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SYNTHESIS AND COLLOIDAL-CHEMICAL PROPERTIES OF NEW SURFACE-ACTIVE DERIVATIVES OF MALEIC ACID

Makhkamov R.

Kurbanbaeva A.

Holmuminova D.

Saidkulov F.

Nurmanova M.

Samandarov Sh.

Saidakhmedova H**.**
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

Abstract

The purpose of this work was synthesis of new surface-active derivatives of maleic acid and establishing correlations between their colloid-chemical properties. The well-known methods for synthesis and determining the properties of surfactants were used in the work. The new surface-active derivatives of maleic acid were synthesized and their colloid chemical properties investigated. The synthesis of new surfactants was carried out by condensation of maleic anhydride with ethylenglicols and the reaction product was esterified with primary alcohols. The surface activity and foaming ability of the obtained new surfactants in aqueous solutions were studied. The obtained results showed that with an increase in the length of the aliphatic hydrocarbon chain, the surface activity of benzoic acid derivative surfactants increases. The analysis of results showed a good correlation between the foam forming ability and the surface activity of the studied surfactants. Based on the studies it was established that the stability of foams is significantly determined by the interaction of surfactant molecules in the monolayer.

Keywords: Synthesis, surfactants, colloid-chemical property, surface activity, foam-forming ability.

Introduction

Water-soluble derivatives of maleic acid with a diphilic structure occupy a special place among new types of surfactants. The water solutions of surfactants cover the surfaces of solids and liquids with the thin monomolecular layers and regulate technological processes. Because of such property surfactants have found wide application to improve the quality of various materials [1-4]. A lot of technological processes cannot proceed without the participation of surfactants, including stabilization of foams, modification and protection of various surfaces [5-9]. In this regard, it is very relevant and interesting to study the colloid-chemical properties and effect of new surfactants on stabilization of disperse systems. [10-15]. In this regard, surface active derivatives of maleic acid deserve attention due to their practicality in both aqueous and non-aqueous solutions. They have a long hydrocarbon chain and their length are different. It is known that the chemical structure and length of hydrocarbon chains can affect the properties of surfactant solutions [11-14]. The surface-active derivatives of maleic acid have well-balanced hydrophilic-lipophilic properties and can form a micellar structure in both aqueous and oily media, depending on the concentration and temperature of the system [16-20]. The interest in surfactants based on maleic acid is also due to their valuable colloidal-chemical properties and the possibility of obtaining model compounds with the required functional groups. They combine high surface-active properties, good biodegradability, low toxicity to warm-blooded animals and relatively low cost. Due to these properties, they are used in various fields of industry, agriculture and in everyday life. However, few studies have been carried out on benzoic acid derivative surfactants. In this regard, in this work, synthesis of maleic acid derivative surfactants and their colloid-chemical properties were studied. 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.

Methods and Materials

The purpose of this work is synthesis of new surface-active derivatives of maleic acid and establishing correlations between their colloid-chemical properties. To achieve the goal, the following tasks were set: the synthesis of new surfactants based on maleic acid, and study their surface activity and foam-forming abilities.

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.

Foaming ability. The foaming ability was determined at a temperature of 293K, while 100 ml of a freshly prepared surfactant solution with a certain concentration was shaken in a graduated container for 60 s. Then the height of the foam column at the initial moment in the graduated container was measured.

Thin layer chromatography. Thin layer chromatography (TLC) was carried out at room temperature in two systems: a. acetone, toluene, ethanol 3:1:1. b. acetone, benzene, ethanol 2:1:2. 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.

Hydrophilic-lipophilic balance. The hydrophilic-lipophilic balance (HLB) for the surfactants was calculated by group numbers according to the equation: $HLB = HLBgf – nHLB_{CH_2}+7$, where HLBgf is the HLB of hydrophilic groups, HLB_{CH_2} is the HLB for the $-CH_2-$ group.

The vacuum distillation and recrystallization methods were used to purify the surfactants.

Results and Discussions

The model compounds based on the reaction of maleic anhydride with ethylene glycols and monohydric alcohols have been synthesized. In the first stage of obtaining a surfactant by a thermal addition reaction, the interaction of 2 moles of maleic anhydride with one mole of di- or tetroethylene glycol, at a temperature of 80-85°C and constant stirring for 7 hours, dimaleatoxyethanes were isolated.

