

Water as a Potential Molecular Probe for Functional Groups on Carbon Surfaces

by

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Abstract

A new and simple method, using water as a potential molecular probe, is proposed for the determination of the concentration of surface oxygen groups on carbon adsorbents. The procedure is based on a determination of the Henry constant between a water molecule and a functional group from the volume integration of the Boltzmann factor over the accessible space around the functional group. Three porous carbons are used in this study to test the new method: A-5, RF-100 and RF-200. The results obtained are in good agreement with those measured by Boehm titration. This new method can be applied to adsorbents containing small concentrations of oxygen groups where the Boehm titration method may give unreliable results.

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1. Introduction

Water is of immense importance to many problems in different scientific disciplines, including chemistry, biology, geology, nanotechnology, and materials technology. One such problem is water adsorption in activated carbon of high surface area; several applications of carbon adsorbents such as the removal of organic pollutants from aqueous streams, recovery of VOCs, the production of clean fuels etc., involve aqueous components. The interaction of water with carbon depends critically on the concentration of hydrophilic groups whose interaction with water is much stronger than the dispersion force interaction between water and carbon itself. The hydrophilic moieties are present as functional groups attached either to the basal plane, or to the edges of graphene layers. It is important to the successful application of carbon adsorbents in processes involving water and competing organic species to understand, at a fundamental level, how water molecules interact with the functional groups. Insight into these processes can be gained by carrying out water adsorption measurements at very low loadings, where the intrinsic interaction between a water molecule and a functional group can be quantified.

The relationship between the amount adsorbed and the gas phase pressure is an adsorption isotherm. At low enough pressures interactions between adsorbate molecules are negligible and the isotherm is linear. The isotherm slope under these conditions is the Henry constant and represents the partition of concentration between the gaseous adsorptive and the adsorbate phases, and it is therefore a measure of the intrinsic interaction between an adsorbate molecule and the solid adsorbent [1-3]. When water is adsorbed in activated carbon, the primary interaction is between water and the functional groups.

Adsorption on carbons has a very long history, e.g. C.W. Scheele in 1773 and the F. Fontana, in 1777, investigated the uptake of gases by charcoal. Therefore, the experimental work of water adsorption in carbon materials might date back to the early literature to give a complete overview. Nevertheless, simulation studies from the 1980s onwards, have shed much new light on the mechanism of water adsorption on carbons [4-22]. Early simulation studies concentrated on the direct interaction between water and a pure graphene surface [23-27], but since graphene is hydrophobic, in the sense that the water-graphene interaction is much weaker than the intermolecular interaction between water molecules, water only adsorbs at pressures greater than the saturation vapor pressure. This theoretical observation contradicts the experimental data, where isotherms show that there is a strong uptake of water in carbonaceous adsorbents in the reduced pressure range between 0.3 and 0.8, depending on pore size. This contradiction has inspired many attempts to account for the factors that lead to the enhanced affinity between water and a carbon adsorbent. These factors are often referred to as adsorption heterogeneity [28], and are categorized as either structural or energetic heterogeneity. Structural heterogeneity could result, for example, from defects in the graphene layers or from the overlap of adsorbent forces in spaces very close to a molecular width. Even this strong enhancement of the adsorption potential energy is not sufficient to explain the experimental observations [29]. The only possible enhancement that can reconcile simulation results and experimental data is an increase in adsorption energy from electrostatic interactions between water molecules and partial charges, most probably due to residual polar groups attached to the edge sites of carbon adsorbents, and usually described as functional groups [30-34]. Water molecules initially adsorbed at these sites can act as an anchor for further molecules which can attach to them and grow into a cluster. This process cannot be regarded as adsorption, in the sense that water is held directly by the adsorbent substrate, but rather as the growth of a “liquid-like” water cluster. One implication

of this is that this cluster growth does not conform to the conventional thermodynamics of adsorption, in which the amount adsorbed decreases with an increase in temperature. The significance of functional groups in water adsorption in porous carbons has been investigated in a number of computer simulations [11, 15, 17, 21, 22, 29, 35-38]. Several oxygen-containing groups (e.g. carboxyl [22], carbonyl [22, 39], and hydroxyl [15, 22] groups) have been studied for the effects of concentration and local distributions on the adsorption of water.

