dr inż. **Andrzej MIZERSKI,**
mgr inż**. Michał LANGNER**
The Main School of Fire Service, Warsaw, Poland

PROPERTIES OF FOAMING CONCENTRATES CONTAINING MIXTURES OF SODIUM DODECYL SULFATE AND COCAMIDOPROPYL BETAINE

Streszczenie

Autor przedstawia wyniki badań dotyczących wpływu dodawania cocamidopropylu betainy na właściwości koncentratów zwierających siarczan dodectyl sodu. Podaje wyniki badań dotyczące ciśnienia powierzchniowego, siły spieniania, zwilżania oraz stabilności piany. W konluzjach udowadnia, iż istnieje wpływ dodanych środków na badane właściwości.

Summary

Results of testing the influence of additives of cocamidopropyl betaine on the properties of concentrates containing sodium dodecyl sulfate have been presented. The surface tension, foaming power, wetting power and stability of stabilised foams have been measured. The occurrence of synergetic effects has been found within those properties.

Introduction

Compounds of surface-active agents have an essential role in rescue operations. Foaming concentrates, fire-fighting wetting agents and preparations used to wash off surfaces contaminated by oil should be mentioned here first of all. Lately, there appeared a new generation of foaming agents, the so called: “class A”. Such compounds may be used to produce foam at very law concentrations of solutions, even below 0.5%. It is possible thanks to the application of new methods, the so called: “Compressed Air Foam System” (CAFS) and other related methods. They enable us to extend the use of foams for class A fire suppression. The use of foam for enclosure fires makes the fire fighting operations shorter and substantially limits the fire and post-fire damage. On the other hand, during fire fighting

action in the open, application of solutions of foaming agents of low concentrations may reduce ecological damage.

Activities aimed at lowering the production costs and reducing the adverse environmental impact lead to decreasing the content of surfactants in concentrates. However, it must result in worsened usability, foaming and wetting power being the most important ones. But it is possible to decrease the general content of surfactants without worsening the usability values if mixtures of various surface-active agents are applied. To this end, synergetic effects involving disproportionate intensification of specified parameters connected with surface activity are utilised [1, 2].

Results

Surface activity of compositions containing mixtures of sodium dodecyl sulfate (SDS) and cocamidopropyl betaine (CAB) was examined.

Sodium dodecyl sulfate having the degree of purity specified as "pure", was produced by STANDARD Industrial and Commercial Enterprise in Lublin.

Cocamidopropyl betaine was used in a form of a commercial preparation named Betaine CAB. It is an ampholytic surfactant based on natural coconut acids with the biggest share of lauric acid. Formula of betaine CAB and spatial structure of a particle for lauryl radical are presented in fig.1.

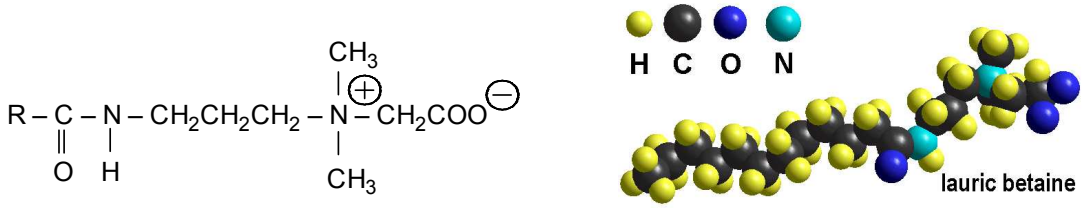

Fig. 1. Betaine CAB – lauric betaine

A commercial preparation produced by ICSO Chemical Production Sp. z o.o., Kędzierzyn – Koźle used for testing was a water concentrate containing ca. 30% of active substance.

Butyldiglycol was used as organic solvent to prepare concentrates to act. It is diethylene glycol monobutyl ether often used for fire recipes of foaming agents. It has no foaming properties but it raises the foaming power of surfactant. Reagent of „pure" degree of purity made by FLUKA was used for testing.

Each composition contained 20% w/w of active substances, 25% of butyldiglycol and 55% of distilled water. Four compounds of the following composition of surfactant fraction were tested:

- 100% SDS,
- 100% CAB,
- 10% CAB, 90% SDS,
- 20% CAB, 80% SDS.

The surface activity of tested concentrates was characterised by the following features:

- surface tension,
- wetting power,
- foaming power.

Surface tension

Surface tension was tested by DuNoüy ring method, by using tensiometer produced by CSC Scientific Co. Inc. In all cases, the experiment was started from a solution of tested concentrates having concentration of 4% while each consecutive solution was prepared by double dilution. Minimum 3 trials were made for each solution if differences between results were not greater than 0.3 mN/m. Distilled water having temperature of 20 ± 1^{o}C. The isotherms of surface tension obtained by the tests are presented in fig. 2.

