Analysis of the Dielectric Permittivity of Suspensions by Means of the Logarithmic Derivative of Its Real Part

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INTRODUCTION

The low-frequency dielectric dispersion (LFDD) of colloidal suspensions has recently gained significance as an experimental technique for their characterization because of its extreme sensitivity to the structure of the electric double layer (EDL) surrounding the particles, under conditions of both equilibrium and nonequilibrium (1–5). The method involves the determination of the (complex) permittivity \( \varepsilon^*(\omega) \) or conductivity \( K^*(\omega) \) as a function of the frequency of an externally applied AC field. The amplitude and characteristic time of the relaxation eventually observed contain a great deal of information about the particles size and shape, their zeta potential, and even the possible presence of a dynamic (field-responsive) Stern layer (6–13). The basic principles of the measuring methods are easy to understand: all that is needed is to measure the amplitude and phase of the current transported between the electrodes containing the sample for each frequency of the applied potential difference. There is, however, a serious difficulty that has likely prevented the method from being more extensively used: this is the phenomenon of electrode polarization (EP). Recall that it is related to the existence of the metal/electrolyte solution interface, which manifests itself as a potential barrier at the latter and can be modelled as a complex impedance \( Z_{EP} \) in series with the true sample impedance, \( Z^* \) (14–16). The important point here is that the presence of \( Z_{EP} \) can lead to apparent low-frequency dielectric constants much higher (even orders of magnitude higher) than the actual value of the suspension. Furthermore, the frequency range in which EP contributions are most important always contains the low-frequency plateau of the real part of the dielectric constant of the dispersed system and may hide the main relaxation frequency (the \( \alpha \)-relaxation, true fingerprint of the EDL polarization) of the dielectric spectrum.

So far, some methods have been devised to eliminate (or, more properly, reduce) the effects of EP in LFDD measurements. These mainly include measuring at variable distance between electrodes (1), using four-electrode cells (3, 17, 18), or the so-called quadrupole technique (19, 20). But even with these sophisticated and well-established techniques, the low-frequency
Experimental data may lead to just qualitative or semiqualitative frequency side. Even then, the uncertainties associated to experimental data may lead to just qualitative or semiqualitative conclusions.

A similar analysis can be carried out with the imaginary part, $\varepsilon''(\omega)$, of the complex dielectric constant. A possible way to obtain the imaginary part of the dielectric constant from experimental data is to use the real part of the conductivity,

$$\varepsilon''(\omega) = \frac{\text{Re}(K'(\omega)) - K_{\text{DC}}}{\omega \varepsilon_0},$$  

where $K_{\text{DC}}$ is the direct current conductivity (or low-frequency value of $\text{Re}(K'(\omega))$), and $\varepsilon_0$ is the permittivity of vacuum. The main drawback of the method is, however, the extreme sensitivity of the conductivity to even small temperature changes. Furthermore, EP also affects the accuracy of $K_{\text{DC}}$.

The search of the loss peak of the $\alpha$-relaxation could also be performed through Kramers–Krönig transformation of the real part (27),

$$\varepsilon''(\omega) = -\frac{2 \omega}{\pi} \int_0^\infty \frac{\varepsilon'(\omega') - \varepsilon_\infty}{\omega'^2 - \omega^2} d\omega',$$

where $\varepsilon_\infty$ is the high-frequency value of $\varepsilon'(\omega)$. Nevertheless, numerical integration of Eq. [2] requires reliable data on $\varepsilon'(\omega)$ in a wide enough frequency range, including of course the critical region of EP predominance.

Recently, Wübbenhorst and Turnhout (28, see also Ref. 27) proposed a different, very promising approach to the calculation of $\varepsilon''(\omega)$ from raw $\varepsilon'(\omega)$ data: they use the fact that the logarithmic derivative of $\varepsilon'(\omega)$ with respect to $\omega$ is, except for a constant factor, practically identical to $\varepsilon''(\omega)$. The method could be specially suited for colloidal suspensions, in which the aqueous dispersion medium can be sufficiently conductive for significantly interfering LFDD data. In order to explore its possibilities, we will first apply it to theoretical data calculated by means of the well-known DeLacey–White theory of LFDD in colloids (8). Next, we will check the procedure using experimental data on the dielectric permittivity of suspensions of polymeric spheres.

