

Freezing in Mesopores: Aniline in Silica Glasses and MCM-41

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1. ABSTRACT

We report a study of the freezing of aniline in silica porous materials, using dielectric relaxation spectroscopy and light transmission measurements. The porous materials include controlled pore glasses with pore sizes H in the range 7.5 to 50 nm, Vycor glass ($H=4.1$ nm) and MCM-41 ($H=2.8$ nm). The freezing temperature is lowered due to the confinement, and in the larger pores crystallization occurs. In the MCM-41 material no crystallization is observed; instead a glassy phase is formed at low temperatures. In Vycor the experiments indicate a mixture of microscopic domains of crystal and glass at low temperature. The results are consistent with recent molecular simulation results.

2. INTRODUCTION

Both experimental and molecular simulation studies of freezing and melting in porous materials suffer from several difficulties [1]. Difficulties in the experiments include the lack of well-characterized porous materials, difficulty in identifying the nature of the adsorbed phases, and long-lived metastable states. In the simulations, large systems and finite size scaling analysis may be needed to feel confidence in the results, and models of the porous materials may be over-simplified. The somewhat complementary nature of the difficulties in experiment and simulation make it profitable to use both approaches in a combined study. We have therefore adopted such a strategy in our recent work in this area [2-7].

For simple adsorbates composed of spherical molecules in pores of simple geometry, it is possible to map out freezing phase diagrams based on the simulation studies [3,6]. A corresponding states analysis [3] of the partition function for such a system shows that the freezing temperature in the pore, $T_{f,pore}$, relative to the value for the bulk material, $T_{f,bulk}$, is a function of three variables: H/σ_{ff} , α , and σ_{fw}/σ_{ff} , where H is pore width, σ is the molecular diameter, subscripts f and w refer to fluid and wall, respectively,

and α is a dimensionless ratio of the fluid-wall to the fluid-fluid attractive interaction when the molecular centers are at the minimum of the potential well. In practice it is found that the freezing and melting behavior is insensitive to the diameter ratio, σ_{fw}/σ_{ff} , for small molecules except when the pore width approaches the molecular diameter (molecular sieving regime). The qualitative behavior (whether the freezing temperature goes up or down, types of new phases occurring, etc.) is found to be controlled to a large extent by α , while H/σ_{ff} determines the magnitude of shifts in transition temperatures. The global freezing behavior predicted in the simulations is in qualitative agreement with the experimental measurements that have been reported [6].

In this paper we report new measurements of freezing and melting behavior for aniline in controlled pore silica glasses (CPG), Vycor and MCM-41 having a range of pore widths from 2.8 to 50 nm. The results are discussed in terms of the global freezing behavior predicted in molecular simulations.

3. METHODS

Freezing of a dipolar liquid is accompanied by a rapid decrease in its electric permittivity [8-10]. Following solidification, dipole rotation ceases and the electric permittivity is almost equal to n^2 , where n is refractive index, as it arises from deformation polarisation only. Investigation of the dynamics of a confined liquid is possible from the frequency dependences of dielectric properties, which allows both the determination of the phase transition temperature of the adsorbed substance and characteristic relaxation frequencies related to molecular motion in particular phases.

The temperature of the phase transition to the solid state has also been determined recently by the light transmission method, recording changes in intensity of the light beam passing through the medium studied. At the melting/freezing transition, the number of absorption centers (nuclei of the new phase) changes discontinuously, leading to a sudden change in intensity of the light beam.

3.1. Dielectric relaxation spectroscopy

The complex electric permittivity, $\kappa = \kappa' + i\kappa''$, where $\kappa' = C/C_0$ is the real, and $\kappa'' = \tan(\delta) / \kappa'$ is the complex part of the permittivity, was measured in the frequency interval 300 Hz - 1 MHz at different temperatures by a Solartron 1200 impedance gain analyser, using a parallel plate capacitor made of stainless steel. From the capacitance, C , and the tangent loss, $\tan(\delta)$, the values of κ' and κ'' were calculated [2]. The temperature was controlled within 0.1K using a platinum resistor Pt(100) as a sensor and a K30 Modinegen external cryostat coupled with a N-180 ultra-cryostat.