Clearly it is important, and could be critical in any application of carbon for the adsorption of mixtures involving water, to determine the concentration of functional groups. Several techniques, such as Boehm titration [40, 41], temperature programmed desorption [42], Fourier transform infrared spectroscopy [42, 43] and X-ray photoelectron spectroscopy [44] have been used. Among these Boehm titration is the most common, partly because of its relative simplicity, and partly because expensive and specialized apparatus may not be available in many laboratories. Even though Boehm titration is relatively simple, it involves wet chemistry, and for an accurate and reliable determination of the functional group concentration a large quantity of sample is required. Many of the advanced carbonaceous materials that have been recently synthesized, are often available only in small quantities; therefore determination of the functional groups on these small samples may be subject to large errors. Furthermore, the wet chemistry involved in Boehm titration changes the surface properties. To circumvent these problems we are proposing, in this paper, a new method for the estimation of functional group concentration. The idea is to determine the interaction between a water molecule and a functional group using a statistical mechanical calculation of the Henry constant between one water molecule and one functional group from the volume integration of the Boltzmann factor over the accessible space around the functional group.

2. Experimental

2.1. Materials

We used a range of porous carbons that have different concentrations of functional groups and different porous structures: (1) pitch-based activated carbon fibre (ACF), A-5 (supplied by Ad'all Co. in Japan), and (2) resorcinol-formaldehyde resin based carbon cryogels, RF-100 and RF-200, synthesized in our laboratories. The details of the synthesis of RF carbons are reported in previous publications [45, 46]. These carbons are mainly hydrophobic, and the surface oxygen groups are present only in small quantities and were identified as carboxylic, lactonic, and phenolic.

2.2. Measurement

Water adsorption on the porous carbons was measured at 263-298K using a constant volume adsorption apparatus (BELSORP-max, BEL Japan). Before each measurement, the samples were degassed at 473K for 5h under vacuum at pressures less than 0.1mPa to remove any physically adsorbed components.

The concentrations of surface functional groups were measured by Boehm titration [40] and are listed in Table 1. Approximately 0.1g of the adsorbent was added to excess (100cm³) standard base solution (0.01N NaOH, 0.001N Na₂CO₃, and 0.001N NaHCO₃), and the acidic oxides on the carbon surface were determined by back-titration with HCl after allowing the mixture to stand for 48h at 298K.

Table 1. Concentration of functional groups on A-5, RF-100, and RF-200 from Boehm titration

Adsorbent	Carboxylic [mmol/g]	Lactonic [mmol/g]	Phenolic [mmol/g]
A-5	0.103	0.000	0.184
RF-100	0.027	0.068	0.198
RF-200	0.012	0.100	0.176

3. Theory

Henry's law can be written in the form:

$$C = \frac{K}{R_g T} P \quad (1)$$

where C is the amount adsorbed, P is the absolute pressure, R_g is the gas constant, T is the temperature of the system, and K is the Henry constant. Since the gas phase is rarefied, it is assumed to be ideal in the above equation. If the amount adsorbed is expressed as mol/g of the solid, K will have unit of m^3/g .

The contribution to the Henry constant from one site is given by [3]:

$$K_\alpha = \iint_{\Omega} \exp[-\beta\varphi(\mathbf{r}, \boldsymbol{\omega})] d\mathbf{r} d\boldsymbol{\omega} - \iint_{\Omega} H[-\varphi(\mathbf{r}, \boldsymbol{\omega})] d\mathbf{r} d\boldsymbol{\omega} \quad (2)$$

where Ω is the domain accessible to the adsorbate molecule, $\beta = 1/k_B T$, φ is the potential energy of interaction between a water molecule, at the position \mathbf{r} , orientation $\boldsymbol{\omega}$, and the site, and H is a Heaviside step function. Here we use the symbol K_α , with the subscript α , to denote the Henry constant contributed by one functional group α in order to distinguish it from the experimental Henry constant K , which is a measure of the interaction between an adsorbate molecule and all the adsorption sites on the surface. K_α has the unit of m^3 per functional group.

