

# **Brookhaven Instruments Corporation**

# ZetaPlus

Zeta Potential Analyzer

Instruction Manual

**Brookhaven Instruments Corporation** 

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#### PLEASE READ

This is the instruction manual for your Brookhaven Instrument's ZetaPlus instrument. Please read it carefully before making measurements. The installation section describes procedures for checking that the instrument and software are working properly. Familiarize yourself with the software by running the program with some of the data sets that are provided for this purpose. If you have any questions, comments or suggestions, please contact Brookhaven Instruments.

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# I Introduction

The ZetaPlus is an automatic instrument designed for use with suspensions of particles or solutions of macromolecules. Generally speaking particles with diameters from 10nm to  $30\mu$ m (depending on particle density) can be measured. The software for instrument control and data analysis is written for use in the Microsoft Windows environment though a DOS version is also available.

The technique employed - electrophoretic light scattering (ELS) - is based on reference beam (modulated) optics and a dip-in (Uzgiris type) electrode system. It is also known as Laser Doppler Velocimetry (LDV). It has several advantages including:

- Speed Typically 1 to 2 minutes
- Accuracy  $\pm 2\%$
- Small Sample Volume 1.5 ml
- Calibration
   None required
- Disposable Cuvettes Eliminates contamination!
- Versatility Measures zeta potential of particles, polymers, emulsions, colloids, etc. in water and polar solvents\*.

\* For measurements in high salt (e.g. physiological ionic strength), viscous media, non-polar solvents or near the Iso-electric point please inquire about the ZetaPALS option.

Sample preparation is quick and easy, though some care should taken to avoid dust (particularly with samples having a small particle size and/or low particle concentration).

Computer control makes the instrument easy to operate. The software is menudriven with friendly screens designed to guide and inform at each stage of the operation. Common problems are identified and accentuated and simple remedies are suggested by the software. After pressing the <u>Start</u> button, everything else is automatic, including the calculations.

Please read the chapters on **Installation**, **Self Test**, **Software Operation** and **Diagnostics** before attempting to use the instrument. The chapter entitled **Theory and Data Interpretation** is not essential for correct instrument setup and operation. However, an understanding of these principles will help the user to apply the results in a better informed fashion.

The technical and sales personnel at Brookhaven will be pleased to render any assistance regarding questions that you might have about the ZetaPlus that have not been clarified by a careful reading of this manual.

# I.I Specifications

Zeta Potential Range	: -150 to + 150 mV
Size Range	: 10nm to 30 $\mu$ m (depending on particle density)
Accuracy	: ± 2%
Repeatability	: $\pm$ 2% with dust free samples
Laser	: 35 mW solid state laser, red (660 nm wavelength). Complies with BRH 21CFR 1040:10 as applicable. Optional 50mW green (532nm)laser, ~10x sensitivity incr.
Temperature Control	: 6 °C to 74 °C in steps of 0.1 °C
Sample Volume	: 1.5 ml
Measurement Time	: Typically 1 to 2 minutes
Results	: Modal values for Zeta Potential and Electrophoretic Mobility. Distributions of zeta potential and mobility. <b>Can characterize and display multi-modal</b> <b>distributions</b>

# II Installation

Your ZetaPlus is shipped to you with the software already installed, however you may need to periodically update the software to the latest version. To install the ZetaPlus software in Windows:

1) Insert the install diskette into the drive (for example in a:).

- 2) From the Windows Start menu select Run...
- 3) The **Run** dialog box will appear as shown in Figure (1)

Run		<u>?</u> ×
2	Type the name of a program, folder, doc resource, and Windows will open it for yo	ument, or Internet ou.
<u>O</u> pen:	a:\setup	<b>_</b>
	OK Cancel	Browse

Figure 1.The Run dialog box in Windows98

4) Run **setup.exe** by entering it on the command line preceded by the drive letter.

#### a:\setup

The software will be installed in the sub-directory **ZetapW** in the directory **BICW**. It is strongly recommended that the installation directories be allowed to remain as named by the setup software and not be altered in any way.

A data directory for the storage of measurement data will also be created. This will be a sub-directory of the **ZetapW** directory called **DATA**.

# III. Running the ZetaPlus

Since the software is written to operate in the Microsoft Windows environment it is necessary to launch the application by double clicking on the ZetaPlus icon (located in the Brookhaven Instruments Corp. program group). For more information on this refer to your Microsoft Windows manual.

Brookhaven Instruments - Zeta Potential Analyzer - 🗆 × File Graphs pH Conductance Mode Setup Help Mena bar ZR3-runs (Run 1) Grapical results display 1.0 Power Measurement Completed 0.5 Measurement status 0.0 -150.0 0.0 150.0 Zeta Potential (mV) Run 1 Zeta Potential Zoom -Zeta Potential Measurement Parameters: Run Zeta Potential (mV) Half Width (mV) 1 -54.91 2.39 Conductance = 330 μS 2 -59.57 3.63 Current = 1.89 mA -55.45 3 3.00 Tabelar results **Electric Field** = 15.69 V/cm -48.67 4.13 4 Sample Count Rate = 787 kcps 2.48 5 -54.16 -61.61 5.37 6 Ref. Count Rate = 3733 kcps 7 -55.64 7.22 Measurement parameters 8 -58.87 2.52 9 -52.99 2.32 10 -37.12 1.93 Mean -53.90 3.50 Std. Error 2.19 0.53 Start Runs Action **Hide Graph** Action bettons bettons Parameters Clear Copy To Clipboard

Figure 2 shows the main screen of the windows ZetaPlus software.

Figure 2. ZetaPlus Windows Software main screen with annotations of functional areas.

#### **III.1 Making a Measurement**

1. Take a fresh, clean sample cell.

2. Pour 1.6 ml of sample into the sample cell. It is strongly recommended that you use a well characterized sample like the BI-ZR3 to familiarize yourself with the instrument before attempting to measure unknown samples. See section V.7 for details on sample preparation for BI-ZR3.

3. Insert the electrodes fully into the sample cell (figure 3). Take care to use a tissue to catch any sample spilling over.



Figure 3

Inserting the electrodes into the sample cell: make sure that the electrodes are fully inserted

- 4. Slide back the door on the top of the ZetaPlus.
- 5. Inside you will find a cable terminated with an RJ11 (common telephone jack type) connector.
- 6. Plug the connector on this cable into the mating connector on the top of the electrodes you should hear a faint click when the connection has been made properly.
- 7. Insert the sample cell into the sample cell holder such that the connector with the cable coming out of it is pointing to your right hand side.
- 8. Ensure that the sample cell is inserted all the way into the sample cell holder.
- 9. Close the sliding door.

Now move the mouse to the **Parameters** button on the bottom of the screen ('Action Buttons' as shown in figure 2) and click the left button. (Please note that the unless otherwise specified we will henceforth refer to clicking the left button whenever we write 'click' or 'double click').

Parameters	×
Sample ID	Unknown Sample
Operator ID	Unknown Operator
Notes	Notes
Cycles	5 Batch # 1
Runs	10 <b>PH</b> 7.00
Temperature	25.0 deg. C Concentration 2.00 mg/mL
Suspension	Aqueous Particle Size 96.0 nm
Viscosity	0.890 cp
Ref. Index	1.330
Dielectric Constant	78.54
Auto Save Re	esults 🔽
	OK Cancel

Figure 4. ZetaPlus parameters panel

Figure 4 shows the **Parameters** menu on the ZetaPlus software. Refer to **Appendix 2** for a detailed explanation of each of the parameters shown here. For a standard measurement simply enter the **Sample ID** and **Operator ID** as a means of identification. Click on **OK**.

On the Menu Bar, click on **Conductance** and then on **Measure Sample Conductance** (Figure 5).



			-	-	-	_
Eiguro 6	Monu	oploation	for	mogouring	aamala	aanduatanaa
Fluule 5.	wenu	SEIECTION		ineasunnu	Samue	CUNULLANCE

Figure 6 shows the sample conductance measurement window. If you are measuring the BI-ZR3 (made up in 1mM KCI, at 25 °C as prescribed) then the sample conductance should read 320  $\mu$ S ± 10%. As shown in figure 6, the software allows the user to set a value for the applied current that would be used to measure the

sample conductance. In most cases (except for a sample with either a very low or a very high conductance) it is advisable to use the default value set by the **Auto** parameter. Feel free to click on the **Measure Again** button to measure a few times to convince yourself that the reading is reasonable and reliable.

Measu	ire Condi	uctance	
•	•		
Applied Current	(mA) —		
Auto	1.30		
⊖ User	0.14		
	ults ——		1
Current	1.30	mA	
Electric Field	11.13	V/cm	
Conductance	310	uS	
		Measure Ag	ain
		Print	
		OK	

Figure 6. Measuring the Sample's Conductance

We are now ready to attempt a zeta potential measurement. Click OK in the **Measure Conductance** page. Control will be returned to the main page of the ZetaPlus Windows software. Click on **Start**.

As it attempts to begin a measurement, the instrument will:

- First wait for the sample temperature to become stable at the temperature requested by the user (in the **Parameters** page).
- Next it will try to adjust the amount of light scattered by the sample so that a suitable ratio is maintained between the intensities of the reference beam and the light scattered by the sample.
- Finally it will determine the magnitude of current appropriate to the sample so as to generate an electric field of around 15V/cm.

Once these operating parameters are determined to be within acceptable limits, the instrument looks for stable operating conditions. In this state, the software will not apply an electric field to the sample until it detects three consecutive power spectra with peaks located at the reference frequency (250Hz,  $\pm$ 4Hz). After this, the instrument is finally ready to measure zeta potential. No user interventions should be required at this stage. By default, the instrument will measure three runs each comprising of five cycles and report the results in both a tabular and graphical form.

Figure 7 shows some results reported for the BI-ZR3 reference material. Please refer to Section V.7 for information on the preparation and use of this substance to check the performance of the ZetaPlus instrument.

👖 Brookhaven In	struments - Ze	ta Potential A	nalyzer				_ 🗆 ×
<u>File G</u> raphs <u>p</u> H	<u>Conductance</u>	<u>M</u> ode <u>S</u> etup <u>I</u>	<u>H</u> elp				
ZR3-runs	(Run 1)		2	1.0 J	19		T
Measurem	ent Com	pleted		0.5 0.0 -150	0.0 Zeta Po	0.0 tential (m∨	150.0
Zeta Potential	•			Zoom	Zeta Potenti	al 🗾	Run 1 🚔
	Run Zet	a Potential (	mV) Half	Width (mV	)		
	1	-54.91	and a second	2.39	80		
	2	- 59.57		3.63			
	3	-55.45		3.00			
	4	-48.67		4.13			
	5	-54.16		2.48			
	6	-61.61		5.37			
	7	- 55.64		7.22			
	8	-58.87		2.52			
	9	- 52.99		2.32			
	10	-37.12		1.93			
	Mean	-53.90	2	3.50			
	Std. Error	2.19		0.53			
S	tart		Runs			Hide Gra	aph
C	lear		Parameters	•	Co	py To Cli	pboard

Figure 7: Zeta potential results for BI-ZR3

If the operator has chosen multiple cycles per run an additional column labeled Sample Quality will appear in the main table above. When the number of cycles is greater than 1 the instrument repeats the measurement up to three times the number of cycles given in order to obtain agreement of the number of cycles requested. The Sample Quality is the ratio of the number of cycles requested and the total number of cycles needed to obtain agreement of the given number. If the **Show Status on Main Screen** check box is selected from the **Setup** / **Instrument Parameters** menu, then the **Measurement Parameters** will be displayed in a separate box to the right of the tabular results as shown in figure 8.

🛚 Brookhav	en Instruments - Zeta	Potential Analyzer			
Eile <u>G</u> raphs	<u>pH</u> <u>C</u> onductance <u>M</u> o	ode <u>S</u> etup <u>H</u> elp			
ZR3-ru Measur Zeta Poten	ns (Run 1) rement Comp	leted	1.0 0.5 0.0 -150.0	0.0 Zeta Potential (m	∨) Run 1 ●
Run 7e	eta Potential (mV)	Half Width (mV)		Measurement Pa	arameters:
1	- 54 . 91	2.39		Conductores	- 220 5
2	- 59.57	3.63		Conductance	- 330 µ S
3	- 55.45	3.00		Current	= 1.89 mA
4	-48.67	4.13		Electric Field	= 15.69 V/cm
5	-54.16	2.48		Sample Count Ra	te= 787 kcps
6	-61.61	5.37		Ref. Count Rate	= 3733 kcps
7	- 55.64	7.22			2010 C + 200 - 200
8	- 58.87	2.52			
9	-52.99	2.32			
10	- 37.12	1.93			
Mean	-53.90	3.50			
Std. Error	2.19	0.53			
	Start	Run	21	Hide G	raph
	Clear	Parame	eters	Сору То С	lipboard

Figure 8. Displaying Measurement Parameters on the main screen.

