

Effect of α - and β -Polymethylenaphthalenesulfonate upon Properties of Cement Grout and Concrete

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Abstract

The following five oligomers of polymethylene naphthalenesulfonates with plasticizing properties of cement grouts were synthesized by the modified procedure. Condensation of sodium salt of α - and β -naphthalenesulfonic acid with formaldehyde in a ratio of 1: 1 leads to the formation of α -PNS-1 (2,7-polymethylenaphthalene- α -sulfonate of sodium), and β -PNS-3 (5-7-polymethylenaphthalene- β -sulfonate of sodium), increase of the ratio of 1: 3 - to trisubstituted cycle of α -PNS-2 (5-7,3-3-polymethylenaphthalene- α -sulfonate of sodium), β -PNS-4 (5-7, 6-6-polymethylene-naphthalen- β -sulfonate of sodium), which modification leads to the formation of β, β' -PNS-5 (β, β' -PNS-5 4-4, 8-8-polymethylenaphthalene-1,5-oxymethylene-2,6(β, β')-disulphonate of sodium). Testing the synthesized additives on the plasticizing properties, on the strength and kinetics of the hardening cement grouts showed that PNS-1 by PNS-4 all proposed types of PNS increase the plasticity from P1 to P3 and in accordance with the State Standard 24211-2008 are plasticizers, increasing the concrete strength from 27 to 30%. PNS5 increases the plasticity from P1 to P5 and in accordance with the State Standard 24211-2008 are superplasticizer, increasing the concrete strength up to 60%.

Keywords: polymethylenaphthalenesulfonate, plasticizer, cement, concrete, strength

1. Introduction

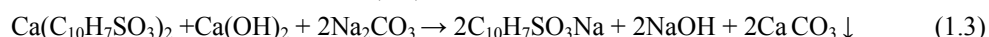
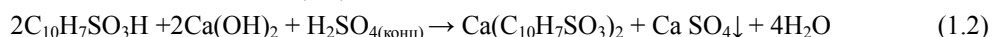
Current global production of naphthalenesulfonic acids and formaldehyde condensation products make about 1.25 million tones in the world, and according to the forecast they will annually grow by 5-6% from 2011 until 2015 (Zhunuspayev et al., 2011; Schmidt and Fehling, 2003; Yamada, 2011; Karpelov, 2010). Various superplasticizing agents are produced worldwide based on the sulphonated polymethylenaphthalenesulfonates (PNSs). They are as follows: C-3, SMF, Dofen DF, Kratasol, Superplast, Polyplast, Ferrokrit, Vilakom, Rheobuild 2000 (Russia); Agiplast (Rhona, France); Cormix (Rhodia, Great Britain); Chiso fluid (Chiso, France); Lomar D (Diamond Shamrock, USA); Mighty (Cao Soar, Japan); Fluimax (Maxfer, Italy); PSP (Protex Industries, USA). However, the opportunities of synthesis of new naphthalene-based products having plasticizing properties have not been exhausted so far. Plasticizing properties of products also depend on molar mass distribution (MMD) of oligomers that depends on conditions of production of PNS (Saveliev, 2009; Kastornov, 2007).

This is due to the fact that during the sulfonation of naphthalene it is theoretically possible the exist of 48 mono-, di-, tri- and tetrasulfonic acids. However, the number of isomers, which can be obtained is practically limited by 2 mono-, 6 di-, and 3 tri- and 1 tetra- sulfonic acids (Donaldson, 1963; Orekhov et al., 2007). Taking into consideration versatile possibilities of synthesis of PNS having plasticizing properties of cement grouts, the goal of this work was to test polymethylenesulfonates as plasticizing additives to concrete obtained by sulfonation of naphthalene with its subsequent polycondensation with formaldehyde and extraction of products, differing from conventional PNS production methods.

2. Materials and Methods

2.1 Synthesis of Naphthalene Sulphonates

Synthesis of naphthalenesulphonates were carried out in the following sequence of reactions and processes: 1) naphthalene, by interacting with an excess of concentrated sulphuric acid at a certain temperature, forms a naphthalenesulfoacid (NSA); 2) by adding calcium hydroxide, naphthalenesulfonic acid is converted into calcium salt of naphthalenesulfonic acid (CaNSA) and at this an excess of sulphuric acid is also neutralized as the precipitation of calcium sulphate into precipitate (precipitate is filtered); 3) by adding sodium, calcium salt of naphthalenesulfonic acid is converted into sodium salt, the excess of calcium hydroxide is precipitated as calcium carbonate (calcium carbonate is filtered); 4) the synthesized and purified from the reaction byproducts, sodium salt of naphthalenesulfonic acid is released in pure form after vacuum distillation of the water. Mentioned above transformation is expressed by the following equation:



During the sulfonation of naphthalene, both naphthalene-1-sulfonic acid and naphthalene-2-sulfonic acid (reaction 2.1) are formed. The rate of sulfonation into α - and β -position changes depending on the concentration of sulphuric acid and reaction temperature.

