

# Study of the relation between diffusion and sedimentation of charged silica sols by dynamic light scattering, ultracentrifugation, and turbidimetry

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(Received 24 July 1984; accepted 3 October 1984)

Measurements of the diffusion coefficient, the sedimentation constant and the turbidity by dynamic light scattering, ultracentrifugation and turbidimetry, respectively, of a charged silica sol as a function of the colloid concentration are reported. The strong repulsive interparticle interactions give rise to a spectacular increase of the inverse osmotic compressibility with concentration. It is found that the generalized Einstein relation between the sedimentation and diffusion coefficients and the osmotic compressibility is satisfied, within the experimental accuracies, at finite concentrations.

## I. INTRODUCTION

Since the advent of photon correlation spectroscopy (PCS), the diffusion coefficient of colloidal particles in solution or in suspension can be measured fast and accurately.<sup>1-3</sup>

For very dilute systems these measurements provide information about single particle properties such as particle size and shape. In the case of more concentrated solutions or suspensions PCS experiments also give insight in the particle interactions.<sup>4-18</sup> A comprehensive review has been given by Pusey and Tough.<sup>19</sup> Apart from experimental complications such as the occurrence of multiple scattering at higher concentrations and the polydispersity of the colloidal particles, the extraction of the information from diffusion coefficients is also complicated by the nature of the interactions themselves. In particular it has been shown that the concentration dependence of the collective or mutual diffusion coefficient of colloidal particles is caused by both static and hydrodynamic interactions.<sup>20</sup> To evaluate the contribution from these two types of interaction to the concentration dependence of the diffusion coefficient requires therefore the necessary theoretical relations.

During the last ten years much work has been done to establish the required expressions.<sup>19-36</sup> One of the methods used is to relate the concentration dependence of the diffusion coefficient to that of the sedimentation coefficient and the osmotic compressibility of the system using a generalized Einstein relation. Such an approach is particularly attractive since it allows a consistency check on independent measurements of the abovementioned quantities.

Although initially the theoretical treatments of the concentration dependence of the friction and/or sedimentation coefficient for a system of hard spheres did not all agree<sup>19-36</sup> it is now generally accepted that the formulations given by Burgers,<sup>21</sup> Batchelor,<sup>35</sup> and Felderhof<sup>32</sup> provide the correct answer.

The relation between diffusion and sedimentation coefficient and osmotic compressibility for a hard sphere system was verified experimentally.<sup>17</sup> A study of a microemulsion system where, besides hard sphere repulsions, attractive interactions play an important part was less successful, presumably due to the unstable character of the particles.<sup>18</sup>

Here a colloidal suspension of charged silica particles (Ludox HS) is investigated by dynamic light scattering, ultracentrifugation, and turbidimetry. In the system studied important repulsive interactions between the particles are present. The main aim is to verify experimentally whether the generalized Einstein relation between osmotic compressibility, diffusion, and sedimentation coefficient holds in this case.

## II. EXPERIMENTS AND RESULTS

### A. Material

The silica sols were obtained from Ludox HS 40 (Dupont de Nemours Co). The stock solution containing about 40 wt. % of colloidal silica was cleared from aggregates by filtration with glass fiber filters (Millipore AP 40). The filtrate was diluted with a  $10^{-5}$  M NaOH solution in freshly distilled water. The pH of the diluted samples was adjusted at 9.7 by adding a few drops of a  $10^{-4}$  M HCl solution. The pH of the samples was measured with an Orion research model 601 pH meter equipped with an Ingold glaselectrode.

The weight fractions of silica were determined gravimetrically by evaporation and drying at 110 °C to constant weight, whereby the electrolyte content, amounting to about 0.4% for the stock solution, is neglected. The concentrations  $c$  in grams silica per  $\text{cm}^3$  of solution were obtained by multiplying the weight fractions with the measured densities of the solution. The errors on  $c$  are estimated to be 0.5%.

The dimensions of Ludox HS silica particles were determined by electron microscopy by Dezelic *et al.*<sup>37</sup>

and more recently by Ramsay *et al.*<sup>38</sup> The first authors report an arithmetic mean average diameter of  $19.07 \pm 0.22$  nm, the latter give  $16.5 \pm 0.21$  nm.

