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ORIGINAL CONTRIBUTION

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Removal of solvent-based ink from printed surface of HDPE bottles by alkyltrimethylammonium bromides: effects of surfactant concentration and alkyl chain length

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Abstract Three alkyltrimethylammonium bromides (i.e., dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide or DTAB, TTAB, and CTAB, respectively) were used to remove a blue solvent-based ink from a printed surface of high-density polyethylene bottles. Either an increase in the alkyl chain length or the surfactant concentration was found to increase the deinking efficiency. Complete deinking was achieved at concentrations about 3, 8, and 24 times of the critical micelle concentration (CMC) of CTAB, TTAB, and DTAB, respectively. For CTAB, ink removal started at a concentration close to or less than its CMC and increased appreciably at concentrations greater than its CMC, while for TTAB and DTAB, significant deinking was only achieved at concentrations much greater than their CMCs. Corresponding to the deinking efficiency of CTAB in the CMC region, the zeta potential of ink particles was found to increase with increasing alkyl chain length and concentration of the surfactants, which later leveled off at some higher concentrations. Wettability of the surfactants on an ink surface increased with increasing alkyl chain length and concentration of the surfactants. Lastly, solubilization of ink binder in the surfactant micelles was found to increase with increasing alkyl chain length and surfactant concentration. We conclude that adsorption of surfactant on the ink pigment is crucial to deinking due to modification of wettability, zeta potential, pigment/water interfacial tension, and dispersion stability. Solubilization of binder (epoxy) into micelles is necessary for good deinking because the dissolution of the binder is required before the pigment particles can be released from the polymer surface.

Keywords Deinking · Alkyltrimethylammonium bromide · HDPE waste bottles · Zeta potential · Contact angle

Introduction

Steady growth of demand in plastics for packaging leads to increasing demand in natural gas and petroleum as the raw materials for plastic production. Growth of demand in plastics translates into steady growth in plastic wastes as a consequence. One good way of dealing with such a problem is through recycling, but it has been reported that recycled plastics often bear poor physical and mechanical properties when compared to virgin ones [1, 2]. One such cause of the deterioration in the properties is the ink that is normally present on plastic surfaces. For example, the deterioration effects of residual ink on physical properties upon reextrusion of polyethylene (PE) films were evident in a previous work [3]. Therefore, the removal of ink from the plastic surface prior to recycling is necessary. Generally, ink can be removed by either physical [4] or chemical [3, 5–7] means. Chemically, ink can be removed by organic solvents, but due to their toxicity, alternative deinking media are desirable. Due to their biodegradability, nontoxicity, and nonvolatility, surfactants in aqueous solutions are good candidates for such a task.

Basically, surfactant-based separation processes [8, 9], in adaptation to the deinking process [3, 5–7], involves three sequential steps of surfactant adsorption, ink detachment, and solubilization. In the adsorption step, surfactant monomers adsorb onto solid surfaces of both ink and plastic, resulting in a decrease in the interfacial tension values of both polymer–water and ink–water [6]. If the reduction in the interfacial tensions reaches a point where the summation of the interfacial tensions of polymer–water and ink–water is equal to or less than that of ink–polymer, it is thermodynamically favorable for the ink to detach from the polymer surface [6]. Rubbing the polymer surface against another solid and the application of shearing forces from agitation help remove loosened ink and maintain dispersion of the detached ink particles [6]. Solubilization of molecularly dispersed dyes or binder molecules into micelles can also help increase deinking efficiency [3, 5–7]. In all of these steps, the type of surfactants used has been found to play an important role [3, 5, 7].

Previous studies on surfactant-based deinking process have been carried out on surfaces of either plastic films [3, 5, 7] or rigid plastics [6] to remove either water-based [3, 5] or solvent-based [6, 7] ink using an anionic surfactant [3], nonionic surfactants [3, 5, 7], an amphoteric surfactant [3, 7], and cationic surfactants [3, 6, 7]. For either water- or solvent-based ink, cationic surfactants were the most effective in ink removal at concentrations well above their critical micelle concentrations (CMC) and at high pH levels (generally greater than or equal to 11) [3, 6, 7]. It was also found that increased temperature during deinking, increased presoaking time in the surfactant solutions prior to mechanical agitation, and increased shaking time helped increase deinking efficiency [5–7]. The cationic surfactants which have been previously investigated were hexadecyltrimethylammonium bromide, which is also known as cetyltrimethylammonium bromide (CTAB; $C_{16}H_{33}{}^{+}N(CH_3)_3Br^{-}$) [3, 6, 7] and hexadecylpyridinium chloride (CPC; $C_{16}H_{33}{}^{+}N(C_5H_5)Cl^{-}$) [3], but CPC was observed to degrade at high pH levels.

Solvent-based inks, which are normally used to print on PE surfaces by a screen-printing technique, are composed mainly of binders, solvents, pigments, and additives [10]. A typical composition of screen-printing ink for PE bottles is 5% organic pigment, 11% titanium oxide, 82% epoxy resin, and 2% napthenate catalyst [11]. For PE printing, alkyd normally used as a binder is usually replaced by epoxy resin, which is polymerized by a catalyst during drying. Epoxy resins are linear polymers with chains of low to medium molecular weights [12]. The adhesion between the epoxy resin with pigments and plastic surfaces is due to van der Waals, electrostatic, and chemical bonding, among others. Hence, for successful deinking, the epoxy binder resin must be removed so that the ink can be removed from plastic surfaces.

