

Effect of Salt on the Mechanism of Adsorption of Aromatics on Activated Carbon[†]

Hassan A. Arafat, Marcus Franz,[‡] and Neville G. Pinto*

Department of Chemical Engineering, University of Cincinnati, Cincinnati, Ohio 45219

Received September 30, 1998. In Final Form: January 12, 1999

The effect of KCl on the adsorption of phenol, toluene, and benzene on activated carbon, with different degrees of surface oxygenation, was investigated. Different trends of salt effect were observed for each compound. The observed KCl effects were interpreted on the basis of electrical charge neutralization on the carbon surface and the adsorbate molecules, water adsorption, and the "salt out" effect. In particular, water adsorption was found to be crucial in reducing the adsorption capacity of the activated carbon. The influence of water adsorption was more pronounced on carbon surfaces with higher amounts of oxygen-containing groups. This was additionally confirmed by measurements using flow microcalorimetry.

Introduction

Activated carbon is a complex and heterogeneous material with unique adsorption characteristics. The main features that give this material these characteristics are its porous structure, surface area, and surface properties.¹ Although activated carbon has been known for a long time for its abilities to adsorb a wide spectrum of organic compounds, the mechanisms behind this adsorption process are not yet well understood, and much confusion exists in the literature regarding these mechanisms.

The surface of activated carbon can be divided into three main parts: the carbon basal planes, which constitute the majority of the carbon surface (more than 90% of the surface), sites formed by heterogeneous oxygen-containing groups, which are mainly located at the edges of the graphitic basal planes,² and metal impurities¹ (ash). Although oxygen-containing complexes form a small fraction of the carbon surface, they are very active and have a significant influence on the adsorption capacity.³ These groups can alter the hydrophobicity, adsorptive behavior, and electrical charge characteristics of the carbon surface.^{4,5}

Dissolved salts in aqueous media have been found to influence the adsorption capacity of many organics on activated carbon. This influence is particularly important in applications where salts exist naturally in water, such as drinking water treatment systems.⁶ It has been suggested^{4,7,8} that salts are involved in a variety of mechanisms including interactions with adsorbates both

in solution and on the carbon surface, and in the alteration of carbon's surface charge. It is expected, therefore, that the influence of salt on adsorption capacity will change according to the ionic nature, hydrophobicity, size, and solubility of the adsorbate.

A review of the literature shows that, in general, increasing the salt concentration yields an increase in capacity.^{7–13} Sodium ions were reported to increase the adsorption of organic humic substance,⁷ dissolved organic matter,¹³ *p*-nitrophenol (PNP),⁸ aniline, and benzoic acid⁹ under specific pH conditions. Calcium ions were also reported to enhance the adsorption of lauryl sulfate¹² and synthetic dissolved organic materials (DOMs).¹³ There are, however, exceptions. Nelson and Yang¹⁴ have reported that the effect of sodium phosphate on the adsorption of chlorophenol was absent at low concentration levels (less than 5 mM salt). Snoeyink et al.⁸ indicated that NaCl was found to have no effect on PNP at salt concentrations below 0.01 M.

Differing explanations have been proposed to interpret salt effects in the above-mentioned studies. It has been suggested that positive salt cations neutralize the negative charge of the carbon surface, enabling it to adsorb more molecules.^{7,11,12} Others have suggested that positive salt cations act directly on the negative adsorbate ions. This can take two forms: the salt cation might pair with the negative adsorbate and reduce the ionic repulsion among molecules adsorbed on the surface⁸ or it might act as a shielding force (due to its positive charge) between adjacent, negative adsorbate molecules.

The present study was undertaken to provide a clearer understanding of the influence of salt ions on the adsorption process. This was achieved by studying the salt effect on three different aromatic adsorbates (phenol, toluene, and benzene) and by using carbons with different amounts of hydrophilic oxygen groups on their surfaces. By changing the functional group on the adsorbate's aromatic ring, the relationships between solubility, hydrophobicity, and

[†] Presented at the Third International Symposium on Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids, held in Poland, August 9–16, 1998.

* Corresponding author.

[‡] Current address: Freiberg University of Mining and Technology, Freiberg, Germany.

(1) Puri, B. In *Chemistry and Physics of Carbon*; Walker, P., Ed.; Marcel Dekker: New York, 1970; Vol. 6.

(2) Coughlin, R.; Ezra, F. *Environ. Sci. Technol.* **1968**, *2*, 291.

(3) Leon y Leon, C.; Radovic, L. In *Chemistry and Physics of Carbon*; Thrower, P., Ed.; Marcel Dekker: New York, 1994; Vol. 24.

(4) Leng, C. C. Ph.D. Dissertation, University of Cincinnati, Cincinnati, OH, 1996.

(5) Matsumura, Y.; Yamabe, K.; Takahashi, H. *Carbon* **1985**, *23*, 263.

(6) Sontheimer H.; Crittenden, J.; Summers, R. S. *Activated Carbon for Water Treatment*; DVGW-Forschungsstelle: Germany, 1988.

(7) Lafrance, P.; Mazet, M. *J. Am. Water Works Assoc.* **1989**, *81*, 155.

(8) Snoeyink, V.; Weber, W.; Mark, H. *Environ. Sci. Technol.* **1969**, *3*, 918.

(9) Cooney, D.; Wijaya, J. *Proceedings of the Second Engineering Conference on Fundamentals of Adsorption*; Engineering Foundation: New York, 1989.

(10) Randtke, S.; Jepsen, C. *J. Am. Water Works Assoc.* **1982**, *74*, 84.

(11) McKay, G. *Chem. Technol. Biotechnol.* **1982**, *32*, 759.

(12) Mazet, M.; Yaacoubi, A.; Lafrance, P. *Water Res.* **1988**, *22*, 1321.

