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# Frequency Dependence of Electroacoustic (Electrophoretic) Mobilities

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The direct characterization of electrokinetic mobilities in concentrated ( $>1\%$  (v/v)) dispersions is now feasible by using electrokinetic sonic amplitude (ESA) measurements of the acoustic pressure amplitude response to an applied radio frequency (rf) field. The calibration of such measurements in terms that can be related to static electrophoretic mobilities rests on the theoretical ratio of dynamic and static mobilities,  $|\mu(\omega)/\mu(0)|$ , where  $\omega$  is the angular frequency of the applied rf field. We report here dynamic and static electrophoretic measurements for colloidal polystyrene and poly(methyl methacrylate) latexes, alumina, and silica, and we examine the self-consistency of these measurements for three theories of the frequency dependence of the mobility ratio,  $|\mu(\omega)/\mu(0)|$ . The motion of particles in an oscillating electric field results from the applied electrical force and the opposing drag (velocity) and inertial forces. A theory due to O'Brien gives good self-consistency. Another theory, due to Babchin, Chow, and Sawatzky, differs significantly from the O'Brien theory in the treatment of particle drag. Scaling for these drag effects shows that both theories give nearly the same account of inertial or particle density effects. A more recent theory of Sawatzky and Babchin numerically matches the O'Brien theory over a considerable range in frequency, particle size, and particle density and provides an analytical rationalization for the scaling observed between the O'Brien and the Babchin, Chow, and Sawatzky theories.

## Introduction

The measurement of electrokinetic sonic amplitude (ESA) is an emerging technique<sup>1-7</sup> for the rapid and repeatable electrokinetic analysis of colloid dispersions at moderate to high concentrations (0.5–20% (v/v)). ESA is the ratio of (induced) pressure wave and (applied) rf-field amplitudes. This pressure wave arises from the vibration of charged particles in ionic environments; particle vibrations occur at the same frequency as the applied field. An ultrasonic transducer contacted with one of two parallel plate electrodes has been developed to provide experimental measurements of ESA.<sup>1,3</sup> With the exception of colloid vibration potential measurements<sup>8,9</sup> (which also require auxiliary conductivities), such measurements in concentrated dispersions are not easily and rapidly available by other techniques such as moving boundary<sup>10-13</sup> and mass transport methods.<sup>14</sup> Because the

ESA instrumentation involves various gain factors and instrumental constants, there is a need in the case of more fundamental studies, or in those applied areas that depend on electrophoretic mobility and zeta potential, for critical methods of instrument calibration.<sup>15</sup> Such calibrations are required in order to convert ESA signals to dynamic mobilities. This conversion requires a theoretical basis for the correspondence between static mobilities (and  $\zeta$  potentials) and dynamic mobilities (at the frequency of ESA measurement).

## Theoretical Background

Expressions derived by O'Brien<sup>2</sup> and by Babchin et al.<sup>3</sup> for ESA in the case of parallel plate geometry can be written in the generalized form

$$\text{ESA} = c \Delta\rho \phi \mu(\omega) G(\omega, \phi) \quad (1)$$

where  $c$  is the speed of sound in the dispersion,  $\Delta\rho$  is the difference in density between the continuous phase and the particle,  $\phi$  is the particle volume fraction,  $\mu(\omega)$  is the dynamic electrophoretic (electroacoustic) mobility at angular frequency  $\omega$ , and  $G(\omega, \phi)$  is a geometrical and acoustic-coupling factor. The expression of eq 1 is valid only in the so-called *linear regime* in  $\phi$ , where significant particle-particle interactions have been neglected, where particle effects on the speed of sound propagation are insignificant, and where higher order volume-conservation effects (particle-boundary layer backflow effects)<sup>6</sup> are insignificant. There are, at present, three theoretical descriptions of the relationship between the dynamic elec-

