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Report

Prepared

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Reviewed by:

Sean Race

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Document:1

A handwritten signature in black ink that reads "Sean Race". The signature is written in a cursive style with a horizontal line underneath it.

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Introduction

The Acorn Area measures the wetted surface area of suspensions using a patented proton NMR technique. This method relies on the observation that **liquid on the particle surface has a relaxation time orders of magnitude smaller than bulk liquid** (i.e., liquid far away from the particle surface). The relaxation time of the dispersion is comprised of the response from both bulk and surface liquid, shifted from the bulk liquid in proportion to the quantity of liquid on the particle surface. The method assumes that the liquid in the sample can be classified into either surface liquid or bulk liquid. This is, in general, a good assumption as the enhancement of relaxation of liquid associated with the presence of a particle surface decrease rapidly with distance from the particle surface.

The method is independent of the particle size distribution and shape. However, the calculation of an absolute particle surface area requires a value for k_a , a parameter which characterizes the relaxation time shift per unit area for a given particle-liquid combination.

Determination of k_a requires a reference material, i.e., a particle of known surface area dispersed in the test liquid. When monitoring changes in particle surface area for a given particle-liquid combination (for example in milling), the differences in relaxation time are absolute and so determination of a specific value for k_a is not necessary.

Changes to the particle interface are altered by the presence of other substances, such as surfactants. Surfactant addition to the bulk liquid has a minimal effect on the relaxation of the bulk liquid. Accordingly, this method can be used to quantify the adsorption of a monolayer of surfactant on the particle surface, and can also be used to study competitive adsorption of two surfactants on the particle surface. It can also be used to observe particle flocculation and sedimentation.



Equipment

Measurements were performed on a standard Acorn Area (13MHz NMR) device using AreaQuant software version 0.9.3. The sample temperature of ~23°C.

Verification

Prior to the actual sample measurement the Xigo Nanotool's verification reference solution was used to ensure that the instrument was properly functioning and that the reference frequency was correct. The verification standard is an aqueous solution of a paramagnetic material that replicates the relaxation behaviour of a concentrated particulate dispersion without the complications associated with concentrated dispersions, such as settling, flocculation, etc. The verification standard has a relaxation time of approximately 45ms.

Sample Identification & Preparation

Seven samples were tested at a range of concentrations and particle sizes shown in Table 1 of the appendix. Note that all samples were tested at a pH of 10. Weight % ws determined using TGA.

Repeatability

Table 2 illustrates the repeatability for the samples analysed. Measurements in triplicate were performed. In general, the repeatability was excellent, better than 1% for the most part. The precision could be improved by increasing the number of scans and implementing temperature control, however, the results are indicative of the precision of the measurement.

Discussion of Results

In general, the surface area data correlates with particle size with the notable exception of samples 6 & 7, with and without MEA. The sample with MEA, S6, shows similar behaviour to that of sample S2, while the lack of MEA significantly alters the measured surface area by approximately 50%. While the actual surface area is probably identical, the surface chemistry of the two samples are markedly different, requiring a different k_a to produce meaningful surface area measurements.

Table 1: Sample Data

Sample	Name	Solid Content %	Particle size nm	pH	Area m ² /g	T2
						ms
S1	20190410-C106-2ETOH	17.19	161	10	57.4	549
S2	20190410-C106-ETOH	23.4	54	10	91.5	276.4
S3	20190410-C106-MEOH	20.8	21	10	132.2	219.7
S4	20190410-C106-IPA	21	86	10	76.8	360.2
S5	20190410-C106-TPOS	13.13	115	10	147.1	326.8
S6	20191210-PDU-MEA	11.23	54	10	85.8	592
S7	20190321-PDU-NoMEA	20.217	54	10	42.8	593

Table 2 Repeatability

Silica
Repeatability

2ETOH

	SA T2	Mxy
R1	57.43	236.9
R2	57.54	236.6
R3	57.86	234.9
Avg	57.61	236.1333
STDev	0.223383	1.078579
COV	0.4%	0.5%

