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Advanced NMR-Based Techniques for Pore Structure Analysis of Coal

Final Project Report

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Summary

During the 3 year term of the project, new methods have been developed for characterizing the pore structure of porous materials such as coals, carbons, and amorphous silica gels. In general, these techniques revolve around; 1) combining multiple techniques such as small-angle x-ray scattering (SAXS) and adsorption of contrast-matched adsorbates or ^{129}Xe NMR and thermoporometry (the change in freezing point with pore size), 2) combining adsorption isotherms over several pressure ranges to obtain a more complete description of pore filling, or 3) applying NMR (^{129}Xe , $^{14}\text{N}_2$, $^{15}\text{N}_2$) techniques with well-defined porous solids with pores in the large micropore size range ($> 1 \text{ nm}$).

The conventional approach for determining the surface area/micropore volume of

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coals is to apply Dubinin-Radushkevich analysis of carbon dioxide adsorption isotherms. However, that assumes a specific (Gaussian) form of the adsorption potential which means that the shape of the pore size distribution is fixed. We show using two families of microporous carbons that this assumption may be relaxed and the Dubinin-Astakov theory employed instead if carbon dioxide adsorption data over the complete relative pressure range of pore filling is obtained. Using this approach, one obtains not only the micropore volume and average interaction energy but a parameter which describes the general nature of the adsorption energy distribution assuming that it is monomodal. We have compared these results for a large number of carbon samples to pore structure parameters measured using nitrogen adsorption, carbon tetrachloride activity, accessibility of molecular probe molecules, small-angle x-ray scattering (SAXS), and ^{129}Xe NMR.

Small-angle x-ray (or neutron) scattering is a powerful method for pore structure analysis since it allows the determination of structural information over a wide range of length scales. However, it suffers from some uncertainty which primarily result from models necessary to relate scattering information to structural information. However, we have shown that if one performs SAXS measurements as a function of the degree of loading of a vapor adsorbate with the same electron density as the porous solid (contrast matching), a more complete picture of the porous solid is obtained.

By making ^{129}Xe NMR measurements as a function of pressure and temperature at temperatures below the freezing point of liquid xenon, a new means of performing thermoporometry was established. Thermoporometry normally employs calorimetric measurements to determine the fraction of pore volume with specific freezing points. The freezing point is subsequently related to pore size. However, by using NMR measurements, a much richer body of information is obtained since one can obtain the distribution of fluid density at any temperature (i.e., the volume fraction of various phases (solid, liquid, dense fluid) since the xenon shift is related to density and the relative spatial proximity of the phases by performing 2-D experiments.

Size analysis in the large micropore size range (1-2 nm) is difficult for a variety of reasons including difficulty in obtaining materials with known size and pore geometry in this range. We have synthesized and purified a nearly phase-pure form of the tubular aluminosilicate, imogolite, which has a nominal diameter of 1.2 nm. By replacing some silicon with germanium, the pore size can be varied in a systematic manner. We have used this material to explore the suitability of ^{129}Xe NMR as well as $^{14}\text{N}_2$ and $^{15}\text{N}_2$ NMR as pore size probes in this size range.

As a result of this work, eight refereed publications have either been published, are in press, or have been submitted. Two graduate students obtained MS degrees in chemical engineering with full support from the project. One student was hired by a carbon company, the Cabot Corporation, who is having the student remain at the University to pursue his PhD in the area of adsorption and the second student is working for a chemical company in Houston.

I. Background

One of the main problems in coal utilization is the inability to properly characterize its complex pore structure. Coals typically have micro/ultra-micro pores but they also exhibit meso and macroporosity. Conventional pore size techniques (adsorption/condensation, mercury porosimetry) are limited because of this broad pore size range, microporosity, reactive nature of coal, samples must be completely dried, and network/percolation effects. Small angle scattering is limited because it probes both open and closed pores. Although one would not expect any single technique to provide a satisfactory description of a coal's structure, it is apparent that better techniques are necessary. Small angle scattering could be improved by combining scattering and adsorption measurements. Also, the measurement of NMR parameters of various gas phase and adsorbed phase NMR active probes can provide pore structure information. We investigate the dependence of the common NMR parameters such as chemical shifts and relaxation times of several different nuclei and compounds on the pore structure of model microporous solids, carbons, and coals. In particular, we study the interaction between several small molecules (^{129}Xe , $^{14}\text{N}_2$, $^{15}\text{N}_2$) and pore surfaces.

II. Work completed during the project

II.1. Analysis of adsorption

II.1.A Background

As early as 1947, the Russian scientist Dubinin had suggested the use of Polanyi's Potential Theory (1) for characterizing microporous materials (2). Central to Dubinin's treatment is the Theory of Volume Filling according to which the primary physical phenomena occurring during adsorption in micropores is not surface coverage by a layer of molecules but rather, the filling of the pore volume space. Dubinin empirically showed that the quantity of vapor adsorbed by zeolites is proportional to the geometrical pore volume and not, as had been thought, the geometrical surface area (3). Thus, the defining characteristic of a microporous material is the micropore volume, as opposed to surface area.

Dubinin demonstrated that benzene adsorption data on several activated carbons could be linearized by the Dubinin-Radushkevich equation (3):

$$\ln V = \ln V_0 - (RT/E)^2 [\ln (P_0/P)]^2$$

Plotting $[\ln (P_0/P)]^2$ versus $\ln V$, the intercept yields the limiting micropore uptake, V_0 , (with known density of the adsorbed phase, this gives the micropore volume), and the slope yields the characteristic adsorption potential, E . It has been postulated that E is inversely related to pore size. Several relationships have been proposed between E and pore width (4,5) but it seems reasonable to expect that the relationship will not be unique but depend on both the chemical and physical nature of the material. Therefore, it is impossible to state with certainty, the micropore size from a single adsorption isotherm. The most dependable method for pore size determination may be molecular exclusion studies using molecules of different sizes but this is time consuming. For most studies (other than those involving molecular sieve materials) it may be sufficient to determine the characteristic adsorption potential, E .

Excellent reviews of the Potential Theory already exist (3,5-7) so the reader is referred to these for a detailed description of the theory. We will restrict ourselves to the specific problems arising during the application of Potential Theory to

micropore characterization. It is observed that while the DR equation gives linear plots for many materials, there are many others for which the plots are not linear (7-9). In particular, deviations are observed when the DR equation is applied to data at higher relative pressures. Rand has reviewed the types of deviations from linearity exhibited by DR plots (8). Apparently the deviations are due to inhomogeneities in pore structure. To counter these problems with the DR equation, Dubinin and Astakhov proposed the DA equation (3) which is similar in form to the DR equation but more general because of the introduction of an additional parameter, n :

$$V = V_0 \exp [-(A/E)^n]$$

where the exponent of 2 is replaced by the variable, n . n is determined by fitting experimental data to a linearized form of the DA equation. It is observed that n is closer to 3 for zeolites and unactivated or molecular sieve carbons. For highly activated carbons, which have broad pore size distributions, n approaches 1 (3). Therefore, the value of n may be an indication of the degree of pore size heterogeneity in a material. The DA equation has been criticized because of the lack of theoretical justification for the addition of the parameter n .

Another problem in the application of the DA equation is that unrealistic values of limiting uptake V_0 may be obtained (6). We note that the vast majority of gas adsorption experiments are carried out using N_2 at 77 K, or CO_2 at 273 K, up to a pressure of ~ 1 atm. only. Thus, while the DR equation can give rise to curved plots, making it impossible to accurately determine the parameters E and V_0 , the DA equation has met with limited acceptance because of the confusion surrounding the significance of the exponent n , and the uncertainty whether the micropore volumes obtained are in fact correct. However, the DR and DA equations, though semi-empirical in nature, are convenient for obtaining information about micropore structure from a single adsorption isotherm. Thus, it is of utility to eliminate the confusion that exists with regard to its application.

For applying the DA or DR equations to experimental data, it is first necessary to know the range of relative pressures over which the equations are applicable. In the past, the bounds of application of Potential Theory seems to have been dictated

by the availability of experimental data rather than theoretical considerations. For example, many authors have recommended CO₂ adsorption for the characterization of microporous materials (10-12) but in most cases, the data used only covers a narrow range of relative pressures. Some authors have applied the DR equation to nitrogen adsorption for relative pressures above 0.4 (where mesopore filling is expected to occur) and even, approaching 1. Significant deviation from linearity of DA/DR plots is observed in such cases due to capillary condensation. It seems clear that the DR and DA equations should only be applied to the range of micropore filling and application beyond that range could lead to incorrect results. For N₂ (77 K) adsorption, there is reasonable agreement as to the point on the isotherm where mesopore filling begins ($P/P_0 \sim 0.4$) (13). Unfortunately, nitrogen is not the best adsorbate for characterizing microporous materials for reasons such as restricted diffusion effects at 77 K and the fact that a large part of the micropore filling region cannot be recorded because it occurs at very low relative pressures (14). For these reasons, CO₂ adsorption at 273 K has been suggested as a better method for micropore characterization. We estimate that for CO₂ at 273 K, the mesopore filling begins at about $P/P_0 \sim 0.8$. This analysis is carried out using the data of Everett and Burgess (15) to find the lowest relative pressure at which a capillary meniscus is stable based on tensile strength arguments, and from the application of the Kelvin equation to determine the lowest relative pressure at which condensation in mesopores will occur (13). This analysis should not be considered exact but provides an estimate of P/P_0 to which the DA equation may be applied without serious error.

