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Graphical Abstract

Surface pressure (mN/m) vs. Area per molecule (Å²) for C18E1.
Highlights

- A series of monolayer compounds was synthesized.
- Their performance as monolayers was investigated under static and dynamic conditions.
- Molecular simulation used to assist in interpretation of experimental results.
- Increasing the hydrophilic headgroup with one ethylene oxy improved monolayer lifetime.
- Design principles for future engineering of improved suppressants were suggested.
Rational design of monolayers for improved water evaporation mitigation

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Abstract

Seven chemically designed monolayer compounds were synthesized and investigated with comparison to the properties and water evaporation suppression ability of 1-hexadecanol and 1-octadecanol. Increasing the molecular weight and polarity of the compound headgroup drastically altered the characteristics and performance of the monolayer at the air/water interface. Contrary to the common expectation the monolayer’s lifetime on the water surface decreased with increasing number of ethylene oxy moieties, thus optimal performance for water evaporation suppression was achieved when only one ethylene oxy moiety was used. Replacing the hydroxyl headgroup with a methyl group and with multiple ethylene oxy moieties resulted in a loss of suppression capability, while an additional hydroxyl group provided a molecule with limited performance against water evaporation. Theoretical molecular simulation demonstrated that for exceptional performance, a candidate needs to possess a high equilibrium spreading pressure, the ability to sustain a highly ordered monolayer with a stable isotherm curve, and low tilt angle over the full studied range of surface pressures by simultaneously maintaining H-bonding to the water surface and between the monolayer chains.

Keywords
Monolayer; water evaporation; molecular dynamics simulation; wind resistance; 1-octadecanol; ethylene glycol mono-octadecyl ether

1. Introduction

Monolayers are one-molecule thick surface films formed by certain amphiphilic molecules such as fatty alcohols and their derivatives. They have been used as the basis for a number of different applications, such as, membranes for molecular separations,[1-2] biomedical systems for tissue engineering and drug delivery,[3-5] packaging and coating materials,[6-7] and water evaporation mitigation.[8] Water is one of the scarcest resources and it is likely to have significant impact on the economic development of many countries, including their population and agricultural industries. Rideal[9] first reported that monolayers reduce the rate of water evaporation as they have the ability to form closely packed films, restricting the loss of water molecules. Subsequently, Langmuir and Schaefer made the first quantitative measurements of the
evaporation resistance ($r$) of monolayers and demonstrated an Arrhenius-type dependence of the resistance to permeation by evaporating water molecules with temperature.[10] Since these discoveries, considerable attention has been directed towards effective suppression of water evaporation, especially from large open water bodies.[11-13]

1-Hexadecanol (cetyl alcohol) and 1-octadecanol (stearyl alcohol) in particular have received much attention for their ability to reduce water evaporation.[12, 14] In order to be useful as evaporation suppressants, surface films need to have a high equilibrium surface pressure, and a reasonably good ability to reduce evaporation at this pressure. 1-Hexadecanol and 1-octadecanol have been shown to have reasonable static evaporation suppressant capabilities, saving up to 50% of water lost under suitable conditions.[15] However, these molecules have generally not been considered to be sufficiently effective as water evaporation suppressants in practical systems due to their rapid loss from the water surface, as well as difficulty in obtaining reliable suppression performance observed under laboratory conditions.[8] Brooks and Alexander[16] demonstrated that the loss of these molecules is primarily due to volatilization into the air, with dissolution into solution only becoming more significant at temperatures below 20°C. However, despite this important finding almost no effort has been made to address this problem so far.

For many years, important studies at the laboratory scale were carried out in order to identify the desired properties and conditions required to understand the mechanism by which monolayers reduce water evaporation. Laboratory studies also provide a first test for the effectiveness of selecting and developing new materials capable of reducing evaporation. The most commonly used technique to obtain information about the properties of monolayers is the Langmuir trough, used to generate isotherms of surface pressure as a function of area per molecule. Other important data obtained from a Langmuir trough include the equilibrium film pressure, the surface pressure at which the molecules are in equilibrium and are usually packed closely together in the solid-like or liquid-condensed phases. It is in the solid phase where the high surface pressures will allow the monolayer to attain the highest water evaporation resistance and, in some cases, drive any impurities out of the monolayer film.
Compounds with 12 or more carbon atoms in the aliphatic chain and with a hydrophilic headgroup can form stable and insoluble monolayers. Increasing the alkyl chain length of the molecule increases the evaporation resistance but also reduces the rate at which the solid material spreads across the water surface. Unsaturation and branching of the hydrocarbon chain can adversely affect how the molecules will pack together in the monolayer and this has been extensively investigated.[17] Thus, further improvement needs to be explored at the headgroup section of the molecules. However, there is little understanding of how the structure of the hydrophilic headgroup affects monolayer stability properties.

Furthermore, a film that is considered stable on the Langmuir trough may not be stable on the surface of an open water reservoir. A common problem in the field is the lack of film stability against wind and wave action, which can profoundly accelerate the loss of the monolayer material. Previous research has stated that exposure to wind of a velocity greater than 10 km/hr (2.7 m/s) destroys the monolayer thereby markedly reducing its ability to control water evaporation.[18] However; despite these statements limited knowledge is available about wind resistance of monolayer molecules on a laboratory scale.

In this paper we report on the properties of a series of chemically designed compounds with different headgroups and their performance under static and wind conditions. The design and choice of these monolayer compounds allows for studying the effect of structure on properties such as their life-time at the air/water interface, performance against wind, and ability to reduce water evaporation. These properties are investigated by using a laboratory method developed for measuring water evaporation resistance of monolayers under wind stress to determine the continuous rate of water loss as a function of time using these compounds. The study is also intended to provide insight into the monolayer system to maximize its functionality by bridging the gap between laboratory-based experiments and those performed in the field by reflecting the dynamic conditions obtained in nature.

