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Surface adsorption and spontaneous aggregation of rhamnolipid mixtures in aqueous solutions

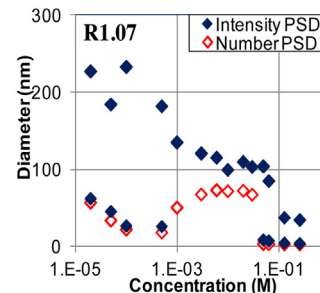
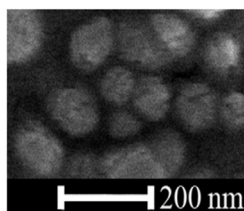
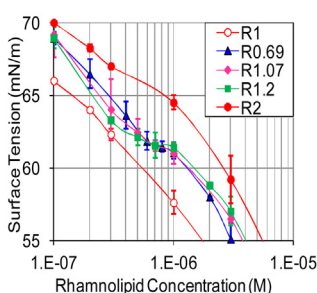
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HIGHLIGHTS

- Rha-C₁₀-C₁₀ and Rha-Rha-C₁₀-C₁₀ show different phase behaviors in their monolayers.
- Monolayer composition of RL mixtures become equal at a surface pressure of 10 mN/m.
- Vesicle formation was observed before the critical micelle concentration.
- Micelles are formed in Rha-Rha-C₁₀-C₁₀ only after vesicle-micelle transition.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface tension related properties of pure rhamnolipids R1 (Rha-C₁₀-C₁₀), R2 (Rha-Rha-C₁₀-C₁₀) and their mixtures with R2/R1 molar ratios of 0.69, 1.07, and 1.2 are investigated at their natural pH with and without bulk phase additives. Surface tension, dynamic light scattering, UV–vis spectrophotometric measurements and observations by scanning electron microscope and cross polarized light microscope were used to evaluate the surface adsorption and spontaneous aggregation of rhamnolipid mixtures in aqueous solutions. Structural changes taking place in the surface monolayers with an increase in the bulk concentration of rhamnolipid mixtures were evaluated through analysis of surface tension measurements. Interactions of the two hydrophilic groups, carboxylic acid and rhamnosyl groups, of the rhamnolipids through electrostatic forces and hydrogen bonds, respectively, were elucidated with the use of electrolytes and rhamnose in the bulk phase. Self-assembly of rhamnolipids correlated well with the state of the monolayer. Vesicle formation was observed at concentrations below the critical micelle concentration (cmc). This critical concentration for spontaneous vesicle formation was correlated with the onset of condensed phases in the monolayer. Micelles could only be observed at very high concentrations, about hundred times the cmc, in solutions of R2 and its mixtures with R1. Vesicles of R2 were found to be more uniform than the vesicles of R1. This difference in aggregation behavior could be due to the different stabilization mechanisms of the aggregates.

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1. Introduction

Biosurfactants produced by microorganisms have ecological superiority over conventional petroleum based surfactants in terms of biocompatibility and biodegradability. Among these biosurfac-

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tants, rhamnolipids are considered to be the most promising due to their synthesis by different strains of *Pseudomonas aeruginosa* bacteria, utilizing a wide range of renewable raw materials as their carbon source, including industrial wastes [1–3]. Their chemical resistance, effectiveness of reducing the surface tension over a wide range of electrolyte compositions and pH [4], and antimicrobial activity [5–7] leads to their use in different applications including foam fractionation [8] separations [9], and drug delivery [10]. These applications are based on the surface and aggregation behavior of the surfactants; namely, the ability to lower surface tension, their critical aggregation (cac) and micelle (cmc) concentrations, and the types, sizes, and homogeneity of their aggregates. Biosurfactant aggregates are under focus as plausible candidates for monodisperse, nearly spherical, unilamellar vesicles for drug delivery applications [11].

Microorganisms adjust the composition of their secretions according to their needs [4], so the rhamnolipids (RL) are produced as a mixture of molecular homologues, called congeners, the composition of which depend on the bacterial strain, growth conditions and carbon source used for their nutrition [1,3,5,6,12–14]. Up to 58 congeners were identified by Abdel-Mawgoud et al. [13]. The hydrophilic section of a rhamnolipid molecule is constituted of one or two rhamnose groups attached to carboxylic acid groups, designated as mono-rhamnolipids and di-rhamnolipids, respectively. The hydrophobic section is made up of the hydrocarbon chains of the carboxylic acids. Number of carboxylic acid groups ranges between one and three, the most common being two carboxylic acid groups per molecule [13]. The congeners also differ in the number, length and saturation of the hydrocarbon chains. The length of the chains ranges from eight to sixteen, with two identical chains, or two chains with number of methyl groups not too different from each other such as 8–10 and 10–12. A double bond may exist between methyl groups next to the carboxylic acid group such as 10–12:1, or 12–12:1. Nomenclature used for rhamnolipid structures indicate the number of both the rhamnose and the carboxylic acid groups: For example, the most common mono-rhamnolipid congener with ten carbon atoms in the two carboxylic acid groups as Rha-C₁₀-C₁₀ and the di-rhamnolipid congener, as Rha-Rha-C₁₀-C₁₀, used in this work. In this text, the nomenclature for these two congeners will be further simplified as R1 and R2, respectively.

