*Article*

Solvent-Relaxation NMR as a tool to study particle dispersions in non-aqueous systems

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**Abstract:** Determination of the spin-spin NMR relaxation rate of the water in aqueous particulate dispersions has been shown to be a convenient and facile experimental approach to probe the composition of near particle surface structures. Here, a systematic study has been undertaken of both nonaqueous and mixed aqueous-nonaqueous solvent particulate dispersions to explore the universality of the solvent relaxation technique. As in the aqueous case, a linear relationship between the surface area present and the solvent relaxation rate is observed, confirming the rapid exchange of the solvent molecules between the surface and the bulk and thereby illustrating the viability of the experimental methodology to study such systems. Crucially, the surface enhancement effect was considerably weaker in nonaqueous systems compared with aqueous dispersions and reflects a potential limitation of the wider deployment of this experimental methodology.

**Keywords:** Spin-spin NMR relaxation time; specific relaxation rate; average relaxation rate; solvent composition; hydrophobic hydration; solvent polarity

1. Introduction

Many commodity products, such as lubricants, detergents, paints/inks, foodstuffs, and drug formulations, involve the manipulation of particulate suspensions, often dispersed at high volume fractions.1-4 Thus, the characterisation of the surfaces within such particulate suspensions is a necessary first step in the optimisation of those formulations.

NMR presents a family of experimental methodologies that can probe concentrated, opaque systems such as particulate dispersions, yielding a variety of dynamic characterisations - diffusion rates5, 6, relaxation times7, 8 - as well as structural information, *e.g*., solid-state spectra9, 10 which can be used to investigate the molecular environment of near-surface species. Over the past few years, the solvent-relaxation NMR approach has been particularly insightful in characterising aqueous dispersions, both theoretically and experimentally11-18. The present work focuses on assessing whether the measurement of solvent relaxation times (rates) in binary aqueous-nonaqueous solvent blends or, indeed, non-aqueous dispersions offer the same experimental potential as aqueous dispersions.

2. Materials & Methods

2.1. Materials

A selection of silica substrates has been studied here; three hydrophobic fumed silica powders and two silica dispersions, as in **Table 1**.

**Table 1.** List of silica substrates used to perform the experiments. The particle size for Ludox SM30 and IPA-ST is provided by the manufacturers.

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| --- | --- | --- |
| **Material** | **State** | **Supplier** |
| Aerosil R104 (particle size 10 – 30 nm, surface area 140 m2·g−1) | Powder | Evonik Degussa,Germany |
| HDK H18 pyrogenic silica (particle size 15 – 50 nm, surface area 124 m2·g−1) | Powder | Wacker Chemie AG, Germany |
| Cab-O-Sil TS-720 (particle size 15 – 45 nm, surface area 122 m2·g−1) | Powder | Inoxia UK Ltd |
| Ludox SM30(particle size 8 nm) | 30 $wt \%$ suspension in water | Sigma Aldrich, UK |
| IPA-ST(particle size 10 – 15 nm) | 38 wt% dispersed in isopropanol (IPA) | Nissan Chemical Corporation |

The solvents toluene (99+%), ethanol (EtOH) (99+%, absolute), methanol (MeOH) ($>=$99.5 %), decane (99+%), *p*-xylene (99+%), and isopropanol (IPA) (99+%) were obtained from either Fisher Scientific UK Ltd or Alfa Aesar UK and used as received.

2.2. Methods

Measurement of the spin-spin relaxation time ($T\_{2}$) of the solvent(s) were carried out on a bench-top Xigo Nanotools Acorn AreaTM spectrometer operating at a resonance frequency of 13 $MHz$, using a CPMG19, 20 pulse sequence. The magnetisation decay curve – ($M\_{xy}\left(t\right)$) *versus* time ($t$) – was recorded with a spacing of 0.5 ms between 90° and 180° pulses and a recycle delay of about 5$T\_{1}$ between each cycle to allow for full recovery of the magnetisation between acquisitions. The sample environment was equilibrated at 25 (± 0.5) ℃. The signal was averaged over three scans. The built-in Acorn AreaQuant software was used to fit all the relaxation decay curves, which we show were well-described by a single-exponential expression.

