Dielectric relaxation in polystyrene suspensions. Effect of ionic strength

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Abstract

The study of the conductivity and dielectric response of colloidal suspensions in a.c. fields of frequency ω can help in improving our understanding of the electrical characteristics of the solid–liquid interface in colloidal systems. In fact, the strong dielectric dispersion shown by such systems at low frequencies is intimately related to the polarization of the double layer surrounding the particles. In this work, we present recent data on the real and imaginary parts of the conductivity and dielectric constant of spherical polystyrene suspensions as a function of the frequency of the applied field, and of KCl concentration in the dispersion medium. The conductivity and dielectric increments are compared to the predictions of accepted theoretical models. The qualitative agreement between both types of data is excellent, although the experimental results are significantly higher than the theoretical ones. Reasons for such discrepancies are discussed in the light of recently reported determinations.

Keywords: Complex conductivity; Dielectric constant; Dielectric relaxation; Ionic strength; Polystyrene suspensions

1. Introduction

When an alternating electric field $E = E_0 \exp(i\omega t)$ is applied to a colloidal suspension, the polarization generated at the solid/liquid interface is in general out of phase with respect to the applied field. This phase difference corresponds to a relaxation effect in the dielectric quantities characterizing the system, which will in turn depend on the properties of both the colloidal particles and the dispersion medium.

Although different approaches have been published to explain the relaxation phenomena observed in colloidal systems [1–7], one of the most general models has been developed by DeLacey and White [8] (DW hereafter). Their theory is valid for dilute suspensions and low frequencies of the applied electric field ($\omega \ll 10^9 \text{ s}^{-1}$), and for whatever values of the parameter $ka$ ($k^{-1}$ is the Debye–Hückel length [9] and $a$ is the particle radius), the zeta potential ($\zeta$) of the particles, and the composition of the ionic dispersion medium.

According to these workers (and also to most experimental results), the complex conductivity $K^*(\omega)$ of a suspension of volume fraction $\phi$ depends linearly on the latter quantity for sufficiently dilute suspensions

$$K^*(\omega) = K^*_c(\omega) + \phi \delta K^*(\omega) + O(\phi^2)$$

where $K^*_c$ is the complex conductivity of the pure
electrolyte solutions, and $\Delta K^*(\omega)$ is the conductivity increment due to the presence of the particles. In terms of real and imaginary parts, Eq. (1) can be written

$$K^*(\omega) = K(\omega) + \omega \epsilon_0 \epsilon''_r(\omega) + \i \omega \epsilon_0 \epsilon'_r(\omega)$$

where $K(\omega) + \omega \epsilon_0 \epsilon''_r(\omega)$ is the so-called suspension conductivity, $\epsilon'_r(\omega)$ and $\epsilon'_r(\omega)$ are, respectively, the real and imaginary parts of the complex dielectric constant of the system, $\epsilon_0$ is the permittivity of a vacuum, $\epsilon_{rd}$ is the electrolyte dielectric constant, and $K^\infty$ is the d.c. conductivity of the pure electrolyte solution.

DeLacey and White [8] proposed expansions similar to Eq. (1) for $K(\omega)$, $\epsilon'_r(\omega)$ and $\epsilon'_r(\omega)$

$$K(\omega) = K^\infty + \phi \Delta K(\omega) + O(\phi^2)$$

$$\epsilon'_r(\omega) - \epsilon_{rd} + \phi \Delta \epsilon'_r(\omega) + O(\phi^2)$$

$$\epsilon''_r(\omega) = \phi \Delta \epsilon''_r(\omega) + O(\phi^2)$$

Hence

$$\Delta K^*(\omega) - \Delta K(\omega) + \omega \epsilon_0 \Delta \epsilon''_r(\omega) + \i \omega \epsilon_0 \Delta \epsilon'_r(\omega)$$

The DW model allows us to compute both the real and imaginary parts of $\Delta K^*(\omega)$ (see Ref. [10] for the separation of the two contributions $\Delta K(\omega)$ and $\omega \epsilon_0 \Delta \epsilon''_r(\omega)$ to the real part).

The aim of this paper is to determine the complex conductivity and dielectric constant of polystyrene suspensions in the presence of KCl solutions, and to compare such data with the theoretical predictions of the DW model. Specifically, the quantities of interest will be $\Delta \epsilon'_r(\omega)$, $\Delta \epsilon'_r(\omega)$, and the so-called specific conductivity increment, $Sci(\omega)$:

$$Sci(\omega) \equiv \text{Re}[\Delta K^*(\omega)] - \text{Re}[\Delta K^*(0)]$$

which, from Eq. (1), must be independent of the volume fraction.

