Research article

Design and performance optimisation of detergent product containing binary mixture of anionic-nonionic surfactants

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A B S T R A C T

The manufacture of detergent products such as laundry detergents, household cleaners and fabric softeners are of increasing interest to the consumer oriented chemical industry. Surfactants are the most important ingredient in detergent formulations, as they are responsible for the bulk of the cleaning power. In this research, a methodology has been developed to design a detergent product using computational tools. Different surfactant systems, such as single anionic, single nonionic, and binary mixtures of anionic-nonionic surfactants are covered in this work. Important surfactant properties such as critical micelle concentration (CMC), cloud point (CP), hydrophilic-lipophilic balance (HLB) and molecular weight (MW) have been identified. A group contribution (GC) method with the aid of computer modelling was used to determine the CMC, CP, and MW of surfactant molecules. The design of a surfactant molecule can be formulated as a multi-objective optimization problem that tradeoffs between CMC, CP, HLB and MW. Consequently, a list of plausible nonionic surfactant structures has been developed with the selected surfactant being incorporated into a binary surfactant mixture. Additives such as antimicrobial agents, anti-redeposition agents, builders, enzymes, and fillers were also considered and incorporated into a hypothetical detergent formulation together with the binary surfactant mixture. The typical ingredients and their compositions in detergent formulations are presented in the final stage of the detergent product design.

1. Introduction

1.1. Background

One of the most prominent applications of detergents is for domestic cleaning. The global market value of laundry detergents was valued at USD 60.9 billion in 2012 (Bianchetti et al., 2015). Detergents are complex mixtures of surfactants, builders, bleaching agents, enzymes and other minor additives (Pedrazzani et al., 2012). Surfactants are the active ingredients in detergent formulations as they are responsible for the bulk of the cleaning power. They can be divided into 3 main groups: anionic, non-ionic and cationic. Anionic surfactants are effective at removing soil but are sensitive to the presence of multivalent ions present in hard water. Nonionic surfactants have high solubility and are virtually immune to the effects of hard water but are less effective than anionic surfactants at removing soil. Cationic surfactants are generally used as fabric softeners.

Detergent formulations usually incorporate a mixture of anionic and nonionic surfactants as the properties of surfactant mixtures are easier to tune than those of single surfactants. A key advantage of utilizing surfactant mixtures is their lower Critical Micelle Concentration compared to pure anionic surfactants. Additional advantages include increased tolerance towards hard water compared to pure anionic surfactants and a higher effective Cloud Point for the nonionic surfactant(s) in the mixture (Na et al., 1999). Therefore, it is important to select an optimum mixture of surfactants so that the end-use specifications can be achieved.

The computational tools have been recently employed in producing other types of chemicals and many of those designed chemicals have been tested in the laboratory for their performance. The computational design and validation of insect repellent lotions and sunscreen lotions have been performed by Conte et al. (2011, 2012). The developed methodology also highlighted the importance of a combined computational and experimental approach in the design of personal care products. In another contribution, a green diesel blend has been designed using

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computer aided molecular design tools (Phoon et al., 2016). The designed fuel's properties are validated experimentally.

In this work, we have developed a methodology to design a new nonionic surfactant that can be combined with an anionic surfactant to form a mixture with improved properties in terms of CMC. Key properties of nonionic surfactants were studied, and property constraints were set according to the product application. Besides, Computer-Aided Molecular Design (CAMD) techniques were applied to identify the nonionic surfactants that satisfy the desired target properties. Next, multi-objective optimization was carried out to determine an optimum molecular structure after trading off between the surfactant properties. A new finding is expected to be obtained in this research, where CMC is set as primary objective in optimization to design a new nonionic surfactant. Product formulation has been done using the molecular structure found from optimization and suitable additives identified along with their appropriate composition.

1.2. Surfactant properties

The key surfactant properties that are to be considered during the design are Critical micelle concentration (CMC), cloud point, Hydrophilic-lipophilic balance (HLB) and molecular weight.

Critical micelle concentration (CMC) is an important characteristic of surfactants, it is defined as the concentration of the surfactant at which micelles start to form, and any additional surfactant added to the system will go into the micelles. When surfactants in solution have reached the CMC, they undergo spontaneous self-association to form micelles. With the formation of micelles, dirt and oil can be solubilized and lifted off the surface and dispersed into the solution. The CMC corresponds to the minimum value of surface tension – the surface tension decreases as the surfactant concentration increases up to the CMC (Rosen and Kunjappu, 2012). The CMC is also influenced by external factors such as temperature, pressure, pH and the surfactant's chemical structure. The determination of the critical micelle concentration of a surfactant is traditionally done by experimentation. Various studies have correlated the CMC values of surfactants with their molecular structure. Li et al. (1998) proposed s-UNIQUAC (segment-based universal quasi-chemical model) and SAFT (statistical associating fluid theory) equations capable of accurately representing the activity coefficients and CMC values of surfactants in aqueous solutions. Saunders and Platts (2004) developed models for the prediction of CMC for anionic and nonionic surfactants based on the structure of their hydrophobic chain and ethylene oxide groups. Cheng and Chen (2005) utilized a modified excess Gibbs energy model (m-Aranovich and Donohue (m-AD) model) to calculate the CMC values of nonionic polyoxyethylene alcohol surfactants. In a study by Mattei et al. (2013), a group contribution property model has been developed to estimate the critical micelle concentration of nonionic surfactants based on the Marrero and Gani group contribution method.

Cloud point is defined as the temperature at which the mixture starts to phase separate, thus becoming cloudy (Rosen and Kunjappu, 2012). Cloud point is an important characteristic for nonionic surfactants as it is correlated with their wetting, cleaning and foaming ability. The polyoxyethylene chains of nonionic surfactants exhibit an reverse solubility versus temperature in water. The solubility of nonionic surfactants is due to their ability to form hydrogen bonds, these bonds are temperature sensitive and will be broken once the temperature is raised to the cloud point, due to high surfactant molecular activity (Sheng, 2011). When the surfactant molecules become dehydrated the solution becomes cloudy. Hydrophilic-lipophilic balance (HLB) is a measure of the balance between the hydrophilic and lipophilic groups of a surfactant molecule (Rosen and Kunjappu, 2012). The HLB number indicates the tendency of the surfactant to solubilize in oil or water, forming either a water-in-oil or oil-in-water emulsion. Low HLB numbers are assigned to surfactants that tend to more soluble in oil while high HLB numbers are assigned to surfactants that tend to more soluble in water.

The molecular weight of a surfactant is often used as a general indication of toxicity and biodegradability. As mixed surfactant systems of anionic and nonionic surfactants are most commonly used in detergency focused applications, their discharge into the environment is of great concern. Cowan-Ellsberry et al. (2014) surmised that the alkyl chain length of the surfactant molecule is the most important determinant of its aquatic toxicity. Additionally, they noted that linear alkyl chained surfactants degrade much faster than highly branched surfactants. Liwarska-Bizukojc et al. (2005) reported that the toxicity of surfactant molecules increased as their molecular weight increased while Warne and Schifko (1999) observed an increase in the toxicity of the nonionic surfactants when the number of ethoxylate groups increased. Morrall et al. (2003) reported that the toxicity of a surfactant is depend on its alkyl chain length and number of ethoxylates groups. Therefore, it can be deduced that in general, the lower the molecular weight of a surfactant, the higher its biodegradability and the lower its toxicity.

Hydrophilic-lipophilic balance (HLB) is a measure of the balance between the hydrophilic and lipophilic groups of a surfactant molecule (Rosen and Kunjappu, 2012). The HLB number indicates the tendency of the surfactant to solubilize in oil or water, forming either a water-in-oil or oil-in-water emulsion. Low HLB numbers are assigned to surfactants that tend to more soluble in oil while high HLB numbers are assigned to surfactants that tend to more soluble in water. A summary of function of HLB values are listed in Table 1.