2.1.1 Synthesis of naphthalene- α -sulfosodium (α -NSNa)

Synthesis of naphthalenesulfonates was carried out in a round bottom flask with a backflow condenser, a stirrer with a hydraulic lock and a thermometer, lowered into reaction mixture up to the bottom of the flask.

Into a flask 72 ml of sulphuric acid was poured, was cooled with ice up to 0 °C, 103,4 g of (0,8 mol) of naphthalene, crushed in a porcelain mortar were added by small portions, so that the temperature in the reaction flask did not rise above 2°C. A reaction mixture was stirred for 2 hours at a temperature of 0-15 °C, after this the temperature in water bath was raised up to 60°C and heating was continued for 6 h. We left it to stand overnight, 500 mL of ice was added into the thick reaction mixture, then poured out into a tall glass beaker of capacity of 700 ml, placed into a cold water bath. When stirring 260 g of calcium hydroxide was added by small portions, so that the temperature did not rise above 60°C. Calcium sulphate is filtered on a Buchner funnel under vacuum, and 65 g of Na₂CO₃ was added to the filtrate until basic medium. The formed calcium carbonate of the reaction mass of milky color was filtered on a Buchner funnel. From the filtrate of yellow color, water was distilled off in a water jet pump vacuum at a bath temperature of 80-90°C. A white crystalline product was obtained, which was dried in air for 6 hours. We received 175 g. Output is 95%.

2.1.2 Synthesis of naphthalene- β -sulfosodium (β -NSNa)

Into a flask 72 ml (1,35 mol) of sulphuric acid was poured, 103,4 g of (0,8 mol) of naphthalene, crushed in a porcelain mortar were added by small portions, a reaction mixture was stirred for 6 hours by heating in sand bath up to a temperature of 160 °C. We left it to stand overnight, 200 mL of ice was added into the thick reaction mixture, then poured out into a tall glass beaker of capacity of 700 ml, placed into a cold water bath. When stirring, 274 g of calcium hydroxide was added by small portions until disappearance of acid medium. A mixture is strongly thickening, so 300 ml of ice was also added. Calcium sulphate was filtered on a Buchner funnel under vacuum, and 72 g of Na₂CO₃ was added to the filtrate until basic medium. The formed calcium carbonate of the reaction mass of milky color was filtered on a Buchner funnel. From the filtrate of yellow color, water was distilled off in a water jet pump vacuum at a bath temperature of 80-90 °C. A white crystalline product was obtained, which was dried in air for 6 hours. We received 180 g. Output is 97%.

2.1.3 Synthesis of naphthalene- β, β' -sulfosodium (β, β' -NSNa)

In a three-necked flask 128 ml of sulphuric acid was poured, after which 102,5 grams of naphthalene, powdered in a porcelain mortar were added by portions during 30 - 40 min with vigorous stirring. The reaction mass was heated at a temperature of 155 - 160 °C in a sand bath for 8 hours. After this, the reaction mixture was cooled up to 60 °C and was poured into glass beaker, having ice (300 ml), under stirring 385 g of calcium hydroxide was added by portions until the disappearance of the acid medium, a strong warming is observed, so a glass beaker with the reaction mass was put in an ice bath. Calcium sulphate was filtered on a Buchner funnel, washing by 300 ml of water. To the resulting solution of volume of 700 ml, 32 g of sodium carbonate was added until basic (pH 8) medium and the precipitated calcium carbonate was filtered. Water was distilled off under water pump vacuum at a bath temperature of 70 - 80 °C. Remaining white crystalline product was dried at room temperature.

The product was obtained with a mass of 118 g. Output is 44.4%.

3. Procedure of Obtaining of PNS

Naphthalene and formaldehyde at 1:1 and 1:3 ratios (mole) were condensed for obtaining the PNS. For this into three necked flask 76,00 g (0.33 mol) of α - or β -naphthalenesulfonate was placed, 500 ml of distilled water was poured, 14,5 ml (0.33 mol) of 40% aqueous formaldehyde solution and was acidified with 9 ml hydrochloric acid up to pH 1. When stirring the reaction mixture was heated at 80-95 °C for 4-8 hours. Then the reaction mixture was neutralized with a concentrated alkaline solution up to pH 10, water was distilled off at 90 °C in water jet pump vacuum, the precipitate was dried at room temperature. The α -naphthalenesulfonate and formaldehyde condensation products are conditionally designated as α -PNS-1, and β -PNS-3. Similarly, we carried out the condensation with an excess of formaldehyde and 115.1 g (0.5 mol) of naphthalenesulfonic acid and 112.5 mL (1.5 mol) of formalin, and we obtained the products, which are conditionally designated as α -PNS-2 and β -PNS-4.

