

# ACTIVATED CARBON SURFACE PROPERTIES AND GAS PHASE FILTER PERFORMANCE

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## Abstract

The surface properties of activated carbon play an important role in the adsorption and desorption of volatile organic contaminants (VOCs). At low VOC challenge concentrations, the adsorbent-adsorbate interactions and the microporous nature of activated carbon adsorbents dictate filter life and efficiency. Therefore, understanding the chemical and physical nature of activated carbons is critical for optimizing filter design. Previously, we have reported on the use of inverse gas chromatography (IGC), in combination with Linear Free Energy Relationships (LFERs), to rationalize the magnitude of specific and nonspecific interactions between VOCs and activated carbon surfaces. Through additional IGC analysis, along with Potentiometric and Boehm titrations, the reported LFER coefficients for three activated carbons are critically evaluated.

## Introduction

Activated carbon based filters are typically used as an effective means of controlling volatile organic carbon (VOC) to acceptable levels in many different applications. In designing these chemical filters for critical applications at low VOC concentrations it is important to understand the contributions that govern the adsorption and desorption processes within activated carbon's porous structure. By low concentration we refer to a concentration that is essentially infinitely dilute, or where adsorption takes place to the point of forming less than a monolayer of adsorbate on the adsorbent surface and micropores are incompletely filled. For example, in many of our industry's applications, activated carbons are designed into chemical filters that operate at challenge concentrations in the parts per trillion to the parts per million range. It has been well documented that the adsorbent surface chemistry and its micropore structure become even more critical at these lower VOC concentrations.

Recently, the authors have used Linear Free Energy Relationships (LFERs) to evaluate the surface properties of three commercially available activated carbons and have attempted to use these relationships to rationalize chemical filter performance for specific VOC's (Dallas et al, 2006). This paper extends that work to draw comparisons between the LFER coefficients and the surface properties of activated carbons through the use of the Potentiometric and Boehm titration methods.

The reader is referred to (Dallas et al, 2006) for a detailed overview of the LFER method. Herein, we will only briefly describe the model equation and the molecular parameters included. In the LFER approach, a free energy related measurement, such as the elution temperature from an inverse gas chromatographic (IGC) experiment, is used as the dependent variable and is regressed against a series of probe molecule descriptors defined by Abraham et al:

$$T_R = SP_o + m V_x + r R_2 + s \pi_2^H + a \Sigma \alpha_2^H + b \Sigma \beta_2^H \quad [1]$$

where,  $T_R$  represents the free energy related measurement (IGC elution temperature) and the probe adsorbate descriptors are: 1)  $V_x$  is the McGowan characteristic volume that is calculated from the molecular structure (Abraham and McGowan 1987); 2)  $R_2$ , adsorbate excess molar refraction, which reflects an adsorbate's ability to interact with an adsorbent through  $\pi$ - and n-electron pairs; 3)  $\pi_2^H$  adsorbate dipolarity/polarizability; 4)  $\Sigma \alpha_2^H$ , solute hydrogen bond donor acidity; and 5)  $\Sigma \beta_2^H$ , solute hydrogen bond acceptor basicity (Burg et al, 2003; Abraham et al, 1994; Abraham, 1999).

In Equation 1,  $SP_o$ ,  $m$ ,  $r$ ,  $s$ ,  $a$  and  $b$  represent the intercept and the regression coefficients. The magnitude of the regression coefficients is representative of the properties of the adsorbent surface. For example, the  $s$  coefficient indicates the degree to which the adsorbent surface can interact with the infinitely dilute adsorbates through dipole-dipole and dipole-induced dipole interactions. The  $a$  coefficient reflects the magnitude of the contributions made from the basicity of the activated carbon surface, whereas the  $b$  coefficient models the magnitude of the surface's acidic contributions to the elution temperature. A relatively large positive value of a coefficient indicates that this

interaction contributes to the adsorption process. By comparing the LFER coefficients for a series of adsorbents it is possible to rationalize the relative importance of nonspecific and specific adsorbate-adsorbent interactions on each adsorbent.

The following LFER equations were obtained for the three activated carbons studied in reference (Dallas et al, 2006):

$$T_R (\text{Carbon B}) = -126 + 365 V_x + 44 R_2 + 66 \pi_2^H + 72 \Sigma \alpha_2^H \quad [2]$$

$$R = 0.991 \quad \text{S.E.} = 7 \quad n = 12$$

$$T_R (\text{Carbon C}) = -86 + 326 V_x + 59 R_2 + 51 \pi_2^H + 40 \Sigma \alpha_2^H + 47 \Sigma \beta_2^H \quad [3]$$

$$R = 0.957 \quad \text{S.E.} = 15 \quad n = 12$$

$$T_R (\text{Carbon F}) = -97 + 364 V_x + 34 R_2 + 81 \pi_2^H + 116 \Sigma \alpha_2^H \quad [4]$$

$$R = 0.965 \quad \text{S.E.} = 16 \quad n = 12$$

Where R is the correlation coefficient, S.E. is the standard error of the regression, and n is the number of adsorbates studied.

