

Effects of Linker Molecules to Adsorption of Rhamnolipid Biosurfactant onto Aluminum Oxide Surface

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Abstract --- Rhamnolipid biosurfactant is not only environmentally friendly but also effective in adsorbing on metal oxide surface. However, the hydrophilic property of rhamnolipid tends to decrease its solid-liquid adsorption capacity. Rhamnolipid surfactant can be modified to enhance its hydrophobicity by adding some linker molecules to the solution. Therefore, effects of linker molecules to the adsorption capacity of rhamnolipid biosurfactant on aluminum oxide surface were evaluated. Results showed that the longer carbon chain in linker molecules (1-butanol, 1-octanol and 1-dodecanol) and the higher rhamnolipid adsorption capacity were observed. Surfactant mixed with 1-butanol (4-Carbon atom) showed the lowest rhamnolipid adsorption capacity of 0.10 mmol per gram while the 8-Carbon atom of octanol yielded the highest amount of 0.30 mmol per gram. This result can be attributed to the coiling effect of the linker molecules (1-dodecanol), which hinders the interaction between the head group and the metal oxide surface which created a gap between adjacent adsorbed surfactant molecules. This was the consequent to a less adsorption capacity for the longer chain linker.

Keywords --- Adsorption, Rhamnolipid, Linker molecule

I. Introduction

Surfactants are amphiphilic molecules consist of both hydrophobic and hydrophilic moieties, which caused them accumulate at the interface between two immiscible fluid phases [1], reduce the interfacial tension (IFT) [2], and adsorb toxic [3]. Surfactants are categorized by their head groups whether they are nonionic, anionic, cationic or amphoteric.

Using absorbent material as intermediates is one of prevalent methods for both of industry and environment. Various forms of adsorbent materials have been developed to improve the effectiveness in the adsorption process. Surfactants can adsorb onto the adsorbent material and perform an interesting adsorption behavior that

capable to improve the overall adsorption performance. However, surfactants are synthetic chemical which commonly known as toxic and hardly degrade as it will remain for a period of time before destroyed by nature. As a result, surfactants are limited to use for the pollution control purpose in an environmental applications. According to this work, the biological surfactant (Biosurfactant) then has been adopted for a better solution. Not only is can biosurfactant synthesized by bacteria, yeast and mold (produced from renewable resources), but they are also bearing preference characteristics for the low toxicity and biodegradable in nature which benefit to the environment[4].

Rhamnolipid biosurfactant has been widely used to absorb toxins from the environment (e.g. phenanthrene, cadmium, PAHs etc.) [5, 6, 7, 8]. However, the relatively hydrophilic property of its molecule is limiting the overall adsorption efficiency. Therefore, this research aims to improve rhamnolipid hydrophobicity by adding some linker molecules to the solution which can be lead to the better performance efficiency. Linker molecules known as long chain linear alcohol, which are 1-butanol, 1-octanol and 1-dodecanol were selected to use in this study. Furthermore, the comparison for each linker system was also evaluated.

II. Materials and Method

A. Materials

The biosurfactant used in this study was rhamnolipid biosurfactant, JBR 515 (15 %w/v), purchased from Jeneil Biosurfactant Co. (Saukville, Wisconsin, U.S.A.). The biosurfactant was received as a mixture of 50 %w/v monorhamnolipid (C₂₆H₄₈O₉, MW = 504) and 50 %w/v dirhamnolipid (C₃₂H₅₈O₁₃, MW = 650) with an average molecular weight of 577 gram per mole. It is an anionic surfactant and was produced by *Pseudomonas aeruginosa*.

The linker molecules used in this study were selected from different type of alcohols with the different number of carbon chain length: butan-1-ol (C₄H₁₀O), 1-octanol (C₈H₁₈O) and 1-dodecanol (C₁₂H₂₆O). All linker molecules were purchased from Acros (Geel, Belgium) with 99% purity.

The solid oxide used in this study was aluminum oxide or alumina (Al₂O₃), which was purchased from Aldrich chemical company (Milwaukee, WI, U.S.A.).

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Alumina has a particle size of about 150 mesh. The specific area obtained from the manufacture is 155 m²/g, and pH of the point of zero charge (PZC) of aluminum oxide is 9.1.

The electrolyte concentration was controlled using 1mM of sodium chloride (NaCl). The solution pH was adjusted by using NaOH and HCl solutions. All chemicals were used as received without further purification. All solutions used in this work were prepared with double distilled water which having a resistance of 18.2 M ohms.

B. Experimental method

1. Critical micelle concentration measurement

Surface tension was measured by Wilhelmy plate tensiometer (DCAT 11, data physics, Filderstadt, Germany) with a platinum plate at room temperature (25 ± 2 °C) in a presence of 1.0 mM of NaCl electrolyte concentration. The relationship between surface tension and surfactant concentration were plotted to determine the critical micelle concentration (CMC) as summarized in Table I.

