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ENTITLED..... OSMOTIC PRESSURE MEASUREMENTS OF POLYSTYRENE COLLOID

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OSMOTIC PRESSURE MEASUREMENTS

OF

POLYSTYRENE COLLOID

BY

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THESIS

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INTRODUCTION

An osmometer was built to measure the osmotic pressure and the phase potential of colloidal suspensions as a function of volume fraction. Monodisperse polystyrene lattices suspended at different ionic strengths were used to test the osmometer. The osmotic pressures, measured as a function of the volume fraction, were compared to an empirical expression. The calculated surface potentials were also compared to literature. Recommendations were made for future work in this and other areas.

LITERATURE SURVEY

Several interaction forces exist between particles in a colloidal suspension. The forces that contribute to the stability or instability of the suspension include electrostatic, van der Waals, Born, steric, solvation, and magnetic. Some of these originate at the double layer which is caused by excess charge at the colloid-solution interface. Most important are the repulsive forces, because they determine whether the dispersion remains stable or undergoes flocculation. When the repulsive forces are strong, the colloidal particles become ordered into a regular array. This array resembles a crystal lattice which changes its structure from body-centered to face-centered cubic symmetry as the repulsive forces become stronger (8) to allow for closer packing. When the center-to-center distance between particles is the same as the wavelength of visible light, Bragg diffraction results in iridescence (8). As the repulsive forces are decreased, the spheres move about and the lattice can become disordered. This will occur if the suspension is diluted, excess electrolyte is added (less electrolyte with higher valencies), or the temperature is increased (3).

The repulsive forces between the colloid particles can be measured when the suspension is allowed to equilibrate with a pure fluid through a semipermeable membrane (3). The

repulsion forces due to the dialysate are on both sides of the membrane, therefore, the measured pressure is caused only by the colloidal particles. This is the osmotic pressure.

Russel and Benzing (2) found that osmotic pressure increased with increasing volume fraction and decreasing ionic strength for ordered polystyrene lattices.

APPARATUS

The original experimental apparatus (Fig. I) built to measure osmotic pressure was similar to that used by Vilker, Colton, and Smith (9). The osmometer cell was comprised of two plexiglas chambers connected by a semipermeable membrane. The membrane was impermeable to colloid but allowed free passage of the solvent. Metal screens supported the membrane on both sides so that pressure could be applied in either direction. Rubber o-rings sealed the unit together. Attached to the top of each chamber were 1-ml pipets. A precision pressure controller was connected to one of the capillaries. The pressure controller was a 1-L volume cell with two manometers, a connecting pressure release valve, and a pipet bulb connected by Tygon tubing. The connected manometers were filled with low-density red oil and were able to detect changes in pressure from 20-mm down to several microns of mercury. These pressures were much smaller than those measured by Vilker, et. al.

Unlike Vilker's et. al. apparatus, a second hole was made next to each pipet. This second set of holes was made to accommodate electrodes. They would allow simultaneous measurements of the potential across the membrane and the osmotic pressure.

Another change from Vilker's et. al. apparatus was the size of the chambers. Although the total volume of the cell was fixed to remain constant, the individual chamber volumes

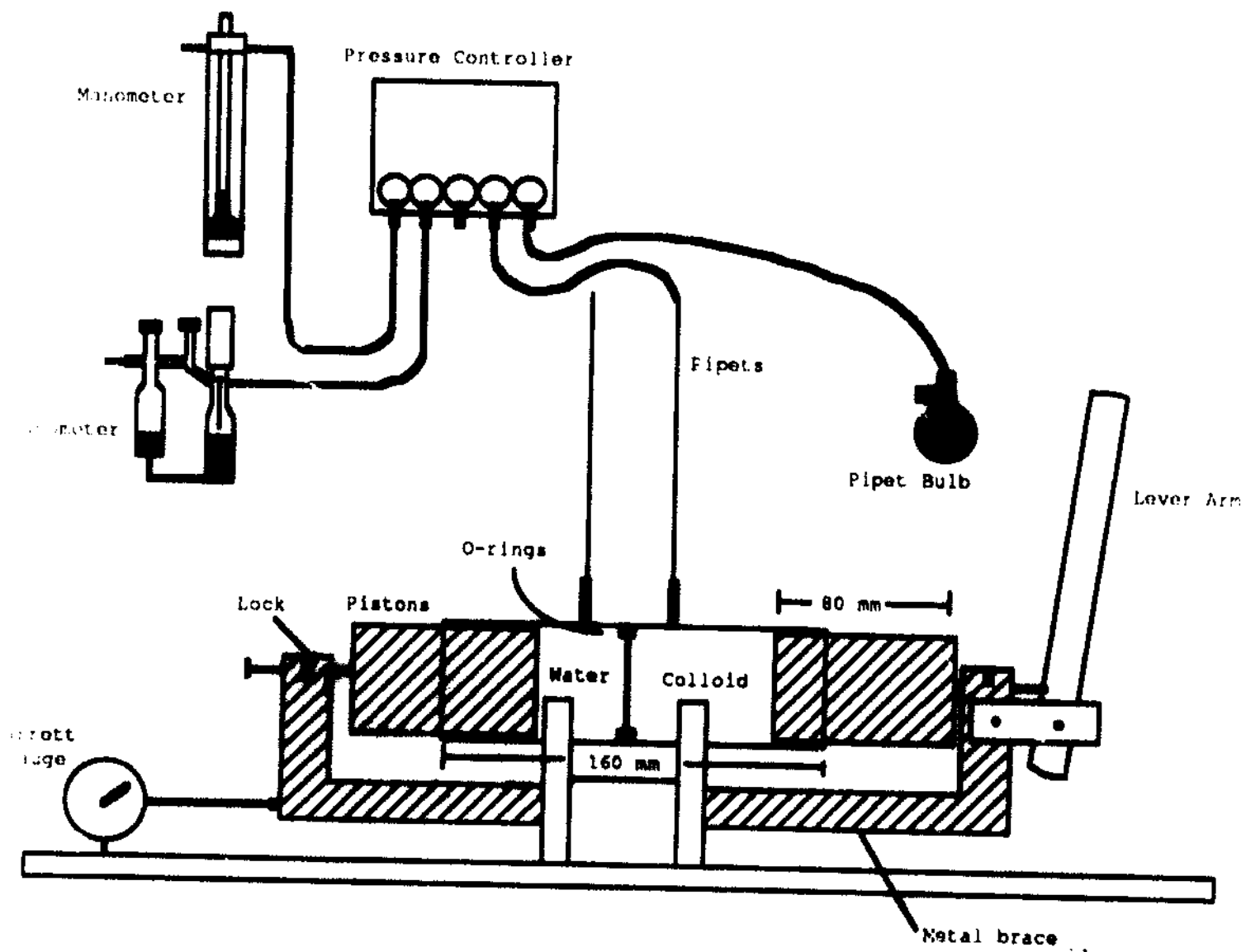


Figure I. Osmotic Pressure Chamber

changed. This allowed measurements of various volume fractions without opening up the cell. The pistons that slid inside each tube were locked to a metal brace so that as one piston moved in, the other moved out (shaded area, Fig. 1). A lever arm connected to the metal brace moved the pistons. A Starrett gauge that read in inches (accurate to ± 0.0001 inches) was also connected to the metal brace. This gave an accurate measure of the length that the pistons were moved. The pistons also had a narrow tunnel drilled through the center which could have been used to eliminate air bubbles.

As the lever arm was moved, the pistons were moved to one side and a pressure built up on the side that was losing volume. This applied pressure forced fluid up into the pipet. Then, pressure was applied into the pipet by squeezing the pipet bulb and slowly opening the valve leading to the pipet. The aim was to apply the exact pressure necessary to force the height of the liquid levels in the pipets to remain equal and constant. This applied pressure was the osmotic pressure.

This task was more difficult than anticipated. It was difficult to know when the system was at equilibrium, because as equilibrium approached, the fluid levels change more slowly. Also, near equilibrium, a very small pressure (1/2 mm Hg) would change the liquid level heights by several millimeters. Therefore, instead of measuring the applied pressure, the pressure controller was disconnected and the system was allowed to reach equilibrium without any external

forces.