To understand the inter-atomic interactions of amphiphilic monolayers at the water surface relevant to their evaporation suppressing and wind resistance properties we used all-atomic Molecular Dynamics simulations. We have previously shown[19-21] that differences among the
headgroups can be accounted for by analysing the specific interactions responsible for monolayer stability and water evaporation mitigation properties. In this paper we employ a combined experimental and theoretical approach to unveil the reasons why 1-hexadecanol and 1-octadecanol have a much shorter lifetime under wind conditions. We develop a theoretical understanding of the performance of these new monolayer architectures in terms of lifetimes on the water surface and water evaporation suppression under static and dynamic conditions for rational design of improved monolayers for water evaporation mitigation.

2. Materials and Methods

2.1. Materials

1-Hexadecanol (C16OH), 1-octadecanol (C18OH) and 1-octadecyl glyceryl ether (C18G1) were purchased from Sigma Aldrich. Ethylene glycol monoolein ether (C18E1), diethylene glycol monoolein ether (C18E2), triethylene glycol monoolein ether (C18E3), ethylene glycol monomethyl monoolein ether (C18E1Me), diethylene glycol monomethyl monoolein ether (C18E2Me) and triethylene glycol monomethyl monoolein ether (C18E3Me) were synthesized according to a general method.[22] Synthesis and characterization details can be found in Supplementary Information.

2.2. Preparation of monolayer solutions

The monolayer compounds were made up into solutions of a known concentration of 1 mg/ml in hexane (AR grade, Chem-Supply).

2.3. Apparatus

A Teflon® Langmuir trough (76 cm x 10 cm, Nima Technology Ltd) Model 711D with a single Delrin® barrier (11.2 cm x 1.6 cm) was used to characterise the properties of the monolayer film. Before each experiment, the trough and barrier were thoroughly cleaned with chloroform (AR grade, Chem-Supply) and a Wilhelmy plate (2.35 cm x 1 cm, Whatman CHR1 filter paper) was attached to the pressure sensor. The trough was then filled with Milli-Q water (18.2 MΩ.cm Millipore) and allowed to equilibrate with the air at a temperature of 25±1 °C. The water surface
was swept clean until the surface pressure reading was zero. Generally 50 μL of the solution containing the monolayer was applied to the water surface (700 cm² area) using a microsyringe, unless otherwise stated. The monolayer film was left for 30 minutes to allow the solvent to evaporate. [23] Once the Langmuir trough was prepared the following characterisation studies of the deposited film were conducted.

2.4. Surface pressure/area isotherms
The Delrin® barrier was used to slowly compress the monolayer film at a rate of 50 cm²/min while measuring the surface pressure as a function of the area per molecule (Å²/mol) until the monolayer reached its collapse pressure. The barrier was then opened at the same speed of 50 cm²/min and the surface pressure was also recorded. This isotherm cycle was repeated three times to confirm the stability of the monolayer film and to ensure the reproducibility of the data.

2.5. Equilibrium surface pressure
In this instance, the barrier was used to close ¾ of the trough (approx. 175 cm², barrier is closer to the pressure sensor) and then a solution of the monolayer forming material in hexane was added on the water surface. The quantity of solution added contained three times the amount required to cover the water surface in the designated area with a close-packed monolayer, termed three theoretical monolayers. This amount is calculated using the area required to occupy one monolayer molecule (Å²) and the area of the Langmuir trough used. The surface pressure was allowed to equilibrate for 30 minutes before the data was recorded. The barrier was then opened slightly and closed again to a different position on the trough and allowed to equilibrate for another 30 minutes and the pressure reported. This step was repeated a third time and an average of the three measurements was taken.

2.6. Loss of monolayer material
50 μL of the monolayer forming material was applied to the water surface and left for 30 minutes. The barrier was then used to compress the monolayer to a surface pressure of 27 mN/m, after which the barrier was instructed to hold the monolayer constant at that pressure. This surface pressure was chosen for all measurements to allow direct comparison between the performances of different compounds. This pressure is also the highest value which could be
used to compare these investigated compounds as C18E3Me has a collapse pressure of 28 mN/m. As the monolayer material disappeared, the barrier was forced to compress the monolayer to maintain this surface pressure. The change in surface area over time was recorded continuously for 24 hours. This was then subsequently correlated to the rate of loss of monolayer material, and the results were presented as the percentage of monolayer material remaining on the water surface as a function of time. The water level in the trough was maintained by placing the tip of a separating funnel (held by a retort stand) filled with Milli-Q water on the side of the barrier without monolayer. The change in height allowed water in the separating funnel to flow, thus maintaining the water level in the trough relatively constant. An average of three runs was taken for reproducibility.

2.7. Static evaporation resistance
The Langmuir-Schaefer method[10] was applied by using a desiccant to measure the rate of water evaporation at the equilibrium surface pressure. The water surface in the Langmuir trough was closed by ⅔ using the barrier (250 cm²) where 3 times the monolayer material was applied to the water surface. The monolayer film was left for 30 minutes to let the solvent evaporate.[23] The desiccant used was dried, finely ground lithium chloride (LiCl, 99 %, Sigma-Aldrich) contained in a metal container (8.5 cm diam.) with a base of permeable cloth covered with a lid, which was weighed on a digital balance. Then the lid was removed and the desiccant container was suspended 2 mm above the water surface for 30 minutes on the monolayer covered area. This distance was held constant for all experiments and the percentage of the interfacial area covered by the desiccant was approx. 90 %. After the specified time the desiccant container was removed, the lid fixed and then reweighed. The difference in mass weighed before and after amounted to the loss of water due to evaporation during that time. This measurement was repeated three times for both a clean water surface and a monolayer covered area and the average taken. After every run, care was taken to ensure the desiccant (LiCl) was dried and mixed thoroughly to avoid caking or adhesion to the permeable cloth. The percentage of water evaporation saving was then calculated with respect to the amount of water evaporated from the clean water surface.

