Dynamic electrophoretic mobility of concentrated suspensions
Comparison between experimental data and theoretical predictions

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Abstract

In this paper, we first report dynamic mobility ($\mu^*$) data obtained with an electroacoustic technique (electrokinetic sonic amplitude (ESA)) on suspensions of alumina with varying volume fractions and ionic strengths. The frequency interval was 1–18 MHz for these measurements. We found the expected reduction of the modulus of $\mu^*$ with volume fraction associated to the hindering of the particle motion by the interaction with its neighbors. More illustrative is the behavior of the phase angle, normally negative (the mobility lags behind the applied field) but sometimes positive in the frequency region of the Maxwell–Wagner relaxation. This behavior is related to the phase angle of the induced dipole moment. From phase data, we also concluded that the effect of the dipole mentioned is weakened by partial neutralization of the dipoles induced on neighbor particles. Our results indicate that dynamic mobility data are little affected by the possible presence of stagnant-layer conductivity, which adds to the advantage of being suitable for concentrated systems. Furthermore, a good sensitivity to changes in particle size by, for instance, aggregation was also detected. The main features of the experimental mobility spectra were compared with the predictions of two models, one based on direct estimation of particle–particle interactions and the other based on the cell concept. We found that the predictions of the cell model agree best with data obtained at the lowest frequencies (close to the Maxwell–Wagner relaxation), whereas for higher frequencies it appears as if the interaction model would better capture the effects of inertia.

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1. Introduction

Electroacoustic techniques are recently gaining interest from the colloid science community as powerful tools to obtain information on the electrical state of many interfaces, particularly in a number of situations where traditional electrokinetic methods are of limited use. One of such situations is that of concentrated suspensions and slurries, in which we can get no information on the behavior of individual particles by performing, for instance, microelectrophoresis experiments. Take off of electroacoustic methods has also been favored by the commercial availability of sophisticated, highly automated devices which, in turn, have driven theoretical treatments dealing with very different problems.

There are two such techniques. One involves the generation of a pressure wave when an ac electric field is applied to the suspension: the amplitude of the sound wave, $A_{ESA}$, is known as electrokinetic sonic amplitude, and so we speak of the ESA effect. The second method, reciprocal of ESA, is based on the determination of the electric potential induced by the passage of a sound wave through the system. It is called colloid vibration potential (CVP) or colloid vibration current (CVI) depending on the quantity measured.

After the very early works in the subject, particularly those by Debye, and Booth and Enderby [1–4], O’Brien [5,6] carried out an investigation on the physical foundations of electroacoustic techniques, based on the concept of dynamic electrophoretic mobility, $\mu^*$, a complex quantity that is in...
fact proportional to the ESA signal, from which it can be derived [6]:

\[ A_{ESA} \propto \phi \rho_p - \rho_m \rho_u^* d \]  

(1)

where \( \phi \) is the volume fraction of solids and \( \rho_p (\rho_m) \) is the density of the particles (the dispersion medium), and the dynamic mobility relates the electrophoretic velocity of the particle to the electric field, if this is alternating.

In the case of the CVI method, its interpretation in terms of dynamic mobility is also possible, and a formally identical expression can be given for colloid vibration current, \( I_{CV} \), [7]:

\[ I_{CV} \propto \phi \rho_p - \rho_m \rho_u^* d \]  

(2)

Current technology allows to obtain the dynamic mobility from either \( A_{ESA} \) or \( I_{CV} \) data, and the problem can thus be reduced to evaluate \( \rho_u^* d \) and relate it to the zeta potential, the particle shape and dimensions, the ionic composition of the medium, and, very important, the volume fraction of solids.