Although the solid surface includes all accessible adsorption sites available to water, the exponential function in Equation (2) means that the strongest sites will dominate the Henry

constant. In the specific example of water on carbon adsorbents, these sites, as discussed above, will be the residual functional groups containing oxygen, rather than sites on the basal plane of the graphene layer.

The rigid non-polarizable SPC/E model [47] was used to model water. The model has a single LJ site located at the centre of the oxygen atom and three fixed point charges representing the charge distribution of the molecule. Two positive charges (q^+) are located at the centres of the hydrogen atoms, and a single negative charge (q^-) is located at the centre of oxygen atom; the molecular parameters of the SPC/E model are listed in Table 2.

Table 2. Molecular parameters of the oxygen functional groups [22] and water model [47]

Model	Interacting site	σ (Å)	ϵ/k_b (K)	q (e)
water	O	0.3166	78.2	-0.8476
	H	0.0	0.0	0.4238
carbonyl	C ^a	0.0	0.0	0.5
	O	0.296	105.8	-0.5
hydroxyl	C ^a	0.0	0.0	0.2
	O	0.307	78.2	-0.64
	H	0.0	0.0	0.44
carboxyl	C ^a	0.0	0.0	0.08
	C	0.375	52	0.55
	O(=C)	0.296	105.7	-0.5
	O(-H)	0.3	85.6	-0.58
	H(-O)	0.0	0.0	0.45

^a Carbon located in plane of graphene sheet.

The intermolecular interaction energy between a water molecule i and a functional group j ,

$\varphi_{i,j}$, is given by:

$$\phi_{i,j} = 4 \sum_{\alpha=1}^A \sum_{\beta=1}^B \varepsilon_{i,j}^{\alpha,\beta} \left[\left(\frac{\sigma_{i,j}^{\alpha,\beta}}{r_{i,j}^{\alpha,\beta}} \right)^{12} - \left(\frac{\sigma_{i,j}^{\alpha,\beta}}{r_{i,j}^{\alpha,\beta}} \right)^6 \right] + \frac{1}{4\pi\varepsilon_0} \sum_{a=1}^A \sum_{b=1}^B \frac{q_i^a q_j^b}{r_{i,j}^{a,b}} \quad (3)$$

where a parameter $X_{i,j}^{\alpha,\beta}$ is associated with a site α on i and a site β on j . The parameters $\sigma_{i,j}^{\alpha,\beta}$ and $\varepsilon_{i,j}^{\alpha,\beta}$ are the cross collision diameter and the cross well depth of interaction energy, respectively, and are calculated from the Lorentz-Berthelot rule. The parameter q_i^λ is the partial charge on the site λ of i , and ε_0 is the permittivity of a vacuum. Three oxygen-containing functional groups were considered in this study: carbonyl, hydroxyl, and carboxyl groups which are the most pronounced hydrophilic sites of carbon adsorbents [12, 41]. Their molecular parameters are also given in Table 2.

Figure 1 presents the schematic diagram of the simulation box containing one functional group attached to the edge of graphite whose structure consists of 11 Bojan-Steele surfaces finite in the z -direction and infinite in the x -direction. These surfaces were positioned parallel to each other and perpendicular to the XY plane. The Bojan-Steele potential [48-51] was used to describe the interaction energy of water and Bojan-Steele surface, the results are presented in Figure 2. It is seen that the potential profile has a wave shape, which is a characteristic of the edges of graphene layers.

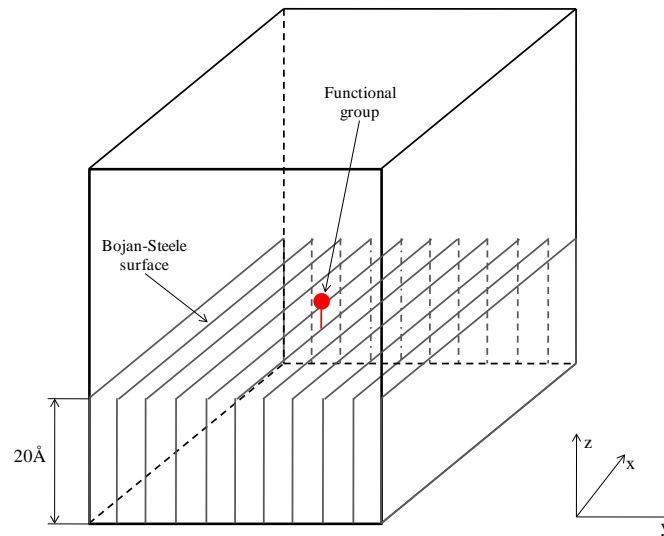


Figure 1: Schematic diagram of the simulation box containing one functional group attached to the edge of graphite consisting of 11 Bojan-Steele surfaces

