Liquid Toner Charging Mechanisms: Electrophoretic Mobilities of Copper Phthalocyanine Pigment Dispersions

Roland I. Keir, Anthony Quinn, Paul Jenkins, John C. Thomas, John Ralston
University of South Australia, Adelaide, S.A., Australia
and Olga Ivanova
Research Laboratories of Australia, Adelaide, S.A., Australia

Abstract

Electrophoretic mobilities of copper phthalocyanine (CuPc) particles dispersed in Isopar G™ are reported. The mobilities were measured as a function of particle charging agent (PCA) concentration using Phase Analysis Light Scattering (PALS). The role of Particle Stabilizing Agents (PSAs) at the particle surface was also investigated. An equilibrium site binding model can describe the experimental data adequately. Conductivity measurements and adsorption isotherms facilitate an overall description of particle charging in these systems.

Introduction

The charging and stability of particles suspended in nonpolar media are of particular interest in relation to liquid toners. Image quality depends upon the ability to design ink toner systems that are stable, highly charged and well dispersed. Whereas charging processes in aqueous media are well understood, there is considerable debate about the role of surfactants and polymers in nonpolar dispersions.[1,2]

It has been shown that the electrophoretic mobility of a particle in nonpolar media can be controlled by use of surfactants at the particle-solvent interface.[3-5] Furthermore, a number of models have been developed to describe the charging mechanisms that occur in these systems.[6,7]

The aim of the present research is to investigate the influence of additives such as particle charging and stabilizing agents on the electrophoretic mobility of CuPc particle dispersions. The development of a state-of-the-art Phase Analysis Light Scattering apparatus[8] has enabled the rapid, reliable measurement of nonpolar dispersions with very low electrophoretic mobilities. We report an investigation of a number of simple toner systems and relate the results to a refined site-binding model.[9]

Experimental

A CuPc ink concentrate (10 wt%) was ball-milled for 72 hours. The concentrate was diluted to 1 wt% using Isopar G™, with varying amounts of Particle Charging Agent, $ZrO(Oct)_2$, and Particle Stabilizing Agent (PSA 1 or PSA 2). PSA 1 was based on an acrylic copolymer containing an amide functional group and PSA 2 was based on a methacrylate polymer. A description of the samples is given in Table 1. The 1 wt% dispersions were tumbled overnight before being analyzed. For PALS, the dispersions were centrifuged lightly to reduce the particle concentration.

The conductivities were measured with a Scientifica conductivity meter (Model 627). Adsorption isotherms for $ZrO(Oct)_2$ dispersions were obtained using the depletion technique. Inductively Coupled Plasma (ICP) was used to determine residual Zr. The PALS measurements were performed using apparatus constructed in our laboratories. The typical electrode voltage of 160 V was applied across an electrode gap of 2.13 mm. The electrodes were made from bright palladium. The electrophoretic mobilities were determined from the amplitude-weighted phase difference signal.[8] All measurements were recorded at 25ºC. Details of the above techniques can be found in a previous paper.[9]

Table 1. Ink dispersions used. Concentrations refer to 1 wt% pigment dispersions.

	Description	Change in Series
S1	CuPc + Isopar G	$ZrO(Oct)_2$ (0 to 1 wt%)
S2	+ 0.1 wt% PSA 1	$ZrO(Oct)_2$ (0 to 1 wt%)
S3	+ 0.2 wt% PSA 1	$ZrO(Oct)_2$ (0 to 1 wt%)
S4	+ 0.1 wt% PSA 2	$ZrO(Oct)_2$ (0 to 1 wt%)
S5	+ 0.2 wt% PSA 2	$ZrO(Oct)_2$ (0 to 1 wt%)
S6	+ 0.06 wt% $ZrO(Oct)_2$	PSA 1 (0 to 2 wt%)
S7	+ 0.06 wt% $ZrO(Oct)_2$	PSA 2 (0 to 2 wt%)

