EFFECT OF ALKYL SULFONATES ON FREEZING RESISTANCE OF CEMENT MORTARS

Eduard PIIROJA[a], Helle LIPPMAA[a], Lembi-Merike RAADO[b], and Nonna NIKITINA[a]

[a] Tallinna Tehnikaülikooli polümeermaterjalide instituut (Department of Polymeric Materials, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn (Estonia)
[b] Tallinna Tehnikaülikooli ehitustootluse instituut (Department of Building Production, Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)

Abstract. Use of alkyl sulfonate fractions (with overall hydrocarbon chain-length range of C_8–C_{20}) as admixtures to improve the freezing resistance of Portland cement/sand mortars was studied. Alkyl sulfonates were synthesised from hydrocarbon mixtures obtained by polyethylene waste pyrolysis. They act as air-entraining agents but do not show plasticising effect. All of the three different fractions improve freezing resistance but higher than 9% air contents are detrimental to the strength values. The best compromise is the fraction C_8–C_{10} in 0.02% amount that raises the freezing resistance by 22–28% as estimated from the values of the dynamic modulus of elasticity measured after 200 freezing/thawing cycles. Under these conditions, the bending and compression strength retain not less than 90% of the values measured for the reference mortar after a six-month hardening period.

Key words: alkyl sulfonates, cement mortars, air content, mechanical strength, freezing resistance, polyethylene waste pyrolysis, alkenes.

1. INTRODUCTION

Polyolefinic wastes can be utilized by pyrolysis to obtain a mixture of hydrocarbons, which can be used as a raw material for organic synthesis [1, 2]. Thermal destruction of polyethylene (PE) in a film-type bubble reactor [3] in the temperature range of 450–550°C (350–450°C for polypropylene) with an inert gas as a heat-carrier, bubbled through the polymer melt, appeared to be the best solution in obtaining n-alkane/ 1-alkene mixture as the only product.

Under the conditions used, no aromatic compounds or oxidation products formed. Polypropylene (PP) gives substantially shorter chain-length compounds (C_2–C_{16}) than PE (C_7–C_{32}) in average, with double bonds positioned at C_1 like in the PE pyrolysis products. The formation of

branched structures is evident with PP. The hydrocarbon chain-length diminishes at higher pyrolysis temperatures [4]. A composition of the product mixture formed in PE pyrolysis, and distilled fractions were determined by gas-chromatography and structure by IR and NMR (both ^{1}H and ^{13}C) spectrometry [5]. It was not possible, though, to determine from the spectrum of the mixture whether dienes with double bonds at both ends of the chains had formed in the process. The chain-length ranges of six vacuum-distilled (at 20 mm Hg) fractions (total boiling range 150–300 °C) were: C_7, C_8–C_{10}, C_9–C_{11}, C_{10}–C_{13}, C_{13}–C_{15}, C_{15}–C_{17}, C_{18}–C_{20}. In the fractions, alkane content varies from 49 to 61% and the values of average molecular weight are in the range of 124–261.

One aspect of this study was further utilization of PE wastes, i.e., the PE pyrolysis products. The alkane/alkene mixtures obtained can be used as a raw material for various organic syntheses [2]. One of the compound classes most usually synthesised is alkyl sulfonates, which belong to one of the cheapest types of surfactants.

Another aim was to study the application of possibilities of various chain-length alkyl sulfonates, synthesised from alkane/alkene mixtures. Various surfactants (anion-active included) are well-known admixtures in the composition of cement mortars as agents for plasticising or air-entraining or both. Increased air content of Portland cement-based mortars is widely used to improve their freezing resistance. Often fatty acid sodium salts with average alkyl chain-length of C_8–C_{12} are used. Typical examples are sodium lauryl sulfate and sodium oleate [6, 7]. Addition of air into mortar composition serves two purposes: increasing the freezing resistance or reducing the water demand of concrete mortars to improve their slump properties. These changes in properties are ascribed to the formation of a cellular structure and overall increase in void volume. Void formation level in the range of 5–10% is usually achieved with the air-entraining salts if about 0.05% of the amount of cement weight is added. Generally, improvement of freezing resistance is accompanied by notable reduction of the strength values at a constant water/cement (W/C) ratio. Hence, in addition to the chemical nature, optimum carbon chain-lengths of admixture surfactants and their amounts are crucial in reaching compromise between the improved freezing resistance and the still acceptable strength values.