2.8. Evaporation reduction under exposure to wind
A gravimetric method was used to measure the evaporation reduction under exposure to wind. The wind was generated by a centrifugal fan (RS Components Pty Ltd) connected to a wind tunnel made in-house as illustrated in Figure 1. The wind tunnel ensured that the air flow out of the tunnel was laminar, and the wind speed was set at 25 km/hr (7.0 m/s, measured by a hot wire anemometer (Control Company) placed at the mouth of the wind tunnel). The mouth of the wind tunnel was positioned at the end of a digital balance (Mettler-Toledo Limited) where a plastic rectangular container (10.5 cm x 16.3 cm) filled with 800 mL of Milli-Q water was placed on top. The digital balance was connected to a computer installed with the BalanceLink® program, which was set to record the mass of the container and water every minute. Films of three theoretical monolayers were applied on the water surface and left for 30 minutes before turning on the fan. As an example, the quantity required to cover one closely packed monolayer of C16OH on the water surface is 0.0287 mg using the following values: area of container 171.2 cm², area occupied by one monolayer molecule 24 Å² and the molecular weight of C16OH is 242.44 g/mol. Therefore, three theoretical monolayers of C16OH is 0.0861 mg, which can be converted to a volume of 86.1 μL of 1 mg/mL solution. The change in weight of the container and water was monitored for two hours. A container of water with no monolayer was used as the control. An average of three measurements was taken for each compound.

Figure 1. Schematic diagram of wind tunnel set up

2.9. Molecular Dynamics (MD) simulations

Molecular Dynamics (MD) simulations have been demonstrated to be a useful and well validated technique for modeling monolayer and bilayer systems. Reviews demonstrating the suitability of these methods can be found in references [19-21, 24-26]. GROMACS[27] software package was used with the OPLS[28] forcefield to model C18OH, C18E1, C18E2, C18E3Me and C18G1 monolayers, representing at least one molecule from each class of monolayers (see Figure 2).
Each system was constructed by placing 80 molecules aligned parallel to the z-direction in periodic unit cells with dimensions 40 x 40 x 140 Å. The cell size in the z-direction was chosen to accommodate a water layer ≥ 20 Å thick situated directly beneath the headgroup and a vacuum space of approx. 100 Å in length above the hydrophobic tails to mimic a quasi 2D interface.

The OPLS[28] forcefield was employed as it was previously found to efficiently and accurately model the inter-atomic interactions in octadecanol monolayer/water systems[21]. The TIP4P[29] model was used to represent the water molecules. The particle mesh Ewald method[30] was employed to calculate the electrostatic interactions with the real space part of the Ewald sum and the Lennard-Jones van der Waals interaction cutoffs at 13 Å. To eliminate any inherent strain in the initial system, the steepest descent method was used to minimize the potential energy with the convergence criterion set to 1 kJ/mol. Following this, MD was performed in the NPT (constant number of particles (N), constant pressure (P), constant temperature (T)) ensemble for 10 ns with an integration time step of 1 fs. The temperature was maintained at 298 K using the thermostat of Bussi et al.[31] while the surface pressure was maintained using the Berendsen coupling regime.[32] The systems were considered equilibrated when fluctuation in the x-y box vectors was below approx. 0.2 Å, at which point the thermodynamic properties, volume and total energy reached equilibrium. The data acquisition was performed over the final 5 ns with surface pressure coupling applied in the x-y directions.

The performance of the molecules was assessed over a range of surface pressures. Each system was initially coupled to a surface pressure of 50 mN/m and MD was performed. The surface pressure was then decreased by 5 mN/m until a surface area change of at least 3 Å² per molecule was observed, at which point the surface pressure was decreased by 2.5 mN/m. At very low surface pressure (< 20 mN/m) the step size was reverted back to 5 mN/m to retain computational tractability. The pressure was reduced until signs of instability were observed, such as pore formation in the monolayers.

Specific interactions between monolayer chains as well as between the chains and water were characterized as a function of surface pressure. The average number of hydrogen bonds
occurring between donor-acceptor pairs was calculated based on the cutoff criteria for the hydrogen donor-acceptor angle (≤ 30°) and the donor-acceptor distance (≤ 3.5 Å). [33] We also calculated the average radial tilt angle of the chains with respect to the interfacial normal. These theoretically calculated properties are presented in Table 1, and are compared with experimental values where available.

3. Results and Discussion

It can be strongly argued that while wind is a factor affecting the lifetime of the monolayer, a more fundamental issue is the stability of the monolayer material on the water surface. Early reports describe the loss of 1-hexadecanol and 1-octadecanol, [16, 34-36] with Brooks and Alexander demonstrating this loss is predominately due to volatilization. [16] However, despite this issue the majority of research has continued to focus on the use of these monolayer molecules. In a 2008 review of the current state of monolayer technology Barnes stated that it is clear that better monolayer materials are required. [8] In order to achieve this, it is first important to understand the performance of current materials and then develop a design strategy to overcome the limitations.

