Adsorption of Organics from Aqueous Solution on Surface-Modified Active Carbons : A Critical Review

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1. INTRODUCTION

It is now clear which features of carbon surface chemistry¹⁾ are important for effective adsorption of organic pollutants from water^{2), 3)}. These are briefly summarized here and illustrated in Sections 2-4.

The origin of the negative charge on the carbon surface is not controversial: dissociated acidic functional groups. Three possible sources of the positive charge must be considered, however: (a) basic oxygen-containing functional groups, (b) protonated amino groups (for nitrogen-rich carbons), and (c) graphene layers acting as Lewis bases and forming electron donor-acceptor (EDA) complexes with H₂O molecules. For most carbons, the relative contributions of basic oxygen and graphene layers to the positive charge are the key issue: electrostatic repulsion of adsorbates from the graphene layers can be much more detrimental for adsorbent effectiveness than repulsion from the basic oxygen functional groups.

Electrophoretic mobility studies on activated carbon and carbon black particles, and their comparison with the results for amphoteric oxides, contain clues about the contributions of functional groups and graphene layers to the development of surface charge. A common observation for activated carbons is that the absolute value of the positive charge is often much smaller than that of the negative charge³⁾.

Taken together, these and other results³⁾ strongly suggest the following: (1) there is an important contribution of the graphene layers to the positive surface charge of carbon adsorbents; and (2) the widely held belief that surface charge develops as a consequence of both deprotonation and protonation of the same oxygen functional groups should be discarded. Instead, protonation of the basal plane is considered to be much more important for the applications of interest here.

2. ROLE OF ELECTROSTATIC INTERACTIONS

The benefits of establishing connecting points, and thus achieving cross-fertilization, between the disciplines of electrochemistry and liquid-phase adsorption are discussed in some detail elsewhere^{1), 3)}. Here we briefly review the effects of pH on surface chemistry (or vice versa) and on the uptake of weak organic electrolytes. It should be noted with distress, however, that there continue to appear reports in peer-reviewed journals in which the pH of the adsorption experiment is not even mentioned, let alone controlled.

In the pioneering work of Mattson et al.⁴⁾, a decrease in p-nitrophenol uptake with increasing pH was noted, but it was attributed to increasing solubility rather than electrostatic repulsion. In this and many other subsequent studies³⁾, the pH effect was noted but its critical link to both surface chemistry and adsorption behavior had not been made. As early as 1937, however, in a paper whose dubious distinction is that it has zero citations in 35 years (according to the Science Citation Index, 1961-1997), Frampton and Gortner⁵⁾ studied charcoal surface chemistry using electrokinetic techniques. They did not report variations in the point of zero charge (PZC) as a function of charcoal pretreatment (e.g., H₂ at 1000°C, N₂ at 900°C, HNO₃, etc.); but they did measure the electrophoretic mobilities in water and found them to be all negative (of the order of 3-4 μm/s/V/cm) and insensitive to treatment conditions. They concluded therefore that (a) "electrokinetic data do not indicate a difference between 'basic' and 'acidic' charcoal" and (b) "apparently the adsorption of weak electrolytes from aqueous solution on charcoal is molecular rather than ionic." In the first edition of the classic monograph *Active Carbon*^{6a)}, Hassler cites this work to affirm that the "electrokinetic behavior of carbon does not appear to be altered by the adsorption of weak organic acids or bases;" in the subsequent edition^{6b)}, however, the same statement is made without any references. Also intriguing is the omission from this second edition of a graph showing the influence of pH on the electrophoretic mobility and the amphoteric character of activated carbons. In fact, the relevant changes between the two editions have hindered our understanding of electrostatic interactions because, for a long time, when surface charge has been invoked, if at all, active carbons had been assumed to possess only a negative surface charge.