2.2.1. Theory

In a simple colloidal dispersion, the relaxation behaviour of the solvent molecules can be modelled as a weighted average of two contributions connected through a rapid exchange between the bulk state with a long $T\_{2}$ and a highly constrained interfacial state, with a considerably shorter $T\_{2}$. The overall relaxation time for rapid exchange yields:

|  |  |
| --- | --- |
| $$\frac{1}{T\_{2}}=\frac{1-p\_{bound}}{T\_{2}^{free}}+\frac{p\_{bound}}{T\_{2}^{bound}}$$ | (1) |

where $T\_{2}$ is observed spin-spin relaxation time, $p\_{bound}$ is the fraction of time that solvent molecules spend in the bound environment with a shorter relaxation time $T\_{2}^{bound}$, whereas $T\_{2}^{free}$represents the relaxation time of free solvent molecules. 4, 21 In Equation (1), (${1}/{T\_{2}}$) is the effective relaxation rate, which is designated as $R\_{2}$. An enhancement in the relaxation rate corresponds to an increase in the residence time or the number of solvent molecules at the surface. Relaxation data are often presented in a normalised form to minimise the effects of instrument-dependent variables as the specific relaxation rate ($R\_{2SP}$), *i.e*., normalised to the relaxation rate of the bulk dispersion solvent ($R\_{2}^{°}$), Equation (2).4

|  |  |
| --- | --- |
| $$R\_{2SP}=\frac{R\_{2}}{R\_{2}^{°}}-1$$ | (2) |

where $R\_{2}$ is the relaxation rate of the solvent within the dispersion and $R\_{2}^{°}$ is the relaxation rate of the pure solvent.

3. Results and Discussion

The technique has been widely used to characterise *aqueous* colloidal dispersions 12, 15, 16, 18, and a range of exemplar data have been summarised on the double-logarithmic representation in **Figure 1.** In the standard representation, $R\_{2SP}$ is presented as a function of silica surface area, which is a proxy for *pbound*, and both are linearly correlated with the concentration of particles. As may be seen, in all cases, each particulate dispersion shows a relaxation enhancement determined by the nature through which the water molecule is constrained at the surface. If the solvent interacts strongly with the surface, the anisotropic motion leads to efficient relaxation, and the relaxation rate increases. For aqueous systems, there is a linear correlation between $R\_{2SP}$ and surface area, with the absolute effect – the surface enhancement - reflecting the hydrophilicity of the surface **Figure 2**.



**Figure 1*.*** Variation of $R\_{2SP}$ for various nanoparticulate systems in aqueous media: cationic polystyrene latex (triangles down)15, Ludox SM40 (stars) and TM40 (hexes)16, Snowtex 50 silica (triangles up)12, colloidal silica (Bindzil 40/220) (open circles) and alumina-modified silica (Bindzil 309/220) (squares)18 in water as a function of particle surface area (${m^{2}}/{ml}$). The solid lines are guides to the eye.



**Figure 2.** Solvent-specific relaxation rate enhancement for all the particles dispersed in aqueous and non-aqueous solvents. For non-aqueous dispersions, the EtOH mole fraction for EtOH/decane, EtOH/toluene, and EtOH/*p*-xylene was $\~$0.68, $\~$0.58, and $\~$0.62. The IPA-ST was dispersed in pure IPA. For aqueous dispersions, the solvent was pure water. The data extracted from \*22, and \*\*12, 15, 16, 18.

3.1. Comparison of aqueous and non-aqueous single solvent particle dispersions

Similar exemplar and comparator data for a series of aqueous and non-aqueous silica nanoparticles in a range of solvents are presented in **Figures 3-4**. Again, the standard representation of $R\_{2SP}$ as a function of particle surface area is used. As in the aqueous case, all data follow a linear relationship 13,18 indicative of fast exchange. There is a very sensitive coupling of the solvent/surface pairings. Fairhurst *et al*.23 have proposed an interpretation of these enhancements in terms of the Hansen Solubility Parameter (HSP)24, in that liquids with strong interactions with the surface have a faster relaxation rate, thereby exhibiting the highest surface enhancement. There was a correlation with the macroscopic stability of the dispersions in that the solvents that exhibited weak interactions with the surfaces settled relatively quickly compared with the same particles suspended in solvents that showed a high affinity with the surface. Collectively, these studies, therefore, conclude that the technique is also applicable to non-aqueous dispersions, though the magnitude of the effect is somewhat smaller.



**Figure 3*.*** Solvent-specific relaxation rate of IPA-ST (black circles) and Ludox SM30 (open squares) as a function of particle surface area (${m^{2}}/{ml}$). The $R\_{2SP}$ data for IPA-ST and Ludox SM30 are normalised to the relaxation rates of pure IPA and water, respectively. The error bars are the standard deviation of three measurements of each sample. The solid lines are guides to the eye.



**Figure 4.**Solvent-specific relaxation rate of Aerosil in *p*-xylene (triangles), COS (circles) and HDK silica (squares) in toluene as a function of surface area (${m^{2}}/{ml}$). The $R\_{2SP}$ data for Aerosil, COS and HDK were normalised to the relaxation rates of pure p-xylene and toluene, respectively. The error bars are the standard deviation of three measurements of each sample. The solid lines are a guide to the eye.

