Experimental report

18/08/2018

Proposal: **1-04-97** **Council:** 4/2015

Title: Fluid transport and pore accessibility in the Early Carboniferous Laurel Formation, Canning Basin, Australia

Research area: Other...

This proposal is a continuation of 9-10-1394

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Samples: 9 natural rocks (shales),

Instrument	Requested days	Allocated days	From	To
D11	2	2	22/05/2018	24/05/2018
S18	14	14	04/06/2018	18/06/2018

Abstract:

We propose to investigate the pore size dependent accessibility, adsorption and desorption of geological fluids in Paleozoic sedimentary rocks from the Canning Basin using SANS and USANS. We will employ contrast matching with CD_4 and CO_2 fluids pressurised up to 650 bar.

The rock samples were either sliced off from solid cores or selected from cuttings samples at various depths in three wells that span the length of the Fitzroy Trough, a Paleozoic depocentre that hosts conventional hydrocarbon accumulations of Devonian and Carboniferous age. Selected samples were characterised using standard geochemical methods and contain small amounts of organic matter that are thermally mature and within either the oil or gas window.

The pore space topology of such rocks is often fractal on the linear scale from nanometers to tens of micrometers. It is a surprising result of only few previous experiments that a significant fraction of pores may not be accessible to invading fluids, with no obvious trend with the pore size. Also, there are indications that in the smallest of nano-pores the adsorption mechanism is pore size dependent and dominated by the condensation phenomena.

Report for experiment 1-04-97 (instruments D11 and S18)

18 August 2018

SANS and USANS experiments were performed on coarse grains (diameter ca. 0.5 mm) of Palaeozoic sedimentary rocks extracted from several wells in Australia. Deuterated methane, CD_4, was used as a contrast match fluid in the pressure range from 0 (vacuum) to 800 bar. There were three types of experiments performed: (1) SANS and USANS measurements at vacuum, (2) determination of the contrast match pressure at a fixed Q-value using stepwise increased gas pressure and (3) SANS and USANS measurements at the contrast match (zero average contrast, ZAC) pressure.

The ZAC pressure was calculated and then confirmed experimentally for each sample as a pressure for which the scattering of neutrons by the rock matrix is closely matched by the scattering of neutrons by the condensed CD_4 gas. The usefulness of the contrast matching technique stems from the fact that at ambient conditions both the accessible (to CD_4 in this case) and inaccessible pores contribute to the scattering intensity, whereas at the ZAC conditions only the inaccessible pores are active scatterers. Therefore, the accessible and inaccessible parts of the pore space in the rock can be quantified separately.

Drawing on experience gained during experiments 9-10-1394, CRG-2102 and CRG_2171 (which were the first SANS and USANS experiments at such high gas pressure performed at ILL) we worked with an improved high pressure cell equipped with Ti windows. Full sets of SANS and USANS data were collected for 9 planned samples and preliminary data were acquired for additional 6 samples. Both SANS and USANS data were isotropic. The data were reduced and analysed using standard methods. In particular, the fraction of pores accessible to invading gas versus the pore size was determined in the pore size range from 10 nm to 10 μm. For pores smaller than about 10 nm a strong capillary condensation effect was observed. Furthermore, the polydisperse spheres (PDS) model implemented in the PRINSAS software was used to fit the combined SANS and USANS curves [1]. Total porosities, pore size distributions and specific surface areas were computed from the fits.

These results are being further analysed in preparation for publication. In the following we show examples of data interpreted so far. Each figure is followed by brief explanations.

As shown in Fig. 1 for sample S5-073, in the middle-Q range the scattering intensity at ZAC is smaller than scattering at ambient pressure by a factor of up to about 5, depending on the Q-value. This indicates that a significant part of the pores is not accessible to the invading CD_4 fluid. In the small-Q range the two curves converge, and for $Q<10^{-4}$ $Å^{-1}$ the USANS intensity measured at ZAC is slightly larger than that measured at ambient conditions. This is most likely caused by multiple scattering and needs to be verified. The latter effect was observed for some samples only.