The first attempts at changing the osmotic pressure were unsuccessful. The lever arm lacked control. A small change in the a.m position resulted in a large movement of the pistons. In one attempt, colloid shot out of the top of the pipet after lightly squeezing in on the arm. Modifications were then made. The lever arm was replaced with long screws, bars, and wing nuts (Fig. II). The screws were locked in place by a top screw in each bar. As the wing nut was tightened, the pistons moved toward the nut. Turning the wing nut offered much more control.

After changing the lever arm, the pistons still did not move smoothly. A wooden block was cut and tapped down in between the bar and the cell. This ended the strain on the bar caused when the wing nut was turned. This piece was a successful addition to the apparatus.

Bubbles trapped between the piston and the chamber posed another problem, because they altered the volume and pressure of the solution. O-rings were inserted on the inside ends of the pistons to avoid the compression and decompression of the air pocket.

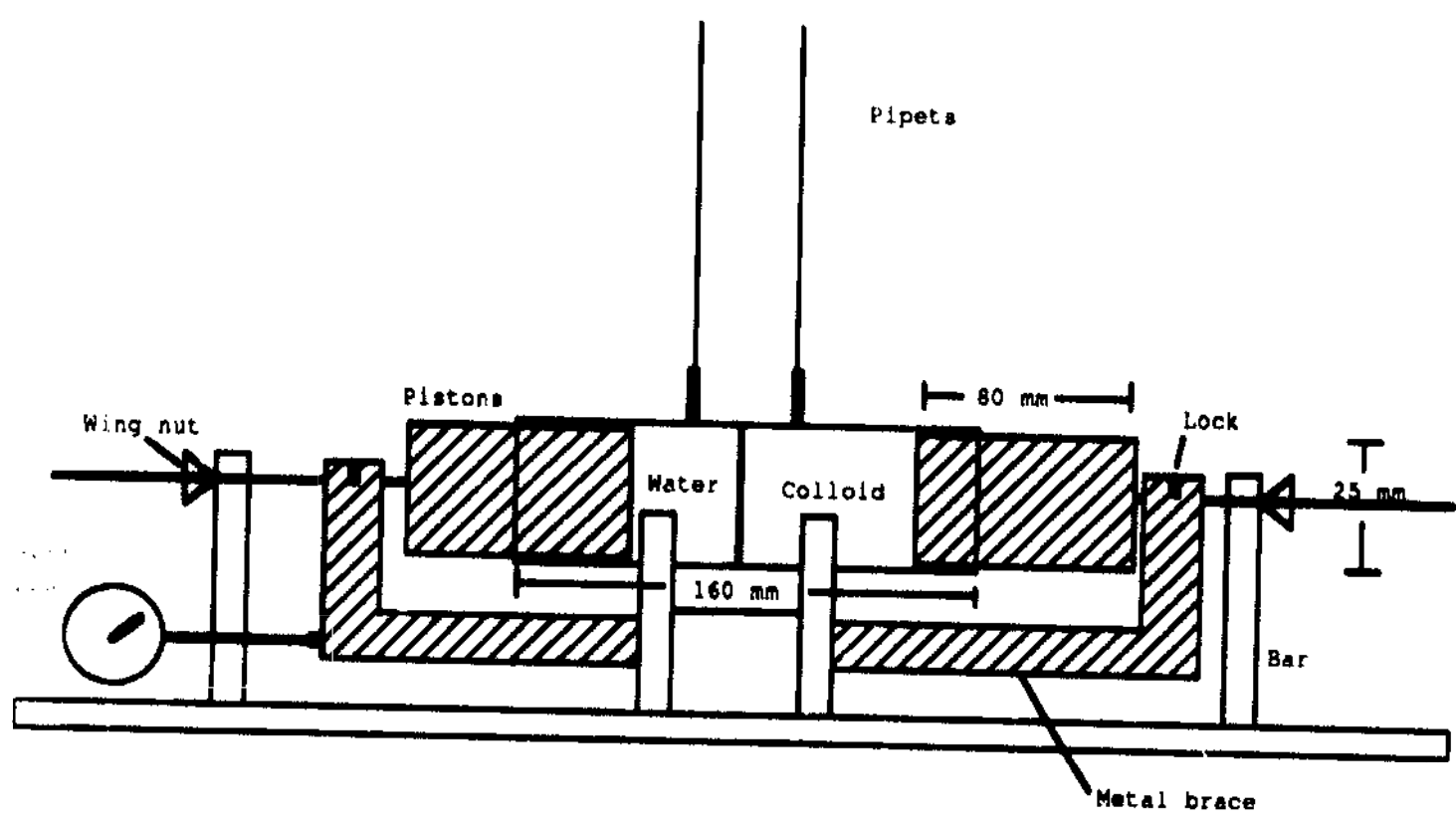


Figure II. Modified Osmotic Pressure Chamber

PROCEDURE

Colloid Fabrication

Monodisperse polystyrene particles with a diameter of 1100 angstroms were fabricated according to a recipe by Juang and Krieger (6). Two-hundred fifty milliliters of styrene were distilled under 25-inches of mercury vacuum at 60°C. To remove the inhibitor and other impurities, the first 25-mls. and the last 25-mls. of distillate were discarded. Then, the purified styrene and 2-liters of water were each purged with nitrogen gas for forty minutes. A 65°C constant temperature bath was set up and the reaction vessel was equipped for continuous agitation at 150-160 rpm. Then, appropriate concentrations of the buffer solution, electrolyte, ionic comonomer and initiator solutions were prepared (Table I).

The distilled water was poured into the 2-liter flask and the agitator was turned on. The solutions were then added in the following order: buffer solution, electrolyte, styrene, ionic comonomer, and initiator. The constant temperature water bath was covered with tin foil to prevent evaporation of the water. After several hours, the agitator speed was reduced to 70-75 rpm. The reaction was left to run for 24 hours. The initially clear solution turned milky white overnight indicating the presence of colloidal particles.

After 24 hours, the colloid was cooled, filtered, and cleaned. The colloid was deionized with Amberlite ion

Table I. Recipe for 1.5-liters of monodisperse polystyrene latex (1100 angstrom diameter).

Name	Solution	Quantity (mls.)
Distilled water	H ₂ O	1108
Buffer solution	.003 M KH ₂ PO ₄	25
Electrolyte	.240 N KOH	25
Styrene	styrene	167
Ionic comonomer	.073 M NaSS*	125
Initiator	.167 M K ₂ S ₂ O ₈	50

* Sodium salt of styrene sulfonic acid

exchange resin. Enough resin was added to equal about one third of the total volume. The beads turned from brown to purple as the colloid was "cleaned up." The mixture was then filtered through glass wool to remove the beads.

Several two foot strips of dialysis tubing were boiled for an hour, and then filled with the colloid. Some of the strips were dialyzed against distilled water, 10^{-4} M HCl, and 10^{-3} M HCl for one week. The latex was thus forced to be in equilibrium with ionic strengths equal to 10^{-5} , 10^{-4} , and 10^{-3} mol/L.

Conductivity and pH measurements of the colloid dialyzed against distilled water were 61.32 micromhos and 6.47, respectively. These were of the expected order (6). The scanning electron microscope revealed monodisperse particles with a diameter of 1100 angstroms (Fig. III).

Colloid Concentration

Initial attempts to concentrate the colloid inside the pressure cell were unsuccessful. The right chamber was filled with colloid and the left chamber was filled with dialysate. The pistons were locked in place, and the pipet holes and electrode holes were plugged. Then, dialysate was forced out of the colloid and across the membrane by pushing the colloid piston into the cell, which pulled the dialysate piston out. In concentrating the colloid from an approximate volume fraction of .07 to .20, a layer of coagulated colloid 2 to