The aniline sample was twice distilled under reduced pressure and dried over Al_2O_3 . The conductivity of purified aniline was on the order of $10^{-9} \Omega^{-1}m^{-1}$. The porous silica samples used were the commercially available Controlled Pore Glass (CPG) from CPG Inc., with a pore size distribution of about 5% around the mean pore diameter. Different CPG samples having average pore diameters ranging from 50 nm to 7.5 nm were used. We also studied confinement effects in Vycor glass from Corning Inc., having a mean pore size of 4.1 nm, and a silica - based MCM-41 material with mean pore diameter of 2.8 nm. The pore samples were heated to about 600 K, and kept under vacuum ($\sim 10^{-3}$ Tr) for 6 days prior to the introduction of the fluid. The MCM-41 samples

were synthesized at A. Mickiewicz University, and were characterized using x-ray diffraction and nitrogen adsorption measurements [11]. The characterization results for MCM-41 showed that these crystalline materials consisted of uniform pores in a hexagonal arrangement with a narrow pore size distribution (dispersion less than 5%).

For an isolated dipole rotating under an oscillating field in a viscous medium, the Debye dispersion relation is derived in terms of classical mechanics,

$$\kappa^* = \kappa'_{\infty} + \frac{\kappa'_s + \kappa'_{\infty}}{1 + (i\omega \tau)}, \quad (1)$$

where ω is the frequency of the applied potential, and τ is the orientational relaxation time of a dipolar molecule. The subscript "s" refers to static permittivity (low frequency limit when the dipoles have enough time to be in phase with the applied field). The subscript ∞ refers to the high frequency limit, and is a measure of the induced component of the permittivity. The dielectric relaxation time was calculated by fitting the dispersion spectrum of the complex permittivity near resonance to the Debye model of orientational relaxation of the induced component of the permittivity.

3.2. Light transmission method

The light source was a He-Ne laser of 6 mW power, whose light beam was split into two beams by a set of prisms. One beam was collected directly by a photodiode, while the other was passed through the measuring cell and the focusing lens and was directed to the second photodiode. The signals from both photodiodes were analysed by the differential amplifier. The measuring cell was thermostatted by a cryostat N-180, and temperature was measured by a copper-constantan thermocouple, with an accuracy of ± 0.1 K. The relative change in the light intensity after passing through the sample studied is proportional to the voltage change at the photodiodes and characterises the absorption of a given medium. A strong increase in the light absorption is observed in the vicinity of the phase transition as a consequence of the appearance of many nuclei of the new phase, which act as absorption centres. The systems studied are transparent in the liquid state, and the change in light absorption at the solid – liquid phase transition is easily seen.

4. EXPERIMENTAL RESULTS

The dielectric relaxation method was applied to study the process of freezing and melting for samples of confined liquid aniline in CPG, having mean pore sizes of $H = 50, 25,$ and 7.5 nm, and in Vycor with $H = 4.1$ nm. The sample was introduced between the capacitor plates as a suspension of CPG or Vycor in pure aniline. Therefore, the capacitance measurement yields an effective relative permittivity of the suspension of porous silica glass in pure aniline. Results of the measurements of C for aniline in these silica glasses as a function of T at a frequency of 0.6 MHz are shown in Fig.1(a-d). There is a sharp increase in C at $T = 267$ K corresponding to the melting point of pure aniline, due to the contribution to the orientational polarisation in the liquid state from the permanent dipoles [2,7]. The second sharp increase at 262 K (Fig. 1a), 260 K (Fig. 1b), 246 K (Fig. 1c) and about 227 K (Fig. 1d) is attributed to melting in the pores. The signal corresponding to melting becomes increasingly rounded as the pore size becomes smaller (Fig. 1d), suggesting a heterogeneous melting process in the pores.

