



CABOT

Titration of Surface Modified Pigment Particles

*Friedrich von Gottberg
Yuan Yu*

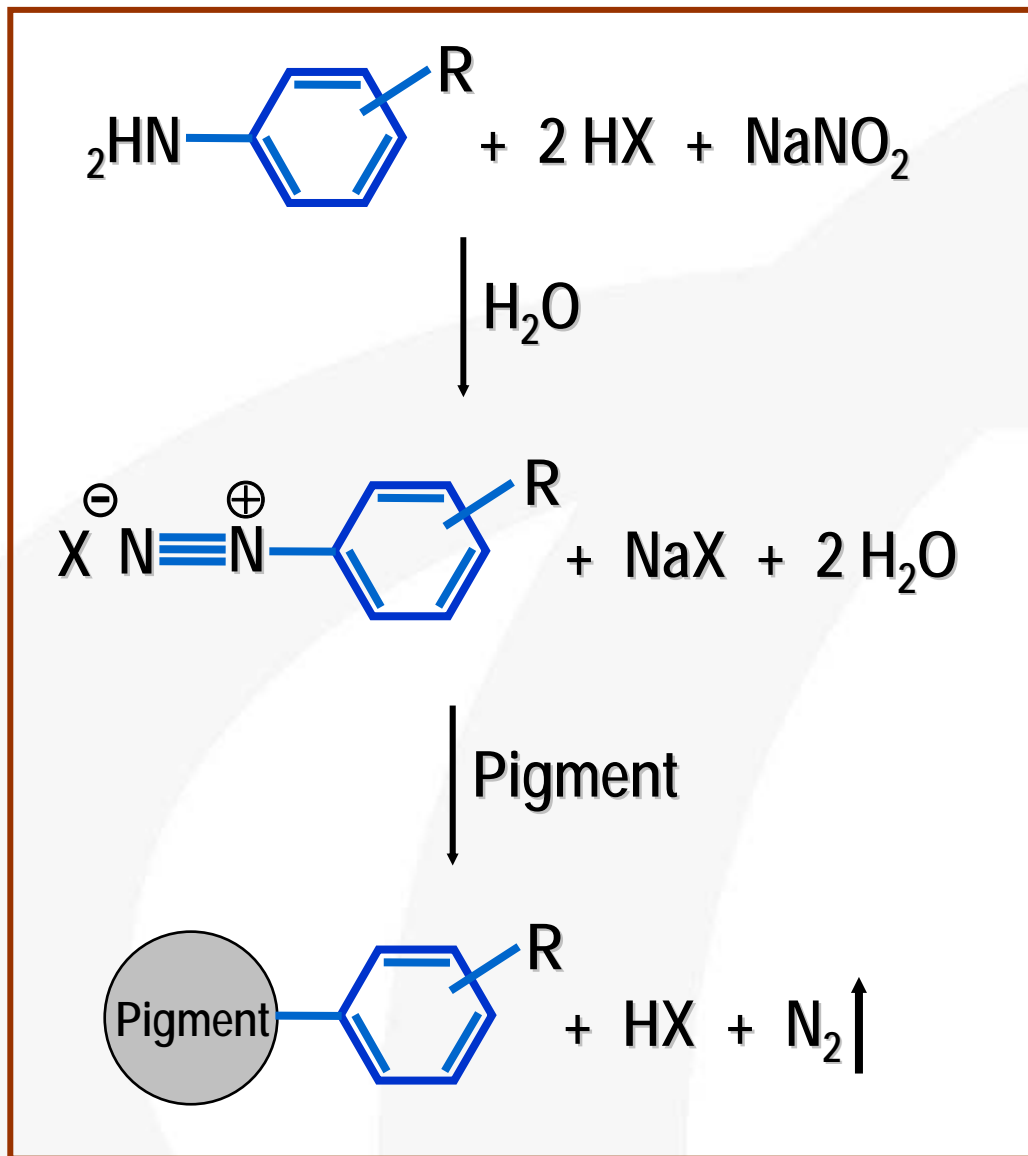
NIP-20, IS&T, Salt Lake City, UT, 11/2004

Outline

- Surface Modified Pigment Particles
- Motivation for Titration Studies
- Brief Review of Henderson-Hasselbalch Equation
- Titration of Carboxylic Acid Modified Carbon Black
 - pKa of surface functional groups and correction with diffusive layer model (DDL)
- Titration of PEI Attached Carbon Black
- Summary



