Electroacoustic and dielectric response of suspensions of zeolites A and Y

James K Beattie,* Alex M Djerdjev and Sophie E Gibb

School of Chemistry, University of Sydney, Sydney NSW 2006, Australia.
E-mail: j.beattie@chem.usyd.edu.au; Fax: 61 2 9351 3329; Tel: 61 2 9351 3797

Received (in Montpellier, France) 23rd May 2003, Accepted 23rd June 2003
First published as an Advance Article on the web 26th August 2003

The dynamic electrokinetic mobility spectra and dielectric response of suspensions of zeolites A and Y have been measured. The dynamic mobility data cannot be fit with the surface conductivity calculated from the zeta potential, but require the inclusion of a large stagnant layer conduction, which is attributed to ionic conduction within the micropores. With the constraint of a constant particle size the electroacoustic spectra give surface conductivity parameters which agree with those measured independently from the dielectric response. Negative zeta potentials that vary with salt concentration are then obtained from the electroacoustic spectra.

Introduction

There have been surprisingly few reports of the measurement of the zeta potentials or electrokinetic properties of suspensions of zeolite particles.[1] As part of a study of the high frequency electrokinetic properties of porous particles, we have made electroacoustic and dielectric response measurements of suspensions of zeolites A and Y.

The zeolite framework consists of SiO_4 and AlO_4 tetrahedra linked by common oxygen atoms. The composition of a zeolite is given by $M_{y/m}{}^{m+}[(AlO_2{}^-)_y(SiO_2)_x]\cdot zH_2O$, where M is a cation with charge m, $x+y$ is the number of tetrahedra in the unit cell and z is the number of water molecules. Zeolite A is a "low" silica zeolite with a ratio of silicon to aluminium (Si/Al) in the framework of 0.7 to 1.2. A typical unit cell consists of $8 \times Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$. Zeolite Y is an "intermediate" silica zeolite with Si/Al > 1.5–3. A typical unit cell of zeolite Y consists of $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]\cdot 250H_2O$.[2]

Zeolite A consists of a framework of truncated octahedrons (β-cages) connected by cubes (double four rings). Formed within the unit cell is a truncated cuboctahedron or α-cage. The free diameter of the cavity within the β-cages is 0.66 nm and that within the α-cages is 1.14 nm. There are two types of three dimensional, intersecting channels formed by the 6 openings into the α-cage. These "windows" are formed by a ring of 8 oxygen atoms with a diameter of about 0.42 nm. Smaller channels, also three dimensional and intersecting, lead into the β-cages and have a diameter of about 0.22 nm.

Like zeolite A, zeolite Y has β-cages; however, they are linked by hexagonal prisms or double six rings rather than double four rings. This creates a void space called a supercage which is 2.5 nm in diameter, larger than the α-cages in zeolite A. The main channels are formed by windows of 12 oxygen atoms, with a diameter of about 0.74 nm. The smaller windows into the β-cages are 0.22 nm in diameter as for zeolite A.[2]

The porosity of the two zeolites is about the same with a porosity of 47% for zeolite A and 48% for zeolite Y. The main channel in both zeolites will be called the pore diameter; therefore zeolite Y has a pore diameter of 0.74 nm and zeolite A has a pore diameter of 0.42 nm.

Electroacoustics

An electroacoustic effect is generated when an alternating electric field is applied to a dispersion of charged colloidal particles: the particles move backwards and forwards at the same frequency as the applied field. The fluid surrounding the particles is displaced by this motion. A density difference between the particles and the fluid generates a sound wave called the electrokinetic sonic amplitude (ESA). From measurement of the ESA, the dynamic mobility (ac electrophoretic mobility) can be determined.[3]

The ESA can be measured using an electroacoustic device called the AcoustoSizer (Colloidal Dynamics, Warwick, RI). The AcoustoSizer software converts the ESA into the dynamic mobility using the formula

$$\mathrm{ESA} = A\phi(\Delta\rho/\rho)\langle\mu_\mathrm{d}\rangle \quad (1)$$

where A is an instrument factor, ϕ is the volume fraction of particles in suspension, $\Delta\rho$ is the density difference between the particles and the surrounding medium, ρ is the density of the medium and $\langle\mu_d\rangle$ is the particle averaged dynamic mobility.

The ESA and dynamic mobility are both complex quantities. The magnitude of the dynamic mobility is the velocity of the particle per unit field strength. The argument of the dynamic mobility is the phase difference ($\omega\Delta t$) between the particle velocity and the applied field. The particle motion lags the applied field when the inertia of the particle is sufficiently large that the particle cannot keep up with the changing direction of the applied field.

When obtained over a range of frequencies the ESA can be used to determine the zeta potential, ζ, and size of solid colloidal particles.[3]

$$\mu_\mathrm{d} = (2\varepsilon/3\eta)\zeta G^*(\omega a^2/v)[1+f^*] \quad (2)$$

Here ε ($=\varepsilon_0\varepsilon_w$) and η are the permittivity and viscosity of the solvent, respectively. $G^*(\omega a^2/v)$ is a function which takes into account the particle inertia and f^* describes the polarisation of the double layer and particle and will be defined later.

In the AcoustoSizer-I, the field is applied at thirteen frequencies from 0.3 to 11.15 MHz. This allows solid particles from about 0.1 to 10 μm in diameter to be sized. Particles that are smaller than 0.1 μm remain in phase throughout the range of

frequencies applied. This allows their zeta potential to be determined, but not their size. For particles larger than about 10 μm a dynamic mobility cannot be obtained as the ESA signal is too small. The AcoustoSizer-II applies the field at thirteen frequencies from 1 to 20 MHz. This extends the lower limit of sizing to about 50 nm.

