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ORIGINAL CONTRIBUTION

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Dielectric relaxation pattern of dilute colloidal suspensions

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Abstract An immediate method of analysis of the relaxation characteristics of a colloidal suspension, like of 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, irregardless of the changes in ionic drag coefficients.

Key words Dielectric relaxation – dielectric constant – standard electrokinetic 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, $\varepsilon_r^*(\omega) = \varepsilon_r'(\omega) - i\varepsilon_r''(\omega)$ (ω is the angular frequency of the applied field). Although plots of either $\varepsilon_r'(\omega)$ or $\varepsilon_r''(\omega)$ vs. frequency are often analyzed, it is also interesting to consider the so-called

Cole–Cole representation, i.e., $\varepsilon_r''(\omega)$ vs. $\varepsilon_r'(\omega)$. Although this type of plotting the data does not add any information to that already contained in the frequency spectrum of either $\varepsilon_r'(\omega)$ or $\varepsilon_r''(\omega)$, 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, ϕ, will be considered:

$$\varepsilon_r'(\omega) = \varepsilon_{re} + \phi \Delta\varepsilon_r'(\omega) \tag{1}$$

$$\varepsilon_r''(\omega) = \phi \Delta\varepsilon_r''(\omega) , \tag{2}$$

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

$$\Delta\varepsilon_r''(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\Delta\varepsilon_r'(\omega') - \Delta\varepsilon_r'(\infty)}{\omega'^2 - \omega^2} d\omega' , \tag{3}$$

where $\Delta\varepsilon_r'(\infty)$ is the high-frequency limit of $\Delta\varepsilon_r'(\omega)$. In a previous paper [19] we found an excellent agreement between values of $\Delta\varepsilon_r''(\omega)$ 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 $\Delta\varepsilon_r'(\omega)$ or $\Delta\varepsilon_r''(\omega)$ with the zeta potential, ζ, or κa (κ 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 $\Delta\varepsilon_r''(\omega)$ 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., $\max(\Delta\varepsilon_r''(\omega)) < [\Delta\varepsilon_r'(0) - \Delta\varepsilon_r'(\infty)]/2$. Furthermore, it can be shown that the angle β 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 κa or ζ.

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 $\Delta\varepsilon_r''(\omega) - \Delta\varepsilon_r'(\omega)$ plots, as obtained from the standard model, are also valid for the DSL theory. In Fig. 2 we have shown our computation based on $\Delta\varepsilon_r'(\omega)$ data reported by Saville [23], after making use of the Kramers–Krönig relation Eq. (3). Different values of the theoretical parameter α (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 β) are clearly confirmed for the DSL model, whatever the value of α.

