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Quarter report #3, 3/1/92-6/30/92
Advanced NMR-Based Techniques for Pore Structure Analysis of Coal

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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. We believe that measurement of the NMR parameters of various gas phase and adsorbed phase NMR active probes can provide the resolution to this problem. We will 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 will study the interaction between several small molecules (^{129}Xe, ^{3}He, $^{2}H_2$, $^{14}N_2$, $^{14}NH_3$, $^{15}N_2$, $^{13}CH_4$, $^{13}CO_2$) and the pore surfaces in coals. These molecules have been selected for their chemical and physical properties. A special NMR probe will be constructed which will allow the concurrent measurement of NMR properties and adsorption uptake at a variety of temperatures. All samples will be subjected to a suite of "conventional" pore structure analyses. These include nitrogen adsorption at 77 K with BET analysis, CO_2 and CH_4 adsorption at 273 K with D-R (Dubinin-Radushkevich) analysis, helium pycnometry, and small angle X-ray scattering as well as gas diffusion measurements. The project combines expertise at the UNM (pore structure, NMR), Los Alamos National Laboratory (NMR), and Air Products (porous materials).

Work completed during the last quarter

We now have two suites of well-characterized microporous materials including oxides (zeolites and silica gel) and activated carbons from our industrial partner, Air Products in Allentown, PA. Our current work may be divided into three areas: small-angle X-ray scattering (SAXS), adsorption, and NMR.

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1. SAXS.

We are also just starting SAXS-contrast matching experiments. For these, we use an adsorbate which has the same electron density as the solid. Therefore, we observe scattering from the adsorbate-vapor interface instead of the solid-vapor interface (if no adsorbate) or a complex combination of the solid-adsorbate and adsorbate-vapor interfaces if an adsorbate is used with different electron density. This type of experiment should enable a new level of pore structure information to be obtained from SAXS experiments.

The SAXS study of samples of a phase-separated and leached glass (CPG-75) adsorbed with various quantities of dibromomethane (as indicated by the relative pressure of dibromomethane) gave us very interesting results. As P/P_0 (relative pressure) increases, the amount of dibromomethane in the sample increases resulting in multilayer adsorption. This changes the internal surface area and surface roughness of the sample and the change should be reflected in the porod slopes. Our results at present do not show a significant pattern of the change of the porod slopes. Comparison of the smeared and the desmeared data does not show the characteristic difference of 1 in the porod slopes. The above difference varies from 0.5 to 1.0. The position of q (the scattering vector) of the peak maximum changes slightly for different levels of adsorption. As the relative pressure of the adsorbent increases, the curves become well-defined and the porod and guinier regions can be distinguished more easily as can be seen from Figure 1. The peaks in this figure are characteristic of the scattering length. The table below shows the variation of the scattering length with the relative pressure of the adsorbent.

Relative Pressure of the adsorbent(%)	The position of the peak maximum (1/Å)	length scale(Å) ($2\pi/q$)
0	0.03114	201.77
10	0.03114	201.77
24	0.02941	213.64
37	0.03114	201.77
57	0.03114	201.77
69	0.02764	227.32
100	0.02595	242.13

The table shows that the length scale of scattering increases as the relative pressure of the adsorbent increases. The reason for the inconsistencies in the data may be due to the sample cells used. Because of X-ray absorption considerations we had to limit our sample cell to a capillary of 1 mm in diameter. Having flattened cells may help