The electroacoustic behaviour of porous particles can be different from that of solid particles because the electrical double layer, which surrounds the exterior of a solid particle, also can extend within the pore network of a porous particle. Porous particles have a much greater surface area than solid particles and therefore the double layer is potentially much more extensive. The electrical driving force on a particle (solid or porous) must be balanced by an equal and opposite force on the double layer which results in a zero total electric force on the particle. If a porous particle has a much more extensive double layer than a solid particle, the force on the double layer is much greater and the force driving the motion of the porous particle will be greater.[4]

We describe elsewhere the electroosmotic effects observed in the electroacoustic behaviour of mesoporous silica chromatography supports.[5] Here we report electroacoustic measurements on suspensions of two microporous zeolites with different pore sizes.

Dielectric response

When an alternating electric field is applied across a dispersion, the resulting macroscopic current has a phase and amplitude that depend upon the frequency of the applied field. This frequency dependent behaviour is the dielectric response or dispersion. It may be used to determine electrical and surface properties of colloidal particles. Whilst many previous studies have focused on the low frequency dielectric response, in this work the dielectric response is measured in the MHz region. The theoretical analysis is that developed by O'Brien and summarised below.[6]

If a field of frequency ω is applied to an electrolyte solution (expressed in complex notation in exponential form as $E = E_0 e^{i\omega t}$), the resulting current is

$$\begin{aligned} J &= (K^{\infty} + i\omega\varepsilon_0\varepsilon_w)E \\ &= K_e^* E \end{aligned} \tag{3}$$

where K_e^* is called the *complex conductivity* of the electrolyte and contains components due to the conductivity of the ions (K^{∞}) and the relative permittivity (which is a measure of the polarisation) of the water molecules (ε_w).

When a field is applied to a colloidal suspension, the water molecules in the continuous phase polarise very quickly. Water molecules on the surface of a particle create a polarisation charge distribution which redirects the electric field tangential to the surface. The ions in the double layer surrounding the particle are then swept around the particle by the field, backwards and forwards, as it changes direction. This creates a charge separation whereby the centre of charge of the double layer is displaced back and forth. At large distances from the particle, the electric field that this motion causes is the same as that caused by an alternating dipole and it is useful to express the effect as the dipole strength, S, of the particle and its double layer.

In response to the migration of ions in the double layer, a backfield, δE, is established which opposes this redistribution of charge. The backfield has a component directed tangentially to the particle surface which reduces free charge transfer from the front of the double layer and a component normal to the surface which reduces the charge build up in the rear of the double layer by pushing charge into the surrounding electrolyte. The rate of change of charge in the rear of the double layer is obtained by subtracting the backfield components from the applied field contribution to charge transfer. This is described by an equation with an exponential solution with a relaxation time given by

$$t \approx \frac{\frac{\varepsilon}{K^{\infty}}}{1 + Du} \tag{4}$$

where Du is termed the surface conductance parameter or the Dukhin number. Surface conductance refers to the enhanced conductivity near the surface of a particle due to the presence of the double layer ions.

Because Du is usually of order 1 at most, the time for free charge in the double layer to rearrange is approximately[7] $t \approx \frac{\varepsilon}{K^{\infty}}$, and decreases with increasing electrolyte concentration. Therefore, if the dispersion has time much greater than $\frac{\varepsilon}{K^{\infty}}$ to respond to the applied field (that is, the frequency is much less than $\frac{K^{\infty}}{\varepsilon}$), a backfield due to charge transfer can be established and come to equilibrium with the applied field.

Because more counterions travel to the rear of the double layer than pass out into the surrounding electrolyte, there is an increase in charge density at the back of the particle, and a decrease at the front. These regions of higher and lower ion density will eventually cancel out by diffusion of ions from areas of high concentration to those of low concentration. The time for this to occur is about the time required for an ion to diffuse through a particle radius, that is, a time of order $\frac{a^2}{D}$, where D is the ion diffusivity[6] and causes a lower frequency relaxation in the dielectric dispersion spectrum, typically in the KHz region.

In summary, the dipole strength can be determined by measuring the conductivity of the suspension. For suspensions of particles with thin double layers ($\kappa a \gg 1$), the suspension conductivity is related to the particle average dipole strength per unit field, $\frac{\langle S \rangle}{\langle E \rangle}$, by

$$K^* = (K^{\infty} + i\omega\varepsilon_0\varepsilon_w)\left[1 + \frac{N_p\langle S \rangle}{\varepsilon_0\langle E \rangle}\right] \tag{5}$$

where N_p is the particle number density and ε_0 is the permittivity of a vacuum. For the case of spherical particles of radius a, eqn. (5) can be rewritten as

$$\mathrm{S} = \frac{1}{4\pi\varepsilon_0 a^3}\frac{\langle S \rangle}{\langle E \rangle} = \left(\frac{K^*}{K^{\infty} + i\omega\varepsilon_0\varepsilon_w} - 1\right)\cdot\frac{1}{3\phi} \tag{6}$$

where ϕ is the volume fraction of the particles. The LHS of eqn. (6) is the non-dimensional dipole strength S.

In order to calculate the dipole strength the Laplace equation is solved subject to the boundary conditions of charge conservation in the electric flux in the double layer and the continuity of the potential from the double layer to the bulk electrolyte solution, the "polarised double layer" assumption of Dukhin.[8] Using $\psi = -E.\mathbf{x}$ far from the particle, where $\boldsymbol{x}$ is the position vector, the solution is[9]

$$\psi = -Er\cos\theta\left(1 - \frac{f^* a^3}{r^3}\right) \tag{7}$$

where

$$f^* = \frac{1 + i\omega' - \left(2Du + i\omega'\frac{\varepsilon_p}{\varepsilon_w}\right)}{2(1 + i\omega') + \left(2Du + i\omega'\frac{\varepsilon_p}{\varepsilon_w}\right)} \tag{8}$$

and $\omega' = \frac{\omega\varepsilon}{K^{\infty}}$. Here ε_p is the relative permittivity of the particle; for particles of low dielectric constant this term is insignificant.

