



Application of ionic liquids as charge control agents of pigments and preparation of microcapsules as electronic inks through electro spraying

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ABSTRACT

In the present study, we have used two ionic liquids (ILs) with different alkyl chain lengths belonging to the imidazolium family to prepare electronic ink (E-Ink). To apply bromide as an anion, compounds such as 1-Butyl-3-methylimidazolium bromide and 1-octadecyl-3-methylimidazolium bromide were utilized as charge control agents. We prepared the E-Ink containing copper phthalocyanine blue15:3 (PB15:3) nanoparticles, which had been modified with ILs in tetrachloroethylene (PCE). As-prepared samples were characterized using Fourier-transform infrared technique, thermogravimetric analysis, high resolution transmission electron microscopy, field emission scanning electron microscopy, energy-dispersive x-ray spectroscopy, X-ray diffraction, dynamic light scattering and ζ -potential approaches. Based on the obtained results, ILs had been successfully covered onto the surface of PB15:3 nanoparticles. Thereafter, to prepare E-Ink microcapsules, the electro spraying method with a coaxial nozzle was used. According to optical microscopy data, the size of microcapsules was smaller than 200 μm . Application of ionic liquids improved zeta potential and electrophoretic mobility properties. In the future, these materials and their modified structures can be considered as appropriate candidates for application as molecular charge control agents. Moreover, we demonstrated that electro spraying is a suitable approach for producing E-ink microcapsules.

1. Introduction

In the past few decades, electrophoretic displays (EPDs) have attracted a great deal of scientific interest, due to their low cost, low weight, low power consumption and safety compared to ordinary papers [1–4]. EPDs are known as non-emitting displays and a kind of reflective displays that act based on the movements of charged nanoparticles in a dielectric media towards the electrode with opposite charge [5–8]. The electrical and optical properties of suspended nanoparticles in a dielectric media are of great significance. Several important parameters such as nanoparticle size, size distribution and surface charge as well as their response to the applied electric field are determinant in the final characteristics of E-Ink and hence, the resulting electrophoretic display. Therefore, during the past decade, researchers have tried to improve these properties. In particular, a lot of studies have been recently performed on surface modification of nanoparticles to improve their surface charge (of positive or negative type) and their application as an E-Ink.

The most commonly-used modifiers in these studies include anionic, cationic and non-ionic surfactants among which, one can name cetyltrimethylammonium bromide (CTAB) [9,10], polyethylene [11,12], sodium dodecyl sulfate (SDS) [2,9], polyvinylpyrrolidone (PVP) [3,9], polyvinylpyrrolidone (PVP) [3,9] octadecylamine (ODA) [1,13–15], sodium oleate [16,17], and hyperdispersant [5,6,17,18]. Due to their unique features, ionic liquids (ILs) have been recently used for pigment modification for application as charge control agent (CCA) [19,20]. For first time, we have synthesized two ionic liquids with geminal dicationic structure and used them as CCA for copper phthalocyanine as E-Ink, which were associated with appropriate results for zeta potential [19].

The microcapsulation method was first introduced by Jacobson in 1998 to improve the stability of electronic ink as a suspension [21]. In recent years, E-Ink microcapsules have been produced using various methods such as in situ [11,22–24], coacervation [7,25,26], emulsification [5,27] and recently, electro spray [28] techniques. The aim of electro spraying, as an encapsulation method, is to provide an active

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protection for the core material from the external environment. Using this technique, one can produce small particles from fluids with certain viscosities under electric fields. Application of a high voltage in the nozzle and collector plate produces a strong field along the gravity direction. In this method, droplet size distribution is controlled via the electric field voltage [29]. Due to application of a conductive fluid, the outer surface of the liquid is pulled into the nozzle opening. Force towards the collector plate can be controlled by the produced electric field and finally, the micro- or nano-scale droplet is produced by overcoming the surface tension force [30–32]. In this manner, it is possible to produce mono-dispersed particles.

Therefore, the aims of this study were to (1) use a combination of ionic liquids with structures similar to the molecular modifiers, such as CTAB, and (2) prepare electrophoretic ink microcapsules through coaxial electro-spraying. Hence, we used copper phthalocyanine15:3 (PB15:3) modified with two ionic liquids with different chain lengths (as the IL-based charge control agents for the first time) as the core, and utilized sodium alginate, which is a natural polymer, as the shell. In this regard, imidazolium and Br-were selected as cation and anion, respectively. As a result, we developed a stable dispersion of the modified PB15:3 in PCE as the electrophoretic fluid and subsequently, prepared microcapsules through electro-spraying as a simple microcapsulation process. Finally, to characterize the modified pigments and electro-sprayed microcapsules, hydrogen nuclear magnetic (^1H NMR), field emission scanning electron microscopy (FE- SEM), high resolution transmission electron microscopy (Hr-TEM), Fourier-transform infrared (FT-IR), thermogravimetric analysis (TGA), energy-dispersive x-ray spectroscopy, X-ray diffraction (XRD) and ζ -potential methods as well as optical microscopy were utilized.