Two independent approaches have been followed to solve specifically the problem of volume fraction dependence in the case of concentrated dispersions. O’Brien et al. use a “first-principles” approach, considering the ac electrophoresis of pairs of interacting particles [8] or the more realistic situation of a particle interacting with its nearest neighbors [9–12]. Another evaluation, first carried out by Dukhin et al. [13,14], is based on a so-called “cell model”, that has also been successfully applied to the analysis of a variety of electrokinetic phenomena in concentrated suspensions, including electrophoresis, sedimentation potential or dielectric dispersion [15–19]. In this sort of calculation, the hydrodynamic and electrical interactions between particles are accounted for in an averaged form by solving the electrokinetic equations for a single spherical particle of radius \( a \), enclosed by a spherical shell of solution of radius \( b \), concentric with the particle. The radius of the sphere is chosen in such a way that the volume fraction of solids is the same in the cell and in the suspension:

\[ \phi = \left( \frac{a}{b} \right)^3 \]  

(3)

In this paper, our aim is to report experimental dynamic mobility data on suspensions of alumina of different volume fractions and ionic strengths, analyzing the features presented by the modulus and phase of \( \rho_u^* \) and checking these results against predictions of the two types of models described.

2. Experimental

2.1. Materials

The hydrated alumina used for the preparation of the suspensions was provided by Dispersion Technology Inc. (USA), and was given to us in the form of a concentrated suspension in an unknown dispersion medium. SEM micrographs showed that the particles were crystalline and moderately polydisperse. Their average hydrodynamic radius was 165 ± 30 nm, as measured by photon correlation spectroscopy in a Malvern 4700c PCS device (Malvern Instruments, UK).

The original suspensions were repeatedly washed with KCl solutions of concentration ranging between \( 5 \times 10^{-5} \) and \( 10^{-3} \) mol/l. The process was carried out by centrifugation at 8500 \( \times g \) in a Kontron T-124 centrifuge, and redispersion in the desired KCl solution. The volume fraction of solids, \( \phi \), in the suspensions prepared was determined from the dry weight of known volumes using \( \rho_p = 2.42 \) g/cm\(^3\) as the density of alumina.

2.2. Methods

The classical or dc electrophoretic mobility of the particles, \( u_e \), was measured in dilute suspensions (\( \phi \sim 10^{-4} \)) in the desired KCl concentration at pH 6, using a Malvern Zetasizer 2000 (Malvern Instruments, UK). These measurements provided an alternative or complementary way to evaluate the electrokinetic or zeta potential of the particles.

The basic quantity of interest in this work was the dynamic or ac mobility of the particles, \( u_e^* \), a complex quantity measured for a frequency range between 1 and 18 MHz in an Acoustosizer II (Colloidal Dynamics, USA). Like other electroacoustic techniques, the method is particularly suitable for the evaluation of the electrokinetic properties of concentrated systems [1,7].

3. Results and discussion

3.1. dc mobility and zeta potential

Fig. 1 shows the electrophoretic mobility of alumina particles as a function of KCl concentration. Previous
determination of the isoelectric point (pH$_{iep}$ or pH of zero zeta potential) yielded a value of pH~4, hence the negative mobility at the pH of the measurements. A significant feature of Fig. 1 is the increase in $|u_e|$ with ionic strength, using a complete theory of electrophoresis, like O’Brien and White’s [20], the zeta potential, $\zeta$, was also found to increase in absolute value with the concentration of KCl. Such an increase is against the predictions of classical models of electrokinetic phenomena, the compression of the electrical double layer upon adding indifferent ions should lead to a reduction in $|\zeta|$. The “anomalous” behavior of $|\zeta|$ has been reported by many other authors [21,22], and there seems to be a general agreement that it is originated by the existence of a finite stagnant-layer conductivity (SLC), and that a theory assuming that SLC $\neq 0$ leads to correct $\zeta$-concentration dependences [23,24]. We will not pursue this topic at this stage, but will come back to it the following sections.

3.2. Dynamic mobility of alumina suspensions: experimental data

We measured the dynamic mobility of alumina particles in suspensions with varying volume fractions ($\phi$~2.5–20%) and KCl concentrations. The ESA instrument provides experimental data of the modulus and phase of the complex dynamic mobility $u^*_e$. Because this quantity has been found to depend strongly on both the ionic strength and the volume fraction, we must show all data in order to discuss such effects. This is done in Figs. 2–5. The following features of these figures must be mentioned:

(i) In whatever conditions, increasing the volume fraction provokes a reduction in the mobility. This was to be expected, as it is predicted by all theoretical models [7,11,12] and justified because of the hydrodynamic and
electrostatic interactions (at non-zero frequencies of the applied field) of a given particle with its neighbors. 