The field due to the potential in eqn. (7) is the same as would be produced by a dipole in a uniform field with dipole strength

$s = -4\pi a^3 \varepsilon_0 f^* E$. Because E is approximately uniform except near the particles, the volume average field $\langle E \rangle$ can be used. For more concentrated suspensions a cell model must be used to account for particle-particle interactions. In this case:

$$S = \left(\frac{1}{4\pi\varepsilon_0 a^3} \frac{\langle S \rangle}{\langle E \rangle} \right) = -\frac{f^*}{1 + \phi f^*} \quad (9)$$

When $\omega \gg \frac{K^\infty}{\varepsilon}$, and for dielectric particles, the suspension behaves as a non-conductor and f^* reduces to the value for an uncharged particle, that is

$$f^* \approx \frac{\varepsilon_w - \varepsilon_p}{2\varepsilon_w + \varepsilon_p} = 0.5$$

If the particle permittivity, ε_p, were equal to that of the electrolyte solvent, ε_w, for example, the dipole strength would go to zero at high frequencies. The high frequency limit thus gives a measure of the permittivity of the colloidal particles.

For $\omega \ll \frac{K^\infty}{\varepsilon}$ $\left(\text{but } \omega \gg \frac{D}{a^2} \right)$, then the suspension behaves as a conductor provided the particles are charged. In this case f^* is approximately

$$f^* = \frac{1 - 2Du}{2(1 + Du)} \quad (10)$$

Hence the value of the dipole strength at this low frequency limit gives a measure of the surface conductance. In the absence of surface conductance $f^* = 0.5$ and $S = -0.5$.

Experimental

Materials

Samples of zeolite A and zeolite Y were gifts from Dr S. Carr (Sydney). The volume average median diameter and size distribution (68%) of the particles were obtained from transmission electron micrographs of a sample of about 150 particles of each type of zeolite. Zeolite A had a size of 3.1 μm (2.1–4.7 μm); zeolite Y had a size of 0.48 μm (0.33–0.70 μm).

Electroacoustic measurements

The zeolite particles were dispersed in UltraPure water at a volume fraction of 1–2% of solid material. This corresponds to a particle volume fraction of about 2–4% when the porosity of the zeolite structure is considered. The dispersions were sonicated for half an hour and shaken vigorously before use. The zeolite Y dispersion was measured at pH 9.00 and the zeolite A dispersion was measured at pH 8.50. The pH was maintained during the experiment to within ±0.05 of a pH unit by addition of drops of 1 M NaOH. Electroacoustic measurements were made on an Acoustosizer-I and flow through AZR-II (Colloidal Dynamics Inc, Warwick, RI).[3]

The zeolite samples used in the flow through cell were the same samples that had previously been measured on the AZR-I. After ageing for several months the supernatant was removed and MilliQ water added to replace the NaCl solution. The pH was then adjusted to pH 9 with NaOH (0.1 M) and the process of decanting-resuspending was repeated until the conductivity was sufficiently low (approximately 0.03 S m^{-1}). Water was added to give a total volume of approx. 80 mL and to ensure that the volume of particles in solution was approx. 5%. The samples were sonicated for 10 minutes and the pH readjusted to pH 9. The sample was contained within a condenser flask maintained at 25 °C with a water bath (Julabo, F20) and the sample was pumped during measurement. NaCl (1.0 M) was added dropwise to the desired conductivity and the pH maintained by addition of NaOH or HCl (0.1 M). After equilibration for 5 min the mobility was remeasured. The process of salt addition and pH adjustment was repeated until the conductivity was sufficiently high (approx. 0.5 S m^{-1}). The sample was then removed and the volume fraction determined by drying to a known mass to constant weight. The effect of the salt addition was ignored because the total volume added was less than 1 mL. The mobility was then reanalysed for the correct volume fraction.

In order to convert the measured electrokinetic sonic amplitude (ESA) into the dynamic mobility the density of the zeolites as given by Breck was used.[2] The hydrated particle densities are 1.99 g cm^{-3} for zeolite A and 1.92 g cm^{-3} for zeolite Y. A value for the permittivity of the zeolites was calculated using the imaginary component of the equation for the effective conductivity of a concentrated suspension of non-conducting spheres[6] given by

$$\varepsilon_p = \varepsilon_w \frac{(1 - \Phi)}{\left(1 + \frac{\Phi}{2}\right)} \quad (11)$$

where Φ is the fraction of solid material in a particle and $(1 - \Phi) \times 100\%$ is the percent porosity. (The porous particles are therefore treated as a dispersion of solid particles (the silica walls) in an electrolyte solution (the fluid in the pores), For zeolites A and Y the theoretical ε_p value is about 35.

The conductivity of the zeolite A dispersion was varied between 0.02 S m^{-1} and 0.26 S m^{-1} by addition of NaCl (1.9–21 mM). The zeolite Y dispersion was measured between 0.033 S m^{-1} (3.0 mM) and 0.51 S m^{-1} (47 mM). Background measurements were made on salt solutions at the same concentration and under the same conditions. This is to account for the ESA effect produced by the motion of the electrolyte ions in the alternating field.