The HLB of a nonionic surfactant can be determined using the ratio of the molecular weight of the hydrophilic portion of the surfactant (Griffin, 1954). Davies (1957) also suggested another method to determine HLB value based on the chemical groups of the molecule. A completely hydrophobic surfactant molecule has a HLB value of 0, while a completely hydrophilic surfactant molecule has a HLB value of 20. The calculated HLB values from both methods can be used to predict the surfactant properties of a surfactant molecule, where a value from 1 to 3 indicates a antifoaming agent; a value from 3 to 6 indicates a W/O emulsifier; a value from 7 to 9 indicates a wetting agent; a value from 8 to 12 indicates an O/W emulsifier; a value from 13 to 16 is typical of detergents; a value of 15–20 indicates a hydrotrope (Fung et al., 2007).

1.3. Types of surfactant

Surfactants are amphiphilic organic compounds – composed of a hydrophobic hydrocarbon chain and a hydrophilic group. They are classified by their net charge into three main groups: anionic, cationic, and nonionic. Surfactants function by lowering the surface tension of a liquid allowing the liquid to spread evenly over a surface more easily; the surfactants adsorb onto the soil allowing them to remove the soil from the surface into the bulk liquid. It is important to note that after the soil is removed, it should be stabilized and suspended (via emulsification and dispersion) in the wash liquor to be washed away via mechanical agitation (St. Laurent et al., 2007).

Anionic surfactants are known to be effective at removing soil, clay, dirt and oily stains. Anionic surfactants ionize in the presence of water and become negatively charged, they then bind to positively charged particles such as clay (Williams, 2007). Anionic surfactants, in general, tend to generate more foam than other classes of surfactants. Anionic

Table 1. Function of HLB values with its solution appearance and emulsion type.

Description	HLB	Emulsion
No emulsion	1–4	None
Poor emulsion	3–6	Water into oil emulsions
Milky emulsion after vigorous agitation	6–8	Water into oil emulsions
Stable milky emulsion	8–10	Oil into water emulsions
Translucent to clear emulsion	10–13	Oil into water emulsions
Clear emulsion	13+	Oil into water emulsions

surfactants are used in greater volume than any group of surfactants due to their ease of production and low cost of manufacture. Examples of anionic surfactant families are alkyl sulfates (AS), linear alkylbenzene sulfonates (LAS), and alpha olefin sulfonates (AOS).

Nonionic surfactants are mostly ethylene oxide adducts, with the polyoxyethylene group as the hydrophilic part of the surfactant molecule. Nonionic surfactants are frequently used as their physical properties such as HLB can be easily adjusted by modifying the length of its hydrophilic chain. Nonionic surfactants have good cleaning power, are milder to human skin, and are highly soluble (Fung et al., 2007). Differing from anionic surfactants, nonionic surfactants are virtually unaffected by the presence of multivalent ions in hard water. Nonionic surfactants are also very effective at stabilizing emulsions. The detergency, wetting, and general usefulness of nonionic surfactants make them widely used in industrial and household products, especially detergents. Examples of nonionic surfactant groups are alcohol ethoxylates (AE), glucamides, ethoxylated amides (EA), alkyl polyglycosides (APG) and carbohydrate-derivate ethoxylates (CDE). Alcohol ethoxylates can be considered the most important of the nonionic surfactants as a wide variety of properties can be achieved by simply varying the alkyl chain length and the number of ethylene oxide moieties (Showell, 2005).

Cationic surfactants are generally based on a quaternary ammonium structures with several alkyl chains attached to a nitrogen atom which carries a positive charge (Yu et al., 2008). Cationic surfactants can be used as antistatic agents for hair conditioners due as they possess anti-static properties. Cationic surfactants are the active agents in fabric cleaners, and they work by reducing the friction between the fibers and the skin. Cationic surfactants are rarely utilized in detergents as they tend to rapidly adsorb onto soil without detaching (St. Laurent et al., 2007).

1.4. Surfactant mixtures

Mixture of surfactant is applied in detergent formulation to accomplish required detergent quality and satisfied cleaning performance. Nonionic surfactant has been extensively used in detergent formulations in combination with anionic surfactant. In a detergent containing both nonionic and anionic surfactant, the anionic surfactant contributes to cleaning performance in soil removal and nonionic surfactant contribute to make the surfactant system less sensitive to water hardness. Nonionic surfactant also increases the solubility of the surfactant mixture due to the ethylene oxide units belong to nonionic surfactant which is highly hydrophilic in nature. Furthermore, synergism occurred when nonionic surfactant mixed with anionic surfactant, results in reduction in the surface tension value of mixed surfactant (Jadidi et al., 2012). On top of that, the CMC of mixed surfactant also will be shifted to lower values compared to that of single anionic surfactant. Therefore, different type of nonionic surfactants is studied and modelled in this research and combine with an anionic surfactant to form a surfactant mixture at the later stage of work.

1.5. Computer-aided molecular design (CAMD)

Chemical product design is defined as "the process of determining new and suitable chemicals for a certain application" and is a laborious trial-and-error procedure that is constrained by both time and resources (Maranas, 1996). Design efforts are high-throughput and focus on small class of chemical compounds. To keep up with the increasing demand for new chemical products, more effective approaches must be utilized. The existence of computational tools enables design problems to be solved much more rapidly, thus the field of computer-aided molecular design (CAMD) is of paramount importance for chemical product design. CAMD is a systematic approach to design an optimal molecular structure, which combines molecular modelling technique, thermodynamics and numerical optimization (Gani et al., 2003). Property prediction uses the given chemical structure of a molecule to predict its properties, this is known as the forward problem; CAMD is the inversion of property prediction by

predicting the chemical structure of a molecule from a given set of target properties, this is known as the reverse problem. There are several quantitative structure property relationships (QSPRs) that are often used in CAMD, such as group contribution methods, topological indices and signature descriptors (Ng et al., 2015).

Group contribution (GC) methods are the most popular QSPRs in CAMD as they exhibit good accuracy and a great degree of applicability. Group contribution methods operate on the assumption that some of the properties of atoms or molecular functional groups remain constant in many different molecules. The properties of a molecule can be predicted by identifying the existing functional groups within it (Cignitti et al., 2015). Joback and Reid (1987) developed a GC method which extends the group increment idea to model many different properties with the same set of groups. In a study by Constantinou and Gani (1994), a two level GC method was developed which considered both the first order groups and second order groups to estimate the properties of pure compounds. The most widely used group contribution method in CAMD is that of Marrero and Gani (2001). In the Marrero and Gani group contribution method, molecular groups are classified as 1st order, 2nd order and 3rd order, where an increase in order provides more structural information about the molecule.

Signature descriptor is another useful QSPR method, which attempts to retain all the structural and connectivity information for every atom in a molecule. The approach has been applied by Stanton and Jurs to correlate the surface tension of organic molecules with charged partial surface area (CPSA) descriptor (Stanton and Jurs, 1990). In the studies done by Nelson and Jurs (1994), the aqueous solubility of organic compounds was correlated to molecular structure for hydrocarbon, halogenated carbons, ethers, and alcohols by using 10 descriptors. Moreover, Huibers et al. (1996) has proposed to correlate the critical micelle concentration of nonionic surfactant with 3 descriptors. The major advantage of signature descriptors is that they can be manipulated through simple functions to represent groups from group contribution method, which means that the large amount of QSPRs derived from group contribution method is accessible using signature descriptor.

CAMD has been recognized as an important tool that can be applied for the design of different classes of chemical products. In the past, most of the applications of CAMD had been focused on the design of solvents and other bulk chemicals. However, in the recent years, CAMD have been successfully integrated into the design of other types of chemical products such as insect repellent and paint (Conte et al., 2011), adhesives (Jonuzaj et al., 2019) and biofuel additives (Mah et al., 2019). A general framework that can be used in the design of chemical products can be found in the literature (Zhang et al., 2017). One of the key differences in the design of chemical products from the bulk chemicals is the specific nature of design approaches that are appropriate for each class of these products. However, many of the chemical products consists of molecules that provide the key functionalities to the molecule. Products such as detergents, pharmaceutical products and agrochemicals. Therefore, it is expected that unique tools will be developed for the design of chemical products that make use of CAMD.

