

Effects of temperature and concentration on mechanism and kinetics of thermally induced deposition from coffee extracts

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1 Production of soluble (instant) coffee powders typically involves extraction of roasted coffee by
2 water followed by evaporation in order to concentrate extracts before spray or freeze drying to
3 produce dry coffee powder. In the course of evaporation, deposition of dissolved material from
4 coffee extracts is a major cause of fouling at heat exchange surfaces of evaporators. Therefore in
5 order to improve design and optimization of evaporation processes of coffee extracts, a better
6 understanding of deposition mechanism and kinetics is needed. We used Optical Waveguide
7 Lightmode Spectroscopy (OWLS) to monitor the initial formation of nanometer scale deposits on
8 surfaces exposed to coffee extracts. OWLS measurements were complemented by light scattering
9 from extract solutions, gravimetry of macroscopic deposits and scanning electron microscopy
10 imaging of deposited layers. Primary molecular-scale layers of about 1 mg/m² were rapidly
11 formed in the first stage of deposition even at ambient temperature, followed by the secondary
12 deposition with kinetics strongly dependent on temperature. Secondary deposition rates were low
13 and largely independent of the extract concentration at ambient temperature, but became strongly
14 dependent on extract concentration at elevated temperatures. In particular, activation energies for
15 deposition between 25 and 70°C were much higher for the original extract (13.3% w/w solids)
16 than for diluted extracts (up to 1.3% w/w solids). Furthermore, heating of the original extracts
17 above 60°C resulted in rapid aggregation of suspended macromolecules into large clusters, while
18 only gradual aggregation was observed in diluted extracts.

19

20 **Keywords:** coffee extracts; deposition; aggregation; fouling; evaporation; heat exchange

21

22

Introduction

23

24 Deposition and fouling play an important role in various industrial and biomedical applications,
25 such as filtration, heat exchange, evaporation, deposition in blood vessels, implant
26 biocompatibility and others. There are instances where deposition is desired, as long as it can be
27 controlled, but others where it is not. Typical examples are in food processing industries, where
28 various liquids (solutions or dispersion) are treated in falling film evaporators in order to produce
29 more concentrated solutions. Extensive fouling of evaporator surfaces can occur over a period of
30 hours to days, depending on properties of a particular system. Fouling leads to build-up of a thick
31 layer deposited on the evaporator surface, which causes a gradual decrease in the efficiency of the
32 heat transfer and the eventual interruption of the production process in order to proceed to surface
33 cleaning.

34 Various characterization methods have been used to study fouling kinetics. Macroscopic
35 deposits can be conveniently studied using gravimetry, which has the advantage of relative
36 simplicity and direct data interpretation. Quartz crystal microbalance has been used to study
37 protein adsorption and it provides useful quantitative information related to mass and viscoelastic
38 properties of deposited material (Höök et al., 2002). Another useful technique widely used in
39 fouling studies is optical microscopy, providing visual characterization of deposited layers down
40 to the micrometer scale. Scanning electron microscopy or atomic force microscopy can provide
41 details in the nanometer range, but they typically require sample manipulations, which may lead
42 to significant changes with respect to its original morphology. This especially concerns biological
43 systems, which are often sensitive to changes in the environment.

44 On the other hand, spectroscopic characterization methods can provide molecular level insight
45 into the mechanisms governing the deposition process, especially at its early stages. Surface
46 spectroscopic techniques, such as Optical Waveguide Lightmode Spectroscopy (OWLS), have
47 the advantage of non-destructive, in situ monitoring of solid-liquid interfaces and provide a useful
48 tool to study adsorption and deposition at solid-liquid interfaces. A limitation of this and similar
49 reflectance-based techniques (e.g., ellipsometry, reflectometry) is that there is a limited extent of
50 the deposit thickness that can be measured, typically not exceeding few tens of nanometers.
51 OWLS is especially suitable to study interfaces interacting with dense and/or dark suspensions,

52 since this waveguide-based method does not require the reflecting laser beam to pass through the
53 suspension.

54 The extracts obtained from ground roasted coffee beans are darkly colored mixtures containing
55 proteins, polysaccharides and organic acids in both soluble and insoluble (colloidal) form
56 suspended in an aqueous matrix. We note that there is a significant amount of lipids in (roasted)
57 coffee beans, but lipids are poorly soluble in water and their concentration in coffee extracts is
58 therefore very low. We are not aware of any previous studies on deposition from coffee extracts
59 or similar systems. Most of previous studies about surface fouling refer to the deposition of
60 proteins, mostly of animal origin. When protein solutions come into contact with an interface a
61 spontaneous deposition is typically observed. Published studies have been mostly focused on
62 protein-surface interactions, mainly at ambient temperature. Protein deposition is affected by pH,
63 electrolyte concentration and temperature, which may specifically affect the protein functional
64 groups or change its geometrical arrangement. Polysaccharides, which represent a significant
65 component of the coffee extracts, tend to copolymerize with proteins at elevated temperatures
66 (Maillard reaction), and the resulting copolymers are also expected to be subject to fouling.

