ARTICLE TYPE

A Method for Studying the Diffusion of Quaternary Ammonium Cations Through Polyelectrolyte Phases†

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The mobility of organic cations in polymeric phases is an important property to consider when using these materials as active ingredients in coatings. Here we describe a method for extracting such compounds from polymeric samples and how analysis of these extracts can yield insights about the diffusivity of molecules in a polymeric phase.

1 Introduction

Diffusion in polymeric phases is an important phenomenon which influences many fields. The ability to control the release of active compounds from a polymeric vehicle may be influenced by the diffusivity of these compounds, especially when strong interactions exist between the active compound and the vehicle. Particularly interesting are those cases in which these interactions can be modified to tune the diffusivity of the mobile compound.

In order to assess how different structural features assess the diffusivity of an analyte, the kinetics of analyte release must be measured. The methods used to effect this measurement are highly dependant on both the nature and quantity of the analyte of interest.

Table 1 Some typical methods used to detect different types of analyte

Analyte	Detection Method	Sensitivity
Transition metal	Flame Photometry	10-1000 ppm
	Flame AAS	1-100 ppm
	Flame AES	< 1 ppm
Organic Cations	HPLC-MS	10ppb - 10 ppm
	GC-MS	10ppb - 10 ppm
	qNMR	10 - 1000 ppm

While HPLC-MS and GC-MS are by far the most sensitive techniques for the investigation of organic compounds, much time and effort must be spent developing and optimizing analyte extraction, pre-concentration and detection methods. Alternative methods, such as flame-photometry and quantitative NMR spectroscopy require less method development but are concomitantly less sensitive. The aim of this work was to establish whether the kinetics of the ion exchange of quaternary ammonium cations could be studied using a combination of flame photometry and qNMR.
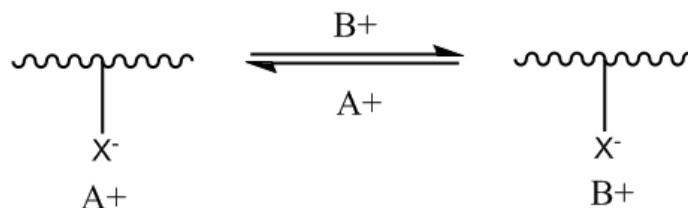
1.1 Ion Exchange

Fig. 1 Basic outline of the ion exchange equilibrium, where an incoming ion B+ can displace a resin associated ion A+

1.2 Basic Principle

Ion exchange describes the phenomenon in which an ion exchange material in some initial ionic form will, in contact with a solution containing some ion of a different type to that already contained within the resin, will take-up that ion while releasing the initial ion.

$$R\bar{A} + B^+ \leftrightarrow R\bar{B} + A^+ \tag{1}$$

This phenomenon is of great utility in a large number of industrially important processes; notably the preferential extraction of radioactive isotopes from the waste produced by nuclear reactors.

1.3 Ion Exchange materials

A typical ion exchange material consists of a crosslinked polymeric matrix containing acidic or basic side chains (depending upon whether cation or anion exchange is the desired be-

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haviour of the resin). One of the most popular co-polymers used as a matrix for ion-exchange material is styrene-divinylbenzene (SDVB)(see figure 2).
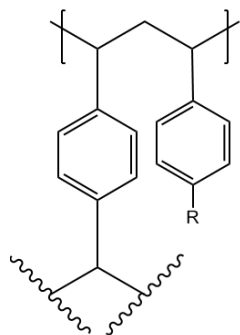

Fig. 2 The styrene-divinylbenzene co-polymer is one of the most popular skeletons for ion exchange resins. R may be any acidic or basic group, dependant upon whether cation or anion exchange functionality is desired

SDVB based resins are particularly attractive due to the ease with which polymer beads of a well controlled size distribution may be obtained. This is achieved by inverse phase suspension free radical polymerization of the monomers in water. As we shall later discuss, this size control is critical for the production of ion exchange resins which behave in a well defined and predictable manner.

