Surfactants in Street Dust and their Deposition on Glass Surfaces

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Abstract: In this study, the dust (total) at exterior surfaces of windows and street dust (<63 μm) in the vicinity of both busy and quiet streets were sampled in order to determine the concentration of anionic and cationic surfactants, as well as anions (sulfate, nitrate and chloride) to indicate its possible sources. The sampling locations were Bandar Baru Bangi, Bandar Kajang and Seremban, which were selected due to the traffic density in those areas. Samples obtained were analyzed by colorimetric methods using Methylene Blue Active Substances (MBAS) for anionic surfactants and Disulphine Blue Active Substances (DBAS) for cationic surfactants. The results obtained indicate that the concentration of surfactants was higher in busy areas for both windows and street dust in comparison to quiet areas; although, the difference noted was insignificant (p>0.05). Such that, it is suggested that combustion in car engines is mostly likely to be the source of surfactants in both areas. Additionally, the positive correlation recorded between surfactant and nitrate concentration (R²adj = 0.51) added further support to surfactants mainly being produced as a result of vehicular emissions. On the other hand, the insignificant correlation between both surfactants in street dust and on windows in busy areas suggests that the presence of surfactants originated from different sources.

Key words: Surfactant, dust, colorimetric method, busy and quiet streets

INTRODUCTION

Surfactants in atmospheric aerosols are commonly described as water soluble materials containing oxygenated and macromolecular polar organic substances, usually found in fine mode aerosols (Kanakidou et al., 2005). Generally, a surfactant (a contraction of the term surface-active agent) is a substance that has the property of absorbing onto surfaces of the system due to their amphiphilic nature (Petrovic and Barcelo, 2004). The surfactant molecule has two parts with different characteristics; the long hydrocarbon chain that forms a nonpolar tail and the carboxylic acid group that forms a polar head. The interaction of both head and tail at the surface/interface results in a formation of surfactant monolayer which can reduce the surface tension (Latif and Brimblecombe, 2004).

Surfactants can be derived from natural and anthropogenic sources. However, combustion activities which usually produce soot, are the major source of surfactants in the atmosphere, particularly in urban area (Spyridopoulos and Simoros, 2004). Many researchers have found that the black crust (known as soot) on building surfaces consisted of carbonaceous materials derived mainly from the combustion of diesel engines. The soot particles emitted from the exhausts of automobiles

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are heterogeneous substances with a highly oxidative surface (Clague et al., 1999) and soot oxidation processes which lead to the formation of polar surface groups, such as carboxylate, are one of the sources of surfactants in the atmosphere (Smith and Chughtai, 1995). These oxidation processes generate oxygen-containing functional groups (often aromatic polyacids), which increase the polarity of the surface of the soot particles and cause solubility and surface activity to occur (Laiti and Brimblecombe, 2004). Apart from that, motor vehicles contribute not only soot but also substantial amount of Volatile Organic Compounds (VOC). Gas-phase oxidation of VOCs has the ability to produce Semi-Volatile Organic Compounds (SVOC) which then condense to form Secondary Organic Aerosols (SOA) (Seinfeld and Pankow, 2003). Substantial fraction of organic compounds represented by SVOC contains hydroxyl and carboxyl groups and hence is surface active.

It has been reported that the ability of surfactants to reduce surface tension may lead to allergies, asthma and dry eyes (Poulsen et al., 2000; Zimmer et al., 2002). This phenomenon indicates that surfactants potentially have an impact on human health. Furthermore, it is noted that surfactants may also have a negative environmental impact. Sukhapan and Brimblecombe (2002) have indicated that the presence of surfactants in the atmosphere can in fact lead to the formation of cloud albedo which can affect the global climate.