To store the results of the measurement click on **File in the** Menu Bar, and then on **Database**. The Database screen will appear (figure 9). The Upper half of this screen contains information on the **Folders** defined in the software. The bottom area of the screen is devoted to **Files** that exist in a given **Folder**. A **Folder** is a device in which several **Files** can be stored (for house keeping purposes). Note that (in figure 9) several **Folders** have been created (by clicking on **Create Folder**). Note also that the Folder "Sample Data" is "open". Any files saved will now be saved in this Folder. The Database Manager allows the user to manipulate (create, print, delete, import) both Folders and Files.

If you wish to save data to a different folder select it (by clicking on it). Click on Exit to return to the main screen. Click on **File** and then on **Save**. The measurement you just made has now been saved in the **Folder** you selected ("Sample Data" in this case).

Current Folder: Sample Data				
🗀 Arch				
🛅 Estee Lauder				
💼 Folder 1				
🛅 McGill				
💼 Pfizer				
🗁 Sample Data				
iles in Sample Data: 22 Files	Selected: 1			
Sample Id:	Date:	Time:	Batch:	
.993 um Latex, repeat 1	May 10, 1994	11:28:54	0	
.993 um Latex	May 10, 1994	11:24:38	0	
Tri-Modal, Mixed IDC Mobility	May 6, 1994	21:37:56	0	
	A 25 1004	15:05:00	0	
AI2O3 in 1mM KCl, pH 11.23	ADI 20, 1994			
Al2O3 in 1mM KCl, pH 11.23 Al2O3 in 1mM KCl, pH 10.25	Apr 25, 1994 Apr 25, 1994	14:39:24	0	_
Al2O3 in 1mM KCl, pH 11.23 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 9.4	Apr 25, 1994 Apr 25, 1994 Apr 25, 1994	14:39:24 14:21:38	0 0	-
Al2O3 in 1mM KCl, pH 11.23 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 8.14	Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994	14:39:24 14:21:38 13:50:07	0 0 0	•
Al2O3 in 1mM KCl, pH 11.23 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 8.14 Sort Files By:	Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Open File	14:39:24 14:21:38 13:50:07	0 0 0 ort Files	•
Al2O3 in 1mM KCl, pH 11.23 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 8.14 Sort Files By:	Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Open File	14:39:24 14:21:38 13:50:07	0 0 ort Files	•
AI2O3 in 1mM KCI, pH 11.23 AI2O3 in 1mM KCI, pH 10.25 AI2O3 in 1mM KCI, pH 9.4 AI2O3 in 1mM KCI, pH 8.14 Sort Files By: © Date/Time © Sample Id	Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Open File Print Selected Files	14:39:24 14:21:38 13:50:07 Imp Reload	0 0 ort Files Archive F	 ile
Al2O3 in 1mM KCl, pH 11.23 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 8.14 Sort Files By: © Date/Time © Sample Id © Batch	Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Delete Selected Files	14:39:24 14:21:38 13:50:07 Imp Reload Archive S	0 0 ort Files Archive F Gelected F	ile:

Figure 9. The File, Database screen

### **III.2 Operating on Stored Data**

Stored data files can be operated upon in a number of ways. To demonstrate this we will use the demonstration data files provided with the software. These files are stored in a **Folder** called Demo. Click on **File** and then on **Database**. In the **Folder** section of the **Database** screen, (figure 9) click on Demo. Note that the **Folder** icon for the Demo **Folder** changes from a closed to an open **Folder**. Note also that the Files associated with the Folder Demo are now displayed in the lower portion of the screen (figure 10).

Current Folder: Demo				
🗁 Demo				
🛅 Folder 1				
🛅 ZR2				
Files in Domo: 19, Files Soloots	ad- 1			
Sample Id:	Date:	Time:	Batch:	
Phthalocyanine Blue Dye #36	May 25, 1994	22:05:59	0	
Phthalocyanine Blue Dve #18	May 25, 1994	20:21:54	0	
Phthalocyanine Blue Dye #12	May 25, 1994	19:16:04	0	
993 um Latev s/n 1168 rene	a May 10, 1994	11:32:14	0	
		44 04 00	Ω	
.993 um Latex, s/n 1168, repe	a May 10, 1994	11:31:28	U	
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe	a May 10, 1994 a May 10, 1994	11:31:28 11:30:32	0	
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe	ea May 10, 1994 ea May 10, 1994 ea May 10, 1994	11:31:28 11:30:32 11:28:54	0	•
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe	ea May 10, 1994 ea May 10, 1994 ea May 10, 1994	11:31:28 11:30:32 11:28:54	0	•
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe Sort Files By:	a May 10, 1994 a May 10, 1994 a May 10, 1994 Dpen File	11:31:28 11:30:32 11:28:54	0 0 ort Files	•
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe Sort Files By: © Date/Time	a May 10, 1994 a May 10, 1994 a May 10, 1994 Den File	11:31:28 11:30:32 11:28:54	0 0 ort Files	
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe	a May 10, 1994 a May 10, 1994 a May 10, 1994 Den File Print Selected Files	11:31:28 11:30:32 11:28:54 Imp Reload	0 0 ort Files Archive Fi	.▼ le
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe	a May 10, 1994 a May 10, 1994 a May 10, 1994 Depen File Print Selected Files	11:31:28 11:30:32 11:28:54 Imp Reload	0 0 ort Files Archive Fi	ile ile
.993 um Latex, s/n 1168, repe .993 um Latex, s/n 1168, repe	a May 10, 1994 a May 10, 1994 a May 10, 1994 Delete Selected Files	11:31:28 11:30:32 11:28:54 Imp Reload	0 0 ort Files Archive Fi Selected F	ile

Figure 10: Files in the Demo Folder

A file can be opened by first selecting it (by clicking on it) and then clicking the **Open File** button. A **File** can be deleted by selecting it and then clicking the **Delete File** button.

#### III.2.1 Two Variable Plots

The ZetaPlus software can be used to plot one variable against another. This is particularly useful when plotting zeta potential as a function of pH (the so called Iso Electric Plot). Click on Graphs and then on Two variable Plots (figure 11).



The software will display the two-variable plots screen (figure 12). In the lower portion of the screen you will see the files available. Select all the  $Al_2O_3$  files (click on the first, hold down the shift key, scroll down the screen and then click on the last). Click **OK**.

Valiable Graphs - Select Files				
Select the files to graph.				
Current Folder: Domo				
Files in Demo: 18, Files Selected: 9				
L	_			
Sample Id:	Date:	Time:	Batch:	_
Sample Id: Al2O3 in 1mM KCl, pH 5.7	Date: Apr 25, 1994	Time: 13:31:34	Batch: 0	
Sample Id: Al2O3 in 1mM KCl, pH 5.7 Al2O3 in 1mM KCl, pH 8.14	Date: Apr 25, 1994 Apr 25, 1994	Time: 13:31:34 13:50:07	Batch: 0 0	
Sample Id: Al2O3 in 1mM KCl, pH 5.7 Al2O3 in 1mM KCl, pH 8.14 Al2O3 in 1mM KCl, pH 9.4	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994	Time: 13:31:34 13:50:07 14:21:38	Batch: 0 0 0	
Sample Id: Al2O3 in 1mM KCl, pH 5.7 Al2O3 in 1mM KCl, pH 8.14 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 10.25	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994	Time: 13:31:34 13:50:07 14:21:38 14:39:24	Batch: 0 0 0 0	
Sample Id: Al2O3 in 1mM KCl, pH 5.7 Al2O3 in 1mM KCl, pH 8.14 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 11.23	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994	Time: 13:31:34 13:50:07 14:21:38 14:39:24 15:05:00	Batch: 0 0 0 0	•
Sample Id: Al2O3 in 1mM KCl, pH 5.7 Al2O3 in 1mM KCl, pH 8.14 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 11.23 Tri-Modal, Mixed IDC Mobility	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 May 6, 1994	Time: 13:31:34 13:50:07 14:21:38 14:39:24 15:05:00 21:37:56	Batch: 0 0 0 0 0 0	
Sample Id: Al2O3 in 1mM KCl, pH 5.7 Al2O3 in 1mM KCl, pH 8.14 Al2O3 in 1mM KCl, pH 9.4 Al2O3 in 1mM KCl, pH 10.25 Al2O3 in 1mM KCl, pH 11.23 Tri-Modal, Mixed IDC Mobility .993 um Latex, s/n 1168, initi	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 May 6, 1994 May 10, 1994	Time: 13:31:34 13:50:07 14:21:38 14:39:24 15:05:00 21:37:56 11:24:38	Batch: 0 0 0 0 0 0 0	•
Sample Id: AI203 in 1mM KCI, pH 5.7 AI203 in 1mM KCI, pH 8.14 AI203 in 1mM KCI, pH 9.4 AI203 in 1mM KCI, pH 10.25 AI203 in 1mM KCI, pH 11.23 Tri-Modal, Mixed IDC Mobility .993 um Latex, s/n 1168, initi	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 May 6, 1994 May 10, 1994	Time: 13:31:34 13:50:07 14:21:38 14:39:24 15:05:00 21:37:56 11:24:38	Batch: 0 0 0 0 0 0	•
Sample Id: AI203 in 1mM KCI, pH 5.7 AI203 in 1mM KCI, pH 8.14 AI203 in 1mM KCI, pH 9.4 AI203 in 1mM KCI, pH 10.25 AI203 in 1mM KCI, pH 11.23 Tri-Modal, Mixed IDC Mobility .993 um Latex, s/n 1168, initi Sort Files By: © Date/Time	Date: Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 Apr 25, 1994 May 6, 1994 May 10, 1994	Time: 13:31:34 13:50:07 14:21:38 14:39:24 15:05:00 21:37:56 11:24:38	Batch: 0 0 0 0 0 0	•

Figure 12: Selecting files for the two-variable plot.

Figure 13 show the two variable plot that results. Note that you may to select variables independently for either the X or the Y axis. By moving the cursor to the point where the Zeta Potential is zero one can locate the so called iso electric point (IEP) for  $Al_2O_3$  (in this case at pH=8.28 as seen in figure 13). The table above the graph can be used to read the values for the individual samples. Change the variables and observe how they plot versus each other.

Two V	ariabl	e Graphs											×
San	nple ld	1			I	Date	Time	рH		Ze	ta Pote	ential (	mV)
AI20	03 in 1	mM KCl, p	H 3.05		Apr	22, 1994	20:36:42	3.05			35	.67	<b></b>
AI20	03 in 1	mM KCI, p	H 3.73		Apr 3	22, 1994	20:13:39	3.73			33	.59	
AI20	03 in 1	mM KCI, p	H 4.6		Apr 3	22, 1994	20:01:10	4.60			34	.05	
AI20	03 in 1	mM KCI, p	H 5.7		Apr 3	25, 1994	13:31:34	5.70			35	.72	
AI20	03 in 1	mM KCI, p	H 6.3		Apr 2	22, 1994	19:55:43	6.30			33	.82	
AIZO	J3 IN 1	тм ксі, р	H 8.14		Apr .	25, 1994	13:50:07	 8.14			3.	42	<u> </u>
Zeta Potential (mV)	40 20 - -20 - -40 - 0		1 2		4	5	6 7	 9	10		т 12	13	1
× Y	( Axis Axis	pH Zeta Po	tential	<ul> <li></li> <li></li> </ul>	8.28 -0.12	mV					<u>L</u> eft Copy T Print	o Clip	<u>R</u> ight board Exit



# III.2.2 Comparing Results

Results from various samples may be compared with each other in one of two ways.

# III.2.2.1 SPC Charts

**SPC** (Statistical Process Control) charts are useful tools for comparing measurements with each other as well as with upper and lower control numbers (decided arbitrarily). Click on **Graphs** and then on **Build SPC Chart**. Select the files that you wish to mark for SPC (as in the two variable plot case described above – except that this time choose the group of 993um latex samples). Figure 14 shows the resulting SPC chart. With the upper and lower control limits (UCL and LCL) set as shown in figure 14, it is immediately apparent that the third sample is out of range and should, perhaps, be investigated more closely (or dropped altogether).



Figure 14: An SPC chart example.

# III.2.2.2 Comparing Data Graphically

The ZetaPlus software also allows you to compare results vis-à-vis the complete distribution of zeta potentials (or mobility). Click on **Graphs** and then on **Compare Measurements**. As in the case of the **SPC** chart, you will need to select files that you wish to compare. At this point, scroll down (in the files section of the screen) and mark five of the 0.993  $\mu$ m latex files for comparison. Click **OK**. Figure 14 shows the resultant screen. Note that the drop box on the bottom right hand side of the screen selects the variable to plot. The default variable (as shown in figure 14) is zeta potential. You may change this to Mobility, Frequency Shift or Frequency. A cursor is available to move along the presently selected curve (the X and Y values of the graphs for any given cursor position are displayed on the bottom of the screen). You may change the presently selected curve by clicking on **the Next Measurement** button. If a measurement is made up of more than one **Run** then you may change the **Run** currently displayed by changing the number in the **Run** Box.



Figure 15 : Comparing graphs from data in different files.

