Salt enhanced solvent relaxation and particle surface area determination via rapid spin-lattice NMR

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ABSTRACT

This paper demonstrates the influence of surface charge chemistry on the application of nuclear magnetic relaxation measurements (NMR relaxometry) for the in situ determination of particle surface area, in the presence of high electrolyte concentration. Specifically, dispersions of titania, calcite and silica with and without 1 M KCl were investigated. The addition of salt, showed no significant change to relaxation measurements for titanium dioxide; however, a significant rate enhancement was observed for both calcite and silica systems. These differences were attributed to counterion layers forming as a result of the particles surface charge, leading to an increase in the relaxation rate of bound surface layer water. Further, changes appeared to be more pronounced in the silica systems, due to their larger charge. No enhancement was observed for titania, which was assumed to be due to the particles being at their isoelectric point, with no resulting counterion layer formation.

Solvent relaxation was further used to successfully determine the surface area of particles in a dispersion using a silica standard reference material, with results compared to Brunauer-Emmett-Teller (BET) and spherical equivalent estimations. Two different dispersions of titanium dioxide, of different crystal phases, were shown to have NMR surface area measurements in good agreement with BET. Thus showing the technique was able to measure changes in surface charge when surface chemistry remained relatively similar, due to the reference silica material also being an oxide. In contrast, the NMR technique appeared to overestimate the calcite surface areas in reference to BET, which was assumed to occur due to both better dispersion in the liquid state of nanocrystallites and potential ion enhancement from the solubility of the calcite. These results highlight the potential of this technique as a fast, non-destructive and non-invasive method for dispersion analysis, but also show the competition between surface area and surface chemistry interactions on measured relaxation rates.

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1. Introduction

Particulate suspensions are present in numerous industries including pigments, cosmetics, pharmaceuticals and foods, and frequently, are at high concentrations [1]. Particle surface area is an important consideration, as an increase in the concentration of colloids in a dispersion results in a larger total surface area available, thus increasing the potential for surface reactions with the surrounding environment. The surface area of a particle is often determined for dry powders by Brunauer-Emmett-Teller (BET), whereby, nitrogen gas molecules physically adsorb onto a particle surface in layers [2,3]. Critically, BET is not capable of determining the total particle surface area for particles in solid-liquid (S-L) dispersions [4] and is considered to be somewhat time-consuming thus reducing its versatility, as some samples require extensive degas times, up to 24 h. Moreover, BET is dependent on the temperature and de-gas conditions used to obtain measurement reproducibility [5]. Mercury porosimetry and gravimetric analysis are alternative techniques for the measurement of surface area, although they also require dry powders [6]. It is well known that the drying of suspensions frequently leads to aggregation and agglomeration [7], resulting in measurements that are unreliable and misrepresentative of the particle surface area in a S-L dispersion [8].

Nuclear magnetic resonance (NMR) is commonly used for the identification of unknown compounds, while the use of proton relaxation rates allows the surface area to be obtained for any particle, of any size or shape [8]. Relaxation NMR (relaxometry) is a rapid non-invasive and non-destructive method to study the behaviour of liquids in porous and non-porous media [4,8]. It offers the potential for high speed data

acquisition, where relaxation measurements can be obtained between 5 and 15 min [4,8].

Relaxometry has previously been used to characterise many types of colloidal dispersions and interfacial phenomena, as recently reviewed by Cooper et al. [9]. Some examples include; polymers in aqueous solution and gels [10,11], polymer melts entanglement [12], polymer adsorption in the presence of electrolytes [13,14] and surfactant polymer interactions [15,16]. Furthermore, it has provided useful insight into competitive adsorption processes [17,18], and allows for a detailed understanding of the nature of the bound and free solvent sites in colloidal systems.

In 1987, Davis et al. [4], explored the use of solvent NMR to determine surface area and compared their findings to BET data [4]. Three different amorphous fumed silica powders were studied, these samples all had negligible internal porosity and therefore only a single exponential relaxation rate was observed, compared to a possible biexponential relaxation indicating water in pores [4]. Nearly three decades later, Fairhurst et al. [8], investigated dispersion and formulation behaviour of nanostructured carbon materials including graphene oxide, nanographite and porous graphene using NMR relaxometry [8], where particle aggregation and the influence of milling methods were also characterised [8]. Chen et al. have correlated relaxation NMR studies to determine the surface area of highly porous metal-organic frameworks to BET and Langmuir surface area measurements [19,20].

Relaxation NMR has also been used extensively to probe particle internal structure; for example, in geophysical well logging to estimate hydrocarbon-reservoir properties which include rock porosity, pore-size distribution, and permeability [21], while several studies have been conducted on the use of relaxation rates to examine porosity [22–25]. Literature has also shown that relaxation NMR measurements are useful to determine the specific surface area of porous cement materials [26], and study the effects of water reducing agents on sealing materials in cement [27].