Surface Modification with Diazonium Chemistry



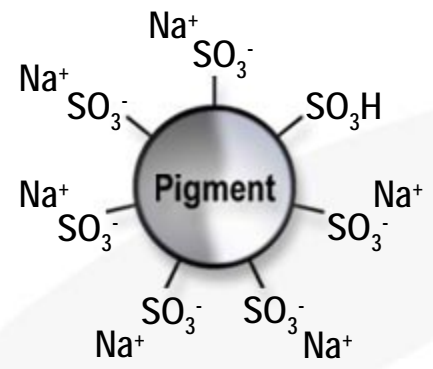
R = COOH
 SO₃H
 Polymers
 Mixed

US Patents
 5,554,739
 5,922,118

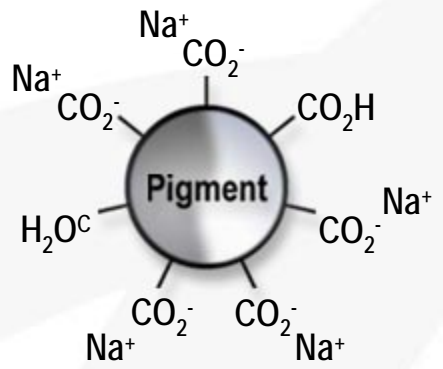


Commercial Products and the Role of pKa

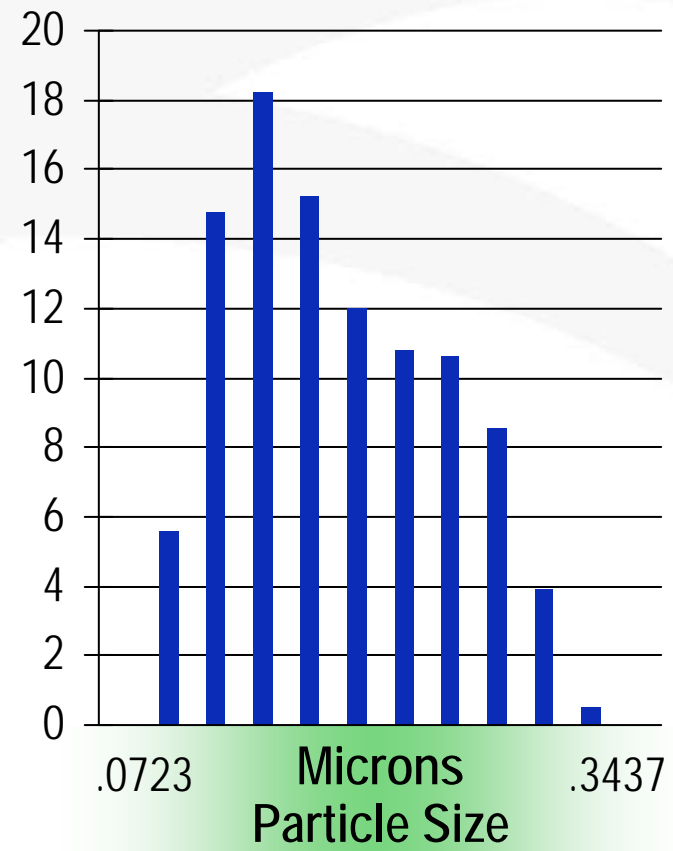
Cab-O-Jet® 200



Cab-O-Jet® 300



Frequency



Print Performance		
	COOH	SO ₃ H
Optical Density	1.5	1.4
Waterfastness	Yes	No



Motivation and Objectives

- Titration of oxidized CB had been reported before
 - Do not have well defined chemical groups
- Surface chemical modification provided a unique opportunity to study the interaction among well defined surface groups
- Another method to determine treatment level
- Understand impact of pKa on surface modified pigment behavior
- Understand surface potential as a function of pH



Henderson Hasselbalch Equation



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{HA}]_o = [\text{HA}] + [\text{A}^-]$$

$$\alpha = \frac{[\text{A}^-]}{[\text{HA}]_o}$$

To simplify this study and data interpretation activity coefficients have been omitted