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troacoustic mobility and the static value (O'Brien,<sup>2</sup> Babchin, Chow, and Sawatzky,<sup>3</sup> and Sawatzky and Babchin<sup>7</sup>). The O'Brien (OB) result, valid for large  $\kappa a$  where  $\omega a^2/D \gg 1$  ( $D$  is the electrolyte diffusion coefficient), may be written<sup>16</sup>

$$|\mu(\omega)/\mu(0)| = |[1 - i\alpha(3 + 2\Delta\rho/\rho)] / [9(1 + (1-i)(\alpha/2)^{1/2})]|^{-1} \quad (2)$$

where  $\alpha = \omega a^2/\nu$ ,  $a$  is the particle radius, and  $\nu$  is the kinematic viscosity ( $\eta/\rho$ , where  $\eta$  and  $\rho$  are the viscosity and density, respectively, of the continuous phase). The corresponding result of Babchin et al.<sup>3</sup> (BCS) is written<sup>17</sup>

$$|\mu(\omega)/\mu(0)| = 6\pi\eta[(6\pi\eta\mathcal{R})^2 + (4\omega\pi\rho_{\text{eff}}a^2/3)^2]^{-1/2} \quad (3)$$

where  $\mathcal{R} = 1 + \alpha/\delta$ ,  $\delta = (2\nu/\omega)^{1/2}$ , and

$$\rho_{\text{eff}} = \rho_0 + (9/a)[\eta\rho/(8\omega)]^{1/2} + \rho/2 \quad (4)$$

where  $\rho_0$  is the particle density. A more recent theory, due to Sawatzky and Babchin<sup>6,7</sup> (SB), develops a frequency-dependent "Henry function",  $f_1(\kappa a, a/\delta)$ , which modifies the BCS theory to give the modulus<sup>18</sup>

$$|\mu(\omega)/\mu(0)| = |f_1(\kappa a, a/\delta)/f(\kappa a)| \eta[(\eta\mathcal{R})^2 + (2\omega\pi\rho_{\text{eff}}a^2/9)^2]^{-1/2} \quad (5)$$

where  $f(\kappa a)$  is the standard Henry function and

$$f_1(\kappa a, a/\delta) = 1 + (1-i)\kappa a/(\delta\beta) + \kappa^2 a^2/2 [e^{\kappa a} E_5(\kappa a) - e^{\beta a} E_5(\beta a) - 3i/2 (\delta^2/a^2) \{e^{\beta a} [E_5(\beta a) + (a/\delta)(1-i)E_4(\beta a)] - [1 + (a/\delta)(1-i)]e^{\kappa a} E_5(\kappa a)\}] \quad (6)$$

and where  $\beta = \kappa + (1-i)/\delta$  and the  $E_n$  are exponential integrals.<sup>19</sup> This frequency-dependent Henry function simplifies, in the limit of large  $\kappa$ , to an expression involving the first two terms. This simplification gives a theoretical basis for a scaling phenomenon between the BCS and the OB and SB theories which we examine in the Discussion. Our main purpose in this report is to present data for a range of materials and concentrations that allow us to critically compare the self-consistency of these theoretical expressions.

## Experimental Section

Dispersions of a (surface) carboxylated polystyrene latex (PS), a poly(methyl methacrylate) latex (PMMA), alumina (AKP), and silica (TM) were utilized for our electrophoretic and electroacoustic measurements. The PS dispersion was obtained from Dr. Richard Sutton (Life Sciences Research Laboratories, Eastman Kodak Co.) as a nominally 11.0% (w/w) (10.5% (v/v)) suspension. The particle density was determined to be 1.0541 g/cm<sup>3</sup> by density gradient centrifugation, and the average particle radius of  $302 \pm 23$  nm was determined by image analysis of transmission electron micrographs. The PMMA dispersion was made by suspending the MP-1201 poly(methyl methacrylate) latex of Soken Chemical and Engineering (Nachem, Braintree, MA) in distilled water at a level of 10% (v/v) by sonication. The particle density of 1.191 g/cm<sup>3</sup> was determined<sup>15</sup> by density gradient centrifugation and the average particle radius of  $162 \pm 9$  nm was determined by image analysis of transmission electron micrographs.

