Barite crystallization in presence of novel fluorescent-tagged antiscalants

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Abstract

Formation of barite crystals in a bulk supersaturated aqueous solution at ambient temperature is studied in presence of two novel fluorescent-tagged antiscalants: a bisphosphonate 1-hydroxy-7-(6-methoxy-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)heptane-1,1-diyldi-(phosphonic acid), HEDP-F, and a co-polymer of N-allyl-4-methoxy-1,8-naphtalimide with acrylic acid, PAA-F1 by fluorescent microscopy, scanning electron microscopy (SEM), turbidimetry, dynamic light scattering (DLS) and a particle counter technique. Both scale inhibitors at a 20 mg dm^{-3} dosage are found to be effective in supersaturated BaSO₄ solutions with saturation index (SI) 10 at 25°C (0.001 mol·dm⁻³). Herewith PAA-F1 reveals a higher efficacy than HEDP-F. At the same time a dramatic impact of foreign background "nanodust" particles on antiscalant efficacy is detected and interpreted in terms of barite nucleation. It is demonstrated, that barite nucleation takes place exclusively on "nanodust" particles as a bulk heterogeneous process. Thus an antiscalant molecule acts not so much as barite nuclei surface modifiers, but as the modifiers of "nanodust" particles. It is shown that inter alia the lower efficacy of HEDP-F relative to PAA-F1 is associated with insoluble barium salts formation by the former reagent (tentatively by Ba₂HEDP- $F \cdot nH_2O$ or BaH₂HEDP- $F \cdot mH_2O$). Thus an efficacy evaluation may be strongly affected by the way of antiscalant introduction into the system. Being initially added to the barium brine both antisclants demonstrate greater difference in barite scale inhibition, than in the case of the sulfate brine. Both fluorescent-tagged reagents reveal perfectly an antiscalant location on barite crystals. Despite expectations they cover BaSO₄ crystal surface uniformly, and indicate no special concentration of antiscalant on crystal's kinks, edges etc. Thus the scale inhibitors affect rather the primary nucleation step of barite solid phase formation than the secondary one (macro-crystal growth phase).

Keywords: barite, fluorescence, fluorescent-tagged antiscalants, fluorescent microscopy, turbidimetry, dynamic light scattering, scale inhibition mechanism, polyacrylate, bisphosphonate.

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Introduction

Barium sulphate scale formation is a matter of significant problems in the oil recovery industry. Barite scale deposits can precipitate in the pipes and this affects oil production by restricting fluid flow [1, 2]. Barite scale is difficult to remove [3], and its formation can lead to an additional increase in operating costs [1-3]. A common strategy to reduce barite scale formation is the addition of phosphonates [4-6] or of polyacrylates [1, 7] to the seawater injected in the reservoir to inhibit BaSO₄ nucleation or growth. However, irrespective of numerous studies over past five decades [8-17], the mechanisms of barite formation from aqueous solutions, and of the influence of additives still remain unclear [1, 2, 5, 15, 16].

Thus a better understanding of the mechanism of barite formation from the bulk aqueous solutions in presence of additives may help in the design of more effective strategies for barite scale prevention. A possible solution might be associated with antiscalant molecule visualization during BaSO₄ crystallization from a supersaturated barite aqueous solution. Such visualization can be provided by fluorescent-tagged antiscalants, developed over past decade for scale inhibitor on-line monitoring in industrial water circulation facilities [18]. Surprisingly, till 2019 no attempts have been registered to apply these compounds to the scale formation mechanism studies. Our first publication in this field [19] revealed serious gaps in the conventional scale inhibition theory in relevance to gypsum scale formation. Our recent study is focused on the visualization of two different fluorescent-tagged antiscalants during barite crystals formation in a bulk supersaturated aqueous solution at ambient temperature, Figure 1.

The first one belongs to the phosphonate group: 1-hydroxy-7-(6-methoxy-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)heptane-1,1-diyldi(phos-phonic acid), HEDP-F [19], while the second one represents a co-polymer of N-allyl-4-methoxy-1,8-naphtalimide with acrylic acid, PAA-F1 [20]. The barite scale formation process was monitored by fluorescence microscopy, scanning electron microscopy (SEM), light scattering technique (dynamic light scattering, DLS; Tyndall's effect, particle counter measurements) and turbidity measurements. Some supplement information was obtained from X-Ray diffraction and chemical speciations. At this point, both solid and liquid phases are monitored along each other.



Figure 1. Naphthalimide-tagged bisphosphonate HEDP-F and polyacrylate PAA-F1 molecular structures.

1. Experimental

1.1. Reagents and stock solutions

Analytical grade chemicals were used for brine preparations. Stock solutions of barium chloride and sodium sulfate were prepared from the corresponding crystalline solids (Sigma-Aldrich; EKOS-1, Russia) using deionized water. The deionized water and the final brines were filtered through 0.45 µm Millipore nylon filters.

