

NMR Studies of Phase Separation of a Binary Liquid in a Porous Glass

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The phase separation behavior of critical aniline-cyclohexane in Vycor porous glass is compared with bulk behavior using high resolution NMR and NMR microimaging methods. The NMR features of this liquid in Vycor are inconsistent with both the random field Ising picture and the single-pore picture. Instead, continuous composition gradients produced by an interplay of molecular sedimentation and self-diffusion, and perhaps wetting, are inferred from the NMR measurements.

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Recently, numerous studies of the phase separation of binary liquids confined in porous glasses have been reported [1–7]. The theoretical and numerical work relied mostly upon the results of light- and neutron-scattering studies. Two essential features emerged from these efforts to probe and understand the equilibrium and phase separation behavior of binary liquids in porous glasses: the effects of confinement and of the randomness of porous media. In the present work, a variety of NMR experiments were performed on the aniline/cyclohexane (AC) critical mixture in Vycor porous glass (70 Å pore diameter) and in bulk. Self-consistent NMR results reveal new static and dynamic properties of this confined mixture which are contrasted to those inferred from previous studies [1–7].

Measurements of Bloch decays, of spin relaxation times T_1 and T_2 , and hole burning experiments were performed on a Bruker WM spectrometer operating at 250 MHz for ^1H . Self-diffusion coefficients and NMR microimaging spectra were obtained on a Bruker MSL spectrometer operating at 300 MHz for ^1H . Temperatures were controlled to $\pm 0.1^\circ\text{C}$ (at 250 MHz) and to $\pm 0.5^\circ\text{C}$ (at 300 MHz).

The bulk AC mixture exhibits an upper consolute solution temperature T_c of 30.0°C at a critical mass fraction of 53% of cyclohexane [8]. Spectroscopic grade cyclohexane and deuterium oxide were used without further purification, while aniline was distilled [8]. Cylindrical samples of commercial Vycor porous glass, 3.5 mm in diameter by 15 mm in length, were cleaned [9], and soaked for 24 h in the AC critical mixture at 38.0°C . The samples were then wiped, wrapped with teflon tape, and placed in D_2O in 5 mm NMR tubes in the magnet. D_2O served as a frequency reference and for shimming the magnetic field.

High resolution ^1H NMR line shapes of the cyclohexane in the AC critical mixture in bulk and in Vycor are shown for various temperatures in Figs. 1(A) and 1(B), respectively. In bulk AC above T_c , the resonance position of a component is determined to a very good approximation by the weighted averages of the magnetic susceptibility of each component and van der Waals interactions among

components [8,10]. Consequently, the resonance position is a linear function of the phase composition. Below T_c , two-phase coexistence causes line splitting. In Fig. 1(A), the larger resonance corresponds to the cyclohexane in the cyclohexane-rich phase, while the smaller resonance originates from the cyclohexane in the aniline-rich phase. Line shapes of cyclohexane in the AC critical mixture in Vycor [see Fig. 1(B)] exhibit no line splittings or displacements over a period of 25 days for $0 < T < 40^\circ\text{C}$. These results indicate the absence of macroscopic phase separation as is also observed in light- and neutron-scattering studies [1–4].

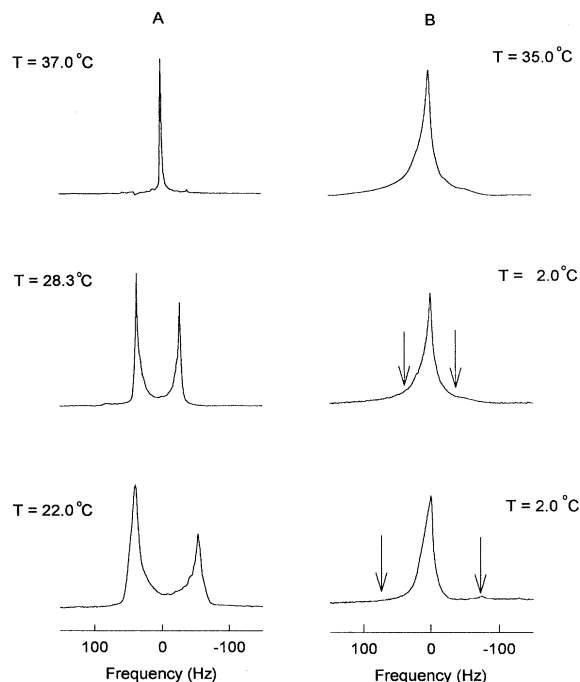


FIG. 1. ^1H NMR absorption line shapes of cyclohexane in AC critical mixture in bulk (A) and in Vycor (B). Arrows in (B) indicate the expected positions of the resonances for cyclohexane in AC bulk mixture.