Similar results (not shown) were obtained from the light transmission measurements, which were carried out for aniline in CPG, Vycor and MCM-41 as a function of temperature. Melting temperatures were indicated by sharp increases in the photodiode voltage, which is proportional to the intensity of the light beam passing through the sample. Melting temperatures were in good agreement with those determined from dielectric relaxation spectroscopy, except for Vycor where a somewhat lower melting temperature of 229.8 K was observed. For MCM-41 a melting transition was observed at 223.1 K.

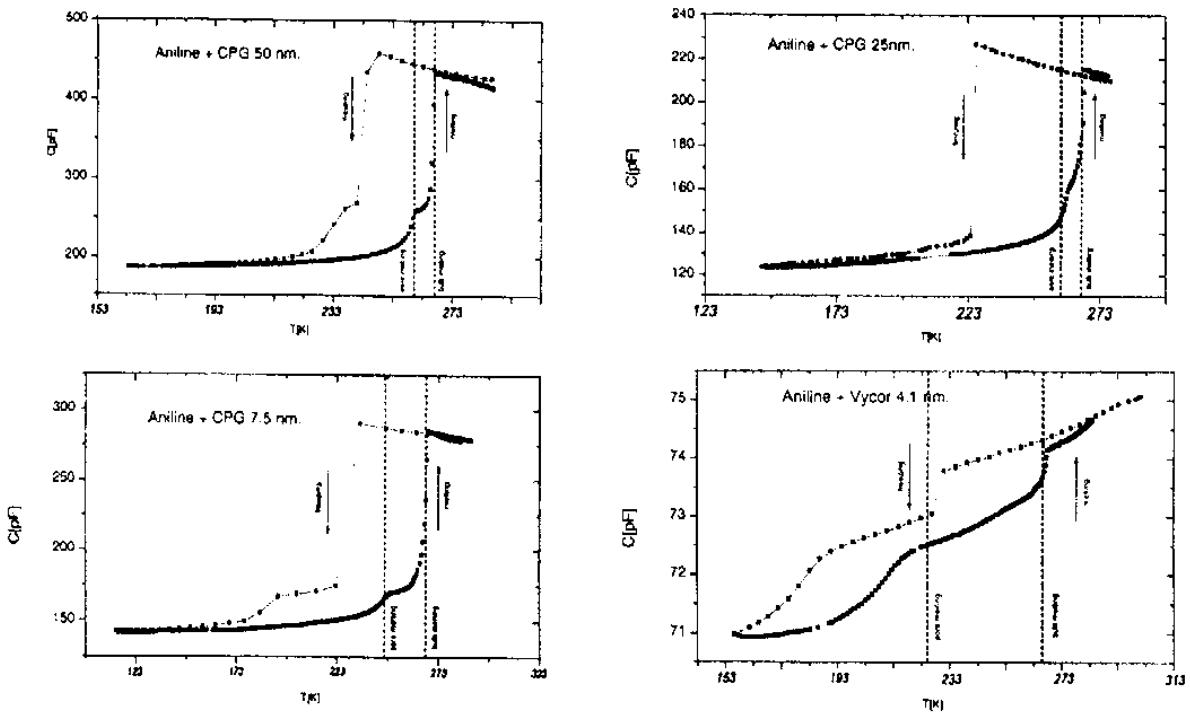


Fig. 1 (a-d) Capacitance C vs. temperature T for Aniline in CPG and Vycor for different pore widths at frequency $\omega=0.6$ MHz.