### B. Density measurements

The densities in  $\text{g/cm}^3$  of the solutions were measured up to the fourth digit after the decimal point with an Anton Paar DMA 40 densitometer. The temperature of  $25.00^\circ\text{C}$  was controlled within  $\pm 0.01^\circ\text{C}$  by circulating water from a Schott CT 1150 thermostat. The values of the densities are given in Table I. From the slope of the density as a function of the concentration a value of  $0.56 \pm 0.02$  was obtained for the buoyancy factor  $(1 - \bar{v}\rho_1)$ , where  $\bar{v}$  is the partial specific volume ( $\text{cm}^3/\text{g}$ ) of suspended material and  $\rho_1$  is the solvent density. In order to determine the buoyancy factor more accurately the densities of a second set of solutions was determined at  $25.00 \pm 0.01^\circ\text{C}$  within  $\pm 2 \cdot 10^{-6} \text{ g/cm}^3$  with an Anton Paar DMA 60/602 densitometer yielding a numerical value of  $0.565 \pm 0.003$  for the factor  $(1 - \bar{v}\rho_1)$ . This implies a density of the colloidal particles of  $2.29 \pm 0.01 \text{ g/cm}^3$  in agreement with the value of  $2.279 \text{ g/cm}^3$  reported by Dezelic and Kratochvil.<sup>39</sup>

### C. Refractive index measurements

The refractive index  $n$  of the solvent and of the solutions was measured with a Jena Optik Pulfrich refractometer model PR2 at the following wavelengths: 404.7; 435.8; 467.8; 476.5; 480.0; 488.0; 496.5; 508.1 and 514.5 nm. The temperature of  $25.00^\circ\text{C}$  was controlled within  $\pm 0.03^\circ\text{C}$  by circulating water from a Neslab EX 200 thermostat. The specific refractive index increment  $(\partial n/\partial c)$  was determined by the procedure described by some of the authors.<sup>40</sup> The probable error on  $(\partial n/\partial c)$  is  $\pm 0.001 \text{ cm}^3/\text{g}$ . In Table II the values of the solvent refractive index and of  $(\partial n/\partial c)$  are given as a function of wavelength.

### D. Turbidity measurements

The difference in absorption between the solutions and the solvent was measured with a Kontron Uvikon 810 double beam spectrophotometer, using 10 cm path length cells (Hellma) at the same wavelengths as for the

TABLE I. Concentration ( $c$ ), densities ( $\rho$ ), sedimentation coefficients ( $s$ ), and diffusion coefficients ( $D$ ) of the investigated silica sols.

$c$ ( $\text{g/cm}^3 \times 10^2$ )	$\rho$ ( $\text{g/cm}^3$ )	$s$ ( $\text{s} \times 10^{11}$ )	$D$ ( $\text{m}^2/\text{s} \times 10^{11}$ )
0.487	0.9998	2.14	2.24
0.622	1.0013	2.07	2.35
0.779	1.0014	2.16	2.43
0.997	1.0027	2.08	2.47
1.100	1.0039	2.02	2.51
1.394	1.0057	1.89	2.56
1.417	1.0068	1.90	2.59
1.659	1.0069	1.86	2.61
1.781	1.0076	1.86	2.61
2.210	1.0093	1.79	2.68

TABLE II. Solvent refractive index ( $n$ ) and specific refractive index increments  $(\partial n/\partial c)$  as a function of wavelength ( $\lambda_0$ ).

$\lambda_0$ (nm)	$n$	$(\partial n/\partial c)$ ( $\text{cm}^3/\text{g}$ )
404.7	1.342 38	0.064
435.8	1.339 82	0.064
467.8	1.337 76	0.062
476.5	1.337 23	0.066
480.0	1.337 07	0.063
488.0	1.336 63	0.065
496.5	1.336 21	0.064
508.1	1.335 72	0.064
514.5	1.335 40	0.064

refractive index determinations. The bandwidth was 2 nm and the temperature of  $25.0 \pm 0.1^\circ\text{C}$  was controlled by circulating water from a VEB U1 thermostat through a jacket surrounding the cells. The measurements were carried out under control of an Apple IIe microcomputer. Data analysis was also performed with this microcomputer.

