

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231669875>

Effect of Particle Size Distribution on the Accuracy of Electroacoustic Mobilities

ARTICLE *in* LANGMUIR · FEBRUARY 1992

Impact Factor: 4.46 · DOI: 10.1021/la00038a011

CITATIONS

13

READS

14

2 AUTHORS, INCLUDING:



Peter J. Scales

University of Melbourne

194 PUBLICATIONS 3,925 CITATIONS

SEE PROFILE

Effect of Particle Size Distribution on the Accuracy of Electroacoustic Mobilities

Peter J. Scales* and Eileen Jones

ICI Corporate Colloid Science Group, P.O. Box 11, The Heath, Runcorn, WA7 4QE, U.K.

Received January 16, 1991. In Final Form: September 12, 1991

The measurement of electrokinetic mobilities in concentrated dispersions (>1% v/v) using the electrokinetic sonic amplitude (ESA) technique at a frequency of 1 MHz is considered. The correlation of such measurements to mobilities measured using classical techniques such as microelectrophoresis rests in the theoretical ratio of the high frequency or dynamic mobility (μ_ω) and the electrophoretic mobility (μ_e). This ratio varies greatly as a function of particle radius at constant frequency. We report an overview of the predictions of the theory of O'Brien (*J. Fluid Mech.* 1988, 190, 71) and the correlation of measurements for both colloidal silica and titania where the particle size distribution is not necessarily monodisperse. The results demonstrate the need to carefully consider both particle size and size polydispersity for adequate correlation of electrokinetics measured by the electroacoustic technique to those measured using conventional electrophoresis.

Introduction

The measurement of particle "electrokinetics" in dispersions of colloidal particles in aqueous solution is paramount to the prediction of flocculation, aggregation, and stability behavior. It is however a drawback of many conventional electrokinetic techniques such as microelectrophoresis, streaming potential, and sedimentation potential that they operate in a solids regime that does not always superimpose on the real systems they mimic. As such, extrapolations of the measured data to systems at lower or higher dilution are typical. This procedure is not always straightforward, and in, for example, the adsorption of amphiphiles onto solid surfaces, the ratio of adsorption surface area to solution volume is such that no real comparison should be made.

An electroacoustic technique for measuring particle electrokinetics in high solids dispersion has now been commercialized (e.g., Matec Instruments Inc.).¹ The technique addresses many of the shortfalls of classical techniques and utilizes a basic physical effect first described by Debye in 1933.² The output of electroacoustic instruments, seen as a result of the movement of charged particles or ions in an oscillating acoustic field is termed the ultrasonic or colloidal vibration potential (UVP or CVP). Conversely, for the reverse experiment, in which particles moving in an oscillating electric field produce an acoustic wave, the output is termed the electrokinetic sonic amplitude (ESA).

A rigorous theoretical development of the relationship between UVP, ESA, and shear plane potential, or for the purpose of this paper, the ζ potential and the electrophoretic mobility (μ_e) has been presented by O'Brien,³ Marlow et al.,⁴ and Babchin et al.⁵ In summary, they predict the relationship between ESA, UVP, and a high frequency or dynamic mobility (μ_ω) to be of the form

$$\text{UVP}(K^*) = \text{ESA} = c\Delta\rho\phi\mu_\omega\gamma \quad (1)$$

where K^* is the complex conductivity of the dispersion,

c is the speed of sound in the fluid, $\Delta\rho$ is the density difference between the particle and the fluid, ϕ is the volume fraction of particles in the fluid, and γ is a geometrical and acoustic coupling factor.