In order to obtain PNS with stronger plasticizing properties, researches on improving methods of synthesis of PNS by correcting the main parameters of synthesis have been suggested.

The parameter adjustment of synthesis was carried out in such a way that these changes have contributed an increase of share of high molecular fractions of oligomers namely. As a result of c adjustments, a new laboratory model has been synthesized, which is conventionally designated as PNS-5, which differs by duration of the synthesis stage, i.e. sulfonation, condensation and neutralization. Basic conditions for the synthesis of samples of PNS are presented in Table 1.

Table 1. Condition of synthesis of samples of PNS –K series

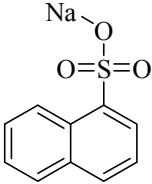
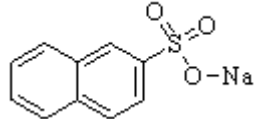
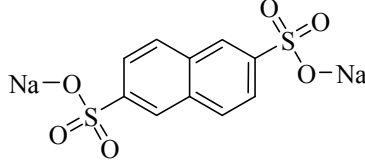
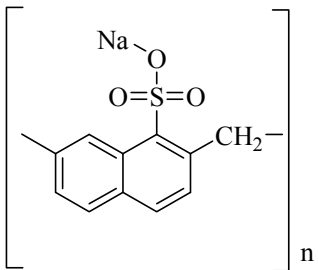
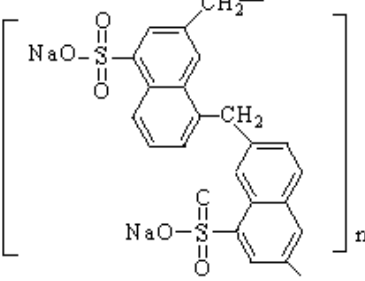
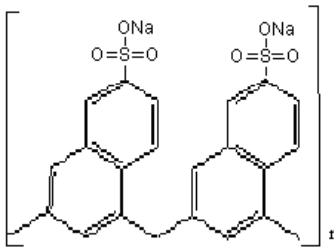
Name of PNS	Ratio of NSA/CH ₂ O, mol	Synthesis duration, τ , hour			Concentration after reaction, %	
		Sulfonation	Condensation	Neutralization	SO ₄ ⁻²	PNS
PNS -1	1/1	6	3	0,5	2,7	33,8
PNS -2	1/3	6	4	0,5	2,0	35,0
PNS -3	1/1	6	3	0,5	1,8	35,0
PNS -4	1/3	6	4	0,5	-	36,0
PNS -5	1/3	8	6	2	-	36,0

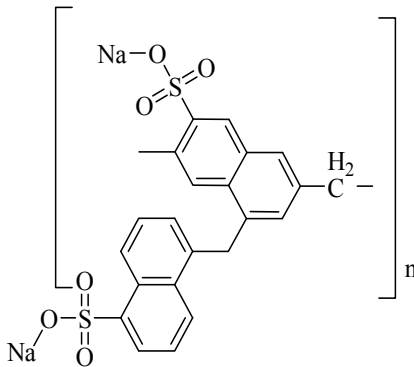
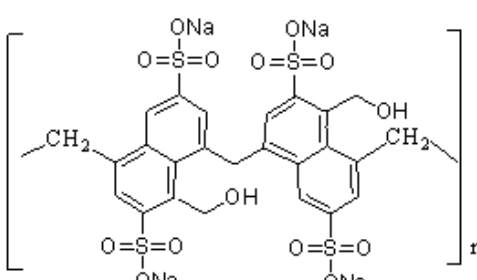
Composition and structure of the following synthesized polymethylenenaphthalenesulfonates: α -PNS-1 (2,7-polymethylenenaphthalene- α -sodium sulfonate), α -PNS-2 (5-7,3-3-polymethylenenaphthalene- α -sodium sulfonate), β -PNS-3 (5-7-polymethylenenaphthalene- β -sodium sulfonate) and β -PNS-4 (5-7,6-6-polymethylenenaphthalene- β -sodium sulfonate) were determined using UV, infrared and NMR spectroscopy methods. Structure of synthesized naphthalenesulfonic acids and polycondensation products, established by NMR spectroscopy and conditions for their production are represented in Table 2 (Arynov et al., 2014).