The goal of this work is to use accepted methods for evaluating the surface chemistry of activated carbons and use their results to rationalize the coefficients obtained from our previous LFER (Dallas et al, 2006).

## Experimental

Three activated carbons were used without further modification except for the sample preparation required by the respective measurement being employed as described below. These carbons identified in this work use the same designations given in (Dallas et al, 2006). Carbon B is a wood-based activated carbon. Carbons C and F are coconut shell-based activated carbons. The IGC methods used to obtain the elution temperature of twelve probe adsorbates are also outlined in (Dallas et al, 2006).

### ***pH Measurement:***

0.4 g of dry carbon powder was added to 20 ml of water and the suspension was stirred overnight to reach equilibrium. Then the samples were filtered and the pH of the filtrates was measured.

### ***Boehm Titration:***

One gram of carbon sample was added to each of the 50 ml of 0.05N solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. The vials were sealed and shaken for 24 h. The samples were filtered. 10 mL of each filtrate was pipetted out and the excess of base or acid was titrated with 0.1N HCl or NaOH, respectively. The number of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxyl, phenolic, and lactonic groups; Na<sub>2</sub>CO<sub>3</sub> carboxyl and lactonic; and NaHCO<sub>3</sub> only carboxyl groups (Boehm, 1966; Elsayed and Bandosz, 2002). The total number of acidic and basic groups is calculated based on the amounts of sodium hydroxide and hydrochloric acid reacted.

### ***Potentiometric Titration:***

The potentiometric titration measurements were performed with a DMS Titrino 798 automatic titrator: Metrohm, Brinkmann Instruments, USA. The experiment was performed by placing 0.100 g samples in a container thermostatted at 298 K with 50 mL of 0.01 M NaNO<sub>3</sub>. The suspensions were stirred and equilibrated overnight in saturated N<sub>2</sub> gas environment to eliminate any interference by dissolved CO<sub>2</sub>. Prior to the experiment the suspensions were made acidic by adding measured volumes of 0.1N HCl to lower the pH to around 3. NaOH was used as titrant. Titration curves representing the variations in pH with the volumes of 0.1N NaOH added were obtained. The carbon suspension was stirred throughout the measurement. Because of the buffering effect of water at pH < 3 and > 11, experiments were carried out in the pH range 3-11.

It is assumed that the system under study consists of acidic sites characterized by their acidity constants, K<sub>a</sub>. The population of sites can be described by a continuous pK<sub>a</sub> distribution, f(pK<sub>a</sub>). The experimental data was

transformed into a proton binding isotherm,  $Q(\text{pH})$ , which represents the total amount of protonated sites.  $Q(\text{pH})$  is related to the  $\text{pK}_a$  distribution by the following integral equation:

$$Q(\text{pH}) = \int_{-\infty}^{+\infty} q(\text{pH}, \text{pK}_a) * f(\text{pK}_a) d\text{pK}_a \quad [5]$$

From this equation, the distribution of acidity constants  $f(\text{pK}_a)$  and their population can be obtained. The solution of the equation is attained using the numerical procedure SAIEUS (Solution of Adsorption Integral Equation Using Splines) (Bandosz et al, 1997). Based on the spectrum of acidity constants,  $\text{pK}_a$ , and the history of the carbon samples (origin, activation method, chemical modification), the detailed surface chemistry is evaluated.

## Results and Discussion

### Boehm Titration:

Table 1 presents the results obtained from the Boehm titrations along with the pH values of the three carbon surfaces. The data reported indicates that the carbons differ in their acidity as a result of the activation method and organic precursor (Bansal et al, 1988). The total number of groups and their distributions within various categories result in different values of the surface pH. We note that the pH values reported herein are slightly different than those reported in (Dallas et al, 2006) due to the use of a different method which ensures consistency with other literature values. Although the three carbons have similar equilibrium surface pH's in the neutral range, the distribution of surface groups obtained from the Boehm titration results are quite different. The pH values indicate that carbon C is the most acidic and Carbon B is the most basic surface. The slightly higher pH of Carbon B's surface is attributed to the presence of a significant amount of basic groups relative to the amount of acidic groups. The neutral pH of carbon C and F is essentially due to their surfaces consisting of an almost even balance of acidic and basic groups. The lower pH for carbon C is consistent with the presence of greater amounts of carboxyl groups on its surface relative to carbons B and F. Figure 1 provides a comparison between the equilibrium pH and the number of acidic and carboxylic groups. Although the pH differences between the three carbons are small, there exists a very good correlation with the individual number of groups.

