Crown ether bis-diazo dyes for aqueous inkjet inks by microemulsion technique

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Abstract

Three newly synthesized crown ether dyes were used as colorants for microemulsion based aqueous inkjet inks. The microemulsions were formulated using the standard phase diagram method and were characterized by dynamic light scattering. The stability, conductivity, viscosity, surface tension and such other properties of the microemulsions were also studied. The microemulsions were then used in formulating inkjet inks that contained the dissolved dyes in the volatile nano sized oil droplets as well as in the interfacial area of the droplets. Hence the use of the microemulsions as the vehicle for the ink resulted in better dye loading. Moreover the use of crown ether dyes gave better fastness properties for the inks due to the non-covalent interactions between the cellulose of the paper and the oxygen in the macrocyclic ring.

Keywords: Crown ether bis-diazo dyes; inkjet inks; microemulsion, nano oil droplets, non-covalent interactions

1. Introduction

All conventional inkjet inks include a vehicle and a coloring element, called a colorant. The vehicle is the portion of the ink that holds it onto the printing medium such as paper, glass, ceramics, etc while the colorant entrained in the medium gives the visible image. The vehicle includes components such as solvent, solubilizing agent, viscosity modifier, pH buffer, biocide, antioxidant and many more.

The use of microemulsions as vehicles for inkjet inks was reported in 1991 by Miller et al [1]. This invention greatly diminished the problems associated with prior inkjet inks. The characteristic properties of microemulsions like high thermodynamic stability, ultralow interfacial tension and large interfacial area make them a competent vehicle in inkjet inks. Since then various microemulsions and related systems have been used in formulating inkjet inks. The microemulsion technique has constantly been improvised to give bleedless and non-threading prints [2], fast drying inks [3], liquid crystalline inks [4] etc. In addition other microemulsion systems for inkjet inks have also been reported [5-10].

On the other hand the colorants used in inkjet inks can essentially be divided into two major classes: Dyes and Pigments. Dyes are the colorants which dissolve in the medium of the ink. Hence based on the solvent used, they maybe classified as water-based and solvent-based dyes. Pigments on the other hand are insoluble and have to be solubilized using a dispersant which acts as a bridge between the solvent of the ink and the surface of the pigment molecules.

Dyes being soluble in the medium provide high color brilliance and a large color gamut. On the other hand, pigments are less used because they posed serious problems due to their insolubility like nozzle clogging and pigment settlement in the...
ink. But they are characterized by good fastness properties which make them attractive for printing on packaging materials, hoardings etc. [11,12]

Thus depending on the type of colorant used, the inkjet inks formulated will have certain limitations restricting its versatility. Hence it is a great technical challenge to formulate inkjet inks which gives overall performance and cost effectiveness.

In the present investigation we have addressed the above aspects by formulating some microemulsions as vehicles for inkjet inks and some newly synthesized crown ethers dyes as solvent soluble colorants for the inks. Microemulsions as discussed are competent vehicles for inkjet inks while the crown ether dyes are known to give high solubility as well as excellent light and water fastness by interaction with the printing substrate [13]. The robust features of the crown dyes have not yet been used in microemulsion inkjet inks. Hence in the present investigation some newly synthesized crown ether dyes 3a, 3b and 3c as described in an earlier report [14] were used as hydrophobic colorants dissolved in the oil phase of the microemulsion based ink formulation.

The microemulsions formulated were the oil-in-water type microemulsions which contained the hydrophobic colorant in its nano sized droplets. Toluene was selected as the oil phase, propan-1-ol as the co-solvent and octyl phenol ethylene oxide condensate (TX-100) as well as polyoxyethylene (20) sorbitan monooleate (Tween 80) as the surfactants.

Hence an attempt has been made to combine the fastness and strength of the crown dyes with the outstanding features of a microemulsion based ink. The microemulsion based inkjet inks thus formulated were found to be thermodynamically stable, displayed excellent fastness, had the features of dye based inks prior to printing and the features of pigment based inks after printing.

