

Zeta potential is an indicator of dispersion stability. The zeta potential of any dispersion is influenced by the surface chemistry. The surface chemistry can be changed by any number of means including a change in the pH, salt concentration, surfactant concentration, and other formulation options. It is, therefore, frequently desirable to determine how pH affects the zeta potential of a dispersion. An isoelectric point measurement studies how pH influences zeta potential and determine at which pH the zeta potential equals zero.

Introduction

Zeta potential is the potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle – see Figure 1.

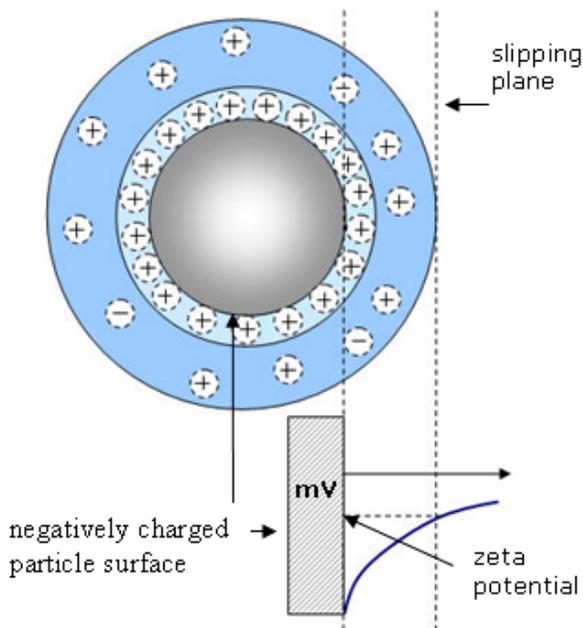


Figure 1: Zeta potential of a negatively charged particle

According to general colloid chemistry principles, an electrostatically stabilized dispersion system typically loses stability when the magnitude (i.e. absolute value) of the zeta potential decreases to less than approximately 30 mV. As a result, there will be some region surrounding the condition of zero zeta potential (i.e. the isoelectric point, or IEP) for which the system is not particularly stable. Within this unstable region, the particles may agglomerate, thereby increasing the particle size. Determining the pH conditions where the zeta potential becomes zero (the IEP) is, therefore, a common use for zeta potential analyzers.

Materials

Two samples were analyzed for this study, noted as creamer A and creamer B. Both are powders used as a cream substitute in coffee. Both samples were dispersed in 18 megohm DI water.

The titration was performed using 1 N HCl and 1 N KOH solutions. The pH was measured using a HORIBA model F-50 pH meter.

The sample is an emulsion once added to the water. The particle size distribution of the emulsion from sample B was analyzed using both the SZ-100 DLS system and the LA-960 laser diffraction analyzer. The large particle size and polydispersity index from the SZ-100 result indicated the presence of large particles outside of the range of any DLS system. This was confirmed by the particle size result recorded by the LA-960 – see Table 1.

D10	0.127 μm
D50	0.284 μm
D90	14.29 μm

Table 1: Particle size distribution of sample B determined with the LA-960

Experimental

The zeta potential of both samples was analyzed using the HORIBA SZ-100 nanoPartica system (Figure 2).



Figure 2: The SZ-100 nanoPartica system

The sample preparation for both samples was identical:

- Add 100 mL of DI water into a beaker
- Add 0.1 g of sample to the water
- Agitate for 5 minutes
- This becomes the base sample to be titrated

The titration was performed manually following this procedure:

- Extract a 10 mL of the base sample using a disposable pipette into a glass beaker.
- Add a few drops of HCl to lower the pH or KOH to raise the pH to reach the desired pH.
- Extract a few mL of the sample with a disposable pipette and fill the disposable zeta potential cell without introducing bubbles.
- Place the zeta potential cell into the SZ-100.
- Measure the zeta potential 3 times and record the average value.

The SZ-100 was placed in zeta potential measurement mode (the same system is also capable of measuring particle size, molecular weight, and second virial coefficient.) The settings for the measurements were:

Smoluchowski assumption for κa
 Measurement duration = 120 sec
 Standard calculation

Results and Discussion

The pH vs. zeta potential plot for sample A and B is shown in Figure 3. The IEP of sample A was determined to be 4.1 and for sample B the IEP was never reached. The value for sample A was near the expected value based on past experience with this sample. The data for sample B was puzzling until the ingredient list was read and the long list of stabilizers added to this product was realized.