Despite the number of previous studies, in wide research areas, there are still significant questions related to the application of NMR relaxometry for the measurement of colloidal surface areas, which has so far limited its wider use. In particular, is the influence of electrolyte conditions on the surface relaxation of solvent molecules, and whether bound counterion monolayers, enhance or reduce the relaxation rate. Flood et al. [13] studied the relative relaxation enhancement (R_{sp}) of four salts (NaCl, MgCl$_2$, CaCl$_2$ and LaCl$_3$) in water at a concentrations of 5 mM (below levels that led to aggregation excluding LaCl$_3$) with increasing concentrations of silica (0–10 wt%). They found the addition of salt led to an increase in the magnitude of R_{sp} which was dependent on the concentration and valency of the salt [13]. They suggested the addition of salt increases the silica-solvent affinity, in other words, there is an increase in the strength of binding of water at the silica surface as a function of ionic strength [13].

Although Flood et al. [13] were the first to conduct a valency and concentration study on the effects of salts to silica measured through NMR relaxation, there has been little progression within this area. Schwarz et al. [28] also carried out an NMR relaxation study on negatively charged sulphate-stabilised polystyrene latex nanoparticles (466 nm) in the presence of 0.25 M NaCl [28]. Consistent with Flood et al. [13] they reported a relaxation rate enhancement in the presence of salt, which they attributed to sodium ions forming a screening layer around the negatively charged latex particles [28]. It was assumed this screening caused an increase in the 'immobilised' water compared to the unscreened charges (where the term 'immobilised' referred to either increasing the amount of bound water to the particle surface, or, a reduction in the dynamics of the bound water) [28]. Additionally, Katika et al. [29] observed that chalk saturated with Mg-rich brines caused a shift in T$_2$ (spin-spin relaxation) to faster relaxation rates [29]. However, in their case, it was concluded that this result was due to precipitation within the pore space leading to an increase in the specific surface area [29].

While these few studies have indicated that electrolyte interactions generally result in an increase in relaxation rate, the underlying mechanism is still unclear. In addition, it is not known whether particle surface charge or magnitude may alter these effects. Importantly for application, there are also imperative questions as to what extent these effects may dominate or confound the use of these measurements for specific surface area analysis, greatly limiting the potential of NMR relaxation for on-line surface area measurements of concentrated slurries, for example [30].

To better understand these related phenomena, this paper presents NMR relaxation measurements in various systems, with changes in both particle surface area and interfacial chemistry. Titanium dioxide, calcium carbonate and silica were selected, due to their likely differences in particle charge at neutral pH [31–33]. Additionally, their fine and cohesive nature, resulting in broad size distributions are representative of many commonly encountered industrial suspensions [34]. Systems with and without 1 M KCl were characterised, where the high salt concentration was thought to considerably enhance any potential ion effects, but also induce particle aggregation (and thus lower total surface area).

2. NMR surface area theory

A dispersion constituting a single liquid and single particulate material is simplified to contain two liquid domains that have different relaxation rates [25,26], where a monolayer coverage of fluid on the particle surface is assumed. The first domain being the bulk liquid (R_b) which is far away from the particle surface and the second the bound solvent (R_s), which is the liquid molecules on the surface of the particle [4]. The liquid bound at the particle surface has a relaxation time orders of magnitude shorter than the comparative bulk (2–3 s), as their motion becomes anisotropic and restricted, thus enhancing the relaxation rate [8,17]. However, only a single average relaxation time is observed due to the fast interchange of the bulk and bound solvent [8,17]. The average relaxation rate (R_{av}) is weighted by the quantity of fluid in each domain, whereby the domains are additive as shown by Eq. (1) [8]. Here, R_{av}, R_b and R_s (ms^{-1}) are various solvent relaxation rates, detailed above, ψ_p is the particle to liquid volume ratio (dimensionless), S (m^2/g) is the total surface area per unit weight, L (m) is the surface layer thickness of the bound liquid, while ρ_p is the bulk particle density (g/m^3).

$$R_{av} = \psi_p \, S \, L \, \rho_p \, (R_s - R_b) + R_b \tag{1}$$

The use of a standard reference material of a known surface area, allows a constant to be defined K_a, which for a given interface, can in principle be obtained for any material. This parameter is a surface specific relaxation constant (g/m^2/ms), shown by Eq. (2), where, K_a is dependent on both particle type, associated surface chemistry and solvent [8]. While, this dependency has limited the techniques use in some systems, nonetheless, it still provides a simple and rapid method to extract important information regarding changes in wetted surface area. Similar theory has previously been denoted for the online surface area measurements of concentrated slurries [30].

$$k_a = L \, \rho_b \, (R_s - R_b) \tag{2}$$

The particles' specific surface area for a given particle system is calculated by substituting Eq. (2) into Eq. (1) and rearranging, as shown by Eq. (3) [8]. Here, R_{sp} is known as the specific relaxation enhancement (Eq. (4)) which is a dimensionless number [9,17].

$$S = \frac{R_{sp} R_b}{K_a \psi_p} \tag{3}$$

$$R_{sp} = \frac{R_{av}}{R_b} - 1 \tag{4}$$