A Bidirectional Acid-Base Charging Model for Triboelectrification: Experimental Verification by Inverse Gas Chromatography and Xerographic Charging of Toner and Carrier

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Abstract

Inverse Gas Chromatography (IGC) has been applied to study surface acid and base properties of xerographic developer materials. The data is interpreted using the recently proposed surface states bidirectional charge transfer model. In that model, charge exchange occurs between Lewis acid and basic surface states on both surfaces in both directions, with the net charge on a material the result of the sum of the charge transfer in both directions. In previous work, model carrier and toners were prepared, blending the toner particles with nano-particulate metal oxide surface additives. It was shown that the IGC K_a and K_b, the Lewis acid and Lewis base parameters, within the bidirectional charge model, fit very well the charge on the surface additives in these model toners. The current study extends that previous work, by measuring the IGC parameters, as well as xerographic charging, for a series of "real", rather than model toners, without surface additives. The complete set of toners was studied with two different carriers to form a triboelectric series that is consistent with the bidirectional acid-base charge transfer model. The magnitude and the sign of the charge exchanged between the toner surface and the carrier is determined by the relative surface K_a/K_b acid/base parameters for the toner and carrier surfaces. For toner surfaces with K_a/K_b greater than that of the carrier surface, predicted and observed toner charge is negative; while for toner surfaces with K_a/K_b less than that of the carrier surface, the predicted and observed toner charge is positive. It is further shown that the K_a/K_b parameters can be interpreted as defining work functions for these toner and carriers.

Introduction

In our previous work, a theoretical model was proposed that links the surface acid and base parameters of xerographic developer materials, as measured by Inverse Gas Chromatography (IGC), to the triboelectric charging of those materials.[1,2] The model fits within the surface states model, in the high density of states,[3-7] as described in detail previously.[1] IGC measured acid and base parameters represent the ability of materials to accept or donate electrons, respectively.[8,9] It was shown that toner charging with metal oxide surface additives, such as SiO_2, TiO_2, and Al_2O_3, agree very well with the model, and thus are well predicted by the IGC determined K_a and K_b values. For these oxides, it was also shown that the measured work functions, measured by Kelvin

potentials,[10] are also predicted by the K_a and K_b values determined by IGC. Thus, for metal oxides it has been shown that the work functions are controlled by the surface acid base properties.

In the current work, the relationship between the charging of parent toners without surface additives and the IGC determined K_a and K_b values are investigated. The results are compared to the predictions of our theoretical model based on IGC parameters, and interpreted in terms of a work function model.

Experimental

Six different styrene-acrylic cyan toners were evaluated in this study. These were not model materials, as in the previous work, but rather represent "real" toners with variations in composition and process. All toners were approximately the same size, 8 μm. Two different carriers were evaluated, carrier "A", which was 65 μm diameter, and carrier "B", which was 35 μm diameter. For each carrier the toner TC was kept constant, but it was different for each carrier. Samples were conditioned overnight at 20% RH. Toner samples with carrier A were charged on a paint shaker, with carrier B they were blended in a Turbula mixer, in both cases for 30' to reach an "equilibrium" tribo charge. Charge was measured as the peak of the q/d distribution on a Xerox charge spectrograph.

Acid and base interaction constants, K_a and K_b respectively, were obtained from IGC measurements, following well established procedures,[8,11,12] as detailed in our previous study.[2] The toner and carrier materials were packed directly into stainless steel columns, housed in a Varian 3400 gas chromatograph. The experimental uncertainty in acid-base parameters is about ± 8%.

Results and Discussion

The Acid-Base Charge Model

A brief summary of our acid-base charging model is described below. All details have been published previously.[1] In the high density surface-state charge model,[3] the charge of the toner is:

$$\text{Toner } q/m = A\,[\Phi_c - \Phi_t] \tag{1}$$

Here Φ_t and Φ_c are the toner and carrier work functions, respectively. The A factor is a composite of terms defined previously.[1,3] In this study, the data set for each carrier is at

equilibrium charge, with a fixed toner/carrier geometry and TC. Thus, the A factor is a constant for each carrier. However, data with carrier A and carrier B do have different A values.

