Solution Properties of New Biosurfactants and Their Effect on The Modification of Surfaces

Makhkamov R.* Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan. 77a, Mirzo Ulugbek street, 100170 Tashkent, Uzbekistan.
*e-mail: ravshanmak@gmail.com, tel.+998998214336

Samandarov Sh. Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan. 77a, Mirzo Ulugbek street, 100170 Tashkent, Uzbekistan.

Saidkulov F Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan. 77a, Mirzo Ulugbek street, 100170 Tashkent, Uzbekistan.

Makhkamova I. Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan. 77a, Mirzo Ulugbek street, 100170 Tashkent, Uzbekistan.

Nurmanova M Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan. 77a, Mirzo Ulugbek street, 100170 Tashkent, Uzbekistan.

Saidakhmedova H. Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan. 77a, Mirzo Ulugbek street, 100170 Tashkent, Uzbekistan.

ABSTRACT

Biosurfactants are surface active amphiphilic compounds of biological origin and produced by many different microorganisms. The microorganisms including bacteria, fungi and algae are the most efficient organisms at producing biosurfactants. The biosurfactants offer many advantages compared to the synthetic surfactants: they are environmentally friendly, have useful properties including bioavailability, biodegradability, activity under extreme conditions, low toxicity and structural diversity. The purpose of this work was obtaining new biosurfactants from microorganisms, investigating the colloid-chemical properties of new biosurfactants, the efficiency of biosurfactants water solutions on wettability of different surfaces and establishing correlations between colloid-chemical properties of new surfactants. The modern methods for determining the colloid-chemical and solution properties of biosurfactants were used in the work. The contact angles of biosurfactant water solutions on different hydrophilic and hydrophobic surfaces were investigated. It has been established that the contact angles of biosurfactant water solutions on the hydrophilic surfaces (aluminum, copper, steel, glass) significantly depends on the composition and structure of biosurfactant molecules. It has been shown, that the compositions with low biosurfactant concentrations have higher contact angles and the hydrophobization of aluminum, copper, steel and glass surfaces takes place. At high biosurfactant concentrations, the contact angles sharply decreased due to the fact that during adsorption, the biosurfactant molecules oriented by the polar groups to the surfaces. The concentration dependence of the contact angle passes through a minimum only for hydrophilic surfaces aluminum, copper, steel and glass as a monolayer of surfactant molecules was formed on the hydrophilic surface with orientation by polar groups to the solid surface. It has been established that the increase in the cosine of the contact angle at higher biosurfactant concentrations was associated with the hydrophilization of the hydrophilic surfaces due to the formation of micelles on hydrophilic surfaces. For a hydrophobic surfaces, such as polyethylene, plexiglass and paraffin, the cosine of the contact angle increased monotonically with the increase in the biosurfactant concentration. It has been established that the effect of the biosurfactant structure on the adsorptive modification of surfaces occurs only at low biosurfactant concentrations by the formation of a monolayer.

Keywords: Biosurfactants, solution properties, wettability, contact angles, hydrophilic and hydrophobic surfaces, surface modification.

