Titration of Surface Modified Pigment Particles

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Abstract

Surface modified pigments are playing an increasingly important role in high performance inkjet inks. Titration has been developed as a quantitative tool to evaluate pigment particles bearing weak acid or base functional groups. The value of total titratable groups in mmol/g pigment indicates the level of surface modification. The dissociation constants (pK_a or pK_b), which can be derived from the mathematical treatment of the titration curve, provide an insight into the colloidal stability as a function of pH. Titration studies of pigment particles have been reported before; however, due to poorly determined functional groups, data interpretation has been difficult. Cabot's surface modification technology, which introduces specific functional groups to the pigment surface, provides a unique opportunity for a systematic investigation. In this paper, a range of surface modified pigment particles has been investigated. The impact of ionic strength (I_m), inkjet ink components, and the nature of the surface functional groups have been studied and related to the pigment stability. The discrepancy between apparent pK (as measured experimentally) and the functional group pK is explained using a diffuse double layer (DDL) correction term. Using this method, the stability of the pigment dispersions can be better understood and the ability to destabilize these systems in a controlled manner through pH, ionic strength, or other environmental changes can be anticipated.

Introduction

Pigmented inks are widely used in inkjet applications[1-3] with stability and reliability performance matching dye based inks. The next generation of pigment colorants needs to be engineered to provide superior print quality: high optical density, durability, gloss, chroma, and less inter color bleeding. Most of the pigment-based inks on the market today are electro-static or electro-steric stabilized by weak acid groups such as carboxylic acid. An understanding of the nature and concentration of surface charge groups and the charge density as a function of pH is valuable for formulating, troubleshooting, and failure mode analysis of pigmented inks. In this report, potentiometric titrations of surface modified carbon blacks (CB) will be discussed.

Pigment Titration

Titrations of weak acid and base functional groups on CB surfaces have been investigated before.[4] Those CBs were surface oxidized creating a wide range of functional groups. As a result, the data interpretations are complex. Surface modification chemistries developed by Cabot offer a unique opportunity to study the titration behavior of well-defined functional groups on CB surface.[1-3] Titrations of polyelectrolytes and latex have been investigated extensively and the theory should be applicable for surface modified pigment particles. The extended Henderson-Hasselbach equation (Equation 1) has been used to express the titration behavior of many polyelectrolytes.[5]

$$pH = pK - n\log[(1-\alpha)/\alpha]. \tag{1}$$

The α is the degree of dissociation; pK is the apparent dissociation constant, and n is indicative of the interaction between the neighboring ionized groups. Since the precise physical meaning of n is not well understood, Equation 1 remains a phenomenological equation. The value for pKa can then be calculated from the Y-intercept of the Henderson-Hasselbach (HH) plot of pH vs. ($-\log[(1-\alpha)/\alpha]$).

Experiment and Samples

Material

Black Pearls™ 700 (BP700) with different surface functionalities were prepared and processed according to published patent procedures.[2,3,6] The dispersions for this study were supplied in 10 to 15% solid in DI-water. Standardized solution of NaOH, HCl, and other chemicals were purchased from Aldrich.

Measurement

Titration measurements for this report were carried out on a Metrohm 736 GP Titrino titrator. In a typical measurement 5 g of dispersion was diluted to 50 g with DI-water, and pH of the mixture was adjusted to 12 with 1 N NaOH. Then the solution was titrated with 0.1 N HCl to the end point. We have also titrated the dispersions with 0.1 N NaOH (pH of the dispersions were first adjusted to 2 with 1 N HCl) and in the presence of non-ionic surfactant, they all gave similar results.

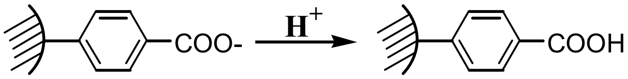
Data Processing

The titration curve was derivertized to determine the start and end points of the titration (See Figure 1). At the starting point the α=1 and at the end point the α=0, those values were then used for HH plot (See Figure 2). It is commonly assumed that inflection points in acid-base titration correspond to the equivalence point. This is, however, not generally true. Meites and Goldman had published a series of excellent papers on that subject.[7] Within the pK and concentration ranges of this investigation, we found that the correction term is small and our data interpretation is adequate.