In our acid-base charge model, toner charge is related to both acid and base properties of toner and carrier surfaces. While the model is applicable to any type of charge transfer, the excellent correlation of the electron donor/acceptor parameters, K_a and K_b, with charging data (shown by the data in ref. 2 and *vide infra* by the current data) suggests that charge transfer for these materials is due to electrons. Thus, the following discussion will assume electron transfer. This choice doesn't affect the conclusions here: other charge carriers could fit within the model.

Thus, in the exchange of charge between two materials, charge can transfer in either or in both directions:

a) electron transfer from toner electron donor (basic) sites to carrier electron acceptor (acidic) sites, which results in positive toner charge, and;

b) electron transfer from carrier electron donor sites to toner electron acceptor sites, which results in negative toner charge.

The effective work function of carrier or toner materials is the average of the work function of their respective acid and base sites, $\Phi_c = (\Phi_{ac} + \Phi_{bc})$ and $\Phi_t = (\Phi_{at} + \Phi_{bt})$, with Φ_{at} representing acidic toner sites, Φ_{bc} basic carrier sites, Φ_{bt} basic toner sites, and Φ_{ac} acidic carrier sites. The observed work function is then a global average over the work functions of individual acid and base sites.

Through Gibbs type relationships, we can relate the acid and base parameters to their corresponding chemical potentials, and thus to the apparent work functions, where Φ^o is a constant:[1]

$$\Phi_t = \tfrac{1}{2} \Phi^o + \tfrac{1}{2} kT \ln (K_{at}/K_{bt}); \; \Phi_c = \tfrac{1}{2} \Phi^o + \tfrac{1}{2} kT \ln (K_{ac}/K_{bc}) \quad (2)$$

Eq. (2) predicts that the apparent toner work function is directly related to the log of the ratio of K_a to K_b values, for toner acid and base sites, respectively. A larger acid to base ratio results in a larger work function; a smaller ratio, a smaller work function.

Substituting Eq. (2) into Eq. (1) gives:

$$\text{Toner } q/m = -(A/2) kT [\ln (K_{at}/K_{bt}) - \ln (K_{ac}/K_{bc})] \quad (3)$$

Eq. (3) predicts that a plot of toner charge vs. $\ln(K_{at}/K_{bt})$, for a fixed carrier, is linear with a slope of $-(A/2)kT$. That is, negative toner charge increases with an increasing ratio of toner acid to base parameters, if K_{at}/K_{bt} is greater than K_{ac}/K_{bc}. Similarly, it predicts that positive toner charge increases with decreasing ratio of toner acid to base parameters, if K_{at}/K_{bt} is smaller than K_{ac}/K_{bc}. Finally, Eq. (3) predicts that toner charge is zero if $K_{at}/K_{bt} = K_{ac}/K_{bc}$, where toner and carrier acid/base ratios are equal.

Previous Verification of Acid-Base Model for Metal Oxide Toner Additives

In our previous study,[2] toner charge was shown to correlate well with IGC determined K_a/K_b ratios for model toners covered with metal oxide surface additives. Those developers were selected so that the developer charging was dominated by the charging of the metal oxide on the toner with the carrier PMMA polymer coating. The effect of the toner resin itself was not studied. The results for the three hydrophilic oxides, SiO_2, TiO_2, and Al_2O_3, and

two hydrophobic oxides, Wacker H2050™ SiO_2 and Degussa R812™ SiO_2 measured previously, are reprised here in Fig. 1.
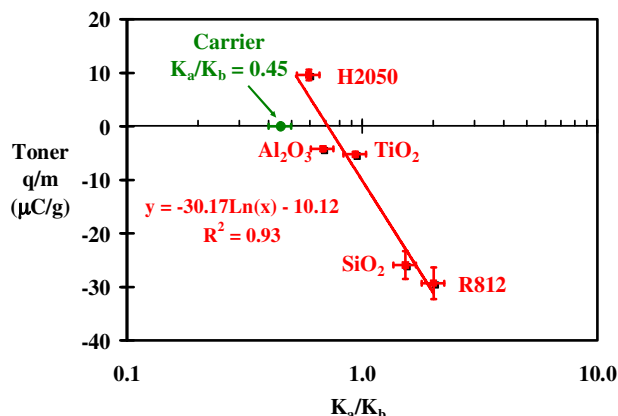