This study is aimed at determining the concentration of anionic surfactants such as Methylen Blue Active Substances (MBAS) and cationic surfactants, for example, Dusulphene Blue Active Substances (DBAS) in dust from the windows and street dust in the vicinity of busy and quiet streets. The surface-active agents are delivered to windows and roadside dust through adsorption and precipitation, respectively. According to Pio et al. (1998), carbonaceous compounds accumulate and affect impervious surfaces through the deposition process, forming a so-called organic film which contributes to the blackening and soiling of the surface; providing the rational for conducting the sampling on the surface of windows. An additional objective of this research is to explore any correlation between surfactant concentration and that of major atmospheric pollutants (e.g., Cl^-, NO_3^- and SO_4^{2-}).

**MATERIALS AND METHODS**

**Sampling Locations**

Sampling was conducted for 1 month starting from December 2006 until January 2007. Several sampling locations were selected based on the traffic density in those areas. Six roads situated in Kajang and Seremban were categorized as busy roads, while another six in Bangi and Seremban were labeled as quiet areas (Table 1). Busy roads can be defined as those used by over 5,000 cars a day, whilst quiet roads were ones used by less than 5,000 cars.

<table>
<thead>
<tr>
<th>Table 1: Sampling sites</th>
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<tbody>
<tr>
<td>Streets</td>
<td>Sites</td>
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<tr>
<td><strong>Busy</strong></td>
<td></td>
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<tr>
<td>Kajang</td>
<td>S1-Abdul Aziz street</td>
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<tr>
<td></td>
<td>S2-Abdul Aziz street</td>
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<tr>
<td></td>
<td>S3-Harun street</td>
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<tr>
<td>Seremban</td>
<td>S4-Rasah street</td>
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<tr>
<td></td>
<td>S5-Dato’ Bandar Tunggal street</td>
</tr>
<tr>
<td></td>
<td>S6-Dr. Krishnan street</td>
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<tr>
<td><strong>Quiet</strong></td>
<td></td>
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<tr>
<td>Bangi</td>
<td>QS 1-Kompleks Bangi</td>
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<td></td>
<td>QS 2-Kompleks Bangi</td>
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<td>QS 3-Kompleks Bangi</td>
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<td>Seremban</td>
<td>QS 4-Tak Ungku street</td>
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<td></td>
<td>QS 5-Blossom street</td>
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<td></td>
<td>QS 6-Rahang street</td>
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Table 2: Distance between window panes and adjacent streets (m)

<table>
<thead>
<tr>
<th>Easy streets</th>
<th>Quiet streets</th>
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</thead>
<tbody>
<tr>
<td>S1-8.0 m</td>
<td>QS 1-11.0 m</td>
</tr>
<tr>
<td>S2-6.0 m</td>
<td>QS 2-11.0 m</td>
</tr>
<tr>
<td>S3-1.5 m</td>
<td>QS 3-11.0 m</td>
</tr>
<tr>
<td>S4-8.0 m</td>
<td>QS 4-15.0 m</td>
</tr>
<tr>
<td>S5-2.0 m</td>
<td>QS 5-20.0 m</td>
</tr>
<tr>
<td>S6-1.5 m</td>
<td>QS 6-11.0 m</td>
</tr>
</tbody>
</table>

**Sampling of Dust on Glass Window Surfaces**

For the first stage of sampling, the dust on the exterior of window panes was collected by scrubbing the outside surface of the window with dry Kim Wipe laboratory tissues and then left for 1 week before the next sampling were conducted. The distance between window pane and adjacent streets are summarized in Table 2. Simultaneously, contamination from window materials was avoided by leaving a gap of 10 cm from the frame around the outside of each window pane. After sampling, all Kim Wipes were stored in plastic zipper bags to avoid any possible contamination of samples prior to preparation and analysis. The total masses of material collected from the windows were determined gravimetrically with Kim Wipes weighed on an electronic analytical balance (Mettler Toledo-Dragon, 204) and measured to the nearest 0.0001 g, both before and after sampling. Next, to prepare the sample, Kim Wipes in 50 mL of ultra pure water were sonicated in order to accelerate the extraction of organic matter from the deposited dust (Lee et al., 2001), then was filtered into a volumetric flask using 0.2 μm, 47 mm cellulose acetate filter paper (Whatman) and made up to 100 mL with water.