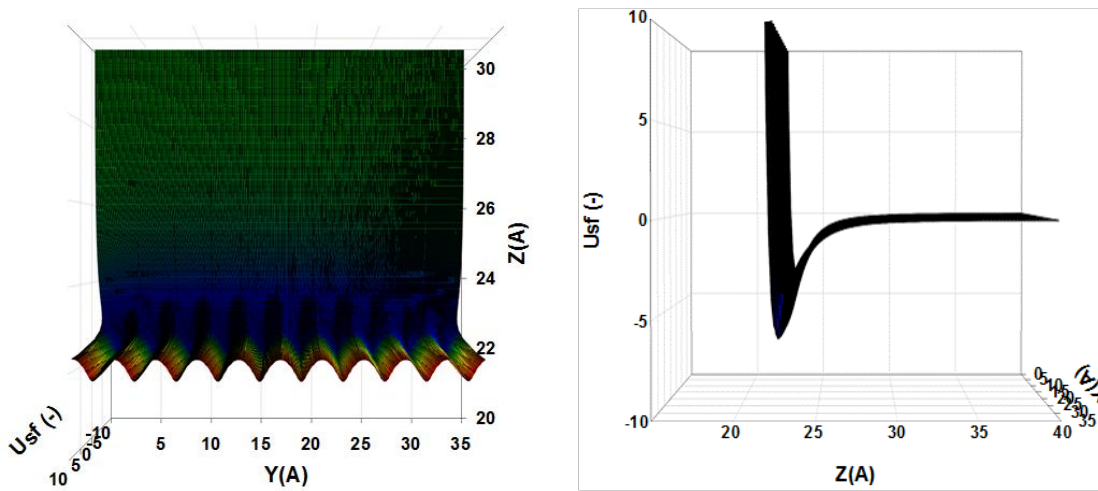


Figure 2: Solid-fluid potential profile for water on pure graphite consisting of 11 Bojan-Steele surfaces.

The theoretical Henry constants contributed by one functional group, carbonyl, hydroxyl, carboxyl, whose side views are shown in Figure 3, are shown in Figure 4 for a range of temperature. At the temperatures studied (263-298K) the carboxyl group gives the highest K_a , which is about two orders of magnitude higher than the carbonyl and hydroxyl groups.

Therefore, if the adsorbent contains carboxyl groups, water molecules will tend to cluster around carboxyl groups, irrespective of the presence of other functional groups unless their concentrations are at least two orders of magnitude greater than that of the carboxyl group. It has also been reported in the literature that carboxyl groups exhibit the highest affinity towards water molecules [12, 41]. Therefore, water adsorption on carbon adsorbents that have carboxyl groups and other oxygen groups attached, is dominated by the interaction between water and carboxyl groups at zero loading.

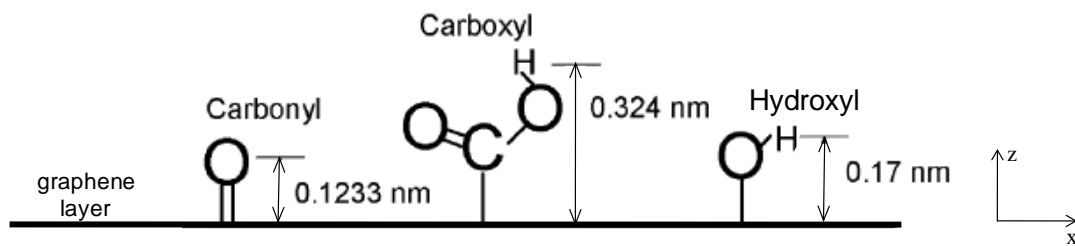


Figure 3: Side projections of functional groups attached at the edge of graphene layer

