Mobility measurements by phase analysis

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A new instrument, based on the principle of phase analysis light scattering (PALS) for the measurement of electrophoretic mobilities, has been produced. Such measurements are particularly useful in the study of dispersions in nonpolar and highly conducting media. The current PALS configuration can be used to measure mobilities up to 3 orders of magnitude lower than with the conventional Doppler mode. The device has a number of new features; in particular, all the signal processing is digital and the optical system features a reference beam configuration. Data are presented to show that on suitable samples both the PALS technique and conventional laser Doppler electrophoresis can be performed on the same instrument and the techniques are in good agreement. © 2001 Optical Society of America

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1. Introduction

An understanding of many aqueous dispersions is based on their electrophoretic mobilities, which is of importance in determining, for example, suspension stability, rheological properties, and coating behavior. This arises because the mobility, defined as the velocity the particle attains per unit electric field, can be related to the so-called zeta potential. This potential is defined to be the potential at the surface of shear where the particle with a shell of electrostatically attracted counter ions moves through the bulk solution. The value of the zeta potential is not the same as the surface potential because of the presence of counter ions; however, it is the relevant potential for calculating the interaction energy of the dispersion.

The electrophoretic mobility μ_e can be shown[1] to be related to the zeta potential by

$$\mu_e = \frac{\zeta \epsilon f(\kappa a)}{\eta(T)}, \tag{1}$$

where $\eta(T)$ is the viscosity, T is the absolute temperature, ϵ is the dielectric constant of the dispersing medium, $f(\kappa a)$ is a function of the particle size (radius a), and $1/\kappa$ is the thickness of the double layer of counter ions and ions that surround an individual particle.

In many aqueous-based dispersions with a moderate ion concentration and not too low particle size, where κa is 100 or more, $f(\kappa a) = 1.5$, and Eq. (1) becomes the so-called Smoluchowski relationship. For particles in nonpolar media, where $\kappa a < 1$, $f(\kappa a) = 1$ and Eq. (1) becomes the Hückel relationship. For intermediate values of κa and for a wide range of zeta potential values, the form of $f(\kappa a)$ can be evaluated only numerically.[1]

For aqueous systems to which the Smoluchowski relationship applies, at 25 °C, where the viscosity of water is 0.8905 cP and the dielectric constant is 79, we have a mobility of $1.0 \times 10^{-8}\ \mathrm{m^2V^{-1}s^{-1}}$ corresponding to a zeta potential of 12.6 mV. Values of mobility in the range of $\pm 7 \times 10^{-8}\ \mathrm{m^2V^{-1}s^{-1}}$ and zeta potentials in the range of ±90 mV are common in aqueous colloids and many biological systems.

Typically, as the surrounding ion concentration increases, the zeta potential and hence the mobility both fall, owing to the shielding effect of the ion atmosphere around the particle. For example,[2] human red blood cells (RBCs) in physiological saline conditions (0.145-M NaCl, pH of 6.8) have a mobility of $-1.07 \times 10^{-8}\ \mathrm{m^2V^{-1}s^{-1}}$. In conventional electrophoresis instruments, electric fields of the order 1000 $\mathrm{Vm^{-1}}$ are used, so that velocities of the order of 10–100 μm/s must be measured. This can be done by laser Doppler electrophoresis (LDE). However, for many nonaqueous dispersions (and some other cases) the situation differs. The change of $f(\kappa a)$ from 1.5 to 1 has a marginal effect: more important are the effects of changes in the viscosity and the dielectric constant. For example, a dispersion in toluene has a

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Table 1. Mobility Ratio for Particles with the Same Zeta Potential in Various Media

Liquid	Viscosity η (cP)	Dielectric Constant ϵ/ϵ_0	Mobility Ratio μ_L/μ_w
Water	00.89	78.0	1.000
Methanol	00.54	33.0	0.700
Toluene	00.56	02.4	0.050
Ethylene glycol	17.00	40.0	0.030
Glycerol	01.20	43.0	0.400
Oleic acid	26.00	02.5	0.001
n-Octane	00.54	02.0	0.040
1:4 Dioxane	01.26	02.2	0.020

viscosity of 0.56 cP, which would tend to raise the mobility for a given zeta potential. Conversely, the dielectric constant for toluene is 2.38 (owing to the low polarizability of a nonpolar molecule). The resultant effect of both changes is to reduce the mobility by a factor of approximately 20. Other examples are given in Table 1.

The stabilization and behavior of suspensions of solids or liquids in low dielectric media are of considerable interest. Systems of this type are widely used in the paint and coatings industry; in lubrication technology; in pharmaceutical, agrochemical, and cosmetic formulations; in reprographic applications; and in the development of high-performance ceramics and magnetic recording hardware.