This equation relates the measured quantities to other experimentally available quantities. It predicts that the measured "ESA" in an electroacoustic experiment is a linear function of the dynamic mobility, μ_ω , and is deemed to be valid in the so-called linear regime in ϕ . It is assumed in this regime that particle effects on the speed of sound propagation are insignificant, as are particle-particle interactions and volume conservation effects.^{6,7} Recent work has demonstrated good linearity for a range of solids for $\phi \leq 0.05$.⁹

There are at present three theoretical descriptions of the comparison between μ_ω and μ_e .^{3,5,8} In one of these, O'Brien³ writes down an approximate relationship between μ_ω and ζ for the case where κa is ≥ 10 , namely

$$\mu_\omega = (2\epsilon\zeta/3\eta)(1 + f)G(\alpha) \quad (2)$$

where ϵ is the dielectric permittivity of the fluid, η is the fluid viscosity, f is a complex function of the frequency of the applied field and the diffusivity of the electrolyte ions in solution, and $G(\alpha)$ is most easily visualized as a "damping" term and is a complex function of the frequency of the applied field (ω), the average radius of the particles in solution, and the kinematic viscosity (ν), such that

$$\alpha = \omega a^2/\nu \quad (3)$$

and

$$G(\alpha) = \left(1 - \frac{\frac{1}{9}i\alpha(3 + \frac{2\Delta\rho}{\rho})}{1 + (1-i)\sqrt{\alpha/2}} \right)^{-1} \quad (4)$$

where ρ is the fluid density.

At high κa , the ratio of μ_ω to μ_e may then be approximated as

$$|\mu_\omega/\mu_e| = {}^{2/3}(1 + f)G(\alpha) \approx G(\alpha) \quad (5)$$

The alternative theory of Babchin, Chow, and Sawatzky⁵

* To whom correspondence should be addressed at the School of Chemistry, University of Melbourne, Parkville 3052, Australia.

(1) Oja, T.; Petersen, G. L.; Cannon, D. W. Eur. Pat. Appl. 84106668, 1984. Matec Instruments Inc. U.S. Patent 4,497,208, 1985.

(2) Debye, P. *J. Chem. Phys.* 1933, 1, 13.

(3) O'Brien, R. W. *J. Fluid Mech.* 1988, 190, 71.

(4) Marlow, B. J.; Fairhurst, D.; Pendse, H. P. *Langmuir* 1988, 4, 611.

(5) Babchin, A. J.; Chow, R. S.; Sawatzky, R. P. *Adv. Colloid Interface Sci.* 1989, 30, 11.

(6) Babchin, A. J.; Sawatzky, R. P.; Chow, R. S.; Isaacs, E. E.; Huang, H. In *International Symposium on Surface Charge Characterization*, San Diego, CA, August 1990; Oka, K., Ed.; Fine Particle Society: Tulsa, OK, 1990; pp 49-50.

(7) Kozak, M. W.; Davis, E. J. *J. Colloid Interface Sci.* 1988, 127, 497.

(8) Sawatzky, R. P.; Babchin, A. J. *J. Fluid Mech.*, to be submitted for publication.

and a modification of this theory by Sawatzky and Babchin⁸ give a comparative modulus of the form

$$\left| \frac{\mu_\omega}{\mu_e} \right| = \frac{f_1(\kappa a, a/\delta)}{f(\kappa a)} \left(\frac{\eta}{\sqrt{(\eta R)^2 + (2\omega\pi\rho_{\text{eff}}a^2/9)^2}} \right) \quad (6)$$

where

$$\delta = \sqrt{2\nu/\omega} \quad R = 1 + (a/\delta)$$

$|f_1(\kappa a, a/\delta)|$ is a frequency-dependent "Henry function" and

$$\rho_{\text{eff}} = \rho_0 + \frac{9}{a} \sqrt{\frac{\eta\rho}{8\omega}} + \frac{\rho}{2} \quad (7)$$

The expressions due to both O'Brien³ and Sawatzky and Babchin⁸ have been shown to be theoretically self-consistent at a frequency of 1 MHz.⁹ Another numerical treatment also shows good agreement for $\kappa a \gg 10$.¹⁰ For $\kappa a \leq 10$, differences due to an expected breakdown in the O'Brien theory are observed.