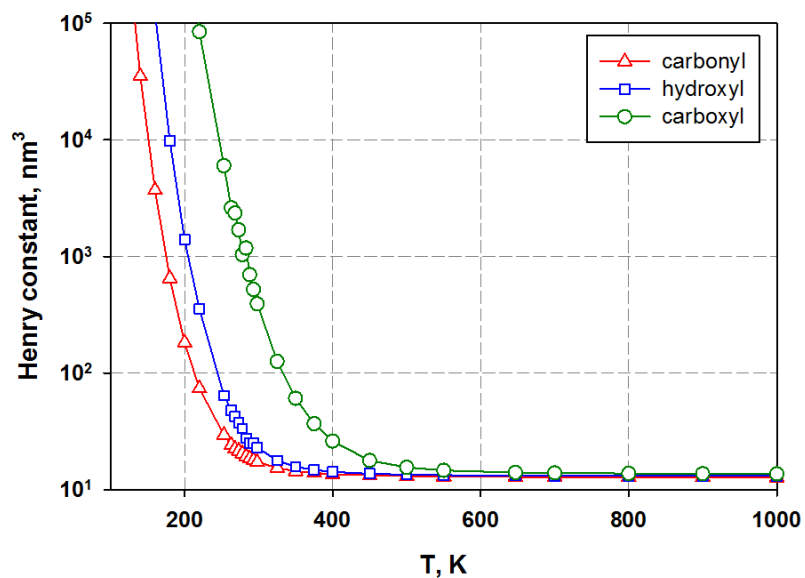


Figure 4: Theoretical Henry constant K_a contributed by functional groups as a function of temperature: carbonyl (triangles), hydroxyl (rectangles) and carboxyl (circles)

Knowing the experimental K and theoretical K_α contributed by a carboxyl group, the concentration C_α of carboxyl groups on the carbon can be calculated in mol/g from:

$$K = C_\alpha K_\alpha N_A \quad (4)$$

where N_A is the Avogadro number.

4. Results and discussion

Water adsorption isotherms at various temperatures on the porous carbons, A-5, RF-100 and RF-200, are presented in Figure 5. The insets show the isotherms at low pressure on a log-log scale and can be seen to obey Henry's law initially.