Unfortunately, knowledge of the electrophoretic properties of suspensions in nonpolar liquids is much less well developed than that in aqueous suspensions. A prime reason is that the measurement of particle mobilities in media of low dielectric constant has previously been experimentally more difficult than the corresponding measurement in aqueous systems.[3] In addition to lower dielectric constants, the viscosities of many organic liquids are higher, thus reducing electrophoretic mobilities even more. This is clearly illustrated with the examples of some common organic liquids in Table 1. A low dielectric constant causes additional problems of cell capacitances and discontinuous electric fields when a driving potential is applied.[4]

Many applications, particularly in the cosmetic and personal care industries, utilize oils and waxes for the preparation of water-in-oil emulsions and also as emollients. While some oils, such as isopropyl myristate, have a moderate value for the dielectric constant and the viscosity, silicone oils are insulators and can have viscosities that are many orders of magnitude greater than water, making measurement even more difficult, if not impossible, with conventional instrumentation.

Nonaqueous systems are not the only ones that pose a challenge; there are many aqueous examples. We have already mentioned that, as the electrolyte concentration of a solution increases, the particle mobility decreases owing to the shielding effect of the ion atmosphere around the particle. Although in the medical and biomedical areas organisms such as bacteria and blood cells are suspended in water under physiological conditions, which results in a reduction in mobility of nearly an order of magnitude compared with distilled water,[5] some body fluids can exceed the electrolyte concentration of normal physiological solutions by an order of magnitude.[6]

Severe difficulties also arise in obtaining reliable data in environmental applications where the solution conductivity is >1 S/m, as in brine and seawater.[7,8] Finally, particles that are sterically stabilized by adsorbed nonionic surfactants, macromolecules, and synthetic polymers all have electrophoretic mobilities at or near zero. Even electrostatically stabilized suspensions have little charge and, hence, low mobilities if brought close to their isoelectric points.

2. Conventional Laser Doppler Electrophoresis

Before I describe how the new apparatus addresses the measurement of such dispersions, I will briefly review the operation of conventional LDE and its limitations.

Conventional LDE is based on the mixing of scattered light from a sample of a suspension of colloidal particles moving in an electric field, with light directly from the source. The scattered light is frequency shifted by the Doppler effect, and optical mixing of this with the unshifted reference beam light leads to a beating at a frequency that is dependent on the speed of the particles. A phase modulation can be applied to the reference beam to generate an additional frequency shift to the spectrum. This allows for either a positive or a negative frequency shift that is due to the movement of particles to be distinguished (provided that this shift is less than the modulation frequency) because the two shifts are additive. Inasmuch as the direction of the electric field is known, the sign as well as magnitude of the electrophoretic mobility can be determined. The limitation of this method, when a mobility is low, arises from the small displacement of the particles over a given time. If the displacement is less than q^{-1} (q being the scattering vector as defined below), the signal will not produce a complete cycle of 2π and cannot be accurately measured by use of either spectral analysis or correlation techniques. Note that the addition of the modulator frequency does not materially alter this argument because we are now trying to quantify a shift of less than one cycle added to many. In conventional dynamic light scattering (where we measure the mean-square displacement rather than the mean displacement itself) we can still measure small displacements simply by waiting a sufficient amount of time for them to become commensurate with q^{-1}. This option is not a good one in an electrophoresis experiment as the continual application of a field in one direction for periods longer than a few seconds can lead to electrode polarization. Similarly, increases in the field from the usual 1000 V/m or so lead to excessive joule heating and other undesirable effects; irregular motions at high fields have been observed in conventional microelectrophoretic instruments.[9] In addition, a phenomenon known as dielectrophoresis can occur at high fields when there is a large difference in dielectric constant between particle and medium.[10] With truly nonpolar suspensions, where conductive effects should be absent, the existence of small flows that are due to temperature gradients can mask the very low mobilities ($<10^{-10}$ $\mathrm{m^2V^{-1}s^{-1}}$) that are to be measured. Additionally, the presence of Brownian motion added to any electrophoretic motion makes the measurement of a small mobility less precise as this random motion broadens the peak that is due to any directed motion and makes its accurate location more difficult.

3. Phase Analysis Light Scattering

One can overcome the difficulties outlined above by recasting the problem somewhat. The time derivative of the phase is equivalent to the frequency

$$\frac{\mathrm{d}\Phi_s(t)}{\mathrm{d}t} = \omega_s = \mathbf{q}\cdot(\mathbf{v}_e \pm \mathbf{v}_c). \tag{2}$$

With the electrophoretic velocity $\mathbf{v}_e(t) = \mu_e \mathbf{E}(t)$ and ensemble averaging over all particle velocities in the scattering volume, the time derivative of the phase can be written as

$$\frac{\mathrm{d}\Phi_s(t)}{\mathrm{d}t} = \mathbf{q}\cdot[\langle\mu_e\rangle\mathbf{E}(t) \pm \mathbf{v}_c], \tag{3}$$

where $\langle\mu_e\rangle$ is the first moment of the mobility distribution, because all velocities contribute to the phase shift, Φ_s is the Doppler-shifted phase of the scattered light, ω_s is the shifted frequency, $\mathbf{v}_e$ is the velocity vector that is due to an electrophoretic mobility, $\mathbf{q}$ is the momentum transfer vector, and $\mathbf{v}_c$ represents a field-independent collective velocity, that is due to, e.g., thermal convections. Thus, by measuring the time series of the phase rather than the frequency, the same information can be obtained. However, only a tiny fraction of the Doppler cycle is required; as a result, the sensitivity is up to 1000 times higher, enabling the determination of extremely low velocities of the scatterers. We apply phase modulation, so that the Doppler frequency of a zero mobility particle is equal to the modulation (reference) frequency ω_0. We can measure the deviation of the actual frequency that is present in the detected scattered light signal $S(t)$ by performing a phase comparison of $S(t)$ with the imposed modulator frequency ω_0. The phase differences Φ_s as a function of time are extracted from the measured time series $S(t)$ simply by multiplying it with the sine and cosine of the time series of the reference modulator frequency ω_0 as follows [Eqs. (4)–(8)]:

$$S(t) = A\exp[-j(\omega_0 t + \Phi_s)]. \tag{4}$$

Multiplying $S(t)$ with the complex $S_{\mathrm{ref}}(t)$,

$$S_{\mathrm{ref}}(t) = \exp(j\omega_0 t) = \cos(\omega_0 t) + j\sin(\omega_0 t), \tag{5}$$

yields

$$\begin{aligned} A\exp[-j(\omega_0 t + \Phi_s)]\exp(j\omega_0 t) &= A\exp(j\Phi_s) \\ &= A\cos(\Phi_s) + A\sin(\Phi_s). \end{aligned} \tag{6}$$

Now both the phase Φ_s and amplitude A can be extracted by the well-known trigonometric relations

$$\Phi_s = \arctan[\sin(\Phi_s)/\cos(\Phi_s)], \tag{7}$$

$$|A| = \mathrm{ampl} = (\{[A\cos(\Phi_s)]^2 + [A\sin(\Phi_s)]^2\})^{1/2}. \tag{8}$$

Similar equations can be derived for nonsinusoidal fields. In particular, for a square-wave-type field with alternating polarities, the phase differences would be linear in time [see Eq. (3)]. If the mobility were truly zero, the relative phase of the two would be constant; if a small mobility were present the relative phase would shift, and small phase shifts could be detected by a phase comparator. The essence of the extra precision is that phase comparison takes place over many cycles of the applied electric field whereas spectral analysis is sensitive to the period of one cycle. This comparison can be carried out in a variety of ways. In the original phase analysis light scattering (PALS) development[11,12] an analog lock-in amplifier was used; the instrument described in this study uses digital signal processing.

From Eq. (3) the average phase change as a function of time in integral form can be shown[12] to be

$$\Delta\Phi_s = \Phi_{te} - \Phi_0 = \langle A\rangle\mathbf{q}\left\{\left[\int_0^{te}\langle\mu_e\rangle\mathbf{E}(t) \pm \mathbf{v}_c\right]\mathrm{d}t\right\} \tag{9}$$

and, for a sinusodial electric field with frequency $\nu = \omega_e/2\pi$ (Hz),

$$\Delta\Phi_s = \langle A\rangle\mathbf{q}\{[\langle\mu_e\rangle\mathbf{E}_0\cos(\omega_e t_e)/\omega_e] \pm \mathbf{v}t_e\}, \tag{10}$$

with $\langle A\rangle$ being the first moment of the amplitude distribution. Equation (10) is equivalent to Eq. (3) in Ref. 12, because the phase differences are invariant to amplitudes. The extracted mobility μ_e is the mean mobility for the sample inasmuch as the average of all the phase changes that are due to the many particles is detected. The magnitude of the scattering vector is defined to be $q = (4\pi n/\lambda_0)\sin(\theta/2)$, where λ_0 is the wavelength in vacuum, θ is the scattering angle, and n is the refractive index of the suspending liquid. $\Phi(t)$ is the amplitude weighted phase at time t, $\langle A\rangle$ is the mean signal amplitude, $\langle\mu_e\rangle$ is the mean electrophoretic mobility, $E(t)$ is the electric field, and v_c is some collective motion (that is due to temperature gradients, for example), assumed to be constant over the time interval of the field application. The electric field $E(t)$ is applied from $t = 0$ to $t = t_e$. It is also obvious that the term $\Delta\Phi_s$ represents the total distance that the scatterer traveled during time t_e.

To perform the electrophoresis experiment we apply a rather higher frequency field than the more usual 0.5–1.0 Hz used in conventional LDE. The

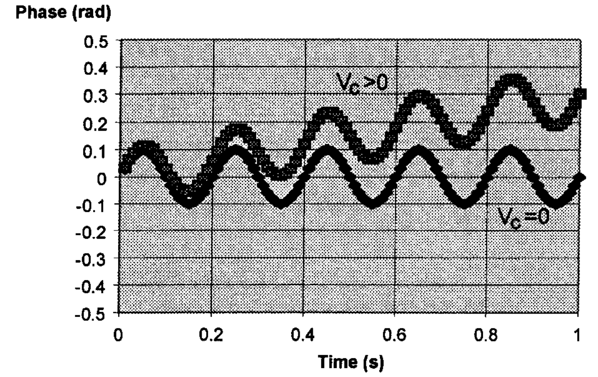


Fig. 1. Amplitude-weighted phase difference spectra for $\mathbf{V}_c = 0$ and $\mathbf{V}_c > 0$.

