

Adsorption of Anionic Surfactant by Activated Carbon: Effect of Surface Chemistry, Ionic Strength, and Hydrophobicity

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Received March 3, 2001; accepted August 4, 2001

This work investigates the interrelationship between the adsorbent surface chemistry and relative hydrophobic nature and the solution ionic strength and solution hydrophobicity during dilute anionic surfactant solution adsorption. The adsorbents were coconut- and coal-based, steam-activated carbons and wood-based, acid-activated carbons. The adsorptives were dodecanoic acid and octanoic acid dissolved in water or strong caustic solution. The activated carbons (ACs) were immersed in the strong caustic solution at different temperatures for various lengths of time prior to adsorption measurements. The oxygen content and surface functional group chemistry of each AC sample was analyzed using elemental analysis and X-ray photoelectron spectroscopy. The equilibrium solution concentration of each surfactant was determined using gas chromatography–flame ionization detection techniques. The amount of surfactant adsorbed by each AC indicates that an inverse linear relationship exists between the amount of surfactant adsorbed and the adsorbent oxygen content. Although the steam-activated carbons offer lower pore volumes than the acid-activated carbons, they exhibit the higher adsorption capacity. The high solution chemistry pH promotes adsorbent surface oxidation and anionic surfactant dissociation, leading to an interfacial repulsion force and decreased C₁₂- and C₈-acid adsorption. Overall, this study demonstrates that both the surface chemistry and the solution properties should be considered for an adsorption analysis since each has a significant influence on the adsorption process.

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Key Words: activated carbon; oxygen content; surface functional groups; anionic surfactant adsorption; porous carbons.

INTRODUCTION

Surface-active agents, or surfactants, are used widely in many industrial and commercial products and processes throughout the world. Surfactants are not only related to soaps and detergents in daily life, they are also in heavy demand for industrial processes requiring colloid stability, metal treatments, mineral flotation, pesticides, oil production, pharmaceutical formulation, emulsion polymerization, and particle growth (1, 2). The broad range of surfactant applications may also cause side effects in the

environment and in these industrial processes. The application of surfactants can also produce environmental pollution and raises a series of problems for wastewater treatment plants (3). Furthermore, surfactants adsorb readily on crystal surfaces owing to their surface activity, leading to crystal growth inhibition (4–6). From this perspective, surfactants should be removed from selected stages of the industrial process or wastewater emission systems.

Surfactant adsorption has been studied extensively. Additionally, several materials have been investigated as surfactant adsorbents. These include layered double hydroxides (1, 7), zeolites (7, 8), silica (9), mineral oxides (alumina) (1, 6, 7, 10–12), polymers (13), natural and synthetic fibers (14), and activated carbons (ACs) (8). Different adsorption mechanisms and models have been proposed, depending on the adsorbent–adsorbate system. The different surface chemistry as well as the different physical properties of the above adsorbents affect the surfactant adsorption mechanism. These differences are especially manifest during adsorption processes occurring during “critical” industrial conditions, such as sugar crystal growth and crystal recovery.

AC is used as an adsorbent in many industrial applications as an economic mass separation agent to raise the final product quality. Drinking water and wastewater treatment processes and the food and chemical industry processes are typical examples (15–18). More recently, ACs are increasingly used as adsorbents for the purification of process streams *within* industrial chemical processes, again owing to their high adsorption efficiency (19). Rudzinski and co-workers have investigated AC to adsorb organic impurities from liquid solution (20). Mechanisms of adsorption in the systems were proposed based on a multi-site occupancy model of an energetically heterogeneous AC surface. As mass separation agents ACs present useful physical and chemical properties. These include high specific surface areas (typically between 1000 and 2000 m² g⁻¹), wide pore size distributions (including micropores and mesopores) (17, 18, 21–26), hydrophobic surfaces (27), and variable surface functional groups (21, 26, 28). Each property supports the application of ACs as adsorbents for surfactant concentration reduction or removal.

Most commercially available ACs are generated from low-cost materials of high carbon content, such as coconut shells, agricultural waste, coal, and wood. From the adsorption experimental point of view, the relatively hydrophobic character and

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high specific gravity of ACs makes their separation from the solution phase a simple operation (21). The physical properties of ACs mentioned above, as well as their relatively inexpensive availability, make them suitable for use as adsorbents in large-scale continuous processes. If the industrial uses involve high-temperature calcination processes (over 800°C), then the AC can be discarded by incineration, particularly if the AC produces a low ash content (4). Otherwise, relatively moderate regeneration processes need to be developed that impress minimal impact on the principal property used in the adsorption process.

Previous research has demonstrated that the carbon matrix often contains oxygen, nitrogen, hydrogen, phosphorus, and/or sulfur (16–18, 21, 29). Oxygen is an important element that can form surface functional groups bonded on the edge of carbon, with the graphitelike crystallites offering properties that may be interpreted from a study of organic functional group chemistry (15–18, 26). The most commonly encountered oxygen functional groups are carboxylic acid, carbonyls, phenols, and lactones (15, 16, 18, 26, 30). The proportion or concentration of these groups on the AC surface depends on the precursor material and on the activation method (17). The presence and concentration of surface functional groups affect the relative hydrophobicity of the AC, and thus play an important role in influencing the adsorption capacity and the mechanism for adsorptive removal (18, 25, 27).

A considerable amount of research has been published where an AC has been used as the adsorbent in dilute aqueous solutions and in mixtures of pure solvents. In contrast, very few publications exist that discuss solution adsorption in extreme pH conditions, such as $\text{pH} < 1$ or $\text{pH} > 13$. Part of this literature recognizes the fact that surfactant adsorption is a complex process (7). It is well-known that the surface charge of an AC is pH dependent, which will affect the mechanism of surfactant adsorption (31). The study of surfactant adsorption based on an electrostatics interaction mechanism has been well developed (1, 2, 6, 32, 33). However, few studies include anionic surfactant adsorption. We have not identified any literature discussing anionic surfactant adsorption by ACs from solutions of extreme pH, > 14 . This paper discusses the recent findings for such a system. The anionic surfactants of interest are dodecanoic and octanoic acids adsorbed by a coconut-, a coal-, and a wood-based AC, exposed to three different treatments. To investigate the effect of high ionic strength and pH conditions on adsorption, we adsorb these surfactants from a continuous phase of either a caustic solution ($\text{pH} > 14$) or a water phase. The information presented in this paper will lead to a better understanding of the mechanism of surfactant adsorption by these ACs by clarifying the roles of adsorbent porosity and surface chemistry and the continuous phase solution properties on the surfactant adsorption process.