67 Considering interphase interactions of deposited entities with solid surfaces, we can divide the
68 deposition processes into two main groups:

69 *i)* The first group involves monolayer systems, where the main driving force for the deposition
70 is due to the interaction potential difference between a bulk solution and a solid surface.
71 Electrostatic double layer repulsion prevents charged polymer colloids from aggregating to each
72 other, resulting in a stable deposited monolayer on the solid surface, which is made resistant
73 against further deposition by the same electrostatic repulsive forces which keep suspended
74 colloids stable in the bulk solution.

75 *ii)* The second group involves multilayer systems, where the repulsive interactions between the
76 primary deposited layer and the bulk solution entities are reduced, so that subsequent deposition
77 on the top of the primary layer can proceed. Multilayer growth can be achieved by altering the
78 bulk solution composition, mainly through changes of pH and/or electrolyte concentration or, as
79 in the system studied here, by increasing the temperature. Typically, fouling phenomena occur
80 through the multilayer deposition. In this case the deposition is driven by interactions of
81 previously deposited entities with those in the bulk, similar to aggregation in the bulk solution
82 itself, so that fouling becomes independent from surface properties of the original substrate after
83 the first few layers are deposited.

84 Multilayer film deposition at ambient temperature was studied by Picart et al. and Lavallo et al.
85 (Picart et al., 2001; Lavallo et al., 2004), where well defined polyelectrolyte multilayers and
86 multilayer polyelectrolyte/protein films were investigated by OWLS and scanning angle
87 reflectometry. It was shown that OWLS was able to monitor the deposition process from the
88 initial deposited layer up to a thickness of more than 40 nm, while reflectometry could be used
89 only after a few nanometers have been deposited up to about the same maximum thickness. This
90 study of polyelectrolyte multilayer growth pointed out the important role of solution pH and
91 charge distribution inside the film on the layer buildup mechanism.

92 Studies of Griesser et al. (Griesser et al., 2002) on the deposition of complex protein mixtures
93 (differing in the isoelectric point) for different bulk solution electrolyte concentrations on
94 variously grafted polysaccharide layers and polymer coatings showed that coatings with
95 substantial surface charge can be resistant to protein adsorption of the same charge, although they
96 cannot be considered as a universal protein-resistant surface for all protein mixtures.

97 The effect of temperature, particularly at elevated temperature, on the deposition process has
98 been rarely investigated. As reported in the review by Nakanishi et al. (Nakanishi et al., 2001),
99 this may be in part related to the associated experimental difficulties. The most commonly
100 temperature driven fouling system studied in the literature is milk (Changani et al., 1997; Jong,
101 1997; Visser & Jeurink, 1997; Anema, 2000). This is a complex mixture of proteins, fats,
102 carbohydrates, minerals and enzymes. There are two major components playing a role in milk
103 fouling. Deposits formed between 60°C and 100°C are predominantly proteinaceous (with β -
104 lactoglobulin as the dominant protein), while deposits formed above 100°C are rich in minerals.
105 Thermal properties and aggregation and deposition behavior of proteins are in general strongly
106 dependent on pH and on the presence of other components, such as calcium ions, lactose or
107 casein. Upon heating at neutral pH, the proteins initially unfold and expose their inner
108 hydrophobic cores and free thiol groups, which initiates their spontaneous aggregation and can
109 also lead to their deposition on surfaces (Kroslak et al., 2007; Vogtt et al., 2011; Grancic et al.,
110 2012). At ambient temperature β -lactoglobulin forms monolayer due to its interaction with the
111 bare surface, which is the typical behavior observed for various proteins (Relkin, 1996; Van
112 Tassel, 2003; Voros, 2004; Sava et al., 2005).

113 The main scope of this work was to investigate the mechanism and kinetics of surface
114 deposition from coffee extract induced by an increased temperature. Using the temperature
115 control setup developed for the OWLS instrument allowed us to obtain unique insights into the

116 deposition process in these systems. A better qualitative and quantitative understanding of the
117 deposition process should provide a rational basis for possible process modifications leading to
118 decreased fouling, thus improving the heat transfer in evaporators used for the production of
119 concentrated extracts.

120 In the following we investigate the primary layer formation on several different surfaces at
121 ambient temperature and at various pH and electrolyte concentrations. Next, we investigate the
122 secondary deposition driven by temperature on the primary layers previously deposited on a silica
123 surface. The structure of deposited layers is also analyzed using scanning electron microscopy
124 while the macroscopic deposition kinetics at longer times is measured by gravimetry. Light
125 scattering is used to monitor the corresponding aggregation processes in the bulk suspension for
126 variously diluted extracts at elevated temperatures.

127

128 **Optical Waveguide Lightmode Spectroscopy**

129

130 Optical waveguide lightmode spectroscopy is based on measurements of changes of the
131 effective refractive index of an optical waveguide when a thin film forms at the waveguide
132 surface. The presence of the thin film changes the evanescent electromagnetic field in a close
133 vicinity of the waveguide surface and it influences the light reflection from the waveguide
134 surface. This results in a shift of the incidence angle of a light beam leading to a lightmode
135 guided along the waveguide. By measuring the incidence angle α corresponding to the resonance
136 maximum of the light incoupled in the waveguide it is possible to determine an effective
137 refractive index N of the light propagating along the waveguide and from that the thin film
138 (deposited) mass per surface area (please see further details in Supplementary Information).