In the present contribution, a series of alkyltrimethylammonium bromides (i.e., dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide or DTAB, TTAB, and CTAB, respectively) with different alkyl chain lengths (i.e., 12, 14, and 16 carbon atoms of the alkyl tail group for DTAB, TTAB, and CTAB, respectively) were investigated for the removal of blue solvent-based ink from the printed surface of high-density polyethylene (HDPE) bottles. The effects of these cationic surfactants and their concentration on deinking, zeta potential of ink particles, wettability of printed surfaces, and solubilization of binder were investigated.

Experimental

Materials

High-density polyethylene sheet samples used in this work were obtained from commercial-drinking-water blow-molded bottles produced by SVB Drinking Water Company (Thailand). Printing of these bottles was done at CK-Plastic Company (Thailand). Prior to printing, the HDPE bottles were flame-treated. A blue ink formulation (UPE-B4009/2) from Uni Ink Company (Thailand) was printed on the treated surface using the screen-printing technique. The printed part of the bottles was then cut into 8×40-mm square sheets.

N-Dodecyltrimethylammonium bromide (99% purity; powder) and *n*-tetradecyltrimethylammonium bromide (98% purity; powder) were purchased from Aldrich (USA), while *n*-hexadecyltrimethylammonium bromide (CTAB) (98% purity; powder) was purchased from Fluka (Switzerland). Sodium hydroxide (NaOH) (98% purity), purchased from EKA Noble (Sweden), and hydrochloric acid (HCl) (AR grade), purchased from BHD (Germany), were used for pH adjustment. All of these chemicals were used as received.

Ink powder was prepared by mixing the as-received ink with an appropriate solvent, and the mixture was thoroughly pasted on a 15×10-in. glass plate. The layer of ink was made as thin as possible to hasten the drying. The painted glass was later dried in an oven at 60°C overnight, after which the ink was scraped off from the glass surface, ground in a mortar, and finally sieved into powder of 100 mesh or less. The as-prepared ink powder was kept in a desiccator prior to further use.

CMC measurement

The CMC of DTAB, TTAB, and CTAB was determined by measurements of both conductivity and surface tension values of each surfactant solution as a function of surfactant concentration using an Orion 125 conductivity meter and a KRÜSS DSA10-Mk2 drop-shape analyzer. The solution temperature was maintained at 30±1°C. The CMC of each cationic surfactant (i.e., CnTAB) was determined from the break points observed in the plots of conductivity and surface tension as a function of linear (for measurements based on the conductivity values) or logarithm (for measurements based on the surface tension values) scale of CnTAB concentration.

Wettability measurement

Wettability of CnTAB on printed HDPE surface could be inferred from contact angles of drops of CnTAB solutions on the surface using the sessile drop method [13]. The apparatus was composed of a closed chamber of 21×27×15 cm in dimension, which was constructed from acrylic sheets. A hole of 0.5 cm in diameter, used as a microsyringe holder, was located on top of the chamber. A Nikon Coolpix 995 with microlens attachment was set on a camera holder in front of the chamber. Prior to measurements, the temperature of the chamber was equilibrated to 30±1°C, and the chamber atmosphere was saturated with moisture from a water-filled beaker placed within the chamber. The relative humidity in the chamber was maintained in the range of 90–93% to limit evaporation of water from drops of CnTAB solutions during measurement. For each sample solution, advancing contact angles were measured on drops of between 10 and 80 μl in a stepwise manner from the addition of 10 μl of the sample solution. For each measurement, the sessile drop was allowed to set not more than 1 min before a photograph of the drop was recorded digitally. This is insufficient time for equilibration, so the reported value is a dynamic contact angle. Adobe Photoshop version 5.5 software was used to analyze the digital files recorded, and the data for each sample solution were averaged from at least three readings. It was found that, for all of the sample solutions, the standard deviation for all of the measured values of contact angles was within ±5.5°.

Zeta potential measurement

A very small amount of the as-prepared ink powder was added into a CnTAB solution. The pH level of the mixture was adjusted to 12, and the mixture was stirred for 24 h. The temperature of the mixture was equilibrated to 30±1°C. The as-prepared mixture was then transferred to an electrophoretic cell of a Zeta-Meter ZM 3.0+ zeta meter equipped with a microscope module. After applying a suitable voltage according to the solution conductivity, the time for any observable ink particle to move for a certain distance was measured. For a given data set, at least 20 ink particles were monitored, from which the average time was calculated. The average time was then used to calculate the average zeta potential value for that particular data set. The point of zero charge (PZC) of ink pigment particles in distilled water was determined as the pH at which the zeta potential of the ink particles equals zero.