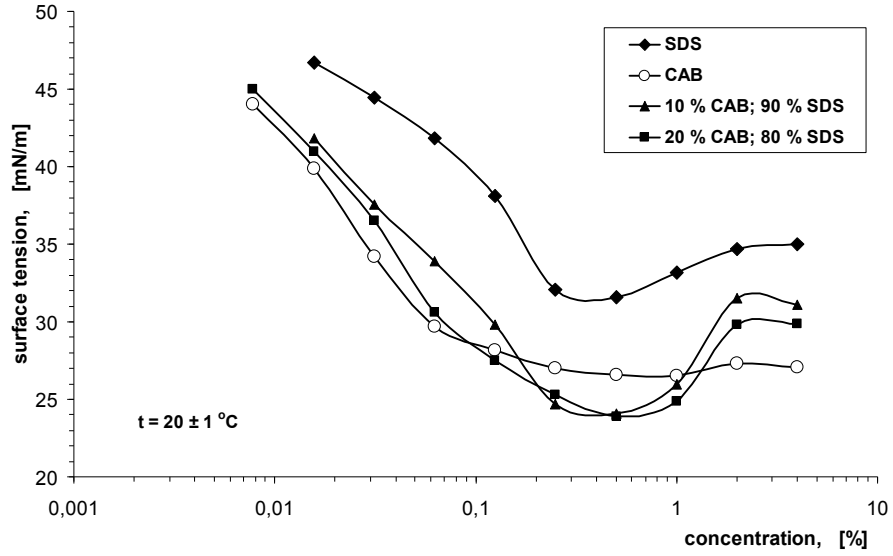

Fig. 2. Surface tension isotherms of tested concentrates (t = 20 ± 1 ^{o}C)

Minimal values on surface tension isotherms testify to the presence of impurities having strong surfaces activity.

Wetting power

In order to evaluate wetting power of surfactants in dynamic conditions a very convenient method is used in textile industry [3]. It is determined by measurement of the sinking time of technical cotton disc immersed in a solution of tested substance.

Measurement was started from 4% concentration and each consecutive solution was prepared by double dilution. At the last concentration of solution of the tested concentrate, the sinking time of disc exceeded 200s. Solutions were prepared by the use of distilled water. The temperature of water and tests was $20 \pm 2^{o}C$.

Results are presented in fig. 3.

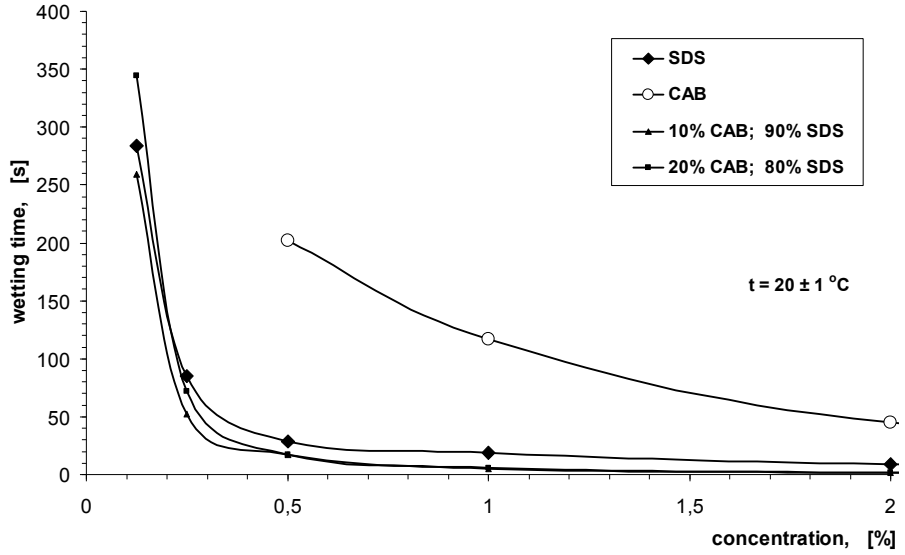

Fig. 3. Wetting power of tested concentrates

Foaming power

Foaming power of surfactants depends upon their chemical structure, concentration in water solution, temperature, presence of additives in the solution, such as foam stabilizer or electrolyte, and upon the way of producing foam and features of the test stand [4, 5]. Most often, the volume of foam obtained from a specified volume of the solution on a given test stand is considered as the foaming power.