(13) Karanfil, T.; Kilduff, J.; Schlautman, M.; Weber, W. *Water Res.* **1998**, *32*, 154.

(14) Nelson, P.; Yang, M. *Water Environ. Res.* **1995**, *67*, 892.

ionic charge of the adsorbate, on one hand, and salt concentration, on the other, were observed and used to obtain insight on the adsorption mechanism. By changing the degree of carbon surface oxygenation, the interactions between the salt ions and the carbon surface were also examined.

Experimental Section

(a) Materials. Kureha LP spherical bead activated carbon (BAC) (0.5 mm diameter) purchased from Kureha Chemical Industry Company (NY) was used in this study. The LP carbon, which is made from petroleum pitch, was conditioned upon receiving by boiling in deionized water for 1 h and then drying in an oven at 110 °C for 24 h. This carbon will be referred to as LP-DI. To study the influence of surface oxygen groups on adsorption, the LP-DI carbon was oxygenated with air in a tubular furnace at 350 °C. A 3 g sample was placed in a quartz container, which was then placed in the furnace for 60 min under a constant flow of air. The sample was then cooled to room temperature in air. Previous analyses in our lab have shown that this treatment increases the content of both carbonyl- and carboxyl-type oxygen groups on the surface.¹⁵ This was confirmed using linear temperature-programmed desorption (LTPD) experiments, which are described elsewhere.⁴ The oxygenated carbon will be referred to as LP-air. Deoxygenated carbon was obtained by heating the LP-DI carbon to 850 °C in the tubular furnace under a constant flow of nitrogen for 1 h. It was then cooled to room temperature under a flow of nitrogen and stored in a nitrogen atmosphere. This carbon will be referred to as LP-N₂.

All of the organic compounds and salts used in this study were purchased from Fisher Scientific (Pittsburgh, PA) in the highest purity available, and no further purification was performed.

(b) Measurements of Surface Area and Pore Size Distribution. A Micromeritics Gemini 2360 (Norcross, GA) BET apparatus was used to measure the surface area of the carbons used. The surface area measurements were repeated twice for each carbon, and the experimental error for these measurements was found to be in the range 2–5%. Average values for BET surface areas are reported. Surface area measurements were performed with both degassed and non-degassed carbon samples. Degassing was achieved by placing the sample under a flow of helium for 2 h at 100 °C. Pore size distribution was measured using a Micromeritics ASAP 2010 machine with nitrogen, utilizing the Barrett, Joyner, and Halenda (BJH) method (ASTM D4641-94).

(c) Surface Charge Measurements. To quantify the point of zero charge (PZC), 0.1 g of LP carbon was added to 0.02 L solutions of 0.1 N NaCl, whose initial pH had been adjusted with NaOH or HCl. The containers were sealed and placed on a shaker for 24 h, after which the pH was measured. The PZC occurs when there is no change in the pH after contact with the carbon.

(d) Adsorption Isotherm Measurements. Equilibrium isotherms were determined using the bottle point method, following the ASTM standard procedure (ASTM D3860-89a). All isotherms were measured in controlled (buffered) pH solutions to exclude any effects of pH variations on the solubility of the adsorbate or the charge of the carbon surface. Prewedged amounts of carbon (ranging from 20 to 300 µg) were placed in 50 mL bottles with two blank solution bottles left without carbon to test for evaporation. Each point on the isotherm is the average of three bottle measurements. The adsorption solutions were prepared by dissolving the organic adsorbate in the buffer solution. The bottles were then filled with 50 mL of solution, leaving no headspace to minimize evaporation, and covered with Parafilm and caps and then placed on a shaker for a period of 7 days. The equilibrium time was determined from preliminary kinetic studies. After equilibration, a UV spectrophotometer (Shimadzu, UV160U) was used to measure the adsorbate concentration in the solution. Wavelengths of 270, 253, and 260 nm were used for phenol, benzene, and toluene, respectively. The equilibrium amount adsorbed on the carbon was then calculated by a mass balance. All equilibrium isotherms were measured in buffered solutions at a pH of 11.6. The buffers were

Table 1. Surface Area and PZC Measurement

carbon	surface area (m ² /g)		difference of surface area between degassed and nondegassed surfaces (%)	PZC
	degassed	not degassed		
LP-DI	1112	1044	6.5	7.15
LP-air	1465	1132	29.4	2.8
LP-N ₂	1032	988	4.5	9.2

prepared using 0.02, 0.05, 0.07, 0.2, 0.5, 0.7, and 0.8 M KCl/NaOH in deionized water.

(e) Flow Microcalorimetry (FMC) Heat Measurements. Heat of adsorption measurements were used to show the effects of surface oxygenation and KCl salt on water adsorption on the carbon surface. A Microscal flow microcalorimeter, Model 3vi (Microscal LTD., London, U.K.) apparatus was used for this purpose in a thermostated room (ambient temperature is 23 °C). A detailed description of the apparatus can be found in the literature.¹⁶

The FMC flow cell was filled with a mixture of 7 mg of carbon (the amount of carbon was accurately weighed in each case) and purified quartz sand. The latter was used to "dilute" the carbon sample to shorten the time of adsorption. A test was performed on a blank sample (sand only without carbon) to estimate the contribution of the heat of adsorption on sand to the total heat. It was found that this contribution was negligible compared to the heat evolved from activated carbon. The dry adsorbent in the cell was evacuated to 0.2 mmHg for a period of 12 h to ensure the removal of any air or moisture from the carbon pores. DI water was then introduced into the cell, and the heat of wetting of activated carbon was measured. DI water was then percolated through the sample at the rate 3.3 mL/h. After the attainment of thermal equilibrium (about 20 min), the flow was switched from DI water to a solution of 0.02 M KCl (in DI water). The thermal signal due to the introduction of salt was measured. Thermal equilibrium was subsequently achieved, at which point a new solution at a higher salt concentration was introduced, and the additional (incremental) heat released was measured. This process was continued for a series of increasing salt concentrations. For each change in solution, 15–30 min elapsed before the thermal equilibrium was re-established. To ensure that the heat of mixing was not a significant part of the heat measured, preliminary experiments were performed with an inert material (sand) in the cell. It was determined that the heat for mixing solutions in the concentration range of interest is negligible.