Linewidths of the cyclohexane resonances of AC in the porous glass, 15–30 Hz at half-height in Fig. 1(B), could originate from magnetic field inhomogeneities, a dispersion of chemical environments, or spatial configurations of microscopic domains of equilibrium compositions with possible rapid molecular diffusional exchange. Magnetic field inhomogeneities due to the Zeeman field and other internal relaxation effects yield a combined broadening of 1.5–2.0 Hz for the resonance of cyclohexane in bulk and in the bulk AC critical mixture above T_c [see Fig. 1(A)]. Composition differences across phase boundaries produce magnetic field gradients; across the bulk interface these gradients broaden the linewidths by 15–20 Hz [see Fig. 1(A)]. In addition, such gradients shift the resonance position by 5–250 Hz for domain sizes $<10 \mu\text{m}$ [10]. In the random field Ising picture [1,2,5] and the single-pore picture [4,6,7] of binary fluids in porous media, microscopic domains with, respectively, the equilibrium composition or slightly shifted composition due to wetting are presumed to exist. Thus, the resulting gradients would produce broadening about the expected resonance positions indicated by the arrows in Fig. 1(B). Broadening due to possible wetting or hydrogen bonding of surfaces is estimated at 5–10 Hz from relaxation measurements. Rapid molecular diffusional exchange between microscopic domains would lead to averaging of the susceptibility effects, with the motionally modulated resonance appearing at an intermediate position between the arrows as observed in Fig. 1(B). Hole burning experiments, as will be discussed next, eliminate this possible interpretation.

Figure 2 displays the selective saturation of the ^1H cyclohexane resonance in the AC critical mixture in bulk [Fig. 2(A)] and in Vycor [Fig. 2(B)] at 28.0 °C. In the bulk, the cyclohexane resonance in the cyclohexane-rich

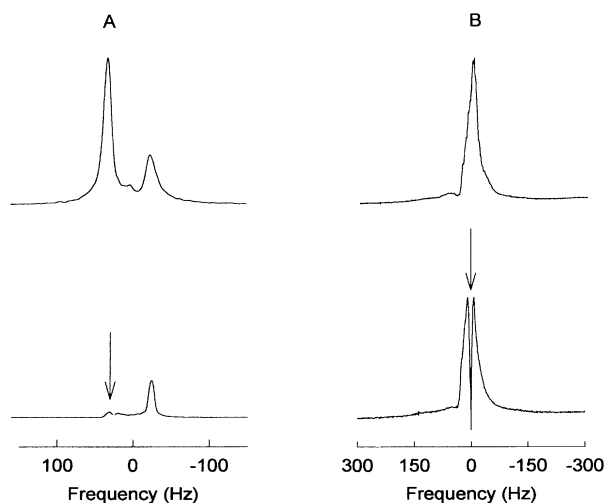


FIG. 2. Unsaturated (top) and saturated (bottom) power spectra of the cyclohexane ^1H resonance of the AC critical mixture in bulk (A) and in Vycor (B) at 28.0 °C. Arrows indicate the selective irradiation frequencies.

phase was completely saturated after 60 s of the selective irradiation of its peak with a 180 mG rf field. In the Vycor sample, the irradiation procedure (60 s duration with a 180 mG rf field) on the cyclohexane resonance produced a hole in the spectrum. The duration of the irradiation was much longer than spin-lattice relaxation times which are 5 s for the cyclohexane protons in the critical mixture in bulk and in Vycor at 28.0 °C. These results unambiguously demonstrate the presence of inhomogeneous broadening for the cyclohexane resonance of AC in Vycor. If microscopic domains of different composition occurred, as advocated in the random field Ising picture [1,2,5] and in the single-pore picture [4,6,7], with rapid molecular diffusional exchange, hole burning at the position indicated in Fig. 2(B) would not be possible. To corroborate this observation, selective irradiations were performed, within 100 Hz on each side of the resonance position in Fig. 2(B). In these experiments, the resonance remained unaffected, establishing unequivocally the absence of rapid diffusional molecular exchange between microscopic domains of different compositions, assuming they existed.

To confirm the lack of microscopic domains with different compositions and with possible slow molecular diffusional exchange, measurements of self-diffusion coefficients, D , in the AC critical mixture in the porous glass were performed at 24.0 °C. These NMR results are compared with bulk behavior in Table I. The reduction of D (pure cyclohexane) in porous glass, i.e., $\frac{1}{3}$ of the bulk value, can be readily understood on the basis of the tortuosity and the reduced dimensions of the porous network [12]. D (cyclohexane in the AC critical mixture) in Vycor is about $\frac{1}{5}$ of D (pure cyclohexane) in Vycor. However, only part of this ratio can be attributed to porous glass effects, since D (cyclohexane in the bulk AC critical mixture) is $\frac{1}{2}$ of D (bulk cyclohexane). In Vycor, presumably the glass surface induces hydrogen bonding and wetting effects which further reduce the self-diffusion coefficients of AC. By assuming a simple 1D random walk, and with D (cyclohexane in the AC critical mixture) in Vycor, the average displacement of a cyclohexane molecule in 1 s is

TABLE I. Self-diffusion coefficients $D \times 10^5 / (\text{cm}^2/\text{s})$ measured by NMR at 24 °C.