Introduction

Biosurfactants are surface active amphiphilic compounds of biological origin and are produced by a large variety of microorganisms. The microorganisms including bacteria, fungi and algae are the most efficient microorganisms at producing biosurfactants [1-4]. The biosurfactants offer many advantages compared to synthetic surfactants: they are environment friendly, have bioavailability, biodegradability, activity under extreme conditions, low toxicity and structural diversity [2-6]. On the basis of their chemical structures, biosurfactants can be divided into the following classes: lipopeptides, glycolipids, lipoproteins, phospholipids and polysaccharides. The biosurfactants can reduce surface and interfacial tensions between immiscible liquids and can make mixtures of solvents with different polarities compatible. Despite the presence of numerous studies on the production of biosurfactants, the discovery of new microbial surfactants and investigating their properties are very important and useful. Biosurfactants can be used in different fields of industry, environment protection, pharmacy and medicine, food and cosmetics [7-8]. Therefore, greater attention has been paid during recent years to the isolation of biosurfactants, studying properties and finding their applications. Several studies have been reported on the isolation and characterization of new biosurfactants, and investigating new fields of application for biosurfactants [9-10]. The high surface activity of the new biosurfactants provide reasons to believe that they have the property of adsorptive modification of different hydrophilic and hydrophobic surfaces [11-12] In this regard, the investigation of adsorptive modification of various surfaces with new biosurfactants water solutions was very interesting. The adsorption of biosurfactants from water solutions is one of the main methods for regulating the disperse systems of various nature [13-15]. The main method for studying the adsorption of biosurfactants on solids is to determine the adsorption isotherms. From the appearance of such isotherms, a conclusion can be drawn about the nature of adsorption (mono- or poly-layer) [16-18]. However, from the isotherms it is impossible to draw a conclusion about the structure of the adsorption layers. This requires additional information, first of all, on the orientation of surfactant molecules on the outer surface of the layer facing the solution [19-20]. Such information can be obtained by determining the contact angles of surfactant water solutions on different surfaces, which can reflect the orientation of the adsorbed surfactant molecules on the surfaces [21-22]. In this regard, we have investigated the contact angles of new biosurfactants water solutions on different hydrophilic and hydrophobic surfaces. Obtained results of study of the contact angles of new biosurfactants water solutions on different surfaces will provide a very important information for surface modification by new biosurfactants and be useful for creation of new modified materials. Due to this, the colloid-chemical properties of new biosurfactants were studied in this work. The article presents the materials and methods used in the work, the results of the study and their discussion, conclusion based on the analysis of the results and a list of references.

Materials and methods

The purpose of this work was investigating the solution properties of new biosurfactants and wettability of different surfaces by water solutions of the biosurfactants and establishing correlations between their colloid-chemical properties. To achieve the goal, the following tasks were set: investigation of colloid-chemical properties, to study the wettability of hydrophilic and hydrophobic surfaces by water solutions of new biosurfactants; to find-out correlations between their colloid-chemical properties. The following methods and materials were used in this research work.

Determination of surface tension. The surface tension of surfactant solutions was determined using tensiometer DCAT-9T at different temperatures and concentrations. In order to obtain statistically significant results, each measurement was repeated 5 times.

Thin layer chromatography. Thin layer chromatography (TLC) was carried out at room temperature in two different systems. For the study, ascending TLC was used in chambers preliminarily saturated with solvent vapors forming the mobile phase. Chromatography was carried out on plates with a polar stationary phase on aluminum and polymer matrices.

Refractive indices of aqueous solutions of surfactants. An Easy plus refractometer was used to determine the refractive index (n_D^{20}) of aqueous solutions of the obtained new surfactants. The refractive index of aqueous solutions was measured at a temperature of 293 K.

Density of surfactant samples. To determine the density (d_4^{20}) of new surfactants a density meter Easy plus was used. The density of the obtained surfactants was measured at a temperature of 293 K.

Extraction and purification of biological surfactants. Biological surfactants were isolated by acid precipitation and purified by solvent extraction. The Lactobacillus pentosus were planted in medium with nutrients and stored in a thermostat at a constant temperature. Each experiment was conducted at different temperatures in a thermostat. After incubation at a constant temperature for 144 hours in a thermostat, the cells were removed from the cultural liquid by centrifugation for 15 minutes at a constant temperature. The cell-free supernatant thus obtained was acidified with a 10% aqueous solution of acetic acid and the resulting mixture was stored for 15 hours at a constant temperature in an incubator to enhance the precipitation of biological surfactants. The precipitate formed as a result of storage in a thermostat was separated by centrifugation for 20 minutes. The thus isolated precipitate was extracted several times with ethyl alcohol at room temperature. The resulting extract was filtered and then the ethanol solvent in the extract was distilled under reduced pressure. The residue in the flask after distillation was dissolved in acetone and reprecipitated with n-hexane. The biological surfactants isolated after reprecipitation were dried in a thermostat under reduced pressure. Biological surfactants obtained in this way were brown colored viscous substances with a peculiar odor. Depending on the temperature of the medium with nutrients during the experiments obtained biosurfactants have names EFS-1, EFS-2 and EFS-3.

