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Original contribution

Insights into adsorption behaviour of binary liquid mixtures in porous media using fast field cycling NMR

J. Ward-Williams, L.F. Gladden*

Department of Chemical Engineering and Biotechnology, University of Cambridge, West Cambridge Site, Philippa Fawcett Drive, Cambridge CB3 0AS, UK

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ABSTRACT

Fast field cycling, FFC, NMR relaxometry experiments are reported in the frequency range of 10 kHz–40 MHz to characterise the adsorption behaviour of cyclohexane:THF (non-polar:polar) and THF:methanol (polar:polar) binary liquid mixtures adsorbed on a γ-alumina surface of catalytic interest. Laplace inversion of the relaxation rate data is employed to identify the chemical species in the binary mixture. In both systems studied, the more polar molecule preferentially interacts with the surface compared to the co-imbibed species. The relaxation rate data were analysed to explore the relative influences of surface dynamics and surface accessibility on the observed relaxation rates. For both binary systems, the change in relaxation behaviour with composition is interpreted as a change in the surface accessibility of each species caused by a micro-phase separation at the pore surface.

1. Introduction

Many analytical techniques have been applied to the characterisation of homogeneous systems on the molecular level, allowing deep insights into the chemical and physical processes that occur [1,2]. In contrast, heterogeneous systems are much less well understood, despite their frequent occurrence in industrial processes [3]. Much of this lack of understanding stems from the experimental difficulties associated with characterising these systems, as well as extending this characterisation to the high temperatures and pressures at which they operate. Nuclear Magnetic Resonance, NMR, is a promising tool for overcoming this knowledge gap, as the technique can be applied from room temperature and pressure up to industrial conditions [4]. In addition, NMR offers many different ways to deconvolute complex problems; i.e., by separating out regions of interest spatially using imaging [5], or by partitioning the NMR signal based on distinct chemical [6] or dynamical [7] environments. In this paper we will focus on the latter of these methods, and will show the application of fast field cycling, FFC, NMR to the characterisation of surface dynamics and surface accessibility of binary liquid mixtures within the pore space of a catalytically-relevant γ-alumina system.

Studies of the adsorption behaviour for single-component liquids in fully- and partially- saturated porous media have been widely reported within the literature using both NMR and non-NMR techniques [8,9], but comparatively few studies exist for liquid mixtures [10,11]. In recent years the application of neutron scattering and infrared spectroscopy has provided important physiochemical insight into the intraparticle adsorption behaviour of liquids in porous media [12–14], with a growing focus on the micro-phase separation at the fluid-surface interface. In the case of binary systems this separation ranges from full to only partial demixing, with the extent of this micro-phase separation being a function of the properties of the porous medium as well as the properties of the liquid. As micro-phase separations leads to a surface layer of composition influenced by preferential adsorption of one (or more) of the components, the composition of liquid imbibed within the nanoporous extrudate will not necessarily be equivalent to the composition of the liquid that the porous medium was initially immersed in. Further, the composition of the surface-influenced (adsorbed) layer may differ, for the same reason, from the composition of the bulk pore liquid. In addition, cooperative or competitive binding effects may alter the surface dynamics of adsorbed molecules. Therefore, in order to fully characterise these systems it is necessary to measure both the composition of the imbibed liquid as well as the dynamics of each component. This information is encoded into the NMR longitudinal relaxation rate, $R_1 = 1/T_1$, of the system and can be interpreted through an extension of the two phase fast exchange model [15].

In the case of a pore of volume V the filling factor of species i can be expressed as:

$$f_i = \frac{V_{i,ads} + V_{i,bulk}}{V}, \tag{1}$$

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* Corresponding author.

E-mail address: lfg1@cam.ac.uk (L.F. Gladden).

