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A Novel Surfactant Molecular Design with Optimal Performance, Safety and Health Aspects for Laundry Detergent

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Surfactants are one of the main ingredients in laundry detergent formulation used to improve the wetting ability of water, loosens and removes oil with the aid of wash action. Sodium lauryl sulfate (SLS) and diethanolamine (DEA) are two examples of chemicals used as surfactants in laundry detergents. Exposure to SLS and DEA has the potential to cause skin and eye irritation. In this study, surfactant candidates were designed by using Computer-aided Molecular Design (CAMD) tools with the integration of safety and health properties. The CAMD start with problem formulation, followed by model development, molecular design, optimization model and performance analysis. The important surfactant properties such as critical micelle concentration (CMC), hydrophilic-lipophilic balance (HLB) and molecular weight (M_W) were considered. The safety and health properties of surfactant candidates are assessed using index-based methodology. The surfactant candidates with optimum property functionality, safety and health performance are presented. The potential surfactant candidate, 1-aminomethyl-2,3,4,5,6-pentamethylnonane-1,8-diol is suggested to be implemented into in the laundry detergent formulation as it offers lower CMC (0.00228 mol/L) and minimum safety and health risks (total index score of 6) to consumers.

1. Introduction

Surfactants are crucial ingredients in liquid laundry detergents, which enhances the water's wetting ability, function in loosen and removal of oil with the aid of wash action and also aids in emulsification, solubilization or suspension of soils in the wash solution. The chemicals used as surfactant in the currently available laundry detergents have the potential to cause health effects to human body. Exposure to the two most commonly used surfactants; sodium lauryl sulfate (SLS) and diethanolamine (DEA), are found to result in irritation to eyes and skin. SLS is commonly used as anionic surfactant in laundry detergent, which acts as a foaming agent. Its function is to aid the mechanism of laundry washing and increase the washing efficiency. The toxicity profiles of SLS has shown that the exposure to this substance will lead to irritation of the skin and eyes (Cara et al., 2015). DEA will result in irritation of nose and throat due to acute inhalation exposure to it. For dermal exposure, it will lead to skin irritation (New Jersey Department of Health,2000).
An alternative molecule needs to be identified to replace the harmful chemicals as surfactants in liquid laundry detergent. Limited work has been done to identify hazardous chemicals used in product design. Most of the product design works have considered the aspect of safety represented by the flammability potential, while for environment, is by the value of LC_{50}. Liu et al. (2019) have presented an optimization-based framework where

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one of the case studies shown was on the design of surfactant with the aim to minimize the environmental toxicity. An extensive work on surfactant selection have incorporated the safety and environmental toxicity aspects (Mattei et al. (2014) and (2012). There is a research gap identified for health aspects in most of the product designs. The risk assessment works of hazardous chemicals have been done on the finished products and the supply chain (Ju, 2017). In order to assess the safety and health aspects into surfactant design, safety and health hazard sub-indexes are utilized. A score is given to the molecule to indicate the level of hazard of each sub-index. A higher number indicates a higher degree of potential safety and health hazard and vice versa. In this work, the safety and health sub-indexes used are adopted from Inherent Safety Index (ISI), and Inherent Occupational Health Index (IOHI) and National Fire Protection Association (NFPA) health hazard rating. ISI is a safety index which is widely used during the safety assessment of chemical process synthesis (Heikkila, 1999). For IOHI, it is a health index which assess the possible health risks of different chemical substances for chemical process pathway selection during the research and development (Hassim and Hurme, 2010). Safety and health properties of a chemical substance such as flammability, explosiveness and acute toxicity can be evaluated through the NFPA health hazard rating (National Fire Protection Association, 2007).

