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Historical Perspective

Electrokinetic detection of the salt-free condition in colloids. Application to polystyrene latexes<sup>☆</sup>A.V. Delgado<sup>a,\*</sup>, S. Ahualli<sup>a</sup>, F.J. Arroyo<sup>b</sup>, M.L. Jiménez<sup>a</sup>, F. Carrique<sup>c</sup><sup>a</sup> Departamento de Física Aplicada, Facultad de Ciencias, and MNat Unit of Excellence, Universidad de Granada, 18071 Granada, Spain<sup>b</sup> Departamento de Física, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain<sup>c</sup> Departamento de Física Aplicada I, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

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## ABSTRACT

Because of their singular phenomenology, the so-called salt-free colloids constitute a special family of dispersed systems. Their main characteristic is that the dispersion medium ideally contains only the solvent and the ions compensating exactly the surface charge of the particles. These ions (often called released counterions) come into the solution when the surface groups responsible for the particles charge get ionized. An increasing effort is nowadays dedicated to rigorously compare theoretical model predictions for ideal salt-free suspensions, where only the released counterions are supposed to be present in solution, with appropriately devised experiments dealing with colloids as close as possible to the ideal salt-free ones. Of course, if the supporting solution is aqueous, the presence of atmospheric contamination and any other charged species different from the released counterions in the solution must be avoided. Because this is not an easy task, the presence of dissolved atmospheric CO<sub>2</sub> and of H<sup>+</sup> and OH<sup>-</sup> from water dissociation cannot be fully discarded in aqueous salt-free solutions (often denominated realistic in such case). Ultimately, at some point, the role of the released counterions will be comparable or even larger in highly charged concentrated colloids than that of added salts. These topics are covered in the present contribution. The model results are compared with experimental data on the dynamic mobility and dielectric dispersion of polystyrene spheres of various charges and sizes. As a rule, it is found that the model correctly predicts the significance of alpha and Maxwell-Wagner-O'Konski relaxations. Positions and amplitudes of such relaxations are well predicted, although it is necessary to assume that the released counterions are potassium or sodium instead of protons, otherwise the frequency spectra of experimental mobility and permittivity differ very significantly from those theoretically calculated. The proposed electrokinetic evaluation is an ideal tool for detecting in situ the possible contamination (or incomplete ion exchange of the latexes). A satisfactory agreement is found when potassium counterions are assumed to be in solution, mostly if one considers that the comparison is carried out without using any adjustable parameters.

## 1. Introduction

Disperse systems ideally containing only the dispersed entities and the counterions (*added* or *released* counterions hereafter) released by them when surface charge is generated (salt-free colloids), are gaining interest because of the many physical phenomena and applications in which they are involved, particularly in the biomedical field. For instance, it can be recalled that the electro-hydrodynamic separation of DNA from BSA is favoured in salt-free solutions [1], or that the dyeing of cotton is improved while wastewater contamination is reduced if the

dyeing is performed in salt-free media [2,3]. Salt-free extraction of biosurfactants produced by *Lactobacillus pentosus* is advantageous because the presence of sodium chloride is phytotoxic [4]. Stabilization of halobacteria cells in media deprived of salt allows to precisely determine the protein content and biomass of the bacterial cells [5]. More fundamental phenomena can also be mentioned, such as the non-monotonic dependence between the electrophoretic mobility of particles and their volume fraction in suspension [6], the formation of ordered phases undergoing phase transitions at low volume fractions, resembling molecular or atomic crystals (thus named colloidal crystals

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or glasses [7–11]), or the different frequency relaxations of the particles' electrical polarization as compared to usual, added salt suspensions [12–14]. This explains the increasing interest in understanding the phenomena associated to salt-free systems, particularly their electrokinetic properties, that is, those associated to the response of the colloids to the application of external electric fields, notably if these are alternating ones [15].

Many of the phenomena involved in the examples mentioned regard concentrated colloids, i.e., those in which the volume fraction of the suspended particles is above roughly 1%. Here the theory of electrokinetic phenomena in such systems comes into play. Obvious complications related to hydrodynamic and electrical interactions between particles, and even to proper definitions of the main quantities of interest, arise in these systems, already in the “simpler” case of colloids in added-salt solutions [16–18].

Because of the importance of external salt control in systems that we think as salt-free, it is an essential step to check that no contamination has occurred during the colloid manipulation. If ions from water dissociation and atmospheric CO<sub>2</sub> dissolution are considered, the resulting colloid is denominated *realistic salt-free*. In this work, we propose to use electrokinetics in ac fields with those checking purposes. We start with a model and calculation previously elaborated by the authors dealing with alternating current (or ac-) electrophoresis and electric permittivity of the colloid (concentrated and salt-free) as a function of the frequency of the field in the linear-response regime [15]. Experiments will be performed for evaluating both quantities in polystyrene latexes of different particle diameters and surface charges. The comparison between the theoretical results and the experimental determinations will show that “contamination” of otherwise salt-free suspensions can be unequivocally detected.

## 2. Theoretical background

Our target system will be a colloid composed of spherical particles of radius  $a$  and surface charge density  $\sigma_p$ , electric permittivity  $\epsilon_p$ , and mass density  $\rho_p$ , with volume fraction of solids  $\phi$ . The particles are dispersed in an aqueous medium (mass density  $\rho_m$ , electric permittivity  $\epsilon_m$ , viscosity  $\eta_m$ ) containing those ions produced by the generation of  $\sigma_p$  (released counterions with charge  $z_e e$ , opposite in sign to  $\sigma_p$ , being  $e$  the elementary charge) plus H<sup>+</sup> and OH<sup>-</sup> from water dissociation, and H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> from atmospheric CO<sub>2</sub> dissolution. Eventually, external salt (KCl) may be added at known concentration. Ideally, the released counterions will be H<sup>+</sup>, assuming that exhaustive dialysis against water of the samples fully exchanges potassium ions from the initiator (typically potassium persulfate, also responsible for the sulfate end-groups on the particles) by protons from water. The interactions between the particles will be accounted for by using the Kuwabara's cell model [17,19], according to which the mentioned interactions can be simulated by studying a single particle confined in a sphere of fluid concentric with it and with radius  $b$  such that the particle volume fraction in the cell is made coincident with that of the whole colloid: ( $\phi = (a/b)^3$ ).