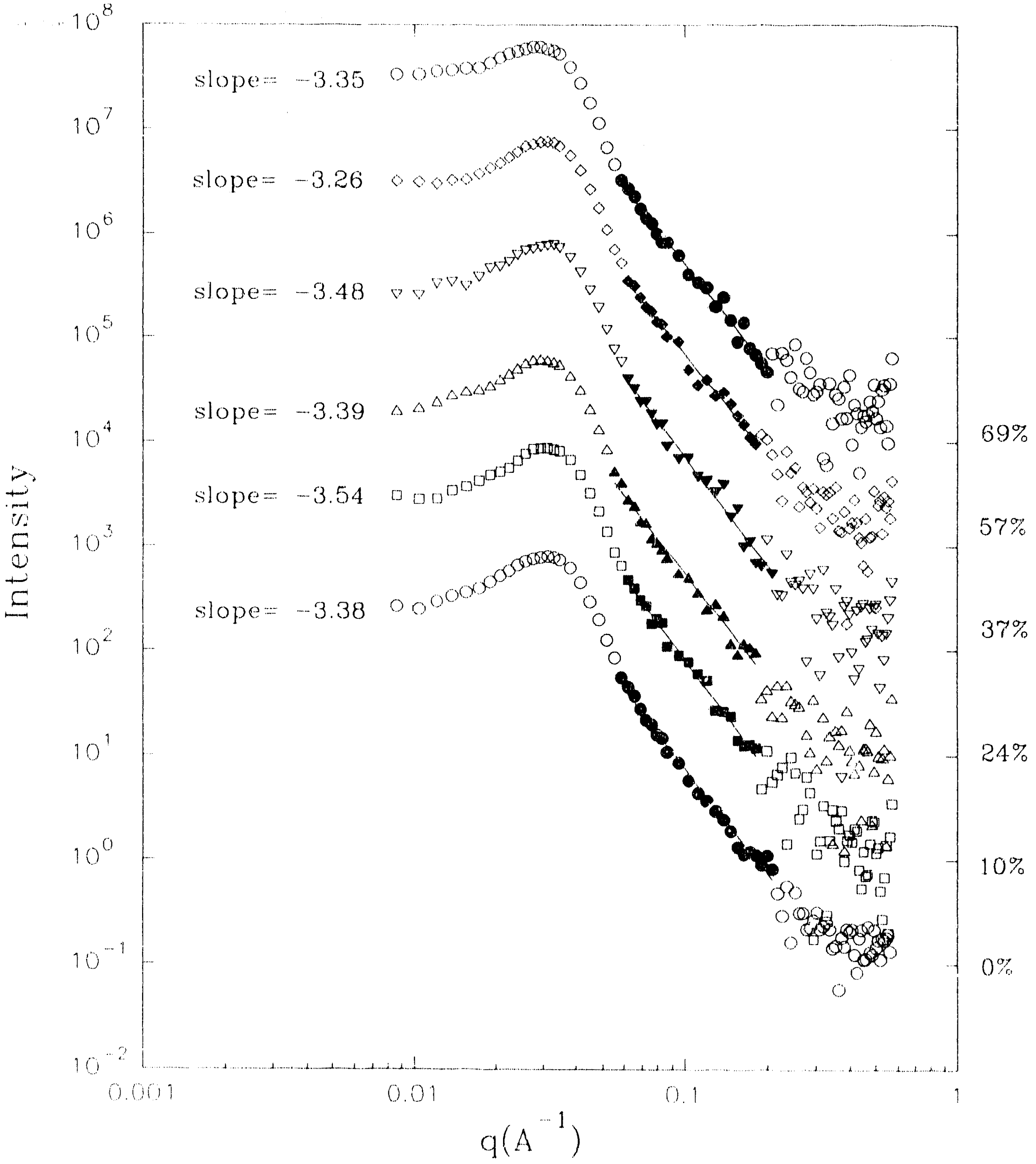

fig. 1 CPG adsorbed with different amounts of dibromomethane

may help to obtain better data. The flat cells have a larger and more uniform surface area for the x-rays to pass through and this will remove edge effects. Edge effects arise from the x-rays shining on the edge of the sample cell. This results in incorrect data which can lead us to wrong results. At present, the various variables affecting the flattening of the sample cells are being determined. We are currently expanding this study to employ several different CPG samples with different pore size/scattering lengths.

The carbon adsorbents from Air Products and Chemicals Inc. gave us results that were very encouraging (see Figure 2). Independent studies on the carbon samples showed similar results. The radius of gyration, corresponding to a feature size, is obtained from a Guinier analysis of the scattering curves of Figure 2 as shown in Figure 3. These results are tabulated in the table below:

SAMPLE ID	%CCL4	SAXS1 (Å)	SAXS2 (Å)
7461-071.03	30	6.0	6.0
7461-071.18	113	6.8	7.5
7461-071.19	81	6.2	6.9
7461-071.20	60	6.1	6.5
7461-071.21	102	6.6	7.3

For the 7461-071 series, we find that with increasing CCl_4 activity the size of the pores increases. These results are in agreement with the literature. Figure 2 shows the porod analysis of the samples which gives us a measure of the surface area and the surface roughness. There is a general increase in the porod slope with increasing pore size indicating a smoother pore surface. We are currently performing more extensive analysis of this scattering data.