(ii) In addition, the phase angle is in general negative, i.e., the velocity lags behind the applied ac fields. This must be due to two phenomena that, for certain frequency ranges, act against the electrophoretic motion. One is the particle and fluid inertia that becomes increasingly important for frequencies above $f_I \approx \eta/\rho_m a^2$ ($\approx$5 MHz for our particles), where $\eta$ is the viscosity of the liquid medium, this is the manifestation of the time needed for the particles to acquire their steady velocity after a variation of the applied force. Because of this inertia, the phase lag of the mobility will become increasingly negative with frequency for $f > f_I$.

Furthermore, the action of the field provokes the polarization of the electrical double layer inducing a frequency, and zeta potential, dependent dipole moment. In order to understand in a qualitative way the influence of that dipole on the dynamic mobility, we have used the Delacey and White’s theory [25], valid for dilute suspensions, to calculate the induced dipole coefficient $C_0^*$ related to the dipole moment $d^*$ as follows: $d^* = 4\pi\varepsilon_m C_0^* E$, where $\varepsilon_m$ is the electric permittivity of the dispersion medium. Recall that in this theory no contribution of stagnant-layer conductivity is assumed, but this is not essential for our qualitative arguments.

It is known [26] that, for large $\kappa a$, the dc electrophoretic mobility is very approximately determined by the induced dipole coefficient by means of the relation:

$$\mu_e = \frac{\varepsilon_m}{\eta} \left(1 - C_0\right),$$

Fig. 4. Modulus (left) and phase angle (right) of the dynamic mobility $u^*_{e}$ of alumina particles as a function of frequency and volume fraction, in $5 \times 10^{-4}$ mol/l KCl solutions.

Fig. 5. Modulus (left) and phase angle (right) of the dynamic mobility $u^*_{e}$ of alumina particles as a function of frequency and volume fraction, in $1 \times 10^{-3}$ mol/l KCl solutions.
Fig. 6. Modulus (a) and phase angle (b) of \((1 − \varepsilon_1)/\varepsilon_0\) for 150 nm particles with the zeta potentials indicated, in \(2 \times 10^{-4}\) mol/l KCl solutions. The suspensions are assumed to have low volume fractions of solids.

which O’Brien [5] has shown to be also valid for alternating fields. We can wonder whether a similar dependence between \(u_e\) and \(\phi\) exists for ac fields, so we will focus ourselves on the frequency range of interest from the electrokinetic point of view. From the ac version of Eq. (4) we can conclude that the phase angle of \(u_e\) is given by \(\text{Arg}(1 - \varepsilon_0^*|\varepsilon_0|)\), and \(|\varepsilon_0^*|\) will depend on \(1 - \varepsilon_0^*|\varepsilon_0|\). Fig. 6 shows \(1 - \varepsilon_0^*|\varepsilon_0|\) and \(\text{Arg}(1 - \varepsilon_0^*|\varepsilon_0|)\) as a function of frequency for low and moderate zeta potential. Both the low-frequency (or \(\alpha\), with frequency \(\omega_\alpha\)) and the Maxwell–Wagner (MW, with characteristic frequency \(\omega_{MW}\)) relaxations are observed. Note how, for sufficiently high \(\eta_\alpha\), \(|\varepsilon_0^*|\) should increase around \(\omega_{MW}\), as experimentally found, because of the raise in \(|1 - \varepsilon_0^*|\) (Fig. 6a). For similar reasons, the phase angle of \(u_e\) can increase, and even become positive, as that of \((1 - \varepsilon_0^*|\varepsilon_0|)\) displays a maximum around the Maxwell–Wagner relaxation frequency (Fig. 6b).