The structure of the paper is as follows. In the following section, we will give the theoretical background of the method. After describing the experimental details of the dielectric measurements in suspensions, we will show the results, both theoretical and experimental, and check the validity of this procedure.

### THEORETICAL BACKGROUND

As mentioned, EP contributes to erroneous measurements of the dielectric permittivity of conducting samples mainly in the low-frequency region, close to the frequency interval in which the $\alpha$-dispersion of colloidal systems can be expected to occur. Although the impedance associated with electrode polarization decreases with frequency, it is still not negligible when the dielectric relaxation of the suspension takes place (typically in the kilohertz range). Very often (the phenomenon is more significant the higher the conductivity of the dispersion medium) the magnitude of EP impedance is so high that the LFDD of the suspension can be hidden.

In order to analyze the EP contribution, we will follow the approach by Cirkel et al. (16). Let us assume for the moment that the measuring cell consists of two planar electrodes separated by a distance $L$; the cell contains a simple ionic solution or even a colloidal dispersion, but it will be admitted that in the frequency range of interest no relaxation occurs, that is, the dielectric permittivity of the system is frequency-independent, and equal to some value $\varepsilon_\infty$. Assuming further that the electrodes are ideally polarizable, and hence that there is no charge transfer or ionic adsorption on their surfaces, it can be shown that the complex dielectric constant of the system depends on frequency as follows:

$$\varepsilon_p^*(\omega) = \varepsilon_m^* \left[ 1 - \frac{1}{1 + i \omega/\omega_0} \left( 1 - \sqrt{\frac{\omega_0}{\omega}} \right) \right]^{-1},$$

where $\omega_0$ is associated to the electric double layer relaxation around the electrodes,

$$\omega_0 = \kappa^2 D,$$

$\kappa$ being the reciprocal Debye length, and $D$ the average diffusion coefficient of ions in solution. For example, $\omega_0 \approx 2 \times 10^7$ rad/s for a $10^{-3}$ M KCl solution. The second frequency appearing in Eq. [3] is related to the migration of the ions from one electrode to the other:

$$\omega_L = \frac{4D}{L^2},$$

and its typical value is $9 \times 10^{-4}$ rad/s for a 3-mm electrode separation.

From Eq. [3] it can be found that the high-frequency behavior of the real and imaginary parts of the dielectric constant of the system behave at high frequencies as

$$\varepsilon_p' - \varepsilon_m' \propto \left( \frac{\omega}{\omega_0} \right)^{-3/2},$$

$$\varepsilon_p'' \propto \left( \frac{\omega}{\omega_0} \right)^{-1}.$$
The important point in connection with our discussion is that the characteristic frequency \( \omega_c \) in Eq. [6] depends on the electrode separation, \( L \), since it is a combination of both \( \omega_0 \) and \( \omega_L \),

\[
\omega_c = \omega_0^{2/3} \left( \frac{\omega_L}{2} \right)^{1/3} \propto L^{-2/3},
\]

from which it is immediately clear that the effect of electrode polarization on the dielectric constant of the system relaxes at lower frequencies the larger the electrode separation.

The alternative approach proposed in Ref. (28) introduces a new function,

\[
\epsilon''(\omega) = -\frac{\pi}{2} \frac{\partial \epsilon'}{\partial \ln \omega},
\]

that for the case of electrode polarization, under the preceding assumptions shows the following high-frequency asymptotic behavior:

\[
\epsilon''(\text{EP}) \propto \omega^{-3/2} L^{-1}.
\]

These dependencies of \( \epsilon''(\text{EP}) \) on the frequency and electrode-spacing are in fact the most relevant aspects of this derivation. On one hand, the EP contribution decreases, at a given frequency, when \( L \) increases, while the imaginary part of the EP dielectric constant is independent on \( L \) (Eq. [6]). On the other hand, \( \epsilon''(\text{EP}) \) decreases faster than the imaginary part of the dielectric constant because of its \( \omega^{-3/2} \) dependence, in contrast to the \( \omega^{-1} \) dependence of \( \epsilon'' \). In conclusion, it is more likely for the logarithmic derivative to be able to separate the two main relaxation peaks for colloidal suspensions (one corresponding to the electrodes, and the other to the \( \alpha \)-relaxation of the colloid) than for the imaginary part of the dielectric constant. We need only to place the electrodes far enough, always within the limits of the parallel-plate capacitor approximation.