Fig.1 and **Fig.2** are from our own recent work. **Fig.1** illustrates the fact that the uptake of methylene blue (a cationic species at low pH) is controlled by both the pH of the solution and the surface chemistry of the adsorbent. Clearly, the notion that this uptake is a good measure of the total surface area of the adsorbent, which still prevails in certain segments of the activated carbon community³⁾, should be discarded. In contrast, **Fig.2** illustrates the fact that, for another activated carbon, electrostatic interactions may be of lesser importance over a wide pH range. But clearly, such a conclusion cannot be generalized. This particular carbon has a very low PZC, electrostatic repulsion occurs only at low pH (<PZC) and the uptake of anilinium cations at pH=1.5 is greatly suppressed.

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The important work of Müller and coworkers^{7)–9)} regarding pH effects on the adsorption of weak organic electrolytes has been ignored by the environmental electrochemistry community³⁾, but in the adsorption community it resonated clearly, albeit slowly. Their model for single-solute systems is discussed in more detail in Section 4 and elsewhere³⁾. The authors noted that "certain combinations of solute pK, solute concentration, and

Fig.1 Effect of solution pH on the adsorption isotherms of methylene blue³⁵⁾.

Fig.2 Effect of solution pH on the adsorption isotherms of aniline³⁵⁾.

surface charge are predicted to result in" an adsorption maximum with hydrogen ion concentration⁷⁾, " this being a frequently reported experimental finding. In particular such "adsorption maximum is found in a pH range where the solute exists mostly as a counterion and where the effect of pH on ionization of the solute is stronger than that on the decrease of the magnitude of the surface charge⁷⁾". Clearly, the emphasis here is on electrostatic adsorbate/adsorbent interactions. The authors do acknowledge that "[a]romatic solutes adsorb onto activated carbon by interaction of the aromatic ring with the carbon surface" and that "changes in the electron density of the aromatic ring affect the affinity to adsorb⁸⁾", although their reference for the latter statement should be³⁾ the work of Coughlin and coworkers^{10)–12)} and not the cited study of Mattson et al.⁴⁾. The adjustable parameters in their model were not subjected, however, to scrutiny that would reveal the importance of this non-electrostatic contribution to the overall adsorption potential (see Section 4). The dominant effect of electrostatic interactions was illustrated by showing (a) a dramatic decrease in the uptake of benzoic acid ($pK_a=4.2$) as the pH was raised from 4.5 to 11.0 for a carbon whose PZC was 6.7; (b) a gradual increase in the uptake of aniline ($pK_a=4.2$) by the same carbon as the pH was raised from 2.0 to 10.8; and (c) a gradual decrease in the uptake of p-nitrophenol ($pK_a=7.3$) as the pH was raised from 2.05 to 10.6 for a carbon whose PZC was 5.8.

In the mainstream literature on the adsorption of organics, this appreciation of the importance of electrostatic interactions, and its further development, was a very slow process. It had been hampered by uncertainties regarding the key aspects of the chemistry of the carbon surface and by efforts to find a direct relationship between specific features of this chemistry and carbon's adsorptive properties. For example, in the work of Mazet et al.¹³⁾ both positive and negative zeta potentials of powdered activated carbons (PAC) are reported, with the isoelectric point (IEP) values ranging from below 3 to above 6, and it is apparent that electrostatic interactions are important but not dominant. Particularly instructive are the results for phenol and benzoic acid (see Table 1), both showing monotonically decreasing uptakes with increasing pH in agreement with the reversal of zeta potential from positive to negative in the same pH interval. The authors attribute these results to the effects of solubility, adsorbate dissociation (ionization), surface charge

Table 1 Effect of pH on the Adsorption of Phenol and Benzoic Acid for As-Received and Chemically Modified Activated Carbons.

Adsorbent ^a	pH	Zeta potential (mV)	Capacity (mmol/g)	
			Phenol	Benzoic acid
Heat-treated Filtrisorb 400	3.0	14	0.99	1.16
	5.6	3	1.08	1.06
	7.2	−4	0.93	0.82
As-received Filtrisorb 400	3.0	−4	1.02	1.0
	5.6	−20	0.78	0.71
	7.2	−28	0.73	0.65
Oxidized Filtrisorb 400	5.6	−26	0.43	0.57
	7.2	−32	0.37	0.50

^a Heat treatment in N_2 at 800°C for 4 h; oxidation in boiling conc. HNO_3 for 1 h.

