Chapter 15

Fluorescent Markers in Water Treatment

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Additional information is available at the end of the chapter

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Abstract

Both phosphonate- and polymer-based scale inhibitors have a broad spectrum of applications in water treatment technologies. However, the "online" monitoring of antiscalant content in an aqueous phase is still a challenge for researchers. A possible solution is provided by the fluorescent markers added to the feeding water. These can be either an antiscalant tagged or may represent the independent species. The review summarizes both the advantages and the drawbacks of these approaches along with such markers' classification, with a special emphasis on the novel fluorescent-tagged phosphonates. Besides, some unique opportunities provided by the fluorescent-tagged antiscalants for reverse osmosis membrane mapping, scale inhibition traceability, and a scale inhibitor localization in a circulation water facility are also considered and discussed.

Keywords: scale inhibition, fluorescent markers, water treatment

1. Introduction

Fluorescence is the emission of light by a substance that has absorbed light with a different wavelength or electromagnetic radiation. It has many practical and valuable applications, including in mineralogy, gemology, medicine, chemical sensors (fluorescence spectroscopy), fluorescent labeling, dyes, biological detectors, environmental monitoring, cosmic-ray detection, and, most commonly, fluorescent lamps [1–5]. However, in the field of water treatment, it has gained increasing interest mostly in the last decade [6–8]. The water treatment technologies use fluorescence phenomenon for the oil component control in wastewater [9], gaseous oxygen monitoring in wastewater [10], water leaks in industrial pipelines [11], for the total bacterial count [12], and for online scale inhibitors' content monitoring [6–8, 13]. Besides, the problem of a scale inhibition mechanism is still actual and requires applications of fluorescent-tagged inhibitors [14]. All these applications are to be considered in a recent review.

2. Fluorescent monitoring of a scale inhibitor content

Scale formation in the upstream oil and gas industry, reverse osmosis desalination processes, steam generators, boilers, cooling water towers, and pipes is a serious problem, causing significant plugging of wells, pipelines, membranes, and increasing the production cost [15]. A widely used technique for controlling scale deposition is an application of chemical inhibitors [16, 17]. Commonly used commercial antiscalants are represented by chemical families: polyphosphates (hexametaphosphate (HMP), tripolyphosphate (TPP), etc.), organophosphonates (aminotris(methylenephosphonic acid), ATMP; 1-hydroxyethane-1,1-bis(phosphonic acid), HEDP; 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC); ethylenediaminetetra(m ethylenephosphonic acid), EDTPH, etc), and organic polyelectrolytes (polyacrylates (PA), polycarboxysulfonates, (PCS)). Among these, the organophosphonates are dominating the world market at present. At the same time, phosphorus-based inhibitors are hardly biodegradable and persist for many years after their disposal, which lead to eutrification problems. Phosphorus discharges are therefore regulated in many countries worldwide, and permissible limits are constantly decreasing [18].

Increasing environmental concerns and discharge limitations have forced the scale-inhibitor chemistry to move toward "green antiscalants," that are readily biodegradable and have minimal environmental impact [17, 18]. Intensive efforts have been applied recently to develop the "green" alternatives to organophosphonates and nonbiodegradable polyacrylates. Among these novel inhibitors, such chemicals as polymaleates (PMAs), polyaspartates (PASPs), polyepoxysuccinates (PESAs), as well as their various derivatives, including co-polymers with PA, are worth mentioning [19, 20].

The concentration of polymeric antiscalants in the circulating system is usually changed by evaporation of water, reagent sorption on the pipe surfaces, and by a periodical discharge of the circulating water with some deposit. Therefore, an adequate monitoring of the polymer concentration is needed to minimize the consumptions of both scale inhibitor and water. Along with conventional monitoring methods based on UV–vis or potentiometry, the intensity of fluorescence emitted from either indifferent markers or a covalently bound to polymer tracer becomes a matter of choice [6].

The conventional monitoring methods for PA and for other polymeric antiscalants are classified into four groups [21]: (i) monitoring a spectral change caused by the interaction of PA with some metal-reagent complex (e.g., Fe^{3+}– SCN^{-} [22], Hg^{+}–diphenylcarbazide [21]); (ii) monitoring the concentration of an inert tracer added in proportion to PA by potentiometry or spectrophotometry (e.g., Li^{+}, K^{+}, Br^{-}, I^{-}, transition metal ion, dye) [23–25]; (iii) monitoring the intensity of fluorescence emitted from a tag covalently bound to PA [26, 27], and (iv) monitoring a change in spectroscopic characteristic on the interaction of PA with a metachromic or fluorochromic dye or a change in turbidity on the interaction of PA with a cationic surfactant [28–31]. Each of the abovementioned approaches has both advantages and the drawbacks. Indeed, the light absorption of PA complexes can be masked by the corrosion byproducts (formation of iron and copper complexes), by water background cation (iron, calcium, magnesium, copper) complexes formation, as well as by calcium carbonate and calcium sulfate colloid formation. At the same time, the indifferent markers do not guarantee the correct

PA concentration indication. Due to the differences in chemical properties of PA and a marker, the latter could have a different sorption ability relative to PA in a particular system. Therefore, the marker can provide either overestimation or an underestimation of PA content with a sequence of time. The PA-tagged fluorescent markers are treated as more reliable, although the more expensive solution [6]. Besides there is a risk of the PA antiscaling ability change due to the fluorescent fragment implementation. Thus, the chemical behavior of PA and of a corresponding PA-tagged fluorophore would be somehow different.