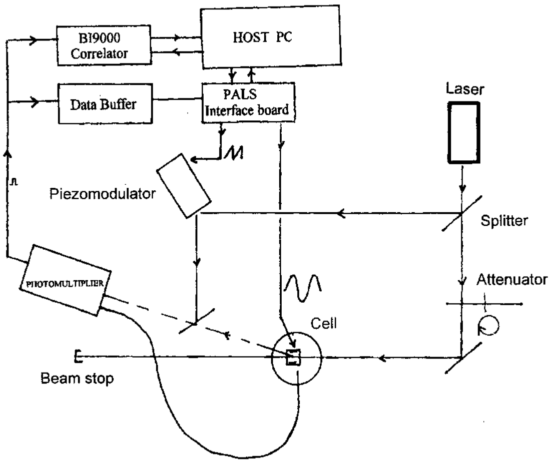


Fig. 2. Schematic diagram of the instrument.

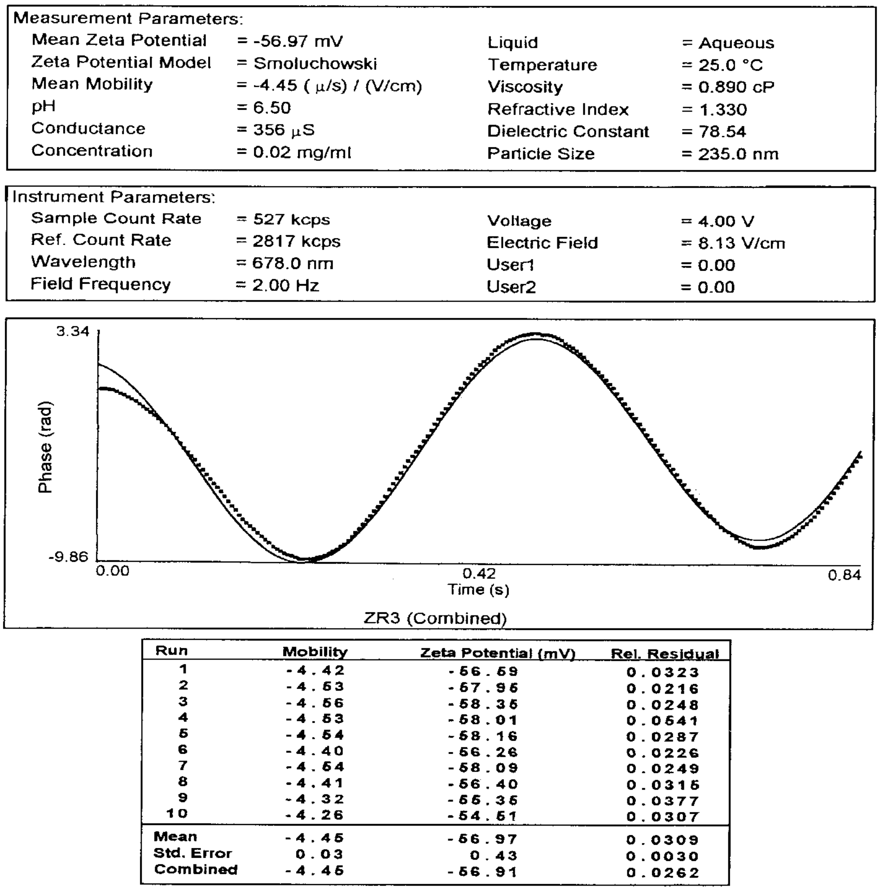
phase change, since the start of the experiment, is then seen to oscillate as shown in the lower curve in Fig. 1. If a sinusoidal field is applied, a sinusoidal oscillation will be detected. If a square wave is applied, the phase changes linearly in each half-cycle of the waveform, reversing direction when the field switches. Obviously the total phase excursion depends on the time of application (or inverse frequency) of the field. The signal fluctuates in amplitude because of the relative motion of the particles and fluctuations of concentration. It has been previously shown[12] that weighting the phase with the amplitude of the signal was of benefit because the phase cannot be determined accurately when the signal amplitude is small. Inasmuch as the phase difference function is synchronous with the field, it can be readily averaged over a number of separate applications of the field to yield high-quality results. Another important aspect of the PALS data reduction is the fact that, with $\langle \mu_e \rangle$ being the first moment of the mobility distribution, averaging over many cycles removes the diffusive term from the result.

The presence of a collective motion is shown in the upper curve in Fig. 1. It can be seen that by suitable data treatment the collective motion can be separated from the electrophoretic motion. Indeed, by adjustment of the reference frequency to account for the frequency shift of v_c, this collective term can be virtually eliminated.

4. Instrumental Details

To the best of my knowledge, the instrument described in this paper is the first to adapt the PALS methodology to utilize the much more robust and simple optical arrangement of the homodyne method and has been designed based on the configuration of the Brookhaven ZetaPlus (an instrument based on conventional laser Doppler technology) in which the method of applying the phase modulation frequency also differed from that used by Miller *et al.*[12] Finally, a major objective was to reduce the total size of the original apparatus and to design a commercially practical unit. The original PALS system was configured on a large optical bench and used a rack of analog electronics.