Source : Ref.13

and electrostatic repulsion and conclude "that the electric charge of PAC is an important parameter for the adsorption of organic solutes." **Table 1** also illustrates the neglected point that, on a given adsorbent, the uptake of phenol is comparable to that of benzoic acid, despite the fact that the latter is much less soluble (see Section 3); the authors mention the "existence of a polarity due to π electrons (in phenol, for example)," but they interpret this also as an electrostatic rather than a dispersion effect.

The recent studies by Newcombe and coworkers^{14) - 18)} concerning the complex fundamental issue of adsorption of natural organic matter (NOM) are important contributions to our understanding of electrostatic interactions. This is also an important practical issue in water treatment because NOM adsorption leads to carbon fouling. They performed measurements of both the isoelectric point and the point of zero charge and investigated their relationship with the adsorption and regeneration behavior of several commercial activated carbons. **Table 2** summarizes the surface charge characteristics of virgin and spent commercial activated carbons. The significance of the differences between PZC and IEP is discussed elsewhere¹⁹⁾. Of interest here is the decrease in PZC with increasing adsorption of humic and fulvic acids, as well as the increasing negative charge of the adsorbent. This result led the authors to conclude¹⁶⁾ that "the surface charge properties of the GAC are largely determined by the adsorbed material, rather than the carbon surface itself." When applying these concepts to chemical regeneration of GAC from an operating water treatment plant, the authors¹⁴⁾ noted that in prior studies "no attempt was made to investigate the surface chemistry of the interactions taking place at the carbon-water interface. As a result the findings have often been poorly understood, incorrect conclusions have been drawn and the possibility of chemical regeneration has not been fully explored." To remedy this situation, the authors^{14) - 15)} analyzed the surface chemistry of virgin, spent and regenerated activated carbon and speculated that the effectiveness of the selected regeneration protocol was due to the creation of "an environment of lower pH within the pore structure, enhancing adsorption of organics" by virtue of "a large decrease in the electrostatic repulsion between the surface and the adsorbing species." In a more incisive study of the same issue, Newcombe¹⁷⁾ set out to determine "how surface concentration and pH affect the degree of ionization, the conformation, and the change in the free energy of dissociation of the adsorbed material, and how the effects may be explained in terms of the properties of both the humic material and the carbon surface." Most recently, the same research group tackled the key issue of the relative importance of electrostatic and nonelectrostatic effects¹⁸⁾ in

the adsorption of NOM by studying the effectiveness of electrostatic screening (using an added salt) in the case of two chemically different commercial activated carbons. Those results are discussed in more detail elsewhere³⁾.

3. ROLE OF DISPERSION INTERACTIONS

Nonspecific dispersion interactions between the adsorbent and the adsorbate are the dominant driving force for the adsorption of gases and vapors. Therefore, in the absence of molecular sieving effects, the entire carbon surface is "active" in the removal of gaseous or vapor-phase pollutants. In contrast, removal of inorganic solutes from aqueous solution takes place predominantly on specific sites on the carbon surface, e.g., by ion exchange, and very high concentrations of solute or surface functional groups are necessary for achieving high removal efficiencies^{2) - 3)}. Here we summarize how the interplay of electrostatic and dispersion interactions governs the adsorption of organic pollutants on activated carbons.

Our interest in this topic was sparked by intriguing initial results for adsorption of benzoate, oxalate and fumarate anions on chemically modified (oxidized vs. nitrified) activated carbons²⁰⁾. For example, both oxidation (which reduced the PZC of the carbon) and nitrification (which raised the PZC) were found to suppress the uptake of benzoic acid; this is contrary to the expectations based on electrostatic arguments alone. On the basis of these and other findings, we proposed the following mechanisms of adsorption^{20) - 21)}: (a) adsorption of benzoate (aromatic) anions occurs primarily on the graphene layers of carbon and the electron-withdrawing effects of nitrogen and carboxyl functional groups suppress the π - π interaction of the graphene layers with the adsorbate's aromatic rings; (b) adsorption of aliphatic anions occurs also predominantly on the graphene layers and the same electron-withdrawing effects enhance their interaction with the carboxyl anions. More recently, we studied in more detail the relative importance of dispersion and electrostatic adsorbate/adsorbent interactions as we examined the uptakes of methylene blue and nitrophenol, as well as those of benzoic, oxalic and fumaric acids²¹⁾. In agreement with our earlier findings, we concluded that, while electrostatic interactions are important, dispersion interactions appear to be dominant in the adsorption of aromatic solutes. On the other hand, electrostatic repulsion appears to be much more important for the adsorption of aliphatic anions.