Recently, all the publications on the covalent binding of a fluorophore fragment to the antiscalant molecule are restricted by either the polyacrylate or polyaspartate moieties [6–8, 13, 32–36]. Any reports on the fluorescent-tagged phosphonate-based antiscalants are missing, although the online phosphonate monitoring is no less actual.

2.1. Inert tracers added to polymeric antiscalants

Irrespective of a broad spectrum of the commercially available fluorescent dyes, the number of reagents that have a high quantum yield in an aqueous medium is relatively small [37]. It should be noted that the fluorescence intensity strongly depends on pH, background cation concentration, and bioimpurities, normally present in the circulating systems. Besides, some dyes may change the color of industrial water. Therefore, it is desirable to use those reagents that have maximal light absorption in the ultraviolet spectral range, while the emission spectrum is likely to correspond to the visible blue light.

Usually the fluorescent marker molecules combine sulfo-1,8-naphtalimide with some carboxylate or sulfo-groups to provide an aqueous solubility (fluorescein, rhodamine, sodium 1,3,6,8-pyrene-tetrasulfate) [38–40]. These reagents have high quantum yield, chemical, and photostability

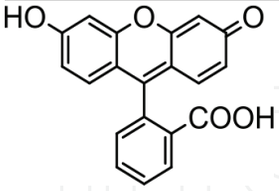
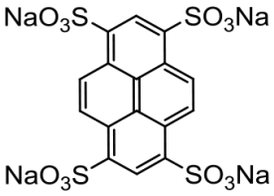
Dye formula	Absorption maximum in H_2O, nm	Fluorescence maximum in H_2O, nm	Quantum yield, %
 Fluorescein	473 (Buffer pH 5.0); 490 (Buffer pH 9.0)	514 (Buffers pH 5.0, pH 9.0)	92
 1,3,6,8-pyrene tetrasulfonic acid tetrasodium salt	374	403	56

Table 1. The excitation and emission properties of fluorescein and of 1,3,6,8-pyrene tetrasulfonic acid tetrasodium salt [11, 41].

[11, 41] as shown in **Table 1**. Besides, Kurita Water Industries Ltd. offers a 2-phenylbenzimidazole as a marker [42], while Kemira Oyj proposes a lanthanoid-based tracer [43].

2.2. Fluorescent-tagged scale inhibitors

An antiscaling ability of fluorophore-tagged polymers relative to their non-tagged analogues was reported in a very few studies [6, 44–46], as shown in **Table 2**. Usually the implementation of a fluorophore fragment either does not change the inhibitor efficacy or even provides some enhancement.

Fluorescent-tagged scale inhibitors *	Concentration scale inhibitors, mg·dm^{-3}	Inhibitor efficacy, %	Reference
$CaCO_3$ scale			
PA-F1	10	49 ± 3	[6]
PA-F2	10	51 ± 2	[6]
MA-AA-F1	10	44 ± 2	[6]
MA-AA-F2	10	54 ± 2	[6]
PA	10	70 ± 2	[6]
FPASP	6	90	[44]
PASP	6	70	[44]
$CaSO_4$ scale			
PA-F1	10	73 ± 3	[6]
PA-F2	10	78 ± 2	[6]
MA-AA-F1	10	61 ± 2	[6]
MA-AA-F2	10	65 ± 2	[6]
PA	10	58 ± 2	[6]
AA–APEM–APTA	9	96	[45]
AA–APEM	9	95	[45]
PAA	9	85	[45]
$Ca_3(PO_4)_2$ scale			
FPASP	12	95	[46]
PASP	12	30	[46]

PA-F1: co-polymer acrylic acid–N-allyl-4-methoxy-1,8-naphtalimide. **PA-F2:** co-polymer acrylic acid–N-allyl-2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzamide (N-allylamidefluorescein). **MA-AA-F1:** co-polymer acrylic acid–fumaric acids–N-allyl-4-methoxy-1,8-naphtalimide. **MA-AA-F2:** co-polymer acrylic acid–fumaric acids–N-allyl-2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzamide (N-allylamidefluorescein). **PA:** Na-salt of polyacrylic acid (Shandong TaiHe Water Treatment Co.Ltd.). **FPASP:** fluorescent polyaspartic acid was synthesized with partially ethanolamine-modified polysuccinimide, p-toluenesulfonyl chloride and 3-amino-9-ethyl carbazole. **AA–APEM–APTA:** co-polymer acrylic acid–oxalic acid–allylpolyethoxy carboxylate–8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine). **AA–APEM:** co-polymer acrylic acid–oxalic acid–allylpolyethoxy carboxylate. **PAA:** poly(acrylic acid), MW 1800 Da.

Table 2. An antiscaling ability of fluorophore-tagged polymers relative to their non-tagged analogues.