Note that as Q-values increase in the large-Q region, the SANS intensity measured at 800 bar of CD_4 first matches and then exceeds that measured at ambient conditions. This is an indication of capillary condensation in the small pores. (Sedimentary rocks are often surface fractal scatterers, and the approximate relationship between the average pore diameter, D, and the Q-value is $D \approx 5/Q$ [2]).

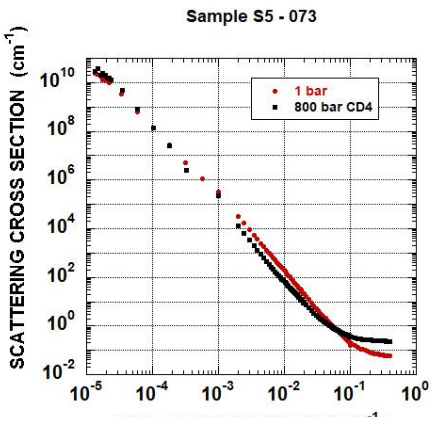

Figure 1. Combined SANS and USANS data, reduced to the absolute scale. Red circles – ambient conditions, black squares – near-ZAC condition at the room temperature. ZAC pressure of CD_4 calculated for this sample is 930 bar, which is about 15% larger than the maximum pressure certified for the pressure cell used in this work. For the purposes of contrast matching such a mismatch is not very significant (see caption to Fig.5).

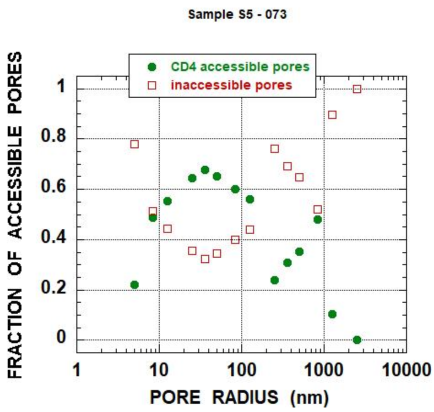

Figure 2. Fraction of pores accessible (green full squares) and inaccessible (red open squares) to CD_4 in sample S5-073.

In Figure 2, data for pore radii less than about 20 nm are distorted by capillary condensation, and for pore radii larger than about 1000 Å by the multiple scattering effects. Nevertheless, in the range of reliable results the fraction of inaccessible pores is significant (30% - 50%), which may adversely affect both the gas sorption capacity and fluid flow properties of the rock.

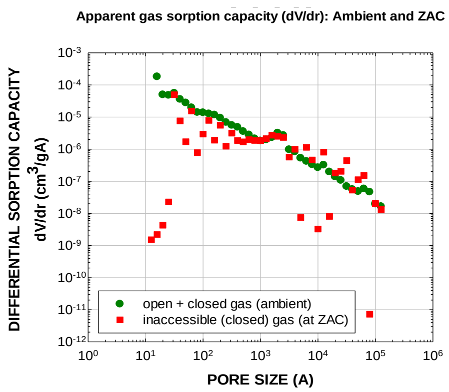

Figure 3. Total gas sorption capacity (green circles) and inaccessible gas sorption capacity (red squares) calculated from SANS/USANS data acquired from sample S5-073.

The actual (real) differential sorption capacity is the difference between the green circles and red squares (Fig. 3). Results shown in Fig. 3 were obtained after the large-Q background was automatically subtracted from both data sets. This creates artefacts (1) for small pore sizes (too small values for inaccessible sorption capacity, owing to excluded contribution from the gas trapped by capillary effects) and (2) for large pore sizes (too small values for the total sorption capacity, most likely owing to multiple scattering. For this sample a large fraction of gas resides in closed pores and cannot be produced.