Determination of wettability of surfactants. The wettability of solid surfaces with surfactants water solutions was characterized by the values of the contact angle on different surfaces. The measurements were carried out on using Theta Flow optical tensiometer by projecting the deposited drop onto the screen. The drop was applied using a micro-syringe in a strictly defined amount.

Results and discussions

The isolated and purified biological surfactants were weighed and aqueous solutions with different concentrations were prepared from them. The surface activity of new biological surfactants in water solutions were investigated. The results of a investigation of the surface tension of aqueous solutions of the studied new biologic surface-active substances are presented in Table 1 below.

Table 1. The surface tension of water solutions of the studied biosurfactants.

Surfactant	T, K	Surface tension σ (мН/м) of biosurfactant water solutions at different concentrations ($C \cdot 10^2$) mol/L)								
		0,02	0,04	0,08	0,16	0,31	0,62	1,25	2,5	5
EFS-1	293	71,9	71,2	68,5	63,8	53,9	46,8	39,9	35,6	34,4
	303	71,1	69,9	67,2	62,5	52,5	45,7	39,2	34,1	33,5
	313	69,9	68,4	66,3	58,7	51,3	44,5	37,4	33,8	32,8
	323	68,6	67,6	64,7	57,3	49,9	43,8	36,7	32,7	31,5
	333	67,8	66,5	62,8	53,5	48,7	42,6	35,8	31,9	30,6
EFS-2	293	69,9	67,9	63,9	57,8	53,9	41,9	34,8	31,9	30,5
	303	68,7	65,8	62,7	56,5	48,7	40,7	32,9	30,8	29,6
	313	67,9	64,5	59,9	54,7	45,8	39,8	30,8	28,7	28,8
	323	65,4	62,8	58,8	52,6	44,6	38,9	29,8	27,6	27,7
	333	64,7	60,9	57,5	50,9	43,9	37,6	28,7	26,7	26,9
EFS-3	293	69,2	66,5	62,9	57,9	52,9	41,1	33,8	31,7	30,8
	303	67,9	64,7	61,8	56,8	47,7	40,2	32,7	29,8	28,7
	313	66,8	63,4	58,9	53,7	44,9	38,9	30,3	28,5	27,9
	323	64,3	61,6	57,7	51,9	43,8	37,8	29,7	27,6	26,7
	333	62,4	60,4	56,9	49,8	41,8	37,5	28,8	26,9	25,5

Analysis of the experimental data in Table 1 showed that, in terms of surface activity, the studied biosurfactants were ranked in the following order: EFS-3> EFS-2> EFS--3. The analysis of obtained results showed that with the increase of surfactant concentrations in water solutions the surface activity of new biosurfactants were increased. This result is connected with increase of adsorption capacity of new biosurfactants depending on the increase of biosurfactant concentration in water solutions. The analysis of experimental results in Table 1 also showed that with the increase of the temperature of the disperse system the surface tensions of water solutions of new biosurfactants were decreased. This result was connected with increase of adsorption of new biosurfactants molecules on the solution surface with the increase of the temperature of the disperse system. To get information on the orientation of biosurfactant molecules on the outer surface of the layer facing the solution we have studied new biosurfactants by determining the contact angles of biosurfactant water solutions on different surfaces. Such investigation will also provide information on the orientation of the adsorbed biosurfactant molecules on the surfaces. For this purpose, the contact angles of biosurfactant water solutions on different hydrophilic and hydrophobic surfaces such as aluminum, copper, steel, glass, polyethylene, plexiglass and paraffin were investigated. The contact angles of new biosurfactant water solutions on aluminum, copper, steel and glass surfaces depending on the biosurfactant concentrations are shown in Table 2. Analysis of the data presented in Table 2 showed that the contact angles of surfactant water solutions on the hydrophilic surfaces (aluminum, copper, glass and steel surfaces) significantly depends on the composition and structure of surfactant molecules. Obtained results showed, that lower concentration of biosurfactant in the water solution, higher the contact angle. It is interesting to note that at low biosurfactant concentrations, the hydrophobization of aluminum, copper, glass and steel surfaces takes place. Obtained results in Table 2 also showed that the treatment of hydrophobic surfaces with the diluted biosurfactant water solutions increased the contact angles on such surfaces.