**Sampling of Street Dust**

The dust along the roadside was carefully collected at the same location as window dust by using the same brush which was shaken and wiped clean between samplings. Each sample was stored in a plastic zipper bags. The samples were then sieved using a 0.63 μm size sieve. After which dust samples (50 mg) were diluted to 100 mL in a volumetric flask of ultra pure water. The extracts were shaken for approximately 5 min, filtered into a volumetric flask using 0.2 μm 47 mm cellulose acetate filter paper (Whatman) and made up to 100 mL with water.

**Determination of Surfactants**

Surfactants can be categorized into 4 main types: anionic, cationic, amphoteric and non-ionic (Myers, 1988; Fan, 2006). However, in this study, anionic and cationic surfactants were the main focus as both are more highly present in the atmosphere in comparison to other types of surfactants. The presence of surfactants was determined using cationic dyes to detect anionic surfactants and anionic dyes to detect cationic surfactants. This method operated on the principle of the formation of an ion-association complex between anionic or cationic surfactants and cationic or anionic dyes, respectively. The use of appropriate dyes was followed by spectrophotometric measurement of the intensity of the extracted coloured complex (Latif et al., 2005). This methodology has previously been used for sea-spray samples by Oppo et al. (1999) and cloud water by Cini et al. (2002) The methodology also has been employed previously to study the presence of atmospheric surfactants in aerosol samples (Sukhapan and Brimblecombe, 2002; Latif and Brimblecombe, 2004).

**Determination of Anionic Surfactant as Methylene Blue Active Substances (MBAS)**

The sample solution (20 mL) was put into a 40 mL vial (vial A) equipped with a screw cap and Teflon liner. The alkaline buffer (2 mL), neutral methylene blue solution (1 mL) and then chloroform (5 mL) were added to vial A in that order. The vial was tightly closed using a holed screw-cap and Teflon liner before being vigorously shaken for 2 min using a vortex mixer. After being shaken, the screw-cap was loosened to release the pressure inside and awaited the separation phase. Once the two
phases were separated a Pasteur pipette was used to transfer the chloroform layer into the new vial (vial B) that contained ultrapure water (22 mL) and acid methylene blue solution (1 mL). Vial B was shaken using a vortex mixer for 2 min. The cap was then loosened for few seconds and re-tightened. After the chloroform had completely separated from the water (after 2 min), the chloroform layer was collected using a Pasteur pipette and placed in a 10 mm quartz cell. The absorbance of the chloroform phase was measured by using a ultra-violet spectrometer at a wavelength of 630 nm (Latif and Brimblecombe, 2004).

**Determination of Cationic Surfactants as Disulphine Blue Active Substances (DBAS)**

The determination of cationic surfactants using anionic dyes operates on a similar principle as determination of anionic surfactants using cationic dyes (see section 2.4). A volume of the sample solution (20 mL) was placed in a 40 mL vial equipped with a screw cap. An acetate buffer (2.0 mL) and then 1 mL disulphine blue solution were added to the solution. After 5 mL of chloroform was added, the solution was vigorously shaken for a minute using a vortex mixer. The cap was loosened for a few seconds to release the pressure and then re-tightened. The vial was inverted and left until the two phases were completely separate (around 2 min). Some of the chloroform layer was removed using a Pasteur pipette and placed in the 10 mm quartz cell, its light absorbance was then measured at a wavelength of 628 nm (Latif and Brimblecombe, 2004).

**Determination of Anion**

Anions were analyzed using ion chromatography (DIONEX 4000i Ion Chromatograph), which is an analytical method for detection of ionic species. Ion chromatography is a separation technology which uses an anion exchange column to separate anions moving through the column, which are then measured by a detector system at the column outlet (Jeffery et al., 1989).