In order to verify the linear dependence of the absorption with cell length the absorption of a suspension was measured with cells with path lengths of 1, 2, 5, and 10 cm. Within better than the experimental accuracy, actually within  $\pm 0.001$  absorption unit, the absorption was found to be direct proportional to the cell length.

The excess turbidities of the solutions are given in Table III as a function of wavelength and concentration. The probable errors are about  $\pm 2 \cdot 10^{-4} \text{ cm}^{-1}$ .

### E. Sedimentation

The sedimentation coefficients of the dispersions were determined with a Beckman Spinco E Analytical Ultracentrifuge equipped with Schlieren Optics. All measurements were performed with a An-D rotor at  $25.0 \pm 0.5^\circ\text{C}$ . The rotor speed was 11,272 rpm. For each solution a set of ten photographs of the Schlieren pattern as a function of sedimentation time was recorded. These photographs were analyzed with a Joyce-Loebl microcomparator model 3CS-MK3.

The sedimentation coefficients were determined from the slope of a plot of the logarithm of the peak positions of the almost symmetrical Schlieren pattern as a function of time. The rms deviations from a straight line were about 1%. The probable errors on the sedimentation coefficients are about  $\pm 2\%$ . The results are given in Table I.

### F. Dynamic light scattering

The diffusion coefficients were obtained with a Malvern 4300 PCS system including a 96 channel K7023 correlator operated in scaling mode. The light source was a Lexel 85.5 Ar-ion laser used at a wavelength of 488 nm and at a power of about 10 mW. Data analysis was performed on line with a Hewlett-Packard 9825A calculator. All measurements were performed at  $25.00 \pm 0.1^\circ\text{C}$  and at a scattering angle of  $90^\circ$ .

The normalized scattered intensity time autocorrelation functions  $g_2(t)$  were fitted to the following equation<sup>41</sup>:

TABLE III. Excess turbidities in  $\text{cm}^{-1}$  of the silica sols as a function of wavelength and concentration.

$c$ ( $\text{g}/\text{cm}^3 \times 10^2$ )	$\lambda_0$ (nm)								
	404.7	435.8	467.8	476.5	480.0	488.0	496.5	508.1	514.5
0.487	0.0317	0.0237	0.0179	0.0167	0.0162	0.0151	0.0140	0.0127	0.0121
0.622	0.0384	0.0286	0.0216	0.0200	0.0195	0.0182	0.0170	0.0155	0.0148
0.779	0.0459	0.0344	0.0262	0.0245	0.0238	0.0223	0.0209	0.0192	0.0207
0.997	0.0581	0.0434	0.0331	0.0308	0.0300	0.0282	0.0264	0.0241	0.0231
1.100	0.0614	0.0457	0.0345	0.0321	0.0312	0.0293	0.0274	0.0249	0.0238
1.394	0.0794	0.0595	0.0453	0.0423	0.0411	0.0386	0.0361	0.0353	0.0340
1.417	0.0767	0.0570	0.0430	0.0400	0.0388	0.0363	0.0339	0.0309	0.0295
1.659	0.0874	0.0649	0.0489	0.0455	0.0442	0.0414	0.0387	0.0352	0.0337
1.781	0.0942	0.0700	0.0528	0.0491	0.0477	0.0446	0.0417	0.0379	0.0362
2.210	0.1126	0.0840	0.0636	0.0592	0.0575	0.0539	0.0504	0.0459	0.0439

$$g_2(t) = \exp(-2\langle\Gamma\rangle t)(1 + \mu_2 t^2). \quad (1)$$

In Eq. (1),  $t$  represents a time delay and  $\langle\Gamma\rangle$  is an average time decay constant; the factor  $\mu_2/\langle\Gamma\rangle^2$  was taken as a measure for the deviation from a single exponential decay of  $g_2(t)$ . Values of  $\mu_2/\langle\Gamma\rangle^2$  in the range 0.02 to 0.04 were obtained indicating that to a very good approximation  $g_2(t)$  is a single exponential. This was confirmed by fitting  $g_2(t)$  with the aid of Eq. (2):

$$g_2(t) = \exp(-2\langle\Gamma\rangle t). \quad (2)$$

The values of  $\langle\Gamma\rangle$  found by fitting to Eq. (1) were recovered within 0.5%.