MATERIALS AND METHODS

Solutions were prepared using organic molecule-free 18-M Ω resistance water produced by a Milli-Q water purification sys-

tem. All chemicals used in this work were supplied as analytical grade (Sigma–Aldrich, Australia) and used without further purification. High-purity, instrument-grade hydrogen, oxygen, and nitrogen gases, which were supplied by CIG (Australia) as 99.99% purity without further purification, were used for gas chromatography GC and X-ray photoelectron spectroscopy XPS analysis. All the glassware used was cleaned with a permanganic acid solution and rinsed with Milli-Q water, followed by placement in a furnace at 450°C for 4 h to remove residual adsorbed surfactant and organic materials.

Activated Carbon Samples

Three AC samples (carbon A, B, and C) are chosen for this study. The coconut-based, steam-activated carbon A, and the wood-based, phosphoric acid-activated carbon C were supplied by PICA (Australia). Char Processors (Western Australia) provided sample B as a coal-based, steam-activated adsorbent.

All three AC samples were prepared separately under three different conditions prior to use in the experiments described herein. The ACs were washed with the Milli-Q water to remove any residual, physically adsorbed activating chemicals to provide a reproducible surface for the solution adsorption measurements. Washing was continuous until the effluent conductivity matched the influent value. After washing, these samples were oven-dried overnight at 110°C and stored in a desiccator until used. Such samples are referred to as washed (-W) sample.

Portions of the washed carbons were exposed to 2 M sodium hydroxide (NaOH) solution as a preparation to investigating whether the surface chemistry and/or adsorption capacity of the ACs was affected by contacting either carbon with this caustic solution. This exposure involved two different processes: either immersion in NaOH at 25°C, or refluxed in 2 M NaOH solutions. The former treatment consisted of thoroughly mixing the samples in 2 M NaOH solution for 24 h at 25°C. After this treatment, the samples were filtered, washed, and dried as per the original samples and stored in a desiccator. These samples are referred to as treated (-T) samples. The latter treatment process involved suspending each AC sample in 2 M NaOH and refluxing for 4 h at ambient pressure. After this period, the samples were washed and dried as per the original sample and stored in a desiccator. These samples are referred to as refluxed (-R) samples.

Surfactant Adsorption

Two anionic surfactants used in this study were dodecanoic acid (C_{12}) and octanoic acid (C_8) with $> 99.0\%$ purity, supplied by Sigma (Aldrich, Australia). Dodecanoic acid is representative of the surfactant mixture found in a typical Bayer alumina process stream. The C_{12} acid exhibits very low solubility in pure water (≈ 0.4 mg/L), but dissolves readily in 2 M NaOH solution up to 1.0 mg/L. To prepare 1.0 mg (C_{12})/L solutions, 20 mL/L *iso*-propanol (IPA) was added, greatly improving C_{12} solubility. Since the C_8 acid is more soluble than C_{12} , no IPA was required to prepare solution concentrations up to 1 mg (C_8)/L in either solvent system.

Adsorption was carried out using a batch method with the surfactant adsorption isotherms determined in the same manner. In each case, a mass of AC, 0.50–1.40 mg, was accurately weighed using a Cahn microbalance. The AC samples were placed separately into 40-ml vials. A series of aqueous surfactant solutions was prepared, with various initial concentrations ranging from 0.1 to 1.0 mg/L. A fixed volume of solution (35 ml) was transferred to the vials containing the carbon. The solid–solution system contained in the vials was mixed well by tumbling end-over-end on a rotating wheel maintained at a constant temperature of 25°C. After 24 h, the carbons were removed from the surfactant solution using centrifugation at a rotation speed of 3000 rpm. A portion (25 ml) of this separated solution phase was then transferred to clean vials. The surfactant concentration in the equilibrium solution was determined using GC and a pre-determined calibration curve. Isotherms were constructed from a mass balance analysis.

The residual dissolved surfactants (either C₁₂- or C₈-acid) were extracted from the aqueous solutions using methyl-*t*-butyl ether at pH <1. The surfactants dissolved in the organic phase were then reacted with diazomethane (CH₂N₂) to convert the polar surfactant molecules to nonpolar methylated molecules. These methylated surfactants gave a sharp peak when separated on the nonpolar GC column. A HP 5890 series II gas chromatograph with a flame ionization detector was used to determine the peak profile, and hence the surfactant concentration. We used a BPX5 column (SGE, Australia) for surfactant separation measuring 25 m long and 0.22 mm in diameter. The packing had an effective film coating thickness of 0.25 μm.

Activated Carbon Micropore Volume Analysis

The pore volumes of the ACs were evaluated from nitrogen adsorption isotherms measured at 77 K, using a computer-controlled, stainless steel volumetric instrument employing a static equilibrium measurement methodology. Samples were outgassed at 398 K for 12 h to a background pressure <5 × 10⁻⁶ Torr (34). Adsorption capacities in terms of micropore volumes and mesopore volumes were calculated by applying the α_s method (35). The amount adsorbed was converted to liquid volume using a molar volume of liquid nitrogen of 35 cm³ mol⁻¹.

Surface Functional Groups and Oxygen Content

AC surface functional groups were determined using X-ray photoelectron spectroscopy (XPS). These analyses were performed using a PHI model 5600 hemispheric electron spectrometer with the pass energy set at 18 eV for surface analysis and 26.8 eV during depth profiles. The X-ray source was non-monochromatized K_α operating at 300 W. The main chamber pressure was ≈10⁻⁹ Torr. The spectrometer energy scale was calibrated using the Fermi edge and the 3d_{5/2} line (367.9 eV) for silver. Complementing this calibration, the retardation voltage was calibrated from the positions of the Cu 2p_{3/2} (932.7 eV) and Cu 3p_{3/2} (75.1 eV) peaks relative to the expected voltages.