The AKP dispersion was made by milling  $\alpha\text{-Al}_2\text{O}_3$  (AKP-30, Sumitomo Chemical Co. Ltd., Tokyo) at 67.07% (w/w) (33.8%

**Table I. Physical and Electroacoustic/Electrophoretic Properties of Sample Dispersions**

dispersion	$\rho$ , g/cm <sup>3</sup>	radius ( $a$ , nm)	$\kappa a$	$dS/d\phi$ , mPa m/V	$\mu(0)$ , ( $\mu\text{m/s}$ ) (cm/V)
PS	1.054	302	99	-2.76 <sup>b</sup>	-5.13 <sup>a,b</sup>
PMMA	1.191	162	53	-7.27 <sup>c</sup>	-3.80 <sup>a,c</sup>
AKP	3.98	169 <sup>i</sup>	55	139.5 <sup>d</sup>	4.06 <sup>a,d</sup>
TM	2.20	11.5	3.8	-43.4 <sup>e</sup>	-2.41/ <sup>f</sup> 3.41 <sup>g</sup> (-3.4 $\rightarrow$ -4) <sup>h</sup>

<sup>a</sup> Measured by microelectrophoresis. <sup>b</sup> pH 6.8. <sup>c</sup> pH 10. <sup>d</sup> pH 4. <sup>e</sup> pH 9. <sup>f</sup> Calculated using instrumental factors derived from  $|\mu(\omega)/\mu(0)|$  ratios of Babchin, Chow, and Sawatzky. <sup>g</sup> Calculated using instrumental factors derived from  $|\mu(\omega)/\mu(0)|$  ratios of O'Brien. <sup>h</sup> Range of values reported for similar colloidal silica (refs 27-29). <sup>i</sup> Volume mean radius.

(v/v)) in a high-speed Cowles mixer for 24 h at pH 4. The density of 3.98 g/cm<sup>3</sup> was taken<sup>20,21</sup> as that of bulk alumina. The median (geometric mean) radius, 195 nm, was determined by centrifugal size analysis (Shimadzu Model SA-CP3) from replicate determinations. The cumulative weight percent was plotted on logarithmic probability paper and yielded an excellent fit to a straight line; the mass distribution therefore was well approximated by a log-normal distribution. The geometric standard deviation determined from the slope of the straight line was 1.366. By use of the Hatch-Choate relationships,<sup>22-24</sup> various averages could be determined from these geometric mean and standard deviation parameters. The arithmetic average, volume mean, and geometric mean radii determined were 153, 169, and 146 nm, respectively. The volume mean radius of 169 nm was used in our electroacoustic calculations (Tables I-III).

The silica dispersion TM was obtained by dilution of 52.1% (w/w) Ludox-TM (Du Pont; lot 3-88). A particle density of 2.20 g/cm<sup>3</sup> was used as assigned by Alexander and Iler;<sup>25</sup> this value is quite close to the value of 2.17 g/cm<sup>3</sup> reported by Klingbiel et al.<sup>15</sup> and obtained by measuring densities of distilled water dilutions of the stock dispersion. An average particle radius of  $11.5 \pm 2.3$  nm was determined by image analysis of transmission electron micrographs. A summary of these physical properties is given in Table I.

Static electrophoretic mobilities were determined by microelectrophoresis. A Model Mark II microelectrophoresis apparatus (Rank Brothers, Cambridge) was used. The cell constant for the flat cell in this apparatus was calibrated by using ac conductivity measurements at 2000 Hz and by a dc method comparing potentials measured across this cell and across precision resistors. A cell constant of  $61.7 \pm 0.6$  cm<sup>-1</sup> was obtained. Particles at the stationary layer were timed moving in both directions by reversing the polarity of the 7.28 V/cm electric field.