All stock solutions were tested by DLS for the presence of background nanoparticles. It was found that all of them have 1 nm size particles and a sufficiently smaller amount of 200 to 400 nm particles. These exist as impurities in all samples and are characterized by Malvern correlation coefficients ranging from 0.05 to 0.08. Besides, both brines have been analyzed for the background solid suspended particles content operating with a particle counter SLS-1100 (Particle Measuring Systems Inc.), Table 1.

Particle counter channel	≥100 nm	≥ 200 nm	≥ 300 nm	≥ 500 nm				
Sample	Number of solid suspended particles in 1 ml							
Barium chloride, $0.02 \text{ mol} \cdot \text{dm}^{-3}$	4150	1900	890	470				
Sodium sulfate, $0.02 \text{ mol} \cdot \text{dm}^{-3}$	5170	4300	3100	2500				
Deionized water	660	75	36	13				
TAP water	300 000	53 000	14 000	6 000				

Table 1. Cumulative numbers of the background solid suspended particles in the brines estimated with particle counter SLS-1100 after nanofiltration.

It was demonstrated that irrespective of the filtration procedure all the initial solutions still contain a significant amount of solid suspended particles, including rather large ones (much bigger than an average filter pore size). This could be explained by deviations from the mean value in the pore size distribution as well as by some microcracks in filtering material.

The 1-hydroxy-7-(6-methoxy-1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)heptane-1,1-diyldi(phos-phonic acid), HEDP-F and a co-polymer of N-allyl-4-methoxy-1,8-naphtalimide with acrylic acid (PAA-F1) were synthesized as described elsewhere [19, 20]. PAA-F1 represents an acrylate polymer (molecular mass *ca*. 4000 Da) with 0.5% mass of fluorophore fragment.

1.2. Sample preparation and barite precipitation tests

Two synthetic brines were prepared with deionized water: a barium containing brine $(BaCl_2 \cdot 2H_2O, 0.02 \text{ mol} \cdot dm^{-3}, \text{ pH 6})$ and a sulfate containing brine $(Na_2SO_4, 0.02 \text{ mol} \cdot dm^{-3}, \text{ pH 6})$. Being mixed at ambient temperature with deionized water at different volume ratios (1:1:n; n corresponds to H₂O volume), these brines give a supersaturated barium sulfate solutions with pH 6 within the concentration range from 0.01 to 0.00001 mol \cdot dm^{-3}. The corresponding background electrolyte (NaCl) concentration was changing therefore from 0.02 to 0.00002 mol \cdot dm^{-3}.

In a present study the saturation index SI at 25°C is denoted as:

$$SI = [BaSO_4]_{init} / [BaSO_4]_{equil}$$
(1)

where $[BaSO_4]_{init}$ corresponds to the barite concentration in aqueous solution at the moment, when the brines get mixed, while $[BaSO_4]_{equil}$ indicates the equilibrium concentration. According to [11] the solubility product K_{sol} of $BaSO_4$ in water at 25°C corresponds to: $-\log K_{sol} = 9.959$. A presence of some background NaCl slightly increases this value. We take roughly $[BaSO_4]_{equil} = 0.00001 \text{ mol} \cdot \text{dm}^{-3}$ for all samples used. Therefore 0.01 mol $\cdot \text{dm}^{-3}$ initial concentration of $BaSO_4$ corresponds to a saturation index $SI \sim 1000$, *etc*.

After the brines get mixed, an aqueous phase was analyzed immediately for turbidity and by DLS technique. Unless specifically stated an antiscalant solution in all cases was initially added to the deionized water, then this water was mixed with sulfate brine, equilibrated for 30 minutes, and then the barium brine was added to this mixture. BaSO₄ crystals were sampled for fluorescent, X-Ray diffraction and SEM analysis after several days equilibration with an aqueous phase. To do this, *ca*. 1 ml of BaSO₄ saturated solution with crystals was put on the glass surface and the liquid phase was cautiously soaked by a filter paper, while the residual solid phase was dried on the air. Alternatively, the fluorescent analysis of crystals was performed directly in the liquid phase.

Besides barite scaling, some blank experiments were run with antiscalant solutions in presence of barium ions in order to estimate the possible side equilibria:

$$2Ba^{2+} + H_2HEDP - F^{2-} + 2H_2O \leftrightarrows Ba_2(HEDP - F) \cdot nH_2O_{solid} + 2H_3O^+$$
(2)

$$Ba^{2+} + H_2hedp - F^{2-} \leftrightarrows BaH_2(HEDP - F) \cdot mH_2O_{solid}$$
(3)

$$nBa^{2+} + H_xPAA - F1^{(2n-x)-} + xH_2O \leftrightarrows Ba_n(PAA - F1) \cdot nH_2O_{solid} + xH_3O^+$$
(4)

1.3. Fluorescent microscope measurements

Confocal microscopy measurements have been run with laser scanning confocal microscope LSM-710-NLO (Carl Zeiss Microscopy, Germany), 20×Plan-Apochromat objective (NA=0.8). The samples were placed onto the Petri dish with a glass bottom 0.16 mm thick. The fluorescence of the HEDP-F and PAA-F1 was recorded in the wavelength range of 460–600 nm, when excited by laser radiation with a wavelength of 488 nm. As a result, the distribution of HEDP-F or PAA-F1 (green pseudo-color in images) and images in the transmitted light mode was obtained.