1.6. Bilevel optimization

Bilevel optimization is a mathematical program, where an optimization problem contains another optimization problem as a constraint (Sinha et al., 2018). During large-scale optimization and decision-making process, it is common to realized that the outcome of any solution taken by the upper level authority (leader) to optimize their goals is affected by the response of lower level entities (follower). Bilevel optimization problem often appear as leader-follower problems and the basic principle is to have the main optimization problem optimized while recognizing that the second level problems are independently optimized. Therefore, the lower level problems are required to have an optimized solution while optimizing the main objective. Ideally, the constraints of the lower level objectives can be the results of single objective optimization results

of the lower level problems itself. However, this will provide the real optimal solution for the primary objective only if all the objectives are not conflicting. A more realistic approach is to set a certain fraction of the optimal value of lower level objectives to be set as constraints in the bi-level optimization formulation.

This approach has been applied in several applications where there is a main optimization target and also a number of important secondary targets. For instance, in the design of integrated biorefineries, Andiappan et al. (2015) has optimized the reaction pathways by keeping economic performance as the main objective while environmental burden and heat of reaction as the secondary objectives. Other applications of this approach are in supply chains (Roghanian et al., 2007) and production planning (Cao and Chen, 2006). In the design of surfactants, since CMC is the key property to be targeted, CMC has to be prioritized in the design whereas the cloud point and HLB must be as close as the best possible values. Therefore, bi-level optimization allows us to model CMC as the as the upper level objective while keeping CP and HLB as secondary objectives.

Objective Function:
Minimize CMC
Subject to:

$\{Cloud\ Point \geq w1 \times Maximum\ Cloud\ Point\}$

$\{HLB \geq w2 \times Maximum\ HLB\}$

$\{w3 \times Molecular\ Weight \leq Minimum\ Molecular\ Weight\}$

1.7. Problem statement

This research aims to apply CAMD techniques to identify an optimum nonionic surfactant which could be combined with an anionic surfactant to form a mixture that satisfies the primary objective of critical micelle concentration (CMC) while also fulfilling the secondary objectives of cloud point (CP), hydrophilic-lipophilic balance (HLB) and molecular weight (MW).

The proposed objectives of this research are:

1. Design a feasible nonionic surfactant to be mixed with an anionic surfactant; the combination of surfactants and their proportions should satisfy the target properties of the mixture.
2. Create a detergent formulation using the surfactant mixture and the appropriate additives.

2. Methodology

A multistage framework has been developed to design a new surfactant molecule that fulfils the needs of the detergent product. It consists of 5 major steps and their associated sub-steps arranged in a systematic manner that incorporates the relevant chemical property models and computer aided molecular design (CAMD) tools as shown in Figure 1.
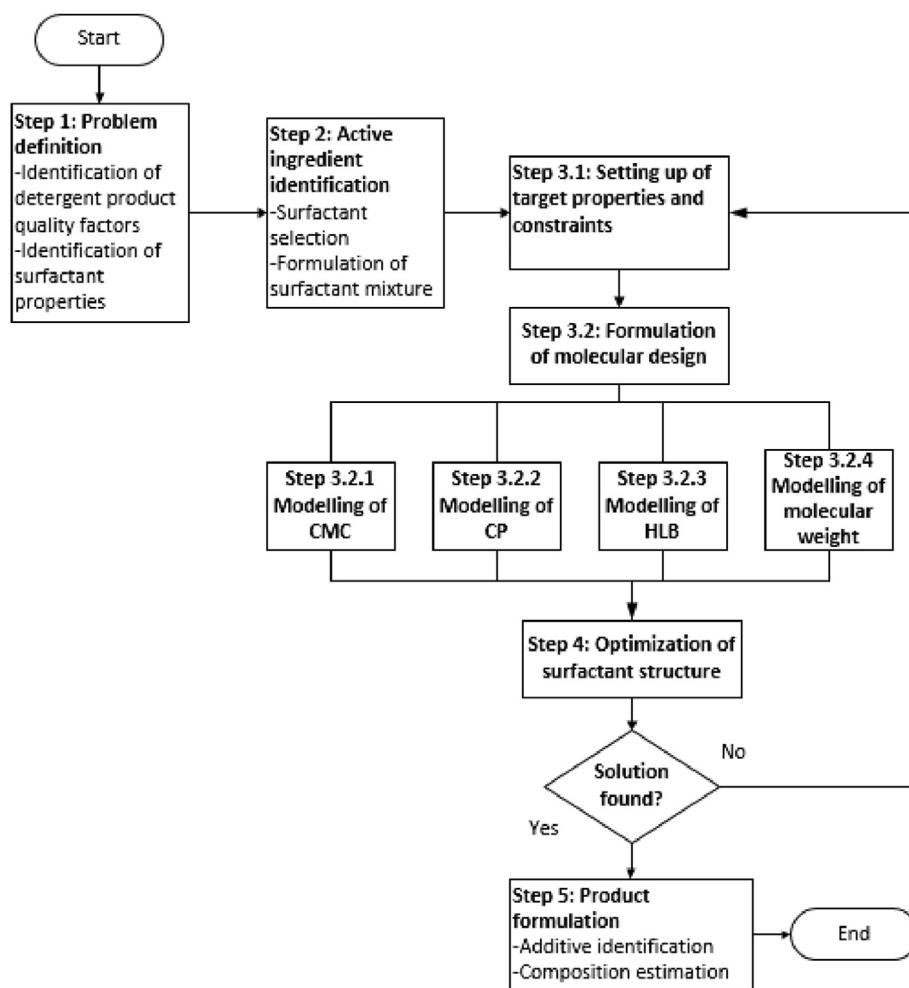

Figure 1. CAMD framework for detergent design.

2.1. Problem definition

2.1.1. Identification of detergent product quality factors

It is the essential to produce a detergent product that can carry out cleaning work efficiently and meet the needs of the consumer, thus ensuring customer satisfaction. The desired quality factors of the detergent product have been identified.

The quality factors for the detergent are:

- Dissolves quickly and completely in water
- No decomposition of detergent components at wash temperature
- High cleaning power
- High biodegradability
- Safe to discharge into the environment

The performance of a detergent product is closely linked to its surfactants' properties. Hence, it is important to identify and achieve the target properties in the surfactant modelling process.

2.1.2. Identification of surfactant properties

The surfactant requirements are derived from detergent quality factors that are then translated into surfactant target properties. The translated properties are shown in Table 2.

2.2. Surfactant identification and selection

Active ingredient refers to the most important chemicals in the formulation; they satisfy the main needs of the product and define the function of the product itself. The surfactant(s) is one such key ingredient and plays a pivotal role in the detergent formulation. Detergents usually consist of a mixture of different types of surfactants in order to maximize cleaning capability while remaining mild to the skin.

Laundry detergents, in general, use a mixture of anionic and nonionic surfactants (instead of a single surfactant) in their formulations to ensure satisfactory product performance (Showell, 2005; Smulders et al., 2007). In this work, a binary mixture of an anionic surfactant and a nonionic surfactant is used. Anionic surfactants display excellent cleaning performance while being relatively cheap. Sodium dodecyl sulfate (SDS) is the anionic surfactant of choice as it is widely used in both research and industrial applications. Its critical micelle concentration (CMC) is reported to be 8.2×10^{-3} M at 25 °C (Mukerjee and Mysels, 1972), by mixing this surfactant with the nonionic surfactant modelled in this research the CMC of the mixture can be lowered below that of the anionic surfactant.

Nonionic surfactants are largely unaffected by the presence of multivalent ions (hardwater) in water and are comparatively mild to dyes, fabrics, and skin than other surfactants. As such they tend to be used in combination with anionic surfactants. The nonionic surfactant will be designed using computer modelling, group contribution methods, and mathematical optimization. The generated nonionic surfactant will then be mixed with the anionic surfactant to form the mixed surfactant system. Four types of nonionic surfactants were chosen to be modelled – linear alcohol ethoxylates, branched alcohol ethoxylates, ethoxylated amides and carbohydrate-derivative ethoxylates.