Results and Discussion

(a) Characterization of Activated Carbon. LP carbon has been previously analyzed in our laboratory⁴ and was found to be ash-free. Ash constituents (metals) usually give hydrophilic sites on the carbon surface. Thus, for an ash-free carbon the only hydrophilic sites are those composed of nonmetallic, non-carbon, groups, in particular, oxygen-containing groups.

It has been found that the oxygenation process to form LP-air from LP-DI carbon increases the oxygen-containing complexes on the carbon surface by 110%, while deoxygenation of LP-DI to LP-N₂ reduces the amount of these groups by 40%.⁴ Using linear temperature-programmed desorption⁴ (LTPD) and FT-IR spectroscopy,¹⁵ the type of oxygen groups on the surface was also probed for LP-DI, LP-air, and LP-N₂. It was found that the quantity of both carboxylic- and carbonyl-type oxygen groups increased with oxygenation of the surface and decreased with deoxygenation.

BET surface areas were measured for all the carbons used and are shown in Table 1. The measurements were made with both degassed and non-degassed carbons. The main objective of degassing was the removal of adsorbed

(15) Leng, C. C.; Pinto, N. *Carbon* **1997**, *35*, 1375.

(16) Groszek, A.; Partyka, S. *Langmuir* **1993**, *9*, 2721.

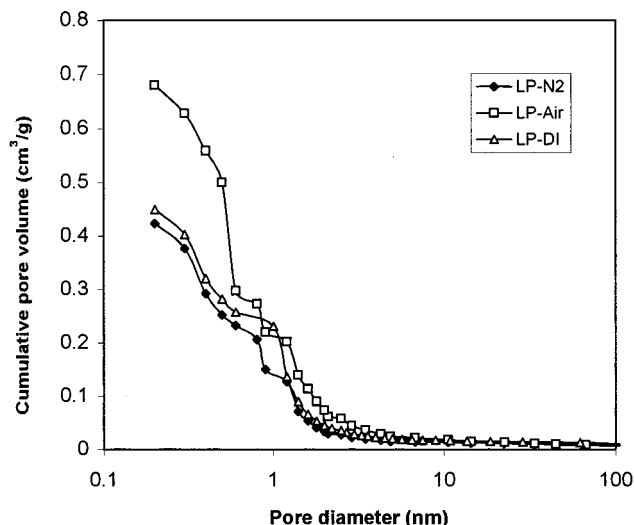


Figure 1. Pore size distribution for LP carbon.

water molecules. On comparing surface areas of the degassed LP samples, it is seen that the oxidation leads to an increase of 32% for LP-air compared to LP-DI. This large difference is attributed to the partial activation of carbon during the oxygenation process at high temperature. This takes place by partial gasification of the carbon to produce CO and CO₂. As a result of this gasification, more of the finer micropores are generated, as will be discussed later. The surface areas of LP-DI and LP-N₂ are, in contrast, close to each other, with the LP-N₂ area being 7% less than that for LP-DI. This slight reduction in area can be attributed to the loss of oxygenated sites that formed part of the original surface area or to the formation of a graphitized surface. However, the latter is unlikely at the deoxygenation temperature used.^{3,17}

When degassed and non-degassed surfaces are compared, it is seen that the degassed surfaces consistently have a larger BET area. The difference is highest for oxygenated carbon (LP-air) and lowest for deoxygenated carbon (LP-N₂). Surface oxygen is responsible for attracting water molecules, which form clusters through H-bonds around hydrophilic oxygen groups (such as carboxylic and phenolic-type groups) and lead to the blockage of smaller pores, reducing the accessible surface area. Although the difference in surface area for degassed and non-degassed LP-N₂ is around the upper limit of the experimental error, the larger difference for LP-DI and LP-air along with the consistent trend of increasing difference with surface oxygenation supports this argument. Also, as will be shown later, heat of wetting data indicate the same effect of oxygen on water adsorption.

The cumulative pore size distribution for the three carbons is displayed in Figure 1. The majority of the pore volume was found to be in the micropore (less than 2 nm) and, to a lesser extent, the mesopore (2–10 nm) range. Macropores constituted a very small fraction of the total pore volume. This is anticipated in this high-surface-area carbon. It was also observed from Figure 1 that while LP-DI and LP-N₂ had similar pore size distributions, the oxygenation to LP-air affects the pore size distribution. This has also been reported by others.^{18,19} More mesopores,

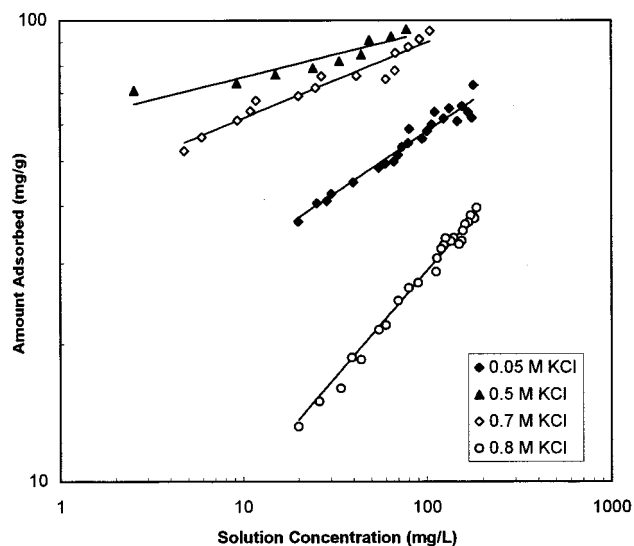


Figure 2. Adsorption isotherms of phenol on LP-air at pH 11.6 and 23 °C in the presence of KCl.

