Dielectric relaxation pattern of dilute colloidal suspensions

Abstract An immediate method of analysis of the relaxation characteristics of a colloidal suspension, like any dielectric, is based on the so-called Cole-Cole representation (imaginary part versus real part) of its complex dielectric constant in a wide frequency range. In this work, we show theoretical plots calculated according to the models developed by DeLacey and White (J Chem Soc Faraday Trans 2 77:2007-2039), and by Rosen et al. (J Chem Phys 98: 4183-4194; this model uses the dynamic Stern layer theory). Both theoretical approaches to the dielectric relaxation pattern of a colloidal suspension are compared to each other, and to experimental data obtained on polystyrene suspensions. Although no significant differences are found between the theoretical predictions of the relaxation patterns (except for the values of the dielectric constant; the DSL model yields higher polarizabilities of the suspensions), none of the models can exactly reproduce the frequency dependence of the dielectric constant of a colloidal system. We propose a modification of DeLacey and White's model to include the possibility that the ionic drag coefficients depend on the ion position in the double layer. The final results show that the general trends of the frequency dependence of the quantities involved are not modified, regardless of the changes in ionic drag coefficients.

Key words Dielectric relaxation - dielectric constant - standard electrophoretic model - dynamic Stern layer model - position-dependent drag coefficient

Introduction

Both theoretical [1–9] and experimental [10–17] data on the dielectric response and conductivity of a dilute colloidal suspension in the presence of AC fields show significant relaxation processes at low frequencies (up to the radiofrequency range). The explanation for the existence of such processes relates them to the polarization of the electric double layers surrounding the particles: the ion cloud, due to the finite time constants for the diffusive transport processes occurring in it, cannot follow the changes of the applied field when the oscillation period of the latter is small as compared to the characteristic diffusion times of ions in the double layer. As a consequence, the polarization is out of phase with respect to the applied field, and hence the strong dielectric dispersion typical in colloidal systems for the frequency range above mentioned.

The quantity of interest is the complex dielectric constant of the colloidal suspension, \( \varepsilon^*(\omega) = \varepsilon'_*(\omega) - i\varepsilon''*(\omega) \) (\( \omega \) is the angular frequency of the applied field). Although plots of either \( \varepsilon'_*(\omega) \) or \( \varepsilon''*(\omega) \) vs. frequency are often analyzed, it is also interesting to consider the so-called
Cole–Cole representation, i.e., $\varepsilon'(\omega)$ vs. $\varepsilon''(\omega)$. Although this type of plotting the data does not add any information to that already contained in the frequency spectrum of either $\varepsilon'(\omega)$ or $\varepsilon''(\omega)$, it helps to easily establish the analogies and differences between the various dielectric models. Moreover, there exists a very close relation between the form of the relaxation patterns in these plots, and the specific mechanisms responsible for the dielectric response observed [18].

In this work, both types of representation will be considered. A linear relationship between the dielectric constant and the volume fraction of solids, $\phi$, will be considered:

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \phi \Delta \varepsilon'(\omega)$$  \hspace{1cm} (1)

$$\varepsilon''(\omega) = \phi \Delta \varepsilon''(\omega)$$  \hspace{1cm} (2)

where $\varepsilon_{\infty}$ is the dielectric constant of the pure electrolyte solution. Since $\Delta \varepsilon'(\omega)$ and $\Delta \varepsilon''(\omega)$ (the intrinsic quantities containing all the information on the effect of the particles with their double layers on $\varepsilon'\omega$) are based on the same polarization mechanisms, $\Delta \varepsilon'(\omega)$ can be calculated from $\Delta \varepsilon'(\omega)$ using the following version of the Kramers-Krönig equation [18, 19]:

$$\Delta \varepsilon'(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\Delta \varepsilon''(\omega') - \Delta \varepsilon''(\infty)}{\omega^2 - \omega'^2} d\omega'$$  \hspace{1cm} (3)

where $\Delta \varepsilon'(\infty)$ is the high-frequency limit of $\Delta \varepsilon'(\omega)$. In a previous paper [19] we found an excellent agreement between values of $\Delta \varepsilon'(\omega)$ obtained by means of Eq. (3), and those computed by numerically solving the theoretical equations of DeLacey and White [1].

