Appendix C

Paper III

Verification of the Electroacoustic Calibration Standard: Comparison of the Dynamic Mobility of Silicododecamolybdate and Silicododecatungstate Acids and Salts

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Verification of the Electroacoustic Calibration Standard: Comparison of the Dynamic Mobility of Silicododecamolybdate and Silicododecatungstate Acids and Salts

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The dynamic mobility spectra of solutions of silicododecamolybdate and its potassium salt and of silicododecatungstate acid have been measured with a prototype of the Acoustosizer-II apparatus and compared with the dynamic mobility of the electroacoustic standard solution of potassium silicododecatungstate. The ratio of the dynamic mobilities can be calculated independently from known physical quantities such as the conductivity of the solution, the mass of the ions, and their ionic mobilities. Within experimental errors, the observed ratios are in good agreement with the calculated values, providing an independent verification of this standard for the measurement of absolute z potentials by electroacoustic.

Introduction

The electroacoustic signal amplitude (ESA) is an electroacoustic effect generated when an alternating electric field is applied to a colloidal suspension. Charge on the particles causes them to move in response to the field. This motion and their density difference from the surrounding fluid generate an ultrasonic wave in the suspension. As the frequency of the applied field increases, the inertia of larger particles causes them to lag behind the applied field. This leads to a reduction in the magnitude of the ESA effect and a phase lag between the ultrasonic signal and that of the applied electric field. This phase lag is a measure of the mass of the particles, which, if their density is known, enables evaluation of their size. Only when this phase lag is properly evaluated, which requires measurement of the frequency dependence of the ESA signal, can the charge on the particles then be obtained from the magnitude of this signal.

An instrument, the Acoustosizer (Colloid Dynamics Inc., Warwick, RI), has been designed to make these frequency-dependent measurements of the dynamic mobility. To obtain the correct ESA signal, the instrument must be calibrated at each frequency of measurement to account for the frequency dependence of the electronics and of the physical components such as the transducer that converts the ultrasonic effect to an electrical signal.

Instead of using a colloidal suspension for calibration, an inorganic salt was chosen. This avoids the problems and expense associated with obtaining a standard colloidal suspension with known and reproducible properties not subject to alteration by contamination, aging, and so forth. Electrolytes also give ESA signals, which are generally small. Heavy, dense ions can give conveniently measurable signals, however, so the potassium salt of the Keggin ion silicododecatungstate was used as the calibration standard. This had the additional advantage that the quantity that determines the ESA signal from a solution of this salt could be independently evaluated from the literature. Hence, an absolute determination of the z potential of colloidal suspensions could be made with the Acoustosizer once the instrument had been properly calibrated with this electrolyte.

The electroacoustic signal of the electrolyte, ESA, has to be normalized for the effects of the acoustic impedance of the sample on the ultrasonic signal that reaches the transducer. This is done by measuring a reference signal with air in the measuring cell and then with the electrolyte in the cell. This normalized signal is given by

\[
ESA(f; \Delta \rho) = By
\]

where \(S(f)\) is the Fourier transform of the reference signal with air in the cell, \(S(f)\) is that with the electrolyte in the cell, \(B\) is the instrument constant that is to be determined, and \(y\) is a factor which depends on the properties of the electrolyte.

Each of the ion species of an electrolyte can generate an ESA signal, so the term \(y\) is given by a sum over all of the species,

\[
y = \sum_j \phi_j \Delta \rho_j \rho_j \mu_j
\]

where \(\phi\) is the volume fraction of the species, \(\Delta \rho\) is the density difference between the ion \(j\) and the solvent of density \(\rho\), and \(\mu\) is the ionic mobility of species \(j\).

The product of the volume fraction and density terms can be calculated as

\[
\phi(\Delta \rho; \rho) = \eta_j \nu_j - \nu \rho_j
\]

where \(\eta_j\) is the number density, \(\nu_j\) is the ionic mass, and \(\nu\) is the partial molar volume of the \(j\)th species. The molar of the ion is that of the unhydrated species; any density changes that occur because of hydration effects are taken into account by the partial molar volume term. Because


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the partial molar volume of the potassium silico tungstate salt is known from the literature, eq 3 can be calculated independently.