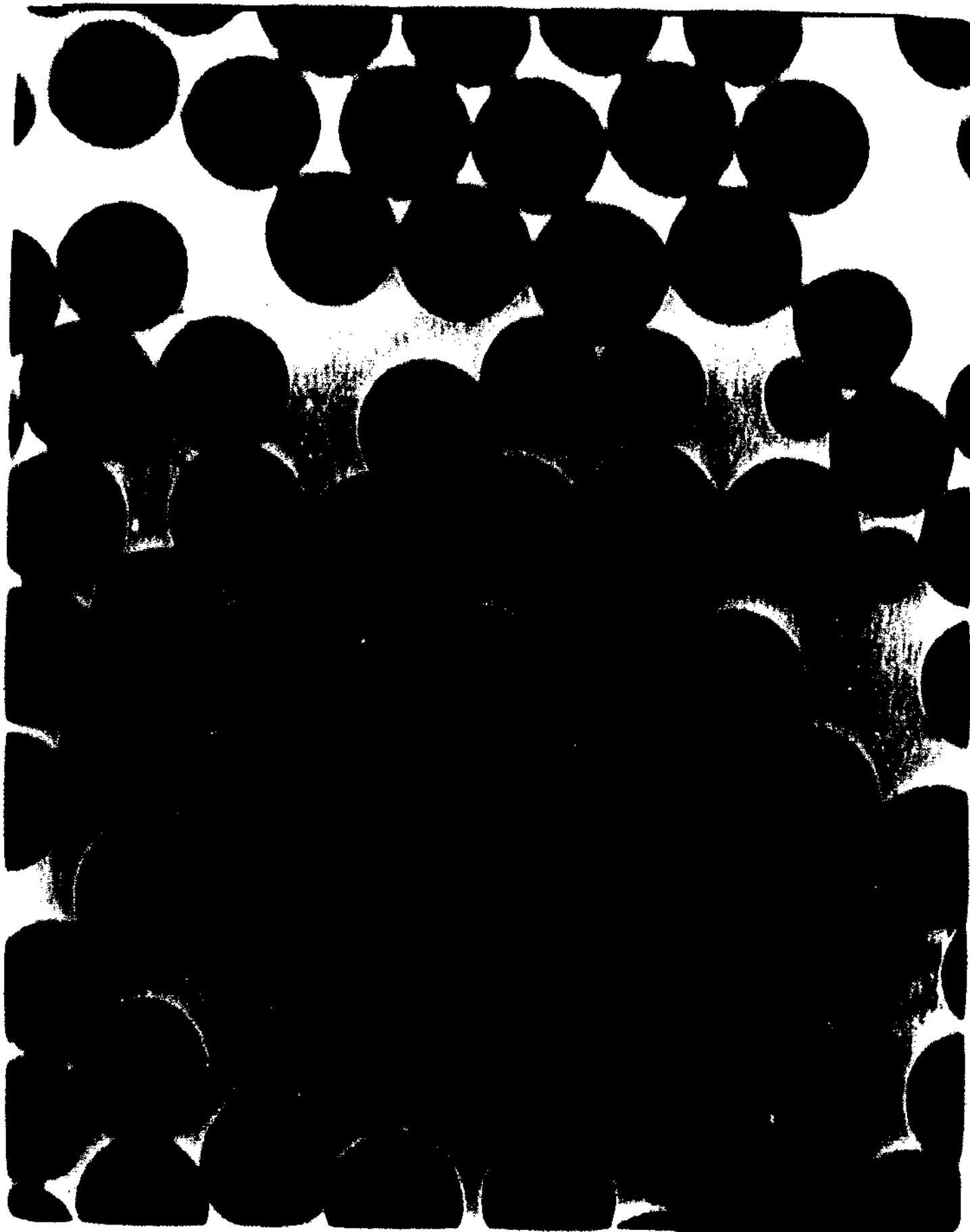


Figure III. SEM photo at 100,000X magnification showing monodisperse polystyrene particles.

3-mm thick was formed on the membrane. Also, the screens holding the membrane buckled 3-mm because of the pressure.

A second attempt to concentrate the colloid inside the cell was also unsuccessful. The cell was filled, the pistons were locked in place, the electrode holes were plugged, and pipets were inserted into the top. As pressure was applied, the liquid level in the pipet containing the colloid rose, and the liquid level in the pipet containing the dialysate fell. Several minutes went by and the liquid levels only moved a few millimeters. To speed up the process, air pressure was applied to the pipet on the colloid side. This had the same effect as using the pistons, and colloid coagulated on the membrane.

An alternate method of concentrating the colloid was then developed (Fig. IV). A 15-inch strip of dialysis tubing that was boiled for one hour was filled with the colloid; only one end was tied. The other end was sealed to rubber tubing that was connected to a nitrogen cylinder. The tube was placed in a 1500-ml graduated cylinder which was filled with water. The cylinder was opened to deliver 5-psi of nitrogen. The colloid was compressed to an approximate volume fraction of .30 after four days. It had yellow, pink, green, and purple irridescent blotches and strips. No coagulation was seen on the inside of the dialysis tubing.

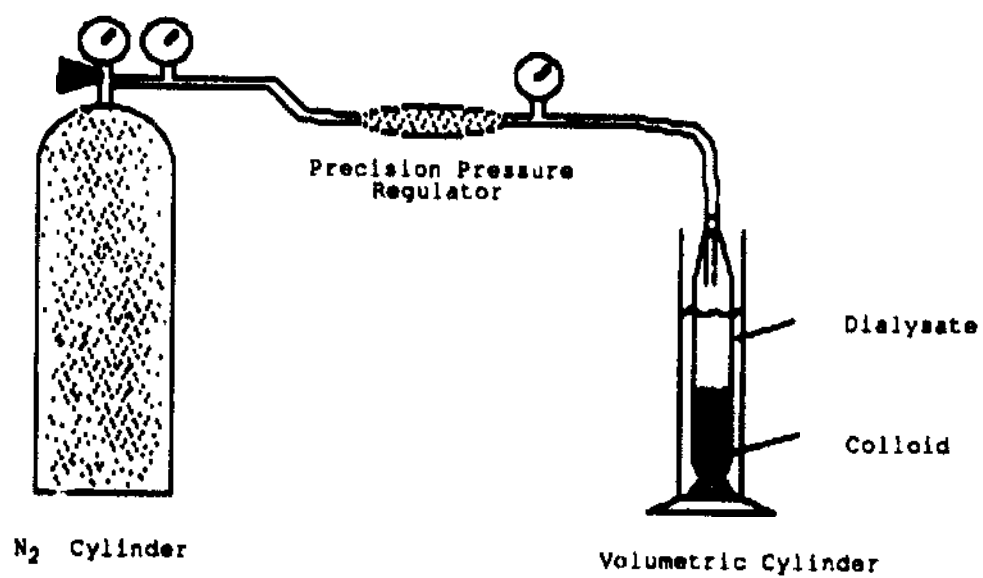


Figure IV. Apparatus used to concentrate the colloid.

Filling the Pressure Cell

The entire cell was cleaned thoroughly and all o-rings were greased lightly with Dow Corning vacuum grease so that the pistons could slide easily. Then, the membrane, screens, and both pistons were inserted. The colloid side was filled first. The cell was tipped on an angle and filled slowly with a disposable pipet, making sure no air bubbles were trapped along the bottom or sides. Once the liquid level reached the top openings, the pipet was inserted and tightened down, again avoiding air bubbles. Then, the plug was carefully inserted into the electrode hole and screwed down. This forced colloid up into the pipet. More colloid could be forced up into the pipet by slowly, squeezing in on the piston.

The dialysate was then poured into the other chamber. It was easiest to insert the plug first, then the pipet. Dialysate was forced up into the pipet by the pressure exerted from the colloid. Extra dialysate was inserted into the pipet using the disposable pipet, or carefully squeezing in on the piston.

The long screws were then tightened and the chamber was locked in place. The wooden block was tapped into place. Next, 50-microliters of red oil (specific gravity .826 at 25°C) were added to the top of each pipet using a syringe. This hindered evaporation of the fluids and gave a crisp meniscus that was easily read. Measurements began after 24 hours (Fig. V). This was long enough so that the liquid levels in the