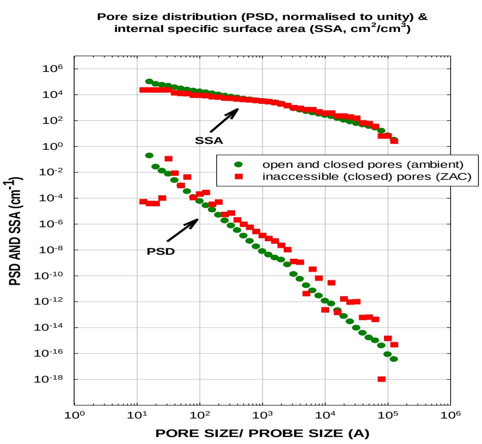

Figure 4. PSD versus pore size (normalised to unity) and SSA versus probe size (in absolute units) computed from the SANS/USANS data acquired from sample S5-075.

Figure 4 shows the results of calculation of (1) specific (internal) surface area versus probe (measuring stick) size, and (2) pore size distribution for all pores (green circles) and inaccessible pores (red squares), for sample S5-075. As well as for data shown in Fig.3, these results were obtained after the large-Q background was automatically subtracted and are subject to similar artefacts.

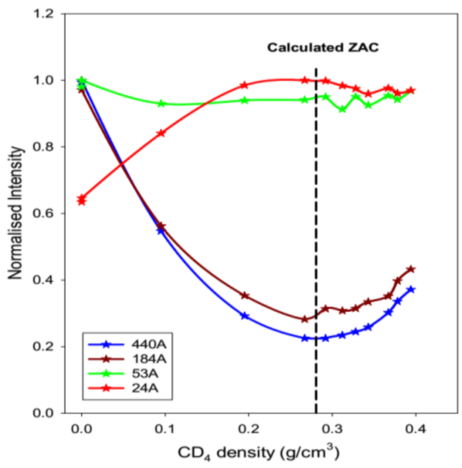

Figure 5. SANS intensity measured for sample K-944 at various pressures of CD4 at four Q-values. Pore sizes shown in the legend were calculated as R=π/Q. Corresponding Q-values were 7.1×10^{-3} (blue line), 1.71×10^{-2}, 0.59 and 0.13 $Å^{-1}$. Note that a density mismatch with the ZAC value of 10% does not affect SANS intensity significantly. At p=800 bar (used for most of the samples studied in this project) such a density mismatch corresponds to CD_4 pressure mismatch of +/- 200 bar.

Figure 5 illustrates an experimental method for finding the ZAC pressure (and, consequently, gas density) for a particular rock sample. Since the maximum gas pressure that could be obtained with our pressure cell was 800 bar (which corresponds to the density of CD_4 of 0.394 g/cm^3), the measurements illustrated in Fig.5 were performed on a (coal) sample for which the ZAC pressure expected from its density and elemental composition was 270 bar (corresponding to CD_4 density of about 0.26 g/cm^3), i.e. well within the experimentally accessible pressure range. A series of SANS measurements in the full Q-range of D11 were performed at increased pressures from vacuum to 800 bar, plus a control measurement at p=1 bar at the end.

The blue (R=440Å) and brown (R=184Å) curves illustrate the variation of SANS intensity (normalised to p=1 bar) in the region of fractal scattering. The minimum scattering intensity (marked "calculated ZAC") occurs close to the expected fluid density of 0.26 g/cm^3 at the ZAC point.

In contrast, the green curve (R=53Å), which corresponds to a Q-value at the cross-over of the scattering curves acquired at p=1 bar and at the ZAC pressure, is practically pressure-independent. This is caused by the pressure-independent average density of CD_4 fluid, which is adsorbed by a combination of the external pressure and capillary forces in pores of this particular size. For even smaller pores (R=24Å, red curve) the density of CD_4 in confinement gradually increases with the external gas pressure, until it reaches saturation at the external driving pressure of about 200 bar.

References:

[1] A.L. Hinde (2004), J. Appl. Crystallography **37**, 1020-1024.

[2] A.P. Radlinski, C.J. Boreham, P. Lindner, O.G. Randl, G.D. Wignall and J.M. Hope (2000), Organic Geochemistry **31**, 1-14.