Liquid–liquid phase separation in micropores

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Abstract

Phase separation of binary liquids with an upper critical temperature in porous materials is studied by 1H NMR cryoporometry and cross-relaxation spectroscopy and by 15N NMR spectroscopy. The first method provides domain size distributions of the separating minority component while the other ones verify the segregation of the two liquids on molecular level. We find that metastable structures are formed manifested by bimodal domain size distributions. The kinetic arrest of domain growth may be imposed upon by bottlenecks in the porous structure that block diffusion of entire droplets. Practical applications, if one of the liquid components is polymerized, include mobile polymer particles trapped in porous matrix that can serve, e.g., as filters with microscopically amphiphilic pathways.

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1. Introduction

Upon cooling, many binary liquid mixtures phase separate. The temperature of phase separation is defined as the critical or consolute temperature $T_c$, the variation of which with the composition of the mixture defines the coexistence line of the liquid–liquid phase diagram. If occurs in bulk, liquid–liquid phase separation usually results in two distinct liquid layers, with the more dense liquid at the bottom. As many other phase transition phenomena, such liquid–liquid phase separations may be modified if the initial homogeneous (at $T > T_c$) mixture is imbibed in a porous matrix [1]. Experimental observations are apparently contradicting each other as concerning the size, morphology, and composition of liquid domains that arise below $T_c$; considering that the presence of the porous matrix significantly complicates (e.g., via opacity or background scattering) the analysis of data obtained by many methods this is not that surprising. Similarly, predictions of theoretical methods which emphasise different features of the matrix are often at odds with each other. Here we present a new experimental approach [2,3] to the problem.

2. Experimental

The observational method is based on 1H and 15N nuclear magnetic resonance (NMR) and is applied to the selected model mixture of nitrobenzene and n-hexane that is imbibed in controlled porous glass from CPG, Inc (Lincoln Park). The pores in the glass form a randomly interconnected network with average pore diameters 7.5, 24, 73, and 127 nm in the different investigated samples. Since the NMR signal arises exclusively from the pore-filling liquid the only significant disturbance to the data by the glass matrix is the broadening of the NMR peaks by the slight random variation of the magnetic field within the sample volume [4]. In case of 1H NMR, the chemical shift difference is, nevertheless, large enough to obtain separate nitrobenzene and hexane peaks in the spectrum. In 15N NMR, it is only nitrobenzene molecules that contribute to the observed signal. The NMR experiments were performed on Bruker DMX 200 (1H) and AMX 300 (15N) spectrometers.

In the 1H cryoporometry [5,6] experiments, the samples are cooled from above $T_c$ ($= 293$ K at 36% volume fraction of nitrobenzene) to far below (ca. 250 K) the freezing point ($= 272.5$ K) of the nitrobenzene-rich phase [2,3]. Importantly, the cooling rate in those
experiments was about 0.2 K/min. We also note that experiments performed after keeping the system at a constant temperature below $T_c$ but above 250 K did not significantly alter the obtained domain size distributions. At low temperature, the nitrobenzene peak disappears from the $^1$H spectrum which is a consequence of (i) freezing of the nitrobenzene-rich domain of the sample and (ii) detecting the $^1$H NMR signal by a spin-echo pulse sequence [7,8] with the echo time set to a few milliseconds that effectively cancels signal from solid nitrobenzene whose spectrum is very broad. Upon increasing the temperature from this point, the nitrobenzene signal successively reappears as a result of melting. The temperature at which a particular domain melts depends on the domain size $d$ as given by the well-known Gibbs–Thompson equation [9]. Hence, by recording the temperature dependence of $^1$H nitrobenzene NMR intensity, the size distribution of the phase-separated nitrobenzene-rich domains can be measured; the temperature-dependent NMR intensity data were processed as described in detail in [3].

