

Spectroscopy Focus

The Physical Characterisation of Suspensions and Slurries

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A significant number of commercial products involve, either in the final state or at some stage of their production, suspensions of particulate materials dispersed into liquid vehicles often at high volume fraction. Quality dispersions are needed in applications as diverse as cosmetics, pharmaceuticals, and ceramics, but it is often under-appreciated that, in order to be properly formulated, these suspensions or slurries must be analysed as they are prepared and without dilution. The characteristics of the solid-liquid interface control dispersion behaviour and can influence, among other things, important processes such as adsorption, flotation, and, in concentrated suspensions, rheological behaviour. Here we introduce a new methodology of studying concentrated dispersions in-situ.

NMR (Nuclear Magnetic Resonance) relaxation is a well-established method for characterising liquids and solids and more recently dispersions [1]. The methodology is straightforward and the combination of highly customisable digital radio frequency devices and the miniaturisation of affordable magnet systems (made using rare earth composites) has made it possible to create small desk-top spectrometers with advanced features that are useful for routine laboratory measurements. The basic NMR experiments have also

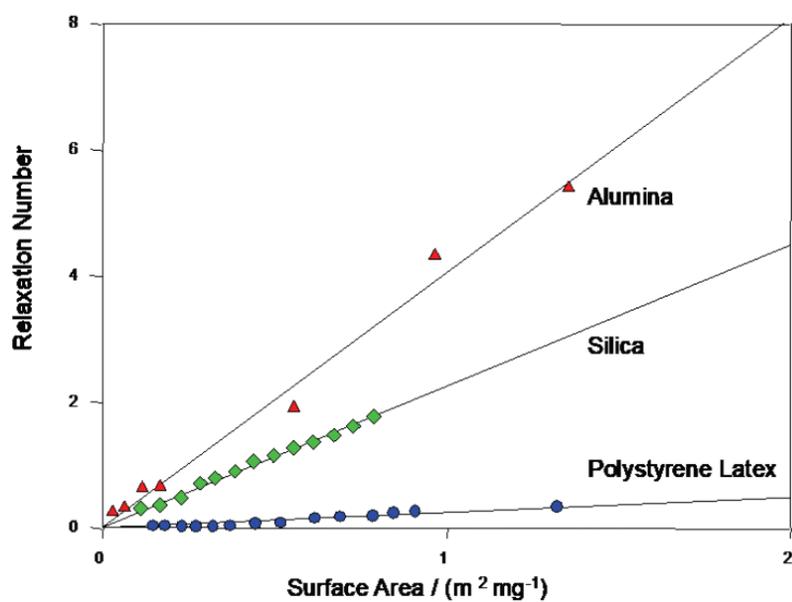


Figure 1: NMR relaxation numbers for a series of concentrated dispersions.

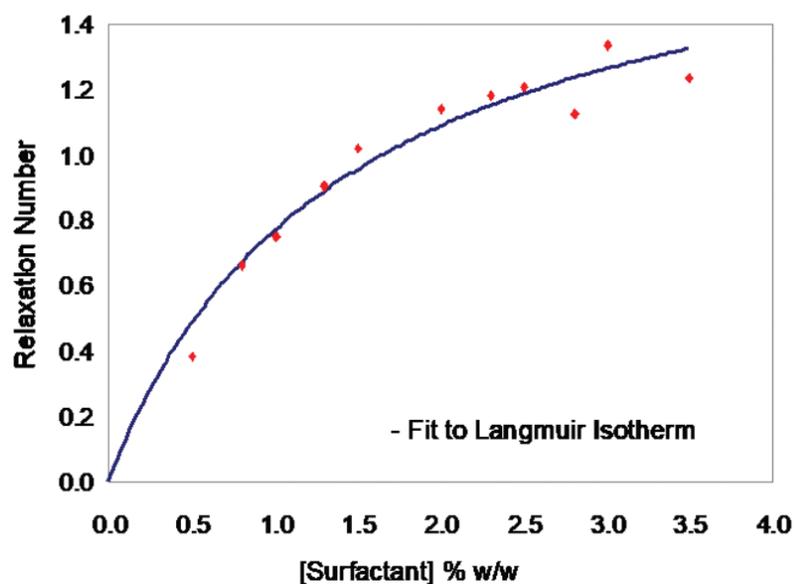


Figure 2: NMR Surfactant Isotherm.

been refined to take into account limitations of magnet homogeneity and stability.