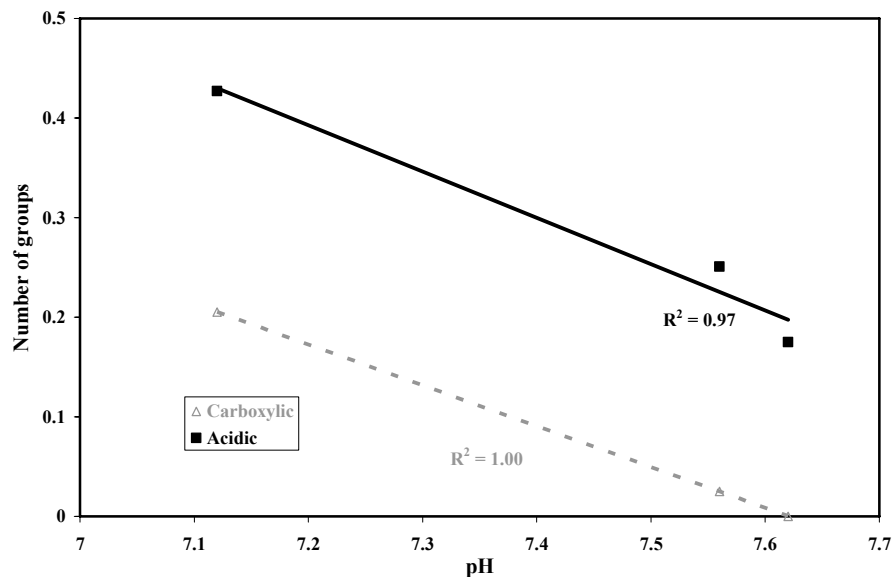
**Table 1:** Results of Boehm Titration (mmol/g)

Sample	pH	Carboxylic groups [mmol/g]	Lactonic groups [mmol/g]	Phenolic groups [mmol/g]	Amount of acidic groups [mmol/g]	Amount of Basic groups [mmol/g]	Total amount of groups [mmol/g]
Carbon B	7.62	~0	~0	0.175	0.175	0.691	0.866
Carbon C	7.12	0.205	~0	0.222	0.427	0.565	0.992
Carbon F	7.56	0.025	0.075	0.150	0.251	0.381	0.632

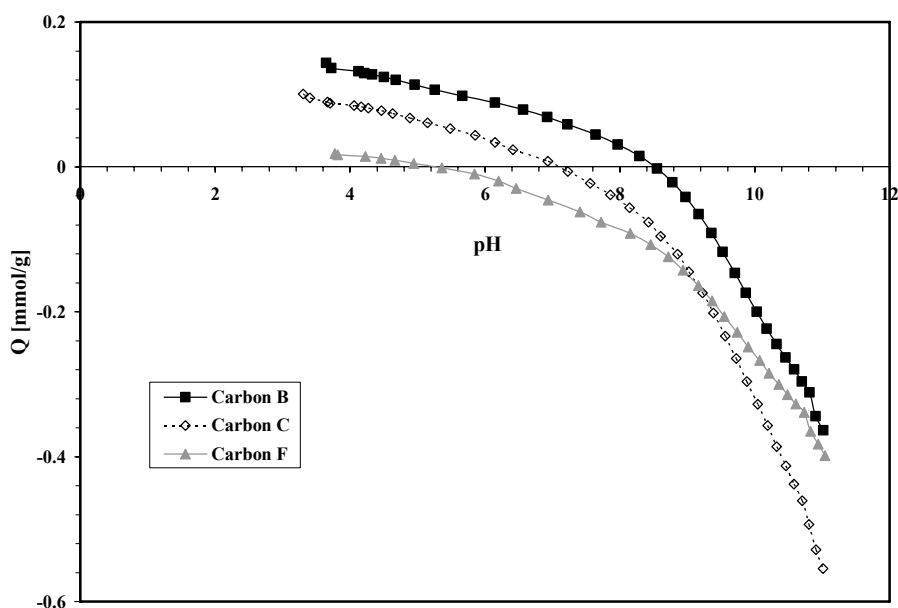
### Potentiometric Titration:

The changes in the degree of surface acidity were also studied using potentiometric titration. The proton binding curves given in Figure 2 were deconvoluted using the numerical SAIEUS procedure (Solution of Adsorption Integral Equation Using Splines) (Jagiello et al, 1994). From proton binding curves, the  $\text{pH}_{\text{PZC}}$  (pH at the point of zero charge) could be estimated (Jagiello et al, 1995). The  $\text{pH}_{\text{PZC}}$  values are determined to be approximately 8.5, 7.3, and 5.4 for carbons B, C, and F, respectively.

