

Mixtures of Rhamnolipid Biosurfactant and Linker Molecule for Enhancing Styrene Adsolubilization

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Abstract— Rhamnolipid biosurfactant modified-surfaces were prepared to adsolubilize styrene in their admicellar structures with and without a coupling of linker molecules; three systems of alcohol containing different number of carbon atoms in alkyl chain (1-butanol, 1-octanol and 1-dodecanol). The effects of linker molecules to styrene adsolubilization on the rhamnolipid biosurfactant modified-surface were investigated. The partitioning of styrene into an admicelle is described by the admicellar partition coefficient (K_{adm}). Results showed that rhamnolipid biosurfactant with the present of linker molecules had the larger K_{adm} value than those containing of surfactant alone ($K_{adm}= 3042$). In addition, K_{adm} values increased with respect to the carbon atoms in alcohol molecules. In considering the effect of linker molecules, the K_{adm} for the mixture of dodecanol (12-Carbon), octanol (8-Carbon) and butanol (4-Carbon) were 4070, 3759 and 3612, respectively. The result indicated that the adsolubilization capacity increased with increasing carbon chain lengths of linker molecules, since linker molecules can enhance the adsolubilization capacity of styrene by enlarging the adsolubilization region in the admicelle through partitioning with surfactant tails.

Keywords— Adsolubilization, Rhamnolipid, Linker molecule, Styrene

I. Introduction

Biosurfactants are groups of surfactants which can be produced from microorganisms such as bacteria, fungi and yeast [1]. The advantage of biosurfactants, when compared to synthetic surfactants, is that can work in extreme conditions of temperature, pressure, pH and salinity [1], are biodegradable in nature, have low toxicity and are environmental friendly [2, 3]. The general structure of surfactant molecules are divided into two parts, a polar or hydrophilic head group (water-like) and a non-polar or hydrophobic tail group (oil-like). These properties are promoted to create an accumulation of surfactant monomers between air-liquid and solid-liquid as a hydrophilic-hydrophobic interface/surface. Therefore, aggregated surfactants can reduce interfacial tension between

that two interfaces, for example water-oil and increase the solubility of oil molecules into the surfactant micelles. Biosurfactants are widely used for environmental and industrial applications, such as cosmetics, toiletries, wetting agent, emulsifier, detergent and foaming agent as well as commonly applied in environmental and agricultural purposes e.g. enhanced oil recovery, wastewater treatment, antimicrobial, antifungal and antiviral agents [3]. In particular, biosurfactants have been used to modify adsorbent in order to increase organic contaminant removal efficiency. When, surfactant monomers adsorb at the solid-liquid interface, they are capable of solubilizing organic solutes solubilized in aqueous phase into the hydrophobic core of adsorbed surfactant aggregates, known as admicelle or hemimicelle depending on whether they form bilayer or monolayer coverage, this process known as adsolubilization [4]. Admicelle is a bilayer structure of surfactant in which the tail group of the first and the second layer binding together to create a hydrophobic area inside the adsorbed aggregate.

Rhamnolipids are classified as anionic biosurfactants, produced by *Pseudomonas aeruginosa*. Their unique molecular structure typically consist of one or two rhamnose sugar connected to β -hydroxydecanoic acid with glycosidic bond. Previous studies showed that rhamnolipids were used in the treatment of contaminated soil and water through various technologies for example, soil washing, heavy metal and organic compound removal, bioremediation and oil spills treatment [3]. Thus, rhamnolipids is an interesting alternative to be applied in environmental applications.

The purposes of this study is to investigate the impact of linker molecules on styrene adsolubilization in a rhamnolipid biosurfactant admicellar system on an aluminum oxide surface. The linker molecules used in this study are three alcohols with varying number of carbon chain length (1-butanol, 1-octanol, and 1-dodecanol). The comparison of styrene adsolubilization with the presence and the absence of linker molecules were also evaluated.

