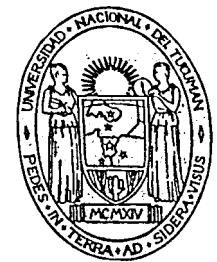


EXPERIMENTAL DETERMINATION OF THE LOW AND HIGH-FREQUENCY DIELECTRIC DISPERSION PARAMETERS OF AQUEOUS SUSPENSIONS OF LATEX PARTICLES FOR DIFFERENT COUNTERION AND CO-ION DIFFUSION COEFFICIENTS

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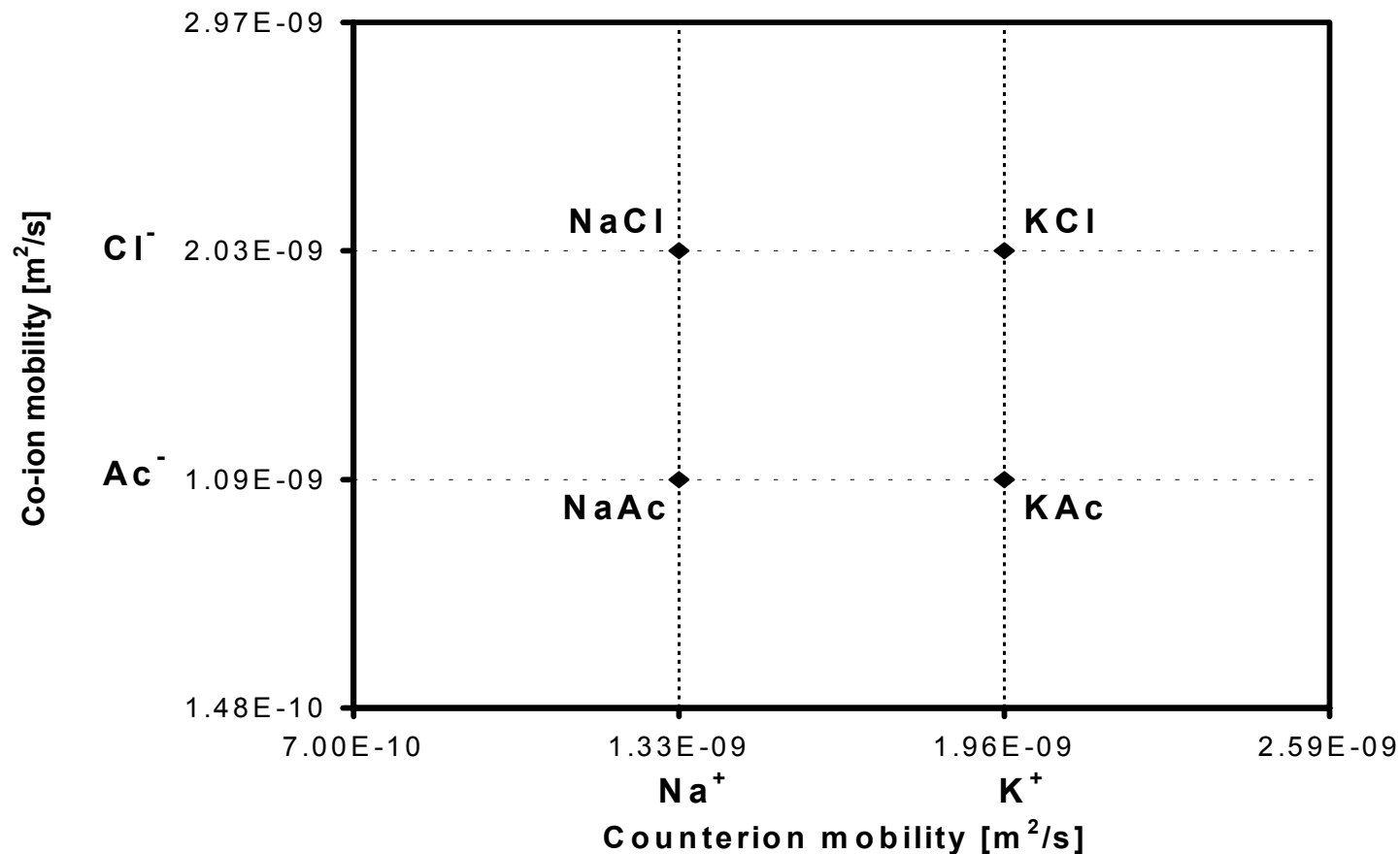
AIMS