Figure 1. *Toner surface additives charge dependence on log (K_a /K_b).*

As predicted by Eq. (3), the toner charge is increasingly negative as the toner K_a/K_b ratio increases, with the expected logarithmic dependence. Also as predicted by Eq. (3), within experimental error, the charge exchanged is zero when the K_a/K_b ratio for the metal oxide additives is the same as the carrier K_a/K_b ratio. Neither K_a nor K_b alone correlated with toner charge.[2] Thus, for metal oxide particles charging against a PMMA coated carrier, the acid-base bidirectional charge model verified well.

Also in the previous study, oxide work functions determined by CPD, for the three hydrophilic oxides, were evaluated in light of the oxide surface acid and base constants, K_a and K_b, determined by IGC. The result is reprised in the semi-log plot in Fig. 2. Oxide work functions are plotted with respect to the corresponding oxide K_a/K_b ratios. The plot shows the expected linear dependence of oxide work function with oxide $\ln (K_a/K_b)$, as predicted by Eq. (2). And as predicted, the more negative charging the oxide, the larger the K_a/K_b ratio, and the larger the work function.
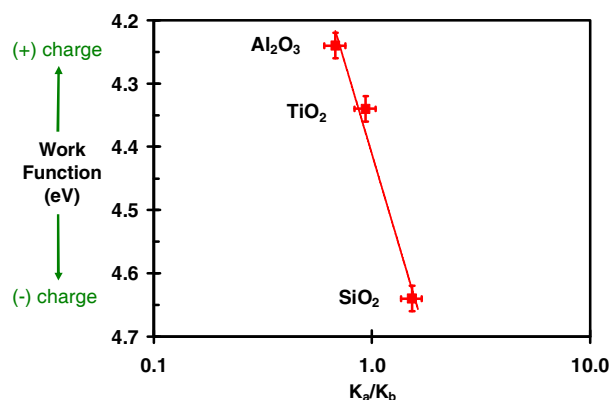

Figure 2. *Dependence of oxide work functions on oxide (K_a/K_b) ratio.*

Verification of Acid-Base Model for Toner Particles

Thus, our previous work has shown that metal oxide additives charging against a carrier follows our acid-base model. However,

that work did not study the effect of either changing the toner particle itself or changing the carrier, two aspects that will now be addressed. Charge was measured for six cyan toners, all without additives, on two different carriers, carrier "A" and carrier "B", under dry conditions. Charging was compared to the IGC determined K_a/K_b ratio, measured on dry samples. The toner charge with carrier A is plotted with the toner K_a/K_b ratio in Fig 3.
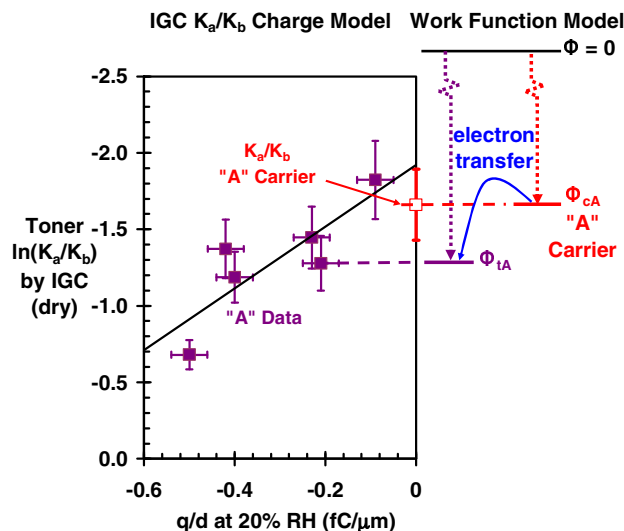

Figure 3. The relationship between toner ln (K_a/K_b) values and toner charge for six toners charged with carrier A, and the comparison to a work function model

The K_a/K_b ratio is plotted on the y-axis, with charge on the x-axis, to more clearly show the relationship of the K_a/K_b ratio to the work function model. For this set of six toners charged with carrier A, the plot of ln (K_a/K_b) is linear with toner charge, measured as peak q/d, with charge increasing with K_a/K_b ratio. Within experimental error, the point of zero toner charge is the point where toner and carrier K_a/K_b ratios are equal. That point is predicted to be -1.92±0.44 (95% CI) from the intercept of the toner data, in agreement with the measured value from the carrier of -1.66±0.2. Varying the toner particle composition changes the charge and K_a/K_b values in a manner totally consistent with Eq. (2).