In the present report, the foaming power was tested by the so called: "beating method". It is one of the first methods used to evaluate a foaming power. It consists in

energetic mixing of foaming solution with air by plane and backward motion by using a perforated disc mounted on the end of a long bar as the agitator. Foaming is carried on in a measuring cylinder, which enables to directly read out the volume of the produced foam. It is not a standard method but, due to its simplicity, it is often used in manufacturers' quality control laboratories where performance of a big number of comparative testing is required. The volume of produced foam is there a measure of the foaming power.

In order to produce the foam, 100 cm^3 of solutions of tested concentrates in distilled water of temperature 20 ± 1^oC were used. The foaming was carried on in a measuring cylinder having the volume of 1 dm^3 by 60 mixer's motions with a frequency of 1 motion per second. The measurements were started from 4% concentration of solution and the concentration of each consecutive solution was twice less. The tests were ended when the volume of foam obtained from consecutive solution was smaller than 500 cm^3. For each foam its half value was measured, i.e. the time of leakage of half volume of the solution (50 cm^3) there from. Results are provided in table 1. For comparison, results of the tests concerning Forexpan, foaming agent of class A have been added. No half values were measured in that case because, opposite to the tested concentrates, Forexpan contains the foam stabilizer and half values for the same concentrations are many times higher.

Table 1.

Foaming power of solutions of tested concentrates V_p – foam volume [cm^3]; $W_{50\%}$ – half value [s]

c [%]	foaming power								
	SDS		CAB		10 % CAB		20 % CAB		Forexpan
	V_p	$W_{50\%}$	V_p	$W_{50\%}$	V_p	$W_{50\%}$	V_p	$W_{50\%}$	V_p
0.25	–	–	–	–	900	137	850	145	800
0.5	550	140	550	31	1000	241	1000	202	900
1	1200	431	1100	175	1200	330	1200	337	1200
2	1200	320	1200	249	1200	247	1200	281	1200
4	1200	312	1200	260	1200	193	1200	264	1200

Results of foaming power studies were verified by using the tested concentrates with 2% addition of dodecanol as the foam stabilizer. The content of water in concentrates (53%) was respectively lower. The foam was produced by the use of a laboratory fine-bubble foam generator [6] as illustrated in fig. 4.

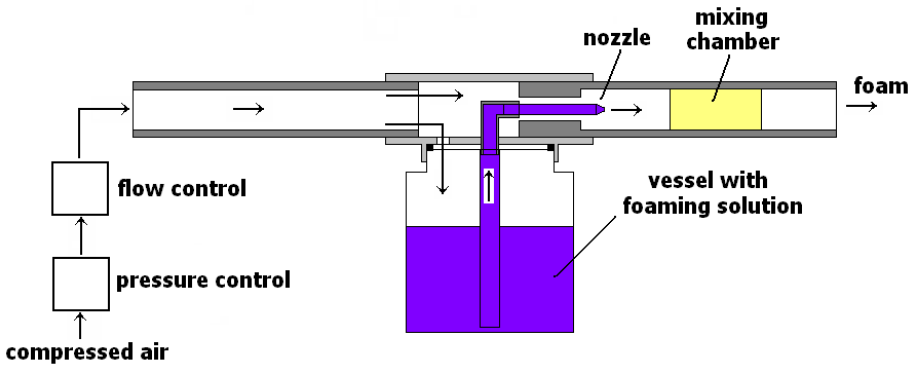

Fig.4. Laboratory foam generator

The air stream having appropriate pressure and capacity flows to the facility by flowing around the nozzle spraying the foaming solution. It is then forced from vessel to the nozzle through a portion of air directed there. Mixture of dispersed solution and the air flows through the chamber with filling where the foam is produced and intensively mixed. The foam at the mouth stream is very uniform and fine-bubbled. In the presented tests, the equipment worked at the overpressure of 0,05 Mpa and the flow of air of 600 dm^3/h. The foam was produced of the concentrates' solutions in distilled water of 1% and 2% concentrations. The measurements included the foam value and the features characterising the speed of outflow of solution from the foam: accumulation time τ_o (the time from the moment the foam has been produced to the time when the first drops of solution appear under the layer of foam); W_5, the five minute value (volume fraction of solution that has flown out from the foam within first 5 minutes); $W_{25\%}$, the 25% value (the time of the flow of half initial volume of solution from the foam). The course of solution's drainage was tested at the stand complying with PN-EN 1568. Results are presented in table 2.

Table 2.