$2C_2H_2(CO)_2O+HO(CH_2CH_2O)_{nH}$ =

$HOOCCH=CHCOO(CH_2CH_2O)_n\text{-}OCCH=CHCOOH$

n = 2, 4.

From the obtained adduct, by interaction with monohydric alcohols in a toluene medium at a temperature of 105-110°C, in the presence of catalysts, monoalkyl esters of dimaleatoxyethane were obtained. A Dean-Stark trap was used to separate the reaction water.

$HOOCCH=CHCOO(CH_2CH_2O)_n\text{-}OCCH=CHCOOH + ROH$ =

$HOOCCH=CHCOO(CH_2CH_2O)_n\text{-}OCCH=CHCOOR + H_2O$

where n=2, 4, $R=C_7H_{15}$, $C_{10}H_{21}$

The reaction products were washed with water until neutral (according to litmus) and dried by azeotropic distillation with toluene. After distilling off toluene and excess alcohol under reduced pressure, the main reaction product was isolated by reprecipitation from an acetone solution with petroleum ether. The reaction product yield averaged 75-80% of theoretical.

From the obtained monoalkyl esters of succinooxyethanes, by interaction with solutions of alkali metal hydroxides, ammonia and ethanolamines, different alkali, ammonium and ethanolammonium salts of monoalkyl ethers of succinooxyethanes were obtained:

$HOOCCH=CHCOO(CH_2CH_2O)_n\text{-}OCCH=CHCOOR + MOH$ =

$ROOCCH=CHCOO(CH_2CH_2O)_n\text{-}OCCH=CHCOOM$

where n=2-4, R= C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, M=Na^+, K^+, NH_4^+, Li^+, $H_3NC_2H_4OH$, $H_2N(C_2H_4OH)_2$, $HN(C_2H_4OH)_3$.

The resulting reaction products were purified by distillation under vacuum and reprecipitation from an acetone solution with petroleum ether. The physicochemical properties of the obtained derivatives of maleic acid are presented in table. 4.

Below are examples of the synthesis of surface-active derivatives of maleic acid.

Monoethanolammonium salt of heptyl ether 1.4-dimaleate dioxyethane (M-1). In a three-necked flask with a capacity of 250 ml, equipped with a dropping funnel, a reflux condenser (with a Dean-Stark trap) and a mechanical stirrer, 19.6g (0.2 mol) of maleic anhydride and 10.6g (0.1 mol) of diethylene glycol. The contents of the flask were heated at 75-80°C for 7 hours with constant stirring. At the end of the reaction, the product is purified by reprecipitation from an acetone solution with dry petroleum ether. Received 29.23g (96.8% of theoretical) adduct 1 (1,4-dimaleate dioxyethane), which is a viscous liquid of light yellow color.

To 30.2g (0.1 mol) of adduct 1 was added 100 ml of toluene and dissolved with stirring. To the solution was added 1 ml of concentrated sulfuric acid and heated to a temperature of 110-115°C and 11.6g (0.1 mol) of heptanol was added dropwise with constant stirring during 30 minutes. The contents of the flask were heated for an additional 30 minutes. The end of the reaction was monitored by the volume of water released in the Dean-Stark trap. Upon completion of the reaction, the reaction mixture was washed with distilled water until neutral with litmus and dried over anhydrous Na_2SO_4 by azeotropic distillation with toluene. After distilling off toluene and an excess of alcohol, 36.1g (86.4% of theoretical) adduct 2 (heptyl ether of 1,4 - dimaleate dioxyethane) was isolated.

41.8g (0.1 mol) of the obtained adduct 2 was placed in a round-bottom flask equipped with a mechanical stirrer and a dropping funnel, 50 ml of acetone was added and it was dissolved with stirring. Then to the resulting solution at room temperature with constant stirring was added dropwise 6, 1g (0.1 mol) of monoethanolamine in 25 ml of acetone during 30 minutes. After the addition of all monoethanolamine was complete, the reaction mixture was stirred for an additional 30 minutes. After the end of the reaction, when dry petroleum ether is added to the reaction mixture, the reaction product precipitates, which is purified by recrystallization from an acetone solution with ether.

