BINARY MIXTURES OF FLUOROCARBON SURFACTANTS IN AQUEOUS SOLUTION. I.

Teodor DEHELEAN

Romanian Academy, Institute of Chemistry, Timişoara

În lucrare sunt prezentate rezultatele cercetărilor privind caracterizarea unor amestecuri de fluorotenside.

Comportarea amestecului de perfluorooctilsulfonat de potasiu şi perfluorooctanoat de tetraetilamoniu a fost cercetată cu scopul de a determina compatibilitatea componenţilor şi efectele superficiale ale amestecului în soluţii apoase, urmărind variaţia tensiunii superficiale în funcţie de concentraţie, concentraţiile critice micelare, proprietăţile spumogene şi de udare. Rezultatele cercetărilor prezintă interes din punct de vedere ştiinţific şi sunt utile pentru aplicaţii practice. Pentru determinări s-au folosit metode moderne de analiză şi programe de calcul pentru determinarea unor caracteristici.

S-au constatat efecte sinergetice în ce priveşte proprietăţile superficiale. Compuşii sunt activi în mediu apos, sunt perfect compatibili, fiind vizaţi pentru a fi folosiţi în concentrate emulsionabile cu scopul de a obţine emulsii apoase stabile şi reversibile.

Introduction

Virtually used surfactants are quite often mixtures, as they are synthesized as mixtures, or they are mixed in order to increase the performances of individual components by synergistic actions.

The mixed fluorocarbon surfactant systems are often researched for some theoretical and practical reasons:

- the great efficiency of fluorocarbon surfactant mixtures provides the reduction of necessary fluorine surfactants;
- the mixtures of fluorocarbon surfactants have special properties; in aqueous diphase systems and in some solvents, the mixtures of fluorocarbon surfactants reduce the superficial tension, and the interfacial tension. For example, an aqueous scum formed of mixtures of fluorocarbon surfactants in a hydrocarbon solvent produce the preferential adsorption of fluorocarbon surfactants to the water-air interface;
- mixtures of fluorocarbon surfactants are of great interest for the study of micelles structure. Perfluor radicals are hydrophobic and oil repellent too. Phobic interactions of fluoride and catenaries of the mixtures of fluorocarbon surfactants are the causes of some imperfect behaviour and they sometimes produce demixing. Research is made on the producing of mixed micelles and the coexistence of two kinds of micelles for a better understanding of micellar solutions.

Because of the great theoretical and practical interest on the mixtures of fluorocarbon surfactants, it is not surprising at all that an excellent monograph on mixed surfactant systems have been realized and some other works on this field have been published [1-9].

Abe and his collaborators studied mixed surfactant mixtures such as the cethoxyl alcohol with 20 moles ethylene oxide ($C_{16}H_{33}O(C_2H_4O)_{20}H$) and ammonium perfluorooctanoate, $C_7F_{15}COONH_4$, and proving the forming of mixed micelles [2].

Guo and his collaborators researched mixtures of sodium perfluorooctanoate (SPFO) and ionic, amphoteric or nonionic hydrocarbon surfactants by RMN and superficial tension measurements [3].

Tamori and his collaborators made researches on the interactions between basic cationic fluorocarbon surfactants and different hydrocarbon surfactants [4].

Matsuki and his collaborators studied the miscibility of lithium tetradecyl sulfate (LiTS) and lithium perfuoroctanfluorosulfonated (LiFOS) in aqueous solution [5,10].

Experimental researches

We have analyzed the results of the experimental researches on the mixtures of tetraethylamonium perfluorooctanoate, $C_7F_{15}COON(C_2H_5)_4$, (TEAP), and potassium perfluorooctansulfonate, $C_8F_{17}SO_3K$, (PFOSK), and we present them in this work. Mixtures of TEAP:PFOSK have been prepared and e have made researches in mixture reports: 0:1; 1:1; 2:1; 3:1; 4:1 and 1:0.

Tetraethylamonium perfluorooctanoate, $C_7F_{15}COON(C_2H_5)_4$ (TEAP), in normal conditions it is a white fine powder, slightly soluble in water, forming clear solutions.

It is compatible with anionic surfactants. The product is stable in hard water and in caustic alkali solutions, and it is not resistant to acids.

Potassium perfluorooctansulfonate, $C_8F_{17}SO_3K$, (PFOSK), is, in normal conditions, a white hygroscopic solid product, in crystal form, slightly soluble in water. It is the potassium salt of the perfluorooctansulfonated acid. The perfluorooctansulfonated acid is available on the market as a solution 50% in water, and the potassium salt is obtained by neutralizing this solution with potassium hydroxide, KOH.

Sodium laurylsulfate, $C_{12}H_{25}SO_3Na$, (LSNa), it is often used as a standard in comparing the physical and chemical properties and for the practical performances of different surfactants. In these researches we have used reacting sodium laurylsulfate c.p. Merck.