The toner particle K_a/K_b values, and thus charge, are also consistent with the proposed work function model, where the work function of the toner and carrier are directly related to the ln (K_a/K_b) of the materials.[1,2] As the K_a/K_b ratio of the toner or carrier material increases, the corresponding work function, Φ, would increase. If the work functions of toner and carrier are equal, the charge exchanged is zero. As the work function of the toner becomes larger than that of the carrier, the electron transfer is from the carrier to the toner, providing negative charge to the toner.

The same six toners were also evaluated as developers with a second carrier "B". The resulting toner charge is plotted with respect to the corresponding K_a/K_b values as shown in Fig. 4.
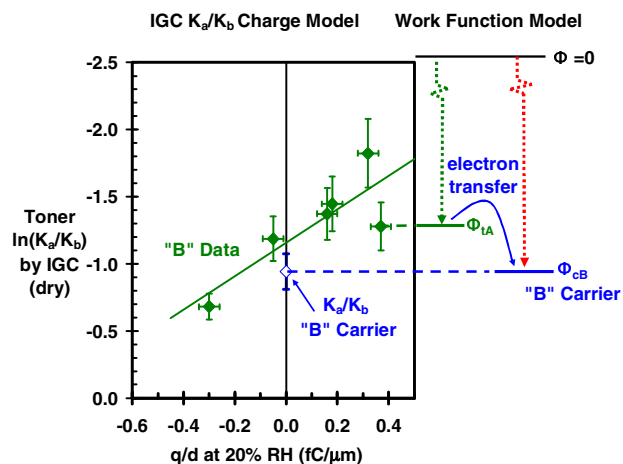

Figure 4. The relationship between toner ln (K_a/K_b) values and toner charge for six toners charged with carrier B, and the comparison to a work function model.

As for carrier A, the plot of ln(K_a/K_b) for the same six toners on carrier B is linear with the toner charge. Again, within experimental error, the point of zero charge for the toner is the point where the toner and carrier K_a/K_b ratios are the same (toner data predict -1.15±0.21 at 95% CI compared to the measured value of -0.94±0.13 for carrier B). For carrier B, the carrier K_a/K_b ratio is significantly shifted with respect to that for carrier A. As a result, the four toners with smallest K_a/K_b ratio (most negative ln K_a/K_b) have a smaller K_a/K_b ratio than the carrier, and thus these toners now charge positive not negative. As before, the two toners with the highest K_a/K_b ratio, where the ratios are larger than for the carrier, show negative charge. As with carrier A, the toner particle composition changes the charge and K_a/K_b values in a manner totally consistent with Eq. (3). Further, the effect of the shift in the carrier K_a/K_b on charge is also as predicted by Eq. (3).
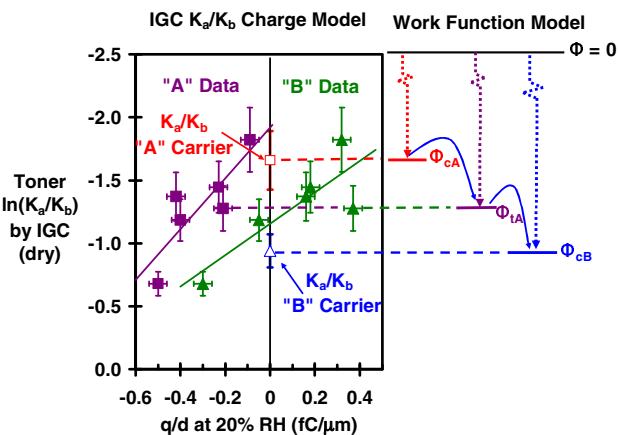

Figure 5. The relationship between toner ln (K_a/K_b) values and toner charge for six toners charged with carrier A and carrier B, and the comparison to a work function model.

