

EXCLUSION OF SALT SOLUTIONS FROM ACTIVATED CARBON PORES AND ITS RELATIONSHIP TO CONTACT ANGLE ON GRAPHITE

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Abstract

The exclusion of salts from the pores of activated carbon granules is demonstrated clearly. In soaking experiments, the concentrations of solutions of K_2CO_3 , K_2HPO_4 and K_3PO_4 inside the pores are less than in the bulk solutions. This phenomenon is observed by measuring the bulk concentration, which increases upon the addition of carbon. This suggests that these salts are repelled by the carbon surface. In incipient wetness experiments, the three aforementioned salts do not enter the carbon at concentrations greater than ~ 1 M. The contact angles of these three salt solutions on highly oriented pyrolytic graphite surfaces rise with concentration and approach 90° , which suggests that these solutions would not enter activated carbon pores. By contrast, soaking, incipient wetness and contact angle measurements for salts like $ZnCl_2$ and $Zn(CH_3COO)_2$ show preferential adsorption by soaking (the salt is depleted from the solution), high maximum incipient wetness volumes at high solution concentrations and a reduction of contact angle with increase in concentration. It is therefore found that the behavior of these solutions on graphite surfaces approximates the solution behavior on activated carbon that is low in acidic surface functional groups.

Introduction

It has been known for many years that the impregnation of activated carbon with strategically selected compounds can improve its ability to remove toxic gases [Bush 1946]. Carbon can be impregnated by stirring it in an aqueous solution of the desired compound ("soaking method"). Alternatively, carbon can be impregnated via the incipient wetness (imbibing) method, which involves adding just enough solution to the carbon granules so that they remain free flowing and appear dry, that is stopping just before the granules start to stick together.

Earlier work has shown that, when soaking at high concentrations, certain salts adsorb preferentially onto activated carbon [Czarny 1971, Westreich 2006], while others behave as spectators, that is they do not adsorb. A third category of salts is excluded from the activated carbon surface. Czarny *et al.* identified the preferential adsorption of $ZnCl_2$, $CaCl_2$, $CdCl_2$, and $HgCl_2$, as well as the exclusion of $MgCl_2$ and $BaCl_2$. The present work identifies the exclusion of the salts K_2CO_3 , K_2HPO_4 and K_3PO_4 when soaking activated carbon. In addition, the incipient wetness method does not work for certain salt solutions, which do not enter the carbon pores. This work attempts to combine the observations of incipient wetness experiments and preferential adsorption and exclusion in soaking experiments with the contact angle of the salt solutions on graphite surfaces.

Experimental Methods

Commercially available Kuraray GC (referred to subsequently as GC), an acid-washed coconut shell-based granular activated carbon (0.4% w/w ash), with particle mesh size of 12 x 35 (0.5 – 1.7 mm), was used. A Brunauer-Emmett-Teller (BET) surface area [Brunauer 1938] of about $1500 \text{ m}^2 / \text{g}$ was previously determined [Westreich 2006]. Boehm titrations [Boehm 1964, Boehm 1994] have also been previously carried out on the activated carbon [Westreich 2006]. The results of the Boehm titrations for GC are given in Table 1.

Table 1. Results of Boehm titrations of Kuraray GC carbon.

Base	$KHCO_3$	K_2CO_3	KOH
mmol acidic groups / g untreated GC	0.00 ± 0.01	0.07 ± 0.01	0.09 ± 0.01

The maximum incipient wetness volumes were determined by adding small increments of solution to 10 g of carbon in a screw-top jar. The jar was then shaken so that the solution could be distributed uniformly. Solution was added until the carbon granules began to stick to each other or to the walls of the jar. The volume added to this point is called the *imbibing limit*, and was determined from measurements of mass and density of the solution. The imbibing limit per gram of carbon is

called the *specific imbibing limit*.