3D images were obtained by registering a series of fluorescent images with a step of 5 μ m along the Z axis, followed by 3D image reconstruction using ZEN program (Carl Zeiss Microscopy, Germany).

Also the high-resolution microscopy camera AxioCam HRc (Carl Zeiss Microscopy, Germany) was used for taking microphotographs in polarized light.

1.4. DLS measurements

Liquid phase was monitored by the dynamic light scattering technique. DLS experiments were performed at 25°C with Malvern Nano ZS instrument (λ =633 nm, operating power 4 mW) at Θ =173°.

1.5. SEM crystal characterization

The precipitated solids, after being triply rinsed with deionized water and air drying at 50°C, were characterized by scanning electron microscopy (SEM, Hitachi TM-3030). The sample examinations by SEM were done at 15 kV accelerating voltage in a Charge-Up Reduction Mode with crystal phase located on a Conducting Double-Sided Tape and the working distance 4.1 mm.

1.6. Turbidity measurements

For turbidity measurements UV-Vis double beam Spectrophotometer Unico 2804 was used (wavelength range 190–1100 nm, slit width 1.8 nm; light source – wolfram halogen or deuterium lamp). Turbidity was measured in 1 cm quartz cuvettes at wavelength 400 nm at ambient temperature.

1.7. Chemical speciations

Chemical speciation modeling of equilibria was performed with SPECIES software [21], using $\log K = 2.49$ for barium complex formation equilibrium with sulfate anion (5) at ionic strength 0 and 25°C [22].

$$Ba^{2+} + SO_4^{2-} \leftrightarrows [BaSO_4]_{liq}$$
(5)

Hereinafter $[BaSO_4]_{liq}$ is denoted as a sulfate soluble complex of barium cation. When solubility product of barite is excluded, then for an aqueous solution with $[Ba^{2+}] = [SO_4^{2-}]$ = 1 mmol·dm⁻³ chemical speciations reveal 20% (mol) of $[BaSO_4]^{liq}$ formation, while for 0.1 mmol·dm⁻³ – 3% (mol) and for 10 mmol·dm⁻³ – 57% (mol). However, if the solubility product of barite is included, then for $[Ba^{2+}] = [SO_4^{2-}] = 1$ mmol·dm⁻³ aqueous solution chemical speciations indicate 99% (mol) of solid barite formation and an absence of $[BaSO_4]^{liq}$ species. However, a homogeneous equilibrium (Eq. 5) occurs much faster than the barite solid phase formation (Eq. 6)

$$Ba^{2+} + SO_4^{2-} \leftrightarrows BaSO_{4solid} \tag{6}$$

Thus $[BaSO_4]_{liq}$ should be always considered as a possible intermediate species in barite formation scheme.

1.8. X-Ray diffraction analysis

After being triply rinsed with deionised water and air drying at 50°C, the precipitated solids were characterized by powder X-ray diffraction (XRD), (Bruker D8 Advance diffractometer; Cu $K\alpha$; Ni-filter; LYNXEYE detector). The XRD phase identification was done with Joint Committee on Powder Diffraction Standards (JCPDS) database. All the crystals isolated in present work are identified as barite.

2. Results and discussion

An experimental study of barite scaling at ambient temperature is a challenge for researcher. Due to a very poor solubility of $BaSO_4$ a reliable detection of its crystals formation in a liquid phase at low barium and sulfate concentrations (0.00001 – 0.0001 mol·dm⁻³) by conventional methods becomes hardly possible. Meanwhile, for 0.01 to 0.0001 mol·dm⁻³ solutions the process of solid phase formation takes a few seconds, insufficient for clear monitoring of different crystal formation steps. Thus the data presented below characterize $BaSO_4$ scaling in 0.001 to 0.0001 mol·dm⁻³ supersaturated aqueous solutions.

2.1. DSL and fluorescent studies of HEDP-F and PAA-F1

As far as calcium salts of HEDP-F form insoluble species with an excess of calcium ions [19], it was reasonable to study preliminary both fluorescent-tagged antiscalants for their own crystal phase formation with barium ions. Indeed DLS indicates formation of sustainable solid microparticles monomodal fraction formation with a mean hydrodynamic diameter of 230 ± 60 nm for PAA-F1 and of 1400 ± 300 nm for HEDP-F, Figure 2.



Figure 2. Particle size distribution by intensity for PAA-F1 (a) and HEDP-F (b) aqueous solutions in presence of $0.02 \text{ mol} \cdot \text{dm}^{-3} \text{ BaCl}_2([PAA-F1]=[HEDP-F]=10 \text{ mg} \cdot \text{dm}^{-3})$ 50 minutes after contact of barium and antiscalant brines at pH 4 to 6. Solid and dashed lines represent two measurement replicates.