139

140

Experimental

141 ***Materials***

142 The dry solid content of the coffee extract (provided by Nestlé Product Technology Centre
143 Orbe, Switzerland) considered in this work is 13.3 wt% and the pH is 5.0. The dry mass of the
144 suspension is constituted of 7.4% proteins, 35% carbohydrates, 3.2% minerals and 54.4% other
145 organic molecules like melanoidines, organic acids and ash. At the natural pH of the coffee
146 extract (pH 5) most of the proteins are negatively charged (36%), 1.2% are positively charged,
147 30% are polar uncharged (mainly aliphatic), 23% are aromatic and the rest is not determined. The

148 sediments constitute 2% of the overall dry content. All solutions were prepared with ultra pure
149 water (Millipore, 18M Ω) degassed under vacuum before use in order to reduce bubble formation
150 in the spectroscopy cell.

151 Silica-Titania planar waveguides (OW 2400) were purchased from Microvacuum Ltd.
152 (Budapest, Hungary). They consist of a 1-mm-thick AF45 glass substrate and a 180-nm thick
153 Si_{0.75}Ti_{0.25}O₂ waveguiding surface layer, with dimensions of 1.2x0.8x0.1cm. The isoelectric point
154 (IEP) of silica is 3.0 and of titania around 5.5 (Kosmulski, 2001). The waveguide layer has an
155 approximate thickness of $t_F \sim 180$ nm and a refractive index of $n_F \sim 1.76$. Five different surfaces
156 have been used in this study to investigate the ambient temperature deposition process. These
157 include the negatively charged silica and niobia surfaces, the positively charged alumina surface,
158 and the hydrophobic polystyrene (PS) and poly(ethylene glycol)-3.5-poly(L-lysine) (PEG-3.5-
159 PLL) surfaces. At elevated temperature only the silica modified surface has been used.

160 All the surfaces mentioned above have been obtained through a suitable coating procedure,
161 covering the original waveguide film with layers 10-15 nm thick. The silica and alumina coated
162 waveguides were purchased from Microvacuum Ltd. (Budapest, Hungary). The IEP of alumina is
163 8 (Kosmulski, 2001). The niobia coated waveguides were sputter coated on the original
164 waveguide, using reactive magnetron sputtering (PSI, Villigen, Switzerland). The IEP of niobia is
165 4.3. Before each deposition experiment, all oxide surfaces were activated in NaOH solution at pH
166 11 for 3 hours. Afterwards, the waveguides were rinsed with Millipore water and dried with
167 nitrogen. This procedure activates the hydroxyl groups on the accessible surface.

168 A polystyrene (PS) layer approximately 15 nm thick was coated on the silanized original
169 waveguide using 1% polystyrene dissolved in toluene at rotation speed 3000 rpm for 1 minute
170 (Extrand, 1994; Schubert, 1997). PS used in this study was PS Standard 30'000 from Sigma-
171 Aldrich (Product Number 81408) with $M_p=32500$, $M_n=31000$, $M_w=32000$, $M_w/M_n=1.02$.
172 Silanization by hexamethyldisilazane, from Fluka, (Lot. No. 427155/1 44601) was used to make
173 the originally hydrophilic oxide surface hydrophobic (Huang, 2002). PEG-3.5-(PLL), a
174 polycationic co-polymer (grafting ratio of 3.5; Huang, 2002), positively charged at neutral pH
175 (Huang, 2002), was spontaneously adsorbed on the negatively charged original surface from
176 aqueous solution. PEG-3.5-(PLL) modified waveguides were obtained from the Laboratory of
177 Surface Science and Technology, Department of Materials, ETH Zurich.

178 Prior to the SLS measurements the coffee extract was filtered with a 0.8 μ m filter (Millipore) in
179 order to remove bigger aggregates from the coffee extract. This does not change significantly the

180 overall dried mass of the filtrate compared to the original extract. The removal of these particles
181 is needed to reduce skewing of the measurements caused by big aggregates.

182 ***OWLS***

183 Deposition experiments were performed in OWLS apparatus type OWLS 110 made by Micro
184 Vacuum Ltd, Budapest, Hungary with an integrated temperature control unit. The waveguide is
185 placed in a measuring cell, which is a channel 8mm long with rectangular cross section (0.8mm
186 high and 2 mm wide) with a volume of 12.8 μ l, with entrance and exit ports to allow for
187 continuous flow through. All delivery tubes and the measuring cell are made of PTFE. The flow
188 through operation mode has been selected in order to guarantee exposure to a fresh extract with
189 constant composition over time. The waveguide parameters n_f and t_f are measured through a
190 preliminary set of experiments where water is flushed through the deposition cell at ambient
191 temperature.

192 In the deposition experiments at ambient temperature the waveguide surface was exposed to the
193 coffee extract for at least one hour leading to completion of the primary deposited layer on the
194 bare surface. The flow rate is held constant at 1ml.min⁻¹ by the programmable syringe pump Vit-
195 Fit (Lambda, Czech Republic). After deposition, the sample is washed with water for at least 1
196 hour at ambient temperature. This was found sufficient to wash out all the electrolytes adsorbed
197 on the deposition process. For the runs at higher temperatures, a specific experimental procedure
198 has been developed which is described in detail in Supplementary Information. After each
199 deposition experiment the waveguide was cleaned by a short exposure to a strong oxidizing agent
200 (3 seconds in chromic acid), followed by water rinsing. After the cleaning procedure, the position
201 of the resonance spectra was checked and compared with the initially measured one to check that
202 no waveguide damage occurred during cleaning.