The $^1$H NMR cross-relaxation and $^{15}$N NMR spectra were used to control and verify the phase separation of the nitrobenzene- and hexane-rich domains above freezing. Dipole–dipole cross-relaxation between $^1$H nuclei is strongly ($\propto r^{-6}$) dependent on distance $r$ between the involved nuclei [10]. Hence, strong cross-relaxation, manifested by strong corresponding cross-peaks in the conventional 2D NOESY [10] spectra, is expected between the nitrobenzene and hexane peaks in the molecular mixture above $T_c$. Far below $T_c$, where the minority concentration is low in any of the phase separated domains, one expects small cross-peaks. On the other hand, the chemical shift of the $^{15}$N nuclei of nitrobenzene varies a lot with the molecular environment (solvent effect) [11]. Hence, at the onset of phase separation one expects a splitting of the $^{15}$N spectra with the larger and smaller peaks arising from nitrobenzene molecules in the nitrobenzene-rich and hexane-rich domains, respectively. Exchange of nitrobenzene between the two sorts of domains may modify this signature.

3. Results and discussion

The obtained pore size distributions are shown in Fig. 1. The first point is that, in contrast to conclusions drawn from data in related systems [12], microscopic phase separation indeed occurs in the present porous glasses; there are domains with distinct molecular composition and thereby distinct freezing point. On the other hand, $^1$H PGSE NMR diffusion data indicate that the domains are small on the $\mu$m scale [3]. This phase separation is not a consequence of freezing: below $T_c$, the $^{15}$N NMR spectrum (not shown) is split into two lines, one small (from nitrobenzene molecules in the hexane-rich domains) and one large (from the nitrobenzene-rich phase). Moreover, $^1$H cross-relaxation NMR data show a drastic decrease of molecular contact between nitrobenzene and hexane upon cooling the sample below $T_c$ (see Fig. 2) but keeping it unfrozen.

As the average pore size increases, the relative (w.r.t. the average pore size) size of the formed nitrobenzene domains clearly increases. While at the smallest pore diameter apparently no nitrobenzene domain fills a pore completely, at the highest pores size nitrobenzene seems to fill completely those pores that contain nitrobenzene-rich domains. At intermediate pore sizes, we obtain a mixture of these two scenarios. Of the two structures, the incomplete filling of pores must be the less stable state.

Since the hexane-rich phase always contains some nitrobenzene, Ostwald (Lifshitz–Slyozov) ripening [13,14] of the system via molecular nitrobenzene diffusion is an ever present domain growth mechanism. However, the ripening rate depends on nitrobenzene and hexane molecular parameters and should thereby be roughly independent on pore size. This is clearly not the case. Hence, we suggest the following growth mechanism. Upon cooling the sample below $T_c$, small ($\sim$nm) initial droplets are formed dominantly by molecular diffusion. This process, driven by the difference in chemical potential, can continue as droplet ripening and thereby lead to droplet growth. There are two important limitations. First, on lowering the temperature the nitrobenzene concentration in hexane and thereby the diffusion flux decreases. Second, the rate of growth of
droplet size decreases even in bulk and at constant temperature with time $t$ as $\frac{d}{dt} \sim t^{-2/3}$ [13,14]; in a porous system, a further decrease is expected [15]. Hence, droplet coalescence and/or relaxation of droplet shape (for droplets extended over the pore correlation length) by hydrodynamic flow may take over as a dominant mechanism [13]. At the same thermal history and liquid composition, this cross-over appears at a given droplet size $d_{\text{cross}}$. The further history of droplet growth depends on the relation between $d_{\text{cross}}$ and the pore size $d$: in case of $d \sim d_{\text{cross}}$, droplet diffusion is slow [16] and hydrodynamic flow may be hindered by bottlenecks and thereby cannot contribute to further droplet growth.

4. Conclusions

Phase separation of liquids in random porous networks shows as surprising variation by average pore size. The explanation may involve cross-over between different droplet growth mechanisms and the relation of the cross-over droplet size to pore size. Further experiments, especially those that measure droplet dissolution instead of droplet growth may help to clarify this phenomenon.

Irrespective of its reasons, this phase separation phenomenon suggests a way to produce polymer particles embedded in but not immobilized by a porous matrix. By choosing polymerizable liquids as the inner phase within pores and by polymerizing them after phase separation, one creates a new porous network where not only is the average pore size smaller but the adjacent pore walls are chemically different within a single correlation length. Such a structure may act as a filter with large chemical selectivity.

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References