An external electric field varying harmonically with frequency  $\omega$ ,  $\mathbf{E}e^{-i\omega t}$  is assumed to be applied to the suspension. As a result of the action of the field on both the particle and its ionic atmosphere (forming the electrical double layer, EDL, altogether), the particle will move with its electrophoretic velocity  $\mathbf{v}_e e^{-i\omega t}$  (with the same frequency as the field, but with certain phase lag, so that  $\mathbf{v}_e$  will be a complex quantity, and the same will happen to the (dynamic or ac-) electrophoretic mobility  $u_e$ , defined by the relation  $\mathbf{v}_e = u_e \mathbf{E}$ ). Only the basic equations and boundary conditions will be shown here. The details of the equations linearization can be found in previous works [15,20–22]. The equations are:

### a) Poisson equation

$$\nabla^2 \Psi(\mathbf{r}, t) = -\frac{\rho_{elec}}{\epsilon_m} \quad (1)$$

$$\rho_{elec} = \sum_{j=1}^5 z_j n_j(\mathbf{r}, t)$$

where  $\Psi(\mathbf{r}, t)$  is the electric potential at position  $\mathbf{r}$  and time  $t$ , and the volume charge density in the liquid medium,  $\rho_{elec}$ , is given in terms of the number concentrations  $n_j$  of all ions present, namely, H<sup>+</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> ( $j = 1, 2, 3$ ), and, as mentioned, K<sup>+</sup> and Cl<sup>-</sup> ( $j = 4, 5$ ) if salt is added to the realistic salt free case. The possibility that K<sup>+</sup> is present as released counterion (instead of H<sup>+</sup>) will also be considered.

### b) Navier-Stokes equation for incompressible fluid

$$\rho_m \frac{\partial}{\partial t} [\mathbf{v}(\mathbf{r}, t) + \mathbf{v}_e \exp(-i\omega t)] = \eta_m \nabla^2 \mathbf{v}(\mathbf{r}, t) - \nabla p(\mathbf{r}, t) - \rho_{elec}(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0 \quad (2)$$

where  $\mathbf{v}(\mathbf{r}, t)$  is the fluid velocity with respect to the particle, and  $p$  is the local pressure.

### c) Nernst/Planck equations for the transport of ions ( $j = 1, \dots, 5$ )

$$\mathbf{v}_j(\mathbf{r}, t) = \mathbf{v}(\mathbf{r}, t) - \frac{D_j}{k_B T} \nabla \mu_j(\mathbf{r}, t) \quad (3)$$

$$\mu_j(\mathbf{r}, t) = \mu_j^\infty + z_j e \Psi(\mathbf{r}, t) + k_B T \ln n_j(\mathbf{r}, t)$$

Here  $k_B T$  is the thermal energy,  $D_j$  is the diffusion coefficient of the  $j$ -th ionic species, and  $\mu_j(\mathbf{r}, t)$  is its electrochemical potential, with  $\mu_j^\infty$  its standard value.

### d) Continuity equations for the conservation of ionic species ( $j = 1, \dots, 5$ )

$$\nabla \cdot [n_j(\mathbf{r}, t) \mathbf{v}_j(\mathbf{r}, t)] = -\frac{\partial}{\partial t} [n_j(\mathbf{r}, t)] \quad (4)$$

The first boundary condition comes from the electroneutrality of the cell. One starts by expressing the equilibrium ionic concentration (depending only on the radial coordinate  $r$  for symmetry reasons) in terms of the equilibrium potential through a Boltzmann factor:

$$n_j^0(r) = b_j \exp\left(-\frac{z_j e \Psi^0(r)}{k_B T}\right) \quad (5)$$

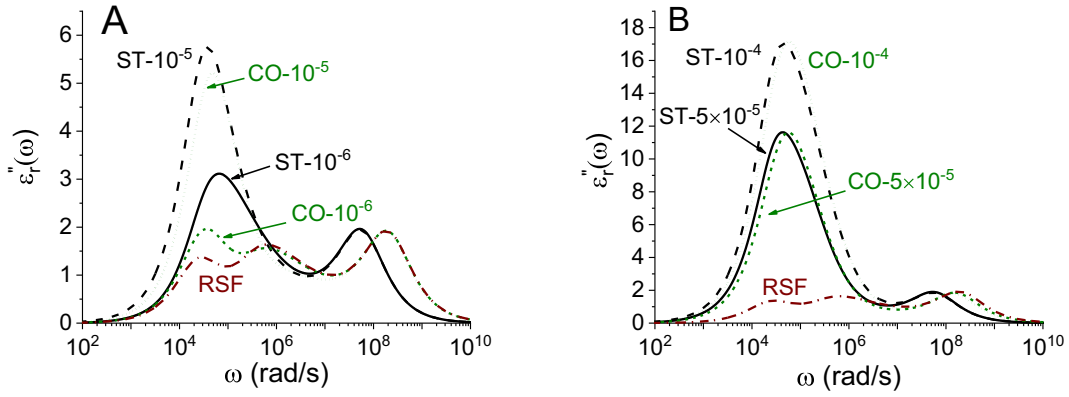
The factors  $b_j$  refer to the corresponding ionic concentration at a position where the potential vanishes. At equilibrium, the charge conservation reads:

$$\int_a^b \rho_{elec} 4\pi r^2 dr = -4\pi a^2 \sigma_p \quad (6)$$

and the electric field at equilibrium must be zero on the cell limit because of electroneutrality, according to Gauss law:

$$\left. \frac{d\Psi^0}{dr} \right|_{r=b} = 0 \quad (7)$$

The equilibrium quantities are linearly perturbed by the applied electric field, and this is made explicit by writing (the perturbation to the quantity  $X$  is given by  $X(\mathbf{r}, t) = X^{(0)} + \delta X(\mathbf{r}) \exp(-i\omega t)$ ,  $X^{(0)}$  being its equilibrium value):



**Fig. 1.** Frequency dependence of the imaginary component of the relative permittivity of suspensions with  $\phi = 0.01$  volume fraction of solids (spheres of radius  $a = 250$  nm; surface charge density  $\sigma_p = -10 \mu\text{C}/\text{cm}^2$ ). Three cases are considered: realistic salt-free (RSF), standard (ST), and complete (CO) (released counterions, ions from  $\text{CO}_2$  and water dissociation, and added KCl) models. Added KCl concentrations in the CO case as indicated; A:  $10^{-6}$  and  $10^{-5}$  mol/L, and B:  $5 \times 10^{-5}$  and  $10^{-4}$  mol/L. The surface charge counterions are assumed to be  $\text{H}^+$ .