### **III.3 Summary**

Thus far we have learnt how the ZetaPlus software may be used to measure sample Conductance, pH and zeta potential. We have also examined as to how the software save results and how these results can be recalled and operated upon in a number of ways (SPC, Comparison, Two variable Plots etc.). A few additional details are provided in the appendices. Please read Chapter IV on Theory for details on how the instrument works and Chapter V for tips on sample preparation.

# **IV THEORY**

#### IV.1 How the ZetaPlus works

Particles dispersed in a liquid often have a charge on the surface. If we apply an electric field in the liquid then these charged particles will move towards either the positive or the negative pole of the applied field. The direction they select is a clear indication of the sign of the charge they carry. The velocity with which they translate is proportional to the magnitude of the charge. Thus we need to measure both the direction and the velocity of the particles under the influence of a known electric field and then calculate mobility and zeta potential from this information.

The ZetaPlus system has a laser beam which passes through the sample in a cell which carries two electrodes to provide the electric field. The light which is scattered by the particles is Doppler shifted because the scattering particles are moving in the electric field



Figure 16: Overview of the ZetaPlus Instrument

The frequency of light scattered into the detector is Doppler shifted by an amount proportional to the velocity of the particles. Unfortunately practical frequency shifts are of the order of a 100 Hz. Keeping in mind that the frequency of the laser is of the order of  $10^{14}$  Hz – a change of  $10^2$  in  $10^{14}$  is the proverbial drop in the ocean and quite impossible to detect. To overcome this we make use of the principle of optical heterodyning (figure 17). A portion of the beam is split off (the reference beam or the local oscillator) and then re-combined with the scattered beam after it is modulated at 250 Hz. What this means that in the absence of an electric field, a power spectrum of the signal from the detector would have a sharp peak at 250 Hz. When an electric field is applied, any resultant Doppler shift would occur from this frequency – now of course to is easy to detect a shift of 100 Hz from 250 Hz. Also this automatically allows for detection of sign. The opto-electronics is arranged such that if the resultant shift is less than 250 Hz, the sign of zeta potential is negative and visa versa.



Figure 17: Heterodyne optics used for zeta potential measurement.

# **IV.2 Colloid Fundamentals**

A brief, simplified description of the solid-liquid interface follows. The reader should not assume this description is complete. On the contrary, these few pages constitute nothing more than a sketchy outline, just enough to understand what is being measured and a glimpse at its significance. For a deeper understanding, please read one or more of the references listed.

Almost all solids acquire a surface charge when placed in polar liquids. This is the rule, not the exception. The charge can arise in many different ways. Among the more common are:

- Ionization of surface groups such as carboxyl and amino groups.
- Adsorption of ions such as surfactants, multivalent ions, and polyelectrolytes.
- Unequal dissolution of the ions comprising the surface molecules such as metal oxides and silver halides.

Each of these categories is rich with examples of how the surface charge arises and changes with solution conditions such as:

- pH
- Ionic Strength
- Addition of adsorbed ions
- Addition of surface active agents (ionic or nonionic)
- Addition of reagents that chemically bond to the surface
- Order of addition of various species.

The surface charge, more specifically the surface charge density, plays an active role in colloidal stability. A simple definition of a colloid is: a particle or molecule with at least one dimension less than, approximately, 1  $\mu$  and all dimensions greater than, approximately, 1 nm. Examples include most polymers, latexes, carbon blacks, liposomes, many pigments, some ceramics, clays, etc., etc. The list is too long to enumerate. An enormous number of commercial preparations fall into the category of colloidal dispersions.

The surface area per gram of material for colloidal-sized particles is orders of magnitude larger than it is for particles larger than, approximately, 10  $\mu$ . Therefore, surface effects, which are normally negligible, become dominant in the description of colloidal behavior. It is the surface charge density, for example, which is responsible for the repulsive force between charged, colloidal particles.

Colloidal dispersions are inherently unstable. On a macroscopic basis, it is predicted, from the second law of thermodynamics, that small particles will coalesce into big ones to reduce the surface area. On a microscopic basis, attractive forces are <u>always</u> present pulling the particles together. The attractive forces are present even for completely nonpolar particles. Such forces have their origin in the momentary, induced dipole effects that arise when nonpolar particles approach each other at random due to diffusion. These forces, variously called London, Van der Waals, or dispersion forces, are also responsible for the liquefaction of the noble gases such as Helium, Neon, and Argon.

The dispersion forces are often just as large as any permanent dipole forces of attraction. This may seem unusual until you look at some typical cases as enumerated in most physical chemistry textbooks. Another surprise, for the novice, is the long range over which these forces are important. For simple molecules, the dispersion forces, indeed, all the attractive forces vary as  $r^7$  where r is the intermolecular distance. The attractive part of the potential energy varies as  $r^6$  but for colloidal particles this simple description is insufficient. For colloidal particles the attractive force is the sum of the individual molecular forces, summed over all pairs. The final result depends on shape, but the important point is this: the potential energy of attraction varies between D<sup>-1</sup> and D<sup>-2</sup>, depending on shape, particle size dimensions, and distance of approach, where D is the shortest distance between particles. Thus, colloidal particles attract each other over much longer ranges than individual molecules, and this will lead to aggregation unless a repulsive force is present.

What then, is responsible for colloid stability? In general, there are two answers: electrostatic and steric repulsion. For suspensions in water and other highly polar liquids electrostatic repulsion is the more common. The name "electrostatic" is misleading in the sense that the particles, solvent molecules, and ions are always in motion. It is used, however, because much of the theory is based on relatively simple electrostatic equations; and because it is assumed that the time averaged results can be calculated from an electrostatic theory. The final result is known as the DLVO theory after the proposers--Derjaguin, Landau (Russia) and Vervey, Overbeek (The Netherlands). Its success over the last 50 years is testimony to the reasonable character of the assumptions underlying the theory. Though few practical applications have been fully interpreted with the DLVO theory, it is the best foundation currently available for describing colloid stability, dispersion, and aggregation processes.

#### **IV.3 Electrophoresis**

Due to the existence of surface charge, particles will move when placed in an electric field, **E**. This phenomenon is called electrophoresis. Microelectrophoresis is the common name given to the motion of charged colloidal particles in a liquid. Specifically, the particles move with an average drift velocity, **V**<sub>S</sub> toward the electrode of opposite charge. At low field strengths the drift velocity is proportional to the electric field, and the proportionality is expressed as

 $V_s = \mu_e E$ , where  $\mu_e$  is defined as the electrophoretic mobility.

There are three other related electrokinetic phenomena: electroosmosis, streaming potential, and sedimentation potential. Each have their own specific applications.

For colloidal dispersions the most useful technique is electrophoresis. Due to the cell design in the ZetaPlus, only electrophoresis is important in what follows. This is a distinct advantage over other instruments where, in addition to the electrophoretic effect, the electropsmotic effect must be taken into account; otherwise, calculated electrophoretic velocities are in considerable error.

The electric field is commonly given in units of volts/cm (V/cm), and it's value ranges from near 0 to a few tens of V/cm. The electrophoretic velocities that develop are in the range of 0 to a few hundred microns/second ( $\mu$ /s). Mobilities are in the range of 0 to ±10 Mobility Units.

Mobility units are commonly given in  $(\mu/s)/(V/cm)$  or  $\mu s^{-1}V^{-1}cm$ . This mixture of length units--microns and centimeters--is awkward by SI standards, yet it results in convenient dimensions for mobilities between 0 and ±10. Conversions to cgs and mks units are simple:

1 Mobility Unit ( $\mu_e$ ) = 1 $\mu s^{-1} V^{-1} cm = 10^{-4} cm s^{-1} V^{-1} cm$	(cgs)
1 Mobility Unit (μ <sub>e</sub> ) = 10 <sup>-8</sup> ms <sup>-1</sup> V <sup>-1</sup> m	(mks)

The mks units are the preferred SI units. Nevertheless, the common practice of using mobility units will be followed throughout the rest of this manual as, indeed, this practice is followed in much, but not all, of the literature on this subject.

[Note: The greek letter  $\mu$ , pronounced mu, is sometimes used to designate both the electrophoretic mobility and a unit of length, namely, micron (10<sup>-6</sup> meters). In this manual the subscript e is used to designate the electrophoretic mobility,  $\mu_e$ . In the scientific literature it is not always done this way. In addition, it is difficult to put subscripts on the computer monitor and printouts. This manual is consistent with but other works are not and the reader should be careful.]

A positive mobility of a particle means it's surface is positively charged; a negative mobility means the surface is negatively charged. Most surfaces are negatively charged under normal solution conditions, though by changing the solution conditions, a positive charge may result. The sign of the mobility, therefore, is a very important quantity. If a particle with a negative surface charge is mixed with a particle with a positive surface

charge, the result is an unstable dispersion that will aggregate. (The later statement needs modification if long-chain polymers are also attached to the surface. These long chains provide steric repulsion, the name given to entropic and osmotic effects that would drive the particles apart. In what follows, it will be assumed that only simple electrostatic repulsion is significant.)

When the mobility is zero, the velocity is zero, and it implies that electrostatic repulsion is small. Under this circumstance particles will aggregate, because, again, the attractive forces are always present.

# IV.4 The Double Layer

In the early simple theories of the charged solid-liquid interface, it was assumed that a layer of counter ions--ions oppositely charged to those on the surface--lined up to surround the surface. These counter ions were held rigidly in place by the electrostatic forces and moved with the particle. This model gave rise to the name electrical double layer. Figure 18 shows a simple picture of this for a flat surface.



Figure 18. Rigid and Diffuse models of a simple Double Layer

The name has been used ever since although it was recognized that such a simple model could not suffice to describe all the known phenomena. For example, although the counter ions must be attracted to the surface more strongly than the co-ions--ions of the same charge as those on the surface--both the counter and co-ions in the bulk of the solution are continually jostled by the thermally driven, random motions of the solvent molecules. This picture leads to the model of the diffuse electrical double layer. The concentration of counter ions is higher near the surface, and it decreases steadily to the concentration in the bulk liquid. Likewise, the co-ions are depleted near the surface, and their concentration increase until it reaches the level in the bulk liquid. Figure 19 shows a simple picture of this for a flat surface.



Figure 19. Relative concentrations of co- and counter-ions near a surface

Under a variety of simplifying, yet reasonable assumptions (see the references), this model leads to the following equation for the electrostatic potential y as a function of distance x from the particle surface:

$$y = y_0 e^{-\kappa x}$$

where  $y_0$  is the potential at the surface and  $\kappa$  is a parameter that measures the decay of the potential with distance.

Although this equation is based on a much too simplistic model--many more sophisticated models are discussed in the book by Hunter – it does embody several aspects of the diffuse electrical double layer theory that are important even in the more advanced theories. First, like y, the zeta potential (discussed below) decreases in an exponential fashion. Second, the parameter  $\kappa^{-1}$ , called the double layer thickness, plays an important role in determining the distance from the particle surface over which various electrical potentials are significant.

The double layer thickness is a function of the temperature, the dielectric constant of the liquid, and the ionic strength due to free ions (typically, added salt like KCI) in the bulk of the liquid. The double layer thickness is defined mathematically in Appendix I, and values are calculated under a variety of conditions. In Appendix II, the ionic strength is defined mathematically, and formulas are given for various types of electrolytes.

For 1:1 electrolytes such as KCI, it is useful to remember that the double layer thickness is approximately 100 nm at  $10^{-5}$  Molar, 10 nm at  $10^{-3}$  Molar, and 1 nm at  $10^{-1}$  Molar. Thus, at low concentrations  $\kappa^{-1}$  is large, and the repulsive forces are long range. At high concentrations,  $\kappa^{-1}$  is small, and repulsive forces are short range. You can coagulate an electrostatically stabilized colloid by adding enough salt.

The double layer thickness also plays a crucial role in more advanced theories where the calculation of the zeta potential depends on the value of the dimensionless product  $\kappa a$ , where "a" is the radius of the particle. This is discussed further in the section on zeta potential.

# **IV.5 Electrokinetic Unit**

Experimentally it is the velocity of the charged particle that is measured. The mobility is calculated from the measured velocity. Theoretically it is the zeta ( $\zeta$ ) potential that is important in determining the magnitude of the electrostatic repulsive force. Unfortunately, there is no independent method for determining  $\zeta$  potential; in microelectrophoresis it is always calculated from the mobility. In addition, there are no primary standards available for determining the accuracy of a  $\zeta$  potential calculated from a measured mobility. These two facts have serious consequences for the science of colloids, yet it does not hinder the usefulness of such measurements for many, many practical purposes associated with the determination of stability.

The  $\zeta$  potential is the electrostatic potential at the surface of shear. It is not the potential at the surface of the particle. The surface of shear extends out from the particle surface. This surface separates the electrokinetic unit from the bulk of the solution. It is the kinetic unit that moves. The kinetic unit consists of the particle, ions adsorbed onto the surface, counter ions contained within the surface of shear, plus solvent molecules strongly attached to the surface ions and counter ions in the double layer. In addition, if long-chain surfactants or polyelectrolytes are attached to the surface, then they, and any solvent molecules strongly associated with them, also constitute part of the electrokinetic unit. It is this kinetic unit that moves as a single entity through the surrounding liquid.