and many more micropores, are generated as a result of the oxygenation process. As mentioned in the discussion on BET surface area, this increase in meso- and micropores is attributed to the partial activation of the carbon during the oxygenation process. This is consistent with the higher BET area obtained for LP-air. It should also be noted that the oxygenation process did not affect the macroporous portion of the carbon, which was also reported by Moreno-Castilla et al.¹⁹

Finally, measurements of point of zero charge (PZC) for all three carbons are presented in Table 1. It is observed from these data that PZC decreases with surface oxygenation. This trend has been discussed in the literature.^{20,21}

(b) Effects of KCl on Adsorption Isotherms. The effects of KCl on the adsorption of phenol on LP-air are shown in Figure 2. The data were obtained at 23 °C and a pH of 11.6. Four isotherms, each at a different KCl concentration (0.05, 0.5, 0.7, and 0.8 M), are shown. Also shown, as solid lines in Figure 2, are Freundlich isotherm characterizations of the experimental data. These were obtained using the best-fit coefficients shown in Table 2. It must be emphasized that the Freundlich model was selected only because it provides a simple and effective representation of the trends observed. This in no way is meant to imply that the model assumptions are valid for this case. In fact, there is evidence in the literature⁴ that the underlying mechanisms for phenol adsorption are quite different from those presumed for the Freundlich isotherm.

To more clearly see the effect of KCl, the amount of phenol adsorbed on carbon in equilibrium with a solution concentration of 80 mg/L (q_{80}) and the amount adsorbed in equilibrium with a solution concentration of 20 mg/L (q_{20}) have been plotted against salt concentration in Figure 3. The adsorption capacity for phenol on LP-air increases with KCl concentration from 0.05 to 0.5 M. Further increase in the salt concentration to 0.7 M reduces the adsorption capacity, and there is a dramatic reduction in capacity with a further increase to 0.8 M KCl.

The increase in capacity from 0.05 to 0.5 M KCl can be explained on the basis of mechanisms proposed earlier.

(17) Otake, Y.; Jenkins, R. *Carbon* **1993**, *31*, 109.

(18) Choma, J.; Burakiewicz-Mortka, W.; Jaroniec, M.; Li, Z.; Klinik, J. Proceedings of 3rd International Symposium on Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids, August 9–16, 1998, Torun, Poland, Sklad: K. Nieszporek Druk, 1998.

(19) Moreno-Castilla, C.; Carrasco-Marin, F.; Maldonado-Hodar, F.; Rivera-Utrilla, J. *Carbon* **1998**, *36*, 145.

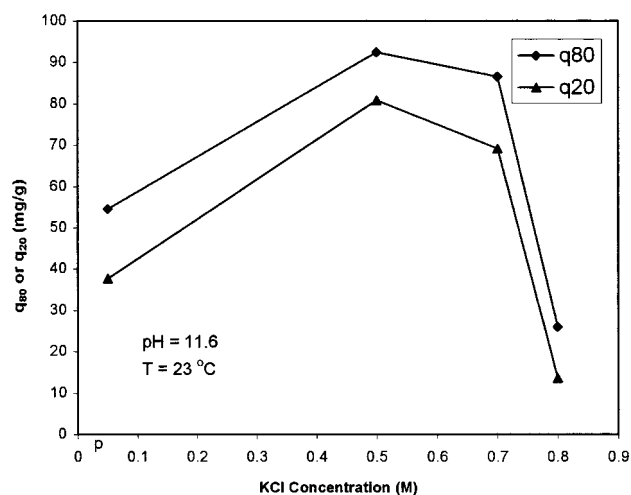
(20) Stumm, W. *Chemistry of the Solid Water Interface*; John Wiley: New York, 1992.

(21) Radovic, L.; Ume, J.; Scaroni, A. In *Fundamentals of Adsorption*; LeVan, M., Ed.; Kluwer Academic Publishers: Boston, Massachusetts, 1996.

Table 2. Coefficients for Best-Fit Freundlich Isotherms^a

carbon	KCl concn (M)	adsorbate	<i>K</i>	<i>1/n</i>
LP-DI	0.5	Phenol	33.97	0.195
	0.8	Phenol	13.24	0.411
LP-air	0.05	Phenol	17.01	0.266
	0.5	Phenol	60.66	0.096
	0.7	Phenol	42.57	0.162
	0.8	Phenol	3.39	0.465
LP-air	0.05	Toluene	645.8	0.042
	0.2	Toluene	499.3	0.0067
	0.5	Toluene	382.8	0.0807
	0.7	Toluene	290.2	0.038
LP-DI	0.02	Benzene	15.38	0.688
	0.07	Benzene	16.67	0.624
LP-air	0.02	Benzene	5.785	0.773
	0.05	Benzene	10.91	0.527
	0.07	Benzene	15.96	0.393
	0.2	Benzene	14.92	0.427
	0.5	Benzene	13.79	0.508
	0.7	Benzene	7.945	0.729

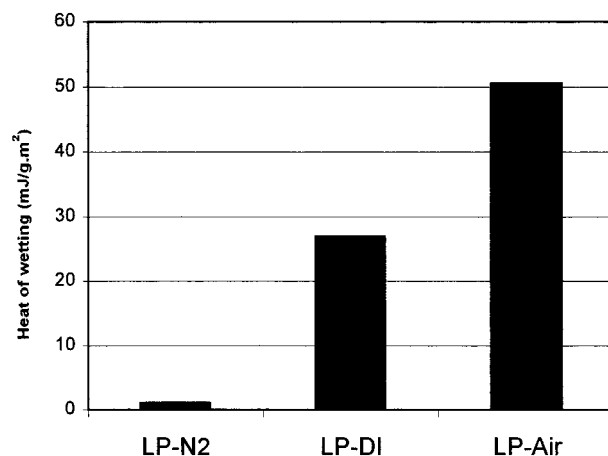
^a The form used for the Freundlich isotherm is $q = KC^{1/n}$, where q is the amount adsorbed (mg/g), C is the adsorbate concentration in solution (mg/L), and K and $1/n$ are constants.