2. Experimental

2.1. Instrumentation

The average particle size or droplet size of the samples was measured at 25 °C by dynamic light scattering with the Brookhaven-90Plus/BI-MAS Instrument (15mWAr solid state laser, wavelength 635 nm, detector angle 90°, dispersant refractive index 1.33). The particle size (according to the particle number distribution) was taken as a mean value of three measurements. Samples were filtered prior to measurements through a 0.2 μm filter. Electronic spectra were recorded on a Hitachi U-3210 UV-visible spectrophotometer with matching 10 mm quartz cells.

Conductivity measurements were performed with Ecoscan Handset conductivity meter from Eutech Instruments at 25 °C with variations of ± 1 °C. Surface tension was measured using a Surface and Interfacial Tensiometer (DU-NUY’s type)-SIT-78 from S. C. Dey and Company.

2.2. Chemicals and Reagents

All the chemicals used were of analytical reagent grade of Sigma, Aldrich, E-Merck or Qualigens unless otherwise specified. The solvents used for absorption studies were rigorously purified by standard procedures [15].

The crown ether dyes 3a, 3b and 3c were synthesized as reported earlier [14] (Fig. 1).

2.3. Phase diagrams

The phase diagrams were constructed using the conventional titration technique. Toluene and a short chain alcohol (butan-1-ol or propan-1-ol) were selected as the oil component and co-solvent, respectively, in the microemulsion systems. The surfactants selected for the studied were TX-100 and Tween 80.

The pseudo-ternary phase diagrams of oil, surfactant, co-solvent and water were set up using the water titration method. The mixture of oil, surfactant and co-solvent at predetermined weight ratios was diluted with water by sequential addition of 10 μL of water using a micropipette. No heating was necessary during the preparation and all mixing was done at room temperature (25 ± 1 °C). However, the system was stirred using a magnetic stirrer to ensure a thorough mixing. After each mixing, the sample was allowed to settle and its physical condition (clarity and flow) was reviewed. If required, the sample was sonicated for 1 to 2 minutes to remove air bubbles and to enable a better visual examination.
2.4. Physical stability

The formulated microemulsions were subjected to temperatures ranging from -15 °C to 70 °C. After each temperature change the microemulsions were allowed to attain room temperatures and their physical condition was visually examined.

![Synthetic scheme for dyes](image)

Fig.1. Synthetic scheme for dyes 3a, 3b and 3c

2.5. Solubility of the dyes

A stock of the formulated microemulsions was prepared and the dyes 3a, 3b and 3c in excess were added. They were stirred overnight and then filtered through a 0.2 μm filter paper. The samples were diluted using propan-1-ol and the concentrations of the dyes were determined spectrophotometrically by using a calibration curve constructed with solutions of the dye in propan-1-ol.

2.6. General procedure for the preparation of the inks

From the microemulsions formulated as shown in Fig 2 and 3, a few were chosen to formulate inkjet inks depending on the viscosity and surface tension (microemulsions having viscosity less than 3 cP and surface tension nearly 27 N/m). The ink formulations were prepared as shown in Table 1. The rest of the components were added in their appropriate quantities. They were then dissolved in the formulations; the inks were filtered through a 0.2 μm filter and then filled into color printheads of an HP 3325 Hewlett-Packard printer. The prints taken were then used for studying the performance and durability of the inks.

2.7. Fastness properties of the inks formulated

The light fastness and water fastness of the inks were assessed using standard procedures [16,17]. The prints of the dyes were subjected to 1 year exposure in an Atlas HPUV indoor exposure system along with the standard blue dyes. After exposure, the prints were compared with the standard blue dyes and assessed on a scale of 1-8. The prints were evaluated
for water fastness by dripping 200 ml of water on the printout tilted at 45 degrees. Standard grey dyes were also subjected to the same conditions. The decrease in color was measured by comparing with the standards and rating on a scale of 1-5.

