Understanding the Influence of Surface Acid and Base Properties and Water on Work Functions and Triboelectric Charging Using Inverse Gas Chromatography

Rick Veregin, Maria McDougall, Mike Hawkins, Cuong Vong and Vlad Skorokhod, Xerox Research Centre of Canada, Mississauga, Ontario, Canada and Henry Schreiber, Department of Chemical Engineering, École Polytechnique, Universite de Montréal, Montréal, Québec, Canada

Abstract

Inverse Gas Chromatography (IGC) has been applied to study surface Lewis acid and base properties of xerographic developers. Model carrier and toners were prepared and the toners blended with metal oxide surface additives: silica, titania and alumina. The effect of additives on charging, work functions and surface chemistry, as measured by IGC, was studied. All properties were evaluated as a function of relative humidity, to improve understanding of the effect of water as relative humidity increases. Results under dry and wet conditions generally support a work function model for charging, where work functions are determined by surface acid-base properties. Adsorption of water onto surfaces can be followed by IGC, work functions and charging. All provide a consistent picture that water adsorption leads to surfaces that have essentially the properties of adsorbed water at sufficiently high RH.

Introduction

Metal oxide surface additives, such as SiO_2, TiO_2, and Al_2O_3, are ubiquitous in toners. One key function of these oxides is to control toner charging. In turn the charge provided by the oxide is controlled by the oxide work function.[1] In order to understand the chemical basis for oxide work functions and charging, Inverse Gas Chromatography (IGC), a powerful method to study surfaces, has been used to measure Lewis acid and base parameters for developer materials. These parameters represent the ability of materials to accept or donate electrons, respectively.[2,3] Recently we developed a surface state model for triboelectrification that integrates Lewis acid-base concepts, and their IGC related parameters, which enables prediction of charging and work functions.[4,5] In further work, we showed that work functions and charging of oxide additives are in good agreement with this Lewis acid-base surface state model.[4,6]

Fig. 1 shows a schematic of this Lewis acid-base surface state model,[5] where ϕ_{at}, ϕ_{bt} are work functions for acidic and basic toner sites, and ϕ_{ac}, ϕ_{bc} work functions for acidic and basic carrier sites. As the model shows, the observed work function of toner, or carrier, is an average over all acid and base sites. This results because charge exchange, mediated by electrons, is bidirectional: both from toner basic (donor) sites to carrier acidic (acceptor) sites and from carrier basic sites to toner acidic sites.

There are two key predictive equations from this model. Eq. (1) predicts a material's work function based on that material's acid and base parameters. For toner these are K_{at} and K_{bt}, respectively, which are measured by IGC. Here, R is the gas constant, T is temperature and ϕ^o is a constant, representing the work function of the reference state for the K_a and K_b values, which can be obtained from the fit of Eq. (1) to the experimental data.

$$\phi_t = \phi^o + \tfrac{1}{2} RT \ln (K_{at}/K_{bt}) \tag{1}$$

Eq. (1) shows that the apparent measured toner work function is directly related to the ratio of the K_a to K_b values for the toner acid and base sites. For carrier, there is a similar equation, where the acid and base parameters are K_{ac} and K_{bc}.

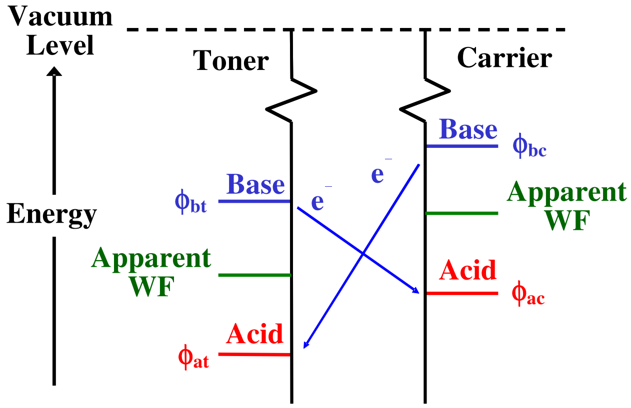

Figure 1. *Toner-carrier charge exchange interactions for Lewis acid-base surface state model. Arrows show the direction of the electron flow.*

Eq. (2) expresses toner charge based on the acid and base parameters of the toner and carrier.

$$\text{Toner } q/m = -(A/2)\, RT\, [\ln (K_{at}/K_{bt}) - \ln (K_{ac}/K_{bc})] \tag{2}$$

Eq. (2) predicts that toner q/m for fixed carrier, is linear with ln (K_{at}/K_{bt}), with slope $-ART/2$. A is constant.[5] Negative charge increases with increasing toner acid-base ratio, and charge is zero if the carrier and toner acid base ratios are equal, $K_{at}/K_{bt} = K_{ac}/K_{bc}$.