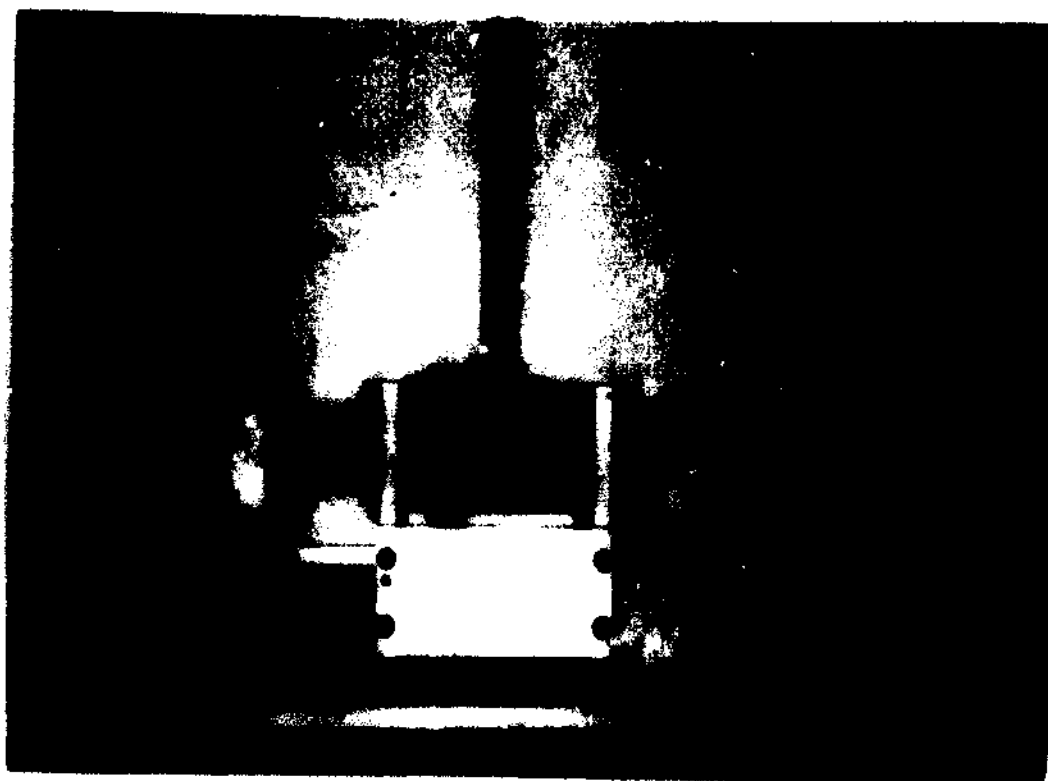


Figure V. Photo of the working osmometer.

pipets did not change when checked at two hour intervals. The initial position of the pistons, the Starrett gauge, and the height of the liquid levels in the pipets were recorded. After 24 hours, the wing nut was carefully turned to obtain a less concentrated volume fraction. Osmotic pressures were calculated from the data.

RESULTS AND DISCUSSION

The measured osmotic pressures increased with increasing volume fraction and decreasing ionic strength (Fig. VI), as expected (3). The osmotic pressure curve was predicted from an empirical expression for particles of a diameter equal to 1100 angstroms from the following expression:

$$\pi \text{ (mm H}_2\text{O)} = (\rho RT)/L \cdot (1 + \phi + \phi^2)/(1 - \phi)^3. \quad (1)$$

The expression assumed that the particles were hard-spheres and was predicted for disordered suspensions. The particles did not act like hard spheres with their known diameter, however, because the interaction forces hindered the particles from coming close together. To correct for these repulsive forces, the predicted curve was shifted back onto each of the experimental curves. An "effective" hard-sphere diameter was found using:

$$d_{H-S} = (\phi_{H-S} / \phi_{exp})^{1/3} \times d_{exp}, \quad (2)$$

which was derived from the number density:

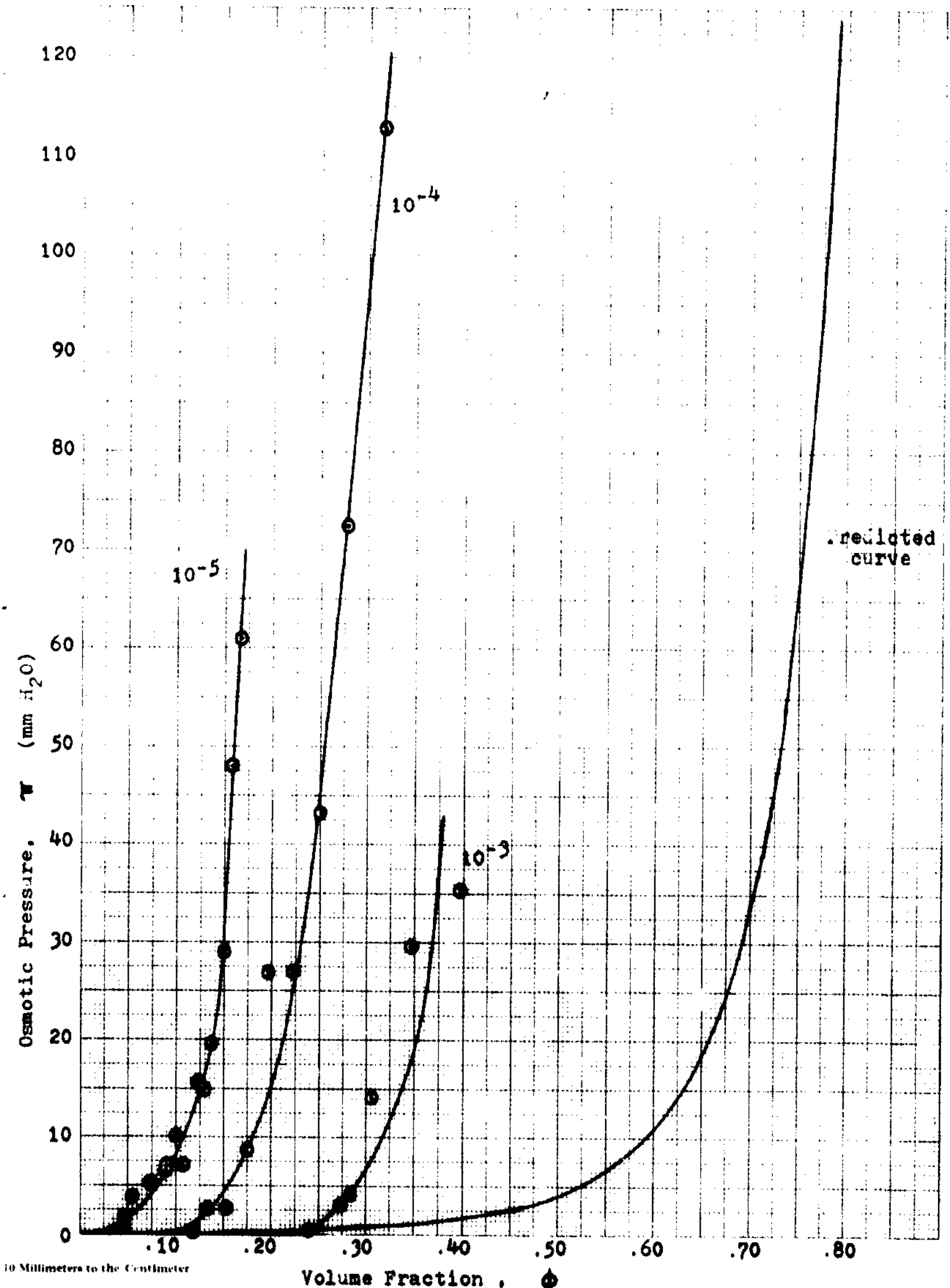
$$\rho = \phi / (4/3 \pi r^3) = \phi / (1/6 \pi d^3), \quad (3)$$

assuming when:

$$\pi_{\text{hard-sphere}} = \pi_{\text{exp}}, \quad (4)$$

$$\rho_{\text{actual}} = \rho_{\text{hard-sphere}}. \quad (5)$$

Figure VI. Osmotic Pressure as a Function of Volume Fraction.



The effective hard-sphere diameters were larger than the physical diameters because they accounted for the interparticle repulsion. The effective diameters found for the lattices of ionic strengths 10^{-5} , 10^{-4} and 10^{-3} were 1809 Å, 1525 Å, and 1357 Å, respectively.