Table 2. Target properties translated from requirements.

Surfactant Requirement	Surfactant target properties
Dissolves rapidly water	Hydrophilic-lipophilic balance
Does not decompose at wash temperature	Cloud point
High cleaning power	Critical micelle concentration
High biodegradability	Molecular weight
Safe to discharge into the environment	Molecular weight

2.3. Surfactant design

2.3.1. Setting up target property constraints

Before proceeding to the modelling stage, it is necessary to decide on the constraints for the selected surfactant properties. The CMC of the nonionic surfactant was set to be equal to or lower than that of Sodium Dodecyl Sulfate (SDS) which is around 8.2×10^{-3} M at 25 °C (Mukerjee and Mysels, 1972). The cloud point of the nonionic surfactant was set to be 20° higher than the highest washing temperature in Asia (Smulders et al., 2007) to ensure that the surfactant has little to no chance of decomposing during the wash cycle. Therefore, lower limit of the cloud point of the nonionic surfactant was set to be 60 °C.

The HLB of the nonionic surfactant is set to be between 13 and 16 which is the standard HLB range for detergent products (Griffin, 1949) and to ensure that the product exhibits high detergency and forms a clear solution (Fung et al., 2007). The molecular weight of the nonionic surfactant is desired to be as low as possible as the toxicity of surfactants (anionic and nonionic) was found to increase with molecular weight, the maximum molecular weight is set to be 640 – which is the molecular weight of the largest surfactant tested by Liwarska-Bizukojc et al. (2005). The property constraints are shown in Table 3.

The design of the surfactant structure was framed as a mixed integer nonlinear programming (MINLP) problem which includes the target property constraints and their appropriate models, this was later solved using the program LINGO v18 with the Global solver (LINDO Systems Inc. 2018).

2.3.2. Selected models & decomposition of molecular structure

The models used for the estimation of the CMC and the CP of the nonionic surfactants in this work were developed by Mattei et al. (2013, 2014) while Griffin's method (Griffin, 1954) was used to estimate the HLB of the nonionic surfactants. Before the models can be applied, the molecular structures of the surfactants must first be decomposed into first order groups, the first order groups for each nonionic surfactant type are:

- Linear alkyl ethoxylate: CH_3, $CH_2(1)$, CH_2O, CH_2CH_2O, $CH_2(2)$, OCH_2CH_2OH
- Branched alkyl ethoxylate: CH_3, $CH_2(1)$, $CH_2(2)$, $CH_2(3)$, CH, $CH_2O(1)$, $CH_2O(2)$, OCH_2CH_2OH
- Ethoxylated amide: CH_3, $CH_2(1)$, CH_2NH, CH_2COO, CH_2CH_2O, $CH_2(2)$, OCH_2CH_2OH
- Carbohydrate-derivate ethoxylate: $CH_3(1)$, CH_2, CH_2COO, CH_2CH_2O, $CH_3(2)$

2.3.3. Modelling the critical micelle concentration

The critical micelle concentration of the nonionic surfactants was modelled by using a group contribution method developed by Mattei et al. (2013) as shown in Eq. (1).

$$-\log(CMC) = \sum_i N_i C_{i,cmc} + \sum_j M_i D_{j,cmc} + \sum_k O_k E_{k,cmc} \qquad (1)$$

Table 3. List of surfactant properties with appropriate model.

Surfactant properties	Constraint		Method used
	Lower Bound	Upper bound	
Critical Micelle Concentration, CMC	-	8.2×10^{-3} M	Group contribution method
Cloud point, CP	60 °C	-	Group contribution method
Hydrophilic-lipophilic balance, HLB	13	16	Griffin's method
Molecular weight	-	640	Group contribution method

where $C_{i,cmc}$ is the contribution of the first-order group of type-I that occurs N_i times. $D_{j,cmc}$ is the contribution of the second-order group of type-j that occurs M_j times. $E_{k,cmc}$ is the contribution of the third-order group of type-k that occurs O_k times. The group contribution of each first order group to the CMC is taken from Table 4. When the group contribution for a first order group is unavailable, other property models can be used to predict the value. In this work, the missing group contribution was predicted using a Quantitative Structure Property Relationship (QSPR) model developed by Huibers et al. (1996).

2.3.3.1. QSPR model to predict critical micelle concentration. In many cases the intended target properties cannot be predicted solely by a single model.

Molecular signature descriptor is one of the many quantitative structure property relationships (QSPR) that can be used for property prediction, the signature descriptors can represent the building blocks of a molecule and can even account for the contributions of second and third order groups. Therefore, if a molecule can be written in the form of a signature descriptor, different mathematical formulations (including group contribution methods) can be processed on the same platform (Faulon et al., 2003a, 2003b). The molecular signature descriptor model (Equation 2) proposed by Huibers et al. (1996) was employed to predict the group contribution of the CH$_2$NH group to the CMC of the nonionic

surfactants, it includes three descriptors: i) the Kier and Hall index of zeroth order (KH0), ii) the average information content of second order (AIC-2) and iii) relative number of nitrogen and oxygen atoms (RNNO).

$$\log(CMC) = -1.80 - (0.567 KH0) + (1.054 AIC2) + (7.5 RNNO) \quad (2)$$

The formulas and the calculations for the group contribution of the CH$_2$NH group are shown in the Table 5.

The group contribution value of the CH$_2$NH group to the CMC of the nonionic surfactants is calculated to be 0.461 and is incorporated in Eq. (1) for the calculation of the CMC of the Ethoxylated Amine family of nonionic surfactants.

2.3.4. Modelling the cloud point

The group contribution method in the work of Mattei et al. (2014) was applied to model the CP of the nonionic surfactants (Equation 7).

$$CP^2 = \sum_i N_i C_{i,cp} + \sum_j M_j D_{j,cp} + \sum_k O_k E_{k,cp} \quad (7)$$

where $C_{i,cp}$ is the contribution of the first-order group of type-I that occurs N_i times. $D_{j,cp}$ is the contribution of the second-order group of type-j that occurs M_j times. $E_{k,cp}$ is the contribution of the third-order group of type-k that occurs O_k times. The group contribution of each first order

Table 4. Critical micelle concentration of each first order group for all nonionic surfactant.

Symbol	Linear alkyl ethoxylates		Branched alkyl ethoxylates	
	First order group	CMC Group contribution (M)	First order group	CMC Group contribution (M)
X1	CH$_3$	-0.223	CH$_3$	-0.223
X2	CH$_2$(1)	0.434	CH$_2$(1)	0.434
X3	CH$_2$O	-0.431	CH$_2$(2)	0.434
X4	CH$_2$CH$_2$O	0.003	CH$_2$(3)	0.434
X5	CH$_2$(2)	0.434	CH	1.009
X6	OCH$_2$CH$_2$OH	-0.571	CH$_2$O(1)	-0.431
X7			CH$_2$O(2)	-0.431
X8			OCH$_2$CH$_2$OH	-0.571

Symbol	Ethoxylated amides		Carbohydrate-derivate ethoxylates	
	First order group	CMC Group contribution (M)	First order group	CMC Group contribution (M)
Y1	CH$_3$	-0.223	CH$_3$(1)	-0.223
Y2	CH$_2$(1)	0.434	CH$_2$	0.434
Y3	CH$_2$NH	0.461	CH$_2$COO	-0.458
Y4	CH$_2$COO	-0.458	CH$_2$CH$_2$O	0.003
Y5	CH$_2$CH$_2$O	0.003	CH$_3$(2)	-0.223
Y6	CH$_2$(2)	0.434		
Y7	OCH$_2$CH$_2$OH	-0.571		

Table 5. Formula and calculation of descriptors.