Solubilization measurement

The ink can be considered to be composed of colored pigment particles and binder (epoxy resin), which can be solubilized in a surfactant solution. The solubilization capacity of ink binder in CnTAB solutions was measured by mixing a weighed amount of the as-prepared ink powder (ca. 10 mg) in 15 ml of an as-prepared CnTAB solution, with its pH level being adjusted to 12, in a 50-ml Erlenmeyer flask. The flask was then placed in a shaking water bath, the temperature of which was equilibrated to 30±1°C, and the shaking cycle of which was set at 200 cycles/min for 4 h. The solution was later filtered to remove undissolved ink particles (pigments) using a Whatman No. 7402-001 filter paper with average pore size of 0.2 μm. The UV absorbance of the filtrate was measured by a Shimadzu UV-2550 UV-visible spectrophotometer at a wave length of 273.8 nm. The absorbance for accurate measurements should be between 0.1 and 0.8. If a sample solution showed an absorbance beyond this range, it was diluted until the reading was within the optimum range. The actual “quantitative” absorbance for the solution after dilution was calculated back from the amount of water used to dilute the original solution. The plot of the absorbance vs CnTAB concentration was a qualitative measure for the amount of ink binder solubilized in CnTAB solutions.

Deinking experiment

To investigate the effects of the alkyl chain length and surfactant concentration on deinking efficiency, DTAB, TTAB, and CTAB solutions were prepared at different concentrations, and the pH level of the surfactant solutions was adjusted to 12. The as-prepared printed HDPE specimens were first presoaked (without shaking) in 15 ml of a surfactant solution for 2 h and further soaked with shaking at 200 cycles/min for another 2 h in a shaking water bath. The temperature of the bath was equilibrated to 30±1°C. After the required time was reached, the specimens were washed with deionized water and later dried in open air at room temperature overnight. The amount of ink on the plastic before and after deinking was measured using the optical scanning method [6]. In this method, each plastic sample was carefully positioned on an HP ScanJet 4C optical scanner and scanned using the factory settings. The scanned files were analyzed by an Adobe Photoshop version 5.5 software by counting the number of pixels (equivalent to the amount of ink present) on the plastic surface. The amount of ink removed (%) was then calculated using the following relationship [6]:

$$\text{Ink removed}(\%) = [(\text{pixels}_{\text{before deinking}} - \text{pixels}_{\text{after deinking}}) / \text{pixels}_{\text{before deinking}}] \times 100 \quad (1)$$

Viscosity measurement

The viscosity of each CnTAB solution was measured in comparison with that of water by a Ubbelode viscometer. The Ubbelode tube containing a sample solution was partially submerged in water, the temperature of which was equilibrated to 30±1°C. Prior to each measurement, the sample solution was filled in the Ubbelode tube and was left for temperature equilibration for 15 min. During measurement, the solution was then raised up and then allowed to flow gravitationally. The elapsed time for the solution to flow passing two marked lines was recorded. The measurement was repeated five times, from which an average value was calculated. The viscosity of the solution is assumed to relate to that of water according to the following relationship [14]:

$$\frac{\eta_1}{\eta_0} = \frac{\rho_1 t_1}{\rho_0 t_0} \quad (2)$$

where η is viscosity, ρ is density, and t is the measured elapsed time. “1” represents the measured CnTAB solution, and “0” represents water.

Results and discussion

Critical micelle concentration

From the plots of conductivity against the concentration of DTAB, TTAB, and CTAB solutions (results not shown), a break point was observed at the concentrations of 16.29, 3.75, and 0.97 mM, respectively, while from the plots of surface tension against the logarithm of concentration of the respective CnTAB solutions (see Fig. 1), a break point was observed at the concentrations of 13.77, 3.70, and 0.93 mM, respectively. These surface tension-based values are taken as the CMC of the cationic surfactants. Obviously, the CMC of these surfactants decreased with increasing alkyl chain length due to the increased driving force for micelle formation from increased hydrophobicity of the tail group. When comparing the experimental CMC values with the reported values of 16.00 mM for DTAB [15], 3.60 mM for TTAB [16], and 0.92 for CTAB [17] (all at 25°C), the obtained values seem reasonable except for the value of DTAB from the surface tension method, which was much lower than the reported value of 16.00 mM. The discrepancy in the observed CMC value of DTAB from the drop-shape analysis and that from the conductivity may be due to the fact that the calculation of the surface tension from the shape of a pendant drop depended very much on input values of both the density and the viscosity of the measured solution; therefore, a slight inaccuracy in either value or both values could lead to an erroneous result.

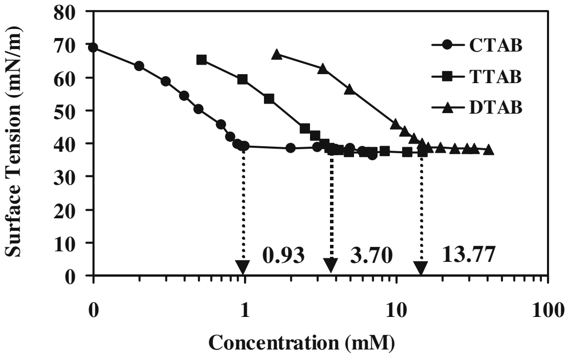


Fig. 1 Surface tension of CnTAB solutions as a function of initial CnTAB concentration. *Arrows* indicate CMC values

Wettability

A photograph of a sessile drop on a flat plastic surface showing the contact angle is shown in Fig. 2. Wetting is the first step for the deinking process, which results from adsorption of surfactant molecules onto the surfaces of both HDPE and printed ink. As a result, the interfacial tensions of ink/water and HDPE/water are lowered, and the contact angle of the surfactant solution onto the solid decreases. If the contact angle attains 0°, complete wetting occurs. A contact angle of 90° or greater would indicate a nonwetted surface. The case with which a hydrophobic polymer surface is wetted is often quantified by a “critical surface tension” characteristic of that plastic [18]. This is the maximum surface tension of a pure single-component