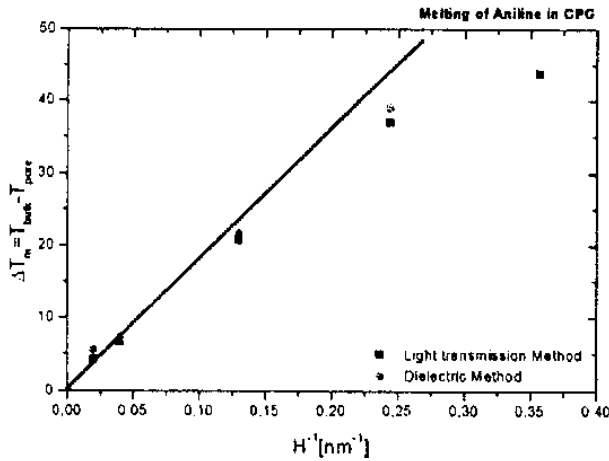


Fig. 2. Shift in the melting temperature ΔT_m as a function of $1/H$ for Aniline in CPG, Vycor and MCM-41. The straight line is a fit to the data for H values of 25 nm and above, and is consistent with the Gibbs-Thomson equation.

The size dependence of the melting temperature of the confined aniline is shown in Figure 2. The linear relationship between the shift in the pore melting temperature and the inverse pore diameter for larger pore widths is consistent with the Gibbs-Thomson equation [1], but strong departures from this linear behaviour are observed for smaller widths, particularly below pore widths of about 10 nm. Such departures arise from the assumptions made in the derivation of the Gibbs-Thomson equation, and have been observed in other systems [e.g. 1,2,4]. The dielectric and optical measurements are in generally good agreement.

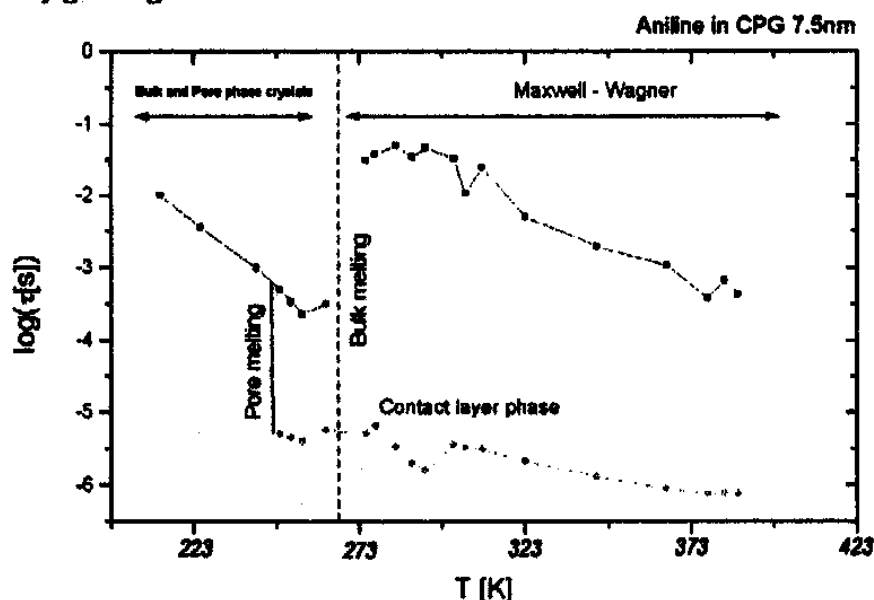


Fig. 3. τ vs. T for aniline in CPG with average pore size of 7,5 nm.

The spectrum of the complex permittivity (κ' and κ'' vs ω) was fit to the dispersion relation, Eq.(1), to determine the dielectric relaxation time τ . The frequency range in this study encompasses the resonant frequencies corresponding to the dielectric relaxation in solid and glass phases. According to Eq.(1), κ' shows a point of inflection and κ'' goes through a maximum at the resonant frequency. Therefore, from a spectrum plot of κ' and κ'' vs $\log_{10}(\omega)$, the relaxation time can be calculated as the reciprocal of the frequency corresponding to a saddle point of the κ' function or a maximum of the κ'' function. An alternative graphical representation of the Debye dispersion equation is the Cole-Cole diagram in the complex κ^* plane [2].