- **To measure the low and high frequency dielectric dispersion parameters of monodispersed polystyrene particle suspensions for different counterion and co-ion diffusion coefficients at 25 °C.**
- **To describe and interpret the dielectric behavior using the experimental results, theoretical models, and numerical calculations.**

MATERIALS AND METHODS

Four aqueous electrolyte solutions were prepared using equal molar concentrations (0.29 mM) of **NaCl**, **KCl**, **NaAc**, and **KAc**.

The electrolyte solutions were selected in order to have symmetrical and non symmetrical solutions in what concerns with the diffusion coefficient:



The suspensions were prepared using the electrolyte solutions and **polystyrene particles** (Interfacial Dynamics Corp., surfactant-free white sulfate latex) of **radius $a = 0.5 \mu\text{m}$** and $0.012 \mu\text{m}$ standard deviation. In all the suspensions, the particle **concentration** was **1%** in volume.

The value of $\kappa a = \sqrt{\frac{2e^2 C_{\infty}^{\pm}}{\epsilon_0 \epsilon_e kT}} a$ was constant and equal to **28** for the temperature of the measurements (**$25 \pm 0.2^\circ\text{C}$**).

The measurements were made in the **frequency range** between **100 Hz** and **10 MHz** using a **Hewlett Packard 4192A Impedance Analyzer** under computer control.

The **variable spacing measurement cell** has flat 15 mm diameter **electrodes of platinum recovered with platinum black** and is connected to the instrument using coaxial cables in the Five-Terminal Pair configuration (5T) [*Honda, Hewlett Packard, Yokogawa (1989)*].

All measurements were performed using the same pair of electrodes that were platinized prior to each measurement.

The distance between electrodes should be adjusted depending on the conductivity of the sample. In this case the conductivity was low ($\sigma \approx 0.004$ S/m), so we used **shorter spacing** values to avoid stray field effects: **between 3 and 1 mm** in 0.5 mm intervals [*Tirado, Arroyo, Delgado, Grosse, J. Colloid Interface Sci., 227, 141 (2000)*].

The **calibration** of the instrument was made using the **cuadрупolar method** [*Grosse, Tirado, IEEE Trans. Instrumentation and Measurement, 50, 5 (2001)*], besides the standard short and open circuit calibration, using the cell filled with the electrolyte solution as a load.

CORRECTIONS TO THE VARIABLE SPACING TECHNIQUE

The variable spacing technique is based on the assumption that the measurement cell impedance increases linearly with the electrode spacing. Unfortunately, this relationship is not exact but a good approximation. The main reason is the variable thickness of the volume charge close to the electrodes, that depends on the value of the conduction current density in the cell, which is related to the electrode spacing.

The measurements are usually made using a constant value for the oscillator voltage U , while the value of the conduction current I^* flowing across the sample increases when the electrode spacing decreases. In this study, the measurements were made keeping the real part of I^* constant, so that, at each electrode spacing and at each frequency, U was adjusted accordingly.

A notable improvement in the experimental results was achieved by implementing constant current measurements (Figure 1).