Figure 20 shows <u>only</u> one of many possible pictures of a more complicated, flat surface without long-chain polymers. Notice the various mathematical planes that can be drawn to distinguish various layers of entities associated with the surface. The exact location of these various planes depends on the model chosen to describe the solid-liquid interface. And, of course, any model is only an approximation to reality there are no physical planes, only narrow regions over which something of interest changes.



Figure 20. Simple Double Layer model with some terms identified.

The various potentials associated with the model of the surface in Figure 20 are shown in figure 21.

There is a sharp increase in viscosity between the bulk liquid and the kinetic unit at the shear plane, also called the shear surface. And, in principle, the dry particle size is less than the size of the kinetic unit. In practice, however, the difference is usually smaller than the random error in the measurement of the size, except for the case of small particles with long-chain surfactants attached.

Figure 21. Potentials in the Double layer model

For example, the extent of the inner layers is determined by the sum of ionic radii and the diameter of any strongly attached solvent molecules. This sum varies from 0.1 to 0.2 nm up to 1 nm for highly charged surfaces with large counter ions attached. For dry particle sizes greater than 10 nm, the difference is usually less than the experimental error associated with the size measurement. Yet, it is the nature of the surface and the resultant inner layers that controls the stability of the colloid.

The size of the kinetic unit, also called the hydrodynamic size, is also the size that is measured in sedimentation and dynamic light scattering (DLS) measurements, such as the one provided as an option with the ZetaPlus. In DLS measurements the diffusion coefficient of the kinetic unit is measured from which a hydrodynamic diameter is calculated. The hydrodynamic diameter is another name for the diameter of the electrokinetic unit.

(In the case of small particles with long-chain polymers adsorbed onto the surface, the extent of the inner layer compared to the dry particle size may be significant. These are often called "Hairy" particles because the long-chain polymers, if they stick out into the inner layers, are thought to resemble hair.)

# Zeta Potential Calculation:

It is worthwhile repeating the fact that velocity is measured but mobility and the  $\zeta$  potential are calculated. The calculation of mobility is simple and straight forward. The calculation of the  $\zeta$  potential is not. Mobility is not a direct measure of repulsive force; the  $\zeta$  potential is. Otherwise, one could entirely ignore the  $\zeta$  potential in favor of  $\mu_e$  as a measure of repulsive force. It is possible to measure the same mobility for two different samples under two different sets of solution conditions. The mobilities are, in this case, the same; however, the  $\zeta$  potentials may be completely different. If you want to know about the repulsive forces, then, in principle, you need to calculate the  $\zeta$  potential.

The relationship between  $\zeta$  potential and mobility depends on the theoretical model chosen. There is no standard substance with a certified zeta potential. Nor is there any known method of calculating the  $\zeta$  potential independent of a mobility measurement when using the electrophoretic technique. Therefore, one is forced to rely on model calculations.

There are two classic models that result in two classic limits: the Smoluchowski and the Hückel equations. They each apply in opposite limits. These limits have a common root: the magnitude of the dimensionless product  $\kappa a$ , where a is the radius of the kinetic unit. Most undergraduate physical chemistry textbooks develop the Hückel theory of ionic activities and their role in thermodynamic calculations. Simple ions are very small: as a result,  $\kappa a <<1$ .

For example, most simple ions have radii less than a nanometer. Since  $\kappa$  is less than 0.1nm<sup>-1</sup> at 10<sup>-3</sup> M KCI, it is fairly easy to satisfy the Hückel limit for ions. In this limit the relationship between mobility and zeta potential is:

Hückel Limit  $\mu_e = (2e\zeta)/(3\eta)$  for  $\kappa a \ll 1$ .

where  $\eta$  is the viscosity of the suspending liquid.

In the opposite limit,  $\kappa a$  is very large, and the limiting equation is:

Smoluchowski Limit  $\mu_e = e\zeta/\eta$  for  $\kappa a >>1$ .

For most colloidal particles of interest dispersed in water or highly polar liquids, it is nearly impossible to satisfy the Hückel limit; and, yet, it is not easy to completely satisfy the Smoluchowski limit either. For example, most colloids range in size from 100 to 1,000 nm. In  $10^{-3}$  M KCl,  $\kappa$ a will vary from 10 to 100.

In general, mobility is related to the  $\zeta$  potential by the following equation:

where,  $f(\kappa a, \zeta)$  is a model-dependent function. In the simplest model, that of Henry, for 1:1 electrolytes,

$$f(\kappa a, \zeta) = f(\kappa a) = 3/2 - 4.5/(\kappa a) + 37.5/(\kappa a)^2 - 330/(\kappa a)^3$$
  $\kappa a > 1.5$ 

In the limit of  $\kappa a \gg 1$ , this equation yields the Smoluchowski equation. For  $\kappa a \sim 1$ , Henry provided another equation, and, in the limit  $\kappa a \ll 1$ , this equation yields the Hückel expression. Henry's equations provided confirmation of the two limiting results as well as the first glimpse of the function  $f(\kappa a)$ . Henry's equations are strictly valid only for  $\zeta \ll 25.7$  millivolts. It is plotted as the dashed line in Figure IV-5 along with the more exact computer solutions for the function  $f(\kappa a, \zeta)$  with  $\zeta = 25.7, 51.4, 77.1$ , and 102.8 millivolts. These are numbered 1,2,3 and 4 in the figure. All these curves are for charged particles in 1:1 electrolytes such as KCI. These more exact results include the effects of relaxation and retardation. (For more details see the book by Hunter.)

Several interesting features can be deduced from these curves. First, large differences may occur between the true  $\zeta$  potential and that calculated using the Smoluchowski limit. Second, for  $\zeta$ =25.7 mV, the Henry approximation is quite adequate. Third, the curves decrease from the Smoluchowski limit for decreasing  $\kappa$ a, and they decrease more rapidly for larger  $\zeta$  potential.



FIGURE 22:  $f(\kappa a, \zeta)$  for  $\zeta = 25.7(1)$ , 51.4(2), 77.1(3), and 102.8(4) mV. Calculated for a 1:1 electrolyte at 25 °C. See Fig. 23 for reference.



FIGURE 23:  $f(\kappa a, \zeta)$  for  $\zeta = 51.4$  at 25 °C for various electrolytes. Ref: Wiersema, Loeb, and Overbeek, J. Colloid Interface Sci., <u>22</u>, 78, (1966).

Figure 23 is a plot of the function  $f(\kappa a, \zeta)$  when  $\zeta = 51.2$  millivolts for a variety of different types of electrolytes. The curves are labelled with the counter-ion valency given first. The higher the counter-ion valency, the greater the difference between the Smoluchowski limit and the more exact result.

Taken together, these results suggest the following: if at all possible, make measurements in 1:1 electrolytes at  $10^{-3}$  to  $10^{-2}$  M salt so that the difference between the Smoluchowski limit and the more exact results is smaller; and, if  $\zeta$ < 25.7 mV, the Henry equation provides a good, first-order estimate. For  $\kappa a > 100$ , Henry's equation even provides a good approximation when  $\zeta$ <51.4 mV.

#### IV.6 Smoluchowski Limit

As was mentioned above, for typical colloids and salt concentrations, it is much easier to arrange for  $\kappa a >1$  than it is to arrange for  $\kappa a <1$ . Therefore, the Smoluchowski limit is more appropriate for measurements on colloids than the Hückel limit. In addition, the Smoluchowski equation is much simpler to apply than any of the more exact results. For these reasons, the Smoluchowski equation is used, almost exclusively, to convert mobilities to zeta potential, except by specialist colloid chemists who are aware of the errors that may occur.

Matters are complicated for broad particle size distributions. What then is the correct particle radius to use? Ideally, one should measure the mobility and particle size for individual particles. This should be done for a large enough number of particles to get adequate statistics. Then, for each particle,  $\kappa a$  is calculated, followed by a calculation of the zeta potential for each particle.

At the present time no instrument, commercially available, is capable of doing this. Practically, one has three choices. (1), make  $\kappa a$  very large by, typically, making measurements at high salt concentrations (10<sup>-2</sup> M KCI) such that the Smoluchowski limit applies. (2), ignore the problem, in which case the Smoluchowski limit is applied anyway.(3) In the ZetaPlus, the default calculation employs the Smoluchowski limit. The user can choose the Henry equation (Hückel), provided an average particle radius is available. The default, average radius is 250 nm. A better result is obtained by measuring the size distribution. If you purchased the BI-MAS option for your ZetaPlus system measure the particle size and use one half of the Effective Diameter for the particle radius.

In the Smoluchowski limit, every mobility unit corresponds to 12.8 millivolts at 25 °C. This is a very useful number to remember. For example, Henry's equations are good approximations when the potential is less than 25.7 mV. This corresponds to 2 mobility units. As another example, consider the case of strong repulsion. This corresponds to a zeta potential of, very roughly, 50 or more millivolts. Using 12.8 mV/mobility unit, this equals, roughly, 4 mobility units.

Even though the default calculation is the Smoluchowski limit, it is worthwhile remembering that the actual zeta potential may differ. One can estimate how large the errors can be by using the curves in Figures 22 and 23. It can be shown that the errors can be as large as 20% using the Smoluchowski equation at  $\kappa a = 10$ , and these errors can be reduced to about 10% with the Henry equation. If you want to do even better, then consider the O'Brien & White solution described in Hunter's book. Warning: Unless you also know the particle size **and** have fixed the ionic strength using a 1:1 salt solution, it is not worth the effort, considering the difficulties involved.

# **V** Sample Preparation

# V.1 General Comments

For many methods of analysis and, in particular, particle sizing (PS) and zeta potential ( $\zeta$ ) measurements, the preparation of wet suspensions having a defined dispersion state - which does not essentially change even during measurement - is possibly the most important prerequisite. Frequently, it is very difficult to meet this demand in a simple way since complete knowledge of the physicochemical conditions of the dispersed system to be investigated is lacking. Nevertheless, there are some general recommendations and guidelines which, if followed, will result in suspensions having reproducible dispersion characteristics. Although a great deal of empirical experience is available unfortunately there are no real "text-books" of sample preparation. The closest is "Dispersions of Powders in Liquids" by G.D.Parfitt (Elsevier, 1969).

Materials for analysis are usually available in two forms:

- 1. As a concentrated suspension, typically 1vol% to 40vol%.
- 2. As a dry powder.

These two different conditions need to be addressed separately in order to prepare a sample for analysis by electrophoretic light scattering where the maximum particle concentration that can usually be tolerated is 0.01 vol%.

# V.2 Concentrated Suspension

This is the most straightforward situation; it is a matter of diluting the suspension. However, simply diluting into pure water is **never** appropriate. This is because, for the given system, a particular chemical equilibrium exists between the particle surface and the solution. For example, there will usually be an equilibrium amount of an adsorbed species (polyelectrolyte, surfactant etc.) on the particle surface. If the suspension is diluted with pure water such material will desorb from the particle surface to establish a new equilibrium: the more dilute, the more will come off. Since the  $\zeta$  potential (and, thus, stability) is directly affected by the solution conditions it follows that the  $\zeta$  potential of such a diluted suspension will not, and can not, be the same as that of the concentrate. Not appreciating this fact has led to the belief that measurements of  $\zeta$  potential in dilute solution can not provide relevant in formation about industrially important suspensions which are normally manufactured as concentrates. This is not so.

The correct way to dilute a concentrated suspension is to first centrifuge it to obtain a sample of the supernatant mother liquor. It is then a simple matter to resuspend a few drops of fresh concentrate in the mother liquor. In this way the chemical equilibrium is always maintained while reducing the particle number concentration to the appropriate level.

If measurements of  $\zeta$  potential are required as a function of some variable - say additive concentration, or pH - then, ideally, each adjustment should be made at the concentrate level followed by the dilution process as outlined above.

Sometimes the centrifugation/resuspension technique is not practicable; the amount of concentrate is too small to obtain sufficient "diluent"; the particles are too small or have too low a density to allow separation in a standard laboratory centrifuge. In such circumstances the most appropriate way to dilute the concentrate is to prepare a diluent having, as a minimum requirement, a pH and electrolyte concentration as close to that of the mother liquor as possible.

# V.3 Dry Powder

This is the more usual and more problematical case because, depending upon the material properties and conditions of preparation and storage of the material, three different particle species must always be expected. These are:

- 1. Crystals or primary single particles
- 2. Aggregates
- 3. Agglomerates (Aggregates of Aggregates)

The proportion of each species results from a variety of different binding mechanisms. The process of "dispersion" entails overcoming these different binding forces by use of **both** physicochemical and mechanical means.

The final dispersed state is influenced by three fundamental processes which take place:

- 1. Wetting of the solid surface
- 2. Dispersing of the particles
- 3. Stabilizing of the dispersed suspension

The physicochemical ways in which all three processes can be influenced are too numerous to cite here. They are covered in most textbooks of colloid and surface chemistry (see **Bibliography**). The following problems must, however, be addressed:

- 1. Selection of the suspension liquid.
- 2. Selection of the type and concentration of the dispersing aids (i.e. wetting agent, de-agglomerating agent and stabilizing agent).
- 3. Selection of the type and duration of the mechanical dispersing treatment.

