Correlation of the Dielectric and Conductivity Properties of Polystyrene Suspensions with Zeta Potential and Electrolyte Concentration

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In this work we present recent data on the dielectric properties and conductivity of anionic polystyrene suspensions. Our main aim is to analyze how such properties correlate with the zeta potential of the particles and the electrolyte concentration in the dispersion medium. The results will be compared to the predictions of the standard dielectric model of suspensions (DeLacey, E. H. B., and White, L. R., J. Chem. Soc., Faraday Trans. 2 27, 2007 (1981)). Our data indicate that the correlation between the properties analyzed and both the zeta potential and electrolyte concentration follows qualitatively the predictions of the standard model in all cases. Like previously reported results, data presented here confirm that more general models, that include dynamic processes in the inner part of the double layer are needed to explain the dielectric response of colloidal systems.


INTRODUCTION

The analysis of the conductivity and dielectric response of a colloidal suspension in an AC field can yield considerable information on the electrical characteristics of the solid–liquid interface. Such phenomena are much more precise fingerprints of colloidal systems than electrophoretic mobility or DC conductivity measurements. This is because the relaxation processes taking place in the double layer for low frequencies (sub-MHz range) of the applied field are most sensitive to the exact nature of the interface (1–4).

The standard electrokinetic model, and in particular the rigorous theory of DeLacey and White (4) (DW hereafter) of the dielectric response of dilute suspensions cannot quantitatively explain the experimental results obtained with a number of different solid–liquid systems, mainly in the case of latexes (5–10). Thus, recent studies have incorporated considerations about surface conductance into the body of equations of the standard theory (11), and have analyzed the effect on the dielectric properties and complex conductivity of ionic adsorption and lateral transport in the inner part of the double layer. This approach has been named the dynamic Stern layer model (12, 13) (DSL in what follows).

The results of these recent models show better quantitative agreement between experimental results and theoretical data, although some assumptions are needed concerning the concentrations and mobilities of ions in the (thin) region between the solid surface and the slipping plane to obtain the best approximate agreement with the measured results. In any case, both the standard DW model and the DSL approach predict similar qualitative relations between the quantities of interest and both the zeta potential (ξ) and the electrolyte concentration. Hence, the comparison between the experimental dependence of those quantities on both ξ and the concentration, and the predictions of either of the models concerning such dependence seems of interest.

The aim of the present work is to carry out such a comparison using anionic latexes. It will be shown that excellent qualitative agreement does exist between theory and experiment when the DW model is used. Although the current version of the DSL (13) model does not completely fit the measurements on amphoteric latexes studied by Myers and Saville (5) and Rosen and Saville (6), it can be expected that the DSL theory will improve the agreement from a quantitative point of view.

However, it seems clear that the standard DW model is a solid basis for more general theories, and in fact it correctly predicts the trend of variation with frequency, ξ potential, or ionic strength in many instances. Before proceeding with our discussion we will describe the notation used in the next section.

NOTATION

The complex conductivity \( K^*(\omega) \) of a dilute suspension in an AC field of frequency \( \omega \) can be expressed as a series expansion in the volume fraction \( \phi \) (4),

\[
K^*(\omega) = K_0^*(\omega) + \phi \Delta K^*(\omega) + O(\phi^2),
\]

where \( K_0^*(\omega) \) corresponds to the complex conductivity of the electrolyte dispersion medium. \( \Delta K^*(\omega) \) contains all the
information concerning the effect of the particles and their
double layers in terms of AC conductivity. In terms of real
and imaginary parts, it can be written

$$K^*(\omega) = K(\omega) + \omega \varepsilon_0 \varepsilon'_r(\omega) + i \omega \varepsilon_0 \varepsilon'_i(\omega)$$  \[2]\n
$$K^*_s(\omega) = K^\infty + i \omega \varepsilon_0 \varepsilon_{rd}$$  \[3]\n
where $K(\omega)$ is the part of the conductivity not associated to
dielectric losses, $\varepsilon'_r(\omega)$ and $\varepsilon'_i(\omega)$ are, respectively, the real
and imaginary parts of the complex dielectric constant of
the suspension, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_{rd}$ is the di-
electric constant of the solution, and $K^\infty$ is its DC con-
ductivity. For dilute suspensions, series expansions like [1] can be
proposed:

$$K(\omega) = K^\infty + \phi \Delta K(\omega) + O(\phi^2)$$  \[4]\n
$$\varepsilon'_r(\omega) = \varepsilon_{rd} + \phi \Delta \varepsilon'_r(\omega) + O(\phi^2)$$  \[5]\n
$$\varepsilon'_i(\omega) = \phi \Delta \varepsilon'_i(\omega) + O(\phi^2).$$  \[6]\n
$\Delta K^*(\omega)$ can be experimentally determined if the complex
admittance $Y^*(\omega)$ of a conductivity cell of constant $C_s$ filled
with the suspension is measured at each prescribed frequency,$\omega$.

$$K^*(\omega) = C_s Y^*(\omega)$$  \[7]\n
for different volume fractions.

The quantities of interest in this work will be $\Delta \varepsilon'_r(\omega)$, the
increment of the real part of the dielectric constant, Eq. [5],
and the specific conductivity increment, $\text{Sci}(\omega)$,

$$\text{Sci}(\omega) = [\text{Re}[K^*(\omega) - K^*(0)]]/\phi,$$  \[8]\n
or, using Eq. [2],

$$\text{Sci}(\omega) = [K(\omega) + \omega \varepsilon_0 \varepsilon'_r - K(0)]/\phi.$$  \[9]\n
As demonstrated before (14, 15), $K(\omega)$ is in fact in-
dependent of frequency ($K(\omega) = K(0)$) and, as a consequence,

$$\text{Sci}(\omega) = \omega \varepsilon_0 \Delta \varepsilon'_r(\omega) = \text{Re}[\Delta K^*(\omega) - \Delta K^*(0)].$$  \[10]\n
where use has been made of Eqs. [6], [2], and [1]. Since
the numerical solution of the equations of the DW model
yields the complex quantity $\Delta K^*(\omega)$, both $\text{Sci}(\omega)$ and
$\Delta \varepsilon'_r(\omega)$ can thus be calculated and compared to experimen-
tal data.

EXPERIMENTAL

The polystyrene latex was prepared without surfactant ad-
dition following the method described by Goodwin et al.

$\phi = 24.5 \pm 0.5\%$. Electron micrographs (TEM and SEM)
showed the sphericity and monodispersity of the particles,
their average diameter being $610 \pm 10$ nm.

Different methods have been proposed to obtain suspensions
of different volume fractions for a given electrolyte
concentration (9). In this work, the technique employed
consisted of repeated cycles of centrifugation and redisper-
sion in solutions of the desired concentration.

The zeta potential of the particles, a determinant parame-
ter of their dielectric behavior in suspension, was calculated
from their electrophoretic mobility determined with a Mal-
vern Zeta Sizer 2c device. O'Brien and White's model of
electrophoresis (17) was used to carry out such calculations.

The complex admittance of the suspensions was measured
by means of an HP-4192A LF impedance analyzer from
Hewlett-Packard. The conductivity cell connected to the an-
alyzer was designed similarly to that described by Springer
(18); the technique of variable separation between the (plat-
inized) platinum electrodes was used to reduce the effect of
both parasitic impedances and electrode polarization (19,
20). The cell with suspension was thermostatized at 25.00 ±
0.05°C and kept under N₂ atmosphere. The frequency of
the electric field applied to the suspensions varied between
1 kHz and 200 kHz, and their volume fractions ranged from
$5 \times 10^{-3}$ to $5 \times 10^{-2}$. The linearity of the dependence of
$K^*(\omega)$ with $\phi$ for each frequency was experimentally found
for this range of values of $\phi$.

FIG. 1. Zeta potential of the polystyrene particles as a function of KCl
concentration.
FIG. 2. Specific conductivity increment of the suspensions plotted against frequency for different KCl concentrations.

FIG. 3. Increment of the real part of the dielectric constant of the suspensions plotted against frequency for several KCl concentrations.

FIG. 4. Comparison between theoretical and experimental specific conductivity increments as a function of zeta potential.