ESA signals were measured at 25 °C with a Matec Applied Science (Hopkinton, MA) MBS-8000 electrokinetic sonic analysis system. The instrumentation was controlled by Matec STESA software in the single-point mode. A low volume parallel-plate flow-cell (Matec Model PPL-80) was used for sampling the dispersions. It should be noted that the extant theoretical developments are based on parallel-plate electrode geometry.<sup>2,3,7</sup> A Wavetek Model 23 waveform generator was used as a radio-frequency source. The frequency of the applied rf field was tuned so that the electrode separation was  $3/2$  wavelengths of the pressure (acoustic) wave. The ESA signal,  $S$ , was monitored with an Iwatsu Model SS-5510 oscilloscope. All electrophoretic measurements were done on samples with continuous phases adjusted to 0.01 M KNO<sub>3</sub>. The ESA apparatus was first adjusted, following the manufacturer's recommendation, to give an ESA signal,  $S$ , of -3.67 mPa cm/V for a 10% (v/v) suspension of

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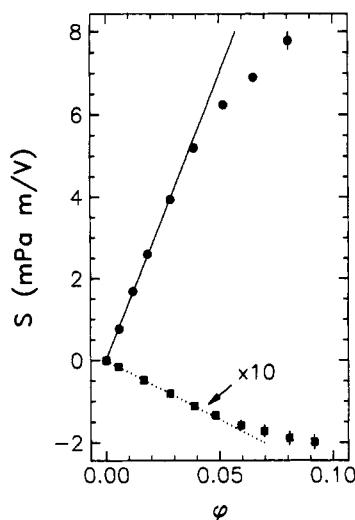
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**Figure 1.** Electrokinetic sonic amplitude signal,  $S$ , as a function of volume fraction ( $\phi$ ) for the polystyrene latex (■, PS, pH 6.8, ordinate values magnified 10 $\times$ ) and for the alumina (●, AKP, pH 4). Experiments were done at 25 °C in 0.01 M KNO<sub>3</sub>. The straight lines fit the data in the linear regimes and have slopes of  $-2.76$  and  $139.5$  mPa m/V respectively for PS (without magnification) and AKP. The error bars correspond to standard deviations of repetitive trials.

Ludox-TM. Measurements were made as a function of volume fraction ( $\phi$ ) by dilution with 0.01 M KNO<sub>3</sub> preadjusted to the desired continuous phase pH (6.8 for PS; 10 for PMMA; 4 for AKP; 9.5 for TM).

### Results

The average static mobilities for the PS (pH 6.8), PMMA (pH 10), and AKP (pH 4) dispersions are listed in Table I. The static mobility of  $-5.13$  ( $\mu\text{m/s}$ ) (cm/V) for PS is considerably greater than the  $-3.5$  ( $\mu\text{m/s}$ ) (cm/V) reported by Ottewill and Shaw<sup>26</sup> at the same ionic strength (0.01 M). Our PS latex was engineered, however, to have a significantly higher surface carboxylation than were the polystyrene latexes studied by Ottewill and Shaw.

The mobility of  $4.06$  ( $\mu\text{m/s}$ ) (cm/V) for AKP is comparable to values of  $3.6$ – $4$  ( $\mu\text{m/s}$ ) (cm/V) over the pH 5–3 interval reported by DeLiso et al.<sup>27</sup> for aqueous alumina dispersion in  $10^{-3}$  M KCl. Kimura et al.<sup>28</sup> reported a  $\zeta$  potential of 49 mV for AKP-30 in 0.01 M NH<sub>4</sub>Cl. They obtained this value by using microelectrophoresis and the Smoluchowski equation. This  $\zeta$  potential corresponds to a static mobility of  $3.8$  ( $\mu\text{m/s}$ ) (cm/V), in reasonable agreement with the value we obtained. Velamakanni and Lange<sup>29</sup> used microelectrophoresis to study a related alumina, AKP-50 (median of the mass distribution indicated an average radius of 135 nm), in 0.01 M NH<sub>4</sub>Cl over the pH range of 4–5. They reported a  $\zeta$  potential determined from the Smoluchowski equation of  $62 \pm 3$  mV; this potential corresponds to a mobility of  $4.7$  ( $\mu\text{m/s}$ ) (cm/V).