2. Surfactant adsorption study

Rhamnolipid biosurfactant and surfactant-linker mixtures were prepared to adsorb onto aluminum oxide (Al₂O₃) surface at a room temperature (25 ± 2°C) in a presence of an electrolyte concentration of 1.0 mM NaCl with the solution pH of 8.0 – 8.5. The adsorption studies were conducted in 40 mL vials containing 0.01 g. of aluminum oxide with varying surfactant concentrations. The solution was equilibrated by shaking at 150 rpm for 48 hours. After shaking 12 hours, the solution pH was measured and adjusted using NaOH and/or HCl solution until the solution pH was constant at the desired level. After equilibration, the solution was centrifuged to remove the aluminum oxide. The surfactant concentration were analyzed by HPLC (LC 1100, Agilent) with C18 column, acetonitrile and water (55:45) as the mobile phase and detected by an evaporative light scattering detector (ELSD).

III. Results and discussion

The adsorption isotherms were obtained by analysis of aqueous surfactant concentrations before and after adsorption on an aluminum oxide surface. Fig.1 shows the adsorption isotherm of rhamnolipid, rhamnolipid/butanol, rhamnolipid/octanol and rhamnolipid/dodecanol. For all systems, adsorption increases with increasing surfactant concentration prior to plateau adsorption according to the S-shaped isotherm that show the characteristics of regions II, III

and IV as expected from theory [1]. However, analytical limits prevented the measurement of surfactant concentrations in Region I. In this study, regions II and III are of the greatest interest as this is where monolayer (hemimicelles) and bilayer (admicelles) coverage occurs, respectively. The transition point between regions III and IV represented the CMC values from the surfactant adsorption isotherm of the Rhamnolipid alone, rhamnolipid/butanol, rhamnolipid/octanol and rhamnolipid/dodecanol that summarized in Table I. The maximum adsorption was evaluated as the mean value at the plateau region of the surfactant adsorption isotherm as summarized in Table II.

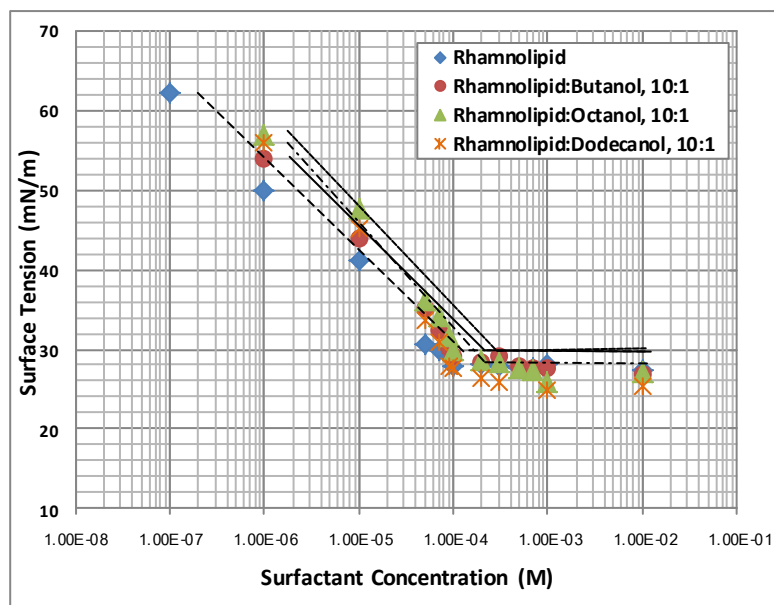


Fig. 1 The surface tensions of Rhamnolipid, Rhamnolipid/Butanol, Rhamnolipid/Octanol and Rhamnolipid/Dodecanol system

The maximum adsorption for rhamnolipid, rhamnolipid/butanol, Rhamnolipid/Octanol and Rhamnolipid/Dodecanol were reported as 0.12, 0.10, 0.30 and 0.15 mmol/g, respectively (table II).

Rhamnolipid mixed with 1-butanol had the lowest maximum adsorption onto aluminum oxide due to hydrophilic, the effectiveness of adsorption is declined could be attributed to the higher HLB determined from the surface tension data (Table I). The greatest amount for maximum adsorption onto aluminum oxide was found in the system of rhamnolipid mixed with 1-octanol. (Table II).

Table I. CMC values, Minimum surface tension, Surfactant adsorption and Area per molecule from surface tension of all surfactant system.