Diffusion coefficients were calculated by

$$D = \langle\Gamma\rangle/q^2, \quad (3)$$

where  $q$  is the modulus of the scattering vector, given by

$$q = 4\pi n \sin(\theta/2)/\lambda_0. \quad (4)$$

Here  $\theta$  is the scattering angle,  $n$  the solvent refractive index, and  $\lambda_0$  the wavelength *in vacuo* of the incident radiation. The values of the diffusion coefficients are reported in Table I. The probable errors are  $\pm 3\%$ .

### III. DISCUSSION

The main aim of this study is to experimentally verify the validity of the generalized Einstein relation between diffusion coefficient  $D$ , sedimentation coefficient  $s$ , and osmotic compressibility at constant temperature and solvent chemical potential<sup>42</sup> for this system.

$$\frac{D}{s}(1 - \bar{v}\rho_1) = (\partial\pi/\partial c)_{T,\mu_1}. \quad (5)$$

In Eq. (5)  $\bar{v}$  is the partial specific volume of suspended particle,  $\rho_1$  is the solvent density,  $c$  is the concentration in mass per unit volume of solution, and  $\mu_1$  is the chemical potential of the solvent.

The osmotic compressibility can be related to the excess turbidity of the suspension. For a nonabsorbing colloidal system the loss in intensity by transmission of a light beam through the suspension is given by the sum of the intensities scattered in all directions. For unpolarized incident light with unit intensity, the time averaged excess intensity scattered by a unit of volume of suspension at a distance  $R$  large compared to the wavelength of light in a unit solid angle in direction  $\theta$ , with respect to the incident direction, is given by

$$I(q) = KcM(1 + \cos^2\theta)S(q)P(q). \quad (6)$$

Here  $M$  is the molar mass of the particles,  $S(q)$  is the static structure factor,  $P(q)$  is the single particle scattering factor, and the optical factor  $K$  is given by

$$K = \frac{2\pi^2 n^2 (\partial n/\partial c)^2}{\lambda_0^4 N_A}, \quad (7)$$

where  $N_A$  is Avogadro's number.

The turbidity  $\tau$  is related to  $I(q)$  by

$$\begin{aligned} \tau &= \int_0^\pi \int_0^{2\pi} I(q) \sin\theta \, d\theta \, d\varphi \\ &= HcMQ(\lambda). \end{aligned} \quad (8)$$

TABLE IV.  $Hc/\tau \times 10^7$  ( $\text{g}^{-1}$ ) of the silica sols as a function of wavelength and concentration.

Concentration $c$ ( $\text{g}/\text{cm}^3 \times 10^2$ )	$\lambda_0$ (nm)									Average
	404.7	435.8	467.8	476.5	480	488	496.5	508.1	514.5	
0.487	2.32	2.30	2.14	2.42	2.21	2.36	2.30	2.31	2.30	2.29 <sub>4</sub>
0.622	2.45	2.44	2.27	2.57	2.34	2.49	2.41	2.41	2.40	2.42 <sub>1</sub>
0.779	2.56	2.53	2.35	2.64	2.41	2.55	2.46	2.45	2.16	2.45 <sub>6</sub>
0.997	2.59	2.57	2.38	2.68	2.44	2.58	2.50	2.49	2.48	2.52 <sub>3</sub>
1.100	2.71	2.69	2.51	2.84	2.59	2.75	2.65	2.66	2.65	2.67 <sub>2</sub>
1.394	2.65	2.62	2.43	2.74	2.49	2.64	2.55	2.38	2.35	2.53 <sub>9</sub>
1.417	2.79	2.78	2.60	2.94	2.68	2.85	2.76	2.76	2.75	2.76 <sub>8</sub>
1.659	2.87	2.86	2.68	3.02	2.76	2.93	2.84	2.84	2.82	2.84 <sub>6</sub>
1.781	2.86	2.85	2.66	3.01	2.74	2.92	2.83	2.83	2.81	2.83 <sub>4</sub>
2.210	2.97	2.94	2.74	3.10	2.82	3.00	2.90	2.90	2.88	2.91 <sub>7</sub>

TABLE V. Inverse osmotic compressibilities as determined from the turbidity measurements ( $RTHc/\tau$ ) and from the ratio  $[D(1 - \bar{v}\rho_1)/s]$  as a function of concentration. The concentration 0 represents the values extrapolated to infinite dilution.