The yield of the reaction product was 43.2g (90.1% of theoretical).

The synthesized compounds isolated in pure form had characteristic IR absorption in the range of 1200-1030 and 920-766 cm-1, due to the presence of the carboxylate ion, and peaks at 3800-3200 and 1735 cm-1, assigned to the hydroxyl and ester groups, respectively. The results of microchemical elemental analysis and studies of the functional composition of the obtained adducts are in good agreement with the theoretically calculated. The physical properties and IR spectrum of some of the synthesized surface-active derivatives of maleic acid are shown in Table 1.

Table 1. Physical properties and IR spectrum of some of the synthesized surface-active derivatives of maleic acid.

Surfactants*	n^{20}	IR-spectrum, см$^{-1}$				HLB*	Density, d^{20}	Mol. weight
		COOR, v	COOM, v	OH, v	OH, δ			
MO-1	1,4684	1730-1720	1600-1570	3600-3300	1640-1620	15,9	1,05	461
MO-2	1,4696	1730-1720	1600-1560	3580-3300	1630-1620	15,9	1,07	505
MO-3	1,4714	1730-1720	1590-1570	3580-3300	1630-1620	15,9	1,11	549
MO-4	1,4866	1700-1680	1650-1580	3480-3450	1650-1600	9,8	1,12	549
M-12	1,4884	1700-1680	1650-1580	3480-3440	1650-1600	11,7	1,14	593
M-13	1,4912	1715-1670	1650-1580	3500-3450	1650-1600	13,6	1,16	637
M-21	1,5623	1735-1700	1600-1560	3550-3400	1645-1600	11,2	1,15	591
M-22	1,5628	1735-1705	1590-1560	3560-3450	1640-1610	13,0	1,17	635
M-23	1,5640	1735-1710	1590-1560	3500-3480	1640-1610	13,1	1,19	679

*Chemical formula of surfactant: $ROOCCH{=}CHCOO(CH_2CH_2O)_n{-}OCCH{=}CHCOOM$

For surfactant MO-1 n=2, R= C_4H_9, M=Na^+; for MO-2 n=2, R= C_6H_{13}, M=Na^+; for MO-3 n=2, R= C_8H_{17}, M=Na^+; for MO-4 n=2, R= $C_{10}H_{21}$, M=Na^+.

The stabilization of foam dispersions by the new maleic acid derivative surfactants have been investigated. The results of investigation of the foam forming and stability of foam dispersions by the aqueous solutions of surface-active derivatives of maleic acid is shown in table 2. The results obtained for the foaming ability of maleic acid derivatives are compared with some physical and colloidal-chemical properties of their solutions. Analysis of the obtained results in table 1 indicates that compounds with the hydrocarbon chain C_8H_{17} - $C_{10}H_{21}$ have the highest foaming ability. With a further increase of the hydrocarbon chain length, a slight decrease in the foaming ability of surfactant was observed due to a decrease in the solubility of the surfactant.

Table 2. The foam forming ability and surface tension of surfactant water solutions depending on the oxyethylation degree (n) and hydrocarbon chain length at 313K.

n	The volume of foam (V, ml)/surface tension (σ, mN/m) of surfactant water solutions					
	$-C_2H_5$	$-C_4H_9$	$-C_6H_{13}$	$-C_8H_{17}$	$-C_{10}H_{21}$	$-C_{12}H_{25}$
1	222.5 / 38.15	232.0 / 36.51	250.5 / 34.41	260.0 / 32.63	270.0 / 32.53	271.0 / 32.14
2	230.0 / 37.80	244.5 / 36.14	258.0 / 33.92	271.0 / 32.21	282.0 / 32.12	275.0 / 32.05
3	254.0 / 37.40	265.0 / 35.92	280.0 / 33.63	295.0 / 31.93	310.0 / 31.60	306.0 / 31.10
4	265.0 / 37.20	280.0 / 35.84	296.0 / 33.42	306.0 / 31.81	324.0 / 31.40	314.0 / 30.91

It should be noted that the surface activity and foam forming ability of surfactants are interrelated, and this is due to the similarity of interfacial processes for the considered parameters, which are important for the formation of monolayers at the liquid-gas interface and formation and stabilization of foams. The correlation between foam forming ability of new surfactants and the nature of the surfactant counterion has been investigated. The obtained results are shown in table 3.