Results and Discussion

The dependence of the electrophoretic mobilities on the amount of $ZrO(Oct)_2$ present in the dispersions is shown in Figure 1 for series S1 to S5. There is a maximum in the

mobility for each series. Thus a maximum in charging occurs at approximately 0.06 wt% $ZrO(Oct)_2$, after which, the mobility decreases due to neutralization of the charged sites on the pigment surface. Furthermore, the addition of stabilizing agents increases the overall electrophoretic mobilities of the dispersions. For example, the addition of 0.1 wt% of PSA 1 increases the mobilities by approximately 30%. The addition of 0.1 wt% of PSA 2 results in even larger mobilities. Overall, the functional form of the data remains the same, suggesting that charge neutralization is associated with the quantity of $ZrO(Oct)_2$ present.
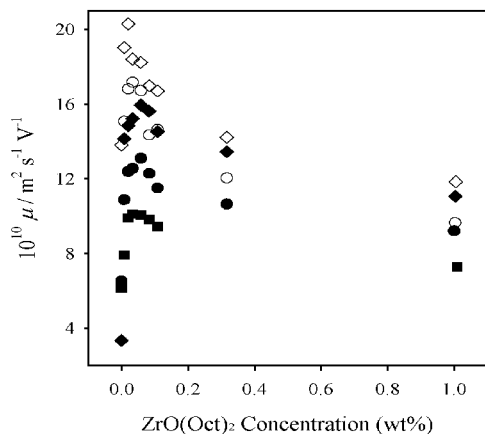

Figure 1. Electrophoretic mobility vs. ZrO(Oct)$_2$ concentration for S1 (squares), S2 (filled circles), S3 (open circles), S4 (filled diamonds) and S5 (open diamonds).

Figure 2 shows the variation of electrophoretic mobility with PSA 1 or 2 concentration at a fixed $ZrO(Oct)_2$ concentration of 0.06 wt%, which corresponds approximately to the maximum in mobilities reported in Figure 1. Here the mobility increases to a maximum and decreases sharply at polymer concentrations of ~ 0.2 wt% for both polymers. This corresponds to polymer monolayer coverage of the particles (not reported here). Above 0.2 wt% polymer, the particles are covered in a monolayer (or more) of polymer and the decrease in the mobility may be due to a shift in the location of the shear plane.[10]

The conductivity of each series was measured and the results are given in Figures 3 and 4. In Figure 3, the lowest conductivities were for series S1, the dispersion without PSA additives. The presence of 0.1 wt% PSA 2 results in a higher conductivity than does 0.1 wt% PSA 1. Furthermore, the dispersions containing 0.2 wt% PSA 1 and PSA 2 have conductivities that are convergent. This can be explained by Figure 4, which shows the conductivities for series S6 and S7. It is evident that dispersions containing PSA 1 have much higher conductivities than those containing PSA 2. This implies that in the presence of increasing amounts of PSA 1, the number of charge carriers in solution increases. Note also that below 0.2 wt% polymer concentration, the PSA 2 dispersions have higher conductivities than those containing PSA 1. This explains the trend seen in Figure 3

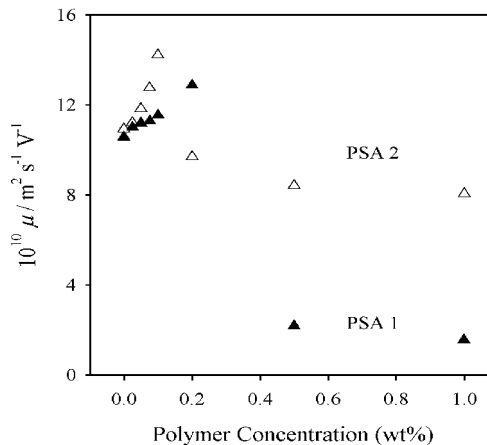(i.e. where systems containing PSA 1 display higher conductivities).

Figure 2. Electrophoretic mobility vs. PSA concentration for a fixed 0.06 wt% ZrO(Oct)$_2$ concentration. S6 (filled triangle) and S7 (open triangle).

Further comparison of Figure 4 can be made with the mobilities reported in Figure 2. A crossover occurs in both cases at ~0.2 wt%. At higher polymer concentrations there are more ions present in the dispersions containing PSA 1 but the mobilities are lower than those of the PSA 2 dispersions. This indicates that free PSA 1 increases the conductivity of the dispersions by its interaction with $ZrO(Oct)_2$. However, PSA 2 has a greater ability than PSA 1 to assist $ZrO(Oct)_2$ in charging the surface, even when PSA 2 is fully covering the surface. An interaction between $ZrO(Oct)_2$ and PSA 2 on the surface is implied.
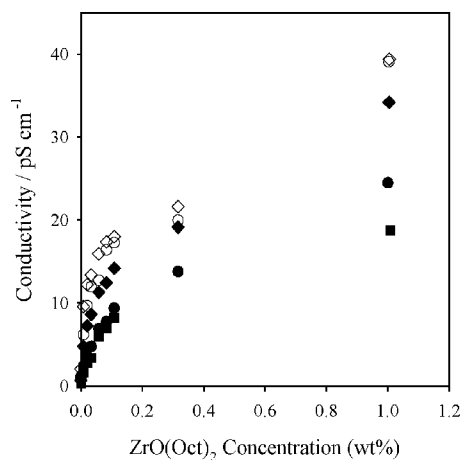

Figure 3. Conductivity vs. ZrO(Oct)$_2$ concentration for S1 (squares), S2 (filled circles), S3 (open circles), S4 (filled diamonds) and S5 (open diamonds).