A number of researchers^{4,5,11} demonstrate excellent agreement between calculated ζ potentials from electroacoustics and microelectrophoresis for a range of solids using the above theoretical treatments. Often however, the magnitude of the ζ potentials calculated from dynamic mobilities are significantly different from potentials calculated from other electrokinetic techniques. Work in our laboratories suggests the discrepancy to be due in part to an inappropriate input value of the particle radius into the conversion of ESA signal to ζ potential. This is obviously not problematic for colloidal stable, monodisperse particle dispersions, but samples such as commercial pigments and most particulate oxides would rarely fit into such a description. The aim of this study was therefore to elucidate the sensitivity of the electroacoustic technique to the input value (into the theory) of both the particle radius and any size polydispersity and the ramifications of these factors for the accurate prediction of particle ζ potentials. This was seen as a major consideration for the use of this technique for the in situ measurements of electrokinetics in high solids dispersions in both a research and a developmental environment.

In brief, the work plots the relationship between μ_e and μ_ω as a function of particle radius and density using eqs 1–4. O'Brien³ has already plotted this relationship as a function of frequency, but in the present experimental context, the relationship at constant frequency is also required. Comparisons of mobilities are then made for both monodisperse and polydisperse particle distributions.

Experimental Section

A Matec Instruments MBS-8000 system was used for electroacoustic measurements. Ancillary equipment included a Wyse AT compatible computer and a Marconi Model 2022C frequency synthesizer capable of signal generation in the 0.01–1000 MHz range. In the MBS-8000 system, a SP-80 model electroacoustic probe was attached to a SSP-1 model titration assembly. This consisted of a stirred Teflon sample holder with conductivity cell, pH electrode, temperature probe, and stirrer. A Hamilton Microlab 900 automatic burette was used for titrations of acids and bases. This combination of equipment allowed simultaneous measurement of pH, conductivity, temperature, and ESA signal. Solutions of potassium hydroxide and hydrochloric acid were used for pH adjustment. The ionic strength of particle dispersions was adjusted using KCl or KNO₃. Water was distilled and passed through a "Milli-Q" water purification system. Details of the

Table I. Characteristics of Solids Used in Electroacoustic Experiments^a

| solid | diameter (N4) | diameter (LS130) | density, g cm ⁻³ | CV, % |
|------------------|---------------|------------------|-----------------------------|-------|
| TiO ₂ | | 2.45 | 4.25 | 55 |
| SiO ₂ | 0.60 | 0.60 | ~2.0 | 11 |

^a Sizes are in microns and represent the distribution average (mean) particle size.

solids used in the initial characterization experiment are shown in Table I. Particle sizes were determined using a Coulter N4 PCS instrument, a Coulter LS130 laser diffraction particle sizer, and/or transmission electron microscopy (TEM). The coefficient of variation of the distributions (CV) is shown in the last column. The SiO₂ sample was prepared using the Stöber synthesis.¹² The TiO₂ sample was ex. Tioxide (TSM-1 grade) and had been sedimented, dried, and heated to 70 °C to remove a known organic impurity.

The MBS-8000 instrument was used to measure an ESA signal for a particle dispersion. Samples were typically 200 cm³ in volume. Dispersion was achieved through use of a high-speed disperser fitted with a high shear head (tip speed 10 m s⁻¹) and ultrasonication for short periods at high power. Measurements were nominally made at a volume fraction (ϕ) of 2.5%. The measured ESA signal was converted to dynamic mobility and ζ potential values after input into the software of particle radius, volume fraction, and supporting electrolyte information. The sign of the particle charge was determined after calibration of the instrument with a Ludox silica (Ludox TM ex. Du Pont) at 25 ± 0.2 °C. All experiments were then conducted at this reference temperature using Ludox as a reference. The calibration procedure determined the frequency of maximum signal. This was usually 1.0 ± 0.1 MHz. The instrument factor (γ) was then adjusted to give the manufacturer's recommended value. The electrophoretic mobility of highly dilute particle dispersions was characterized using a Malvern Zetasizer IIC instrument incorporating a cylindrical cell and a pH probe attached to the measurement chamber outlet.