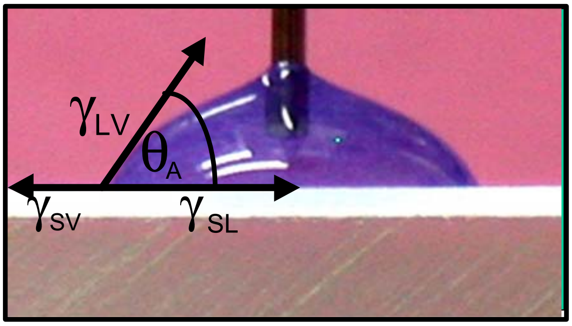


Fig. 2 Schematic for sessile-drop contact angle method. θ_A is the advancing contact angle; γ_{SV}, γ_{SL}, and γ_{LV} are solid–vapor, solid–liquid, and liquid–vapor interfacial tensions, respectively

liquid which would yield a contact angle of 0° on that polymer. For example, the critical surface tension of PE has been reported to be 31–33 mN/m [18]. This value will vary with molecular weight, surface treatment, and other factors. Although never intended to apply to surfactant solutions, the critical surface tension concept is often applied to these [19]. The plateau surface tensions (at concentrations above the CMC) of DTAB, TTAB, and CTAB are about 40 mN/m (see Fig. 1), which might indicate that these surfactant solutions would not completely wet the HDPE surface even above the CMC.

The critical surface tension is a crude, empirical approach to wettability of hydrophobic surfaces. A general description of wetting through the contact angle (θ_A) is from the Young equation [19]:

$$\cos\theta_A = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{3}$$

where γ_{SV}, γ_{SL}, and γ_{LV} are surface tensions between solid–vapor, solid–liquid, and liquid–vapor interfaces, respectively. For advancing contact angles as measured here, γ_{SV} can be assumed to be constant because the liquid has not been exposed to the dry surface area ahead of the advancing drop. Surfactants cause improved wetting (by reducing θ_A) via adsorption at the liquid–vapor and solid–liquid interfaces, reducing both γ_{LV} and γ_{SV}, respectively.

The wettability in terms of advancing contact angles of CnTAB solutions on printed HDPE surface as a function of CnTAB concentration is illustrated in Fig. 3. For a given type of CnTAB, the contact angle decreases with increasing CnTAB concentration. At a given concentration, the contact angle of CTAB solution was the lowest, while that of DTAB was the highest. From the results obtained, it can be concluded that the wettability of CnTAB solutions on a printed HDPE surface increased with an increase in both the alkyl chain length and the CnTAB concentration.

Since the hydrophilic head group of these cationic surfactants is the same, the only difference among these surfactants is the length of the hydrophobic tail groups. Due to the similarity among the hydrophilic head groups of these surfactants, the electrostatic interaction among the head groups of adjacent surfactant molecules of these surfactants is similar. An increase in the length of the hydrophobic tail group increases the van der Waal interaction among the tail groups of adjacent surfactant molecules, as well as between the tail groups of some surfactant molecules and some part of printed HDPE surface which is hydrophobic, and the hydrophobic surface of the unprinted HDPE surface [20, 21]. Hence, CTAB molecules which have the longest alkyl chain length among the cationic surfactants investigated can adsorb onto the hydrophobic part of ink surface (i.e., polymeric binder) much better than those of TTAB and DTAB, which showed the lowest adsorption. As a result, an increase in the alkyl chain length of CnTAB increased hydrophilicity of the solid surface, reducing both γ_{LV} and γ_{SL} values, which consequently cause the contact angles to decrease or the wettability on the ink surface to increase.

Since surfaces of both HDPE and some part of the printed ink are hydrophobic, adsorption of CnTAB molecules on these surfaces is a monolayer coverage with tail-in and head-out arrangement. Conversely, on some hydrophilic parts of the printed ink, a bilayer probably forms head groups down in the first layer and head groups out toward the solution for the second layer.

Zeta potential

Figure 4 shows the zeta potential of ink particles in water as a function of pH level. The PZC is defined as the pH at which there is no net charge on the solid surface and where the zeta potential is zero. According to Fig. 4, the PZC for the ink particles investigated was found at a pH level of about 3.3. This means that the ink particles exhibited a positive charge when pH<3.3, while they exhibited a negative charge when pH>3.3, and the charge of the ink particles became more negative with increasing pH level.