Results and Discussion

Our study started with the simplest system: CB modified with carboxylic acid groups as shown in Scheme 1.[1]

Scheme 1: BP700 with surface carboxylic acid groups



The titration curve of Cab-O-Jet™ 300, a commercial grade of CB dispersion with benzoic acid functional groups, is shown in the Figure 1. The derivative curve clearly shows the start and end points of titration. The distance between those two inflection points is the total titratable groups, which gives 0.25 mol/Kg of solid for this example. This number matches well with the total titratable groups determined by other methods, e.g. counter ion analysis. Potentiometric titration has been developed into an indispensable tool at Cabot to study the level of surface modification on pigment particles.

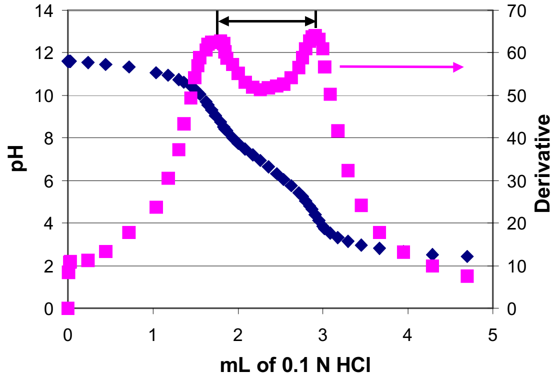


Figure 1. Titration of Cab-O-Jet™ 300

The HH plot of Cab-O-Jet™ 300 titration is shown in Figure 2. Apparent pKa of 6.6 is determined from the Y-intercept of the HH plot. The pKa of simple benzoic acid is around 4.2. Why is there the discrepancy?

The answer lies in the differences between the individually soluble molecules and a collection of those molecules on the pigment surface. When titrating functional groups on the pigment surface, a large number of those groups are located in close proximity to each other and their dissociation behavior is markedly different from soluble molecules. For example, once some of the acid groups on the surface have been de-protonated and charged, it will be increasingly difficult to de-protonate other acid groups due to electrostatic interaction that opposes the de-protonation. As a result, the proton concentration at pigment surface for Cab-O-Jet™ 300 will always be higher than that of the bulk solution. The concentration of proton on the Inner Helmholtz Plane (IHP) $[H^+]^{(S)}$ can be related to the proton concentration in the bulk solution $[H^+]^{(b)}$ with the so-called diffuse double layer model (DDL). In this model, all the surface charges locate at the IHP with a characteristic surface potential Ψ_0. DDL model is depicted in Figure 3.

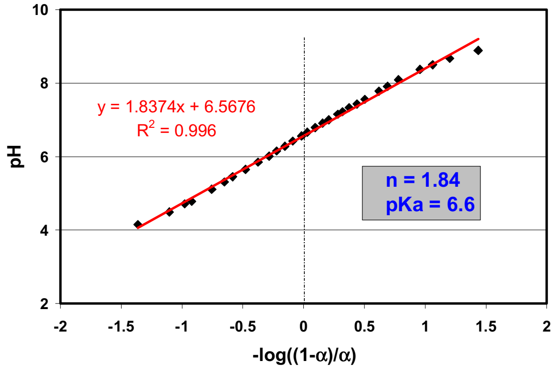


Figure 2. HH Plot of Cab-O-Jet™ 300 Titration

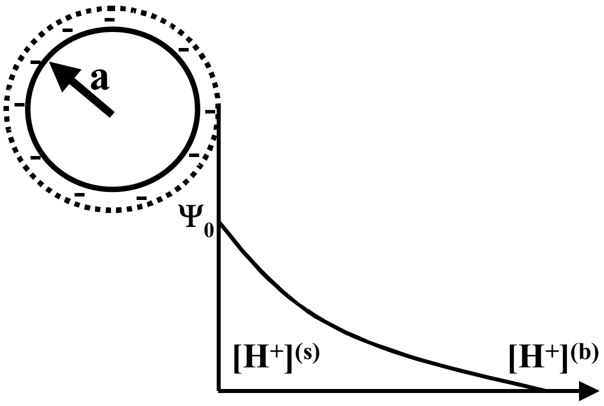


Figure 3. DDL model of a charged particle surface

The proton concentration at IHP can be related to the bulk concentration by Equation 2.[8,9]

$$[H^+]^{(s)} = [H^+]^{(b)} e^{\frac{-e\psi_0}{kT}} \tag{2}$$

Dissociation constant for a weak acid (K_{a0}) at the IHP can then be expressed as in Equation 3.