203 ***Gravimetry***

204 Gravimetry measurements were used as complementary experiments for OWLS measurements.
205 While the OWLS was used in this work to track deposition for surface coverages up to 30 mg.m⁻²,
206 in order to study the deposition at longer times, when thicker deposits are obtained, we used
207 gravimetry, the lower detection limit of which for the given experimental system is about 50
208 mg.m⁻². Gravimetry is probably the most conventional method to study macroscopic deposition.
209 It is based on weighing the difference between adsorbent weight before and after the adsorption
210 process, and therefore its sensitivity is limited by the accuracy of the weighting procedure. The
211 silica plate was placed into a gravimetry cell, constituted by a channel 180 mm long, with

212 rectangular cross-section 0.5 mm high and 18 mm wide. All delivery tubes were made of
213 stainless steel and the gravimetry cell was made of alumina. The channel geometry has been
214 selected so that we can use the hydrodynamic model for laminar flow between two infinite
215 parallel plates to calculate the hydrodynamic regime inside the channel. Using this model we can
216 determine the flow rate to be fed to the channel so that the velocity gradient at the surface of the
217 waveguide is equal to that in the OWLS cell. The calculated velocity gradient in the OWLS cell
218 is about 500 s^{-1} , which corresponds to a volume flow rate in the channel of $32 \text{ ml} \cdot \text{min}^{-1}$. A
219 peristaltic pump was used to deliver the extract preheated to the desired temperature shortly
220 before entering the measurement cell. The entire gravimetry cell was held at constant
221 temperature. Washing with pure water was performed for one hour after the cooling step as in the
222 OWLS experiments.

223 ***Light scattering***

224 Light scattering experiments were performed on coffee extract in order to compare the
225 aggregation in the liquid bulk with the surface deposition. All measurements have been taken
226 with a small angle light scattering instrument (Mastersizer 2000 by Malvern) after preliminary
227 filtration with $0.8 \mu\text{m}$ filter. The original extract was heated and kept for one hour at constant
228 temperature in the range $25\text{-}80^\circ\text{C}$ so as to undergo Brownian aggregation. Samples were
229 withdrawn at fixed times and quickly diluted 200 times with pure water in order to stop
230 aggregation and avoid multiple scattering in the light scattering measurements. Alternatively, the
231 extract was immediately diluted and then heated at the desired temperature so as to monitor
232 directly in-situ the aggregation process by light scattering without any sampling procedure.

233

234 **Results and discussion**

235

236 ***Estimation of OWLS parameters***

237 In order to evaluate the deposited mass from the measured $N(TE)$ we need to supply optical
238 parameters which correspond to the conditions inside the deposition cell. The refractive indices
239 n_s and n_c , for the waveguide support and the cover liquid, respectively have been taken from the
240 literature or measured independently at various temperatures and are summarized in **Table 1**. The
241 waveguide thickness t_F and refractive index n_F may vary slightly depending on the
242 measurement conditions and therefore have been evaluated before each experiment.

243 Let us now consider the evolution of the derivative of the dielectric constant with respect to the
244 mass concentration of deposit $dc/d\varepsilon$ (see Supplementary Information for further details). For
245 this the refractive indices of variously diluted coffee extracts were measured by refractometer at
246 wavelength 632.8nm for four different temperatures (20, 25, 40, 60°C). The measured values are
247 provided in **Table 1** where x_E represents the weight concentration of solid content in coffee
248 extract suspension. Since the relative dielectric constant can be computed from the refractive
249 indices in the table as $\varepsilon = n_c^2$, the derivative $dc/d\varepsilon$ (where $c=x_E$) can be readily obtained. This
250 procedure has been repeated at the four considered temperatures and obtained values are fitted by
251 following expression, where T is given in °C:

$$252 \quad \left(\frac{dc}{d\varepsilon}\right)_T = -3.47 \cdot 10^{-6} T^2 + 4.028 \cdot 10^{-3} T + 1.642 \quad [g/cm^3] \quad (1)$$

253 As can be seen for this particular case, the term $dc/d\varepsilon$ changes just very little within measured
254 temperature range 20-60°C (i.e. a temperature change of 40°C leads to an increase of 3%). Here
255 we can notice that the value determined experimentally at ambient temperature for the coffee
256 extract (1.74 g.cm⁻³) is similar to the value conventionally used to determine the deposited mass
257 from various biomolecular systems (~1.89 g.cm⁻³) (Defejter, Benjamins & Veer, 1978).

258 ***Deposition at ambient temperature***

259 A typical result of the OWLS measurement is shown in **Figure 1** in terms of mass deposited
260 during a primary exposure of two waveguides, the silica and the polystyrene coated ones, to the
261 coffee extract (solid concentration 13.3 wt%). After equilibration with pure water the extract was
262 pumped at constant flow rate through the measuring cell, and at the end of the deposition process
263 the flow was switched back to pure water and the washing process started. These two times are
264 indicated by arrows in the figure. Typical deposition coverage was about 1 mg.m⁻² after washing
265 with pure water for one hour at ambient temperature.