The applicable physical and chemical properties of products have been determined using appropriate experimental methods and techniques.

The superficial tensions in the aqueous solutions have been determined by the platinum ring method agreed by ISO (International Standard Organization), using KRÜSS apparatus. For the determination of the micellar citric concentration, aqueous solutions with a concentration of 1% have been prepared, and they were progressively diluted with distilled water, the superficial tension being constantly measured. The mixture having been agitated 10 minutes, right after the preparation of solutions, all determinations were made at a temperature of 20^0C.

Based on results, using a performing calculation program, the TESCRIS program, the variation of the superficial tension has been graphically represented, depending on the active substance concentration and the micellar citric concentrations and the appropriate superficial tensions have been determinated [7,8].

The frothing properties of the products and mixtures have been determined using the Ross-Miles method.

The characteristics of scum have been determined conform to STAS 577-68.

The wetting power has been determined conform to STAS 6097-68.

The results of determination and the superficially active main properties are presented in tables 1…4.

In table 1 there are shown the variations of superficial tensions of aqueous solutions of the studied mixtures, based on the concentration at 20°C, comparative with sodium laurylsulfate (LSNa), considered to be the standard.

Table 1

The variation of superficial tension of aqueous solutions of the TEAP:PFOSK mixtures, at 20°C, comparative with LSNa

Mixture TEAP:PFOSK	The superficial tension, expressed in mN/m, based on the total concentration in the active substance, expressed in %							
	1,000	**0,500**	**0,250**	**0,125**	**0,062**	**0,030**	**0,016**	**0,008**
0:1 (PFOSK)	25,50	30,00	36,60	40,00	42,00	45,00	50,00	56,00
1:1	30,20	29,25	32,40	35,50	38,25	40,50	43,00	44,00
2:1	33,50	34,00	36,50	42,00	45,20	49,00	59,00	62,00
3:1	32,00	35,00	37,50	45,00	48,00	50,50	58,50	62,50
4:1	33,50	35,25	36,00	37,00	44,00	52,50	57,15	60,10
1:0 (TEAP)	20,00	19,51	21,62	30,76	40,00	45,60	57,33	58,00
(LSNa)	38,70	38,80	38,90	43,00	51,60	57,80	64,20	65,40

In table 2 there are shown the results of determinations regarding the frothing properties of mixtures TEAP:KOFS, in distilled water, and in table 3 there are the characteristics of the scum in the solutions of the respective mixtures.

Table 2

The frothing properties of the mixtures of TEAP:KOFS, in water, at 20°C

Time (min)	Scum volume in mL, based on the total concentration in the active substance, expressed in %											
	0:1		**1:1**		**2:1**		**3:1**		**4:1**		**1:0**	
	1,00	**0,50**	**1,00**	**0,50**	**1,00**	**0,50**	**1,00**	**0,50**	**1,00**	**0,50**	**1,00**	**0,50**
0	240	210	250	200	250	240	300	200	350	250	500	300
5	200	80	200	150	200	200	300	100	280	225	470	250
10	160	70	50	5	190	100	250	50	275	50	250	150
30	150	30			150	50	200	25	245	10	200	100
60	100	20			50	25	100	25	150		200	50
120	60						50		50		150	50

Table 3

The characteristics of the scum in the aqueous solutions of TEAP:KOFS mixtures, at 20°C

Mixture TEAP:KOFS	Total concentration, expressed in %	The time of separation of 50% of the scum,expressed in seconds	The frothing power, expressed in ml.	The stability of the scum after 30 minutes, expressed in %	Frothing coefficient
0:1 (PFOSK)	1,00 0,50	30 10	240 210	62,50 14,28	4,8 4,2
1:1	1,00 0,50	50 20	250 240		
2:1	1,00 0,50	60 30	250 240	60,00 20,80	5,00 5,80
3:1	1,00 0,50	120 60	300 200	66,66 12,50	6,00 5,00
4:1	1,00 0,50	150 60	350 250	70,00 4,00	7,00 5,00
1:0 (TEAP)	1,00 0,50	180 10	500 300	40,00 33,30	10,00 6,00

Using the calculation and graphical representation TESCRIS program, the micellar citric concentration and the corresponding superficial tensions have been determined, based on the data in table 1, conform to the table 4. In table 4 are shown the results of the determinations wetting times too, using untreated cotton 100% and solution 1% as a stability sample.

Table 4

The main superficially active properties of the mixtures TEAP:KOFS, in water, at 20°C

Properties of mixtures TEAP:KOFS	Micellar critic concentration MCC, %	Superficial tension of MCC, mN/m	The wetting time of 0,5% of the solution, expressed in seconds	The solution's aspect 1% (solubility)
0:1 (PFOSK)	0,0183	34,33	1 sec.	clear
1:1	0,0120	28,27	1 sec	clear
2:1	0,0284	34,47	1 sec	clear
3:1	0,0272	37,83	1 sec	clear
4:1	0,0226	36,92	1 sec	clear
1:0 (TEAP)	0,055	19,07	2 sec	clear
(LSNa)	0,0127	36,98	12 sec	clear

The results of determination and the superficially active main properties are presented graphic in fig. 1…3.