Environment	Cyclohexane	Aniline
Bulk ^a	1.32	
AC bulk mixture (50%/V cyclohexane): upper phase ^b	1.3	1.5
AC bulk mixture (50%/V cyclohexane): lower phase ^b	0.6	0.4
Vycor porous glass ^a	0.39	
AC critical mixture in Vycor porous glass ^a	0.085	0.071

^aThis work: error estimates $\pm 10\%$.

^bReference [11]: error estimates $\pm 15\%$.

estimated at 10 μm , or roughly 385 pores and pore interconnections, assuming 70 \AA pore diameters and 190 \AA pore to pore distances [9,13]. Thus, the presence of microscopic domains with different compositions, with or without slow molecular diffusional exchange, is incompatible with the diffusion results and the line shapes of Fig. 1(B).

Hence, the cumulative high resolution NMR results on the AC critical mixture in Vycor are inconsistent with the claim of microscopic domains of the size of pores in the single-pore picture [4,6,7]. Similar arguments applied to microscopic domains extending over several pores exclude the random field Ising picture [1,2,5] as a possible explanation of these NMR observations. Furthermore, measurements of spin relaxation times revealed only single component exponential decays; no activated dynamics associated with the random field picture can be perceived at the molecular level. Instead, the NMR features of the AC critical mixture in the porous glass indicate the presence of composition variations without distinct interfaces. From the linewidths in Fig. 1(B), and from the composition dependence of resonance positions [8,10], one infers a dispersion of chemical composition ranging from $\pm 3\%$ to 5% about the critical composition in the Vycor porous glass.

NMR microimaging experiments were performed in order to examine the composition profiles over macroscopic length scales. The ^1H nuclear spin density profiles along the gravitational direction (z) in the AC critical mixture in bulk and in Vycor, respectively, 25 min and 14 days following a thermal quench from 38 to 24 $^\circ\text{C}$, are shown in Figs. 3(A) and 3(B). In the bulk critical mixture, a sharp interface, which appears within a few minutes after the temperature quench, separates the upper and lower phases. Hydrodynamic instabilities and domain sedimentation in the late stage of phase separation [14] drive the mixture to the final two-phase equilibrium configuration within about 60 min under the experimental conditions. Slight concentration gradients along the z direction, due to molecular sedimentation, are expected to occur over a period of about 2 weeks in the absence of hydrodynamic perturbations [15]. In Fig. 3(A), intensity attenuations of about 15% arise in both phases due to self-diffusion during the experiments. Further attenuations at the edges of the sample result from inhomogeneities of the pulsed magnetic field gradients and rf excitation pulses. Figure 3(B) shows a nonuniform spin density profile of AC in Vycor, which developed gradually over a period of several days along the z direction in the sample. During the same period, the spin density profiles in the x and y directions remained uniform for the bulk mixture and for the mixture in Vycor. Visualization studies (unpublished) during the initial soaking of the Vycor revealed an isotropic invasion process which lasts about 20 min. Following the invasion processes, the high resolution NMR spectra [see Fig. 1(B)] remained relatively constant over periods of several days which indicates that the local com-