Surfactant	HLB	CMC from surface tension (mM)	Minimum surface tension		Surfactant adsorption Γ (mmol/1000m ²)	Area per molecule from surface tension (Å ² /molecule)
			(mN/m)	SD		
Rhamnolipid	22.00 - 24.00*	0.1	28.02	0.09	0.989	167.8
Rhamnolipid/Butanol	20.64 - 22.45	0.15	28.25	0.35	1.074	154.5
Rhamnolipid/Octanol	20.46 - 22.28	0.2	28.24	0.53	1.188	139.8
Rhamnolipid/Dodecanol	20.29 - 22.11	0.15	25.36	0.60	1.261	131.6

*From [10]

TABLE II. Transition points, Maximum adsorption (q_{max}), Molecule per area and Area per molecule from adsorption isotherm of all surfactant system.

Surfactant systems	Transition point (mM)	Maximum adsorption (q_{max})		Molecule per area (molecule/nm ²)	Area per molecule from adsorption isotherm (Å ² /molecule)
		mmole/g	SD		
Rhamnolipid	0.7	0.12	0.12	0.470	212.8
Rhamnolipid/Butanol	0.5	0.10	0.10	0.406	246.3
Rhamnolipid/Octanol	0.6	0.30	0.30	1.158	86.3
Rhamnolipid/Dodecanol	0.4	0.15	0.15	0.597	167.3

The result from Fig.1 showed that rhamnolipid mixed with 1-dodecanol performed the highest average plateau value of adsorption for all system. However, the summary data obtained from adsorption isotherm in Table II indicated that maximum adsorption amount (q_{max}) found to be in the rhamnolipid mixed with 1-octanol (0.30 mmole/g). The result in Table II also showed that the adsorption amount increased with an increasing of carbon atom in the linker molecule. Some contradictory found for the rhamnolipid mixed with 1-dodecanol (0.597 molecule/nm²) that showing two time smaller for the effective area per molecule than those in rhamnolipid mixed with 1-octanol (1.158 molecule/nm²). This result can be attributed to the coiling effect of linker molecules [9], which hinders the interaction between head group of surfactant and alumina surface, which created a gap between the adjacent adsorbed surfactant molecules. Consequently, the unarranged of adsorbed surfactant on the solid surface was affected to the adsorption effectiveness.

Comparison between adsorption of two immiscible phases which are the air-liquid interface and the liquid-solid surface as summarized in Table I and Table II, respectively. The result showed an unequal of the adsorbed area used for both systems that the air-liquid interface required the smaller adsorbed site than those needed in liquid-solid surface. The reason for this could be due to the larger head of the surfactant cannot adsorb into a very small pore in alumina surface, resulting in larger areas are require for surfactant aggregate.

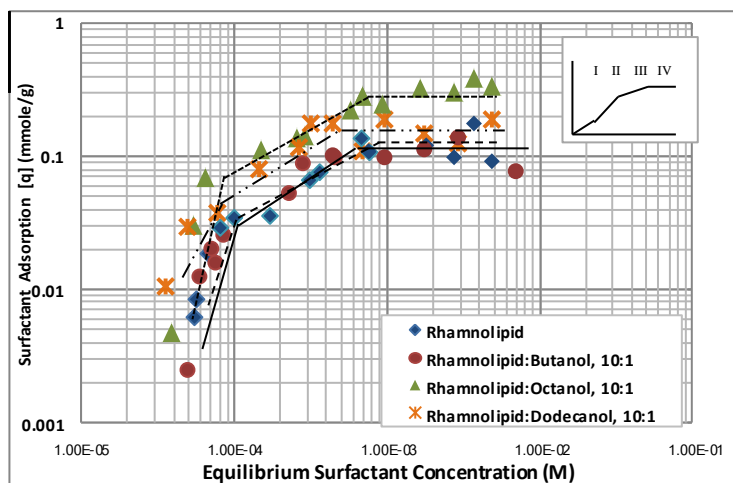


Fig.2 Adsorption isotherms of Rhamnolipid, Rhamnolipid/Butanol, Rhamnolipid/Octanol and Rhamnolipid/Dodecanol system in 0.001 M NaCl and for a solution pH of 8.0 - 8.5 onto aluminum oxide.

IV. Conclusions

This study aims to examine the adsorption of rhamnolipid biosurfactant on metal oxide by adding some linker molecules to the solution for improving adsorption efficacy. The lowest maximum adsorption onto aluminum oxide was rhamnolipid mixed with 1-butanol system while the greatest maximum adsorption amount onto aluminum oxide was rhamnolipid mixed with 1-octanol. This result can be attributed to the coiling effect of the linker molecules and surfactant arrangement.

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This study examines the adsorption of rhamnolipid biosurfactant on metal oxide when adding some linker molecules to the solution that can improve adsorption efficacy.