The behavior of the relaxation times as a function of temperature for aniline in CPG of 7,5 nm pore size are depicted in Fig. 3. For temperatures greater than 246 K (melting point inside the pores), there are two different relaxations. The longer component of the relaxation that is of the order of 10×10^{-3} s is divided into three regions. The response in the region $T > 267$ K is due to Maxwell-Wagner polarization.

This relaxation mechanism occurs for heterogeneous system due to interfacial polarization, when a slightly conducting liquid is enclosed in an insulating material, and has a relaxation time of the order 10^{-3} s; the porous glass particles, suspended in bulk aniline were electrically neutral. The response in the region $246 < T < 267$ K corresponds to the relaxation of the bulk crystal; the Maxwell-Wagner effect disappears because the porous glasses particles are arrested in the crystalline matrix of bulk aniline, thereby preventing interfacial dispersion. The shorter relaxation component, of the order 10^{-5} s, is too slow to represent the liquid phase relaxation in the pore. However, for dipolar liquids confined in nanopores, the molecules in the contact layer show a slower dynamics, with a relaxation time of the order of 10^{-5} s [12,13]. Thus, the shorter branch of the relaxation time that occurs above 246 K can correspond to the response of the contact layer. The response of the liquid phase in the bulk and in the inner layers of the pore are not accessible in our experiments, as the sub-nanosecond relaxation times characteristic of liquids is not affected by the frequency range we use in our experiment. The disappearance of the 10^{-5} s branch at 246 K is due to the freezing of the liquid in the pores. Below this temperature, the millisecond relaxation time corresponds to the crystal phase relaxation in the bulk [7] and in the pore.

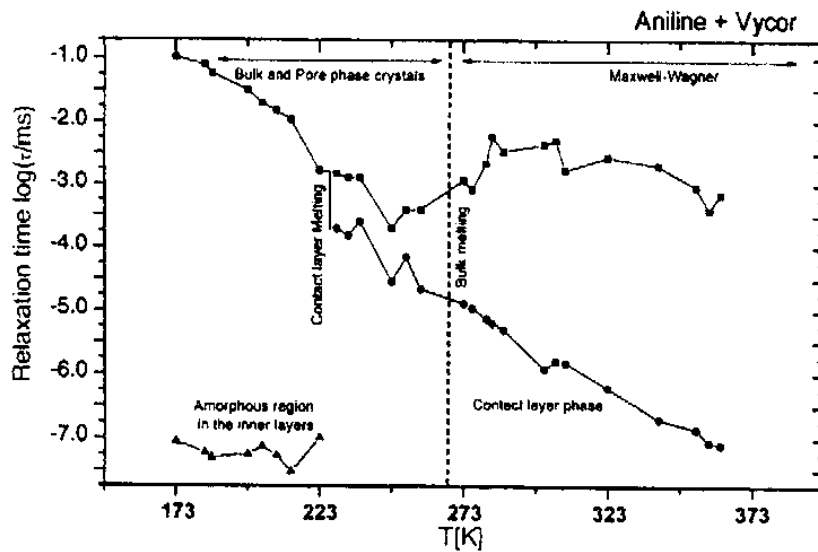


Fig. 4. τ vs. T for aniline in Vycor with average pore size of 4.1 nm.

For mean pore diameters larger than 7.5 nm, the behavior of the relaxation time with temperature is similar to that shown in Fig. 3, and suggests that at lower temperatures the phase in the pore is a continuous (presumably defective) crystal; i.e. molecules have a single relaxation component throughout the confined crystalline phase. For smaller pores, e.g. Vycor with $H = 4.1$ nm, the behavior is quite different. In Fig.4 the corresponding relaxation times for aniline melting in Vycor glass are shown. The 10^{-5} s branch of the relaxation time shows a sharp increase at $T = 230$ K, which is taken to be the melting temperature inside the pores. The millisecond branch is again divided into three regions: $T > 267$ K (Maxwell-Wagner effect), $230 < T < 267$ K (bulk crystal phase) and $T < 230$ K corresponding to the crystalline phase relaxations in the bulk and in the pore.