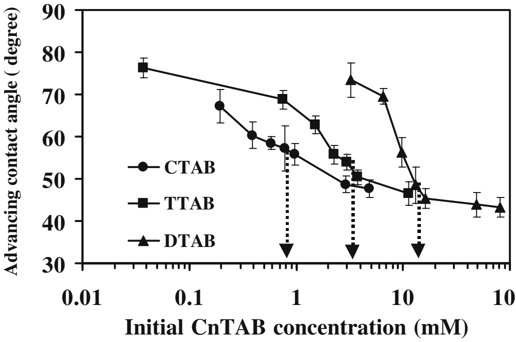


Fig. 3 Advancing contact angles of CnTAB solutions on printed HDPE surface as a function of initial CnTAB concentration. *Arrows* indicate CMC values

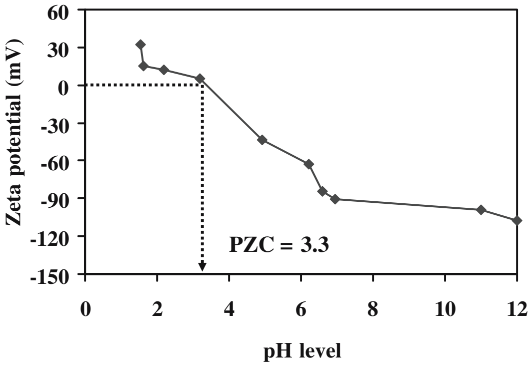


Fig. 4 Zeta potential of ink particles in water as a function of pH level

The ink particles are very highly negatively charged (−108 mV) at pH 12, which was the deinking condition.

Figure 5a illustrates the zeta potential of ink particles in CnTAB solutions at pH 12 as a function of CnTAB concentration. For a given CnTAB solution, the zeta potential of ink particles increased monotonically with increasing CnTAB concentration up to a critical value, after which the zeta potential reached a constant value. Initially, the zeta potential of ink particles in DTAB solution held a negative charge at concentrations lower than about 0.17 mM and became positive and increased with further increasing concentration to reach a constant value at a concentration of about 80 mM. For TTAB and CTAB solutions, the observed zeta potentials of ink particles were positive even at the very low concentrations investigated. At a given concentration, the zeta potential of ink particles in CnTAB solutions increased with increasing alkyl chain length of CnTAB molecules.

The zeta potential of ink particles in CnTAB solutions at pH 12 is plotted as a function of the normalized CnTAB concentration in Fig. 5b. The normalized concentration is the surfactant concentration/CMC. Obviously, this type of plots accented the importance of the CMC value on the zeta potential of ink particles in CnTAB solutions. The initial abrupt increase in the zeta potential of ink particles was observed in all CnTAB solutions, and after the concentrations of about five times of the CMCs for DTAB and CTAB and about two times of the CMC for TTAB, the zeta potentials of ink particles in these surfactant media became constant, with its value increasing with increasing alkyl chain length of the CnTAB molecules. It should be noted that the zeta potential of about −108 mV shown in Fig. 5b was the zeta potential value of ink particles in water at pH 12, and it could not be included in Fig. 5a because of the use of the logarithmic scale of the *x*-axis.

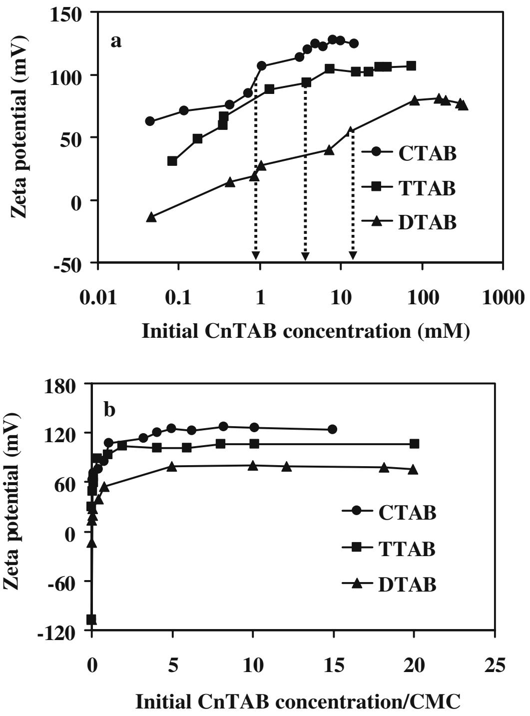


Fig. 5 Zeta potentials of ink particles in CnTAB solutions at pH 12 plotted as a function of **a** initial CnTAB concentration and **b** normalized CnTAB concentration. *Arrows* indicate CMC values

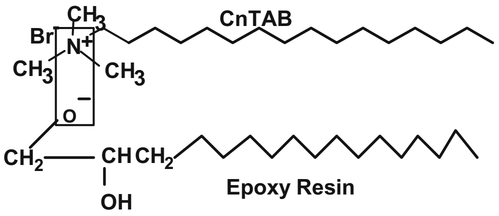


Fig. 6 Electrostatic interaction between positively charged head group of a CnTAB molecule and negatively charged moiety of an epoxy molecule

In analogy to the wettability results (see advancing contact angle results in Fig. 3), the zeta potential of ink particles increased with an increase in both the alkyl chain length and the CnTAB concentration. The most likely explanation may be based on the interaction between the tail groups of CnTAB molecules and the ink surface. On the first approximation, the increased adsorption of CnTAB molecules with longer alkyl chain length on the hydrophobic part of the ink particles could modify the charge of the ink surface into a more positive value (see Fig. 5).