Properties of fine-bubble foam produced of tested compositions with addition of stabilizer

c [%]	composition	Ls	T_0 [min]	W_5 [%]	$W_{25\%}$ [min]	$W_{50\%}$ [min]
1	SDS	32.7	3	11.5	8.5	17.5
	CAB	24.4	2	4,7	13.5	25.5
	10 % CAB	26.1	4	1.2	15.0	23.5
	20 % CAB	25.7	5	0	18.5	30.0
2	SDS	58.2	4	3.7	9.5	21.0
	CAB	38.0	8	0	20.0	31.5
	10 % CAB	55.6	5	0	18.0	30.0
	20 % CAB	54.1	8	0	23.5	36.5

Discussion of results

For the purpose to evaluate the results of measurements of surface tension and wetting power of the tested concentrates, they have been compared with results of similar measurements for fire concentrates. The following agents were used: two typical foaming agents of type S, i.e. SAT 10 and Roteor M 3%, a foaming agent of class A: Forexpan and fire wetting agent: Netzmittel H 1%. Surface tension isotherms and wetting curves are illustrated in figs. 5 and 6.

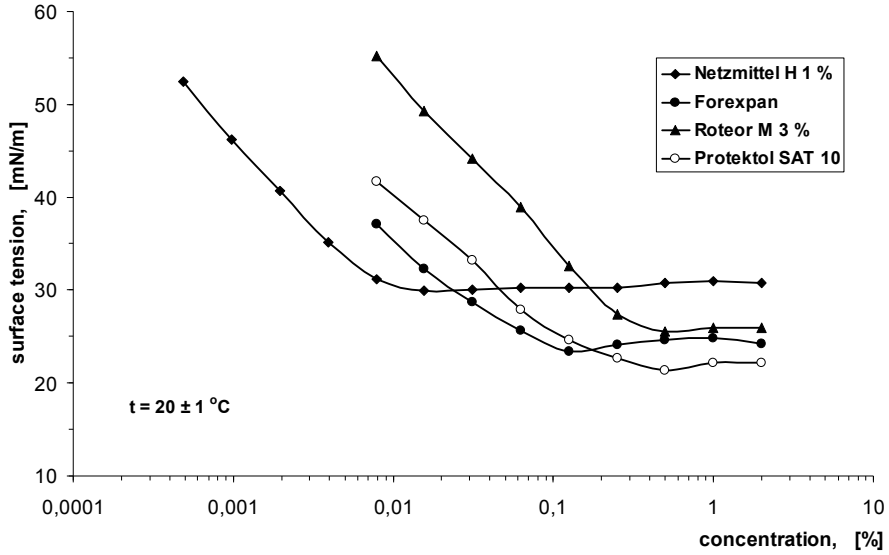

Fig. 5. Surface tension isotherms for fire concentrates of surface active substances

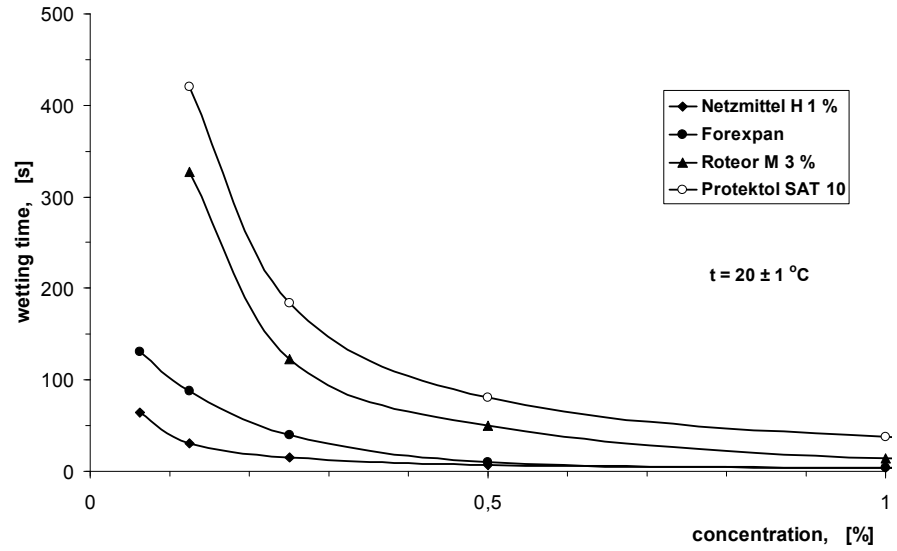

Fig. 6. Wetting power of fire concentrates

It is characteristic that solutions of concentrate of the best wetting values have surface tensions (ca. 30 mN/m) substantially higher than those of foaming agents (20 – 25 mN/m).