1.4 The Kinetics of Ion Exchange

The kinetics of ion exchange are well understood, with the first pioneering studies undertaken by Boyd at the beginning of the 20th century[1]. The early consensus which was established is that diffusion of ions is the rate-controlling step in ion exchange reactions. There are however two separate diffusive mechanisms which may dominate, depending on reaction conditions, the structure of the ion exchange resin and the nature of the ions undergoing exchange.
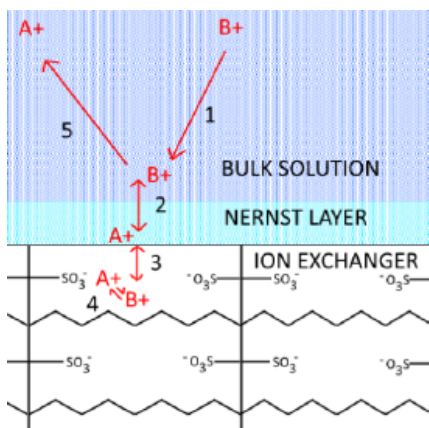

Fig. 3 Ion exchange consists of a number of steps; 1+5: diffusion of ions through the bulk solution, 2: diffusion of ions through the Nernst Layer, 3: diffusion of ions through the polymeric phase, 4: exchange of ions at the ionic polymer side chain

Figure 3 shows the various sub-processes which make up the overall ion exchange process. It is widely accepted that of all these processes, only diffusion through the Nernst layer and the ion exchanger itself are rate controlling (processes 2 and 3 respectively).[2]

When studying the ion exchange reaction it is important to determine which diffusion type is rate controlling; not only are they subject to significantly different mathematical interpretations, they shed light on diffusion in different regions. In other words, to study diffusivity of a molecule within a polymeric phase, particle diffusion not film diffusion must be rate controlling. Table 2 shows how the reaction conditions can be modified in order to influence which process will be rate controlling.

Table 2 The effect of different reaction conditions on the two potential rate controlling diffusion types

Condition	Particle Diffusion	Film Diffusion Control
Ion mobility in particle	$\propto$ mobility	No effect
In bulk solution	No effect	$\propto$ mobility
Particle size	$\frac{1}{r^2}$	$\propto \frac{1}{r}$
Capacity of exchanger	no effect	$\propto \frac{1}{X}$
Nature of ionic groups	$\propto$ strength of electrostatic interaction	No effect
Degree of cross-linking	$\propto \frac{1}{crosslinkdegree}$	No effect

1.5 Measuring Ion Exchange Kinetics

Boyd proposed the following set of equations for the ion exchange reactions (table 3).

Table 3 Equations describing the ion exchange reaction as stated by Boyd[1]. D^i = Inter-diffusion coefficient, F = Fractional approach to equilibrium, r_0 = ion exchange particle radius, Δr_0 = thickness of the Nernst layer, t = time.

Description	Model
Film diffusion in a sphere	$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{\left(-\frac{D^i \pi^2 n^2 t}{r_0^2} \right)}$
Film diffusion in a polymer slab	$F = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} e^{\left[-(2n-1)^2 \frac{\pi^2 D^i t}{4 x_0^2} \right]}$
Diffusion through the Nernst Layer	$log(1 - F) = -\left(\frac{\left[\frac{3D^i}{r_0 (\Delta r_0) \kappa} \right]}{2.303} \right) t$

Thus measurement of the extent to which ion exchange reactions have reached equilibrium will permit estimation of the inter-diffusion coefficients for the ion exchange reactions on the involved resin systems. The fractional approach to equilibrium can be monitored by following the ionic composition of the bulk solution or the ion exchange resin; the advantages and disadvantages of each approach are summed up in table 4

Table 4 Both strategies for studying ion exchange reactions have benefits and drawbacks

Strategy	Positive Aspects	Negative Aspects
Bulk electrolyte monitoring	Compatible with industrial practice	Requires complicated experiment
	Very precise and accurate	Ambiguity about effect of column flow dynamics
	Easily fits required constraints	May require sample preconcentration
Particle content monitoring	Less complicated instrumentation	Requires many distinct observations
	No sample preconcentration required	Incompatible with industrial practice

Where possible, the best approach is of course to combine particle composition analysis with electrolyte composition analysis to come up with a comprehensive trace of the concentrations of the various analytes throughout the reaction. However where this is not possible, one can still deduce the concentration profile of the unmeasured as the velocity of ingress and egress are identical.