Inhibitor, 10 mg·dm^{-3}	**Cation**									
	Ca^{2+}		Mg^{2+}		Zn^{2+}		Cu^{2+}		Fe^{3+}	
	Cation concentration, mg·dm^{-3}									
	20	200	10	100	2	20	0.5	5	0.3	3
	Fluorescence intensity change relative to the cation-free solution, %									
PA-F1	100 ± 1	93 ± 1	100 ± 1	100 ± 1	97 ± 1	96 ± 1	91 ± 1	74 ± 1	99 ± 1	94 ± 1
PA-F2	58 ± 1	43 ± 1	66 ± 1	62 ± 1	85 ± 1	42 ± 1	96 ± 1	48 ± 1	108 ± 1	94 ± 1
MA-AA-F1	81 ± 1	71 ± 1	91 ± 1	84 ± 1	93 ± 1	85 ± 1	90 ± 1	74 ± 1	94 ± 1	62 ± 1
MA-AA-F2	87 ± 1	81 ± 1	100 ± 1	138 ± 1	93 ± 1	90 ± 1	88 ± 1	69 ± 1	92 ± 1	60 ± 1

Table 3. The dependence of inhibitor fluorescence intensity on inorganic cation concentration (pH 8.0, 25°C) [6].

However some more experimental work has to be done in this field to make the situation clear.

Only a single paper reports on the influence of the background cations on the quantum yield of an antiscalant [6], as shown in **Table 3**. The corresponding data clearly indicate that cations can either increase or sufficiently diminish the fluorescence intensity of some reagents, while some others stay insensitive to this influence. Anyhow this property has to be taken into account for any particular application of a tracer.

A covalent implementation of the fluorescent fragment into the polymer moiety can be performed in two ways. The first one assumes an attachment along with the polymer formation process. Another one is based on the fluorophore binding to the readymade polymer matrix. The first approach is used for the radical involved synthesis of co-polymers bearing carboxylate, sulfonic, or polyalkylenoxyde groups (acrylic, methacrylic, or maleic acids) and the dyes with an active double bond. The reaction runs in an aqueous solution being initiated by persulfates, by H_2O_2, benzoylperoxide, or by 2,2′-azobisisobutyronitrile (0.1–1.0%, mass). Also, such molecular mass regulators as sulfur compounds [47] or sodium hypophosphite are used [48]. These regulators keep the molecular masses within 2000–200,000 Da. The low molecular mass Mw of a polymer (1000 Da < Mw < 10,000 Da) is known to provide the most effective scale inhibition.

Generally, the fluorescent markers should meet the following requirements: (i) synthetic availability of the dyes capable for polymerization; (ii) a dye chemical stability during polymerization; (iii) a minimal influence of a dye on the polymer structure and on its Mw; (iv) the polymer structure, which should not affect the optical properties of a marker.

Fluorescent monomers used for a scale inhibitor implementation could be classified into three main categories: (i) aromatic hydrocarbons and their derivatives, for example, polyphenilic hydrocarbons, hydrocarbons with arylethylene or arylacetylene groups, and so on; (ii) heterocyclic monomers; and (iii)monomers with a carbonyl group.

Polyphenylhydrocarbons demonstrate an intensive fluorescence within a violet-to-blue visible spectrum region. Among these there are vinylanthracene (Rhodia Operations) [49], potassium

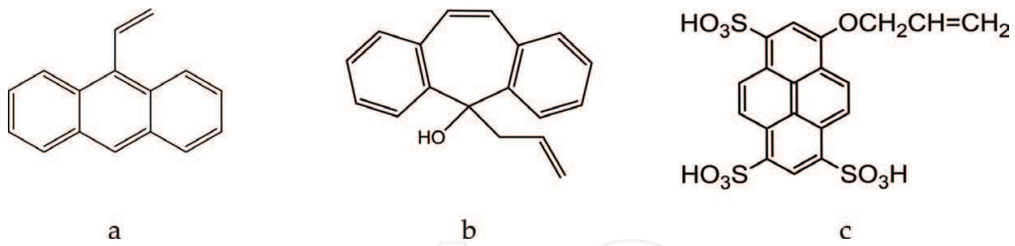
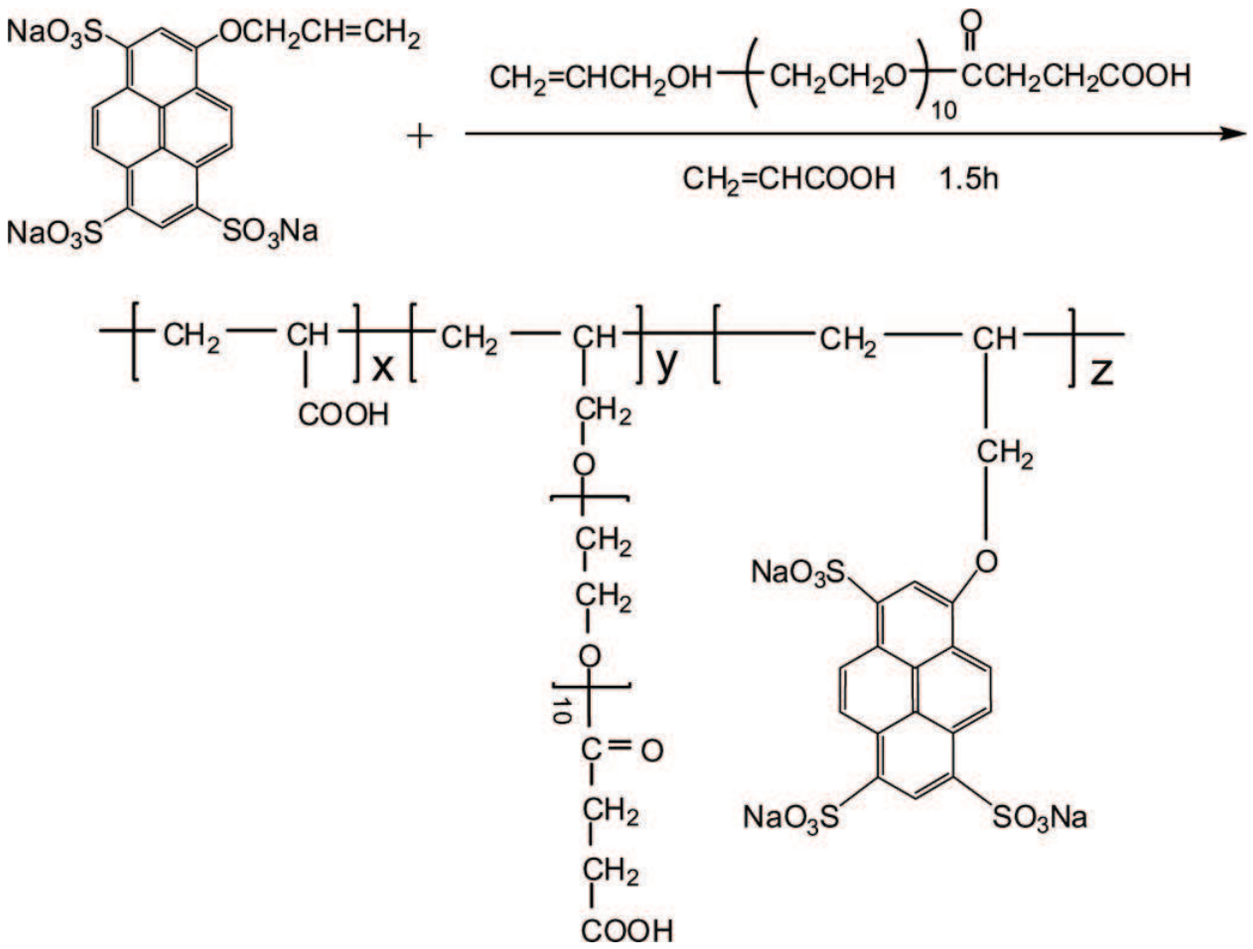