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

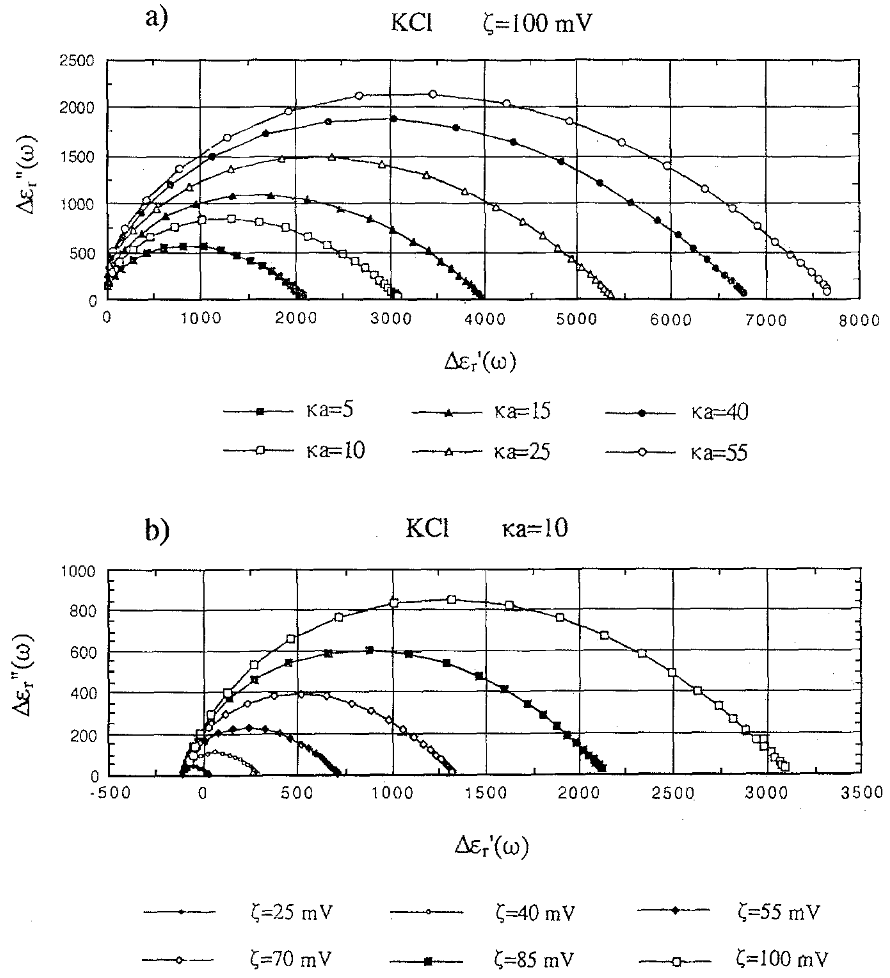

Fig. 1 Cole–Cole diagrams for the increment of the complex dielectric constant of the suspensions: a) $\kappa a = 10$ and different ζ values;
b) $\zeta = 100$ mV and different κa values. Electrolyte: KCl, DW model

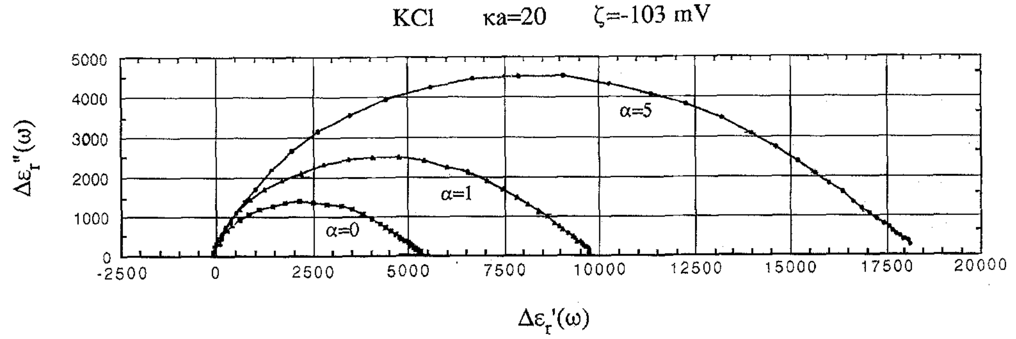

Fig. 2 Cole–Cole diagrams for the increment of the complex dielectric constant of the suspensions, for $\kappa a = 20$, $\zeta = -103$ mV and different values of α (see text). Electrolyte: KCl, DSL model (ref. [23])

most of the experimental Cole–Cole diagrams reported in the literature for the complex dielectric constant of dispersions are symmetrical, and conform to the so-called depressed semicircle response [10, 11, 17]: when $\varepsilon_r''(\omega)$ (or $\Delta\varepsilon_r''(\omega)$) is plotted against $\varepsilon_r'(\omega)$ (or $\Delta\varepsilon_r'(\omega)$) a semicircle is obtained having its center below the real axis. This type of behavior was first interpreted in an empirical way by Cole and Cole (ref. in [26]), according to the equation:

$$\varepsilon_r'(\omega) - i\varepsilon_r''(\omega) = \varepsilon_{r\infty} + \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{1 + (i\omega\tau_0)^{1-\alpha}}\,, \tag{4}$$

with $\alpha < 1$, where ε_{rs} and $\varepsilon_{r\infty}$ correspond to the values of the dielectric constant for low and high frequencies,