The general arrangement of the Brookhaven ZetaPALS is shown in Fig. 2. A laser beam is split to produce a scattering beam and a reference beam. The latter can be modulated by a piezoelectric phase modulator at frequencies in the 62.5–2000-Hz range. Scattered light at 15 deg is combined with this reference beam to produce a homodyne signal or, with the reference beam interrupted, a self-beat signal for particle size analysis by dynamic light scattering. The use of the reference beam configuration is also a significant departure from the original PALS device of Miller *et al.*[12] and allows considerable ease in alignment and optical stability because flare light from the walls of the cell becomes unimportant as a source of error. The reference beam configuration is also an asset in the measurement of weak scatterers such as small particles or dispersions of low refractive-index contrast. A fiber optic also allows dynamic light scattering to be performed at a 90-deg scattering angle. The ratio of scattered-to-reference signal is optimized by automatic adjustment of a continuous attenuator in the incident beam path. The scattered light is detected by a photomultiplier or an avalanche photodiode and passed to both a data buffer for spectral (or phase) analysis and an (optional) digital correlator for particle size analysis. The sample is in a 1-cm-square cuvette thermostated by a Peltier device. The electrodes plug into the cell and provide a field that can be reversed automatically and is remote from any cell wall. The cell configuration, based on that used in the Brookhaven ZetaPlus, avoids the troubling factor of electro-osmosis and, in addition, no alignment to a stationary level is required; both effects are discussed in detail elsewhere.[13,14] A further advantage of the cell configuration is that there is no necessity to refocus the optics when working with media of differing refractive indices. Electrodes of gold or palladium are available, the latter being preferred when conductive (polar) dispersions are to be measured. In conventional LDE the field



Measurement Parameters:
Mean Zeta Potential = -56.97 mV
Zeta Potential Model = Smoluchowski
Mean Mobility = -4.45 (μ/s) / (V/cm)
pH = 6.50
Conductance = 356 μS
Concentration = 0.02 mg/ml
Liquid = Aqueous
Temperature = 25.0 °C
Viscosity = 0.890 cP
Refractive Index = 1.330
Dielectric Constant = 78.54
Particle Size = 235.0 nm

Instrument Parameters:
Sample Count Rate = 527 kcps
Ref. Count Rate = 2817 kcps
Wavelength = 678.0 nm
Field Frequency = 2.00 Hz
Voltage = 4.00 V
Electric Field = 8.13 V/cm
User1 = 0.00
User2 = 0.00

ZR3 (Combined)

Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	-4.42	-56.59	0.0323
2	-4.53	-57.96	0.0216
3	-4.56	-58.35	0.0248
4	-4.53	-58.01	0.0541
5	-4.54	-58.16	0.0287
6	-4.40	-56.26	0.0226
7	-4.54	-58.09	0.0249
8	-4.41	-56.40	0.0315
9	-4.32	-55.35	0.0377
10	-4.26	-54.51	0.0307
Mean	-4.45	-56.97	0.0309
Std. Error	0.03	0.43	0.0030
Combined	-4.45	-56.91	0.0262

Fig. 3. Brookhaven Instruments Corporation Zeta potential reference sample ZR3 by use of PALS. The dotted curve represents measured data points. The photon count intensities were measured in kilocounts/s (kcps).

current is regulated, and the electric field is computed from the current and measured conductance, which is carried out at high frequency.

The whole instrument is controlled by a host PC. For phase analysis we add an additional electronic module that contains a slave digital signal processor. This processes the 16-bit photon count signal to produce phase estimates at intervals that are a multiple of the fundamental sampling time and a small fraction of the electric field period. This measurement is synchronized with the applied electric field. The cell can be driven by fields up to 60 kVm^{-1} at frequencies from dc to >1 MHz, with either a square- or a sine-wave format. The frequency is generated by a high-precision numerically controlled oscillator and has a wide dynamic range.

5. Experimental Details

A number of samples were studied by both conventional LDE and the new PALS methodology. Since, as yet, no standard types of nonaqueous dispersion are available that have been characterized by LDE, the samples used initially were aqueous-based dispersions. Various materials were simply dispersed in a range of different electrolytes between 10^{-4} M and above 1 M. The materials and solution conditions were chosen to provide examples of both positively and negatively charged surfaces; a particle size range of 49-nm (polystyrene latex) to 7 μm (human RBCs) was covered by the different samples. Measurements were conducted at a temperature of 25 °C by use of the standard temperature control system fitted to the PALS instrument.