The resultant position of the C_{1s} photo-peak due to adventitious hydrocarbon was found at 284.8 eV. A 45° takeoff angle was employed in all XPS measurements. The photo-peak area was used to calculate the atomic concentrations for each element. The listed sensitivity factors were based on both the instrument and stand-alone data analysis software.

In combination with the XPS analyses, an elemental analysis was also performed. This analysis gave a higher sensitivity for the element quantitative analyses, especially for the oxygen content analyses. The elemental analysis was performed using a CamScan CS44 FE instrument, with the samples being attached to a stub via double-sided tape. The element contents of carbon, oxygen, and phosphorous in the AC sample were measured using a 10–20 kV acceleration voltage, with the X rays analyzed at a takeoff angle of 48.6°.

RESULTS AND DISCUSSION

Correctly interpreting surfactant adsorption in an aqueous solution is a complex and challenging procedure. The multicomponent nature of the adsorptive system leads to complex interactions between the surfactant adsorptive and the AC adsorbent. Various mechanisms are involved (7). The physical and chemical characteristics of each AC also affect surfactant adsorption. To present a systematic analysis of the surfactant–AC system, we begin by addressing the influence of the solvent conditions on AC physical and chemical properties. Once these details are established, we define the adsorption isotherms and interpret the amount adsorbed in terms of the adsorbent properties and in terms of the solution properties, from which we propose a systematically derived, qualitative mechanism for C₁₂ and C₈ adsorption.

Activated Carbon Characterization

The pore volumes of the ACs (A, B, and C) that were treated by the three different procedures are summarized in Table 1. Micropore volumes were determined from α_s analyses of each isotherm, prepared by comparing the amount adsorbed with

TABLE 1
The Volumes of Total Pore, Micropore, and Mesopore Assessed From the α_s-Plot Method Using W, T, and R Samples of Carbon A, B, and C

Carbon	V _{total} (ml/g)	V _{micro} (ml/g)	V _{meso} (ml/g)
A-W	0.74	0.69	0.04
A-T	0.76	0.70	0.06
A-R	0.75	0.68	0.07
B-W	0.87	0.44	0.43
B-T	0.95	0.46	0.49
B-R	0.97	0.43	0.54
C-W	1.30	0.48	0.82
C-T	1.20	0.50	0.69
C-R	1.19	0.58	0.61

standard adsorption data obtained from a certified nonporous carbon black (34). Examination of Table 1 shows that carbon A offers the highest micropore volume, carbon B the least, and carbon C an intermediate volume. In contrast, the order of the *total* pore volume is $C > B > A$. A comparison of the total pore volume of each carbon shows that carbon A is the least sensitive to the strong base treatments. The data in Table 1 also suggest that the mesopore volume of sample A is negligible compared with its total pore volume and that of samples B and C.

The nitrogen adsorption data for carbon B reflects a modest absolute change to the mesopore volume after exposure to either strong base treatment condition. There is a 12% *relative* increase in total pore volume after reflux. The micropore volumes remain essentially constant. The overall changes for sample B-T and B-R suggest that the temperature of the treatment has more effect on the total pore volume than the length of time of exposure to the caustic conditions. The increased pore volume suggests that either some new mesopores form during the caustic treatment or some carbonaceous material or functional groups initially blocking the entrance to some mesopores may be removed during the strong caustic treatment. Recently, we showed that the Horvath–Kawazoe method of micropore width distribution analyses for these B-samples exhibits a relative widening of the width distribution, accompanied by a modest decrease in the relative volume adsorbed with pore width (36).

Of the three carbons studied in this work, carbon C is the most affected by the base treatment, especially after the re-

flux treatment, sample C-R. The micropore volume for samples C-T and C-R increase 4% and 21%; however, mesopore volumes show a relative decrease of 18% and 34%. Since the mesopore volume is considerably larger than the micropore volume, and has a greater impact on the total pore volume, there is an overall decrease (8%) in the total pore volume. To appreciate the causes of these changes, we should consider the source of activation (phosphoric acid) and the possibility of residual acidic surface functional groups, not removed during water washing, reacting with sodium hydroxide solution. We suggest that the residual acid groups react with the strong base at room temperature, resulting in selective dissolution or leaching of some chemically bound phosphate groups. Some mesopores possibly fracture, and some of the smaller mesopores may develop into micropores during the treatment condition.

Activated Carbon Surface Chemistry

AC surfaces exhibit chemical heterogeneity due to the presence of several types of heteroatoms, oxygen, nitrogen, hydrogen, phosphorus, and/or sulfur, contained within the carbon matrix (16–18, 21, 29). Oxygen offers a strong influence on solution adsorption, especially when it is bonded to an edge within the carbon surface (15–18, 21, 26).

XPS was employed to evaluate the surface chemical structure of the ACs used in this study. Figure 1 shows a representative XPS spectrum. We applied the spectrum of various C–O and C–C structures to deconvolute the C_{1s} spectrum. Consequently,