2. Methodology

The main objective in this work is to generate surfactant candidates which are safer and less harmful to substitute SLS and DEA in laundry detergent formulation by using computer-aided molecular design (CAMD) method. The product design steps in this work are referred from the methodology proposed by Ten et al. (2015), where a list of molecules which achieve the design objectives was generated by CAMD. The design objectives are the molecules generated should be less harmful and hazardous, and able to perform well as surfactant. After that, the generated molecules were analyzed based on their safety and health performances by applying safety and health sub-indexes to ensure that the only molecule which is safer and less harmful is selected. The first stage is problem formulation. This stage starts with the identification of the requirement of a chemical product. The product specifications in terms of targeted properties need to be defined to determine the functionality and behavior of a product (Ten et al., 2015). The molecule generated should be less hazardous and less toxic. At the same time, the performance of surfactant as cleaning and wetting agent should not be compromised and its function must be maintained as well. The design objectives of this work are to minimize the score of safety and health index and also the value of Critical Micelle Concentration (CMC). CMC is a surfactant concentration where above this concentration may result to no micelles formed. Below this concentration limit, all additional surfactant molecules will form micelles (Mattei et al., 2013a). The presence of micelles in solutions is to promote the generation of foams sufficiently. It is not only to offer excellent cleaning efficiency but also provide a good sensory feel to consumer. The lower the CMC of the surfactant, the higher the foam-ability. The upper bound of CMC is set to be lower than 0.01 mol/l following the CMC constraint presented by Mattei et al. (2014). The other properties considered in this work include boiling point (Tb), freezing point (Tf), molecular weight (Mw), surface tension (σ) and hydrophilic-lipophilic balance (HLB). The Tb is set to be higher than 50°C and Tm is set lower than 25 °C. This is to ensure that the laundry detergent exist in liquid form in room temperature. The Mw is set to be between 60 g/mol and 550 g/mol. Surface tension, (σ) is the ability of the surfactant to wet the surface to be cleaned. According to Michele et al. (2013), the value of σ is set to be lower than 33 mN/M to ensure its efficiency as detergent surfactant. The HLB is a scale based on the size and strength of hydrophilic compared to lipophilic groups in a molecule of surfactant (Tadros, 2013). Based on Tadros (2013), the value of HLB for a surfactant should be in between 7 and 15, to function as wetting agent and detergent surfactant. The safety properties were represented by the values of flammability and explosiveness. The flammability (FL) of a molecule was evaluated by referring to its flash point (Fp) and Tb. For explosiveness (EX), it is calculated by the value of lower explosion limit (LEL) and upper explosion limit (UEL). The health properties were represented by volatility and toxicity potential based on the property prediction model developed by Hukkerikar et al. (2012). Three health properties were considered that include volatility measured through Tb, acute toxicity from oral exposure of rat by lethal dosage (LD50), and the permissible exposure limit (PEL). PEL is known as the concentration limit of a chemical substance through the dermal and inhalation routes with the basis of 8 h daily. The upper boundary and lower boundary of the surfactant functionality properties are shown in Table 1.

The next stage is model development. For this stage, all the target properties involved in problem formulation have to be calculated through the property prediction models. The property prediction model used in this study is Group Contribution method (GCM). By using GCM, the physical and chemical properties of a molecule are able to be estimated based on its molecular structure. In this method, the property of a compound is a function of structurally-dependent parameters, where the frequency of each group occurring in the molecule multiply by

Table 1: Upper boundary and lower boundary of the properties

Product Attribute	Property (unit)	Lower bound	Upper bound
Performance	σ (mN/m)	-	33
	HLB	7	15
	CMC (mol/L)	-	0.01
Health	T_b (°C)	50	-
	PEL(ppm)	-	-
	LD_{50} (mg/kg)	-	-
Safety	F_p (°C)	-	-
	E_X (vol %)	-	-
Functionality	T_m (°C)	-	25
	M_w (g/mol)	60	550

its contribution is summed up (Marrero and Gani, 2001). The property-estimation model proposed by Marrero and Gani is as shown in Eq(1):

$$f(x) = \sum_i N_i C_i + w \sum_j M_j D_j + z \sum_k O_k E_k \quad (1)$$

where C_i is contribution of the first-order group of type-i that occurs N_i times, D_i is contribution of the second-order group of type-j that occurs M_j times and E_k is contribution of the third-order group of type-k that has O_k occurrences in the compound. The w and z are binary integers that allow user to decide for the inclusion of second-order and third-order group contributions in property estimation. There are three level of estimation in Marrero-Gani (MG) Model. Primary level estimation uses contributions from first-order groups which describe a broad selection of organic compounds. For the higher levels of estimation, they involve polyfunctional and structural groups in which more information is provided (Marrero and Gani, 2001). In this work, the design of simple-structured chemical compounds is considered, since they are easier to be synthesized. Besides, the inclusion of higher-order groups will increase the complexity of the optimization model. Only first-order groups were considered, where w and z were assigned value of zero. The appropriate property prediction models were identified in order to calculate the properties involved in the design. The σ for the molecules was calculated following Conte et al. (2008). HLB was calculated by using equation shown by Guo and Rong (2006). T_b,T_f, M_W and LD_{50} were calculated by using equations provided by Hukkerikar et al. (2012b). PEL and F_P were calculated by using equation shown by Hukkerikar et al. (2012a). E_X for the molecules was calculated following equation provided by Frutiger et al. (2016). σ for the molecules was calculated by using Eq(2) (Conte et al., 2008).