266 It can be seen that in the case of the hydrophobic polystyrene coated waveguide the deposited
267 mass increased almost instantaneously to about 2 mg.m⁻², and then under very slow growth,
268 which in the following we refer to as the secondary growth. During washing there was a rapid
269 decrease of the deposited mass to about 1 mg.m⁻², followed by a period of time where the mass
270 decrease was so slow that we can consider the deposit as stable in time. When the silica surface
271 was exposed to the extract, the deposited mass was growing rapidly for a longer time, i.e. about
272 half an hour, followed again by a steady but very slow increase corresponding to the so-called
273 secondary growth. Also in this case washing starts very fast and then slows down considerably,

274 leading to a stable deposit. The mass measured at this point represents the amount of material
275 irreversibly deposited on the surface, since the waveguide is at the same conditions as at the
276 beginning of the experiment (in contact with pure water at ambient temperature). And this will be
277 referred to in the following as irreversible primary layer.

278 It is worth noting that while the response of the neutral polystyrene surface is almost
279 instantaneous, the one of the charged silica surface is slower and more pronounced. This is due to
280 the fact that in the second case not only the extract material, but also all the various electrolytes
281 present in the solution are adsorbed or deposited on the surface. These species are however
282 removed during washing, so that it can be observed that the irreversibly deposited amount is very
283 close to that obtained for polystyrene. This can be confirmed by the data reported by Nellen et al.
284 (Nellen et al., 1992) for simple electrolyte solutions, which indicate typical saturation times of
285 about 40 min.

286 The sensitivity of the silica waveguide to electrolytes is well known and the usual way to
287 eliminate it is to use a background medium with the same electrolyte composition as the covering
288 liquid under examination. Since the coffee extract used here was a complex buffering mixture, it
289 was not possible to prepare a matching background medium. Therefore, in addition to the
290 deposition of the extract components, we need to take into account the partitioning equilibrium
291 between the solution and the solid surface. The closer the solution pH is to the isoelectric point of
292 a given surface, the less significant the adsorption of electrolytes is (Sefcik et al., 2002). When
293 the silica surface is exposed to an electrolyte solution at pH=3, which corresponds to its
294 isoelectric point, there is no charging response from the waveguide surface, similarly to the case
295 of neutral polystyrene surface.

296 In **Figure 2** we show the results of deposition measurements for multiple subsequent exposures
297 of a silica coated waveguide to the coffee extract. The first exposure leads to the formation of an
298 irreversible primary layer of about 1.2 mg.m^{-2} as shown in **Figure 1**. The second and third
299 exposures exhibit a very similar behavior. It is worth noticing that for all three subsequent
300 exposures, although the secondary growth region was extended over different times, the final
301 irreversible deposit was substantially the same. This indicates that the material deposited during
302 secondary growth is weakly bounded to the surface and is easily removed by washing with water.

303 The values of the irreversibly deposited mass obtained after the primary exposure to the extract
304 on various surfaces are summarized in **Table 2**. Note that the obtained values are in the same
305 range as those observed for pure proteinaceous solutions deposited on silica surfaces (Nakanishi

306 et al., 2001). Silica and niobia surfaces (isoelectric point at pH 3 and 4, respectively) are
307 negatively charged in contact with the extract at its native pH 5 and exhibit the same thickness of
308 the deposit. A comparable deposited mass was observed on polystyrene (neutral hydrophobic
309 surface) after 15min of exposure, thus confirming that the irreversible primary layer builds up
310 almost completely after quite a short time. The amounts deposited on PEG-3.5-PLL (positively
311 charged at pH 5 since it contains sterically isolated amine groups) and alumina surfaces
312 (positively charged) were smaller than those in the previous cases. It is remarkable that the
313 extract dilution does not lead to any substantial difference in the deposited amount of primary
314 layer, as shown by data in **Table 2** for silica coated waveguide.

315 These data confirm the result reported by Paschke et al. (Pasche et al., 2005) that the
316 electrostatic potential of the waveguide surface has only a moderate influence on the secondary
317 deposition and can be efficiently screened by the thin primary irreversible layer, whose properties
318 govern the following deposition process. This can be justified by the fact that the extracts
319 considered here contain a substantial amount of soluble ions so that the expected electrical double
320 layer thickness is below 1 nm. Therefore electrostatic surface effects act only over a very short
321 range, which is moreover further screened by the irreversible primary layer.

322 ***Deposition at elevated temperatures***

323 Prior to the deposition measurements, the temperature response of the bare waveguide in pure
324 water was investigated. The waveguide thickness t_F and refractive index n_F were evaluated (see
325 Supplementary Information) with the n_c and n_s values reported in **Table 1**. As shown in
326 **Figure 3**, an increase in the waveguide thickness and a decrease in refractive index were
327 observed with increasing temperature. We note that the temperature response slightly varies
328 between individual waveguides, although the general trend is always the same and relative
329 changes in waveguide properties are very similar. As indicated by Saini et al. (Saini et al., 1994)
330 the change in the waveguide thickness can be attributed to thermal dilatation of the waveguide
331 material.