**RESULTS AND DISCUSSION**

The results showed that along busy streets, the concentration of Methylene Blue Active Substances (MBAS) and Disulphine Blue Active Substances (DBAS) was 0.07±0.02 and 0.04±0.03 μmol m⁻², respectively. The μmol m⁻² unit was used in order to represent the amount of surfactants deposited on the surface of the glass windows. It was found that the concentration of anionic surfactants (as MBAS) was higher in comparison to cationic surfactants (as DBAS) in the atmosphere. From observation, the traffic density which was high along the busy streets probably generated more soot particles to be oxidized to form surfactants; thus explaining the high concentration of negatively-charge surfactants in the busy areas (Latif and Brimblecombe, 2004).

Another point to note is that diesel soot, in comparison to petrol soot, could make a large contribution to the surfactants load in aerosols. According to Sakumai et al. (2003), diesel exhaust particles can be formed as ultrafine particles in high concentrations and can contain high levels of organic compounds and soot. It was found that the hydrocarbon mixtures of diesel fuels were in the range from C₁₅ to C₇₂ with boiling points between 174 and 360°C (Omar et al., 2006). This indicates that more particulate organic compounds are generated when combustion takes place in vehicles engines, suggesting the possibility that surfactants might be derived from diesel soot. This result also mirrored those from a previous study (Latif et al., 2005) which indicated that the concentration of anionic surfactants was higher in diesel soot than in petrol soot and soot from wood.

Along quiet streets, the average concentration of surfactants, as MBAS and DBAS was 0.05±0.01 and 0.07±0.02 μmol m⁻², respectively. In contrast with the busy streets, the quiet ones provided more cationic surfactants than anionic surfactants with the high amount of cationic surfactants usually dominated by organic nitrogen, possibly originating from soil (Latif et al., 2005). It is possible that the
dust deposited onto the streets simply originated from wind-blown soil particles generated from private gardens, plantations along the road side and even from road medians planted with grass and shrubs. It has been found that the decomposition of plants and insects would convert large organic nitrogen molecules into water-soluble salts containing ammonium ions (NH$_4^+$) (Miller, 1982). Since, the cationic surfactants comprised positive charges such as ammonium ions, it can be inferred that cationic surfactants come from the soil. In addition, the use of artificial fertilizers containing ammonium salts is also considered to be a likely contributing factor to the high concentration of cationic surfactants in soil. Meteorological factors such as wind also might explain how the particulates containing organic nitrogen may have managed to travel over great distances (Wilkening et al., 2000; Gyan et al., 2005). The ability of soil particulates remain in the troposphere for only a few weeks before removal by precipitation or by gravitational settling, would be expected to lead to high concentrations of DBAS in quiet areas (Highwood and Kinnersley, 2006).

Comparison of Surfactants in Street Dust from Busy and Quiet Streets

Street dust collected from busy streets contained much higher amounts of MBAS (0.70±0.07 μmol g$^{-1}$) in comparison to dust from quiet streets (0.58±0.09 μmol g$^{-1}$), where the difference noted was significant (p<0.05). Since the initial samples were in a solid form, the data was presented in terms of concentration of surfactants per mass of dust. This result indicates that urban soil might contribute to the presence of anionic surfactants in street dust. Urban soils, according to Plaster (2003), can be defined as those soil found within cities, towns or metropolitan areas, where particles deposited upon the soil are generated from a range of human-related sources, such as vehicular emissions, industrial discharge and urban development. A study conducted by Arslan and Güzir (2005) indicated that vehicular emission is commonly known to be a significant and increasing source of soil pollution in urban environments and it is possible that surfactants might be derived from this polluted soil. Additionally, humic materials are acknowledged as being a possible source of atmospheric surfactants in the atmosphere. The amount of surfactant from street dust was expected to originate from the photo-oxidation of primary humic material driven into the atmosphere from soil, as proposed by Tegen and Fung (1995). Surfactants in street dust can also be a secondary product of the oxidation of soot particles; e.g., HULIS produced when soot is exposed to ozone (Deccarsi et al., 2002). Consequently, it is suggested that anthropogenic sources might influence the concentration of surfactants in street dust.