$$\begin{aligned} \delta\Psi(\mathbf{r}) &= \psi(r)E\cos\theta \\ \delta\Psi_p(\mathbf{r}) &= \psi_p(r)E\cos\theta \\ \delta\mu_j(\mathbf{r}) &= -z_j e \phi_j(r)E\cos\theta \end{aligned} \quad (8)$$

$$\delta\mathbf{v}(\mathbf{r}) \equiv \mathbf{v}(\mathbf{r})_{r,\theta,\phi} = \left( -\frac{2}{r}\chi(r)E\cos\theta, \frac{1}{r}\frac{d}{dr}[r\chi(r)E\sin\theta], 0 \right)$$

where  $\psi(r)$ ,  $\psi_p(r)$ ,  $\phi_j(r)$  ( $j = 1, \dots, 5$ ),  $\chi(r)$  are auxiliary functions of the radial coordinate  $r$ , and  $\theta$  is the angle between the field direction and the position vector. This allows to convert the partial differential equations into ordinary ones, as detailed in [15,21,22] (the subscript “p” refers to the particle interior).

The next boundary conditions regard the facts that both the perturbed potential and normal displacement must be continuous:

$$\begin{aligned} \delta\Psi_p(\mathbf{r})|_{r=a} &= \delta\Psi(\mathbf{r})|_{r=a} \\ \epsilon_m \nabla \delta\Psi(\mathbf{r}) \cdot \hat{\mathbf{r}}|_{r=a} - \epsilon_p \nabla \delta\Psi_p(\mathbf{r}) \cdot \hat{\mathbf{r}}|_{r=a} &= 0 \end{aligned} \quad (9)$$

The conditions for the fluid velocity include: i) it must be zero on the particle surface; ii) its radial component coincides with that of the electrophoretic velocity far from the particle; iii) the vorticity vanishes on the cell surface (Kuwabara conditions). They read, respectively,

$$\begin{aligned} \mathbf{v}(r=a) &= 0 \\ v_r(r=b) &= -\mathbf{v}_e \cdot \hat{\mathbf{r}} \\ \boldsymbol{\omega}(r=b) &= \nabla \times \mathbf{v}(r=b) = 0 \end{aligned} \quad (10)$$

In addition, the particles are impenetrable to ions:

$$\mathbf{v}_j \cdot \hat{\mathbf{r}}(r=a) = 0 \quad (11)$$

Regarding the perturbation of counterion number concentration  $\delta n_j$  (see Eqs. (3), (8)) on the cell boundary, we choose the Dirichlet condition, as proposed by Shilov et al. [23]:

$$\delta n_j(r=b) = 0 \quad (12)$$

For the perturbation of the potential, we also follow the Dirichlet boundary condition [23]:

$$\delta\Psi(\mathbf{r}, t)|_{r=b} = -\mathbf{E} \cdot \mathbf{r}|_{r=b} \exp(-i\omega t) \quad (13)$$

The final condition comes from the establishment of the equation of motion of the cell. The resulting system of equations can be solved numerically by means of a Matlab® routine. As shown in [15], the two basic quantities (both complex) that describe the electrokinetic response are calculated as follows:

a) *Dynamic electrophoretic mobility:*

$$u_e(\omega) = \frac{2\chi(b)}{b} \frac{1}{1 + \frac{\rho_p - \rho_m}{\rho_m} \phi} \quad (14)$$

b) *Relative permittivity of the colloid:*

$$\begin{aligned} \epsilon_r^*(\omega) &= \epsilon_r'(\omega) - i\epsilon_r''(\omega) \\ \epsilon_r'(\omega) &= -\frac{\text{Im}[K^*(\omega)]}{\omega\epsilon_0} \\ \epsilon_r''(\omega) &= \frac{\text{Re}[K^*(\omega) - K^*(\omega \rightarrow 0)]}{\omega\epsilon_0} \end{aligned} \quad (15)$$

where  $K^*(\omega)$  is the complex electrical conductivity of the suspension, which in turn can be also obtained after solving the system:

$$K^*(\omega) = \sum_{j=1}^5 \left[ \frac{z_j^2 e^2 D_j}{k_B T} \frac{d\phi_j}{dr} \Big|_{r=b} - 2 \frac{z_j e \chi(b)}{b} \right] \times b_j \exp \left[ -\frac{z_j e \Psi^o(b)}{k_B T} \right] + i\omega \epsilon_m \frac{d\psi}{dr} \Big|_{r=b} \quad (16)$$

We will not go into details regarding the model suitable for a colloid containing added salt with concentration such that the released ions are negligible. This has been previously studied by different authors [24–26], and it can be considered a *standard model* in this context: only ions introduced in the solution by dissolving some salt are then considered. In the following we just show some results and compare the electrokinetic behaviour of spheres in the presence of ac electric fields both in the salt-free and salt-added cases. We assume that the suspension has been extensively dialyzed against water, so that the counterions of the charged groups are  $\text{H}^+$ , although, as mentioned, an incomplete exchange may retain  $\text{K}^+$  ions from the initiator. Interestingly, our method allows detection of its presence because of the enormous difference between the diffusion coefficients of  $\text{H}^+$  and  $\text{K}^+$ . Even if no further ions are added, it is quite possible that the solution is contaminated by atmospheric  $\text{CO}_2$  dissolution (hence  $\text{HCO}_3^-$  will also be present), and even that the dissociation of water also provides additional ions (we speak then of realistic salt-free colloids).

### 3. Some predictions

In a subsequent section we will show how the model can be used for explaining experimental data on the dynamic mobility and electric permittivity of polystyrene latexes. But let us for the moment consider purely theoretical results regarding the expected behaviours of these

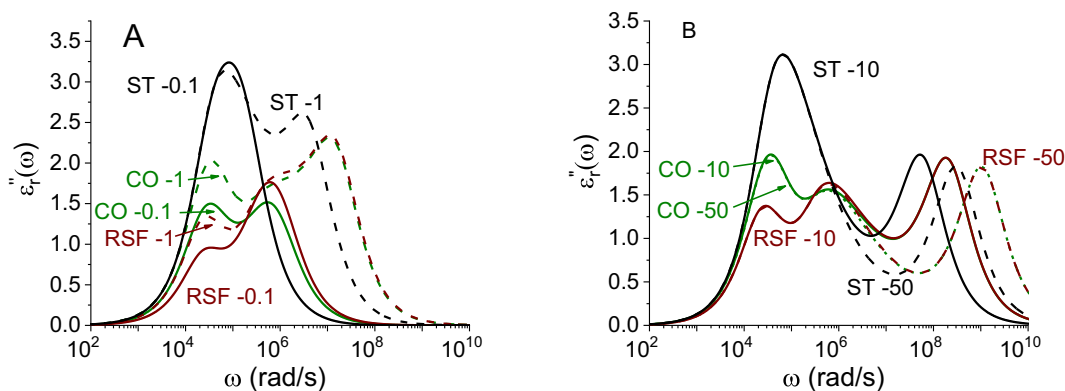


Fig. 2. Same as Fig. 1, but for  $[KCl] = 10^{-6}$  mol/L, and different surface charge densities:  $\sigma_p = -0.1$  and  $-1 \mu\text{C}/\text{cm}^2$  (A) and  $\sigma_p = -10$  and  $-50 \mu\text{C}/\text{cm}^2$  (B).