Figure 1. 9-vinyl anthracene (a), 2-allyldibenzosuberenol (b), and 8-(allyloxy)-1,3,6-pyrene trisulfonic acid (c) chemical structures.

2-alkyloxonaphtyl-6,8-disulfonate (China National Offshore Oil Corp.) [50], 2-allyldibenzosuberenol, and 9-allyl-9-hydroxyanthrene (Kurita Water Industries Ltd.) [51], as shown in **Figure 1**.

Numerous research groups synthesize a marker monomer via the 8-hydroxypyrene-1,3,6-trisulfonic acid (pyranine) interaction with allylchloride (**Figure 1c**) [52, 53]. Such a monomer reveals an intensive fluorescence with a maximum at 431 nm. Quantum yield is high. It depends on pH and varies within 80–90%. Then, these fluorescent monomers are co-polymerized (radical polymerization) with an antiscalant-forming monomers, for example, acrylic acid and so on. (**Scheme 1**) [8].



Scheme 1. Preparation of co-polymer acrylic acid-oxalic acid-allylpolyethoxy carboxylate-8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt.

A co-polymerization of the pyranine-based monomers with maleic anhydride is also possible [35, 53–56]. The fluorescence intensity of an antiscalant correlates well with the fluorophore content in the scale inhibitor (R~0.99), while the detection limit ranges from 1 to 2 $mg \cdot dm^{-3}$ [35, 53–56]. Among the numerous water treatment reagents developed by Nalco Chemical Co. there are two fluorescent monomers of the pyranine group [57], as shown in **Figure 2**.

Besides antiscalants, these monomers can also be implemented into some biocides. However, the Nalco Chemical Co. also uses some inert tracers along with the polymer-tagged ones.

Another important group of fluorophore monomers is represented by 5- and 6-member heterocycles [44, 49], particularly by a vinylimidazolic monomer [58], as shown in **Figure 3**.

Among the fluorophores with a carbonyl group, it is reasonable to mention an inhibitor with a fluorescence fragment dimethyl-(4-(7-methoxylcoumarin))-methyl-(acryloyloxy)-ethyl-ammonium bromide [59], as shown in **Figure 4**. It reveals the maximal fluorescence intensity at 390 nm.

Several publications report on the naphthalic acid-based markers for biochemical analysis application [60, 61]. An interest in these reagents is associated with both synthetic availability of some valuable 1,8-naphthalimide derivatives and with promising optical properties [62–64]. Ecolab Inc. (USA) has proposed fluorescent monomers derived from 3,4-7H-benzo[d,e] anthracenedicarboxylic acid for the antiscalant labeling [65]. Among these N-(3-N′,N′-Dimethylaminopropyl)benzo(k,l)xanthene-3,4-dicarboxylic imide of 2-hydroxy-3-allyloxypropyl quaternary salt seems to be the most interesting, as shown in **Figure 5**.

A considerable attention is paid to the 1,8-naphthalimide derivatives in relevance to the desalination processes (reverse osmosis) [66–68], as shown in **Figures 6** and **7**.