2. Adsorption.

High pressure methane adsorption measurements have been completed on four of the carbon samples. Adsorption isotherms are shown in Figure 4. Replotting the adsorption data in terms of the D-R equation, surface areas may be obtained as shown in Figure 5. For the three samples in the coconut char activation series (.16, .18, .19), correlation is observed between methane surface area, SAXS results, and the $\%CCl_4$ activity as measured by Air Products and which should be a rough measure of micropore size. These results are summarized below. We are currently finishing the adsorption measurements for the remaining samples.

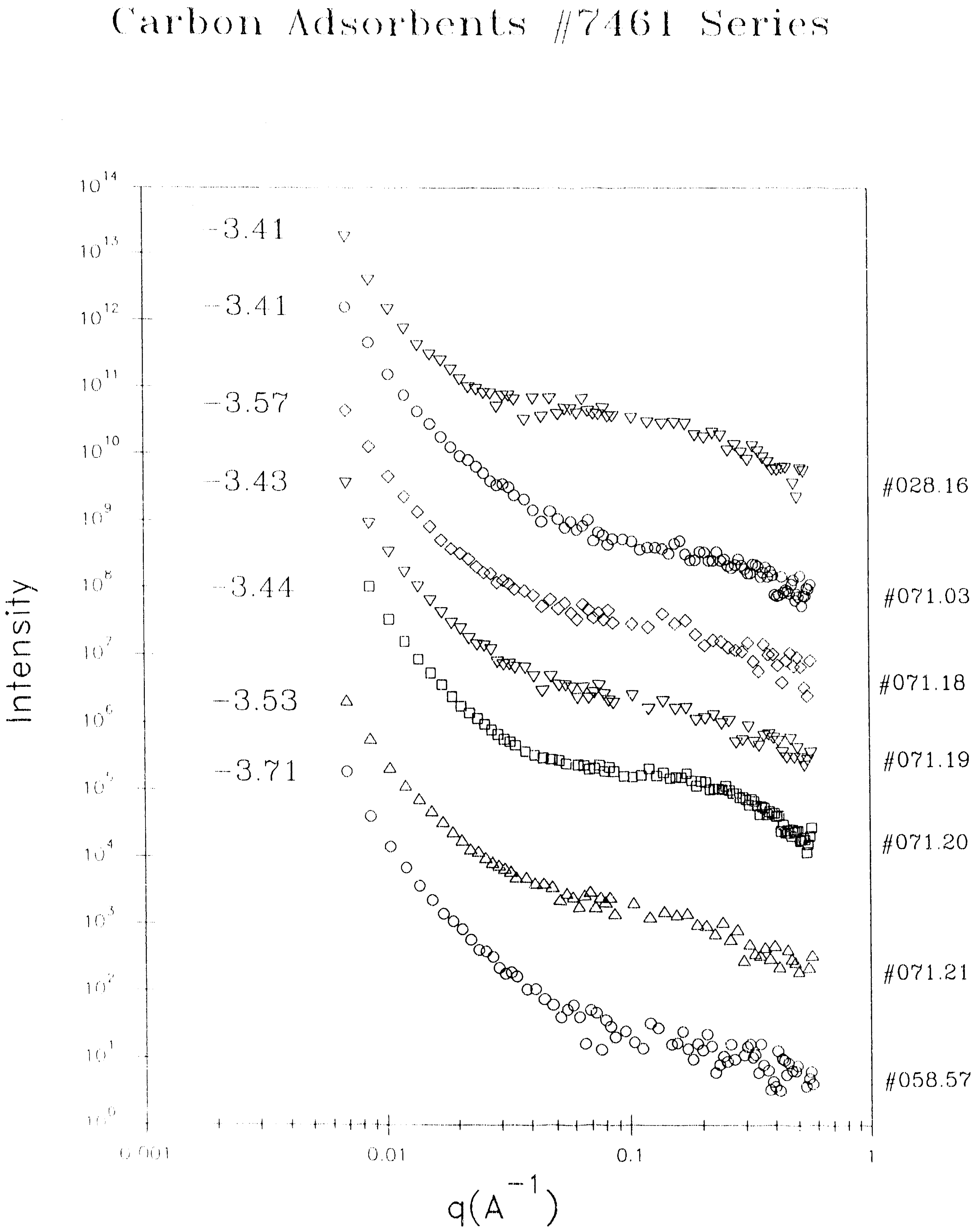

Figure 2   Scattering curves for Air Products carbons.