In case of PAA-F1 the colloid solution remains stable over several weeks and no solid phase deposition is observed. Alternatively, HEDP-F forms in presence of barium ions small individual crystals, Figure 3.



Figure 3. Fluorescent images of Ba-(HEDP-F) aqueous solution ($[Ba^{2+}] = 0.02 \text{ mol} \cdot dm^{-3}$; [HEDP-F] = 10 mg·dm⁻³ or 0.02 mmol·dm⁻³) two days after preparation at ambient temperature, pH 4.8. Scale bar corresponds to 50 microns.

Thus the side equilibria (2)-(4) really take place, and may occur during barite formation in presence of antiscalants, like it was found for HEDP-F during gypsum precipitation [19]. Respectively, it is reasonable to add antisclant initially to a sulfate brine,

but not to the barium or calcium one. Otherwise much of scale inhibitor would be disabled in calcium environment long before the experiment starts. This conclusion is in a very good agreement with data reported in [23].

2.2. DSL, SEM and turbidity studies of barite blank solutions

A mixture of barium and sulfate brines at 1:1 volume ratio and at different water content leads to an almost immediate bulk barite solid particles formation, detected by both the Tyndall effect and by DLS technique within $BaSO_4$ concentration range from 0.01 to 0.00001 mol·dm⁻³, Figures 4a,b, and 5. However, the clear turbidity is observed only for 0.01 to 0.005 mol·dm⁻³ $BaSO_4$ concentrations. The more diluted solutions remain visually transparent and generate no barite deposits. Thus below 0.005 mol·dm⁻³ a solid barite phase exists in the form of a stable colloid solution.



Figure 4. Tyndall's effect for 0.01 (a) and 0.001 (b–d) mol·dm⁻³ BaSO₄ aqueous solutions in presence of 50 mg·dm⁻³ HEDP-F (c) and PAA-F1 (d) 120 sec after barium and sulfate brines get mixed at ambient temperature.

DLS of concentrated $BaSO_4$ solution reveals multimodal particle size distribution unstable in time due to a fast particles growth and precipitation. At the same time a $0.0001 \text{ mol} \cdot \text{dm}^{-3}$ barite solution demonstrates a stable reproducible bimodal distribution with one peak corresponding to 370 ± 80 nm, and another one – to 80 ± 20 nm, Figure 5.



Figure 5. DLS particle size distribution by intensity for barite $0.0001 \text{ mol} \cdot \text{dm}^{-3}$ aqueous stock solution 10 minutes after barium chloride and sodium sulfate brines get mixed at pH 6. Solid and dashed lines represent two measurement replicates.

Formation of barite particles is detected practically immediately after the saturated solutions are prepared. Taking into account the presence of foreign background solid suspended particles in both brines, Table 1, the fast BaSO₄ particles formation and growth corresponds well to the heterogeneous nucleation scenario [24, 25]. Heterogeneous nucleation is characterized by a lower free energy barrier, and a smaller critical nucleus size, relative to the homogeneous nucleation [24]. The turbidity of concentrated barite solutions increases fast after the brines get mixed, stays constant for a while, and then decreases steadily due to the crystals precipitation, Figure 6a.



Figure 6. A time dependence of 0.001 mol·dm⁻³ barite solutions turbidity in a blank experiment (a) and in presence of 20 mg·dm⁻³ HEDP-F (b,c) in deionized water (a,c) and in TAP water (b).

Barite crystals, isolated from a $0.01 \text{ mol} \cdot \text{dm}^{-3}$ BaSO₄ aqueous solution have a star-like shape, Figure 7, and this form does not change significantly for the more diluted solutions. At the same time the mean crystal size is evidently smaller for a solid faze isolated from a more concentrated barite solution.

The BaSO₄ crystals in our experiments look a bit different from those presented in [26, 27], but they are very similar to those presented in [28–30]. Anyhow the X-ray analysis conforms that they belong to barite. Indeed the barite crystal form depends significantly on a supersaturation degree [30, 31].



Figure 7. SEM images (a, b) and polarized light microphotographs (c, d) of $BaSO_4$ crystals deposited from 0.01 mol·dm⁻³ (a, b) and 0.002 mol·dm⁻³ (c, d) barite solutions at ambient temperature, pH 6. Scale bar for microphotograph's images corresponds to 20 microns.