II. Materials and Method

A. Materials

The rhamnolipid biosurfactant JBR 515 (15 %w/v) was purchased from Jeneil Biosurfactant Co. (Saukville, Wisconsin). JBR 515 consist of 50 %w/v monorhamnolipid ($C_{26}H_{48}O_9$, MW = 504) mixture with 50 %w/v dirhamnolipid ($C_{32}H_{58}O_{13}$, MW = 650) and has an average molecular weight of 577. The rhamnolipid biosurfactant was anionic surfactant and was produced by *Pseudomonas aeruginosa*, as seen in Figure 1.

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Three alcohols with different number of carbons chain lengths were used as a linker molecule in this research: 1-butanol (C₄H₁₀O), 1-octanol (C₈H₁₈O) and 1-dodecanol (C₁₂H₂₆O). All linker molecules were purchased from Acros (Geel, Belgium). The physical and chemical properties of linker molecules are shown in Table I.

Aluminum oxide or alumina (Al₂O₃) was purchased from Aldrich (Milwaukee, WI, USA). Alumina has a particle size of about 150 mesh. The specific area obtained from the manufacture is 155 m²/g and the point of zero charge (PZC) pH of aluminum oxide is 9.1 [5].

Styrene with 99% purity was purchased from Acros (Geel, Belgium). All chemicals were used as received without further purification. All solutions were prepared with de-ionized water with a resistance of 18.2 MΩ cm. The plastic and glassware were rinsed several times with de-ionized water prior to use.

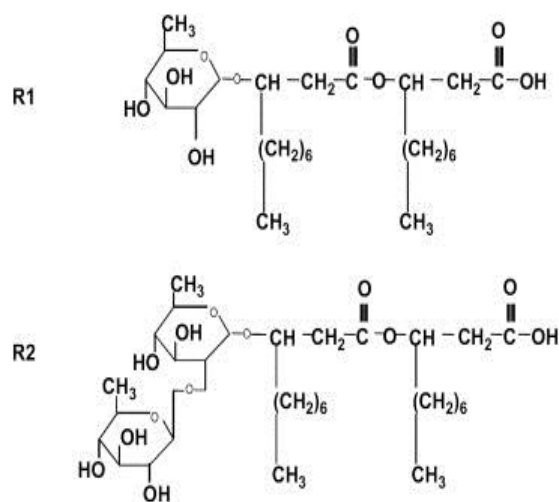


Figure 1. Structures of the rhamnolipids: (R1) 1-(carboxymethyl)octyl 3-[(6-deoxy-alpha-L-mannopyranosyl)oxy]decanoate and (R2) Decanoic acid, 3 [[6-deoxy-2-O-(6-deoxy-alpha-L-mannopyranosyl)-alpha-L-mannopyranosyl]oxy]-, 1-(carboxymethyl)octyl ester

TABLE I. PROPERTIES OF LINKER MOLECULE

Linker molecules	Molecular		MW	Density (g/ml)
	Formula	Structure		
1-butanol	C ₄ H ₁₀ O		74.12	0.81
1-octanol	C ₈ H ₁₈ O		130.23	0.82
1-dodecanol	C ₁₂ H ₂₆ O		186.33	0.83

B. Styrene adsolubilization

The adsolubilization of styrene were conducted in batch experiment at room temperature (25 ± 2 °C), an electrolyte concentration of 1.0 mM NaCl and the solution pH of 8.0 – 8.5 adjusted by using NaOH and HCl were used. The appropriate surfactant concentration was selected to be a 95% lower than the CMC which was obtained from the surfactant adsorption isotherm. At this concentration, the maximum adsorbed admicelles were formed onto aluminum oxide surface without any micelles formation in aqueous solution. The surfactant solutions with known concentrations were added to 40 mL vials containing 0.01 g of aluminum oxide with varying styrene concentrations. The vials were sealed with Teflon-line screw caps (PTFE) followed by shaking at 150 rpm for 48 hours. The aqueous phases containing surfactant and styrene were analyzed by HPLC (LC 1100, Agilent) with C18 column type. The mobile phase in this analysis was acetonitrile and water (55:45). The concentration of surfactant and styrene in the solution were detected by evaporative light scattering detector (ELSD) and UV detector at 247 nm, respectively.