Therefore, the study focused on the possibility of using alkyl sulfonates synthesised as cement mortar admixtures, the effect of the amount and the chain-length of these admixtures on the freezing resistance and particularly on strength properties of sand/Portland cement mortar.

2. EXPERIMENTAL METHODS

2.1. Synthesis of alkyl sulfonates

Alkyl sulfonates were synthesised from the crude alkane/alkene mixture and all the distilled (Vigreux column of 3 theoretical plate

efficiency) fractions reacting them with $Na_2S_2O_5/H_2O$ in 2-propanol solution, with benzoylperoxide an initiator and cobalt acetate as an accelerator. The presence of cobalt acetate does not noticeably influence the yield. The synthesis conditions and reactant ratios were optimised. Hydrogen sulfite has to be taken in excess (1.2–1.5). The reaction time depends on the alkene chain-length; the longer the length, the slower is the reaction. For shorter 1-alkenes, the optimum yield was obtained in 4-hour reaction at 2-propanol boiling temperature with a very slow further gain [8].

- Molar amounts or ratios of reagents:

Alkenes	1	always 0.35 moles;
$(C_6H_5CO)_2O_2$	0.02–0.04	initiator;
$Co(OCOCH_3)_2$	0.0–0.04	accelerator;
$2\text{-}C_3H_7OH$	11	solvent, always 300 ml;
$Na_2S_2O_5/H_2O$	1/1.1	

- Reaction conditions:

Temperature 82°C; air bubbling rate 0.015 m^3/h; reaction time 2.5–6h; solvent 2-propanol, added stepwise, average yield 75%. After cooling, the reaction product formed three layers. The phases obtained after separation were treated either with additional 2-propanol or octane to get rid of the unreacted hydrocarbons and other additives [8]. To characterise the three alkyl sulfonate fractions chosen as the most promising, as the results of preliminary experiments show [9]. The yield dependence on carbon chain-length and the time dependence of the yield are illustrated in Figs. 1 and 2.
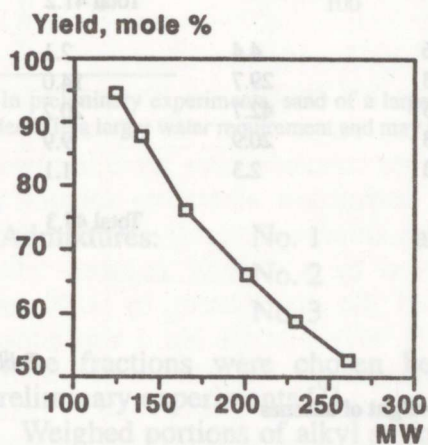

Fig. 1. Dependence of the yield of alkyl sulfonates on carbon chain-length.
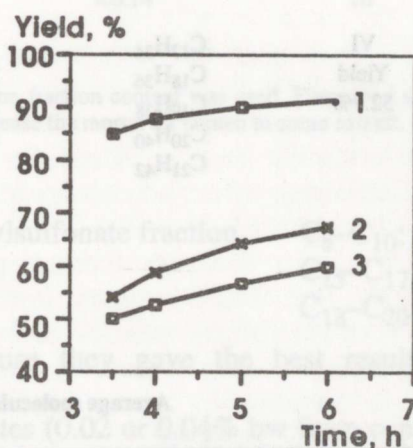
Fig. 2. Time dependence of alkyl sulfonate yield; 1, C_8–C_{13} (M = 139); 2, C_{14}–C_{19} (M = 230); 3, C_{17}–C_{21} (M = 261).

The composition of alkyl sulfonates, which are too corrosive for straight gas-chromatographic analysis, can be estimated by comparing of the composition of the corresponding alkenic fractions before and after

sulfonation reaction at optimum reactant molar ratio: alkenes/hydrogen sulfite/benzoylperoxide/water/2-propanol = 1/1.2/0.02/0.5/11 (Table 1) and by changes in average molecular weights (Table 2).