However, there is a new branch of relaxation times of the order of a few hundred nanoseconds which occurs below the melting temperature of aniline in the pores ($T < 230$ K). This strongly suggests that the confined crystalline phase is not homogeneous, but that there are regions that are glasslike (amorphous), having a relaxation component of the order one hundred ns. Thus, for pore diameters as small as 4.1 nm, the confinement poses a serious constraint on the formation of a homogeneous crystalline phase in the pore. The exact structure of the confined crystalline phase cannot be determined from dielectric relaxation spectroscopy experiments alone. One would need to resort to more direct methods, such as x-ray diffraction and molecular simulation, in order to obtain the fluid structure of the inhomogeneous crystalline phase.

The light transmission measurements for aniline in MCM-41 ($H=2.8$ nm) showed only one signal, corresponding to a phase transition at 223.1 K. Dielectric relaxation measurements showed that the distribution of the relaxation times vs temperature was similar to that for nitrobenzene in MCM-41 [4], and qualitatively different from the behavior in Vycor. The melting transition at low temperature is absent for the 10^{-5} s branch; this branch of the relaxation time does not show any discontinuity. Once again there is a branch of relaxation times of the order of a few hundred ns, suggesting the presence of an amorphous region, which appears at a temperature of about 223 K, corresponding to the temperature of the phase transition observed in the light transmission experiments. We conclude that the pore size of 2.8 nm is too small for even partial crystallization to occur.

H/nm	H/σ_H	T/K	Ordered phase
Bulk	...	266.8	Crystal
50 (CPG)	100	262	Crystal
25 (CPG)	15	260.2	Crystal
7.5 (CPG)	9	246.1	Crystal + glass
4.1 (Vycor)	5.6	229.8	Glass
2.8 (MCM-41, Si)	5.6	223.1	Glass

Table 1. Melting temperatures: Experimental measurements.

The melting behavior of aniline is summarized in Table 1 for a range of pore sizes in various silica-based pores. Aniline freezes to a crystalline structure when confined in the larger pores $H \geq 7.5$ nm ($H \geq 15\sigma_H$). For a pore size of 4.1 nm, only part of the fluid freezes, with the rest forming an amorphous phase. Morishige and Kawano [14] reached similar conclusions in their x-ray diffraction study of freezing of N_2 and CO in MCM-41 materials of varying pore diameter. For these latter fluids, the x-ray studies indicated a homogeneous crystalline phase for pore diameters greater than 6 nm ($H \geq 16\sigma_H$). For smaller pore sizes, the x-ray diffraction patterns were consistent with a partially crystalline confined phase coexisting with an amorphous phase. For pore size of 2.8 nm the confined fluid does not undergo a freezing transition; however a glass transition is observed.

5. DISCUSSION AND RESULTS

The proposition that the quasi-two-dimensional contact layer may exist as a hexatic phase [6] implies that at higher temperatures, the "hexatic" contact layer can undergo a transition to an orientationally disordered, liquid-like contact layer. In Fig.4 the disappearance of the μ s branch at 363 K suggests such a transition from a hexatic (with μ s relaxation time) to a liquid-like contact layer (with nanosecond relaxation time). Such a transition is a Kosterlitz-Thouless (KT) transition [15,16], and involves a large entropy change. In two dimensions, the specific heat shows a nonuniversal peak at the KT transition. Previous DSC measurements [4] for the case of nitrobenzene adsorbed in Vycor and MCM-41 showed an additional peak at a temperature of about 373 K, which is consistent with the KT behavior (hexatic to liquid transition). These results are in qualitative agreement with recent molecular simulation results [6].

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