NEW TYPES OF SEQUESTRATE AGENTS AND CHELATING SURFACTANTS

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***Abstract**: This work evaluates the development of sequestering agents and chelating surfactants. These agents are the substances capable of removing a metal ion from a solution system via formation of a complex ion that does not possess the reaction activity of the ion removed. These agents are being used to eliminate the water hardness and some metals, such as iron; both having found a wide applicability in the textile industry. Surface activity of chelating surfactants was measured of stalagmometric method. The sequestration capacity was measured at 20 °C and 90 °C using media with different pH and in combination with precipitating opacity titration — the so-called Hampshire test.*

***Key words**: sequestering agents, chelating surfactants, surface activity, sequestering capacity*

1 INTRODUCTION

The sequestrate agents and surfactants are of textile auxiliary agents. Textile auxiliary agents are possible to define as compounds produced by chemical way and their mixtures. These mixtures make easy, speed up, improve or enable at all a technological treatment and are used at production and textile finishing. Those are the most frequent used as a component of detergents, then in the areas of textile finishing (mainly in a pre-treatment) but in further areas, e.g. dyeing cellulose materials or softening of water.

Sequestrate agents are generally compounds creating chelates, what are specific kinds of complex compounds surrounding the cation (such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}). The polyvalent cation is central atom and it is strongly locked by other inversely charged ions or a neutral molecule. Nowadays, several types of sequestering agents are in use, namely: polyphosphates, aminopolycarboxylates, hydroxycarboxylates, polyaminophosphonate and polyhydroxyphosphonate or polymeric carboxylic acid. [1]

Most traditional chelating agents do not break down readily in the environment. An increasing pressure on cleanness of wastewater and the use of biodegradable washing components and finishing baths of textile productions leads to new opinions on recently used sequestrates. These new types of sequestrate agents are for example: polycarboxylic compounds containing nitrogen (nitrolotriacetic acid [2], glutamic acid [3], aspartic acid and its derivates [4,5,6], agents basis of imidodisuccinic acid, polyasparic acid, hydroxyethylimidoacetic acid [7,8]); copolymers of acrylic acid with monosaccharides or oligosaccharides [9]; copolymers of acrylic acid with vinyl acetate [10]; grafted polysaccharides [11].

Surfactants are surface-active substances. Surfactants have a bipolar chemical structure - each containing one hydrophilic and one hydrophobic part. Surfactants accelerate the technological processes, reduce friction, stabilize disperse systems and affect the physical - mechanical properties. Since surfactants reduce the surface tension of solvents, facilitate the dissolution and removal of impurities. [12] The oldest and most widely used surface active agents is soap. Its disadvantage is the poor stability in hard water, which limits its utilization.

Then the chelating surfactants should combine the properties of surfactants and sequestering agents. There are various ways of preparations of chelating surfactants, when the starting materials are phthalic anhydride, citric acid and polyethylene glycol [13] or the synthesis of itaconic acid, phthalic anhydride, citric acid and oxypropylated diols [14] or fumaric acid with polyoxyethylated stearyl ether [15]. Another option is to prepare a mixture of amides of polyaminopolycarboxylic acids and their salts, alternatively mixtures of detergents containing self-sequestering molecules of tenside [16].

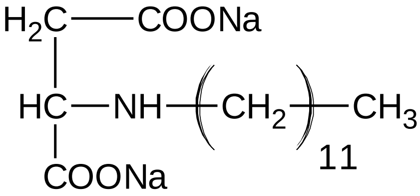
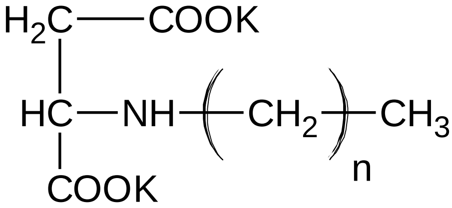
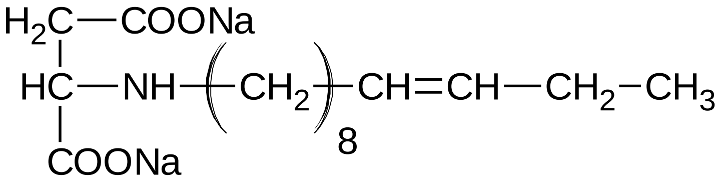
New types of biodegradable sequestering agents and chelating surfactants (derivatives of aspartic acid) were synthetized at Institute of Chemistry and Technology of Macromolecular Material of University of Pardubice. Basic properties (sequestering capacity and surface activity) were tested in this work.