Suspension of latex particles in aqueous KCl electrolyte solutions

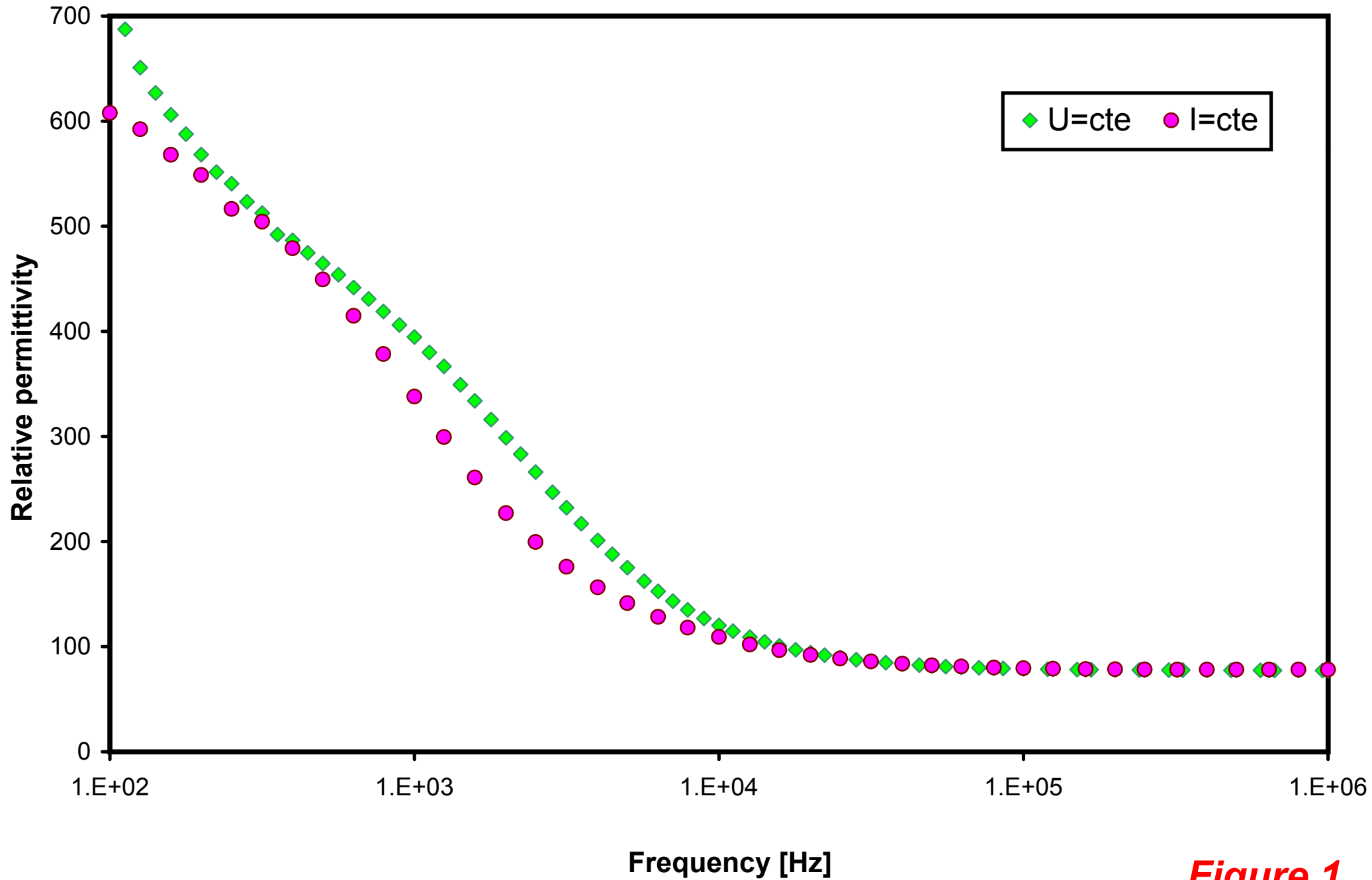


Figure 1

EXPERIMENTAL RESULTS

- The experimental permittivity and conductivity spectra, for different counterion and co-ion diffusion coefficients appear in figures 2 to 5. They clearly show two dispersion regions.
- The strong permittivity increase at low frequencies corresponds to the alpha dispersion. The variable spacing technique, combined with a Short-Open-Load calibration performed at all the measurement frequencies using a load impedance value close to that of the sample, assures that this increase is not due to an electrode polarization artifact.
- Furthermore, a second dispersion region exists at around 1 MHz that corresponds to the Maxwell-Wagner-O'Konski relaxation.