quantities in some representative cases. Fig. 1 shows the frequency spectra of the dielectric constant; we have chosen to represent the imaginary component,  $\epsilon_r''(\omega)$  (Eq. (15)), as it allows a more clear display of the frequency features.

Recall that in this representation, every maximum occurs at a characteristic frequency associated to a relaxation process: as the frequency is increased, slower processes cannot follow the field oscillations and disappear (or relax). Going in the order of increasing frequencies, we first observe the  $\alpha$ - or concentration polarization-relaxation: a cloud of neutral salt is formed at distances about  $a$  from the particle's surface, because of the different transport numbers of coions and counterions in the electrical double layer [27]. This process is more important for larger ionic strength (Fig. 1) and for larger, but moderate, surface charge density (Fig. 2A): in both cases, the strength of the induced dipoles is bigger and hence the significance of the  $\alpha$ -process is more important. The characteristic frequency of this process is given by ( $D$  is an effective or average diffusion coefficient) [28].

$$\omega_\alpha \simeq \frac{2D}{a^2} \quad (17)$$

If the field frequency is increased above that value, another maximum, i.e., another relaxation is found. This is the Maxwell-Wagner-O'Konski (MWO) process, with frequency [27,28]:

$$\omega_{MWO} = \frac{(1-\phi)K_p + (2+\phi)K_m}{(1-\phi)\epsilon_p + (2+\phi)\epsilon_m} \quad (18)$$

( $K_p$  and  $K_m$  are, respectively the electrical conductivities of the particle –including its double layer-, and the medium). This relaxation takes

place when the ions in the EDL cannot follow the field oscillations to the extent of deforming the diffuse ionic atmosphere, which remains spherical, non-deformed beyond this frequency. Finally, a high frequency maximum is observed: this is another Maxwell-Wagner event (MWC hereafter), in this case associated to the counterion condensation layer [29–33], typically highly conductive (that is, characterized by a large  $K_p$ , and hence relaxing at a higher frequency, according to Eq. (18)) as compared to the diffuse layer. Since the layer is fed with the highly-mobile  $\text{H}^+$  counterions, it appears at frequencies  $\omega_{MWC}$  higher than in the standard model, where counterions are only slower  $\text{K}^+$  from the externally added solution. The separation between MWO and MWC processes is more significant for larger surface charge, as shown in Fig. 2. Note also that the  $\alpha$ -relaxation is dominant in all the studied wide ranges of ionic strength or surface charge conditions, and this is the reason why the MWO relaxation appears negligible for the standard model, when concentration polarization is most noticeable. It can also be observed that the increase in  $\sigma_p$  produces an intense effect on the condensation layer, but it leaves almost unaffected the diffuse region. A final comment is in order, regarding the shift from complete (CO) to standard salt-added (ST) descriptions: note in Fig. 1 how the latter model is adequate for external salt concentration above  $\sim 5 \times 10^{-5}$  mol/L, as indicated by the proximity between standard and complete predictions, noticeably showing a single, rather weak MWO relaxation.

One can now wonder to what extent these processes manifest themselves in the dynamic mobility spectra, taking into account that both the dielectric constant and the mobility are controlled by the polarization mechanisms of the colloid [27,28,34–36]. Such information is contained in Fig. 3 (effect of added salt concentration) and Fig. 4 (effect

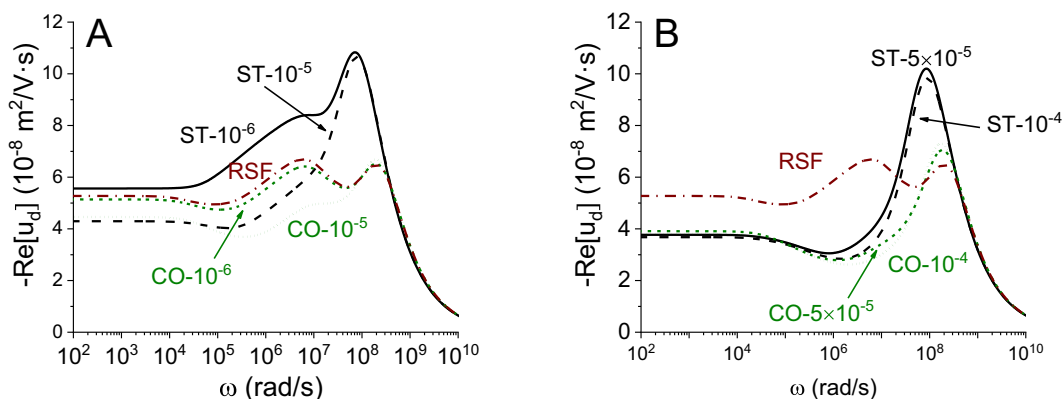


Fig. 3. Frequency dependence of the real component of the dynamic mobility of suspensions with  $\phi = 0.01$  volume fraction of solids (spheres of radius  $a = 250$  nm; surface charge density  $\sigma_p = -10 \mu\text{C}/\text{cm}^2$ ). Three cases are considered: realistic salt-free (RSF), standard (ST), and complete (CO) (released counterions, ions from  $\text{CO}_2$  and water dissociation, and added KCl) models. Added KCl concentrations in the CO case as indicated; A:  $10^{-6}$  and  $10^{-5}$  mol/L, and B:  $5 \times 10^{-5}$  and  $10^{-4}$  mol/L. The surface charge counterions are assumed to be  $\text{H}^+$ .