Solving equation 5 provides the distribution of the acidity constants,  $f(\text{pK}_a)$ , for each carbon surface. Based on the previous studies (Habgood and Flood, 1967; Kortum et al, 1961), the groups with  $\text{pK}_a < 8$  are classified as carboxylic acids and those with  $\text{pK}_a > 8$  are classified as phenols and quinones. The acidity constant distribution for each carbon is presented in Figure 3. The amount of each species calculated by integration of each peak and the peak positions are collected in Table 2. Analysis of the  $\text{pK}_a$  distributions reveals similar trends to the ones observed from the Boehm titrations. As shown in Figure 4, a good correlation is observed between the total group amounts on the three carbon surfaces calculated from both titrations methods. The deviation from unity in the slope, the presence of a positive intercept, and the correlation coefficient are related to the slightly different experimental conditions and the limitations of potentiometric titration below  $\text{pK}_a$  3 and above  $\text{pK}_a$  11. However, if we consider the standard error of the slope and the intercept obtained from the data fit, these fitting parameters are found to be statistically unity and zero, respectively. The advantage of potentiometric titration is in the distinct distribution of species having  $\text{pK}_a$  in the range between 3 and 11 (Jagiello et al, 1994).



**Figure 1:** Comparison between equilibrium surface pH and the number of groups.

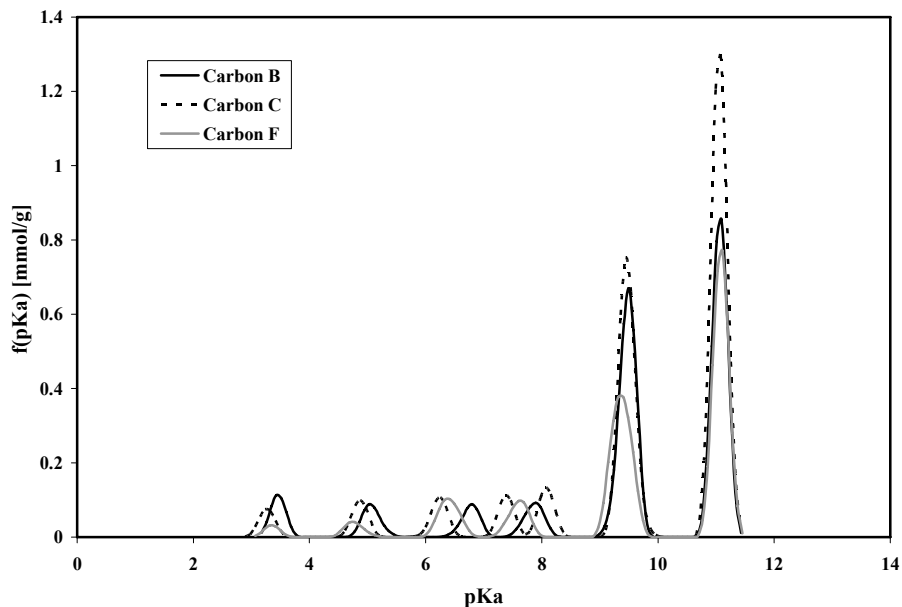


**Figure 2:** Proton binding curves.

***Evaluation of IGC LFER Coefficients:***

The results from the Boehm and potentiometric titrations given above are used to rationalize the LFER coefficients obtained for the IGC elution temperatures of twelve probe adsorbates on each of the three carbon surfaces given in equations 2-4 (Dallas et al, 2006). Table 3 provides a listing of results from these correlations.