Results and Discussion

As an adjunct to the understanding of comparative experiments between electrophoretic and electroacoustic mobilities, it was considered important to visualize the fundamental differences between the two measurements as a function of particle size. Qualitatively, by examining eqs 2 and 4, one observes that the $G(\alpha)$ term will cause μ_ω to go to zero as the frequency of the applied field and/or the size of the particles in the dispersion increases. The practical significance of these effects may be computed for fixed frequency taking into account that apparatus such as the Matec MBS-8000 operate at a frequency of 1 MHz. Calculations of the effect of particle radius and density on the measured ESA signal were achieved by writing a subroutine to the "MOBILITY" program of Chan and White.¹³ The ratio of μ_ω to μ_e as a function of particle radius and at various particle densities is shown in Figure 1. The calculations were made for a dispersion of particles in which κa was ≥ 20 (a KCl concentration of 0.1 mol dm⁻³) and ζ was low (i.e., ~30 mV). The dielectric permittivity of the solid was assumed to be low (i.e., ≤ 5). The phase lag or phase angle (θ) of the signal as a function of the same variables is shown in Figure 2. Examination of these two figures shows a very strong predicted dependence of both μ_ω and θ on the particle radius for a frequency of 1 MHz.

The dependence of signal on particle size and density is similar for both higher and lower frequencies except

(9) James, R. O.; Texter, J.; Scales, P. J. *Langmuir* 1991, 7, 1993–1997.

(10) White, L. R. University of Melbourne, private communication.

(11) O'Brien, R. W.; Midmore, B. R.; Lamb, A.; Hunter, R. J. *Faraday Discuss. Chem. Soc.* 1990, 90, 301.

(12) Stöber, W.; Fink, A.; Bohn, E. J. *Colloid Interface Sci.* 1968, 26, 62.

(13) MOBILITY: O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* 1978, 74, 1607.

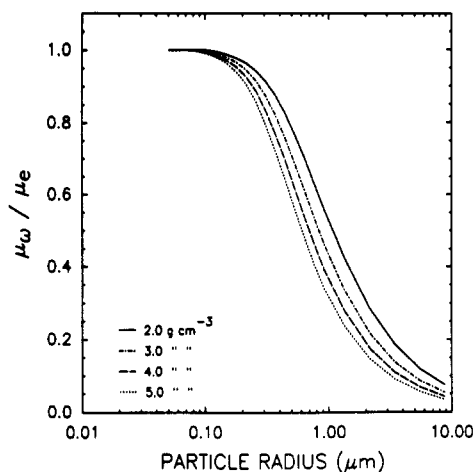


Figure 1. Ratio of the dynamic to the electrophoretic mobility for particles of various densities as a function of particle radius at a frequency of 1 MHz. Data is for KCl at 0.1 mol dm⁻³, a particle dielectric permittivity of 5 and for a value of the ζ potential of 30 mV.

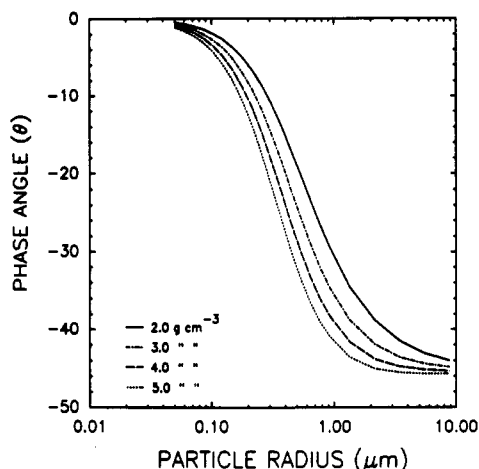


Figure 2. Phase angle versus particle radius for various particle densities and a frequency of 1 MHz. Other parameters are as for Figure 1.