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where $V_{i,ads}$ and $V_{i,bulk}$ are the adsorbed and bulk pore volumes of species i. To simplify the model we assume that there is no interspecies relaxation, and that all species occupy the same volume, giving:

$$\frac{1}{T_{1i,\mathrm{obs}}} = \frac{1}{T_{1i,\mathrm{bulk}}} + p_{i,ads}\left(\frac{1}{T_{1i,\mathrm{ads}}} - \frac{1}{T_{1i,\mathrm{bulk}}}\right) \tag{2}$$

$$\approx \frac{1}{T_{1i,\mathrm{bulk}}} + \frac{V_{i,ads}}{V\, f_i}\left(\frac{1}{T_{1i,\mathrm{ads}}}\right), \tag{3}$$

where $T_{1i,\mathrm{obs}}$ is the measured longitudinal relaxation rate, and $p_{i,\ \mathrm{ads}} = V_{i,\mathrm{ads}}/(V_{i,\mathrm{ads}} + V_{i,\mathrm{bulk}})$ is the relative surface volume fraction of species i. The subscript 'ads' identifies the molecules influenced by the surface and not just the molecules in the monolayer adjacent to the surface. It is immediately obvious from Eq. (3) that the relaxation rate will vary with the composition of each component in the mixture, even if the surface dynamics leading to relaxation remain fundamentally unchanged. This complicates the analysis, and means that relaxation measurements performed at a single magnetic field strength are unlikely to be able to provide enough information to accurately distinguish between changes in the composition of the surface adsorbed phase and any underlying changes in the surface dynamics. A potential solution to this problem is to measure the T_1 relaxation of the system as a function of the applied magnetic field using FFC-NMR. For liquids adsorbed on a porous medium that is free from paramagnetic impurities the relaxation rates at low fields tend to be dominated by a series of surface binding events separated by bulk excursions [16,17]. This process modulates the intramolecular dipole-dipole coupling, and leads to a decay of the correlation function that occurs several orders of magnitude slower than the decay observed in bulk liquids. The resultant relaxation dispersion profiles often follow a power law frequency dependence, the exponent of which contains information about both the adsorption strength and the surface geometry [16]. The high sensitivity of FFC-NMR to the former has previously been demonstrated for a range of liquids imbibed in an alumina-supported metal catalyst [18].

Despite the wealth of dynamical information FFC is able to provide, its application to liquid mixtures within porous media has thus far been limited to the study of immiscible mixtures of water and oil in rock cores [19]. This limitation is due in part to the relatively poor magnetic homogeneity provided by the switchable electromagnets that are integral to this technique. This prevents the spectroscopic resolution of multiple components, leaving a numerical deconvolution of multiple relaxation rates as the only remaining approach for studying complex systems [20]. Recently it has been shown that existing inverse Laplace and exponential fitting methodologies are highly effective at characterising multiple environments arising from single-component liquids adsorbed on heterogeneous metal oxide catalysts, even in the absence of spectral resolution [21]. Application of these techniques to binary liquid mixtures should therefore allow a deeper understanding of the relaxation behaviour of adsorbates as a function of composition, which is a necessary precursor to the in situ monitoring of catalytic reactions with FFC-NMR.

2. Materials and methods

Methanol, tetrahydrofuran (THF, with 250 ppm BHT stabiliser) and cyclohexane were obtained from Alfa Aesar with a purity of > 99%. The polarities of these liquids are 0.762, 0.207 and 0.006 respectively relative to the polarity of water [22]. Methanol-d_1 was purchased from Fluorochem Ltd. with an isotopic enrichment of > 99%. The γ-alumina catalyst was obtained from Alfa Aesar in the form of 1/8″ diameter cylindrical extrudates with typical lengths of 1/8–1/4″. Pore size determination was performed using a Micromeritics TriStar 3000 automated gas adsorption analyser and the N_2 adsorption data were then calculated using the Barrett–Joyner–Halenda, BJH, method. A narrow and monomodal pore size distribution was observed, centered about a modal value of 10 nm. ESR measurements on the alumina sample are reported elsewhere [21], and showed a negligible quantity (< 10 ppm) of paramagnetic iron.