To complete the calculation of y, the ion mobilities, \( \mu_i \), must be evaluated. For dilute solutions, these are the same as in a steady electric field, for the masses of the ions are too small for the inertia effects that are observed with colloidal particles. Hence, the mobilities could be obtained from limiting equivalent conductance data. At higher concentrations, however, ion interactions occur to alter the mobilities. It was shown that the ion mobilities were independent of frequency over the frequency range of 0.5-11 MHz of the AcoustoSizer. It was known that the ratio of cation to anion mobility was independent of concentration up to 10^-4 M for silicodentanoguanide. With the assumption that this is also true for solutions of the potassium salt with conductivities from 0.1 to 1.0 S/m (5 x 10^-3 to 1.0 S/m), y is given by

\[
y = \frac{\rho_i}{\rho_j} \left[ \frac{(m_j - \rho_j) \rho_i}{z_j^2 (m_j - \rho_j) \rho_i} \right] \tag{4}
\]

where the \( \rho \) signs refer to the charge on the ions, \( z \) is the valency of the ion, and

\[
r = \frac{\rho_i}{\rho_j}. \tag{5}
\]

The conductivity of the electrolyte is given by

\[
K = n_e \epsilon \sigma_e \varepsilon_0 (1 + r) \tag{6}
\]

so eq 4 can be written as

\[
y = \frac{K}{\sigma_e \varepsilon_0 (1 + r)} \left[ \frac{(m_i - \rho_i) \rho_j}{z_i^2 (m_j - \rho_i) \rho_i} \right] \tag{7}
\]

From data in the literature, O'Brien et al. were able to calculate for y and K in SI units

\[
y = -(3.02 \times 10^{-5}) \text{N K}^{-1} \tag{8}
\]

Note that ages 7 and 8 were misprinted in the original literature. From this relationship, the magnitude of the electromosmetric signal from a solution of potassium silico-dentanoguanide can be calculated from a simple measurement of the conductivity. This relationship has been tested only indirectly. Using it, a mobility of \( 3.7 \times 10^{-8} \Omega^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) was measured for a suspension of 22 nm silica particles of Lodex TM. This was compared to a value of \( 3.4 \times 10^{-8} \Omega^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) obtained by James et al. measured at 1 MHz on the single-frequency Malvern BSA-8000 instrument that had been calibrated with a latex suspension, the mobility of which was theoretically calculated from O'Brien's model. The first measurements of the ESA signal from a silicodentanoguanide solution on the ESA-8000 gave an instrument constant consistent with measurements on other salts and on Lodex. Finally, reasonable \( z \) potentials and particle sizes have been obtained on many samples with the AcoustoSizer calibrated with this standard.

In view of the importance of this method for the absolute determination of \( z \) potentials with electromosmetry, we have independently tested this calibration standard by measuring the dynamic mobility of solutions of the closely related silicodentanoguanide ion. Baker and Pope have shown that these two systems have identical diffusion coefficients, which reflects their virtually identical size, structure, and charge. They do not differ significantly in mass, however, (SilicoDentanoguanide ion weight = 1397 and Silicodentanoguanide ion weight = 1810), so a large difference in their ESA signals is expected according to the theory described above.

Experimental Section

The 13-molybdenic acid hydrate, K_2[H_2MoO_4(OH)_2]_2H_2O, was obtained from Sigma Chemicals. The 15-tungsten acid hydrate, K_2[H_2WO_4(OH)_2]_2H_2O, was from Fluka Chemicals and of purum p.a. quality. (The potassium salt of silicodentanoguanide acid, K_2[H_2(SiW_12O_40)(OH)]_2H_2O, was from Cedral Dynamic Pty. Ltd. and is the salt used for calibration of the AcoustoSizer. Potassium hydrate was from Anachem Chemicals with a minimum assay of 99% and a maximum limit of impurities of 1.5%.)

Because of the variable and uncertain numbers of waters of hydration of the acids, the concentration of the silicodentanoguanide acid was determined by analysis of the solution for Mo by flame atomic absorption spectrometry on a Varian model Spectra AA-800. The concentration was then adjusted to be 0.05 M. A solution of the potassium salt was then obtained by neutralization of the acid with 4 equiv of KOH. For the silicodentanoguanide, the concentration was adjusted such that the solution of the potassium salt obtained from the acid gave a mobility similar to that obtained from the K_2[H_2(SiW_12O_40)(OH)]_2H_2O standard solution, also 0.05 M.

Electrosmotic measurements were made on a prototype of the AcoustoSizer-II, a flow through version with a smaller sample cell. This instrument operates from 1 to 50 MHz, slightly higher frequencies than the AcoustoSizer-I. The temperature was maintained at 25.0 ± 0.5 °C.