All produced additives of PNSs are brown liquids with minor precipitation, well soluble in water, density of 1.15-1.17 g/cm³, pH=8-10, total weight percentage of oligomers is 35-37%.

Table 2. Molecular structures of the synthesized HCNa and PNS and their production conditions

No	Code	Name	Structural formula	Reaction temperature, °C	Output, %

1	α -HCNa	naphthalene -1(α)-sulfosodium		60	95
2	β -HCNa	naphthalene - β - sulfosodium		160	97,0
3	β,β -HCNa	naphthalene -2,6(β,β')-disulfosodium		160	44,4
4	α -PNS-1	2,7-polymethylene naphthalene - α -sulfonate of sodium		90-95	98,0
5	α -PNS-2	5-7,3-3-polymethylene naphthalene - α -sulfonate of sodium)		90-95	52,6
6	β -PNS-3	5-7- polymethylene naphthalene - β - sulfonate of sodium		90-95	99,0

7	β -PNS-4	5-7,6-6- polymethylene naphthalene- β - sulfonate of sodium		90-95	69
8	β, β' -PNS-5	4-4, 8-8- polymethylene naphthalene -1,5-oxy methylene-2,6(β, β')-disulfonium		90-95	74

4. Results

Research of PNS as plasticizing additives in concrete

Research of influence of additives on the mobility of concrete mixtures was carried out in accordance with the State Standard 10181.1-2000. Influence of additives on the concrete compressive strength was determined in accordance with the State Standard 10180-90, for which samples the following samples depending on the used material were prepared:

1. Samples with dimensions of 2x2x2 cm, in amount of 10 pc were prepared from the cement. Test of samples was carried out on a hydraulic press of 2PG -10, No 953 with the scale of "A" 0 ... 5m (16.6 kgs), "B" 0-10t (33.2 kgs), measurement error is $\pm 1\%$.

2. Physical and mechanical properties of binder were determined in accordance with the State Standard 310.4-81. Samples - beam of size of 4x4x16 cm, in the amount of 6 pcs were prepared. Test of beams on bending was performed on test machine of MII-100 № 210 in accordance with the State Standard 10180-78 with a scale of 0 ... 200 kgf/cm; measurement error is $\pm 1\%$.

3: Determination of concrete compressive strength was carried out in accordance with the State Standard 10180-78. Samples - cubes with size of 10x10x10 cm were manufactured. Test of cubes was carried on a hydraulic press PSU-125 № 1415, with the scale of "A" 0-50t (100 kgs), "B" 0-125 t (250 kgs), measurement error is $\pm 1\%$. Samples were prepared by series of 48 by 6 samples in each.

Measuring the pH value was carried out using a digital pH meter of type of EhWRO with an accuracy of 0.01. Indications were recorded after the installation of equilibrium, which occurred after 6 minutes.

The molecular weight of oligomers were determined by the method of mass spectrometry with matrix-assisted laser dissociation / ionization combined with time of flight mass analyzer (MALDI-TOF) (Krasnov, 2012; Giannuzzi and Stevie, 2004).

The effectiveness of PNS-5 as an additive in cement mortars and concrete was determined in comparison with the indicative characteristics of known superplasticizer of "Kratasol" of the firm of "Krata-Asia" (Russia). Additives were introduced with the mixing water, the measurement was carried out after two minutes of stirring of the suspension.

Identification of synthesized naphthalenesulfonic acids and oligomers of polymethylenenaphthalenesulphonates,

also their quantitative determination in aqueous solutions were performed by spectrophotometer Varian Cary-50 in the range of 190-1100 nm with a resolution of 1.5 nm.

Normal consistency and setting time of cement paste was determined using the instrument Vick in accordance with the State Standard 310.3 - 76.

Selection of concrete mixtures was carried out in accordance with the methodology, developed in, by the use of additives of various types in technology of precast and monolithic concrete (Nesvetaev et al., 2001; Frenkel, 1979; Kogay et al., 2008; Kazitsina and Kupletskaia, 1989; Batrakov, 1998; Bazhenov et al., 2006).

The mobility of the concrete mixture was determined using a standard cone.

The synthesized substances have been tested as additives to concrete. The data on the effect of 4 oligomers of PNS on the properties of concrete are represented below.

Testing the effect of PNS additives upon the following 3 properties:

- plasticizing ability (GOST 30459-2008, p.8.1);
- strength (GOST 30459-2008, p.9.2);
- structure kinetics (GOST 30459-2008, p.9.1).

Works cubes were filled with Standardcement cement of PC-400D-0 grade, sand and macadam from the Badam quarry.