Table 1

Composition of alkenes before and after the reaction

Fr. No.	Composition	Before, %	After	
			%	g/100 g initial
II	C_8H_{16}	5.9	3.5	0.4
Yield	C_9H_{18}	30.5	7.1	0.8
87.8%	$C_{10}H_{20}$	35.9	37.6	4.6
	$C_{11}H_{22}$	23.8	38.5	4.7
	$C_{12}H_{24}$	3.4	11.8	1.5
	$C_{13}H_{26}$	0.5	1.5	0.2
			Total	12.2
V	$C_{14}H_{28}$	7.5	3.9	1.6
Yield	$C_{15}H_{30}$	19.9	16.5	6.8
58.8%	$C_{16}H_{32}$	28.3	28.2	11.6
	$C_{17}H_{34}$	27.3	29.8	12.3
	$C_{18}H_{36}$	12.4	15.8	6.5
	$C_{19}H_{38}$	4.6	5.8	2.4
			Total	41.2
VI	$C_{17}H_{34}$	6.6	4.4	2.1
Yield	$C_{18}H_{36}$	37.3	29.7	14.0
52.7%	$C_{19}H_{38}$	39.5	42.7	20.2
	$C_{20}H_{40}$	15.3	20.9	9.9
	$C_{21}H_{42}$	1.3	2.3	1.1
			Total	47.3

Table 2

Average molecular weight of alkenes

Fr. No.	Boiling range, °C at 20 mm Hg	Average molecular weight	
		before	after
I	150–175	139	144
V	250–285	230	234
VI	285–300	261	264

2.2. Mortar test specimens

The mortar specimens with dimensions of $4 \times 4 \times 16$ cm were prepared from the 1/3 Portland cement/sand mixtures according to EVS 637:1993 standard (Eurostandard ENV 197-1 EVS 637-1:1993). The mixtures were prepared in a Hobart type mixer. The W/C ratio was chosen to guarantee the flow of the sand/cement/water mixtures within 120–130 mm.

Reference mortar specimens were prepared without admixtures. For the purposes of comparison, one series was made with specimens containing special air-removal agent (TG 4250).

* Materials:

Portland cement PT 42.5 EVS 635:1993 (Kunda Nordic Cement);

sand from Kiiu quarry, fractionated according to EVS 637:1993 (Table 3).

Table 3

Fractional composition of sand*

Mesh, mm	Residue, total %	Particle diameter, mm	Content, %
2	0	–	
1.25	22	1.25–2.00	22
0.63	58	0.63–1.25	36
0.315	78	0.315–0.63	20
0.14	90	0.14–0.315	12
0	100	<0.14	10

* In preliminary experiments, sand of a larger fine fraction content was used. Finer sand usually leads to a larger water requirement and may increase the mortar air conten to some extentt.

Admixtures: No. 1   alkylsulfonate fraction C_8–C_{10};
   No. 2 C_{15}–C_{17};
   No. 3 C_{18}–C_{20}.

These fractions were chosen because they gave the best results in preliminary experiments [9].

Weighed portions of alkyl sulfonates (0.02 or 0.04% bw from cement) were dissolved in mortar mixing water.

* Hardening and testing of specimens:

Before testing of bending and compression strength, specimens were hardened for 28 days or 6 months under ambient conditions at 20°C. Standard equipment was used to determine the air content in mortars. The freezing resistance was determined after alternating freezing/thawing cycles using dynamic modulus of elasticity E_D as a characteristic parameter. The schedule of cycles: 8 h at –18°C; 8 h at +20°C (specimens

soaked in water). Changes of E_D were measured after 100, 150 and 200 freezing/thawing cycles, respectively.

To estimate the times for hardening schedules of the mortar specimens properly, the setting times of the cement pastes unmodified and modified with alkyl sulfonates were determined according to the EVS 637-4 standard (Table 4).

Effect of alkyl sulfonates on the cement paste setting rate

No.	Admix. No.	W/C	Setting, hours and minutes		
			initial	final	time
1	–	0.265	3.24	5.04	1.40
2	1	0.263	3.53	5.23	1.30
3	2	0.263	4.04	5.51	1.45
4	3	0.264	3.33	5.18	1.45

In the presence of alkyl sulfonates, the rate of the starting phase of setting was retarded to some extent, leading to prolonged overall setting times. No. 1 (C_8–C_{10}) is an exception, exerting no retarding effect on the setting rate.