II.1.B Experimental

For this work, we analyzed two sets of microporous carbons from Air Products. The first, the AC1 series, consisted of five progressively activated coconut shell carbons. The role of activation on changing pore size distribution is shown in Figure 1. The second, the AC2 series, consisted of eight unrelated microporous carbons from a variety of sources. A list of these materials is given in Table 1:

Table 1. Source of carbon samples in series AC1 and AC2.

Sample ID	Material	Source
AC1-03	Activated carbon	Coconut
AC1-18	Activated carbon	Coconut
AC1-19	Activated carbon	Coconut
AC1-20	Activated carbon	Coconut
AC1-21	Activated carbon	Coconut
AC2-09	Carbon adsorbent	Coconut
AC2-16	Chemically activated	Pitch
AC2-17	Carbon adsorbent	Coke
AC2-23	Carbon adsorbent	Coconut
AC2-31	Carbon adsorbent	Peat
AC2-32	Carbon adsorbent	Petroleum
AC2-33	Carbon adsorbent	Wood
AC2-57	Molecular sieve carbon	Coconut

Adsorption experiments were carried out using nitrogen (UHP) at 77 K and CO₂ (UHP) at 273 K. All samples were outgassed at 10⁻³ Torr and 383 K for at least 10 hours. N₂ adsorption was measured with a Quantachrome Autosorb-1 or Micromeritics ASAP 2000 automated analyzer. These instruments allow the precise determination of adsorption isotherms between about 10⁻² Torr and 800 Torr. CO₂ adsorption was carried out at 273 K using an ice-water bath. Two sets of CO₂ measurements were made for each sample; low pressure measurements that were made with an ASAP 2000M analyzer, and high pressure measurements to 30 atm. that were undertaken with a VTI Corp. HPA 100 automated volumetric adsorption system. To determine CO₂ adsorption at 273 K to P/P₀ = 0.8, it is necessary to perform measurements at high pressure (P₀ = 35.3 atm), far above the range of commercial low-pressure instruments, which operate below 850 Torr. The complete isotherm was obtained by combining the low and high pressure measurements. DA and DR analysis was carried out using the ASAP 2000M software.

**Figure 1. A simple picture of the activation process in carbons.
(the spheres represent adsorbate molecules)**

The degree of activation of the materials in the AC1 series was determined from the carbon tetrachloride activity. CCl_4 activity is defined as the quantity of CCl_4 adsorbed at a given relative pressure, normalized by the total pore volume as measured by nitrogen adsorption. This indicates the volume of pores accessible to

CCl_4 ($\sigma \sim 6 \text{ \AA}$) relative to the total pore volume from N_2 adsorption at 77 K. CCl_4 activities greater than 100% are caused by CCl_4 condensation around particles.

II.1.C Results

In Figure 2, a typical DR plot for CO_2 adsorption on the AC1 series is presented. The significant nonlinearity over the entire range of relative pressure and the problems associated with extrapolation are apparent. The deviation from linearity is of type "B" as classified by Rand (8). If one used a smaller range of P/P_0 , it is obvious that different values would be obtained for the slope and intercept depending upon the particular range selected. However, when the same data is plotted in DA coordinates, it is linearized well over the entire relative pressure range (see Figure 2). Comparison of the limiting micropore uptake calculated using both DR analysis and DA analysis of the same CO_2 data is given in Table 2 for all samples studied. The density of adsorbed CO_2 was taken to be equal to 0.919 g/cm^3 (16). For many samples, there are differences of over 100% between the two methods which raises the question of which analysis (DR or DA) of the same data yields the micropore volume with the most physical significance.

Figure 2. DR plot for CO_2 (274 K) adsorption on AC1-18

Figure 3. DA plot for CO_2 (274 K) adsorption on AC1-18

Table 2. Comparison of limiting micropore volumes using the DA and DR equations for CO₂ (274 K) adsorption on AC1 and AC2 carbons.

Sample ID	Limiting micropore volume from DR (cm ³ /g)	Limiting micropore volume from DA (cm ³ /g)
AC1-03	0.338	0.367
AC1-18	0.521	0.859
AC1-19	0.453	0.66
AC1-20	0.406	0.491
AC1-21	0.496	0.812
AC2-09	0.278	0.259
AC2-16	0.803	1.535
AC2-17	0.619	1.338
AC2-23	0.318	0.566
AC2-31	0.365	0.6
AC2-32	0.41	0.863
AC2-33	0.287	0.897
AC2-57	0.213	0.211

Nitrogen adsorption isotherms for all samples were of Type 1 according to the IUPAC classification (17). The molecular sieve carbon AC2-57 exhibited low pressure hysteresis which is typical of materials for which restricted diffusion of the adsorbate, or swelling of the adsorbent occurs (13). The total pore volume was obtained from the volume of nitrogen adsorbed at $P/P_0 \sim 0.995$ using an adsorbed phase density of 0.807 g/cm³ (13). The BET "surface area" was calculated using five points in the relative pressure range of 0.05 to 0.2. Although the BET surface area has no physical significance for microporous materials, we report it for purposes of comparison. In Table 3, micropore volumes calculated from DA analysis are listed along with total pore volumes from nitrogen adsorption. The values of the DA/CO₂ micropore volume are quite reasonable based on comparison with the total pore volume from nitrogen adsorption. For all samples but two, the N₂ and DA/CO₂ pore volumes are within 10%. For the molecular sieve carbon, AC2-57, the DA/CO₂ volume is almost double the pore volume from nitrogen adsorption, and this is readily explained when one considers the possibility of restricted diffusion during adsorption of nitrogen into the pores of the molecular sieve at 77 K. Sample AC2-33

has a N₂ pore volume which is much larger than the CO₂ micropore volume, presumably the result of the presence of mesoporosity.

Table 3. Summary of results on AC1 and AC2 series carbons

Sample ID	CCl ₄ activity, %	BET surface area, (m ² /g)	Total (N ₂) pore volume, (cm ³ /g)	Micropore volume from CO ₂ DA, (cm ³ /g)	DA exponent from CO ₂ DA analysis
AC1-03	30	689	0.352	0.367	1.81
AC1-18	113	1774	0.938	0.859	1.35
AC1-19	81	1256	0.635	0.66	1.45
AC1-20	60	985	0.51	0.491	1.68
AC1-21	102	1654	0.857	0.812	1.39
AC2-09	-	477	0.24	0.259	2.1
AC2-16	-	2652	1.459	1.535	1.24
AC2-17	-	2742	1.451	1.338	1.37
AC2-23	-	1010	0.509	0.566	1.43
AC2-31	-	1140	0.579	0.6	1.51
AC2-32	-	1489	0.929	0.863	1.34
AC2-33	-	1556	1.178	0.897	1.22
AC2-57	-	292	0.102	0.211	2.17

One of the possible reasons for uncertainty in the DA-derived micropore volume values is that a limited relative pressure range was employed (6). Therefore, the DA equation was applied to data obtained over two ranges of relative pressure; $10^{-5} < P/P_0 < 0.03$ (corresponding to the range of operation of a commercial low-pressure instrument), and $10^{-5} < P/P_0 < 0.8$ (corresponding to the complete range of micropore filling as used in Tables 2 and 3). Micropore volumes obtained from application of the DA equation over the two ranges are tabulated in Table 4. The exponent n obtained for the two ranges of relative pressure is also presented. For some samples, there are wide discrepancies between the results from the two pressure ranges. Therefore we ascribe the confusion that has existed about the results from DA analysis to the fact that it was not carried out over the complete range of micropore filling. In effect, the data analyzed represented only a partial filling of the micropore volume. It is therefore not surprising that problems were encountered in interpretation of the data.

Table 4. Comparison of results from application of the DA equation to CO₂ (274 K) adsorption over the complete P/P_O range ($10^{-5} < P/P_O < 0.8$) and low pressure ($10^{-5} < P/P_O < 0.03$) only.