2. Experimental

Surfactant free polystyrene suspensions were prepared following the method proposed by Goodwin et al. [11]. The latex obtained was repeatedly centrifuged (Kontron T-124 high speed centrifuge, 7500 rev min$^{-1}$) and redispersed in water (twice distilled, Milli-Q reagent water system, Millipore). The latex was then serum replaced for 15 days, until a final filtrate conductivity close to 1 $\mu$S cm$^{-1}$ was obtained. The final polystyrene suspension had a volume fraction $\phi = 0.245 \pm 0.005$, gravimetrically determined. Transmission and scanning electron micrographs showed the particles to be spherical and monodisperse, with an average diameter of 610 ± 10 nm.

In order to determine the complex conductivity, it is essential to be sure that the dispersion medium contains the electrolyte concentration (KCl in this case) to be studied, given the significant effect that even small amounts of ionic impurities have on conductivity measurements. Although there are a number of techniques available for the purpose [12], the method employed consisted of repeated (10–12 cycles were sufficient) centrifugation of appropriate amounts of latex in the desired KCl concentration until the conductivity of the supernatant was equal to that of the solution.

For the determination of the zeta potential of the particles, a fundamental quantity for explaining the dielectric response of the colloidal system [8], the electrophoretic mobility of dilute polystyrene suspensions was measured as a function of KCl concentration by means of a Malvern Zeta-Sizer 2c instrument. The zeta potential was computed from electrophoresis data using the theory of O'Brien and White [13].

The conductivity and dielectric response of the suspensions were measured with a HP-4192 LF impedance analyzer (Hewlett-Packard). The conductivity cell connected to the analyser was built following a design very similar to that published by Springer [14]. Thus the technique of variable separation between the (platinized platinum) electrodes was used to eliminate as much as possible the disturbing effects of parasitic impedances and electrode polarization [15,16]. Details of the cell geometry and of the method followed are given elsewhere [17]. The cell was filled with the suspension and thermostated to 25.00 ± 0.1°C (Haake F3K), and kept under a nitrogen atmosphere. From direct measurements of the complex admittance of the suspension in the conductivity cell as a function of electrode distance, both the real and
imaginary parts of $K^*(\omega)$ and of the dielectric constant were obtained in the 1–200 kHz frequency range.

Since all models concerning the dielectric relaxation of colloidal systems assume that such quantities as $\Delta K$, $\Delta \varepsilon'$, and $\Delta \varepsilon''$ are independent of the volume fraction, special attention was paid to check that this was indeed so with our experimental data, since such $\phi$-independent behaviour indicates that no interactions exist between the particles, which is a necessary condition for models such as DW to be valid.

3. Results and discussion

3.1. Experimental values of $K^*(\omega), \varepsilon'_(\omega)$ and $\varepsilon''(\omega)$

In this section we will show some experimental results of the quantities of interest for suspensions in $10^{-4}$ M KCl of different volume fractions. Fig. 1 shows, for example, the conductivity of the suspensions (referred to the low frequency or d.c. value) as a function of frequency, for volume fractions up to $5.66 \times 10^{-2}$. Note first that this conductivity increment is zero at $\phi=0$ for the whole frequency range.

![Graph showing conductivity increment of polystyrene suspensions referred to its d.c. values, for different volume fractions in $10^{-4}$ M KCl.](image)
range studied, as expected since the relaxation frequency of the pure liquid must be around 1 GHz.

Noticeable relaxation processes are clearly observed in Fig. 1 for non-zero volume fractions, the conductivity increase with frequency being the higher the larger the volume fraction of the suspensions, owing to the increase in the number of particles contributing to the relaxation effects observed. It is easy to show that the conductivity variations are larger than they would be if they were just a consequence of temperature drifts or fluctuations.

The real part of the dielectric constant, $\varepsilon'_r$, is plotted, for the same suspensions, in Fig. 2. The relaxation phenomena are again observed: since they are related to the finite time needed by the charge transport processes that polarize the double layers [5,8], it is reasonable that, as the frequency increases, $\varepsilon'_r$ tends to the electrolyte dielectric constant $\varepsilon_{rd}$. For high frequencies, the oscillating dipoles induced by the electric field are unable to follow the rapid variations of the latter, and hence do not contribute to the polarizability of the system. This type of behaviour has also been

![Graph](image)

Fig. 2. Real part of the dielectric constant of polystyrene suspensions plotted vs. frequency, for different volume fractions (electrolyte, $10^{-4}$ M KCl).
observed with, for example, amphoteric latexes [18,19].