Table 2. The cosine of the contact angles of biosurfactant water solutions on different hydrophile surfaces depending on the concentration of biosurfactants

Biosurfactant	Surface	Biosurfactant concentration in water solution (C %) / The cosine of the contact angles (CosΘ)										
		0,013	0,025	0.05	0,15	0,25	0,35	0,45	0,55	0,65	0.85	1.00
EFS-1	Steel	0,42	0,38	0.36	0,43	0.52	0.63	0.66	0.71	0.72	0.72	0.72
	Glass	0.87	0.86	0.85	0.84	0.88	0.93	0.95	0.96	0.96	0.96	0.96
	Aluminum	0,61	0,56	0.52	0,59	0.69	0.78	0.84	0.85	0.86	0.86	0.86
	Copper	0,58	0,53	0.49	0,56	0.65	0.72	0.79	0.81	0.83	0.84	0.84
EFS-2	Steel	0.37	0.34	0.32	0.36	0.44	0.54	0.62	0.64	0.66	0.66	0.66
	Glass	0.85	0.84	0.82	0.81	0.84	0.88	0.91	0.92	0.93	0.93	0.93
	Aluminum	0.54	0.49	0.47	0.44	0.53	0.68	0.79	0.82	0.86	0.88	0.88
	Copper	0.50	0.47	0.45	0.41	0.51	0.64	0.75	0.81	0.85	0.86	0.86
EFS-3	Steel	0.31	0.28	0.26	0.31	0.35	0.46	0.52	0.58	0.61	0.61	0.61
	Glass	0.81	0.79	0.78	0.77	0.79	0.84	0.86	0.88	0.88	0.88	0.88
	Aluminum	0.49	0.43	0.39	0.33	0.48	0.56	0.71	0.73	0.74	0.74	0.74
	Copper	0.45	0.41	0.36	0.30	0.45	0.52	0.69	0.71	0.72	0.72	0.72

Obtained results in Table 2 showed that at high biosurfactant concentrations, the contact angles were sharply decreased. Obviously, these results were due to the fact that during adsorption, the biosurfactant molecules were oriented by their polar groups to the hydrophobic surfaces. At a certain biosurfactant concentration in water solution, at which the maximum filling of the monolayer took place, the values of the contact angles reach minimum values. The values of the contact angles were decreased with the increase in the hydrophobic nature of the biosurfactant. Lower critical micelle-forming concentration (CMC) values of studied new biosurfactants the validity of this assumption. It is interesting to note that the concentration dependence of the contact angle passes through a minimum only for hydrophilic surfaces (aluminum, copper, glass, steel surfaces). This can be explained by the fact that a monolayer of biosurfactant molecules is formed on the hydrophilic surface with orientation by polar groups to the solid surface, and by hydrophobic chains to water. During the adsorption of the second surfactant layer with the orientation of polar groups to the water, the surface is again hydrophilized, the contact angle decreases, and a minimum is observed on the concentration dependence of the contact angle. It should be noted that the concentration corresponding to the maximum contact angle is in the concentration range between the CMC and the concentration at which the maximum build-up of the adsorption layer of biosurfactant molecules occurs at the solution-air interface. The increase in the cosine of the contact angle at higher surfactant concentrations is associated with the hydrophilization of the surface due to the formation of surface micelles.

The new biosurfactant water solutions were also investigated on polyethylene, plexiglass and paraffin surfaces depending on the biosurfactant concentration and contact angles were determined. The contact angles of new biosurfactant water solutions on polyethylene, plexiglass and paraffin surfaces depending on the concentration are presented in Table 3. Analysis of the results presented in Table 3 showed, that for hydrophobic surfaces (polyethylene, plexiglass and paraffin surfaces), the cosine of the contact angle has been increased monotonically with the increase in the biosurfactant concentrations. It should also be noted, that the isotherms of the dependence of the contact angle on the biosurfactant concentration for hydrophobic surfaces are similar to the surface tension isotherm

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Table 3. The cosine of the contact angles of biosurfactant water solutions on different hydrophobic surfaces depending on the concentration of biosurfactants.