The purpose of this work is to compare the dielectric patterns predicted by two rather different models, and to consider if some improvements could be achieved in their predictions of experimental facts by assuming that the mobilities of ions in the double layer depend on their distance to the particle surface in a physically reasonable manner.

The first model (DW hereafter) was developed by DeLacey and White [1], and it can be considered the standard, or classical, description of the dielectric response of colloidal suspensions, Experimental results [10–17; see however, ref. 20] suggest, however, that this model underestimates the measured dielectric increments, although the predicted trends of variation of either $\Delta \varepsilon'(\omega)$ or $\Delta \varepsilon''(\omega)$ with the zeta potential, $\zeta$, or $ka$ ($k$ is the reciprocal double layer thickness, and $a$ is the particle radius) are parallel to those found experimentally [20, 21].

The quantitative differences between the DW model and experimental results has prompted other authors to consider relaxation mechanisms associated not only to the polarization of the diffuse part of the double layer, but also to adsorption and transport in the inner part of the double layer [22–25]. These are called dynamic Stern layer (DSL) models of dielectric relaxation; specifically, the results obtained by Rosen et al. [22] and Saville [23] will be used to compute Cole–Cole plots that can be compared to those obtained from the DW theory, in order to ascertain whether that additional mechanism modifies the standard relaxation pattern of a dilute colloidal suspension.

### Cole–Cole plots of colloidal suspensions

When the DW model is used to predict such diagrams, results like those shown in Fig. 1 are obtained. The plots are not symmetrical (as expected from raw $\Delta \varepsilon'(\omega)$ data, see refs. [1,19]). This lack of symmetry is intrinsically related to the differential equations of the model and to the hydrodynamic, electrical and diffusive mechanisms assumed to explain the ionic transport in the double layer under the influence of the AC field. Note in fact how the curves in Fig. 1 correspond to depressed Cole–Cole plots, i.e., $\max(\Delta \varepsilon'(\omega)) < \frac{[\Delta \varepsilon'(\omega) - \Delta \varepsilon'(\infty)]}{2}$. Furthermore, it can be shown that the angle $\beta$ between the tangent to the plot and the real axis tends to $-\pi/4$ at low frequencies, and to $\pi/2$ at high frequencies, irrespective of the values of either $ka$ or $\zeta$.

As mentioned above, several authors [12, 22, 23] have shown that the differences previously found between experimental and theoretical estimations of the dielectric response in different suspensions [12–14] decrease when surface conductance and ionic adsorption are incorporated to the standard model. We will now consider whether or not our previous considerations on the $\Delta \varepsilon'(\omega) - \Delta \varepsilon'(\omega)$ plots, as obtained from the standard model, are also valid for the DSL theory. In Fig. 2 we have shown our computation based on $\Delta \varepsilon'(\omega)$ data reported by Saville [23], after making use of the Kramers–Krönig relation Eq. (3). Different values of the theoretical parameter $\alpha$ (describing the ratio of the surface to the integrated conductance in the diffuse double layer, associated to a given ionic species, the counterion in this case) are included. The characteristics mentioned above for the plots (depressed Cole–Cole plots, limiting values of $\beta$ are clearly confirmed for the DSL model, whatever the value of $\alpha$.

These results suggest that the modification of the boundary conditions on the particle surface, introduced by the DSL model in order to account for the global dielectric behavior of the system, does not modify the shape of the relaxation pattern of the colloidal suspension. In this respect, it can be concluded that the divergences found between the experimental and theoretical DW relaxation patterns, still remain in the same way for the DSL model. This can be demonstrated by considering the fact that...