The salt solutions were prepared from $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (subsequently referred to as $\text{Cu}(\text{Ac})_2$, $\text{Zn}(\text{Ac})_2$), $\text{C}_6\text{H}_5\text{COONa}$ (sodium benzoate, subsequently referred to as NaBz), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , KCl , K_2CO_3 , KH_2PO_4 , K_2HPO_4 , and K_3PO_4 . The $\text{Cu}(\text{Ac})_2$, NaBz, CuCl_2 , ZnCl_2 , KCl , K_2HPO_4 , and K_3PO_4 were obtained from Aldrich (ACS reagent grade). The $\text{Zn}(\text{Ac})_2$ and K_2CO_3 (technical grade) were obtained from 3M Canada. KH_2PO_4 was obtained from Anachemia (ACS reagent grade).

Contact angle and surface tension were measured with a FTA 135 drop shape analyzer. The following procedure was employed. A pendant drop of about 2 mm in diameter was formed using a syringe, and the syringe was slowly lowered until the drop made contact with the graphite. The drop was held for a count of one second, and then the syringe was slowly raised up. A digital snapshot was taken, and the contact angle was measured. The graphite samples used were highly oriented pyrolytic graphite (HOPG), obtained from SPI Supplies, of grades SPI-1, SPI-2 and SPI-3. No noticeable differences in contact angle measurements were observed among the three grades, and most measurements were taken using SPI-1. The HOPG was freshly cleaved with adhesive tape before each measurement. All contact angle measurements are an average of 3-5 data points.

Soaking studies were performed by stirring carbon for one hour in solutions of $\text{Zn}(\text{Ac})_2$, K_2CO_3 , KH_2PO_4 , K_2HPO_4 , K_3PO_4 and KCl ; 4 g of carbon were soaked in various volumes of solution. One hour was determined to be long enough by verifying that there was no significant change in concentration for samples soaked between 30 minutes and 2 hours. For the low solution volume to carbon volume ratios chosen to emphasize the effect of salt exclusion, two samples each of 4 g of carbon in 10 mL of solution and 8 g of carbon in 16 mL of solution were stirred for each initial solution concentration selected. Concentrations of initial and equilibrium solutions of K_2CO_3 , KH_2PO_4 , K_2HPO_4 and K_3PO_4 were determined by potentiometric titration, using a Mettler DL21 titrator. $\text{Zn}(\text{Ac})_2$ adsorption was determined by gravimetry. KCl solutions were analyzed for their potassium content by atomic absorption (AA) spectroscopy at Dalhousie University's Minerals Engineering Centre.

Results and Discussion

Equilibrium isotherms were determined for $\text{Zn}(\text{Ac})_2$, K_2CO_3 , K_2HPO_4 , KH_2PO_4 and KCl by soaking experiments on GC [Westreich 2007]. Preferential adsorbers such as $\text{Zn}(\text{Ac})_2$ cause the solution to be depleted due to salts adsorbing on the carbon [Westreich 2006]. In order to determine the concentration inside the carbon granules, C_{in} , the following equation was employed:

$$C_{in} = [C_o V - C_{eq}(V - V_{imbibe})] / V_{imbibe} \quad (1),$$

where V_{imbibe} is the solution volume inside the granules, taken to be the specific imbibing limit for water in GC (0.7 mL / g) times the mass of carbon used in the experiment. C_o is the initial concentration, V is the total solution volume, and C_{eq} is the equilibrium concentration.

The solution in the interior of the granules can be modelled in a number of ways. Two possibilities are of particular interest. In one case (model 1), the interior volume V_{imbibe} is uniformly filled with solution of concentration C_{in} . The other possibility (model 2) is that a portion of this volume, closest to the carbon surface, is filled only with water, *i.e.* with a concentration of 0, while the rest of the interior is filled with solution at a concentration C_{eq} , equivalent to that outside of the granules. In model 2, C_{in} is the average concentration inside the granules. Curve fitting shows that both models, uniform interior solution and interior with two distinct layers, agree well with the data [Westreich 2007]. However, model 2 is perhaps more intuitive, as it implies a region in which the salts are repelled by the carbon surface. In other words, there is a stronger attraction between the salts and water than between the salts and the carbon surface.