From the above, one may expect that the faster decrease of \( \epsilon''(\text{EP}) \) with frequency might lead to the assumption that its value can be negligible when the \( \alpha \)-relaxation of the colloidal suspension becomes important, so that it may be possible to get rid of the disturbing EP effects.

Furthermore, according to Böttcher and Bordewijk (27), \( \epsilon''(\omega) \) is a good approximation to the actual dielectric loss for the case of broad loss peaks like those usually found in the \( \alpha \)-relaxation (or double-layer relaxation) characterizing the polarization of the electric double layer. Below we will check to what extent this approximation is valid. If it can be acceptable, the logarithmic derivative will have a double advantage: it will help us in separating the electrode effects from the dielectric constant of the suspension, and it furthermore will give information on the imaginary part of the latter.

**DATA TREATMENT**

According to Eq. [8], \( \epsilon''(\omega) \) can be obtained if \( \epsilon'(\omega) \) data are available through a wide enough frequency range. The numerical procedure of Savitzky and Golay (29) is then used to compute the logarithmic derivative. In the presence of electrode polarization, and in view of Eq. [9], the appearance of the plot will be as schematically shown in Fig. 1a, assuming that the system (the colloidal suspension in our case) has a single relaxation \( \omega_{rel} \) in the frequency range of interest. If the relaxation frequency \( \omega_{rel} \) is sufficiently above that of the electrode polarization (as it is often the case), the contribution of the latter can be subtracted, and the true \( \epsilon'' \) data of the suspension obtained (Fig. 1b).

Since it is often found that the dielectric spectra of suspensions are asymmetric (30), we used the Havrišák–Negami relaxation function (31) to fit the remaining points as in Fig. 1b. This relaxation function is

\[
\epsilon'(\omega) = \epsilon'(\infty) + \frac{\epsilon'(0) - \epsilon'(\infty)}{1 + (i \omega \tau)^a} \omega^b,
\]

where \( \epsilon'(0) \) and \( \epsilon'(\infty) \) are, respectively, the high and low frequency limits of the dielectric constant of the suspension, and \( \tau \), \( a \), \( b \) are parameters of the relaxation. Note that \( \tau \) will be used in this work as an approximate measure of the characteristic time of the relaxation process. The parameters \( a \) and \( b \) are determined by the frequency width of the dispersion, whereas \( b \) is specifically related to its asymmetry. Once the best-fit parameters are
obtained, the real part $\varepsilon'(\omega)$ (now free of disturbing electrode effects) is reconstructed by taking the real part of Eq. [10].

**COMPARISON WITH PREDICTIONS OF THE STANDARD ELECTROKINETIC THEORY**

According to the DeLacey and White theory (8), the real and imaginary parts of $\varepsilon^*\omega$ can be computed if the dipole induced in the double layer by the external field is known for each frequency. In fact, it can be shown that

$$
\varepsilon'(\omega) = \varepsilon'_s + 3\phi\varepsilon_e \left[ C_1(\omega) - \frac{K^\infty}{\omega\varepsilon_0\varepsilon'_s} C_2(\omega) \right]
$$

[11]

$$
\varepsilon''(\omega) = 3\phi\varepsilon_e \left[ \frac{K^\infty}{\omega\varepsilon_0\varepsilon'_s} (C_1(\omega) - C_1(0)) + C_2(\omega) \right].
$$

[12]

where $\phi$ is the volume fraction of solids, $\varepsilon'_s$ and $K^\infty$ are, respectively, the dielectric constant and DC conductivity of the dispersion medium, and $C_1$ and $C_2$ are the real and imaginary parts of the induced dipole coefficient, $C_0^s = C_1 - iC_2$. Here,

$$
d^* = 4\pi\varepsilon'_e\varepsilon_0a^3(C_1 - iC_2)E
$$

[13]

is the complex dipole moment, $a$ is the radius of the particle (assumed to be spherical), and $E$ is the external field. The corresponding volume-fraction independent quantities (so-called dielectric increments) are given by

$$
\Delta\varepsilon'(\omega) = \frac{\varepsilon'(\omega) - \varepsilon'(\infty)}{\phi}
$$

and

$$
\Delta\varepsilon''(\omega) = \frac{\varepsilon''(\omega)}{\phi},
$$

[14]

where $\varepsilon'(\infty)$ is taken as the value of $\varepsilon'$ at a frequency large enough compared to $\omega_{\text{rel}}$. The same definitions apply to $\Delta\varepsilon'_D$ and $\Delta\varepsilon''_D$, obtained from $\varepsilon'_D$ and $\varepsilon''_D$, respectively.

