Liquid–liquid phase separation in micropores

Rustem Valiullin [a,b], Dulce Vargas-Kruså [a], István Furó [a,*]

[a] *Physical Chemistry, Department of Chemistry, Royal Institute of Technology, SE-10044 Stockholm, Sweden*
[b] *Department of Molecular Physics, Kazan State University, 420008 Kazan, Russia*

Abstract

Phase separation of binary liquids with an upper critical temperature in porous materials is studied by ^{1}H NMR cryoporometry and cross-relaxation spectroscopy and by ^{15}N 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 ^{1}H and ^{15}N 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 ^{1}H NMR, the chemical shift difference is, nevertheless, large enough to obtain separate nitrobenzene and hexane peaks in the spectrum. In ^{15}N NMR, it is only nitrobenzene molecules that contribute to the observed signal. The NMR experiments were performed on Bruker DMX 200 (^{1}H) and AMX 300 (^{15}N) spectrometers.

In the ^{1}H 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