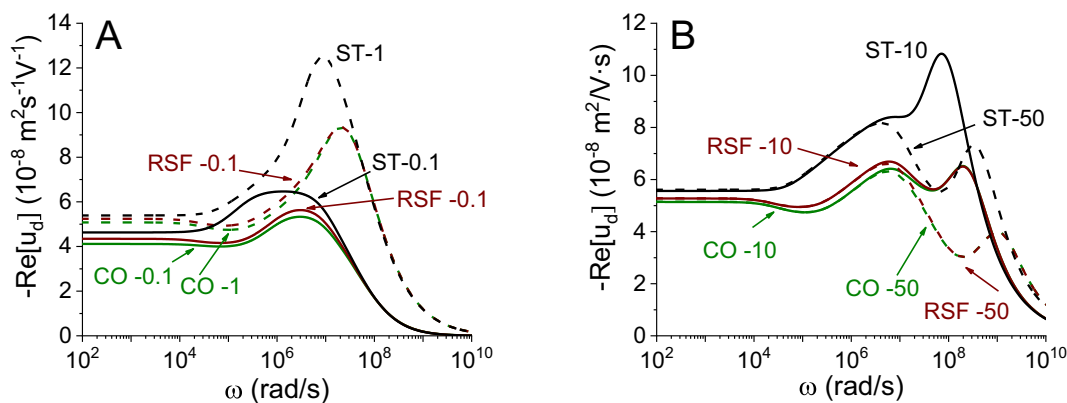


Fig. 4. Same as Fig. 3, but for  $[KCl] = 10^{-6}$  mol/L, and different surface charge densities:  $\sigma_p = -0.1$  and  $-1 \mu\text{C}/\text{cm}^2$  (A), and  $\sigma_p = -10$  and  $-50 \mu\text{C}/\text{cm}^2$  (B).

Table 1

Sample identification.

Sample	Diameter (nm)	Surface charge density* ( $\mu\text{C}/\text{cm}^2$ )
185/33	$185 \pm 2$	-33
500/14	$518 \pm 5$	-14
500/38	$520 \pm 5$	-38
1000/32	$1074 \pm 8$	-32

\* Reported by the manufacturer.

of particle charge density). There can be observed parallelisms between these Figures and those referring to the permittivity, but also differences. First of all, the alpha, low-frequency relaxation is only found for the highest particle charges, and it appears as a shallow minimum: the concentration polarization, if present, reduces the strength of the electric dipole induced by the field [27] that commonly brakes the particle motion, and as a consequence, increases the electrophoretic mobility; when it relaxes at  $\omega_\alpha$ , the mobility decreases. Interestingly, the effect is by no means as intense as it is in the case of the dielectric constant. (See Fig. 4.)

The MWO and MWC relaxations are well observed, but as mobility elevations: these relaxations mean the disappearance of the dipole associated to the diffuse layer (or condensation layer) polarization. Less polarization means more significant effect of the external field and thus larger mobility. But a new process comes into play regarding mobility when the frequency of the field increases beyond the MW relaxations: a clear reduction and tendency to zero known as inertial relaxation is predicted [25,37,38], and associated to inertia of the liquid and the particle motions, unable to follow the fast field oscillations. The characteristic frequency of this kind of process can be roughly expressed in dilute systems as [37]:

$$\omega_{in} = \frac{\eta_m}{\rho_m a^2} \quad (19)$$

which corresponds to  $\sim 1.5 \times 10^7$  rad/s for the 250 nm particles exemplified above.

#### 4. Experimental

Four spherical polystyrene latex samples, with different diameters and surface charges were investigated, all of them manufactured by Ikerlat Polymers, Spain. They were used as received, without further cleaning or ion-exchanging.

They were manufactured in three different diameters and similar surface charges, and with the same diameter and different charges, with the aim of analyzing independently both effects, namely that of particle size and of surface charge, on the electrokinetics of the particles. Table 1

allows the particle identification (labels in the form “D/C”, where D means diameter in nm and C surface charge in  $\mu\text{C}/\text{cm}^2$ ). According to the manufacturer, the surface charge was determined by potentiometric titration, after changing the counterions to  $\text{H}^+$  by extensive dialysis.

All latexes were manufactured in 10% volume fraction of solids. They were diluted to the desired particle concentration using deionized and filtered water (Milli-Q Academic, Millipore, France). The dilution experiments were carried out in air, without attempting to control the atmosphere, so that dissolution of atmospheric  $\text{CO}_2$  cannot be discarded. The type and concentration of ions in the dispersion medium was determined after centrifugation of the mother suspensions, by means of ion chromatography using a 940 Professional IC Vario, Metrohm, Switzerland) system, capable of detecting  $1 \mu\text{g}/\text{L}$  of the ions of interest, potassium in our case.

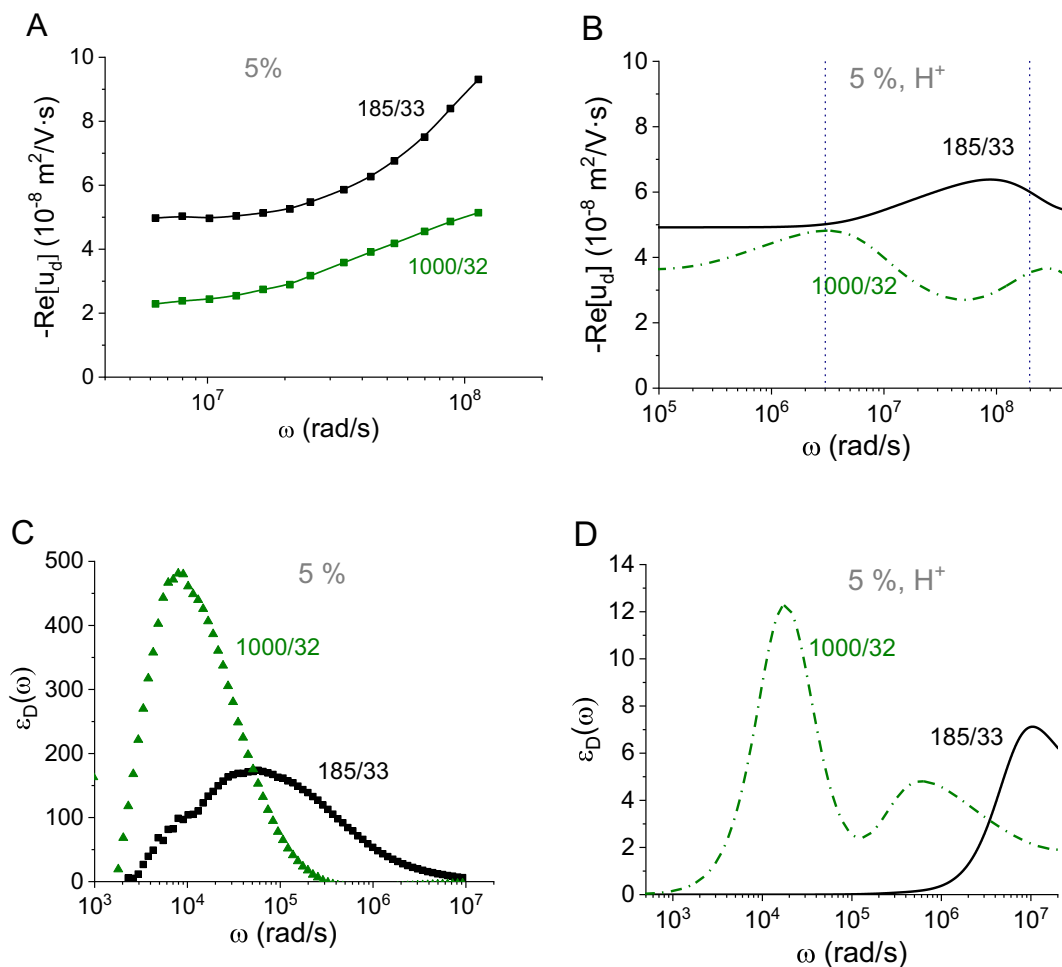
The dynamic mobility of the latexes was determined by the electroacoustic method known as ESA (Electrokinetic Sonic Amplitude), using the Acoustosizer IIC (Colloidal Dynamics, USA). The mobility is obtained from the evaluation of the pressure wave generated when an alternating electric field with frequency in the range 1 to 18 MHz is applied to the system. The signal detection relies on the existence of surface charge and a density mismatch between the particles and the medium [25,37–40].