Sample ID	V _{mic} from low pressure data (cm ³ /g)	V _{mic} from data over complete pressure range (cm ³ /g)	DA exponent from low pressure data	DA exponent from data over complete range
AC1-03	0.436	0.367	1.67	1.81
AC1-18	1.132	0.859	1.22	1.35
AC1-19	0.658	0.66	1.44	1.45
AC1-20	0.579	0.491	1.56	1.68
AC1-21	0.989	0.812	1.29	1.39
AC2-09	0.286	0.259	2.01	2.1
AC2-16	1.459	1.535	1.25	1.24
AC2-17	1.346	1.338	1.37	1.37
AC2-23	0.726	0.566	1.32	1.43
AC2-31	0.792	0.6	1.38	1.51
AC2-32	0.56	0.863	1.54	1.34
AC2-33	0.521	0.897	1.45	1.22
AC2-57	0.169	0.211	2.39	2.17

To further investigate the meaning of the three parameters V_O, E, and n, we studied how they varied with activation in the AC1 series of carbons. The three parameters are plotted against the CCl₄ activity for the AC1 activated series in Figures 4 and 5. The micropore volume from CO₂/DA increases with activation as does the total pore volume from nitrogen condensation (Figure 4). Also, the characteristic adsorption potential, E, decreases with progressive activation (Figure 5). From our physical picture of activation (Figure 1), the pore volume should increase, the pore size should increase (hence, the adsorption potential should decrease assuming pore surface chemistry is not changing), and heterogeneity should increase. The DA exponent, which is thought to be a measure of heterogeneity, decreases and approaches values close to unity with activation (Figure 5). Therefore, it seems reasonable to state that the DA exponent reflects the degree of heterogeneity (size and/or chemical) of the material.

Figure 4. Variation of total pore volume and micropore volume of AC1 series with activation

Figure 5. Variation of characteristic adsorption potential E and DA exponent n for AC1 series with activation

Figure 6. Relation between characteristic adsorption potential E and DA exponent n for both series

The three parameters V_O , E , and n also correlate with one another (Figures 6 and 7), and it is interesting to note that they seem to preserve their relationship with activation. We note that these same trends in V_O , E , and n hold true even for the more general, AC2, series. This is rather surprising considering the different precursors and processes with which these materials were manufactured.

II.2.D Discussion

It is clear that application of the DR equation can give rise to results much different from those obtained from application of the DA equation. Adsorption data giving rise to curved DR plots can be linearized using the DA equation as a result of the extra degree of freedom (the exponent) associated with the DA equation. The DR equation is just a special case of the DA equation with n equal to 2. Application of the DR equation is, in effect, an imposition of a specific distribution of adsorption

potentials on the experimental data. The problem is compounded since many users of commercial instruments employ a limited relative pressure range with DR analysis and therefore, nonlinearities are not as apparent. We believe that the observation that the DA equation gives rise to results different from other methods is a result of applying the DA equation over limited P/P_0 ranges (corresponding to an incomplete range of micropore filling). Table 4 shows that application of the DA equation to data over an incomplete range of pore filling could lead to values of limiting uptake that are either much larger or smaller than the actual limiting uptake calculated from data over the entire range of micropore filling. Whether this deviation is towards the higher or lower side depends on the adsorption potential distribution of the material being studied.

To further investigate the physical meaning of the exponent, n , the change in the potential distribution with activation of the AC1 series was assessed. The distribution of potentials for each sample can be determined by numerical differentiation of the experimental data. The distribution is a continuous curve of $(-dV/dA)$ plotted versus the potential, A , and represents the distribution of pore volume with potential. The area under the curve directly gives the limiting micropore uptake, V_0 . The characteristic adsorption potential, E , is the volume averaged potential. For large n , E coincides with the modal adsorption potential.

It is apparent that the shape of the potential distribution curve is not dependent on any one parameter, but on both E and n . To illustrate, theoretical potential distributions were generated keeping two of the three parameters constant and varying each in turn. The effect of V_0 can be eliminated by normalizing the distribution by V_0 and hence, does not affect shape, only the magnitude. The effects of E and n on the distribution are more complex. For constant E and V_0 , (Figure 8) increasing n results in narrower distributions. At n equal to 1, the potential distribution assumes an exponential form. For high n values, the distribution becomes symmetrical and E coincides with the mode of the distribution. The ratio on the left hand side approaches unity as n becomes large, and thus the peak of the distribution occurs at E .

Figure 8. Adsorption potential distribution as a function of n .

Figure 9. Adsorption potential distribution as a function of E .

In real systems, n is rarely observed to be greater than 3. Fixing n and V_0 , and changing E , the distribution changes shape, though differently from how it changes with n (see Figure 9). The distribution becomes flatter and shifts to higher values of

A_{mode} with increasing E , as opposed to the previous case, where an increase in n causes the distribution to become more "peaked" about the modal potential value.

Plotting the distributions for the activated AC1 series from the experimental data (Figure 10), we find that the simple trends obtained while varying only one parameter (E or n), are not observed. The change in the potential distribution with activation is thus rather more complex than would have occurred if only one of the parameters was changing. When both E and n are changing, it is difficult to predict the effect of any one parameter on the distribution. The change in the distribution with activation is a net result of the simultaneous change in E and n .

Figure 10. Experimentally determined adsorption potential distributions for AC1 series of activated carbons

The trends observed between E and n persist for the general AC2 series (Figures 6 and 7). Thus the trends observed for the progressively activated AC1 series may be part of a more general trend which exists for all microporous carbons. From the physical picture of activation (Figure 1), prior to activation, the material has a relatively homogeneous pore size (n larger than 1), with a small average pore width (hence, large E). On activation, existing pores are widened to cause an increase in the pore width (decrease in E) and a greater range of pore sizes (causing n to approach a value closer to 1). If one considers that at a greater activation, the

difference in size between the largest and smallest micropores is much larger than it was prior to activation, it will be intuitively obvious why activation increases heterogeneity. This may be part of the reason why the trends in V_O , E , and n persist for all the samples studied and not only for the AC1 activated series of carbons.

II.1.E Conclusions

The DA equation needs to be applied carefully so that i) only the data from the micropore filling region is analyzed using the DA equation, and ii) the entire range of micropore filling is covered by the data. In this way, two of the commonly observed problems with the DA and DR equations can be avoided; deviations of the DR/DA plot from linearity caused by data from the capillary condensation region, and incorrect values of micropore volume that are sometimes obtained when the DA equation is used. The DA equation provides a useful semi-empirical method of characterizing the micropore structure of carbons, and if used with care, can provide useful information about structure in the micropore size range from a single adsorption isotherm. However, the distribution of potential does not necessarily directly give pore size information.

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II.2. Comparison of methods

II.2.A Background

The determination of pore size distribution information for microporous, amorphous materials is more problematic than for materials with larger pores as the limits (theoretical and practical) of common techniques are often exceeded. The determination of pore size information from adsorption and condensation of gases such as nitrogen at 77 K works well in the mesopore size range yet is limited for microporous solids because of the inability to accurately relate adsorption isotherms to pore size. Many approaches are available for relating adsorption isotherms to adsorption potential and hence, to pore size. However, acceptance of these approaches is limited because of the effects of unknown surface-adsorbate interactions, unknown pore shape, etc. which can cause very different size information to be calculated from the same adsorption data.

In contrast to adsorption techniques, small angle scattering has the advantage of being primarily a physical probe. By changing the instrumental setup and/or the source wavelength (x-rays, neutrons, light), large pore size ranges can be investigated (<1 nm to >10 μm). This is an advantage for materials which may exhibit fractal pore structure over several orders of magnitude in pore size. One shortcoming of scattering techniques is the difficulty in relating scattering data (typically, intensity versus scattering vector) to the solid's physical structure. Data analysis requires pore shape assumptions and the extraction of structural information is often sensitive to the data analysis scheme employed. For carbons, most scattering studies have employed x-rays (SAXS) in order to probe the length scales of interest (0.1 nm to 10 nm). A previous study on activated carbons showed that small angle scattering can provide the radius of gyration for some samples depending upon their size range [1]. For those samples the r_g , obtained from the Guinier region, correlated well with the micropore size obtained from adsorption. However, scattering failed to correlate with the adsorption data at very small pore sizes. One reason is that the minimum size covered by normal SAXS is at wave vectors near $0.5 \text{ \AA}^{-1}$ implying that the length scales of interest are smaller than normal spatial resolution limits ($\sim 0.2\text{-}0.4 \text{ nm}$). In their study of natural coals,

Ciccariello et al. suggested that for better structural analysis, one also should have data from the wide angle x-ray scattering (WAXS) region ($0.5 < q < 1 \text{ \AA}^{-1}$) [2]. To our knowledge, there are a limited number of combined SAXS and WAXS studies on carbons in the literature, presumably a result of limited access to these two techniques.

With SAXS, the length scales are associated with electron density variations in the sample but it is not possible to determine if the features are pores, solid features, or regions of varying solid density arising from solid-phase heterogeneity. Only by combining SAXS with other techniques such as adsorption or NMR can unambiguous pore structure information be obtained.