2.3. Fluorescent and turbidity studies of barite solutions in presence of antiscalants

The turbidity measurements with antiscalants have been done for a middle supersaturation range of barite (0.001 mol·dm⁻³). For the lower concentrations, the turbidity was not detectable, while for the higher BaSO₄ content the time difference with the blank

experiment was too small at any reasonable antiscalant concentration. Meanwhile, the common 10 mg \cdot dm⁻³ dosages of antiscalants are also not capable to provide a meaningful difference in barite scale formation even for 0.001 mol \cdot dm⁻³ BaSO₄ concentration, while 50 mg \cdot dm⁻³ antiscalant dosage suppresses completely the Tyndal's scattering, Figure 4 c,d. Thus 20 mg \cdot dm⁻³ antiscalants concentrations were run to inhibit 0.001 mol \cdot dm⁻³ barite scaling in turbidity tests, Figures 6, 8, 9.



Figure 8. A time dependence of 0.001 mol·dm⁻³ barite solutions turbidity in deionized water (a,c) and in TAP water (b): blank experiment (a); experiments in presence of 20 mg·dm⁻³ (b,c) of PAA-F1.



Figure 9. A time dependence of 0.001 mol·dm⁻³ barite solutions turbidity in presence of 20 mg·dm⁻³ of HEDP-F in deionized water with HEDP-F initially added: to the sulfate brine (a); to the barium brine (b).



Figure 10. A time dependence of 0.001 mol·dm⁻³ barite solutions turbidity in presence of 20 mg·dm⁻³ of PAA-F1 in deionized water with PAA-F1 initially added: to the sulfate brine (a); to the barium brine (b).

It is demonstrated that both antiscalants really slow down the crystals formation process in barite supersaturated solutions in deionized water, Figure 6c, and 8c. However, in a TAP water HEDP-F appears to be less efficient relative to PAA-F1. A comparison of curves 6b and 6c (Figure 6) reveals a drastic difference between barite scaling in deinonized and TAP water in presence of one and the same amount of HEDP-F (20 mg·dm⁻³). It indicates clearly an important role of "nanodust" particles present in amount at least one order of magnitude higher in TAP water, than in deionized water, Table 1. A corresponding increase of calcium and of some other background ions content due to TAP water (0.00004 mol·dm⁻³) is negligible in comparison with barium content in the model solutions (0.001 mol·dm⁻³), and is unable to make any impact on "barite – HEDP-F" interaction. Figures 8 and 9 demonstrate that an increase in barite/HEDP-F (barite/PAA-F1) mole ratio in deionized water, as well as a corresponding increase of "nanodust" particles per one mole of antiscalant promote scaling. Notably, there is no induction time in curves 8b and 9b relative to the blank experiments. However the turbidity maximum in presence of antiscalants is much lower than that one of a blank experiment. Thus it seems that much less barite nuclei form in presence of antiscalants. However, those BaSO₄ particles that manage to appear grow thereafter pretty fast. They form rather big aggregates, and then pass an intensive sedimentation without any noticeable influence of scale inhibitors.

The most impressive results are obtained by fluorescent microscopy, Figures 11 and 12. In presence of both antiscalants the form of barite crystals does not change relative to the blank solution. At the same time the mean crystal size becomes smaller. Evidently HEDP-F and PAA-F1 are adsorbed on $BaSO_4$ crystals, covering uniformly the whole barite

surface. There is no evidence of antiscalant molecules special concentration on the barite crystal kinks, edges, *etc.* as recent inhibition theory predicts [32]. This could be seen especially clearly from the 3D image, Figure 12.



Figure 11. Fluorescent images of barite crystals in aqueous phase, formed in presence of $10 \text{ mg} \cdot \text{dm}^{-3}$ of HEDP-F (a) or PAA-F1 (b) obtained from 0.002 mol $\cdot \text{dm}^{-3}$ BaSO₄ stock solution. Scale bar corresponds to 20 microns.



Figure 12. Fluorescent 3D image of barite crystals formed in presence of $10 \text{ mg} \cdot \text{dm}^{-3}$ of HEDP-F obtained from 0.002 mol·dm⁻³ BaSO₄ stock solution. Scale bar corresponds to 20 microns.

Moreover, fluorescent images demonstrate that antiscalants are rather covering the already formed macro-crystals than the initially formed barite nuclei. Otherwise the fluorescence would concentrate mostly inside the $BaSO_4$ crystal, but not on their surface.

Notably, fluorescence of HEDP-F on barite crystals, Figures 11 and 12, is sufficiently different from the images of the same antiscalant on gypsum surface [19]. In case of gypsum, the HEDP-F molecules did not cover the surface of $CaSO_4 \cdot 2H_2O$ crystals, but they get completely concentrated in their own solid phase. Tentatively it is $Ca_2HEDP-F \cdot nH_2O$.

This difference may be explained: (i) by a disparity in relative solubility of $CaSO_4 \cdot 2H_2O$, $BaSO_4$, Ca_2HEDP -F $\cdot nH_2O$ and Ba_2HEDP -F $\cdot mH_2O$; (ii) by a distinction in $CaSO_4 \cdot 2H_2O$ and $BaSO_4$ supersaturation levels used in [19] and in present work; and (iii) by a dissimilarity in HEDP-F affinity to the $CaSO_4 \cdot 2H_2O$ and $BaSO_4$ surface. Anyhow the comparison of HEDP-F fluorescence on barite and gypsum crystals indicates clearly, that an antiscalant's behavior may be very flexible depending on the scale nature and experimental conditions. Thus any scale requires an individual adjustment of even one and the same antiscalant.

