It was dried in an oven at 110°C overnight prior to evacuation at 70°C for three hours and was stored in a desiccator.

## RESULTS

The conductance readings obtained using NaCl solution of various concentrations are given in *Fig. 1*. Conductance was found to
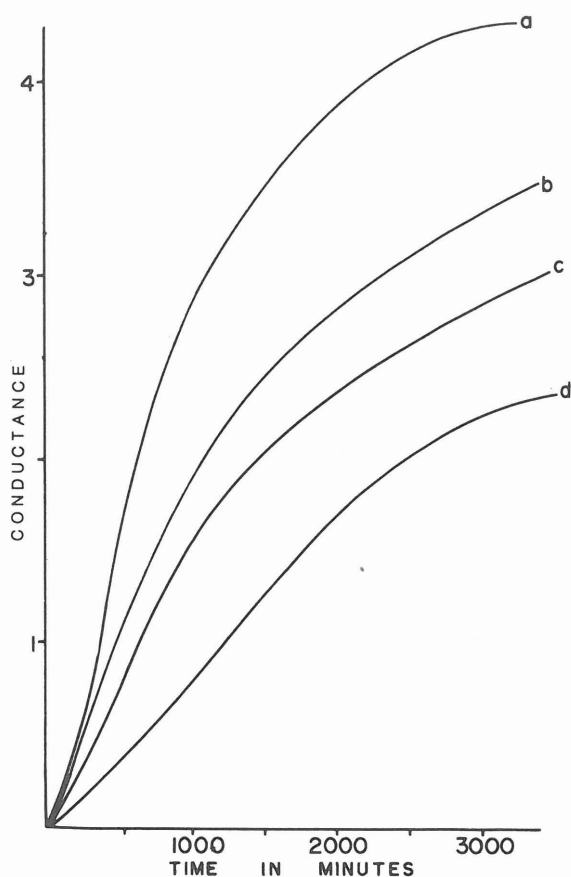


*Fig. 1. Conductance of activated carbon immersed in NaCl at four different concentrations:*
*a — 1 x 10⁻⁵M, b — 2.5 x 10⁻⁵M,*
*c — 5 x 10⁻⁵M, d — 1 x 10⁻⁴M.*
*Final conductance was read after 4320 minutes.*

increase with time in a manner similar to that when only pure distilled water was used. In each case the initial slow increase of the conductance was followed by an accelerated phase before a final slow period as the maximum value, $\sigma_f$, was approached. The initial inductive period seems to be lengthened with increasing NaCl concentration. The rate of increase of the conductance and its final value were also smaller as NaCl concentration was increased. The maximum increase in the conductance, $(\sigma_f - \sigma_0)$, was found to be $4.35 \times 10^{-6}$, $3.727 \times 10^{-6}$, $3.217 \times 10^{-6}$ and $2.459 \times 10^{-6}$ $\Omega^{-1}$ respectively in increasing order of NaCl concentration.

The results analysed according to the equation given above, are plotted in *Fig. 2*. The limit of applicability of the equation has been found to be up to about 73% of sorption fraction, $(\sigma - \sigma_0 / \sigma_f - \sigma_0)$, similar to when only distilled water was used. As is obvious from *Fig. 2*, deviation did occur at small sorption fractions and became more significant as the concentration of NaCl was increased. The slope of the curve, which is proportional to $\delta/\eta$, decreased as the concentration was increased.

The final conductance of activated carbon immersed in HCl of various concentrations, KCl and LiCl of $1.00 \times 10^{-3}$M are given in Table 1.
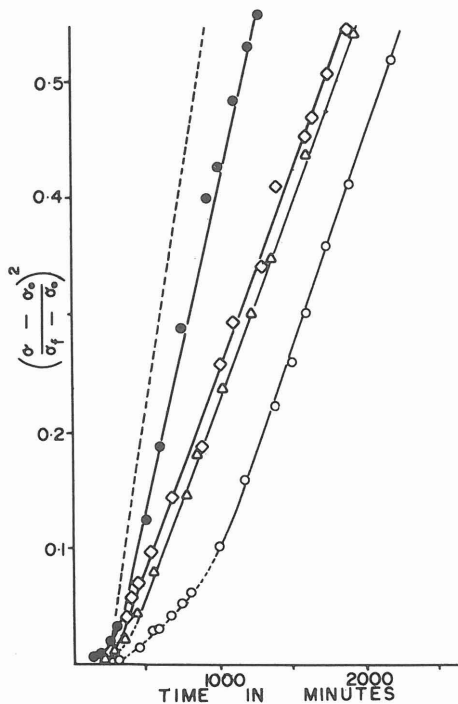


Fig. 2. The plot of $(\sigma - \sigma_0 / \sigma_f - \sigma_0)^2$ for activated carbon immersed in NaCl of four different concentrations.