3.1. Investigation of 1-hexadecanol and 1-octadecanol.

1-Hexadecanol (C16OH) and 1-octadecanol (C18OH) are fatty alcohols and their structures are shown as 1 and 2 in Figure 2.
**Figure 2.** Structures of monolayer compounds: 1 – 1-hexadecanol (C16OH), 2 – 1-octadecanol (C18OH). Class 1 compounds: 3 – ethylene glycol mono-octadecyl ether (C18E1), 4 – diethylene glycol mono-octadecyl ether (C18E2), 5 – triethylene glycol mono-octadecyl ether (C18E3). Class 2 compounds: 6 – ethylene glycol monomethyl mono-octadecyl ether (C18E1Me), 7 – diethylene glycol monomethyl mono-octadecyl ether (C18E2Me), 8 – triethylene glycol monomethyl mono-octadecyl ether (C18E3Me). Class 3 compound: 9 – 1-octadecyl glyceryl ether (C18G1).

While both C16OH and C18OH perform adequately well in terms of forming a good monolayer and reducing the evaporation of water, their long term performance in suppressing water evaporation is not good. They are susceptible to loss from the water surface (predominately to volatilization)[16] and this has become an important drawback for their water evaporation suppression performance. In the study of the loss monolayer material from the water surface, compounds were individually applied to the water surface in a Langmuir trough as a solution in hexane. Hexane was chosen as the nonpolar spreading solvent to avoid loss of the monolayer film into the water subphase, as reported if ethanol or mixtures of ethanol are used as the spreading solvent.[37] The rate of material loss from the water surface was monitored by the change in surface area over time when a surface pressure of 27 mN/m was maintained. The
change in surface area over time was then correlated to the decrease in the amount of material. Brooks and Alexander have previously reported on the loss of C16OH and C18OH.[16] In this paper similar experiments were repeated in order to have direct comparison to other compounds later used in this study (Figure 5).

Under static conditions, C16OH or C18OH showed approx. 30-40% saving of water from evaporation within 30 minutes. Under dynamic conditions, the performances of C16OH and C18OH were measured using a laboratory wind test method, and are compared to a control sample where no monolayer was used with the results shown in Figure 3.

![Graph showing mass of water lost over time for C16OH and C18OH compared to a control with no monolayer.](image)

**Figure 3.** Mass of water lost over time for C16OH and C18OH compared to a control with no monolayer under exposure to wind at 25 km/hr applied at 3 theoretical monolayers from a 1 mg/ml hexane solution.

It can be seen that both C16OH and C18OH are not only lost relatively rapidly from the water surface, similar to what was observed by Brooks and Alexander,[16] but they also perform poorly as evaporation suppressants in the presence of wind with the water savings decreasing with time. The rapid loss of monolayer is likely due to their volatility and inability to hold onto the air/water interface. Therefore, a series of monolayer compounds was synthesized to study new monolayer structures which can overcome these limitations.
3.2. Design principles for improved performance of new monolayer materials

To improve the monolayer’s water suppression ability under wind, both its resistance to being lost from the water surface and ability to control water evaporation under wind stress need to be improved. Based on this understanding new monolayers were developed using the following two approaches:

- **Increase the molecular weight of the monolayer compound** – this was designed to improve resistance to loss by decreasing the vapour pressure. This concept is illustrated in Figure 2 for C16OH and C18OH, where C18OH has a longer lifetime on the surface than C16OH. However, a good monolayer needs to be able to self-spread on the water surface and be capable of self-healing. As the alkyl chain gets longer, this requirement becomes more difficult to fulfill as the spreading rate decreases with increasing chain length. Hence, further increase in the molecular weight has to be in the hydrophilic head region of the molecule.

- **Increase the polarity** – this was designed to increase the “anchoring” of the molecule to water via additional hydrogen bonding, hence less volatilization, thereby improving the monolayer resistance to being lost to the water and wind. Alternative polar head groups such as carboxylic acid or amide were considered during the design phase, however previous research has shown monolayers containing these groups demonstrate negligible water savings,[38] primarily due to their low equilibrium spreading pressure.[8]

Based on the two approaches described above, a range of target molecules was synthesized and tested for their ability to remain on the water surface, as well as their wind resistance. Seven molecules, falling into three classes, which comply with the improvement strategy, are shown as 3 – 9 in Figure 2. These molecules all contain an “anchor” group in the hydrophilic head. In the case of Class 1: ethylene glycol mono-octadecyl ether (C18E1), diethylene glycol mono-octadecyl ether (C18E2) and triethylene glycol mono-octadecyl ether (C18E3) have the addition of one, two or three ethylene oxy moieties to 1-octadecanol (C18OH), providing one, two or three additional hydrophilic ether linkages, respectively. This design strategy is intended for these compounds to have a greater proportion of the molecule attracted to the water phase and to be progressively less volatile. However, there is an expected limitation on the number of ethylene oxy units which
can be added before the compound is no longer insoluble and capable of forming a stable monolayer on the surface, instead being more likely to behave as a surfactant to form micelles in solution. In the Class 2 compounds there is addition of a methyl group to the ethylene glycol head: ethylene glycol monomethyl mono-octadecyl ether (C18E1Me), diethylene glycol monomethyl mono-octadecyl ether (C18E2Me) and triethylene glycol monomethyl mono-octadecyl ether (C18E3Me). The methyl group was chosen to counteract the hydrophilicity of the extra ethylene oxy moieties by essentially replacing the hydroxyl group with the less hydrophilic methyl ether. Class 3 contains octadecyl glyceryl ether (C18G1), providing not just an ether linkage, but also two hydroxyl groups instead of one as in the Class 1 molecules, further increasing the polarity of the headgroup. All of these molecules not only have increased molecular weight compared to C16OH and C18OH, but they also have increased polarity. Studies on the properties and performance of these three classes of monolayer compounds were then carried out with both experiments and molecular simulations.