The surface potentials, ψ_0 , of the particles were derived by following the method developed by Beunen and White (4) in which the hard-sphere diameters can be calculated from the solvent ionic strength and particle surface potential. Their equation also assumed no overlap of the particles:

$$d_{\text{eff}} = 2a + a \int_2^{20} (1 - \exp(-u(x)/kT)) dx, \quad (6)$$

where x was the center-to-center separation in units of the particle radius a (4). The energy $u(x)$ was given by:

$$u(x) = 4 \pi \epsilon a^2 \psi_0^2 (1/x) \exp(-\kappa a (x-2)), \quad (7)$$

and the inverse screening length by:

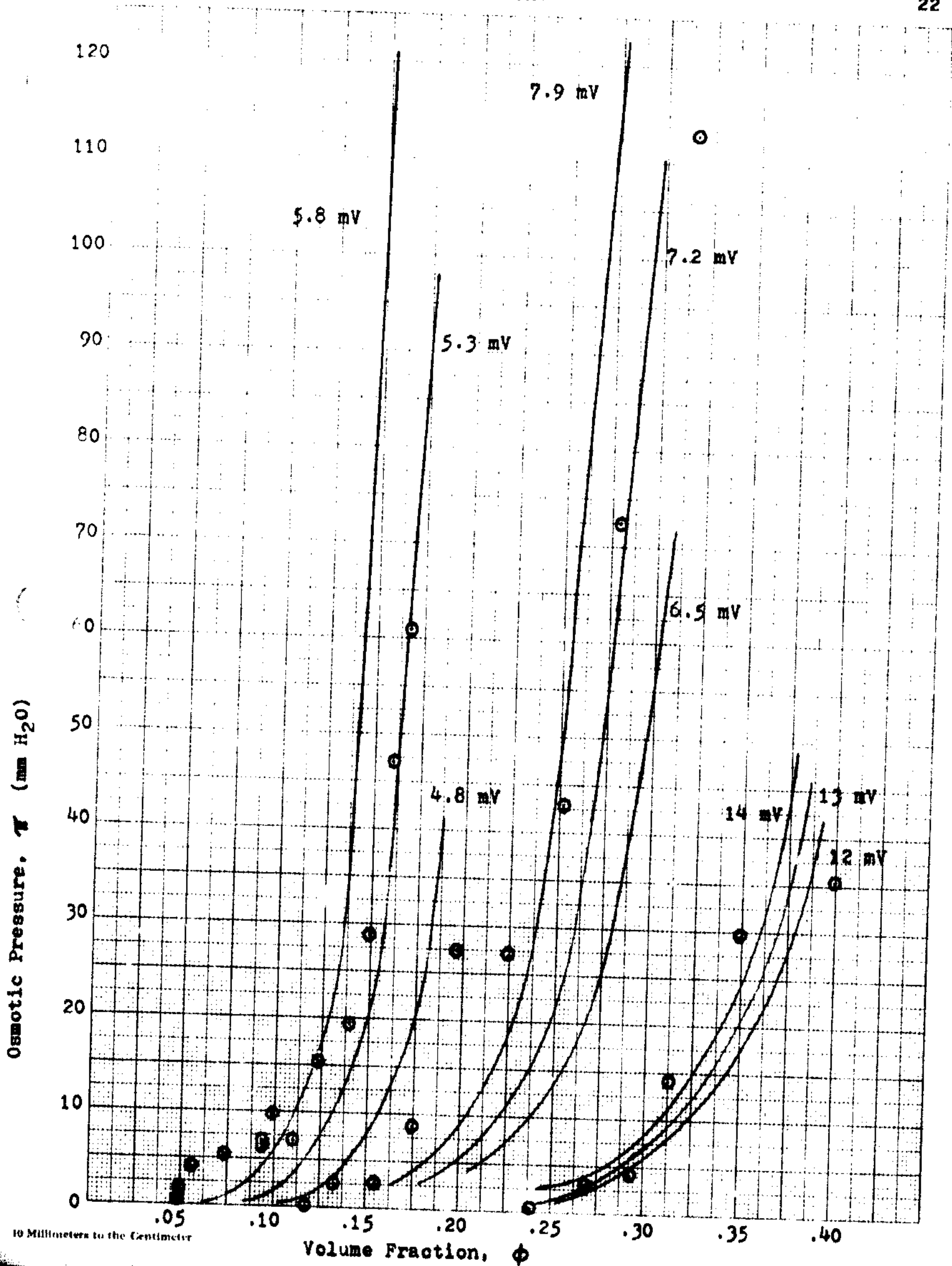
$$\kappa^2 = (2\rho L^2 e^2 I) / (\epsilon RT). \quad (8)$$

The expressions accounted for the electrostatic interaction, neglecting the van der Waals attraction because it was assumed to be small (3). The solutions were by trial and error, matching the effective diameter calculated from shifting the predicted curve over, to the effective diameter calculated from the above equation. The calculated surface potentials

for the particles of ionic strengths 10^{-5} , 10^{-4} , and 10^{-3} , were 5.3 mV, 7.2 mV, and 13 mV, respectively. These were low compared to similar particles by Russel and Benzing (2) which had a surface potential of approximately 25 mV. The surface potential was the only adjustable parameter in the calculations. The disagreement may indicate that the predicted osmotic pressure is a function of more than one variable.

Calculated surface potentials were changed by $\pm 10\%$ of the calculated values to show the dependence of the osmotic pressure (Fig. VII). All of the calculated curves were too steep, demonstrating that the expression used for disordered suspensions may need to be altered if used to predict osmotic pressures for ordered lattices.

Figure VII. Calculated Osmotic Pressures as a Function of Volume Fraction.



CONCLUSIONS AND RECOMMENDATIONS

An osmometer was successfully built to measure the osmotic pressure as a function of the volume fraction of colloid. Although the apparatus was equipped to simultaneously measure the pressure and the potential, time constraints only allowed investigation of the former.

The experimental and calculated data of the polystyrene lattices lacked quantitative agreement. However, predictions were based on a liquid state theory by the suspension structure. It was known that the suspension was in an ordered state. Continuing work should include a comparison of the experimental osmotic pressures with those predicted for ordered suspensions (2,5,9). Also, the assumption of constant surface potential may have been incorrect, and agreement may have improved if the surface potential was varied (with the volume fraction of polystyrene) using the same equations (3).

Future work may investigate the relationship between the measured osmotic pressure and potential difference across the osmometer membrane. This would be a useful tool for systems in which the pressures are too small to be measured. Of particular interest, are the osmotic pressures involved in the liquid-vapor phase change of this colloidal system. Understanding the interaction forces of all phases may someday allow us to alter the controlling parameters and create a stable flawless high-density solid.

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APPENDICES

ABBREVIATIONS

a	particle radius (A)
d_{eff}	effective or hard-sphere diameter (A)
e	charge of an electron (C)
ϵ_0	permittivity in a vacuum ($C^2/J \cdot m$)
ϵ_r	permittivity of water
G	Starrett gauge reading (inches)
H	height (mm)
I	ionic strength (mol/kg)
k	Boltzmann's constant (J/K)
K	inverse screening length (m^{-1})
l	length (mm)
L	Avogadro's number (mol^{-1})
M	molarity (mol/L)
r	radius (m)
r_D	Debye screening length (m)
R	gas constant (J/mol \cdot K)
T	temperature (K)
$u(x)$	potential at x radii from the particle (J)
V	volume (L)
ϕ_{exp}	experimental volume fraction
ϕ_{H-S}	hard-sphere volume fraction
π_{calc}	calculated osmotic pressure (mm H ₂ O)
π_{exp}	experimental osmotic pressure (mm H ₂ O)
ρ	density (kg/m^3)
ψ_0	surface potential (J/C)

Table II. Raw Data For Colloid Dialyzed Against Distilled Water.

Starrett Gauge (inches)	Pipet Height		Volume Fraction	π Osmotic Pressure (mm H ₂ O)
	Colloid (mm)	Water (mm)		
0.9949	130.5	70.5	.168	61.1
0.9534	114	86	.149	28.8
0.9754	97	50	.159	47.8
0.9309	76	57	.140	19.5
0.9084	73.5	59	.132	15.0
0.8829	70.5	55.5	.124	15.4
0.8251	60	53.5	.109	6.83
0.7873	73.5	64	.101	9.87
0.7177	74.0	67.5	.089	6.83
0.7177	69.0	63	.089	6.31
0.5895	68	63	.073	5.25
0.3729	65	61.5	.056	3.68
0.2202	18	17.5	.048	0.54
0.2202	20	18.5	.048	1.55

Table III. Raw Data For Colloid Dialyzed Against 10^{-4} M HCl

Starrett Gauge (inches)	Pipet Height		ϕ Volume Fraction	π Osmotic Pressure (mm H ₂ O)
	Colloid (mm)	Water (mm)		
1.7146	153	42	.317	113
1.6602	117	46	.279	72.6
1.6146	90	48	.253	43.1
1.5530	81	55	.225	26.9
1.4761	79	53	.197	26.8
1.3900	73	65	.174	8.6
1.3070	69	67	.156	2.5
1.1732	72	70	.133	2.5
1.0500	70	70	.118	0

Table IV. Raw Data For Colloid Dialyzed Against 10^{-3} M HCl

Starrett Gauge (inches)	Pipet Height		Volume Fraction	π Osmotic Pressure (mm H ₂ O)
	Colloid (mm)	Water (mm)		
1.7975	118	85	.400	35.4
1.7381	99	71	.348	29.6
1.6875	95	86	.313	10.4
1.6540	74	71	.293	4.0
1.6160	81	79	.274	3.0
1.5371	73	73	.240	0
1.6160	79	74	.274	6.0
1.6540	88	77	.293	12.4

Table V. Calculated Effective Diameters For Particles Dialyzed Against Distilled Water.