Further validation of these conclusions was achieved²²⁾ by contrasting the behavior of three chemically different carbons in adsorbing two vastly different aromatic solutes: nitrobenzene

Table 2 Electrochemical Properties of a Granular Activated Carbon^a Before and After Adsorption of Natural Organic Matter (NOM).

Sample ^b	PZC	IEP	Surface change (mC/m ²)	
			pH=7.0	pH=8.0
Virgin GAC	7.3	3.0	+0.3	-0.6
Spent GAC (3.5 mg DOC/g)	6.4	2.7	-1.9	-4.6
Spent GAC (10.0 mg DOC/g)	4.5	2.4	-5.3	-8.4

^a Filtrasorb 300 (Calgon Carbon Corp.)

^b DOC = dissolved organic carbon (measure of NOM concentration)

Source: Ref. 16.

is a very weak Lewis acid that possesses the electron-withdrawing NO_2 group, while aniline is a predominantly cationic species at $\text{pH} < 4.6$ which also possesses the electron-donating NH_2 group. The chemical differences among the carbons were produced by incorporating O- or N-containing functional groups on the carbon surface. While the effects of the former on the adsorption of phenol and other aromatics are well documented (though not necessarily well understood)^{2), 3)}, the effects of the latter, as well as the interplay of (a) surface groups, (b) solution pH, and (c) effective charge on the carbon surface, had not received adequate attention in the literature. The results showed that for aniline, dispersion interactions are dominant at high pH, while at low pH both types of interactions are important. In contrast, for nitrobenzene surface chemistry effects on the dispersion interactions alone were the key to understanding the uptake variations over the entire pH range.

A dissenting view with respect to these conclusions about the relative uptakes of aliphatics and aromatics had been presented by Kamlet et al.²³⁾ in their analysis of correlations based on linear solvation energy relationships (LSER). The adsorbability of an organic solute was expressed in terms of its molar volume, its dipolarity or polarizability and its hydrogen bond acceptor character. The key results are summarized in **Table 3a**. On the basis of these results, the authors concluded that "when the aromatic solutes were included [together with aliphatic solutes], however, the quality of the correlation dropped dramatically." They had "considered that the differences might be attributable

to specific interactions of the aromatic solutes with the π electrons of the activated carbons, but this would have led to higher calculated [adsorbability] values, whereas in most instances the experimental values are lower than calculated." They were thus forced to conclude that there is "no self-consistent rationale to accommodate the aromatic and the aliphatic results in the same correlation."

A critical analysis of the results of this study reveals, however, some obvious errors in data analysis and presentation (e.g., a mix-up between experimental and predicted adsorbability values). A corrected summary of the relevant results is presented in **Table 3b** using two sets of parameters^{24), 25)}. The trend is less confusing and its implication is exactly the opposite to the conclusion drawn by the authors: in 5 out of 7 cases the experimental adsorbability values for aromatic solutes are higher than the calculated values. The importance of delocalized π electrons and π - π interactions in aromatic systems is now consistent with the discussion presented above. Indeed, the exciting hydrogen storage results of Chambers et al.²⁶⁾ may be a very dramatic demonstration of the (heretofore mostly neglected) role of graphite's delocalized π electrons in adsorption processes. If "a new theory of intermolecular forces will be needed²⁷⁾" to explain the much larger H_2 storage capacity of graphite vs. activated carbon, as well as the almost unbelievable storage capacity of graphite nanofibers, electron density in the graphene layers at different interlayer spacings must be the keystone of such a theory.