Conventional LDE was performed on a Brookhaven ZetaPlus. For this instrument the electric field is applied for as long as approximately 1 s in each direction and the resultant Doppler shift for the two directions was averaged. The instrument checks the apparent mobility with no field applied and waits until the Doppler shift is less than 4 Hz before taking data. This procedure largely eliminates the effects of thermal collective motion of the particles that would otherwise distort the electrophoretic motion. In contrast, the Zeta PALS can measure the collective motion directly which, as we have shown above, can be separated from the electrophoretic motion. The example given in Fig. 3 illustrates such an effect. In addition, the Zeta PALS has the ability to adjust the phase demodulation frequency, thus compensating for any substantial thermal or other drift in the course of the experiment. Measurement times on

Table 2. Comparison of Electrophoretic Mobilities by Conventional and PALS Measurements

Sample	Mobility by LDE (or Accepted Value)[a] × 10^{-8} $m^2V^{-1}s^{-1}$	Mobility by PALS × 10^{-8} $m^2V^{-1}s^{-1}$
Brookhaven reference material ZR3 (a blue-colored organic dye) dispersed in 1-mM KCl	−4.50 ± 0.10	−4.45 ± 0.03
Colloids in unfiltered (raw) water with 0.075-mg/l KCl	−1.1 ± 0.2	−1.07 ± 0.04
NIST reference material SRM1980 in water adjusted to pH 3.4 with HNO_3	2.54 ± 0.10 (NIST)	2.48 ± 0.02
Human RBCs in Dulbecco's phosphate buffered saline solution (0.145M NaCl, pH of 7.4)	−1.07 ± 0.02 (Ref 2)	−1.08 ± 0.015
Ferrite in dodecane	?	0.013 ± 0.0015
TiO_2 in ethanol	?	−0.503 ± 0.010
Same TiO_2 dispersed in toluene	?	0.255 ± 0.010
Same TiO_2 after drying, dispersed in toluene	?	0.155 ± 0.011
Same TiO_2 dispersed in xylene	?	0.095 ± .005
Casein in polyethylene glycol	?	−0.025 ± .002

[a] The ? means data were not available, because the classic LDE method is not sensitive enough to yield meaningful results.

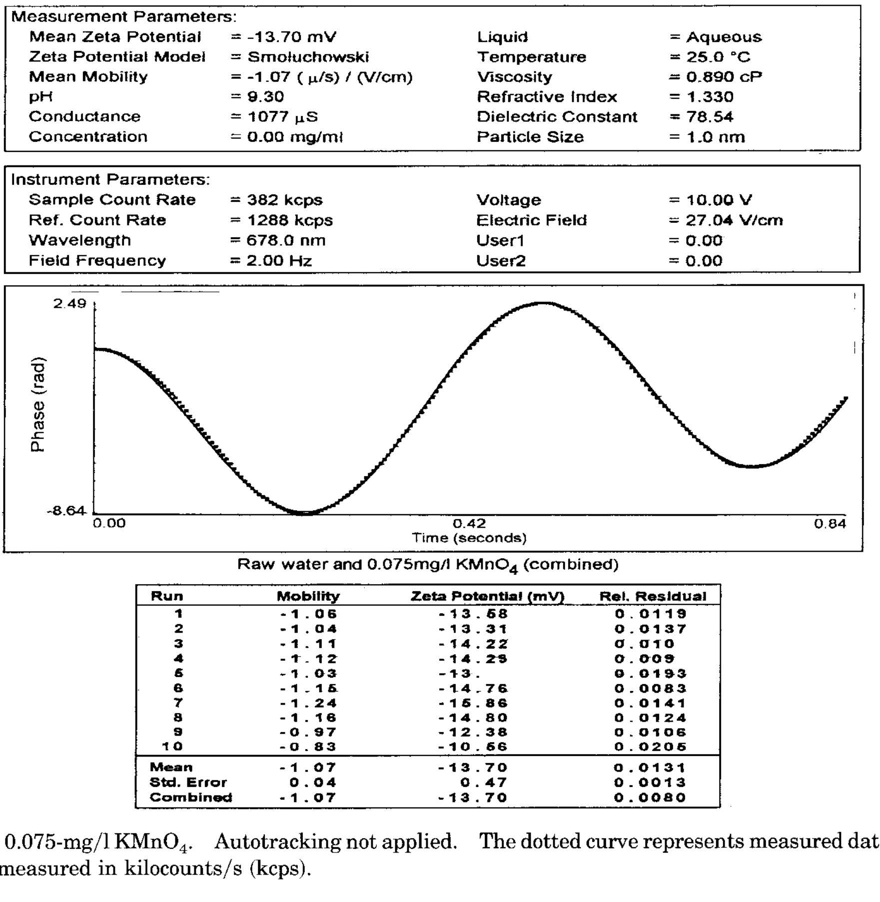
the Zeta PALS are typically less than 20 s or so, and during this time some 30 separate phase spectra are collected and averaged.

6. Results of First Set of Samples

The first set of samples for which electrophoretic mobilities are reported are listed in Table 2. When an error figure is quoted it represents the standard error of the mean for between five and ten repeated measurements.

Sample A is used within Brookhaven as a material for initial optical alignment and to check the ZetaPlus; the electrophoretic mobility value of −4.5 $m^2V^{-1}s^{-1}$ has been established by many measurements over more than a year. The agreement between the two techniques is excellent.