Henderson Hasselbalch Equation, con't

$$K_a = \frac{[H^+][A^-]}{[HA]_0 - [A^-]} = \frac{[H^+]\alpha}{1 - \alpha}$$

$$\log(K_a) = \log(H^+) + \log\left(\frac{\alpha}{1 - \alpha}\right)$$

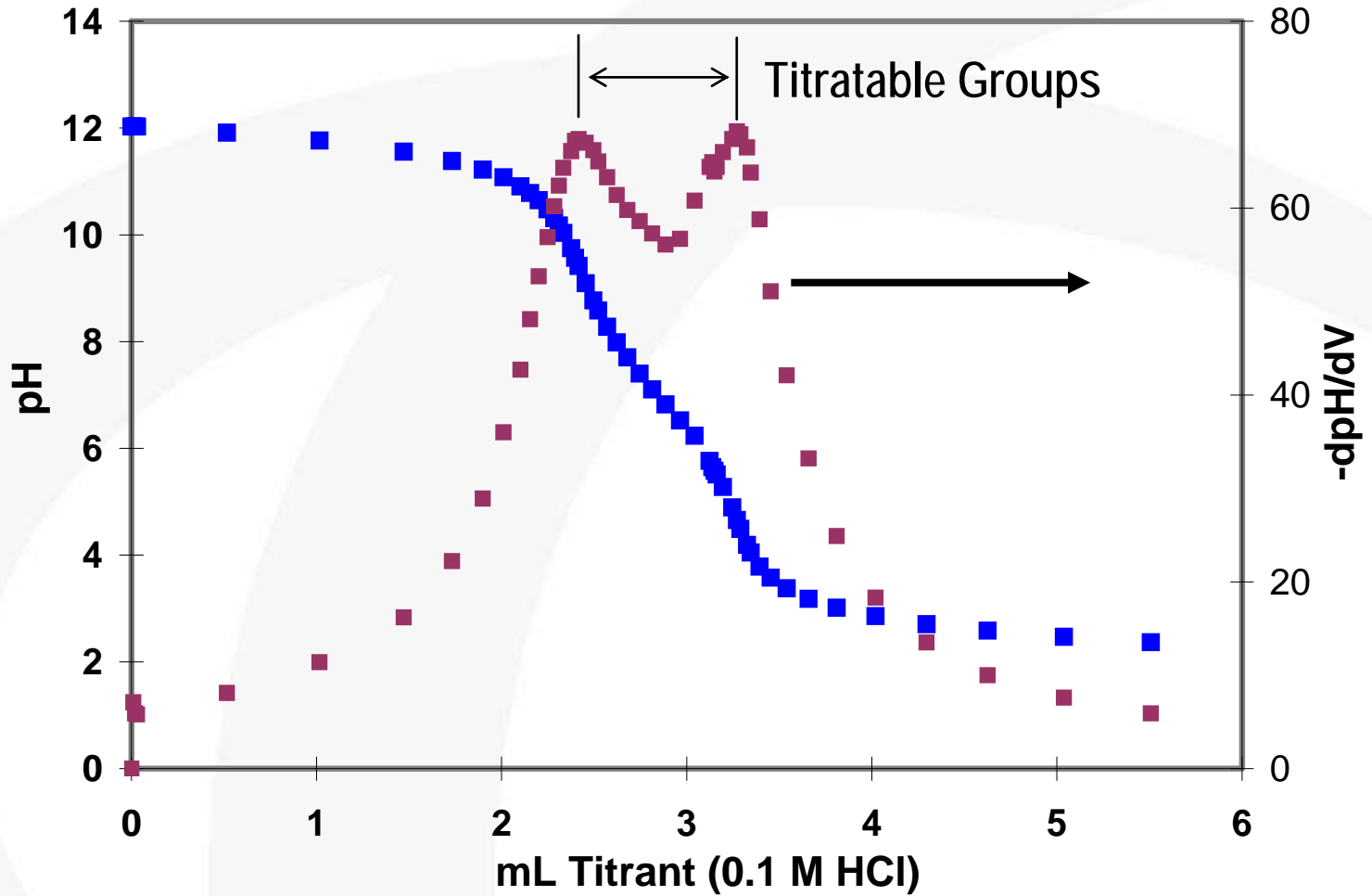
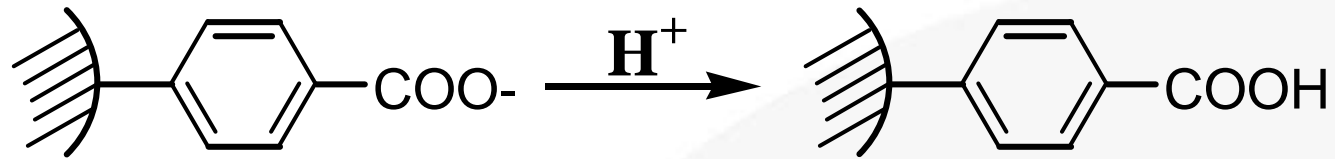
$$pH = pK_a - \log\left(\frac{1 - \alpha}{\alpha}\right)$$

