CORRELATION OF ZETA POTENTIAL OF INK AND INK REMOVAL FROM HIGH DENSITY POLYETHYLENE SHEETS BY ALKYLTRIMETHYlammonium BROMIDES

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Abstract

Zeta potential of ink with three different cationic surfactants: dodecyl-, tetradecyl-, and hexadecyl or cetyl-trimethylammonium bromides (i.e., DTAB, TTAB, and CTAB, respectively) was measured at two pH levels of 11 and 12. These surfactants are chemically different in the number of carbon atoms of the alkyl tail group (i.e., 12, 14, and 16 for DTAB, TTAB, and CTAB, respectively). The zeta potential of ink particles increases and fractional ink removal increases with increasing alkyl chain size and increases with surfactant concentration, plateauing at some higher concentration. The zeta potential of each surfactant at pH 12 was higher than that at pH 11, while the efficiency for ink removal of these surfactants worked particularly well at pH 12. Inducing a higher negative charge on the ink particles by increasing pH or surfactant hydrophobicity and concentration is correlated with ink removal as repulsion between ink particles and polymer surface increases and dispersion stability of detached ink particles increases, presumably due to increased surfactant adsorption on the ink particles.

Keywords
Plastic deinking, Alkyltrimethylammonium bromide, and Zeta potential

Introduction

The stability of colloid is resulted from the balance of the repulsive force between colloidal particles and the force of Van der Waals attraction. If the repulsive force is greater than the attraction force, the particles tend to discrete and disperse in suspension. On the other hand, the colloidal particles can aggregate and precipitate out from the solution if repulsive force is reduced (Hiemens, 1986). The interaction between the same charged particles is responsible for repulsive force. One can visualize a single charged particle suspending in the solution is surrounded by cluster of oppositely charged ions. There are two distinct layers of the oppositely charged ions according to the Double Layer Theory. Therefore, it is very difficult to measure the surface potential (the actual charge on the particle surface). The practical measurement of particle charge is actually the charge at the junction of the stern layer and the diffuse layer, which is known as the zeta potential theory. For a case of very low electrolyte concentrations, the value of zeta potential is very close to the surface potential. However, in highly concentrated solutions e.g. saline water, the double
layer and the potential curve are compressed resulting in the zeta potential to be much lower than the surface potential (Hiemens, 1986).

For the process of paper deinking, negatively carboxylate group in water-based ink can react with anionic surfactants such as sodium octanoate sulfate (C8) and sodium dodecanoate sulfate (C12) due to the positive charge of calcium bridge. Increasing concentrations of both anionic surfactants and calcium cause the zeta potential of ink to decrease because the negative charge of surfactant simply neutralizes the positive charge of calcium ions around negative ink particle (Riviello et al., 1994).

The solution pH is another important parameter affecting on the zeta potential of particles. It was reported that the zeta potential of polytetrafluoroethylene [PTFE] in 0.001 M KCl with alkyltrimethylammonium bromide gradually decreased from 0 to –30 mV when the pH in the solution was increased. The change in zeta potential value is caused by COOH group on PTFE surface which is a product of hydrolysis of C=O (Juan et al., 1996). Another case of effect of pH is the interaction of lysozyme and n-alkyltrimethylammonium bromides at pH 3.20. Lysozyme which is protein is protonized and hence there is no electrostatic interaction with the cationic surfactant. On the other hand, at pH 7 and 10 the lysozyme is deprotonized and turns to have negative charge so that it can react with positive charge of C_{10}TAB, C_{12}TAB and C_{14}TAB. As a result, the zeta potential of lysozyme changes from negative to positive charge when concentration of these three surfactants were increased (Wang et al., 1999). Moreover, with increasing surfactant concentration, zeta potential also increases (Wang et al., 1999; Ajay and Sharad, 1996).

Chain length of surfactant has been reported to affect zeta potential. The zeta potential of kaolinite in alkyltrimethylammonium bromide with 1.0 mM NaCl was found to increase with increasing chain length of alkyltrimethylammonium bromide. (Wang et al., 1999). This result agrees with the zeta potential of PTFE in alkyltrimethylammonium bromide solution. (Ajay and Sharad, 1996).

Ink removal from plastic sheets is the process of detaching the binder and ink. Similar to laundering, deinking process consists of two sequential steps of detachment of soil (ink) from substrate (plastic surface) and dispersion of soil in a washing bath by mechanical action (Borchart, 1994; Rosen, 1989). Normally, water cannot wet both the plastic sheet and the printed ink. During deinking, added surfactant adsorbs on ink/binder interface and the plastic surface, resulting in decreasing both ink/water and binder/water interfacial tensions, and enhancing the formation of a water layer between ink/binder particles and the plastic surface (Rosen, 1989; Broze, 1991). As analogous to detergency, surfactant can liquefy ink and ink can flow or be removed from surface (Borchart, 1994). Moreover, surfactant can aid antiredeposition by dispersing solid ink particles by adsorption on the ink surface, emulsifying liquid ink droplets, and solubilizing ink molecules in micelles.