**Figure 3.** Effect of KCl on phenol adsorption on LP-air.

At the high pH of 11.6, at which the isotherms in Figure 2 were obtained, the carbon surface is negatively charged,^{20,21} since pH 11.6 exceeds, by far, the PZC for both LP-air and LP-DI. Phenol, which has a pK_a of 9.99,²² exists in solution in its dissociated form as a negative phenolate ion. The addition of KCl causes a partial neutralization of the negative charge on the carbon surface and a consequent compression of the electrical double layer by the K^+ cation. This enables the carbon to adsorb more of the negative phenolate ions, since the repulsive forces between the surface and the phenol are reduced. Similar explanations have been given by other researchers for other organic materials.^{7,11,12}

The K^+ ions can also enhance the adsorption capacity by pairing with the phenolate ions, hence, reducing the repulsion between the adsorbate and the carbon surface, as well as between adjacent phenol molecules adsorbed on the surface. This was proposed earlier by Snoeyink⁸ for *p*-nitrophenol and by Cooney and Wijaya⁹ for benzoic acid.

The reduction in capacity observed at concentrations above 0.5 M KCl appears to be related to water adsorption. It has been suggested^{4,23–25} that water cluster formation

**Figure 4.** Heat of wetting for LP carbon.

on surface hydrophilic oxygen groups, such as carboxylic groups, affects adsorption in two ways. First, since these hydrophilic groups are located on edges of the graphitic basal planes, due to the “free valence” in the basal planes at these sites,² the formation of water clusters at these sites hinders access to the basal planes. This is supported by the BET data in Table 1, which show lower surface area values for the non-degassed samples as compared to the degassed ones.

Further evidence of the water adsorption on hydrophilic oxygen groups is obtained from the heat of wetting data, shown in Figure 4. The heat of wetting of LP-air is 247% that for LP-DI, while the heat of wetting for LP-N₂ is only 3.7% that of LP-DI. The difference in the heat of wetting values can be attributed to the formation of H-bonds between water molecules and the oxygen in the hydrophilic groups (especially carboxylic groups). Additional heat can also evolve due to secondary water adsorption, through H-bonds, around the first layer of adsorbed water. It is interesting to observe here that the differences in evolved heats of wetting between different LP carbons (247% for LP-air and 3.7% for LP-N₂) do not correspond directly to the relative amounts of oxygen groups on these carbons (110% for LP-air and 40% for LP-N₂), which indicates a secondary water adsorption process.

A second possible influence of water adsorption is interference with surface carbonyl groups. These groups can adsorb aromatics through donor–acceptor complex formation.²⁶ Because the carbonyl and carboxylic groups are generally in close proximity on the surface (at edge sites), water cluster formation on carboxylic groups is suspected to block adsorption on the carbonyl sites. Water adsorption is expected to increase with increasing salt concentration because of ion exchange between H^+ and K^+ ions at the surface COO^-H^+ (carboxylic) and $O-H^+$ (phenolic/hydroxylic) groups. Puri and Mahajan²⁷ have reported that the replacement of H^+ with alkali ions on charcoal causes charcoal to adsorb more water.

If water cluster formation is indeed the cause of the decreased capacity observed at higher salt concentrations (Figure 3), it is to be expected that the effect would be reduced if the number of surface oxygen groups were reduced. To test this, phenol isotherms were measured on

(23) Mahajan, O.; Moreno-Castilla, C.; Walker, P. *Sep. Sci. Technol.* **1980**, *15*, 1733.

(24) Dubinin, M. *Carbon* **1980**, *18*, 355.

(25) Youssef, A.; Ghazy, T.; El-Nabacrawy, Th. *Carbon* **1982**, *20*, 113.

(26) Mattson, J.; Mark, H.; Malbin, M.; Weber, W.; Crittenden, J. J. *Colloid Interface Sci.* **1969**, *31*, 116.

(27) Puri, B.; Mahajan, O. *Soil Sci.* **1962**, *94*, 162.

(22) Dean, J. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992.

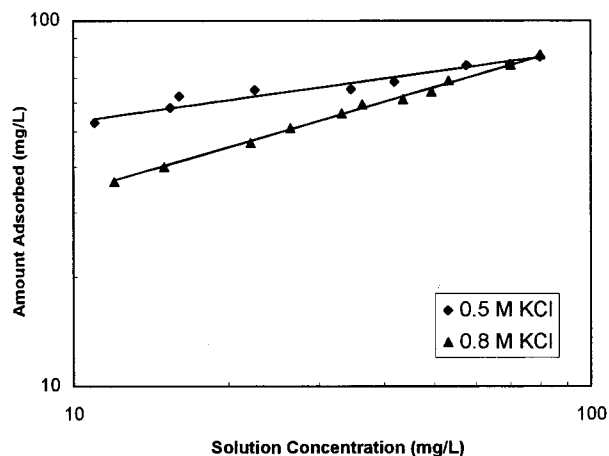


Figure 5. Adsorption isotherms of phenol on LP-DI at pH 11.6 and 23 °C in the presence of KCl.