$c$ ( $\text{g}/\text{cm}^3 \times 10^2$ )	$RTHc/\tau$ ( $\text{m}^2/\text{s}^2 \times 10$ )	$D(1 - \bar{v}\rho_1)/s$ ( $\text{m}^2/\text{s}^2 \times 10$ )	$RTHcs/\tau D(1 - \bar{v}\rho_1)$
0	5.40	5.33	1.01
0.487	5.67	5.91	0.96
0.622	6.00	6.41	0.94
0.779	6.09	6.36	0.96
0.997	6.24	6.71	0.93
1.100	6.62	7.01	0.94
1.394	6.29	7.65	0.82
1.417	6.86	7.70	0.89
1.659	7.06	7.93	0.89
1.718	7.01	7.93	0.89
2.210	7.23	8.46	0.85

Here  $H = 16\pi/3$  K and

$$Q(\lambda) = \frac{3}{8} \int_0^\pi S(q)P(q)(1 + \cos^2 \theta) \sin \theta d\theta. \quad (9)$$

For particles small compared to the wavelength of the light  $P(q)$  is unity. In the limit of vanishing  $q$ ,  $S(q)$  is given by<sup>43</sup>

$$\lim_{q \rightarrow 0} S(q) = \frac{RT}{M} \left( \frac{\partial \pi}{\partial c} \right)_{T, \mu_1}^{-1}. \quad (10)$$

Using Eq. (10) and putting  $P(q) = 1$  in Eq. (9) leads to the following relation between the excess turbidity and the osmotic compressibility:

$$\tau = HcRT \left( \frac{\partial \pi}{\partial c} \right)_{T, \mu_1}^{-1}. \quad (11)$$

If this relation holds, the ratio  $Hc/\tau$  should be independent of the wavelength. The measured ratio  $Hc/\tau$  is given in Table IV as a function of wavelength and particle concentration. Since these values show no systematic wavelength dependence and since the particle diameter is less than  $1/20$  of the wavelength of the light at all investigated wavelengths, it seems reasonable to assume that Eq. (11) holds for the investigated system. Values of the inverse osmotic compressibility are now calculated with Eq. (11) at each concentration using average values of  $Hc/\tau$ , which are all listed in Table IV. The values of  $RTHc/\tau$  so obtained are given in Table V and are plotted in Fig. 1 as a function of concentration. The probable errors are about 5%. Clearly the inverse osmotic compressibility is strongly increasing with the colloid concentration. A least squares fit to the following linear function of concentration

$$\left( \frac{\partial \pi}{\partial c} \right)_{T, \mu_1} = \frac{RT}{M} (1 + \alpha \phi) \quad (12)$$

gives a weight averaged molar mass  $M_w = 4.6 \pm 0.2 \times 10^6$  Daltons and  $\alpha = 39 \pm 4$ . In Eq. (12),  $\phi = c\bar{v}$  represents the colloid volume fraction. For purely hard sphere repulsion theory predicts a value of 8 for  $\alpha$ .<sup>44</sup> The strongly increasing dependence of  $(\partial \pi / \partial c)_{T, \mu_1}$  with  $\phi$  can be attributed to the long ranged electrostatic repulsions between the particles. The more precise relation of  $\alpha$  to the surface charge density or surface potential will be discussed in a more detailed study of the investigated system.