III. Results

Adsolubilization is the process of organic solutes partitioning from the aqueous phase and adsorbing the admicelles on the adsorbent. The partitioning of organic solutes into an admicelle is described in term of the admicellar partition coefficient, K_{adm} , as follows:

$$K_{adm} = \frac{X_{adm}}{X_{aq}}$$

X_{adm} and X_{aq} are the mole fraction of organic solute in the admicelle and the aqueous phase, respectively. X_{adm} and X_{aq} values can be calculated as follows:

$$X_{adm} = \frac{(C_{i,s} - C_{f,s})}{(C_{i,s} - C_{f,s}) + (S_i - S_f)}$$

$$X_{aq} = \frac{C_{f,s}}{C_{f,s} + 55.55}$$

where $C_{i,s}$ and $C_{f,s}$ are the initial and equilibrium concentrations of the organic solute, respectively. S_i and S_f are the initial and equilibrium concentrations of the surfactant that were added as monomers, respectively. All material concentrations are expressed in mole per liter.

The adsolubilization isotherm (Figure 2) is plotted between the mole fraction of styrene in the admicelle (X_{adm}) versus the mole fraction of styrene in the aqueous phase (X_{aq}). From Figure 2, it can be seen that as the equilibrium concentration of styrene increased, the adsolubilization of styrene in the admicelles also increased for all surfactant (with and without the linker molecules). The styrene admicellar partition coefficient values (K_{adm}) are summarized in Table II. The results showed that rhamnolipid biosurfactant mixed linker

molecule showed greater styrene adsolubilization capacity than rhamnolipid biosurfactant alone. From Figure 2 and Table II, the system with the presence of linker molecules showed higher styrene adsolubilization compared to the system without linker molecules ($K_{adm}=3042$). Regarding the effect of linker molecules, the K_{adm} of the dodecanol system ($K_{adm}=4070$) was higher than that of the octanol system ($K_{adm}=3759$) and that of the butanol system ($K_{adm}=3612$), respectively. The result indicated that the adsolubilization capacity increased when the number of carbons in the linker molecule chain increased. The rationale of this finding can explain that the linkage between linker molecule and the surfactant tail are affected to an increasing of hydrophobicity for each surfactant monomer. Therefore, the admicelle can provide larger space to adsolubilize organic solute into their aggregates. As a result, the enhancement of styrene adsolubilization capacity was observed.

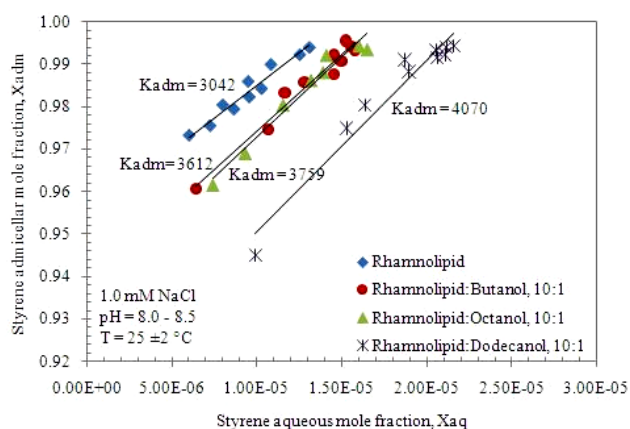


Figure 2. The relationship between styrene admicellar mole fraction (X_{adm}) and styrene aqueous mole fraction (X_{aq}) of rhamnolipid biosurfactant mixtures at 1.0 mM NaCl, equilibrium pH of 8.0 – 8.5 and a temperature of 25 ± 2 °C