- The experimental data were analyzed considering the Nettelblad-Niklasson expression [*J. Colloid Interface Sci.* 181, 165-168 (1996)] combined with a Debye type high frequency term:

$$\varepsilon_s(\omega) = \varepsilon_{s\infty} + \nu \left[\frac{\delta\varepsilon_L (1+W)}{(1+W)^2 + W^2 (1+SW)^2} + \frac{\delta\varepsilon_H}{1+(\omega \tau_H)^2} \right] \quad \text{s}\equiv\text{suspension; L}\equiv\text{low; H}\equiv\text{high}$$

$$\sigma_s(\omega) = \sigma_s(0) + \nu \left[\frac{\varepsilon_0 \delta\varepsilon_L \omega W (1+SW)}{(1+W)^2 + W^2 (1+SW)^2} + \frac{\varepsilon_0 \delta\varepsilon_H \omega^2 \tau_H}{1+(\omega \tau_H)^2} \right] \quad W = \sqrt{\frac{\omega \tau_L}{S}}$$

$\sigma_s(0)$ \equiv low-frequency conductivity of the suspension, $\varepsilon_{s\infty}$ \equiv high-frequency permittivity of the suspension, ν \equiv volume fraction occupied by the particles.

- The fitted curves are shown in figures 2 to 5 together with the experimental data.
- The fitted values of the 7 macroscopic parameters appear in Table A. The value of the parameter S had to be set equal to one, since it could not be determined in view of the precision of the experimental data.