At a pH of 12, the cationic head groups of CnTAB molecules can associate with the negative moieties of the epoxy molecules via electrostatic interaction, as depicted in Fig. 6. The hydrophobic tail groups of the CnTAB molecules can interact with the tail groups of adjacent CnTAB molecules and with the hydrophobic part of the epoxy molecules. As stated previously, a longer alkyl chain length of CnTAB molecules leads to an increased van der Waal interaction among the tail groups of adjacent CnTAB molecules, resulting in a higher density of CnTAB molecules adsorbed onto the ink surface. The binding of more CnTAB molecules in turn causes the charge of the ink

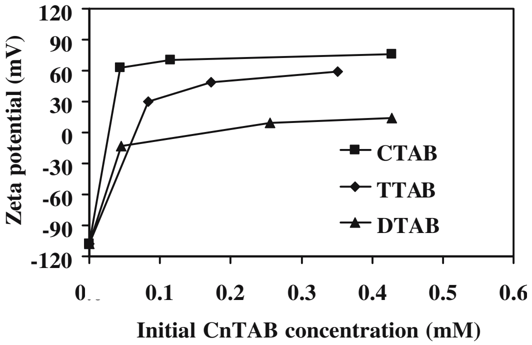


Fig. 7 The point of charge reversal of ink particles in CnTAB solutions at pH 12. Note that the zeta potential value of about −108 mV was the zeta potential value of ink particles in water at pH 12

surface to become more positive. The offered explanation agreed well with the point of charge reversal (PZC) observed in Fig. 7 (i.e., blown-up plots from Fig. 5a shown with the linear scale on the *x*-axis). With increasing alkyl chain length of the CnTAB molecules, the PZC was observed at about 0.17 mM for DTAB, 0.07 mM for TTAB, and 0.03 mM for CTAB. Therefore, charge reversal of the ink occurs at a lower concentration as the alkyl chain length of the surfactant increases. The results are consistent with the observed increase in the wettability with increasing alkyl chain length of the CnTAB molecules in the framework of increasing surfactant adsorption with increasing alkyl chain length and increasing surfactant concentration.

Solubilization

Solubilization of ink binder in surfactant micelles is a very important step for the deinking process. Removal of the binder from the surface is necessary to permit removal of the colored pigment particles (deinking). It has been hypothesized in a previous work that it is the negative charge on the binder (carboxylate groups) which is the cause of the effectiveness of cationic surfactants relative to surfactants of another charge [3]. Figure 8 shows quantitative absorbance of ink-containing CnTAB solutions as a function of CnTAB concentration above the corresponding CMCs of CnTAB to illustrate the solubilization capacity of ink binder in CnTAB micelles. Evidently, the solubilization of ink binder in CnTAB micelles increases with an increase in both the alkyl chain length and concentration of CnTAB. Due to the similarity in their chemical structures, solubilization of epoxy-based ink in CnTAB micelles could be compared with the solubilization of amphiphilic hemicyanine dye in CTAB micelles [22].

Solubilization of epoxy-based ink is due to three basic factors: incorporation of the hydrophobic portion of the epoxy molecule into the micelle core, electrostatic binding between the positively charged head groups of CnTAB molecules at the outer surface of micelles and the negatively charged carboxylate groups on the binder, and the ion–dipole attractions between the hydrophilic head groups of the surfactants and the π-electrons of the aromatic rings in the epoxy molecules solubilized in the palisade layer of the micelles. The aggregation number of alkyltrimethylammonium halide (CnTAX) micelles was shown to increase with increasing alkyl chain length (with the even number of carbon atoms between 12 and 18) [23], which implies that the diameter of CnTAB micelles also increases with increasing the alkyl chain length. As the alkyl chain length of the surfactant increases, the volume of the hydrophobic core increases as micelle diameter increases [24], and the increased micellar volume tends to increase solubilization [22] due to hydrophobic bonding between surfactant and epoxy.

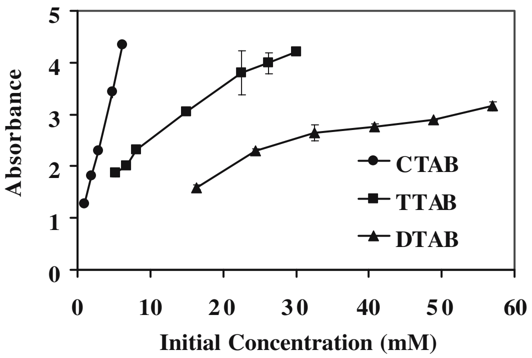


Fig. 8 Solubilization capacity of ink components in CnTAB solutions at pH 12 as a function of initial CnTAB concentration as indicated by adsorbance at 273.8 nm

Deinking performance

The use of CnTAB solutions for removing solvent-based ink from a printed HDPE surface was carried out at a pH level of 12 and a temperature of 30°C. Figure 9a shows the ink removed as a function of CnTAB concentration, while Fig. 9b shows the ink removal as a function of normalized CnTAB concentration (i.e., CnTAB concentration divided by corresponding CMC value). According to Fig. 9, significant ink removal occur at concentrations much greater than the corresponding CMCs (CMC of 16.29 mM for