Correlation Between Surfactants in Dust from Windows and Street Dust

The concentration of both MBAS and DBAS in dust from glass surfaces had an insignificant correlation (p>0.05) with the concentration of MBAS and DBAS in street dust, both in busy and quiet areas (Fig. 1a, b, 2a, b). It can therefore be proposed that the presence of surfactants on the windows were not influenced by the presence of surfactants in street dust. Work by Miguel et al. (1999) found that road dust present on the surface of streets in Southern California consisted of a complex mixture of soil dust, deposited motor vehicle exhaust particles, tire dust, brake lining wear dust, plant fragments and other biological materials. Thus, street dust can be defined as an agglomeration of multiple sources contributions which originated from anthropogenic or biogenic sources (Rogge et al., 1993a).

Possible sources of surfactants can be indicated by the size of the dust particles collected. A study by the Bascom (1996) discovered that particles generally derived from combustion sources (vehicles, power plants, etc.) are smaller whilst those from abrasion (road dust, wind blown soil) are often larger. From this experiment, it was found that the dust collected from the windows contained a higher amount surfactants compared to street dust, which was due to the small size of dust particles. Penttinen et al. (2001) reported that the number of particles (and surface area) to mass ratio increases
Fig. 1: Correlation between MBAS in both dust from glass window and street dust at vicinity of the (a) busy streets and (b) quiet streets

\[ y = 0.0021x + 0.6911 \]
\[ R^2 = 0.0256 \]

Fig. 2: Correlation between DBAS in both dust from glass window and street dust at vicinity of the (a) busy streets and (b) quiet streets

\[ y = -0.0031x + 0.6122 \]
\[ R^2 = 0.0862 \]

with decreasing size, hence, providing a higher concentration of surfactants. Thus, it can be suggested that surfactants deposited on the glass windows were originated from combustion activities. Research
conducted in Pasadena indicated that the lower molecular weight range C_{17}-C_{20} is typical for vehicle exhaust emissions (Simoneit, 1984, 1985; Rogge et al., 1993a). According to Cirelli et al. (2008), surfactants was usually found in the range between C_{17}-C_{20}.

**Surfactants and Anions (NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}^{2-} and Cl\textsuperscript{-})**

The distribution of anions in both busy and quiet areas shows that the concentration of anions was dominated by Cl\textsuperscript{-}, followed by NO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}^{2-} (Fig. 3) Levels of chloride (Cl\textsuperscript{-}) were found to be higher, providing another indication of the possibility of MBAS from the natural source of the sea surface microlayer (Latif et al., 2005). A study by Zhang et al. (2007) also indicated that the Cl\textsuperscript{-} ion is commonly of marine origin and whilst there was a considerable distance between the sampling areas and the sea, meteorological factors such as wind could have enabled dust particles from the sea to have been distributed over the sampling area. According to Wrobel et al. (2000), wind velocity is capable of sustaining small particles (with a diameter of 25 μm or less) in the air and moving them great distances. Open burning activities could also explain the presence of Cl\textsuperscript{-} in fine ambient particles as research undertaken by Liu et al. (2000) suggested that during atmospheric movement from the fire source regions to the receptor sites, the Cl\textsuperscript{-} in the KCl particles is released by acidification reactions with SO\textsubscript{2} from various sources, some which may be emitted during the fires. Thus, this phenomenon could explain the high concentration of Cl\textsuperscript{-} found in urban areas.