3.3. Surface pressure/area isotherms
Pressure/area isotherms of the newly-made monolayer compounds spread from hexane are shown in Figure 4(a) and (b). The monolayer film properties obtained from these and related experiments are listed in Table 1.
Figure 4. Surface pressure/area isotherms for C18OH compared with (a) Class 1 compounds: ethylene oxy derivatives and Class 3: octadecyl glyceryl ether, (b) Class 2 compounds: ethylene oxy methyl ether derivatives. Rectangular highlighted section of the isotherms is used for comparison with simulation in Figure 8.
Table 1. Monolayer properties of investigated compounds spread from hexane obtained from experimental and simulation.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>EXPERIMENTAL</th>
<th>SIMULATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area(^a) (Å(^2)/mol)</td>
<td>Equilibrium spreading pressure (mN/m)</td>
</tr>
<tr>
<td>C16OH</td>
<td>24 ± 0.2</td>
<td>42</td>
</tr>
<tr>
<td>C18OH</td>
<td>23 ± 0.1</td>
<td>39</td>
</tr>
<tr>
<td>Class 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18E1</td>
<td>21 ± 0.2</td>
<td>48</td>
</tr>
<tr>
<td>C18E2</td>
<td>30 ± 0.2</td>
<td>41</td>
</tr>
<tr>
<td>C18E3</td>
<td>43 ± 0.3</td>
<td>34</td>
</tr>
<tr>
<td>Class 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18E1Me</td>
<td>18 ± 0.4</td>
<td>39</td>
</tr>
<tr>
<td>C18E2Me</td>
<td>26 ± 0.4</td>
<td>39</td>
</tr>
<tr>
<td>C18E3Me</td>
<td>74 ± 0.4(^c)</td>
<td>27</td>
</tr>
<tr>
<td>Class 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18G1</td>
<td>30 ± 0.3</td>
<td>38</td>
</tr>
</tbody>
</table>

\(^a\) Extrapolated from the solid phase of the isotherm from both experimental and simulation curves
\(^b\) Calculated at 30 minutes
\(^c\) Has no solid phase; extrapolated from upper end of liquid phase of isotherm.

It can be seen that the length of the ethylene oxy headgroup in Class 1 affects the way the molecules pack at the air/water interface, with the longer headgroups being less likely to form closely packed films. C16OH, C18OH, C18E1 and C18E2 all reach a similar collapse pressure of 50 mN/m, and their isotherms appear to have a solid phase: a steep curve when the molecules are tightly packed as shown in Figure 4(a) (C16OH isotherm not shown). It is in this phase that a monolayer is expected to provide the best evaporation resistance. C18G1 (from Class 3) containing the extra hydroxyl group also reaches a high collapse pressure and has a steep curve indicating close-packing. Table 1 shows that in the case of C16OH, C18OH and C18E1 they pack to 21-24 Å\(^2\)/molecule while both C18E2 and C18G1 packs to 30 mN/m, and C18E3 packs to 43 Å\(^2\)/molecule.

Class 2 contains ethylene oxy moieties, where the hydroxyl headgroup is replaced with a methyl group. The hydrophilicity of the extra ethylene oxy groups would be somewhat negated and the molecule might be more likely to stay at the air/water interface. Compared to C18OH, the Class 2 compounds, C18E1Me, C18E2Me and C18E3Me, vary in their collapse pressures from 50, 40 and 30 mN/m, respectively, as shown in Figure 4(b). C18E1Me and C18E2Me appear to reach
the solid phase upon compression, while C18E3Me does not. C18E3Me collapses below 30 mN/m and does not appear to reach the solid phase with the highest packing achieved at 74 Å²/molecule, which was extrapolated from the upper end of the isotherm.

3.4. Survival of the monolayer
As previously mentioned, the loss of the monolayer material itself from the water surface is a crucial problem. The ability for the new molecules to remain on the water surface is shown in Figure 5 compared to C16OH and C18OH. It can be seen that C18E1 has superior resistance to loss from the water surface when compared to C18OH, with very little material lost over 24 hours (Figure 5(a)). However, as the size of the hydrophilic head is increased to contain two or three ethylene oxy moieties (C18E2 or C18E3), the ability of the monolayer to stay on the surface of the water is reduced with C18E2 being lost at a similar rate to C16OH, and C18E3 rapidly disappearing from the surface. In the case of these molecules, it is likely that dissolution of some of the monolayer material into the water subphase begins to occur, with C18E3 being lost particularly fast likely due to the structure approaching a surfactant rather than an insoluble monolayer material. The poor performance of C18E3 agrees with the observations from its isotherm that C18E3 does not form a good, close-packed monolayer film on the water surface. In fact C18E3 has been found to have a critical micelle concentration of 4200 μM indicating it is relatively water soluble.[39] In addition, the increased polarity of C18G1 in Class 3 also results in an improved lifetime over C18OH with less than 10 % material lost over 24 hours; a similar result to that obtained for C18E1. This may be due to the fact that both hydroxyl groups in C18G1 are able to hydrogen bond substantially with the water providing its strong anchoring characteristics.
Figure 5. The percentage of monolayer material remaining on the water surface as a function of time for (a) Class 1 and 3, and (b) Class 2 compounds, compared to C16OH and C18OH at a surface pressure of 27 mN/m.