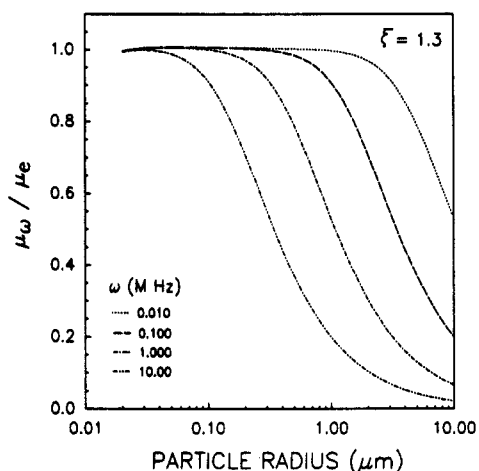


Figure 3. Ratio of the dynamic to the electrophoretic mobility versus particle radius for a particle density of 2 g cm⁻³. Calculations are for a ζ value of 30 mV and for a range of frequencies.

that the position of the dependence shifts. This dependence for a range of frequencies is shown in Figures 3 and 4. It is interesting to note the sensitivity of μ_ω to particle size in the radius range 0.2–1.0 μm at the routinely used frequency of 1 MHz. It will be noted that κa is increasing

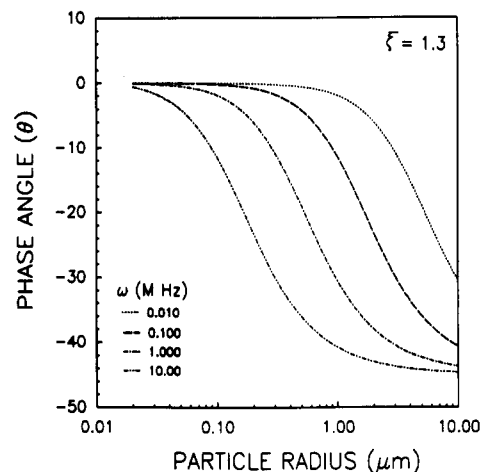


Figure 4. Phase angle versus particle radius for a particle density of 2 g cm⁻³. Other parameters are as for Figure 3.

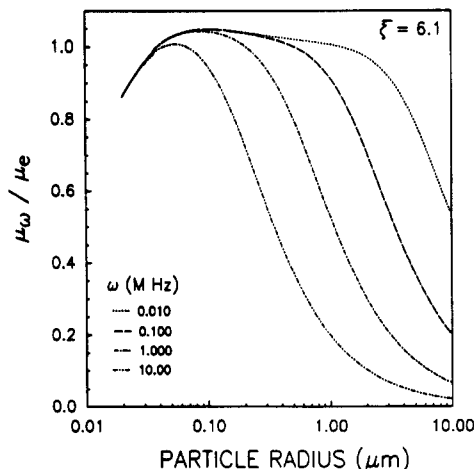


Figure 5. Ratio of the dynamic to electrophoretic mobility versus particle radius for a particle density of 2 g cm⁻³. Calculations are for a ζ value of 150 mV and for a range of frequencies.

with particle radius in Figures 1–4. The consequence of this at low values of ζ is minimal due to insignificant relaxational effects.¹⁴ However, at high values of ζ , these effects are no longer trivial and low κa dependences are expected. Plots of mobility ratio and phase angle versus particle size using the same parameters as for Figures 3 and 4 except at a high value of ζ (i.e., ~150 mV) are shown in Figures 5 and 6, respectively. A KCl concentration of 0.1 mol dm⁻³ was once again assumed to give continuity of ionic strength and a κa value greater than 20 for the entire concentration range. Although potentials of 150 mV are rarely if ever measured at this electrolyte concentration, the calculations serve to demonstrate the contribution of relaxation effects. The maximum in the mobility ratio versus radius curve in Figure 5 for low κa is assumed to be due to breakdown in the theory.

It is of interest to note that the mobility ratio slightly exceeds unity under certain conditions. This may appear contradictory but is in line with O'Brien's prediction of the possibility of a particle actually leading the field under the suggested conditions. At no stage however does the magnitude of μ_e approach the Smoluchowski value in this particle radius regime.