To study the ion exchange process a number of steps must be carried out:

- Controlled exposure of a sample of ion exchange particles to an electrolyte solution

- Recovery and washing of the bead sample

- Extraction of analytes from the bead sample

- Quantitation of extracted analytes

We endeavoured to adapt or develop techniuqes for these processes as follows.

2 Experimental

3 Procedure for the investigation of ion exchange profiles

3.1 Part A: preparation of electrolytes

In all ion exchange reactions the external electrolyte concentration was initially 0.50M. These electrolyte solutions were made up by dissolving the requisite amount of the desired salt in distilled water; the required masses of the various compounds used is given below.

Table 5 The required masses to make 0.5M electrolyte solutions of the various salts used.

Salt	Mass (g/L)
tetramethylammonium chloride	54.8
sodium chloride	29.22
hydrogen chloride	41.3 (37% HCl solution)

3.1.0.1 Part B: Preparation of ion exchange beads in the appropriate form

Before ion exchange reactions could take place, the ion exchange beads were converted to the appropriate form. This was accomplished in the following fashion.

A 1M electrolyte (saturated solution for DDDMAC) solution was prepared according to the values in table 5. In a 250ml conical flask, 2g of ion exchange resin were added to 100ml of the electrolyte and the contents of the flask were stirred overnight. Subsequently, the contents of the flask were filtered under reduced pressure and rinsed with distilled water (500ml) to remove supernatant electrolyte from the surface of the polymer particles.

3.2 Part C: Ion exchange reaction

The exchange of the didecyldimethylammonium cation for the sodium cation on AG50WX8 shall be used as a representative example. All exchange reactions follow the same procedure and differ only in the nature of the electrolyte, the specific number and time of samples and the quantity of observations made.

Quaternized AG50WX8 containing didecyldimethylammonium cations (0.2g) was placed in a sieve mesh basket. This basket was pressed onto a rubber bung attached to the end of the drive shaft of an overhead stirrer. The stirrer was switched on and set to rotate the basket at a speed of 200 $\pm$ 20 RPM, confirmed by use of an infra-red tachometer (part number HDE-R07, HDE).

A jacketed reaction vessel was prepared by the addition of of 0.5M NaCl solution (500 ml). A thermometer was suspended in the solution and the temperature was recorded. If the experiment was to be conducted at an elevated temperature then the electric blanket was activated and set to maintain the desired temperature.

Once the stability of the rotational velocity of the basket was confirmed, by observing a deviation of no greater than 20 RPM over a ten second period in the shaft speed, the vessel containing the electrolyte solution was placed below the basket and raised such that the basket was partially submerged (50% of the depth of the basket) in the solution. For small time periods (less than 120 seconds) this was achieved my manually holding the vessel in place underneath the rotating basket. For longer time periods, the vessel was manually raised underneath the basket and a lab jack was placed underneath the vessel to hold it in place. The vessel was kept in place while the basket was stirred until 5 seconds before the target observation time, at which point the vessel was lowered and the overhead stirrer switched off to allow the electrolyte solution to drain from the mesh basket. Once basket appeared empty of solution, a beaker of distilled water (500 ml) was raised underneath the basket which was stirred at the previously set speed for 5 seconds. Finally the beaker was lowered and

the basket again allowed to drain before the basket was removed from the apparatus. Paper towel was wrapped around the mesh basket to absorb any remaining distilled water before the solid was removed from the basket and weighed.

For interruption tests, the above was modified in the following manner. A suitable interruption period was identified (typically 30 seconds after the start of the reaction) and the ion exchange reaction was conducted as usual up to this time. The basket was then drained and stirred in distilled water for 30 seconds. Finally, the distilled water was drained and the basket returned to the electrolyte solution and stirred for the determined period. Finally the reaction was stopped and the solids extracted as previously described.

3.3 Flame Photometric analysis of resin contents

Ion exchange particles subjected to the ion exchange procedure as described previously (see paragraph 3.2) were placed in a Leur lock plastic syringe between plugs of glass wool in an arrangement which allowed various eluent solutions to be poured through the ion exchange particles without contaminating the eluted solution with solid matter. A P-200 Gilson pipette tip was affixed to the tip of the syringe which was then pushed through a rubber septum forming an air tight gasket. In a 500ml glass Buchner flask was placed a 50 ml plastic falcon tube supported by glass beads to elevate the tube towards the top of the flask. The syringe was placed in the top of this Buchner funnel.