Suspension Liquid For the vast majority of  $\zeta$  potential measurements water is the normal suspension liquid. It is sufficient here to point out that distilled water and deionized water are not the same. Certainly for Particle Size (PS) measurements water should be filtered, preferably through a 0.2um filter to remove dust, before use. Water must **never** be stored in soda glass containers. Storage in "plastic" containers is acceptable only after cleaning to remove plasticizers and organic processing aids used in the manufacture of the containers.

Natural materials (clays, minerals) as well as many synthetic materials (oxides) are invariably contaminated with organic and electrolytic debris. For critical work in colloid and surface chemistry the suspension liquid should first be "conditioned" by filtering the liquid through a packed bed of the dry powder material. The filtrate is then used to prepare any suspensions. This procedure is of less importance for water but is absolutely critical when using solvents particularly those of low permittivity/conductivity (such as dodecane,toluene).

# V.4 Dispersing Aids

In order to maintain the highest degree of dispersion a number of conditions are necessary.

**First**, the solid must be wetted by the liquid as spontaneously and completely as possible. This process is controlled by the contact angle, q, of the liquid at the material surface and the liquid-air interfacial tension, $g_{L/A}$ . Favorable wetting conditions are achieved when both q and  $g_{L/A}$  are as small as possible.

Materials which naturally have a high contact angle with water are termed "hydrophobic" (or water hating). Examples are some polymer surfaces such as PTFE (Teflon), paraffin wax and graphitic carbon (graphite).

Materials with a low contact angle are termed "hydrophilic" (or water loving). Examples are glass surfaces, metal hydroxides and proteins.

Hydrophilic surfaces can be made hydrophobic and vice-versa. A clean glass surface can be made hydrophobic by a coating of paraffin wax; the wax surface can be made hydrophilic by adsorbing a protein.

Surface-active materials (surfactants) have a strong affinity for interfaces because they contain both hydrophobic and hydrophilic regions. As such they are able to reduce  $g_{L/A}$ . Surfactants can be used as wetting agents. There are four basic types of surfactants (see "Colloidal Surfactants by K.Shinoda, Academic Press, 1969):

- 1. <u>Nonionic</u>: The hydrophilic part is polar but uncharged. Common examples are the polyethylene oxides.
- 2. <u>Anionic</u>: The hydrophilic part contains a negatively charged group. An example is linear alkylbenzene sulphonate (LAS).

- 3. <u>Cationic</u>: The charged group is positive. Examples are the quaternary ammonium compounds.
- 4. <u>Ampholytic</u>: The molecule contains groups which are positive and negative depending on solution conditions. An example is alkyl betaine.

**Second**, electrostatic forces of repulsion should be as high as possible. In a given system, the electrostatic energy of repulsion of particles is greatest if the interfacial potential and double layer thickness are large. The latter condition occurs at low ionic strength (low electrolyte concentration). The surface potential can be increased by using so-called potential determining ions. Example are H<sup>+</sup> for a quartz surface and Ag<sup>+</sup> for a silver iodide surface. To make use of this mechanism necessitates some prior knowledge of the surface chemistry of the material to be dispersed. A very useful parameter is the isoelectric point (i.e.p.) and this can be readily determined using  $\zeta$  potential measurements (see Section VIII).

Alternatively, a molecule containing a large polar (charged) head group can be adsorbed at the surface of the material. Such a molecule should **not** reduce the interfacial tension,  $g_{L/A}$ , i.e. it is not a surfactant. The family of ionic phosphates are very effective in aqueous suspensions. All these dispersing aids are ionic - they are electrolytes. Please note that acids and bases are also electrolytes. So, if too high a concentration is used then the double layer thickness will be decreased and this can promote aggregation (see Appendix I).  $\zeta$  potential measurements are, again, an ideal way to determine the optimum concentration for dispersion.

**Third**, the van der Waals energies of attraction between the particles should be kept as low as possible. The smaller the energy of attraction the more similar are the Hamaker constants for the particle and the liquid. This is a very complex matter and beyond the scope of this manual. Suffice to say that materials such as oxides, metals have very unfavorable Hamaker constants. Surfactants, polyelectrolytes and proteins all have Hamaker constants close to water. Thus, an adsorption layer can "mask" the Hamaker constant of the material surface.

A further effect of an adsorbed layer of macromolecules is the formation of a structuremechanical barrier (called a steric barrier) which can provide very long term stabilization even under extreme solution conditions. The best examples of polymeric stabilizers are the block and graft copolymers such as the Pluronics. The behavior of polymers is very concentration dependent. For normal sample preparation for  $\zeta$ potential measurements steric stabilization is unnecessary. For more detailed reading on this topic see "Polymeric Stabilization of Colloidal Dispersions" by D.H.Napper, Academic Press, 1983.

# V.5 Mechanical Dispersing Treatment

For maximum stability the total energy of interaction should have a high repulsion barrier. The combination of electrostatic and van der Waals attraction results in the total interaction,V<sub>max</sub>, between two suspended particles (the DLVO theory).

Even with a high energy barrier aggregation can reoccur because of the use of excess thermal or mechanical agitation during the dispersing process. An increase in thermal or mechanical energy increases the possibility of the collision of particles. The maximum collision energy attained using even an ultrasonic bath of low power (50W) is well in excess of a typical  $V_{max}$  of five to ten  $k_BT$ . High power sonicators are often over 400W and they also generate considerable heat - enough to boil water! All electrostatically stabilized systems have a critical coagulation temperature. In addition, nonionic surfactants have a "cloud point". This is the temperature at which the surfactant molecule becomes insoluble. Both these critical temperatures can be as low as 40 °C.

The rule is to use the absolute minimum amount of thermal/mechanical agitation. The choice of adequate dispersing aids will itself result in a reduced need to use agitation. Any agitation should be applied in short periodic bursts and not continuously. This latter situation results only in a steady state condition. For most materials the maximum total agitation time should need never exceed one minute. If it is taking longer then it is most likely that the wrong dispersing aids are being used. For maximum efficiency the one minute total time period should be broken into eight periods of fifteen seconds on and fifteen seconds off.

# V.6 Examples

Here are two typical preparations of suspensions that have been used as zeta potential reference colloids. Remember, there are no true standards.

### **Polymer Latex Microspheres**

Example A uniform sized polystyrene latex:

Supplier:	Interfacial Dynamics Corporation
	4814 NE 107th. Avenue, Suite B
	Portland, OR 97220 U.S.A.
	Tel:503-256-0076 Catalogue#: 10-38-30 Note: The cost is approximately \$90 for 15ml.

This latex is prepared surfactant-free. The microspheres, as supplied, are suspended only in distilled water. The suspension contains nominally 8% solids and the particle size is certified as 753nm (c.v.3%).

## The Suspension Fluid

The suspension fluid for zeta potential measurement is a one millimolar aqueous solution of potassium chloride. To prepare this simply dissolve 0.07456 gram of potassium chloride into one liter of distilled, or deionized, water.

[Note: 1mM KCl(aq) =  $10^{-3}$  mol dm<sup>-3</sup> = 0.07456 g KCl per liter of water.]

Dilute 0.25ml of the concentrated polymer latex suspension into one liter of the suspension fluid. This is the working solution.

The surface functional groups on the latex are sulphate and hydroxyl. The isoelectric point of the material is at a pH value <2. Under all normal conditions the zeta potential will be negative.

# A Metal Oxide Powder

Example: An alumina-coated titanium dioxide pigment

Supplier: E.I.Dupont de Nemours & Co. Customer Service Center Wilmington, DE 18989 U.S.A. Tel: 302-774-2102

Catalogue#: "Ti-Pure" R900, rutile titanium dioxide [Note: A sample as large as 25kg can usually be obtained free of charge.]

Prepare a suspension for zeta potential measurement as follows:

- 1. Weigh out one gram of the pigment.
- Add one or two drops of a 0.1% Triton X-100 solution just sufficient to thoroughly "wet" the powder to produce a slurry. Stir and mix well with a spatula. [Note: Triton X-100 is a nonionic surfactant manufactured by Rohm & Haas.]
- 3. Add 20mL of suspension fluid (see below).
- 4. Sonicate for one minute using a 50W probe (or equivalent bath) for one minute (see page 7-5).
- 5. Make up to one liter with suspension fluid, stirring continuously.
- 6. Age for 24 hours, if possible with continuous stirring or rolling.
- 7. Dilute 10mL of the above solution to 500mL with suspension fluid. This is the working solution.

# The Suspension Fluid

The surface functional group on the pigment is hydroxyl. The isoelectric point of this material is at a pH value of about 8.5. A suspension can be prepared having either a positive, or a negative, zeta potential.

1. For a positive zeta potential.

The suspension fluid is a one millimolar aqueous solution of potassium nitrate adjusted to pH4 using one to two mL of standard dilute (0.1M) nitric acid. To prepare, simply dissolve 0.1011 grams of potassium nitrate into one liter of distilled, or deionized water. Then, using a pH meter, or pH paper, to monitor the pH value adjust to pH4 with the nitric acid.

### 2. For a negative zeta potential

Use a suspension fluid of 0.05% w/v aqueous solution of sodium pyrophosphate.

# V.7 Preparation and Measurement of the BIC Reference Material ZR3

BI-ZR3 is a zeta potential reference material for use with Brookhaven's ZetaPlus and ZetaPALS instruments. The sample is a colloidal pigment, blue in color. Since there are no universally accepted zeta potential standards, only reference materials are available to check the proper operation of zeta potential instruments. The BI-ZR3 is such a material. Brookhaven has made measurements on this sample over a long period of time, under a strict set of sample preparation conditions. As long as the user prepares the sample as described below, and as long as the materials is not used beyond the expiration date printed on the bottle, the value of any single zeta potential measurement using any ZetaPlus or ZetaPALS will be within the range -49 mV to -57 mV; whereas, the average of many runs should be -53 +/- 4 mV.

BI-ZR3 comes in two forms: a concentrated aqueous suspension and a powder.

**7.1** Preparing a sample and making a measurement from the concentrate.

**A.** Use only **de-ionized water** to prepare 100 mL of a 10 mM KCl solution. Since the molecular weight of KCl is 74.6 g/mol, add 74.6 mg to 100 mL of de-ionized water. This is the stock solution. Then add 90 mL of de-ionized water to 10 mL of the stock solution, resulting in a final dilution to 1 mM KCl. **All measurements will be made with the 1 mM KCl.** 

[DO NOT USE TAP WATER. The residual ions in tap water vary greatly from placeto-place. Furthermore, the residual metal ions found in tap water specifically absorb on the surface of the pigment, dramatically changing the zeta potential. For example, using tap water in our laboratory to make up the 1 mM KCl, reduces the zeta potential by 50%.] **B**. Add 1 mL of the BI-ZR3 concentrate to 400 mL of the 1 mM KCI. This diluted BI-ZR3 is the sample to be used for all further steps in this procedure.

#### NOTE: Experienced ZetaPlus or ZetaPALS users may skip steps C,D,E, and F.

**C**. Soak the ZetaPlus or ZetaPALS electrodes for approximately 1 minute in a few millilitres of the diluted BI-ZR3.

**D**. Clean a cell for use in the ZetaPlus or ZetaPALS. Add Approximately 1.5 mL of the diluted BI-ZR3, and slowly insert the electrodes into the cell. Take care that the electrodes are completely immersed in the sample, that no bubbles are trapped between or on the electrodes, and that any excess sample is wiped from the outside of the cell walls.

**E**. Attach the electrodes to the cable inside the ZetaPlus or ZetaPALS, and insert the cell into the cell holder.

**F**. With the temperature set at 25° C, wait several minutes for thermal equilibrium.

**G.** Initiate a measurement with the ZetaPlus or ZetaPALS of the ZR3. The conductance should be 320  $\mu$ S (microsiemens) ± 10%, provided the electrodes are fully covered by the liquid in the cell. If it is not, something is either wrong with your instrument or the sample or your sample preparation. Check first for any entrapped air. Next, use the ZetaPlus or ZetaPALS to measure the conductance of the stock 10 mL KCI solution without particles. The reading should be roughly 3,000  $\mu$ S. Next measure the conductance of the 1 mM KCI solution without particles. The reading should be 320  $\mu$ S ± 10%.

**H**. Watch the reference frequency. It should settle down to 250 Hz, the peak shape being relatively sharp and clean, ignoring any noise below the 10% level. If, after several minutes, a sharp, clean peak is not centered at 250 Hz, replace the sample with a Static Scatterer that Brookhaven supplies at no charge. If the Static Scatterer shows a sharp, clean peak at 250 Hz, then the BI-ZR3 concentrate is no longer viable. Discard it, and prepare a fresh sample from the dry power as described below, or order a fresh sample from Brookhaven. If the Static Scatterer does not show a sharp, clean peak at 250 Hz, contact Brookhaven immediately for assistance.