Term	Formula	Calculation
KH0	$KH0 = \sum_{i=1}^{N} (\delta_i^v)^{-\frac{1}{2}} (3.)$ Where $\delta_i^v = \frac{Z_i^v - H_i}{Z_i - Z_i^v - 1} (4.)$ Z_i = total number of electrons Z_i^v = number of valence electrons H_i = number of hydrogens directly attached to the atom	$KH0 = \left(\frac{5-1}{7-5-1}\right)^{-\frac{1}{2}} + \left(\frac{4-2}{6-4-1}\right)^{-\frac{1}{2}}$ $= 0.5 + 0.707$ $= 1.207$
AIC2	$AIC2 = -\sum_{i=1}^{Nclass} \frac{n_i}{n} \log_2 \frac{n_i}{n} (5.)$ n_i = number of atoms in the ith class n = total number of atoms in the molecule or fragments	$AIC2 = -\left[\frac{1}{5}\log_2\frac{1}{5} + \frac{1}{5}\log_2\frac{1}{5} + \frac{3}{5}\log_2\frac{3}{5}\right]$ $= 1.371$
RNNO	$RNNO = \frac{number\ of\ N\ \&\ O\ atom}{total\ number\ of\ atom\ in\ the\ molecule} (6.)$	$RNNO = \frac{1}{5} = 0.2$

group to the CP is taken from Table 6. As the contributions of all the molecular groups are available, the use of other QSPRs is unnecessary.

2.3.5. Modelling the HLB

The HLB is calculated by taking the ratio of the molecular weight of the hydrophilic portion of the molecule to its total molecular weight and multiplying it by 20 (Griffin, 1954), this is shown in Eq. (8).

$$HLB = \frac{M_H}{M_H + M_L} \times 20 \tag{8}$$

where M_H is the molecular weight of hydrophilic portion and M_L is the molecular weight of lipophilic portion of the surfactant molecule. The hydrophilic group for each nonionic surfactant is identified and listed in Table 7.

2.3.6. Modelling the molecular weight

The molecular weight of the generated surfactant is calculated by summing up the molecular weight of all the first-order groups within the molecule (Equation 9).

$$MW = \sum_i N_i MW_i \tag{9}$$

The molecular weight of each first order group is taken from Table 8.

2.3.7. Calculation of mixed surfactant CMC

The CMC of the mixed surfactant system was calculated using a model developed by Rubingh (1979) which applies regular solution theory to the mixed micelle, the equation is shown below:

$$\frac{1}{C_{1,2}} = \frac{\alpha_1}{f_1 C_1} + \frac{1 - \alpha_1}{f_2 C_2} \tag{10}$$

where α is the mole fraction of surfactant 1, C_1, C_2 and $C_{1,2}$ are the CMC values of the surfactant 1,2 and mixed surfactant respectively, f_1 and f_2 are activity coefficients of surfactant 1 and 2 in the mixed micelle. Due to the unavailability of information, the ideal approximation is assumed, therefore $f_1 = f_2 = 1$, and the equation is then simplified to:

$$\frac{1}{C_{1,2}} = \frac{\alpha_1}{C_1} + \frac{1 - \alpha_1}{C_2} \tag{11}$$

Azzam (2001) reported that a binary anionic-nonionic surfactant system (at mole fraction of 0.4 or lesser of anionic surfactant) possessed a lower critical micelle concentration than a singularly anionic surfactant system. The experiments conducted by Azzam (2001) show that the minimum CMC of the mixed surfactant system is attained at a mole fraction of 0.2 anionic surfactant and 0.8 nonionic surfactant. In this work, the aforementioned values of surfactant mole fraction are taken for the calculation of the CMC of the mixed system and for the product formulation in the next section.

2.4. Optimization of surfactant properties

As previously discussed in this work, CMC is a fundamental property of surfactants – below the value virtually no micelles form making detergency impossible. Therefore, the CMC was set as the primary objective of the optimization problem, other target properties such as cloud point, HLB, and molecular weight were of secondary concern so long as their values fell within the set constraints. A systematic multi-objective optimization approach was implemented in this research that considers CMC, cloud point, HLB, and molecular weight simultaneously. In the past, both fuzzy optimization methods and bi-level optimization methods have been used to solve chemical product design (CPD) problems (Ng et al., 2014). If an overall better product is desired with no preference to any specific property, fuzzy optimization may be utilized with the constraints set such that all the target properties are fulfilled to a

Table 6. Cloud point of each first order group for all nonionic surfactant.

Symbol	Linear alkyl ethoxylates		Branched alkyl ethoxylates	
	First order group	CP Group contribution (K^2)	First order group	CP Group contribution (K^2)
Y1	CH_3	64351	CH_3	64531
Y2	$CH_2(1)$	-2214.9	$CH_2(1)$	-2214.9
Y3	CH_2O	8910.4	$CH_2(2)$	-2214.9
Y4	CH_2CH_2O	6695.5	$CH_2(3)$	-2214.9
Y5	$CH_2(2)$	-2214.9	CH	-65736
Y6	OCH_2CH_2OH	33508	$CH_2O(1)$	8910.4
Y7			$CH_2O(2)$	8910.4
Y8			OCH_2CH_2OH	33508
Symbol	Ethoxylated amides		Carbohydrate-derivate ethoxylates	
	First order group	CP Group contribution (K^2)	First order group	CP Group contribution (K^2)
Y1	CH_3	64351	$CH_3(1)$	64531
Y2	$CH_2(1)$	-2214.9	CH_2	-2214.9
Y3	CH_2NH	0	CH_2COO	-2770.6
Y4	CH_2COO	-2770.6	CH_2CH_2O	6695.5
Y5	CH_2CH_2O	6695.5	$CH_3(2)$	64351
Y6	$CH_2(2)$	-2214.9		
Y7	OCH_2CH_2OH	33508		

Table 7. Hydrophilic group of each nonionic surfactant.

Nonionic surfactant	General formula	Hydrophilic group
Linear alkyl ethoxylates	$C_nH_{2n+1}O(C_2H_4O)_mH$	CH_2CH_2O
Branched alkyl ethoxylates	$(C_{(n-2)/2}H_{n-1})CHCH_2O(C_2H_4O)_mH$	$CH_2(2)$, $CH_2O(2)$
Ethoxylated amides	$C_nH_{2n+1}NHCH_2COO[C_2H_4O]_mH$	CH_2NH, CH_2COO, CH_2CH_2O
Carbohydrate-derivate ethoxylates	$C_nH_{2n+1}COO[C_2H_4O]_mCH_3$	CH_2COO, CH_2CH_2O

Table 8. Molecular weight of each first order group for all nonionic surfactant.

Symbol	Linear alkyl ethoxylates		Branched alkyl ethoxylates	
	First order group	MW Group contribution (g/mol)	First order group	MW Group contribution (g/mol)
MW1	CH_3	15	CH_3	15
MW2	$CH_2(1)$	14	$CH_2(1)$	14
MW3	CH_2O	30	$CH_2(2)$	14
MW4	CH_2CH_2O	44	$CH_2(3)$	14
MW5	$CH_2(2)$	14	CH	13
MW6	OCH_2CH_2OH	61	$CH_2O(1)$	30
MW7			$CH_2O(2)$	30
MW8			OCH_2CH_2OH	61

Symbol	Ethoxylated amides		Carbohydrate-derivate ethoxylates	
	First order group	MW Group contribution (g/mol)	First order group	MW Group contribution (g/mol)
Y1	CH_3	15	$CH_3(1)$	15
Y2	$CH_2(1)$	14	CH_2	14
Y3	CH_2NH	29	CH_2COO	58
Y4	CH_2COO	58	CH_2CH_2O	44
Y5	CH_2CH_2O	44	$CH_3(2)$	15
Y6	$CH_2(2)$	14		
Y7	OCH_2CH_2OH	61		

higher level of satisfaction as compared to the previous product. However, in the design of detergents, bi-level optimization is more appropriate because of the precedence given to one of the target properties. Via bi-level optimization, the second-level objectives, i.e. properties with no target ranges specified are optimized first before optimizing the main objectives. Since the solution of a bi-level optimization problem depends on the priority given to the secondary problems, the solution is not exact and depends heavily on the level of importance of secondary targets, The solution obtained from bi-level optimization will provide the optimal surfactant structure which can be taken further for product formulation. If a solution is not generated at this stage, the property targets needs to be revisited and more realistic targets must be provided for the design.