The ^{129}Xe NMR of adsorbed xenon has been promoted as a technique for characterization of porous materials, especially microporous zeolites [3,4]. The stated rationale for this technique is the high sensitivity of the ^{129}Xe chemical shift to the xenon mean free path. Fraissard and coworkers measured ^{129}Xe chemical shifts extrapolated to zero xenon pressure at 297 K in zeolites and established a correlational equation that relates the chemical shift to the pore size. Operationally, the ^{129}Xe chemical shift is measured at several pressures and extrapolated to zero pressure to determine the shift associated with xenon-surface interactions (as opposed to xenon-xenon interactions). For many materials the ^{129}Xe shift versus pressure is nonlinear which is inconsistent with the simple mean free path arguments and requires further empirical corrections to the correlational model.

The extension of ^{129}Xe NMR to amorphous solids with a broad pore size distribution is even more problematic. Conner and co-workers [5] measured ^{129}Xe chemical shifts in silica powder compacts. The shift versus pressure curves are nonlinear and the pore sizes calculated from the NMR data were more than an order of magnitude smaller than those predicted from gas adsorption or a knowledge of the silica primary particle size and packing behavior. There are a few published applications of ^{129}Xe NMR to carbons and coals [6-9]. Wernett and co-workers [6] used ^{129}Xe NMR to study pore structure in Spherosorb porous carbon

and a coal. They assumed cylindrical pore geometry and applied the same equation relating ^{129}Xe chemical shift and pore size derived for zeolites [6]. The NMR derived pore size for the Spherisorb sample agreed with the reported of 15 Å pore size. For coal, they noted several peaks in the xenon spectra which they attributed to xenon in pores and to xenon dissolved in the coal matrix depending upon whether the peaks shifted with changing pressure and on the peak intensities. The pore sizes calculated were not compared to other size characterization methods. Tsiao and Botto [7] extensively studied three Argonne Premium Coal samples using ^{129}Xe NMR. They typically observed four peaks; one assigned to free gas and another to xenon dissolve in the coal. The peaks assigned to xenon in pores increased in shift with an increase in pressure but at higher pressures, the shifts decreased. This unexpected decrease was attributed to swelling of the coal as a result of xenon adsorption. Suh and co-workers [8] combined ^{129}Xe NMR and nitrogen adsorption at 77 K to study several carbons before and after mild oxidative treatments. They found that even though N_2 adsorption indicated negligible change in the pore size following oxidation (calculated from t-plot analyses) the xenon shift changed dramatically yielding a large apparent pore size change. Bansal and coworkers [9] also combined ^{129}Xe NMR and nitrogen adsorption to study porous carbons. They used ^1H NMR of methane in conjunction with the ^{129}Xe NMR to correct for ^{129}Xe chemical shift effects that might be due to paramagnetism in the carbon. They assumed a flat plate geometry and used the corrected ^{129}Xe chemical shifts to estimate the size of the solid platelets which form the structure of the porous carbon structure.

The objective of this study is to apply both x-ray scattering and ^{129}Xe NMR spectroscopy to two series of carbons which have been well characterized by CO_2 adsorption as described in II.1 in order to evaluate the utility of these techniques for carbon characterization. One series of carbon samples were progressively activated from the same precursor and the second series consisted of carbons from a wide range of sources.

II.2.B Experimental

NMR data was acquired on a Varian Unity spectrometer which operates at 4.7 tesla with a nominal ^{129}Xe NMR frequency of 110.6 MHz. The spectra are Fourier transforms of Bloch decays, acquired in a one pulse sequence with a 90° pulse width. At the maximum xenon loading, the free gas NMR resonance was usually observed. The ^{129}Xe chemical shifts are referenced to free xenon gas extrapolated to zero pressure. A special adsorption NMR probe was used for all experiments. Essentially the sample is contained in a 16 mm outer diameter and 16 mm long Pyrex cylinder which is connected to a gas handling system. The entire probe is contained in a cryostat for accurate temperature control. This system allows simultaneous measurement of adsorption isotherms and acquisition of ^{129}Xe spectra with good temperature control. Natural isotopic abundance xenon gas was cleaned by several freeze-pump-thaw cycles at 77 K before use in the NMR experiments. Xenon adsorption isotherms were measured by the volumetric method at 299 K in the NMR probe. The amount of adsorbed xenon is given as the number of xenon atoms adsorbed per gram of sample. Before analysis, samples were outgassed at 573 K and 0.01 torr for 8 hours.

Small angle and wide angle x-ray scattering (SAXS & WAXS) were performed at the University using a Rigaku 12 kW rotating anode x-ray generator. For SAXS, a Rigaku Kratky camera was used with a M-Braun linear position sensitive detector. The q range covered with the Kratky system was 0.007 to $0.55 \text{ \AA}^{-1}$. SAXS data was desmeared by Schmidt's method [10]. WAXS was performed using an INEL x-ray diffractometer operating in the transmission mode with single slit (200 μm). A curved, CPS-120, 120° position sensitive detector was used for data collection with the higher angle region ($60^\circ < 2\theta < 120^\circ$) blocked by a lead insert. No desmearing process was performed. The q range covered for WAXS was from 0.2 to $4 \text{ \AA}^{-1}$.

All scattering data are presented as intensity versus wavevector, $q = 4\pi/\lambda \sin(\theta/2)$. Data from WAXS is matched with the SAXS data by applying a constant factor to match the intensity in the q range of 0.2 to $0.5 \text{ \AA}^{-1}$. An excellent match over

this range was observed for all the samples. The maximum q value used for the combined data is approximately $1\text{\AA}^{-1}$ (immediately before the amorphous peak for most samples in this study).

II.2.C Results: SAXS and WAXS

WAXS and SAXS intensity plots are presented in Figure 1 for the five samples of the AC1 series which are produced from the same precursor but with different degrees of activation. Although the curves look similar, with linear regions at small and high q values, the samples exhibit subtle differences in the q range of 0.03 to $0.3\text{\AA}^{-1}$. These differences are more apparent from the radius of gyration for each sample calculated from the Guinier region of Figure 1 as reported in Table 1.

Figure 1 Combined SAXS and WAXS scattering plots for the AC1 series of progressively activated carbons.

Figure 2 shows the 8 carbons of the AC2 (random) series. Differences between the samples are apparent although the large intensity range covered serves to hide these differences when all samples are compared at once. Samples AC2-09, AC2-17, and AC2-33 have similar large scale structure as indicated by the features at q equal to 0.02-0.03 $\text{\AA}^{-1}$. This feature probably results from either a characteristic platlet or primary particle size. However, the AC2-09 and AC2-17 samples have a much narrower size distribution in the micropore region, which is revealed by the well defined R_g region. The lack of a sharp knee in the q range of 0.1 to 1 $\text{\AA}^{-1}$ for some samples indicates a relatively wide micropore size distribution. This point will be discussed in more detail subsequently.

Figure 2 Combined SAXS and WAXS scattering plots for the AC2 series of randomly selected carbons.

Size information from Guinier analysis of the combined SAXS/WAXS curves presented in Figures 1 and 2 are listed in Table I. We note that the radius of gyration does not directly yield a "pore size" but rather is proportional to the actual size with the proportionality constant depending upon pore shape. We estimate the accuracy of these R_g values to be $\pm 0.1 \text{ \AA}$. The activated AC1 series shows only small variations in size whereas the random series exhibits a much wider range of sizes.

Table I. The radius of gyration calculated from the Guinier region of the combined SAXS/WAXS curves for the progressively activated (AC1) and random (AC2) carbon series.

Activated		Random	
AC1-03	5.4 $\text{\AA}$	AC2-09	5.7 $\text{\AA}$
AC1-18	6.4 $\text{\AA}$	AC2-16	6.4 $\text{\AA}$
AC1-19	5.7 $\text{\AA}$	AC2-17	6.4 $\text{\AA}$
AC1-20	5.9 $\text{\AA}$	AC2-23	6.7 $\text{\AA}$
AC1-21	6.4 $\text{\AA}$	AC2-31	9.1 $\text{\AA}$
		AC2-32	8.2 $\text{\AA}$
		AC2-33	10.2 $\text{\AA}$
		AC2-57	5.6 $\text{\AA}$

Although the determination of one or more characteristic sizes is possible from scattering if Guinier regions are observed, the quantitative determination of size distribution information is difficult. Qualitatively, the smoother, longer stretching of a scattering curve indicates a wider size distribution. This is directly shown by a Guinier plot ($q^4 \cdot I$ vs. q) as discussed by Kaeler [11]. Figure 3 shows this comparison between AC2-17 and AC2-33. AC2-17 exhibits a fairly narrow peak at $q=0.4 \text{ \AA}^{-1}$ and AC2-33 monotonically increases into the high q region which suggests a much wider distribution.

Figure 3 Guiner plot for samples AC2-17 and AC2-33.