I. Check the version number of your software. If the number is less than 3.22, set the CYCLES to 1 and the RUN number to 1. Make five single measurements, saving all of them. Make two more fresh samples, and repeat the measurements.

If you have Version 3.22 or higher, set the CYCLES to Off; set the RUN number to 1. When you initiate a measurement, five will automatically be made and averaged. All five runs will be saved, as well as each of the five. Make two more fresh samples, and repeat the measurements.

**J**. If your version number is less than 3.22, mark all 15 for use in the SPC table. If the average is  $-53 \pm 4$  mV, the results are acceptable. If you feel that any of the 15 individual runs are outliers, either high or low values, reject them. We reject values that are higher than the average plus three times the standard error, or lower than the average minus three times the standard error. Average the remaining runs using the SPC feature.

If you have Version 3.22 or higher, mark the three average runs for use in the SPC tables. If the average is  $-53 \pm 4$  mV, the results are acceptable. If you feel that any of the 15 individual runs are outliers, mark all 15 for use in the SPC table. Examine these for any outliers, either high or low values. We reject values that are higher than the average plus three times the standard error, or lower than the average minus three times the standard error. Average the remaining runs using the SPC feature.

**7.2** Preparing a sample from the dry powder.

**A**. To prepare a fresh sample of the concentrate, add 100 mg of the BI-ZR3 dry powder to 20 mL of 1 mM KCI. [See section I for preparation of 1 mM KCI.]

**B**. Continue with the measurement from section I.B.

NOTES: Besides the warning about using de-ionized water, the user should be aware of the following. According to classic theory, it is to be expected that the absolute value of the zeta potential will decrease with increasing amounts of three electrolyte ions. For example, we find for BI-ZR3 -58 mV using only de-ionized water, -56 mV in 0.5 mM KCl, and -52 mV in 2 mM KCl.

# Appendix 1: Bibliography

D.H. Everett, **Basic Principles of Colloid Science**, published by The Royal Society of Chemistry, 1988. This excellent, introductory, yet in-depth text can be purchased by writing to: The Royal Society of Chemistry, Distribution Centre, Blackhorse Road, Letchworth, Herts. SG6 1HN, United Kingdom.

P.C. Hiemenz, **Principles of Colloid and Surface Chemistry,** second edition, Marcel Dekker publisher, 1986. Attractive forces, double layer theory, and electrokinetic phenomena are discussed in Chapters 11, 12 and 13. Sample calculations are shown. If you can't get Everett's bo ok, get this one.

A. Kitahara and A. Watanabe, editors, <u>Electrical Phenomena at Interfaces</u>, **Fundamentals, Measurements and Applications,** Marcel Dekker publisher, 1984. Part III of this book is devoted entirely to applications including chapters on detergency, flotation, fibers, paper, electrocapillary emulsification, pigments and paints, cosmetics, antirusting, electrokinetic phenomena in biological systems, and reproduction in copying and electrophoretic display. This English language book grew out of a famous 1972 textbook published in Japanese: *Kaimen Denki Gensho-Riron, Sokatei, Oyo.* 

D.J. Shaw, <u>Electrophoresis</u>, Academic Press, 1969. Long out of print, if your local library has a copy, read the first 5 chapters, about 85 pages. These pages contain a concise review of double layer theory and how zeta potential is calculated from mobility. An excellent summary.

R.J. Hunter, **Zeta Potential in Colloid Science. Principles and Applications**, Academic Press, 1981. The bible for anyone seriously interested in zeta potential. Each chapter contains a wealth of references to the original research. Written at the graduate student and research level.

H.G. Barth editor, <u>Modern Methods of Particle Size Analysis</u>, Wiley-Interscience 1984. Chapter 3 is an introduction to particle sizing using dynamic light scattering techniques.

G. D Parfitt, **Dispersion of Powders in Liquids**, Elsevier 1969. For information on sample preparation.

K. Shinoda, <u>**Colloidal Surfactants**</u>, Academic Press 1969. On the use of surfactants as wetting agents.

D. H. Napper, **<u>Polymeric Stabilization of Colloidal Dispersions</u>, Academic Press 1983. For more information on sample preparation and colloid stability.** 

# Sample ID

**Sample ID** should be used as a label to clearly identify the sample being measured. This is the label under which it will be saved (and later identified for retrieval) in the built-in database by the ZetaPlus software, therefore the use of a meaningful **Sample ID** is strongly recommended. **Sample ID** can be up to 30 characters in length and can contain numbers, alphabets, special characters (like \$,#,@ etc.) and even blanks.

# **Operator ID**

**Operator ID** can be used as a means of identifying the person who conducted the measurement. **Operator ID** can be up to 30 characters in length and can contain numbers, alphabets, special characters (like \$,#,@ etc.) and even blanks.

# Notes

The **Notes** parameter should be used to store additional information either about the sample, or about the conditions a particular measurement was made. **Notes** can be up to 50 characters in length and can contain numbers, alphabets, special characters (like \$,#,@ etc.) and even blanks.

# Cycles

A **Cycle** is defined as the collection of data from the sample during the application of an electric field once in the positive and once in the negative direction, i.e. during one complete field reversal. **Cycles** must be an integer between 1 and 5.

# Runs

A **Run** is said to consist of the number of **Cycles**, i.e. a **Run** is merely the average of the number of **Cycles** selected by the user. **Runs** must be an integer between 1 and 10.

### **Batch Number**

**Batch Number** is a parameter that may be used to identify the batch from which a particular sample was elected. **Batch Number** must be an integer with a value less than 99999.

### рΗ

The **pH** of the sample can either be entered by the user or (if the built in **pH** meter is used) by the ZetaPlus software. This value of **pH** will be used to plot iso-electric graphs and other two parameter plots.

### Temperature

This parameter is used to set and control the sample **temperature** in the ZetaPlus. Temperature is a real number with acceptable values between 6.0 and 74.0 degrees Celsius.

#### Concentration

This is a parameter that may be used to remind the user of the concentration (in mg/ml) at which the sample being measured was prepared. **Concentration** may be entered as a real number less than 99999.99.

## Suspension

This parameter refers to the continuous phase of the sample. For example the BI-ZR3 is a colloidal **suspension** of blue particles in water. Therefore the **suspension** is aqueous. The software provides a list of commonly used suspensions that can be selected using the drop box menu. If your **suspension** is not listed you may enter it manually (make sure to then enter the corresponding values for viscosity and refractive index).

# **Particle Size**

The particle size of the sample may be entered here. This parameter is not presently used in any calculations. **Particle Size** is a real number.

# Viscosity

The **viscosity** of the liquid phase (in cP) of the sample can be entered here. If the **Suspension** is selected from the list box provided then the value for viscosity is calculated automatically (depending on the temperature requested). If a **suspension** not listed is used, then this parameter is made available for the user to enter manually.

# **Refractive Index**

Like the **Viscosity** parameter, if a preprogrammed **Suspension** is selected then this parameter is calculated automatically. If a **suspension** not listed is used, then this parameter is made available for the user to enter manually.

# User1 and User2

These parameters are meant to provide the user with the ability to create parameter names tailored to his/her specific needs.

# Auto Save Results

If **Auto Save Results** is checked then the results are saved automatically at the conclusion of a measurement.

# Appendix 3

# **Main Screen Action Buttons**

#### Start/Stop

Clicking on **Start** will commence a measurement. Once the **Start** button has been clicked (and a measurement started) the button is automatically re-labeled as the **Stop** button. Once the measurement has been successfully completed (or if the **Stop** button is clicked) the button is once again labeled **Start** signaling the instruments readiness to commence a fresh measurement.

#### Runs

The **Runs** button allows the user to change the number of **runs** for an ongoing measurement.

#### Hide Graph/Show Graph

This button can be used to either enable or disable the display of the results in a graphical format.

#### Clear

This button is meant to Clear all data from system memory. If the data has not been already saved then the software will offer the user another oppro

#### **Parameters**

Allows the user to enter and edit sample parameters (Sample ID, Notes, Temperature etc.).

### **Copy to Clip Board**

Copies the contents of the current screen to the windows clipboard. This feature is useful for exporting screens to other windows applications (e.g. Microsoft Word). This feature is available throughout all the screens of the software package.

#### Zoom

Allows the user to look at graphs in expanded screens.

#### **Drop Box for Results table**

Allows the user to change the variable being displayed in the results table. The user may select from zeta potential, mobility, frequency shift and frequency.

#### **Drop Box for Results Graph**

Allows the user to change the variable being displayed in the results graph. The user may select from zeta potential, mobility, frequency shift and frequency.

# Appendix 4

Menu option from the Main Menu Bar

File Menu



# <u>S</u>ave

Saves the data that is being presently operated upon using the Sample ID as the main identifier tag.

# Save <u>A</u>s

Allows the user to save the data under a different name.

Save As		×
Description:	Mixed Alumina	
Folder:	Sample Data	
	Save	
	Cancel	

#### Database

Opens the File Database Manager. From here the user can create/delete folders, delete/archive/load files etc.

tabase				
Current Folder: Sample Data				
Arch				
💼 Estee Lauder				
Folder 1				
🛅 McGill				
Defizer				
🦢 Sample Data				
Files in Sample Data: 22, Files	Selected: 1	Time	Datab:	
	Date.	15.20.40		
ZR 3 REF. INT MM KUI SOlutio	n May 12, 2000	10:38:49	1	1
Polisning Silica Slurry , 3900	Mar 10, 2000	11:01:50		
Mixed Alumina	Sep 29, 1999	08:16:39		
Mixed Alumina	Sep 29, 1999	08:00:29	1	
Phthalocyanine Blue Dye #36	May 25, 1994	22:05:59	0	
Phthalocyanine Blue Dye #18	May 25, 1994	20:21:54	0	
Phthalocyanine Blue Dye #12	May 25, 1994	19:16:04	0	-
- Sort Files Bu:	1			- 1
C Data (Time	Upen File	Imp	ort Files	
• Date/Time	Print Selected Folder	Reload	Archive Fil	e
C Sample Id -				
C Batch	Delete Selected Folder	Archive S	elected Fo	lder
	Create Folder		Exit	

# <u>Rebuild Database File Index</u>

Searches for all data files present and creates a new index file.

# Log File Settings

Allows selection of the parameters that will be reported in the log file.

Please select each data fi	eld to in	clude in	a Log File	entry.	
			_	-	
Sample Id					-
Date					
Time					
Batch					
Zeta Potential					
Mobility					
pH					
Conductance					
Concentration					
Temperature					
Suspension					-

# **Reset Log File**

This will terminate entries being made to the log file and commence entries into a new log file.

# **Report File Settings**

Allows a selection of the parameters to be presented in a text file report format.

Report File Settings		×
Please select each data field to	include in a Report F	ile entry.
Sample Id		🔺 🔺
Date		
l ime Datak		
Batch Start Time - First Measurement (	Start Time	
Zeta Potential		
Mobility		
pH		
Conductance		
Concentration		
Temperature		•
	OK	Cancel

### **Create Report File From Saved Measurements**

Allows the user to select a number of saved data files. Results from these files are then presented in the form of a text file report.

### **Print Report**

Will print a report of the currently selected measurements on the printer.

#### **Print Preview**

Allows the user to preview on the screen before actually printing a report.

# **Report Print Options**

Allows the user to select the parameters to be printed.

Print Options		×
Please indicate the items you wou in the printout.	uld like to include	
Results Summary		
Additional Graphs To Print		880 1939 -
🗖 Zeta Potential	Print Graphs	- 14
🗖 Mobility	Single Page	
Frequency Shift	C Full Page	
Frequency	2	
- 11 - 12 - 12 - 12 - 12 - 12 - 12 - 12		<u> </u>
OK	Cancel	

# **Print Setup**

Allows the user to select the printer, the orientation of the print job (portrait/landscape) and the size and source of the paper to be used for the printing.

Print Setup		×
Printer © Default printer (currently HP LaserJet IIF © Specific printer:	OK Cancel <u>O</u> ptions	
HP LaserJet IIP on \\N1	AS-SERVER\HPCUBE1 (LPT2:)	N <u>e</u> twork
Orientation	Paper	
A C Landscape	Size: Letter 8 1/2 x 11 in ▼ Source: Upper tray	

# **Exit Zeta Potential Application**

Allows the user to exit.

# <u>G</u>raphs Menu

<u>F</u> ile	<u>G</u> raphs	<u>р</u> Н	<u>C</u> onductance		de	<u>S</u> etup	<u>H</u> elp
75	Two	Varia					
<mark>е</mark> г Ме	<u>B</u> uild Com	i SPC pare l	Uhart Measurements		lof	ha	
1410	Data	a Disp	lay Format	- C	ICI	cu	

# Two variable Graphs

Allows the user to select a number of files, the results from which can be plotted by selecting the x-axis and y-axis variable independently.

