

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 silicododecamolybdic acid and its potassium salt and of silicododecatungstic 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 ratios of the dynamic mobilities can be calculated independently from known physical quantities such as the conductivity of the solutions, the mass of the ions, and their limiting 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 ζ potentials by electroacoustics.

Introduction

The electrokinetic sonic amplitude (ESA) is an electroacoustic effect generated when a MHz 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 the signal.

An instrument, the AcoustoSizer (Colloidal Dynamics Inc., Warwick, RI), has been designed to make these frequency-dependent measurements of the dynamic mobility.¹ 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 stan-

dard.² This had the additional advantage that the quantities that determine the ESA signal from a solution of this salt could be independently evaluated from the literature. Hence, an absolute determination of the ζ 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_a , 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

$$ESA_a(S_a - S_a) = B\gamma \quad (1)$$

where S_a is the Fourier transform of the reference signal with air in the cell, S_e is that with the electrolyte in the cell, B is the instrument constant that is to be determined, and γ is a factor which depends on the properties of the electrolyte.¹

Each of the ionic species of an electrolyte can generate an ESA signal, so the term γ is given by a sum over all of the species,

$$\gamma = \sum_j \phi_j(\Delta\rho/\rho)\mu_{Dj} \quad (2)$$

where ϕ_j is the volume fraction of the species j , $\Delta\rho_j$ is the density difference between the ion j and the solvent of density ρ , and μ_{Dj} is the ionic mobility of species j .

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

$$\phi_j(\Delta\rho_j/\rho) = n_j(m_j - \rho v_j)/\rho \quad (3)$$

where n_j is the number density, m_j is the ionic mass, and v_j is the partial molar volume of the j th species. The mass 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

(2) O'Brien, R. W.; Garside, P.; Hunter, R. J. *Langmuir* 1994, 10, 931.

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(1) O'Brien, R. W.; Cannon, D. W.; Rowlands, W. N. *J. Colloid Interface Sci.* 1995, 173, 406.

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

To complete the calculation of γ , the ion mobilities μ_D 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 0.3–11 MHz of the AcoustoSizer-I.¹ It was known that the ratio of cation to anion mobility was independent of concentration up to 10^{-2} M for silicododecatungstic acid.³ With the assumption that this is also true for solutions of the potassium salt with conductivities from 0.01 to 1.0 S/m (5×10^{-4} to 0.1 M), γ is given by

$$\gamma = \frac{n_+ \mu_-}{\rho} \left[(m_- - \rho v_-) + \frac{z_-}{z_+} (m_+ - \rho v_+) r \right] \quad (4)$$

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

$$r = - \frac{\mu_{D+}}{\mu_{D-}} \quad (5)$$

The conductivity of the electrolyte is given by

$$K = n_+ z_+ \mu_{D-} (1 + r) \quad (6)$$

so eq 4 can be written as

$$\gamma = \frac{K}{z_+ (1 + r) \rho} \left[(m_- - \rho v_-) + \frac{z_-}{z_+} (m_+ - \rho v_+) r \right] \quad (7)$$

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

$$\gamma = -(3.02 \times 10^{-9}) K \quad (8)$$

Note that eqs 7 and 8 were misquoted in the original literature.¹ From this relationship, the magnitude of the electroacoustic signal from a solution of potassium silicododecatungstate can be calculated from a simple measurement of its conductivity.

This relationship has been tested only indirectly. Using it, a mobility of $-3.7 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured for a suspension of 23 nm silica particles of Ludox TM. This was compared to a value of $-3.4 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ obtained by James et al. measured at 1 MHz on the single-frequency Matec ESA-8000 instrument that had been calibrated with a latex suspension, the mobility of which was theoretically calculated from O'Brien's model.⁴ The first measurements of the ESA signal from a silicododecatungstate solution on the ESA-8000 gave an instrument constant consistent with measurements on other salts and on Ludox.² Finally, reasonable ζ 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 ζ potentials with electroacoustics, we have directly tested this calibration standard by measuring the dynamic mobility of solutions of the closely related

(3) Kerker, M.; Keller, J.; Siau, J.; Matijević, E. *Trans. Faraday Soc.* 1961, 57, 780.