π experimental osmotic pressure (mm H ₂ O)	ϕ experimental volume fraction	ϕ hard-sphere volume fraction	d effective diameter (angstroms)
65	.170	.748	1802
60	.166	.742	1807
55	.165	.736	1810
50	.164	.730	1808
45	.162	.722	1809
40	.160	.715	1811
35	.157	.700	1809
30	.154	.690	1812

Table VI. Calculated Effective Diameters For Particles Dialyzed Against 10^{-4} M HCl

π experimental osmotic pressure (mm H ₂ O)	ϕ experimental volume fraction	ϕ hard-sphere volume fraction	d effective diameter (angstroms)
120	.324	.789	1479
110	.315	.787	1492
100	.305	.777	1502
90	.295	.770	1514
80	.287	.763	1523
70	.278	.753	1533
60	.269	.742	1542
50	.260	.730	1534
40	.250	.715	1561
30	.235	.690	1575

Table VII. Calculated Effective Diameters For Particles Dialyzed
Against 10^{-3} M HCl

π experimental osmotic pressure (mm H ₂ O)	ϕ experimental volume fraction	ϕ hard-sphere volume fraction	d effective diameter (angstroms)
40	.385	.715	1352
35	.376	.700	1353
30	.367	.690	1357
25	.357	.675	1360
20	.346	.660	1364

Table VIII. Calculated Osmotic Pressures for Hard-sphere Volume Fractions and Ionic Strength 10^{-5} .

Potential ϕ_{eff}	5.3 mV 1809 A		5.8 mV 1902 A		4.8 mV 1711 A	
ϕ Exp. Volume Fraction	ϕ H-S Volume Fraction	π Calc. Osmotic Pressure	ϕ H-S Volume Fraction	π Calc. Osmotic Pressure	ϕ H-S Volume Fraction	π Calc. Osmotic Pressure
.170	.756	72.2	.879	784	.640	16.9
.165	.734	52.8	.853	413	.621	13.6
.160	.712	39.4	.827	239	.602	11.2
.154	.685	28.1	.796	135	.580	8.94
.145	.650	18.7	.750	66.2	.546	6.41
.125	.556	7.06	.646	17.9	.470	3.18
.110	.489	3.78	.569	8.02	.414	1.94
.080	.356	1.10	.413	1.93	.301	0.73
.060	.267	0.54	.310	0.79	.226	0.37

Table IX. Calculated Osmotic Pressures for Hard-sphere
Volume Fractions and Ionic Strength 10^{-4} .

Potential Diff	7.2 mV 1525 A		6.5 mV 1475 A		7.9 mV 1569 A	
ϕ Exp.	ϕ H-S	π Calc.	ϕ H-S	π Calc.	ϕ H-S	π Calc.
Volume Fraction	Volume Fraction	Osmotic Pressure	Volume Fraction	Osmotic Pressure	Volume Fraction	Osmotic Pressure
.324	.863	521	.781	105	.940	7300
.315	.839	304	.759	75.5	.914	2350
.305	.813	183	.735	53.6	.885	926
.295	.786	115	.711	38.9	.856	442
.269	.717	42.1	.648	18.3	.786	104
.260	.693	31.0	.627	14.5	.755	71.1
.250	.666	22.5	.603	11.3	.725	46.8
.238	.626	14.4	.566	7.78	.682	27.1
.220	.586	9.50	.530	5.51	.638	16.4
.200	.533	5.67	.482	3.54	.580	8.94
.180	.480	3.48	.434	2.31	.522	5.11
.155	.413	1.93	.374	1.37	.450	2.66
.034	.387	0.14	.323	0.88	.389	1.86

Table X. Calculated Osmotic Pressures for Hard-sphere
Volume Fractions and Ionic Strength 10^{-3} .

Potential ϕ	13 mV 1357 A		12 mV 1341 A		14 mV 1369 A	
ϕ	ϕ	π	ϕ	π	ϕ	π
Exp.	H-S	Calc.	H-S	Calc.	H-S	Calc.
Volume Fraction	Volume Fraction	Osmotic Pressure	Volume Fraction	Osmotic Pressure	Volume Fraction	Osmotic Pressure
.385	.723	45.5	.689	33.0	.742	59.0
.376	.706	36.5	.681	28.8	.728	46.8
.367	.689	29.8	.665	18.2	.707	37.0
.357	.670	23.5	.647	15.1	.688	29.2
.346	.650	18.7	.627	14.5	.667	22.7
.337	.633	15.5	.610	12.1	.650	18.7
.318	.597	10.6	.576	8.59	.613	12.5
.290	.544	6.29	.525	5.86	.559	7.27
.270	.507	4.45	.489	3.78	.520	5.02

SAMPLE CALCULATIONS

Volume fraction of polystyrene, ϕ

For Table 1, volume fraction was sampled at end of run:

jar + wet colloid	18.0882 g
jar	- 10.3992 g
	<hr/>
	7.6890 g

jar + dry colloid	10.7862 g
jar	- 10.3992 g
	<hr/>
	0.3870 g

water = (7.6890 g - 0.3870 g) · (1 ml/1.0 g) = 7.3020 ml

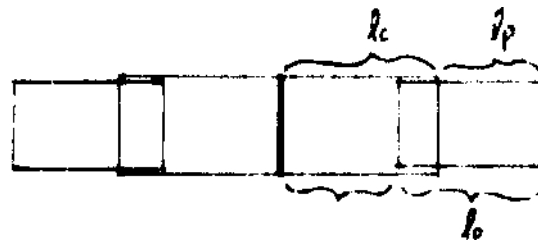
polystyrene = (0.3870 g) · (1 ml/1 g) = 0.3686 ml

$\phi = (.3686 \text{ ml}) / (7.3020 \text{ ml} + .3686 \text{ ml}) = 0.048$

Successive Volume Fractions

For Table I:

$l_c = 81 \text{ mm}$
 $l_o = 86 \text{ mm}$
 $l_p = 32.5 \text{ mm}$
 $G_o = 0.2202 \text{ in.}$



$$\phi_o = x / (l_c - l_o + l_p)$$
$$0.048 = x / (81 - 86 + 32.5)$$

$$x = 0.048 \cdot 27.5 \text{ mm}$$
$$x = 1.32 \text{ mm}$$

$$\phi_n = 1.48 \text{ mm} / (27.5 \text{ mm} - (G - G_o) (25.4 \text{ mm/in}))$$

For Trial 1:

$G = 0.9949 \text{ in.}$

$$\phi_n = 1.32 \text{ mm} / (27.5 \text{ mm} - (0.9949 \text{ in} - 0.2202 \text{ in}) (25.4 \text{ mm/in}))$$

$\phi = 0.168$

Osmotic Pressure, π (mm H₂O)

$$\pi \text{ (mm H}_2\text{O)} = H_{\text{colloid}} (\rho_{\text{colloid}} (\phi) + \rho_{\text{water}}(1-\phi)) / \rho_{\text{water}} - H_{\text{water}}$$

For Table I, trial 1:

$$\rho_{\text{water}} = 1.00 \text{ g/ml}$$

$$\rho_{\text{colloid}} = 1.05 \text{ g/ml}$$

$$\phi = 0.168$$

$$H_{\text{colloid}} = 130.5 \text{ mm}$$

$$H_{\text{water}} = 70.5 \text{ mm}$$

$$\pi = 130.5 \text{ mm} \left(\frac{1.05 \text{ g/ml}(.168) + 1.00 \text{ g/ml}(1-.168)}{1.00 \text{ g/ml}} \right) - 70.5 \text{ mm}$$

$$\pi = 61.1 \text{ mm H}_2\text{O}$$

Calculated Osmotic Pressure Curve

From McQuarrie (7):

$$\pi / (\rho kT) = (1 + \phi + \phi^2) / (1 - \phi)^3$$

$$\rho = \phi / (4/3 \pi r^3)$$

$$R = 8.31441 \text{ J/mol} \cdot \text{K}$$

$$T = 296 \text{ K}$$

$$L = 6.02 \times 10^{-23} \text{ /mol}$$

$$\text{conversions: } 1 \text{ mm Hg} = 133.322 \text{ J/m}^3 = 13.5497 \text{ mm H}_2\text{O}$$

$$\begin{aligned} \pi \text{ (mm H}_2\text{O)} &= (\rho RT / L) \cdot (1 + \phi + \phi^2) / (1 - \phi)^3 \\ &= 9.91822 \times 10^{-5} (\phi + \phi^2 + \phi^3) / (r^3 (1 - \phi)^3) \end{aligned}$$

A program was written to calculate the osmotic pressures for a given radius in microns for volume fractions starting at .05 and going up to 1.00.