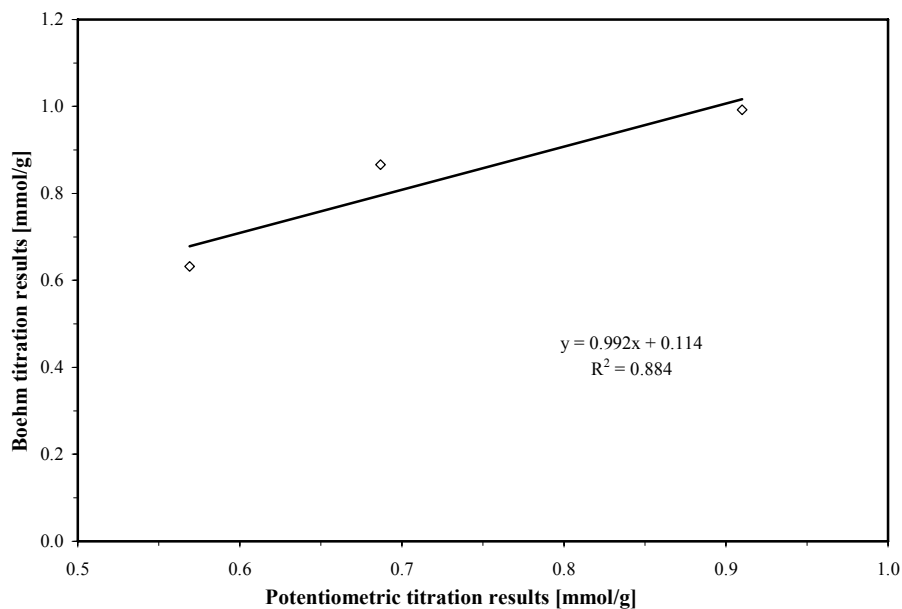
Figure 5 shows the correlations between the LFER *m* coefficient and the total number of surface acid and base groups determined by the Boehm and potentiometric titration methods. This comparison suggests that there is a downward trend in the magnitude of the LFER *m* coefficient with an increase in the total number of acidic and basic groups on the activated carbon surface. Since the LFER *m* coefficient represents the impact of the adsorbates size and shape on the overall IGC elution temperature, it can be hypothesized that by increasing the number of acidic and basic groups on the surface negatively impacts the ability of larger, more bulky, adsorbate molecules to enter the



**Figure 3:** Distribution of acidity constants.

**Table 2:** Potentiometric titration results: Peak position and the number of each group (in parentheses; mmol/g).

Sample	pKa 3-4	pKa 4-5	pKa 5-6	pKa 6-7	pKa 7-8	pKa 8-9	pKa 9-10	pKa 10-12	Total
Carbon F	3.35 (0.011)	4.77 (0.017)		6.40 (0.048)	7.60 (0.043)		9.37 (0.181)	11.08 (0.268)	(0.569)
Carbon C	3.26 (0.036)	4.87 (0.034)		6.23 (0.038)	7.39 (0.039)	8.07 (0.046)	9.47 (0.273)	11.05 (0.453)	(0.910)
Carbon B	3.46 (0.039)		5.07 (0.035)	6.77 (0.035)	7.86 (0.040)		9.47 (0.247)	11.07 (0.292)	(0.687)

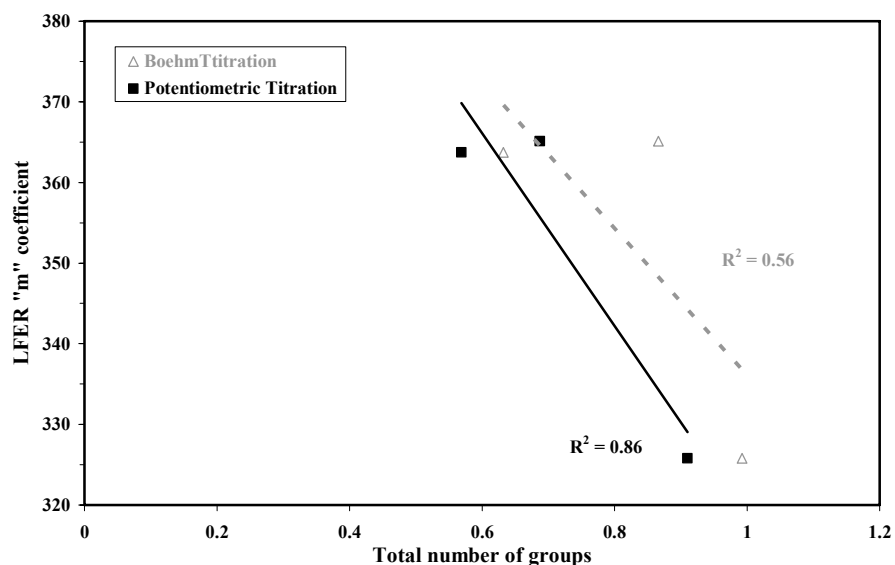


**Figure 4:** Relationship between the total group amounts obtained from the Boehm and potentiometric titration.

**Table 3:** LFER regression coefficients for elution temperatures from the three activated carbons:

Activated Carbon	SP	m	r	s	b	a	R <sup>a</sup>	s.e. <sup>b</sup>	n <sup>c</sup>
Carbon B	-126.2	365.1	44.0	66.0	0	71.8	0.991	7.2	12
Carbon C	-85.7	325.8	58.6	50.8	47.4	39.6	0.957	14.6	12
Carbon F	-97.1	363.7	33.5	80.5	0	116.1	0.965	15.5	12

a. correlation coefficient; b. standard error of the regression; c. number of adsorbates in regression.