Large particle effect

For solid particles of greater than about 1 μm in diameter and at high frequencies, the phase angles of the dynamic mobility need to be corrected for particles that are adsorbed onto the electrodes in the AcoustoSizer cell. Particles (of any size) that are close to the electrodes will experience a force due to their oppositely charged image in the electrode.[10] The particles are drawn towards the electrodes and stick onto them. They no longer move in the applied field and therefore do not contribute to the ESA signal. They also prevent other particles from approaching the electrodes and consequently the ESA signal, which is produced by the particles moving closest to the electrodes, have to travel further before being detected by the transducer. It has been determined experimentally that the signal has to travel an extra distance of about three particle radii, and this can result in a significant change in the phase information contained in the ESA signals.[11] The phase of the dynamic mobility is altered by $3ka$, that is

$$\mu_{\text{app}} = \mu_{\text{true}} \exp(-3ika) \quad (12)$$

where μ_{app} is the apparent dynamic mobility, μ_{true} is the dynamic mobility in the absence of this effect, a is the particle radius and $k = 2\pi/\lambda_s$, where λ_s is the sound wavelength. For particles where $a \ll \lambda_s$ the effect will not be significant.

For zeolite A, which has a particle size greater than 1 micron, the effect of the large particle correction on the argument is significant, especially at high frequencies where a phase change of +20 degrees can occur for a 3 micron particle. The experimental arguments were therefore first corrected for the large particle effect (using $a = 1.55$ μm) and then reanalysed using a spreadsheet version of the dynamic mobility calculation. This calculation also allows the inclusion of the effects of conduction behind the shear plane. It was necessary to include the effect of stagnant layer conduction to fit the data

to a constant size distribution for both zeolite samples and at all conductivities.

Dielectric response measurements

The complex conductivity of the zeolites was measured immediately after the low conductivity ESA measurements. The dielectric measurements were made on a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer (Tokyo, Japan). An alternating electric field is applied across a cell containing a colloidal dispersion and the *complex admittance* of the cell is measured. The admittance, $Y = G + iB$ is the ac analogue of conductance.

The reciprocal of the admittance is called the impedance, Z, and is the ac analogue of resistance. The admittance and impedance are complex quantities. The term G is the (in-phase) conductance, B the (out-of-phase) susceptance.[12]

In these experiments the field is applied over a frequency range of 0.1–40 MHz. These measurements were made on a flow through dielectric response cell which has not been previously reported in the literature. The cell used is an adaptation of a cell used by Midmore *et al.*[7] which was adapted from a cell used by Essex *et al.*[13] It consists of two brass electrodes of dimension $50 \times 18 \times 65$ mm separated by a Perspex spacer which has a circular hole to hold the sample. The volume of the hole is approximately 5 mL. The faces of the electrodes have been gold plated to prevent any chemical reaction at the surface.

The cell is connected directly onto the HP 4194A in order to reduce inductive effects from the leads. The measured impedance of a sample is affected by, for example, leakage paths and interactions in the lead wires. In order to find the true impedance of a sample, it is necessary to calibrate the cell before each use. Three calibration measurements are necessary to determine the cell constants. In this setup, three standard electrolytes were measured (10^{-3}, 10^{-2}, and 10^{-1} M KCl). This procedure is more accurate than the calibration of the static cell which consists of a short circuit measurement, an air measurement and the measurement of one standard electrolyte. This is because the static cell has to be disassembled after the short circuit measurement to introduce the perspex spacer and because the short circuit and air calibration involve the use of an estimated value of conductivity (∞ for the short circuit) and dielectric constant ($= 1$ for air).

The temperature of the cell was maintained by circulating water from a water bath at 25.0 °C through the brass electrodes. The sample was also maintained at 25 °C with a separate water bath. The sample was pumped from the AZR cell into the bottom of the dielectric response cell and back to the AZR cell. Care was taken to ensure that no air bubbles became entrapped during the calibration and measurement. The electrical admittance of the sample is then measured between 0.1 and 40 MHz using a Hewlett Packard 4194A impedance/gain-phase analyser. Since the flow through method requires a large volume of solution, and because the background electrolyte contains NaCl only, it was decided to simulate the background measurements. In this situation, $K^*_{\text{back}} = K^\infty + i\omega\varepsilon_0\varepsilon_w$. Both K^∞ and ε_w will therefore be frequency-independent. Since ε_w is tabulated for a given temperature, it remains only to vary the value of K^∞ for each measurement to obtain a suitable fit to the dipole.

Results

The magnitudes and the phase angles of the dynamic mobility of zeolite A at the 13 frequencies applied in the AcoustoSizer are shown in Fig. 1. The magnitude of the dynamic mobility is negative, which indicates that the zeta potential of zeolite A is negative. The dynamic mobility was measured at electrolyte conductivities from 0.02 to 0.26 S m^{-1}. The magnitudes