Work to date relating IGC determined acid-base parameters, charge, and work functions has been limited to dry conditions, where the effect of water is not dominant. The intent of the current work is to study the effect of high relative humidity (RH), where water plays a dominant role. The study will test our Lewis acid-base surface state model and will provide a deeper understanding of the role of water in triboelectrification.

Experimental

Contact potential differences (CPD) were measured previously using a non-contact, electrostatic voltmeter, and converted to work functions.[1] Surface additives studied were Degussa A300™ SiO_2, P25™ TiO_2 and Al_2O_3 C™. For triboelectric charge, oxides were dry-blended on 4.6 µm PMMA model toner particles for 30 s at 15 krpm, with 100% toner surface coverage.[7] The carrier was a 65 µm irregular iron core, powder-coated with 1 wt% of the above PMMA particles. Developers were prepared at 4% toner concentration, equilibrated overnight at the desired RH, and then paint shaken for 15 min to reach equilibrium charge. Acid and base interaction parameters, K_a and K_b respectively, were obtained from IGC measurements, following well established procedures.[3,8,9] The metal oxide and carrier stationary phases were packed in stainless steel columns, housed in a Varian 3400 gas chromatograph. Substrate temperatures ranged from room temperature to about 80°C. RH was controlled by sweeping the columns with He carrier gas, which first passed through a dead space volume where RH was established with salt solutions of specific concentrations. The dispersive interaction capacity of the stationary phases was obtained from retention volumes of n-alkane probes, injected at extreme dilution. Polar vapors, selected from Gutmann's tabulations,[2] then led to evaluations of K_a and K_b. Retention volumes were collected in at least triplicate, with experimental uncertainty ≤ ±4%. The experimental uncertainty in acid-base parameters is about ± 8%. Further details have been previously published.[6]

Results and Discussion

This work will study the adsorption of water onto the toner oxide additives and onto carrier as measured by IGC K_a/K_b values. It will also study the WF and charge of the oxides and charging of the oxides with water adsorption. As water adsorbs onto a surface with increasing RH, the surface will look more and more like water. One might expect, at high enough RH, that the surface will be only water, and thus it properties will be dominated by those of water.

One can postulate two mechanisms to explain the effect of water on WF and charging. The first is that the WF of water controls charge. That is, water is active in the charge exchange process, and thus at high RH its WF will dominate charge. One might think that water adsorption on toner and carrier leads to all surfaces coming to a common WF: that of surface water. Charge would then go to zero at high RH. However, water adsorbed on a surface can interact with the surface, changing the WF of the adsorbed water. Thus, if carrier and toner (in this study, the oxide) have surface adsorbed water of different WF values, all surfaces will not be the same. Two water covered surfaces thus might still produce some charge, due to the difference in water WF. However, if all surfaces come to the same WF for adsorbed water, charge will also drop to zero.

A second postulate is that water simply interferes with charging: it blocks charge sites on toner and carrier from making contact with each other, disabling charge exchange. The actual WF of the water does not play an active role in charging. For this case we expect charge to decrease to zero when water adsorption completely covers the surface.

In either case, it is also possible that water also reduces charge because it allows charge to dissipate (e.g. back transfer due to conductivity). This can happen if water is an inert blocking layer or if it is an active charging agent due to its WF.

Fig. 2 shows triboelectric charge of toner with varying oxide additives varying with RH. Since the base toner particles and carrier coating are both PMMA, charging only occurs between the oxide and PMMA carrier surfaces (charge is zero without oxide). All oxides show lower negative charge at higher RH, and all are very close to zero charge at 85% RH, although alumina appears slightly positive. Similar results were seen in a previous study,[1] although all intercepts at 100 %RH were identically zero.