2 EXPERIMENTAL

The samples of sequestering agents and chelating surfactants

Four types of chelating surfactants (Tab. 1) and three types of sequestering agents (Tab. 2) were tested in this study. Commercial product (sodium dodecylsulphate – Tab. 1) was used for the comparison of surface activity. The commercial sequestering agent Trilon M (Tab. 2) was used for the comparison of sequestering capacity.

Table 1 Structures of chelating surfactants

Sample	Chemical structure
No. 1	 *N*-dodecyl aspartic acid disodium salt
No. 2	 n = 10-18 *N*-cocoyl aspartic acid dipotassium salt
No. 3	 N-oleyl aspartic acid disodium salt

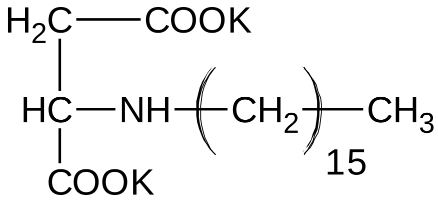
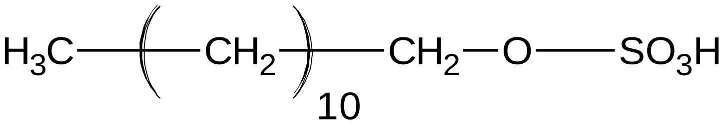
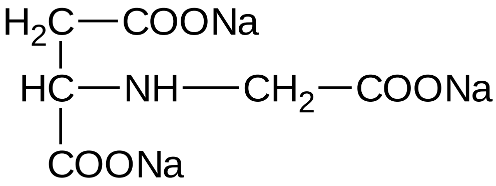
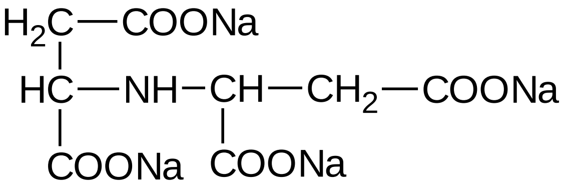
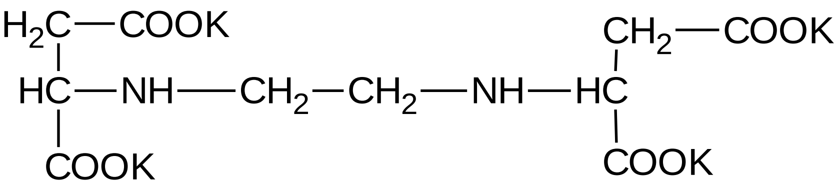
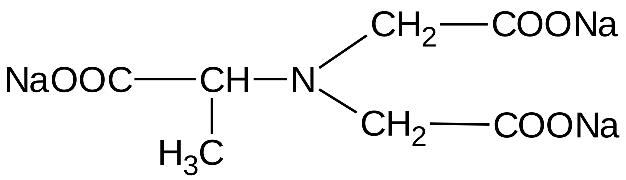
No. 4	 *N*-hexadecyl aspartic acid dipotassium salt
	 Sodium dodecylsulphate

Table 2 Structures of sequestering agents

Sample	Chemical structure
No. 5	 *N*-carboxymethyl aspartic acid trisodium salt
No. 6	 *N*-(1,2-dicarboxyethyl)aspartic acid tetrasodium salt
No. 7	 N,N'-ethylendiamin diaspartic acid tetrapotassium salt

Trilon M	 methylglycindiacetic acid trisodium salt

The evaluation of the sequestration capacity

The sequestration capacity was evaluated with model agents and compared to that of the commercially marketed sequestrate agent. Evaluation of the sequestration capacity was carried out for the Ca2+ ions when using precipitating opacity titration— the so-called Hampshire test [17], at two different temperatures of 20 °C and 90 °C. For the latter, a solution of sequestering agent was tempered at 90 °C and then titrated, when a solution of $CaCl_2.6H_2O$ had been selected as a volumetric solution. The equivalence point was determined via the respective absorbance of the opacity formed during the reaction that was measured at the wavelength of 650 nm in a glass cell (thickness: 1 cm). For this purpose, a spectrophotometer (model Spekol 11; Carl Zeiss Jena, Germany) was used and the data obtained were consequently evaluated with the aid of a standard method of quantitative analysis.