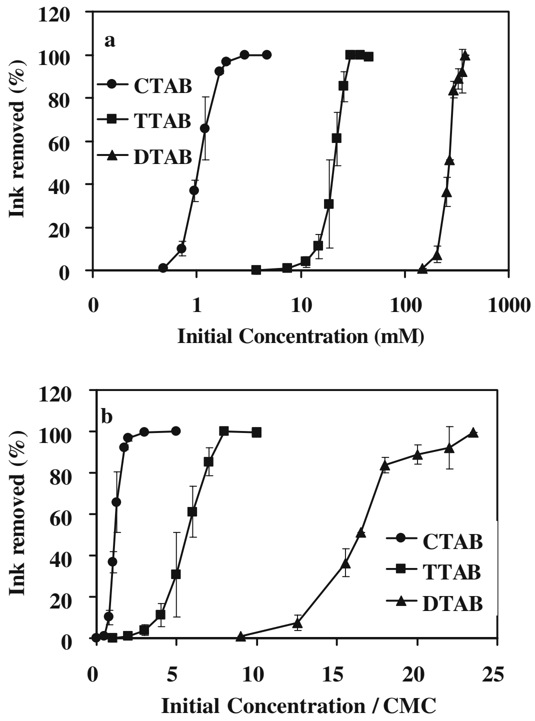


Fig. 9 Percentage of ink removal from printed HDPE surface as a function of **a** initial CnTAB concentration and **b** normalized CnTAB concentration

DTAB, 3.75 mM for TTAB, and 0.97 mM for CTAB). Specifically, 10% of ink could be removed from the surface of printed HDPE sheets when the concentrations of CnTAB solutions were about 13 times the CMC for DTAB, 4 times the CMC for TTAB, and about the CMC of CTAB, respectively, while complete deinking was observed at concentrations of about 24 times the CMC for DTAB, 8 times the CMC for TTAB, and 4 times the CMC for CTAB, respectively. The deinking efficiency of these cationic surfactants was obviously found to increase with increasing both the concentration and the alkyl chain length of the surfactants.

Interestingly, only CTAB showed the ability to remove the ink at concentrations close to its CMC, while a very high concentration was required in the case of DTAB. The zeta potential and wettability results at concentrations less than its CMC imply that CTAB adsorbed onto the ink surface in a much greater extent than both TTAB and DTAB either at constant concentration below the CMC (Figs. 3, 5a, and 7) or at the CMC (Figs. 3 and 5b). We were unable to measure surfactant adsorption onto the ink directly by the solution depletion method because we could not obtain a representative sample of ink by scraping from the plastic surface, and the preprinted ink does not have the same binder/pigment interaction as when printed. Therefore, we hypothesize that surfactant adsorption is responsible for increased zeta potentials and increased deinking. Since surfactant adsorption increases with concentration below the CMC and plateaus above the CMC [25], this plateau behavior in contact angle (Fig. 3) and zeta potential (Fig. 5a) is consistent with the correlation between wettability, zeta potentials, and surfactant adsorption. The critical concentration for the formation of admicelles on the ink surface (i.e., critical admicelle concentration; CAC) is much lower than the critical concentration for the formation of micelles (i.e., CMC) [26, 27]. The longer the alkyl chain length, the lower the CAC is [28]. As a result, CTAB,

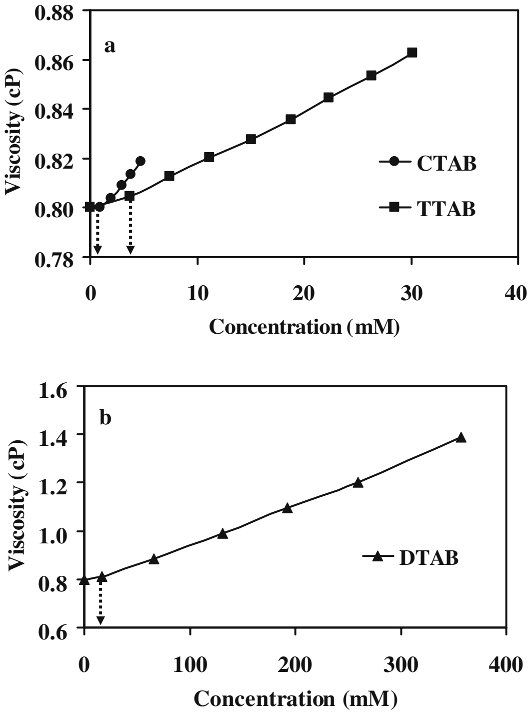
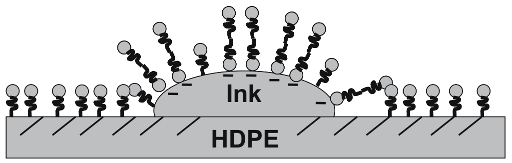
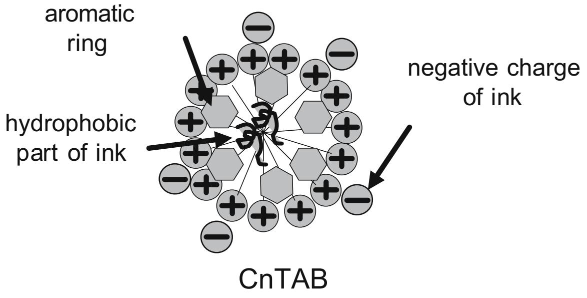


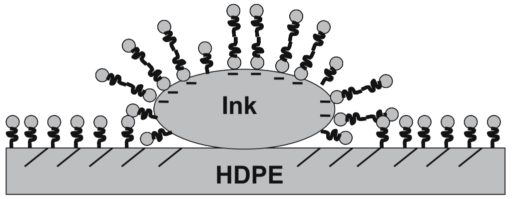
Fig. 10 Viscosity of CnTAB solutions as a function of initial CnTAB concentration for **a** CTAB and TTAB, and **b** DTAB. *Arrows* indicate CMC values