Results for PS and AKP are illustrated in Figure 1. Both of these samples exhibit a *linear regime* at low  $\phi$  ( $<0.05$ ) with slopes of  $-2.76$  and  $139.5$  mPa m/V, respectively, for PS and AKP. The proximity of the PS density of  $1.0541$  g/cm<sup>3</sup> to that of the continuous phase,  $0.997$

g/cm<sup>3</sup>, yields a low  $\Delta\rho$  term (eq 1) and as a result the  $\text{ESA}/G(\omega, \phi)$  signal magnitude is much lower than for the other samples. However, even in these circumstances, adequate signal-to-noise is available. The data illustrated in Figure 1 for PS are means and standard deviations obtained from three separate series of measurements (on different days) on samples prepared by dilution from the stock latex suspension. The relative error *does not exceed* 10%, and this relative error is obtained only at the highest volume fractions studied. The  $\text{ESA}/G(\omega, \phi)$  signal obtained in the limit of  $\phi \rightarrow 0$  (0.01 M KNO<sub>3</sub>) was approximately  $-0.002$  mPa m/V. Although quite small, background electrolyte corrections were made for  $\phi > 0$  in proportion to the volume fraction of the continuous phase,  $1 - \phi$ . Similar results<sup>15</sup> for PMMA and TM yielded slopes of  $-7.27$  and  $-43.4$  mPa m/V, respectively.

Examination of eq 1 shows that the quotient  $\text{ESA}/G(\omega, \phi)$  is a fundamental electroacoustic property of the colloidal suspension, since the  $G(\omega, \phi)$  term varies with the probe and cell geometry. Furthermore, since the analytical form of  $G(\omega, \phi)$  has been derived for only two cases,<sup>30,31</sup> it is convenient to define an instrumental calibration constant,  $\gamma$ , by the relation<sup>15</sup>

$$\gamma S = \text{ESA}/G(\omega, \phi) = c \Delta\rho \phi \mu(\omega) \quad (7)$$

which in the linear  $\phi$  regime ( $\lim \phi \rightarrow 0$ ) gives

$$\gamma dS/d\phi = c \Delta\rho \mu(\omega) \quad (8)$$

The dynamic mobility  $\mu(\omega)$  was calculated from the static value,  $\mu(0)$ , using the theory of Babchin et al.<sup>3</sup> (BCS), the theory of O'Brien<sup>2</sup> (OB), and the theory of Sawatzky and Babchin<sup>6,7</sup> (SB) with eqs 3, 2, and 5, respectively. These respective ratios are listed in Table II for the three samples for which the static mobility was determined by microelectrophoresis. The respective  $\gamma$  values, as calculated from eq 8, are also listed in Table II, as are the averages obtained from the three theoretical treatments of  $|\mu(\omega)/\mu(0)|$ . The  $\gamma$  determined with the theories of O'Brien and of Sawatzky and Babchin seem more consistent in that all three values are greater than unity. The main criterion by which we judge the relative consistency of these theoretical treatments, however, is comparison of the calculated static mobility for TM to experimental estimates. A value of  $-2.41$  ( $\mu\text{m/s}$ ) (cm/V) was obtained from the BCS treatment and  $-3.41$  ( $\mu\text{m/s}$ ) (cm/V) was obtained for the OB and SB theories. Experimental studies of colloidal silicas in the pH range of 9–10 have indicated mobilities in the range of  $-3.4$  to  $-4$  ( $\mu\text{m/s}$ ) (cm/V).<sup>32–34</sup> Ludox-HS, although about half the size of TM, has similar surface properties and a static mobility of approximately  $-3.5$  ( $\mu\text{m/s}$ ) (cm/V) at these alkaline pH. The static result of  $-3.41$  ( $\mu\text{m/s}$ ) (cm/V) calculated by using the OB and SB theories, therefore, appears more self-consistent with respect to this magnitude criterion. This static result, using the linear response theory of O'Brien and White,<sup>35,36</sup> yields a  $\zeta$  potential of  $-71$  mV. This value compares favorably with  $\zeta$  potentials determined from streaming potential measurements, of  $-67$  mV for vitreous silica<sup>37</sup>