332 It is worth noting that in the temperature response experiments conducted in pure water, when
333 the waveguide was cooled down to ambient temperature, the waveguide parameters were slightly
334 different compared to those before heating. This may indicate a gradual hydrolysis and possibly
335 dissolution of the silica coated waveguide, particularly at higher temperatures. Therefore we
336 minimized the heat exposure of the waveguide in water to a minimum necessary time. On the
337 other hand, changes of the waveguide optical parameters were not observed during the extract

338 deposition runs. The thin layer deposited from the extract can effectively protect the waveguide
339 from hydrolysis and dissolution reactions in two ways. First, it can partially isolate the oxide
340 surface from contact with the solution and secondly it reduces the mass transfer from the oxide
341 surface to the bulk liquid. All the other parameters needed to estimate the deposited mass from
342 are reported in **Table 1**.

343 In **Figure 4a** and **Figure 4b** we show a typical deposition experiment for the coffee extract at
344 60°C. All deposition runs started from a waveguide which had already undergone a primary
345 deposition at ambient temperature, and therefore was covered by an irreversible primary layer.
346 Accordingly, we refer to these experiments as secondary deposition runs in the following
347 sections. The adopted experimental procedure is described in the experimental section and in the
348 case of the experiment in **Figure 4** is reported in detail in **Table S1**. The last column in the table
349 refers to the temperature which is shown in **Figure 4a**.

350 In **Figure 4b** the deposited mass is given as a function of time for silica coated waveguide for
351 the different periods listed in **Table S1**. It is seen that as soon as the extract enters the measuring
352 cell (period C) the deposited mass increases abruptly while at later times it follows an almost
353 linear, relatively slow, increase which constitutes the secondary growth of the deposit. The first
354 jump in deposited mass is due to the adsorption of the small electrolytes on the primary
355 irreversible layer. This is a rather fast process and the deposition of large molecules in such a
356 small time is probably negligible for the secondary deposition runs. In order to determine the
357 deposited mass it is necessary to bring the surface of the waveguide after deposition at the desired
358 temperature back to its initial state, i.e. in the presence of pure water at 25°C. The total
359 irreversibly deposited mass of the coffee extract is then computed as the difference between the
360 mass measured at ambient temperature in water before the deposition (point M_1) and after water
361 washing for one hour (point M_2). The corresponding average deposition rate is given as the
362 increment of deposited mass divided by the exposure time at the elevated temperature.

363 It is worth noting that the average deposition rate determined by this method agrees well with
364 the one obtained from the slope of the deposited mass curve as a function of time during period C
365 in shown in **Figure 4b**. This is further supported by data collected for a moderately diluted
366 extract over a range of temperatures shown in **Figure 5**. This confirms that the two ways of
367 measuring the deposition rate, referred to as online and off-line respectively, yield comparable
368 results. Therefore the thickness of the solid layer deposited on the waveguide after a certain
369 duration of the deposition process corresponds to the secondary deposition rate measured during

370 period C. The electrolytes and other reversibly adsorbed species responsible for the sudden jump
371 in the adsorbed mass at the very beginning of period C are all removed during the washing period
372 E.

373 As can be seen from the semi logarithmic plot in **Figure 6**, the deposition rate of the original
374 extract (solid circles) gradually increases by over two orders of magnitude when the temperature
375 increases from 25°C to 65°C, beyond which the deposition rate does not increase any further. The
376 apparent plateau in the deposition rate above 65°C was also confirmed by gravimetry
377 measurements (see below) and it could be due to a diffusion limited regime for the transport from
378 the bulk to the interface.

379 *Effect of extract composition on deposition kinetics*

380 The assembly of molecules and particles among themselves as well as at interfaces is controlled
381 by their mutual interactions. Repulsive interactions, typically electrostatic or steric, between
382 depositing entities are required in order to prevent mutual aggregation as well as surface fouling.
383 Electrostatic interactions between colloidal particles are modulated most readily by solution pH
384 and electrolyte concentration. Coffee extracts considered here contain molecules and colloidal
385 particles with dissociable groups which are negatively charged at the normal extract pH values
386 ~5, as indicated by electrophoretic mobility measurements of diluted extracts (zeta potential -15
387 mV).

388 In an attempt to control deposition kinetics through electrostatic interactions, we studied
389 deposition by modifying pH to values 4.0 and 6.5 (from the natural pH of 5) at ambient
390 temperature and at 65°C. As expected, by increasing pH the negative charges on the colloids
391 increase, thus leading to slower deposition. In particular, the data reported in **Table 3** show that
392 the increase of pH from 4 to 6.5 results in a decrease of the secondary deposition rate by a factor
393 of 2. An even more pronounced decrease was observed at 65°C, with a reduction of the secondary
394 deposition rate by a factor of 5 when increasing pH from 4 to 6.5.