The data in Fig. 2 is in reasonable agreement with either a blocking mechanism or active participation of water through its WF, with near zero charge at high RH, as extrapolation of oxide charging from 85% RH to 100% RH are all close to zero. The alumina charge goes slightly positive, which would not be consistent with a blocking mechanism. However, the positive shift is small, and we cannot say conclusively that it is not zero within experimental uncertainty. Silica extrapolates to positive charge, but it is possible that silica is fully covered with water at 85% RH, in which case the linear extrapolation at higher RH may not correct, and silica would remain at zero charge at RH values about 85%.

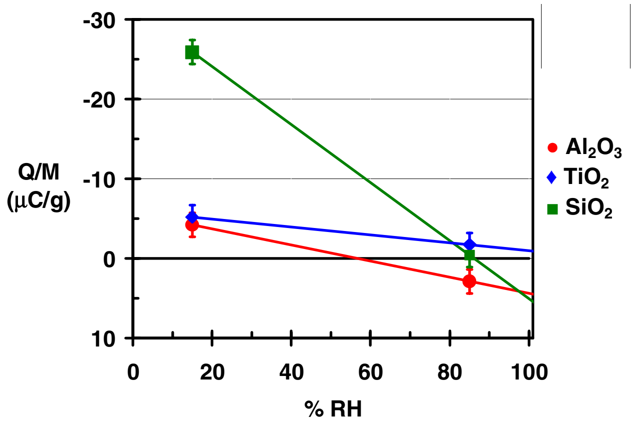

Figure 2. Measured charge with RH of metal oxide on toner vs. PMMA carrier

Fig. 3 shows the K_a/K_b of the oxides and of the carrier measured as a function of RH. The K_a/K_b values for all of the oxides converge on a value of 1.20±0.02 at 100% RH. Clearly at 100% RH all of the surfaces are completely covered with water. Their surface chemistry is not dependant on the nature of the oxide, as there is no exposed oxide surface. Thus, the limiting value for K_a/K_b of 1.20 corresponds to the K_a/K_b of surface adsorbed water. Based on a linear extrapolation the carrier surface K_a/K_b appears to extrapolate to a somewhat different WF than the oxides at 100% RH. However, the observed value of 0.87±0.16 eV (quoted errors are ±s) is within the 95% CI of the oxide limiting value. It should also be noted that the extrapolation from 80% to 100% RH for the PMMA carrier may not be linear, and may adsorb proportionally more water as RH approaches 100%. Note that if the difference in intercept at high RH is real, from Eq. (2) this would predict a negative toner charge with all the oxides at 100% RH, due to the larger K_a/K_b ratio for the oxides compared to carrier. This is not consistent with the data in Fig. 2. Thus, all the oxides, and the carrier surface, do appear to generally approach the same K_a/K_b value at 100% RH, that of surface water.

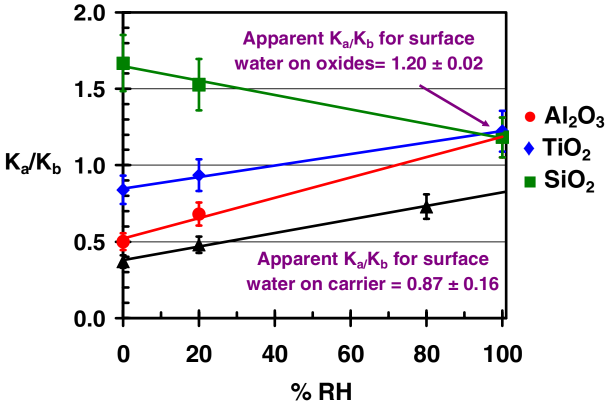

Figure 3. *Measured K_a/K_b values of metal oxide and carrier particles with RH*

Fig. 4 shows the oxide WF as a function of RH. As with K_a/K_b, all oxides converge on a common WF at 100% RH, which corresponds to the WF for complete coverage of adsorbed surface water, 4.19±0.02 eV. This observed WF for surface water is somewhat less than the WF of bulk water,[1] 3.93±0.01 eV. The difference is due to the interaction of adsorbed water with the oxide surface. Clearly the oxide WF at 100% RH is controlled by the WF of water. The large insulative carrier particles are not compatible with the measurement method used to determine oxide WF values,[1] so no WF values for the carrier are available.