Calculation of effective diameters

When: $\pi_{n-s} = \pi_{exp}$,

then: $\rho_{n-s} = \rho_{exp}$,

or: $\phi_{n-s} / (4/3 \pi r_{n-s}^3) = \phi_{exp} / (4/3 \pi r_{exp}^3)$

and then: $\phi_{exp} (d_{n-s}/d_{exp})^3 = \phi_{n-s}$

$$d_{n-s} = (\phi_{n-s}/\phi_{exp})^{1/3} d_{exp}.$$

```
10 INPUT "enter the radius" ;R
20 INPUT "enter the volume fraction" ;F
30 PRINT "Radius = ",R
40 F= .05
50 FOR I = 1 TO 99
60 F=F+.01
70 P=9.918222E-05*F*(1+F+F*F)/(R*R*R*(1-F)^3)
80 PRINT "the osmotic pressure is"; P, " f = ",F
90 PRINT
100 NEXT I
110 END
```

```
10 INPUT "enter the radius" ;R
20 INPUT "enter the volume fraction" ;F
30 LPRINT "Radius = ",R
40 F= .05
50 FOR I = 1 TO 99
60 F=F+.01
70 P=9.918222E-05*F*(1+F+F*F)/(R*R*R*(1-F)^3)
80 LPRINT "the osmotic pressure is"; P, " f = ",F
90 LPRINT
100 NEXT I
110 END
```

Radius = .055	f =	.06
the osmotic pressure is 4.580277E-02	f =	.07
the osmotic pressure is 5.576517E-02	f =	.08
the osmotic pressure is 6.653681E-02	f =	8.999999E-02
the osmotic pressure is 7.818186E-02	f =	9.999999E-02
the osmotic pressure is 9.076977E-02	f =	.11
the osmotic pressure is .1043758	f =	.12
the osmotic pressure is .1190817	f =	.13
the osmotic pressure is .1349761	f =	.14
the osmotic pressure is .1521552	f =	.15
the osmotic pressure is .1707234	f =	.16
the osmotic pressure is .1907946	f =	.17
the osmotic pressure is .2124924	f =	.18
the osmotic pressure is .2359515	f =	.19
the osmotic pressure is .2613186	f =	.2
the osmotic pressure is .2887537	f =	.2100001
the osmotic pressure is .3184316	f =	.2200001
the osmotic pressure is .3505428	f =	.2300001
the osmotic pressure is .3852959	f =	.2400001
the osmotic pressure is .4229191	f =	.2500001
the osmotic pressure is .463662	f =	.2600001
the osmotic pressure is .5077985	f =	.2700001
the osmotic pressure is .5556288	f =	.28
the osmotic pressure is .607483	f =	.29
the osmotic pressure is .6637235	f =	.3
the osmotic pressure is .7247491	f =	.31
the osmotic pressure is .7909998	f =	.32
the osmotic pressure is .8629599	f =	.33
the osmotic pressure is .9411651	f =	.34
the osmotic pressure is 1.026207	f =	.35
the osmotic pressure is 1.118739	f =	

the osmotic pressure is 1.32926	f =	.37
the osmotic pressure is 1.448949	f =	.3799999
the osmotic pressure is 1.579549	f =	.3899999
the osmotic pressure is 1.722171	f =	.3999999
the osmotic pressure is 1.878053	f =	.4099999
the osmotic pressure is 2.048578	f =	.4199999
the osmotic pressure is 2.235295	f =	.4299999
the osmotic pressure is 2.439943	f =	.4399999
the osmotic pressure is 2.664472	f =	.4499999
the osmotic pressure is 2.91108	f =	.4599999
the osmotic pressure is 3.182243	f =	.4699999
the osmotic pressure is 3.48076	f =	.4799999
the osmotic pressure is 3.809797	f =	.4899999
the osmotic pressure is 4.172949	f =	.4999998
the osmotic pressure is 4.574301	f =	.5099998
the osmotic pressure is 5.018509	f =	.5199998
the osmotic pressure is 5.510889	f =	.5299998
the osmotic pressure is 6.057533	f =	.5399998
the osmotic pressure is 6.66543	f =	.5499998
the osmotic pressure is 7.342631	f =	.5599998
the osmotic pressure is 8.098423	f =	.5699998
the osmotic pressure is 8.94357	f =	.5799998
the osmotic pressure is 9.890568	f =	.5899998
the osmotic pressure is 10.95398	f =	.5999998
the osmotic pressure is 12.15083	f =	.6099997
the osmotic pressure is 13.50112	f =	.6199997
the osmotic pressure is 15.02838	f =	.6299997
the osmotic pressure is 16.76046	f =	.6399997
the osmotic pressure is 18.73044	f =	.6499997
the osmotic pressure is 20.97779	f =	.6599997
the osmotic pressure is 23.54982	f =	.6699997
the osmotic pressure is 26.50381	f =	.6799996

the osmotic pressure is 33.84715	f =	.6999996
the osmotic pressure is 38.42423	f =	.7099996
the osmotic pressure is 43.76628	f =	.7199996
the osmotic pressure is 50.03113	f =	.7299996
the osmotic pressure is 57.41628	f =	.7399996
the osmotic pressure is 66.17077	f =	.7499996
the osmotic pressure is 76.61135	f =	.7599996
the osmotic pressure is 89.14468	f =	.7699996
the osmotic pressure is 104.2981	f =	.7799996
the osmotic pressure is 122.7628	f =	.7899996
the osmotic pressure is 145.4562	f =	.7999996
the osmotic pressure is 173.6109	f =	.8099995
the osmotic pressure is 208.9084	f =	.8199995
the osmotic pressure is 253.6785	f =	.8299995
the osmotic pressure is 311.208	f =	.8399995
the osmotic pressure is 386.2259	f =	.8499995
the osmotic pressure is 485.6924	f =	.8599995
the osmotic pressure is 620.1156	f =	.8699994
the osmotic pressure is 805.8323	f =	.8799994
the osmotic pressure is 1069.118	f =	.8899994
the osmotic pressure is 1453.951	f =	.8999994
the osmotic pressure is 2037.512	f =	.9099994
the osmotic pressure is 2963.253	f =	.9199994
the osmotic pressure is 4517.408	f =	.9299994
the osmotic pressure is 7325.032	f =	.9399994
the osmotic pressure is 12923.16	f =	.9499994
the osmotic pressure is 25766.18	f =	.9599994
the osmotic pressure is 62338.06	f =	.9699994
the osmotic pressure is 214707	f =	.9799994
the osmotic pressure is 1752537	f =	.9899994
the osmotic pressure is 5.345241E+18	f =	.9999994
the osmotic pressure is -1824811	f =	1.0099995

the osmotic pressure is -70296.85

f =

1.029999

44

the osmotic pressure is -30241.29

f =

1.039999

Debye screening length, r_D

From Atkins (1):

$$r_D^2 = (eRT) / (2\rho L^2 e^2 I)$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/\text{J}\cdot\text{m}$$

$$\epsilon_r = 80$$

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$T = 296 \text{ K}$$

$$\rho = 1000 \text{ kg/m}^3$$

$$L = 6.02 \times 10^{-23} \text{ /mol}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$r_D^2 = 9.3709 \times 10^{-20} (\text{mol/kg} / I) \text{ m}^2$$

$$I = 10^{-5}, 10^{-4}, 10^{-3}$$

$$r_D = (3.0612 \times 10^{-10}) / \sqrt{I} \text{ m}$$

Calculation of the surface potential, ψ

From Beunen (4):