The evaluation of surface tension

For the measurement there was used a stalagmometric method. It is a relative method, in which are compared the numbers of drops of the known liquid n_1 of known surface tension y_1 with the number of drops of the measured liquid n_x, in which we find the surface tension. Between the measured and reference liquid (in this case distilled water) the following relation holds:

$$\mathbf{n_x . \gamma_x = n_1 . \gamma_1 \rightarrow \gamma_x = n_1 . \gamma_1 / n_x} \qquad (1)$$

$\gamma_1 = 72{,}75 \cdot 10^{-3}\ N.m^{-1}$ (at 20°C)

3 RESULTS AND DISCUSSION

Tables 3 – 6 state values of the sequestrate capacity of chelating surfactants for pH 9 – 12. Measured values are relatively low. This was to be expected due to the number of contained carboxyl groups in the molecule. Values of the sequestration capacity were expected by the chemical structure of the samples. Content of functional groups necessary to the sequestration is important. The best results were achieved by sample no. 1 (N-dodecyl aspartic acid disodium salt) at 20 °C and by sample no. 4 (N-hexadecyl aspartic acid dipotassium salt) at 90 °C.
Tables 7 - 9 state values of the sequestration capacity of prepared samples of sequestrate agents for pH 10 - 13. Table 10 state values of the sequestration capacity of commercial agent Trilon M. The sequestration efficiency depended on the increasing temperature and pH value. It is possible say that the sequestration the efficiency decreases with the increasing temperature. Measured values of prepared samples no.5, 6, 7 at 20 °C are comparable with the commercial sequestrate agent Trilon M. The sequestering ability at 90 °C of these samples is lower. The best results were

achieved by sample no. 6 [N-(1,2-dicarboxyethyl)-aspartic acid tetrasodium salt]. Sequestrate ability is the question of dissociative equilibria of creating complexes with ion Ca^{2+} and sequestrate agent.

Table 3 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 1 (N-dodecyl aspartic acid disodium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	9	9,3	**90 °C**	9	0,3
	10	18,7		10	5,8
	11	32,7		11	3,5
	12	35,0		12	6,9

Table 4 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 2 (N-cocoyl aspartic acid dipotassium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20° C	10	14,8	**90° C**	10	6,6
	11	3,3		11	6,6
	12	6,6		12	1,6

Table 5 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 3 (N-oleyl aspartic acid disodium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	9	7,7	**90 °C**	9	-
	10	21,3		10	21,4
	11	22,2		11	7,0
	12	29,9		12	22,5

Table 6 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 4 (N-hexadecyl aspartic acid dipotassium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	9	9,7	**90 °C**	9	48,4
	10	29,1		10	58,1

	11	19,4		11	77,5
	12	24,2		12	67,9

Table 7 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 5 (N-carboxymethyl aspartic acid trisodium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	10	173,2	90 ° C	10	92,8
	11	165,4		11	68,5
	12	173,1		12	52,5

Table 8 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 6 (N-(1,2-dicarboxyethyl)-aspartic acid tetrasodium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	11	194,4	90 ° C	11	169,3
	12	142,1		12	113,4
	13	209,8		13	101,3

Table 9 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for sample no. 7 (N,N'-ethylendiamin diaspartic acid tetrapotassium salt)

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	10	110,1	90 ° C	10	47,2
	11	104,9		11	47,1
	12	99,8		12	41,9

Table 10 Values of sequestration capacity [mg Ca^{2+}/ g] at 20°C and 90 ºC for Trilon M

	pH	S [mg Ca^{2+}/1g]		pH	S [mg Ca^{2+}/1g]
20 °C	11	203,7	90 ° C	11	166,6
	12	197,5		12	154,3
	13	222,3		13	154,2

Surface activity of prepared chelating surfactants was measured of stalagmometric method. The presence of sufficiently high alkyl is a precondition for an ability of the product to behave itself as a surface-active substance. Measured surface tension is comparable with commercial product of sodium dodecylsulphate – Tab.11; Fig.1. Sodium dodecylsulphate is commonly used anion-active surfactant. The surface activity of the samples no. 2 and no. 3 is significant. Its reflected already at a low concentration 0,1 g/l. Samples no. 1 and no. 4 show at room temperature the lower solubility, which may affect the measured value of the surface tension.