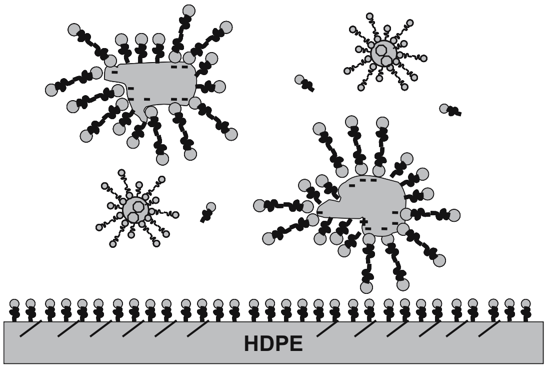
a Step 1: surface adsorption



b Step 2: solubilization of binder



c Step 3: detachment of pigment particles



d Step 4: stabilization and dispersion of detached pigment particles

Fig. 11 Proposed four-step mechanism for removal of solvent-based blue ink from HDPE surface which has the longest chain length, should form admicelles at a lower CAC than the other two cationic surfactants investigated. In addition, the formation of the negatively charged epoxy species could further reduce the critical concentrations where admicelles and micelles are formed [27, 28]. The plateau adsorption level is a result of the relative tendency of the surfactant to form admicelles as compared to the tendency to form micelles. There is generally a small increase in plateau adsorption above the CMC with increasing alkyl chain length [25], explaining higher zeta potentials (Fig. 7) and deinking (Fig. 9) at the CMC with increasing alkyl chain length, although wettability was not systematically affected. All of these result in CTAB being able to remove the ink particularly well at concentrations close to its CMC.

For a given surfactant type, the drastic increase in the ink removal at concentrations much greater than its CMC could be a result of the solubilization of ink components within the inner core of the micelles. The postulation is in excellent agreement with the observed increase in the solubilization capacity of ink component with an increase in both the concentration and the alkyl chain length of CnTAB above the CMC. To verify that the drastic increase in the percentage of ink removal at high CnTAB concentrations was not a result of the change in the morphology of the micelles, the viscosity of the CnTAB solutions investigated was measured. Figure 10 shows viscosity of CnTAB solutions is nearly a linear function of CnTAB concentration above the CMC. This suggests that the spherical morphology of CnTAB micelles was conserved within the corresponding concentration range investigated because an abrupt change in the slope of the plots is expected if the morphology of the micelles changes from spherical to rod-like [29].

The increased viscosity of CnTAB solutions at concentrations much greater than the CMCs is also another factor aiding in stabilizing the pigment dispersion and preventing redeposition of the detached ink particles on the HDPE surface.

Proposed mechanism for deinking process

Based on the results obtained in this work, the proposed mechanism for the removal of solvent-based ink from the HDPE surface consists of four main steps (see Fig. 11): (1) surfactant adsorption on both printed and unprinted HDPE surfaces, (2) solubilization of binder in micelles, (3) detachment of ink from HDPE surface, and (4) stabilization and dispersion of the detached ink particles. At the PZC, stoichiometric pairing between the positively charged head groups of CnTAB molecules and the negatively charged moieties of the ink components is expected. Due to heterogeneity, not all parts of the ink surface is negatively charged, and the general coverage of CnTAB molecules on the ink surface can be either a head-in (to bind with the negatively charged moiety on the surface) or tail-in arrangement (via van der Waal interaction with the hydrophobic part of the surface), while the coverage of CnTAB molecules on the hydrophobic HDPE surface can a be tail-in arrangement only. If adsorption on the charged ink particles is head-down, a bilayer generally forms with the second layer head-out. It is generally difficult or impossible to determine if a tail-down monolayer or bilayer forms because both result in a reduced contact angle (Fig. 3) or increased zeta potential. Admicelle (bilayer) or hemimicelle (monolayer) formation is driven by electrostatic attraction between head groups or tail groups and the surface and lateral attraction between adjacent surfactant tail groups. Due to the latter effect, enough surfactant molecules can adsorb on the surface to reverse the charge on the negatively charged particle to positive (Fig. 5a). Above the CMC, adsorption, wettability, and zeta potentials became constant.

Figure 11a shows a schematic of the hypothesized surfactant adsorption. The ink removal may be caused by the electrostatic repulsion between the head groups of surfactant molecules adsorbing on HDPE and ink surfaces. Once the edge of the ink starts to detach from the HDPE surface, adsorption of surfactant molecules on a newly uncovered surface results in additional electrostatic repulsion between the head groups of CnTAB molecules adsorbing on both HDPE and ink surfaces, leading to further detaching of the ink. Figure 11b illustrates the second step of ink detachment which occurs simultaneously with steps 1 and 3, the solubilization of binder into micelles, which is necessary to permit the pigment particles to detach from the surface effectively (deinking is poor below the CMC in the absence of micelles). Figure 11c shows the detachment of the ink pigment. Figure 11d shows adsorbed surfactant layer on pigment and polymer surface, giving electrostatic stabilization of detached ink pigment. The electrostatic repulsion from the positively charged head groups of CnTAB molecules absorbing on both the detached ink and the HDPE surfaces can help prevent the detached ink particles from redepositing on the HDPE surface. Solubilized binder molecules are unavailable for readsorption or redeposition.

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