- ● $1 \times 10^{-5} M$  ○ $1 \times 10^{-4} M$
- ◇ $2.5 \times 10^{-5} M$  — — pure distilled water
- △ $5 \times 10^{-5} M$

TABLE 1a

Conductance of activated carbon immersed in solutions of HCl (30°C) and NaCl (25°C)

| pH | $(\sigma - \sigma_0) \times 10^6 \ \Omega^{-1}$ | NaCl/$10^{-5}$M | $(\sigma - \sigma_0) \times 10^6 \ \Omega^{-1}$ |
|---|---|---|---|
| 1.8 | 4.373 | 2.5 | 3.727 |
| 3.1 | 2.546 | 5.0 | 3.178 |
| 4.2 | 2.102 | 1.0 | 4.345 |
| 5.9 | 1.920 | 10 | 2.459 |
| 6.7 | 1.906 | | |

TABLE 1b

Conductance of activated carbon immersed in HCl, LiCl, NaCl and KCl ($1 \times 10^{-4}$ M) at 30°C

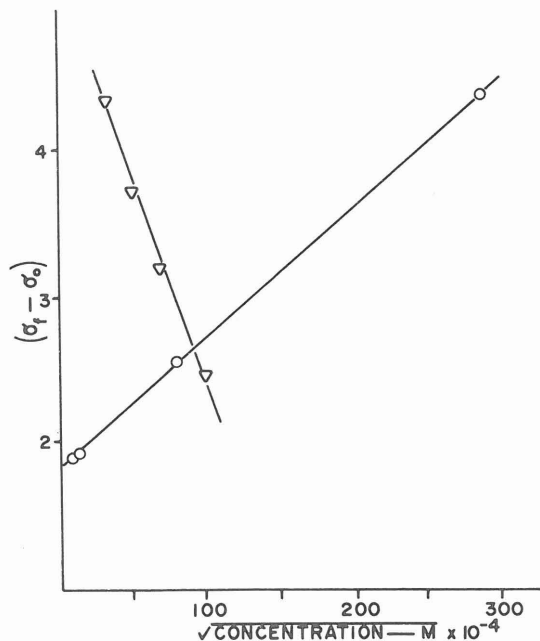| | HCl | LiCl | NaCl | KCl |
|---|---|---|---|---|
| $(\sigma_f - \sigma_0) \times 10^6 \Omega^{-1}$ | 2.398 | 1.985 | 2.017 | 2.117 |
| mobility | 363 | 40.1 | 52.0 | 76.2 |

*Fig. 3. Final conductance difference, ( $\sigma_f - \sigma_o$ ), in $\Omega^{-1}$ plotted against the square root of concentration in molar.*

▽ $Na^+$
○ $H^+$

*$H^+$ gives a direct relationship whereas $Na^+$ gives an inverse relationship.*

*Fig. 3* shows the change in ( $\sigma_f - \sigma_o$ ) with the mobility of three alkali metal ions.

## DISCUSSION

The conductance of activated carbon immersed in aqueous NaCl solution increased with time in agreement with the results found when only distilled water was used. The increment was attributed to the presence of hydrogen ions in the pores resulting from the ionization of the functional groups as water seeped in. The rate of increase in the conductance was determined by the rate of water entering the pores and its final value was determined by the extent to which these pores were filled.

A NaCl solution is more viscous than pure water and has a higher surface tension. High viscosity has the effect of slowing down the flow as is evident from the longer time taken by the sample to attain its maximum conductance as the concentration of the solution was increased, *Fig. 1*. The lower $\sigma_f$ values showed by the conductor at higher NaCl concentrations was probably in part due to the reduced wetting capability of the solutions. As its surface tension was increased, the ability of the solution to fill the available space in the pores was reduced resulting in fewer ions present to carry the charge across the walls of the pores and therefore lowering the final conductance.