2.4. Tentative mechanism of barite crystals formation in the bulk supersaturated solutions

2.4.1. Barite crystals formation without antiscalants

An extremely fast formation of BaSO₄ solid phase in the form of microparticles at any supersaturation level indicates a heterogeneous mechanism of barite crystallization in the bulk aqueous medium in agreement with a classical crystallization theory [24, 25]. Indeed, according to the particle counter data even the deionized water used for the brines preparation and for samples dilution contains no less than 700 solid impurities ("microdust") in 1 ml with the size over 100 nm, Table 1. Unfortunately, the recent counters do not provide numerical data for the particles smaller than 100 nm. In our opinion for the estimation of the total minimal "micro- and nanodust" particle concentration the data of particle counter can be at least dabbled, and therefore it constitutes no less than 1400 units per ml, or $1.4 \cdot 10^6$ particles in a liter. This number can be partly diminished by some extra nanofiltration, but it is impossible to make it negligible. Notably, every brine solution contains much more particles than the deionized water, Table 1. Bearing in mind, that the number of "nanodust" particles with a size below 100 nm in any brine is no less than, that listed in a Table 1, one can take roughly, as the first approximation, that all "nanodust" particles have spherical shape with the mean particle size (hydrodynamic diameter) 100 nm, and their mean concentration 5000 units per one ml, or $5 \cdot 10^6$ per liter. Then the total surface area of "nanodust" would constitute *ca*. $1.5 \cdot 10^{-7}$ m² in one liter of 0.01 mol·dm⁻³ BaSO₄ solution before barite crystals start to form.

On the other hand, any initial brine in our case has from $1.2 \cdot 10^{22} \text{ SO}_4^{2-}$ (Ba²⁺) ions in a liter (0.02 mol·dm⁻³ solution) to $6 \cdot 10^{19}$ ions (0.0001 mol·dm⁻³ solution). Therefore one

has at least 10^{13} SO₄²⁻ (Ba²⁺) ions per one solid nanoparticle in any brine. This is more than enough to cover the "nanodust" surface.

Thus at a moment of any supersaturated barite solution preparation we have two transparent aqueous solutions of solid nanoparticles covered via sorption with either SO_4^{2-} or Ca^{2+} ions, and of "free" either SO_4^{2-} or Ca^{2+} ions respectively (Na⁺ and Cl⁻ are neglected and omitted for simplicity). When the sulfate and calcium brines get mixed, the solid "nanodust" particles become the readymade barite crystals nucleation centers. Tentatively, the following equilibria take place, Figure 13:

$$Ba^{2+} + SO_4^{2-} \leftrightarrows BaSO_{4liqid} \tag{7}$$

(nanodust particle) $nBa^{2+} + nSO_4^{2-} + mBaSO_{4liqid} \leftrightarrows$ (nanodust particle) $(n+m)BaSO_4$ (8)

(nanodust particle) $nSO_4^{2-} + nBa^{2+} + mBaSO_{4liqid} \leftrightarrows$ (nanodust particle) $(n+m)BaSO_4(9)$



Figure 13. Tentative scheme of barite crystals formation from a supersaturated solution (Na⁺, Cl⁻ ions and [BaSO_{4liquid}] complexes are not shown for simplicity).

Notably a relative impact of processes (7), (8) and (9) on barite formation should strongly depend on the stock solutions concentration. Supposing that the homogeneous complex formation process (7) goes much faster than sorption (8) and (9), it is possible to estimate BaSO_{4liqid} concentration. The chemical speciations indicate that at the first moment, when the 0.02 mol·dm⁻³ brines get mixed in 1:1 volume ratio, a complex BaSO_{4liqid} constitutes *ca*. 57% of the total Barium (sulfate) content, while for 0.0002 mol·dm⁻³ brines it becomes negligible (3%).

Solid phase forms very fast, producing an intensive Tyndal's effect and demonstrating clear turbidity. Evidently any aggregate like [(nanodust particle)(n+m)BaSO₄] is bearing an electrostatic charge and therefore has zeta-potential. However it is small and it is not capable to suppress particle aggregation, Table 2. For the sake of simplicity the electrostatic charges are not shown in (8) and (9) schemes.

The [(nanodust particle)(n+m)BaSO₄] may further grow due to BaSO_{4liqid} complexes or Ba²⁺ (SO₄²⁻) free ions accumulation and then may aggregate with each other, regularize their structure and finally form barite crystals. Due to a very low barite solubility this process becomes completed within several tenths of seconds in 0.01 mol·dm⁻³ barite stock solution, Table 2, Figure 4. Then the BaSO₄ crystals pass very fast sedimentation and reveal no Tyndal's effect in a liquid phase, that equilibrates with crystals Table 2.