A comparison of particle mobilities for TSM-1 TiO₂ from electroacoustics (μ_ω) and electrophoresis (μ_e) is shown in

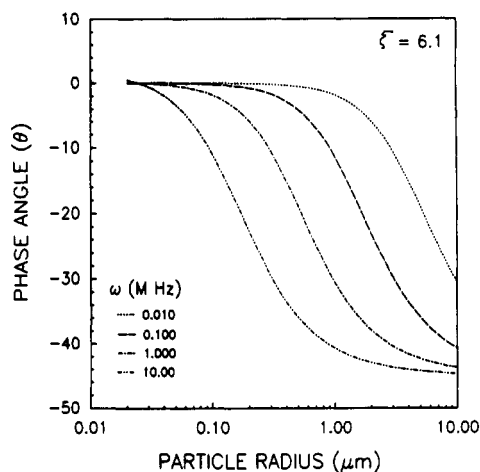


Figure 6. Phase angle versus particle radius for a particle density of 2 g cm^{-3} . Calculations are for a ζ value of 150 mV and for a range of frequencies.

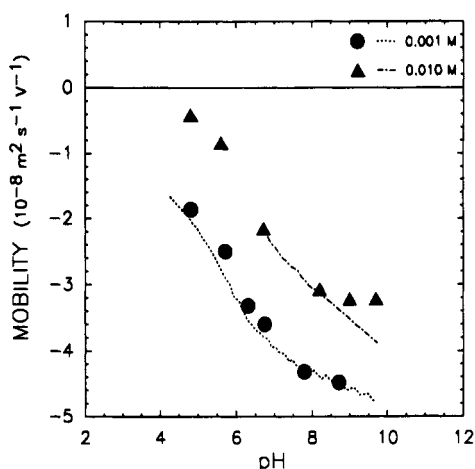


Figure 7. Mobility versus pH for TSM-1 TiO_2 as measured by electrophoresis (points) and electroacoustics (lines).

Figure 7. The data have been plotted against μ_e after correcting the electroacoustics data using a multiplication factor of 2.63. This factor represents a mobility ratio of 0.38 and corresponds to a mean radius of $0.97 \text{ } \mu\text{m}$. Calculations for the measured mean particle radius of $1.22 \text{ } \mu\text{m}$ ($\kappa a = 125$ and 300 corresponding to 0.001 and $0.010 \text{ mol dm}^{-3}$ background electrolyte) suggest a correction factor of 3.60 or a mobility ratio of 0.28 .

The electroacoustics data of Figure 7 have also been corrected for any error due to background electrolyte signal. This correction was found to be insignificant for the lower ionic strength titrations, but since each ESA measurement is a composite of contributions from particle and electrolyte sources, it is important that the magnitude of the electrolyte signal is insignificant for an accurate interpretation of results. Using the ESA data from samples containing only background electrolyte (KCl in this case) and the relationship between ESA and μ_e from eq 1, the electrolyte contribution as a percentage of the total signal can be calculated. Setting an arbitrary error cutoff of say 5% , the required volume fraction of particles in the continuous phase to ensure $\leq 5\%$ error was then calculated as a function of particle density for a value of μ_e of $1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$. Results for two background electrolyte concentrations and a range of particle densities are shown in Figure 8. The lines represent a 5% error cutoff point, so volume fractions of particles above each line for a given particle density and electrolyte concentration represent a measurement regime that will be relatively free of error

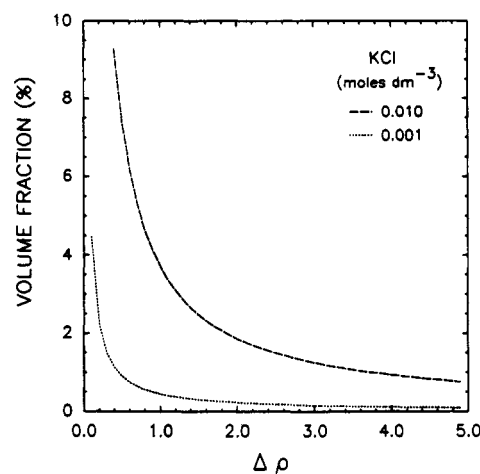


Figure 8. Volume fraction versus density difference for a 5% error cut in electroacoustic experiments for two concentrations of KCl.

