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Extending the range of liquids available for NMR cryoporometry studies of porous materials

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ABSTRACT

Nuclear magnetic resonance (NMR) cryoporometry, although well established, can be limited by the inability of any one liquid to probe a broad range of pore sizes, a relatively small number of commonly-used probe liquids and the requirement to match the probe liquid to the chemistry of the material being studied. Here we demonstrate, for the first time, the use of menthol and t-butanol as probe liquids in NMR cryoporometry measurements. Using appropriate estimates for the values of the melting point depression constant, k_c, and the non-freezing surface layer, $2sl$, NMR melting data was converted into pore size distributions. The melting point depression constant for t-butanol is similar to that of cyclohexane; however due to its functionality, t-butanol may be the preferred liquid used to study the porosity of hydrophilic materials. Menthol, having a larger value of k_c, can accurately analyze larger pore sizes up to 100 nm. This represents the first use of menthol and t-butanol to accurately probe pore dimensions in NMR cryoporometry.

1. Introduction

Nuclear magnetic resonance (NMR) cryoporometry is a well-established technique used to accurately measure the pore size distribution of mesoporous materials [1–6]. Cryoporometry can non-invasively measure the phase transition of a liquid confined in various pore geometries [3]. However, a major disadvantage of the technique is that a single liquid cannot probe a wide range of pore sizes or surface chemistry; a range of liquids, with differing thermodynamic properties, are therefore required to span the full range of pores sizes amenable for NMR investigations.

NMR cryoporometry uses the observed depression in melting point of a confined liquid to obtain a pore size distribution, as introduced by Gibbs and Thomson [7–12]. The melting point depression ΔT_m is predicted by Equation (1)

$$\Delta T_m = T_m - T_m(x) = \frac{4\gamma_{sl} T_m}{x \Delta H_f \rho_s} \tag{1}$$

$$\Delta T_m = \frac{k_c}{x - 2sl} \tag{2}$$

where T_m is the bulk solid melting point, $T_m(x)$ is the melting point of a crystal with diameter x, ΔH_f is the bulk enthalpy of fusion, ρ_s is the density of the solid, and γ_{sl} is the surface energy at the crystal-liquid interface [2]. The parameters in Equation (1) can be collectively reduced to one value, known as the melting point depression constant k_c. Equation (2) takes into account the additional contribution from a non-freezing surface layer, typically labelled as $2sl$.

Values for the two key parameters in cryoporometry analysis, k_c and $2sl$, are seldom agreed upon in the literature. The collection of parameters which define k_c determine the range of pore sizes that a liquid can accurately analyze. An approximation for k_c is obtained from Equation (3):

$$k_c = 2\nu\gamma_{Sl}\frac{T_m}{\Delta H_f} \tag{3}$$

where ν is the molar volume of the liquid, γ_{sl} is the surface energy at the crystal-liquid interface, ΔH_f is the bulk enthalpy of fusion, and T_m is the bulk melting point. An estimate for k_c can therefore be obtained if values are known for the molar volume of the liquid, the free energy at the crystal/liquid interface, and the latent heat of melting.

Potential cryoporometric liquids, with estimates for k_c, have been collated by Petrov and Furo [4], including water, cyclohexane, octamethylcyclotetrasiloxane (OMCTS), menthol, and t-butanol. Cyclohexane and water are two of the most common liquids for cryoporometry analysis due to their favourable melting points and suitable

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melting point depression constants [2,5,6,13–15]. Water (k_c = 49.5 K nm) is well suited for the analysis of hydrophilic materials, such as silica, with pore diameters < 10 nm, whereas cyclohexane (k_c = 103.7 K nm) is more suited to hydrophobic materials, such as porous glasses, with pore diameters between 10 and 50 nm. Glasses smaller in size can be pre-treated with hexamethyldisilazane to make the glass more hydrophobic and promote the wetting of cyclohexane [13]. Larger pore diameters can be probed by two methods. The first is to use appropriately smaller temperature steps for liquids which have a relatively high k_c, although this method will still ultimately fall short when the pore diameter exceeds a certain limit. The second is to use a liquid with a much larger k_c value. OMCTS has been demonstrated as a suitable liquid for larger pore analysis [16]. Despite a similar k_c to cyclohexane, OMCTS can accurately measure the pore size distributions of glass into the micron range when sufficiently small temperature steps are used.

Neither menthol nor t-butanol have been previously used as probe liquids for NMR cryoporometry. The only previous studies of their melting behaviour are provided by Christenson [17], and Qiao and Christenson [18], for t-butanol and menthol respectively. Both studies describe the capillary condensation of the alcohols between mica surfaces and provide estimates of the solid-liquid interfacial tension. With accessible melting points, both liquids are ideal candidates as probe liquids in NMR cryoporometry experiments. In cryoporometry experiments, k_c is typically calibrated against experimental data. However such calibrations are highly susceptible to the choice of fitting function, particularly in estimating the non-freezing surface layer ($2sl$), which can lead to significant errors. We have previously investigated the melting point depression constant, and influence of a non-freezing surface layer, for water confined in mesoporous silica, and applied this methodology to cyclohexane confined within CPGs [6]. Here we extend this methodology to estimate these two parameters for t-butanol and menthol and, hence, demonstrate the suitability of both alcohols for NMR cryoporometry.