Regarding dielectric dispersion measurements, a lab-made parallel plate electrode cell was used [41]. The complex impedance of the cell loaded with the latex to be investigated is determined in a E4980A LCR meter from Agilent (USA) in the frequency range 100 Hz to 2 MHz. By calibration with a KCl solution of known conductivity it is possible to obtain the cell constant for any electrode separation. Finally, the data on impedance can be converted into complex conductivity, and, from this, into real and imaginary components of  $\epsilon_r^*$ . The raw  $\epsilon_r'(\omega)$  data are perturbed by the effect of electrode polarization at low frequency (below 1–10 kHz, depending on the cell design and the ionic concentration of the medium). Several methods have been proposed for, at least partially, eliminating that unwanted contribution [42]. We have chosen the logarithmic derivative method [43]. The procedure involves obtaining the log derivative of  $\epsilon_r'(\omega)$ :

$$\epsilon_D(\omega) = -\frac{\pi}{2} \frac{\partial \epsilon_r'}{\partial \ln \omega} \quad (20)$$

and this quantity has the advantage of displaying very clearly the relaxations (giving maxima close to those of  $\epsilon_r''(\omega)$ ) and being more easily corrected of electrode polarization than  $\epsilon_r'(\omega)$ .





**Fig. 5.** Experimental dynamic mobility (real part, A) and logarithmic derivative of the real component of the dielectric constant (C) of polystyrene latex suspensions with 5% volume fraction. Theoretical model predictions assuming that the counterion is  $H^+$  for the mobility (B) and the logarithmic derivative (D). Samples with the same surface charge density and varying diameter (see Table 1). The dotted vertical lines in (D) correspond to the experimentally accessible frequency interval.

## 5. Results and discussion

### 5.1. Particle size effects for constant surface charge density

Fig. 5A shows the measured dynamic mobility of latex particles of two different sizes and the same charge, for 5% volume fraction. Note that for both sizes the mobility shows a growing trend, corresponding to the MWO elevation. The maximum frequency accessible in the ESA device does not allow to recover the full relaxation. It is also found that neither the  $\alpha$ - nor the MWC-relaxations are observed, and that for the maximum size investigated (1000 nm) the decreasing trend produced by the inertial relaxation is suggested (unlike the small size, where the relaxation would occur at still higher frequencies, see Eq. (19)). As observed, the mobility decreases with size. This is a manifestation of a balance between the increased concentration of released counterions from smaller particles (the concentration ratio equals the inverse of the size ratio) and the particle radius itself, leading to a decrease of the mobility with size [44]. Additionally, the larger particles undergo a deeper alpha decrease for frequencies below the experimental range, also manifested in a decrease of the absolute mobility.

Because the dielectric relaxation is, as mentioned, most sensitive to frequency variations in the low-frequency ( $\alpha$ -region) range, it seems convenient to analyze it in a wide frequency interval. The pertinent data are plotted in Fig. 5C, and they demonstrate indeed that the  $\alpha$ -relaxation, occurring in the 1–100 kHz frequency range (depending on particle size) is the really distinctive feature of the dielectric dispersion of these

polymer latexes. Note also that the relaxation bands are relatively wide in frequency, extending through one or two frequency decades. It is also noticeable that, as often found in dielectric relaxation data of colloids [45], the MWO process is almost negligible in comparison, and that it at most contributes to widening the concentration polarization band.

Regarding the comparison with theoretical predictions (Fig. 5A vs 5B, 5C vs 5D), it is clear that the agreement is very limited with the case of  $H^+$  counterions assumption. Possible reasons regarding non-ideality of the latex particles investigated could be offered. First of all, lack of sphericity of the particles can be discarded: SEM pictures (not shown for brevity) confirm that the particles are spherical as typically found with polystyrene latexes. Furthermore, the position of the relaxations (mainly in the case of the alpha and inertial processes) is strongly dependent on the particle size (c.f. Eqs. (17), (19)), so that a large radius variation could certainly affect the whole frequency-dispersion behaviour. This possibility can also be ignored, since, as reported in Table 1, the width of the particle size range is close to 1%, and this cannot explain the differences between Fig. 5A(C) and 5B(D). Additionally, in all our calculations we have assumed that the particle surface is ideal, that is, smooth, with no roughness. This is important, as the work by Duval et al. [46] showed that even ideal polystyrene particles have some degree of surface roughness: for 100 nm spheres, they found an average thickness of around 1 nm. Since the resulting layer is formed by polystyrene chains, it can be considered as a soft coating on the rigid substrate. Additionally, the authors demonstrated that the layer has a fuzzy distribution of charged polymer segments, instead of an ideal constant-

