

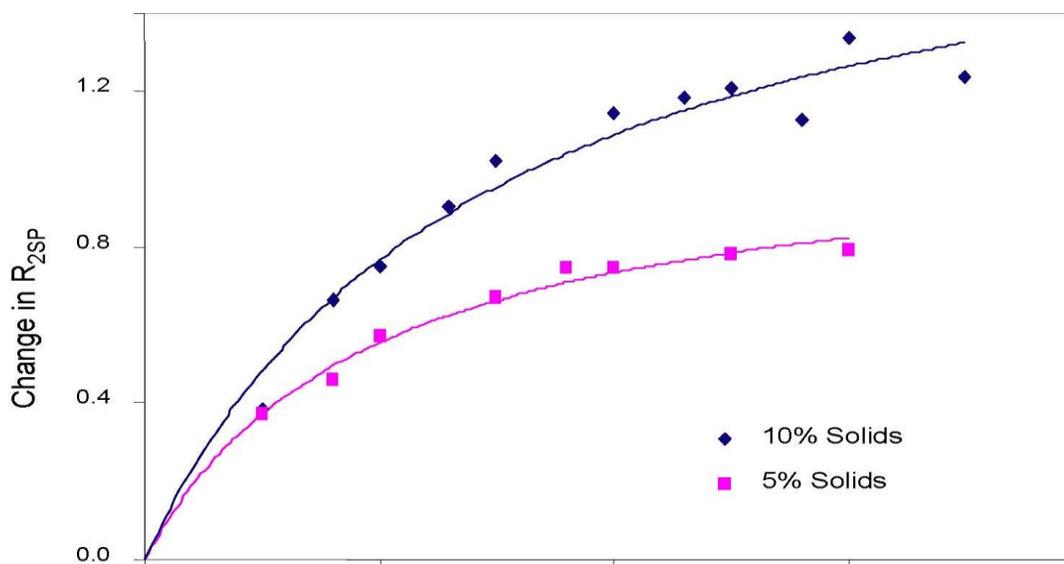
Surfactant Adsorption using the Acorn Area™

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Understanding the extent of coverage of the particle by surfactant is an important part of formulation development in a variety of industries. Inadequate coverage of the particle surface can result in unstable formulations. Surfactants are expensive, hence optimizing their concentration in a formulation is important to producing the best product possible at the lowest costs. Free surfactant in a liquid changes the relaxation time of the liquid only slightly, while surfactant at the particle interface changes the relaxation time of the dispersion to a much larger extent. This property can be used to determine the concentration of surfactant at the interface.

NMR relaxation measurements can be used to determine the adsorption of solutes on to the surface materials. For a solute to be adsorbed it must displace fluid that is already wetting the surface. As such the relaxation time will change. Here we show a simple adsorption isotherm experiment. This type of measurement can be run in real time and could be extremely useful not only in R&D but also to enable manufacturers to optimize the amount of dispersant/stabilizer needed in milling and grinding processes.

In the figure below we show the change in the relaxation rate of two concentrations of the same dispersion as a function of surfactant concentration. As the surfactant at the interface reaches a monolayer of coverage, the relaxation rate plateaus, as shown in the figure:



Small variations in particle size can result in large variations in particle surface area, resulting in inadequate surfactant coverage and unstable dispersions. As the particle size of a material is reduced, the surface area increases in proportion to the particle diameter². Consequently, the surface area-to-volume ratio of the particles increases dramatically. For example reducing the particle diameter from 10 microns to 1 micron increases the surface area/gram by a factor of 100. This is an essential characteristic common to all particulate suspensions. It matters little what the particle shape is - the surface area per mass of any colloid is orders of magnitude larger than it is for particles of even only a few micrometers in size¹. Measurement of the surface area is commonly determined using BET (N₂) gas adsorption but requires the material under test to be a dry powder. However, drying wet suspensions inevitably results in aggregates and agglomerates and, as a consequence, the subsequent surface area measured by gas adsorption will be seriously underestimated. For wet suspensions of particles it is essential, then, that the wetted surface area is measured directly to determine optimal surfactant loading.

The Acorn Area™

The Acorn Area uses a patented technique based on NMR relaxation to determine the wetted surface area of suspensions of particulate materials². The Acorn Area takes advantage of the fact that liquid that is bound to a particle surface has a much smaller relaxation time than the free or bulk liquid. Thus a sample with a high surface area will have a smaller total relaxation time than a low surface area sample because there should be more of the fluid bound to the surface. In contrast to measurement of particle size by dynamic light scattering, where the raw intensity data has to be deconvoluted by means of complex algorithms, the NMR relaxation time can be converted into the absolute surface area by means of a straightforward calculation. As in the BET gas adsorption method, monolayer coverage of fluid onto the particle surface is assumed. NMR measurements make no assumptions about the surface morphology, hence are sensitive to variations in particle shape.

The most common method of surface area determination is nitrogen (N₂) gas adsorption^{3,4}. In this method, N₂ is adsorbed on a sample kept at liquid N₂ temperature at a series of different pressures. It is useful only for dry powders and requires that the sample be degassed to drive off any adsorbed material (sample conditioning); this requires a source of liquid N₂ to maintain the proper sample temperature; and this is also a critical experimental requirement⁵.

¹ D.H. Everett, "Basic Principles of Colloid Science", *RSC Publications*, London (1988)

² US Patent, 7,417,426, August 26, 2008.

³ S.J. Gregg and KSW. Sing, "Adsorption, Surface Area and Porosity", 2nd Edition, Academic Press, London, 1982.

⁴ S. Lowell and J E. Shields, "Powder Surface Area and Porosity", Chapman Hall, London, 1984.

⁵ KSW. Sing, "The Use of Gas Adsorption for the Characterization of Porous Solids", *Colloids and Surfaces*, 38 113 (1989).

It is possible to calculate the surface area from measurements of the particle size but it assumes spherical particles and a monodisperse size distribution, a condition clearly not met by many materials. Any surface area calculated for such materials is, at best, only a crude approximation; it is well-recognized that particle shape, surface irregularities and porosity will inevitably lead to estimated values significantly less than the true value⁶.

In contrast, the Acorn Area measures suspensions directly and requires no sample pretreatment or temperature control. There are no assumptions about the sample particle size (distribution) or shape used in the determination of surface area; it is measured directly. Thus, it is, inherently, a much simpler measurement technique; and as little as 0.5 ml of sample is needed.

The formula for calculating the surface area from the measured NMR relaxation time is:

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

where R_{av} is the average spin relaxation rate constant, ψ_p is the particle volume to liquid volume ratio, \mathbf{S} is the total surface area per unit weight, L is the surface layer thickness of liquid, ρ_p is the bulk particle density, R_s is the relaxation rate constant for the bound solvent and R_b is the relaxation rate constant for the free or bulk solvent.

Using a standard reference material we can define a constant, $K_a = L \rho_p (R_s - R_b)$ so that the equation (1) reduces to:

$$R_{av} = K_a \mathbf{S} \psi_p + R_b \quad (2)$$

The surface area can then be calculated from:

$$\mathbf{S} = R_{sp} R_b / K_a \psi_p$$

where, $R_{sp} = R_{av}/R_b - 1$

A more precise method is to use the slope of a plot R_{sp} as a function of different volume ratios, ψ_p (i.e. concentrations).

⁶ T. Allen, "Particle Size Measurement", Chapman & Hall, 4th Edition, New York, 1990.