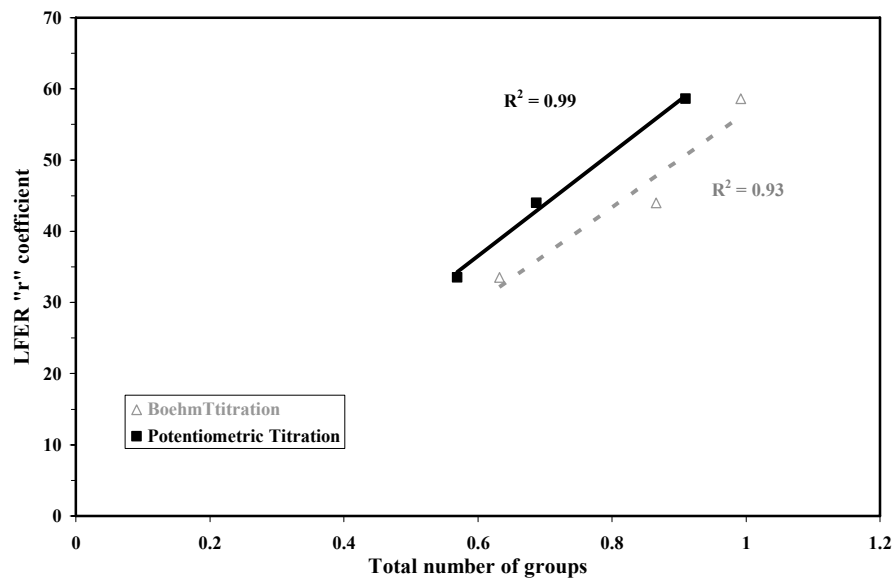
**Figure 5:** Total number of surface acidic and basic groups determined by Boehm and potentiometric titration methods compared with the magnitude of the LFER “m” coefficient.

microporous network of an activated carbon. However, we note that the relatively poor correlations demand that additional carbon surfaces be considered in order to solidify this conclusion.

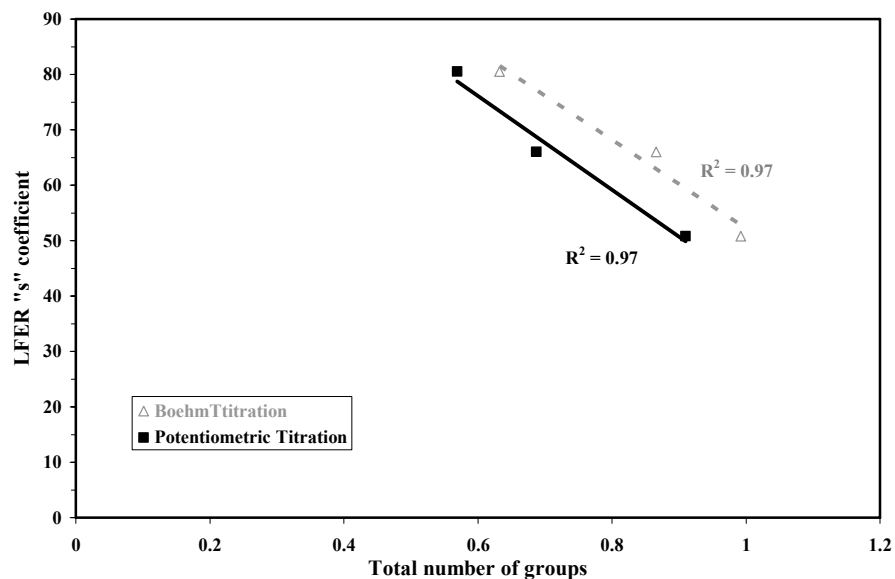
Figure 6 shows the correlations between the LFER *r* coefficient and the total number of surface acid and base groups determined by the Boehm and potentiometric titration methods. Excellent fits to the titration results are obtained. The overall trend of these correlations indicate that as the total number of acidic and basic groups on the activated carbon surface increases, the magnitude of the LFER *r* coefficient increases. This observation reflects the increase in an adsorbate’s ability to interact with an adsorbent through  $\pi$ - and n-electron pairs giving an indication of polarizability.