The value of the main effect was determined by comparing the indicators of concrete quality of control and basic compositions.

For the purpose of study of effect of PNS additive concentration upon *concrete compressive strength* (R_{comp28}) at mature state the used PNS doses were 0.2; 0.3; 0.4; 0.5; 0.6; 0.8% of cement mass (Table 3).

Table 3. Effect of PNS additive concentration upon concrete strength R_{comp28} , and ΔR_{comp28} (reference –K*)

№	Additive name	0,2%		0,3%		0,4%		ΔR_{28}		0,5%		0,6%		0,8%		1,2%	
		R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}	R_{28}^{och}	ΔR_{28}
1	α -PNS-1	59,00	9,26	58,5	8,33	61,5	13,89	65,25	20,83	56,00	3,70	62,5	15,74	57,34	6,19		
2	α -PNS-2	66,93	23,94	66	22,22	67,6	25,19	67,97	25,87	54,34	0,63	61,45	13,8	65,98	22,19		
3	β -PNS-3	55,32	2,44	60,35	11,76	58,68	8,67	65,31	20,94	65,53	21,35	62,37	15,5	63,16	17,78		
4	β -PNS-4	68,11	26,13	67,42	24,85	64,29	19,06	61,74	14,33	52,17	-3,39	57,71	6,87	61,84	14,52		
5	β^{β} -PNS-5	70,5	35,58	71,30	37,12	78,32	50,60	83,22	60,04	83,10	60,00	73,30	37,54	71,10	37,10		

Note: reference K* $R_{ck28}=52,0$ MPa ΔR_{comp28} – concrete compressive strength growth against reference value.

Based on the result of PNS effect upon concrete strength one can say that all proposed 4 types of additives (at concentration of 0.2-0.8% of cement mass) increase concrete strength on day 28. In terms of concrete strength increase on day 28, the most efficient additives at lowest concentrations are those with 0.3 and 0.5% concentration where $\Delta R_{28}=25-29\%$, therefore, further concrete plasticizing properties and *strength testing* were carried out using 0.3% and 0.5% of cement mass (Table 4).

Table 4. Efficiency of PNS additive effect upon *paste fluidity* and *strength*

Additive	Concrete mix properties			The compressive strength, R_{compr} , MPa		Increase of concrete strength on the 28 days. $\Delta R_{28}\%$
	dosage, %	W/C ratio	Settling of cement cone, cm	3 days	28 days	
reference – 3к	0	0,36	2,2	41,5	52,0	-
PNS-1	0,3	0,36	9,0	43,5	58,5	12,5
	0,5	0,36	9,0	43,75	65,25	20,8
PNS -2	0,3	0,36	9,0	48,5	66,00	26,9

PNS -3	0,5	0,36	10,0	42,25	67,97	25,8
	0,3	0,36	9,0	43,0	60,35	16,1
PNS -4	0,5	0,36	9,5	46,75	65,31	25,6
	0,3	0,36	9,0	44,5	67,42	29,6
PNS -5	0,5	0,36	10,0	42,75	61,74	18,7
	0,3	0,36	17	48,14	71,30	37,1
	0,5	0,36	27	59,16	83,22	60,0

Note: W/C ratio is water-cement ratio.

Testing α -PNS-1 (2,7-polymethylenaphthalene- α -sulfonate of sodium), α -PNS-2 (5-7,3-3-polymethylenaphthalene- α -sodium sulfonate), β -PNS-3 (5-7-polymethylenaphthalene- β -sulfonate of sodium) and β -PNS-4 (5-7,6-6-polymethylenaphthalene- β -sulfonate) and β -PNS-5 4-4 polymethylene 8-8-naphthalene-1,5-oxymethylene-2,6 (β , β 1) - and sulfosodium in terms of plasticizing properties, strength and cement hardening kinetics cement showed that 4 types of additives of PNS -1, PNS-2, PNS-3, PNS-4 increase plasticity from P1 till P3 and they are plasticizers of cement grouts, which increase concrete strength and concrete hardening kinetics. PNS-5, synthesized by a modified procedure by all indexes differs significantly, improves the concrete plasticization from P1 to P5 (OK-27cm), the concrete strength increases by 60% ($R_{comp.} = 83.22$ MPa, $\Delta R_{28} = 60,0\%$ R) and is a superplasticizer that increasing concrete strength and accelerating the kinetics of concrete hardening.

4. Discussion

It has been suggested that weak plasticizing action on concrete mixtures of synthesized PNS-1 - PNS-4 are linked by the discrepancy of oligomers MMD to an optimal composition, more precisely, by the low the composition of macromolecular fractions in PNS.