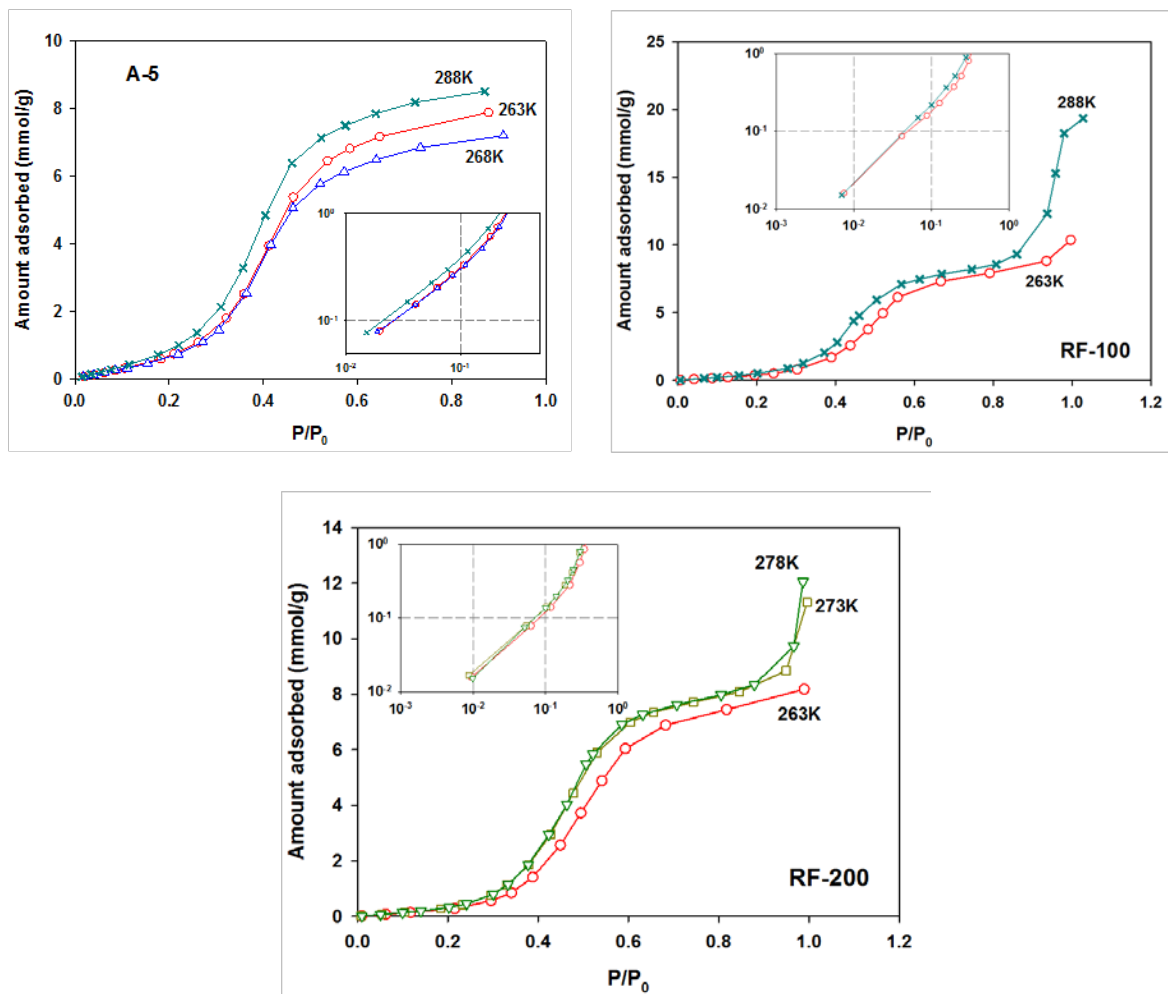


Figure 5: Adsorption isotherms of water on porous carbons: (a) A-5, (b) RF-100 and (c) RF-200

The experimental Henry constants at various temperatures calculated from eq. (1) for water adsorption on these three carbons are tabulated in Table 3, together with the theoretical Henry constant, K_a , contributed by one carboxyl group. To obtain these values of K_a by Monte Carlo integration (eq. 2) we assumed that the carboxyl group is rigid with the hydrogen atom positioned in the same plane as the other atoms giving a C-C-O-H dihedral angle of 180° . The concentrations of carboxyl groups on A-5, RF-100 and RF-200 computed by eq. (4) are given in Table 4. These concentrations are much higher than those measured by Boehm titration.

Table 3. Experimental Henry constant (m^3/g) of A-5, RF-100, and RF-200 and theoretical Henry constant, K_a ($10^{27}\text{m}^3/\text{functional group}$) at various temperatures

	263K	268K	273K	278K	288K
A-5	0.0275	0.0175	-	-	0.00561
RF-100	0.018	-	-	-	0.003
RF-200	0.0105	-	0.0055	0.0038	-
K_a	3079.47	2502.94	1428.61	1110.82	761.14

Table 4. Estimated concentration of carboxyl groups (mmol/g) of A-5, RF-100, and RF-200 with the C-C-O-H dihedral angle of carboxyl model equal to 180°

Adsorbent	263K	268K	273K	278K	288K	Average	Exp.
A-5	14.83	11.61	-	-	12.24	12.89	0.103
RF-100	9.71	-	-	-	6.55	8.13	0.027
RF-200	5.66	-	6.39	5.68	-	5.91	0.012

The carbon atom in the carboxyl group is sp^2 , therefore the carbon and oxygen atoms of this group are positioned in the same plane as the carbon atom attached to the graphene layer, but the O-H group can be rotated about the C-O bond which changes the dihedral angle of the carboxyl group and therefore the Henry constant, as illustrated in Figure 6. The maximum value of the Henry constant is found when the dihedral angle is in the narrowly distributed range centered at 100° . This angle will therefore correspond to the optimum configuration

and will be maintained when water clusters are formed. The Henry constant K_a for the optimum configuration is almost 5 times larger than that for the dihedral angle of 180 degree which gives concentrations of carboxyl groups almost 5 times smaller as shown in Table 5. However, these concentrations are still higher than the experimental values.