Table 1. Ink formulations

<table>
<thead>
<tr>
<th>Component</th>
<th>Ink Formulation 1</th>
<th>Component</th>
<th>Ink Formulation 2</th>
<th>Component</th>
<th>Ink Formulation 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tween 80</td>
<td>10 Wt%</td>
<td>TX-100</td>
<td>10 Wt%</td>
<td>TX-100</td>
<td>10 Wt%</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>3.2 Wt%</td>
<td>Diethylene glycol</td>
<td>3.2 Wt%</td>
<td>Diethylene glycol</td>
<td>3.2 Wt%</td>
</tr>
<tr>
<td>Toluene</td>
<td>10 Wt%</td>
<td>Toluene</td>
<td>20 Wt%</td>
<td>Toluene</td>
<td>15 Wt%</td>
</tr>
<tr>
<td>propan-1-ol</td>
<td>20 Wt%</td>
<td>propan-1-ol</td>
<td>20 Wt%</td>
<td>propan-1-ol</td>
<td>20 Wt%</td>
</tr>
<tr>
<td>Glycerol</td>
<td>7.2 Wt%</td>
<td>Glycerol</td>
<td>7.2 Wt%</td>
<td>Glycerol</td>
<td>7.2 Wt%</td>
</tr>
<tr>
<td>Triethanol amine</td>
<td>0.16 Wt%</td>
<td>Triethanol amine</td>
<td>0.16 Wt%</td>
<td>Triethanol amine</td>
<td>0.16 Wt%</td>
</tr>
<tr>
<td>Sodium penta chlorophenate</td>
<td>0.1 Wt%</td>
<td>Sodium penta chlorophenate</td>
<td>0.1 Wt%</td>
<td>Sodium penta chlorophenate</td>
<td>0.1 Wt%</td>
</tr>
<tr>
<td>EDTA disodiumsalt</td>
<td>0.15 Wt%</td>
<td>EDTA disodiumsalt</td>
<td>0.15 Wt%</td>
<td>EDTA disodiumsalt</td>
<td>0.15 Wt%</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
<td>Water</td>
<td>Balance</td>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3. Results And Discussion

3.1. Phase diagrams

The choice of the oil phase as toluene was governed by the fact that the crown ether dyes employed as colorants in the ink showed excellent solubility in toluene. Moreover the volatility of toluene made it the appropriate solvent for the formulation of inks. The nonionic surfactants chosen were the result of an extensive study on a large number of surfactants which showed that the nonionic surfactants TX-100 and Tween 80 gave very large monophasic regions in their pseudo-ternary phase diagrams with the other components of the system. Short chain alcohols like propan-1-ol and buta-1-ol are known to improve microemulsion formation [18]. Low–molecular weight alkanols affect the interfacial energy by interaction with surfactant monolayers. Hence propan-1-ol and butan-1-ol were chosen as the co-solvents.

The phase diagram of the basic system without the surfactant, namely, of propan-1-ol, toluene and water was studied and it was observed that with large amount of propan-1-ol there was a large area of one-phase solution in the mixture of water, toluene and propan-1-ol. Similarly for butan-1-ol also a monophasic area is observed with large quantities of butan-1-ol. Similar results were reported by Magdassi et al [19] and Siswana et al [20].

The phase diagrams were then evaluated for the different short chain alcohols using TX-100 and Tween 80 as the surfactants. Large monophasic areas were obtained with both co-solvents but propan-1-ol gave a larger monophasic region. Moreover due to the strong odor of butan-1-ol further studies were done using only propan-1-ol as the co-solvent.

In order to obtain larger one-phase regions, phase diagram in which the surfactant concentration was constant i.e the oil phase, the co-solvent and the aqueous phase had 10% wt of the surfactant throughout the phase diagram were plotted. As shown in Fig. 2, with propan-1-ol large monophasic regions were obtained for both TX-100 and Tween 80. An additional one-phase region was observed for both the systems at much higher toluene concentration. Electrical conductivity measurements (Fig. 3) indicated that the continuous phase in the latter region was toluene while in the larger region the continuous phase was water. It can be clearly seen that conductivity monotonically decreases with the increase of the oil. This conductivity behavior indicates the conversion of the oil-in-water microemulsion into a water-in-oil microemulsion. The decrease in conductivity in the first one-phase region was shown at several studies of microemulsion with short alkanol as co-solvent, and its variation may be explained by percolation and effective medium theories [21,22]. Therefore, it can be concluded that TX-100 and Tween 80, leads to formation of either oil in water or water in oil microemulsions.