For the Class 2 compounds, the lifetimes of C18E1Me and C18E2Me on the water surface are much shorter than C16OH as shown in Figure 5(b). C18E3Me is lost faster than all the tested compounds with 50% of the monolayer material lost in less than 30 minutes. It appears that replacing the hydroxyl with a methyl ether headgroup to balance the hydrophilicity does not improve the lifetime of the monolayer material. They tend to give more expanded monolayers than the corresponding Class 1 compounds, the expansion being associated with the reduction in monolayer stability (Figure 4).
3.5. *Equilibrium surface pressure and evaporation resistance*

All these compounds were measured for their equilibrium surface pressure, the pressure when an excess of material is applied to the water surface, and their resistance to water evaporation under static and dynamic conditions. It is the evaporation suppressing ability of the monolayer at this surface pressure that is of particular interest if the monolayer is to be used as an evaporation retardant in the field. It can be seen from Table 1 that C18E1 has the highest equilibrium surface pressure (48 mN/m) and the majority of the compounds with an equilibrium surface pressure below 40 mN/m demonstrate poor performance in terms of monolayer retention on the water surface (shown in Figure 5) and evaporation reduction (water savings below 40 %), with the exception of C18G1. The addition of the glycerol headgroup in C18G1 resulted in a slight improvement in the evaporation reduction of this molecule compared to C18OH; however, the savings are still below that achieved by C18E1. Nevertheless, C18E2 still shows some improved evaporation suppression performance over C16OH. For the methyl ethers, in all cases the replacement of the hydroxyl group with a methyl ether resulted in a decreased evaporation reduction capability from C18E1 with no additional savings from C18E3Me compared to the evaporation savings of C16OH and C18OH. These alterations in the molecule structure give rise to changes in the molecular arrangement of the monolayer and therefore to changes in monolayer characteristics, such as the surface pressure/area isotherms (Figure 4).

Subsequent experiments on evaporation suppression capability under wind stress were performed to further confirm the investigated findings as shown in Figure 6. It can be seen that for the Class 1 molecules, C18E1 and C18E2 both show significantly improved ability to reduce evaporation under exposure to wind when compared to C18OH with C18E1 saving 85 % of the water lost to evaporation under these conditions. C18E3 showed a low evaporation saving effect compared to the control sample without monolayer (Figure 6(a)). This was to be expected considering the surface pressure/area isotherm that was obtained for this film showed poor packing and thus indicated weak lateral interaction within the monolayer. These results are in agreement with those previously obtained results for the ability of the monolayer to remain on the water surface, and again demonstrate that C18E3 is likely to be too hydrophilic and no longer sufficiently water insoluble, hence rendering it relatively less effective as an evaporation mitigation option. However, C18E1 and C18E2 both demonstrate improved ability to control water evaporation
under wind stress when compared to C18OH and also last longer on the water surface, although C18E2 loses material approximately at a similar rate to C16OH (Figure 5(a)). The evaporation resistance of C18G1 under wind in Figure 6(a) again shows a slightly improved performance compared to C16OH and C18OH, saving 64% compared to the control, however, it is still not as good as the performance of C18E1.

Figure 6. Mass of water lost over time for (a) Class 1 (ethylene oxy derivatives) and Class 3 (increased polarity) and (b) Class 2 (ethylene oxy methyl ether derivatives) compared to C16OH, C18OH and a control with no monolayer, under exposure to wind at 25 km/hr.

For Class 2 molecules, all monolayers show reduced ability to suppress evaporation under wind stress when compared to both C16OH and C18OH as seen in Figure 6(b). Despite the fact that C18E1Me appears to form a reasonably close-packed monolayer on the water surface when
compressed, as demonstrated by the surface press/area isotherm (Figure 4), it does not have sufficient hydrophilicity to provide anchoring into the water layer and hence only had a limited evaporation resistance under wind stress. C18E2Me and C18E3Me have previously demonstrated, through the isotherm and stability tests, that they do not form good monolayers on the water surface, which agrees well with the wind stress results.

3.6. Molecular Simulations: Monolayer structure and properties

The experimental data shows that C18E1 is the best performing monolayer in terms of its ability to suppress water evaporation under wind stress. Although an improvement in wind resistance was found for C18E2 and C18G1, there is a limit on how far the hydrophilicity of the headgroup can be increased before reducing the monolayer’s water evaporation suppression capability. In addition, replacing the hydroxyl headgroup with a methyl headgroup provided no suppression capability. To understand the reasons behind the observed behaviours of these molecules at a molecular level, all atom monolayer models were constructed and molecular dynamic simulations were carried out. These simulations also enabled us to elucidate the necessary and sufficient conditions for a monolayer composition and structure to perform as a good water evaporation suppressant.

The monolayer properties were assessed over a range of surface pressures used in experimental measurements. Typical snapshots of the simulated systems at low (< 30 mN/m) and high (> 30 mN/m) pressure are presented in Figure 7. Each system was initially coupled to a surface pressure of 50 mN/m and equilibrated. The surface pressure was then decreased, as described in the experimental methods section, until pore formation in the monolayers was observed. Specifically, fissure in the monolayer appeared exposing the water and creating a ‘pore’ that increased in size (see Figure 7(c)), as did the unit cell, eventually leading to termination of the simulation. This phenomenon has been previously shown to occur in mono/bilayer simulations.[40-42]
Figure 7. Typical cross section snapshot of simulated monolayer systems of (a) high pressure (> 30 mN/m) solid-like phase and (b) low pressure (< 30 mN/m) liquid-expanded (LE) phase. (c) A top view image of pore formation is also shown for those monolayers that formed a pore (C18E1 did not form a pore at any simulated pressure).