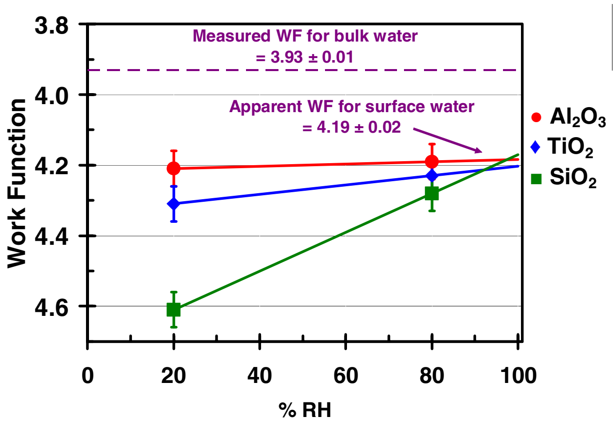

Figure 4. *Work function of oxides under varying RH conditions*

Fig. 5 shows a strong relationship between charge of the oxide on the toners with the PMMA carrier and oxide WF. Higher oxide WF provides increased negative charge. The data shows clearly that oxides provide zero charge at the WF for adsorbed surface water, taken from Fig. 4. Thus, the average measured WF at zero charge, averaged over all the oxides, is 4.21±0.04 eV, identical to the apparent WF for surface water at 4.19±0.02 eV.

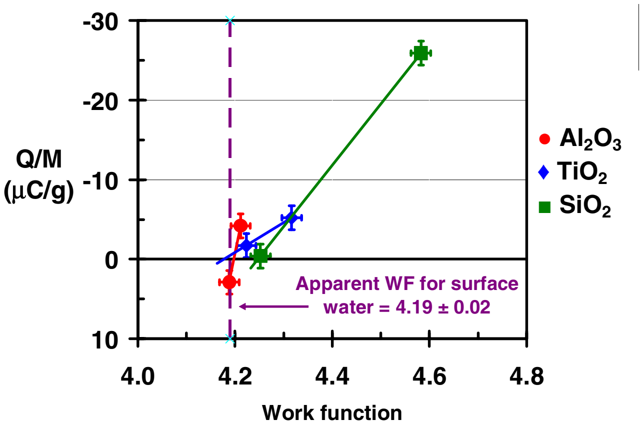

Figure 5. *Charge of oxide particles on toner with oxide work function*

Eq. (1) predicts that the oxide WF should be linearly dependant on the log of the K_a/K_b ratio, with a higher acid-base ratio corresponding to a higher WF. Fig. 6 plots oxide WF with their K_a/K_b values under dry and wet conditions. For each RH, the observed WF is linear with K_a/K_b, and the WF increases with the K_a/K_b ratio, both as predicted by Eq. 1. However, higher RH shifts the linear relationship by -0.25 eV, a shift to lower WF. Clearly, the effect of water on WF is more complex than predicted by Eq. 1, although each RH condition follows Eq. 1 very well. The problem is that Eq. (1) assumes that measured oxide WF and K_a/K_b are that of the oxide surface. It does not include the concept that water on the oxide also contributes to the measured oxide K_a/K_b and WF values. This will be addressed in a future publication.

Note that the shift in WF and K_a/K_b with RH does show a clear trend. The extrapolation from low to high RH, for each oxide, results in all data converging, in both WF and K_a/K_b dimensions, to a single point that intersects the apparent WF and K_a/K_b for surface water. Thus, water does indeed control both K_a/K_b and WF for all the oxides, as relative humidity increases

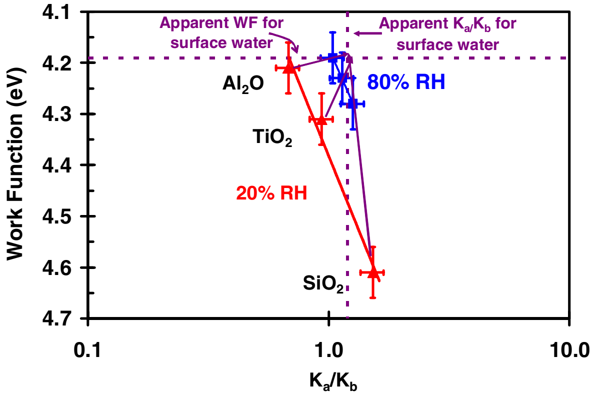

Figure 6. *Work function of metal oxide additives as a function of the IGC determined K_a/K_b ratio, under both wet and dry conditions.*

Eq. (2) predicts that toner charge from the oxides, with a fixed carrier, will be linear with the log of oxide K_a/K_b, as shown in Fig. 7. Also as predicted by Eq. (2), the slope is negative for each data set, with larger K_a/K_b ratios producing more negative toner charge.