Figure 7 shows the correlations between the LFER *s* coefficient and the total number of surface acid and base groups determined by the Boehm and potentiometric titration methods. Again, excellent correlations are obtained with each titration method. However, the observed decreasing trend in the LFER *s* coefficient with an increase in the number of acidic and basic groups is somewhat surprising. As the total number of specific polar groups increases on the activated carbon surface, the overall surface polarity should increase. Therefore, it is expected that dipolar adsorbates would be able to interact more strongly with these surface groups leading to an increase in the IGC elution temperature; however, the trends suggest the opposite. This result may be attributable to the model’s attempt to rationalize balance between surface dipolarity and polarizability using a parameter that is a blend of both dipolarity and polarizability,  $\pi_2^H$ , and a term that models polarizability,  $R_2$ .

The influence of the activated carbon surface basicity and acidity on the overall IGC elution temperature is revealed through the LFER *a* and *b* coefficients, respectively. Figure 8 gives the correlations between the LFER *a* coefficient and the surface basicity measurements. From the potentiometric titration results we have chosen to use the total number of groups having pKa values greater than 8, and for the Boehm titration results we have used the total number of measured basic groups. A good correlation between the LFER *a* coefficient and the potentiometric titration results is observed, whereas a poor correlation is observed with the Boehm titration results. It is expected



**Figure 6:** Total number of surface acidic and basic groups determined by Boehm and potentiometric titration methods compared with the magnitude of the LFER “r” coefficient.

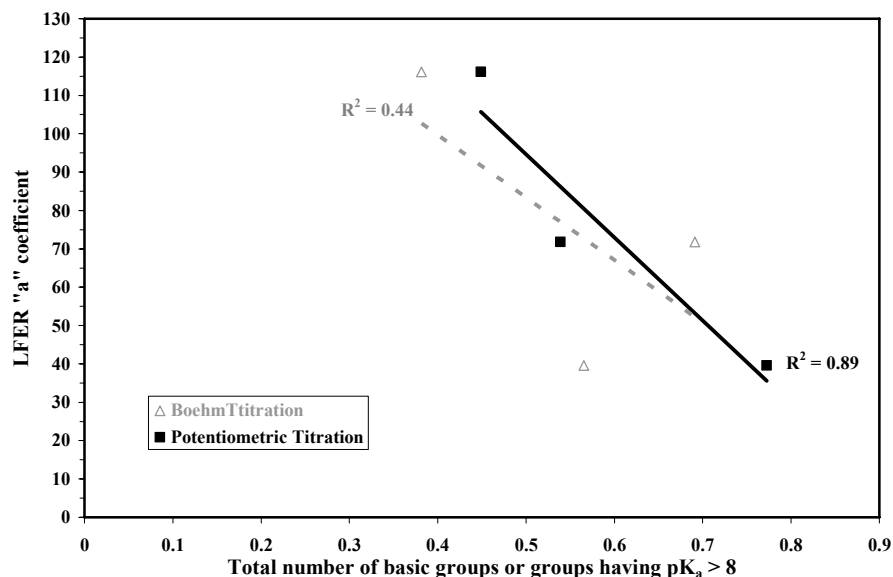


**Figure 7:** Total number of surface acidic and basic groups determined by Boehm and potentiometric titration methods compared with the magnitude of the LFER “s” coefficient.

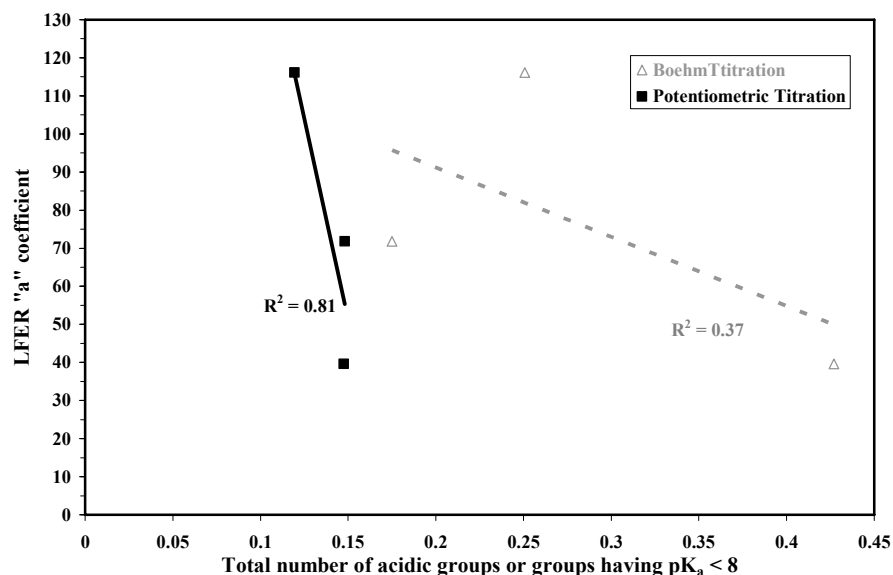
that as the activated carbon surface basicity increases, the magnitude of the LFER **a** coefficient would also increase.. This trend is expected since the **a** coefficient is supposed to reflect the ability of the carbon surface to interact with the adsorbates through the surface accepting a hydrogen bond from the hydrogen bond donating adsorbate. Our observations may be attributable to our use of such few activated carbons and the issues stated above with the potentiometric titration method. Alternatively, we point out that the LFER **a** coefficient should be inversely related to the surface acidity measurements as is shown in Figure 9. The expected trend in the LFER **a** coefficient holds in the case of the surface acidity measurements, but in the case of the surface basicity measurements. In order to unravel this discrepancy we are continuing to evaluate several additional activated carbons surfaces.