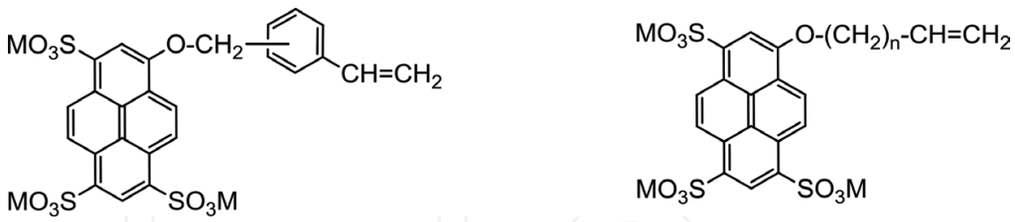


Figure 2. Nalco fluorofores for a covalent attachment to the scale inhibitors [57]; M = H^+, NH_4^+, K^+, Na^+, Cs^+, Rb^+, Li^+; n = 1, 2, 3, 4, 6 or 9.

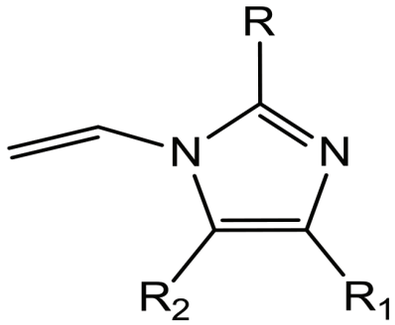


Figure 3. Vinylimidazolic monomer structure; R, R^1, and R^2 are denoted as H, alkyl, aryl, phosphate, nitrate, or sulfate groups.

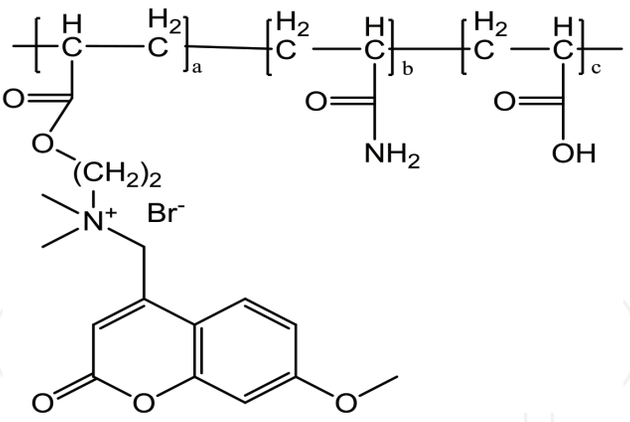


Figure 4. An antiscalant with a dimethyl-(4-(7-methoxylcoumarin))-methyl-(acryloyloxy)-ethyl-ammonium bromide fragment [59].

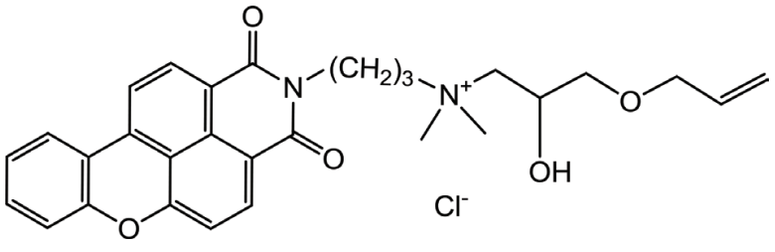


Figure 5. N-(3-N′,N′-Dimethylaminopropyl)benzo(k,l)xanthene-3,4-dicarboxylic imide of 2-hydroxy-3-allyloxypropyl quaternary salt [65].

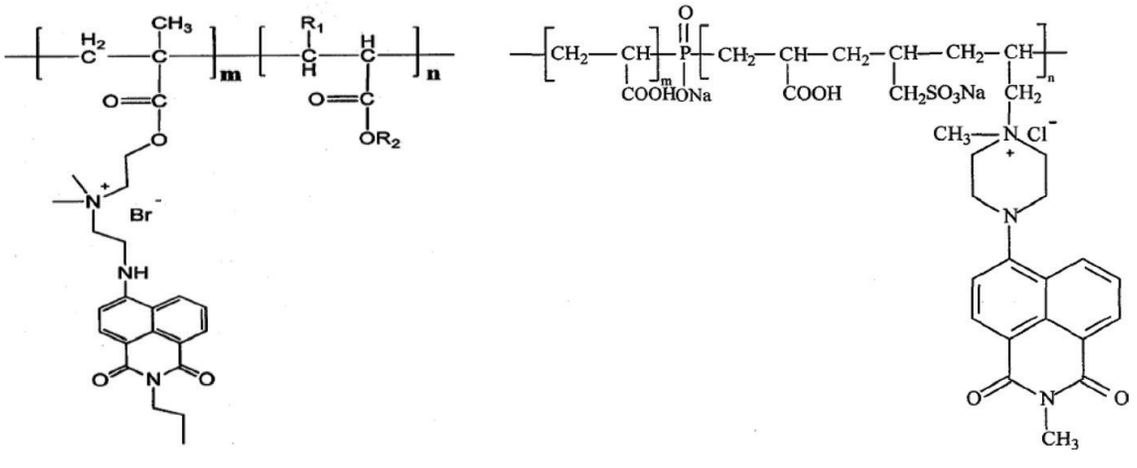


Figure 6. Some 1,8-naphthalimide-tagged antiscalants [66, 67].