Samples were prepared by drying the alumina for 12 h at 120 °C and then soaking the alumina for a further 12 h in a liquid mixture of known composition. The sample was then poured onto filter paper and the extra-pellet liquid was removed shortly prior to analysis. Since preferential adsorption of one component could influence the composition of the mixture within the porous medium, the actual composition of the mixture in the intra-particle space was calculated from the relative signal intensities of the observed relaxation environments. This procedure was applied to the T_1 values measured at each field, and the average value was taken from the 20 measured field values for each mixture.

FFC-NMR experiments were performed on a Stelar Spinmaster Duo relaxometer. For each nuclear magnetic relaxation dispersion, NMRD, profile 20 ^{1}H Larmor frequencies were analysed, logarithmically spaced between 10 kHz and 40 MHz. Each experiment consisted of 64 logarithmically spaced delay times from 1 ms to 5.5 s ($\sim 5 \times T_{1,\mathrm{max}}$). The acquired FFC-NMR data were renormalized such that the signal in each dataset decayed from 1 to 0. The T_1 distribution at each field strength was obtained via an Inverse Laplace transformation using Tikhonov regularisation and was then independently fitted with a bi- or tri-exponential fit depending on whether or not the O^{1}H signal was of sufficient intensity that it could be fitted independently. The reported relaxation rates and relative populations are those extracted from the multi-exponential fits.

3. Results

The compositions of the liquids used to soak the pellets, and the measured intra-particle compositions for each sample are shown in Table 1. In all experiments the intra-particle liquid composition was similar to the composition of the liquid in which it was immersed, however preferential uptake of the more polar of the two components was observed.

Fig. 1 shows the T_1 distributions obtained from the Inverse Laplace transformation of the relaxation rate data at a range of field strengths, for single-component liquids and binary-liquid mixtures adsorbed on γ-alumina. As seen in Fig. 1a, single-component cyclohexane and THF adsorbed on γ-alumina gave rise to only one relaxation environment for all magnetic field strengths. Methanol showed two relaxation environments, consistent with previous studies that showed that the relaxation behaviour of exchangeable and non-exchangeable ^{1}H can be significantly different, even within the same molecule [21]. Fig. 1b shows the data for the cyclohexane:THF mixture. Two dynamical environments were observed, as expected. The narrow and symmetric peaks in the distributions suggested that a multi-exponential fitting procedure was valid. The assignment of the observed relaxation environments to each component was possible through a comparison of the mixture with the single-component relaxation rate data, and then confirmed by

Table 1
The compositions of liquids used for soaking the γ-alumina pellets, and the measured intra-particle composition for each sample.

Cyclohexane:THF composition [mol%]		THF:methanol composition [mol%]	
Initial mixture	Intra-particle	Initial mixture	Intra-particle
35:65	34:66	20:80	17:83
50:50	45:55	40:60	33:67
66:34	62:38	66:34	59:41
75:25	71:29	75:25	67:33
80:20	75:25	80:20	73:27