ETOH

	SA T2	Mxy
R1	91.5	156
R2	91.4	154
R3	91.6	155
Avg	91.5	155
STDev	0.070711	1.414214
COV	0.1%	0.9%

IPA

	SA T2	Mxy
R1	76.1	168
R2	76.7	167.7
R3	77.6	168.5
Avg	76.8	168.0667
STDev	0.754983	0.404145
COV	1.0%	0.2%

MEOH

	SA T2	Mxy
R1	132.6	179
R2	132.7	180.1
R3	131.5	179.5
Avg	132.2667	179.5333
STDev	0.070711	0.777817
COV	0.1%	0.4%

TPOS

	SA T2	Mxy
R1	147.6	205
R2	146.9	206
R3	146.8	207
Avg	147.1	206
STDev	0.43589	1
COV	0.3%	0.5%

PDU MEA

	SA T2	Mxy
R1	86	205
R2	85.7	208.7
R3	85.6	209
Avg	85.76667	207.5667
STDev	0.208167	2.227854
COV	0.2%	1.1%

PDUNO MEA

	SA T2	Mxy
R1	42.7	212
R2	42.8	216
R3	42.8	217
Avg	42.76667	215
STDev	0.057735	2.645751
COV	0.1%	1.2%

Surface area measurement

Sample		
2ETOH		
20190410 C106 (#1)		
Date	User	Instrument
2019-04-12 14:14:50	XIGONANOTOOLS\Xigo Nanotools	
Filename		
2ETOH-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

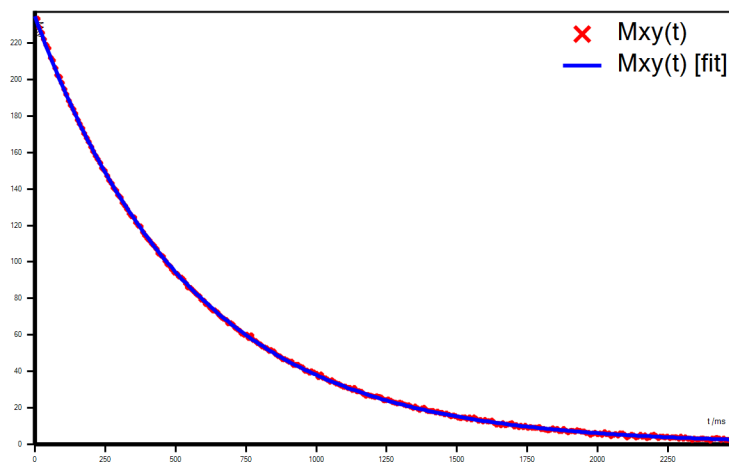
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 312 echo cycles and $\tau=0.5$ ms, averaging 8 scans with a recycle delay of 2500 ms. The experiment was planned based on an anticipated T_2 value of 500 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 57.9 m^2/g of solids. This estimate is based on a T_2 value of 549.3 ms, a specific surface relaxivity k_a of 0.000264 $g/m^2/ms$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.0940.


Table of results

Specific surface area	SA	57.9	m^2/g
Experimentally determined T_2 value	T2A	549.3	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	234.9	arb.
Experimentally determined offset $M_z(t=\infty)$	C	3.4	arb.



M_{xy} fit for T_2 measurement

Notes about the experiment:

 No problems were detected in this experiment



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Surface area measurement

Sample ETOH 20190410 C106 (#2)		
Date 2019-04-12 14:23:19	User XIGONANOTOOLS\Xigo Nanotools	Instrument
Filename ETOH-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