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**Table II. Comparison of Calibration Constants Derived from Data of Table I and the BCS,<sup>a</sup> OB,<sup>b</sup> and SB<sup>c</sup> Theories of Dynamic Mobility**

dispersion	Babchin et al. <sup>a</sup> (BCS)		O'Brien <sup>b</sup> (OB)		Sawatzky and Babchin <sup>c</sup> (SB)	
	$ \mu(\omega)/\mu(0) ^d$	$\gamma$	$ \mu(\omega)/\mu(0) ^e$	$\gamma$	$ \mu(\omega)/\mu(0) ^f$	$\gamma$
PS	0.570	0.894	0.950	1.49	0.949	1.49
PMMA	0.737	1.106	0.987	1.48	0.987	1.48
AKP	0.707	0.908	0.957	1.23	0.957	1.23
TM	0.98	0.97 ± 0.12 <sup>g</sup>	1.00	1.40 ± 0.15 <sup>g</sup>	1.00	1.40 ± 0.15 <sup>g</sup>

<sup>a</sup> Reference 3. <sup>b</sup> Reference 2. <sup>c</sup> Reference 7. <sup>d</sup> Calculated from eq 3 (eq 4.21 in ref 3) at  $\omega = 2\pi$  MHz,  $\eta = 0.89$  cP, and  $\rho = 0.997$  g/cm<sup>3</sup>. <sup>e</sup> Calculated from eq 2 (eq 6.11 in ref 2) at  $\omega = 2\pi$  MHz,  $\eta = 0.89$  cP, and  $\rho = 0.997$  g/cm<sup>3</sup>. <sup>f</sup> Calculated based on theory of ref 7 and provided by A. J. Babchin and R. P. Sawatzky (private communication). <sup>g</sup> Average of determinations for PS, PMMA, and AKP.

(in 0.01 M KNO<sub>3</sub>) at pH 9.5 and -68 mV at pH 9.2 and -74 mV at pH 10 for  $\alpha$ -SiO<sub>2</sub><sup>38</sup> (in 0.01 M NaCl). Good agreement is also obtained with a calculated value of -65 mV, using a surface (hydroxyl) ionization model for SiO<sub>2</sub> in 0.01 M univalent electrolyte.<sup>39</sup>

### Discussion

The essentially identical  $\gamma$  obtained (Table II) for the fairly monodisperse PS and PMMA latexes with the OB and SB theories and the different  $\gamma$  obtained from the BCS theory, provide the best testament for the consistency of the OB and SB theories; all three theories were derived on the basis of dilute dispersions of monodisperse spherical particles. It is noteworthy that inclusion of data for the polydisperse AKP dispersion, *with dramatically different density and opposite surface charge* where a volume mean radius is used, results in average  $\gamma$  with standard deviations of only 10–11%. According to a recent study<sup>40</sup> of the effects of particle size polydispersity on  $|\mu(\omega)/\mu(0)|$  moduli, a log-normal distribution with a geometric standard deviation of approximately 1.4, as we have in the present AKP dispersion, should not significantly perturb the dynamic modulus relative to the monodisperse value. It appears that the discrepancy that exists is likely due to the asymmetry of the alumina particles, an error in the measurement of the volume mean, and/or unidentified experimental error in the microelectrophoresis and electroacoustic measurements. On the other hand, the 10–11% uncertainty we report is encouraging, since one must often be satisfied with 3–10% experimental uncertainties in microelectrophoresis measurements of suspensions much more dilute than those measured electroacoustically in this study.