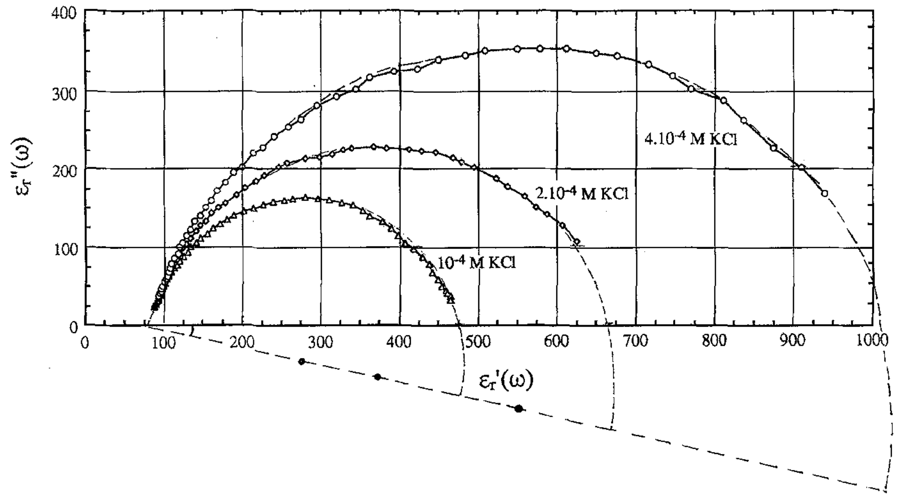

Fig. 3 Experimental Cole–Cole diagrams for the complex dielectric constant of polystyrene suspensions, with particle radius $a = 305$ nm, for different KCl concentrations

respectively, and τ_0 is a characteristic time related to the frequency of the maximum in the $\varepsilon_r'' - \log(\omega)$ plot.

As a clear example of this result, Fig. 3 shows the experimental Cole–Cole plot for the complex dielectric constant $\varepsilon_r^*(\omega)$ of a suspension of spherical polysterene particles, with radius $a = 305$ nm, for different KCl concentrations. A complete description of the material and experimental technique used for the determination of the dielectric quantities, can be seen in [17]. The results in Fig. 3 are in very close agreement with the Cole–Cole Eq. (4), and therefore, with its depressed semicircular dielectric relaxation response; to the authors' knowledge, the latter has not been explained by the existing dielectric relaxation models in suspensions.

Effect of ionic mobilities on the dielectric relaxation pattern

In order to further check whether the standard electrokinetic model (in which interactions between particles are neglected) can be made compatible with relaxation patterns closer to those experimentally found, we analyzed the effect of relaxing the condition that the ionic drag coefficient is constant throughout the double layer. We propose a model in which that coefficient is larger the closer the position of any ion to the particle surface. Some physical justification can be given for that dependence: thus, surface-induced liquid structure, in addition to the usual hydrodynamic effects near a boundary, could account for the slower motion of ions upon approaching the solid/liquid interface.

However, this study is a very rough approximation to the real problem, since the viscosity could certainly be different to that in the bulk liquid medium, whereas the dielectric constant should be a position-dependent tensor as a consequence of solvent structure in the inner part of the double layer. In spite of this, we assume that the macroscopic parameters of the liquid are constant and take their bulk values anywhere in the double layer; it will also be assumed that the laws of continuum mechanics are valid in that particular region surrounding the particles.

We propose a radially-symmetric function for describing the position dependence of the ionic drag coefficient of any ionic species j ($j = 1, \dots, N$):

$$\lambda_j(x) = \lambda_j^{\infty}[1 + \alpha_j e^{-\beta_j(x-\kappa a)}] \qquad j = 1, \dots, N , \qquad (5)$$

where $x = \kappa r$ is the dimensionless distance to the particle center, N is the number of ionic species, and λ_j^{∞} is the corresponding bulk value. α_j and β_j are both adjustable parameters that permit us to modify the decay of λ_j with distance.

It is easy to verify that the boundary conditions of the electrokinetic model remain unchanged; we numerically solved the set of differential equations of the model, and the values of $\Delta\varepsilon_r'$ and $\Delta\varepsilon_r''$ were computed as a function of the frequency, as shown in Fig. 4. The parameter m in these figures represents, in κa units, the distance at which the ionic drag coefficients reduce to their bulk values (we assume the same value of m for both coions and counterions).

Data in Fig. 4 show that increasing m provokes a significant decrease in the values of the dielectric quantities, in perfect agreement with the idea that the higher the value of m, the lower the polarizability of the region surrounding the particles. It is interesting to note that the frequency-dependence of both $\Delta\varepsilon_r'$ and $\Delta\varepsilon_r''$ are essentially identical for different m values. As a consequence, no difference can be expected between the relaxation pattern just described, and those predicted by either the DW or the DSL models. In fact, calculations not shown here demonstrate that the frequency dependence of the angle β is indistinguishable, for any value of m, of those obtained for DW and DSL models.