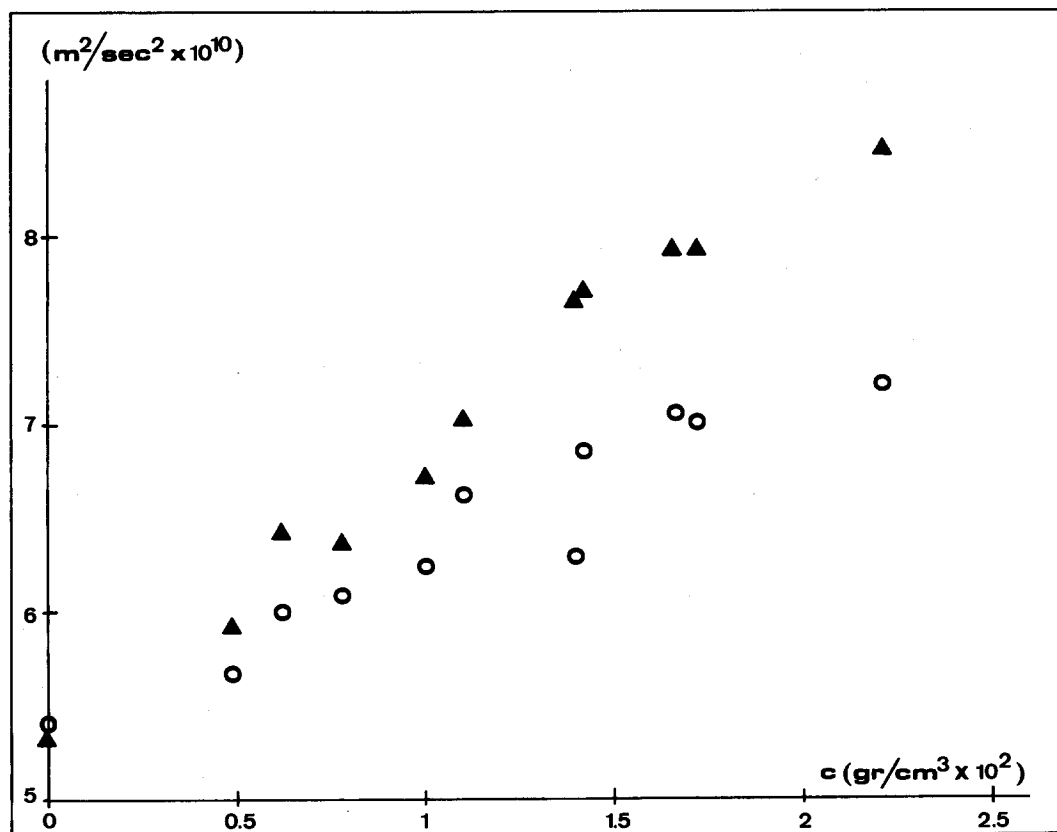


FIG. 1. Inverse osmotic compressibilities as determined from turbidity measurements (O) and from the ratio  $D(1 - \bar{v}\rho_1)/s$  (Δ).

Values of the inverse osmotic compressibility are also calculated using the left-hand side of Eq. (5). The values obtained for  $D(1 - \bar{v}\rho_1)/s$  are given in Table V and plotted in Fig. 1 as a function of concentration. The probable errors are about 6%. Within the estimated experimental error the values of the inverse osmotic compressibilities as obtained from the turbidity measurements agree with those calculated from the ratio  $D(1 - \bar{v}\rho_1)/s$ . However, from the values of the ratio  $RTHc/\tau$  to  $s/D(1 - \bar{v}\rho_1)$  listed in Table V, it appears that the values of  $(\partial\pi/\partial c)_{T,\mu_1}$  determined from the turbidity measurements are systematically lower than the ones determined from the diffusion and sedimentation coefficients. It also looks like that this difference is slightly increasing with concentration.

A possible way to refine the analysis is to take into account that, although the particles are small compared to  $q^{-1}$ , due to the strong interactions, the replacement of the static structure factor  $S(q)$  by its limit  $S(0)$  may introduce concentration dependent effects.<sup>45</sup> This assumption affects not only the analysis of the turbidity data but also the interpretation of the diffusion and sedimentation measurements.<sup>46,47</sup> A preliminary estimate gives rise to about 5% to 10% for this effect for the concentration range examined here, i.e., of the order of the experimental errors. Therefore no definite conclusions about the effect of the interactions on the concentration dependence of the structure factor are possible.

To conclude it is nevertheless clear that the generalized Einstein relation between diffusion coefficient, sedimentation coefficient, and osmotic compressibility holds, within the experimental accuracy, for this system of strongly interacting colloidal particles.

## ACKNOWLEDGMENTS

We thank Ch. De Greef for his excellent technical assistance and M. Weckx for typing the manuscript. This work has been supported by Grant 4.0001.77 of the "Interuniversitair Instituut voor Kernwetenschappen" (Belgium).

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