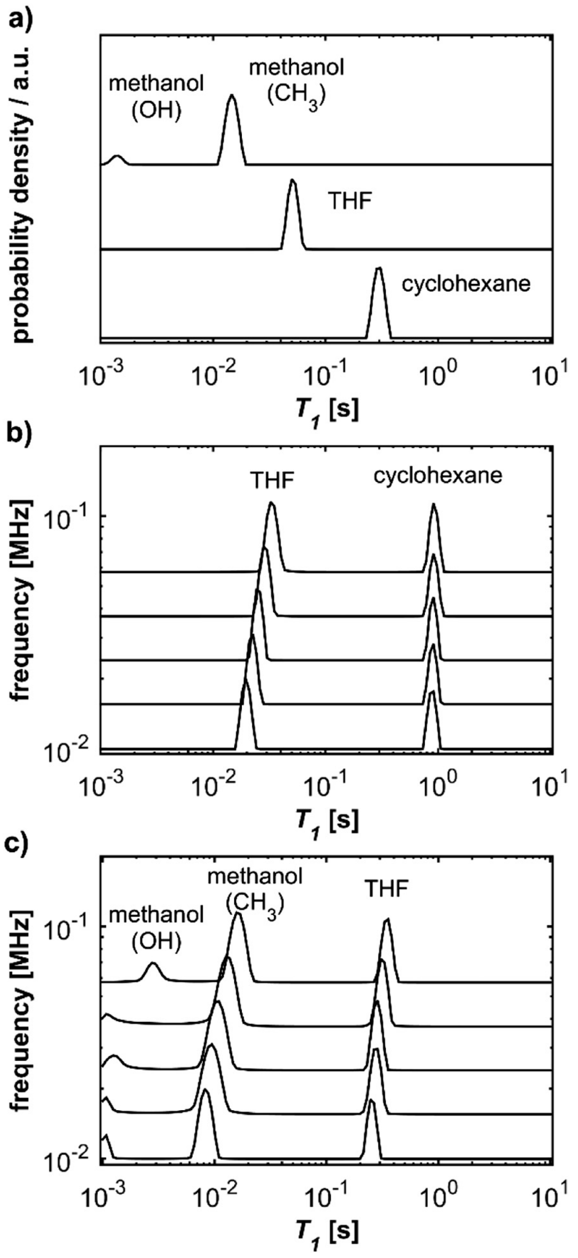

Fig. 1. The T_1 distributions obtained from a) single component liquids and mixtures of b) THF and cyclohexane, and c) methanol and THF adsorbed within γ-alumina. For the single component liquids the T_1 distributions at 24 kHz are shown. For each mixture the distributions obtained at field values of 57, 37, 24, 16 and 10 kHz are shown. All distributions are offset and normalized such that the highest peak has an arbitrary value of 1.

calculation of the relative amounts of each species present based on the analysis of the intensity of the peaks in the T_1-distribution. Fig. 1c shows the data for the THF:methanol mixture. Due to the relatively small signal arising from the methanol hydroxyl group and its inherently high relaxation rate, there was a significant error associated with measuring the NMRD profile of this environment in mixtures containing < 50 mol% of methanol. The measurements of the methyl group relaxation rates, however, were much more reliable across the whole composition range, therefore when referring to methanol for all of the following discussion this refers specifically to the methyl group relaxation rate.

Fig. 2 shows the NMRD profiles of each component in a series of cyclohexane:THF and THF:methanol mixtures imbibed within γ-alumina. These profiles will incorporate the influences of both surface dynamics and mixture composition inside the pore space. Both systems show similar trends in relaxation rate behaviour. The species interacting more strongly with the surface shows an increase in relaxation rate as the mole fraction of that component decreases, whilst the relaxation rate of the species that is less able to interact directly with the surface decreases as its composition decreases. In both binary systems, the relaxation rate of the species that interacts less strongly with the surface decreases below its single-component value and converges to a finite relaxation rate at each field strength. The relaxation rate data for the mixtures compared to the single-component bulk liquid suggest that the behaviour of cycohexane in the cyclohexane:THF mixture is similar to that of cyclohexane in the bulk liquid, whereas THF in THF:methanol is significantly different from the bulk liquid state suggesting that it is still experiencing the influence of the pore surface.