An implementation of a fluorophore into a PASP molecule is normally performed not via co-polymerization but by its attachment the already formed polymer molecule [46, 69, 70]. Some authors propose 3-amino-9-ethylcarbazole [71] or N-(2,3-epoxypropyl)carbazole [72] for the PASP molecule labeling, as shown in **Figure 8**.

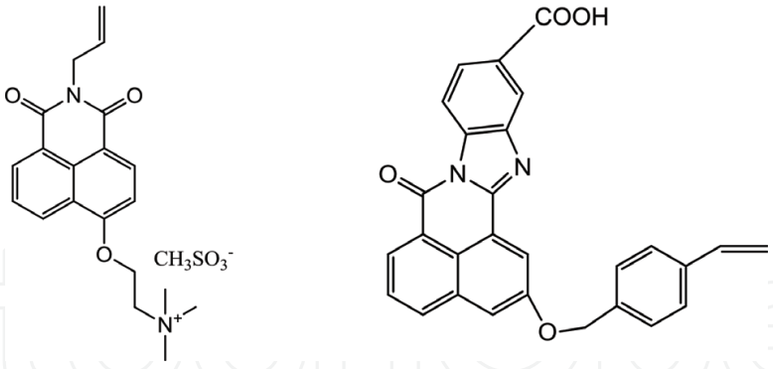


Figure 7. Some 1,8-naphthalimide-based fluorophore monomers developed by Nalco for antiscalant labeling [68].

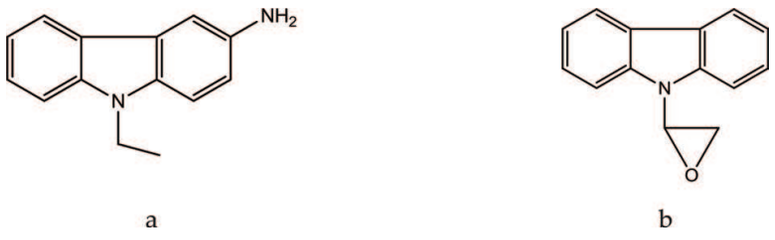
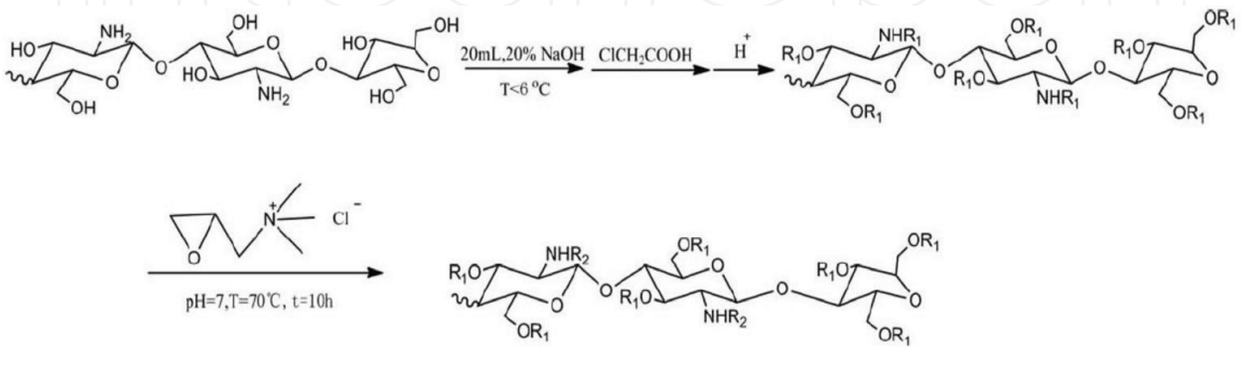


Figure 8. 3-amino-9-ethylcarbazole (a) and N-(2,3-epoxypropyl)carbazole (b) fluorophore structures.

A special attention has to be paid to the communication, where a fluorescence of the inhibitor itself (carboxymethyl ammonium olygochitosan) is reported [73]. This antiscalant does not need any fluorescent marker attachment. The corresponding synthetic method is presented in **Scheme 2**.

It was found that the fluorescence intensity increases under acidic conditions. Thus, the hydrogen bonding and the electrostatic repulsion provide a rigid and densely stabilized structure formation, which is necessary for inducing fluorescence. Hence, the fluorescence of carboxymethyl quaternary ammonium oligochitosan may have been caused by the effect of the n → π* transition between -C=O- and -NH- and the special rigid structure formed by hydrogen bonding and a charge–charge repulsion [73]. The fluorescence maximum corresponds to 460 nm, while the detection limit at pH 5–9 is within 0.61 mg·dm^{-3}.