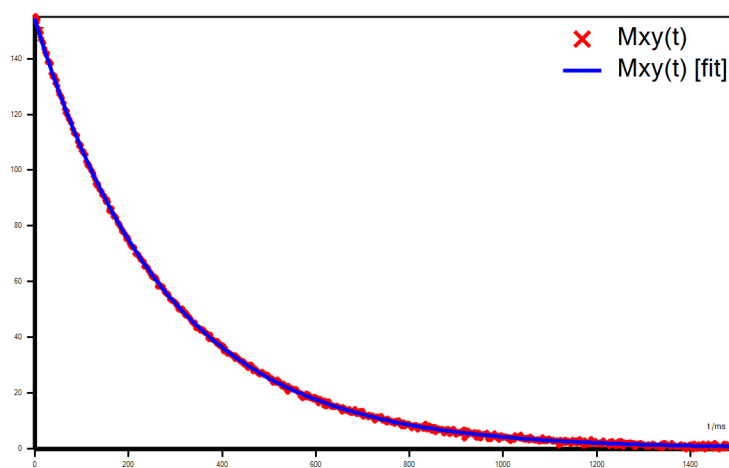
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 750 echo cycles and $\tau=0.5$ ms, averaging 4 scans with a recycle delay of 1500 ms. The experiment was planned based on an anticipated T_2 value of 300 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 91.4 m^2/g of solids. This estimate is based on a T_2 value of 276.4 ms, a specific surface relaxivity k_a of 0.000264 $g/m^2/ms$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.1340.


Table of results

Specific surface area	SA	91.4	m^2/g
Experimentally determined T_2 value	T2A	276.4	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	154.4	arb.
Experimentally determined offset $M_z(t=\infty)$	C	1.7	arb.



M_{xy} fit for T_2 measurement

Notes about the experiment:

 No problems were detected in this experiment



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Surface area measurement

Sample MEOH 20190410 C106 (#3)		
Date 2019-04-12 14:31:06	User XIGONANOTOOLS\Xigo Nanotools	Instrument
Filename MEOH-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

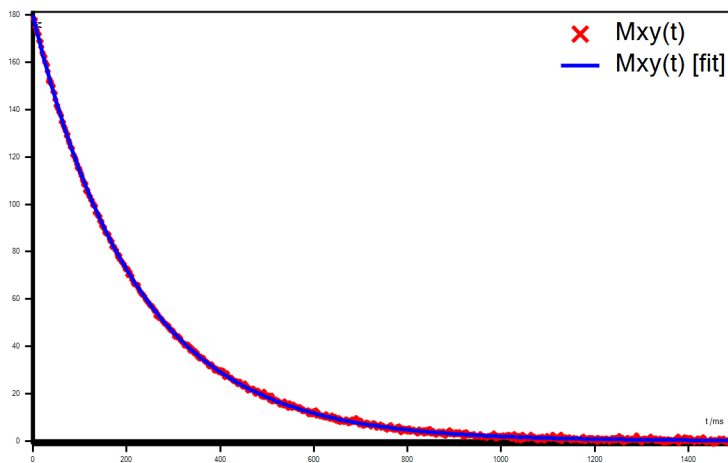
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 750 echo cycles and $\tau=0.5$ ms, averaging 4 scans with a recycle delay of 1500 ms. The experiment was planned based on an anticipated T_2 value of 300 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 132.7 m^2/g of solids. This estimate is based on a T_2 value of 219.7 ms, a specific surface relaxivity k_a of 0.000264 $\text{g}/\text{m}^2/\text{ms}$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.1190.

Table of results

Specific surface area	SA	132.7	m^2/g
Experimentally determined T_2 value	T2A	219.7	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	180.1	arb.
Experimentally determined offset $M_z(t=\infty)$	C	3.5	arb.



M_{xy} fit for T_2 measurement

Notes about the experiment:

No problems were detected in this experiment



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Surface area measurement

Sample IPA 20190410 C106 (#4)		
Date 2019-04-12 14:38:39	User XIGONANOTOOLS\Xigo Nanotools	Instrument
Filename IPA-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