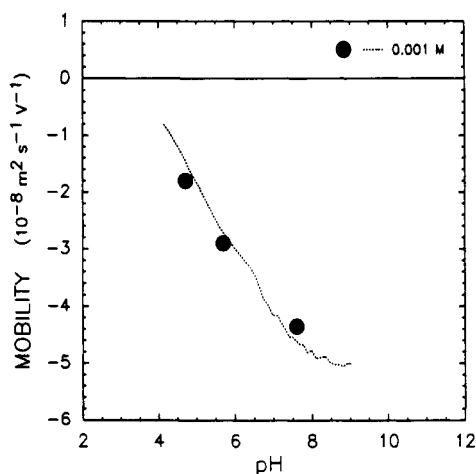


Figure 9. Mobility versus pH for Stöber silica as measured by electrophoresis (points) and electroacoustics (lines).

due to background electrolyte contributions. Figure 8 is not universal in its application due to a different ESA response for each electrolyte, but it nonetheless gives an indication of the importance of the electrolyte signal. The difficulty of making unambiguous measurements on systems where the density difference between the particle and the continuous medium is small is also highlighted.

Returning to the data of Figure 7, the observed correlation in the form of the mobilities for two ionic strengths and the two measurement methods is interesting in that a single multiplication factor suffices to correlate the data. The discrepancy between the techniques is therefore not at all random, and the data suggests that, with errors in density calculations and other experimental factors taken into account, the particle radius as measured by laser diffraction is not representative of the distribution average particle radius in the dispersion during electroacoustics or that the distribution of particle size needs to be considered. This is perhaps not all that surprising as TiO_2 particle distributions are typically polydisperse and even a small number of particles of significantly different radius from the volume average radius may cause the above noted discrepancy.

A comparison of mobilities for an almost monosized ($\text{CV} = 11\%$) Stöber silica is shown in Figure 9. The particles had a radius of $0.30 \text{ } \mu\text{m}$, and a multiplication factor of 1.18 was used to produce correlation of the data from the two sources. This correlates with a particle radius

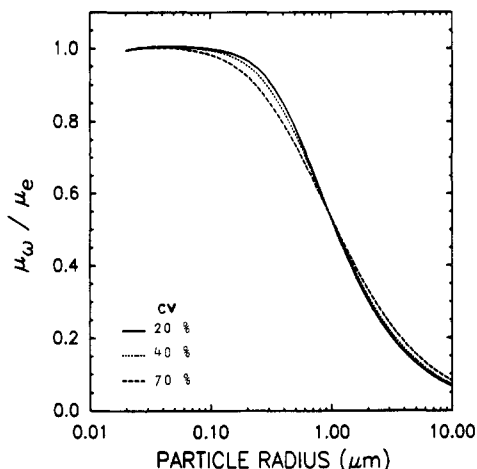


Figure 10. Ratio of dynamic to the electrophoretic mobility versus particle radius for a particle density of 2 g cm^{-3} . Calculations are for a ζ value of 30 mV and for a range of particle size distributions.

of $0.32 \text{ } \mu\text{m}$ which is in excellent agreement with the expected result.