2.5. Product formulation

2.5.1. Additives identification

Additives are components that provide additional functionality to the detergent product. This includes ingredients that supplement the surfactant in order to boost performance as well as components that satisfy specific consumer needs thereby fulfilling higher-order quality factors and distinguishing them from other products in the market (Fung et al., 2007; Smulders et al., 2007). An extensive list of additives is explored at this stage.

Antimicrobial agents are included in the detergent formulations to kill or inhibit the growth of microorganisms. Typical examples of antimicrobial agents are sodium hypochlorite and iodophors (Fung et al., 2007). Sodium hypochlorite is perhaps the most commonly used bleaching agent (paired with laundry detergents or incorporated in cleaning products) and is widely used for hard surface disinfection (Mcdonnell et al., 1999). In spite of its effectiveness at low temperatures, its tendency to damage fabric and its incompatibility with dyes and other detergent ingredients greatly limits its wider use in detergency (Bianchetti et al., 2015). Iodophors are essentially "a combination of iodine and a solubilizing agent" (Rutala and Weber, 2019), these organic complexes are confined within the surfactant micelles and periodically release iodine into the wash solution providing a germicidal effect. Iodophors are recommended for products that will come into direct contact with human skin as they are nonirritating, nontoxic, and nonstaining (Fung et al., 2007; Rutala and Weber, 2019).

Anti-redeposition agents keep soil suspended in the wash liquor and prevents it from resettling onto the fabric; traditional anti-redeposition agents are derived from carboxymethyl cellulose, a more recent anti-redeposition agent is polyethylene glycol (Smulders et al., 2007). The effectiveness of carboxymethyl cellulose is limited to cellulose-based fabrics or cellulose and synthetic fabrics – carboxymethyl cellulose is virtually inert to purely synthetic fabric (Smulders et al., 2007). Polyethylene glycol is a highly effective anti-redeposition agent on both polyester fabrics and polyester-cotton fabrics (Smulders et al., 2007).

Builders are another important detergent additive, their function is to eliminate the effects of water hardness by binding to calcium and magnesium ions thus maximizing the performance of the surfactant (Martín and Martínez, 2013). Examples of builders include precipitating materials such as sodium silicate and ion exchangers such as polycarboxylates and zeolites (Smulders et al., 2007). It is generally ill advised to use precipitating builders in laundry detergent formulations as they can cause damage to both the fabric and the washing machine (Fung et al., 2007). Zeolite A is specifically designed for laundering applications, shields the fibres from damage, and does not deposit on clothing (Smulders et al., 2007).

Bleaching agents can function as both a detergent (either alone or in tandem with the surfactant system) and a antimicrobial agent (Bianchetti et al., 2015). The two types of bleaches used with laundry detergents are chlorine bleaches and oxygen bleaches. Sodium hypochlorite is the most common chlorine bleach and must be sold separately as it is too reactive to be directly incorporated into detergents; care must be taken when using sodium hypochlorite as an overdose could easily lead to color loss and fabric damage (Smulders et al., 2007). Oxygen bleaches such as sodium perborate are considered color-safe bleaches and are more compatible with detergent ingredients, and thus favored over their chlorine counterparts in detergent formulations (Bianchetti et al., 2015).

Binders are used in powdered detergents to ensure that the components are held together in granules (Fung et al., 2007). Example of binders include polyethylene glycol, polyvinylpyrrolidone and polyacrylates. The selection of binding material is dependent on the ambient temperature of the region the product will be sold in; binders with a melting point higher that 40 °C should suffice for most countries, the melting point must also be lower than around 80 °C for ease of processing (Fung et al., 2007).

Enzymes are incorporated primarily for stain removal as they catalyze the breakdown of peptide bonds in complex stains and soils including blood (Martín and Martínez, 2013). Enzymes are highly specific and can only cleave their specific class of biopolymer i.e. protease is particularly

effective on protein and polypeptide based stains (Smulders et al., 2007). The typical enzymes found in laundry detergents are amylase, lipase, protease and cellulase. For a detergent formulation that contains enzymes, certain compounds must be avoided to prevent the enzyme degradation such as but not limited to: cationic surfactants, anionic surfactants of the alkylbenzene sulfonate family, and chlorine bleaches or percarboxylic acid bleaches (Fung et al., 2007).

Corrosion inhibitors are incorporated into detergent formulations in order to prolong the lifetime of washing machines. Sodium silicates are preferred as they can shield the machine parts by forming a protective barrier on the surface (Fung et al., 2007). Sud suppressors are included in detergents to limit foam production as too much foam will inhibit cleaning – the foam cushions the clothes and prevents them from rubbing against each other (Fung et al., 2007). Examples of suds suppressors include soaps and silicones – silicones are preferred as soaps are mediocre antifoams outside of LAS or alcohol ethoxylate systems while silicones perform adequately in most environments (Smulders et al., 2007).

The selection of additives largely follows the heuristics laid out by Fung et al. (2007). Table 9 summarizes the list of additives with selection criteria, examples, and their typical concentrations.

2.5.2. Composition estimation

2.5.2.1. Case study: concentrated laundry powder detergent for hospital usage.
Cleanliness must be continuously maintained in order to prevent hospital-acquired infections, as such the cleaning and disinfection of bedsheets, uniforms, and other patient-contacting fabrics are of paramount importance. In order to achieve high efficiency cleaning, the CMC value should be as low as possible, as such, a mixed surfactant system of an anionic surfactant and a nonionic surfactant is chosen. The anionic surfactant of choice is sodium dodecyl sulfate (SDS). The selected nonionic surfactant will be the optimal solution of a MINLP problem which incorporates group contribution models to model key surfactant properties – a HLB between 12 and 15, a cloud point of $\geq 60\ ^\circ$C, and a molecular weight of ≤ 640.

Additives are selected based on the form of the product and its desired function. To break down blood stains, protease is selected as the enzyme. Iodophors are selected as the antimicrobial agent as they are generally nonirritating, nontoxic, and nonstaining. Polyethylene glycol was chosen as the anti-redeposition agent as it is more effective on synthetic and synthetic-cellulose garments which are more common. Zeolite A is the builder of choice as it is specifically tailored for laundry applications. Sodium perborate was selected as peroxygen bleaches are color and fabric safe while being generally more compatible with most detergents' ingredients. Polyethylene glycol is chosen as binder to increase the cohesiveness of powder while sodium silicate is added as a corrosion inhibitor to prolong the lifetime of the washing machines. Silicones were selected over soaps as sud suppressors due to their greater effectiveness in multiple wash environments. The product formulation and composition are summarized in the Table 10; the composition range for surfactants and fillers were taken from Smulders et al. (2007) while the

Table 9. Summary of additives, their selection criteria, examples, and typical concentrations (Fung et al., 2007).

Additive	Selection Criteria	Examples	Typical amount
Antimicrobial agents	Microbicidal effectiveness	Sodium hypochlorite	0–1%
		Iodophors	-
Anti-redeposition agents	Ability to suspend or disperse soil	Carboxymethyl cellulose	<1%
		Polyethylene glycol	<1%
Binder	Physical properties such as Hamaker constant and Young's modulus	Polyethylene glycol	3–6%
		Polyvinylpyrrolidone	3–6%
		Polyacrylates	3–6%
Bleaches	Potential for colour loss or fabric damage	Sodium perborate	0–13%
		Sodium hypochlorite	0–1%
Builders	Capacity to eliminate alkaline earth ions in water	Zeolites	20–30%
		Polycarboxylates	0–5%
		Sodium silicates	1–20%
Corrosion inhibitors	Corrosion inhibition capability	Sodium silicates	3–15%
Enzymes	Effectiveness and ease of incorporation	Amylase	0.2–1.0%
		Lipase	0.2–0.6%
		Protease	0.1–1.5%
		Cellulase	1–3%
Suds suppressors	Effects on the surfactant system	Soap	-
		Silicones	0–5%

Table 10. Product formulation and composition range (Fung et al., 2007; Smulders et al., 2007).

