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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

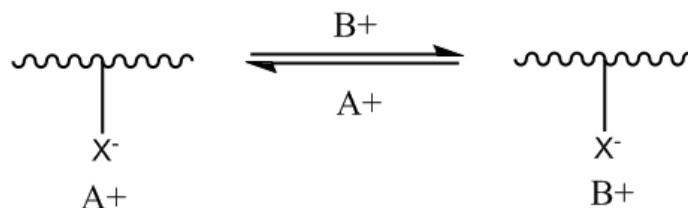


Fig. 1 Basic outline of the ion exchange equilibrium, where an incoming ion B+ can displace a resin associated ion A+

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.



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).

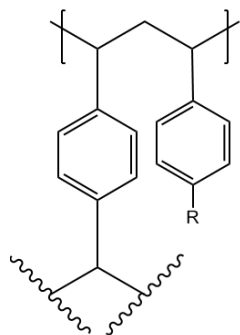


Fig. 2 The styrene-divinylbenzene co-polymer is one of the most popular skeletons for ion exchange resins. R may be any acidic or basic group, dependant upon whether cation or anion exchange functionality is desired

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 century¹. 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.

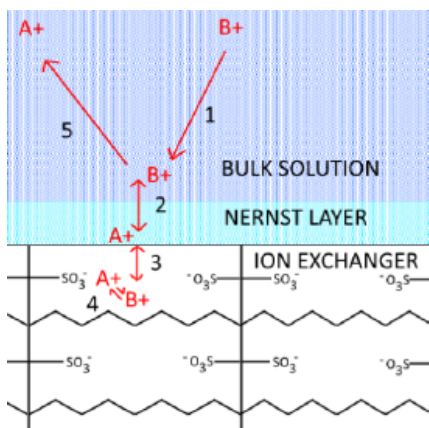


Fig. 3 Ion exchange consists of a number of steps; 1+5: diffusion of ions through the bulk solution, 2: diffusion of ions through the Nernst Layer, 3: diffusion of ions through the polymeric phase, 4: exchange of ions at the ionic polymer side chain

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	$\propto \frac{1}{\text{crosslinkdegree}}$	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 Boyd¹. 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	$F = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} e\left[-\frac{(2n-1)^2 \pi^2 D^i t}{4\Delta r_0^2}\right]$
Diffusion through the Nernst Layer	$\log(1-F) = -\left(\frac{[\frac{3D^i}{2.303}]\right)t$

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 Very precise and accurate Easily fits required constraints	Requires complicated experiment Ambiguity about effect of column flow dynamics May require sample preconcentration
Particle content monitoring	Less complicated instrumentation No sample preconcentration required	Requires many distinct observations 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 techniques 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 didecyltrimethylammonium 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 didecyltrimethylammonium 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 ± 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 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 by 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 ($T=100^{\circ}\text{C}$) 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 ($[\text{Na}^+]=1000\text{ppm}$, 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 1: Preparation of calibration solutions

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_2O 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, $8.6 \times 10^{-5}\text{ moles}$) in D_2O (10 ml).

A 1000 ppm solution of tetramethylammonium chloride was prepared by dissolving tetramethylammonium chloride (7.4mg, $6.8 \times 10^{-5}\text{ moles}$) in D_2O (10 ml). DDDMAC calibration solutions were prepared according to the following table:

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 (T_1): 5 seconds

Table 7 didecyldimethylammonium chloride NMR calibration solutions were prepared as shown

Volume 1000ppm Maleic acid solution (μL)	Volume 200ppm didecyldimethylammonium solution (μL)	Volume D ₂ O	Concentration maleic acid (ppm)	Concentration didecyldimethylammonium (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

- 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

3.5.0.1 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).

3.6 Assesment of [Na+] by Flame Photometry

3.6.1 1: Preparation of a calibration curve

Concentration maleic acid (ppm) Ideally the calibration curve should have samples expected to represent the highest and lowest concentrations of analyte in the data set. The response of the flame photometer to these samples, as compared to a 1000 ppm standard solution is used to estimate the appropriate calibration range for the experiment. Typically for AG50WX8 resins this concentration range will be from 0 - 100 ppm Na+.

3.6.2 2: Analysis of samples

Samples are aspirated in the following manner: Each sample is aspirated 3 times, following the third measurment of a sample the highest calibrant and the blank are reaspirated to ensure stability of the scale. All flame photometry work was conducted on a Jenway 2000 Natural gas flame photometer.

3.7 Quantitative NMR spectroscopy

All NMR spectra were recorded on a JEOL 400 ECS NMR spectrometer, operating at a Magnetic field strength of 9 Tesla (400 MHz).

3.7.1 Preparation of a calibration curve

In all cases, Maleic acid was used as the quantitative NMR standard. Calibration curves for the analysis of tetramethylammonium chloride will be used as a representitive example. A solution of 1000 ppm Maleic acid in D₂O is prepared by dissolving 1 mg maleic acid per ml of D₂O. A solution of 1000 ppm tetramethylammonium chloride is made up by dissolving 7.4 mg tetramethylammonium chloride per ml of D₂O volumetrically.

The total volume of the solution in the NMR sample tube is set at 1ml. At this volume 1μl of stock solution per 1000μl corresponds to 1ppm of sample.

Calibrant solutions are made up such that each solution has a maleic acid concentration of 50 ppm, while the concentration of the tetramethylammonium chloride varies from 10-50ppm.

Collection of NMR spectra is conducted with a view to maximizing the signal to noise ratio for the spectrum. Ideally the signal to noise rati should be 50:1. Signal to noise ratio is improved by increasing the number of scans obtained for a sample.

3.8 Photographic particle size analysis

3.8.1 Calibration of the scale

The camera is suspended over the high contrast background and the scale card is placed on the backing. A photograph of this scale is taken at the level of focus which will be used for photographic particle samples. From this image a scale can be derived (pixels/mm) allowing determination of particle sizes

3.8.2 Particle size analysis

Two cameras were used in the analysis of particle sizes, one USB microscope and one "smaat phone" camera. These two devices provided different levels of zoom permitting particles of different sizes to be analyzed. The method of sample analysis was the

same regardless of camera. A sample of ion exchange particle is deposited on the High contrast background. Some sample manipulation takes place in order to separate (as far as possible) beads from one another to permit clean detection of outlines. Several photographs of each sample are taken.

4 Results and Discussion

5 Conclusions

References

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