Biosurfactant	Surface	Biosurfactant concentration in water solution (C %) / The cosine of the contact angles (CosΘ)									
		0,03	0,05	0,15	0,25	0,35	0,45	0,55	0,65	0.85	1.00
EFS-1	Polyethylene	0.21	0.38	0.48	0.49	0.52	0.62	0.66	0.73	0.74	0.74
	Plexiglass	0.25	0.41	0.49	0.51	0.56	0.68	0.74	0.78	0.79	0.79
	Paraffine	0.16	0.32	0.41	0.44	0.46	0.54	0.56	0.62	0.62	0.62
EFS-2	Polyethylene	0.23	0.29	0.35	0.41	0.46	0.49	0.59	0.63	0.71	0.71
	Plexiglass	0.28	0.32	0.39	0.48	0.52	0.58	0.62	0.68	0.74	0.75
	Paraffine	0.14	0.23	0.28	0.32	0.35	0.45	0.52	0.54	0.56	0.56
EFS-3	Polyethylene	0.19	0.21	0.28	0.35	0.41	0.49	0.55	0.61	0.69	0.70
	Plexiglass	0.23	0.26	0.31	0.38	0.46	0.51	0.59	0.66	0.72	0.73
	Paraffine	0.12	0.18	0.21	0.24	0.28	0.38	0.42	0.46	0.48	0.48

These results can be explained by the fact that only monolayers of biosurfactant molecules can be formed on hydrophobic surfaces, oriented by hydrophobic groups to a solid surface, and hydrophilic groups to the water. The second layer cannot form, as the energy of intermolecular interaction of polar groups with water is greater than with each other. The absence of minima on the dependence of the cosine of the contact angle of paraffin on the biosurfactant concentration confirms the correctness of the formation of a monolayer of surfactant molecules on such surfaces. Thus, the dependence of the contact angle on the biosurfactant concentration for hydrophobic surfaces is similar to the surface tension isotherm, and for hydrophilic surfaces it has the form of a curve with a maximum. The obtained results on the contact angles of the different surfaces with new biosurfactant solutions indicate that the effect of the biosurfactant structure on the adsorptive modification of surfaces occurs only at low surfactant concentrations, under conditions of specific adsorption and formation of a monolayer. At high concentrations above the critical micellar concentrations, the adsorptive modification of surfaces is mainly determined by the structure of the surfactant hydrocarbon chain.

Conclusion

The contact angles of biosurfactant water solutions on different hydrophilic and hydrophobic surfaces such as aluminum, copper, steel, glass, polyethylene, plexiglass and paraffin surfaces were investigated. It has been established that the contact angles of biosurfactant water solutions on the hydrophilic surfaces (aluminum, copper, steel, glass) significantly depends on the composition and structure of biosurfactant molecules. It has been shown, that at low biosurfactant concentrations in the system, higher the contact angle and the hydrophobization of aluminum, copper, glass and metal surfaces takes place. At high biosurfactant concentrations, the contact angles sharply decreased due to the fact that during adsorption, the biosurfactant molecules are oriented by the polar group to the surface. The concentration dependence of the contact angle passes through a minimum only for hydrophilic surfaces (aluminum, copper, glass, metal) as a monolayer of biosurfactant molecules is formed on the hydrophilic surface with orientation by polar groups to the solid surface. It has been established that the increase in the cosine of the contact angle at higher surfactant concentrations is associated with the hydrophilization of the surface due to the formation of micelles on surfaces. For a hydrophobic surfaces (polyethylene, plexiglass and paraffin), the cosine of the contact angle increases monotonically with an increase in the biosurfactant concentration. It was established that the effect of the biosurfactant structure on the adsorptive modification of surfaces occurs only at low biosurfactant concentrations by the formation of a monolayer.

Conflict of interests:

The authors declare no conflict of interests.

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