Hydrochloric acid (1M) followed by distilled water (20 ml) was passed through the syringe to elute the ions within the ion exchange particle sample. After all the eluent had been passed through the syringe, a vacuum was applied to draw any remaining fluid from the sample. The eluents were made up to 50 ml with distilled water and taken for analysis by flame photometry or QNMR spectroscopy. The solid particles were removed from the syringe and dried in an oven (T=$100^o C$) overnight before being weighed to determine the mass of anhydrous polymer present in the sample,.

3.4 Flame photometric analysis of resin eluents

A set of calibration solutions was prepared by dissolving a sodium chloride stock solution ([Na$^+$]=1000ppm, 2.542g/L) with distilled water as described in table 6:

Table 6 The dilution volumes required to prepare standard solutions with various sodium concentrations

Desired concentration (ppm)	volume stock/100 ml
100	10
80	8
60	6
50	5
40	4
30	3
20	2
10	1
8	0.8
6	0.6
4	0.4
2	0.2

The selection of concentrations for calibration solutions was based upon the expected concentration range of sodium in the samples.

Once appropriate calibration solutions had been prepared, the response of a flame photometer (Jenway PFP7) was used to produce a calibration curve. Finally, each eluent solution was aspirated and the concentration of each eluent was determined with reference to the calibration curve.

3.5 QNMR analysis

A set of calibration solutions in the range 0-50ppm prepared according to the following procedure. First, didecyldimethylammonium methylcarbonate (25g, 0.062 moles) was placed in a round bottomed flask and teflon stirrer bar was added. Concentrated HCl (25ml) was added dropwise until no more gas was released from the solution. The resulting mixture was concentrated repeatedly under reduced pressure with the addition of toluene to encourage azeotropic evaporation. After no more solvent could be removed from the residue, a small quantity (2.2mg) was dissolved in D$_2$O such that the concentration was 200 ppm with respect to the didecyldimethylammonium cation.

A 1000 ppm solution of maleic acid was prepared by dissolving maleic acid (10mg, $8.6 \times 10^{-5} moles$) in D$_2$O (10 ml).

A 1000 ppm solution of tetramethylammonium chloride was prepared by dissolving tetramethylammonium chloride (7.4mg, 6.8×10^{-5} moles) in D$_2$O (10 ml). DDDMAC calibration solutions were prepared according to the following table:

Table 7 Volumes used for the preparation of stock solutions for quantitative NMR spectroscopy

Volume 1000ppm Maleic acid solution (μL)	Volume 200ppm didecyldimethylammonium solution (μL)	Volume D$_2$O	Concentration maleic acid (ppm)	Concentration didecyldimethylammonium cation (ppm)
50	50	900	50	10
50	100	850	50	20
50	150	800	50	30
50	200	750	50	40
50	50	700	50	50

TMAC calibration solutions were prepared in a similar fashion with the exception that the volume (in microlitres) of 1000 ppm TMAC solution used to prepare a sample is identical to the desired concentration of TMAC in ppm.

NMR spectra of each calibration solution was then obtained using the following instrument configuration:

- Instrument: JEOL ECS-400 NMR

- Field strength: 9T (400MHz)

- Relaxation time (T1): 5 seconds

- Acquisition period: 2 seconds

- 90 degree pulse width

- Number of scans: 128

- Spin: off

Following the completion of each experiment the FID was subjected to a number of different data processing techniques to find the optimal combination of pre and post transform modifications for optimizing the signal to noise ratio of the spectra without compromising peak shape. Two window functions (single exponential and gaussian) were compared to evaluate their effect on the SNR and peak shape, while the effect of zerofilling was also assessed

3.6 Procedure for the evaluation of a window function - Part 1: Single exponential

Following the aquisition of the sample spectrum, the FID trace is opened in JEOL Delta. The following processing list is applied to the FID:

1. DC balance

2. Single exponential window function

3. Zerofill (once)

4. Fast Fourier Transform

5. Machinephase

6. scale-ppm

7. baseline correct

The width of the single exponential function was varied from 0.2 to 8 Hz. After each processing list was applied the analyte:standard peak ratios were measured. Two analyte signals were observed (0.6-0.8ppm and 1.0-1.2ppm) while the standard signal appeared at 5.8ppm. Peak integration was accomplished using the automated function of Delta. The signal to noise ratio was assessed using the Signal to Noise analysis tool(Analyze > Signal to Noise Calculator). Signal regions were the analyte regions previously described while the noise region was taken to be 0-0.2ppm. Peak broadness was assessed by monitoring the peak diameter as reported by Delta (Main-screen > File-information > Peak-tab).