There are two relaxation processes - R_1 , the spin-lattice relaxation rate and R_2 , the spin-spin-relaxation rate and both can be used in these experiments and each are each sensitive to molecular motion and the local magnetic environment that the spins are in. Although there are many nuclei that can be used we focus here on protons. For convenience, we define a relaxation number, R , which is the normalised relaxation rate and is dimensionless. The R value depends on many factors but those relevant to this work are the value of the pure solvent relaxation rate, the chemical composition of the interface, the available surface area and the strength of solvent or solute adsorption. We essentially measure an average relaxation assuming that the solvent can interact with all the available surface by a process of fast exchange. In this way, the measured R values are proportional to the surface area (A) and the plots of R vs A are linear and have a slope which depends on the surface interactions (Figure 1). This then provides a very useful tool to probe the available interface in dispersions and adsorption with minimal sample preparation. Measurement can be made typically in a few seconds so that dynamic changes such as adsorption or displacement rates of additives, settling, flocculation etc. can be followed.

Techniques based on NMR relaxation avoid these dilution problems, and are able to make measurements on suspensions and slurries prepared at almost any industrially relevant concentration. This not only removes the practical need for dilution - no matter what the application - but also allows monitoring of any dilution process. Importantly, the technique is non-invasive and non-destructive so that samples - at whatever concentration - can be saved and re-measured at some future date. This allows examination of any time-dependent behaviour.

NMR relaxation of the dispersion medium in a suspension is sensitive to some of the key parameters discussed above - including particle concentration, surface area surface structure and porosity as well as solvent type, and solute chemical composition. For example, Figure 1 shows the variation in the NMR relaxation number as a function of particle surface area and type. Samples with higher solvent surface affinity (silica *cf* latex) and elemental composition (alumina *cf* silica) give very different relaxation numbers (normalised to the solvent) and can be used as diagnostic tool and for quality control without the need for dilution. Figure 2 shows the effect of adsorption of surfactant from solution on the relaxation number (normalised to the bare particle dispersion); this can be used to optimise the best surfactant concentration for optimum stability.

The following illustrates a typical scenario where a concentrated dispersion is measured by conventional means and the problems that can arise.

Figure 3, on the left, depicts any concentrated suspension as it is made or formulated

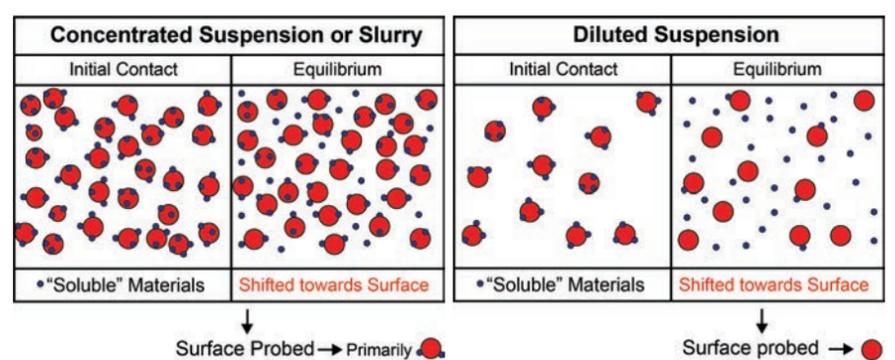


Figure 3: Schematic of a concentrated suspension or slurry at initial contact and at equilibrium.