Suspension of latex particles in aqueous KAc electrolyte solutions

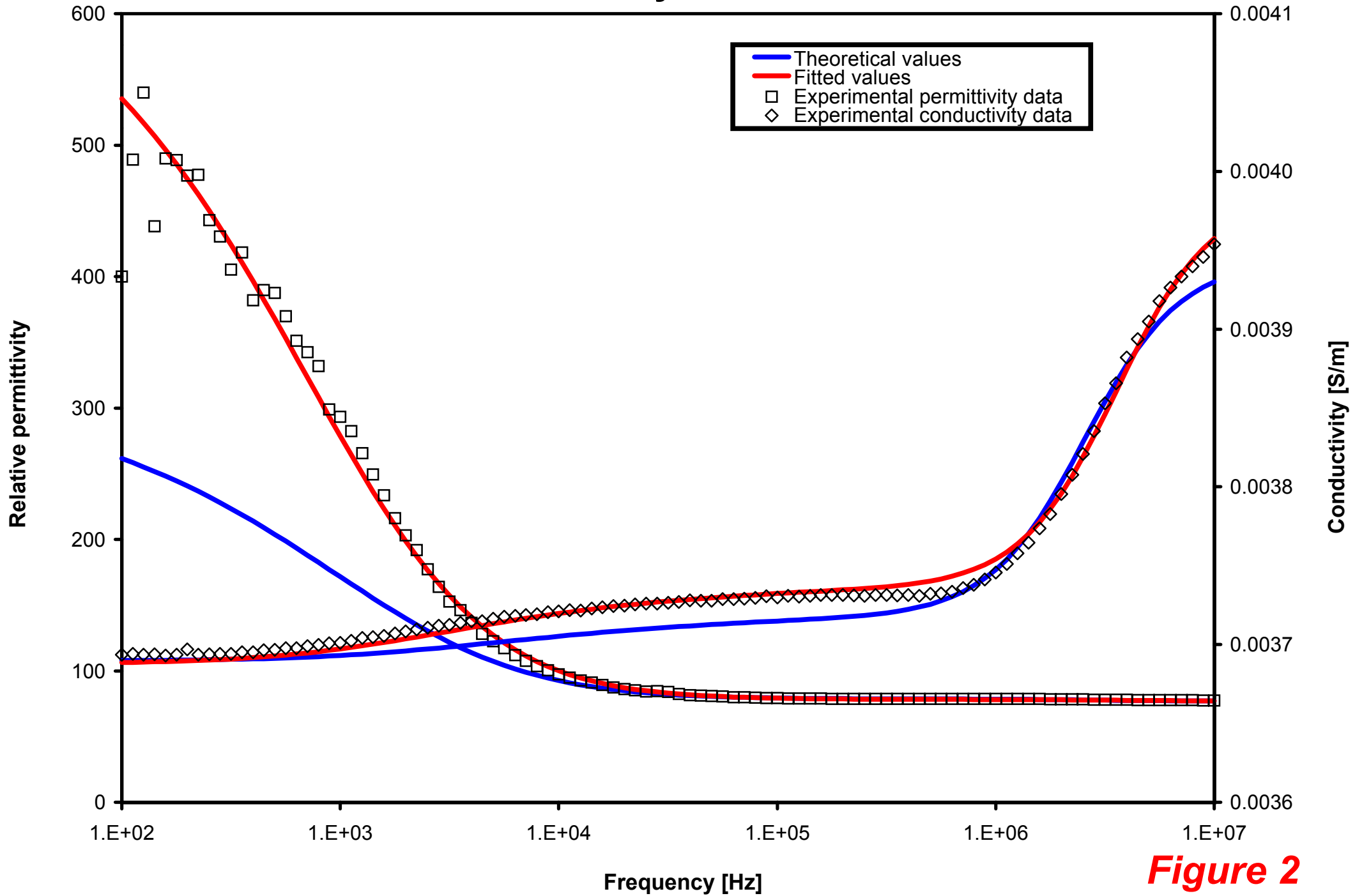


Figure 2

Suspension of latex particles in aqueous KCl electrolyte solutions

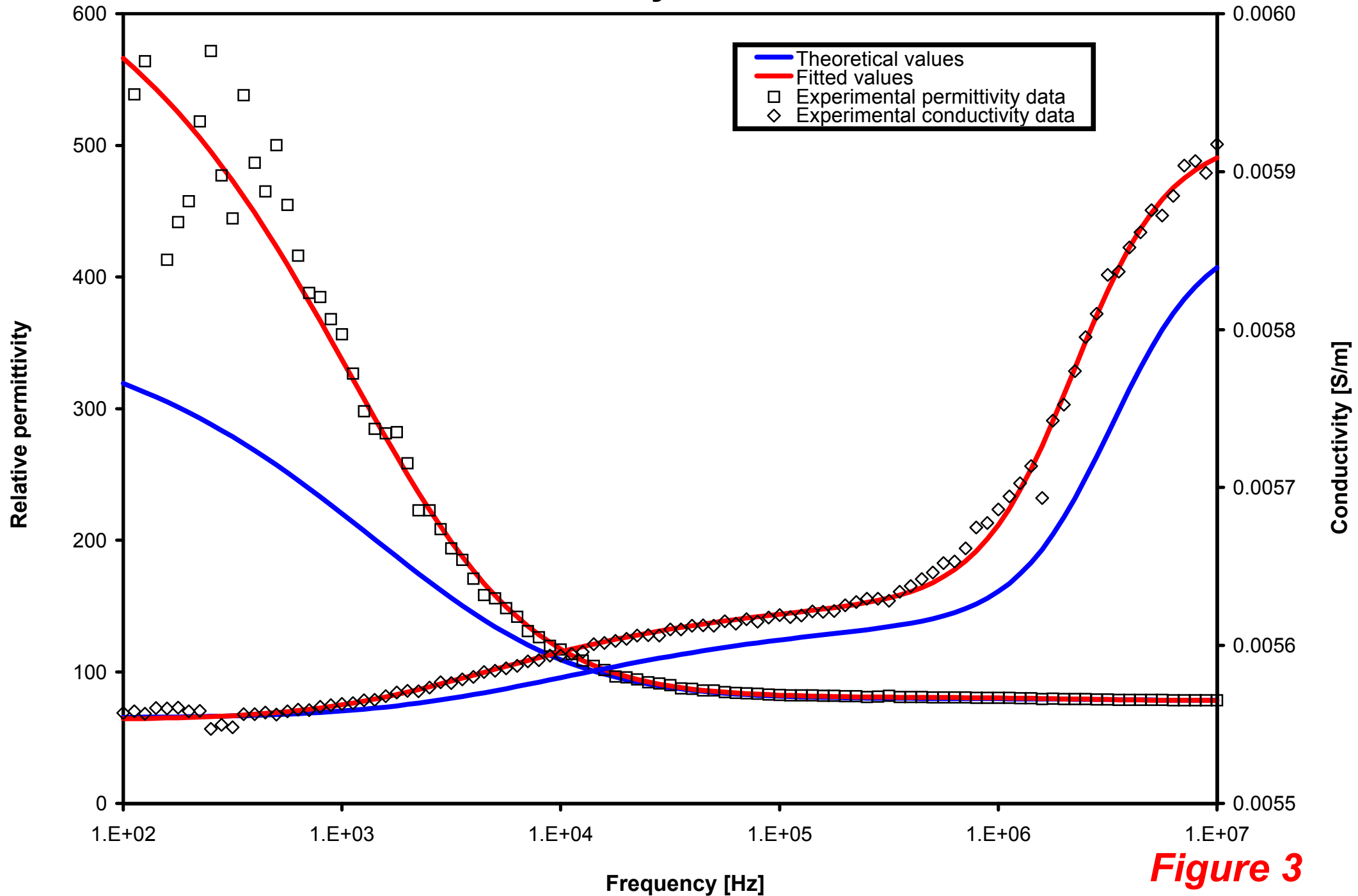


Figure 3

Suspension of latex particles in aqueous NaAc electrolyte solutions

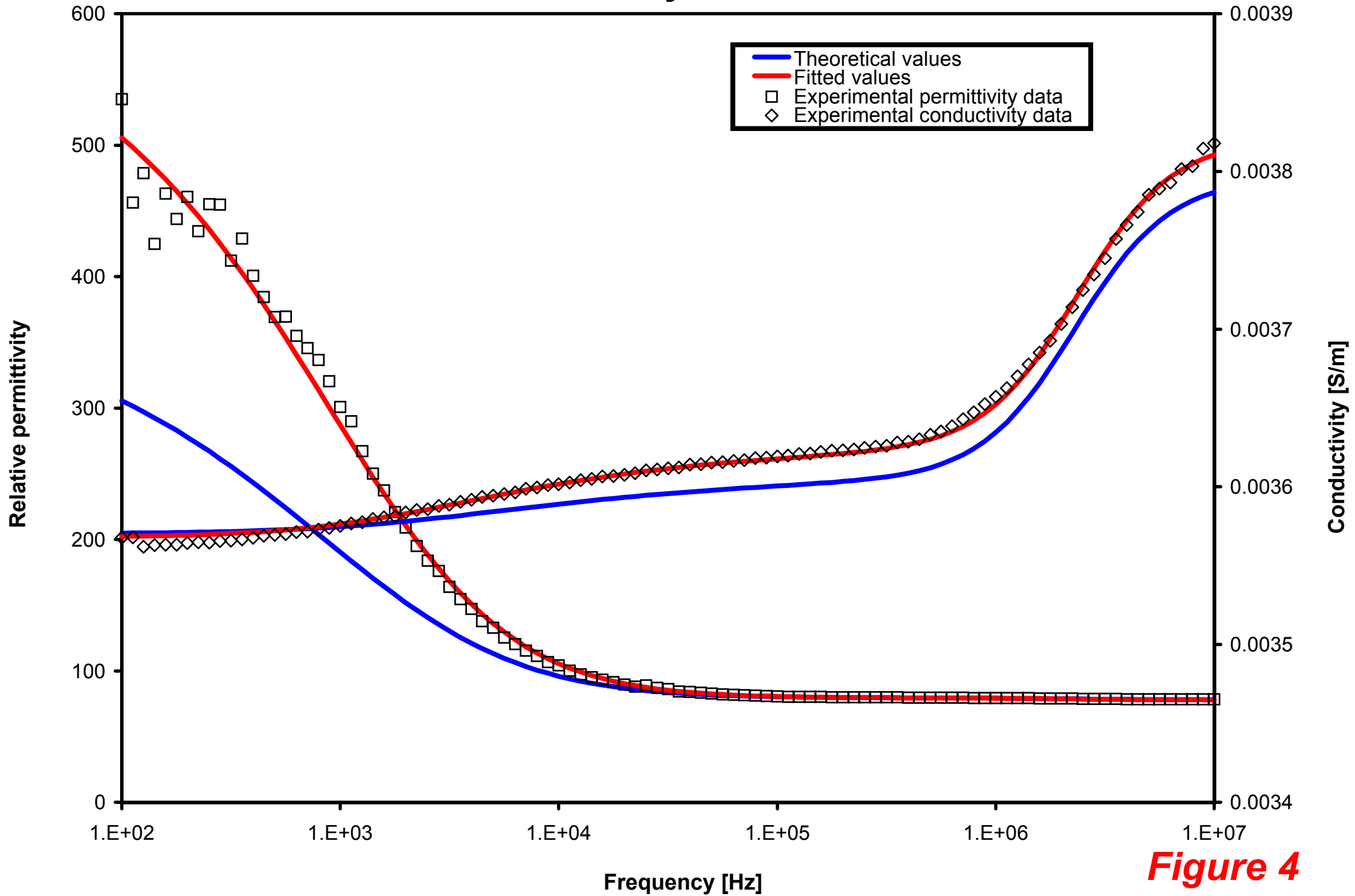


Figure 4

Suspension of latex particles in aqueous NaCl electrolyte solutions

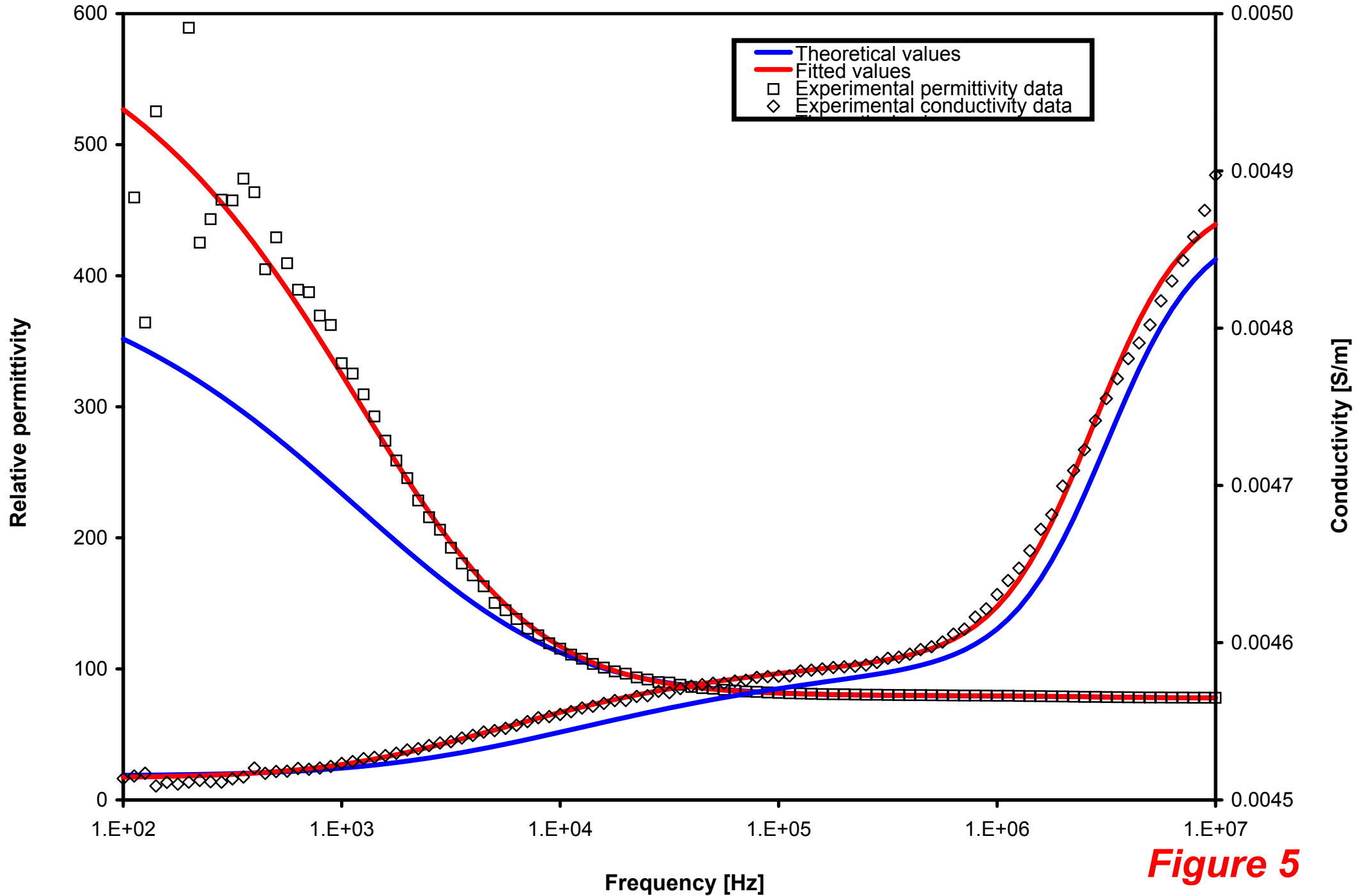


Figure 5

TABLE A: Fitted parameter values