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

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Table 1. Properties of Measured Solutions

3 mM electrolyte	pH	conductivity S/m	$\text{m}^2 \text{C}^{-1}$	$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$
H ₄ [Si(Mo ₃ O ₁₀) ₄]	1.8	0.48	$-(0.75 \times 10^{-9})K$	-0.36×10^{-9}
K ₄ [Si(Mo ₃ O ₁₀) ₄]	2.7	0.18	$-(1.79 \times 10^{-9})K$	-0.32×10^{-9}
H ₄ [Si(W ₃ O ₁₀) ₄]	1.8	0.46	$-(1.15 \times 10^{-9})K$	-0.53×10^{-9}
K ₄ [Si(W ₃ O ₁₀) ₄]	3.0	0.16	$-(3.02 \times 10^{-9})K$	-0.48×10^{-9}

silicododecamolybdate ion. Baker and Pope have shown that these two isostructural ions have almost identical diffusion coefficients, which reflects their virtually identical size, structure, and charge.⁵ They do differ significantly in mass, however ([SiW₁₂O₄₀]⁴⁻ ionic weight = 2875 and [SiMo₁₂O₄₀]⁴⁻ ionic weight = 1820), so a large difference in their ESA signals is expected according to the theory described above.

Experimental Section

The 12-molybdisilicic acid hydrate, H₄[Si(Mo₃O₁₀)₄] \cdot xH₂O, was obtained from Strem Chemicals. The 12-tungstosilicic acid hydrate, H₄[Si(W₃O₁₀)₄] \cdot xH₂O, was from Fluka Chemicals and of purum p.a. quality. The potassium salt of α -silicododecatungstic acid, K₄[Si(W₃O₁₀)₄] \cdot 18H₂O, was from Colloidal Dynamics Pty. Ltd. and is the salt used for calibration of the AcoustoSizer. Potassium hydroxide was from AnalaR Chemicals with a minimum assay of 85% 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 silicomolybdic acid was determined by analysis of its solution for Mo by flame atomic absorption spectroscopy on a Varian model SpectraAA 800. The concentration was then adjusted to be 3.0 mM. A solution of the potassium salt was then obtained by neutralization of the acid with 4 equiv of KOH. For the silicotungstic solutions, 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 K₄[Si(W₃O₁₀)₄] \cdot 18H₂O standard solution, also 3.0 mM.

Electroacoustic 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 20 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 pHs and conductivities of the four different solutions as well as the calculated γ values. The acids show a marked higher conductivity and a lower pH than their respective potassium salts. The pH of both salts is below the pH at which they start to decompose. For the molybdenum salt, this is at pH 4,⁶ and for the tungstate salt this is at a pH between 4 and 4.5.^{6,7} 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 molybdenum electrolytes is consistent with the higher mobility of the molybdenum 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.^{1,5} The calculated values are 2.89 for the tungstate and 2.76 for the molybdate. The measured ratios calculated from the data in Table 1 are 2.88 ± 0.19 for the tungstate and 2.67 ± 0.16 for the molybdate. This coincidence of the conductivity

(5) Baker, L. C. W.; Pope, M. T. *J. Am. Chem. Soc.* 1960, 82, 4176.

(6) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

(7) Kepert, D. L. *Isopolyanions and Heteropolyanions*; Kepert, D. L., Ed.; Pergamon Press: Oxford, 1973; Vol. 4, p 662.