II.2.D Results: ^{129}Xe NMR

While performing ^{129}Xe NMR experiments, we measured xenon pressures and volumes added at 299 K for all samples. Figure 4 contains the xenon adsorption isotherms calculated from this data for the five samples of the AC1 series. Although all of the samples, with the exception of AC1-03, exhibit similar xenon uptake at low pressure, at higher pressures there are significant differences. At low pressure, the AC1-03 sample had the highest uptake but at higher pressures, it had the lowest uptake. This is presumably a result of the AC1-03 sample having both smaller pore sizes and lower total pore volume. Figure 5 contains adsorption isotherms for the AC-2 series. These isotherms have very different appearances in both the total xenon adsorbed at any given pressure and in the overall shape of the isotherm. Presumably this reflects the differences in the pore structure and surface characteristics for these very different samples.

Figure 4 Xenon adsorption isotherms for the AC1 series.

Figure 5 Xenon adsorption isotherms for the AC2 series.

The ^{129}Xe NMR chemical shifts as a function of xenon loading are presented in Figures 6 (AC1 series) and 7 (AC2 series). All xenon shift-loading data is nominally linear. However, large differences in both intercept (zero pressure shift) and slope are observed for different samples.

Figure 6 ^{129}Xe NMR shift referenced to xenon free gas as a function of gas loading for the AC1 series.

The concepts surrounding the ^{129}Xe chemical shift for xenon in confined spaces use an equation relating the measured ^{129}Xe shift to an additive set of chemical shifts ($\delta = \delta_0 + \delta_s + \delta_e + \delta_{\text{Xe-Xe}}\rho_{\text{Xe}}$) where δ_0 is the shift of the reference, δ_e is the shift due to electric fields in the pore space (primarily due to cations), the term $\delta_{\text{Xe-Xe}}\rho_{\text{Xe}}$ is due to xenon xenon collisions as the density of xenon is increased, and δ_s is due to xenon interactions with the surface. It is this latter term that is of interest in determining pore sizes. In most cases the electric field term is considered to be negligible and plots such as those in figures 6 and 7 yield an intercept which is δ_s . By comparing known structures of zeolites and computing the mean free path for the

xenon and empirically relating this to measured chemical shifts, the following relationship is obtained: $\delta_s = 243 (2.054)/(2.054 + \lambda)$ where λ is the mean free path.

Figure 7 ^{129}Xe NMR shift referenced to xenon free gas as a function of gas loading for the AC2 series.

II.2.E Results: Comparison of NMR, Scattering, and Adsorption

Dubinin and Stoeckli [12] and McEnaney [13] proposed correlations for relating the adsorption potential, E , and the SAXS R_g . Our CO_2 adsorption-scattering data does not correlate as well as the benzene data reported by Dubinin ($\pm 4\%$). We believe that this is a result of the fact that the adsorption potential, E , also depends on surface chemistry while SAXS probes only a physical structure. Further evidence for this lack of a general correlation between adsorption and scattering is shown in Figure 8, a plot of E versus radius of gyration. Although there is a general decrease in E with increasing radius of gyration, it is clear that the overall correlation is poor. This is true even for the samples which had been

progressively activated from the same precursor. Actually, a better correlation is observed between the D-A exponent, n , and the radius of gyration. The D-A constant arises when the variation of adsorption potential is not described by a Gaussian distribution (which yields a value of two as in the Dubinin-Radushkevich equation) but is allowed to be an experimentally fit parameter. As the radius of gyration increases, the value of n decreases which is an indication of increased heterogeneity in the sample. As discussed in the preceding section, increasing activation leads to a wider pore size distribution as the size of existing micropores are increased and new, smaller micropores are created. However, it is surprising that the correlation between R_g and n is so good for all of the samples studied, not just the progressively activated AC1 series.

Figure 8. Correlation between SAXS radius of gyration and average energy, E , from D-A analysis of CO_2 adsorption.

Figure 9. Correlation between D-A exponent, n , from CO₂ adsorption and SAXS radius of gyration.

As discussed above, the analyses of the ^{129}Xe NMR shifts versus xenon loading from figures 6 and 7 were done simply following Fraissard's equations which correlate the xenon mean free path with the measured chemical shift. There are clear problems with the intrinsic accuracy of this approach but it can be said that it works remarkably well. In fact, one might ask why application of these simple concepts, under conditions for which they were not derived, should work so well. Proton NMR corrections for paramagnetism as made by Bansal and coworkers [9] would likely make a significant improvement relating the ^{129}Xe shifts to absolute pore sizes. However, in the carbons used in this work, it is likely that the density of paramagnetic centers is relatively constant from sample to sample. Thus, the relative sizes, from sample to sample are well correlated. There is also a question of

interactions between the xenon atoms and the pore walls. In order to relate the mean free path, obtained from this simple analysis, to the actual pore size requires assumptions about the pore shape. We have simply assumed a spherical shape and note that this affects the absolute value of pore size reported but does not affect the ranking of the various samples. The conclusion that one reaches is that the ^{129}Xe analysis is flawed but it is likely that most of the errors come out in the wash and it is reasonable to simply apply Fraissard's mean free path analysis with no corrections. Thus, the goal is not to obtain absolute pore sizes but rather relative pore sizes through a series of samples and to compare those relative sizes to ones measured by another technique, SAXS.

As with the SAXS results, there is an inverse correlation between the NMR measured mean free path and the adsorption potential. In fact, the correlation is quite good with the exception of the point on the lower left of figure 10. This sample, AC2-33, has a small mean free path, measured in the NMR experiments, as well as a low adsorption potential. These measurements were duplicated with two separate samples of the same material and the experimental deviation from the other samples is real. We attribute this difference to the wide pore size distribution of this material as evidenced by the large difference between the micropore and total pore volumes and the fact that this sample had the lowest DA exponent value.

Figure 10 Correlation between the ^{129}Xe NMR mean free path and average energy, E , from D-A analysis of CO_2 adsorption.

Although SAXS, NMR, and adsorption energy distributions are not absolute structure measures, the carbon tetrachloride activity (the fraction of the pore volume measured by nitrogen adsorption which is accessible to CCl_4) is often taken as a more direct probe of micropore size (or at least, the fraction of pores with size greater than ~ 0.5 nm). Figure 11 contains plots of both radius of gyration and xenon mean free path versus the carbon tetrachloride activity, $\%\text{CCl}_4$. Both SAXS and NMR exhibit the same general increasing trends with increasing $\%\text{CCl}_4$. Based on these results, one can conclude that SAXS and NMR give very similar physical structure information which supports $\%\text{CCl}_4$. All three methods are primarily structural probes and thus yield little complementary information.

Figure 11. SAXS radius of gyration, r_g , and ^{129}Xe NMR λ versus $\%\text{CCl}_4$ activity for a series of progressively activated carbons (AC1).

Figure 12. Correlation between the SAXS radius of gyration and the ^{129}Xe NMR mean free path.

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II.3. Contrast matching

II.3.A INTRODUCTION

Small angle x-ray scattering and ultra small angle scattering (SAXS and USAXS) are important techniques for structural analysis of porous materials on the scale of 10 to 2000 Å. In scattering studies, the scattered intensity from a structure with a length d can be expressed as a function of qd , where q is the scattering vector and:

$$q = (4\pi/\lambda) \sin(\theta/2), \quad (1)$$

where λ is the wavelength, and θ is the scattering angle. The scattering data between the interval $0.1 < qd < 1$ can be used to estimate d . For $qd \gg 1$, information about the pore surface properties can be obtained. In this qd interval, the intensity, $I(q)$, is proportional to a negative power of q [1,2]:

$$I(q) = I_0 q^{-\alpha}. \quad (2)$$

From the exponent α , one can ascertain whether pore surfaces are smooth, self-affine or fractal [2,3]. Other information such as molecular weight or surface area can be obtained using I_0 [4,5]. In a two-phase system with constant electron density for each phase, the small angle scattering intensity can be expressed as

$$I_0 = I_c(\rho_1 - \rho_2)^2. \quad (3)$$

Therefore, the intensity will be zero when the electron density of the two phases are equal, even when the phases contain different materials (or a solid and a fluid). This method is typically called contrast matching and is often employed in small

angle neutron scattering. A similar approach is also used in light scattering studies by matching the refractive index but has rarely been used with x-rays.

By combining SAXS with varying loading of a contrast matched adsorbate or varying coverage of a contrast matched surface modification agent, additional structural information may be obtained as compared to scattering or adsorption only. These include pore surface roughness, pore morphology (i.e. positive or negative curvature), and pore size. The change in scattering with adsorption/surface modification is conceptually illustrated in Figure 1. Since SAXS probes only changes in density, one is unable to determine if a particular solid exhibits pores of a given size, d , or a solid particle of the same dimension. However, the change in characteristic size as a function of adsorbate loading should indicate the net curvature of the pore space (see Fig 1.a). Pfeifer and co-workers [6] have previously shown that by measuring the change in surface area as a function of the quantity of a film adsorbed on the pore, the surface roughness could be assessed. This same approach may be combined with SAXS to yield roughness information (see Fig 1.b). A related approach would be to surface modify with a surface modification agent of similar electron density and vary either the extent of coverage or the molecular weight distribution. At higher relative pressures, pore blockage will occur as a result of capillary condensation leading to pore size information (see Fig 1.c). Although some of these concepts have been demonstrated previously with SANS (for example, Ramsey [7]), there has been only limited SAXS/contrast-matching work [8,9]. In this paper, we will demonstrate the approach with SAXS which should make the technique more generally available.