The low (15% RH) and high (85% RH) charge data follow separate, but parallel linear relationships with log (K_a/K_b). Eq. (2) There is an offset between the two data sets, where the 15% data intercepts zero charge at $K_a/K_b = 0.65\pm0.16$, while the 85% data intercepts zero charge at 1.17±0.16. The difference between the two intercepts is a +0.52±0.21 shift with higher RH. Eq. (2) predicts that zero charge should occur when K_a/K_b for the oxide on the toner matches the K_a/K_b of the carrier. Those points, which are the K_a/K_b values for the carrier, are $K_a/K_b= 0.44\pm0.04$ at 15% RH and 0.75±0.06 at 85% RH, a K_a/K_b shift of +0.31±0.07 with RH (all errors ±1s). Within 95% CI, there is agreement between the observed q/m = 0 intercepts and the observed carrier K_a/K_b values, as predicted by Eq. (2). The shift in K_a/K_b for the point of zero charge between 15% and 85% RH is consistent with the shift in the carrier K_a/K_b, due to the adsorption of water. This is a powerful confirmation of the acid-base surface states model. Also, as water is adsorbed on each oxide all data in Fig. 7 converge toward a common point (excepting a slight positive shift for alumina), the apparent K_a/K_b for surface water and zero charge. This is expected if all surfaces, oxide and carrier alike are fully covered with water at sufficiently high RH, and consistent with the other results of this study.

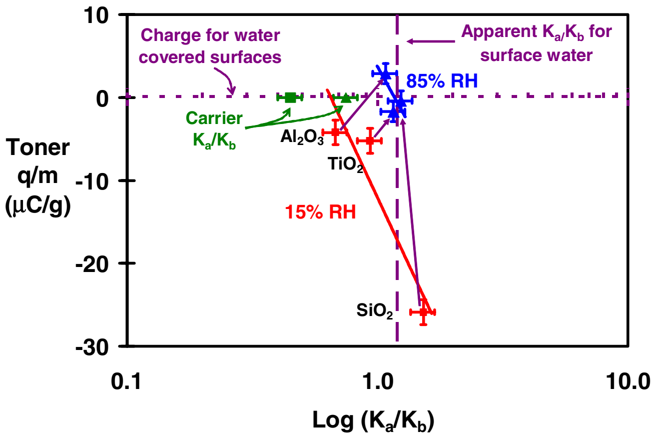

***Figure 7.** Charge of metal oxide additives on toner as a function of IGC determined K_a/K_b ratio under wet and dry conditions.*

Unfortunately, this work cannot distinguish the two different mechanisms for the effect of water on charge. Since water surfaces are totally covered with water at sufficiently high RH, WF and K_a/K_b of all surfaces are essentially identical, that of surface water. Thus, no charge exchange is expected, even if water plays an active role in charge through its WF, as the surfaces are essentially identical. On the other hand, since surfaces are fully coated with water, no charge exchange between the surfaces would be possible if water has a blocking effect on charging.

Conclusions

The acid-base surface state charging model is supported by work function, IGC determined K_a/K_b acid/base ratios, and toner charge with native (untreated) metal oxide surface additives. The model provides a generally consistent fit with data collected at both low and high RH. Charge is controlled by the oxide work functions, which is in turn controlled by the chemistry of the oxide, and by the adsorption of water. At high RH, approaching 100%, all data is consistent with an essentially complete coverage of all surfaces with water. Thus, all properties of the surfaces at high RH reflect those of surface water, both K_a/K_b and WF. We cannot, based on this data, distinguish between a model where water takes an active part in the charging process, via its work function, or plays a passive blocking function, preventing contact of charging sites on the toner and carrier as relative humidity increases. Further work is also needed to incorporate the effect of surface water on work functions in the acid-base surface state charge model.

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Author Biography

Rick Veregin has a B.Sc., M.Sc. and Ph.D in Chemistry. For the last 21 years he has worked at the Xerox Research Centre of Canada, where he manages the Developer Physics group. His interests focus on the interface of chemistry, physics and surfaces in xerographic materials. Rick is a member of IS&T and ACS, and is an author of over 50 refereed publications and an inventor of more than 60 US patents.