Extended Henderson-Hasselbalch Equation

$$pH = pK_a - n \log\left(\frac{1 - \alpha}{\alpha}\right)$$

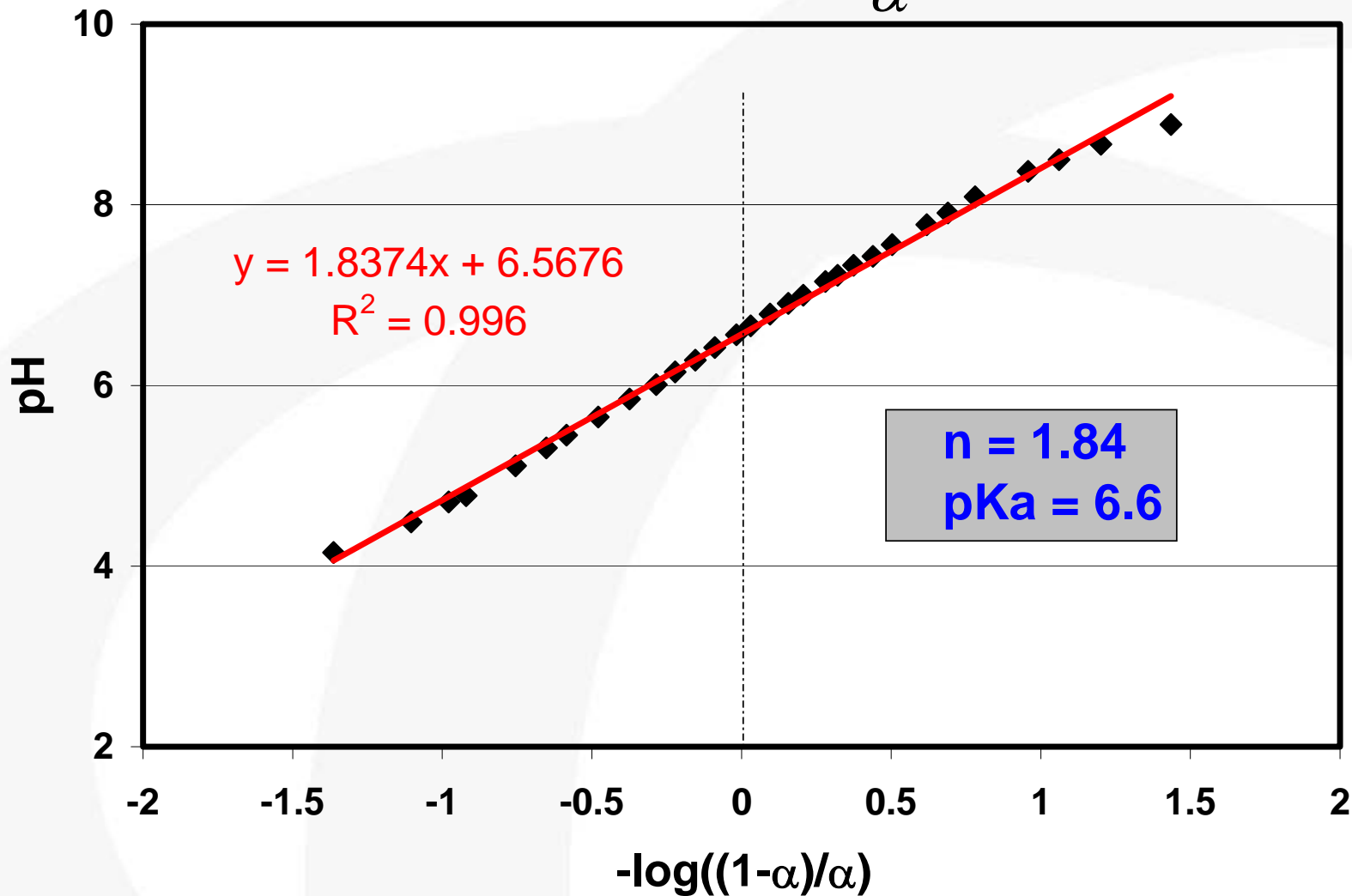


Titration of CB with Surface Carboxylic Acid Groups



Henderson-Hasselbalch Plot

$$pH = pKa - n \log\left(\frac{1-\alpha}{\alpha}\right)$$

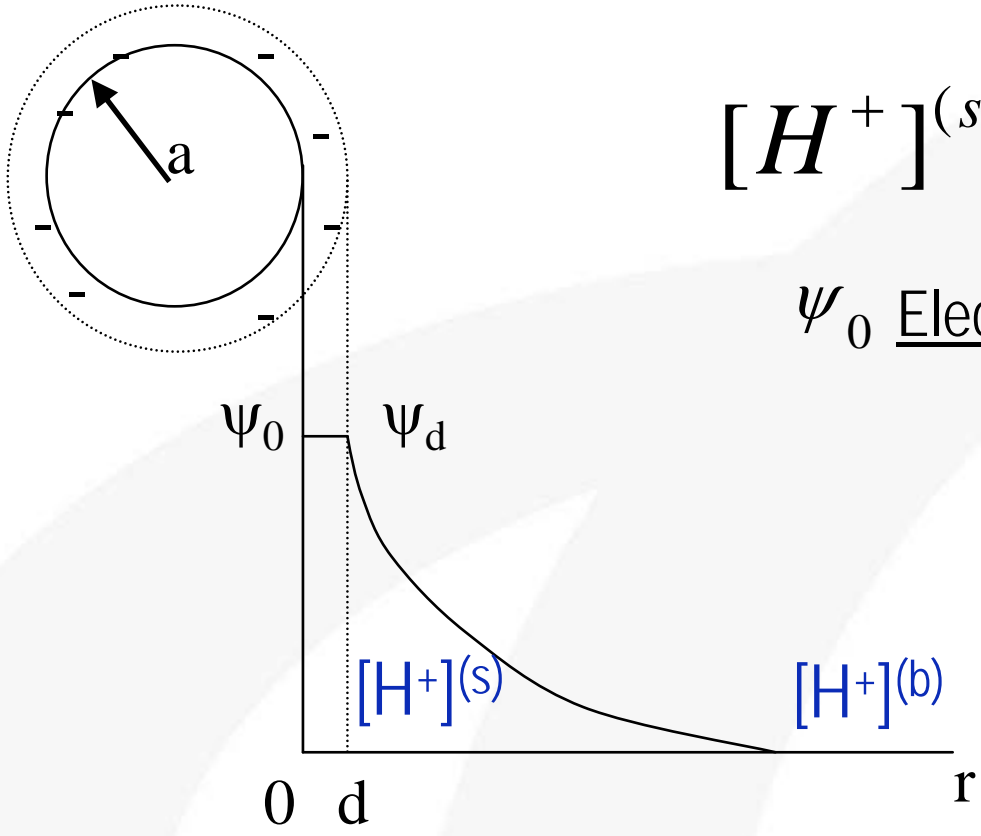


Questions ?

- Why is the pKa so much higher than benzoic acid ?
 - Effective pKa and pKa₀?
 - pKa benzoic acid ~ 4.2
- Why is the slope n so different from unity ?
 - For benzoic acid titration, n = 1
- Could this all be explained by the diffuse double layer ?
 - Surface concentration is different from bulk concentration !



Double Layer: Surface vs Solution



$$[H^+]^{(s)} = [H^+]^{(b)} e^{\frac{-e\psi_0}{kT}}$$

ψ_0 Electrostatic surface potential

$$Ka = \frac{[H^+]^{(s)}[A^-]}{[HA]}$$

Surface dissociation constant