Fig. 1 shows a plot of C_{in} for K_2CO_3 , K_2HPO_4 , K_3PO_4 , KH_2PO_4 and KCl as a function of C_{eq} . Only data points with volume-to-mass ratios of 2.0 and 2.5 are shown, as these give the most easily measured differences between C_{in} and C_{eq} . Assuming that C_{in} is an average value and that in fact the solution inside the granules is divided as discussed in model 2 above, the volume in which the salts are excluded yields an "exclusion thickness". This exclusion thickness is calculated from the data in Fig. 1, and the BET surface area of $1500 \text{ m}^2 / \text{g}$ is used as an estimate of actual interfacial surface area. The values of exclusion thickness are listed in Table 2. A monolayer of water is around 2.8 \AA thick [Wells 1990], so the exclusion thickness value of 2.0 \AA found for K_2CO_3 , K_2HPO_4 , and K_3PO_4 represents roughly 70% of a water monolayer. Further studies of the interactions between salt solutions and the surfaces of both GC activated carbon and graphite surfaces are shown in Figs. 2-3.

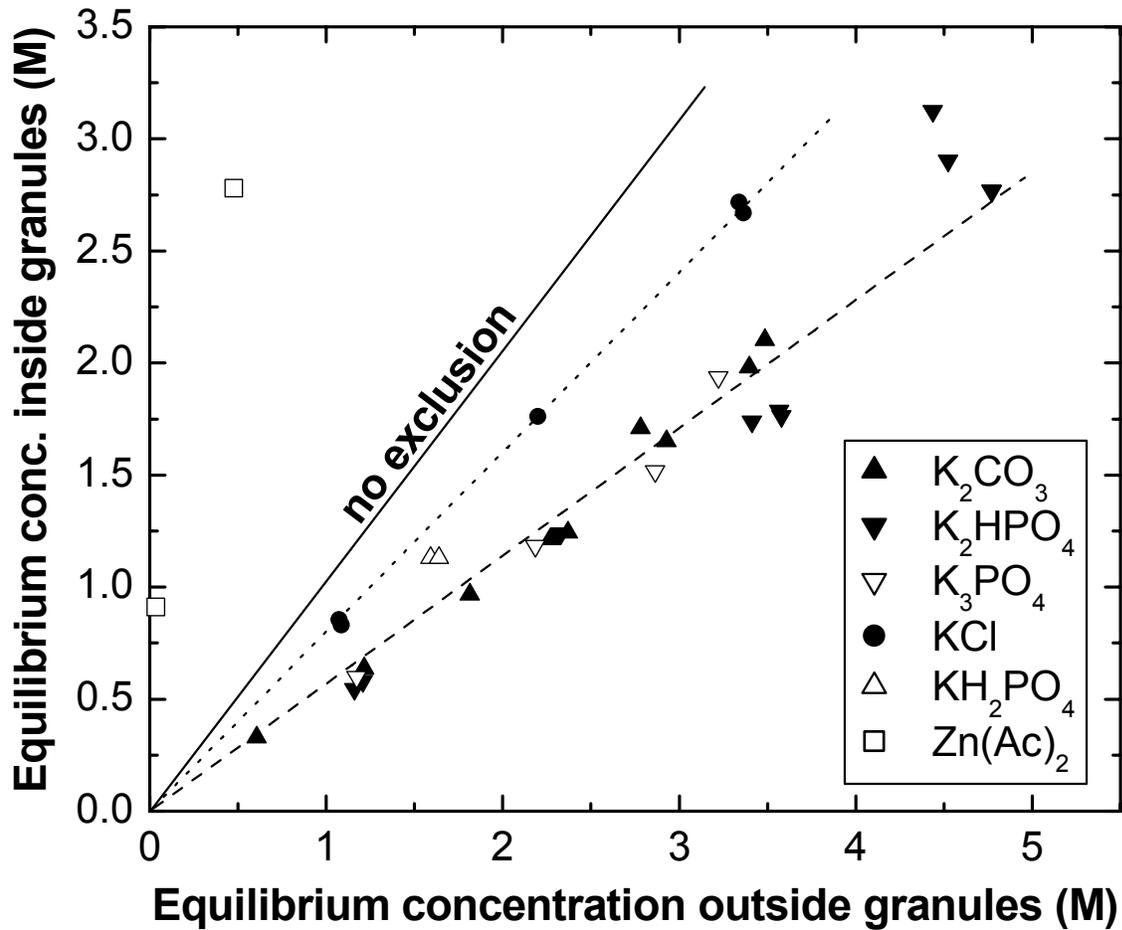


Figure 1. Equilibrium concentrations of some salts inside the granules of GC as a function of the equilibrium concentration outside the granules, derived from soaking studies with solution volume-to-carbon mass ratios of 2.0 and 2.5 mL / g. The solid line has a slope of 1, which is where the data would fall if there were no exclusion. The slope for KCl is 0.80, 0.7 for KH_2PO_4 (no line shown), and 0.57 for K_2CO_3 , K_2HPO_4 and K_3PO_4 . $\text{Zn}(\text{Ac})_2$ clearly shows preferential adsorption behavior.

Table 2. Exclusion thicknesses for salt soaking experiments on GC, as derived from the data in Fig. 1.

Solute	Exclusion thickness (Å)
KCl	0.9 ± 0.1
KH_2PO_4	1.2 ± 0.2
K_2CO_3	2.0 ± 0.1
K_2HPO_4	2.0 ± 0.1
K_3PO_4	2.0 ± 0.1