The adsorption isotherms for series S1 to S5 are given in Figure 5. It is evident that the addition of polymers to the dispersion results in a decrease in the amount of zirconium adsorbed. This may be due to competitive adsorption. There is less $ZrO(Oct)_2$ adsorbed when polymers are present

however, the mobilities (Figure 1) are higher than for the bare pigment dispersion (S1). Therefore, although the polymers compete with ZrO(Oct)$_2$, the ZrO(Oct)$_2$ present on the surface is dissociated to a larger extent, hence giving an increased mobility. Water at the surface of the pigment may also be influenced by the presence of the polymers.[9]
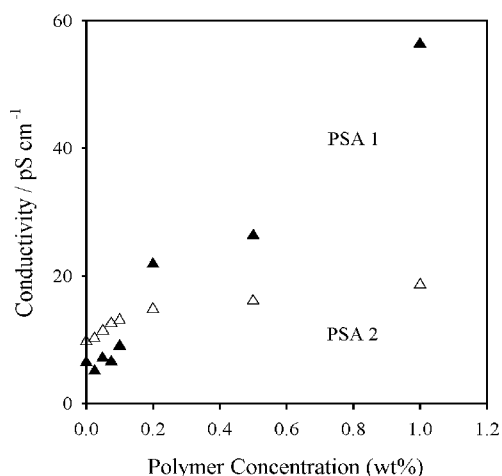

Figure 4. Conductivity vs. PSA concentration for a fixed 0.06 wt% ZrO(Oct)$_2$ concentration. S6 (filled triangle) and S7 (open triangle).
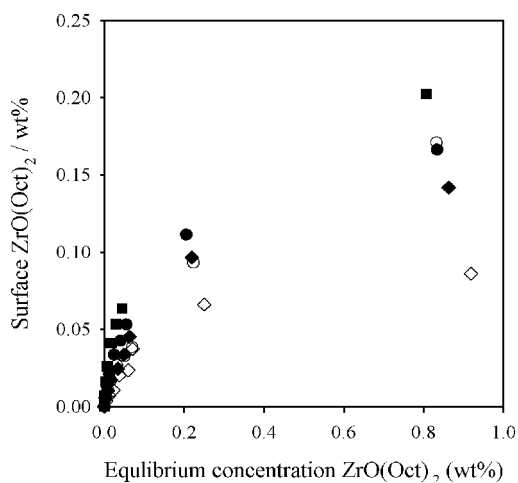

Figure 5. Surface concentration of ZrO(Oct)$_2$ vs. equilibrium ZrO(Oct)$_2$ concentration for S1 (squares), S2 (filled circles), S3 (open circles), S4 (filled diamonds) and S5 (open diamonds).

From a review of the relevant literature it is evident that there are two main schools of thought regarding site-binding and charge generation in non-polar media. Caruthers et al[7] have proposed that particle charging is a result of the formation of micelles in solution and that the neutral micelles then go on to form complexes with the appropriate surface sites. Upon separation of the complex, a charged micelle and a charged surface site results. Kitahara's approach[6] involves the partial dissociation of the PCA,

which then charges the surface. The surface sites are then neutralized at high PCA concentrations by excess counter-ion binding to the charged sites. This was the approach taken by Jenkins et al.[9] After some consideration of the two models it was thought that a modification of the approach of Kitahara using the formalism of Caruthers et al was the most suitable path.

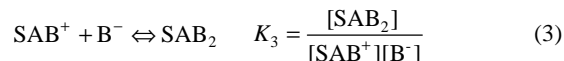The following site-binding model is proposed. We will consider a 2:1 surfactant and denote it as AB$_2$.