The quantities $C_1$ and $C_2$ can be calculated in terms of the zeta potential of the particles, $\zeta$, and of the product $\kappa a$, where $\kappa^{-1}$ is the EDL thickness or Debye length. The theory appears ideal for checking our methodology, since $\varepsilon'$ and $\varepsilon''$ can be computed independently. It should be possible to compare $\varepsilon''(\omega)$ with $\varepsilon''_D(\omega)$, and $\varepsilon'(\omega)$ with the reconstructed real part, $\varepsilon'_D(\omega)$.

Upon numerical integration of the equations of the theory, we first calculated $\Delta\varepsilon'(\omega)$ for a suspension of spheres with $2a = 110$ nm, in $10^{-3}$ M NaCl, for two zeta potentials, namely, $-50$ and $-100$ mV. In Fig. 2a we have plotted $\Delta\varepsilon'(\omega)$ obtained directly from the theory, and in Fig. 2b the corresponding value of the imaginary part, $\Delta\varepsilon''(\omega)$. From the actual real dielectric constant, we computed $\Delta\varepsilon''_D(\omega)$, and the result is also included in Fig. 2b. Note that in the frequency range of interest, $\Delta\varepsilon''(\omega)$ and $\Delta\varepsilon''_D(\omega)$, are very similar. Fitting $\Delta\varepsilon''(\omega)$ with a Havriliak–Negami function, the parameters detailed in Table 1 were obtained. Finally, the reconstructed values $\Delta\varepsilon'_D(\omega)$ were superimposed in Fig. 2a to those calculated directly from the theory. The method proves to reproduce extremely well the real part of the dielectric constant of the suspensions, so we proceed to use it with real experimental data obtained in our laboratory with different kinds of colloidal suspensions. First, we describe in the next section the methodology and data analysis.

**EXPERIMENTAL**

LFDD determinations were carried out with two different latexes. One was an aqueous dispersion of spherical particles

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**TABLE 1**

Best-Fit Parameters of $\varepsilon''_D(\omega)$ in Fig. 2b to a Havriliak–Negami Function

<table>
<thead>
<tr>
<th>$\zeta$ (mV)</th>
<th>$\Delta\varepsilon'(0) - \varepsilon'(\infty)$</th>
<th>$\tau$ (µs)</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-50$</td>
<td>$644 \pm 2$</td>
<td>$2.6 \pm 0.2$</td>
<td>$0.568 \pm 0.003$</td>
<td>$2.91 \pm 0.09$</td>
</tr>
<tr>
<td>$-100$</td>
<td>$2910 \pm 30$</td>
<td>$3.7 \pm 0.8$</td>
<td>$0.55 \pm 0.01$</td>
<td>$2.3 \pm 0.2$</td>
</tr>
</tbody>
</table>

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**FIG. 2.** (a) Full symbols: Theoretical values of $\varepsilon'(\omega)$ for a colloidal suspension of spheres, obtained from DeLacey–White theory (8). Open symbols: values estimated from the logarithmic derivative method. (b) Same as (a), but for the imaginary part of the dielectric constant. In all cases, $a = 55$ nm, and the dispersion medium is a 1 mM aqueous solution of NaCl.
TABLE 2