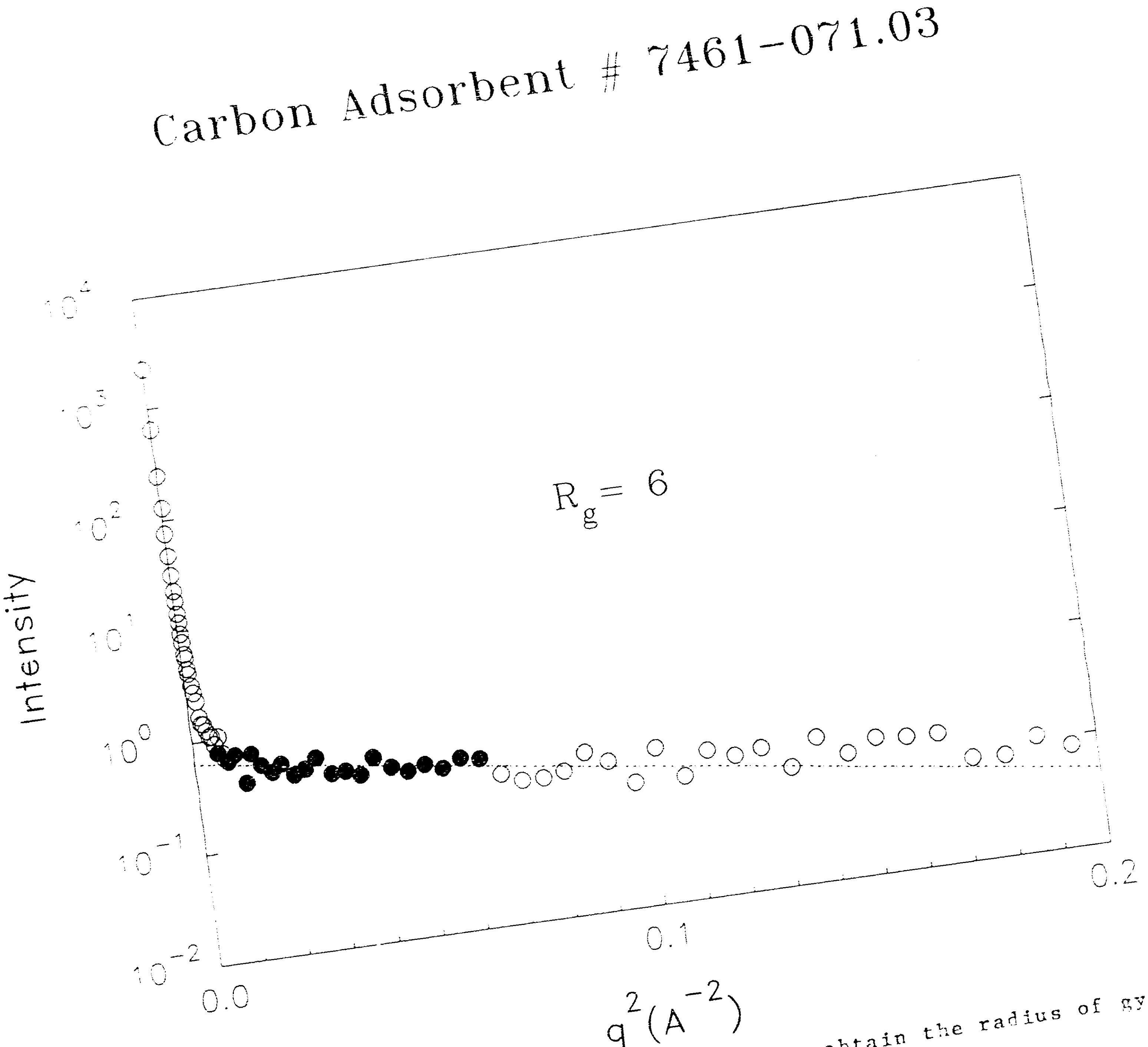

Figure 3 Guinier Plot of SAXS results to obtain the radius of gyration.