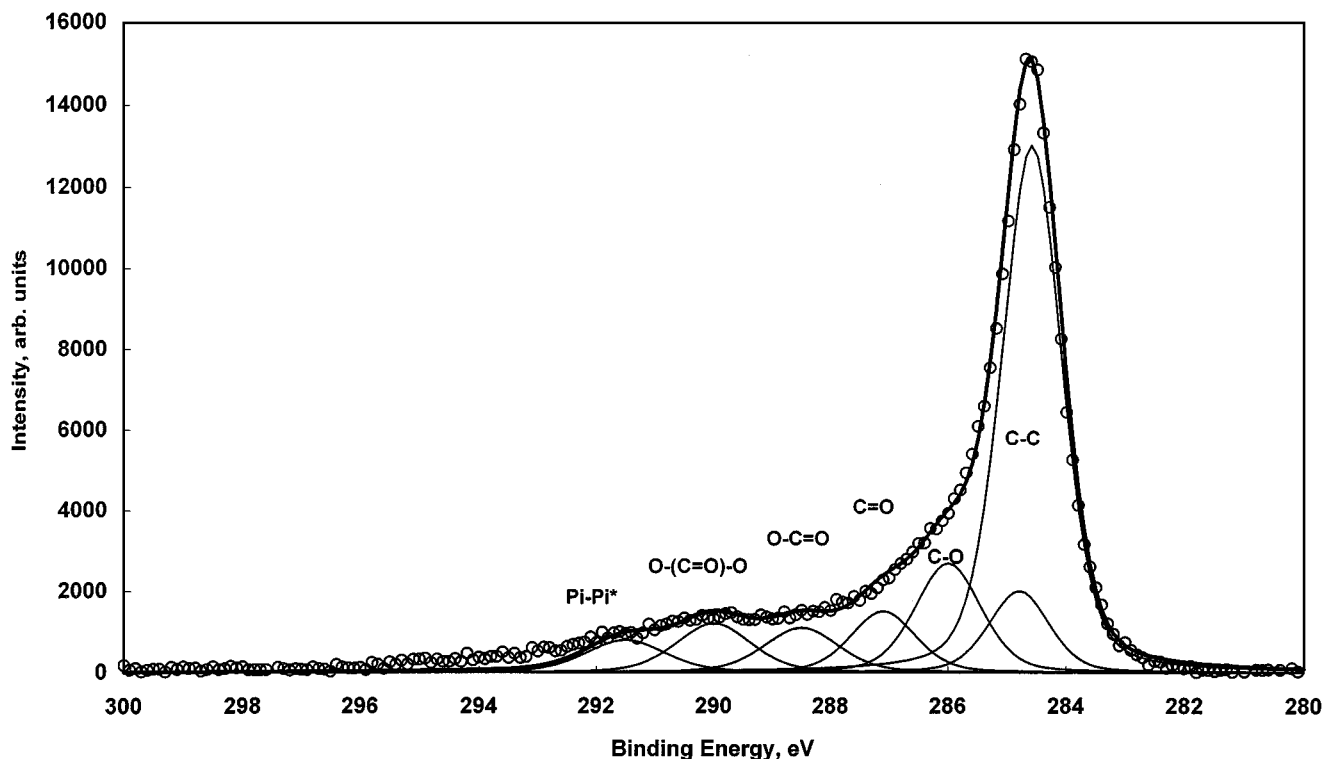


FIG. 1. Deconvolution of the XPS spectrum of sample B-W carbon-peak area into its functional groups.

from the XPS analyses, we suggest the presence of Pi–Pi* aromatic, graphitic, and aliphatic carbon structures coupled with ether or cyano (C–O–R/C–N), carbonyl (C–O), acid (O–C–O), and anhydride (O–(C–O)–O) structures. Toles *et al.* (30) and Solum *et al.* (37) used X-ray diffraction methods to analyze the structure of ACs and found that oxygen acts as a cross-linking element located between disordered polyaromatic sheets. These functional groups are consistent with the titration methods pioneered by Boehm (15) and promulgated more recently by Bandosz (17). Base titration methods react “specifically” to indicate the presence of carboxylic, carboxylic anhydride, ether, carbonyl, phenol, lactol, and lactone groups (15, 16, 18, 26, 30).

The concentration of each functional group determined from XPS spectra is listed in Table 2. The results show that the graphitic structure in the acid-activated carbon C is $\approx 37\%$ of the steam-activated carbons (A and B). In contrast, the concentration of C–C/C–H (aliphatic) structure in carbon C is approximately five times higher than that of A and B. Also, carbon C shows a higher concentration ratio for C–O–R/C–N, C–O, O–C–O, and Pi–Pi* structures. For example, these structures in C–W are, respectively, ≈ 20 , 28, 38, and 16% higher than in A–W or in B–W. The activation method is probably responsible for these differences. We conclude that phosphoric acid-activation creates greater oxygen functionality than steam-activation methods. In general, both carbons A and B have a higher carbon content and lower impurities, such as chemisorbed oxygen, than does carbon C. It is interesting to note that the contribution from the carboxylic group to the C_{1s} spectrum of carbon C decreases with increasing base treatment. Presently, we cannot determine whether this decrease is due to the fact that this is a wood-based carbon or whether it is because this is an acid-activated carbon. Both carbons A and B also contain a percentage of carboxylic groups but their contributions are not affected to the same extent as that of carbon C.

An elemental analysis was made of each AC to determine how the overall oxygen content for each carbon sample may be affected by NaOH treatment. These results are shown in Table 3. Again, carbon C has the highest oxygen concentration and A has the lowest, by as much as 30% of that of carbon C. Carbon

TABLE 3

The Oxygen Content of W, T, and R Samples of Carbon A, B, and C

Carbon	A-W	A-T	A-R	B-W	B-T	B-R	C-W	C-T	C-R
Oxygen (%)	5.3	5.9	5.7	8.8	8.0	7.5	15.9	22.6	18.4

B is intermediate. Similar conclusions can be drawn from the analyses after caustic solution treatment at 25°C. In this case, treatment has a significant influence on oxygen content of the T samples, which may indicate that more surface oxygen groups form after contact with the 2 M NaOH at 25°C for 24 h. This observation suggests that the length of time for carbon contact with NaOH solution influences oxygen functional group creation more than higher temperature, where the oxygen content decreases for each sample.

Effect of Surface Chemistry on Surfactant Adsorption

Pendleton and co-workers (27, 28) and others (38) demonstrated that AC surface chemistry is more important than pore-size distribution in controlling the adsorption of a relatively hydrophobic molecule from dilute aqueous conditions. It is well established that polar molecules interact strongly with polar sites on a surface (39, 40). Previously, Pendleton *et al.* illustrated that the amount of water vapor adsorbed is directly proportional to a carbon's surface–oxygen content (27, 40). Barton and Koresh (39) made similar observations for nitric acid-oxidized carbon cloth. Pendleton *et al.* indicated that a correlation exists between the surface concentration of ionizable groups (determined via conductometric titration) and the B-point amount of water vapor adsorbed by various activated carbons (27, 40). When adsorption occurs from a dilute aqueous surfactant solution, we need to test if the surface oxygen groups that act as “high-energy” adsorption sites for water-vapor molecules manifest themselves as a source of specific interaction during surfactant adsorption.