Characteristics of the Polymer Suspensions Investigated

<table>
<thead>
<tr>
<th>Code</th>
<th>Polymer</th>
<th>Average diameter (nm)</th>
<th>Volume fraction</th>
<th>Electrolyte</th>
<th>C (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquacoat</td>
<td>Ethylcellulose</td>
<td>110 ± 20</td>
<td>0.04</td>
<td>Sodium salicylate</td>
<td>0.1, 0.3, 1</td>
</tr>
<tr>
<td>L-530</td>
<td>Polystyrene</td>
<td>530 ± 30</td>
<td>0.02</td>
<td>KCl</td>
<td>0.5</td>
</tr>
</tbody>
</table>

of ethylcellulose (Aquacoat, a trademark of FMC Corp., USA, kindly supplied by Foret, S.A., Spain) and the other was a commercial polystyrene latex manufactured by Interfacial Dynamics Corporation (Portland, OR). We denote it as L-530 hereafter. The commercial polystyrene latex manufactured by Interfacial Dynamics Corporation is even more efficient for larger cell constants, that is, larger interelectrode distance (i.e., the larger \( \lambda \)). The most interesting feature of Fig. 3(b) is the clear detection of the absorption peak, and hence of the characteristic relaxation frequency can be determined with high accuracy.

(v) Fit the Havriliak–Negami relaxation function to the calculated \( \varepsilon''_0(\omega) \) values, after getting rid of the data corresponding mostly to electrode polarization. This can be done by visual inspection of the plot.

(vi) Reconstruct \( \varepsilon''_0(\omega) \) from the real part of the Havriliak–Negami function with identical parameters.

The procedure can be repeated for different separations, although (and this is one of the advantages of the method) this is not strictly necessary.

RESULTS AND DISCUSSION

Following the procedure described with a suspension of polystyrene spheres (L-530 in Table 2) in 0.5 mM KCl, the results in Fig. 3 were obtained. Figure 3a shows the raw \( \varepsilon'(\omega) \) data both for the suspensions and for the dispersion medium. As observed, EP almost completely masks any relaxation until rather high frequencies are reached. Even the value of the dielectric constant of the solutions (where no relaxations can occur for the frequency interval shown) is hidden by polarization. The drastic change that occurs when \( \varepsilon''_0(\omega) \) is obtained is clear in Fig. 3b: at very low frequencies, the straight-line dependence \( (\varepsilon''_0 \propto \omega^{-3/2}) \), Eq. (9) associated with EP is clearly visible, no matter whether the system contains particles or not. These lines are parallel for the distances examined (with average slope \(-1.632 \pm 0.010\) and shift to lower frequencies the larger the interelectrode distance (i.e., the larger \( \lambda \)). The most interesting feature of Fig. 3b is the clear detection of the absorption peak, and hence of the \( \alpha \)-relaxation characteristic frequency, well separated from EP effects. Note that this is not an artifact: no such peaks are measured when no particles are present. Observe also that, both for the suspension and the solution, the curves corresponding to different distances collapse at moderate to high frequencies into only one, indicating the absence of any EP effects. Figures 3c and 3d show that the reduction of EP effects is even more efficient for larger cell constants, that is, larger electrode separations.

Since we are interested in the effect of the colloidal particles and their double layers on the dielectric dispersion, the quantities that are needed are the real and imaginary dielectric increments. As mentioned above, \( \varepsilon'(\omega) \) will be identified with \( \varepsilon''_0(\omega) \), obtained in turn from \( \varepsilon''_0(\omega) \), after fitting the latter with a Havriliak–Negami function. Table 3 shows the fitting parameters found. Figure 4 shows \( \Delta \varepsilon''_0(\omega) \) and \( \Delta \varepsilon''_0(\omega) \) for L-530 and a cell constant \( \lambda = (43.1 \pm 0.1) \text{ m}^{-1} \) (recall that there is little effect of the electrode separation, provided the peak is well detected, as in Fig. 3). The real part of the dielectric increment is compared to our best estimation based on the electrode separation technique. As observed, the method proposed helps us in obtaining a low-frequency plateau, which can be very useful for characterizing the dielectric response of the suspension. Also, the characteristic relaxation frequency can be determined with high accuracy.
### TABLE 3
Parameters of a Havriliak–Negami Function Fitted to the L-530 Data, for Different Electrode Separations