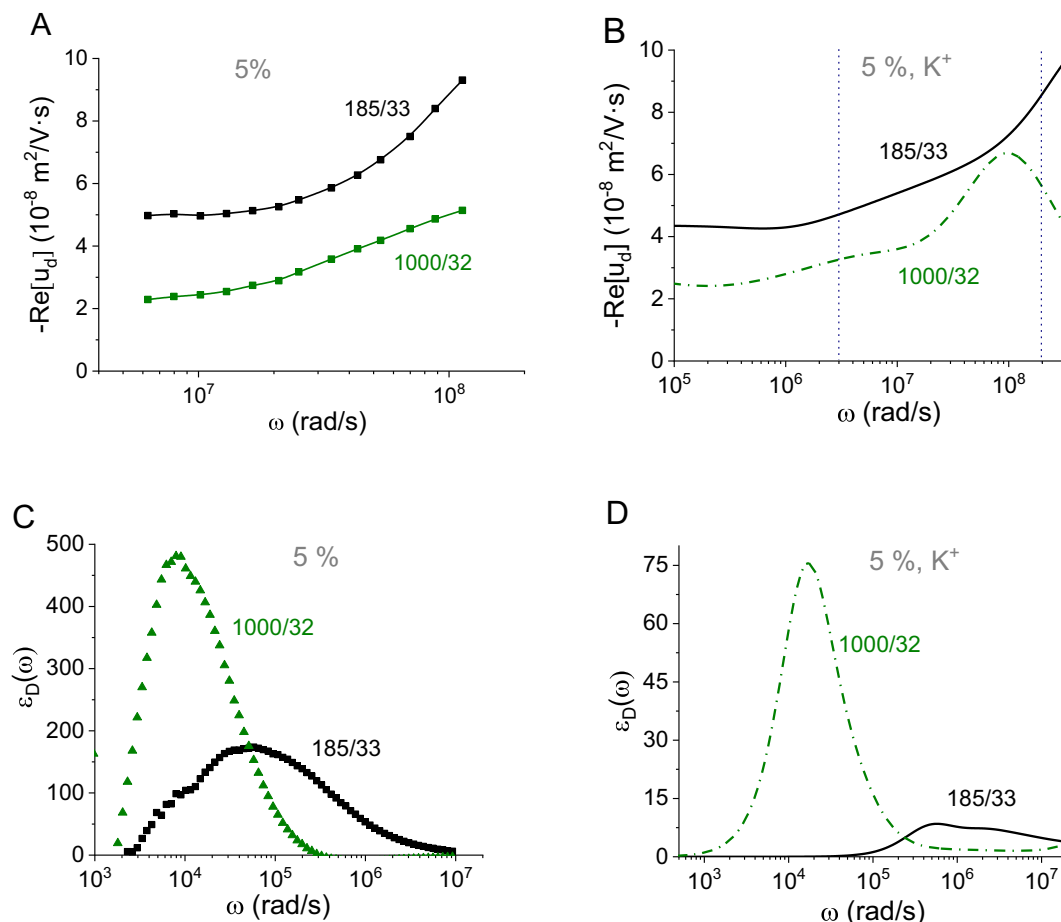


Fig. 6. Same as Fig. 5, but using  $K^+$  as counterion in the model calculations.

density layer with a sharp boundary with the surrounding solution. The presence of a soft coating has indeed consequences on the frequency dispersion of both the dynamic mobility and the electric permittivity [33,47]. If a sharp interface is considered, numerical calculations (not shown for the sake of brevity) demonstrate that even if all the surface charge would be smeared out in the volume of the soft layer (for instance, 100 nm particle radius vs. 5 nm layer thickness) no significant variation in either the mobility spectrum (except some increased significance of the MWO relaxation in the latter case) or in the dielectric dispersion is found.

Nevertheless, works by Duval and Ohshima [48] and by Duval and Gaboriaud [49] have stressed the importance of considering the fuzziness of the layer, particularly in connection with the interface between the membrane of bacteria and surrounding electrolyte medium. The existence of fuzzy surface layer has in fact been reported in very different systems. For instance, Adamczyk et al. [50], when analyzing the viscosity of silica suspensions and comparing each volume fraction dependence with existing models, unequivocally found that a fuzzy gel layer existed on the silica particles in aqueous media.

Numerical calculations of the ac electrokinetic response for soft particles with fuzzy polyelectrolyte layers performed by [51] for

multiple layers demonstrated that the degree of fuzziness (from an abrupt change in polyelectrolyte concentration to a rather extended interface) has a negligible effect on the relaxation frequencies, and it mainly affects the low-frequency value of the dynamic mobility. To the authors' knowledge there is not a model on the ac electrokinetics of salt-free systems with a (either fuzzy or step-like) polyelectrolyte surface layer.

We are left with another possibility. If cleaning of the samples could not be completely achieved because of the high particle concentrations of the mother suspensions, it might occur that a significant portion of the original counterions (potassium) stemming from the ionization of the sulfate-end groups on the particles still remain in solution. Fig. 6 A, B show that the agreement between the mobility model and experiment improves when it is  $K^+$  the assumed counterion (the predictions are very similar for other typical cations, as  $Na^+$ ; any of them could come from the initiator of the synthesis): in this case, the calculations are quite close to the measured data. It must be recalled that no fitting parameters are used for achieving the comparison between calculations and experiment. These results demonstrate that ac mobility is a good indicator of the nature of the counterions in solution (mainly in relation to their diffusion coefficients).

In the case of dielectric dispersion data (Fig. 6 C, D) the comparison is again very satisfactory with the model using  $K^+$ , only some quantitative differences being detected. It is interesting to note that such differences are always in the direction of experimental data being larger than predicted ones. This has also been reported previously [52], and has been typically ascribed to the contribution of the inner part of the EDL (Stern layer) to tangential ionic movements and double layer polarization. The related phenomenology has been widely investigated before [53,54],

Table 2

Potassium concentrations of the 10% mother suspensions.