$$f(x) = \sum_i N_i \sigma_i \quad (2)$$

HLB was calculated by using Eq(3) (Guo and Rong, 2006).

$$HLB = 7 + \sum_i N_i HLB_i \quad (3)$$

CMC was calculated by using Eq(4) (Mattei et al., 2013b).

$$-\log(CMC) = \sum_i N_i CMC_i \quad (4)$$

T_b, T_m, M_W and LD_{50} were calculated by using Eq(5), Eq(6), Eq(7) and Eq(8) (Hukkerikar et al., 2012b).

$$exp(\frac{T_b}{T_{bo}}) = \sum_i N_i T_{bi} \quad (5)$$

$$exp(\frac{T_m}{T_{mo}}) = \sum_i N_i T_{mi} \quad (6)$$

$$M_w = \sum_i N_i M_{wi} \quad (7)$$

$$-log(LD_{50}) - A_{LD50} - B_{LD50} M_w = \sum_i N_i LD_{50i} \quad (8)$$

PEL and F_P were calculated by using Eq(9) and Eq(10) (Hukkerikar et al., 2012a).

$$-log(PEL) = \sum_i N_i PEL_i \quad (9)$$

$$F_p - F_{po} = \sum_i N_i F_{pi} \quad (10)$$

E_X for the molecules was calculated by using Eq(11), Eq (12) and Eq(13) (Frutiger et al., 2016).

$$exp(\frac{T_b}{T_{bo}}) = \sum_i N_i T_{bi} \quad (11)$$

$$exp(\frac{T_m}{T_{mo}}) = \sum_i N_i T_{mi} \quad (12)$$

$$Ex = UEL - LEL \quad (13)$$

The sub-index score is assigned to each safety or health property based on safety and health indexes (Ten et al., 2015). All the sub-index scores of safety and properties are summed up to calculate the total safety and health index score as in Eq(14):

$$I_{SH} = I_V + I_{EL} + I_{AH} + I_{EX} + I_{FL} \quad (14)$$

where ISH is total health and safety index score, Iv is volatility sub-index score, IEL is the exposure limit sub-index score, IAH is acute health hazard index score, IEX is explosiveness sub-index score, IFL is flammability sub-index score. The scores of IV and IEL are referred from Inherent Occupational Health Index (IOHI) by Hassim and Hurme (2010), the scores of IEX and IFL are taken from Inherent Safety Index (ISI), while score of IAH is from National Fire Protection Association (NFPA) health hazard rating.

For molecular design, the potential molecular groups which act as probable building blocks were selected. The molecular blocks were identified based on the molecular blocks that existing in surfactant in laundry detergents which are currently available in market. The molecular blocks selected are $–CH_3$, $-CH_2$, -CH, -OH, $-CH_2O$, $-CH_2NH_2$ and $–OCH_2CH_2OH$. The octet rule of structural feasibility as shown in Eq(15) is imposed to ensure that only feasible molecules are generated.

$$\sum_{i=1}^{G_T} N_i(2 - v_i) = 2g \quad (15)$$

where vi is the valence number of group i, GT is the total number of groups present in the molecule, and g is a constant that takes the values of 1, 0, -1 or -2 for acyclic, monocyclic, bicyclic, and tricyclic compounds. Since there are two target properties to be minimized in this work, fuzzy optimization algorithm was adopted, where max-min aggregation method by Zimmermann (1978) was utilized. For safety and health index score, the highest possible penalty score is 19 and the lowest possible score is 2. The usage of these scores followed the safety and health indexes from ISI, IOHI and NFPA rating. For CMC, the highest possible value is 0.0086 and the lowest value is 0. The degree of satisfaction, λ for safety and health index score and CMC were calculated by using Eq(16) and Eq(17). Another variable known as the least-satisfied degree of satisfaction, λ is introduced, where both λISH and λCMC must be greater or equivalent to the value of λ. The overall objective now is to maximize the value of λ subjected to the constraints given as shown in Eq(18).

$$\lambda_{ISH} = \frac{19 - I_{SH}}{19 - 2} \quad (16)$$

$$\lambda_{CMC} = \frac{0.0086 - CMC}{0.0086 - 0} \quad (17)$$

$$\text{Maximize } \lambda: \qquad \lambda ISH \geq \lambda \text{ and } \lambda CMC \geq \lambda \quad (18)$$

3. Result and discussion

This surfactant design problem is solved using Lingo 18.0, an optimization modelling software. Three surfactants with the best value of λ, A1, A2 and A3 are generated. The International of Pure and Applied Chemistry (IUPAC) name for A1, A2 and A3 are 1-aminomethyl-2,3,4,5,6-pentamethylnonane-1,8-diol, 2-aminomethyl-1-isobutyl-5,6-methylheptane-1,3-diol and 9-amino-(2-hydroxyethoxy)-4,5,6,7-tetramethyl-3-nonanol. The molecular structure of these three molecules are illustrated in Figure1. The properties of the generated molecules are shown in Table 2.