<table>
<thead>
<tr>
<th>Electrode separation (mm)</th>
<th>Cell constant, $\lambda$ (m$^{-1}$)</th>
<th>$\Delta \varepsilon'(0)$</th>
<th>$\tau$ ($\mu$s)</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>12.7 ± 0.1</td>
<td>41,700 ± 240</td>
<td>14.6 ± 0.5</td>
<td>0.884 ± 0.009</td>
<td>1.53 ± 0.04</td>
</tr>
<tr>
<td>7.0</td>
<td>29.6 ± 0.1</td>
<td>24,540 ± 100</td>
<td>15.5 ± 0.3</td>
<td>0.907 ± 0.003</td>
<td>1.440 ± 0.024</td>
</tr>
<tr>
<td>10.0</td>
<td>38.8 ± 0.1</td>
<td>21,920 ± 140</td>
<td>18.0 ± 0.7</td>
<td>0.988 ± 0.012</td>
<td>1.18 ± 0.04</td>
</tr>
<tr>
<td>10.5</td>
<td>40.4 ± 0.1</td>
<td>21,090 ± 110</td>
<td>18.116 ± 0.018</td>
<td>1.013 ± 0.005</td>
<td>1.128 ± 0.007</td>
</tr>
<tr>
<td>11.0</td>
<td>41.9 ± 0.1</td>
<td>20,820 ± 140</td>
<td>17.6 ± 0.6</td>
<td>1.013 ± 0.013</td>
<td>1.13 ± 0.04</td>
</tr>
<tr>
<td>11.5</td>
<td>43.1 ± 0.1</td>
<td>20,450 ± 200</td>
<td>17.4 ± 0.8</td>
<td>1.014 ± 0.018</td>
<td>1.13 ± 0.05</td>
</tr>
</tbody>
</table>

FIG. 3. (a) Raw dielectric constant (real part) of L-530 suspensions and of a 0.5 mM NaCl solution as a function of frequency. (b) Same as (a), but for the imaginary part calculated with the logarithmic derivative method. $\lambda = 12.7$ m$^{-1}$ (■, □), 29.6 m$^{-1}$ (●, ○) and 43.1 m$^{-1}$ (▲, △). (c) and (d) Same as (a) and (b), respectively, but $\lambda = 38.8$ m$^{-1}$ (▼, ▼), 40.4 m$^{-1}$ (●, ○), 41.9 m$^{-1}$ (●, △), and 43.1 m$^{-1}$ (●, ×). First symbols: suspensions; second symbols: solutions without particles.
FIG. 4. Real and imaginary parts of the dielectric increment of L-530 suspension as a function of frequency. Real part obtained by using the logarithmic derivative method (■) and the quadrupole calibration technique (○). Imaginary part, (□) from the logarithmic derivative. Cell constant, \( \lambda = 43.1 \text{ m}^{-1} \) (electrode separation, 11.5 mm).

FIG. 5. \( \varepsilon''_D(\omega) \) for Aquacoat suspensions in solutions of sodium salicylate with concentrations 0.1 mM (■), 0.3 mM (●), and 1 mM (▲). \( \lambda = 24.9 \text{ m}^{-1} \).

Dielectric Spectra of Aquacoat Suspensions: Effect of Ionic Strength

The results obtained with Aquacoat latex at increasing concentrations of sodium salicylate (NaSal) are plotted in Fig. 5, where \( \varepsilon''_D(\omega) \) is shown as a function of frequency for suspensions with \( \phi = 4\% \) in 0.1, 0.3, and 1 mM NaSal solutions. The linear dependence between \( \varepsilon''_D(\omega) \) and log \( \omega \) is clearly observed in all cases, as well as the larger effect of EP for higher ionic strengths. Even in this less favorable case, the absorption peak of Aquacoat is easily detected, so the logarithmic procedure was performed in these suspensions (see Table 4 for the fitting parameters), and Fig. 6 shows the calculated \( \Delta \varepsilon'_D(\omega) \),

### Table 4

<table>
<thead>
<tr>
<th>C (mM)</th>
<th>( \Delta \varepsilon'(0) )</th>
<th>( \tau ) (( \mu \text{s} ))</th>
<th>( a )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2025 ± 25</td>
<td>22 ± 1</td>
<td>1.004 ± 0.001</td>
<td>0.72 ± 0.03</td>
</tr>
<tr>
<td>0.3</td>
<td>2075 ± 25</td>
<td>18.5 ± 0.9</td>
<td>1.003 ± 0.001</td>
<td>0.81 ± 0.03</td>
</tr>
<tr>
<td>1</td>
<td>2975 ± 25</td>
<td>20.6 ± 0.6</td>
<td>0.91 ± 0.01</td>
<td>0.95 ± 0.03</td>
</tr>
</tbody>
</table>