Increasing the number of condensed rings in the PNS-5 were confirmed by the studies of the UV spectra of absorption of the synthesized PNS, and the known superplasticizer of "Kratasol", which also has a naphthalene formaldehyde basis.

UV spectrum of naphthalene in warm water has three types of bands, α -, p, and β -bands, differing from each other by intensity and vibrational structure. α -bands, which are less intense in the area of 325-295 nm, due to the low concentration of naphthalene in water is not detected (naphthalene solubility in water at 200C is 30 mg/l), p-bands are recorded at 285, 276, 266, 257 and 247 nm, which are also of low intensity, and β -bands in the area of 210-220nm is detected by strongly pronounced intense band (Figure 1) (<http://www.chem.asu.ru/org/fcml/fcml04.pdf>; Arynov, 2012; Chemical encyclopedia, 1992).

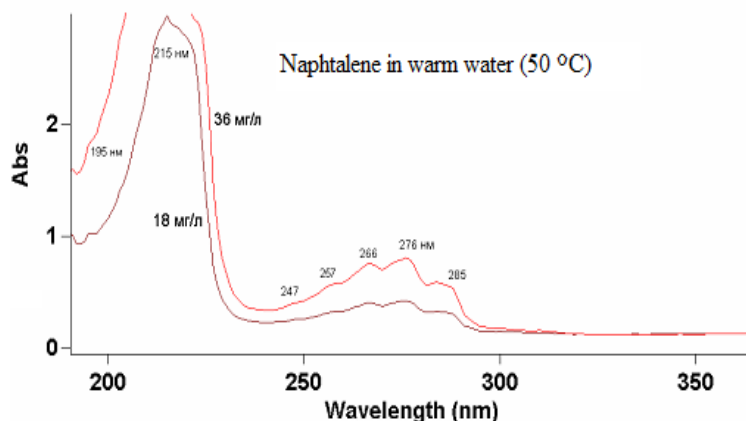


Figure 1. UV spectrum of of naphthalene in a warm (40-450C) water: 1-36mg/l; 2-18mg/l

The synthesized sodium salts of α - and β -naphthalene sulfonic acid in the UV spectrum, both are recorded by two peaks, α -isomer is recorded at a wavelength of $\lambda = 284,0$ nm (intensity = 0.232) and $\lambda = 223,0$ nm (intensity = 1,320), β - isomer-at $\lambda = 275,0$ (intensity = 0.203) and $\lambda = 227,0$ nm (intensity = 1.672) (Figure 2).