Fig. 3 shows the imaginary part of the dielectric constant. Note the clear increase in dielectric losses, associated with $\varepsilon''(\omega)$, upon increasing the volume fraction, in perfect agreement with the results of Fig. 1 and with data from other latexes [20]. The uncertainty in $\varepsilon''(\omega)$ is larger for the lower frequency side due to the remaining effects of electrode polarization. However, the behaviour observed for $\varepsilon''(\omega)$ (with maxima being obtained when the period of the applied field is of the order of some average relaxation time of the double layer) agrees with that found for $\varepsilon'(\omega)$, at least for intermediate and high frequencies [21]. Since the information contained in the frequency dependence of $\varepsilon'$ and $\varepsilon''$ is physically equivalent, we will not discuss further the results in Fig. 3.

A representation of $\varepsilon''$ vs. $\varepsilon'$ (the so-called Cole–Cole plot for the dielectric constant) allows us to rapidly and visually characterize the nature of the relaxation processes which are appropriate for a system. This type of plot is shown in Fig. 4. It is interesting to point out, mainly for the highest volume fractions investigated, the close proximity between these data and those of the empirical
Cole–Cole model [22], according to which the plots must be depressed semicircles (centre below the real axis), according to the equation:

$$\varepsilon_r''(\omega) + i \varepsilon_r''(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{\infty} - \varepsilon_{\infty}}{1 + (i\omega\tau_0)^{1-\alpha}} \quad \alpha < 1 \quad (9)$$

where $\varepsilon_{\infty}$ and $\varepsilon_{\infty}$ correspond to the values of the dielectric constant for low and high frequencies, respectively, and $\tau_0$ is a characteristic time related to the frequency of the maximum in the $\varepsilon_r'' - \omega$ plot.

Experimental results like those in Fig. 4 are frequently found in the literature [14,23,24], although some workers [25] claim that trying to find an interpretation of the data in terms of empirical models is irrelevant.

For each KCl concentration studied, we have calculated the increments $\Delta\varepsilon_r''(\omega)$ and $\Delta\varepsilon_r'(\omega)$, according to Eqs. (5) and (8). The expected non-dependence of these quantities on the volume fraction can be seen in Figs. 5 and 6. The linearity between $K^*$ and $\phi$, expressed by Eq. (1) is thus verified by our systems, and a comparison between our data and DW's predictions must be possible. This will be done in the next section.

### 3.2. Comparison with the predictions of the DW model

In order to carry out the proposed comparison, we must first know the zeta potential of the particles. The values of $\zeta$, computed from electrophoretic mobility measurements, as well as the $k\alpha$ parameter for the different KCl concentrations, are shown in Table 1. Note how $\zeta$ increases in absolute value upon increasing the ionic strength of the solutions. This behaviour has been found in many instances for both cationic and anionic latexes, and different explanations for it have been offered [26].

Like the dielectric response, it must be intimately related to the surface characteristics of the particles. We will return to this problem below.

A comparison between theory and experimental data is shown in Figs. 7–10, using only increments, since they contain all the information. The quantities $\Delta\varepsilon_r''(\omega)$ and $\Delta\varepsilon_r'(\omega)$ can be seen, as a function of frequency, in Figs. 7 and 8 respectively: note the excellent qualitative agreement between both types of data for all KCl concentrations. However, experimental results are about one order of magnitude higher than theoretical predictions, and it is important to note that this situation is very common in previous investigations of these phenomena [18–20,27,28].

Many hypotheses have been proposed to justify such divergence, including the existence of a “hairy layer” on the surface of polystyrene particles [29]. Some experiments carried out with latexes subjected to thermal treatments (such treatments are supposed to yield bare polystyrene surfaces)
showed a significant approximation between theoretical and experimental results [20,27]. In fact, the interesting point is that the dielectric behaviour is critically dependent on the nature of the colloidal particle surface. Nevertheless, similar heat treatments with anionic latexes [28] did not lead to any improvement in the comparison. The topic is still open for discussion.