LP-DI at pH 11.6 and 23 °C in the presence of KCl. Shown in Figure 5 are isotherms at 0.5 and 0.8 M KCl; the solid lines are best-fit Freundlich isotherms, and the coefficients for these lines are reported in Table 2. As before, the adsorption capacity dropped as the KCl concentration was increased from 0.5 to 0.8 M. However, the drop is much smaller for LP-DI as compared to LP-air. Since LP-air has 110% more oxygen complexes on its surface than LP-DI, it is to be expected that the influence of water cluster formation is smaller for the latter, as has been observed.

On the basis of these results it appears that KCl does influence adsorption capacity through two effects that act in opposite directions. At lower salt concentrations, electrostatic effects dominate, leading to an increased capacity, while, at higher salt concentrations, water cluster formation has the strongest influence. The maximum observed in Figure 3 is a consequence of the opposing forces. It stands to reason, then, that if similar measurements are made with a neutral adsorbate, a maximum as in Figure 3 may not be observed, since the electrostatic influence is considerably lessened. It should, however, be noted that while shielding effects will be absent, the influence of salt on the double layer will still be present. Thus, it is not certain that there will not be a maximum. However, it is much less likely to exist than in the case of phenol. To test this, adsorption isotherms for toluene were measured on LP-air at pH 11.6 and 23 °C and are shown in Figure 6. Also shown are best-fit Freundlich lines for which the coefficients are reported in Table 2. Four KCl concentrations were used, 0.05, 0.2, 0.5, and 0.7 M. Once again, to show clearly the influence of salt, q_{80} and q_{20} are plotted in Figure 7 as a function of KCl concentration. Clearly, Figure 7 shows that the adsorption capacity for toluene on LP-air decreases with increasing KCl concentration. This is as expected with the diminished influence of electrostatic interactions. Since toluene is a neutral, nondissociating compound, it does not possess a charge that can be neutralized by the salt cations (or anions). Hence, the effect of salt on minimizing repulsive ionic forces on the surface is absent. As in the case of phenol, the decrease in capacity can be attributed to water cluster formation. Increasing the K^+ concentration in solution increases the ion pairing of K^+ with ionized carboxylic or phenolic groups on the surface. This leads to higher water adsorption and reduces accessibility to the basal plane carbons.

Figures 8 and 9 show the effect of KCl on the adsorption of benzene on LP-air at pH 11.6 and 23 °C. Figure 8 presents three isotherms at the salt concentrations 0.02,

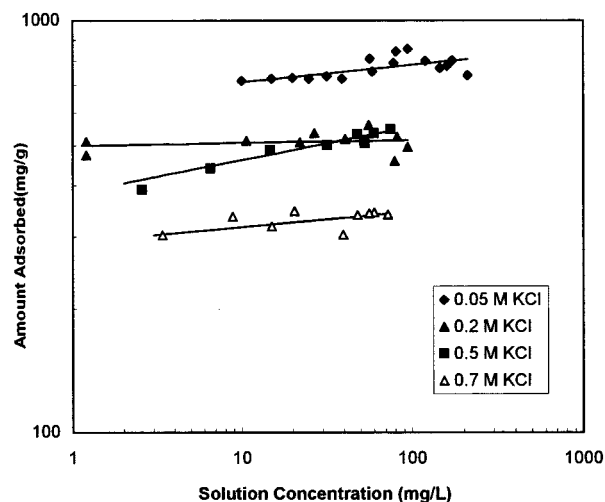


Figure 6. Adsorption isotherms of toluene on LP-air at pH 11.6 and 23 °C in the presence of KCl.

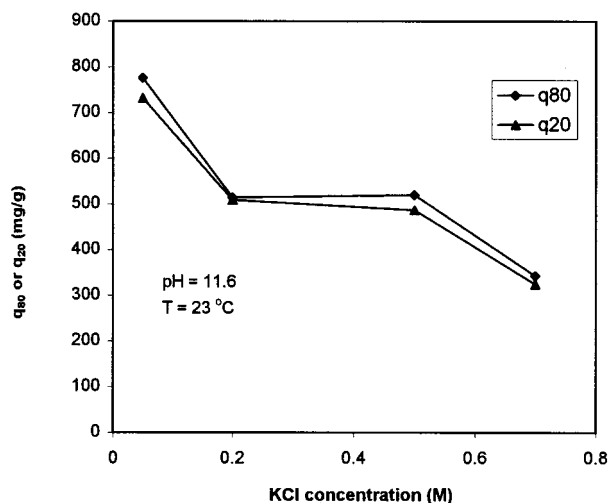


Figure 7. Effect of KCl on toluene adsorption on LP-air.

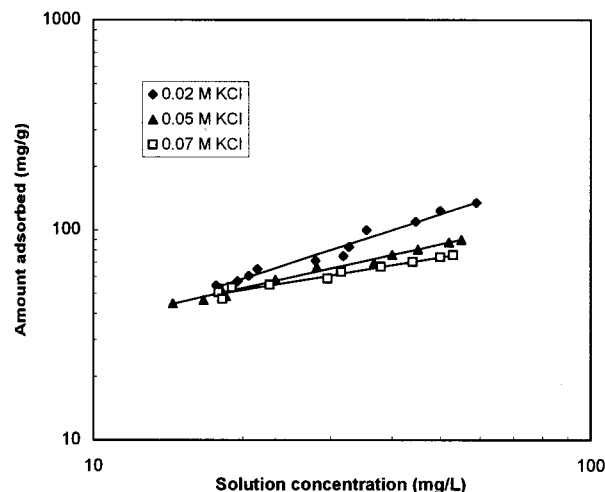


Figure 8. Adsorption isotherms of benzene on LP-air at pH 11.6 and 23 °C in the presence of KCl at low concentrations.

0.05, and 0.07 M KCl, while Figure 9 presents isotherms at the higher salt concentrations 0.2, 0.5, and 0.7 M KCl. The straight lines in these figures are Freundlich best-fit isotherms, and the corresponding coefficients are given in Table 2.