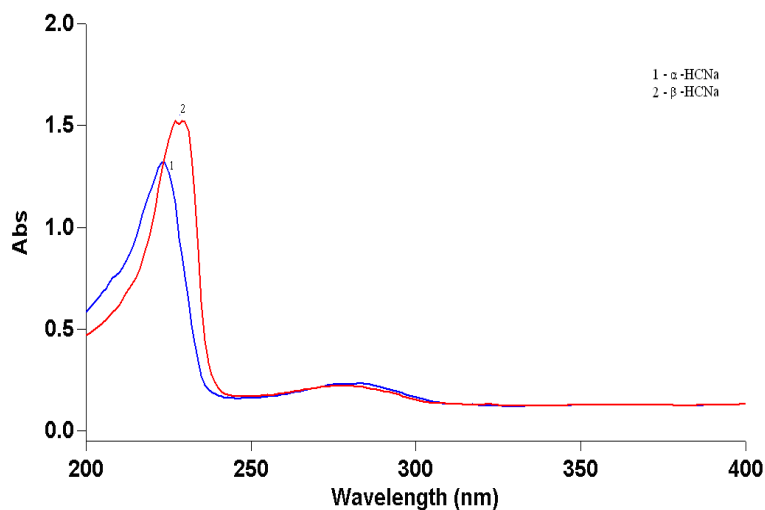


Figure 2. UV spectrum of the sample HCNa- α and HCNa- β

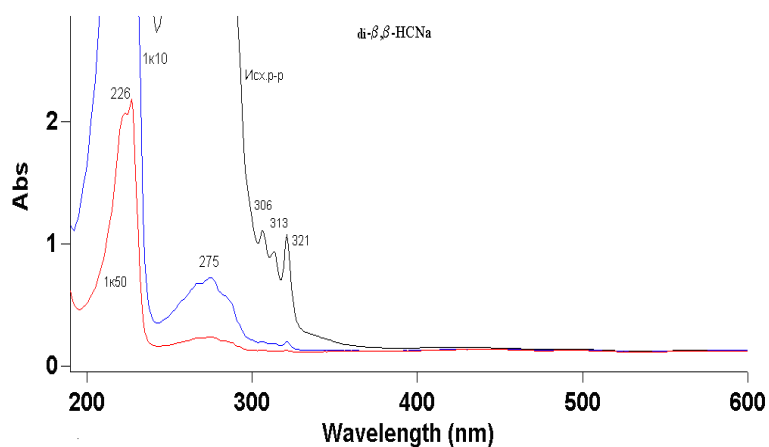


Figure 3. UV spectrum of a sample of di- β,β -HCNa

The introduction of the second sulfonic groups into β -position of naphthalene in UV spectrum is manifested in the form of additional reflections α -, p-bands and weak three peaks of β -bands in the area of 306, 313 and 321nm. Minor changes of all three absorption bands of naphthalene during introduction of sulfonic groups, probably is linked by nekoplanarnostyu of sulfonic groups with the aromatic rings of naphthalene, i.e. delocalized π -bonds of rings weakly interact with double bonds sulfonic groups (Figure 3).

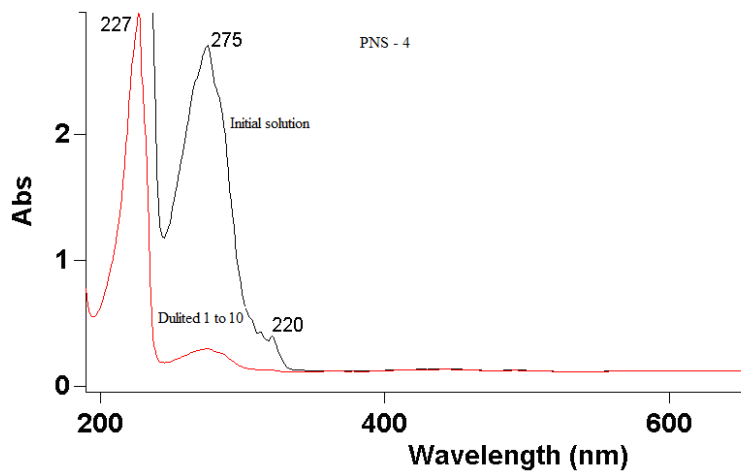


Figure 4. UV spectrum of a sample of PNS – 4

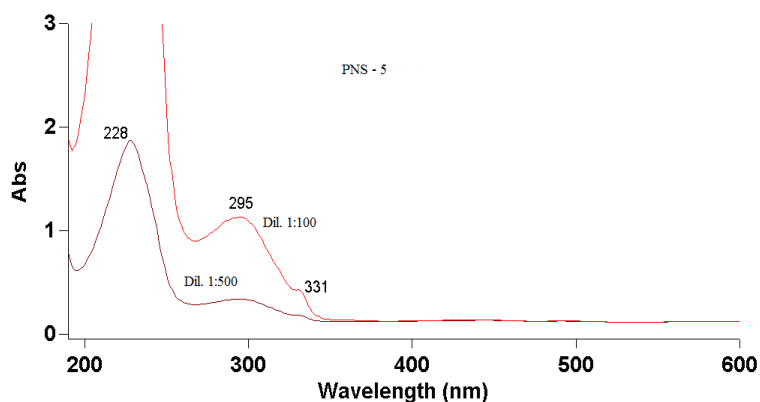


Figure 5. UV spectrum of the sample of PNS-5 with concentrations of: initial = 3 500 mg/l; 1: 100 = 35mg/l; 1: 500 = 7 mg/l.

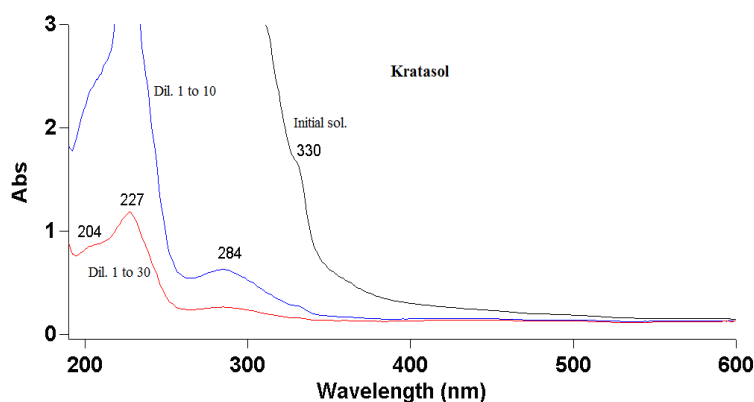


Figure 6. UV spectrum of the sample of "Kratasol" with concentrations of: init. = 350 mg/l; 1:10 = 35mg/l; 1:30 = 12 mg/l