The procedure for the investigation of the various T$_1$ relaxation times in an aqueous sample is as follows.

DDMAC calibration solutions were prepared according to 7. Subsequently the inversion recovery experiment was performed for each sample using the following instrument configuration:

- Instrument: JEOL ECS-400 NMR

- Field strength: 9T (400MHz)

- Relaxation time (T1): 7 seconds

- Tau delays: 0.2, 0.4, ,1, 2 and 6 seconds

- Acquisition period: 2 seconds

- 90 degree pulse width

- 180 degree pulse width

- Number of scans: 256

- Spin: off

FID data was processed in the following fashion:

1. DC balance

2. Single exponential window function, width = 8Hz

3. Zerofill (8 times)

4. Fast Fourier Transform

5. Machinephase

6. Manual 180° phase shift

7. scale-ppm

8. baseline correct

9. Sub-set (isolate desired signal)

Following data processing, the Fourier Transform subset is opened in the Delta Curve-Analysis tool (Analyse > Curve Analysis) and the T_1 relaxation time was calculated using a non-linear inversion recovery curve fitting algorithm.

3.7 Analysis of resin Quat contents by QNMR

Calibration solutions are prepared as previously described. Quaternary ammonium compounds were extracted from extracted from ion exchange particles in the following manner. Beads were subjected to the extraction procedure previously described for the extraction of sodium from ion exchange resins A 1ml aliquot of each resulting eluent solution was lyophilized to remove the HCl and H_2O. Residues were taken for ^1H NMR analysis, each sample was spiked with 50ml 1000 ppm maleic acid solution and the total sample volume was made up to 1ml with D_2O.

3.8 Photographic particle size analysis

Photographs were recorded using a Samsung SM-G900F smart phone camera. The analysis of the particle size distribution of protonated AG50W-X8 beads shall be taken as an example.

The base of a flat Petri dish was covered with black card. Upon this card was placed a laminated scale which was photographed in order to permit later reconstruction of particle dimensions from recorded pixel values. A small quantity (<0.1g) of protonated ion exchange resin was placed on the black card; aggregated particles were separated where possible using a wooden boiling stick. The particles were photographed, the camera being maintained in the same position from which the photograph of the scale was obtained. After each photograph was taken, the sampled particles were set aside and a new set of particles were photographed in the same fashion. The recorded images were processed using ImageJ to determine the average particle radius (radius of the equivalent sphere).

4 Results and Discussion

4.1 Particle size distributions

Boyd's laws for ion exchange require that the radius of the ion exchange particles under investigation be known. In order to simplify the procedure, it was assumed that samples contained spherical particles with a range of radii which could be described by an average radius r_0. Mesh fractions proved to be insufficient descriptors of the particle sizes due to swelling of the particles and the presence of aggregates preventing efficient separation. The fragility of acrylamide co-polymer particles meant that an analytical method was required which would create the minimum risk of bead destruction during analysis. This was necessary because damaged particles would have radii not representative of the particles involved in ion exchange experiments. Thus a method was developed in which photographs of ion exchange particles were analysed in order to extract information about the particle sizes.

Table 8 Measured radii of ion exchange particles in the protonated form

| Co-polymer type	Radius (mm)	Standard deviation (mm)
AG50W-X8	0.41	0.09
AMPS/Acrylamide	1.5	0.3
NA2MA/Acrylamide	1.8	0.5

The developed method proved satisfactory for the analysis of particle sizes. The measured standard deviation in the radius of acrylamide co-polymer particles was fairly large, and contributed significantly to uncertainty in the calculated inter-diffusion coefficients.