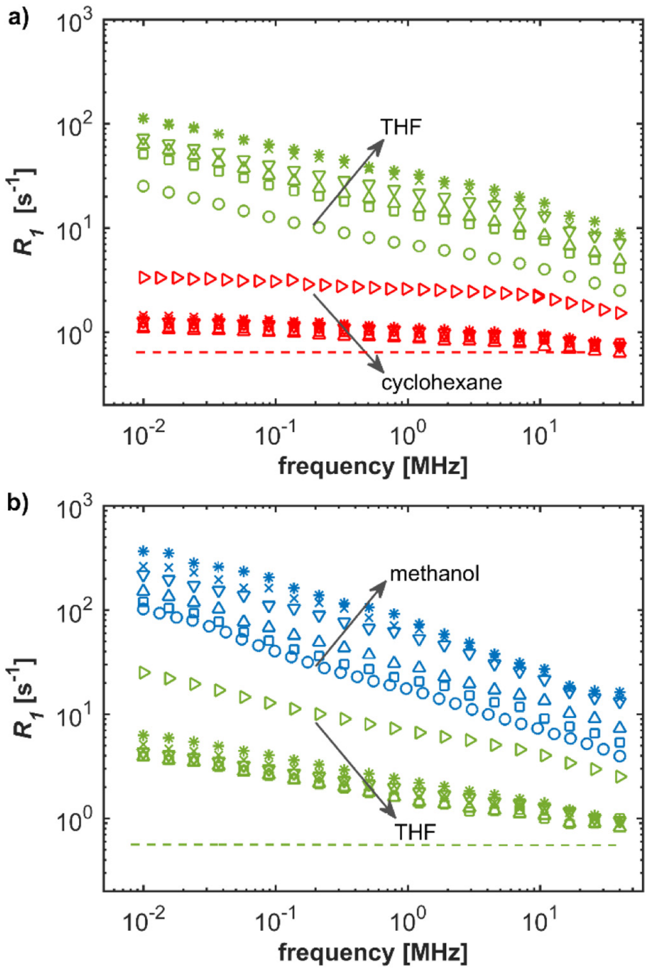

Fig. 2. The NMRD profiles of a mixture of a) cyclohexane:THF at intra-pellet compositions of 0:100 (○), 34:66 (□), 45:55 (△), 62:38 (▽), 71:29 (×), 75:25 (*) and 100:0 (▷) mol%, and b) THF:methanol at compositions of 0:100 (○), 17:83 (□), 33:67 (△), 59:41 (▽), 67:33 (×), 73:27 (*) and 100:0 (▷) mol% imbibed within a γ-alumina catalyst. Dashed lines represent the bulk liquid values for selected components i.e. in the absence of γ-alumina. The arrows indicate the trend in the NMRD profiles with decrease in concentration of each species. [Online, red refers to cyclohexane, green to THF and blue to methanol]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The sensitivity of the relaxation rate to surface dynamics is obtained by renormalisation of the NMRD profiles [23–25]. Fig. 3 shows the results obtained by dividing each NMRD profile by the R_1 value obtained at 10 kHz to generate a master curve for each component of the liquid mixtures. In the case of cyclohexane:THF (Fig. 3a), the relaxation behaviour of both THF and cyclohexane in the mixture at all studied compositions was described well by curves with power law exponents of -0.26 and -0.05, respectively. The same procedure was applied to each of the single-component NMRD profiles of THF and cyclohexane in the same porous medium, which showed excellent agreement with renormalized binary mixture data. These data show that the molecular dynamics are the same across the composition range investigated for each species, and that they are the same to within experimental error as their dynamics when adsorbed as single-component liquids within the same material. However, it is noted that cyclohexane has a relatively weak interaction with the surface even when imbibed as a single-component liquid, therefore significant changes in surface dynamics in moving from the single-component to binary mixture environment were not expected, thereby explaining the behaviour observed in Fig. 3a. The data for THF:methanol are shown in Fig. 3b; the two master curves are fitted with power law exponents of -0.2 and -0.38, respectively. In contrast to the cyclohexane:THF system, whilst the relaxation behaviour of single-component methanol is in good agreement with the renormalized binary data, the data for THF in the THF:methanol binary is significantly different to the single-component THF data. In contrast to cyclohexane, the methanol relaxation rate is highly sensitive to its physical environment and any surface interactions. These data strongly suggest that the dynamics of THF in the THF:methanol system are modified from the dynamics of single-component THF with the γ-alumina surface, but that the THF is still able to interact with the γ-alumina surface.

In summary, initial inspection of the analysis of the chemically-specific FFC-NMR dispersion data suggests that the more polar species in each binary out-competes the co-imbibed species with respect to interaction with the surface. Renormalisation of the dispersion data (Fig. 3) shows that the molecular dynamics of each species remains constant in a given binary mixture; with the more strongly interacting species in each binary characterised by the same surface dynamics in the binary as observed when that component is imbibed as a single liquid. In the present work the relaxation rate of the cyclohexane species did not vary sufficiently between single-component adsorbed liquid and binary mixture to identify changes in surface dynamics in these different environments. However, for THF in the THF:methanol binary there is evidence from the dispersion data and the renormalized dispersion data that THF is still interacting with the surface even though the surface layer is depleted in THF relative to the overall intra-particle composition.