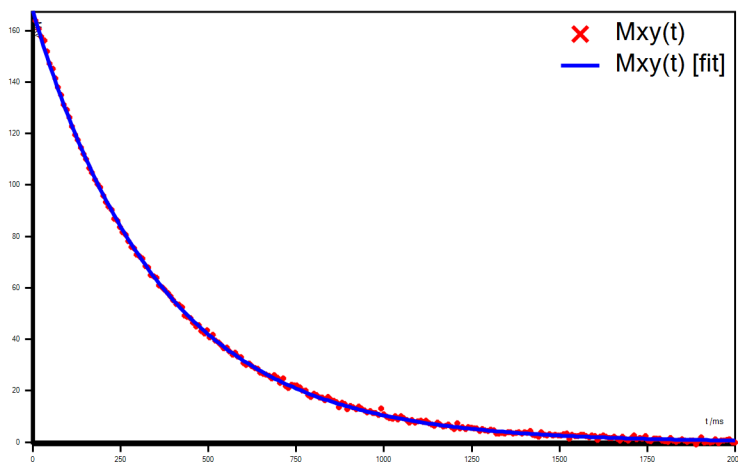
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 250 echo cycles and $\tau=0.5$ ms, averaging 4 scans with a recycle delay of 2000 ms. The experiment was planned based on an anticipated T_2 value of 400 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 76.1 m^2/g of solids. This estimate is based on a T_2 value of 360.2 ms, a specific surface relaxivity k_a of 0.000264 $g/m^2/ms$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.1190.


Table of results

Specific surface area	SA	76.1	m^2/g
Experimentally determined T_2 value	T2A	360.2	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	167.6	arb.
Experimentally determined offset $M_z(t=\infty)$	C	2.5	arb.



M_{xy} fit for T_2 measurement

Notes about the experiment:

 No problems were detected in this experiment



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Surface area measurement

Sample TPOS 20190410 C106 (#5)		
Date 2019-04-12 14:44:37	User XIGONANOTOOLS\Xigo Nanotools	Instrument
Filename TPOS-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

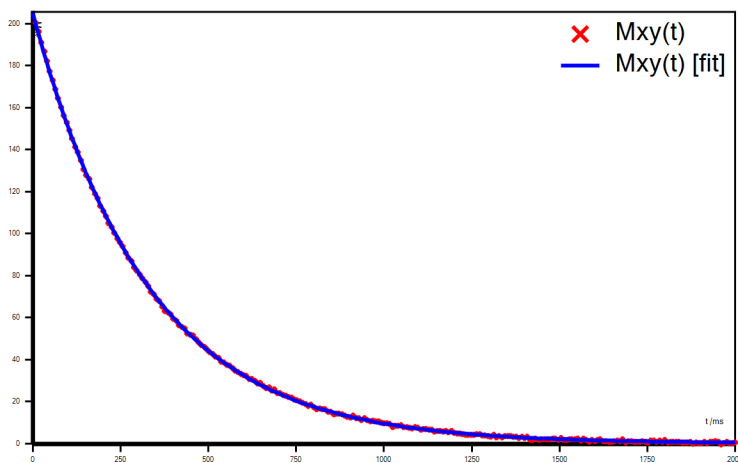
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 250 echo cycles and $\tau=0.5$ ms, averaging 8 scans with a recycle delay of 2000 ms. The experiment was planned based on an anticipated T_2 value of 400 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 147.6 m^2/g of solids. This estimate is based on a T_2 value of 325.4 ms, a specific surface relaxivity k_a of 0.000264 $g/m^2/ms$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.0690.

Table of results

Specific surface area	SA	147.6	m^2/g
Experimentally determined T_2 value	T2A	325.4	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	205.1	arb.
Experimentally determined offset $M_z(t=\infty)$	C	5.0	arb.



M_{xy} fit for T_2 measurement

Notes about the experiment:

No problems were detected in this experiment



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Surface area measurement

Sample PDU-MEA 20181210 C106 (#6)		
Date 2019-04-12 15:24:01	User XIGONANOTOOLS\Xigo Nanotools	Instrument
Filename PDU-MEA-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