II.3.B Experimental

For solids, the electron density ρ_e can be computed from:

$$\rho_e = (v/M)N_0\rho_m \quad (4)$$

where v is the number of electrons per molecule, M is the molecular mass in atomic mass units, ρ_m is the mass density, and N_0 is Avogadro's number. There are a number of liquid halogenated hydrocarbons that have electron density in the same range as silica and carbon and which have a vapor pressure sufficiently high at room temperature to facilitate vapor adsorption experiments. Table I-lists the

1.a Pore Morphology

1.b Surface Roughness

1.c Pore Size

Figure 1. Conceptual schematic of the change of scattering with adsorption /surface modification

electron densities and mass absorption coefficients that we have calculated for a series of fluids with density that bracket silica and carbon (the solids of interest in this study). We should note that there is some uncertainty in the calculated electron density as a result of uncertainty concerning the physical properties (this is particularly problematic for the fluid density in microporous solids) and in solid density since this depends on surface species associated with the solid (eg, surface hydroxyls).

Table I. Electron Density for potential compounds for SAXS contrast matching.

Compound	Mass Abs. coeff. (μ) (cm^2/gm)	Electron Density ($\text{e}^-/\text{\AA}^3$)	Saturation Vap.Press. (torr, 22°C)
graphite (C)	4.22	0.683	NA
silica (SiO_2)	36.41	0.661	NA
bromoform (CHBr_3)	85.84	0.772	6.4
chloroform (CHCl_3)	97.72	0.436	171.7
dibromomethane (CH_2Br_2)	83.31	0.669	39.2
chlorodibromomethane (CHClBr_2)	70.12	0.666	18.5
1,2 dibromoethane ($\text{C}_2\text{H}_4\text{Br}_2$)	77.37	0.601	9.5
bromochloromethane (CHCl_2Br)	57.12	0.556	54.7

For contrast matching/adsorption studies, several porous materials were used; CPG-75, CPG-240, CPG-350 (phase separated and leached glasses with narrow pore size distribution from Electronucleonics), microporous activated carbon produced from coconut char (AC03), Amoco AX-21 high surface area activated carbon, and a silica xerogel made by gelling and drying a 4 nm silica sol (Nalco Co.). Particulate fumed/pyrogenic silica, grades CAB-O-SIL L90 and EH5 (Cabot Co.), were also studied. For loading the contrast matching reagents, two methods were used, one via vapor and one via liquid. For liquid loading, the sample is put in a 1 mm capillary tube, dried under vacuum at 140°C , the liquid is added, and the tube is sealed. Vapor loading is accomplished at ambient temperature with a volumetric adsorption apparatus. The vapor pressure was controlled by the temperature of the liquid in equilibration with the adsorbate. An equilibrium time of 24 hours was used for each adsorption point. Surface area and pore volume for each sample was determined from analysis of low and high pressure portions of nitrogen adsorption isotherms measured at 77 K and are reported in Table II.

Figure 2. Scattering curves of CPG-350 liquid loaded with various halogenated solvents.

Figure 3. Scattering curves of AX-21 liquid loaded with various halogenated solvents.

due to the large mass adsorption coefficient with which we can not obtain adequate signal to noise. From these and similar results for the other porous silica solids, we conclude the solvent dibromomethane is the best for contrast matching of porous silica and carbon.

II.3.C.ii Pore Blocking (Pore Size)

First we use SAXS/contrast matching for pore structure analysis by selective pore filling. The scattering curve of a partially saturated porous samples should exhibit a change in the q value at which the pore size is evident. If there are two different characteristic pore sizes, the smaller one should be filled at lower relative pressure. In order to demonstrate the effects of contrast matching adsorption/condensation on SAXS for surface roughness and pore size, the CPG-75 sample was vapor loaded with dibromomethane at a wide range of relative pressures. The plain (unloaded) CPG-75 has a peak in Figure 4 which shows the characteristic feature of the material (pore dia.~ 80 Å). The slope at large q has been interpreted as a fractal dimension of ~2.2 [12]. At lower relative pressures ($P/P_0 \leq 0.68$), the adsorbate progressively fills the surface roughness. This smoothening is manifested in a flat tail at large q which moves to smaller q as the thickness of the adsorbed dibromomethane film increases. Using the correlation of inverse scattering length ($1/q$) [3], this surface smoothening effect is observed at length scales greater than ~2.5 Å ($q = 0.4 \text{ Å}^{-1}$). The q values at which the curves for the different relative pressures flatten are listed in Table III.

Table III. CPG-75 with various loading of dibromomethane

P/P_0	q value at which the curve flattens (Å^{-1})	min. length at which the surface is fractal (Å)
0.0	0.4	2.5
0.25	NA	NA
0.47	0.33	3.0
0.51	0.31	3.2
0.63	0.33	3.0
0.79	0.3	3.3
0.80	0.23	4.4
0.87	0.14	7.1
0.97	NA	NA

This flattening of the scattering curve indicates that no scattering features are present with length scales smaller than that of the corresponding q value.

Figure 4. Scattering curves of CPG-75 vapor loaded with different relative pressure (P/P_0) of dibromomethane.

At the low adsorbate relative pressures, the 80 Å peak does not move significantly. We think it is because the the film thickness change is small (i.e., less than 10 Å) and because the pores contain regions of both positive and negative curvature. The CPG samples are produced by a spinodal decomposition and subsequent leaching of one phase and although the pore throats in this type of material are cylindrical and of narrow size distribution, TEM indicates a microstructure which does indeed have positive and negative curvature. Since this material exhibits a monomodal pore size distribution, a gradual change in the SAXS pore size is not observed during increasing adsorbate loading but rather a sudden drop in scattering intensity is observed when a relative pressure, P/P_0 , is reached which causes condensation in the majority of the pores. We have calculated this relative pressure value to be ~ 0.8 at room temperature using the Kelvin equation [13] with the physical properties of dibromomethane and the 80 Å pore size. There is still a small hump for the $P/P_0 = 0.97$ vapor loaded sample which implies that the contrast is still not perfectly matched. This is either due to the fact that all of the pores in the sample were not completely filled during the 24 hour equilibration time, or that the material contains structural heterogeneity such as pockets of the second solid phase which were not leached during sample production.

SAXS as a function of dibromomethane loading was also measured for the AC03 activated carbon (see Figure 5). The micropore size is apparent at high q values ($\approx 0.3 \text{ Å}^{-1}$) for the unloaded ($P/P_0 = 0$ sample). According to nitrogen adsorption, pore filling should happen at $P/P_0 \approx 0.1$ to 0.2, from SAXS, the high q scattering feature disappears at $P/P_0 \approx 0.14$. This is the lowest relative pressure that we are able to measure in our system and is consistent with the nitrogen adsorption result. The scattering curve at lower q regime gets steeper indicating that the scattering surface at larger feature sizes, relative to the micropores, become smoother as the vapor loading increases.

Another demonstration of progressive pore filling is obtaining by making physical mixtures of CPG samples with two different pore sizes. Scattering from a mixture of CPG-75 and CPG-240 in a 40:1 volume/volume ratio is given in Figure 6. Also included are scattering curves for each unloaded sample individually. Since our previous results indicate that the pores of CPG 75 will fill in the dibromomethane relative pressure of approximately 0.8, we loaded the mixture to

Figure 5. Scattering curves of AC03 vapor loaded with different relative pressure (P/P_0) of dibromomethane.

Figure 6. The effect of solvent loading (dibromomethane) of mixture of CPG-75 and CPG-240 (40:1 v/v)

a series of relative pressures in the vicinity. As can be seen, it contains two characteristic feature sizes and the smaller pore gets filled at lower P/P_0 and the larger pores shift to smaller sizes and superimpose with the small pores.

II.3.C.iii Pore Morphology

Since SAXS probes changes in electron density, one is unable to determine if the length scale of curvature being probed is a characteristic of the pore or of the solid matrix. However, according to Fig. 1a, the change in characteristic size as a function of adsorbate loading should indicate the net curvature of the surface being probed. Depending upon the surface curvature, the scattering curve will shift to higher or lower q values with increasing adsorbed film thickness.

The Nalco xerogel made from a 4 nm silica sol was used for the pore morphology study. Nitrogen adsorption/condensation showed pores of radius calculated from the desorption branch between 30 to 40 Å. The SAXS data presented in Figure 7 shows similar length scales. Analysis of the scattering data show two feature sizes, an interference peak which corresponds to radius of 51 Å and another one at 30 Å. The radius of gyration (R_g) from SAXS could be due to primary particles, pores or cluster aggregates. Adsorption of dibromomethane at various relative pressures exhibits size changes for these two features are listed in Table IV. It can be clearly seen that the larger R_g varies with vapor loading. This indicates that size 1 is from aggregate structure, and the smaller size 2 could be the pore size and/or the primary particle size. At $P/P_0 \geq 0.75$, all features vanish, due to capillary condensation as observed for the CPG samples.