$$HA \Leftrightarrow H^+ + A^-$$
$$K_{a0} = \frac{\left[H^+\right]^{(s)}\left[A^-\right]}{\left[HA\right]} \tag{3}$$

Combining Equation 2 and 3 and converting it to HH equation gives an equation that related the proton concentration in the bulk solution (pH) with the disassociation behavior at IHP. In Equation 4, pK_{a0} is the dissociation constant of the functional group and pK_a is the measured apparent dissociation constant. In order to calculate the correction factor, we need to estimate the value of Ψ_0 when α=1/2.

$$pH = pKa_0 - \frac{e\psi_0}{kT}\log(e) - n\log\left[(1-a)/a\right]$$
$$pKa = pKa_0 - \frac{e\psi_0}{kT}\log(e) \tag{4}$$

Based on Poisson-Boltzmann equation for 1-1 electrolytes, the charge density at IHP q of an isolated particle with radius of a can be expressed in terms of the surface potential as shown in Equation 5.[10] The second term in the equation gives a first-order correction for the surface curvature. This equation is valid when the thickness of the double layer is sufficiently thin compared with the particle diameter (κa >>1).

$$q = \frac{Q}{4\pi a^2} = \frac{\varepsilon\varepsilon_0 kT}{eZ}\kappa\left[2\sinh\frac{ze\psi_0}{2kT} + \frac{4}{\kappa a}\tanh\frac{ze\psi_0}{2kT}\right]$$
$$\kappa = \left(\frac{e^2\sum n_i^{\,b} Z_i^{\,2}}{\varepsilon\varepsilon_0 kT}\right)^{1/2}, \quad \kappa^{-1} = Debye\ Decay\ Length \tag{5}$$

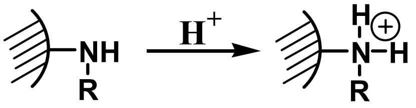
As mentioned before, the system we are studying possesses well-defined surface functional groups, which give us an opportunity to estimate the value of Ψ_0. For Cab-O-Jet™ 300 it is reasonable to have the following assumptions: 50 nm radius and with 2 μmol/m² of surface charge groups. When half of the acid groups have been neutralized in 10 mM of 1-1 electrolyte, the estimated Ψ_0 is 140 mV. Using this number the term $[-e\psi_0/kT\log(e)]$ gives a value of 2.4. This value can then be used to relate the apparent pKa to the pK_{a0} of carboxylic acid as shown in Equation 6. This exercise closes the discrepancy between the effective pKa and functional group pKa. In summary, the measured apparent dissociation constant is related to the functional group dissociation constant by the DDL correction factor.

Extended HH theory in Equation 1 can be modified to Equation 4 to explain the titration behavior of functional groups on particle surface.

$$pK_{a0} - e\psi_0/kT\log(e)$$
$$4.2 + 2.4 = 6.6 \tag{6}$$

This discrepancy between pK has been studied in the polymer systems before, this paper represents the first attempt on the pigment. Equation 4 can be used to correlate a wide range of effective pK with the pK_0 of the same functional group on soluble molecules.

Scheme 2: CB with surface amino functional groups



Recently, Cabot has developed technology of attaching polymers onto pigment surfaces.[11] What would be the dissociation behavior of polymers when they attach to the pigment particle surface? Once again, the well-defined surface structure by Cabot's technology offers us a chance to study the titration behavior of the polymer attached pigment particles. One such system we will report here is the pigment surface modified with poly-ethylene-imine (PEI) with a molecular weight of 1200, as illustrated in Scheme 2. PEI polymer, avaliable from BASF Corporation is prepared from aziridine with a globule structure consisting of primary, secondary, and tertiary amines.