Fwo Va	ariabl	e Grapi	ıs												×
Sarr	nple le	d			D	ate	Time	;		pН		Z	Zeta Pote	ential (	mV)
AI20	)3 in 1	mM KC	, pH 3.05		Apr 2	2, 1994	20:36:	42		3.05			35	.67	
AI20	)3 in 1	mM KC	l, pH 3.73		Apr 2	2, 1994	20:13:	39		3.73			33	.59	
AI20	)3 in 1	mM KC	l, pH 4.6		Арг 2	2, 1994	20:01:	10		4.60			34	.05	
AI20	)3 in 1	mM KC	l, pH 5.7		Apr 2	5, 1994	13:31:	34		5.70			35	.72	
AI20	)3 in 1	mM KC	l, pH 6.3		Apr 2	2, 1994	19:55:	43		6.30			33	.82	
AI20	)3 in 1	mM KC	l, pH 8.14		Apr 2	5, 1994	13:50:	07		8.14			3	.42	<b>-</b>
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Y .	Axis	Zeta	Potential	-	35.67	mV						-	Drint	1	Enit
L													Fint		Exit

# **Build SPC Chart**

Allows the user to select a number of files the results from which are then tabulated in the form of a Statistical Process Control (SPC) table along with upper and lower controls.

SPC Graph					×
Sample ID	Date	Time	Batch	Zeta Potential (mV	)
ZR2	Jul 16, 1997	12:02:05	1	-41.63	
ZR2	Jul 16, 1997	12:29:42	1	-39.59	
ZR2	Jul 16, 1997	12:37:56	1	-42.74	
ZR2	Jul 16, 1997	12:41:43	1	-41.99	
Mean (4 Measurements) Std. Error				-41.49 0.68	
-37.44 Lu -45.54 -45.54					
Results:Total Measurements:4Measurements above UCL:0Measurements within limits:4Measurements below LCL:0	= 0.00% = 100.00% = 0.00%	hart Scale Fixed Automatic	UCL Ctrl LCL	-39.46 Zeta -41.49 Copy -43.51 Prir	Potential 💌 To Clipboard It Exit

#### **Compare Measurements**

Allows the user to select up to 5 files, the results from which can then be overlayed in graphical form for comparison purposes.



### **Data Display Format**

This allows the user to select the format of the displayed graphical data. The user can select between displaying a graph of the raw data or displaying data as a Lorentzian curve.



# <u>p</u>H Menu

Allows the user to measure and/or calibrate the pH probe using the pH meter built into the ZetaPlus.

<u>F</u> ile	<u>G</u> raphs	<u>р</u> Н	<u>C</u> onductance	M	ode	<u>S</u> etup	<u>H</u> elp
		Me	asure pH				
		Ca	librate pH Prob	e			

### **Conductance**

Allows the user to measure the conductance of the sample.

 File
 Graphs
 pH
 Conductance
 Mode
 Setup
 Help

 Measure
 Sample
 Conductance
 Mode
 Setup
 Help

# <u>M</u>ode

Allows the user to select the mode of the measurement in terms of the number of **Cycles** per run to be used. If **Single Cycle** is selected then (regardless of how many **Cycles** were selected in the **Parameters** page) each **Run** will comprise a single **Cycle** only. If **Multiple Cycles** are selected then each **Run** will comprise of the number of **Cycles** specified in the **Parameters** page.



# <u>S</u>etup

The Setup Menu allows the user to control and test a range of Instrument Parameters.



**Instrument Parameters** 

**Set Parameters** 

#### Wavelength

This is the wavelength of the laser and cannot be changed in this menu. If necessary (only in the case of a laser being replaced with one that operates at a different wavelength) it may be changed in the zetapw.ini file.

Instrument Parameters	×
Set Parameters	Measured Parematers
Wavelength 670.0 nm	[] [
Sample Time (microseconds)	Conductance Unknown µS
C Auto Unknown	Electric Field Unknown V/cm
C User 1024	
Current (mA)	Signal Strength
Auto Unknown	Sample Count Rate Unknown
O User 0.15	Ref. Count Rate Unknown
☑ Show status on Main Screen	OK Cancel

# Sample Time

Possible values for sample time are 1024, 512, 256 and 128 micro seconds. When left in the AUTO mode the instrument will select the sample time automatically, depending on the conductance of the sample. A higher sample time implies better resolution in the power spectrum but also means that the sample will be subjected to a larger current for a longer period of time. Sample Time should not be confused with the measurement time, which is the sample time  $\times$  the number of measurement points (4096).

### Current

The current driven through the sample decides the electric field formed in the sample (and hence the electrophoretic velocity induced in the particles). In the AUTO mode a current corresponding to an electric field of about 15 V/cm is applied. If necessary a manual current may also be used.

#### **Measured Parameters**

#### Conductance

The conductance measured in the sample is reported here.

## **Electric Field**

The Electric Field applied in the sample is reported here.

## Signal Strength

The signal strength is the magnitude of scattered light seen by the detector (in counts per second). The Sample Count Rate is the signal scattered by the sample, while the Ref. Count Rate is the signal from the reference beam (local oscillator).

# Appendix 5: Double Layer Thickness

The double layer thickness is defined by the following equation

 $K^{-1} = \{(\epsilon k_B T)/(2e^2. \ 1000.I_c N_{avo})\}^{0.5}$ 

where

$$\begin{split} & \epsilon = \text{Permittivity of Liquid} \\ & k_B = \text{Boltzmann's Constant} = 1.3807 \text{ x } 10^{-23} \text{ JK}^{-1} \\ & T = \text{Temperature in Kelvin (K)} \\ & e = \text{Electronic Charge in Coulombs} = 1.6022 \text{ x } 10^{-19} \text{ C} \\ & I_c = \text{Ionic Strength in units of mol/dm}^3 \text{ (mol/L or M, molar)} \\ & N_{avo} = \text{Avogadro Constant} = 6.0221 \text{ x } 10^{23} \text{ mol}^{-1} \end{split}$$

The permittivity of the liquid is equal to where  $\varepsilon_r$ , the relative permittivity, also called the dielectric constant, is 78.54 for water at 298.15 K. The permittivity of vacuum,  $\varepsilon_0$ , is 8.8542 x 10<sup>-12</sup> F.m<sup>-1</sup> where 1 Farad= 1 C<sup>2</sup>J<sup>-1</sup>. The extra factor of 1000 in the denominator converts I<sub>c</sub> from mol/dm<sup>3</sup> to mol/m<sup>3</sup>. Substituting these values into the equation, one obtains:

 $K^{-1} = \{9.2591 \text{ x } 10^{-20}/I_c\}^{0.5}$  in meters, or  $K^{-1} = 0.3043/I_c^{0.5}$  in nanometers.

The double layer thickness decreases inversely as the square root of the ionic strength. The ionic strength depends on the concentration of free ions and also on their charge. See Appendix II. For simple salts, the double layer thickness in water at 25 °C as a function of concentration is given in the following table:

Double Layer Thickness in Nanometers

Conc.(M)	10 <sup>-7</sup>	10 <sup>-6</sup>	10 <sup>-5</sup>	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-1</sup>
1:1	962	304	96.2	30.4	9.62	3.04	0.962
1:2,2:1	555	176	55.5	17.6	5.55	1.76	0.555
2:2	481	152	48.1	15.2	4.81	1.52	0.481
1:3,3:1	393	124	39.3	12.4	3.93	1.24	0.393
3:3	321	101	32.1	10.1	3.21	1.01	0.321
2:3,3:2	248	78.5	24.8	7.85	2.48	0.785	0.248

#### Interpretation

Much can be learned from such a table. First, in deionized water, here The only free ions are H<sup>+</sup> and OH<sup>-</sup>, the concentration is  $10^{-7}$  M, and the double layer thickness is 962 nm, nearly 1µ. This is the distance over which the repulsive forces are significant. Second, add a little KCI, a 1:1 salt, and, at a concentration of 10 mM (millimolar,  $10^{-3}$  M) the double layer has decreased to 9.62 nm. Third, add too much salt, and the double layer is so small that attractive forces will, sooner or later, cause aggregation.

Fourth, much smaller concentrations of multivalent ions can cause aggregation. Therefore, if working in tap water, it is important to know what the concentrations of the various ions are.

Most measurements are made at or near room temperature, which, for convenience, we define as 25 °C. It is then fair to ask what the variation in the calculated double layer thickness will be with temperature. The following, simple equation may be used to calculate the dielectric constant of water from t = 10 to t = 60 °C to within 0.25% of the actual value is:

 $\epsilon_r = 78.54 \times 10^{-0.0022 \times (t-25)}$ .

As temperature increases the dielectric constant decreases. These two effects tend to offset each other in the calculation of  $\kappa^4$ . The slight decrease in density with increasing temperature causes a slight decrease in concentration and ionic strength, which further offsets the decrease in dielectric constant. Finally,  $\kappa^4$  varies as the square root of all these changes. Putting numbers in shows that  $\kappa^4$  varies by less than +1% from 10 to 40 °C, respectively. Therefore, the values calculated at 25 °C will be sufficient for most purposes regardless of the actual measurement temperature.

# Definition

The ionic strength, on a concentration basis, is defined as follows:

 $I_{c} = 1/2 \cdot c_{i} z_{i}^{2}$ 

where  $z_i$  is the charge number (typically, 1, 2, 3, or 4) on the ith ion and  $c_i$  is the concentration of the ith ion in solution.

[Note: This definition does not include the charged particles themselves. For suspensions, it is strictly true that the charged particle is not in solution; however, for charged polymers of colloidal size, such particles are in solution. Furthermore, whether in solution or not, all charged particles contribute to the overall conductivity. Typical measurements, however, are carried out at sufficiently high, added salt concentration  $(10^{-3} \text{ to } 10^{-2} \text{ Molar})$  so that ignoring any contribution of charged, colloidal-sized particles in the calculation of  $I_c$  does not effect significantly the final results, and the measured conductivity is determined, within experimental error, by the added salt concentration.]

The units of  $I_c$  are the units of  $c_i$ , mol/m<sup>3</sup> in the SI system of units and molar (mol/L or M) in the older chemical literature system of units. Since 1 L is now defined as exactly  $10^{-3}$  m<sup>3</sup> or 1 dm<sup>3</sup>, a 1 M salt solution is equal to  $10^3$  mol/m<sup>3</sup> or 1 mol/dm<sup>3</sup>

Typical added salts include NaCl (1:1),  $CaCl_2$  (2:1), and  $Al_2(SO4)_3$  (3:2). (In addition, samples prepared from so-called city water include smaller amounts of +2 and +3 ions such as Ba<sup>+2</sup> and Al<sup>+3</sup>) Electrolytes are classified according to the charge on the ions. For example, KCl is a 1:1 electrolyte,  $CuSO_4$  is a 2:2 electrolyte, and  $Na_2SO_4$  is a 1:2 electrolyte. When these salts are added in the concentration range of  $10^{-2}$  M or less, they completely dissociate into their separate ions.

The calculation of ionic strength then proceeds as follows:

1:1	l = 1/2[c1 <sup>2</sup> + c1 <sup>2</sup> ] = c
1:2 or 2:1	$I = 1/2[2c1^2 + c2^2] = 3c$
2:2	$I = 1/2[c2^2 + c2^2] = 4c$
1:3 or3:1	$I = 1/2[3c1^2 + c3^2] = 6c$
3:3	$I = 1/2[c3^2 + c3^2] = 9c$
2:3 or 3:2	$I = 1/2[3c2^2 + 2c3^2] = 15c$

Since the double layer thickness varies inversely as the square root of the ionic strength, even relatively small amounts of multivalent ions can decrease the thickness by factors of 2 and 3 fairly readily. This leads to a drastic decrease in the distance over which the electrostatic repulsive force is significant. And, as a result, increases the chance that the particles will aggregate.

# Appendix 7: The Smoluchowski Equation and The Debye - Hückel Approximation

## Smoluchowski Eqn.

In the Smoluchowski limit the electrophoretic mobility, µe is related to the zeta potential through th

where:  $\epsilon$  = Permittivity of Liquid  $\varsigma$  = Zeta Potential  $\eta$  = Viscosity of Liquid

In Appendix I it was stated that  $\epsilon$  for H<sub>2</sub>O at 25 °C is the product of the dielectric constant, 78.54, and the permittivity of vacuum, 8.8542 x 10<sup>-12</sup> J/(V<sup>2</sup>m). The viscosity of water at 25 °C is equal to 0.8904 x 10<sup>-2</sup> g/(cm.s).

One mobility unit is  $1 \mu \text{ s}^{-1}\text{V}^{-1}\text{cm} = 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$ . Therefore, the zeta potential in water at 25 °C corresponding to one mobility unit is equal to  $\varsigma$ = 12.83 mV per mobility unit

# **Debye-Hückel Approximation**

One of the assumptions in Henry's equations is that the potential is small. This same assumption occurs in several other theories of the diffuse double layer, and it has its roots in the Debye-Huckel approximation:

 $\Psi_0 = k_B T/e << 1$ 

Where:

 $k_{\rm B}$  = Boltzmann's Constant = 1.3807 x 10<sup>-23</sup> J K<sup>-1</sup>

T = Temperature in Kelvin (K)

e = Electronic Charge in Coulombs =  $1.6022 \times 10^{-19} C$ 

When evaluated at 25 °C,  $\Psi_0$  = 25.7 mV. In other words, Henry's equations are increasingly more accurate as the zeta potential falls below 25.7 mV. And this corresponds to about 2 mobility units.