Note. Electrode separation: 6.5 mm (\( \lambda = 24.9 \text{ m}^{-1} \)).
TABLE 5
Experimental Mobility and Zeta Potential (via O’Brien and White Theory) as Input Parameters for the DeLacey–White Model

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>C (mM)</th>
<th>(\mu_e) (10^{-8}) m²/Vs</th>
<th>(\zeta) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-530</td>
<td>KCl</td>
<td>0.5</td>
<td>−5.26</td>
<td>−100</td>
</tr>
<tr>
<td>Aquacoat</td>
<td>NaSal</td>
<td>0.1</td>
<td>−3.73</td>
<td>−95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>−3.93</td>
<td>−123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>−4.00</td>
<td>−106</td>
</tr>
</tbody>
</table>

Note. The relative uncertainty of the data is estimated as ±5%.

compared to the values deduced from the electrode separation technique. As observed, the latter tends to overestimate the amplitude of the relaxation, i.e., the value of \(\Delta\varepsilon'(\omega \to 0)\). Let us mention that such overestimation might be due to the absence of reliable low-frequency data because of the fact that the EP effects do not appear to be fully eliminated in standard methods.

Comparison between Experimental Data and Theoretical Predictions

It is well known (see, e.g., Refs. 5, 32) that experimental LFDD data often overestimate theoretical predictions, even if a complete electrokinetic theory like that of DeLacey and White (8) is used. Both theoretically (11) and experimentally (5, 32–34), it has been shown that the disagreement could be reduced if an electrokinetic theory based on the existence of a dynamic Stern layer (DSL) is employed instead of a standard model. In a DSL description, ions beneath the electrokinetic shear plane are assumed to be able to move tangentially to the surface, contrary to so-called standard or classical theories, in which both the fluid and the ions located in the inner part of the double layer are thought of as rigidly bound to the solid, hence completely immobile.

Nevertheless, since results like those in Fig. 6 suggest that part of the overestimation could be associated to the procedure used to get rid of electrode polarization, we will now consider to what extent this is the situation. Thus, we performed measurements of electrophoretic mobility in all the suspensions, and used the O’Brien and White theory (33) to compute the electrokinetic potential, \(\zeta\) (Table 5). This quantity, together with the particle radius and the concentrations, valencies, and mobilities of ions in solution, are the input parameters needed to calculate \(\Delta\varepsilon'(\omega)\) in the DeLacey and White approach.

Figure 7 shows the comparison for latex L-530. Note the very significant differences that still remain between measured (data treatment with the logarithmic-derivative method) and calculated (DeLacey–White theory) values of \(\Delta\varepsilon'(\omega)\). It appears very plausible that consideration of DSL effects is required: the disagreement cannot be reasonably ascribed to improper EP correction.

The comparison between measured and calculated \(\Delta\varepsilon'(\omega)\) data for Aquacoat is much more favorable, as Fig. 8 demonstrates. The agreement is much better, and we could say that the differences are now acceptable, both in \(\Delta\varepsilon'(0)\) and in \(\omega_{rel}\).
In fact, our previous work with these particles (35) has demonstrated that Stern-layer conductance effects are lower in this less-charged polymer than in polysterene, because of the larger particle size of the latter. Furthermore, the agreement can be improved if account is made for the moderate polydispersity of this latex, using the method described in Ref. (12).

CONCLUSIONS

The logarithmic-derivative method for correcting dielectric dispersion data for electrode polarization effects has been applied to the case of aqueous colloidal suspensions. After demonstrating that the procedure can be applied to theoretical results (8), where the real and imaginary parts of the dielectric constant can be independently calculated, we have used it with experimental data on two polymer latexes. The method has been proved to be capable of separating the electrode and particle double-layer relaxations. By fitting a relaxation function to the thus obtained double-layer absorption peak, the real part of the dielectric constant can be reconstructed. The results are compared to the predictions of the DeLacey and White theory: it is found that the agreement between theoretical and experimental results is poor in the case of polysterene latex and reasonably good for these results.

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