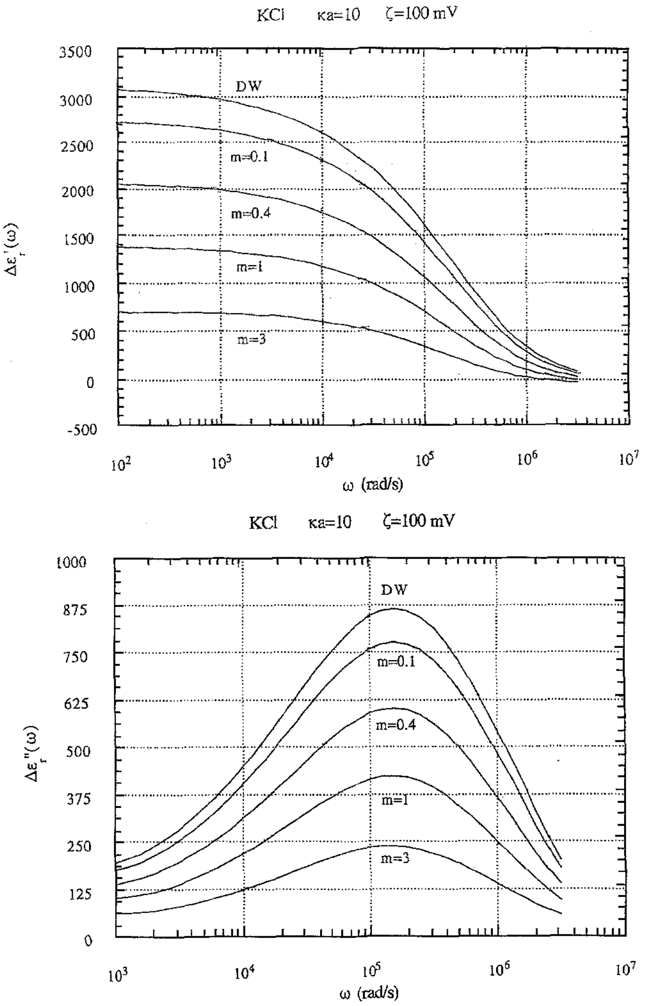

Fig. 4 Frequency dependence of the increment of the real ($\Delta\varepsilon_r'(\omega)$) and imaginary ($\Delta\varepsilon_r''(\omega)$) parts of the complex dielectric constant of the suspensions, for different parameters of the dependent-position ionic drag coefficients (see text) with ($j = 1, 2$ for KCl): $\alpha_j = \beta_j = 0$ for the DW case; $\alpha_j = 50$ for the rest of cases; $\beta_j = 85.1$ for $m = 0.1$, $\beta_j = 21.3$ for $m = 0.4$, $\beta_j = 8.51$ for $m = 1$, and $\beta_j = 2.84$ for $m = 3$

Discussion

The results presented so far point to the conclusion that the shape of the dielectric relaxation pattern is intrinsically related to the diffusive nature of the processes responsible for the dielectric relaxation taking place in the suspensions, irregardless of the ionic characteristics of both the medium and the particles. Apparently, only changes in the absolute values of the quantities of interest (ε_r' and ε_r'', mainly) for any given frequency are to be expected when the ionic characteristics mentioned above are modified. This might explain why the DSL model, incorporating new transport mechanisms associated to surface conductance in the inner part of the double layer, essentially predicts the same relaxation pattern and relaxation frequency as the DW theory.

Turning now to the discussion of the β values characteristic of the different theories, it must be mentioned that only theories assuming that the dispersed colloidal particles are not completely independent of each other predict limiting β values different to those mentioned in this work; in fact, the universal dielectric response model [27] yields $\beta < \pi/2$ in the high frequency limit only when interactions do exist between the individual elements constituting a system. Vogel and Pauly [28] obtained different limiting β values for the case of particles with thin double layers and residual interaction between pairs of particles. It must be mentioned that, because of the considerable experimental difficulties involved in dielectric determinations in concentrated dispersions, this point has been little investigated [20, 29].

The relaxation pattern is the dielectric "fingerprint" of any system. Hence, the important question of if (unlike theoretical calculations) experimental data are well described by the semiempirical Cole–Cole equation (Eq. (5)), seems to be an open problem requiring further improvements of the theoretical models of the dielectric behavior of colloidal systems.

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