In fig.1 there are shown the variations of superficial tensions of aqueous solutions of the studied mixtures, based on the concentration at 20^{0}C, comparative with sodium laurylsulfate (LSNa), considered to be the standard.

In fig 2 there are shown the results of determinations regarding the frothing properties of mixtures TEAP:KOFS, in distilled water, and in fig. 3 there are the characteristics of the scum in the solutions of the respective mixtures

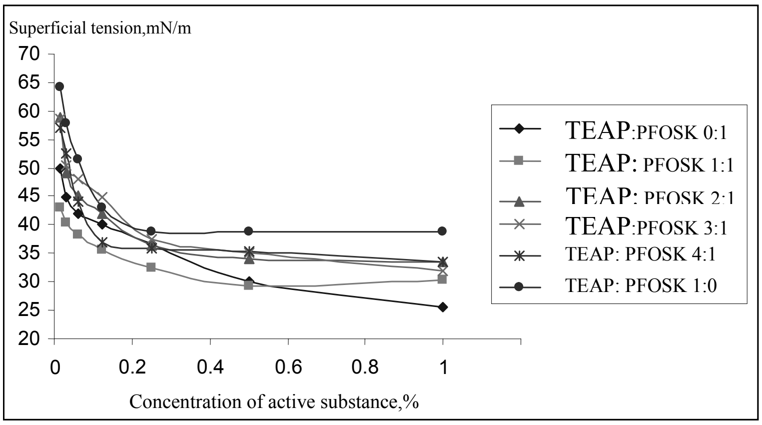

Fig.1. Relationship between the superficial tension and the concentration of the studied mixtures at 20°C.

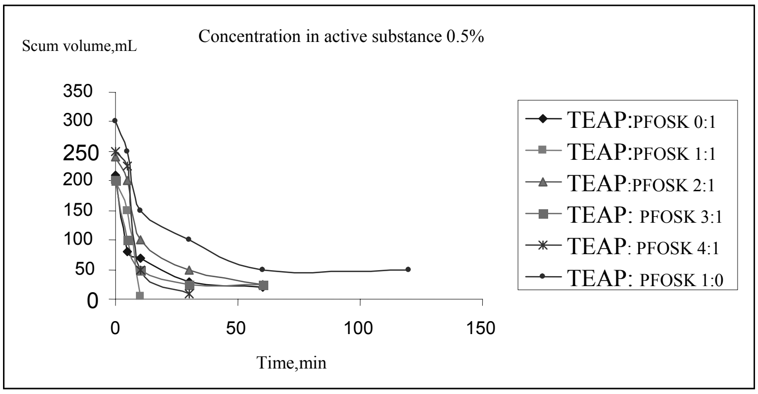

Fig.2. The frothing properties of mixtures NaLS:KOFS, in distilled water.

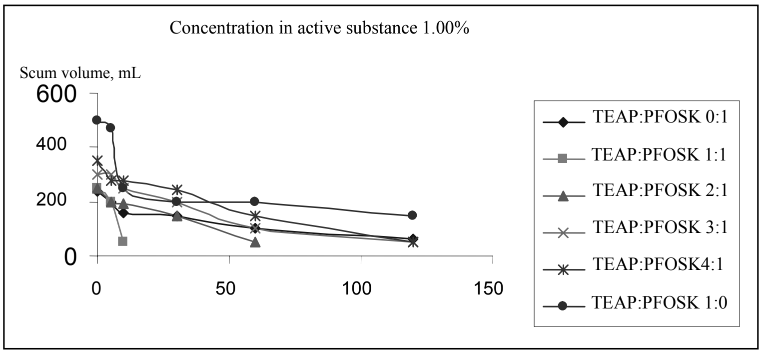

Fig. 3. The characteristics of the scum in the solutions of the respective mixtures.

Conclusions

The results show that the mixtures of sodium laurylsulfate and potassium perfluorooctansulfonate, in proportion of 1:1 up to 4:1, are tensioactive in water medium. The two products are perfectly compatible, the mixture is neutral, soluble in water, and it doesn't precipitate, and by mixing interesting synergetic effects are obtained for industrial applications.

The micellar critic concentrations and the corresponding superficial tensions have been determined using the TESCRIS program. The micellar critic concentrations, which have been determined in the experimental conditions, are bigger than the concentrations of sodium laurylsulfate. The superficial properties don't submit to the addition rule.

The hydrophilic properties of the mixture's compounds improved. The wetting times are more than 10 times smaller in the case of mixture than in the case of hydrocarbonate compound. This type of mixture can be an excellent wetting agent.

The mixtures are two times active and they are to be used in concentrates used as pesticides emulsions for in order to obtain some stable and reversible emulsions.

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