Quantitative similarities and differences among these three treatments of the  $|\mu(\omega)/\mu(0)|$  ratio are illustrated in Table III, where the frequency dependence over 2 decades is listed for conditions applicable for the dispersions examined in this report. It is clear that the OB and SB theories give nearly identical quantitative results. This similarity is reassuring in these moderate to high  $\kappa a$  suspensions, given the fundamentally different symmetries invoked (plane parallel in OB and axisymmetric spherical in BCS and SB) in the respective hydrodynamic solutions. The theoretical result of BCS appears to be more sensitive to frequency and particle size than that of OB and SB. This sensitivity variation is particularly noteworthy (Table III) in the neighborhood of  $\omega/2\pi = 1$  MHz, since the relative mobility ratios drop 2–41% below unity for the BCS treatment and only drop 0–4.4% in the OB theory. The effects of particle size ( $a$ ) and density in the BCS and OB theories are compared in Figure 2. There it appears that

**Table III. Frequency Dependence of Dynamic/Static Mobility Ratios Calculated for PS, PMMA, AKP, and TM Dispersions from the BCS,<sup>a</sup> OB,<sup>b</sup> and SB<sup>c</sup> Theories of Dynamic Mobility**

log ( $\omega/2\pi$ )	$ \mu(\omega)/\mu(0) $					
	PS			PMMA		
	BCS	OB	SB <sup>d</sup>	BCS	OB	SB <sup>d</sup>
5.0	0.844	0.997	0.997	0.913	1.000	1.000
5.2	0.808	0.995	0.995	0.892	0.999	0.999
5.4	0.765	0.991	0.991	0.866	0.998	0.998
5.6	0.714	0.985	0.984	0.834	0.997	0.997
5.8	0.665	0.974	0.973	0.796	0.994	0.994
6.0	0.588	0.956	0.955	0.750	0.989	0.988
6.2	0.515	0.928	0.927	0.696	0.980	0.979
6.4	0.437	0.890	0.887	0.634	0.966	0.965
6.6	0.360	0.838	0.834	0.564	0.944	0.941
6.8	0.286	0.773	0.768	0.488	0.911	0.907
7.0	0.220	0.699	0.692	0.409	0.865	0.859

log ( $\omega/2\pi$ )	$ \mu(\omega)/\mu(0) $					
	AKP			TM		
	BCS	OB	SB <sup>d</sup>	BCS	OB	SB <sup>d</sup>
5.0	0.909	0.998	0.998	0.994	1.000	1.000
5.2	0.886	0.997	0.997	0.992	1.000	1.000
5.4	0.857	0.994	0.994	0.989	1.000	1.000
5.6	0.822	0.989	0.989	0.987	1.000	1.000
5.8	0.777	0.980	0.979	0.984	1.000	1.000
6.0	0.722	0.963	0.963	0.980	1.000	1.000
6.2	0.655	0.935	0.934	0.975	1.000	1.000
6.4	0.575	0.890	0.889	0.968	1.000	1.000
6.6	0.484	0.826	0.824	0.960	1.000	1.000
6.8	0.389	0.742	0.739	0.950	1.000	1.000
7.0	0.298	0.645	0.641	0.937	1.000	1.000

<sup>a</sup> Equation 3 (eq 4.21 in ref 3) with  $\eta = 1$  cP and  $\rho = 1$  g/cm<sup>3</sup>. <sup>b</sup> Equation 2 (eq 6.11 in ref 2) with  $\eta = 1$  cP and  $\rho = 1$  g/cm<sup>3</sup>. <sup>c</sup> References 6 and 7. <sup>d</sup> Numerical values courtesy of A. J. Babchin and R. P. Sawatzky (private communication).

the BCS theory is much *less sensitive* to density variations. For the BCS theory and the particle radii illustrated, only slight variations with density are noticeable with radii in the range of 0.3–10  $\mu$ m. Much greater variability with density is exhibited by the OB theory over this size range, and this variability extends to radii approaching 0.1  $\mu$ m.