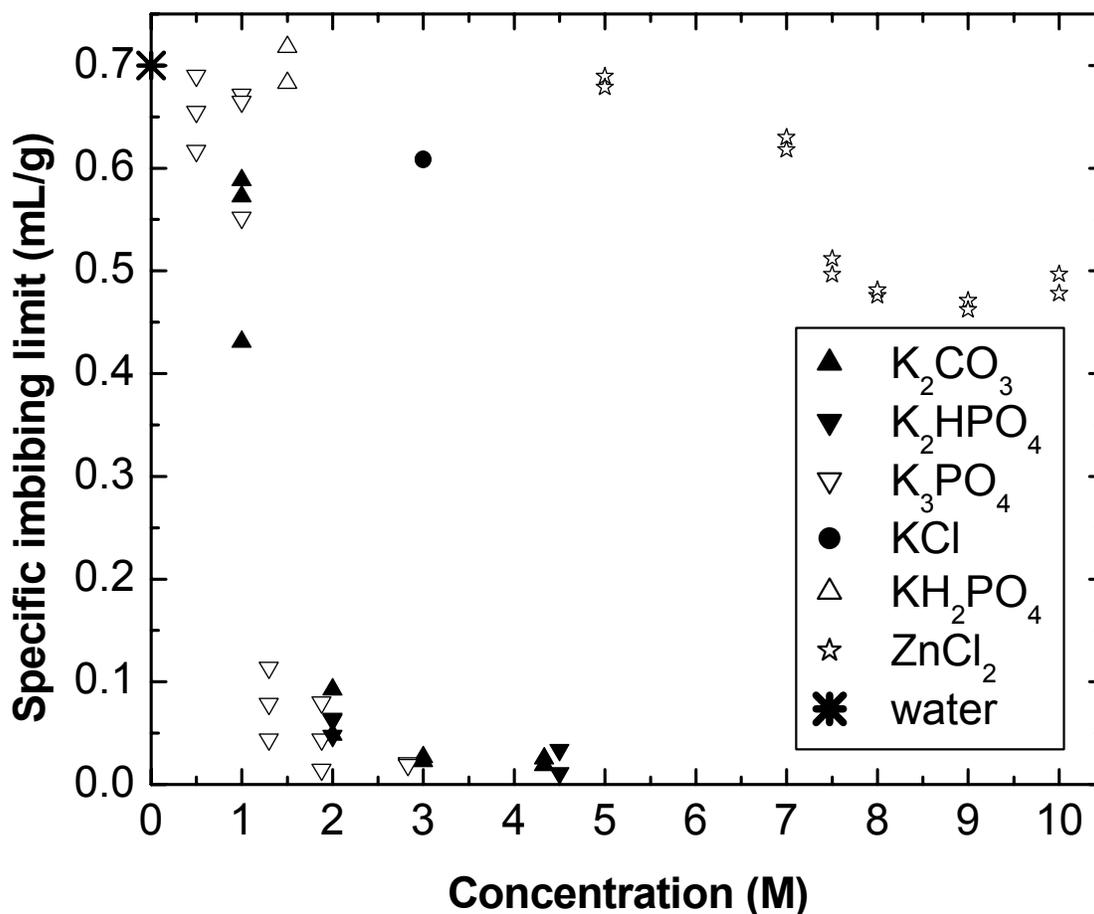


Figure 2. Specific imbibing limits for a number of salts on GC.

Fig. 2 shows the specific imbibing limits for a number of salts as a function of concentration. For both K_2CO_3 and K_3PO_4 , the volume is sharply reduced above 1 M, while for $ZnCl_2$, which was found to be a slightly preferential adsorber in soaking studies [Westreich 2006], the imbibing limit remains high even at high concentrations. Therefore, there appears to be a correlation between a strong reduction of imbibing limit with concentration and exclusion layer determined from the soaking studies described above.

In addition, it has been shown [Fortier 2007] that imbibing and soaking lead to different SO_2 adsorption behaviors for K_2CO_3 on activated carbon. While imbibing at high concentrations is not possible, repeated imbibing with 1 M solutions leads to a higher SO_2 removal capacity than soaking at high concentrations. The same study shows that K_2CO_3 tends to aggregate when loaded by soaking at high concentrations. These findings are in agreement with the idea of an exclusion layer presented in the current work.

Fig. 3 shows contact angles on HOPG for a number of salt solutions. For some of the salts shown in Fig. 3, the contact angle decreases with increasing concentration. These are the same salts that have been shown to display preferential adsorption [Westreich 2006]. For the excluded salts of Fig. 1, contact angles are shown to stay constant or increase with increasing concentration. It should be noted that KCl and KH_2PO_4 , which do not exhibit a sharp reduction in imbibing limit with solution concentration, have contact angles that do not approach 90° at high concentrations, while K_2CO_3 , K_2HPO_4 and K_3PO_4 have larger contact angles and do exhibit the sharp reduction shown in Fig. 2. As the contact angles approach 90° , the solution is not wetting the solid, and thus it is reasonable to associate a lack of entry into pores of an activated carbon having few surface functional groups with a contact angle near 90° on graphite. Thus there is a correlation between the preferential adsorption behavior on GC and decreasing contact angles on HOPG.