TABLE II. SUMMARY RESULT FOR ADSORPTION AND ADSOLUBILIZATION STUDIES OF RHAMNOLIPID BIOSURFACTANT MIXTURES

Experimental systems (Surfactant (fixed at 1.0 mM): Linker)	Maximum adsorption (q_{max}) (mmol/g)	Styrene adsolubilization		
		K_{adm}	r^2	$\log K_{adm}$
Rhamnolipid	0.12 ± 0.03	3042	0.95	3.48
Rhamnolipid:butanol 10:1 v/v	0.10 ± 0.02	3612	0.96	3.55
Rhamnolipid:octanol 10:1 v/v	0.30 ± 0.06	3759	0.96	3.58
Rhamnolipid:dodecanol 10:1 v/v	0.15 ± 0.03	4070	0.95	3.61

The locus of styrene partitioning within surfactant admicelles was evaluated by the shape of the graph shown in Figure 3, which was plotted between the styrene admicellar partition coefficient values (K_{adm}) versus the mole fraction of styrene in the aqueous phase (X_{aq}). It was found that the K_{adm} values for all surfactants decreased as the mole fraction of

styrene in the aqueous phase (X_{aq}) increased. The result showed an agreement with previous studies [4,7], which was reported that styrene partitioned at the region close to the surfactant head group in the admicelle or the so-called palisade layer. This area was acknowledged as a polarity region [4,6]. Thus, the adsolubilization of an intermediate polarity organic solute like styrene (dipole moment = 0.13) tends to perform at the palisade followed by the like-dissolved-like principal.

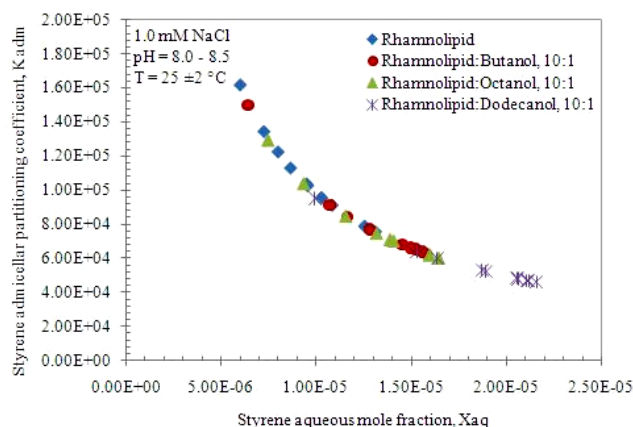


Figure 3. The relationship between styrene admicellar partitioning coefficient (K_{adm}) and styrene aqueous mole fraction (X_{aq}) of the rhamnolipid biosurfactant mixtures at 1.0 mM NaCl, an equilibrium pH of 8.0 – 8.5 and a temperature of 25 ± 2 °C

IV. Conclusions

Surfactant-modified adsorbents have been evaluated for removal of organic contaminants from the environment. This research results demonstrate that the adsolubilization of rhamnolipid biosurfactant mixed with linker molecules showed greater styrene adsolubilization capacity (K_{adm}) than rhamnolipid biosurfactant alone. The adsolubilization enhancement of styrene increased when the carbon chain length of the linker molecule increased due to the linker molecule increasing a larger hydrophobic site for the adsolubilizing styrene into admicelles. Styrene is an intermediate polar organic solute, the result indicated that styrene mainly partitioned into the palisade layer of the admicelle.

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Biosurfactant mixed linker molecule-modified adsorbents have been evaluated for removal of organic contaminants from the environment. This research result indicated that the adsolubilization capacity increased with increasing carbon chain lengths of linker molecules, since they can enhance the adsolubilization capacity by enlarging the adsolubilization region in the admicelle through partitioning with surfactant tails.