The composition of a foaming agent contains substances stabilising the foam, that increase the surface value of a concentrate. Netzmittel H 1% wetting agent contains no such stabilizers and surface tension of its solutions approximate the lowest surface tension of SDS solution (fig. 2). Critical micelle concentration (cmc) presents here an important feature and, for wetting agent, it amounts to ca. 0.015 % and is over 8 times lower than cmc value for Forexpan (ca. 0.125%) and above 30 times lower than cmc for such agents as Protektol SAT 10 and Roteor M 3 %. The difference between Protektol and Roteor, both of which containing similar or the same main active substance, results presumably from the contents of different organic solvents – Roteor contains butanol while Protektol SAT 10 contains butyldiglycol.

The analysis of the course of wetting curves and surface tension curves for fire concentrates confirms the point that it is the value of critical micelle concentration and not the value of surface tension which more determines the rate of wetting, especially as regards porous materials (such as technical fabric). For the same values of cmc, an agent, the solutions of which have higher surface tension, has better wetting power. It results from the fact that the rate of saturating capillaries with liquids is determined by the value of capillary pressure:

$$p_k = \frac{2\sigma \cdot \cos\theta}{r}$$

where: **σ** – surface tension of liquid, **θ** – wetting limit angle, **r** – capillary radius

Limit angles of wetting hydrophobic materials with solutions of surfactants having concentrations higher than cmc have values close to each other [7]. Thus the capillary pressure will be higher for liquid having higher surface tension. Cotton fabric is a porous material. Roteor M 3%, the solutions of which have higher surface tension, should have better power to wet the fabric than Protektol SAT 10, what has been proven by the tests (fig. 5).

The surface tension is being more decreased by CAB than by SDS and critical concentration of CAB is also lower. Adding CAB to SDS drops the surface tension very much as compared with SDS as a single one. The surface tension of mixtures of solutions is also lower than that of CAB solutions. The surface tension of water goes down to 31.6 mN/m and to 26.5 nM/m in SDS solutions and in CAB solutions respectively, while in mixed systems it goes down to 23,9 mN/m. Therefore it is a typical instance of synergetic effect within the scope of surface activity.

Similar synergetic effects may be noticed with respect to the wetting power. Concentrates with addition of CAB wetted markedly better than SDS solutions and clearly

better than CAB as a single one. The wetting power indicated by solutions of a compound containing 10 % CAB approximates that of solutions of Forexpan at concentrations above 0.2%. In that case, it may be believed that wetting power has been visibly improved due to addition of CAB.

The foaming power may be substantially increased by addition of Betaine CAB to SDS. Thus we can expect that working concentrations of foaming concentrates containing the above mixture of surfactants may be relatively low. Tests of stabilised foams indicated (table 2) that 1% solutions of concentrate containing 10% CAB have higher foaming power than solutions of concentrate containing only SDS and the rate of solution's drainage from the foam is ca. 50% lower. Foams with 2% solutions of concentrates with the addition of CAB have foam values slightly lower as compared with that of SDS but they are substantially more stable.

Conclusions

- SDS – CAB mixtures decrease the surface tension more than SDS or CAB every single one. A visible synergetic effect appears for concentrations having values close to the critical micelle concentration.
- Foaming power of 10% CAB – 90% SDS compound, without stabilizer, is better than that of SDS or CAB every single one (what is indicated in table 1). If stabilizer is present in solution, foaming power of mixtures with CAB decreases slightly, but foams stability increases significantly (table 2).
- Wetting power of SDS – CAB compound is higher than that of any of the said substances acting as a single one.
- SDS – CAB concentrates with the addition of stabilizers may be used to produce foams having substantially higher stability than that of SDS stabilised foam and somewhat higher than that of CAB stabilised foam.

References

1. Zieliński R.: „Surfaktanty. Towaroznawcze i ekologiczne aspekty ich stosowania”, Wydawnictwo Akademii Ekonomicznej, Poznań, 2000;
2. Anastasiu S., Jelescu E.: „Środki powierzchniowo – czynne”, WNT, Warszawa, 1973;
3. Norma PN-74/C-04800. Środki powierzchniowo czynne. Oznaczanie zdolności zwilżania.;
4. Bikerman J.J.: „Foams”, Springer Verlag, Berlin, 1973;
5. Тихомиров В.К.: „Пены. Теория и практика их получения и разрушения”, Москва, 1983;
6. Ciosk A., Mizerski A.: „Badania możliwości zastosowania pianotwórczych środków gaśniczych do wytwarzania pian dekontaminacyjnych”, Zeszyty Naukowe SGSP, **5**, 2007;
7. Mizerski A.: „Krytyczna ocena metod pomiaru zdolności zwilżających wodnych roztworów substancji powierzchniowo – czynnych”, Archiwum Spalania, **2**, 2002.