$$pH = pKa - \frac{e\psi_0}{kT} \log(e) - n \log\left(\frac{1-\alpha}{\alpha}\right)$$



Calculation of ψ_0 from Surface Charge Density

From LOW table , when $\kappa a > 0.5$

$$q = \frac{Q}{4\pi a^2} = \frac{\epsilon\epsilon_0 kT}{ez} \kappa \left[2 \sinh \frac{ze\psi_0}{2kT} + \frac{4}{\kappa a} \tanh \frac{ze\psi_0}{2kT} \right]$$

$$\kappa = \left(\frac{e^2 \sum n_i^b z_i^2}{\epsilon\epsilon_0 kT} \right)^{1/2}$$

κ^{-1} : Debye decay length

Estimation of ψ_0 and Correction for pKa

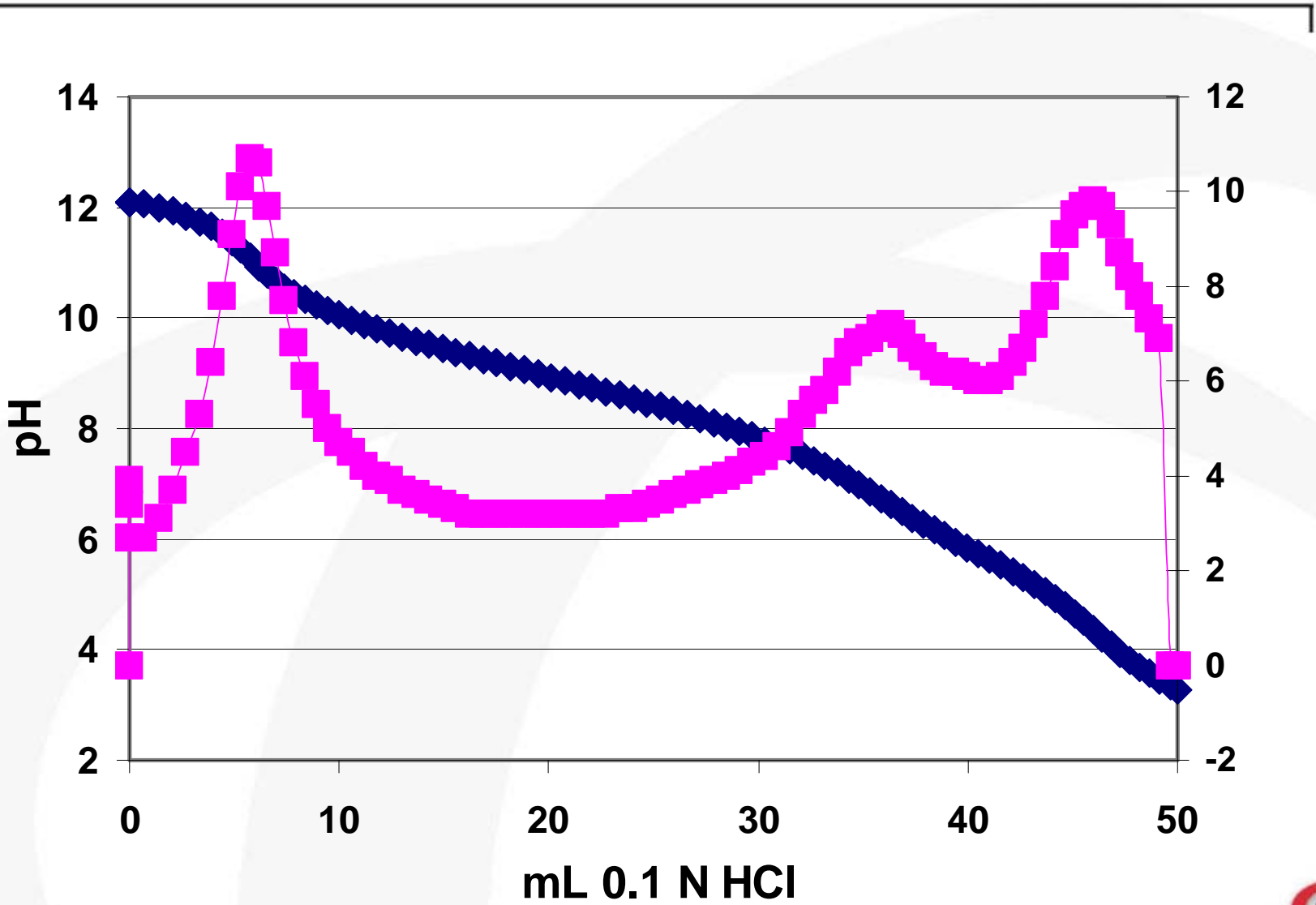
- A 100 nm particle with $2 \mu\text{mol}/\text{m}^2$ of attachment
 - At $\alpha = 0.5$, the surface charge density: $\sim 0.1 \text{ C}/\text{m}^2$
- When $\alpha = 0.5$ in a 0.01 M 1-1 electrolyte
 - $\psi_0 = 140 \text{ mV}$
 - $-e\psi/kT \log_{10}(e) = \sim 2.4$
- Apparent pKa related to pKa_0
 - $\text{pKa}_0 - e\psi_0/kT \log_{10}(e)$
 - $4.2 + 2.4 = 6.6$