3. RESULTS AND DISCUSSION

The results of the first series obtained with the admixture No. 1 (Table 5) show that an increase in the air content of mortars would obviously exceed the optimum level at larger than 0.04% amounts, considering the strength values. So higher concentrations were not used. No plasticising effect was observed at such a low admixture amount, as could be expected. However, workability improved slightly because of a closed cellular structure formed, proved by a slightly reduced water demand. The 0.02% amount increased the air content by 16% and decreased the volume mass by about 3%. When 0.04% No. 1 was added, the changes were by 37 and 4%, correspondingly. The values of bending strength decreased by 5.4 and 9.5% (28-day hardening time) and by 6 and 17% (6-month hardening time) for 0.02 and 0.04% admixture amounts, correspondingly. The reductions in the compression strength values were by 9 and 20% (28-days) but by 8 and 18% after six-month hardening time. It is interesting to note that with a longer hardening period, a more than twofold increase in air content did not have any negative but rather a slightly improving effect on the compression strength, increasing the corresponding value by about 13%. At the same time, compression strength of the reference specimens improved by 10%. So, it can be concluded that in general, alkyl sulfonates do not prevent proper hardening of the mortar specimens. This effect is less pronounced in the bending

Table 5

The effect of alkyl sulfonate admixtures on mortar

No.	c, %	W/C	G, mm	A, %	γ, kg/m³	R_p^{28}, MPa	R_p^{6k}, MPa	R_s^{28}, MPa	R_s^{6k}, MPa	E_D, %		
										F_{100}	F_{150}	F_{200}
				$C_8H_{17}SO_3Na$–$C_{10}H_{21}SO_3Na$								
1*	0	0.46	124	7.5	2240	8.28	9.36	53.7	59.7	100	82.5	79.8
2	0.02	0.44	125	8.7	2180	7.83	8.47	49.0	55.0	100	97.0	102
3	0.04	0.44	124	10.3	2150	7.76	7.75	42.9	49.2	100	96.7	97.0
				$C_{15}H_{31}SO_3Na$–$C_{17}H_{53}SO_3Na$								
1*	0	0.46	124	7.5	2240	8.28	9.36	53.7	59.7	100	82.5	79.8
4	0.02	0.42	120	7.8	2100	7.03	7.37	36.8	33.3	100	96.4	97.0
5	0.04	0.37	125	11.2	1970	5.56	5.66	25.8	25.3	100	105	103
6	0.3	0.37	127	25.0	1720	3.60	3.53	10.4	7.67	77.4	failure	failure
7**	0.04	0.41	111	5.5	2270	–	–	–	–	37.8	"	
				$C_{18}H_{35}SO_3Na$–$C_{20}H_{41}SO_3Na$								
1*	0	0.46	124	7.5	2240	8.28	9.36	53.7	59.7	100	82.5	79.8
8	0.02	0.44	122	10.5	2145	6.28	7.24	28.7	30.0	100	94.5	103
9	0.04	0.44	130	12.0	2065	5.46	6.33	28.0	28.0	100	103	103

* Reference mortar specimen without additives; ** 0.04 + 0.01 TG 4250.

strength behaviour (after-hardening improvement by 8% with 0.02% admixture only). On the other hand, the freezing resistance of mortar specimens increased substantially. After 200 freezing/thawing cycles, the E_D of the reference mortar dropped by 20% against the 2% gain (0.02%) and 3% drop (0.04%), shown by modified mortars. It is also noteworthy that doubled admixture amount had no excessive detrimental effect on the E_D values.

The admixture No. 2 also acts as an air-entraining agent (Table 5, middle part). Although the preliminary experiments showed that that type of compounds lack the properties needed to bring about the plasticising effect in mortars, and they can only be used as air-entrainers, the influence of 0.3% amount of No. 2 was checked (0.3% is a usual amount for plasticisers). It was of interest to compare the deteriorating effect on the strength properties and that brought about by smaller amounts. The water consumption and volume mass reduced to 80 and 77% of the reference mortar, correspondingly. With 0.04% of No. 2, the water consumption reduced to 80% like with 0.3% of No. 2, but the volume mass decreased less than with 0.3% amount, constituting 88% of that of the reference mortar. However, the threefold increase of air content (25%) makes the mechanical structure of mortar too fragile as can be seen from a substantial decrease of the strength values. Obviously, that large amount of such admixture severely interferes with the hardening process. No after-hardening improvement in the compression strength values were observed as it had occurred with the reference mortar specimens. The compression strength was bare 13% of that of the reference after six-month hardening period, the corresponding value for the bending strength was 38%. As to the freezing resistance, the values of E_D also suffered severe reduction, after 100 cycles, the value dropped to 77.4% and specimens decomposed during further cycles.