Table 11 Values of surface tension [mN/m] measured of stalagmometric method

	γ [mN/m]				
c [g/l]	**SDS**	**Sample no. 1**	**Sample no. 2**	**Sample no. 3**	**Sample no. 4**
0,1	71,12	63,26	46,56	60,94	71,56
0,25	62,69	60,63	43,33	49,32	68,47
0,5	53,31	58,39	42,90	46,68	65,39
0,75	48,91	57,25	42,59	44,77	62,36
1	45,00	56,14	42,28	44,10	60,63
1,5	38,46	54,56	41,67	41,87	57,25
2	35,42	52,75	41,08	41,57	56,14

SDS …………….sodium dodecylsulphate
Sample no. 1 ….(N-dodecyl aspartic acid disodium salt)
Sample no. 2 ….(N-cocoyl aspartic acid dikalium salt)
Sample no. 3 ….(N-oleyl aspartic acid disodium salt)
Sample no. 4 ….(N-hexadecyl aspartic acid dikalium salt)

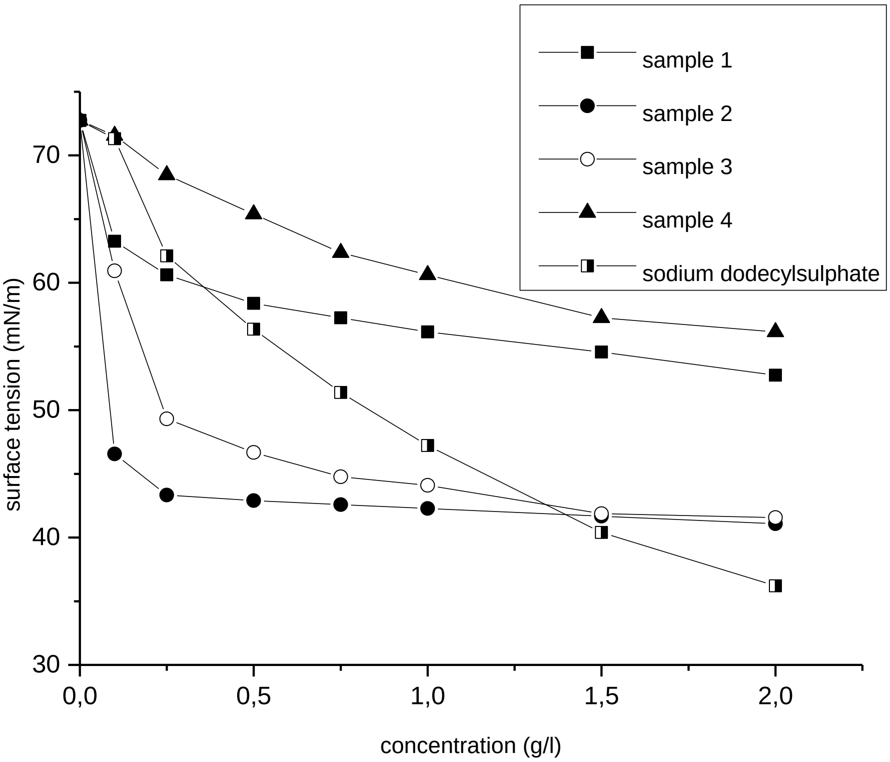


Figure 1 Dependence of surface tension on concentration by prepared samples and by commercial surfactant

4 CONCLUSIONS

In this work basic properties of four prepared samples of chelating surfactants and of three samples of sequestering agent were evaluated. These development samples were prepared by reaction of the appropriate amino compound with maleic anhydride. Prepared samples of chelating agents have a good surface activity. Measured surface tension is comparable with commercial product of sodium dodecylsulphate. The sequestering ability of chelating surfactants is relatively low. There is always a necessary compromise between efficiency and the possible biodegradability. Gained results are materials for next research. Sequestering capacity of prepared sequestering agents is good, comparable with commercial agent. Tested three samples could be used in various operations in the processing of textile materials (e.g. for water softening).

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