The ability of an adsorbate to accept a hydrogen bond from a hydrogen bond donating surface is reflected through the magnitude of the LFER **b** coefficient. Figure 10 compares this coefficient with the surface acidity results

from the potentiometric and Boehm titration methods. From the potentiometric titration results we have chosen to use the total number of groups having  $pK_a$  values less than 8, and for the Boehm titration results we have used the total number of measured acidic groups. We also added the correlation for the number carboxylic groups measured by the Boehm titration method in order to show the effect of strong acidic groups on the magnitude of the LFER **b** coefficient. Although it appears as though the overall trends are in agreement with what is chemically expected, an increasing **b** coefficient with an increasing number of surface acidic groups, there really are too few activated carbons in this data set with significant surface acidic sites to confirm this trend.

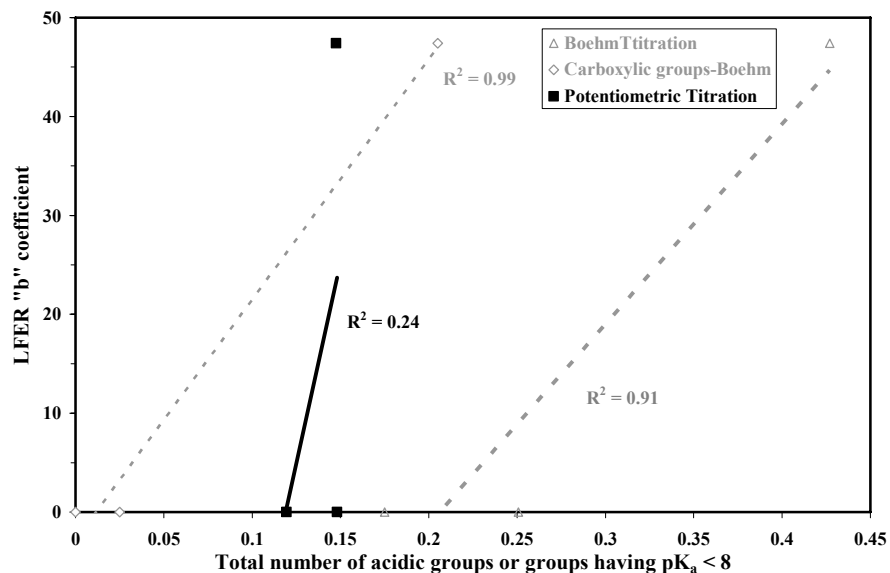


**Figure 8:** Total number of surface basic groups determined by Boehm and potentiometric titration methods compared with the magnitude of the LFER “a” coefficient.



**Figure 9:** Total number of surface acidic groups determined by Boehm and potentiometric titration methods compared with the magnitude of the LFER “a” coefficient.





**Figure 10:** Total number of surface acidic groups determined by Boehm and potentiometric titration methods compared with the magnitude of the LFER “b” coefficient.

### Summary

The surface acidity and basicity of three activated carbons have been evaluated using the potentiometric and Boehm titration methods. The results from these measurements are used to rationalize the magnitude of the coefficients obtained from a Linear Free Energy Relationship analysis of the inverse gas chromatography elution temperatures of twelve probe adsorbates. It has been shown that in most cases the observed trends in the Linear Free Energy Relationship coefficients are in agreement with the surface titration results. However, in order to confirm that there are direct relationships and the trends make chemical sense, it is necessary to expand this study to a wider range of activated carbons.

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