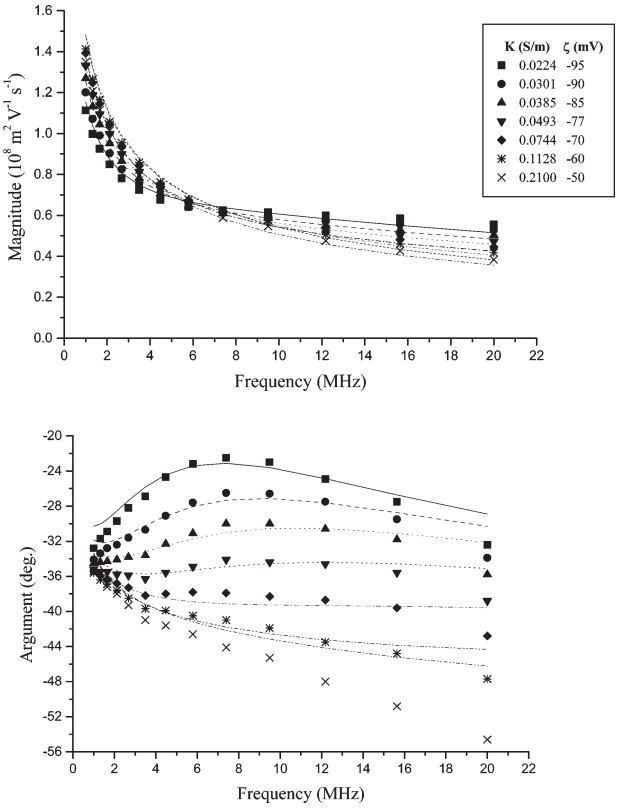

Fig. 1 Magnitude and argument of zeolite A in NaCl at pH 9. Theoretical fit to the mobility with the inclusion of conduction behind the shear plane but excluding the 'large particle effect'.

are slightly dependent on the salt concentration in an unusual way: the magnitudes increase with salt concentration at low frequencies. The usual behaviour is a decrease in magnitude as the increasing electrolyte concentration causes a decrease in the zeta potential.

The phase angles of the dynamic mobility are also unusual in two respects. The phase lag shows a maximum at low salt concentrations which decreases as the salt concentration is increased. And the phase lag is more negative than -45 ° at high frequency and at the highest salt concentrations. This is due to the "large particle effect" caused by particles adhering to the electrodes.[11] Despite this the fit to the mobility with the inclusion of stagnant layer conduction is good, except at the highest salt concentrations where the arguments increase beyond $-45°$, reaching $\sim -55°$ at 20 MHz. The theory does not allow for the argument to increase beyond $-45°$ even when there is conduction behind the shear plane.

The effect of the inclusion of the 'large particle effect' correction is shown in Fig. 2. Only the argument is affected by this correction such that the phase lag is not as large at high frequency. The fits to the dynamic mobility are now in very good agreement with the experimental spectra even at the highest salt concentrations. A median diameter of 3.1 μm with 68% of particles within the range 1.1–8.7 μm was found at all salt concentrations and the particle permittivity was found to be 35. As the salt concentration increased the zeta potential decreased from -118 mV to -77 mV. The size result agrees with the median size from TEM (3.1 μm). The 68% spread from TEM (2.1–4.7 μm) is slightly narrower than the result given by the AcoustoSizer software.

The dielectric response of zeolite A measured at the same salt concentrations and at the same time is shown in Fig. 3. The fits (lines) to the non-dimensional dipole are very good and a constant value of 35 for the dielectric constant of the particle was obtained at all salt concentrations. The value of Du is seen to decrease with added NaCl from a value of $\sim$1.9 to 0.45 over

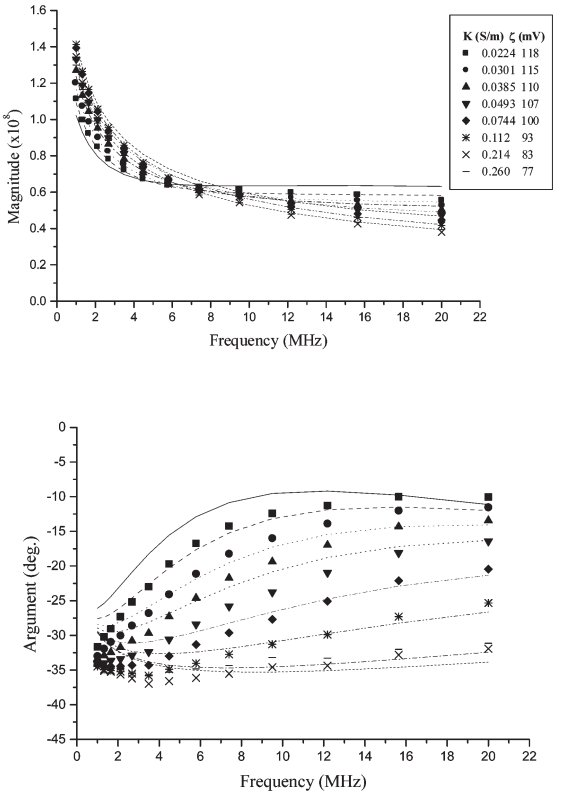

Fig. 2 Magnitude and argument of zeolite A in NaCl at pH 9. Theoretical fit to the mobility accounting for the 'large particle effect'.

the conductivity range measured. In Tables 1 & 2 the parameters for zeolite A required to fit the ESA and DR data are shown. The agreement between Du_{EA} and Du_{DR} is very good when conduction behind the stagnant layer is included in the fit of the dynamic mobility and when the large particle correction is applied (Table 2). When the large particle effect is not included then the agreement is poor (Table 1).

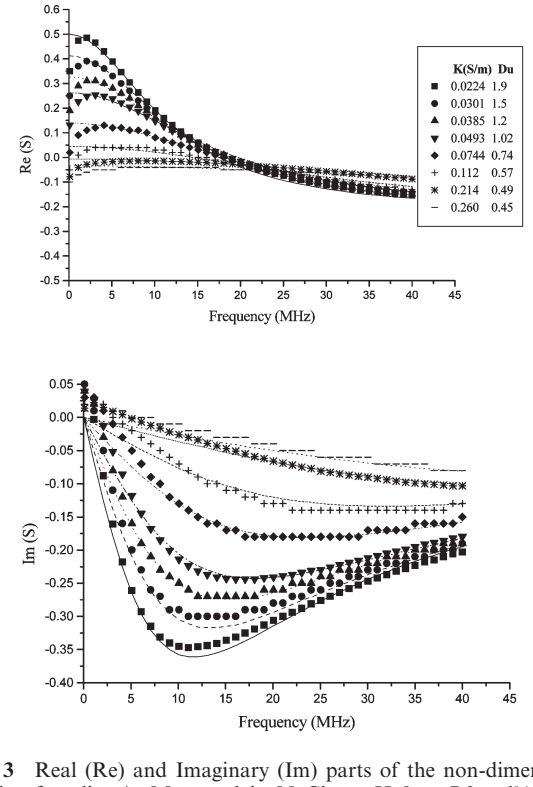

Fig. 3 Real (Re) and Imaginary (Im) parts of the non-dimensional dipole of zeolite A. Measured in NaCl at pH 9 at 7.3 vol%. Lines are theoretical fits to the dipole.