The titration curve and HH plot of the PEI-1200 polymer itself are shown in the Figures 4 and 5. It has two distinctive regions of pKa and the average of the first one is around 8.8, which is about 1-2 units lower than the pK_{a0} of the primary amine, the same DDL explanation applies.

Titration and HH plot of the PEI modified CB are shown in Figures 6 and 7. It is obvious from that data that pigment surface does not seem to impact the dissociation behavior of PEI polymer itself. It is not surprising since the same set of rules that govern the behavior of polyelectrolyte like PEI, also apply to solid pigment particles.

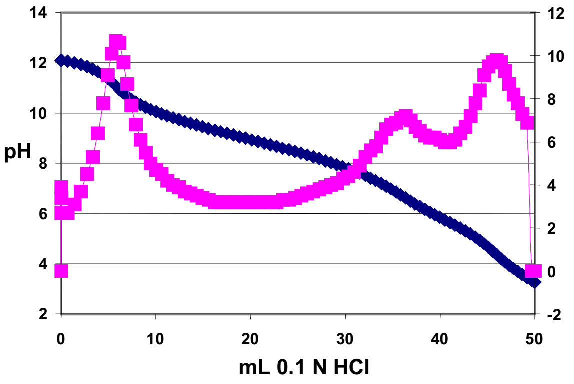


Figure 4. Titration of PEI-1200 polymer

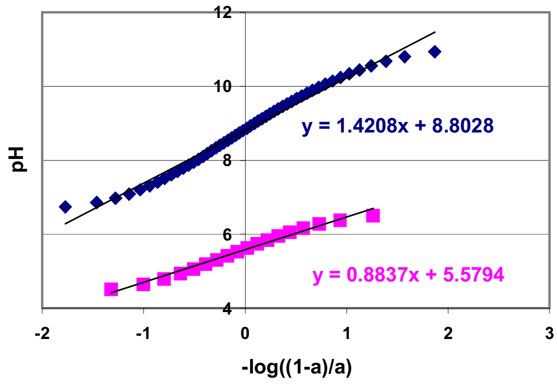


Figure 5. HH plot of PEI-1200 titration

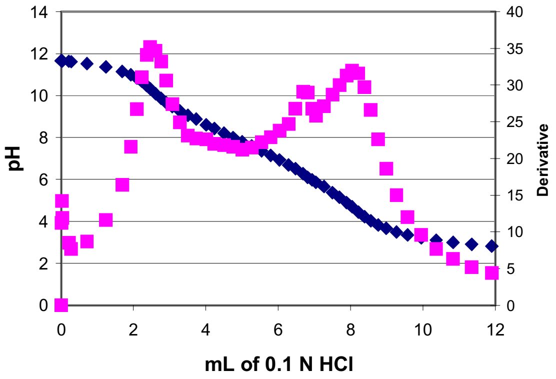


Figure 6. Titration of BP700/PEI-1200

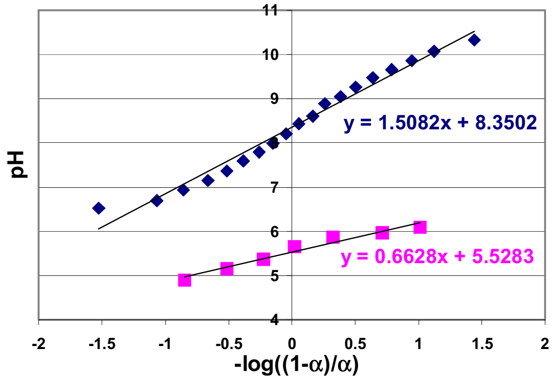


Figure 7. HH Plot of BP700/PEI1200 Titration

Conclusion

Potentiometric titration is an effective analytical method to study weak acid and base functional groups on pigment surface. Functional group density, nature, and its dependence on pH change can be derived from the titration curve. The discrepancy of apparent pK and pK_0 has been explained using DDL model. Well-defined functional groups on the pigment surface by Cabot's technology offers a good starting point for theoretic investigation. This study focused on the titration behavior of CB, and obviously, the learning can be applied to surface modified color organic pigments.[3]

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Biographies

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