Since benzene is a neutral molecule, it was expected that the effect of KCl would be similar to that for toluene.

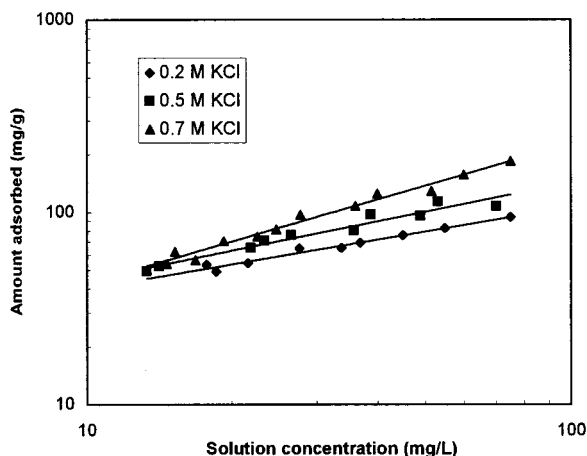


Figure 9. Adsorption isotherms of benzene on LP-air at pH 11.6 and 23 °C in the presence of KCl at high concentrations.

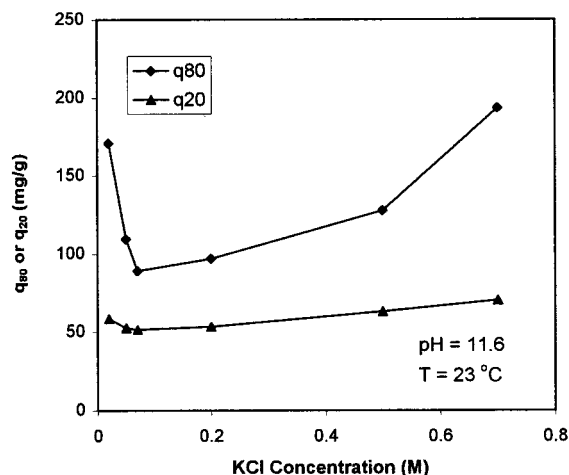


Figure 10. Effect of KCl on benzene adsorption on LP-air.

However, as can be seen from the q_{80} and q_{20} plots in Figure 10, this is not the case. For benzene, in contrast to toluene, there is a minimum observed in the capacity versus salt concentration curves (Figure 10). Also, KCl has a much stronger influence on capacity at q_{80} as compared to q_{20} ; this was not the case for toluene. The behavior in Figure 10 can be explained by the relative hydrophobicities of benzene and toluene. On the basis of the octanol-water partition coefficient (K_{ow}), as an index for hydrophobicity, toluene ($K_{ow} = 537$)²⁸ is considerably more hydrophobic than benzene ($K_{ow} = 131.8$).²⁸ As would be expected, toluene has a much higher capacity on carbon than benzene; this can be seen by comparing appropriate isotherms in Figure 6 with those in Figures 8 and 9. Additionally, the toluene isotherms (Figure 6) are relatively flat, consistent with very strong affinity for carbon. On the basis of these isotherm characteristics, it can be concluded that all of the available adsorption sites for toluene are occupied at a relatively low solution concentration. In contrast, for benzene, the adsorption capacity changes significantly with the liquid concentration. This indicates that, at low equilibrium solution concentration, adsorption has occurred on only part of the sites available, and it is reasonable to assume that these are the more accessible sites. With increasing equilibrium solution concentration, adsorption occurs on progressively less accessible sites. With this recognized, the behavior in

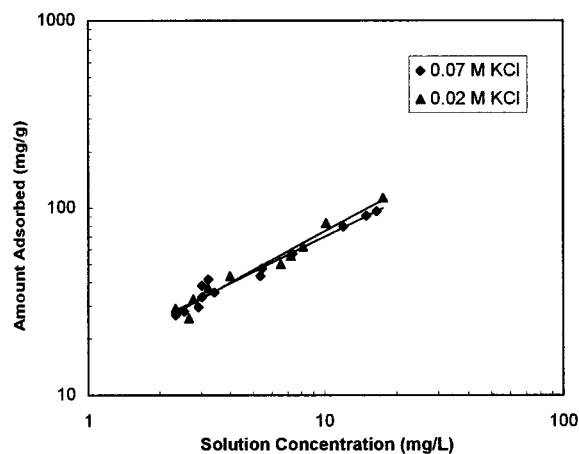


Figure 11. Adsorption isotherms of benzene on LP-DI at pH 11.6 and 23 °C in the presence of KCl at low concentrations.

Figure 10 can be explained. The drop in capacity observed with increasing KCl concentration at lower salt concentrations is postulated to be due to enhanced water cluster formation, as proposed earlier. A stronger effect is observed at q_{80} than at q_{20} , because at the higher solution concentration only the less accessible sites are available for adsorption. These sites are likely to be in smaller pores, which are more easily blocked by the water clusters. For toluene, this difference in behavior between q_{80} and q_{20} is not observed (Figure 7) because the strong adsorption of toluene saturates the surface at a low adsorbate solution concentration. Thus, for both q_{20} and q_{80} curves the less accessible sites are the ones mainly influenced by the changes in KCl concentration.

The increase in capacity observed at higher salt concentrations for benzene can also be explained on the basis of hydrophobicity. Because benzene is hydrophobic, in accordance with Traube's rule,²⁹ the affinity of this adsorbate for the carbon surface will increase as a reaction to increased ionic strength of the solution. This effect counteracts the influence of water clusters and becomes dominant at higher salt concentrations. It is more noticeable at q_{80} than at q_{20} because the benzene solution concentration is higher. Also, this effect does not influence the toluene capacity (Figure 7) because the surface is essentially saturated (flat isotherms) and there is no possibility of further adsorption.