Table 3a Use of Linear Solvation Energy Relationships to Predict the Uptake of Selected Aromatics on a Commercial Activated Carbon.

Adsorbate	Experimental uptake*	Predicted uptake*
Benzene	0.82	1.34
Toluene	1.30	0.51
Ethylbenzene	1.71	0.69
Pyridine	-0.91	-0.25
Benzaldehyde	0.60	1.25
Nitrobenzene	0.91	1.43
Acetophenone	0.71	1.66

*The values shown represent the logarithm of adsorbability (or the partition coefficient between the solution and the adsorbed phase at infinite dilution).
Source : Ref.23.

Table 3b Use of Linear Solvation Energy Relationships to Predict the Uptake* of Selected Aromatics on a Commercial Activated Carbon : Corrected Table 3a (Adapted from Ref. 23).

Adsorbate	Experimental uptake*	Predicted uptake*	
		Ref.24	Ref.25
Benzene	1.34	1.07	0.10
Toluene	0.51	1.58	0.54
Ethylbenzene	0.69	2.01	0.93
Pyridine	-0.25	-0.71	-1.06
Benzaldehyde	1.25	0.59	0.05
Nitrobenzene	1.43	1.13	0.52
Acetophenone	1.66	0.92	0.17

*The values shown represent the logarithm of adsorbability (or the partition coefficient between the solution and the adsorbed phase at infinite dilution).

4. TOWARD A COMPREHENSIVE ADSORPTION MODEL

There are several possible theoretical approaches to the formulation of a suitable model for the adsorption processes discussed above. The most fundamental one is based on the perturbation molecular orbital (PMO) theory of chemical reactivity^{28), 29)} in which the wave functions of the products are approximated using the wave functions of the reactants. A key issue here is the relative importance of the two terms in the expression for the total energy change of the system, which is taken to be a good index of reactivity^{30), 31)},

$$\Delta E_{\text{react}} = \Delta E_{\text{ch}} + \Delta E_{\text{orb}}$$

The question is whether the extent of adsorption is determined by charge control (ΔE_{ch} , i.e., coulombic or electrostatic interactions) or by orbital control (ΔE_{orb} , i.e., attractive interactions between the filled orbitals of the adsorbate and the empty orbitals of the adsorbent).

In a recent interesting study, Tamon and coworkers^{30), 32), 33)} implicitly took the approach that orbital control is dominant. They analyzed the adsorption and desorption characteristics of a series of aromatic compounds at 308 K and uncontrolled pH. (They assume that "since the concentration of aromatic compounds is very low, pH seems to be almost equal to the value of distilled water³²⁾". They do not mention, however, whether the presence of carbon modifies the pH of the suspension, as it often does.) They used the semiempirical MINDO/3 method to determine the HOMO energy levels (E_{H}) for these adsorbates and the LUMO levels (E_{L}) for several adsorbents (including chemically modified activated carbons). The range of calculated $|E_{\text{H}} - E_{\text{L}}|$ values for adsorbates ranging from p-nitrobenzoic acid to aniline on a commercial activated carbon was 6.7–9.0 eV. Low values (< 7.3 eV) coincided with those systems for which irreversible adsorption was found: those adsorbates that possess electron-donating groups (e.g., aniline), i.e., with the highest HOMO levels (or lowest ionization potentials), could not be desorbed easily (using distilled water at 308 K). In contrast, those aromatic species that possess electron-withdrawing groups (e.g., nitrobenzene) were more weakly (reversibly) adsorbed. These findings are in remarkable agreement with our conclusion^{20), 21), 34)} that, when dispersion forces are dominant, the electron-withdrawing effects of nitrogen and carboxyl functional groups suppress the interaction of the basal planes with the adsorbate's aromatic rings. Based on these findings, Tamon et al.³³⁾ proposed a two-state model to explain the appearance of irreversible adsorption of electron-donating compounds, according to which the barrier for going from the precursor (reversible) adsorption state to the irreversible state is higher for the electron-withdrawing aromatic compounds than for the electron-donating compounds. They do not provide a justification for this assumption; instead, they invoke the Hammond postulate according to which "the structure of the transition state will resemble the product more closely than the reactant for endothermic processes whereas the opposite is true for exothermic

processes³³⁾". How exactly is this related to the exothermic adsorption process is not clarified. A more straightforward alternative theory is summarized below³⁾.