The freezing resistance improved at moderate admixture amounts; 0.04% of No. 2 raised the E_D value by 23% relative to that of the reference. At the same time, the compression strength was only 42% of that of the reference.

The plasticising effect was checked at 0.04% admixture amount by adding a special air-control agent TG 4250 (0.01% bw from cement). That provided workability $G = 111$ mm at W/C ratio 0.41. In this case, a substantial loss in its effect on reducing the water content was observed. When workability was brought up to 124 mm, which was the value for the reference mortar in this experiment, the water consumption rose sharply with the progress of air removal. Along with this, the freezing resistance decreased with the E_D dropping to about 38% of the initial value after 100 cycles.

Still longer hydrocarbon-chain alkyl sulfonates (No. 3) have generally shown the same effects as No. 2 (Table 5). It is quite natural because differences in the average chain lengths are quite small. Air content increased by about 60% with 0.04% of No. 3, leading to a reduced water consumption due to excessive air bubble formation, which improved workability. The amount of water needed to provide workability similar to

the reference was only 0.07 L/1 kg of cement (i.e., only about 15%) with No. 3, which, however, is especially detrimental to the compressive strength values. If the values for bending strength still show moderate after-hardening effect and constitute 77% of that of the reference, the compressive strength values retained only 50% of that of the reference after a six-month hardening period. On the other hand, the increased porosity due to larger air content (12% against 7.5% of that of the reference mortar) improved the freezing resistance nearly to the same extent as gained with shorter chain-length admixtures. The E_D value is by 23% higher than that of the reference.

As a result of the comparison of the different alkyl sulfonate fractions according to their effects on Portland cement/sand mortar properties, it can be concluded that all of them reduce water consumption more or less equally, i.e., by about 13–15% (0.02–0.07 L/1 kg Portland cement). No. 2 has the largest reducing effect on the volume mass, the 0.04% amount reducing that value even by 12%, the corresponding values for No. 3 and No. 1 being 8 and 4%. The mechanical strength of the hardened mortar specimens decreased in all cases along with the increasing air contents. Again, the effect is the largest with No. 2. The maximum compression strength value at 0.04% admixture amount was only 42% from that of the reference; in the case of Nos. 3 and 1 the corresponding values were 47 and 82%.

The most important parameter to be considered is the freezing resistance of mortars. It is obvious that all of the three alkyl sulfonate admixtures studied give a positive effect in that respect and could be used as modifiers. All aspects taken into consideration, beneficial effects as well as detrimental ones, an optimum choice can be made. Considering the drawbacks discussed earlier, the strongest beneficial effect was shown by No. 1, which increased the E_D value by 1.27 times (at 0.02% content) after 200 freezing/thawing cycles (Nos. 2 and 3 by 1.21 and 1.29 times, correspondingly) with no substantial impairment of the strength properties. It means that all of them have an improving effect on the freezing resistance but the optimum solution is No. 1 in 0.02% amount from the cement weight.

4. CONCLUSIONS

Alkyl sulfonates with the overall chain-length of $C_8H_{17}SO_3Na$–$C_{20}H_{41}SO_3Na$ appear to be good surfactants and act as air-entraining agents in the composition of Portland cement/sand mortars. An increased content of air leads to the reduction of water consumption and volume mass in the concentration range studied (0.02–0.04%). With 0.04% admixture amounts, the air content varies from 10 to 12% and the volume mass in the range of 1970–2150 kg/m³. As a result of modification the strength of specimens after six-month hardening period is decreased. The compressive strength values constitute only 42–47% of that of the

reference in the case of longer-chain alkyl sulfonates, the values of the bending strength being in the range of 60–80%.

Alkyl sulfonates do not show plasticising properties at concentrations chosen. However, they improve the freezing resistance of mortars substantially. Judging by values of the E_D chosen as a characteristic parameter, the freezing resistance improved by 25–30% after 200 freezing/thawing cycles.