Table 1 Zeta potential and *Du* values of zeolite A as a function of NaCl concentration. Results obtained with the inclusion of stagnant layer conduction but excluding the large particle effect. Measured in NaCl at pH 9 at 7.3 vol% with $d_{50} = 3.6$ μm (2.0–6.5 μm)

K^{∞}/S m^{-1}	c/mM	ζ/mV	Du^{d}	q	Du_{EA}	Du_{DR}
0.0224	1.87	−95	0.027	35	0.95	1.9
0.0301	2.5	−90	0.020	35	0.70	1.5
0.0385	3.4	−85	0.016	35	0.55	1.2
0.0493	4.3	−77	0.011	35	0.38	1.0
0.0744	6.3	−70	0.007	30	0.21	0.74
0.1128	9.3	−60	0.004	20	0.08	0.57
0.210	17.3	−50	0.002	5	0.01	0.50

The experimental dynamic mobility spectra of zeolite Y dispersed in electrolyte solutions of 0.032 S m^{-1}–0.51 S m^{-1} are shown in Fig. 4. The magnitudes in this case increase with increasing salt concentration over almost the entire frequency range. The phase angles again show a dependence on the salt concentration, the phase lag increasing with increasing concentration. In this case with much smaller particles the phase lag is smaller and there is no large particle effect. Very good fits to the experimental data are obtained with the inclusion of stagnant layer conduction. A constant size of 0.61 (0.31–1.2 μm) was obtained at each electrolyte concentration, in fair agreement with the TEM value of 0.5 μm. The zeta potentials obtained from the fits show a maximum at intermediate conductivities and then decrease as expected at higher salt concentrations above 7 mM (Table 3).

The dielectric response of zeolite Y measured at pH 9 and at similar NaCl concentrations is shown in Fig. 5. The dipole was obtained by treating the background electrolyte as a parameter and adjusting K^{∞} along with ε_p and *Du* to obtain the best fit. It is clear that at low electrolyte concentration there is some other relaxation effect dominating the low frequency data and affecting the experimental dipole curves. As a result, the theory is unable to adequately describe the response at low conductivity. At higher salt concentrations better agreement between experiment and theory was obtained. A constant value of 30 for ε_p was found.

Very high *Du* values are required to fit both the electroacoustic and the dielectric results at low conductivities, and the agreement between the two techniques is poor (Table 3). At the higher conductivities, after the zeta potential has reached the maximum the agreement is good. Table 3 also gives the values of Du^{d} for each electrolyte concentration, which reflects the surface conductivity calculated from the zeta potential due to the excess charge in the double layer of a solid particle. Its very low value compared with Du_{EA} and Du_{DR} reflects the large stagnant layer conduction in these systems.

Table 2 Zeta potential and *Du* values of zeolite A as for Table 1 but with the inclusion the large particle effect with $d_{50} = 3.1$ μm (1.1–8.7 μm)

K^{∞}/S m^{-1}	c/mM	ζ/mV	Du^{d}	q	Du_{EA}	Du_{DR}
0.0224	1.87	−118	0.060	30	1.8	1.9
0.0301	2.5	−115	0.048	32	1.55	1.5
0.0385	3.4	−110	0.038	34	1.3	1.2
0.0493	4.3	−107	0.031	35	1.1	1.0
0.0744	6.3	−100	0.022	38	0.84	0.74
0.1128	9.3	−93	0.015	43	0.66	0.57
0.210	17.3	−83	0.009	65	0.57	0.50
0.256	21.3	−77	0.007	83	0.57	0.45

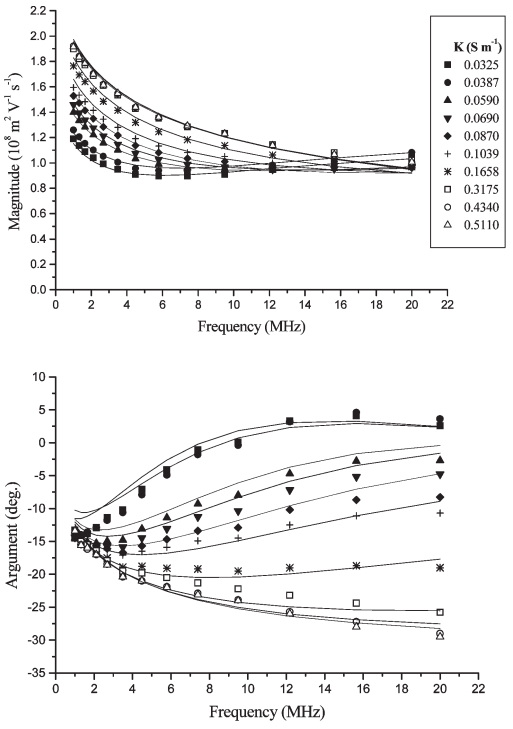

Fig. 4 Magnitude and argument of zeolite Y in NaCl at pH 9. Theoretical fit to the mobility with the inclusion of conduction behind the shear plane.