Ingredient	Chemical compounds	Composition Range (%)
Surfactants	Mixture of Sodium dodecyl sulfate (SDS) and the Ethoxylated Amine ($C_{11}H_{23}NHCH_2COO[C_2H_4O]_8H$)	10–15
Anti-microbial agents	Iodophors	0–5
Anti-redepositions	Carboxymethyl cellulose	<1
Builders	Zeolite A	20–30
Bleaching agents	Sodium perborate	0–13
Binders	Polyethylene glycol	3–6
Enzymes	Protease	0.1–1.5
Corrosion inhibitors	Sodium silicate	3–15
Sud suppressors	Silicones	0–5
Fillers	Sodium sulfate	0–40
Minors and Water	-	Balance

composition range for the remaining additives were taken from Fung et al. (2007).

3. Result and discussion

i) Modelling results before optimization

Suitable nonionic surfactants from 4 different nonionic surfactant families were generated by having LINGO solve a MINLP problem which incorporates all the appropriate models for each surfactant property and their constraints. Multiple solutions were generated, with the optimal solution for each type of nonionic surfactant family being shown in Table 11 with their respective properties.

Optimization was conducted after the basic modelling was completed to obtain the best possible nonionic surfactant for each surfactant family. Bilevel optimization was carried out by considering the significance of the lower level objectives and setting them as constraints for the optimization of the upper level objective. The upper level objective is critical micelle concentration (CMC) while lower level objectives are cloud point, hydrophilic-lipophilic balance (HLB) and molecular weight. In the first stage of optimization the maximum cloud point, maximum HLB and minimum molecular weight were determined for each of the nonionic surfactant families. In the second stage, the values obtained from the first

stage optimization were set as constraints to determine the molecular structure of nonionic surfactant with minimum CMC. Weighting factors of 0.8, 0.2 and 0.8 are assigned to w1, w2, and, w3, respectively. Table 12 shows the molecular structure of the surfactants after bilevel optimization has been conducted.

The CMC of the mixed surfactant system was determined using Eq. (11) using the values of the CMC of the anionic surfactant (sodium dodecyl sulfate) and the nonionic surfactant. Since the CMC of nonionic surfactants are lower than the CMC of anionic surfactant, the mixture can only decrease the effectiveness of the single nonionic surfactant. However, if there are mixing models for other properties are available and applied in optimization, there may be a different non-intuitive optimal solution. Based on the current models, nonionic surfactant from the ethoxylated amide family with the molecular structure of $C_{11}H_{23}NHCH_2COO[C_2H_4O]_8H$ is selected as the final solution. The final solution is applied in the product formulation in Table 10 in the previous section.

3.1. Sensitivity analysis

Different scenarios were considered to study the effect of the weighting factor on the optimization results. The first case, second case, and third case were conducted to study how the optimum molecular

Table 11. Modelling result of each nonionic surfactant before optimization.

ii) Modelling results after optimization

Type of nonionic surfactant: Linear alkyl ethoxylates
General formula: $C_nH_{2n+1}O(C_2H_4O)_mH$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$C_{15}H_{31}O(C_2H_4O)_{10}H$	4.91×10^{-6}	356.52	13.17	668

Type of nonionic surfactant: Branched alkyl ethoxylates
General formula: $(C_{(n-2)/2}H_{n-1})_2CHCH_2O(C_2H_4O)_mH$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$(C_6H_{13})_2CHCH_2O(C_2H_4O)_{10}H$	1.61×10^{-5}	363.83	13.46	654

Type of nonionic surfactant: Ethoxylated amide
General formula: $C_nH_{2n+1}NHCH_2COO[C_2H_4O]_mH$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$C_{14}H_{29}NHCH_2COO[C_2H_4O]_9H$	4.94×10^{-6}	333.09	14.48	667

Type of nonionic surfactant: Carbohydrate-derivate ethoxylates
General formula: $C_nH_{2n+1}COO[C_2H_4O]_mCH_3$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$C_{16}H_{33}COO[C_2H_4O]_9CH_3$	6.32×10^{-6}	393.93	13.35	680

Table 12. Bilevel optimization result on all nonionic surfactant.

iii) CMC of the mixed surfactant system

Type of nonionic surfactant: Linear alkyl ethoxylates
General formula: $C_nH_{2n+1}O(C_2H_4O)_mH$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$C_{10}H_{21}O(C_2H_4O)_7H$	7.41×10^{-4}	343.65	13.22	466

Type of nonionic surfactant: Branched alkyl ethoxylates
General formula: $(C_{(n-2)/2}H_{n-1})_2CHCH_2O(C_2H_4O)_mH$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$(C_4H_9)_2CHCH_2O(C_2H_4O)_7H$	8.95×10^{-4}	348.06	13.22	466

Type of nonionic surfactant: Ethoxylated amide
General formula: $C_nH_{2n+1}NHCH_2COO[C_2H_4O]_mH$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$C_{11}H_{23}NHCH_2COO[C_2H_4O]_8H$	9.96×10^{-5}	333.01	15.11	581

Type of nonionic surfactant: Carbohydrate-derivate ethoxylates
General formula: $C_nH_{2n+1}COO[C_2H_4O]_mCH_3$

Molecular formula	CMC (M)	Cloud point	HLB	Molecular weight
$C_{12}H_{25}COO[C_2H_4O]_6CH_3$	3.52×10^{-4}	379.41	13.09	492

structure would be affected by manipulating the weighting factors for the cloud point, hydrophilic-lipophilic balance (HLB), molecular weight, respectively. The CMC of the optimum molecule changes according to the molecular structure of the optimum result.

Case 1. Manipulating the weighting factor (w1) for the cloud point

The weighting factor for the cloud point, w1, is varied from 0.1 to 0.8, while keeping weighting factors for hydrophilic-lipophilic balance (w2) and molecular weight (w3) constant at 0.2 and 0.8, respectively. The CMC of the optimum molecule is plotted against weighting factor w1, as shown in Figure 2.

Case 2. Manipulating the weighting factor (w2) for the HLB

The weighting factor for the HLB, w2, is varied from 0.1 to 0.8, while keeping weighting factors for cloud point (w1) and molecular weight constant (w3) at 0.8. The CMC of the optimum molecule is plotted against weighting factor w2, as is shown in Figure 3.

Case 3. Manipulating the weighting factor (w3) for the molecular weight

The weighting factor for the molecular weight, w3, was varied from 0.1 to 0.8, while keeping weighting factors for cloud point (w1) and HLB constant (w2) at 0.8 and 0.2, respectively. The CMC of optimum molecule is plotted against weighting factor w3, as shown in Figure 4.