Figure 2 shows adsorption isotherms for C_{12} acid on carbons A–W, B–W, and C–W from 2 M NaOH solution. The

TABLE 2
The Concentration of AC Functional Groups From the XPS Analysis

Functional group	Graphic	C–C	C–O–R	C–O	O–C–O	O–(C–O)–O	Pi–Pi*
A–W	59.9	7.5	12.0	6.7	5.2	4.9	3.7
A–T	58.8	5.9	13.2	7.4	5.9	5.1	3.7
A–R	59.2	8.2	12.5	5.9	5.6	4.6	3.9
B–W	58.3	9.0	12.0	6.7	4.9	5.4	3.6
B–T	57.4	10.1	12.1	6.5	5.1	5.2	3.6
B–R	56.9	10.8	12.0	6.6	5.4	4.8	3.6
C–W	20.1	40.3	14.4	8.6	7.2	5.0	4.3
C–T	22.3	39.1	15.6	7.8	6.7	5.0	3.4
C–R	23.5	37.4	15.0	8.6	6.4	4.8	4.3

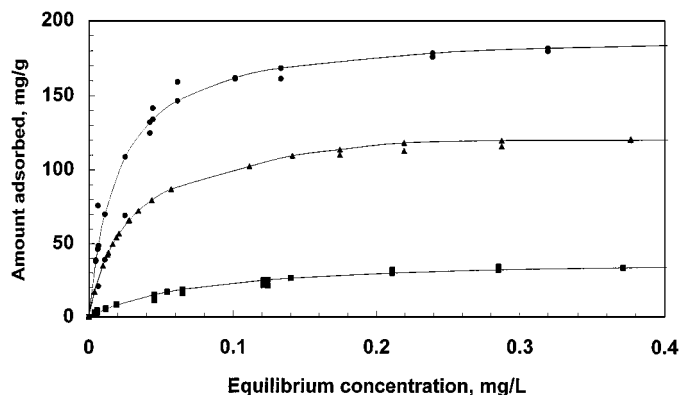


FIG. 2. Surfactant (C_{12}) adsorption isotherms on carbon A–W (●), B–W (▲), and C–W (■) in 2 M NaOH solution at 298 K.

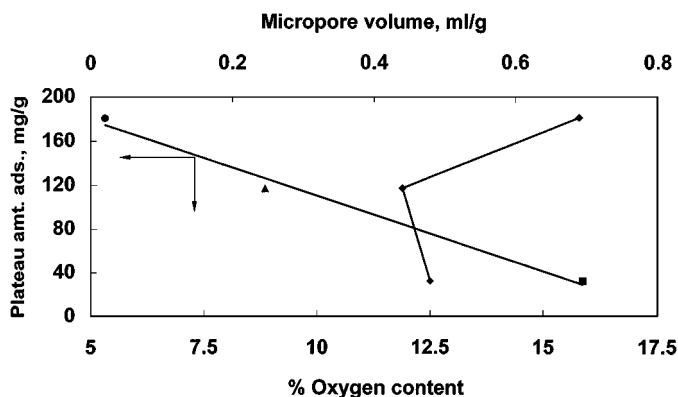


FIG. 3. Correlation between the amount of surfactant (C_{12}) adsorbed at 0.3 mg/L with oxygen content on carbon A (●), B (▲), and C (■) and with micropore volume (◆).

adsorption isotherms reach a plateau amount adsorbed for A, B, and C at ≈ 181 , 117, and 32 mg/g carbon supported by an equilibrium solution concentration of 0.4 mg/L. The general shape of the carbon A and B isotherms suggests that these two carbons have a high affinity for C_{12} , demonstrated by the relatively large amount adsorbed at very low equilibrium solution concentrations. By comparison, the carbon C adsorption isotherm is not regarded as a high-affinity isotherm. Similar results were obtained for the treated and refluxed samples of each carbon. In general, we conclude from these isotherms that carbon A offers the highest affinity and capacity for C_{12} , B is intermediate, and C has the lowest affinity and capacity, irrespective of treatment conditions.

Two contrasting plots of the C_{12} plateau amounts adsorbed for carbons A-W, B-W, and C-W with their oxygen content and with their micropore volume are presented in Fig. 3. The amount of adsorbed C_{12} for each AC may be expressed as inversely proportional to the oxygen content of the adsorbent. The linear regression analysis correlation coefficient, r^2 , for these data is 0.9881. Clearly the higher the carbon oxygen content, the lower the amount of surfactant adsorbed. In contrast, there is no obvious correlation between the amount of surfactant adsorbed and the adsorbent micropore volume. We also suggest that the nature of the precursor material bears no influence on the adsorption process.

Figure 4 shows a plot of the C_{12} adsorption isotherms for carbon C-W, C-T, and C-R from the water phase. Carbon C-W adsorbed the most surfactant, with a plateau at ≈ 77.1 mg/g carbon, while C-T adsorbed the least amount, ≈ 42.6 mg/g, and C-R is intermediate, with a plateau amount adsorbed at ≈ 61.5 mg/g. In Fig. 5 we consider the same starting material to test the suggestion that the precursor material bears no influence on C_{12} adsorption. In comparison with the data in Fig. 3, we consolidate our evidence that the adsorbent surface chemistry influences C_{12} adsorption. Figure 5 shows the plateau amount adsorbed at an equilibrium solution concentration of 0.3 mg/L as a function of the oxygen content of C-W, C-T, and

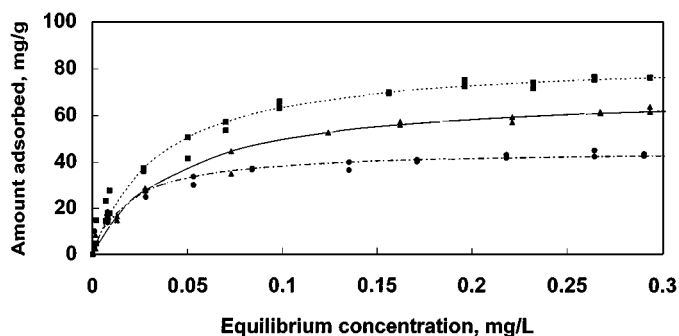


FIG. 4. Surfactant (C_{12}) adsorption isotherms on carbon C-W (.....) (■), C-T (---) (●), and C-R (—) (▲) samples in pure water phase.