3.2. Characterisation of aqueous-alcohol solvents

Many formulations involve solvent blends, either during preparation or in their final form. Several questions arise when considering whether NMR solvent relaxation is applicable to dispersions formed from *solvent blends*, principally whether a single effective relaxation rate is observed and whether any such average rate demonstrates a linear dependence on the surface area, both pre-requisites for Equations (1) and (2). As a first juncture, consider the dynamic averaging operative in the solvent blend itself.

The magnetisation decays for representative binary solvent blends are presented in **Figure S.1** on a semi-logarithmic plot. The data (and fits) have been normalised to the intensity at $t=0$ returned in the fitting route. In all cases, the data follow a single-exponential decay indicating that the measured $T\_{2}$ (and equivalently, the relaxation rate ($R\_{2}$)) reflects a global average of the relaxation processes within the entire solvent. The thus-determined blend $R\_{2}$ was determined for a series of alcohol-aqueous blends, *viz*, methanol (MeOH), ethanol (EtOH), and isopropyl alcohol (IPA) as a function of composition, expressed in terms of the alcohol mole fraction ($χ\_{Alcohol}$). **Figure S.2** presents the *excess relaxation rate* $R\_{2sp}^{excess}$ for these three alcohol-aqueous blends defined as:

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| --- | --- |
| $$R\_{2sp}^{excess}=R\_{2}- R\_{2}\left(linear\right)$$ | (3) |

where $R\_{2}(linear$) is the weighted average expected from two independently relaxing populations of species:

|  |  |
| --- | --- |
| $$R\_{2SP}\left(linear\right)= χ\_{alcohol}R\_{2}^{alcohol}+\left(1-χ\_{alcohol}\right)R\_{2}^{solvent2}$$ | (4) |

This manipulation now highlights the broad maximum in the enhancement in the relaxation behaviour in the water-rich end of the composition range, centred around $χ\_{alcohol}=0.15 (\pm 0.05),$ with the maximum being more evident for the lower molecular weight alcohol blends. It is evident that the number of H-bonded networks between water and alcohol molecules has a significant effect on both the average- and changes in the relaxation rates. The strength of alcohols varies markedly, and the order of variation of the average relaxation rate of alcohols is established as IPA > EtOH > MeOH, consistent with a recent study by Yoshida *et al*.**25**.

3.2. Characterisation of non-aqueous/alcohol mixed solvents

Extending the previous study, a series of binary solvent blends were then explored in which ethanol was mixed with solvents with quite different characters – decane, toluene, and *p*-xylene. Again, all the magnetization decay curves follow a single-exponential form, **Figure S.3**. $R\_{2}$ for the series of ethanol blends with decane, toluene, and *p*-xylene were determined as a function of ethanol mole fraction and are presented in **Figure S.4**. Ostensibly, the data differ markedly from the aqueous-alcohol solvent systems, now demonstrating a seemingly featureless dependence of the average relaxation rate on the alcohol mole fraction. Once correcting the data in terms of the excess relaxation rate, weak retardation is observed in the toluene and *p*-xylene cases, whereas the decane case shows a negligible change in the composition of constituents. Ultimately, these binary blend studies indicate an empirical correlation between the average relaxation rate and solvent polarity, the more polar the solvent, the shorter the relaxation rate ($R\_{2}^{toluene}<R\_{2}^{p-xylene}<R\_{2}^{EtOH}<R\_{2}^{decane}$).

3.3. Characterisation of aqueous binary mixtures – particle dispersions in the aqueous system

Consider now what happens when the silica is added to these solvent blends. The $R\_{2SP} $for two different colloidal particles, Ludox-SM30 and IPA-ST are evaluated as a function of the weight percentage of particles dispersed in IPA/water in **Figures 5-6**. A series of IPA mole fractions in the IPA/water binary mixture were studied. In both silica particles, over the particle concentration range studied, a linear relationship can be seen for $R\_{2SP} $as a function of particle surface area, which indicates the existence of rapid exchange between restricted and non-restricted environments. Interestingly, the relaxation enhancements – the slope of the plots of relaxation rate *versus* particle concentration – decrease with an increase in IPA mole fraction. This indicates the sensitivity of the technique to the polarity of the solvent. The observations are consistent with the data obtained in aqueous systems.



**Figure 5*.*** Solvent-specific relaxation rate of Ludox-SM30 dispersed in IPA/water as a function of Ludox-SM30 surface area (${m^{2}}/{ml}$). The mole fractions of IPA were equal to $\~$0.0 (diamonds), $\~$0.09 (circles), $\~$0.11 (squares), $\~$0.16 (triangles up), and $\~$0.23 (triangles down). The $R\_{2SP}$ data were normalised to the relaxation rate of the equivalent IPA/water binary mixture.