Another possibility is obviously that $\zeta$ is improperly estimated, for example as a consequence of experimental errors in electrophoretic mobility determinations or of the use of a model not suitable to the polystyrene solution interface. However, it must be stressed that the high values of $|\zeta|$ that would be needed to bring theory and experiment closer would be physically unreliable in our case.

Other effects might influence the conductivity and dielectric response of a suspension, for instance, the existence of significant interactions between the particles [28], or the "suspension effect", i.e., the dependence of the electrolyte concentration on the volume fraction of solids, but none of these effects would be important enough to justify the theory–experiment discrepancies [30,31].

In a recent work, Kijlstra [25] modified the double layer model of Fixman [5] to account for the possibility of surface conduction between the
slipping plane and the solid surface. His results suggest that the dielectric response of suspensions is indeed increased in the low-frequency range, giving better agreement with experimental results on spherical silica and haematite. Rosen et al. [32] have elaborated a more general theory based on the so-called dynamic Stern layer hypothesis, which assumes that lateral ionic motion is possible in the region between the solid surface and the slipping plane. These workers have applied their model to the explanation of the dielectric properties of both silica and poly(methyl methacrylate)/poly(acrolein) suspensions. A significant improvement was obtained between experimental and predicted values of the dielectric constant and conductivity of such systems.

Fig. 9 shows the frequency variation of $\Delta\varepsilon''$. 

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**Table 1**

Values of the zeta potential, $\zeta$, and of the parameter $\kappa\alpha$ of polystyrene suspensions as a function of KCl concentration

<table>
<thead>
<tr>
<th>[KCl] (M)</th>
<th>$\kappa\alpha$</th>
<th>$\zeta$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>10.0</td>
<td>-38.6</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>14.2</td>
<td>-54.3</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>20.0</td>
<td>-68.9</td>
</tr>
<tr>
<td>$6 \times 10^{-4}$</td>
<td>24.6</td>
<td>-70.2</td>
</tr>
</tbody>
</table>
Fig. 7. Comparison between theoretical and experimental values of the specific conductivity increment for different KCl concentrations.

Note again the similarity between both trends of variation, although, as before, the experimental data are about ten times larger than theoretical results. Furthermore, the relaxation frequencies are also somewhat different (experimental, $5 \times 10^4$ rad s$^{-1}$; theoretical, $2 \times 10^4$ rad s$^{-1}$): the possible influence of surface conduction on the relaxation mechanisms in the double layer, not considered in the DW model, might explain that difference in
Exp.

![Graph showing \\( \Delta \varepsilon_r(\omega) \) vs. \( \omega \) (rad/s) for different concentrations.](image)

2.10^4 M
4.10^4 M
6.10^4 M

\( \omega \) (rad/s)

Fig. 8. As Fig. 7, for the real part of the dielectric constant.

DW

![Graph showing \\( \Delta \varepsilon_r(\omega) \) vs. \( \omega \) (rad/s) for different concentrations.](image)

10^-4 M
2.10^-4 M
4.10^-4 M
6.10^-4 M

\( \omega \) (rad/s)

Finally, a comparison between theoretical and experimental Cole–Cole plots can be seen in Fig. 10. Note the differences in symmetry: the DW model cannot reproduce the symmetrical nature of

\( \omega_{\text{max}} \), although the theory of Rosen et al. [32] does not predict any important difference between the relaxation frequencies obtained with the DW and the dynamic Stern layer models.
experimental $\Delta \varepsilon'' - \Delta \varepsilon'$ representations. In particular, the fit of the data ($6 \times 10^{-4}$ M KCl) to Eq. (9) yields $\alpha = 0.181 \pm 0.003$, and Fig. 10 shows that the Cole–Cole type semicircle fits the data very well.

4. Conclusions

The results presented in this work lead to the main conclusion that the dielectric response of colloidal dispersions is a powerful technique for
the characterization of the electrical nature of the surface of very different colloids. The DW model qualitatively reproduces the dependence of the various quantities describing the response of the system on frequency, volume fraction or electrolyte concentration. The quantitative discrepancies are still open to further investigation, although data obtained with inorganic colloids such as silica or haematite [19,25] suggest that these particles might be closer to the hypotheses of the theoretical model. In our opinion, quantitative convergence between theory and experiment will come on the basis of further extensive measurements with a large variety of uniform colloids, and improvements of the existing models, mainly by including a more detailed picture of the inner part of the electric double layer.

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References