In this study, zeta potential was used to indicate the adsorption of CnTAB onto printed ink because the both results of adsorption isotherm and zeta potential correspond to each other. (Wang et al., 1999; Ajay and Sharad, 1996, Singh et al., 2001, Hanna, 1990). The measured value of zeta potential provides useful information to establish the polarity and nature of electric charge and possibility of adsorption of surfactants, which usually occurs at the stern’s layer (Karsa, 2000). This leads to a better understanding the deinking mechanisms.
MATERIALS AND METHODS

Materials

Plastic sheets: Printed plastic sheet samples used in this research were cut from the commercially drinking water bottles produced by SVB Drinking Water Co., Thailand. The bottle was made of HDPE and produced by the blow-molding technique with flame treatment prior to printing. Blue ink used for printing by silk screen method is solvent-based ink. The printed parts of plastic bottles were cut to a square-shape with 8x40 mm.x mm..

Chemicals: Cetyltrimethylammonium bromide (CTAB) with 98% purity in powder form was supplied by The Fluka Company, Switzerland. Tetradecyltrimethyl ammonium bromide (TTAB) with 98% purity and dodecyltrimethyl-ammonium bromide (DTAB) with 99 % purity were obtained from Aldrich. Sodium hydroxide with 98% purity was supplied by EKA Noble Company, Sweden. Hydrochloric acid, AR grade, used for pH adjustment was supplied by BHD. All chemicals were used as received.

Ink: Ink flake was scrubbed from blue printed trademark of drinking bottle. Normally, ink is composed of 5.0 % organic pigment, 11.0 % titanium oxide, 82.0 % long epoxy ester or resin and 2.0% and napthenate catalyst.

Epoxy structure

Deinking Experiment

To investigate the effect of surfactant’s alkyl chain length on the deinking efficiency, CTAB, TTAB, and DTAB were used at different concentrations. The base conditions used for deinking experiment were pH 12, shaking time 2 h, soaking time 2 h, and temperature 30°C. Percentage of ink removal was determined as a function of surfactant concentration, pH and temperature. The specimens were soaked in 15 ml deinking solution and agitated in a controlled shaking bath at 200 cycles/min. After that, the deinked specimens were washed in deionized water and dried in the open air at room temperature ( 25-30 °C) overnight.

Calculation of Percentage of Ink Removal

The amount of ink on the plastic surface was determined by optical scanning method using a scanner (HP LaserJet, Model 4C) with the desk scanning software from Hewlett Packard. The scanning data of the printed ink and deinked plastic sheets were recorded and then these files were sent to Adobe Photoshop version 5.0 to count the number of pixels in the histogram mode. The deinking efficiency (in %) was determined by

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\text{Ink removal (in %)} = \left( \frac{\text{No. of pixels before deinking} - \text{No. of pixels after deinking}}{\text{No. of pixels before deinking}} \right) \times 100.
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Critical Micelle Concentration Measurement

The critical micelle concentration (CMC) of CTAB, TTAB, and DTAB were determined by measuring the conductivity of each respective surfactant solution at various concentrations, using a conductivity meter (Orion, model 125). The solution temperature was kept constant at 30 ± 1°C. The critical micelle concentrations of CnTABs were determined from the sharp point of the plot of conductivity value as a function of surfactant concentration.
Zeta Potential Measurement

To measure the zeta potential of ink, ink flakes was obtained by scrubbing the printed ink on the HDPE surface. A small amount of the scrubbed ink was added into CnTAB solution at two pHs of 12 and 11 and then it was stirred continuously for 24 h. by using a magnetic stirrer. The resultant solution was then transferred into an electrophoresis cell of a zeta-potential meter (Zeta Meter, Model 3+). After applying a suitable voltage according to conductivity of particles, time of any particular particle to move to a certain distance was measured automatically. The measured time was then calculated to give a zeta potential value. For each sample, at least 20 particles were monitored and the average value of zeta potential was obtained.