The primary component of the quantitative differences between the OB and BCS theories can be attributed to the treatment of particle velocity and the associated drag. In the OB treatment, the ratio of viscous (velocity) to inertial forces of a particle with 0.1- $\mu$ m radius at a frequency of 1 MHz is on the order of 0.001.<sup>2</sup> A comparable ratio of 1–10 is obtained in the BCS theory (by taking the quotient of Stokes ( $\mathcal{R}$ ) and inertial ( $\rho_{\text{eff}}$ ) terms in the denominator of eq 3). Almost all of this difference can be quantitatively assigned to the inclusion of the  $\mathcal{R}$  term in the BCS treatment of the drag force. If we define

$$P = \mathcal{R} |\mu(\omega)/\mu(0)|_{\text{BCS}} / |\mu(\omega)/\mu(0)|_{\text{OB}} \quad (9)$$

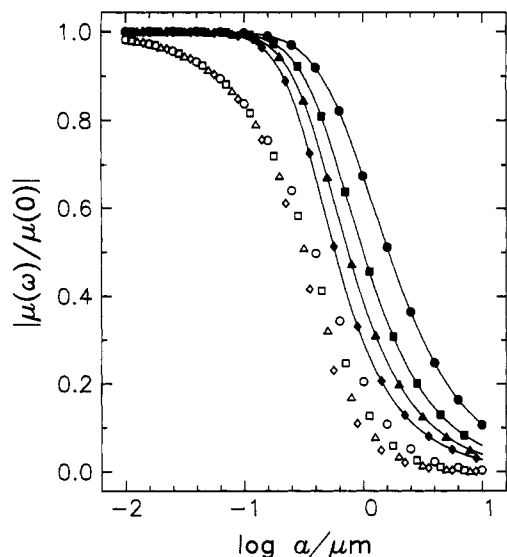
and evaluate this expression for the conditions used in

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**Figure 2.** Particle size ( $a$ ) and particle density dependence of  $|\mu(\omega)/\mu(0)|$  ratio at  $\omega/2\pi = 1$  MHz as calculated from the theories of Babchin et al. (O,  $\rho = 1.1$  g/cm<sup>3</sup>; □,  $\rho = 2.5$  g/cm<sup>3</sup>; Δ,  $\rho = 4$  g/cm<sup>3</sup>; ◇,  $\rho = 6$  g/cm<sup>3</sup>) and O'Brien (●,  $\rho = 1.1$  g/cm<sup>3</sup>; ■,  $\rho = 2.5$  g/cm<sup>3</sup>; ▲,  $\rho = 4$  g/cm<sup>3</sup>; ◆,  $\rho = 6$  g/cm<sup>3</sup>). The viscosity and density of the continuous phase were assumed to be 0.01 P and 1 g/cm<sup>3</sup>, respectively.

generating Figure 2, we find  $P$  decreases from 0.999 to 0.989 as  $a$  increases from 0.01 to 0.1  $\mu\text{m}$ ,  $P$  decreases from 0.989 to 0.843 as  $a$  increases from 0.1 to 1  $\mu\text{m}$ , and  $P$  decreases from 0.844 to 0.714 as  $a$  increases from 1 to 10

$\mu\text{m}$ . For fixed  $a$ ,  $P$  varies by no more than 1% as  $\rho_0$  is varied from 1.1 to 6 g/cm<sup>3</sup>. Hence, the apparent insensitivity of the BCS theory to inertial ( $\rho_0$ ) effects deduced from Figure 2 is a result of the factor  $\mathcal{R}$  that appears in the denominator of eq 3 (Stokes drag term). This factor causes a pronounced  $\mathcal{R}$  weighting of the drag in the BCS treatment of dynamic mobility. The relatively small decreases in  $P$  with increasing  $a$  is a secondary size effect. After rescaling for these effects, both theories exhibit nearly identical variations with particle density. This empirically observed scaling can be derived from the frequency-dependent Henry function of eq 6. Sawatzky and Babchin<sup>6,7</sup> (private communication) have shown, for large  $\kappa a$ , the modulus of this function can be expressed as

$$|f_1(\kappa a, a/\delta)/f(\kappa a)| \approx |1 + (1 - i)(a/\delta)| = |\mathcal{R} - i(a/\delta)| \quad (10)$$

At  $\omega/2\pi = 1$  MHz and the other conditions of this study, this modulus is at most 6% greater than  $\mathcal{R}$ . This frequency-dependent Henry function of the SB theory, therefore, provides an analytical basis for the  $\mathcal{R}$  scaling observed between the OB and BCS theories.

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