Table 2. Literature Data for Calculation of γ

symbol	units	(K ⁺) ₁ [Si(W ₃ O ₁₀) ₄] ⁴⁻	(H ⁺) ₁ [Si(W ₃ O ₁₀) ₄] ⁴⁻	(K ⁺) ₁ [Si(Mo ₃ O ₁₀) ₄] ⁴⁻	(H ⁺) ₁ [Si(Mo ₃ O ₁₀) ₄] ⁴⁻
μ_{D+}	m ² V ⁻¹ s ⁻¹	7.62 × 10 ^{-8a}	36.2 × 10 ^{-8a}	7.62 × 10 ^{-8a}	36.2 × 10 ^{-8a}
μ_{D-}	m ² V ⁻¹ s ⁻¹	-7.74 × 10 ^{-8b}	-7.74 × 10 ^{-8b}	-8.62 × 10 ^{-8c}	-8.62 × 10 ^{-8c}
m_+	kg	64.9 × 10 ⁻²⁷	1.67 × 10 ⁻²⁷	64.9 × 10 ⁻²⁷	1.67 × 10 ⁻²⁷
m_-	kg	4.77 × 10 ^{-28d}	4.77 × 10 ^{-28d}	3.02 × 10 ^{-28d}	3.02 × 10 ^{-28d}
v_+	m ³	1.25 × 10 ^{-28d}	1.12 × 10 ^{-28d}	1.25 × 10 ^{-28d}	1.12 × 10 ^{-28d}
v_-	m ³	7.36 × 10 ^{-28e}	7.36 × 10 ^{-28e}	7.36 × 10 ^{-28f}	7.36 × 10 ^{-28f}
γ/K	m ³ C ⁻¹	-3.02 × 10 ⁻⁹	-1.16 × 10 ⁻⁹	-1.75 × 10 ⁻⁹	-0.74 × 10 ⁻⁹

^a Handbook of Chemistry and Physics, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994; pp 5-90. ^b Reference 3. ^c Figure 1 in ref 5. ^d Ladd, M. Introduction to Physical Chemistry, Cambridge University Press: Cambridge, U.K., 1993; p 284. ^e Kurucsev, T.; Sargeson, A. M.; West, B. O. J. Phys. Chem. 1957, 61, 1567. ^f According to ref 5, the silicomolybdate anion has the same hydrated radius as the silicotungstate anion; additional parameters: $z_+ = 1$, $z_- = -4$, $e = 1.60 \times 10^{-19}$ C, and $\rho = 997$ kg m⁻³.

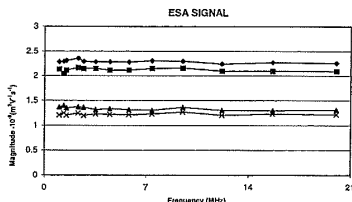


Figure 1. The magnitudes of the ESA signals of 3 mM solutions of (●) H₄[Si(W₃O₁₀)₄], (■) K₄[Si(W₃O₁₀)₄], (▲) H₄[Si(Mo₃O₁₀)₄], and (×) K₄[Si(Mo₃O₁₀)₄].

ratios between the acid and potassium electrolytes confirms the assumption that the ratio of mobility between the cation and the anion is independent of concentration, at least for up to 3 mM solutions.

The γ 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 3.0 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 tungstate species should be about 50% greater than those of the corresponding molybdate solutions.

The magnitudes of the measured dynamic mobility spectra are shown in Figure 1. The instrument was calibrated against air and the potassium silicotungstate standard in the usual way, so that the data 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 AcoustoSizer-I to the 20 MHz limit of the AcoustoSizer-II. The variation in the magnitudes with frequency is about the same for the measurement of the potassium silicotungstate solution that was used for calibration as for the other three solutions. This shows that this variation with frequency is due to noise generated in the apparatus itself. As expected, the phase angles were $0 \pm 2^\circ$ for all the measurements except at the lowest frequency where the two Mo data points were at -5 and -6° .

The experimentally observed magnitudes fell in exactly the predicted order: the acids were slightly higher than the corresponding salts, and the magnitudes for the molybdates were only $2/3$ of those of the corresponding tungstates. The average values of the magnitudes of the mobilities were 2.28 ± 0.03 for the silicododecatungstic acid, 2.12 ± 0.01 for the potassium silicododecatungstate, 1.33 ± 0.04 for the silicododecamolybdic acid, and 1.23 ± 0.01 for the potassium silicododecamolybdate.

Most importantly, the ratios of the mobilities between the tungstate and molybdate species are in good agreement with the values calculated independently. For the potassium salts, this ratio is 1.73 ± 0.02 , and for the acids it is 1.72 ± 0.07 . The ratios calculated from the γ values given in Table 1, obtained from the literature documented in Table 2, are 1.69 for the potassium salts and 1.53 for the acids. Given the disparate sources of data required for the calculation of γ and the error in the measurement of the conductivity, the measured ratios are in very good agreement with these values. This provides a strong test of the validity of the potassium silicododecatungstate standard for the measurement of absolute ζ potentials with the AcoustoSizer.

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