395 The measured secondary deposition rates as a function of temperature are shown in **Figure 6**
396 for extracts at various solid concentrations: the original extract at 13.3 wt% and those diluted with
397 pure water to 1.3, 0.28, 0.14 and 0.034 wt%. We note that due to a strong buffering effect of the
398 coffee extract, the pH values of the diluted extracts were close to that of the original extract (pH
399 5), with the highest value of pH 5.5 for the most diluted extract (0.034 wt%). From the data in the
400 figure we observe that the rate of secondary deposition at the ambient temperature is only little
401 sensitive to the extract concentration. Dilution of the original extract by a factor of up to 400

402 results in not more than a two fold decrease in the deposition rate, which at ambient temperature
403 is only barely distinguishable from the experimental error. In particular, we see that the
404 deposition rate for diluted extracts (solid concentration below 1.3 wt%) is largely independent of
405 the extract concentration. This could be explained by recalling that there is always a reversibly
406 deposited layer present at the surface in contact with the extract. Let us assume that this reversible
407 layer is dense enough at all concentrations considered here so as to effectively saturate the
408 underlying irreversibly bound layer. Then the rate of growth of the irreversible layer may be
409 simply driven by incorporation of the loosely deposited material saturating the interface, and
410 hence it would be essentially independent from the solution composition. However, this does not
411 explain why the deposition rates at elevated temperatures from the original extract are much
412 higher than from diluted ones.

413 In **Figure 7** we show the Arrhenius plot for deposition rates, where the data for the original
414 (13.3 wt%) and the most diluted extract (0.036 wt%) are compared. The activation energy for
415 deposition of the original extract was found to be about 130 kJ/mol, corresponding to an increase
416 of the deposition rate by more than two orders of magnitude between 25 and 65°C. However, the
417 deposition rate for the diluted extract, increased by less than 10 fold between 25 and 70°C
418 corresponding to an activation energy of about 30 kJ/mol. The difference in activation energies
419 between the original and diluted extracts indicates that there is a different deposition mechanism
420 operating in the two cases. In order to consider this in more detail, let us look first at aggregation
421 in bulk coffee extracts upon their heating.

422 As fouling is primarily driven by interactions between depositing entities themselves rather
423 than between depositing entities and the original surface, it is instructive to consider a possible
424 relationship between surface deposition and aggregation in the bulk suspension. Here we used
425 static light scattering to investigate the Brownian aggregation of colloidal particles in the bulk
426 extracts at various dilutions and temperatures. In **Figure 8a** we show the measured scattered light
427 intensity for the 200 times diluted extract after heating for 1 hour at the indicated temperatures.
428 The pattern corresponds to gradual aggregation of smaller particles to larger clusters. There is a
429 strong increase in the mean radius of gyration with increasing temperature, as can be seen in
430 **Figure 9**. The observed behavior is very similar to the one found in **Figure 6** for the rate of
431 deposition.

432 This is further supported by the fact that the activation energy for deposition from diluted
433 extracts observed in **Figure 7** is of the same order of magnitude as for the so-called reaction

434 limited aggregation, where a typical energy barrier for aggregation is on the order of 10kT
435 (Hunter, 2001), corresponding to the activation energy of 25 kJ/mol. These results indicate a
436 correlation between irreversible aggregation in solution at elevated temperatures and secondary
437 surface deposition in diluted coffee extracts.

438 A scattered intensity pattern very different from the one observed in diluted extracts was found
439 when the original extract was heated at higher temperatures, as shown in **Figure 8b**. It appears
440 that large particles of the order of tens of microns emerge after heating at elevated temperatures,
441 although a good portion of the original colloidal particles is still present in the system. This
442 indicates that in the original extract there is an irreversible formation of large aggregates upon
443 heating, indicative of an association or a phase transition, as opposed to the gradual cluster-
444 cluster aggregative growth seen in diluted extracts. These larger aggregates can then either
445 directly assemble at the surface, or be deposited from the solution, in either case leading to much
446 higher deposition rates compared to diluted extracts. These results suggest that the aggregation
447 and deposition mechanisms in coffee extracts are strongly dependent on their concentration. It is
448 worth noting that concentration driven association phenomena have been observed using light
449 scattering in moderately concentrated solutions of peptides (Javid et al., 2011), proteins (Le Bon
450 et al., 1999) and polysaccharides (Burchard, 2001), as well as in coffee extracts using
451 viscosimetry (Redgwell et al., 2005).

452 ***Microscopy and gravimetric study***

453 Scanning electron microscopy images of surfaces before and after deposition were taken in
454 order to complement the information obtained by OWLS. Images of bare silica surface are flat
455 and featureless down to resolution length scales of tens of nanometers, as shown in **Figure S1a**.
456 The primary layers detected by OWLS are not visible by SEM and the corresponding image
457 looks like those of the bare surface, even when a scratch to the primary layer is done. Missing
458 contrast between the original surface and the deposited layer indicates information that the
459 primary layer is uniform and homogeneous at the used resolution.

460 The secondary deposited layer on silica surface exposed to the extract at 50°C for 5 minutes
461 can be made visible through SEM by scratching it to enhance the contrast between the layer and
462 the surface (**Figure S1b**). The mass of the secondary deposit measured by OWLS for these
463 conditions was about $1\text{mg}\cdot\text{m}^{-2}$ which was on the top of the primary layer constituted
464 approximately by another $1\text{mg}\cdot\text{m}^{-2}$. The contrast between surface and deposited layer was
465 stronger in the case where the surface was exposed to the extract at 70°C for five minutes, as

466 shown in **Figure S1c**. In this case the mass measured by OWLS during the secondary deposition
467 was 6 mg.m^{-2} , again on top of 1 mg.m^{-2} of primary layer. Visual inspection of the SEM pictures
468 indicates that in all cases the deposited layers were homogeneous and uniformly covering the
469 exposed surfaces.