4. Discussion

The cyclohexane:THF system in γ-alumina is first considered. As was seen in Fig. 2, the R_1 values of the strongly adsorbed THF component were increased above its single-component value for all field strengths, indicating an enhanced relative surface interaction. As the cyclohexane R_1 values in the presence of THF were concurrently seen to decrease below the value of pure cyclohexane on γ-alumina (and approach that of bulk cyclohexane) it is likely that the binding was competitive in nature rather than cooperative. However, as was shown in Fig. 3, the renormalized NMRD profiles for both THF and cyclohexane suggest that the surface molecular dynamics that underpin relaxation do not significantly change across the composition range and are the same as that observed for the respective single-component species imbibed with the pore space. A possible rationalisation of these two, at first contradictory, results is that a surface-influenced layer of molecules is formed within the pore space, the concentration of which remains constant over all binary compositions studied in this work. The composition of this layer is richer in THF than the bulk pore fluid and hence the intra-particle composition (Table 1). Such extreme micro-phase separation behaviour is expected for a polar (THF) and a non-polar (cyclohexane) mixture adsorbed on a highly polar γ-alumina catalyst based on neutron scattering studies of similar systems [12].

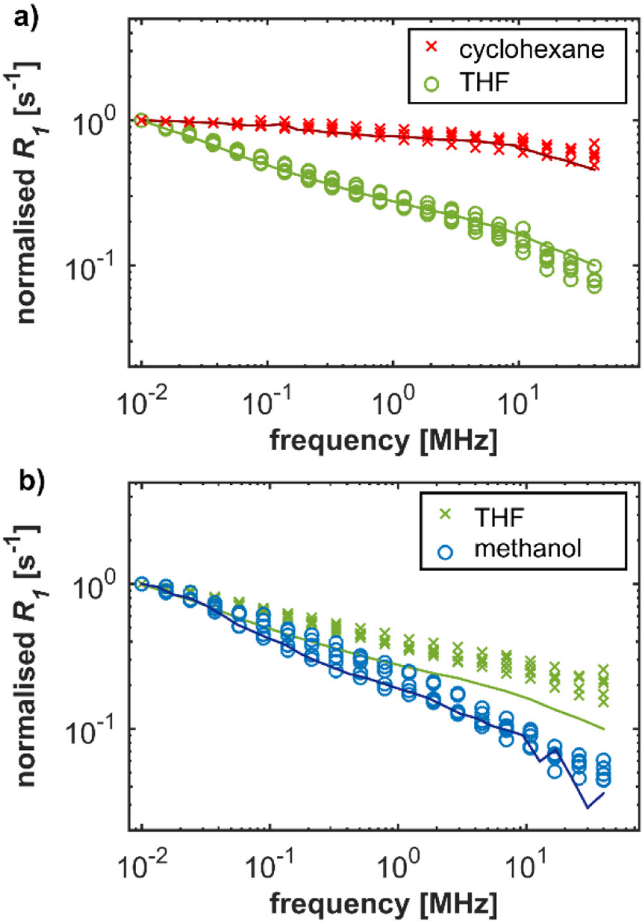

Fig. 3. The renormalized NMRD profiles for each component for all the data shown in Fig. 2: a) cyclohexane:THF, and b) THF:methanol mixtures imbibed within the γ-alumina catalyst. The solid lines represent relaxation rates of the single-component liquids imbibed within the same γ-alumina catalyst. No clear trend is seen between deviation from the renormalized lines and composition for any species. Therefore each species is represented by a single symbol regardless of the composition of the binary liquid mixture.