In the plot of the square of sorption fraction, ( $\sigma - \sigma_o / \sigma_f - \sigma_o$ )$^2$, against time, *Fig. 2*, the two factors operated in opposition. The slope of the curves is proportional to $\delta/\eta$. The data available on the surface tension of NaCl solution (CRC Handbook, 1970 − 71) indicate the ever increasing value of $\delta$ with the increase in concentration. Thus the decrease in the slope as NaCl concentration was increased indicates that the viscosity factor is more prominent, especially when the solution is very dilute.

The increase in the conductance of activated carbon immersed in distilled water at pH 6.7 has been found as $1.906 \times 10^{-6}$ $\Omega^{-1}$ 30°C (Table 1). Since there was no salt added, the final increase has been solely attributed to the presence of $H^+$ in the pores due to the dissociation of the functional groups. One would expect that the change would be much greater if the concentration of $H^+$ was increased. This has been found to be so when measurements were done in aqueous HCl of different concentrations given in Table 1. A plot of ( $\sigma_f - \sigma_o$ ) against the square-root of $H^+$ concentration gave a straight line implying that the Onsager equation may be applied to the system.

A similar plot for the NaCl solutions produced the opposite result, *Fig. 3*. For NaCl, the final change in the conductance ( $\sigma_f - \sigma_o$ ), decreased linearly as the square-root of concentration. The reason for this is still not very clear.

It might have been due to the increase in the surface tension as discussed above but, partially, at least, it could have been due to reduced mobility of the ions resulting from assymetric effects as the concentration was increased. Alternative-
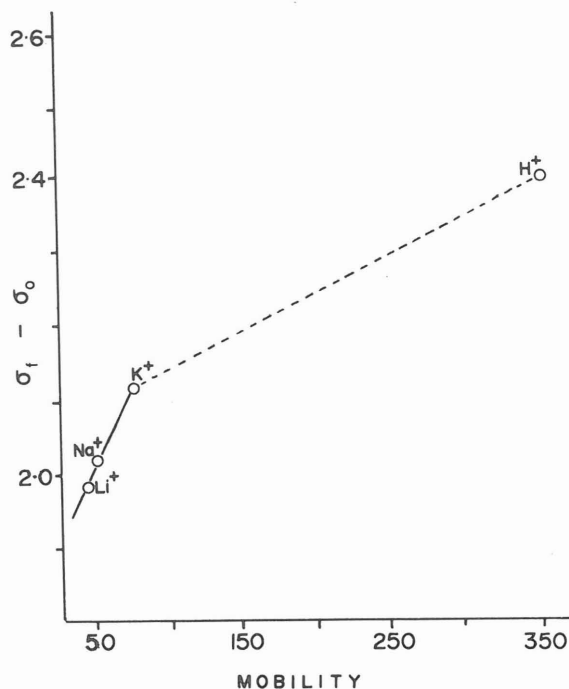
ly, as Na$^+$ ions seeped into the pores, they may have displaced some H$^+$ ions into the bulk through diffusion. This was possible as there was a concentration gradient of H$^+$ ion between the pores in the conductor and bulk solution outside it. The result of this displacement would be a lowering of the concentration of the more mobile H$^+$ ions in the pores thus reducing the conductance.

The effect of mobility of the ions on the conductivity has been clearly shown in *Fig. 4* where ($\sigma_f - \sigma_o$) for four different monovalent cations at the same concentration were measured. This increasing order of mobility has been given as Li$^+$ < Na$^+$ < K$^+$ < H$^+$. The plot of ($\sigma_f - \sigma_o$) against the mobility for each species appears linear for the alkali metal ions. The deviation of H$^+$ in the series above could probably be explained by the totally different mechanism adopted by H$^+$ in its transport in aqueous solution.



*Fig. 4. Final conductance difference, ($\sigma_f - \sigma_o$) in $\Omega^{-1}$ plotted against the mobility of the ions in cm$^2$ volt$^{-1}$ s$^{-1}$. Deviation shown by H$^+$ probably due to the different mechanism adapted in its transport properties in aqueous solution.*

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