RESULTS AND DISCUSSION

1.1 Deinking Performance

Effects of Surfactant Concentration and Alkyl Chain Length

The measured CMC values are 16.29 mM for DTAB, 3.75 mM for TTAB, and 0.96 mM for CTAB. Figure 1 shows the deinking performance as a function of a “normalized” concentration (real concentration devided by critical micelle concentration, concentration/CMC). For any given ink removal, the CnTAB normalized concentration required decreases with increasing alkyl chain length of CnTAB since the critical micelle concentration (CMC) is decreased dramatically as the alkyl chain length increases. Figure 2 shows the deinking performance as a function of surfactant concentration of three different surfactants. The order of deinking efficiency is CTAB>TTAB>DTAB. From the results, it can be concluded that deinking
improves as the alkyl chain length of CnTAB increases. The complete ink removal was found at approximately 3.0xCMC for CTAB, 8.0xCMC for TTAB, and 23.5xCMC for DTAB. For CTAB, the percentage of ink removal abruptly increases when the concentration exceeds the CMC while the percentage of ink removal with TTAB appears at 3.0-4.0xCMC and substantially increases at 5.0xCMC. The ink removal with DTAB occurred at 9.0xCMC, and the minimum concentration of DTAB for the significant ink removal appears at 12.5xCMC. The drastic increase in ink removal with surfactant concentrations greater than their CMC values is resulted from solubilization of ink into micelles being an important mechanism of deinking. As shown in Figures 1 and 2, for the case of TTAB and DTAB, it is necessary to apply very high surfactant concentrations (many times of CMC) to achieve the complete removal of ink. Moreover, the presence of CnTAB also prevents redeposition of detached ink particles because of the same positive charge.Interestingly, there is a dramatic increase in the normalized surfactant with increasing in the alkyl chain length much more than expected as compared to the solubilization capacity (per micellized surfactant molecule). Therefore, increasing chain length leads to enhancing surfactant adsorption, wettability and dispersion stabilization which involve the deinking process. This is because a longer alkyl chain length results in a larger size of micelles, which simply increases the solubilization capacity.

Effect of pH

As seen in Figures 3, 4 and 5, for any given normalized concentration, the percentage of ink removal by CTAB, TTAB and DTAB increases with increasing pH and the solution pH greater than 11.5 is necessary.
for good deinking. For the complete ink removal, the solution pH has to be raised up to 12.0 for all three surfactants. Since the binder of ink used for HDPE is epoxy ester oil. Under certain circumstance at high pH, OH\(^{-}\) group form sodium hydroxide donates electron to these epoxy groups, resulting in association of the positively charged hydrophilic part of CnTAB via electrostatic forces leading to ink removal.

**Zeta Potential of Ink**

**Zeta potential of Ink in Water**

Figure 6 depicts the zeta potential of ink in water as a function of pH showing the point of zero charge (PZC) of ink in water is about 3.3. Therefore, at pH < 3.3, the ink has positive charge and when pH > 3.3, it shows negative charge. In alkaline solution, the epoxy group in ink structure can be dissociated to have negative charge. The more hydroxyl group in the solution or at a high pH level, the more negative charge of epoxy ion in solution is obtained. Therefore, the zeta potential of ink decreases as pH level is increased.
As shown in Figures 7 and 8, when the concentration of any CnTAB increases in the range of CMC, the zeta potential of ink increases abruptly but beyond the CMC, the zeta potential value has a little change. This is because amount of surfactant monomer adsorbed on ink surface increases with increasing surfactant concentration and reaches saturation. Interestingly, in the presence of CnTABs at very high concentration exceeding CMC, the ink surface becomes positively charged.

Zeta potential of ink with CTAB, TTAB, and DTAB at pH 12 and different surfactant concentration is shown in Figure 7. The zeta potential of CTAB is higher than that of TTAB, which is higher than that of DTAB. As described before, CTAB has the highest efficiency for deinking followed by TTAB and DTAB, respectively. This means that CTAB, which has a high number of carbon atoms in alkyl chain length, can adsorb on ink particles more than TTAB and DTAB. Therefore, the ink surface has higher positive charge than TTAB and DTAB. In the same explanation, the zeta potential of ink CTAB is the most positive charge followed by TTAB and DTAB.

As shown in Figures 9, 10, and 11, the zeta potential of ink with any CnTAB at pH 12 is higher than that at pH 11. It can be explained that the zeta potential of ink at pH 12 has more negative charge than that at pH 11 [Figure 6]. This makes the cationic surfactant can adsorb on the ink surface more at pH 12 than that at pH 11. As described before, the best condition for complete deinking by alkyltrimethylammonium bromides
occurs at pH 12. A conclusion can be drawn that an increase in cationic surfactant adsorption will enhance the deinking efficiency. A higher pH value will promote the adsorption of cationic surfactant on ink.

CONCLUSIONS

Quantitative removal of ink is attainable with all three alkyltrimethylammonium bromides studied. As increase in the carbon chain length of the surfactants increases the deinking performance. The percentage of ink removal increases with increasing pH and CnTAB concentration. The zeta potential of ink increases as the alkyl chain length of CnTAB increases and as the solution pH increases. To improve the deinking efficiency, the zeta potential of ink has to be increased. As a result, the adsorption of cationic surfactant is then increased leading to enhance the ink detachment from plastic surface.
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REFERENCES