Table 5. Estimated concentrations of carboxyl groups (mmol/g) of A-5, RF-100, and RF-200 with the C-C-O-H dihedral angle of carboxyl model equal to 100 degree

Adsorbent	263K	268K	273K	278K	288K	Average	Exp.
A-5	2.75	2.84	-	-	3.08	2.89	0.103
RF-100	1.80	-	-	-	1.65	1.72	0.027
RF-200	1.05	-	1.23	1.07	-	1.12	0.012

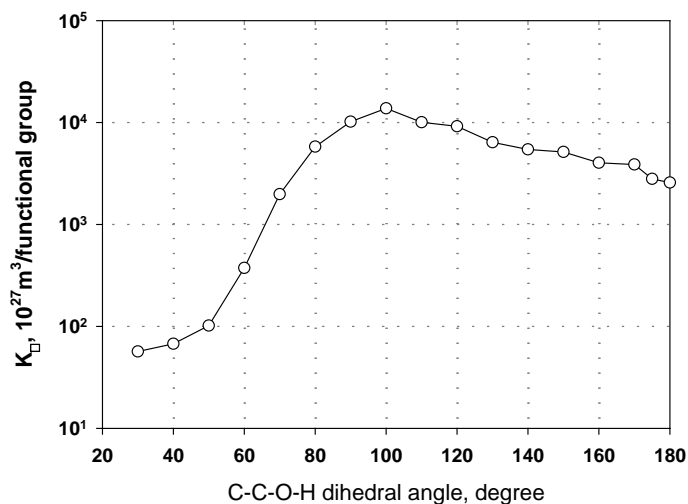


Figure 6: Theoretical Henry constant for a carboxyl group at 263K, as a function of the C-C-O-H dihedral angle

The partial charges used for the carboxyl group in this study were taken from the OPLS potential model of acetic acid [22]. It is possible that these partial charges would be increased when the group is attached to a graphene edge site. Furthermore when a carboxyl group is positioned close to weaker groups, such as carbonyl or phenolic, its partial charges could be enhanced. Therefore, we introduce a factor, F , to estimate the average interaction between a water molecule and a carboxyl group.

$$\Phi_{i,j} = F \cdot \varphi_{i,j} \quad (5)$$

The carboxyl group concentrations estimated for A-5, RF-100 and RF-200 with $F=1.15$ and a C-C-O-H dihedral angle of 100 degree are 0.11, 0.08 and 0.04mmol/g, respectively (Table 6). The corresponding values measured by Boehm titration are 0.103, 0.027 and 0.012mmol/g. Our method gives an excellent agreement with the Boehm titration for A-5, but overestimates the concentrations of carboxyl group in RF-100 and RF-200 as measured by Boehm titration. This difference could be due to a number of factors: (1) uncertainty in the Boehm titration because of the very low concentration of carboxyl groups, and (2) the under-estimation of the partial charges for the RF carbons.

Table 6. Estimated concentrations of carboxyl groups (mmol/g) of A-5, RF-100, and RF-200 with the C-C-O-H dihedral angle of carboxyl model equal to 100° and factor $F=1.15$

Adsorbent	263K	268K	273K	278K	288K	Average	Exp.
A-5	0.12	0.08	-	-	0.14	0.11	0.103
RF-100	0.08	-	-	-	0.08	0.08	0.027
RF-200	0.05	-	0.04	0.03	-	0.04	0.012

5. Conclusions

A new method using water as a molecular probe is proposed to determine the concentration of surface functional groups containing oxygen on a carbon adsorbent. This method is fast and simple to implement experimentally. The results obtained are in fair to good agreement with those measured by the Boehm titration. Moreover, this method can be applied to adsorbents containing a small amount of functional groups where Boehm titration fails.

Acknowledgement: This work is supported by the Australian Research Council. This work was partially supported by the Japan Society for the Promotion of Science, Grant-in-Aid for Young Scientists (B), 24750146.

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