PCA dissociation

$$AB_2 \Leftrightarrow AB^+ + B^- \qquad K_1 = \frac{[AB^+][B^-]}{[AB_2]} \qquad (1)$$
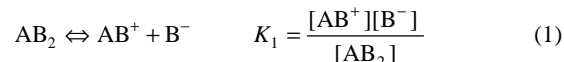
Surface charging (S denotes a surface site)

$$S + AB^+ \Leftrightarrow SAB^+ \qquad K_2 = \frac{[SAB^+]}{[S][AB^+]} \qquad (2)$$
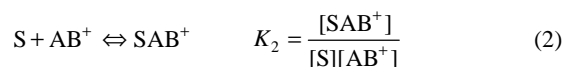
Surface neutralization

$$SAB^+ + B^- \Leftrightarrow SAB_2 \qquad K_3 = \frac{[SAB_2]}{[SAB^+][B^-]} \qquad (3)$$

The total number of sites will be the sum of the free and occupied sites at equilibrium.

$$\text{Total Sites} = [S]_{t=0} = [S]_{t=\infty} + [SAB^+] + [SAB_2] \qquad (4)$$

We are specifically interested in the amount of [SAB$^+$] species present, since these contribute to the electrophoretic mobility of the dispersion. The particle charge, Q, can be related to the mobility, μ, via:

$$Q = 6\pi\eta\mu r \qquad (5)$$

where r is the particle radius. At equilibrium, the total number of charged sites is

$$e[SAB^+]_\infty = QN \qquad (6)$$

Where e is the elementary charge, N is the number of particles per unit volume, Q is the charge per particle and [SAB$^+$]$_\infty$ is the number of charged sites per unit volume.

Therefore, the electrophoretic mobility, the directly observable parameter, can be expressed as

$$\mu = \frac{e}{6\pi\eta rN} \frac{[S]_0}{1 + \dfrac{1}{K_1^{1/2}K_2[AB_2]^{1/2}} + K_1^{1/2}K_3[AB_2]^{1/2}} \qquad (7)$$

which can be expressed simply as a three variable model,

$$\frac{6\pi\eta r\mu}{e} = \frac{a}{1 + b[AB_2]^{-1/2} + c[AB_2]^{1/2}} \qquad (8)$$

Hence, it should be possible to fit this equation to the experimental electrophoretic mobilities using non-linear regression[11] given appropriate initial estimates for each parameter. However, in a three variable model, values of the equilibrium constants cannot be resolved since they are not

independent parameters in the equation. A solution would be to assume a value for the number of surface sites as done by Jenkins et al.[9]
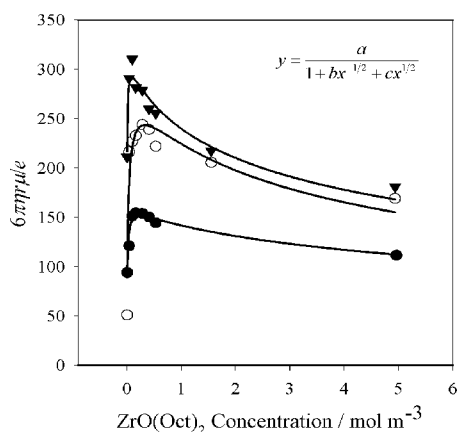

Figure 6. LHS of Eq. (8) vs. concentration of ZrO(Oct)$_2$ for series S1 (filled circles), S4 (open circles) and S5 (triangles).

Figure 6 gives the mobility, represented as the LHS of Eq. (8), as a function of ZrO(Oct)$_2$ concentration for the dispersions containing PSA 2 or bare CuPc. To obtain quantitative information from the model, such as the number of sites per particle, it is necessary to have very high quality electrophoretic mobility data for a series of ink dispersions. Overall, it is evident that the present site-binding model is capable of modelling the data. This is an excellent result for a simple site-binding model that does not invoke the presence of charged micelles. Future research will involve an extension of this model to enable the extraction of the equilibrium constants for the various charging processes occurring in the system.

Conclusion

The electrophoretic mobilities of a number of simple CuPc liquid toner dispersions containing particle charging and stabilizing agents have been determined by Phase Analysis Light Scattering. A site-binding model was presented that can readily describe the data. Conductivity measurements and adsorption isotherms provided supporting evidence.

Acknowledgements

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Biography

Roland Keir received his Ph.D. in Physical Chemistry from the University of New England, Armidale, Australia in 1996. Since then he has worked in the School of Physics and Electronic Systems Engineering and the Ian Wark Research Institute at the University of South Australia. His research has primarily focused on the chemistry and physics of liquid toners, various aspects of colloid chemistry and light scattering instrumentation and techniques. He is a member of the IS&T and the RACI.