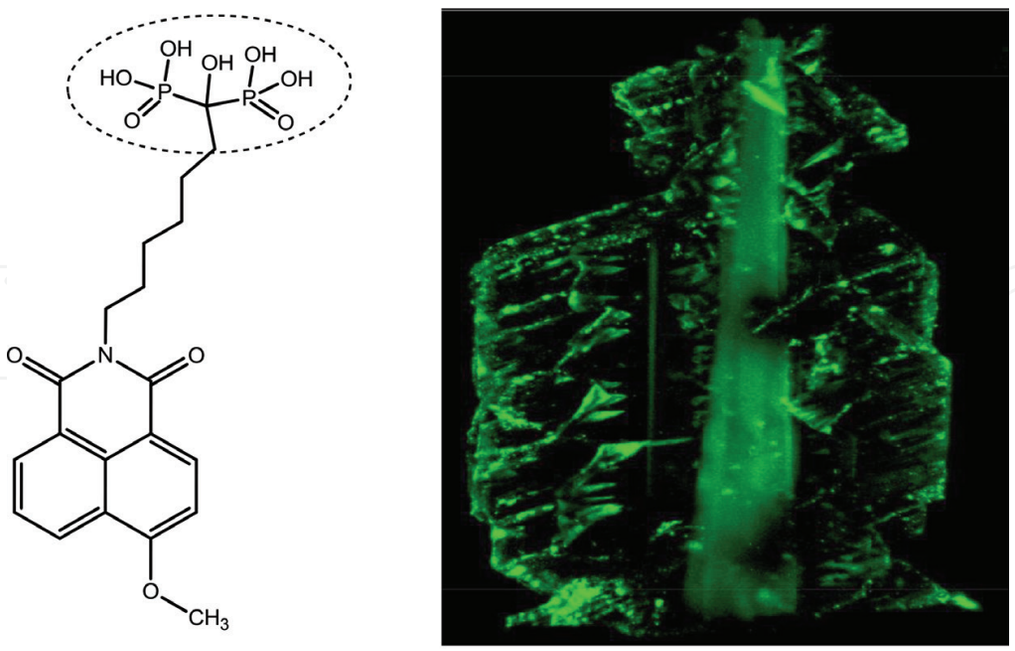


Scheme 2. Carboxymethyl quaternary ammonium oligochitosan synthesis.

2.3. Visualization of scale inhibition mechanisms

Irrespective of the broad, successful, and long-term antiscalant applications, the mechanisms of scale inhibition still appear in the matter of discussions [14, 74–81]. In this sense, the fluorophore-tagged antiscalants can provide the unique and amazing opportunities to get a deep insight of the scale inhibition mechanisms. As far as we know, recently, such reports on the scale inhibition visualization are missing. However, our research group managed to synthesize a conjugate of 1,8-naphthalimide and HEDP: 1-hydroxy-7-(6-methoxy-1,3-dioxo-1*H*-benzo[de]isoquinolin-2(*3H*)-yl)heptane-1,1-diyldi(phosphonic acid), (HEDP-F), as shown in **Figure 9a**. This reagent was tested as an antiscalant in gypsum scale formation experiments performed according to NACE protocol [82]. According to this protocol, a calcium-containing brine and a sulfate-containing brine are mixed to form a supersaturated gypsum aqueous solution in the presence of 0.5–15 mg·dm $^{-3}$ of an inhibitor at ambient temperature. Then, this solution is kept for 24 h at 71°C, cooled, and analyzed for residual calcium content by EDTA titration. In a parallel run, the gypsum crystals have been isolated and analyzed with a fluorescence scanning microscope, as shown in **Figure 9b**.

Unlike the scanning electron microscopy, the fluorescence provides a unique possibility to look inside the crystal. Therefore, all the steps of crystal formation become visible. One can see that the bright crystal rod ("lightsaber"), initially formed by nanoparticles, is completely covered with HEDP-F. Then, this rod becomes the center of gypsum layers' growth without any resistance or involvement of a HEDP-F antiscalant (massive dark layer). Finally, after the gypsum crystal formation is finished, the residual HEDP-F molecules get adsorbed on its surface, particularly at the edges of a crystal lattice, forming the outer layer. This is indicated by green spots and stripes[1]. Evidently,



a b

Figure 9. HEDP-F (a) and an image of a Gypsum crystal, isolated in presence of HEDP-F (b); laser scanning microscope LSM-710 Carl Zeiss, lambda mode with 458 nm excitation; 26.10.2017. Data presented by Semen Kamagurov, Sergey Tkachenko and Maxim Oshchepkov.

[1]A full-scale publication is under in preparation

these data reveal a mechanism, significantly different from the conventional ones [74–81]. By all means the visualization of scale inhibition mechanisms by fluorescent-tagged antiscalants seems to become a very promising tool of the scale inhibition theory development.

Besides, these reagents can provide some unique opportunities for reverse osmosis membrane mapping, scale inhibition traceability in the pipes, and a scale inhibitor localization in a circulation water facility.

3. Gaseous oxygen monitoring in wastewater

Biological treatment of wastewater includes activated sludge aeration. This in turn raises a problem of the gaseous oxygen content monitoring. One of the most promising solutions here is the fiber-optic oxygen sensor application. This method is based on the ability of oxygen molecules to suppress the luminescence of some luminofores [10, 83]. A fruitful application of some pyrene- or decacylene-based fluorophores along with some ruthenium complexe is reported: $(Ru(bpy)_3$, $Ru(phen)_3$, $[Ru(dpp)_2Phen]^{2+}$ (dpp = 4, 7-diphenyl-1,10-phenanthroline, Phen = 1,10-phenanthroline) [84], as shown in **Figure 10**. Also some terbium(III) complexes have been immobilized

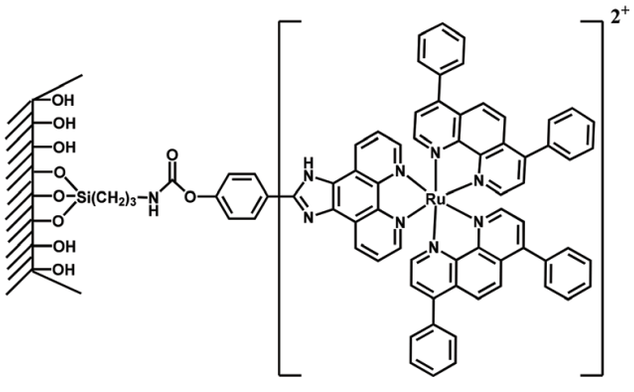


Figure 10. Structure of $[Ru(dpp)_2Phen]^{2+}$.