Functionalization of either the adsorbate or the adsorbent which increases the π -electron density leads to either enhanced or stronger adsorption when the adsorption process is governed by π - π (dispersion) interactions. The converse is also supported by available experimental evidence: functionalization (of the carbon adsorbent or the aromatic adsorbate) which decreases the π -electron density leads to suppressed or weaker adsorption.

As shown in Section 2, however, some adsorption systems involving aromatic adsorbates are very much influenced by electrostatic interactions. Additional examples are cited and discussed elsewhere^{2), 3)}. Clearly, a model that takes into account both electrostatic and dispersion interactions is needed. Such a competitive adsorption model has been presented by Müller and coworkers^{7)–9)}. We used this model to illustrate the possibly dramatic effects of modifications of carbon surface chemistry on equilibrium uptakes of p-nitrophenol²¹⁾. We have also extended it further to evaluate the relative importance of electrostatic and dispersive interactions²²⁾.

5. CONCLUSIONS

In contrast to the optimization of physical surface properties of activated carbons—where we know what is needed for a particular adsorption or water treatment task (an adequate surface area and a specific pore size distribution) and we also know how to achieve it—very few guidelines had been available for the optimization of the chemical surface properties. Much progress has been made in our understanding of the surface chemistry of carbons and in developing techniques of its modification for catalyst support applications. So, in using carbons for water treatment we have long known how to modify their surface chemistry, but only recently have we learned what kind of surface chemistry is most desirable for a specific task. Not unexpectedly, we have also realized that compromises need to be made to meet the sometimes conflicting demands imposed by electrostatic or dispersion forces.

Commonly used modifications of carbon surface chemistry affect the extent of both electrostatic and dispersive interactions. For example, carbon oxidation not only lowers its point of zero charge; it also reduces the dispersive adsorption potential by decreasing the π -electron density in the graphene layers. And conversely, the removal of electron-withdrawing oxygen functional groups not only increases the point of zero charge; it also increases the dispersive adsorption potential by increasing the π -electron density.

A theoretical model that accounts for both electrostatic and dispersive interactions is needed to successfully describe the qualitative trends typically observed. Realistic evaluations of the relative magnitudes of electrostatic and dispersive potentials are also needed to develop reliable quantitative predictions for the removal of organic water pollutants by chemically modified activated carbons. Such predictive capability is now well within our reach.