In case of 0.001 mol dm^{-3} barite stock solution a solid phase is also formed very fast and then also passes sedimentation, Figure 6a. However, the Tyndal's effect is much weaker relative to the 0.01 mol dm^{-3} stock solution, Figure 4a,b. In a 0.0001 mol dm^{-3} BaSO₄ stock solution a solid phase forms also fast, Figure 5, but no visible turbidity, Tyndal's effect and sedimentation are observed.

Barite initial concentration mol·dm ⁻³	Antiscalant mg∙dm ⁻³	рН	ζ- potential, - mV ^a	Tyndal's effect		Particle size, nm	
				а	b	a	b
0.01	0	6.7	_	strong	absent ^c	Unstable size distribution	
0.001	0	6.8	$-8{\pm}4$	present	absent ^c	Unstable size distribution	
0.001	PAA-F1; 20	6.0	-6±3	absent	present	$\begin{array}{c} 33{\pm}8~(30\%^{\ d})\\ 290{\pm}60~(70\%^{\ d})\end{array}$	560±80
0.001	HEDP-F; 20	4.3	-2 ± 5	absent	present	$80\pm20~(20\%^{d})$ $320\pm80~(80\%^{d})$	1000 ± 100

Table 2. Barite aqueous solutions characterization by DLS.

^a10 minutes after supersaturated barite solution preparation; ^b4 days after supersaturated barite solution preparation; ^c all particles are present as a solid phase sediment; ^d Intensity percent in size distribution by intensity.

It should be noted that ζ -potentials of barite particles are too small to provide colloid solution stabilization, Table 2. To reach this goal, one has to arrange $\zeta < -30 \text{ mV}$ or $\zeta > 30 \text{ mV}$.

2.4.2. Barite crystals formation in presence of antiscalants

Both HEDP-F and PAA-F1 are found to suppress barite scaling, Figures 6 and 8. However, they do not provide zeta-potentials, capable to slow down barite nuclei aggregation, Table 2. At the same time none of these antiscalants change the crystal morphology and,

according to fluorescent images, they do not seem to block the barite crystal growth centers (kinks, edges, *etc.*), covering the macro-crystal surface uniformly.

Taking into account the considerations listed in 2.4.1 the total surface area of "nanodust" can be roughly estimated as *ca*. $1.5 \cdot 10^{-8} \text{ m}^2$ in one liter of 0.001 mol·dm⁻³ BaSO₄ solution before barite crystals start to form. One HEDP-F molecule can occupy an area of $12.7 \cdot 10^{-20} \text{ m}^2$ if two bisphosphonate groups are bound to the surface, Figure 14. A 10 mg·dm⁻³ dosage of HEDP-F corresponds to $2 \cdot 10^{-5} \text{ mol·dm}^{-3}$, or $3 \cdot 10^{18}$ molecules per liter. Thus HEDP-F can cover $3.8 \cdot 10^{-1} \text{ m}^2$. Therefore the antiscalant molecules are capable to cover all "nanodust" nucleation centers completely and to isolate them from barium and sulfate ions. Besides, a significant excess of "free" HEDP-F would stay in an aqueous phase.



Figure 14. Tentative location of HEDP-F molecules on the "nanodust" particle surface.

Definitely, this process takes place in a sulfate brine, where HEDP-F is initially added in our experiments. However, an antiscalant is missing in a barium brine, because otherwise it would interact with barium ions and form insoluble Ba₂HEDP-F salts there. Therefore, when 0.1 ml of barium brine is added to 1.9 ml of sulfate/HEDP-F solution (0.1 ml of sulfate brine +0.4 ml HEDP-F concentrate +1.4 ml of deionized water), then HEDP-F species and sulfate anions start to compete for "free" nanodust particles [(nanodust particle)nBa²⁺] – potential nucleation centers of barite, Figure 15. Those "nanodust" particles that manage to be first covered by barium sulfate core, than form the barite nuclei, which grow and aggregate approximately in the same way as in the blank solution. However, the number of such barite growth centers is much less than in a blank solution. Therefore their further aggregation at the initial steps of barite formation becomes slower. This scheme is valid for both HEDP-F and PAA-F1, and it is similar to that one described by us for gypsum [19].



Figure 15. Tentative scheme of barite crystals formation from supersaturated solution in presence of antiscalant (Na⁺and Cl⁻ions are not shown for simplicity).

It should be noted that our interpretation of barite scaling inhibition mechanism does not conflict the previous reports [1, 2, 4, 13, 26, 27, 33], but refines the pre-nucleation step, highlighting the role of "nanodust", evidently present in all recent and previous studies on barite scale inhibition [4–10, 12–20, 26, 27, 33] as well as in all the studies of other scales [28]. Particularly, a recent study [1] suggests, that barium sulphate precipitation occurs *via* the formation of ion associates in solution (ion pairs and/or clusters), that are significantly destabilized in the presence of polyacrylate (PAA) and that pre-nucleation ion associates must form prior to solid BaSO₄ nucleation. Our results agree with these statements, but indicate that a pre-nucleation step takes place not so much as a spontaneous homogeneous ion pairs and/or clusters formation, but as a heterogeneous clusters formation on a "nanodust" particles surface. Thus PAA destabilizes this process by a very clear mechanism of "nanodust" particles surface blockage instead of unclear impact on $BaSO_4$ clusters spontaneous formation.