C-R. Again, an excellent inverse linear correlation exists ($r^2 = 0.9972$).

During water-vapor adsorption, oxygen groups on the carbon surface usually act as the primary adsorption centers. In solution adsorption, one expects the water molecules to show a greater affinity for surface oxygen groups via hydrogen bonding (27, 28) than the more hydrophobic C_{12} surfactant molecules. In both vapor and solution adsorption, the adsorbed water molecules act as polarized secondary adsorption centers, promoting further water-molecule adsorption and cluster formation. These clusters form an envelope extending beyond the localized adsorption centers, reducing the available surface area for adsorption of other adsorptives. Generally, if there is to be adsorption of the adsorptive, part or all of the cluster influence needs to be removed. The size of the envelope will also have an impact on the potential for the hydrophobic parts of the surface to adsorb the nonpolar component of the adsorptive. Thus, it is not unreasonable to assume that high-oxygen-content ACs will adsorb lower quantities of relatively hydrophobic adsorptives. This conclusion is consistent with the data in Figs. 3 and 5 and previous findings by Pendleton *et al.* for 2-methylisoborneol (MIB) adsorption from solution (27, 28).

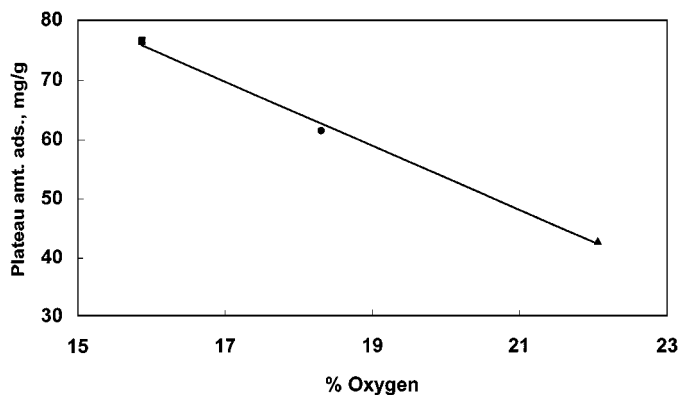


FIG. 5. Correlation between the amount of surfactant (C_{12}) adsorbed at 0.3 mg/L with oxygen content on carbon C-W (■), C-T (▲), and C-R (●).

Effect of Solution Properties on Surfactant Adsorption

Many factors may affect adsorption. From the above, we demonstrate that one needs to consider both the chemical and the physical nature of the adsorbent surface. One also needs to consider the properties of the bulk fluid phase. Although we have not identified all the surface inorganic structures on the ACs used in this work, we know that some of these C–O structures will be susceptible to ionization and/or polarization processes on immersion in the aqueous phase. These sites will provide an electron-rich environment for electrophilic interactions. A complete analysis of the surfactant–AC adsorption process requires that surface group dissociation be addressed as an adsorption variable. One method for performing this analysis is to consider the solution phase as well as its promotion of the specific adsorption of any dissociated surfactant.

We should not attempt to analyze the effects of the solvent phase on adsorption by simply comparing the amounts adsorbed in Fig. 2 with those in Fig. 4. The principal reason for this is the fact that IPA had to be added to pure water-phase systems to promote C₁₂ dissolution. This “cosolvent” was unnecessary when NaOH was the solvent phase. To address this conundrum unequivocally, we added IPA to the NaOH systems with the comparison adsorption data presented in Fig. 6.

For each carbon, we see that adsorption from the water–IPA solution phase renders a higher amount adsorbed than from the NaOH–IPA solvent system. The effect is most pronounced for the carbon C, and carbon A is the least affected. The amount adsorbed from the water–IPA phase for an equilibrium solution concentration of 0.3 mg/L for each carbon, A, B and C, is 275, 234, and 77 mg/g, respectively. For the same solution concentration in the NaOH–IPA phase, the amounts adsorbed are 272, 216, and 43 mg/g, respectively, representing 99, 92, and 56%, respectively, of the amount adsorbed from water–IPA phase. We have found a similar trend for C₈ acid adsorption by these carbons, the only difference being the (expected) lower absolute amount of C₈ adsorbed. To understand these differences in amount adsorbed, we need to consider the effect of the solvent phase on the adsorbent surface chemistry.

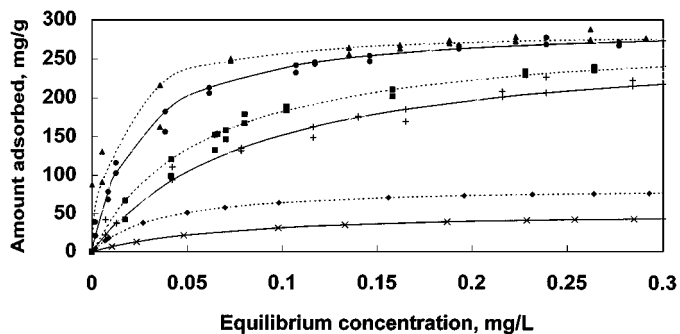
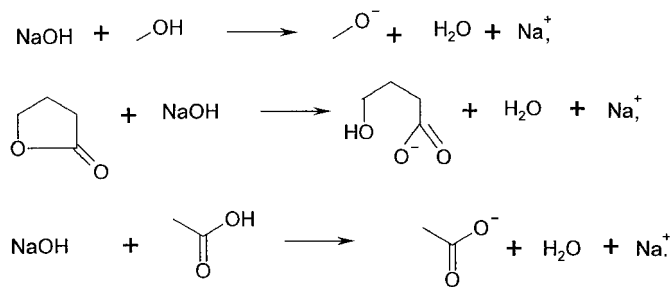


FIG. 6. Surfactant (C₁₂) adsorption isotherms on carbon A, B, and C obtained in 2 M NaOH–IPA solution (—) and in water–IPA solution (·····). The data points for carbon A, B, and C in NaOH–IPA are (●), (+), and (×); in water–IPA phases data points are (▲), (■), and (◆).