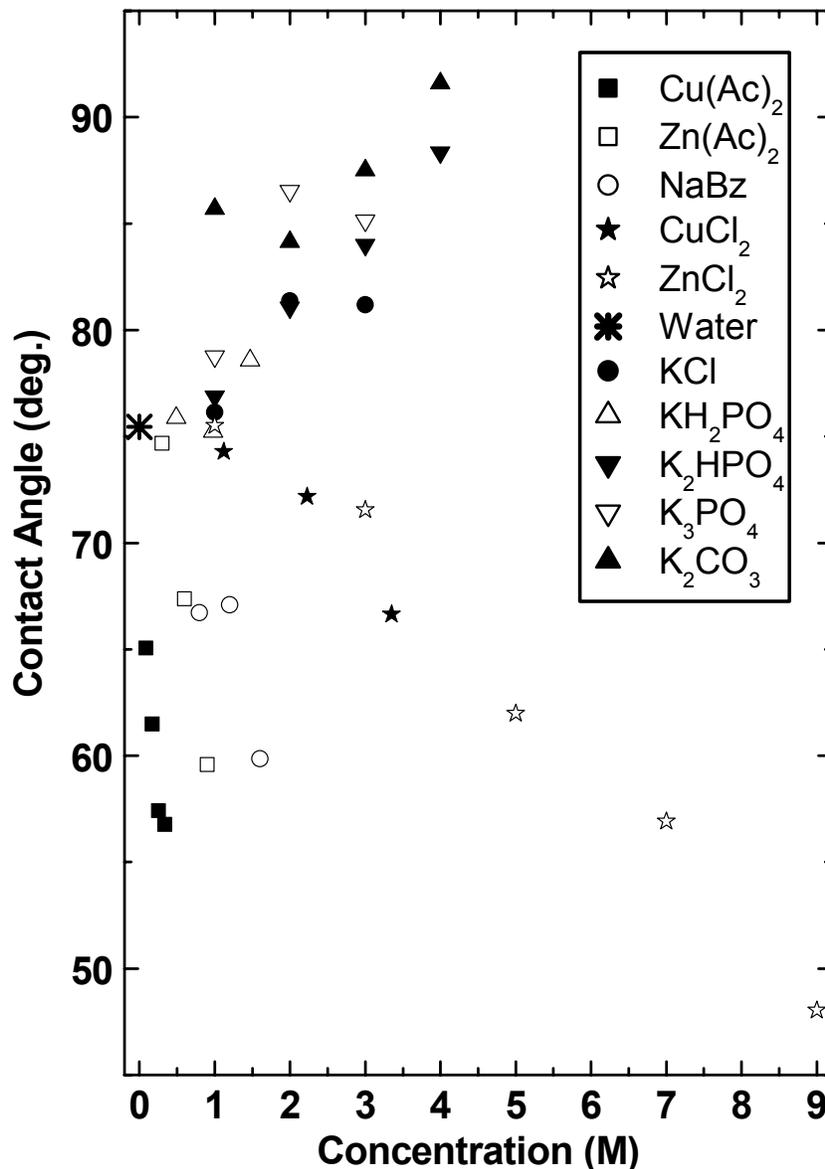


Figure 3. Contact angles for a number of salts on the surface of HOPG.

Stas and Rudko [Stas 1989] found that water and potassium carbonate solutions on carbon plates gave contact angles of 100-110°, and noted that dissolving K₂CO₃ in water-ethanol solutions reduced the contact angle and increased the loading of K₂CO₃ achieved by soaking. Their findings are in agreement with those shown here and in Fortier *et al.*, *i.e.* that concentrated K₂CO₃ solutions have high contact angles on carbon surfaces and they cannot be used to impregnate activated carbon efficiently by soaking or imbibing.

Conclusions

The exclusion of certain salt solutions by activated carbon has been clearly demonstrated by soaking and incipient wetness experiments. The contact angles of these salt solutions tend to increase with increasing concentration, whereas the opposite occurs for salts that preferentially adsorb. Salt solutions that show preferential adsorption in soaking experiments also maintain a high imbibing limit with increasing concentrations. The ability to use contact angle measurements to predict imbibing behavior is a potentially useful rapid screening method, as contact angle measurements can be performed more

quickly than imbibing studies. A short series of contact angle measurements of a salt solution as a function of concentration reveals whether a salt is a preferential adsorber and good imbiber or an excluder and a poor imbiber at high concentration.

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