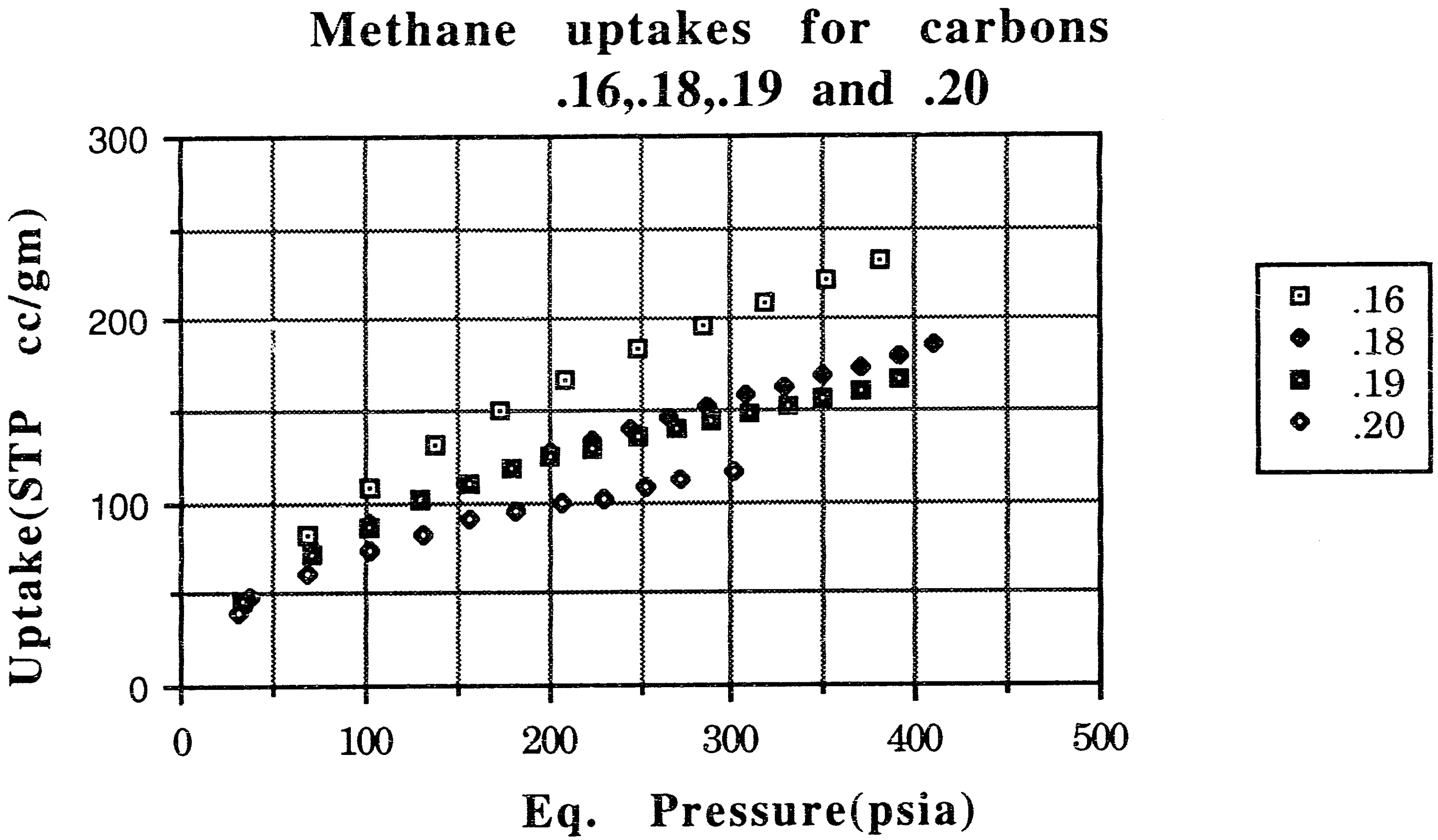

Figure 4 High pressure methane adsorption isotherms for carbons 071.16, .18, .19, and .20.

