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SOLVENT-ASSISTED NMR IMAGING OF HETEROGENEOUS COAL
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INTRODUCTION

Since the early work of Sanada and Honda, solvent swelling has been employed to probe the physical structure of coal (1). The swelling behavior of bituminous coals in various solvents has been used to assess different strengths or types of secondary interactions which determine their macromolecular structures (2-5). The phenomenon of solvent transport into coal during solvent swelling has also been extensively investigated by numerous researchers over the past decade (6-10).

Recently, we have obtained important information concerning solvent accessibility in coals and maceral domains by proton NMR imaging of mobile proton distributions resulting from solvent swelling (11). Images of coals swollen with perdeuterated solvents were used to map mobile phases in the coal macromolecular structure, while images obtained with protic solvents mapped distributions of the ingressed solvent. Three-dimensional back-projection techniques employing a 3-D Radon transform inversion reconstruction algorithm were used to map mobile proton distributions on the basis of T_1 (spin-lattice relaxation time) differences. Contrast based on differences in T_2 (spin-spin relaxation time) was achieved employing 3-D gradient recalled echo pulse sequence for data acquisition, and image reconstruction by 3-D Fourier transform. Both techniques illuminated proton distributions of mobile phases within the solid preferentially. Images with resolutions of 40 to 80 μm showed the presence of different macerals, mineral cleats, microfractures, and the distribution of mobile macromolecular phases in solvent swollen coals. Regions which differed with regard to pyridine accessibility were also contrasted in the images.

Notwithstanding the complications of heterogeneous solvent transport in coals, we were prompted by the initial investigation to elucidate the details of transport behavior of pyridine into coal during swelling. In this study, we present time-resolved proton NMR images of pyridine penetrating a homogeneous sample of high volatile bituminous A rank vitrain (APCS No. 4) that had been pre-extracted with pyridine. In addition to coal swelling in pyridine, we have investigated transient state imaging results from two polymer-solvent systems for comparison; polyethylmethacrylate (PEMA) swollen in methanol, and isobutyl rubber swollen in toluene. A model for case II transport in coals is described.

RESULTS AND DISCUSSION

For the present purposes 2-D images are sufficient to address the question at hand, and their acquisition is suitably fast. In order to ensure that the transport process was also two-dimensional, the upper and lower sample surfaces were protected from solvent infiltration by glass coverslips which restricted the flow of solvent to cross only the exposed faces of the sample. Each sample is rectangular with initial dimensions on the order of 2 x 2 x 1 mm. The experimental protocol involved immersing the sample in the solvent for a period of time, removing it from the solvent bath, acquiring an image, and re-immersing it.

Figure 1 presents transient images together with one-dimensional projections for each of the three macromolecular systems. The first (a) illustrates the swelling behavior of isobutyl rubber in toluene. In the case of a rubbery material, the transport behavior is anticipated to be

Fickian. Analysis of the dynamic behavior of the isobutyl rubber confirms this: during the swelling interval a steep solvent gradient observed in the frame rapidly evolves into a smooth and shallower gradient indicative of a transport mechanism which is essentially Fickian.

Fig. 1 2-D transient proton NMR images and 1-D projections of solvent transport in three macromolecular networks: (a) toluene in isobutyl rubber, (b) methanol in polyethylmethacrylate (PEMA), and (c) pyridine in hv bituminous A vitrain.

The second (b) illustrates the swelling behavior of PEMA in methanol. Clearly evident is a sharply defined solvent front which separates a swollen region from the glassy core. Swelling is essentially complete when the solvent fronts meet at the object center. In general, this behavior is typical of all polymers which pass through a glass to rubber transition during solvent uptake (12). The term case II has been used to describe such transport phenomena (13). Analysis of the transport of pyridine during the swelling of a sample of high volatile bituminous coal (c) clearly reveals a sharp concentration profile during the uptake process which is indicative of case II type transport behavior.

In order to quantify the transient aspects of case II transport, a phenomenological transport model was designed which incorporates the essential characteristics of swelling of materials that exhibit a glass transition accompanying solvent uptake. Solvent induced dilation of a macromolecular network, in either the glassy and or the rubbery states, results from osmotic stresses. Kinetically, the character of transport, hence dilation, is different in the two states. In the glassy state the characteristic relaxation time for diffusion is very long relative to the relaxation time for molecular motion. In the rubbery state, however, diffusion is very rapid relative to molecular relaxation. The point of inversion in the relative magnitudes of the characteristic relaxation times occurs when crossing the phase boundary from the glassy to the rubbery state.

The presence of this osmotic stress is a thermodynamic driving force for rapid expansion at the phase boundary. The net effect of the relaxation at the glass to rubber transition is to convert the problem of solvent transport into a moving boundary value problem; the rate of relaxation in the rubbery region drives the diffusion in the glassy region.

Fig. 2 Dilation data for hVA bituminous vitrain swollen in pyridine and polyethylmethacrylate (PEMA) swollen in methanol fit to case II model with $v_1^* = 0.25$: (A) PEMA, $\beta = 1.0$; (B) vitrain, $\beta = 1.0$; (C) PEMA, $\beta = 10$; (D) vitrain, $\beta = 10$.

Any useful model constitutes a balance between the need to accurately describe a physical process and the desire to remain simple with a minimum number of parameters. Ideally, these parameters have a direct connection with fundamental molecular scale characteristics of the macromolecule. In the case of solvent transport in a system undergoing a glass transition, we can define the uptake behavior using three parameters: a characteristic cooperative diffusion coefficient, D , governing dilation of the network; a molecular relaxation rate constant,

β , which is given by the relationship $\beta = K_{os}/\eta_1$, where η_1 is the bulk viscosity and K_{os} is the osmotic modulus; and a critical solvent concentration, v_2^* , above which there is a transformation of the network from a glass to a rubber.

Figure 2 illustrates the time dependent uptake, L/L_0 , vs. the square root of dimensionless time, τ , for PEMA and the hv bituminous A coal; characteristic curves generated for various values of dimensionless β and v_2^* are also presented. Depending on the magnitude of β , the characteristic shape of the uptake curve plotted as normalized dilation vs. the square root of dimensionless time is observed to evolve from an essentially convex shape at high values to sigmoid shaped uptake curve at the lower values. The convex curves are indicative of constant velocity of solvent front with time; this is consistent with case II behavior and clearly distinguishable from Fickian transport behavior. The cooperative diffusion coefficient and absolute magnitude of β calculated for PEMA and the coal using $v_2^* = 0.25$ are $D_c = 9.4 \times 10^{-8}$ cm²/s, $\beta = 4.2 \times 10^{-6}$ s⁻¹ and $D_c = 7.4 \times 10^{-8}$ cm²/s, $\beta = 3.5 \times 10^{-6}$ s⁻¹, respectively. Quantifying these parameters and searching for the relationship between molecular structure and transport behavior will be the focus of future work.

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