Sample B is a sample of a mixture of particles suspended in unfiltered (raw) water. It was chosen as an example of a weakly scattering system. In addition to the mean values given in Table 2, the



Measurement Parameters:
Mean Zeta Potential = -13.70 mV
Zeta Potential Model = Smoluchowski
Mean Mobility = -1.07 (μ/s) / (V/cm)
pH = 9.30
Conductance = 1077 μS
Concentration = 0.00 mg/ml
Liquid = Aqueous
Temperature = 25.0 °C
Viscosity = 0.890 cP
Refractive Index = 1.330
Dielectric Constant = 78.54
Particle Size = 1.0 nm

Instrument Parameters:
Sample Count Rate = 382 kcps
Ref. Count Rate = 1288 kcps
Wavelength = 678.0 nm
Field Frequency = 2.00 Hz
Voltage = 10.00 V
Electric Field = 27.04 V/cm
User1 = 0.00
User2 = 0.00

Raw water and 0.075mg/l $KMnO_4$ (combined)

Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	-1.06	-13.58	0.0119
2	-1.04	-13.31	0.0137
3	-1.11	-14.22	0.010
4	-1.12	-14.29	0.009
5	-1.03	-13.	0.0193
6	-1.15	-14.76	0.0083
7	-1.24	-15.86	0.0141
8	-1.16	-14.80	0.0124
9	-0.97	-12.38	0.0106
10	-0.83	-10.56	0.0205
Mean	-1.07	-13.70	0.0131
Std. Error	0.04	0.47	0.0013
Combined	-1.07	-13.70	0.0080

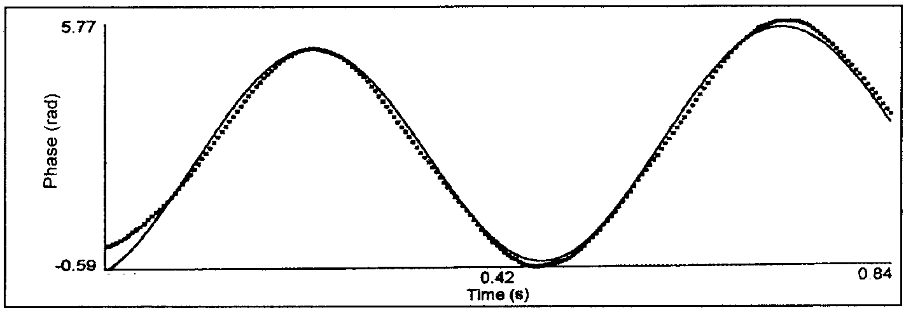
Fig. 4. Raw water and 0.075-mg/l $KMnO_4$. Autotracking not applied. The dotted curve represents measured data points. The photon count intensities were measured in kilocounts/s (kcps).

Measurement Parameters

Avg. Zeta Potential	= 34.99 mV	Liquid	= Aqueous
Zeta Potential Model	= Smoluchowski	Temperature	= 20.0 °C
Avg. Mobility	= 2.48 (µ/s) / (V/cm)	Viscosity	= 1.002 cP
pH	= 7.00	Refractive Index	= 1.331
Conductance	= 1292 µS	Dielectric Constant	= 80.37
Concentration	= 0.25 mg/ml	Particle Size	= 1.0 nm

Instrument Parameters

Sample Count Rate	= 823 kcps	Voltage	= 4.00 V
Ref. Count Rate	= 2270 kcps	Electric Field	= 6.94 V/cm
Wavelength	= 676.0 nm	User1	= 0.00
Field Frequency	= 2.00 Hz	User2	= 0.00



Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	2.48	34.93	0.0116
2	2.51	35.35	0.0127
3	2.51	35.32	0.0145
4	2.51	35.31	0.0158
5	2.42	34.03	0.0125
Mean	2.48	34.99	0.0134
Std. Error	0.02	0.25	0.0008
Combined	2.48	34.99	0.0126

Fig. 5. Electrophoretic mobility of NIST Reference Material SRM 1980. The dotted curve represents the measured data points. The photon count intensities were measured in kilocounts/s (kcps).

experimental data output from the PALS technique is shown in Fig. 4. The zeta potential value, calculated from the mobility data, is −13.70 mV and is not unusual for such samples.

Sample C is the only official reference material for electrophoretic mobility and is manufactured and distributed by the National Institute of Standards and Technology (NIST), Gaithersburg, Md. Figure 5 shows the electrophoretic mobility distribution obtained for the NIST Standard Reference Material 1980 by use of the Brookhaven ZetaPlus. This material is a sample of Goethite [α-FeO(OH)] which, when prepared under standard conditions, has a certified electrophoretic mobility of $+2.53 \times 10^{-8} \pm 0.12 \times 10^{-8}$ $m^2V^{-1}s^{-1}$.[15] The average mobility found from Fig. 5 is $+2.54 \times 10^{-8}$ $m^2V^{-1}s^{-1}$ and a measurement by use of the PALS system gave +2.51 $m^2V^{-1}s^{-1}$; all three values are in excellent agreement.

Sample D was prepared by use of RBCs drawn from the author. For human RBCs, a spread of 2% across the population was routinely observed,[5] depending on the physiological condition of the individual.

In summary, the agreement for all these aqueous-based samples between PALS and conventional LDE measurements is close. It is commonly believed[16] that, for many reasons, an agreement of 5% between different measurements of the electrophoretic mobility of aqueous suspensions and a reproducibility of perhaps 2% can be expected. The PALS technique easily surpasses this criterion.

The remaining measurements were made on samples that were previously beyond the range of conventional LDE, at least for routine applications.