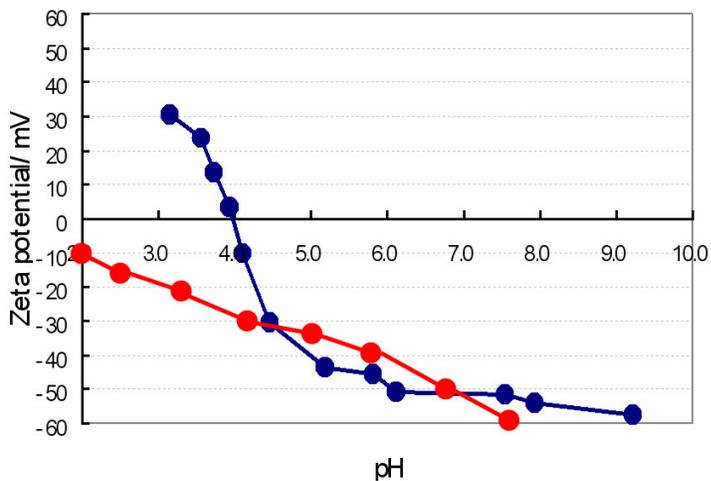


Figure 3: Zeta potential vs. pH graph. Sample A in blue, sample B in red.

A quick study of zeta potential measurement reproducibility was then performed on sample B. The base sample was analyzed 5 times – see Table 2 – and then another identical sample preparation procedure was carried out and this sample was analyzed 5 times – see Table 3. Note that the reported zeta potential value is concentration dependant, which is why these values are higher than was seen in the IEP study.

Run #	Zeta Potential
1	-81,2
2	-80,5
3	-81,6
4	-79,9
5	-80,7
ave	-80,8
st dev	0,65
COV	0,81

Table 2: Zeta potential repeatability sample B prep #1

Run #	Zeta Potential
1	-81,2
2	-79,5
3	-81,6
4	-80,1
5	-79,6
ave	-80,4
st dev	0,95
COV	1,18

Table 3: Zeta potential repeatability sample B prep #2

IEP studies have been published for a variety of samples. Table 4 provides a quick reference to the IEP for many samples. This table is meant for quick reference only and is not intended as a deeply researched or complete list of IEP values. Note further that surface chemistry or structure of some materials can be quite different from bulk chemistry. This is most clear for the case of rutile vs anatase TiO_2 .

Conclusions

The isoelectric point of two emulsion samples was analyzed by determining zeta potential as a function of pH. The reproducibility of sample B was then investigated and showed excellent agreement between two sample preparations.

alpha aluminium oxide Al_2O_3	8-9
alpha iron (III) oxide (hematite) Fe_2O_3	8.4-8.5
antimony(V) oxide Sb_2O_5	<0.4 to 1.9
cerium(IV) oxide (ceria) CeO_2	6.7-8.6
chromium(III) oxide (chromia) Cr_2O_3	6.2-8.1
copper(II) oxide CuO	9.5
delta-MnO2 1.5, beta-MnO2	7.3[5]
gamma aluminium oxide Al_2O_3	7-8
gamma iron (III) oxide (maghemite) Fe_2O_3	3.3-6.7
iron (II, III) oxide (magnetite) Fe_3O_4	6.5-6.8
lanthanum(III) oxide La_2O_3	10
lead(II) oxide PbO	10.7-11.6
magnesium oxide (magnesia) MgO	9.8-12.7
manganese(IV) oxide MnO_2	4-5
nickel(II) oxide NiO	9.9-11.3
silicon carbide (alpha) SiC	2-3.5
silicon dioxide (silica) SiO_2	1.7-3.5
silicon nitride Si_3N_4	6-7
silicon nitride Si_3N_4	9
tantalum(V) oxide, Ta_2O_5	2.7-3.0
thallium(I) oxide Tl_2O :	8
tin(IV) oxide SnO_2	4-5.5
titanium(IV) oxide (rutile or anatase) TiO_2	3.9-8.2
tungsten(VI) oxide WO_3	0.2-0.5
vanadium(V) oxide (vanadia) V_2O_5	1 to 2
yttrium(III) oxide (yttria) Y_2O_3	7.2-8.9
zinc oxide ZnO	8.7-10.3
zirconium(IV) oxide (zirconia) ZrO_2	4-11

Table 4: IEP values for a variety of materials