Figure 4: Schematic of diluted suspension at initial contact and equilibrium.

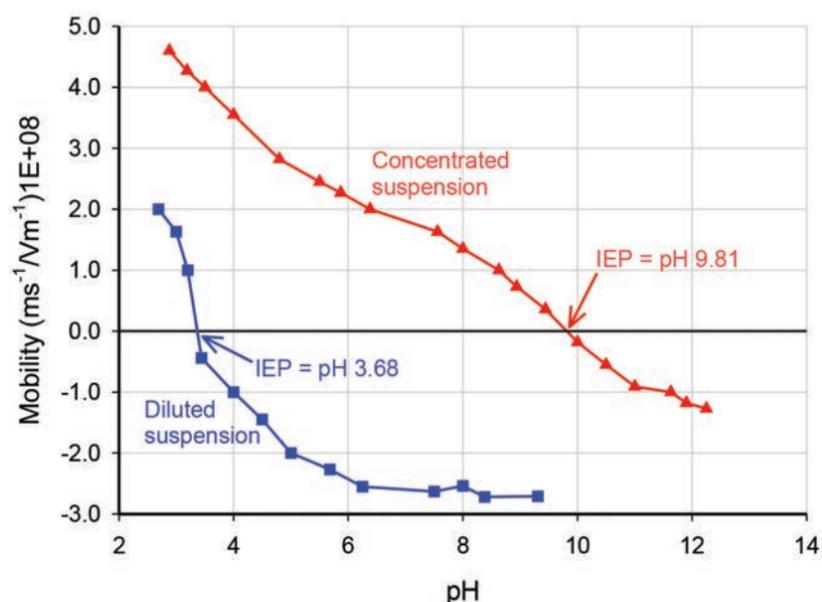


Figure 5: Effect of solids concentration on the mobility of aqueous barium titanate

(called 'initial contact') and provides a representation of particles of a material (red circles) within a liquid (white background). The 'surface chemical nature' of the material is imagined as a series of blue dots. This could be the fundamental functional groups comprising the material, or something adsorbed on the material's surface. On the right-hand side is a depiction of that same suspension in which an 'equilibrium' has been established between adsorption at the particle surface and the concentration of the same moiety in solution. For a given volume of the suspension, the greater the particle concentration is, the less volume of free liquid/solution is available. This means that the solubility limit for any surface species can be exceeded, thus inhibiting any further desorption, dissolution, or dissociation. So, in concentrated suspensions, the chemical equilibrium is always shifted towards the surface, and the little icon at the bottom right-hand side of Figure 3 represents the surface that will be primarily 'probed' (i.e., evaluated/measured/monitored) in such a situation.

In Figure 4 we have the same sample but after being diluted, as can happen when preparing samples for measurement/analysis for example in light scattering. Now the equilibrium is shifted away from the surface and towards the solution - and, the more dilute the suspension, the greater will be this shift.

This can be demonstrated in the following example using electrophoretic mobility measurements of an aqueous suspension of barium titanate, which is used, for example, in the manufacture of ceramic capacitors. The mobility is related to the surface charge of a material; it is a good index of the magnitude of the electrostatic repulsive interaction between particles and can be used to predict and control dispersion stability. The dispersion characteristics of ceramics and refractories affect green body strength and the degree of shrinkage on sintering. Thus, reliable mobility determinations are of practical concern in ceramics preparation, processing, and application. In these samples, the mobility was measured as a function of pH at a high solids concentration (20% w/w) using an electroacoustic device. The suspension was then extensively diluted using deionised water and the mobility measured, again as a function of pH, using an electrophoretic light scattering device and the results compared (Figure 5).