Each system was analysed under varying surface pressure with the goal of comparing with experimental results and determining evaporation retardant characteristics such as anchoring, monolayer stability and small molecule permeation resistance. Surface pressure/area isotherms were calculated for monolayers of each molecule over a range of surface pressures corresponding to a solid-like phase.
Figure 8. Simulated surface pressure/area isotherms (dotted lines) compared with experimental data (solid lines) taken from Figure 4(a).

Pressure/area isotherms obtained for the simulated monolayers of Class 1 and 3 are shown in Figure 8 together with the experimentally obtained isotherms. Monolayers from Class 2 showed significant instability in the time frame of the simulations which made it difficult to directly compare to available experimental measurements. It can be seen from Figure 8, that there is quantitative and qualitative agreement between the Langmuir trough isotherms and the simulated isotherms for Class 1 monolayers, above a certain surface pressure unique to each molecule. At surface pressures below a certain value pore formation was observed corresponding to a coexistence of liquid and gas phases as seen in the experimental pressure/area isotherms at lower pressures. The surface pressure range for stable monolayer systems (prior to pore formation) is presented in Table 1. For Class 2 and 3 monolayers pores formed at relatively high surface pressures signifying the instability. This is likely due to the relatively large head group of Class 2 and Class 3 molecules. In the simulations, both classes exhibited a larger molecular footprint on the water surface which led to higher inter-chain separation (lower monolayer packing density) and larger tilt with respect to the water surface, illustrated by examples shown in Figure 7. The tilt angle as a function of surface pressure is displayed in Figure 9 which shows that Class 2 and 3 molecules, C18E3Me and C18G1 respectively, display on average a larger tilt angle compared to C18OH and Class 1 molecules. Experimental isotherms have similarly shown that C18G1 (Class 3) is less densely packed in the solid phase compared to the Class 1 materials. Overall, this behavior suggests a reduced stability of the Class 2 and Class 3 molecules compared to those from Class 1.
From the isotherms, the equilibrium surface density (area per molecule) of monolayers which affect small molecule permeation[43] was calculated. This was done by extrapolating from the solid phase of the isotherms. These packing density values are displayed in Table 1, together with other related monolayer film properties obtained from the simulations. In agreement with experiment, the simulated C18E1 and C18OH monolayer systems displayed a densely packed structure (21-23 Å²/molecule) within a surface pressure range that extends from 20 to 50 mN/m as can be seen in Figure 8 and from Table 1. Moreover, C18OH and C18E1 reached a lower surface pressure at pore formation compared to the remaining simulated monolayers.

![Graph showing average radial tilt away from the normal to the interface.](image)

**Figure 9.** Average radial tilt away from the normal to the interface, as a function of surface pressure.

The simulated and experimental isotherms in Figure 8 suggest C18E2 also formed a solid phase monolayer. It is in this high pressure solid-like phase that a monolayer is expected to provide the best evaporation resistance. However, both theoretical and experimental results suggest that the length of the ethylene oxy headgroup in Class 1 affects the way the molecules pack at the air/water interface, with the longer headgroups of C18E2 being less likely to form closely packed films at a low surface pressure range. Interestingly, in the simulated isotherm of C18E2, two solid-like areas were identified, with distinct surface densities of 21 and 27 Å² per molecule.
corresponding to surface pressures between 20 and 50 mN/m. These phases differ in molecular tilt angle indicated in Table 1 and Figure 9. It is likely that simulation showed two discreet solid-like areas for C18E2 due to the system size limitations, while experimentally a continuous change between the same packing density values over this pressure range was observed, as shown in Figure 8.

3.7. Molecular mechanisms of evaporation suppression

The simulations enabled us to investigate the molecular mechanisms of interactions between monolayer molecules and water. There are two types of hydrogen bond interaction sites in the headgroups considered: hydroxyl and ethylene oxy groups. Among these, it was found that the terminating hydroxyl group interacts most with water as it is more exposed. The simulations showed that additional ethylene oxy or hydroxyl groups on larger headgroup molecules are indeed capable of forming more H-bonds to water, but this primarily occurs when these molecules are significantly tilted towards the water subphase at low pressure. This observation is confirmed by the plot of H-bond counts versus surface pressure (Figure 10(a)) which shows that the number of hydrogen bonds between the water subphase and the monolayer increases as the pressure is lowered and the chains begin to tilt. It is interesting to note that C18E1 is the only molecule not to significantly compromise its H-bonding as it transitions between high and low surface pressure regions. In contrast, C18E2 shows a large decrease in H-bonding to water as it transitions from a low to high pressure due to its large reduction in tilt angle. Hydrogen bonding between the additional ethylene oxy groups and water is not readily achievable at high surface pressures where the C18E2 chains are largely perpendicular to the water surface, with the additional ethylene oxy groups staying above the water level (Figure 9(a)). Figure 8(b) shows that at low surface pressures the ethylene oxy atoms of C18E2 are more exposed to water at the expense of the monolayer’s ability to maintain a close packed structure and is illustrated schematically in Figure 11. These results indicate that there may be an optimal number of ethylene oxy groups that will simultaneously achieve good anchoring, through H-bonds between the chain and the water subphase, while sustaining the solid-like phase at a wide range of surface pressures.
Figure 10. Average number of hydrogen bonds per frame as a function of surface pressure between (a) monolayer chains and water and, (b) monolayer chains themselves.

Figure 11. Schematic illustrating hydrogen bonding between chains and between chains and water of (a) solid phase and (b) a tilted phase where the headgroup oxygens are more exposed to water.