The question arises therefore as to the effect of size polydispersity on the correlation of experiment and theory. To appraise this question, the effect of a log-normal distribution of particles (by volume) was incorporated into the calculations of the mobility ratio as a function of median particle size. A probability distribution was generated of the form

$$P(a) = \frac{1}{\lambda a \sqrt{2\pi}} \exp\left(-\frac{(\ln a - \ln \bar{a})^2}{2\lambda^2}\right) \quad (8)$$

In this equation, λ is the standard deviation of $\ln a$ and \bar{a} is the median particle radius. The effect of incorporating a log-normal particle size distribution with a CV value of $\sim 20, 40$, and 70% into the mobility ratio calculations for a particle density of 2 g cm^{-3} (low potential case) is shown in Figure 10. This curve is generated by summing $G(a)$ over all of the radius contributions rather than taking a single radius value. The CV = 0% (monodisperse case) is not shown for clarity since it falls almost exactly on the CV $\approx 20\%$ line. Both positive and negative contributions to the mobility ratio are observed as a function of particle size, but no significant deviation in the mobility ratio is noted, even for the relatively polydisperse distribution of CV = 70% . One is led to conclude therefore that the major contributing factor for deviations between theory and experiment for "well-behaved" particle distributions is an incorrect input value of the particle size radius.

For bimodal or indeed multimodal and nonnormal distributions, it is not obvious that calculation of the mobility ratio by incorporation of just the mass average radius into the calculation would produce a representative value. To test this hypothesis, the particle size distribution for the TSM-1 TiO_2 sample as measured on the Coulter LS130 diffraction particle sizer (available in digitized form) was incorporated into the analysis. The experimentally measured distribution is shown in Figure 11. One observes that the distribution is not normally distributed on a log scale, and it was thus seen as a suitable candidate for analysis.

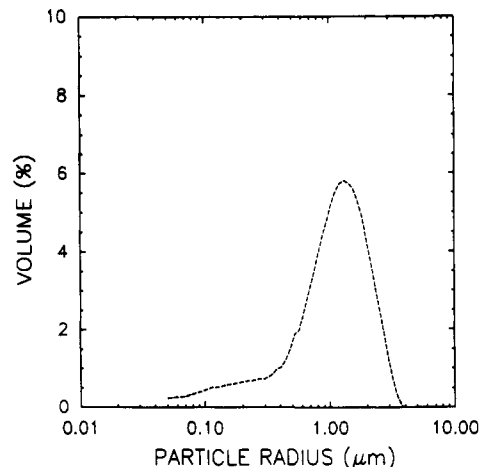


Figure 11. Experimentally measured particle size distribution for a TSM-1 TiO_2 dispersion.

Using the above procedure where $G(a)$ is summed over the entire size distribution, the experimental particle size distribution from Figure 11 resulted in a predicted mobility ratio of 0.363 (multiplication factor 2.75). This is equivalent to a mean particle radius of $1.02 \text{ } \mu\text{m}$ assuming monodispersity. This should be compared to the distribution mean of $1.22 \text{ } \mu\text{m}$. The calculated mobility ratio taking the entire distribution into account is encouragingly closer to the value of 0.38 (particle radius $0.97 \text{ } \mu\text{m}$) required to produce experimental correlation between classical electrophoretic and electroacoustic measurements.

Intuitively, other nonnormal distributions would produce deviations between experiment and the simplest form of the theory. Consideration of the particle size distribution as well as the particle radius is highlighted, and although not representative of a wealth of data, correlation between mono- and polydisperse particle dispersions and for two different densities was considered a reasonable test of the theory. The importance of polydisperse particle distributions to the phase lag or angle of the particles has not been considered experimentally although one would expect a similar approach to be necessary.

Conclusions

The use of electroacoustics as a technique for the in situ investigation of dispersions with solids concentrations of $\phi \leq 0.05$ has been investigated taking current theories into account. The results indicate that the use of the instrument for the accurate measurement of fundamental electrokinetic properties such as ζ is straightforward for monosized particle distributions and for more polydisperse dispersions where the particle size is distributed in a normal fashion about the mean. For bimodal and more diverse particle distributions, a knowledge of the distribution is suggested.

Acknowledgment. We thank ICI (U.K.) for permission to publish this work. Thanks are also extended to Dr. R. Ettelaie for his helpful comments and to Mr. M. Owens for performing a number of complementary electroacoustic measurements.

Registry No. SiO_2 , 7631-86-9; TiO_2 , 13463-67-7.