2. Experimental section

2.1. Material for E-Ink and its microcapsule

1-Methylimidazole (82.1 g/mol), N-methylimidazole and bischloromethyl ether were purchased from Merck Millipore (United States). Copper (II) phthalocyanine 15:3 (dye content > 99%), ethyl acetate (99%), 1-Bromobutane ($\geq 97\%$), 1-Bromooctadecane ($\geq 97\%$), acetonitrile, Anhydrous alcohol, Sorbitan monooleate (Span80), Tetrachloroethylene (PCE, anhydrous, $\geq 99\%$) and Acetonitrile were purchased from Sigma-Aldrich (j). All reagents were used without any further purification. Double distilled water was used throughout the experiments.

Moreover, to prepare microcapsules using polymer of sodium alginate or NaAlg, alginate sodium salt from brown algae and calcium chloride (anhydrous CaCl_2 , $\geq 96.0\%$) were purchased from Sigma-Aldrich (Germany).

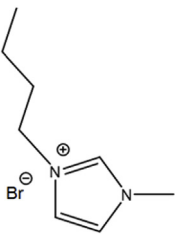
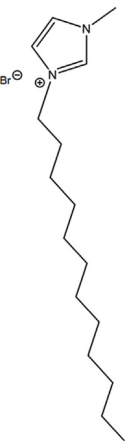
2.2. Synthesis of ionic liquids

To study the application of ionic liquids instead of active surface charge control agents such as CTAB, two ionic liquids (which were structurally similar to CTAB) with different hydrocarbon chain lengths were synthesized.

2.2.1. Synthesis of 1-butyl-3-methylimidazolium bromide ionic liquid (IL-4C)

IL-4C was synthesized according to a previous study by Ehsani et al. [33]. Briefly, 15.00 g (0.10 mol, 1 equiv) of N-methyl imidazole was added to a round bottom flask containing 100 ml of acetonitrile, which was then added with 13.70 g (0.1 mol, 1.0 equiv) of 1-bromobutane. The mixture was heated to reflux at ca. 80°C for 24 h, followed by freezing at ca. 0°C for 12 h. After removal of the volatile material under reduced pressure, the resulting yellow solution was re-crystallized from ethyl acetate to yield a white crystalline solid, which was subsequently dried under vacuum to obtain [bmim]Br in approximately 96% yield.

Table 1
Chemical structure of IL-4C and IL18C.

Chemical Formula	$\text{C}_8\text{H}_{15}\text{BrN}_2$	$\text{C}_{22}\text{H}_{43}\text{BrN}_2$
Chemical Name	1-Butyl-3-methylimidazolium bromide, [bmim]Br	1-octadecyl-3-methylimidazolium Bromide
Chemical Structure		
Abbreviation Name	IL- 4C	IL- 18C

^1H NMR (500, MHz, Chloroform- d): 10.00 (1H, s, NCHN), 7.50 (1H, bs, CH_3NCHCHN), 7.30 (1H, m, CH_3NCHCHN), 4.25 (2H, t, $J = 7.3$ Hz, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 4.10 (3H, s, NCH $_3$), 1.80 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.20 (2H, m, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 0.80 (3H, t, $J = 7.3$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$). The results of elemental analysis were as the following: C (43.85); H (6.90); N (12.78%); Found: C (43.80); H (6.85); N (12.75%).

2.2.2. Synthesis of 1-octadecyl-3-methylimidazolium bromide ionic liquid (IL-18C)

The 1-octadecyl-3-methylimidazolium bromide ionic liquid (IL-18C) was synthesized based on the method previously described by Ehsani et al. [33]. To prepare IL-18C, the stirred solution of 0.10 mol of N-methyl imidazole in 100 mL of acetonitrile was added to 0.10 mol of 1-bromooctadecane. The solution was heated to reflux at ca. 80°C for 48 h and then frozen at -20°C for 12 h. After freeze drying, a white solid with 86% purity was obtained. Table 1 shows the chemical structure of ILs. ^1H NMR (500 MHz, Chloroform- d): 10.54 (1H, s, NCHN), 7.54 (1H, m, CH_3NCHCHN), 7.35 (1H, m, CH_3NCHCHN), 4.26 (2H, t, $J = 7.3$ Hz, $\text{NCH}_2(\text{CH}_2)_{17}\text{CH}_3$), 4.17 (3H, s, NCH $_3$), 1.80 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.30 (30H, m, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_{15}\text{CH}_3$), 0.90 (3H, t, $J = 7.3$ Hz, $\text{N}(\text{CH}_2)_{17}\text{CH}_3$). The results of elemental analysis were as the following: C (63.60); H (10.43); N (6.74%); Found: C (63.57); H (10.33); N (6.64%).

2.3. Modification of PB15:3 with ionic liquids and preparation of the blue electrophoretic liquid

PB15:3 was modified according to a previously published protocol [1]. In this regard, 0.5 g of PB15:3 was added to a 100 mL three-necked flask containing alcohol (50 mL) and 0.1 g of IL-4C. The mixture was refluxed with stirring at 80°C for 1.5 h and then alcohol was removed with a vacuum dryer at 50°C to obtain PB-IL4C. The modification of PB15:3 with IL-18C was performed using the same method (to obtain PB-IL18C).

To prepare the blue electronic ink, 20 mg of Span80 and 5 mg of PB15:3 of unmodified or modified type (PB-IL4C and PB-IL18C, respectively) were added to 10 mL of PCE. The electrophoretic liquid was obtained using a probe sonicator (500 W ultrasonic, Thomas Scientific, United States) for 30 min for homogeneous dispersion.

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