REFERENCES

- 1) C. A. Leon y Leon and L. R. Radovic, in "Chemistry and Physics of Carbon," Vol. 24 (P.A. Thrower, Ed.), Marcel Dekker, New York (1994) pp.213-310.
- 2) L. R. Radovic, in "Surfaces of Nanoparticles and Porous Materials" (J. A. Schwarz and C. J. Contescu, Eds.), Marcel Dekker (1998) in press.
- 3) L. R. Radovic, C. Moreno-Castilla and J. Rivera-Utrilla, in "Chemistry and Physics of Carbon," Vol. 27 (L. R. Radovic, Ed.), Marcel Dekker, New York (1999) in preparation.
- 4) J. S. Mattson, H. B. Mark, Jr., M. D. Malbin, W. J. Weber, Jr. and J. C. Crittenden, *J. Colloid Interf. Sci.* **31** (1969), 116-130.
- 5) V. L. Frampton and R. A. Gortner, *J. Phys. Chem.* **41** (1937), 567-582.
- 6) (a) J. W. Hassler, "Active Carbon," Chemical Publishing Co., Brooklyn, NY (1951) ; (b) J. W. Hassler, "Activated Carbon," Chemical Publishing Co., New York, 1963.
- 7) G. Müller, C. J. Radke and J. M. Prausnitz, *J. Phys. Chem.* **84** (1980), 369-376.
- 8) G. Müller, C. J. Radke and J. M. Prausnitz, *J. Colloid Interf. Sci.* **103** (1985) 466-483.
- 9) G. Müller, C. J. Radke and J. M. Prausnitz, *J. Colloid Interf. Sci.* **103** (1985) 484-492.
- 10) R. W. Coughlin and F. S. Ezra, *Environ. Sci. Technol.* **2** (1968) 291-297.
- 11) R. W. Coughlin, F. S. Ezra and R. N. Tan, *J. Colloid Interf. Sci.* **28** (1968) 386-396.
- 12) R. W. Coughlin and R. N. Tan, in "Water-1968," AIChE, (1968) pp. 207-214.
- 13) M. Mazet, B. Farkhani and M. Baudu, *Water Res.* **28** (1994) 1609-1617.
- 14) G. Newcombe and M. Drikas, *Water Res.* **27** (1993) 161-165.
- 15) G. Newcombe, R. Hayes and M. Drikas, *Colloids Surfaces* **78** (1993) 65-71.
- 16) G. Morris and G. Newcombe, *J. Colloid Interf. Sci.* **159** (1993) 413-420.
- 17) G. Newcombe, *J. Colloid Interf. Sci.* **164** (1994) 452-462.
- 18) G. Newcombe and M. Drikas, *Carbon* **35** (1997) 1239-1250.
- 19) J. A. Menéndez, M. J. Illán-Gómez, C. A. Leon y Leon and L. R. Radovic, *Carbon* **33** (1995) 1655-1657.
- 20) J. I. Ume, A. W. Scaroni and L. R. Radovic, in Proc. 21st Biennial Carbon Conference, Buffalo, NY (1993) 468-469.
- 21) L. R. Radovic, J. I. Ume and A. W. Scaroni, in "Fundamentals of Adsorption" (M. D. LeVan, Ed.), Kluwer Academic Publishers, Norwell, MA (1996) 749-756.
- 22) L. R. Radovic, I. F. Silva, J. I. Ume, J. A. Menéndez, C. A. Leon y Leon and A. W. Scaroni, *Carbon* **35** (1997) 1339-1348.
- 23) M. J. Kamlet, R. M. Doherty, M. H. Abraham and R. W. Taft, *Carbon* **23** (1985) 549-556.
- 24) R. W. Taft, M. H. Abraham, G. R. Famini, R. M. Doherty, J.-L. M. Abboud and M. J. Kamlet, *J. Pharm. Sci.* **74** (1985) 807-814.
- 25) M. H. Abraham, J. Andonian-Haftvan, G. S. Whiting, A. Leo and R. W. Taft, *J. Chem. Soc. Perkin Trans. 2* (1994) 1777-1791.
- 26) A. Chambers, C. Park, R. T. K. Baker and N. M. Rodriguez, *J. Phys. Chem. B* **102** (1998) 4253-4256.
- 27) A. L. Myers, C&E News, August 10 (1998) 6.
- 28) G. Klopman, *J. Amer. Chem. Soc.* **90** (1968) 223-234.
- 29) W. B. Jensen, "The Lewis Acid-Base Concepts," Wiley-Interscience, New York (1980).
- 30) H. Tamon, M. Atsushi and M. Okazaki, *J. Colloid Interf. Sci.* **177** (1996) 384-390.
- 31) Y. Jean and F. Volatron, "An Introduction to Molecular Orbitals," Oxford University Press, New York (1993).
- 32) H. Tamon and M. Okazaki, *J. Colloid Interf. Sci.* **179** (1996) 181-187.
- 33) H. Tamon, M. Atsushi and M. Okazaki, in "Fundamentals of Adsorption" (M. D. LeVan, Ed.), Kluwer Academic Publishers, Norwell, MA (1996) 961-968.
- 34) I. F. Silva, J. I. Ume, A. W. Scaroni and L. R. Radovic, *ACS Preprints (Div. Fuel Chem.)* **41** (1) (1996) 461-465.
- 35) J. I. Ume, PhD Thesis, The Pennsylvania State University, (1995).