On the other hand, the concentration of NO\textsubscript{3} and SO\textsubscript{4}^{2-} were low in both sample areas. This, according to Finlayson-Pitts and Pitts (2000), may be due to NO\textsubscript{3} and SO\textsubscript{4}^{2-} often being higher in aerosols collected from urban areas which are a consequence of human activities such as the use of motor vehicles, industrial activities and open burning. However, there are some factors which might explain the low concentration of both anions in the sampling areas. A decrease in NO\textsubscript{3} could determine the low concentration of NO\textsubscript{2} as it well known that the emission of NO\textsubscript{2} originates from the complete fuel combustion in motor vehicles (Rijnders et al., 2001). However, from observation of the sample sites, complete combustion failed to occur as most of the vehicles were moving at a moderate speed which influenced the efficiency of the combustion process. Consequently, incomplete combustion is likely to have decreased the production of NO\textsubscript{2} and hence, led to a low concentration of NO\textsubscript{2} (Eq. 1):

\[
2\text{NO}_2 + 1/2 \text{O}_2 \rightarrow \text{N}_2\text{O}_3
\]

\[
\text{N}_2\text{O}_3 + \text{H}_2\text{O} \text{(water vapor)} \rightarrow 2 \text{H}^+ + 2\text{NO}_2^{-}
\]  

Additionally, much SO\textsubscript{2} gas is produced by the vehicular combustion process and therefore are a major contributor to the content of SO\textsubscript{4}^{2-} in the atmosphere. Chang et al. (1987) stated that the
formation of $\text{SO}_2^{\text{aq}}$ depends on the concentration of $\text{SO}_2$ gases and it was found that the conversion of $\text{SO}_2$ to $\text{SO}_4^{2-}$ was likely to have decreased due to the high concentration of $\text{SO}_2$. It was rainy reason in Malaysia during the period of sampling. Thus, wash out and dilution processes from rain water are believed to have reduced concentrations of $\text{SO}_4^{2-}$ anion in the samples (Stern et al., 1984). During the dry season, natural sunlight is able to increase the concentration of surfactants (Latif et al., 2005).

The overall correlation of MBAS with anions such as $\text{NO}_2^-$, $\text{SO}_4^{2-}$ and $\text{Cl}^-$ indicate that the correlation of MBAS and anions in busy areas was more marked with $\text{NO}_2^-$, followed by $\text{SO}_4^{2-}$ and $\text{Cl}^-$. Regression analysis of concentrations of MBAS and anions along busy roads show that concentrations of MBAS have an insignificant correlation with concentrations of $\text{Cl}^-$ ($n = 8$, $R^2 = 0.12$, $p>0.05$) and $\text{SO}_4^{2-}$ ($n = 8$, $R^2 = 0.19$, $p>0.05$). Correlation of MBAS in quiet areas with these three anions also indicated the same results with an $R^2$ value of 0.11, 0.11 and 0.06 for nitrate, sulphate and chloride, respectively. As mentioned earlier, $\text{NO}_2^-$ often being higher in aerosols collected from urban areas which are a consequence of human activities such as the use of motor vehicles, industrial activities and open burning (Finlayson-Pitts and Pitts, 2000). The significant correlation of MBAS with $\text{NO}_2^-$ ($n = 8$, $R^2 = 0.51$, $p<0.05$) indicates the possibility of MBAS originating from anthropogenic sources and it was found that $\text{NO}_2^-$ was mainly produced by vehicle emissions. This is considered a good indicator that the combustion of engine fuels is the major source of surfactants in busy areas.

CONCLUSION

Results show that the average concentration of surfactants deposited on glass surfaces was high in busy areas. It was noted that the urban atmosphere was more likely to be dominated by negatively-charge surfactants (anionic surfactants), which indicates that the density of surfactants was influenced by the combustion process of motor vehicles. Furthermore, a strong correlation between anionic surfactants and nitrate provide further support for the contention that vehicular emissions are the principal source of surfactants in urban environments. The insignificant correlation between the concentration of surfactants collected from the windows and the concentration of surfactants collected from street dust shows that surfactants deposited on the window glass directly derived other anthropogenic and natural sources, such as combustion by motor vehicles and from other evaporated chemicals in the environment which have surfactant characteristics.

REFERENCES