SCHEME 1

We conclude from XPS and elemental analyses that some of the oxygen groups on the AC surface are susceptible to chemical change (reaction) during contact with 2 M NaOH solution. Of course, Boehm’s base-titration procedure exploits this fact (Scheme 1). When AC-W is used as the adsorbent for surfactant adsorption from 2 M NaOH, the adsorption conditions of equilibrium time and temperature are equivalent to the conditions that generate AC-T. The initial low oxygen content for carbon A results in a negligible impact of the NaOH treatment on C₁₂ adsorption. The carbon C contains a considerably higher concentration of surface oxygen groups that react with sodium hydroxide, leading to an increased difference in the amount adsorbed from water–IPA compared with that absorbed from NaOH–IPA. Consequently, we suggest that not only is the solvent phase important in considering the mechanism of solution adsorption, but the interaction of the solvent phase with the surface functional groups also needs to be considered as part of the overall mechanism controlling solute (adsorptive)–adsorbent interactions. The plots of the amount of C₁₂ adsorbed by each carbon as a function of surface oxygen content, for each solvent phase in Fig. 6, confirms the linear relationships shown in Figs. 3 and 5. An interesting observation is that an inverse linear relationship also exists for the ratio of the amount adsorbed from water to that adsorbed from NaOH (at 0.3 mg/L equilibrium solution concentration) as a function of carbon-T oxygen content. The regression coefficient for this relationship is 0.9993.

On the other hand, the solution properties also contribute to the adsorption process. Since the C₁₂ acid exhibits such low solubility in water, we classify it as a weakly dissociated organic electrolyte interacting with a hydrophobic and negatively charged surface in an ionic-solution environment. Müller *et al.* (31) discussed the adsorption of weakly dissociated organic electrolytes and commented on the importance of maintaining a constant pH in the continuous phase owing to the change in surface charge (value) with change in solution pH. The maximum adsorptive equilibrium concentration in all aqueous solutions is 0.3 mg/L. Thus, adsorption from 2 M NaOH solutions represents a constant pH. Also, we should expect the surfactant to be completely dissociated at these conditions. On the other hand, at pH 6.5 in pure water solutions, it is only partly dissociated. These conditions contribute to the solution ionic strength, which also can give an indication of the suspension stability via the diffuse electrical double layer surrounding the adsorbents. Müller *et al.* (31)

discussed the role of solution properties and dismissed adsorbent functional group dissociation effects. From the above results, we know that the adsorbents used in this work contain various functional groups that will dissociate, especially in 2 M NaOH solution.

Water is a weak electrolyte with a pK_a of 10^{-7} . A relatively small percentage of H_2O molecules will dissociate to ionic species at pH 6.5. In contrast, NaOH is a strong electrolyte that totally dissociates, forming sodium and hydroxide ions. The pK_a of C_{12} is 4.84; thus, in water at the equilibrium solution concentration of 0.18 mg/L, the approximate concentration where each adsorption plateau commences, the solution contains 94% ionized acid with a solution pH of ≈ 6 . For an initial concentration of C_{12} of 1 mg/L ($5 \mu\text{mol/L}$), it is $\approx 80\%$ dissociated in water phase, giving an equivalent ionic strength of $4 \mu\text{mol/L}$, reducing to $1 \times 10^{-6} \text{ mol/L}$ (or less) during adsorption. We expect that C_{12} acid dissolved in the NaOH solution will give 100% dissociation.

The effect of pH on AC surface charge was investigated previously by Wong (41). Over the pH range 6–13, carbon C remains negatively charged. At pH 6–7, it is very close to zero, but remains negative. The pH for a net zero surface charge on carbon A and B surface is ≈ 6 . The rate of change of charge with pH change is also low for both A and B, offering a net surface charge close to zero over the pH range 5.5–7.5. In this study, the pH of pure water is 6.5. Therefore, almost all three AC surfaces remain negative, albeit close to zero. At pH > 13 , the surface charge on each AC is strongly negative. From an electrostatics perspective, since both C_{12} and C_8 are anionic surfactants, the AC surface charge is unfavorable for a negatively charged adsorptive–adsorbent interaction. A repulsive force is expected (2, 42, 43).

Surfactant Chain Length on Adsorption

Thus far in our analysis we may suggest that surfactant adsorption is a result of one or more interactions at the solid–solution interface. Several driving forces exist in surfactant adsorption. These include hydrophobic bonding, hydrogen bonding, dispersion forces, electrostatic attraction, and ion exchange to replacing counterions (1, 7, 32). The adsorption isotherms shown in Figs. 7a–7c represent C_{12} and C_8 adsorption by carbons A–W, B–W, and C–W from the 2 M NaOH solution phase. Each adsorption system has the same trend. That is, the C_{12} amount adsorbed $\gg C_8$ for a common adsorbent and solution phase; the presence of IPA in solution promotes C_{12} adsorption. In our discussion above, we indicate that the carbon surfaces have a net negative charge when suspended in 2 M NaOH, reducing the potential for anion adsorption. For adsorption to occur at all, and for more C_{12} than C_8 , we suggest that hydrophobic forces may predominate in the adsorption mechanism.