$$u(x) = 4 \pi \epsilon_0 \epsilon_r a^2 \psi_0^2 (1/r) \exp(-K(r-2a))$$

Change r to units of radii by multiplying through by a ($r=xa$)

$$\begin{aligned} u(x) &= 4 \pi \epsilon_0 \epsilon_r a^2 \psi_0^2 (1/xa) \exp(-K(xa-2a)) \\ &= 4 \pi \epsilon_0 \epsilon_r a \psi_0^2 (1/x) \exp(-Ka(x-2)) \end{aligned}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/\text{J}\cdot\text{m}$$

$$\epsilon_r = 80$$

$$a = 5.50 \times 10^{-8} \text{ m}$$

$$K = 1/r_D = 3.2977 \times 10^9 \sqrt{I} \text{ m}^{-1}$$

$$u(x) = 6.50706 \times 10^{-16} (\psi_0^2/x) \exp(-181.4 \sqrt{I} (x-2))$$

$$kT = 1.38066 \times 10^{-23} \text{ J/K} \cdot 296 \text{ K} = 4.08675 \times 10^{-21} \text{ J}$$

$$u(x) / kT = 117547 (\psi_0^2/x) \exp(-181.4 \sqrt{I} (x-2))$$

$$f(x) = 1 - \exp(-u(x) / kT)$$

Finally,

$$\text{def} = 2a - a \int_{x=2}^{x=\infty} f(x) dx$$

where ∞ is taken as 20.

A program was written to calculate the surface potential, ψ_0 , of the polystyrene particles. It used Simpson's rule to evaluate the integral.

In the program, $E = \psi_0$, and $S = I$.

Also, the program was set up to calculate a residual. The surface potential was guessed in millivolts, the ionic strength was entered, and the effective diameter was entered in angstroms. The program calculated:

$$M = (d_{eff} - 2a) / a$$

and

$$S2N = \int_{x=2}^{x=20} f(x) dx$$

giving a residual:

$$R = M - S2N.$$

```
10 DX = .02
20 YI = 0!
30 YJ = 0!
40 YO = 0!
50 Y200 = 0!
60 S2N = 0!
70 M = 0
80 T = 0
90 R = 2!
100 INPUT "enter guess for potential, E ",E
110 INPUT "enter guess for ionic strength, S ",S
120 INPUT "enter effective radius, Deff ",DEFF
130 M = (DEFF - 1100)/550
140 T = SDR(S)
150 ' CALCULATE YO AND Y200
160 G = EXP((-117547!*E*E/R)*EXP(-181.4*T*(R-2)))
170 YO = 1-G
180 R = 10!
190 G = EXP((-117547!*E*E/R)*EXP(-181.4*T*(R-2)))
200 Y20 = 1-G
210 ' CALCULATE INTERMEDIATE VALUES AND SUM RESULT.
220 R = 2!
230 J = 0!
240 FOR I = 2 TO 899
250 R = R + DX
260 G = EXP((-117547!*E*E/R)*EXP(-181.4*T*(R-2)))
270 Y = 1-G
280 IF J=0 THEN S2N = S2N + 4*Y :J=1 : GOTO 300
290 IF J=1 THEN S2N = S2N + 2*Y :J=0
300 NEXT I
310 S2N = S2N + YO + Y20
320 S2N = DX*S2N/3
330 F = M - S2N
340 PRINT "YO is ",YO
350 PRINT "Y20 is ",Y20
360 PRINT "RESIDUAL IS - ",F
370 END
```

```

RUN
enter guess for potential, E .0053
enter guess for ionic strength, S .00001
enter effective radius, Deff 1809
Y0 is .808132
Y20 is 3.349781E-03
RESIDUAL IS - 3.013373E-03

```

```

OK
RUN
enter guess for potential, E .0054
enter guess for ionic strength, S .00001
enter effective radius, Deff 1809
Y0 is .8198266
Y20 is 3.477156E-03
RESIDUAL IS - -3.173721E-02
OK

```

```

1LIST 2RUN 3LOAD" 4SAVE" 5CONT 6,"LPT1 7TRON 8TROFF9KEY 0SCREEN

```

```

RUN
enter guess for potential, E .0072
enter guess for ionic strength, S .0001
enter effective radius, Deff 1525
Y0 is .9524901
Y20 is 3.576279E-07
RESIDUAL IS - 2.071381E-03

```

```

OK
RUN
enter guess for potential, E .0073
enter guess for ionic strength, S .0001
enter effective radius, Deff 1525
Y0 is .9563713
Y20 is 3.576279E-07
RESIDUAL IS - -1.000428E-02
OK

```

```

1LIST 2RUN 3LOAD" 4SAVE" 5CONT 6,"LPT1 7TRON 8TROFF9KEY 0SCREEN

```

```
RUN
enter guess for potential, E .013
enter guess for ionic strength, S .001
enter effective radius, Deff 1357
Y0 is .9999514
Y20 is 0
RESIDUAL IS - 2.268165E-03
```

```
OK
RUN
enter guess for potential, E .014
enter guess for ionic strength, S .001
enter effective radius, Deff 1357
Y0 is .9999901
Y20 is 0
RESIDUAL IS - -.0218603
OK
```

```
1LIST 2RUN 3LOAD" 4SAVE" 5CONT 6,"LPT1 7TRON 8TROFF9KEY 0SCREEN
```

```

20 DX = .02
30 YI = 0
40 YJ = 0
50 Y0 = 0
60 S2N = 0
70 DEFF = 0
80 I = 0
90 R = 2
100 INPUT "enter guess for potential, F = ", F
110 INPUT "enter guess for toxic strength, S = ", S
120 T = SDR(S)
130 * CALCULATE Y0 AND Y20
140 G = EXP((-1175471 * F * E / R) * EXP(-181.4 * T * (R - 2)))
150 Y0 = 1 - G
160 R = 10
170 G = EXP((-1175471 * F * E / R) * EXP(-181.4 * T * (R - 2)))
180 Y20 = 1 - G
190 * CALCULATE INTERMEDIATE VALUES AND SUM RESULT.
200 R = 2
210 J = 0
220 FOR I = 2 TO 899
230 R = R + DX
240 G = EXP((-1175471 * F * E / R) * EXP(-181.4 * T * (R - 2)))
250 Y = 1 - G
260 IF J=0 THEN S2N = S2N + 4 * Y ; J=1 ; GOTO 300
270 IF J=1 THEN S2N = S2N + 2 * Y ; J=0
280 NEXT I
290 S2N = S2N + Y0 + Y20
300 S2N = DX * S2N / 3
310 DEFF = 1100 + 550 * S2N
320 PRINT "Y0 is ", Y0
330 PRINT "Y20 is ", Y20
340 PRINT "deff is - ", DEFF
350 END

```

```

RUN
enter guess for potential, E .0058
enter guess for ionic strength, S .00001
Y0 is .8615354
Y20 is 4.01032E-03
diff is - 1901.301

```

```

OK
RUN
enter guess for potential, E .0048
enter guess for ionic strength, S .00001
Y0 is .7418312
Y20 is 2.74837E-03
diff is - 1711.318

```

```

OK

```

```

1LIST 2RUN 3LOAD" 4SAVE" 5CONT 6,"LPT1 7TRON 8TROFF9KEY 0SCREEN

```

```

RUN
enter guess for potential, E .0079
enter guess for ionic strength, S .0001
Y0 is .9744739
Y20 is 3.576279E-07
diff is - 1569.07

```

```

OK

```

```

RUN
enter guess for potential, E .0065
enter guess for ionic strength, S .0001
Y0 is .9165227
Y20 is 2.384186E-07
diff is - 1475.694

```

```

OK

```

```

1LIST 2RUN 3LOAD" 4SAVE" 5CONT 6,"LPT1 7TRON 8TROFF9KEY 0SCREEN

```



```

1.1A
enter mass for potential, F = .014
enter mass for ionic strength, S = .001
Y0 is      .9999901
Y00 is     0
deff is    1300.023
DE
@UN
enter mass for potential, E = .014
enter mass for ionic strength, S = .001
Y0 is      .9997889
Y00 is     0
deff is    1341.43
DE

```

```

1LIST  2RUN  3LOAD"  4SAVE"  5CONF 6."LPT1 7TRON 8TROFF9KEY  0SCREEN

```