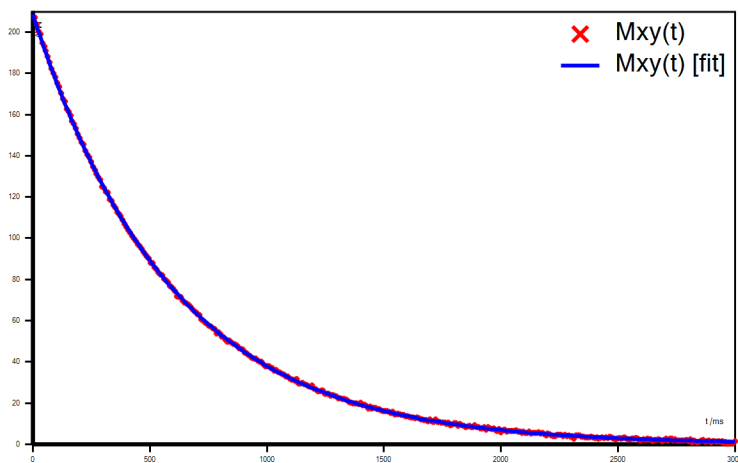
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 375 echo cycles and $\tau=0.5$ ms, averaging 8 scans with a recycle delay of 3000 ms. The experiment was planned based on an anticipated T_2 value of 600 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 86.0 m^2/g of solids. This estimate is based on a T_2 value of 587.6 ms, a specific surface relaxivity k_a of 0.000264 $g/m^2/ms$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.0580.


Table of results

Specific surface area	SA	86.0	m^2/g
Experimentally determined T_2 value	T2A	587.6	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	208.7	arb.
Experimentally determined offset $M_z(t=\infty)$	C	3.4	arb.



Mxy fit for T_2 measurement

Notes about the experiment:

 No problems were detected in this experiment



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Date: ____/____/____

Surface area measurement

Sample PDU-NOMEA 201190321 (#7)		
Date 2019-04-12 15:35:52	User XIGONANOTOOLS\Xigo Nanotools	Instrument
Filename PDU-NOMEA-Surface area measurement-0000.nmrdata		

Surface area measurement using the T_2 -CPMG method

Experimental:

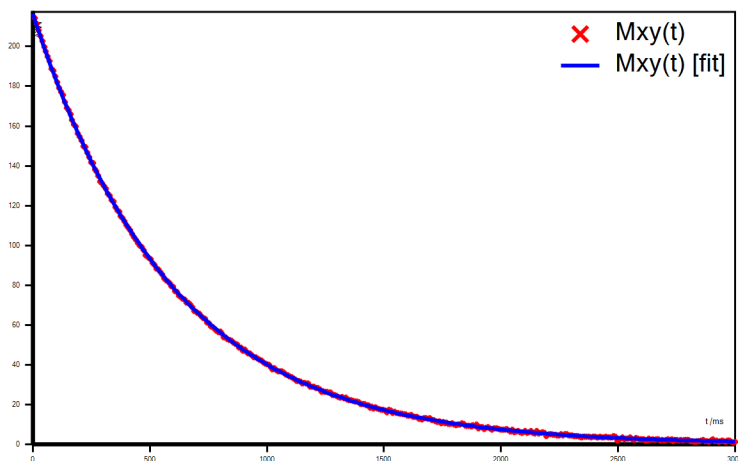
The surface area was estimated using a T_2 measurement obtained from a CPMG sequence with 375 echo cycles and $\tau=0.5$ ms, averaging 8 scans with a recycle delay of 3000 ms. The experiment was planned based on an anticipated T_2 value of 600 ms. Data were phase corrected and fitted to a single exponential with offset.

Results:

The specific surface area is estimated to be 42.8 m^2/g of solids. This estimate is based on a T_2 value of 593.4 ms, a specific surface relaxivity k_a of 0.000264 $g/m^2/ms$, a bulk relaxation time of 2600 ms, and a volume ratio of 0.1150.

Table of results

Specific surface area	SA	42.8	m^2/g
Experimentally determined T_2 value	T2A	593.4	ms
Experimentally determined $M_z(t=0)$ value	Mxy0A	216.6	arb.
Experimentally determined offset $M_z(t=\infty)$	C	3.3	arb.



M_{xy} fit for T_2 measurement

Notes about the experiment:

No problems were detected in this experiment



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