According to Eq. (3) this would require an increase in the term $V_{THF,ads}/f_{THF}$ with decreasing THF concentration, which can be conceptualised as an increase in the bound surface fraction of THF relative to the bulk pore component (i.e. increased surface accessibility) when compared to the single liquid adsorption. This would result in cyclohexane having relatively little access to the alumina surface, and therefore a relaxation rate that is independent of composition, as was observed at even modest mole fractions of cyclohexane.

In the limiting case that the surface volume fraction of each component and the underlying molecular dynamics are constant across the composition range (i.e. $R_{1,surf}(\nu) \approx$ constant at a given field strength) it follows from Eq. (3) that the observed relaxation rate should be directly proportional to $1/f_i$ at each field. This result is tested in Fig. 4a and b. Good agreement with the model was observed for THF at all frequencies, confirming that the THF composition of the surface layer in the pore space is not changing as the initial liquid mixture (prior to imbibition into the porous material) and the average intra-particle composition changes (Table 1). In contrast, cyclohexane shows almost no variation with composition. It is also seen that for the case of single-component cyclohexane inside the pores very different relaxation rates are observed compared to the approximately constant rates seen at all binary compositions. Thus, the data shown in Figs. 2–4 strongly support the hypothesis of a micro-phase separation that leads to a THF-rich phase on the catalyst surface. The observed changes in relaxation rate