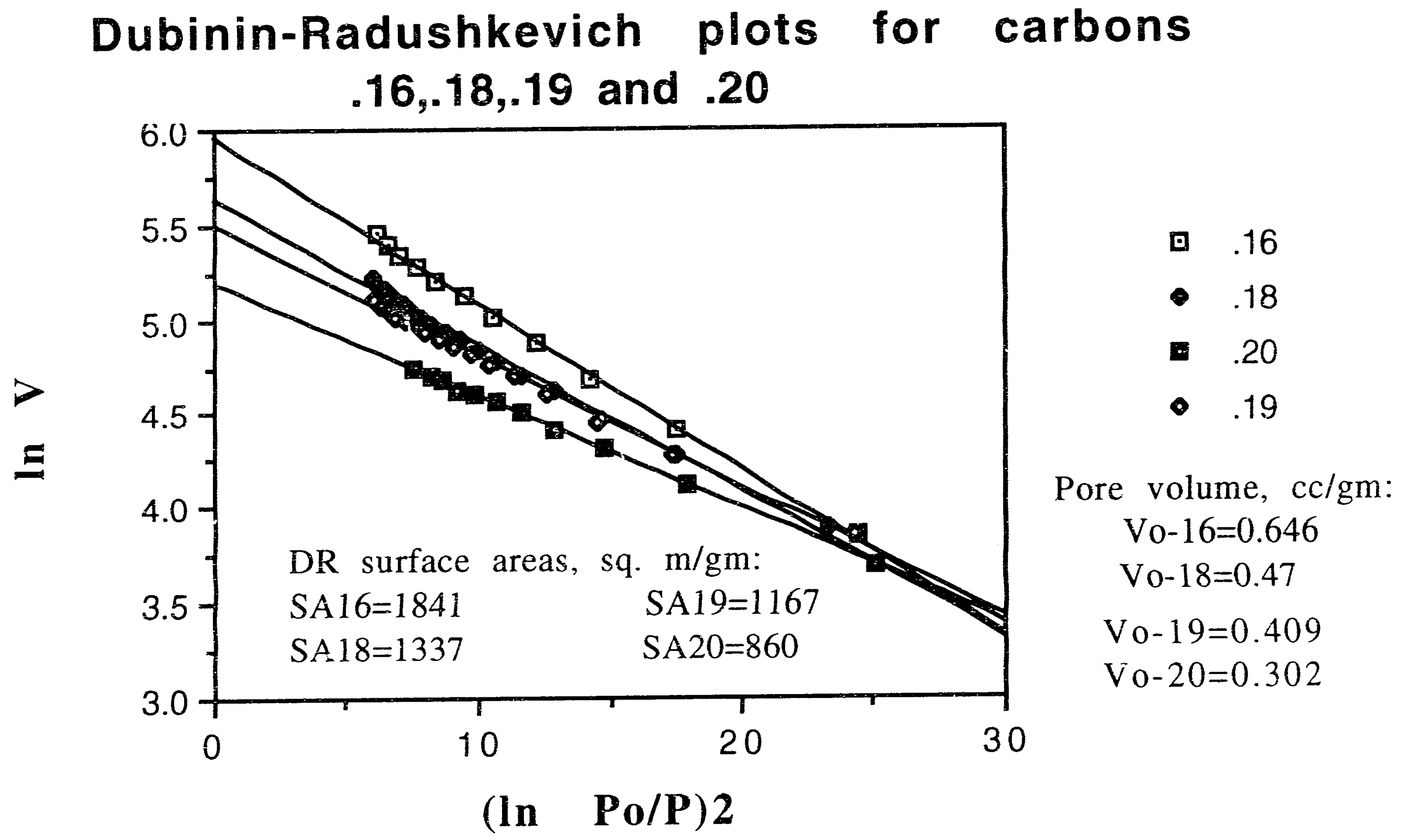

Figure 5 D-R plots for the methane adsorption data given in Figure 4.

Sample	%CCl4	SAXS 1 (Å)	SAXS 2 (Å)	CH_4 SA m^2/g
071.18	113	6.8	7.5	1337
071.19	81	6.2	6.9	1167
071.20	60	6.1	6.5	820

3. NMR Techniques.

Currently, the oxide sample suite is being used to study ^{129}Xe NMR measurements. Ultimately, we plan to study a wide range of NMR-active nuclei as described in the background section but we are currently waiting for the delivery of a low temperature (4 K) cryostat from Oxford Instruments. The low temperature NMR probe has been designed and is currently being constructed. In the meantime, we will concentrate on NMR measurements which can be made at higher temperatures. An example plot of the variation of chemical shift for ^{129}Xe with gas density (molecules/g) of zeolite A is shown in Figure 6. From the extrapolated slope at zero pressure, an estimation of the pore size can be obtained. We are currently exploring the reason for the nonlinearity at low pressure.