4.2 QNMR method development

QNMR was investigated for the quantitative analysis of tetramethylammonium chloride and didecyldimethylammonium chloride in order that the fractional approach to equilibrium of an ion exchange reaction could be monitored. NMR spectra intended for use in quantitative analysis must show good sensitivity (signal to noise ratio of at least 50:1 for analyte and standard peaks) and enough peak separation to ensure unambiguous quantitation may be carried out.

Maleic acid was selected as the quantitative internal standard for QNMR experiments as it gives rise to a single peak at a chemical shift which ensured that it could always be integrated in an unambiguous fashion (δ 6.2 s (2 x HOOC-C$\underline{H}$=CH-COOH, 2H))(see figure 4).

Fig. 4 The NMR spectrum of TMAC and Maleic acid in D_2O
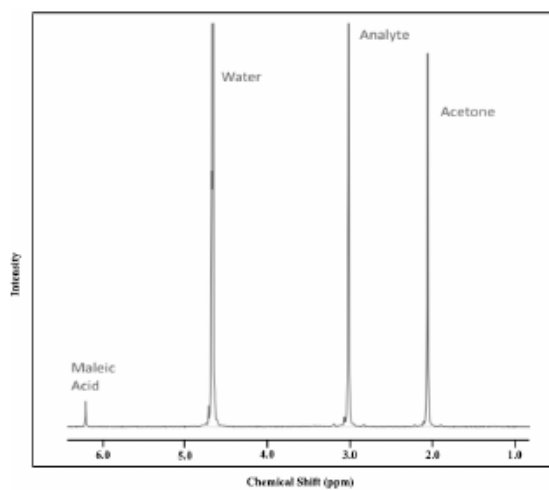
δ(ppm)	Multiplicity	Integration	Environment
2.1	Singlet	N/A	Acetone
3.1	Singlet	N/A	a
4.8	Broad	N/A	Water
6.2	Singlet	N/A	b
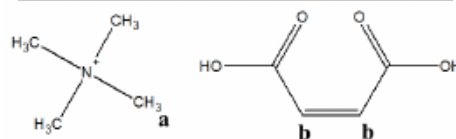
In order to achieve a sufficient signal to noise ratio for the expected lowest analyte concentrations ($\approx$ 10ppm), two approaches were examined; the use of high field instruments to increase sensitivity and optimization of the NMR data processing procedure in order to optimize the signal to noise ratio.

In order to investigate the effect of increasing the instrumental magnetic field strength on the quality of the NMR spectra, a calibration curve was prepared using the Bruker Avance III HD 700 MHz in the NMR department of Newcastle university. The spectra of didecyldimethylammonium chloride solutions in D_2O were collected on both instruments and the spectra compared. The higher field instrument permitted a considerable improvement in spectra sensitivity, yielding an 8 fold improvement in signal to noise ratio (50:400) for a 10 fold reduction in experiment time. While this increased sensitivity of the higher field instrument was appropriate for quantitative analysis of the quats under investigation, it was desirable to find a method which could permit quantitative analysis on the in-faculty NMR instrument equipped with a 400MHz magnet. Therefore attention was turned to optimizing the steps used to process the collected NMR data.

4.2.0.2 Data processing

Two data processing steps were identified for their effect of the signal to noise ratio of the processed spectrum: Application of a window function (also known as adopoziation) and Zerofilling interpolation.

Two window functions were investigated for their effect on the signal to noise ratio of the final spectrum: Single-exponential (SEXP, equation 2) and Gaussian (equation 3).

$$I_t = I_{t=0}e^{-\alpha t} \tag{2}$$

$$I_t = ae^{-\frac{t-b}{2c^2}} \tag{3}$$

Figure 5 shows the effect of applying SEXP functions of varying widths on the signal to noise ratio of processed DDDMAC solution NMR spectra.