Polymer Attached Pigment Particles

- Cabot has extended its pigment surface modification technology from attaching small molecules to attaching polymers.
- What would be the dissociation behavior of the polymers when they are attached to pigment surface?
 - We will exam the titration of poly-ethylene-imine (PEI) attached carbon black particle.
 - PEI-1200: mixture of primary, secondary, and tertiary amines.

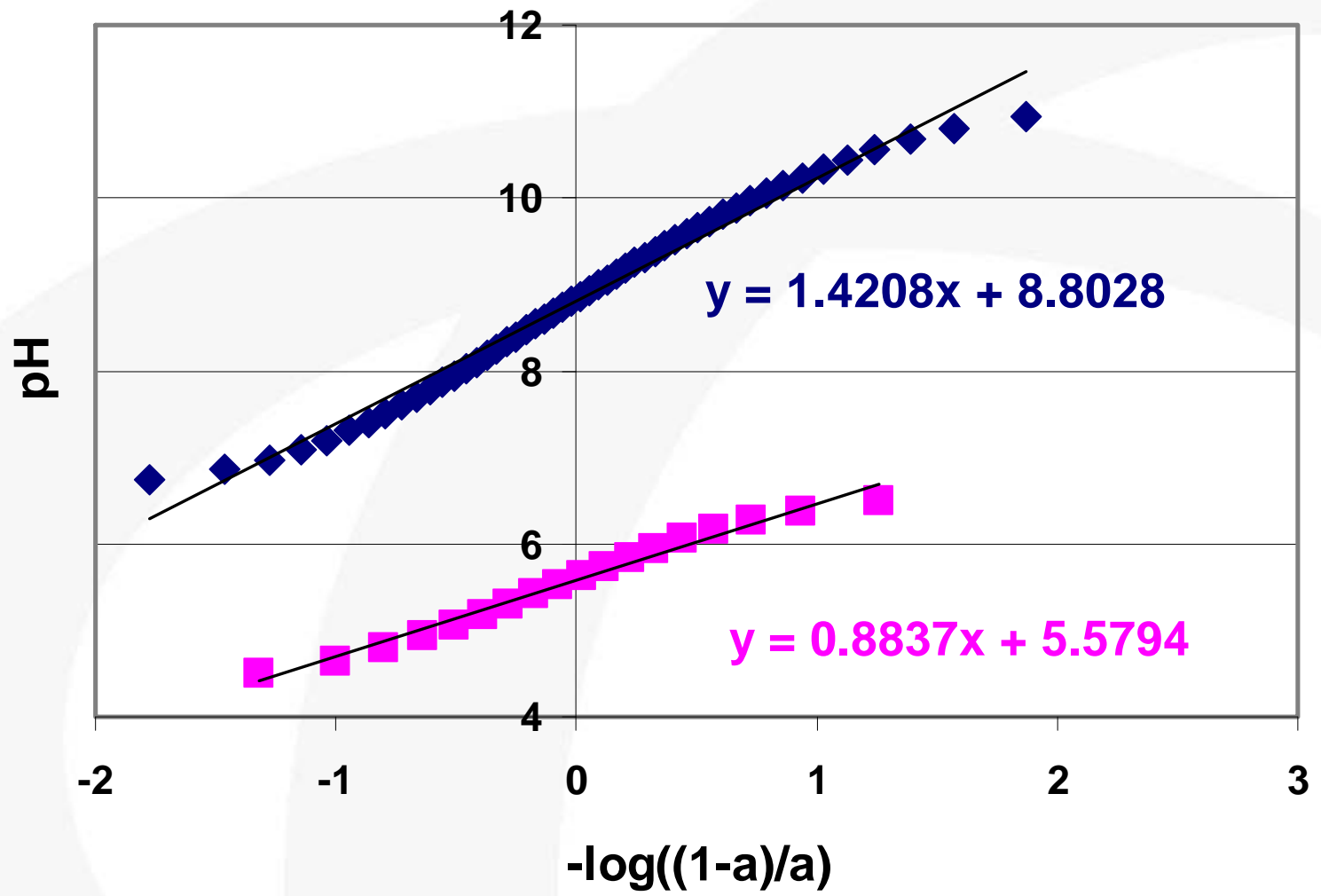


Titration Curve of Pure PEI-1200



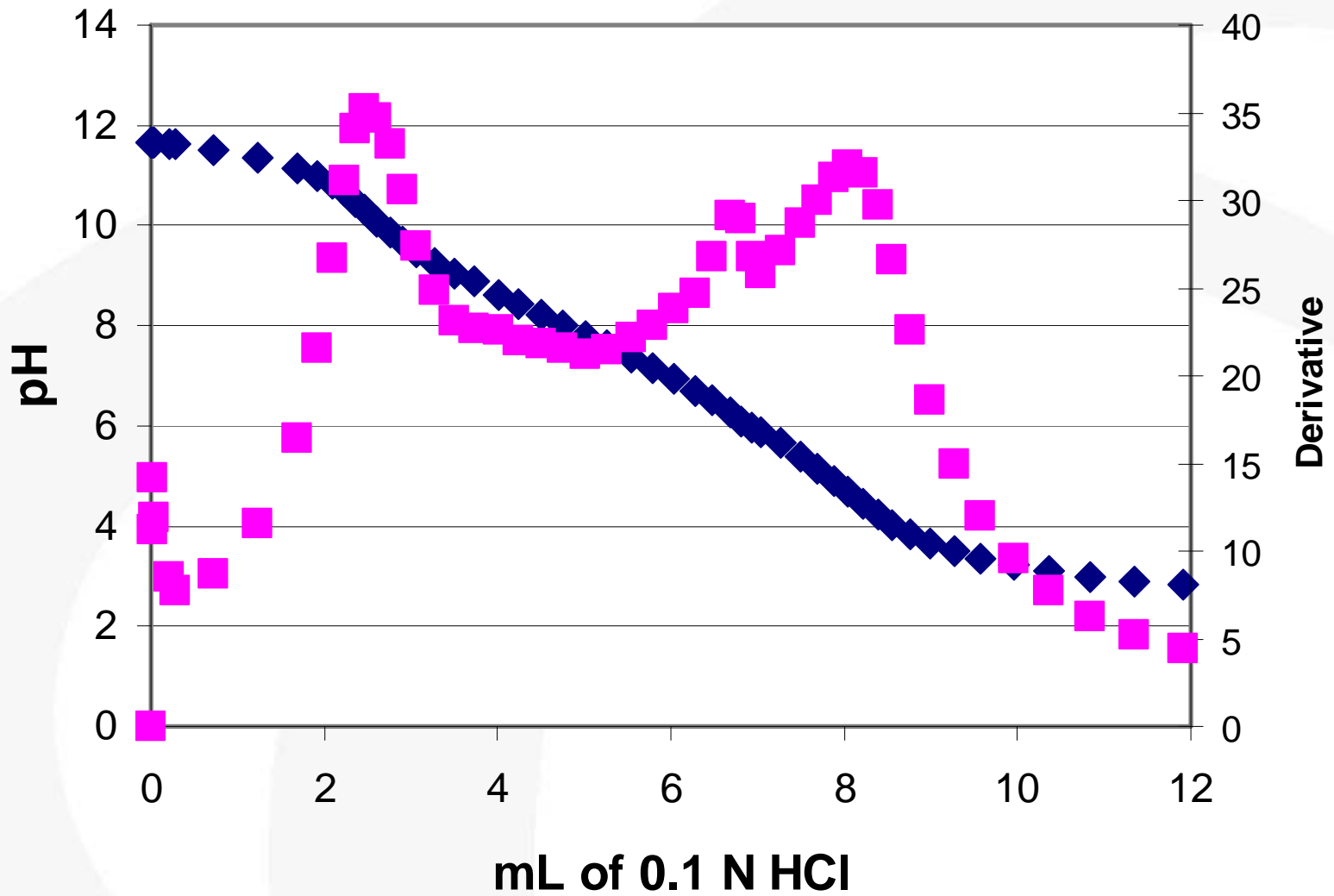