Fig. 5 shows more clearly the relationship between the charge of the six toners on both carrier A and carrier B. In particular, the shift in the carrier K_a/K_b value between carrier A and carrier B is clearly linked to the shift in the charge of the six toners, and to the change in the sign of the charge on four of the toners from negative to positive. The results are clearly consistent with the work function model for these toners and the two carriers.

Fig. 6 shows another way of illustrating all the data in Fig. 5. According to Eq. (3), all the toner data with both carriers should fall along a single line, if $\Delta\ln(K_a/K_b)$ is plotted with the toner charge, where $\Delta\ln(K_a/K_b)$ is defined as $[\ln(K_{at}/K_{bt}) - \ln(K_{ac}/K_{bc})]$, i.e. the difference in the toner and carrier $\ln(K_a/K_b)$ ratios. The expected slope of the line is $-(A/2)kT$ and the expected intercept is zero. Since A is different for the measurements with carrier A and carrier B (TC, carrier size and density), the A value for each dataset was taken as a fitting constant between the two data sets. There are no other adjustable parameters. The plot in Fig. 6 shows an excellent fit to Eq. (3), with a linear dependence of charge with $\Delta\ln(K_a/K_b)$, and a best fit line that passes through the origin, within experimental error, predicting a q/d of -0.11±0.14 for a 95% CI. The direction of charge exchange is negative if $\Delta\ln(K_a/K_b)$ is positive and positive if $\Delta\ln(K_a/K_b)$ is negative, in agreement with the predictions of Eq. (3).
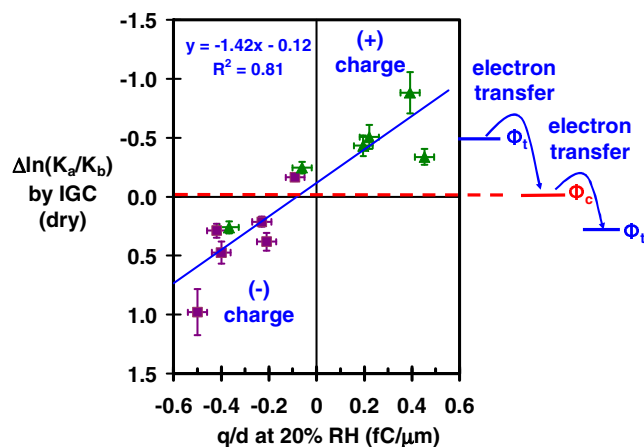

Figure 6. *The relationship between developer $\Delta\ln(K_a/K_b)$ values and toner charge for six toners charged with carrier A and carrier B, and the relationship to the toner and carrier work functions.*

Conclusions

Xerographic toners and carriers have been evaluated for developer charging and for surface acid/base properties using IGC. The results for six different cyan toners charged with either of two different carriers are completely consistent with our previously proposed model for charging. This model proposes bidirectional electron transfer from toner basic sites to carrier acidic sites, and from carrier basic sites to toner acidic sites. The result is a net charge exchange, which is the average over these charge exchange events. The result is an observed charge that increases linearly with $\ln(K_a/K_b)$. Toner charge is zero when the K_a/K_b for the toner and carrier are equal, negative when the toner K_a/K_b is larger than the carrier K_a/K_b, and positive when the toner K_a/K_b is smaller than the carrier K_a/K_b. Each one of these aspects has been verified for the six toners and two carriers, including accurately predicting the point of zero charge and the change of charge from negative to positive. The data is shown to be consistent with the ratio of K_a/K_b determining an "effective" work function that is the average of the work functions of the acid and base sites of each material in the charge exchange. These results, along with our previous results, verify all the predictions of our acid-base mechanism, for different toner particles, different metal oxide toner surface additives, and different carriers.

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Biography

Rick Veregin has a Ph.D. in Chemistry from the University of Guelph (1985). For the last 23 years Rick has worked at the Xerox Research Centre of Canada, where he currently manages the Developer Physics group, focused mainly on developer design for the Xerox Emulsion/Aggregation toner technology. Rick is an inventor on more than 70 US patents and an author of nearly 60 scientific refereed publications. Rick is a member of the IS&T and ACS.