Fig. 5 The effect of increasing SEXP widths on the signal to noise ratio of ^{1}H NMR spectra of aqueous DDDMAC solutions
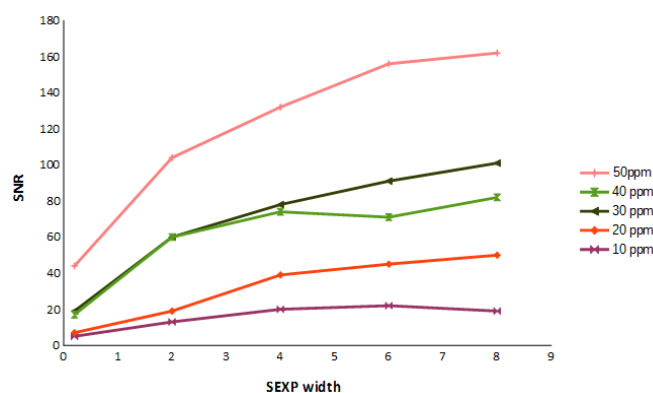
Increasing the width of the function resulted in increasing signal to noise ratios in all cases; the factor by which the SNR was increased was approximately the same in all cases, yielding greater absolute increases in the SNR for more concentrated solutions.

Figure 6 shows the effect of Gaussian window functions of various widths on the SNR of collected spectra.

Fig. 6 The effect of increasing Gaussian widths on the signal to noise ratio of ^{1}H NMR spectra of aqueous DDDMAC solutions
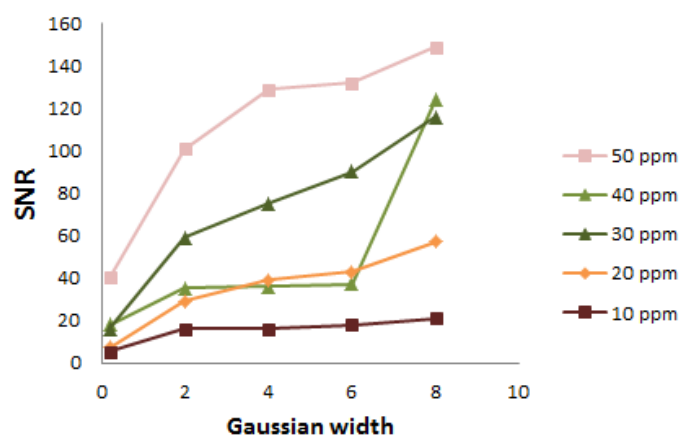
As with a SEXP window function, Gaussian functions of increasing widths lead to improvements in the SNR of collected spectra in all cases. The anomalous recorded SNR for the 40 ppm spectra is due to experimental error. Figure 7 shows a side by side comparison of the effect of SEXP and Gaussian functions. Both functions yielded very similar increases in the SNR for the recorded spectra, with slightly better performance shown for the Gaussian function at high function widths.

Fig. 7 A comparison of the SNR of spectra of 50ppm DDDMAC solutions after applying SEXP and Gaussian functions
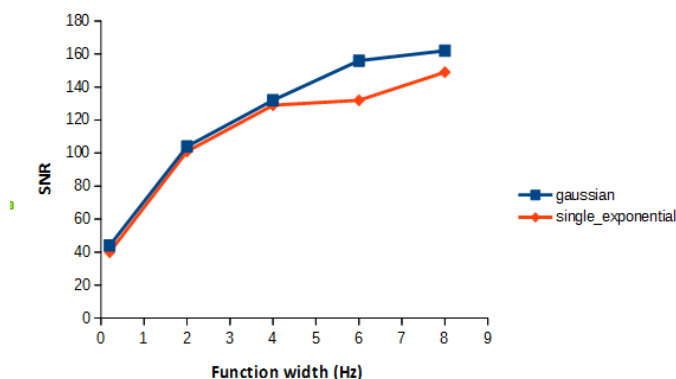

Table 9 shows the effect of both function types on the analyte peak diameter. Gaussian functions resulted in increased peak broadening compared to SEXP functions. For this reason it was decided that a SEXP function of width 8Hz would be most effective.

Table 9 A comparison of the increase in peak diameters for increasing SEXP and Gaussian function widths "*" indicates those diameter changes which are suspect due to SNR limitations

Concentration	10 ppm	20 ppm	30 ppm	40 ppm	50 ppm
% change SEXP	40*	*8	4*	25	12
% change Gaussian	5*	22*	47	42	24

5   Conclusions

References

1 G. Boyd, A. Adamson and M. LS, *J. Am. Chem. Soc*, 1947, **69**, 2836–2848.
2 F. G. Helfferich.