Down-stream operations of separating the bacterial mass and recovery of the surfactants after the microbial production are costly processes [1,15]. Even if the composition of the surfactant solution is identified, the separation of a rhamnolipid mixture into its components is not feasible economically. So, the rhamnolipid mixture is considered as a surfactant on its own, and its physical properties are determined as is [2,3,14,16,17]. The composition of the rhamnolipid mixture was found to affect its surface activity, aggregation behavior and antibacterial properties [5–7,18]. A number of applications are not sensitive to the composition of the rhamnolipid surfactant, but some operations are, as in the case of affinity foam separation of enzymes where di-rhamnolipids are more suitable [9]. The need for research on the effect of individual congeners on the interfacial activity of rhamnolipid mixtures to be used for specific applications has been advocated by several research groups [3,6,13,19]. However, in the current literature, there is only a single work [18] on the comparative effect of the two congeners R1 (Rha-C₁₀-C₁₀) and R2 (Rha-Rha-C₁₀-C₁₀) on the surface and aggregation behavior.

Double chained surfactants with bulky hydrophilic groups coupled with two hydrocarbon chains, such as the rhamnolipids under consideration in this work, attain a cylindrical shape in the fully stretched condition. The shape of the molecule is characterized by the critical packing parameter (cpp), defined as the ratio of the volume of the molecule to the product of its cross sectional area and the fully stretched length of the hydrocarbon groups [20]. Surfac-

tants with packing parameters in the range, $1/2 < cpp < 1$ tend to form bilayers. The aggregation proceeds stepwise with the initial formation of dimers at very low concentrations below surface saturation [21]. Mechanism of dimerization is similar to micellization in that the tails are sandwiched in between the hydrophilic groups in an aqueous environment to minimize their free energy. With an increase in the total surfactant concentration these dimers interact laterally to form bilayers. Besides the fulfillment of cpp conditions, non-ideal mixing of surfactants leading to segregation in the inner and outer monolayers of the bilayer is necessary for spontaneous formation of vesicles [22,23].

Stable vesicles in dilute surfactant solutions at concentrations much below the cmc are stabilized either energetically (enthalpic stabilization), or entropically (entropic stabilization) [24]. In the case of enthalpic stabilization, one of the underlying mechanisms could be the difference in the composition of the two monolayers making up the bilayer. The vesicle radius, determined by the curvature that minimizes the internal energy per molecule, does not change considerably with an increase in surfactant concentration. The vesicles are entropically stabilized through the action of translational entropy at very low concentrations when the composition of the monolayer allows elastic bending of the bilayer from the minimum-free-energy, flat bilayer configuration to a spherical vesicle. Entropically stabilized vesicles are characterized by a broad distribution of sizes around the limiting vesicle size.

The three-stage model proposed by Lichtenberg [25] predicts the observation of three types of aggregations with increasing surfactant concentration: 1. Existence of vesicles from very low concentrations up to a critical concentration, designated as critical vesicle concentration (cvc), 2. Region of mixed micelles and vesicles up to the critical micelle concentration (cmc), and 3. Existence of micelles only at concentrations greater than the cmc. The existence of these three regions are demonstrated for mixtures of double and single chain surfactants [26–31] chosen to mimic the biological processes involving lipid membranes.

Aggregation behavior of rhamnolipids depend on the composition of the hydrophobic chains, number of rhamnosyl groups, concentration of surfactant, presence of electrolytes in the solution, as well as temperature and pH of the medium. Since mixtures of rhamnolipids with different hydrocarbon compositions, and buffers are usually used in the experimental work, there is no general agreement in the spontaneous aggregation behavior of rhamnolipid mixtures in the literature [16,32–36].

In the only work on the aggregation behavior of pure rhamnolipids R1 and R2 and their mixtures [18], small angle neutron scattering (SANS) and dynamic light scattering (DLS) measurements were used to assess the self-assembly trends in solutions buffered to pH=9. In the range of 0.02–0.1M total surfactant concentration, R2 solutions were found to form micelles throughout the concentration range investigated. R1 aggregates were found to be micellar at low concentrations, and lamellar at higher concentrations. Mixed micellar/lamellar aggregations were found for mixtures with mol fractions of R1 greater than 0.5.

In this work the surface tension of R1, R2 and their mixtures in the molar ratio of R2/R1=0.69, 1.07 and 1.2 are determined at 25 °C and natural pH of the medium. The effect of electrolytes and polyalcohols as bulk phase additives on the surface tension is also discussed. In the second part, spontaneous aggregate formation of rhamnolipids R1, R2, and their mixtures are investigated as a function of concentration in the range $1 \times 10^{-5} < C_{RL} < 0.25$ M. The results are confirmed by turbidity measurements and SEM images. Physicochemical quantities derived from the surface tension measurements are associated with the aggregation behavior of rhamnolipid solutions.

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