Comparison of UV spectra of naphthalene, sodium salts of α - and β -HCNa, di- β , β -HCNa, PNS-4, PNS-5 and "Kratasol" indicates that the β -bands of naphthalene in the area of 210-220 nm in all β -HCNa, β -PNS and "Kratasol" are manifested at 227nm. β -bands of aromatic ring at 276 nm, apparently, are displaced depending on

the degree of condensation towards long-wave region (Giannuzzi and Stevie, 2004). In β -HCNa, di- β , β -HCNa and earlier synthesized PNS-4, it is detected at 275 nm (Figures 2-4). In "Kratasole" and PNS-5, this line has a bathochromic shift, in the "Kratasol" it appears at 284nm (Figure 6), and in the PNS-5 at 295 nm (Figure 5), which indicates about increase of the degree of polycondensation of naphthalene sulfoderivatives. Thus, in MMD of PNS-5 the share of oligomers fraction with a large number of condensed rings is more than in PNS- 4 and "Kratasol".

The results of studies of the molecular composition and MMD of PNS oligomers by mass spectrometry with matrix-assisted laser dissociation / ionization coupled with time of flight mass analyzer (MALDI-TOF) follows that in the transition from PNS-1 to the PNS -4 a share of low molecular weight oligomers is slightly reduced, and a share of high molecular weight oligomers (with 13-14 nuclei of naphthalene) smoothly increases, during the transition to an oligomer of PNS-5, a share of fraction of oligomers with the number of nuclei of naphthalene of more than 15 rings sharply increases up to 46-52% (Table 5), which causes the increase of its plasticizing ability.

Table 5. Molecular mass and MMD of synthesized oligomers of PNS

Oligomers of PNS	PNS -1	PNS -2	PNS -3	PNS -4	PNS -5
oligomers with 2-4 nuclei of naphthalene	10-16	12-18	10-18	8-16	6-12
oligomers with 5-9 nuclei of naphthalene	28-35	24-28	22-26	23-25	10-20
oligomers with 10-12 nuclei of naphthalene	38-44	35-42	36-44	34-42	8-12
oligomers with 13-14 nuclei of naphthalene	8-10	8-12	12-16	14-18	14-20
oligomers with number of nuclei of naphthalene more than 15	3-8	3-7	5-10	14-18	46-52

Furthermore, the composition of PNS-5 additionally contains salts of naphthalenesulfonic acid, naphthalenedisulphonic acid and sodium sulphate (Krasnov, 2012; Giannuzzi and Stevie, 2004).

5. Conclusions

Thus, researches show that α -PNS-1 (2,7-polymethylenenaphthalene- α - sulfonate of sodium), α -PNS-2 (5-7,3-3-polymethylenenaphthalene- α - sulfonate of sodium), β -PNS-3 (5-7 polymethylene naphthalene- β -sulfonate of sodium), β -PNS-4 (5-7,6-6-polymethylenenaphthalene- β - sulfonate), and β,β' -PNS-5 (4 -4, 8-8 polymethylene-naphthalene-1,5-oxymethylene-2,6 (β,β') - disulfonate), which synthesized at approximately the same of synthesis parameters (duration of condensations is 3-4 hours) have approximately equal parameters of influence on plasticity (from P1 to P3) and concrete strength $\Delta R_{28} = 20-37\%$.

Adjustment of parameter of PNS-4 synthesis (increase of the duration of condensation up to 6 hours) leads to a sharp increase of indicators (PNS-5) the effect on the plasticity of concrete grouts and concrete strength.

Weak plasticizing action on concrete mixtures of synthesized PNS-1 by PNS-4 is linked with discrepancy of MWD of oligomers by optimal composition, more precisely, by the low composition of high molecular fractions in the composition of PNS. Obtaining PNS with stronger plasticizing properties can be achieved by improving the methods of synthesis of PNS by adjusting the basic parameters of the synthesis. The obtained sample of polymethylenenaphthalenesulfonate (PNS-5) changes the plasticity of the cement paste from P1 to P5, increases the concrete strength by 60% in adulthood and in accordance with the State Standard 24211-2008 and 30459-2008 relates to additives of regulating properties of concrete - superplasticizer, increasing concrete strength and accelerating the hardening concrete kinetics.

At this stage, we not yet managed to make a conclusion by the identification of the reasons of the sharp increase of plasticizing properties of PNS5 (except for the effect of MWD) on concrete grouts and the concrete. For a complete explanation of this positive effect it is necessary to investigate the adsorption properties of PNS-5 molecules in cement systems, which is the subject of further research.

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