Alkyl sulfonates of the shortest chain-length range used ($C_8H_{17}SO_3Na$–$C_{10}H_{21}SO_3Na$ – No. 1) give relatively lower amounts of air (less than 10%), larger volume masses, higher strength values, better workability and also improved freezing resistance (by 22–28% after 200 freezing/thawing cycles). As to the mortar hardening rate, at the admixture amounts 0.02%, no severe interference with the mortar hardening process was observed. With larger amounts, however, after 28-day hardening already, the strength properties deteriorated to an extent that severe interferences with the hardening process were obvious. Therefore, to improve the freezing resistance of Portland cement/sand mortars with no unacceptable impairment of the strength properties, the C_8–C_{10} chain-length fraction of alkyl sulfonates can be suggested as an admixture in the mortar formulations with the optimum amount not larger than 0.02% by weight from cement.

ACKNOWLEDGEMENT

SYMBOLS

c – alkyl sulfonate concentration in cement, %;
W/C   – water/cement ratio;
G – flow of mortar mixture, mm;
A – mortar air content, %;
γ – volume mass of mortar, kg/m³;
R_p^{28} – bending strength after 28-day hardening in water, MPa;
R_p^{6k} – bending strength after six-month hardening in water, MPa;
R_s^{28} – compression strength after 28-day hardening in water, MPa;

R_s^{6k} — compression strength after six-month hardening in water, MPa;

E_D — dynamic modulus of elasticity, determined after 28-day hardening, MPa, presented relative to F_{100} in %;

$F_{100}, F_{150}, F_{200}$ — 100, 150 and 200 freezing/thawing cycles.

REFERENCES

1. Piiroja, E. and Lippmaa, H. Thermal degradation of polyethylene. – Macromol. Symp., 1989, 27, 305–309.
2. Piiroja, E. Processing and utilization of polyethylene wastes. – Trans. Tallinn Tech. Univ., 1990, No. 709, 39–53 (in Russian).
3. Piiroja, E., Rohumägi, M., Vetevool, V., and Viisimaa, M. Pyrolysis Reactor. SU Author Certificate No. 1778145. Inform. Bulletin No. 44, 30 Nov., 1992 (Russian).
4. Piiroja, E. Utilization of polymeric wastes. – Proc. Estonian Acad. Sci. Chem., 1995, 44, 2/3, 218–221.
5. Piiroja, E. and Oja, H. Spectrometric study of polyethylene pyrolysis products. – Trans. Tallinn Tech. Univ., 1990, No. 709, 69–79 (in Russian).
6. ConChem., Conference Proceedings, Karlsruhe, 1993.
7. Ramachandran, V. Concrete Admixtures Handbook. Noyes Publ., 1984, 229–256, 382–433 (in Russian).
8. Piiroja, E. and Nikitina, N. Reaction of alkenes with hydrogen sulfite. – Trans. Tallinn Tech. Univ., 1994, No. 744, 84–91.
9. Piiroja, E., Aas, A., and Arro, M. Effect of alkylsulfonates on cement mortars. – Trans. Tallinn Tech. Univ., 1994, No. 744, 92–99.

ALKÜÜLSULFONAATIDE TOIME TSEMENT-LIIVMÖRTIDE KÜLMAKINDLUSELE

Eduard PIIROJA, Helle LIPPMAA, Lembi-Merike RAADO, Nonna NIKITINA

On uuritud polüetüleeni jäätmete pürolüüsil saadavate süsivesinik-segude sobivust alküülsulfonaatide sünteesiks ja alküülsulfonaatide erineva süsivesinikahela pikkusega fraktsioonide kasutusvõimalusi tsement-liivmörtide külmakindluse tõstmiseks. Sünteesitud alküülsulfonaatidel ei ole kasutatud koguste puhul plastifitseerivaid omadusi. Nende lisand suurendab mörtide õhusisaldust ja parandab töödeldavust. Õhusisalduse teatud piiri ületamisel hakkab alanema proovikehade tugevus. Kolmest erineva ahelapikkusega alküülsulfonaatide fraktsioonist on suhteliselt kõige paremad omadused C_8–C_{10} lisandil, mis tõstab külmakindlust 22–28%, seejuures järelkivinemist takistamata. Lisandi otstarbekas kogus on 0,02% tsemendi kaalust. Kuigi ka pikema ahelaga alküülsulfonaadid parandavad külmakindlust, on tugevusomadusi kahjustavad mõjud (tugevuse alanemine liigse õhusisalduse tõttu) madalaima fraktsiooni puhul kõige väiksemad.