Table IV. Scattering lengths in the Nalco xerogel versus dibromomethane loading

Relative Pressure	Guinier Size 1 (Å)	Guinier Size 2 (Å)	q value for which the curve flattens (Å ⁻¹)
blank	51	29	0.38
0.35	50	34	0.27
0.42	62	36	0.15
0.54	68	35	0.15
0.62	85	30	0.11
0.75	NA	NA	0.06
0.94	NA	NA	0.03

Figure 7. Scattering curves of Nalco xerogel with different relative pressure (P/P_0) of dibromomethane.

II.3.C.iv Surface Roughness

A previous study of silylation with alkoxide-derived silica xerogels showed that the pore size distribution could be narrowed and the pore size reduced by a dimension comparable to the organic group diameter [14]. Silylation appeared to selectively modify the large pores in the size distribution and also smooth the pore surface as observed with SAXS. For highly silylated samples, the SAXS showed a crossover in behavior at a certain q value. Below that region, we obtained a Porod slope less than -4. We attribute this to the "fuzzy boundary" contained on the silica surface arising from the nonuniform change in electron density. Schmidt and co-workers previously observed a decreasing slope with increasing coverage of higher molecular weight silylating agents with values of the slope approaching -5 and attributed this to the presence of a diffuse layer of varying electron density contrast between the silica and the pore (the so-called fuzzy boundary theory) [15,16]. If one can contrast match out this diffuse layer effect, then the study of silylation by SAXS will be more straightforward.

For testing the fuzzy boundary theory, two grades of fumed silica (CAB-O-SIL) were employed. One had a smooth surface (L90) and one with a rough surface (EH5) [17]. Silylation was conducted using DBETCS (dibromoethyl-trichlorosilane; electron density: $0.557 \text{ e}^-/\text{\AA}^3$) since the electron density of the dibromoethyl moiety will be close to that of silica. Since a trifunctional chlorosilane will typically not react all three chlorines with silica surface hydroxyls, samples were washed with water to remove excess chlorine. SAXS results (Figure 8) show that the Porod slope does decrease with increasing concentration of silylating agent. EH5 exhibits a smooth surface (with slope of -4) after silylation whereas the Porod slope for L90 changes slightly for L90. From nitrogen adsorption, as the silylation level increases, the surface area of both L90 and EH5 decrease which also supports a smoothing of the surface.

We extended the study on EH5 to include dibromomethane adsorption. As mentioned above, it has a particle-aggregate structure and a rough surface. We found that when loaded with dibromomethane vapor, the Porod slope does decrease with increasing P/P_0 (Figure 9). EH5 exhibits a smooth surface (with slope of -4) after loading to $P/P_0 = 0.8$ but when loaded at the highest possible relative pressure in our system (~ 0.99), the slope obtained is -4.22 (Table V).

Figure 8. The effect on Porod slope of silylating agent on EH5 and L90.

Figure 9. The effect of various loading (P/P_0) of dibromomethane on EH5.

Table V. Range of scattering vectors and length scales for fractal nature of EH5

P/P ₀	Range of q (Å ⁻¹)		Length scales (Å)		Porod
	q _{min}	q _{max}	L _{min}	L _{max}	Slope
0.0	0.025	0.14	7.0	40	-3.5
0.6	0.02	0.12	8.3	50	-3.7
0.8	0.02	0.11	9.1	50	-4.0
0.99	0.02	0.10	10	50	-4.22

There may be preferential orientation of dibromomethane molecules adsorbed on the surface of EH5. In this case, the film adsorbed on the surface of the sample is not homogeneous in terms of electron density over the surface as it would be for a bulk liquid. Instead of an abrupt density change at the pore-film interface as is normally assumed, the adsorbed layer possesses a distribution of electron density where it changes gradually till it becomes equal to that of the pore volume. This will be a reasonable explanation considering the density differences between Bromine atoms (0.82) and -CH₂ group (0.39). The electron density in the region immediately next to the silica surface increased to a value higher than the silica density and then the density decreased. This could be the profile for a monolayer coverage. For subsequent layers, the electron density will take the value of the bulk density after several monolayers.

Cheng, Cole, and Pfeifer have studied the adsorption of films on fractal surfaces [18] and showed a similar effect. A thick liquid film adsorbed on the fractal surface of a substrate that had the same electron density as the adsorbed film. They found that in this adsorption process, which they call defractalization, an adsorbed film of nominal thickness Δ is adsorbed mainly on the regions of the surface where the surface roughness is characterized by length scales not exceeding Δ . The film tends to smooth out the roughness in these regions, which then appear smooth, and for $q\Delta \gg 1$ the calculated intensity of the small angle scattering can be described by Equation 2, with $\alpha = 4$. On the other hand, for $q\Delta \ll 1$, the surface scatters as if it were fractal, with $\alpha = 6 - D$. Scattering data will provide direct evidence of an effect that the adsorption data could confirm only indirectly.

II.3.D REFERENCES

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II.4. NMR methods

II.4.A Introduction

It is well known that the microscopic behavior of molecules is significantly different when they are confined to small pores. This is the basis for many techniques for measuring pore structure such as analysis of adsorption isotherms and thermoporometry^{1,2}. These effects are the result of the fact that the overall dimension of the pore is within a very few molecular diameters. Similarly, there are a number of unusual phenomena that are associated with molecules in pores but in reality are due to the unusual behavior of those molecules that are in direct contact with the pore wall and it is only in small pores, where the ratio of wall to bulk molecules is large enough, that the phenomena can be observed and studied. This includes such interesting effects as layering transitions and NMR relaxation phenomena. Many of the studies of small molecules in pores are limited to theory and computer simulation because there are few measurement techniques that can directly probe these systems. There are occasional experiments in which unusual results are obtained and which are then interpreted in terms of the pore structure or wall effects. We report here on one such experiment where we observe a ^{129}Xe NMR peak with a chemical shift between that normally seen for solid and liquid

xenon at the particular temperature. This peak is associated with a dense fluid phase due to interactions with the wall of the pore.

The NMR chemical shift is a function of local structure such as chemical bonding, solid state structure, and even collisional frequency³. Early on it was recognized that the chemical shift of ^{129}Xe is a sensitive function of density. Thus, there is a significant difference in the ^{129}Xe NMR shift of solid and liquid⁴. In our work, the shift of solid xenon is at about 293 ppm and the shift of liquid at about 254 ppm near the freezing point, 161.3 K. The reference for ^{129}Xe chemical shifts is the shift of gaseous xenon extrapolated to zero pressure, taken as zero ppm of chemical shift. Since xenon is a large, polarizable atom, each collision of a ^{129}Xe atom produces a chemical shift whose memory persists, resulting in very strong chemical shifts as a function of temperature, pressure and dilution in another gas. Most other atomic or molecular gases have much smaller chemical shift effects, presumably because they have fewer electrons interacting with the surroundings. Jameson and coworkers have made many studies of the effects of pressure and temperature on the chemical shift of ^{129}Xe gas^{5,6}. Recently the ^{129}Xe chemical shift has been extensively promulgated as an indicator of pore size in microporous materials⁷⁻¹⁰.

II.4.B Experimental

In this work we report on the phases of xenon by observing the ^{129}Xe chemical shift in several porous glasses as a function of temperature between the bulk boiling point and the point at which the xenon freezes in the pores (162-65 K). Chemical shifts are reported relative to ^{129}Xe at infinitely low pressure, measured "by substitution". Using this method of measuring shifts, we estimate the error in measurement at ± 2 ppm. These shifts were measured at 110.6 MHz in a specially designed NMR probe that has been described elsewhere¹¹. The porous glasses used in this study are: CPG 75 and CPG 350, obtained from CPG Inc. and Vycor, obtained from Corning Glass Inc. These materials have the following nominal pore diameters as given by the manufacturers: CPG 75 = 7.5 nm, CPG 350 = 35.0 nm, and

Vycor = 4.0 nm. All samples are powders with particle sizes near 50 μ m. The pore structure of these materials was studied in detail by Pfeifer¹².