Sample	$K^+$ concentration (mmol/L)
185/33	$1.190 \pm 0.001$
500/14	$0.018 \pm 0.001$
500/38	$0.388 \pm 0.001$
1000/32	$0.173 \pm 0.001$

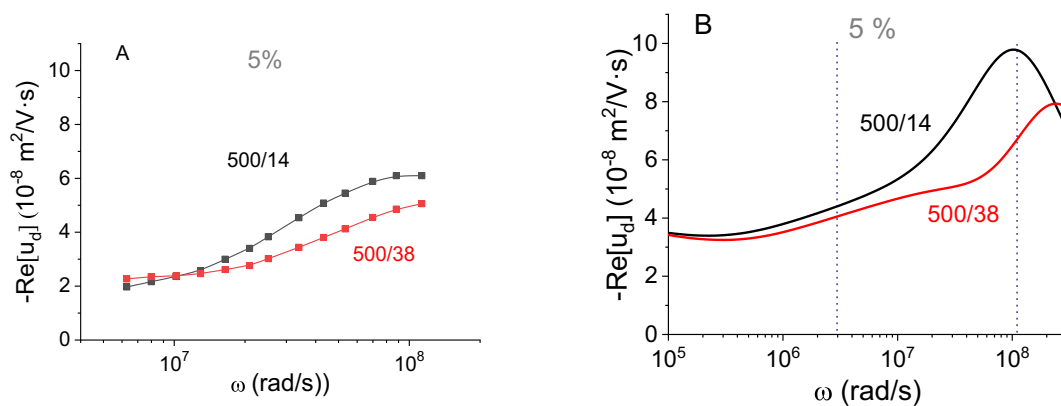


Fig. 7. Real part of the dynamic mobility of latex spheres of the same size and two different charge densities. Experimental data for 5% (A), and corresponding predictions (B) for the model based on  $K^+$  as counterions in solution. The dotted vertical lines in B correspond to the experimentally accessible frequency interval.

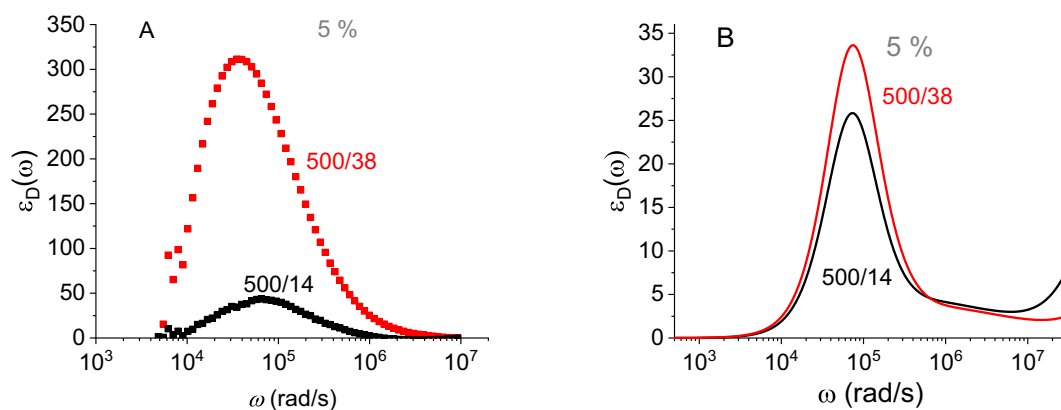


Fig. 8. Same as Fig. 7, but for the logarithmic derivative of the dielectric constant.

and will not be pursued further in the present work.

The hypothesis of the presence of significant amounts of potassium in solution was tested by determining the concentration of such ions in the supernatant of the original suspensions. Table 2 shows the results. Note that  $K^+$  is indeed present in the medium, and that the smallest and most highly charged particles lead to a larger amount of potassium, as expected. In all cases it is justified to consider the presence of  $K^+$  when explaining the electrokinetics of these systems.

### 5.2. The influence of surface charge density

The electrokinetics of polymer latexes for very similar sizes and varying surface charge is discussed in relation to Fig. 7 (dynamic mobility) and 8 (dielectric dispersion). It does not appear necessary to consider again the possibility of explaining the results using the realistic salt-free model with just  $H^+$  counterions, since the agreement in this case (as before) little satisfactory, and the discussion will proceed directly with the calculations based on  $K^+$  as counterions. As observed, for 5% volume fraction (Fig. 7 A, B), there is a reasonable agreement between experimental findings and predictions. Note also that, in spite of the different charge densities, the low-frequency values of the mobility are coincident, both theoretically and experimentally. This can be explained by the fact that, roughly beyond  $1\text{--}2 \mu\text{C}/\text{cm}^2$  charge density, the dynamic electrophoretic mobility is controlled by the counterion condensation effect [55]. Interestingly, the MWC relaxation frequency increases with surface charge, explaining the unexpected result that less charged particles move with larger electrophoretic velocity beyond a certain frequency, as clearly shown in the experiments and theoretically confirmed.

The same can be said about the logarithmic derivative of the dielectric constant in Fig. 8. The more highly charged particles contribute by a larger amount to the dielectric constant of the suspensions, and the MWO processes appear to be partially merged with the  $\alpha$ -relaxation, yielding very wide relaxation bands. It is also found, both theoretically and experimentally, that the larger particles produce larger relaxation amplitude, associated to the greater induced dipole moment, whose dimensions are of the order of the size of the concentration polarization cloud, that is, the particle radius [28,34,35]. The quantitative differences (the experimental data are about 3–10 times larger than the predictions) mentioned above persist in these experiments, and will obey the same physical reasons.

## 6. Conclusions

Because of the growing applications and fundamental behaviour of salt-free systems (i.e., those colloids in which only the particles and the counterions of their surface charge groups are in solution), a systematic study of their electrokinetic response is considered a useful source of information on their structure. This is so because electrokinetic phenomena in alternating fields are a rich source of information on the electrical properties of the interfaces. In this work, we describe a theoretical model including three different possible configurations of these systems: strict salt-free, realistic salt-free (whereby ions from water dissociation and atmospheric  $\text{CO}_2$  contamination are also accounted for), and a general or complete model including also the possibility of additional salt. Experimental data on the dynamic (or ac) electrophoretic mobility and the dielectric dispersion of the suspensions are reported for different combinations of diameters and charges, and several



volume fractions of polystyrene spheres. The mere qualitative observation of the frequency dependencies of both kinds of quantities already demonstrates the interest of these measurements for ascertaining the validity of the salt-free (even realistic) hypothesis. The large difference between the diffusion coefficients of  $H^+$  and  $K^+$  ions provokes very significant changes in the frequency spectra when the latter are present. The contamination (or incomplete ion exchange of the latexes) makes that the mobility or dielectric constant plots vs. frequency of the field are much closer to the theoretical predictions when  $K^+$  is assumed to be the counterion of the surface group. The comparison between theory and experiment in such a case is rather satisfactory, taking into account that the calculations are performed without using any adjustable parameters. It is hypothesized that quantitative differences are associated to the possible role of ions stored in the Stern layer, which have been demonstrated to be able to participate in the electric double layer polarization. Such a role is not contemplated in the model developed here.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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