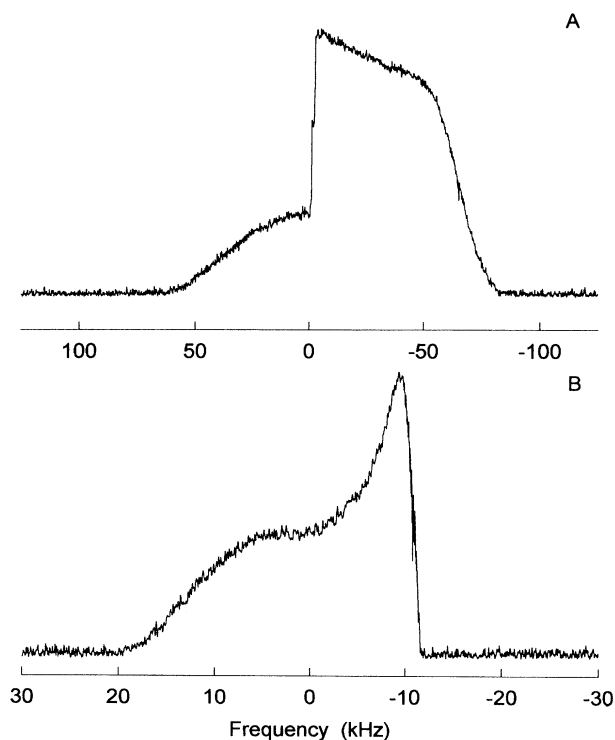


FIG. 3. Profiles of ^1H nuclear spin densities (intensities in arb. units) along the gravitational (z) direction (abscissa in kHz) for AC critical mixture in bulk (A) and in Vycor (B) 25 min and 14 days, respectively, after a thermal quench to 24 $^\circ\text{C}$. Bottom of the samples are in the positive frequencies. Spectra show 3.13 cm of a 4 cm bulk sample in (A) and the whole 1.5 cm Vycor sample in (B).

position is stable. Hence, the microimaging results in Vycor are consistent with an interplay of molecular sedimentation and self-diffusion leading to some molecular segregation and smooth concentration variations over macroscopic distances after several days.

Corroboration for these observations comes from a chemical shift slice selection technique, in which ^1H NMR spectra corresponding to layers of the samples were acquired at different heights along the cylinder axis. Figure 4(A) displays the total ^1H NMR magnitude spectra of the bulk AC critical mixture in selected layers in the lower phase, near the macroscopic interface, and in the upper phase. The cyclohexane resonance occurs close to the 1.5 kHz on the frequency scale, while the aniline aromatic protons are seen around 3.0 kHz. The amine protons of aniline should appear at 2.3 kHz; however, their spectral features are extremely sensitive to quadrupolar relaxation effects at the nitrogen through indirect nuclear coupling. Magnitude spectra of selected layers obtained at similar relative positions in the porous glass are presented in Fig. 4(B). With increasing height in the sample, the cyclohexane/aniline ratio increases gradually which demonstrates that some molecular segregation has indeed

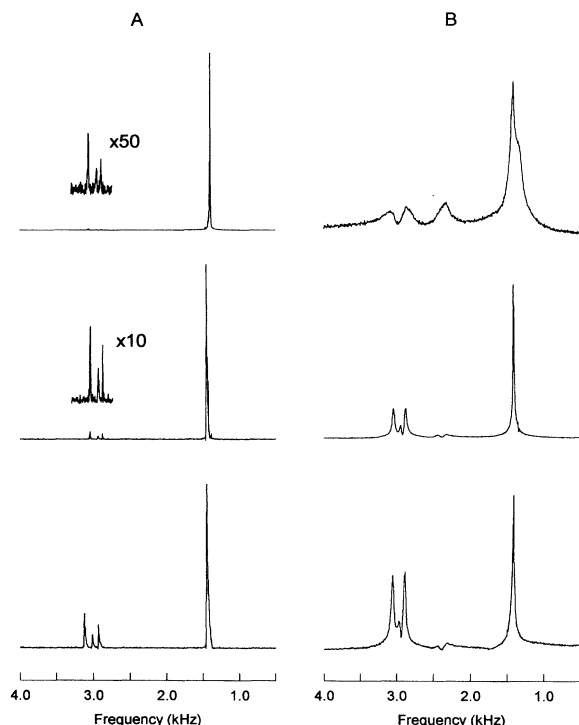


FIG. 4. ^1H NMR chemical shift slice selection spectra at different heights along the z direction for the AC critical mixture in bulk (A) and in Vycor (B) 45 min and 14 days, respectively, after a thermal quench to 24°C . Top, middle, and bottom portions correspond to the relative positions along the z direction in the samples. Spectral intensities were normalized using the cyclohexane resonances. Spectral broadening, due to magnetic field inhomogeneities, does not affect the relative intensities within a single slice; broadening of the line shapes in the top spectrum in (B) arises from slight Zeeman field inhomogeneities present in the upper part of the sample.

occurred in Vycor. Thus, molecular self-diffusion and sedimentation bring about a possible equilibration of the chemical potentials.

In summary, the results of the noninvasive NMR experiments presented here provide new and striking evidence about the behavior of the AC critical mixture in a porous glass. The cumulative high resolution NMR data are inconsistent with the presence of microscopic domains of different compositions. Hence, the random field

Ising picture [1,2,5] and the single-pore picture [4,6,7] developed from the interpretations of light- and neutron-scattering studies on other binary fluids are incompatible with the NMR behavior of AC in Vycor porous glass. While macroscopic phase separation is not observed, the NMR evidence establishes the presence of continuous spatial variations of composition without distinct interfaces. Molecular segregation, based on an interplay between self-diffusion and sedimentation, and perhaps wetting, accounts for the macroscopic composition profiles observed with the NMR microimaging methods.

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