Inter-chain hydrogen bonding statistics are presented in Figure 10(b) and can be expected to have an effect on the stability of the monolayer. When the interactions between water and monolayer headgroups increase (Figure 10(a)), there is a corresponding decrease in the interaction between the headgroups themselves, with C18E1 displaying the smallest change (Figure 10(b)). For
example, as the surface pressure increases and the monolayer enters the solid phase, C18OH shows an increase in the interchain hydrogen bond interaction with a simultaneous decrease in hydrogen bonding to water. The relatively high count of interchain hydrogen bonding explains the good survivability of C18OH as shown by the experimental results presented in Figure 5 which were collected when the monolayer was in the solid-like phase. However, the notable decrease of H-bonding to water results in a reduced anchoring which according to experimental results has a detrimental effect on the monolayer’s ability to mitigate evaporation of water under wind (Figure 6).

C18G1 monolayer presents the highest incidence of chain-water and chain-chain H-bond interactions across the surface pressures investigated, with contributions coming from both OH groups. Consistent with this, experimental measurements of monolayer stability (Figure 6) show that C18G1 has survivability characteristics approaching those of C18E1. However, this molecule exhibits the largest tilt (Figure 9), and greatest surface area per headgroup (Table 1) leading to poor packing which explains its reduced evaporation mitigation ability. This example demonstrates that chain-chain and chain-water hydrogen bonding alone is not sufficient for good and stable evaporation suppression. The ability of the monolayer to pack tightly is another necessary condition.

C18E3Me, though not terminating with a hydroxyl group, did hydrogen bond with water via its ether groups; however the number of interactions was comparatively small and is not presented. Experimental isotherms showed that C18E3Me did not form a stable solid phase monolayer. The simulated C18E3Me systems, having been constructed initially as an ideal solid phase monolayer, also showed signs of structural instability, having the smallest range of surface pressures where a stable monolayer exists, as listed in Table 1. These simulated results are reflected in the survivability and evaporation experiments where C18E3Me performed very poorly in both.

C18E2 has one additional ethylene oxy in the headgroup compared to C18E1 which resulted in an increase in the headgroup gauche conformation at the low surface pressure region, as illustrated in Figure 7. This led to the increased tilt of C18E2 compared to C18E1 due to the
additional exposure of headgroup oxygens to the water as shown schematically in Figure 11. This exposure provided good anchoring to water and explains its relatively strong evaporation mitigation properties under wind. However, at the same time it resulted in the reduced interchain hydrogen bonding for C18E2 compared to C18E1. This explains the relatively poorer survivability of C18E2 as shown experimentally in Figure 5. Overall, C18E2 has a reduced surface pressure range at which good anchoring to water and interchain bonding occurs.

Figure 10(b) shows that C18E1 has a consistent level of inter-chain H-bonding as well as a relatively consistent H-bonding to water along the entire surface pressure range studied. Figure 9 demonstrates C18E1’s relatively low tilt shown across the full range of surface pressures. The stability of this monolayer is further illustrated in Figure 7 where general structure of the C18E1 system is shown to be largely unchanged from the high pressure to the low pressure region systems. It is this consistent chain-water and chain-chain bonding and its ability to maintain solid-like behavior across the entire surface pressure range, that may be responsible for C18E1 being the highest performing evaporation suppressant compared to all other studied candidates.

The analysis of simulation and experimental results allowed us to determine necessary properties of a monolayer material to exhibit superior evaporation performance, (1) the ability to anchor to water and (2) the ability to pack densely. However, unless these properties are available over a large surface pressure range, they may not be sufficient. This is illustrated in Table 2 for all the studied monolayers which demonstrate that C18E1 is the only material possessing the necessary and sufficient properties for good evaporation mitigation.

Table 2. Necessary properties identified for superior evaporation mitigation.

<table>
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<tr>
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<th>Anchoring</th>
<th>Packing</th>
<th>Large surface pressure range for good packing order</th>
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<tbody>
<tr>
<td>C18OH</td>
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<tr>
<td>C18E1</td>
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<tr>
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<td>C18G1</td>
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In summary, the all atom simulations demonstrate that it is the monolayers ability to maintain good anchoring to water and packing over the entire surface pressure range that constitutes a stable and efficient evaporation suppressant.

4. Conclusion

Monolayer compounds possessing aliphatic chains with only a hydroxyl headgroup (i.e. C16OH and C18OH) have previously been found to have a very short half life due to loss of monolayer predominately to volatilization, and in this study have also been shown to perform poorly as evaporation suppressants under dynamic conditions. A series of monolayer compounds was synthesized and their performance at the air/water interface investigated under static and dynamic conditions. Molecular simulation was carried out to assist in the interpretation of the experimental results. Increasing the hydrophilic headgroup improved the monolayer’s lifetime but only if one ethylene oxy residue was used. Therefore, the optimum structure with the best performance was found to be C18E1. It was also found that replacing the hydroxyl headgroup with a methyl group (i.e. Class 2) did not improve the performance of the monolayer compound, while the addition of a second hydroxyl group (C18G1) had limited monolayer performance when compared to C18E1. Combining experiments with molecular simulation, this paper demonstrated that the exceptional performance of C18E1 can be explained by its high equilibrium spreading pressure, the ability to sustain a highly ordered monolayer with a stable isotherm curve and low tilt angle over the full studied range of surface pressures by simultaneously maintaining H-bonding to the water surface and between the monolayer chains. These properties should constitute the design principles for future engineering of improved water evaporation suppressing materials.

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