Results and Discussion

Table 1 presents the measured pHe and conductivities of the four different solutions as well as the calculated y values. The acids show a marked higher conductivity and a lower pHe than their respective potassium salts. The pHe of both salts is below the pHe at which they start to decompose. For the molybdenum salt, this is at pHe 4.5, and for the tungstate salt this is at a pHe between 4 and 4.5. The higher conductivity of the acids is consistent with the higher mobility of the proton compared to that of the potassium cation. The slightly higher conductivity of the molybdexena electrolyte is consistent with the higher mobility of the molybdexena anion compared to that of the tungstate anion.

The expected ratio of the decrease in conductivity for infinitely dilute electrolytes when the acids are replaced with their respective potassium salts can be calculated from eq 6 from data in the literature. The calculated values are 2.89 for the tungstate and 2.76 for the molybdate. The measured ratio calculated from the data in Table 1 are 2.80 ± 0.19 for the tungstate and 2.67 ± 0.16 for the molybdate. This coincidence of the conductivity

Table 2. Literature Data for Calculation of \( \gamma \)

<table>
<thead>
<tr>
<th>symbol</th>
<th>units</th>
<th>( [K' \text{Si(SiO}_2]\text{OH})^+ )</th>
<th>( [K' \text{Si(SiO}_2]\text{OH})^+ )</th>
<th>( [K' \text{Si(MnO}_2]\text{OH})^+ )</th>
<th>( [K' \text{Si(MnO}_2]\text{OH})^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_0 )</td>
<td>( \text{mol}^3 \text{cm}^{-1} )</td>
<td>( 7.62 \times 10^{-14} )</td>
<td>( 9.22 \times 10^{-4} )</td>
<td>( 7.63 \times 10^{-4} )</td>
<td>( 9.22 \times 10^{-4} )</td>
</tr>
<tr>
<td>( p_1 )</td>
<td>( \text{mol}^3 \text{cm}^{-1} )</td>
<td>( -7.7 \times 10^{-14} )</td>
<td>( -6.74 \times 10^{-4} )</td>
<td>( -6.66 \times 10^{-4} )</td>
<td>( -6.74 \times 10^{-4} )</td>
</tr>
<tr>
<td>( m_0 )</td>
<td>( \text{kg} )</td>
<td>( 64.9 \times 10^{-10} )</td>
<td>( 1.67 \times 10^{-15} )</td>
<td>( 64.9 \times 10^{-10} )</td>
<td>( 1.67 \times 10^{-15} )</td>
</tr>
<tr>
<td>( m_1 )</td>
<td>( \text{kg} )</td>
<td>( 6.7 \times 10^{-10} )</td>
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<td>( 6.7 \times 10^{-10} )</td>
</tr>
<tr>
<td>( v_0 )</td>
<td>( \text{m}^3 )</td>
<td>( 1.25 \times 10^{-9} )</td>
<td>( 1.13 \times 10^{-9} )</td>
<td>( 1.25 \times 10^{-9} )</td>
<td>( 1.13 \times 10^{-9} )</td>
</tr>
<tr>
<td>( v_1 )</td>
<td>( \text{m}^3 )</td>
<td>( 7.3 \times 10^{-9} )</td>
<td>( 7.3 \times 10^{-9} )</td>
<td>( 7.3 \times 10^{-9} )</td>
<td>( 7.3 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

Figure 1. The magnitudes of the ESA signals of 3 mM solutions of (1) \( \text{KSi(SiO}_2\text{OH})^+ \) (2) \( \text{KSi(MnO}_2\text{OH})^+ \) and (3) \( \text{KSi(MnO}_2\text{OH})^+ \) ratio between the acid and potassium electrolytes confirms the assumption that the ratio of mobility between the ions and anions is independent of concentration, at least for up to 3 mM solutions.

The factors given in Table 1 were calculated according to eq 7 with the data summarized in Table 2 and are presented first in the general form given by eq 8 and then specifically for these 3 mM solutions. They predict that the dynamic mobilities of the acids should be slightly higher than those of the corresponding potassium salts and that the mobilities of the tourangeau spectra should be about 50% greater than those of the corresponding molibdate solutions.

The magnitudes of the measured dynamic mobility spectra are shown in Figure 1. The instrument was calibrated against air and the potassium silicate glass standard in the usual way, so that the spectra are effectively normalized against this salt. Each curve represents the average magnitude measured on three different samples over a frequency range from 1 to 20 MHz. All of the spectra show an almost constant and thus frequency-independent magnitude, which extends the range of this observation from the 11 MHz upper frequency limit of the Acoostosizer-I to the 20 MHz limit of the Acoostosizer-II.

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