From the modelling results before optimization, it can be observed that the nonionic surfactants that fulfills the upper level objective are obtained. These nonionic surfactants are ranging from 10^{-5} to 10^{-6}, yet all the CMC values are acceptable since they are below the constraint (0.0082M). However, one of the issues detected from the result is the nonionic surfactant generated never fulfill or tolerate all the surfactant properties. For example, the initial solution of linear alkyl ethoxylates has
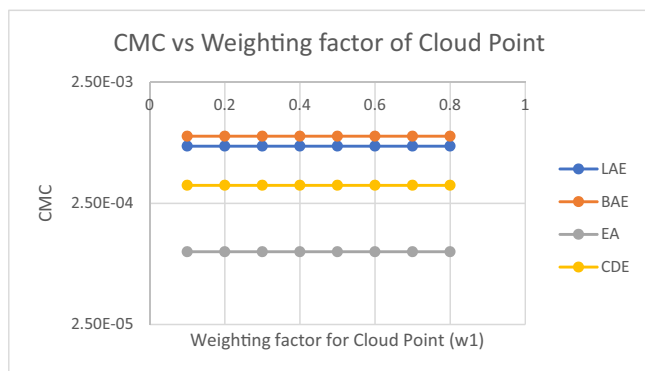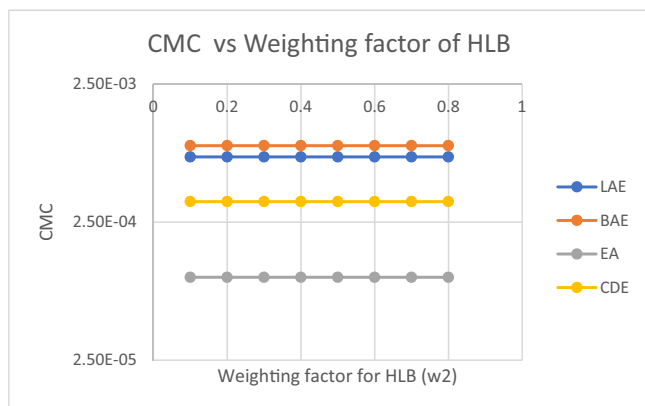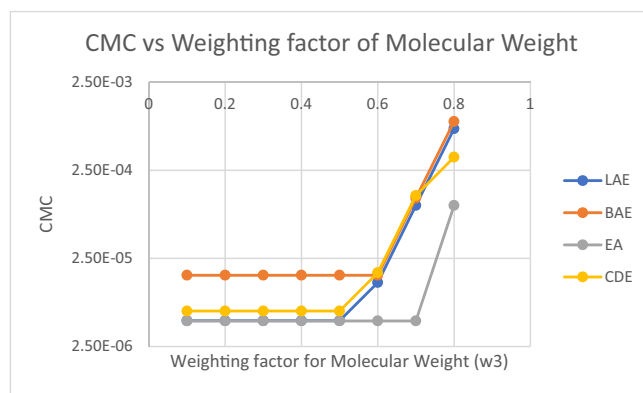

Figure 4. Graph of CMC vs Weighting factor for Molecular Weight (w3).

a very low CMC values (4.91×10^{-6} M), but its molecular weight value is higher (668) compared to other results, even though both values fulfill the constraints established in this research. On the other hand, nonionic surfactant that has comparatively lower molecular weight have slightly higher CMC values from the result before optimization.

The general trend observed from the result is the lower the molecular weight, the higher the CMC values.

The objective of the research required the CMC values to be as low as possible, however the properties of molecular weight should not be neglected and is desired to be as low as possible, since it is an indication of toxicity. Multi-objective optimization has successfully determined an optimum solution for each type of nonionic surfactant, which keeping the CMC value and molecular weight low while fulfill other constraints.

Compared to result before optimization, the result after optimization result has relatively higher CMC values, which CMC values ranging between 10^{-5} and 10^{-6}, shifted to CMC values ranging between 10^{-4} and 10^{-5}.

However, the CMC values are still below the constraint (0.0082M) and thus are acceptable. Optimization has shifted the CMC values to compensate the value of molecular weight, which is initially much higher before optimization.

As a result, the value obtained for molecular weight after optimization are much lower compared to that before optimization, which molecular weight values ranging between 654 and 680, shifted to molecular weight values ranging between 466 and 580.

Among all the nonionic surfactants obtained from the bilevel optimization, the solution with the lowest CMC of 9.96×10^{-5} M is obtained from ethoxylated amide family, with a molecular structure of $C_{11}H_{23}NHCH_2COO[C_2H_4O]_8H$, and lowest CMC value of surfactant mixture of 1.24×10^{-4} M.

In the sensitivity analysis, the graphs in Figure 2 and Figure 3 show a horizontal line for all nonionic surfactant families when the weighting factors w1 and w2 are varied from 0.1 to 0.8. The CMC values remain the same, despite the changing of the weighting factors for the cloud point (w1) and HLB (w2), this indicates that molecular structures of the surfactants from all the tested families are not affected within the range of values tested.

In Figure 4, the optimal molecular structures, and thus the CMCs for all surfactant families, remain the same when the weighting factor for molecular weight, w3, is varied from 0.1 to 0.5. However, between 0.5 and 0.8, CDE and LAE show sharp increases in CMC (close to 10 times in some areas), a similar pattern can be seen in BAE from 0.6 to 0.8, while EA shows a sharp increase (over 10 times) in CMC between 0.7 to 0.8. This indicates that new optimal structures were generated, thus it is concluded that the manipulation of the w3 weighting factor (while keeping w1 and w2 constant) would have the most significant effect on the optimal structures generated.

A few areas of uncertainty were identified in this research. Firstly, the surfactants were modelled using first-order groups alone. In order to set

Figure 2. Graph of CMC vs Weighting factor for Cloud Point (w1).

Figure 3. Graph of CMC vs Weighting factor for HLB (w2).

the structural constraints, the general formula structure of each surfactant family had to be broken down into individual molecular building blocks (first-order groups) with some portions being set to vary while others remained constant. This separation made the inclusion of higher order groups difficult, as portions of the surfactant structure could vary. Even in the instance that a portion of the molecule remained static, there was no guarantee that a group contribution for that exact molecular group existed. In general, access to group contribution information for a larger variety of higher order groups and the incorporation of said groups into the model would significantly boost the accuracy of the group contribution methods used.

Secondly, the modelling of the CMC of the nonionic surfactants does not consider different wash temperatures. As the CMC is influenced by external factors such as temperature, the modelled CMC would not be accurate at wash temperatures aside from 25 °C.

Thirdly, the only mixing rule applied is for the CMC of the mixed surfactant system. By including only one surfactant property, it might not be sufficient to justify any improvement to the overall properties of mixed surfactant system. Besides, the calculation for CMC values of the mixed surfactant system done assuming ideal mixing occurs. In a real mixed surfactant system, interactions exist between the anionic and nonionic surfactants that will affect the final CMC value.

4. Conclusion

A comprehensive framework for detergent design has been presented. All the necessary surfactant properties have been listed together with the constraints required to fulfill the target properties of product. A binary mixture of anionic and nonionic surfactants was identified to exhibit better properties in terms of critical micelle concentration than a single anionic surfactant. Group contribution models were applied to model the critical micelle concentration and cloud point of nonionic surfactant. A QSPR model was also employed for the prediction of the group contribution of a first order group to the CMC when its group contribution data was unavailable. Bilevel optimization was conducted and it shows that the optimum nonionic surfactant is from the class of ethoxylated amides. A mixture of the nonionic surfactant with sodium dodecyl sulfate also possessed the lowest CMC value among the mixtures. It also demonstrates how a binary mixture of anionic and nonionic surfactants can achieve a lower CMC than a singular anionic surfactant. Additives for use in detergent formulations were also studied. The final detergent product, which was designed as a laundry detergent for hospital usage was formulated and detailed in an ingredient and composition list.

The developed methodology can be further enhanced by including more accurate mixing rules to determine the mixed cloud point and mixed HLB of the surfactant mixture as well as other relevant properties. The computational tools can provide guidance in the design of new chemical products and also shortlist the promising ingredients in a chemical product. However, before making the final selection, other relevant properties for which there are no predictive models must also be considered either experimentally or based on databases. Cost factors also needs to be considered before the final selection of ingredients in a chemical product. In addition, the final selection of surfactant mixture and product composition should only be made after experimental verification of properties and to eliminate any undesirable interaction effects.

Declarations

Author contribution statement

Nishanth Chemmangattuvalappil, Newton Well Lo: Analyzed and interpreted the data; Wrote the paper.

Kai Cong Cheng: Conceived and designed the experiments; Performed the experiments.

Zhi Sheng Khoo: Performed the experiments.

Wei Jie Tan: Contributed reagents, materials, analysis tools or data.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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