Although the crystal nucleation theory takes into consideration the possibility of heterogeneous nucleation in the bulk aqueous solution [24], unfortunately the role of "nanodust" in scale formation is so far underestimated. Indeed, many researchers report that they use analytical grade chemicals and some of them claim that all the brines they use have passed filtration, operating usually 0.2 μ m filters in order to remove dust or to reduce its content. However we have failed to find a publication, indicating that someone has ever wondered how much "microdust" and "nanodust" still remain in the system after such a filtration.

Meanwhile our recent data on gypsum scale formation [19, 34, 35], as well as our present work on barite crystallization, reveal that the residual "nanodust" plays a key role in both: the sparingly soluble salt pre-nucleation and nucleation; as well as in an antiscalant efficacy. The latter may reveal itself at the primary steps of inorganic salt crystallization (pre-nucleation; nucleation) and at the secondary step of crystal growth and precipitation. The secondary step is rather well described on the grounds of seeded crystals growth experiments in the supersaturated aqueous solutions [8–10, 36–39]. However, which step determines the total rate of scale deposition in which case is not very clear. At the same time rather little is known about the scale inhibitor behavior at the primary step [1, 2, 13, 15, 32]. Our approach, presented in Figure 13, suggests that ion associates (prenucleation) must form exactly on a "nanodust" particle surface prior to solid BaSO₄ nucleation, while the blockage of "nanodust" by an antiscalant (Figure 15) slows down this process. We suggest that this may be a universal phenomenon during the precipitation of inorganic compounds.

At the same time, our data presented in Figure 9 indicate clearly that the methods of an antiscalant efficacy evaluation based on induction time measurements are rather arbitrary relative to the static experiments with inhibition percent determination. The former ones are likely to depend on the initial nanodust content, than on an antiscalant efficacy.

Besides, our data reveal an importance of the sequence of reagents mixing both in laboratory studies and in industrial applications, Figures 2, 3 and 9. For those antiscalants that form sparingly soluble salts with calcium and barium ions this may lead to conflicting or even confusing results. Thus the data based on the experiments when an antiscalant is placed initially in a barium (calcium) brine [4, 23, 39] may differ drastically from those, where it is initially placed in a sulfate (carbonate) brine [2, 15, 31, 37, 40].

Our last but not least comment relates the application of conductivity as the main indicator of barite solid phase formation [1, 2, 4, 23, 39] *etc.* Actually, a decrease of conductivity in this particular case may indicate both barium soluble sulfate complex

formation and a solid barite occurrence. Recently it is not clear how one can distinguish these events, especially near the saturation point. Thus there is a danger of taking one for the other. Notably, the corresponding stability constants listed in [22] have never been critically evaluated by IUPAC, and might be overestimated due to neglect in colloidal solid barite formation.

Conclusions

A study of barite crystals formation in a bulk supersaturated aqueous solution at ambient temperature in presence of two novel fluorescent-tagged antiscalants: HEDP-F, and PAA-F1 revealed a dramatic impact of foreign background "nanodust" particles on antiscalant efficacy. Such species are normally overlooked by most of researchers active in this field. It is demonstrated, that barite nucleation takes place exclusively on "nanodust" particles as a bulk heterogeneous process. Thus an antiscalant molecule at the first phase of scaling acts not so much as barite nuclei surface modifiers, but as the modifiers of "nanodust" particles.

Both fluorescent-tagged antiscalants are found to be well adsorbed by barite crystals and reveal a perfect contrasting of BaSO₄ solid phase. At the same time none of these antiscalants change the crystal morphology and, according to fluorescent images, they do not seem to block the barite crystal growth centers (kinks, edges, *etc.*), covering the macrocrystal surface uniformly. Such a behavior is sufficiently different from that one observed by us for HEDP-F interaction with gypsum. Thus each sparingly soluble salt case requires a separate consideration.

It is shown that *inter alia* the lower efficacy of HEDP-F relative to PAA-F1 is associated with insoluble barium salts formation by the former reagent (tentatively by $Ba_2HEDP-F \cdot nH_2O$ or $BaH_2HEDP-F \cdot mH_2O$). Thus an efficacy evaluation may be strongly affected by the way of antiscalant introduction into the system. Being initially added to the barium brine both antisclants demonstrate greater difference in barite scale inhibition, than in the case of the sulfate brine.

The fluorescent-tagged antiscalants may become a universal and powerful tool of scale inhibition mechanisms studies, capable to shed light onto the formation of scale in numerous industrial applications.

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