Work planned for next quarter

Our goals for the next quarter include:

1. Complete adsorption measurements (CH_4, CO_2) on the carbon samples.
2. Continue contrast-matching SAXS experiments on CPG phase-separated glasses.
3. Start contrast-matching SAXS experiments on carbon samples.
4. Complete ^{129}Xe NMR experiments on oxide samples.
5. Complete low temperature NMR probe construction.

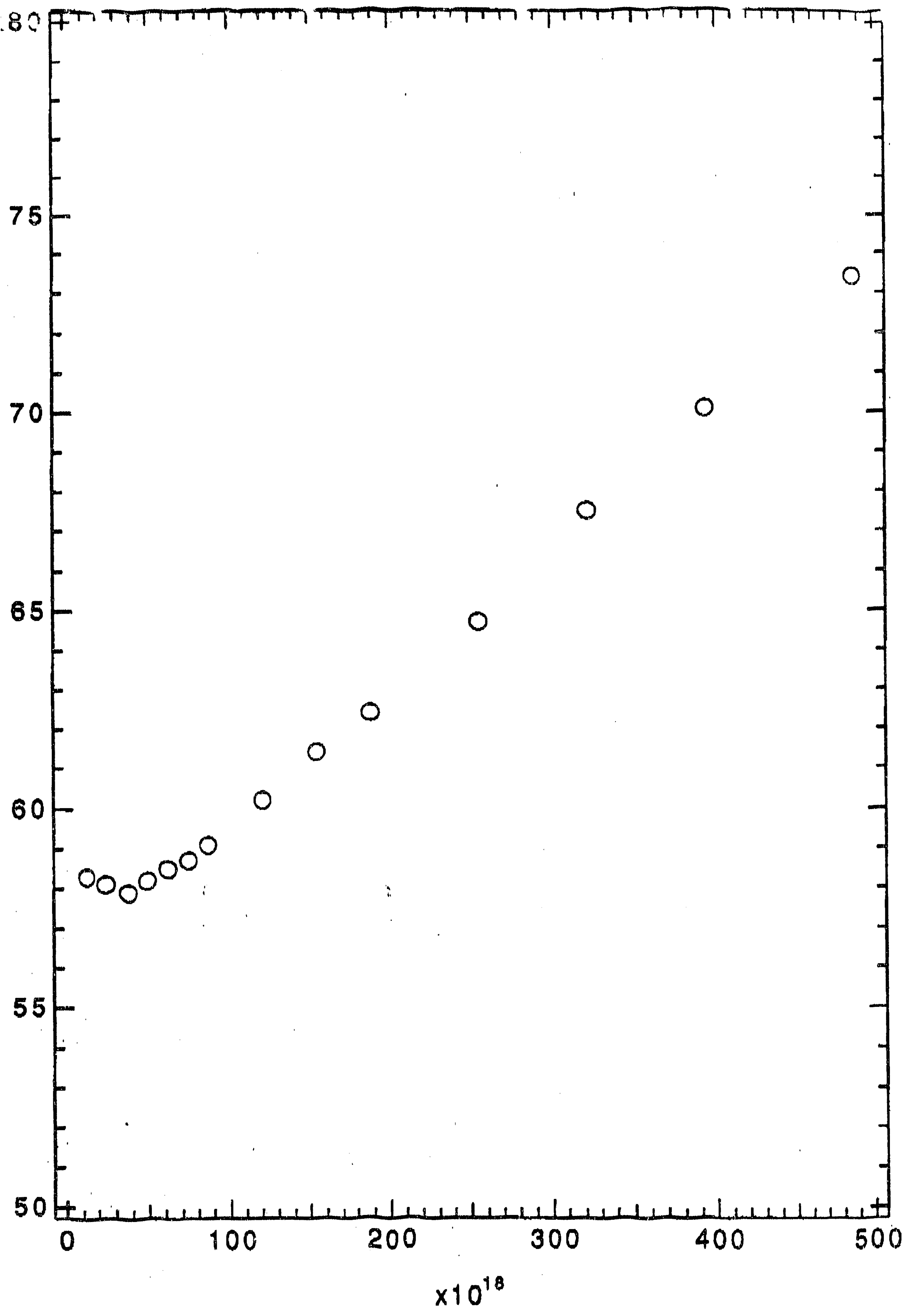

Figure 6 Xe chemical shift as a function of pressure for zeolite A.

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