Summarizing in the \(\omega_{MW}\) region the dynamic mobility may show a phase delay associated to the behavior of \(\varepsilon_0^*|\varepsilon_0|\), and a phase delay because of inertia. Since \(\omega_{MW} = K_m/\eta_\alpha\) (\(K_m\) is the conductivity of the medium), increasing the ionic strength will shift \(\omega_{MW}\) to higher frequencies, thus hiding the raise in the phase by its inertial decrease. This occurs in Fig. 5 \((10^{-3}\) mol/l KCl), whereas in Fig. 4 and, mainly, Fig. 3, the phase increase, and even its positive values are observed.

Note also how the phase difference between the applied field and the particle motion decreases when the content of solids in the suspension increases; in the frequency region controlled by inertia, this phenomenon may be due to the fact that the volume of fluid associated with each particle decreases and so does the inertia of the particle-fluid ensemble. Below \(\omega_{MW}\), the effect of the induced dipole must be weakened by the fields from the dipoles of the surrounding particles [11].

(iii) Concerning the modulus of \(u_e^*\), note how at the lowest electrolyte concentration, it is found to increase with frequency due to the Maxwell–Wagner relaxation around 0.5 MHz (Fig. 2). When the electrolyte concentration is increased, the mobility maximum shifts to higher frequencies, as explained above, in such conditions the fast inertial decrease dominates and almost fully buries the MW increase.

3.3. Comparison with models

Two kinds of theoretical models discussed in Section 1 were used to compare our experimental results to the predictions of the theory. These are the cell model [7,12,14] and the particle interaction model [11]. In all cases, the particle radius was considered fixed (165 nm), and only the zeta potential was used as an adjustable parameter minimizing the differences between calculated and measured mobilities.

Fig. 7 shows the comparison between experimental \(|u_e^*|\) and calculated data of the modulus of the mobility in \(5 \times 10^{-3}\) mol/l KCl solutions. Note that in general both models are capable of properly fitting the data, although cell model calculations sometimes fail to reach the high frequency side because of convergence limitations. In contrast, this model can properly reproduce the maxima in \(|u_e^*|\) at frequencies close to the experimental ones.

Similarly, a good agreement is found in Fig. 8 for a concentration of \(2 \times 10^{-3}\) mol/l KCl. Nevertheless, at higher ionic strengths (Figs. 9 and 10), both models find characteristic inertia frequencies, \(\omega_\alpha\), higher than those experimentally detected. These differences can be explained on the simple basis that, for the particle concentration involved, the aggregation between particles is more likely for these ionic strengths. The dynamic mobility may be sufficiently sensitive as to sense such processes; in fact, if we take an equiva-
Fig. 7. Comparison between the modulus of the dynamic mobility (symbols) and the corresponding theoretical predictions obtained from cell (solid lines) and interaction (dashed lines) model calculations, for the zeta potentials indicated in Table 1. The dc mobility measured in dilute suspensions is shown as a short dotted line labelled “u_e”. Electrolyte concentration 5 × 10^{-5} mol/l.

Fig. 8. Comparison between the modulus of the dynamic mobility (symbols) and the corresponding theoretical predictions obtained from cell (solid lines) and interaction (dashed lines) model calculations, for the zeta potentials indicated in Table 1. The dc mobility measured in dilute suspensions is shown as a short dotted line labelled “u_e”. KCl concentration = 2 × 10^{-4} mol/l.

Fig. 9. Comparison between the modulus of the dynamic mobility (symbols) and the corresponding theoretical predictions obtained from cell (solid lines) and interaction (dashed lines) model calculations, for the zeta potentials indicated in Table 1. The dc mobility measured in dilute suspensions is shown as a short dotted line labelled “u_e”. Electrolyte concentration of 5 × 10^{-4} mol/l.

Fig. 10. Comparison between the modulus of the dynamic mobility (symbols) and the corresponding theoretical predictions obtained from cell (solid lines) and interaction (dashed lines) model calculations, for the zeta potentials indicated in Table 1. The dc mobility measured in dilute suspensions is shown as a short dotted line labelled “u_e”. Electrolyte concentration of 1 × 10^{-3} mol/l.
Fig. 11. Comparison between the modulus of the dynamic mobility (symbols) and the theoretical prediction obtained from cell model calculations (solid lines), for the particle size equal to 300 nm and the zeta potential equal to 70 mV. Electrolyte concentration $5 \times 10^{-4}$ mol/l.

ever, to properly choose the parameters of the system. Note, for instance, how having set the particle size equal to 300 nm in Fig. 11 leads to a very reasonable agreement between the slopes of the decrease in $|u^*_e|$ with $f$ in the high frequency (inertia) regime.