Table 3. The correlation between foam forming ability of surfactants and the nature of the surfactant counterion at 313K.

Surfactant counterion	Volume (ml) of the foam formed by surfactant water solutions					
	$-C_2H_5$	$-C_4H_9$	$-C_6H_{13}$	$-C_8H_{17}$	$-C_{10}H_{21}$	$-C_{12}H_{25}$
Li	249.0	262.0	283.0	295.0	301.5	298.0
Na	243.0	256.0	274.0	288.0	297.0	284.0
K	230.0	244.5	258.0	271.0	282.0	275.0
NH_4	258.0	271.0	291.0	304.0	312.5	274.0

Analysis of the obtained results indicates that surfactant counterions have a noticeable effected on the foam forming ability of surfactant. As shown in the table. 3, the foam forming ability decreases with the increase of the radius of the surfactant counterion, being located in the series NH_4> Li> Na> K. The results obtained can be explained by a change in the hydration of the surface-active ion with an increase in the radius of the surfactant counterion.

Maleic acid derivative surfactants are salts of a weak acid and strong base, and at a constant temperature, in an aqueous medium, they will be partially hydrated and the degree of ionization will depend on the equilibrium between intramolecular bonds and forces of solvation.

$$ROOCH{=}CHCOO(CH_2CH_2O)_nOCHCHCOOM + H_2O =$$
$$ROOCH{=}CHCOO(CH_2CH_2O)_nOCHCHCOOH + MOH$$

Aqueous solutions of these compounds have a pH in the slightly alkaline range. With the addition of mineral acid, the hydrolysis equilibrium shifts to the right, but the solubility of the surfactant decreases, and, consequently, the foaming ability also decreases. If the pH of the surfactant solution gets higher, the hydrolysis equilibrium shifts to the left, the solubility of the surfactant also decreases and, consequently, the foam forming ability of the surfactant decreases. The foam forming ability of maleic acid derivative surfactants depending on temperature of water solutions is shown in table 4. In the neutral surfactant solutions, the increase in temperature promotes an increase in the foam forming ability due to its effect on the degree of surfactant hydrolysis. At the same time, despite the increase in the foam forming ability of the studied surfactants, with increase of the temperature, the stability of the obtained foams decreases.

Table 4. The foam forming ability of maleic acid derivative surfactants depending on temperature of water solutions.

T, K	Volume (ml) of the foam formed by surfactant water solutions						Stability of foam, S
	$-C_2H_5$	$-C_4H_9$	$-C_6H_{13}$	$-C_8H_{17}$	$-C_{10}H_{21}$	$-C_{12}H_{25}$	
293	186,0	194,0	203,0	215,0	259,0	215,0	0,98
303	203,0	211,0	221,5	238,5	269,0	266,0	0,94
313	222,5	232,0	250,5	260,0	279,0	271,0	0,87
323	238,0	246,0	272,5	286,0	286,5	280,0	0,78
333	253,0	261,5	287,0	298,0	289,0	284,0	0,69

Based on the obtained experimental data and correlations it is possible to conclude, that the foaming ability of the studied surfactants is closely related to the structure of their molecules. The established patterns provide a basis for predicting the foaming ability of maleic acid derivative surfactants in various compositions and disperse systems.

Conclusion

The new surface-active derivatives of maleic acid were synthesized and their colloid chemical properties investigated. The synthesis of new surfactants was carried out by condensation of maleic anhydride with ethylenglicols and the reaction product was esterified with primary alcohols. The surface activity and foam forming ability of the obtained new surfactants in aqueous solutions were studied. It has been shown that with an increase in the length of the aliphatic hydrocarbon chains, the surface activity of benzoic acid derivative surfactants increases. It has been established that there is a good correlation between the foam forming ability and the surface activity of the studied surfactants. It has been shown that the stability of foams is significantly determined by the interaction of surfactant molecules in the monolayers. The results of the presented study confirm the results of a number of studies. In the near future, the effect of new benzoic acid derivative surfactants on regulating of rheological properties of disperse systems will be investigated.

Conflict of Interests

The authors declare no conflict of interests.

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