**Figure 6.** Solvent specific relaxation rate of IPA-ST dispersed in IPA/water as a function of IPA-ST surface area (${m^{2}}/{ml}$). The mole fractions of IPA were equal to $\~$0.09 (circles), $\~$0.23 (squares), $\~$0.47 (triangles up), and $\~$1 (triangles down). The $R\_{2SP}$ data were normalised to the relaxation rate of the equivalent IPA/water binary mixture.

3.4. Characterisation of non-aqueous binary mixtures – particle dispersions in non-aqueous system

Representative relaxation decay curves for the solvents in a series of silica dispersions are presented in **Figure S.5**. As in the no-silica case, all the decays were single-exponential, confirming the same global averaging of the relaxation process. The $R\_{2}$ values for each nanoparticulate system are presented as a function of particle surface area, **Figures S.6-S.8**, from which it is clear that the $R\_{2}$ is linearly dependent on the particle surface area in each system – $R\_{2}$ increases linearly with increasing surface area, indicating rapid exchange between the surface and the bulk.

The relaxation rates were normalised to the equivalent solvent blend in the absence of the silica. The relationship between the $R\_{2SP}$ and particle surface area is presented as a function of EtOH mole fractions for COS and HDK silicas in EtOH/toluene, **Figure 7**, for COS and HDK silica in EtOH/decane, and for Aerosil in EtOH/*p*-xylene in **Figures S.9-S.10**, respectively. As expected, it is evident that an increase in particle surface area leads to an increase in the average relaxation rate, but the magnitude of the effect is weaker. There is a weak signature of non-linearity in those systems that gel (*e.g*., EtOH), reflecting the loss of surface area associated with the formation of inter-particle linkage between the particles (that concomitantly leads to an enhancement in viscosity).



**Figure 7.**Solvent-specific relaxation rates of COS and HDK silica dispersions as a function of particle surface area $({m^{2}}/{ml})$. The mole fractions of EtOH in EtOH/toluene mixtures were equal to $\~$0.26 (COS (open squares) and HDK (open triangles down)), $\~$0.32 (COS (squares) and HDK (triangles down)), $\~$0.41 (COS (open circles) and HDK (open triangles up)), and $\~$0.58 (COS (circles) and HDK (triangles up)). The $R\_{2SP}$ data for both COS and HDK silica are normalised to the relaxation rate of the equivalent EtOH/toluene mixture. The error bars are the standard deviation of three measurements for each sample.

These observations are entirely commensurate with the conclusions drawn from the aqueous system. Bringing all these studies together, Figure 8 illustrates (on a double-logarithmic representation) the linear relationship between the $R\_{2SP}$ and particle surface area for a wide range of nanoparticulate systems in aqueous and non-aqueous dispersions. The variation of $R\_{2SP}$ in the non-aqueous solvents yields much smaller enhancements in the average relaxation rates than in the aqueous systems. Thus, it is concluded that solvent-relaxation NMR is a viable experimental methodology with which to study particulate dispersions in non-aqueous media; however, the minor changes observed inherently limit the wider applicability of the methodology, an important contrast with the aqueous system.



**Figure 8*.*** Log-log plot of $R\_{2SP}$ *versus* particle surface area (${m^{2}}/{ml}$) for aqueous and non-aqueous nanoparticulate systems; cationic polystyrene latex15, Ludox SM40 and TM4016, Snowtex 50 silica12, colloidal silica (Bindzil 40/220) and alumina-modified silica (Bindzil 309/220)18 in water (cross symbols), COS and HDK silica in toluene, Aerosil in p-xylene, HDK silica and COS in EtOH/decane, EtOH/toluene, and Aerosil EtOH/p-xylene at different mole % of EtOH.

4. Conclusion

Solvent-relaxation NMR has been utilised to characterise nanoparticle dispersions in a range of binary mixtures of aqueous and non-aqueous solutions. For a range of binary aqueous-alcohol solvent blends, there are inflection points in the relaxation rates at characteristic alcohol mole fractions, due to the arrangement of hydrogen bonds in the system. In non-aqueous binary solvent blends, the average relaxation rates of toluene and *p*-xylene increase with EtOH mole fractions. Surprisingly, decane shows a decrease in the relaxation rate with composition that reflects the solvent polarity. In the case of nanoparticulate dispersions, there is a linear relationship between the specific relaxation rate and the available particle surface area, except where there are macroscopic changes in formulation characteristics, *i.e*., gelation. Importantly, for the first time, these results demonstrate that solvent-relaxation NMR is a viable technique to characterise non-aqueous dispersions; however, the technique is approaching the limit of experimental resolution.

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