Suspension of latex particles in aqueous electrolyte solution of:	KAc	KCl	NaAc	NaCl
$\varepsilon_{s\infty}$	77.0	78.1	77.8	77.6
$\delta\varepsilon_L [10^4]$	6.16	6.13	5.53	5.57
$\delta\varepsilon_H$	125	236	148	193
$\tau_L [10^{-5} s]$	10.9	6.96	8.55	6.30
$\tau_H [10^{-8} s]$	4.46	7.14	6.68	5.78
$\sigma_s(0) [10^{-3} S/m]$	3.69	5.55	3.57	4.51

DISCUSSION

- The Nettelblad-Niklasson expression allows a direct comparison with the theoretical predictions of the Dukhin-Shilov model [*Dukhin, Shilov, "Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes" (1974)*].
- In order to obtain the theoretical parameters it was not possible to choose the ζ potential values that best reproduced the LFDD because, the measured dielectric increments are higher than the maximum predicted by the theory. Therefore, the ζ potential values were chosen to best reproduce the high-frequency dispersion.
- The theoretical parameters so obtained appear in Table B.
- The theoretical curves are shown in figures 2 to 5 together with the experimental data.

TABLE B: Theoretical parameters values

Suspension of latex particles in aqueous electrolyte solution of:	KAc	KCl	NaAc	NaCl
g_L	-0.290	-0.390	-0.356	-0.553
g_H	0.996	0.916	0.963	1.00
$\tau_L [10^{-5} s]$	7.02	4.11	7.39	4.14
$\tau_H [10^{-8} s]$	6.19	4.84	6.89	5.01
$K_{d\infty}$	-0.481	-0.481	-0.481	-0.481
$\zeta [mV]$	-180	-185	-180	-200

- The disagreement between theory and experiment is not due to the approximations made in the Shilov-Dukhin analytical solution because numerical calculations give results that are undistinguishable from the theoretical ones for the studied systems.