Sample E was a proprietary commercial suspension of ferrite in silicone oil sent originally to Brookhaven Instruments for particle size analysis. The stabilizing moiety was believed to be a low molecular weight polymer. The initial material, supplied as a moderately concentrated dispersion, was diluted into dodecane for the PALS measurement. The measured electrophoretic mobility value of 0.013×10^{-8} $m^2V^{-1}s^{-1}$ was the lowest of all the samples chosen for this study, was more than 2 orders of magnitude smaller than any of the aqueous mobility values, and is consistent with what might be expected from a sterically stabilized system. However, by use of the Hückel equation, the zeta potential is calculated to be approximately 15 mV, suggesting an electrostatic contribution to the stability. Aside from the excellent reproducibility of such small measured values, the data clearly highlights the superior

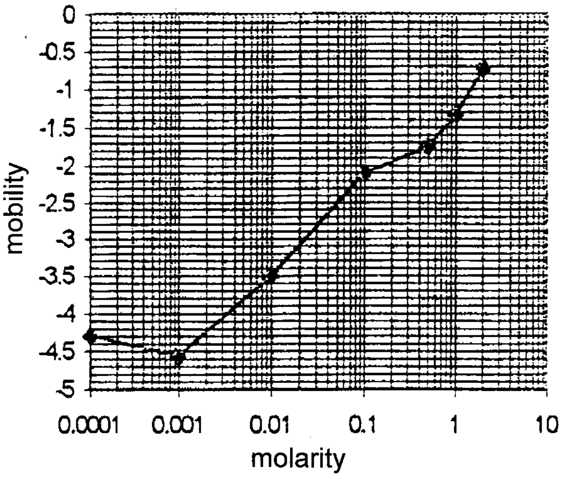


Fig. 6. Silica in increasing salt concentrations.

sensitivity of the PALS methodology. Indeed, the PALS technique is potentially capable of determining electrophoretic mobilities down to 10^{-12} $m^2V^{-1}s^{-1}$.[17,18] This would correspond to only one or two charge sites or groups per particle; clearly, at this level, the term zeta potential would have no meaning.

Although no accepted value for TiO_2 is known, the reversal of sign between polar ethanol and nonpolar toluene or nonpolar xylene is expected on electron donor–acceptor arguments.[19,20] The reduction in the relatively high value of from 0.255×10^{-8} to 0.155×10^{-8} $m^2V^{-1}s^{-1}$ for drying is also explicable when it is recognized that traces of water will stay on the surface of the particle because of the hydrophobicity of the toluene and largely determine the surface charge. It is well recognized that trace amounts of water can dramatically affect the surface charge of particles in nonaqueous media.[21,22]

The final result was obtained on another proprietary commercial sample sent for electrophoretic mobility analysis: casein dispersed in polyethylene glycol (PEG) having an average molecular weight of 200. The measurement was made at 37 °C. Even at this temperature the viscosity is still 27 cP, so a small mobility value is to be expected. This measured value of -0.025×10^{-8} $m^2V^{-1}s^{-1}$ is in contrast with the typical literature value for casein in water of approximately -6.0×10^{-8} $m^2V^{-1}s^{-1}$.[23]

7. Results of Measurements on Quartz Spheroids over a Range of Ionic Molarities

To investigate the performance of the ZetaPALS over a range of salt conditions, rather wider than so far demonstrated, a set of measurements on the reference material BCR66 (Community Bureau of Reference) was performed. This material is a certified reference material made of crushed quartz spheroids of in the range from 0.35 to 3.5 μm,[24] which is used to check the accuracy and precision of particle sizing instrumentation and also as a calibrant. The samples were prepared by simple dispersion of the BCR66 into deionized water that contains different concentrations of KCl by use of 10-s agitation in an ultrasonic bath; no additional dispersing agent was employed. The results obtained are tabulated in Table 3 and plotted in Fig. 6.

As expected for quartz in aqueous suspension, all the measured mobility values are negative. In low electrolyte concentration (<0.01 M) the zeta potential is calculated to be approximately −65 mV, typical of literature values for quartz.[16] The measurements above 0.1 M could not be performed by conventional LDE. Data were obtained even in saturated salt (>4 M), but the reproducibility was not believed to be sufficiently acceptable at this time to justify publication, although, interestingly enough, the mobility obtained was still negative. The general trend of the effect of increasing electrolyte concentration, shown in Fig. 6, including the extremum at 0.001 M (probably caused by a slight specific adsorption of chloride ions) is also in agreement with expectation.

8. Conclusion

The Brookhaven ZetaPALS instrument has been used to measure the electrophoretic mobility of a range of samples, some of which can also be measured by conventional LDE. The agreement between the two techniques, where appropriate, has been shown to be excellent. Examples of measurements on samples beyond the reach of conventional LDE that are due to low dielectric constants, high viscosities, and high ionic strengths, have also been clearly demonstrated; routine measurements of such systems are now possible. With a current sensitivity of up to 3 orders of magnitude better than conventional LDE, the PALS methodology represents a quantum leap in the technological development of commercially available instrumentation to measure the electrophoretic mobility of colloidal dispersions.

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