It is interesting to mention that the phase angle is also very useful in evaluating the validity of the models. Figs. 12–14 show the comparison between theory and experiment (the 5% volume fraction has not been included in these figures to avoid confusion). Although no experimental data are available below 1 MHz, we have performed the calculations down to $\sim 100$ kHz. Contrary to the interaction model, the cell one can properly describe the effect of volume fraction on the phase angle, in particular the phase lead in the MW frequency. This is more significant at low volume fractions, and in some cases it gives rise to crossings (also found in the series of experimental data) of the phase curves at frequencies depending on the ionic strength (which determines the Maxwell–Wagner relaxation frequency).

Let us finally refer to the zeta potentials needed to fit the data. They are summarized in Table 1, and the following features are worth to be mentioned:

(i) $|\zeta|$ decreases with ionic strength, contrary to the trends found in dc electrophoresis (Fig. 1). Although this deserves further investigation, it suggests that at the relatively high frequencies used in ESA experiments stagnant-layer conductivity, if present, plays a rather
Although the trends of solids, suspensions in the indicated KCl solutions, for different volume fractions of Zeta potential (mV) best fitting the dynamic mobility spectra of alumina

<table>
<thead>
<tr>
<th>KCl (mol/l)</th>
<th>φ = 2.5%</th>
<th>φ = 5%</th>
<th>φ = 10%</th>
<th>φ = 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 × 10⁻³</td>
<td>100  80  100  80  100  80  120  90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 × 10⁻⁴</td>
<td>90  80  90  80  95  80  100  90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 × 10⁻⁵</td>
<td>70  80  70  60  70  60  80  70</td>
<td></td>
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</tbody>
</table>

Table 1 corresponds to cell model calculations and column II refers to particle interaction calculations.

little significant role in determining the electrokinetic behavior of the system.

(ii) A slightly higher |ζ| value seems to be needed, whatever the model, to fit the results at highest volume fractions. This probably reflects the limitations of the models to properly account for the collective behavior of the suspensions.

(iii) Although the trends of |ζ| are similar for the two models, it appears that a higher zeta potential results from the cell calculations. However, the differences are only significant at the lowest ionic strengths. We have no clear explanation for this, and more cases should be studied prior to deciding which approximation to the mobility is better, if any.

(iv) We have calculated the best-fit zeta potential for the most dilute suspensions (φ = 2.5%) using a single-particle dynamic electrophoresis model [5]. The results are |ζ| = −75, −80 and −60 mV for KCl concentrations 5 × 10⁻³, 2 × 10⁻⁴ and 5 × 10⁻⁵ mol/L, respectively. Note that they are close to the data in Table 1, and agree with the results obtained using concentrated-suspension approaches for the evaluation of the dynamic mobility.

4. Conclusions

Dynamic mobility data obtained from the ESA signal are coherent with conventional dc electrophoresis measurements performed on dilute suspensions. It appears as if the high frequency data would have the additional advantage of being little affected by the existence of finite stagnant-layer conductivity. Our results also indicate that electroacoustic measurements are extremely sensitive to variations in particle size associated to, for instance, particle growth or aggregation in case of high ionic strength or concentrated suspensions. These advantages of dynamic mobility will be even more appreciated as the theoretical models describing the phenomenon in the case of concentrated systems continue to be improved. In this work, we have compared the predictions of two models, describing the effects of neighbor particles on a given one either through the evaluation of particle–particle interactions or by the use of cell models. We have found that the predictions of the cell model are closer to the experimental frequency dependences at the lowest frequencies (in the vicinity of Maxwell–Wagner relaxation), whereas for high frequency (in the region of inertia effects), the situation is reversed, especially for the most concentrated suspensions.

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