It is clear that not just the shapes of the mobility vs pH profile, but also the iso-electric point (IEP), are totally different for the two suspensions. The IEP is the pH at which the material will have no surface potential (charge) and so such a suspension will be inherently unstable, and all the particles will eventually aggregate. This significant difference can

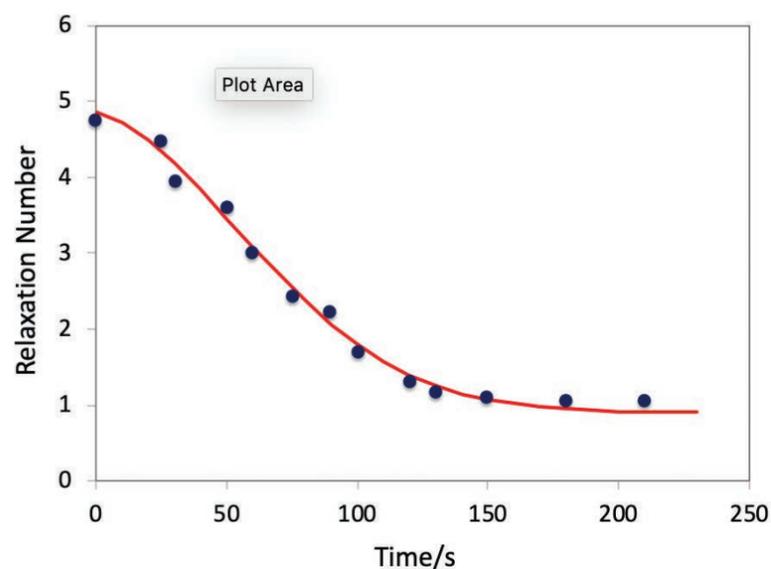


Figure 6: Rate of settling (dispersed area) of an aqueous dispersion barium titanate.

have serious consequences as it impacts, among other things, subsequent formulation - for example, the addition of ionic additives such as surfactants, dispersants and polyelectrolytes - as well as long-term stability.

Figure 6 shows Relaxation experiments on the settling of a concentrated (10% w/w) aqueous dispersion of barium titanate. The relaxation number is directly proportional to the quantity of dispersed area in the sample. The data are highly reproducible and automatic, and allow for a detailed study of the optimum stabiliser concentrations required to control the rate of settling.

The important take-away point is that dilution is never an innocuous process. The consequence is that you will get a value - from whatever characterisation technique used - that is not representative of the original concentrated suspension and so may not translate into a useful performance metric. To avoid this issue, where possible, it is always preferable to make measurements on suspensions or slurries at their use concentration.

This does not mean that you cannot dilute any suspension. There are ways to minimise (but not completely eliminate) the shift in chemical equilibrium that occurs, for example by using the mother liquor from a centrifuged sample of the original suspension but this is often difficult to obtain in practice. More discussion of this issue is beyond the subject of this short note.

Formulations, though initially prepared as concentrates, are sometimes subsequently diluted to obtain the commercial product. However, dilution, if not performed correctly, can lead to suspension instability which can affect, for example, long-term shelf storage. Crucially, if it is necessary to dilute a suspension, then it is essential to check the linearity of any metric as a function of the dilution process. NMR relaxation can play a key role in characterising these suspensions

References

1. C. L. Cooper, T. Cosgrove, J. S. van Duijneveldt, M. Murray, and S. W. Prescott. The use of solvent relaxation nmr to study colloidal suspensions. *Soft Matter*, 9(30):7211-7228, 2013



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Faster Quality Control at Lower Operating Costs with Near-Infrared Spectroscopy

Underestimation of quality control (QC) processes is one of the major factors leading to internal and external product failure, which have been reported to cause a loss of turnover between 10-30%. As a result, many different norms are put in place to support manufacturers with their QC process. However, time to result and the associated costs for chemicals can be quite excessive, leading many companies to implement near-infrared spectroscopy (NIRS) in their QC process.

This new white paper from **Metrohm**, provides a short summary about the importance of QC and QA, while illustrating action points to improve existing QC processes. Furthermore, near-infrared (NIR) spectroscopy is presented as a powerful analysis technique to increase QC efficiency while maintaining the accuracy and precision of the existing analysis method.

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