II.4.C Results and Discussion

Figure 1 contains the ^{129}Xe spectra of xenon as a function of temperature for CPG-75 that is saturated with xenon liquid. We note that the chemical shift of the solid and liquid peaks shift to lower field as the temperature decreases. This change is due to the increase in density upon lowering temperature. There are a number of experimental measurements in the literature that show similar shifts as a function of pressure or temperature⁵. The unusual feature of these spectra is the appearance of a well resolved peak between those associated with the solid and liquid. From the chemical shift, we associate this peak with a phase that is more dense than the normal liquid xenon and yet is less dense than the solid. We shall refer to this phase as a dense fluid phase. We can follow the appearance and disappearance of that phase as a function of temperature both raising and lowering the temperature. Figure 2 contains a plot of the fraction of xenon in each of the three phases as a function of temperature. We note that the interparticle liquid xenon behaves like bulk xenon, freezing at 161 K and producing the plateau between 161 and 154 K. There is a measurable freezing point depression evidenced by the loss of liquid xenon in the pores at about 154 K extending down to about 147 K. As the sample is cooled, the dense fluid appears somewhat before the appearance of solid xenon. By 140 K all the liquid is gone and the xenon exists as either solid or dense fluid. Upon warming the CPG 75 sample, hysteresis in the transition between liquid and dense fluid indicates that the dense fluid is stable to 155 K but above that temperature the transition to normal liquid occurs in a very small temperature range.

The appearance of this dense fluid phase has been duplicated many times with this sample and corroborated by repeating these experiments in porous glasses with both 4.0 and 35.0 nm pores. Generally the chemical shifts of both the solid and liquid phases increases as the temperature is lowered. The chemical shift for the liquid xenon is independent of the pore size but the shifts for solid xenon in the pores decreases with decreasing pore size. The chemical shift of the dense fluid in

Figure 1. A plot of the ^{129}Xe spectra at different temperatures for xenon in CPG-75.

Figure 2. A plot of the fraction of xenon in the three phases, liquid, dense fluid, and solid, as a function of temperature. The data are shown for warming and cooling the sample. Lines are drawn simply to aid the eye.

both CPG 75 and CPG 350 is independent of temperature but the shift for the dense fluid in vycor increases very slightly as the temperature decreases. If the dense fluid were to behave like normal liquid xenon, one would expect the chemical shift to increase with the decrease of temperature. The chemical shift of the xenon in the dense phase is greater in smaller pores with shifts of 289, 285, and 282 ppm in 35, 7.5 and 4.0 nm pores, respectively. The transition temperature from liquid to dense fluid as well as from dense fluid to solid decreases as the pore size decreases. The ^{129}Xe linewidths narrow and then broaden as the temperature is lowered. Below 100 K the linewidths of the dense fluid phase increase rapidly in all samples.

We compared the ratio of the areas of the peaks due to dense fluid and solid xenon at 100 K to an estimate of the surface to free volume. The surface to free volume was obtained by standard nitrogen adsorption at 77 K. Using the physical picture of dense phase on the surface and solid in the center of a pore, *vide infra*, we conclude that the layer of dense phase xenon is two atoms thick. This is reminiscent of results obtained by thermoporometry where it is concluded that there are two layers of water near the surface of pores that do not "freeze" easily¹³.

We questioned the effects of pore size inhomogeneities on the xenon freezing results. In other words, it is possible that small variations in the pore size through the sample will result in solid in large pores, a dense liquid in smaller pores, and liquid in the smallest pores simply due to the freezing point depression as a function of pore size. To resolve this issue, we performed a relatively standard two-dimensional chemical exchange experiment¹⁴, the results of which are shown in figure 3. In this type of two-D spectrum, a slice through the diagonal is equivalent to the one dimensional spectrum; the total number of contour lines in each peak is representative of the intensity of the peak; and the off-diagonal peaks are due to chemical exchange between the species represented by the diagonal peaks. In this particular spectrum, the diagonal peaks are due to the solid and the dense fluid, analogous to the spectrum at 120 K in figure 1. The mixing time in this experiment is only 8 ms. The fact that the off-diagonal peaks are nearly as intense as the on-diagonal peaks indicates that there is very rapid exchange between the two phases.

Figure 3. A two-dimensional chemical exchange plot of xenon in CPG-75 at 125 K. The peaks are associated with xenon in the dense liquid and solid phase. The mixing time in the two-D experiment was 8 ms.

The only model that rationalizes this rapid exchange is one in which the solid and dense fluid are in intimate contact. Thus, solid xenon atoms at the interface with the dense fluid are mobile and there is rapid exchange between the two phases. We have repeated this experiment at many temperatures and mixing times. In the temperature regime just below the freezing point of bulk xenon, we obtain ^{129}Xe peaks for liquid in the pores and solid in the interparticle space. At a mixing time of several seconds, there are virtually no off-diagonal peaks because the time for diffusion into the pores is very slow, *i.e.*, the solid and liquid are not in close contact. That the solid peak in figure 3 is oblate along the diagonal is also an indication of relatively slow exchange between different regions of solid xenon. The breadth of the solid line is due, in part, to a dispersion of bulk magnetic susceptibilities through the sample with different xenon atoms in slightly different magnetic fields. This dispersion is not averaged by motion of the atoms on the time scale of 8 ms (the mixing time) because diffusion in the solid is too slow. Additionally, the peak for the dense fluid is somewhat more round which is an indicator of rapid motion in this phase or for a relaxation determined linewidth. Both of these suggest a phase that is relatively fluid, compared to the solid xenon. This is the underlying reason why we refer to this new phase as a dense *fluid*.

II.4.D Summary

The physical picture that results from this data is one of liquid xenon in the pores of the porous glasses that starts to become a dense fluid phase at about 155 K in CPG 75. Very quickly, at about 145 K the xenon in the pores freezes while there is still a significant amount of the dense fluid phase present. Since the only unusual feature of these samples is the fact that the xenon is contained in pores with relatively large surface to volume ratios, we conclude that the dense liquid phase is associated with xenon atoms at the pore walls. Two dimensional chemical exchange experiments (mixing times of several seconds) performed in the temperature region where peaks due to both dense fluid and liquid xenon are present show very small off diagonal peaks. This indicates that the liquid and dense fluid are not in close contact. At the phase transition, the liquid xenon changes to a dense fluid several

atoms thick at the wall surrounding frozen xenon in the center of the pore. In smaller pores, the core of frozen xenon may be missing at first. As the temperature is lowered, the dense fluid changes to solid down to about 65 K where less than two but more than one surface layer of dense fluid remains. This data can be compared to ^{129}Xe NMR data obtained in Y zeolite which has chambers about 1.1 nm in dimension. In these samples, there is no phase transition, instead the chemical shift of the liquid phase increases monotonically with decreasing temperature down to 70 K. We believe that the dense fluid phase is associated with xenon molecules at the walls of the pores. Thus, we believe that there is a dense fluid layer formed at the wall with liquid xenon in the center. At lower temperatures, the liquid center freezes and then the "crystal" in the center continues to take material from the fluid phase in a rather continuous fashion down to about 60 K where only a small amount of the dense fluid phase remains.

We can make one final observation about this dense phase. There are a number of reports in the literature in which computational methods predict layering¹⁵ and unusual molecular dynamics¹⁶ in pores of molecular dimensions and ordered structures of rare gases in zeolite cages¹⁷. Thus, our data are anticipated in several molecular dynamics calculations. The NMR observations require somewhat special conditions including the large ^{129}Xe chemical shifts as a function of density and pores of just the right size to give relative peak intensities that allow observation of all three phases.

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Appendix

Papers Submitted/Published

- 1) Hua, D.W., D'Souza, J. V., Schmidt, P. W. , and Smith, D.M. , "Pore Structure Analysis Via Small Angle X-Ray Scattering And Contrast Matching," CHARACTERIZATION OF POROUS SOLIDS III, J. Rouquerol, F. Rodriguez- Reinoso, K.S.W. Sing, and K.K. Unger, Editors, Elsevier Press, Amsterdam, 255-262, (1994).
- 2) Earl, W.L., Kim, Y.W., and Smith, D.M., " NMR Measurement of Pore Structure," CHARACTERIZATION OF POROUS SOLIDS III, J. Rouquerol, F. Rodriguez-Reinoso, K.S.W. Sing, and K.K. Unger, Editors, Elsevier Press, Amsterdam, 301-310, (1994).
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- 5) Kim, Y.W., Smith, D.M, and Earl,, W.L., "Evidence for a Dense Liquid Phase in Porous Materials,"transmitted to *Nature*, November, 1994.
- 6) Ghosal, R., Kim, Y.W., Hua, D.W., D'Souza, J.V., Earl,, W.L., and Smith, D.M., "Characterization of Carbon Pore Structure II: Comparison of Adsorption, ^{129}Xe NMR, and X-ray Scattering," transmitted to *Langmuir*, November, 1994.
- 7) Kim, Y.W., Smith, D.M, and Earl,, W.L., " ^{129}Xe NMR Study of Synthetic Imogolite," transmitted to *Langmuir*, August, 1994.
- 8) D'Souza, J. V., Hua, D.W., Schmidt, P. W. , and Smith, D.M. , "Pore Structure Analysis Via Combined Small Angle X-Ray Scattering And Contrast Matched Adsorption," transmitted to *Langmuir*, November, 1994.

Student Thesis Completed

Joseph D'Souza (MS Chem.Eng./UNM) "Scattering studies of microporous carbon."

Ranjan Ghosal (MS Chem.Eng./UNM) "Combined adsorption and NMR studies of porous solids."