Thin Double-Layer Approximation and Exact Standard Prediction for the Dielectric Response of a Colloidal Suspension

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This work deals with the analysis of the applicability of the approximate theory of the dielectric response of colloidal suspensions elaborated by Fixman (J. Chem. Phys. 78, 1483 (1983)) for particles with thin double layers. The predictions of this, comparatively simple, analytical model are compared, for a wide range of the variables of interest, with exact numerical results computed according to DeLacey and White’s standard theory (J. Chem. Soc. Faraday Trans. 2 77, 2907 (1981)). The interest of this comparison lies in the possibility of delimiting to what extent the thin double-layer approximation agrees with the standard model, since new theories, incorporating ionic transport in the inner part of the double layer, have been proposed to explain well-documented discrepancies between theoretical and experimental data on the dielectric behavior of suspensions. Some such models are generalizations of Fixman’s theory, and once the true limits of validity of the latter are established, it will be possible to ascribe the possible differences between measurements and predictions to actual physical facts rather than to errors bound by the use of approximate analytical solutions outside their range of validity.

Key Words: dielectric relaxation; dielectric constant; standard electrokinetic model; thin double-layer approximation.

INTRODUCTION

It is well known that the determination of numerical solutions for dielectric response and electrical conductivity of colloidal suspensions is not an easy task. The first exact numerical results were obtained by DeLacey and White (DW hereafter; Ref. (1)). This model predicts significant relaxation processes in the radio frequency range of the applied field frequency. Such processes are related to the polarization of the electric double layers surrounding the (spherical) particles, as well as to the ionic transport processes occurring when the electric field is applied.

Due to the numerical difficulties involved, the problem has also been approached by other authors searching for analytical or semianalytical solutions. Thus, Dukhin and Shilov (2) derived a thin double-layer approximate formula for the complex conductivity of colloidal suspensions. O’Brien (3) developed a semianalytical theory, valid for zeta potentials, ζ, below 50 mV. Fixman (4) obtained approximate analytical

![Graph](image)

**FIG. 1.** Approximate (full symbols) and numerical (open symbols) values of Δκreff(ω)/Δκeff(ω) plotted as a function of frequency for colloidal particles with ζ = 100 mV dispersed in KCl solutions. Values of κa: ■, Δ = 10; ●, Ω = 25; ●, Ω = 55.

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such suspensions should be significantly lower than in the case of noninteracting particles. Furthermore, the shape of the relaxation spectra obtained was also different.

Given the experimental difficulties involved in the determination of the complex conductivity and dielectric constant of colloidal suspensions, as well as the lack of an exact numerical treatment in this case, we will focus our attention on dilute suspensions. Among the different models above mentioned, this work deals with Fixman (6) and DW (1) models. Both have recently been extended to account for surface conductance contributions (9–13) with the aim of obtaining a better approximation between theoretical predictions and experimental data (14–19). Since such extended treatments have demonstrated to be a good approach to the problem, it is of interest to consider the limitations of the analytical theory and to rigorously establish its range of validity by comparing its results to those provided by the DW theory.

FIG. 2. Same as that described in the legend to Fig. 1 for the real part of the dielectric increment, $\Delta \varepsilon_r$.

solutions applicable to suspensions with low values of $\xi$ and high values of $\kappa a$ ($\kappa$ is the reciprocal double-layer thickness and $a$ is the particle radius). Chew and Sen (5) also found analytical solutions valid to first order in $1/\kappa a$ and low zeta potentials.

In a subsequent paper, Fixman (6) extended his results to values of the dimensionless zeta potential, $\tilde{\xi} (\tilde{\xi} = \xi \kappa^2 aT)$, smaller than 8, and $\kappa a \geq 50$. The results of the model were compared to numerical values previously obtained by the same authors, but such comparison has not yet been carried out with the general DW model. Such a comparison will be considered in the present paper.

Other improvements in these analytical models were proposed by Chew (7) and Vogel and Pauly (8). The latter authors, using the so-called asymptotic matching technique, were able to obtain solutions valid to order $(1/\kappa a)^3$, and, for the first time, considered the much more complex problem of concentrated dispersions of spherical particles. Their results showed that the real part of the dielectric constant of

FIG. 3. Same as that described in the legend to Fig. 1 for the imaginary part of the dielectric increment, $\Delta \varepsilon_i$. 
where \( K(\omega) \) is a real quantity representing the contribution to the conductivity, not due to dielectric losses. \( \epsilon'_r \) and \( \epsilon''_r \) are, respectively, the real and imaginary parts of the dielectric constant of the suspension, and \( \varepsilon_0 \) is the vacuum permittivity. Finally, \( K^{(\infty)} \) and \( \epsilon_{rd} \) are the DC conductivity and dielectric constant of the supporting electrolyte solution.