Figure 11 shows the adsorption isotherms for benzene on LP-DI, in the presence of the two KCl concentrations 0.02 and 0.07 M. Solid lines are Freundlich best-fit isotherms, with their coefficients given in Table 2. When the isotherms in Figure 11 are compared to those in Figure 8, it can be seen that the difference between the 0.02 M and the 0.07 M isotherms is much less for LP-DI as compared to LP-air, with the adsorption capacity being slightly higher for the 0.02 M KCl than for the 0.07 M KCl (the same trend observed for LP-air). Analogous to the case for phenol, the cause of the difference in behavior between the LP-DI and the LP-air is the amount of oxygen groups on the surface. Increasing the KCl concentration does not reduce benzene adsorption on LP-DI to the same extent as that on LP-air, due to water adsorption.

(c) KCl Concentration and Heat Evolution. The FMC technique was utilized to measure heat effects as a function of KCl concentration. Figure 12 shows the incremental heat released as the carbon is equilibrated in a stepwise process with higher and higher salt

(28) LaGrega, M.; Buckingham, P.; Evans, J. *Hazardous Waste Management*; McGraw-Hill: New York, 1994.

(29) Weber, W. *Physicochemical Processes for Water Quality Control*; John Wiley: New York, 1972.

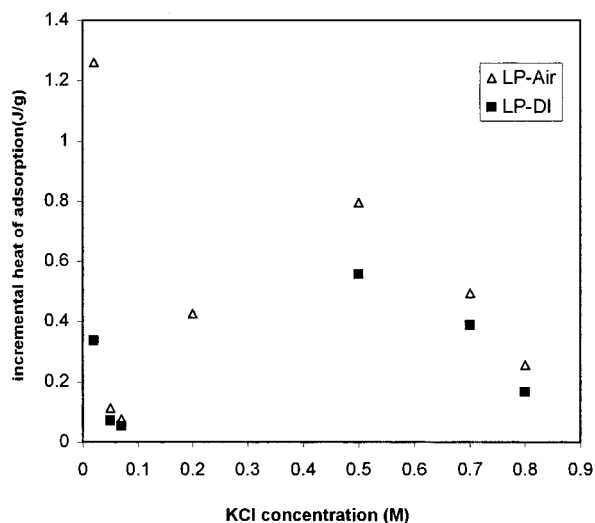


Figure 12. Incremental heats of adsorption on LP carbon.

concentrations. Two features stand out in this figure. First, for all salt concentrations, the oxygenated form of LP carbon (LP-air) has a higher incremental heat than LP-DI. Second, there is a sharp minimum in the incremental heat followed by a maximum at a higher salt concentration.

It is unlikely that the incremental heats in Figure 12 are influenced by interaction between KCl and the basal plane carbon surface, due to the hydrophobicity of this surface. What is more likely is that these heats are rooted in interactions between oxygen sites and KCl and water. This is supported by the differences observed between LP-air and LP-DI.

The shapes of the curves in Figure 12 indicate that at least two mechanisms are involved. From the previous discussion, the heat of ion exchange of K^+ and H^+ and the heat of water adsorption will influence the shape of Figure 12. It is postulated that, at the lowest salt concentration, the heat measured is the net of heat due to ion exchange plus any additional water adsorption due to the presence of K^+ on the surface. As would be expected, there is a significant difference observed between the values for LP-air and LP-DI at this concentration, since the concentration of ionized oxygen sites is significantly different. As the salt concentration is increased further, the incremental heat decreases as the ion-exchange capacity is saturated. This explains the decrease to the minimum point.

The rise in the incremental heat beyond the minimum is puzzling. It is worth noting that the salt concentration at which this minimum occurs coincides closely with the salt concentration at which the minimum was observed

for benzene adsorption (Figure 10). Also, the salt concentration at which the local maximum is observed (≈ 0.5 M) coincides closely with the maximum for phenol in Figure 3. It appears from these results that there is an additional phenomenon influencing behavior at higher salt concentrations. This phenomenon was not identifiable in the adsorption isotherm data but is clearly evident from calorimetric data. The shape of the incremental heat curve beyond the minimum indicates that the phenomenon in question comes into play only at higher salt concentrations. One possible explanation is that the chloride ion interacts with the surface, and this interaction only becomes significant when the concentration of chloride in solution is high. The additional ion adsorption would lead to additional water adsorption as well.

Another possibility is that the behavior beyond the minimum in Figure 12 is rooted in the pore structure. However, since the vast majority of the pores are microporous for both LP-air and LP-DI (Figure 1), this is unlikely because of the rapid kinetics observed in the FMC experiments. It was found that all heat effects were completed within 30 min, strongly suggesting that they are related to occurrences at the mouth of the pores, where the oxygen groups are concentrated. Further investigation on the effect of the anion (Cl^- in this case) on the adsorption process is planned to understand these trends.

Conclusions

The effect of salt on the adsorption of aromatics has been found to be more complex than previously reported. It has been shown that the presence of salt can cause an increase or a decrease in capacity, depending on the nature of the adsorbate and the salt concentration. Thus, the capacity as a function of salt concentration may go through a maximum, as for phenol, or a minimum, as for benzene. The influence of salt is through electrostatic interactions, ion exchange, water adsorption, and the "salting out" effect. Calorimetric data have been shown to also indicate the presence of an additional important effect. This is postulated to be interactions between the Cl^- anion and the surface. Additional investigations are currently in progress to confirm this hypothesis.

Acknowledgment. The authors are grateful for helpful discussions with Prof. R. Scott Summers and Prof. Robert Jenkins that provided insightful interpretation of the data. This work was supported by National Science Foundation GOALI Grant No. BES 9930739, co-sponsored by Calgon Carbon Corporation and E.I. DuPont de Nemours. This support is gratefully acknowledged.

LA9813331