HH Plot of Pure PEI-1200 Titration

- Two pKa: 8.8 and 5.6



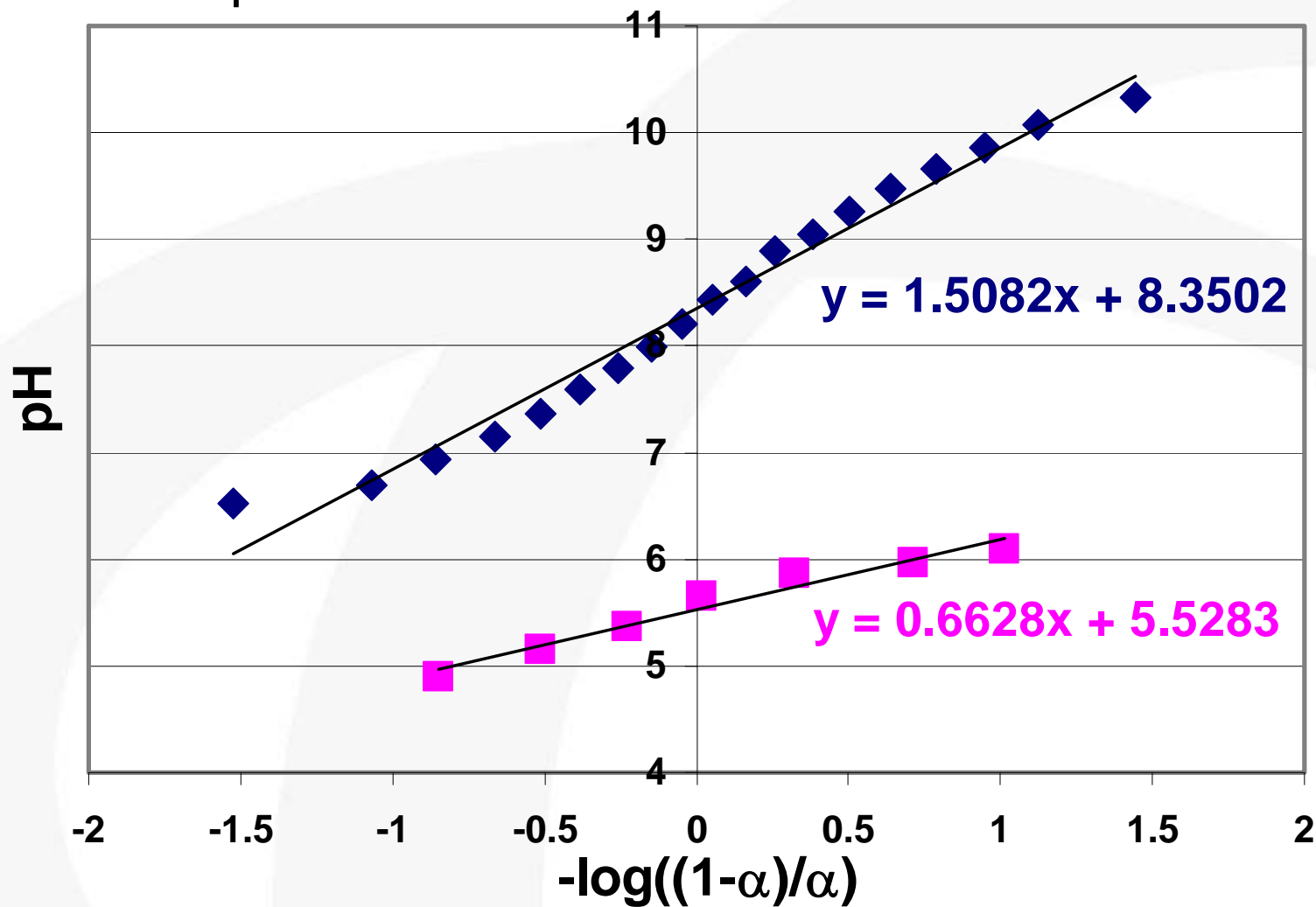
Titration Curve of PEI-1200 Modified CB

• Similar to Pure PEI-1200



HH Plot of PEI-1200 Modified CB

- Two pKa similar to PEI1200



Summary

- Relationship between the measured effective pKa of surface modified pigments and the pKa on the pigment surface has been established with DDL model
- Titration is an effective and simple method to determine treatment levels
- Titration also give the number of surface charged groups as a function of pH
 - critical for understanding stability and impact on IQ
- Titration behavior of poly-electrolyte attached CB is similar to free poly-electrolyte in the solution.



Summary, con't

- Titration studies had been performed with other surface modified pigments
 - Color pigments
 - Pigment with chemically attached polymers
- More work is needed to understand the physical meaning of the slope n and its relation to fundamental surface properties
- **Thank You!**

www.cabot-corp.com
inkjet@cabot-corp.com