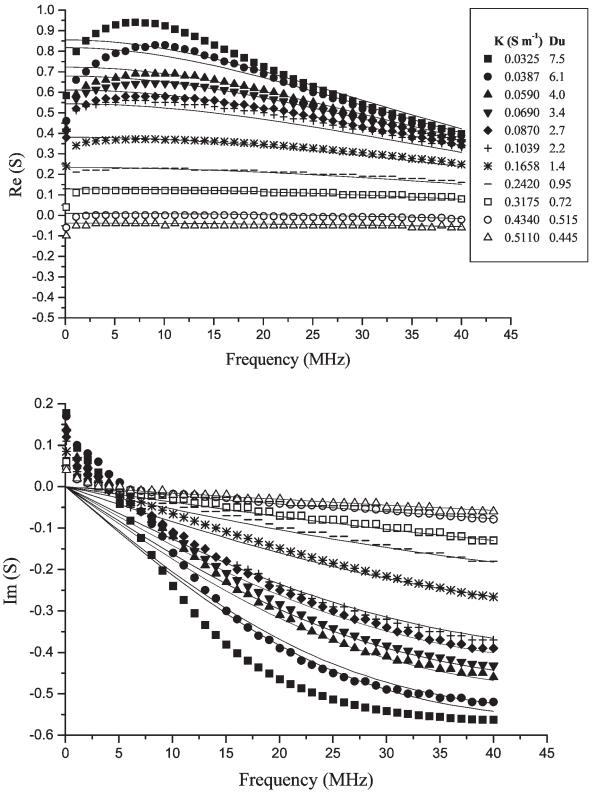

Fig. 5 Real (Re) and Imaginary (Im) parts of the non-dimensional dipole of zeolite Y. Measured in NaCl at pH 9 at 4.5 vol%. Lines are theoretical fits to the dipole.

Discussion

The dynamic mobility spectra of zeolite A is unusual in two respects. The first is the observation of phase angles considerably larger than −45° for the highest conductivity suspensions (Fig. 1). As described above, this arises from large particles adhering to the electrode, effectively causing an increase in the acoustic pathlength to the measuring transducer. Correction for this effect gives the data shown in Fig. 2, all of which can be fitted with a single mean particle size of 3.1 μm, in agreement with a size of 3.1 μm observed by TEM. This gives some confidence in the validity of the large particle effect correction. No such effect is seen in the dynamic mobility spectra of suspensions of zeolite Y (Fig. 4) because the particles are much smaller, with a mean size obtained from analysis of the electroacoustic data of 0.61 μm, compared with that from TEM estimated to be 0.5 μm.

The second aspect is the unusual effects of increasing the electrolyte concentration of the aqueous suspending medium. Typically the effect of increasing salt conductivity is to decrease the magnitudes of the dynamic mobility due to a decrease in the absolute zeta potential, and to have little effect on the phase angles, because the size of the particles is not changed by the addition of salt.

For the zeolite suspensions the magnitudes increase with salt concentration, at the low frequencies for zeolite A (Fig. 2) and across almost the entire frequency range for zeolite Y (Fig. 4). This is ascribed to the very large surface conductivity of these particles. For these suspensions in which the surface conductivity is large relative to the bulk electrolyte conductivity (*i.e.* with a large *Du* number), much of the applied field passes through the particle and does not contribute to the dynamic mobility. As the electrolyte concentration increases, more of the applied field is directed tangentially to the particle surface and the magnitude increases. This effect is smaller for zeolite A, with larger particles, than for zeolite Y, because the *Du* number varies inversely with particle size. In both cases at the highest salt concentrations (lowest *Du* numbers) the magnitudes decrease with frequency in the normal way.

The second effect of the large surface conductivity is seen in the phase angles. At low salt concentrations there is an increase in phase angle with frequency, which in the case of zeolite Y actually leads to positive phase angles, a phase lead. As the salt concentration increases this effect diminishes until at the highest conductivities the phase angles reach limiting values.

The origin of the phase lead is illustrated in Fig. 6. When the electric field E is applied, water molecules are polarised rapidly, at GHz frequencies, to create a back field 180° out of phase with the applied field. Counterions in the double layer are polarised more slowly, at MHz frquencies, in what is termed the Maxwell relaxation, which corresponds to a phase lag in the back field, B. The phase lag of the electroacoustic effect on the resultant electric field R can then appear as a phase lead.

The large back field in these zeolite suspensions arises from a very large stagnant layer conduction. Stagnant layer conduction in solid particles is the ionic conduction that occurs inside

Table 3 Zeta potential and *Du* values of zeolite Y from EA and DR as a function of NaCl concentration. Results obtained with the inclusion of stagnant layer conduction. Measured in NaCl at pH 9 at 4.5 vol% with d_{50} = 0.61 μm (0.31–1.0 μm)

K^{∞}/S m^{-1}	c/mM	ζ/mV	Du^d	q	Du_{EA}	Du_{DR}
0.0325	2.7	−70	0.062	42	2.6	7.5
0.0387	3.2	−75	0.069	41	2.8	6.1
0.0590	4.9	−79	0.063	41	2.6	4.0
0.0690	5.8	−85	0.069	38	2.6	3.4
0.0870	7.3	−88	0.067	39	2.6	2.7
0.1039	8.7	−82	0.054	44	2.1	2.2
0.1658	13.8	−70	0.028	50	1.4	1.4
0.3175	26.5	−55	0.012	60	0.72	0.72
0.434	36.1	−48	0.008	65	0.52	0.52
0.511	42.5	−45	0.006	75	0.45	0.45