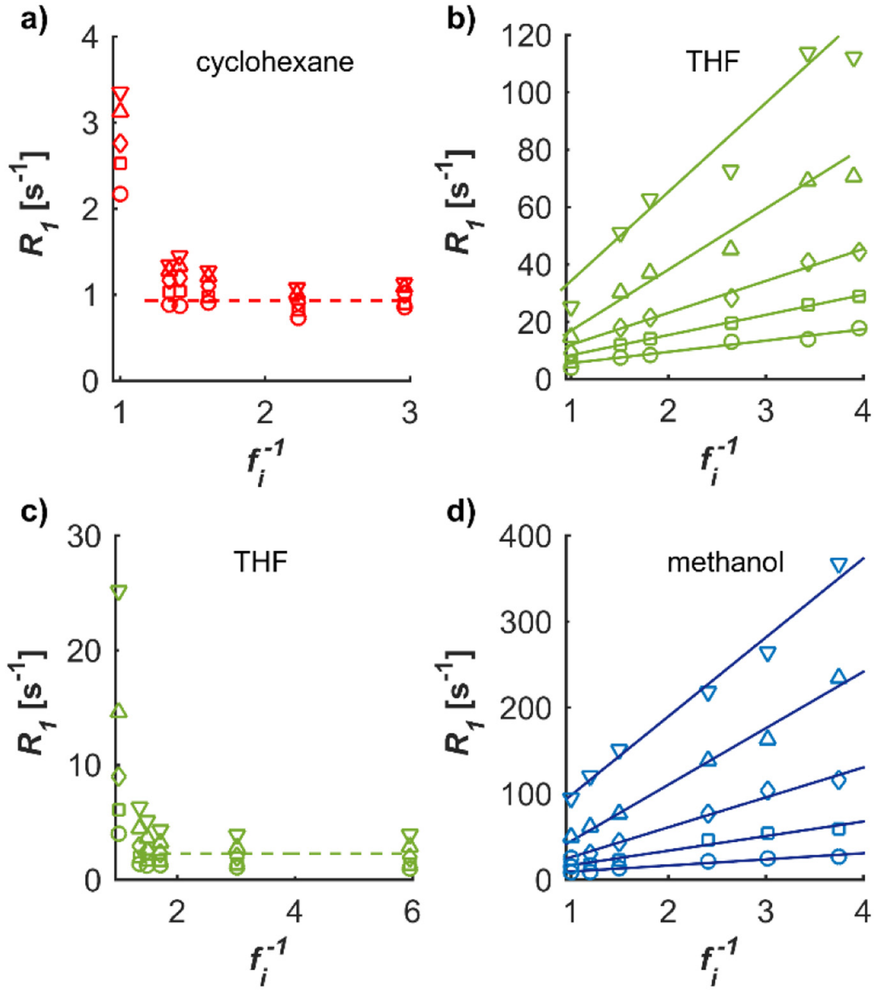

Fig. 4. The relaxation rate as a function of f_i^{-1} for a) cyclohexane in THF, b) THF in cyclohexane, c) THF in methanol, and d) methanol in THF. For each graph the Larmor frequencies of the relaxation field were 11 MHz (○), 1.9 MHz (□), 0.33 MHz (◊), 0.057 MHz (△) and 0.010 MHz (▽). Solid lines represent a fit to Eq. (3) and dashed lines are included as a guide to the eye. The pore filling factor, f_i, is assumed to be identical to the mole fraction which was calculated from the relative populations of each species reported in Table 1.

are predominantly due to changes in the relative weighting of the bulk and adsorbed fraction of THF within the γ-alumina (i.e. surface accessibility) and not a fundamental change in the surface dynamics of either species.

Fig. 4c and d show the analysis for the THF:methanol system. The behaviour of the two components show similar trends to those seen for cyclohexane:THF. The data for the more strongly adsorbing component, methanol, is consistent with a constant surface composition for all initial mixture compositions studied. THF is seen to have an approximately constant relaxation rate. For single-component THF adsorbed within the γ-alumina the relaxation rate increases markedly. These data are consistent with a methanol-rich surface layer forming and inducing a micro-phase separation within the pore space of the γ-alumina; such a layer is consistent with the dynamics of methanol remaining unchanged regardless of whether it exists in the pore space as a single-component or as a component in a binary mixture.

Assessment for competitive adsorption behaviour of the binary mixtures studied here could, of course, be studied using more conventional T_1/T_2 analysis at higher field [7], however the interpretation of the resulting data can be less straightforward. In particular, the transverse relaxation, T_2, is highly sensitive to internal gradients effects and J-couplings, as well as often being far shorter than T_1 – making it a difficult quantity to accurately measure. Further, the bulk pore term in Eq. (2) is much more similar to the surface relaxation rate at the higher fields used for such measurements. This means the bulk pore term cannot be ignored when considering the observed T_1/T_2 ratio, and therefore a great deal of structural information and prior knowledge of bulk relaxation rates is required to interpret these results fully. FFC-NMR allows a far simpler separation of the changes in surface dynamics from changes in surface accessibility (i.e. composition) for adsorbed binary liquid mixtures, even when the liquids within the mixtures are both strongly interacting.

5. Conclusion

Initial FFC-NMR studies of binary liquid mixtures in γ-alumina are reported. Laplace inversion of the data into the T_1 domain allows discrimination of the two chemical species in each binary system. The overall NMRD profiles for each component reveal directly the species which has a greater interaction with the γ-alumina surface. Additional insight into processes occurring within the pore space is given by further analysis of the data. In the first case, renormalisation of the NMRD profiles enables an evaluation of the extent to which surface dynamics change as a function of binary composition. Second, relaxation rates were plotted as a function of overall intra-particle composition, and were fitted to a two phase fast exchange model. A linear relationship between relaxation rate and mixture composition provides evidence that the composition of the surface layers inside the pore, are constant over the range of mixture compositions investigated. For both the cyclohexane:THF and THF:methanol systems the more polar species exhibits the dominant surface interaction. In particular, the more polar species exists in a surface layer phase rich in that species relative to the overall composition inside the pore space. A more pronounced deviation from the bulk liquid relaxation rate was observed for THF in the THF:methanol system compared to cyclohexane in the cyclohexane:THF mixture, suggesting that the surface composition in the latter case had a lower concentration of weakly adsorbed component. The dynamics of the molecular interaction for all species remain relatively unchanged across all mixture compositions, although there is evidence that in the THF:methanol binary, methanol weakens the THF interaction (most likely with the surface) relative to the interaction of single-component THF inside the same porous medium. This work provides a foundation upon which to explore and differentiate chemical-specific molecular dynamics and compositional effects in binary mixtures during adsorption in porous media.

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