2. Experimental

2.1. Materials

Controlled pore glasses were provided by both Sigma-Aldrich (24, 50 and 54 nm) and Prime Synthesis (38, 43, 63 and 100 nm). Their properties are listed in Table 1.

2.2. NMR hardware and temperature control

All NMR measurements were carried out on a Bruker Avance spectrometer, equipped with a 5 mm PABBO BB-1H Z-GRD probe, with a frequency of 300 MHz. To obtain low temperatures, a Bruker BVT3200 temperature control system, with a precision of 0.1 K, was used. The cooling system passes a combination of N_2 gas and air over the sample at a flow rate of 400 l/h operating at 4% cooling with the probe heater set to a maximum of 17% output. Before starting experimental work, the temperature control system was calibrated using a deuterated methanol NMR thermometer, producing a calibration relationship between the nominal spectrometer temperature and actual sample temperature [19]. Further calibrations were performed to determine the stability of the temperature at a given nominal spectrometer temperature and also the time taken for a given temperature change to occur. Before the start of a cryoporometry experiment, the cooling system was allowed to equilibrate with the probe heater. The temperature control unit was optimized to ensure that over- and undershoot of the sample temperature was minimized effectively. Furthermore, the probe was tuned and matched in areas out of sample phase transition to account for the significant temperature changes.

Table 1
Characterisation of controlled pore glasses: Pore diameter, pore volume, grain size, and specific surface area (from N_2 porosimetry). Data supplied by Sigma-Aldrich and Prime Synthesis.

Glass	Pore diameter (nm)	Pore volume ($cm^3.g^{-1}$)	Grain size (mesh)	Specific surface area ($m^2.g^{-1}$)
CPG24	24.0	–	20–80	–
CPG38	38.2	1.10	120–200	113
CPG43	42.8	1.40	120–200	130
CPG50	50.0	0.96	120–200	51
CPG54	54.0	1.06	120–200	44
CPG63	62.6	1.20	120–200	79
CPG100	99.6	1.40	120–200	55

The NMR signal intensities between pore and bulk melting regions have been corrected to account for the effect of Curie's law, where the signal intensity decreases with increasing temperature outside of phase transformations [20]. The intensities are then further normalized to a value where all of the confined water is liquid and the bulk water remains frozen.

2.3. NMR cryoporometry

Cryoporometry measurements were made using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [21,22], comprising a basic spin echo, and carefully selected delay time, Δ, to differentiate between the solid and liquid phases of the sample (pulse sequence can be found in supporting information, Fig. S1). Total delay times of 4 ms and 40 ms for menthol and t-butanol respectively successfully isolated the liquid signal. The sample temperature was reduced until the entire sample was frozen, evidenced by the loss of all liquid signal. The temperature was then increased in increments of 0.2–0.5 K, to initiate and observe the phase transition from solid to liquid, using a minimum equilibration time of 10 min at each temperature to stabilize the signal intensity. Each acquisition comprised of 8 transients of 8192 complex data points.

The melting point depressions obtained by NMR cryoporometry can be converted into pore size distributions using the methodology detailed by Strange et al. [1], using Equation (4):

$$\frac{d\upsilon}{dx} = \frac{k_c}{x^2} \cdot \frac{d\upsilon}{dT} \tag{4}$$

where the change in liquid volume with temperature is denoted by $d\upsilon/dT$, k_c is the melting point depression constant, and x is the pore diameter.

2.4. NMR relaxometry

Transverse relaxation time, T_2, distributions for the liquids were obtained using the PROJECT pulse sequence (pulse sequence, and typical timing parameters, can be found in supporting information, Fig. S2) [23]. Each acquisition comprised of 8 transients of 16384 complex data points, with a maximum experimental time of 8 min. The total delay time was varied from over 10 increments, with exact timings dependent on the liquid used and the phase of the sample. Relaxation time distributions were calculated using CONTIN [24].

3. Results & discussion

To be considered a viable probe liquid for cryoporometry experiments, the phase transition from solid to liquid has to be relatively simple, with the absence of any intermediate stages or plastic crystals, crystalline structures with high molecular mobility [1]. There must also be measurable differences in transverse relaxation time between the pore liquid and the bulk liquid. In order to assess the melting behaviour of t-butanol and menthol, hysteresis data was acquired for the bulk liquids (supporting information, Fig. S3). For both alcohols, as well as the cyclohexane standard, the transition from solid to liquid occurred over