RESULTS AND DISCUSSION

Zeta Potential

Figure 1 shows the variation of the zeta potential of the particles with the concentration of KCl; note the classical maximum in $|\zeta|$ for a concentration of around $10^{-3}$ M. The reasons for the existence of such a maximum have been thoroughly discussed in the literature, and include the presence of a polymeric hairy layer on the surface of the particles (21–23). It has been shown that the maximum disappears, and a monotonic decrease of $|\zeta|$ with concentration is obtained, if surface conductance associated to ionic transport in the Stern layer is assumed (24). These findings suggest that surface conductance could be the answer to the problem. In fact, the DSL model (12) would also predict larger zeta potential values as compared to data obtained using the standard electrokinetic model. Since the effect of the particles on the dielectric response of the system is more important the larger $|\zeta|$, for fixed values of frequency and $\kappa a$ ($\kappa^{-1}$ is
ELECTRICAL PROPERTIES OF POLYSTYRENE SUSPENSIONS

Exp.

\[ \Delta \varepsilon' (\omega) \]

- ζ (mV)

DW

\[ \Delta \varepsilon' (\omega) \]

- ζ (mV)

FIG. 5. Same as Fig. 4, for the increments of the real part of the dielectric constant.

the double layer thickness and \( a \) is the particle radius), a detailed picture of the dynamics of the inner double layer can improve not only the estimation of \( \zeta \), but also the agreement between theory and experiment in AC measurements, as discussed below.

Conductivity and Dielectric Constant of the Suspensions

Figures 2 and 3, respectively, show the quantities \( \text{Sci} \) and \( \Delta \varepsilon'_r \) as a function of \( \omega \) for different KCl concentrations. The increase of both quantities with ionic strength for fixed frequency is clearly seen, in agreement with the increase in \( |\xi| \) with [KCl] observed in Fig. 1 for the concentration range of interest. Note however, that \( \kappa a \) also increases, and hence it is the simultaneous effect of \( \zeta \) and \( \kappa a \) on \( \text{Sci} \) and \( \Delta \varepsilon'_r \) that is experimentally detected.

Similar behavior versus \( \kappa a \) has been described in the literature (5, 7) for amphoteric latexes in the presence of HCl and HNO₃, although in the latter case \( |\xi| \) decreases with \( \kappa a \). Silica suspensions in HCl or KCl solutions showed trends of \( \zeta \) with concentration comparable to those found for amphoteric latexes in HNO₃ solutions, although both \( \text{Sci} (\omega) \) and \( \Delta \varepsilon'_r (\omega) \) decreased with electrolyte concentration (7).

It has been argued that such different behavior must be due to the sensitivity of \( \Delta \varepsilon'_r \) and \( \text{Sci} \) to the peculiar surface characteristics of the various types of particles. However, even the standard model (where essentially no information other than \( \zeta \) and \( \kappa a \) is used) can qualitatively explain all these types of results. When the DSL model is used (12), the trends referred to above can also be explained, although in this case the quantitative agreement does also improve.

Comparison with Theoretical Predictions

The quantities \( \text{Sci} (\omega) \) and \( \Delta \varepsilon'_r (\omega) \) are plotted in Figs. 4–7 as a function of \( \zeta \) and KCl concentration for three frequencies well separated in the measured spectra. It can be observed that the theoretical and experimental trends of

Exp.

\[ \text{Sci}(\omega); \ S/m \]

- \( \omega = 10^4 \) rad/s

DW

\[ \text{Sci}(\omega); \ S/m \]

- \( \omega = 10^4 \) rad/s

FIG. 6. Comparison between theoretical and experimental dependences of the specific conductivity increments on KCl concentrations.
variation are essentially identical, although the quantitative differences are also evident, amounting to about one order of magnitude. As mentioned above (see also Ref. (25)), the extreme dielectric behavior of colloidal latexes cannot be completely explained by assuming ionic transport in the inner double layer (like in the DSL model). In fact, heat treatment of latexes above the glass transition temperature of the polymer (7, 8) brings about a closer approximation between theoretical predictions and experimental relaxation spectra when the standard model is used, whereas realistic values of the DSL parameters are needed to obtain good data fitting (12, 13). Our results agree with those previously published in that polystyrene might not behave as an ideal colloid, and suggest that reliable data for other spherical particles are still needed. Spherical (hydrated) oxides (as described in (28)) could be candidates in the future. Concerning the theoretical treatment, a more complete (and possibly specific for the different transport processes occurring in the double layer) treatment is also in order. Undoubtedly, the DSL model (12, 13, 26, 27) must be the starting point for more rigorous developments.

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