# Appendix 8: Errors in Calculating Zeta Potential

The Smoluchowski equation for calculating zeta potential from the measured mobility is so common place that one forgets that the equation is only an approximation. It is a good approximation when Ka>>I. Often, however, Ka is between 10 and 100. It is worthwhile estimating the errors between the true zeta potential and that calculated using the Smoluchowski and Henry equations.

The tables below take advantage of Figures 22 & 23, which are reprinted from the original work of Wiersma. For the true zeta potential Wiersma calculated the correction factor  $f(Ka, \varsigma)$ . The first column is the true zeta potential. The second column shows the electrolyte. The third column was interpolated from Figures 22 & 23 at Ka = 10. The fourth column is the calculated zeta potential using Smoluchowski's equation. The fifth column shows the percent error using the Smoluchowski equation. The second table uses Henry's equation for a 1:1 electrolyte to estimate the zeta potential. (The 2:1 electrolyte is not applicable since Henry only gave results for the 1:1 case.)

#### For Ka in H2O at 25°C

#### Errors in Calculating Zeta Potential: Smoluchowski

ς <sub>T</sub> (mV)	Elect.	f(κa, ς)	$\zeta_{Smol}(mV)$	%Err
25.7	1:1	1.238	31.8	+19%
51.4	1:1	1.143	58.7	+12%
51.4	2:1	0.833	42.8	-20%

#### **Errors in Calculating Zeta Potential: Henry**

ς <sub>T</sub> (mV)	Elect.	f(κa, ς)	$\varsigma_{\text{Henr}}(mV)$	%Err
25.7	1:1	1.238	28.3	+10%
51.4	1:1	1.143	56.7	+12%
51.4	2:1	0.833	N.A.	+N.A.

In summary, the Smoluchowski equation can lead to errors as large as +20% for  $\kappa a =$  10. Henry's equation is the better choice, with errors as large as +10% for  $\kappa a =$  10. One needs, however, an estimate of the average particle radius to apply the Henry equation.

# Appendix 9: Electrophoretic Doppler Shift

The shift in frequency,  $\omega_s$  of scattered light from a charged particle moving with velocity, **V**<sub>s</sub>, in an electric field, **E**, is given by the dot product of vectors:

$$\omega_s = \mathbf{q} \cdot \mathbf{V}, = \mathbf{q} \mathbf{V}_s \cos \phi$$

where  $\phi$  is the angle between the vectors. When the electrical field is perpendicular to the incident laser beam direction,  $\mathbf{k}_0$  then it can be shown that  $\phi$  is related to the scattering angle  $\theta$  by  $\phi = \theta/2$  for the special case when  $\mathbf{E} \perp \mathbf{k}_0$ 

The magnitude, q, of the scattering wave vector is given by  $q = (4\pi n/\lambda_0)\sin(\theta/2)$  where n is the refractive index of the liquid and  $\lambda_0$  is the wavelength of the laser in vacuum. For water, n = 1.332 in the red end of the visible range of wavelengths; for the solid state laser used in the ZetaPlus,  $\lambda_0 = 0.670 = 0.670 \times 10^{-4}$  cm; and  $\theta = 15^{\circ}$ .

Since  $V_s = \mu_e E$  where  $\mu_e$  is the electrophoretic mobility, the equations and parameters above can be combined to give

$$\omega_s = 3.22 \mu_c E$$
 in rad/s, or  $\nu_s = \omega s/2\pi = 0.513 \mu_e E$  in Hz

where E is the magnitude of the electric field vector in units of V/cm and  $\mu_e$  is in  $(\mu/s)/(V/cm)$ .

When the mobility is low a high field strength is needed to make good measurements, and when the mobility is high a low field strength is needed.

Indirectly, conductivity also plays a part: at high conductivity it is difficult to establish a high field strength. Nevertheless, a reasonable approximation for the maximum of the product  $\mu_e E$  is 400 µ/s. Then a maximum Doppler shift is  $v_s \sim 200$  Hz. In fact, at low scattering angles like  $\theta = 15^\circ$ ,  $v_s$  varies from 0 to100 Hz. These Doppler shifts due to the electrophoretic mobility are added to or subtracted from the applied frequency shift of 250 Hz. If the measured frequency shift is less than 250 Hz, then the calculated electrophoretic mobility and resultant zeta potential must be negative whereas, if the measured frequency shift is greater than 250 Hz, then  $\mu_e$  and the  $\zeta$  potential must be positive.

# Appendix 10: Diffusion & Thermal Broadening Effects

#### Linewidth

The velocity distribution of charged particles moving between two electrodes is broadened not only by the electrophoretic mobility distribution of interest but also by the divisional broadening due to particle size. This latter broadening is, in fact, the principle used for measuring particle size with the BI-MAS particle sizing option. The frequency of the laser line (nearly monochromatic) is broadened by the diffusional motion of the scattering particles. The half-width of the scattered electric field, called the linewidth, is given by

$$\Gamma = D_T q^2$$
 in rad/s

where  $D_T$  is the translational diffusion coefficient and q is the magnitude of the scattering wave vector. This latter quantity is described fully in Appendix V. The diffusion coefficient is related to particle size by

$$D_T = k_B T / (3\pi \eta d_H)$$
 in cm<sup>2</sup>/s

where  $k_B$ , Boltzmann's constant, is 1.380658 x 10<sup>-16</sup> erg/deg; T is the absolute temperature in degrees Kelvin;  $\eta$  is the viscosity in Poise; and  $d_H$  is the equivalent hydrodynamic diameter of the particle with the same diffusion coefficient as the one measured. The subscript signifies that the diameter calculated is the diameter of the kinetic particle including the double layer thickness.

For measurements made at 25 °C (298.15 K) in water,  $\eta = 0.8904$  cP, where one Poise has units of g. cm<sup>-1</sup>.s<sup>-1</sup>. Substituting the parameters above into the equation for the line width, including the equation for q given in Appendix V, yields

$$\Gamma_{15^{\circ}}$$
 (rad/s) = 5137/d(nm) and  $\Gamma_{90^{\circ}}$ (rad/s) = 150,750/n(nm)

or

 $\Gamma_{15^{\circ}}(Hz) = 818/d(nm)$  and  $\Gamma_{90^{\circ}}(Hz) = 24,000/d(nm)$ 

The following table gives some typical examples:

d(nm)	Γ <sub>15°</sub> (Hz)	Γ <sub>90°</sub> (Hz)
10	81.8	2,400
20	40.9	1,200
50	16.4	480
100	8.2	240
200	4.2	120
500	1.6	48
1000	0.8	24
2000	0.4	12
5000	0.2	4.8
10000	0.1	2.4

There are two lessons to be learned from these numbers. First, they show the advantage of making electrophoretic mobility measurements at low angles. The broadening due to translational diffusion is much less at low angles than at high angles. Therefore, the shift and the broadening due to the mobility distribution is easier to extract from the total broadening at low angles. Second, for small particles it becomes increasingly difficult to separate the measured broadening into mobility and particle size effects. In Appendix V it was stated that typical Doppler shifts will be less than ~100 Hz. Depending on the actual shift, the diffusion broadened component for small particles can exceed the mobility shift. Under these circumstances the uncertainty in the peak of the measured frequency distribution becomes greater, and the measured width is dominated by the diffusion effect.

Several other effects also broaden the measured distribution. Of these, thermal effects are the most significant.

To reduce thermal effects wait until the measured peak frequency without the electric field on is  $250 \pm 4$  Hz before proceeding with the measurement. If you use the automatic mode, this condition is implemented since the algorithm waits until the frequency is within 4 Hz of 250 Hz for three successive measurements. You can, however, override this default by pressing any key while waiting for stability. It is suggested that you wait.

When preparing samples take care that the sample temperature is roughly equal to the temperature set on the instrument. If not, you will simply have to wait longer to make good measurements.

Electro-osmotic broadening, an effect that is significant in other instruments, is nonexistent in the ZetaPlus

# **Appendix 11:** Concentration: Definitions and Calculations

A reasonable concentration for measurements with any sedimentation device, including the BI-DCP and BI-XDC, is 0.005 volume fraction, also designated as 0.5% by volume. While there are some cases where a concentration of this magnitude might cause particle-particle interactions and, as a result, distortions in the final answer, this is a good, initial value. If in doubt, make measurements at 0.25% by volume to see if there has been a systematic shift in the results. (Occasionally, depending on the sample, you may be forced to work at higher concentrations in order to get any signal.)

The volume fraction,  $\Phi$ , is a fundamental parameter for describing concentration. The cube root of  $\Phi$  is proportional to the ratio D/L, where L is the average center-to-center interparticle distance and D is the particle size. When the volume fraction is high, the particles are close together, and concentration effects on the measured size are more likely to be important.

 $\Phi$  is defined as,  $\Phi = V_p/V_s = V_p/(V_p + V_l)$ 

where  $V_p$  = the total volume of all particles,  $V_l$  = the volume of the liquid,  $V_s$  = the total volume of th suspension ( particles + liquid).

For example, assume a suspension with 1 mL of particles and 49 mL of liquid. Then,  $\Phi$  = 0.02. The concentration is 2% by volume.

{Note for Chemists: Unless a solution is ideal, the total volume is not equal to the sum of the component volumes. This is due to molecular interactions. Suspensions are not solutions. Only the surface molecules around a stable particle interact significantly, if at all, with the liquid in which it is suspended. Therefore, it is a good approximation to assume that the volumes add. One need not be concerned with partial molar volumes. }

For low concentrations  $V_p \ll V_l$  and  $\Phi \sim V_p/V_l$ . For high concentrations, this approximation is no longer valid.

Another common definition for concentration is the mass fraction defined as the total mass of particles divided by the total mass of suspension. Like the volume fraction, the mass fraction is a true fraction: it has no units. Unlike the volume fraction, the mass fraction is not directly related to particle-particle interactions. In addition, it is not common practice to weigh the liquid used to make a suspension. Instead, the volume of liquid is measured. This practice gives rise to the most common definition of concentration.

Let  $C = M_p/V_1$  where  $M_p$  equals the total mass of particles. For example, if 1 g of particles is added to 50 mL of liquid, then C = 0.02 g/mL.

This is--unfortunately and illogically--often referred to as a 2% solids concentration, or 2% by weight. Notice the mixed units, g/mL. A fraction and the corresponding percent

have no units, as in the case of volume or mass fraction. A further problem arises when a concentration is given only as 2%. It is not clear whether this means volume or mass fraction or C. If in doubt, ask.

With the help of a little algebra, one can relate  $\Phi$  and C. Namely,

$$C = \Phi \rho_p / (1 - \Phi)$$
 or  $\Phi = C / (C + \rho_p)$ 

where  $\rho_p$  is the density of the particle.

For example, if a 30 g sample of particles with  $\rho_p = 1.2 \text{ g/cm}^3$  is suspended in 50 mL of liquid, C = 30g/50mL = 0.6 g/mL, or 60% solids. Using the above equation to calculate  $\Phi$  results in 33.3% by volume.

For low concentrations, C ~  $\Phi \rho_p$ . This is a particularly useful approximation. For example, it was stated at the beginning that making measurements at  $\Phi$  = 0.5% is a good starting point. For polyvinyl chloride, where  $\rho_p$  = 1.38 g/cm<sup>3</sup>, C = 0.5% x 1.38 = 0.69%; and for TiO<sub>2</sub>, where pp = 4.2 g/cm<sup>3</sup>, C = 0.5% x 4.2 = 2.1%.

In preparing samples for particle size analysis it is quite common to use wetting agents and surfactants. These should be used at very low concentrations. In addition, the density of these materials is typically close to 1 g/cm<sup>3</sup>. For these two reasons, it is normal practice to ignore completely the difference between  $\Phi$  and C.

Likewise, when preparing samples for use with the BI-90, BI-FOQELS, ZetaPlus, or BI-200SM (all instruments based on dynamic light scattering), the concentrations are typically between  $10^{-5}$  to  $10^{-2}$  volume fractions. At such low concentrations the difference between suspension volume, V<sub>s</sub>, and liquid volume, V<sub>l</sub>, is insignificant, and the difference between  $\Phi$  and C is, again, often ignored.

Ignoring the difference between  $\Phi$  and C, at low concentrations, is very common and acceptable for rough, qualitative work. It is never acceptable for quantitative work. For example, if you are not sure if the current dilution is sufficient, halve the concentration, and repeat the measurement. It is not too important to know the exact concentration or its definition, if and only if the concentration is roughly in the right range. If, however, you want to plot values against concentration or fit results to an equation in concentration, then you must be quantitative when measuring, diluting and specifying the concentration, especially the units.

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