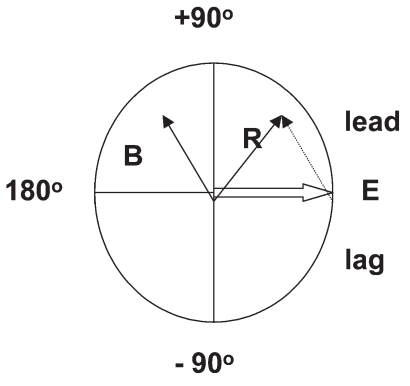

Fig. 6 Resultant vector R of the applied field E and backfield B.

the shear plane from which the zeta potential is measured.[14] In these microporous zeolites it extends to the ionic conduction of the sodium counterions within the micropores.[15,16]

The dynamic mobility spectra could not be fitted to the electroacoustic theory with the surface conductivity value of Du^{d} calculated from the zeta potentials. Instead a scaling factor q was applied that allows the Du value to increase without a concomitant increase in the zeta potential, *i.e.*

$$Du_{EA} = qDu^{d} = Du^{i} + Du^{d}$$

where Du^{i} is a measure of the inner, stagnant layer conduction. Quite large values of q were required (Tables 1–3), reflecting the large internal surface area of the zeolites.

The value of q (and Du_{EA}) was determined by applying a constant size constraint to the fits to the dynamic mobility spectra over the range of salt concentrations. Without this constraint the calculated size and zeta potentials vary in physically unreasonable ways. An independent value of Du can be obtained from the dielectric response measurements, which sample the entire electrical conductivity of the suspension and not just that outside of the shear plane as does the electroacoustic measurement. Table 1 shows that before the large particle correction is applied there is not very good agreement between Du_{EA} and Du_{DR}, but that after that correction is applied (Table 2) the agreement is much better. The Du values decrease as the salt concentration and hence the bulk conductivity increases, as expected, but not as rapidly as the falling zeta potential decreases Du^{i}, so the q value increases.

For zeolite Y the agreement between the electroacoustic and dielectric response Du values is not so good at low conductivities but is good above about 7 mM salt. This may be due to the presence of an additional low frequency relaxation process seen in the dielectric response spectra (Fig. 5) but not included in the analysis. This could be the high frequency tail of the ionic diffusion relaxation process which typically occurs at kHz frequencies, but which frequency increases as the size of the particle decreases. It was not apparent in the dielectric spectra of the larger zeolite A particles.

The zeta potentials of zeolite A are large at low salt concentrations and decrease monotonically with increasing electrolyte, as expected. For zeolite Y there is again an anomaly at low salt concentrations with the zeta potential reaching a maximum of −88 mV at 7 mM salt and then decreasing as expected with increasing electrolyte concentration.

In summary, the electroacoustic spectra reveal that the electrokinetic behaviour of these microporous zeolite suspensions is strongly affected by internal ionic conduction, which can be interpreted as stagnant layer conduction. When this is taken into account satisfactory analysis of the dynamic mobility spectra can be achieved. The validity of the analysis is confirmed by independent evaluation of the surface conductance by dielectric response measurements.

We conclude that stagnant layer conduction must be considered in interpreting electrokinetic measurements of zeolite suspensions, and that, conversely, such measurements can be used to probe the internal conduction of hydrated microporous materials.

Acknowledgements

We thank a referee of an earlier version of this paper for suggesting the interpretation of significant surface conduction. We also acknowledge helpful earlier discussions with Drs Hunter, O'Brien and Rowlands at Colloidal Dynamics. This work was supported by an Australian Postgraduate Award to SG and by a grant from the Australian Research Council.

References

1 T. Mäurer, S. P. Müller and B. Kraushaar-Czarnetzki, *Ind. Eng. Chem. Res.*, 2001, **40**, 2573.
2 D. W. Breck, *Zeolite Molecular Sieves. Structure, Chemistry, and Use.*, John Wiley and Sons, New York, 1974.
3 R. W. O'Brien, D. W. Cannon and W. N. Rowlands, *J. Colloid Interf. Sci.*, 1995, **173**, 406.
4 R. W. O'Brien, *J. Colloid Interf. Sci.*, 1995, **171**, 495.
5 S. E. Gibb, *The electroacoustics of porous particles*, PhD thesis, University of Sydney, 2001.
6 R. W. O'Brien, *J. Colloid Interf. Sci.*, 1986, **113**, 81.
7 B. R. Midmore, R. J. Hunter and R. W. O'Brien, *J. Colloid Interf. Sci.*, 1987, **120**, 210.
8 S. S. Dukhin and V. N. Shilov, *Dielectric Phenomena and the Double Layer in disperse systems and Polyelectrolytes*, Wiley, New York, 1974.
9 C. T. O'Konski, *J. Phys. Chem.*, 1960, **64**, 605.
10 R. J. Hunter, *Foundations of Colloid Science Volume I*, Oxford University Press, New York, 1989.
11 T. Wade and J. K. Beattie, *Colloids Surf. B*, 1997, **10**, 73.
12 N. Balabanian, *Fundamentals of Circuit Theory*, Allyn and Bacon, Boston, 1961.
13 C. G. Essex, G. P. Smith, R. J. Sheppard and E. H. Grant, *J. Phys. E.*, 1975, **8**, 385.
14 J. Lyklema, *J. Phys.: Condens. Matter*, 2001, **13**, 5027.
15 D. C. Freeman Jr. and D. N. Stamires, *J. Chem. Phys.*, 1961, **35**, 799.
16 D. A. Faux, *J. Phys. Chem. B*, 1998, **102**, 10 658.