3.2. Droplet size by dynamic light scattering

Dynamic light scattering was used to measure the droplet sizes in the formulated microemulsions. The particle sizes along with the viscosity and surface tension of the respective formulation is shown in Table 2.
Table 2. The physical characteristics of the formulated microemulsions

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Formulation 1</th>
<th>Formulation 2</th>
<th>Formulation 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cP)</td>
<td>2.25</td>
<td>1.92</td>
<td>2.12</td>
</tr>
<tr>
<td>Surface tension (N/m)</td>
<td>25</td>
<td>27</td>
<td>29</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>10.57</td>
<td>5.19</td>
<td>5.65</td>
</tr>
</tbody>
</table>

Fig. 2 (a) Phase diagram of toluene, water and propan-1-ol with 10% Tween 80 constant throughout the phase diagram (b) Phase diagram of toluene, water and propan-1-ol with 10% TX 100 constant throughout the phase diagram

Fig. 3 (a) Conductivity for Tween 80 microemulsions as a function of toluene concentration (b) Conductivity for TX-100 microemulsions as a function of toluene concentration

3.3. Solubility of the dyes

The solubility of the dyes in various microemulsions is shown in Table 3. Maximum solubility was achieved in the formulation 2. The maximum solubility was observed for dye 3b. The solubility of the dye 3a in the microemulsion as a function of toluene concentration is as shown in Fig 4. It was observed that there was a gradual increase in the solubility with increase in toluene concentration. The concentration of the dye if dissolved only in the portion of toluene present in the microemulsion was also plotted for comparison. It was clearly seen that the microemulsions had a better solubilizing capacity compared to toluene. These results suggest that the solvent soluble dyes are not simply dissolved within the toluene
droplets, but also in the co-solvent and surfactant interfacial layer.

Table 3 Solubility data for the dyes in various microemulsions

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Formulation 1 (wt %)</th>
<th>Formulation 2 (wt %)</th>
<th>Formulation 3 (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1.2</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>3b</td>
<td>1.7</td>
<td>2.6</td>
<td>2.0</td>
</tr>
<tr>
<td>3c</td>
<td>1.6</td>
<td>2.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 4 Solubility of the dye 3a in the toluene fraction and in the formulations as a function of toluene concentration

3.4. Fastness

The light fastness of the dyes on Image™ paper was in the range of 5-6 while the water fastness on all the substrates was in the range of 4-5. The light fastness and water fastness data is summarized in Table 4. The dyes showed good fastness properties compared to the fastness and stability of conventional solvent dyes like CI Yellow 19 and CI Red 8 [22].

The inks showed very high fastness towards light and water probably because of the hydrogen bonding between the hydroxy groups in the cellulose of the paper with the oxygen of the crown ether ring as shown in Fig 5.

Fig 5 Adhesion of the dyes to the paper surface
### Table 7 Fastness data for the formulated inks

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Fastness property studied</th>
<th>Formulation 1</th>
<th>Formulation 2</th>
<th>Formulation 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Light fastness</td>
<td>5-6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Water fastness</td>
<td>4</td>
<td>4-5</td>
<td>5</td>
</tr>
<tr>
<td>3b</td>
<td>Light fastness</td>
<td>5-6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Water fastness</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>3c</td>
<td>Light fastness</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Water fastness</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

### 4. Conclusion

Thus in the present investigation we have successfully formulated environmentally friendly aqueous inkjet inks using the microemulsions method. The inks exhibited:

- Enhanced fastness properties due to the attachment of the crown
- Thermodynamic stability due to the method employed
- Features of a dye based ink prior to printing and the features of a pigment based ink after printing

### References