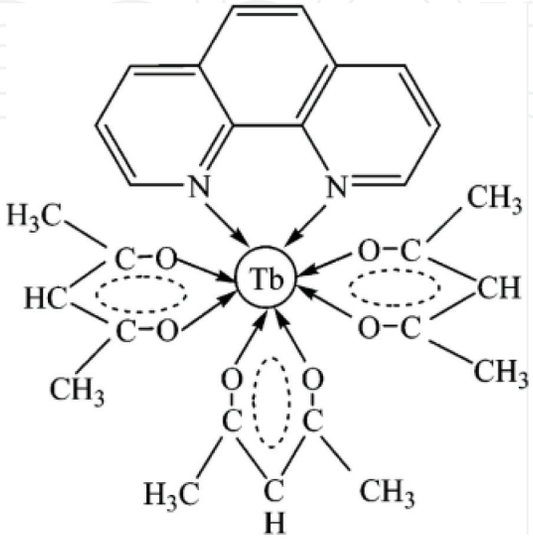


Figure 11. Structure of $Tb(acac)_3phen$.

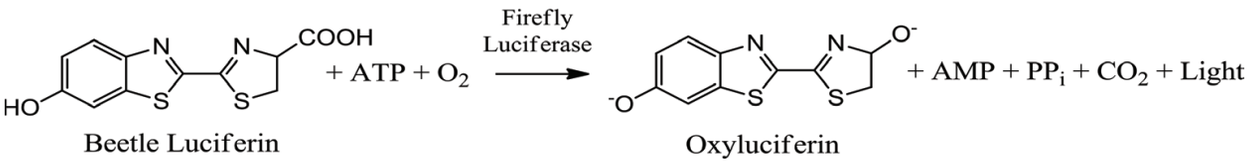
on aluminum oxide ($Tb(acac)_3phen$), where acac-acetylacetone [85], as shown in **Figure 11**, as well as some porphyrin complexes of Pt and Pd [86], is worth mentioning.

The emitted blue light (~ 475 nm) of a photogenerator excites the fluorescence of a specially selected chemical complex, placed at the end of a fiber-optic oxygen sensor (sol–gel matrix). The exited complex generates fluorescence with a wavelength which is around 600 nm. This fluorescence gets suppressed by the oxygen present in a sample [87–89]. This provides an effective oxygen concentration measurement in water within the range from 0 to 40.7 ppm [90].

4. Fluorescent total ATP count in wastewaters

The total bacterial count in wastewater is based on bioluminescence. Normally it is used for the industrial and wastewater quality assessment, while for the drinking water it is not so common. The method is known since 1947, when McElroy has demonstrated that bioluminescence of a glowworm is closely associated with adenosine triphosphate (ATP) content [91]. Thus, the measurement of ATP provides an efficient indication of bacterial pollution of water according to **Scheme 3** [12]:

Analysis involves the firefly luciferase-luciferin system. Its contact with ATP molecules generates the "cold" light, counted by a luminometer within 15–20 s. The sensitivity of analysis is very high. It provides detection of 10^{-17} ATP moles per liter. Recently, there have been some standard solutions for luminometers present at the market: EnSURE™, SystemSURE Plus™ Clean Trace™, NovaLum™, Firefly 2™, Accupoint™, russian-made LYUM-1, Lumitester PD-20™ etc. [92].



Scheme 3. Bioluminescent reaction catalyzed by firefly luciferase.

5. Other applications

Some water treatment facilities require the oil component control in wastewater [9, 93]. Organic pollutants can occur in the cooling water, in the technical-use water, in a boiler-feeding water, and due to the leaks of oils into the steam condensate. For online pollutants' monitoring, the fluorescent sensors are broadly used. The method is highly sensitive. Depending on the type of oil, the detection limits may vary from 1 to 100 ppm. Most of the oils contain some polycyclic aromatic hydrocarbons (PAHs) [94], capable of generating blue or violet fluorescence being exposed to UV irradiation. Usually the excitation light wavelength corresponds to 254 nm, while the detection operates in a 360 nm spectrum range.

Finally, one of the first known applications of fluorophores in water treatment should be mentioned. It is associated with water leaks detection in industrial pipelines. To solve this problem, some fluorescent indicators, for example fluorescein, have been merely added to the circulating water [11].

6. Conclusions

The fluorescent markers added to the circulating water or wastewaters find a broad spectrum of analytical applications for online quality monitoring. The most promising and a fast-developing field is a scale inhibitor concentration detection via antiscalant-tagged reagents. At the same time the visualization of scale inhibition mechanisms by the fluorescent-tagged antiscalants is a very promising tool of the scale inhibition theory development. Besides, these reagents can provide some unique opportunities for reverse osmosis membrane mapping, scale inhibition traceability, and a scale inhibitor localization in a circulation water facility.

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Conflict of interest

For the present study, no economic interest or any conflict of interest exists.

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