In previous research, Pendleton and co-workers have demonstrated the extent of relative hydrophobic nature from water adsorption isotherm analyses (27, 41). Our elemental and XPS analyses rank the order of hydrophobicity of the three carbons

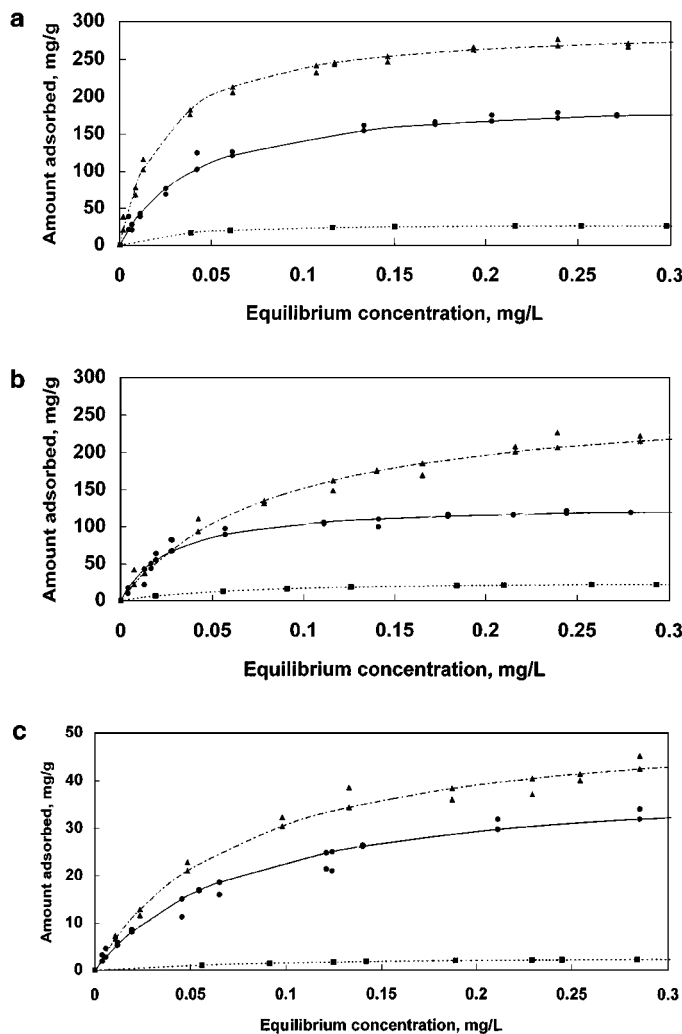


FIG. 7. Surfactant adsorption isotherms on carbon A (a), B (b), and C (c) obtained in 2 M NaOH solution. C_{12} with IPA (---) (\blacktriangle), C_{12} no IPA (—) (\bullet), and C_8 no IPA (.....) (\blacksquare).

herein as $A > B > C$. The relative hydrophobicity of an anionic (or any) surfactant increases with increasing aliphatic carbon chain length (2, 7, 32). The hydrophobic component of surfactants, dissolved in an aqueous solution, will partition more favorably to a hydrophobic environment. At the low concentrations used in these isotherm measurements, we suggest that this environment is more likely to be the carbon surface than the hydrophobic volume created during micelle formation (assuming that solute concentrations exceed the critical micelle concentration). A second driving force for partition is the relative solubility of these two surfactants. C_8 acid is more soluble than C_{12} in either aqueous solution. In fact, IPA was not required to develop aqueous solutions of appreciable concentrations. Thus, the hydrophobic character of the adsorptive probably dominates the chemical potential for adsorption.

There is an interesting outcome on C_{12} adsorption by the carbons owing to the presence of IPA. The amount adsorbed

increases. The same quantity of IPA was used for each isotherm, yet the absolute increased amount adsorbed is 65 mg/g for A-W, 45 mg/g for B-W, and 25 mg/g for C-W. This is an interesting observation, especially since the IPA was added to raise C_{12} solubility. For an increase in solubility, one expects to adjust the partition between dissolved and adsorbed states in favor of the dissolved state. Our data suggest the opposite occurs, consistent with Pavan's observation (7). To understand and interpret this dichotomy, we need to consider the chemical and physical properties of IPA in solution and its behavior as an adsorptive. Previously, Zettlemyer *et al.* (44) interpreted IPA adsorption from the vapor phase in terms of propyl group interaction with the hydrophobic areas of an adsorbent. This mechanism presents an increased hydrophilic surface. From the physiochemical perspective, we can expect that the hydroxyl group will also interact with the polarizable surface functional groups. This mechanism presents an increased hydrophobic surface.

For solution adsorption, the adsorbed water must be displaced prior to the interaction. From our measurements of water displacement by MIB (27), we know that the more (relatively) hydrophobic the surface, the stronger the interaction of the hydrophobic molecule. In the present adsorption mechanism analysis, we can expect that the IPA molecules interact predominantly with the AC surface via hydrophobic interactions, producing an increasingly hydrophilic surface. For an increase in adsorption to occur via this mechanism, we expect an interaction between the hydroxyl group and the polarized group of the surfactant. In contrast, if we consider IPA adsorption via the hydroxyl group-polar surface functional group, we expect this interaction to displace the physically adsorbed water from the polarizable surface functional group, followed by the generation of a surface with an increasingly hydrophobic character. For an increase in adsorption to occur, we can expect the surfactant to adsorb via the aliphatic chain.

CONCLUSIONS

It has been shown that the chemical and physical properties of the acid-activated, wood-based carbon C are most seriously affected by immersion in strong caustic solution. The length of time of exposure in strong caustic solution affects the oxygen content in the carbon samples more than does the effect of temperature. Although XPS analysis is only a surface analysis, such data correlate with bulk elemental analysis and complement such techniques. An inverse linear relationship exists between the amount of C_{12} adsorbed and the adsorbent oxygen concentration. The relatively (low oxygen content) hydrophobic, steam-activated carbons adsorb more C_{12} than does the chemically activated carbon. A greater quantity of surfactant adsorption occurs from aqueous solutions than from strong caustic solutions owing to the combination of adsorbent surface chemistry affected by the NaOH (treatment), solvent, and surface functional group dissociation, leading to electrostatics repulsion effects in NaOH system. We conclude that the adsorbent surface chem-

istry and solution chemistry contribute more to the adsorption process than does adsorbent porosity. Overall, the adsorption interaction is promoted by a combined surface-solute hydrophobic interaction.

ACKNOWLEDGMENTS

The authors acknowledge the Australian Research Council for the provision of an APA(I) research scholarship and a SPIRT grant, Alcoa World Alumina, and the Department of Industry, Science and Resources for financial support throughout this work. The authors also thank Dr. Bill Skinner for the XPS measurements and Dr. Russell Schumann for his assistance during GC measurements.

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