(a) (b) (c)

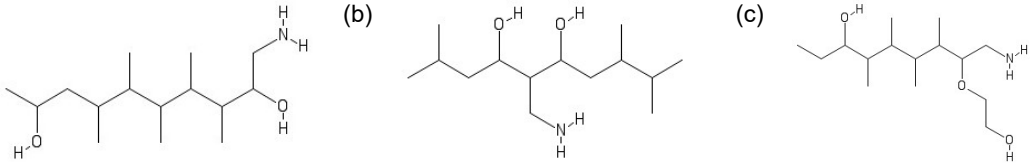

Figure1: Molecular structure (a) A1, (b) A2, and (c) A3.

Table 2: Generated molecules with their properties.

Surfactant	λ	λ_{ISH}	λ_{CMC}	I_{SH}	CMC (mol/L)	σ (mN/m)	HLB
A1	0.735	0.765	0.735	6	0.00228	21.5	7.36
A2	0.405	0.765	0.405	6	0.00512	21.9	7.02
A3	0.228	0.765	0.228	6	0.00664	24.8	7.05
DEA	-	-	-	10	0.00827	-	-
SLS	-	-	-	-	0.00380	-	-

Table 2: Generated molecules with their properties (cont.).

Surfactant	T_b (°C)	T_m (°C)	M_W (g/mol)	PEL (ppm)	LD_{50} (mg/kg)	F_p (°C)	E_X (vol %)
A1	150	22.6	259.00	18.92	321.66	608.85	6.66
A2	150	21.2	245.00	20.93	348.87	542.84	8.78
A3	150	7.1	275.00	10.92	336.00	562.34	12.70
DEA	268	28.0	105.14	0.27	0.68	273.00	8.20
SLS	204	-	288.37	-	1288.00	170.00	-

Since there are several values of safety and health properties for SLS such as PEL and E_X are not available in literature, only DEA is referred for comparison in the term of safety and health aspects. The score of safety and health sub-index is assigned to each molecule as shown in Table 3. All surfactant candidates have the total safety and health index score of 6, which is much lower than DEA. As shown in Table 2, the three generated candidates have larger values of PEL and LD_{50} compared to DEA, indicating that they are less harmful than DEA. DEA and the three molecules are assigned with the same value of FL and E_X sub-index, which is the lowest score in each sub-index. A1, A2, A3 and DEA are considered safe in terms of FL and E_X. All in all, it is clearly stated that A1, A2 and A3 are safer and less harmful compared to DEA and SLS and able to replace DEA and SLS in laundry detergent as surfactant with respect to the safety and health performance.
The CMC value shows the amount of surfactant needed to achieve maximum surface tension reduction; it is crucial for surfactant efficiency. The lower the CMC, the higher the efficiency. A1 has the least CMC value among the surfactants, followed by DEA, A2 and A3. A1 has higher efficiency than SLS and DEA, it is able to replace SLS and DEA as surfactant in laundry detergent. A2 and A3 has poorer functionality performance compared to DEA. However, they are still good candidates to replace DEA in laundry detergent formulation due to their favorable safety and health properties. The results demonstrate that any conventionally used chemical ingredients can be substituted with less hazardous substances without compromising the desired functionalities. This ensures that the potential risks resulted from the consumption of chemical products can be eliminated or reduced to a minimum level.

Table 3: The score of safety and health sub-index.

Surfactant	I_V	I_{EL}	I_{AH}	I_{EX}	I_{FL}	I_{SH}
A1	0	2	2	1	1	6
A2	0	2	2	1	1	6
A3	0	2	2	1	1	6
DEA	0	4	4	1	1	10

4. Conclusions

The safety and health aspects have not been strongly emphasized before into a laundry detergent design. The safety and health aspects were integrated into laundry detergent design besides the property functionalities. The proposed approach may provide alternative surfactant candidates that acquire the desirable functionality properties and at the same time reduce the safety and health impacts to consumer. Based on the results, 1-aminomethyl-2,3,4,5,6-pentamethylnonane-1,8-diol is the most suitable molecule to replace SLS and DEA as surfactant in laundry detergent. Further validation by laboratory experiments is suggested for future work to ensure the functionality performances of the molecule in the final laundry detergent formulation design.

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