The quantities \( \epsilon'_r \) and \( \epsilon''_r \) can also be expanded as a power series in \( \phi \), and, for dilute systems, it can be written

\[
\epsilon'_r(\omega) = \epsilon_{rd} + \phi \Delta \epsilon'_r(\omega) \tag{4}
\]

\[
\epsilon''_r(\omega) = \phi \Delta \epsilon''_r(\omega). \tag{5}
\]

From Eqs. [1-5] it is clear that the knowledge of the real and imaginary parts of \( \Delta K^*(\omega) \) allows one to obtain all the quantities of interest. The following will be chosen for this work:

\[
\Delta \epsilon'_r(\omega) = \epsilon'_r(\omega) - \epsilon_{rd} = \phi \Delta \epsilon'_r(\omega) \text{ for } \omega \text{ of interest.}
\]

\[
\epsilon''_r(\omega) = \phi \Delta \epsilon''_r(\omega).
\]

**NOTATION**

For dilute suspensions with volume fraction \( \phi \), the following linear relationship between the complex conductivity of the suspension, \( K^*(\omega) \), and \( \phi \) can be written

\[
K^*(\omega) = K^*_r(\omega) + \phi \Delta K^*(\omega), \tag{1}
\]

where \( \omega \) is the frequency of the applied AC field and \( K^*_r(\omega) \) is the complex conductivity of the pure electrolyte. \( \Delta K^*(\omega) \), the conductivity increment, is a quantitative measure of the effect of the colloidal particles on the bulk conductivity.

In terms of its real and imaginary parts, [1] can be rewritten as

\[
K^*(\omega) = K(\omega) + \omega \varepsilon_{rd} \epsilon'_r(\omega) + i \omega \varepsilon_{rd} \epsilon''_r(\omega) \tag{2}
\]

\[
K^*_r(\omega) = K^{(\infty)} + i \omega \varepsilon_{rd}, \tag{3}
\]
and $\kappa a$ on the quantities of interest will be considered. According to Fixman (6), even for $\kappa a \sim 20$ the approximation yields results reasonably close to his own numerical calculations. We will show that such facts are confirmed when Fixman's results are compared to DW's, and, furthermore, that the convenient use of the easily computable Fixman's formulas can be extended to still lower $\kappa a$ values if $\xi$ is not very high.

Figures 1–3 show, respectively, $\Delta K_{\text{eff}}$ (normalized by the electrolyte DC conductivity), $\Delta \varepsilon^\prime$, and $\Delta \varepsilon^\prime\prime$, as a function of the frequency of the applied field, for constant $\xi$ (100 mV) and different values of $\kappa a$, and for both models used. It can be seen that, even for $\kappa a$ values as low as 25, the agreement is excellent, the maximum errors in $\Delta K_{\text{eff}}$ amounting to 5%, this figure being lower for the dielectric constant increments (Figs. 2 and 3). This is an interesting result, since the values of $\xi$ and $\kappa a$ included in these figures are very often found

$$\Delta K_{\text{eff}}(\omega) = \text{Re} \{ \Delta K^*(\omega) \}$$  \hspace{1cm} \text{[6]}

$$\Delta \varepsilon^\prime(\omega) = \frac{\text{Im} \{ \Delta K^*(\omega) \}}{\omega \varepsilon_0}$$  \hspace{1cm} \text{[7]}

$$\Delta \varepsilon^\prime\prime(\omega) = \frac{\text{Re} \{ \Delta K^*(\omega) - \Delta K^*(0) \}}{\omega \varepsilon_0}.$$  \hspace{1cm} \text{[8]}

By numerical integration of the differential equations of the DW model, $\Delta K^*(\omega)$ can be computed for each frequency and from it the quantities defined in [6–8] follow. Fixman's analytical expressions for the same quantities are given in Ref. (6).

RESULTS AND DISCUSSION

The predictions of both models will be compared assuming that the spherical colloidal particles are dispersed in KCl solutions of different concentrations. The effects of both $\xi$ and $\kappa a$ on the quantities of interest will be considered. According to Fixman (6), even for $\kappa a \sim 20$ the approximation yields results reasonably close to his own numerical calculations. We will show that such facts are confirmed when Fixman's results are compared to DW's, and, furthermore, that the convenient use of the easily computable Fixman's formulas can be extended to still lower $\kappa a$ values if $\xi$ is not very high.

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under standard experimental conditions; in such cases, the use of approximate analytical formulas is not only convenient but correct, assuming that the approximation of symmetrical electrolyte with equal ionic mobilities is correct. It must be remembered that, for the particle size used in most experiments, a large amount of electrolyte would be needed in order to obtain higher $\kappa a$ values, and under these conditions, the colloidal stability of the system is not guaranteed (20).

The effect of $\zeta$, for reasonable $\kappa a$, on $\Delta K_{\text{eff}}$, $\Delta\varepsilon''$, and $\Delta\varepsilon''$, is plotted in Figs. 4–9. Zeta potential values of 40, 70, and 100 mV are used (dimensionless zeta potentials of 1.6, 2.7, and 3.9 at room temperature, respectively), for $\kappa a = 10$ (Figs. 4–6) and $\kappa a = 25$ (Figs. 7–9). The first feature to be noted in these figures is that, although the case $\kappa a = 10$ is out of the range of validity of Fixman's theory, data in Figs. 4–6 show that the latter is a reasonably good approximation if the zeta potential of the particles is not too high.

For $\kappa a = 25$ (Figs. 7–9) and higher (not shown for brevity) the agreement between analytical and numerical results is excellent in practically all cases, the differences increasing moderately with the zeta potential. Furthermore, the assumption of symmetrical electrolyte, with ions of equal mobility, used in Fixman's model, could be another source of discrepancy. However, this may be a second-order effect, given the demonstrated smaller effects of nonadsorbed coions in many phenomena of colloid science (20).

In conclusion, it can be seen that there exists a wide range of applicability for analytical approximate solutions. Such a range covers many cases of interest in practice. It can be assumed, although a rigorous demonstration is still lacking, that extended theories including surface conductance, based on Fixman and DW models (9, 10), can be applied under the same conditions of $\zeta$ and $\kappa a$ in which those models are valid.

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