470 We further used gravimetry in order to measure the deposition rates at longer deposition times,
471 and therefore for thicker deposited layers. As mentioned above, the gravimetry measurements can
472 be performed only after an appreciable amount of mass has been deposited, which imposes a
473 lower limit to the applicability of this method, which happens to be very close to the upper limit
474 of OWLS. Therefore with this technique one can compare the deposition rates and deposited
475 mass over longer time for dense, concentrated extracts and follow the history of the deposition
476 process beyond the limits of OWLS. This also gives us the opportunity to verify the compatibility
477 between these two techniques.

478 One important aspect in the design of these experiments is that in the measurement cells used
479 for gravimetry and OWLS the hydrodynamic conditions at the deposition surface should be
480 similar. As described in the experimental section this is obtained by a proper design of the
481 gravimetric cell which in the experiments discussed in the following led to a velocity gradient at
482 the surface equal to about 500 s^{-1} . Measurements were performed for the coffee extract at 65°C .
483 The results in **Figure 10** show that the deposited mass as a function of time increases in a log-log
484 plot in a consistent manner going from the short time OWLS measurements (diamonds) to the
485 long-time gravimetric measurements (squares). This results in comparable deposition rates equal
486 to about $1 \text{ mg.m}^{-2}.\text{min}^{-1}$, as determined by the two methods.

487 Gravimetric experiments have been performed using the original extract to measure the
488 deposition rates at higher temperatures, i.e. 73 and 83°C . The obtained values are very similar to
489 the one measured at 65°C , thus confirming the plateau in the deposition rate shown in **Figure 6**
490 which was obtained by OWLS.

491

492

Conclusions

493

494 The deposition kinetics of an industrial coffee extract at wide range of temperatures was
495 studied by OWLS and gravimetry. The first step in deposition formed a primary layer of about 1
496 mg.m^{-2} on all the considered surfaces. At ambient temperature the secondary exposure of the
497 primarily covered surface leads to reversible deposition, attributed to the electrolyte adsorption.

498 Temperature and concentration were found to be the main operating parameter driving
499 deposition, which in the original extract reached a maximum rate at 65°C. Gravimetry was used
500 as an independent method to measure the deposition rates. A comparison of the deposition rates,
501 measured by gravimetry at longer times and by OWLS at shorter times, shows a very good
502 consistency between the two methods. Deposition rates at ambient temperature were only little
503 dependent on extract concentration, although they increase moderately with decreasing extract pH
504 between 6.5 and 4. Activation energies for deposition kinetics were determined for both the
505 original and diluted extracts. The activation energy for the original extract (solid concentration
506 13.3 wt%) was found to be about 130 kJ/mol between 25 and 65°C. However, the activation
507 energy for diluted extracts was only about 30 kJ/mol. This can be due to the fact that the surface
508 in contact with the diluted extracts is saturated with a loosely bound layer of material, which
509 gradually becomes incorporated into irreversibly bound deposits. Therefore the buildup of the
510 irreversibly bound deposit is independent of the extract concentration, provided that it is
511 sufficient to reversibly saturate the available surface. In contrast, the original concentrated extract
512 exhibits an irreversible association of suspended entities to large clusters at elevated
513 temperatures, as indicated by static light scattering, leading to a different deposition mechanism
514 with much higher deposition rates at higher temperatures. Our findings contribute to better
515 understanding of mechanism and kinetics of deposition from protein/polysaccharide aqueous
516 systems, which is a major cause of fouling at heat exchange surfaces of evaporators in production
517 of instant coffee powders and other similar operations. In particular, the knowledge of deposition
518 kinetics and corresponding activation energies will allow to determine time evolution of deposit
519 thickness on evaporator walls and to assess its effect on heat transfer coefficients as a function of
520 operating time and temperature. This will help to guide better design and improved operation of
521 relevant processes in food and chemical processing industries.

522

523

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524

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Table 2. Deposited amount of the irreversible primary layer from the coffee extract on various surfaces at ambient temperature.

Table 3. Influence of pH on secondary deposition rates of concentrated coffee extract.

Table 1. Refractive indices as a function of temperature. T denotes temperature in °C and x_E is the weight concentration of solid content in coffee extract suspension (in g.cm⁻³), $n_{C,E}$ denotes refractive index of coffee extract and n_{C,H_2O} denotes refractive index of water.

Parameter	25°C	T [°C]	Source
n_{C,H_2O}	1.331144	$n_{C,H_2O}^{25^\circ C} - \frac{75453.41\Delta T + 2340.431\Delta T^2 + 6.363191\Delta T^3}{T \cdot 10^7 + 65.7081 \cdot 10^7};$ <i>where</i> $\Delta T = T - 25$	<i>a</i>
$n_{C,E}$	$0.2090x_E + n_{C,H_2O}^{25^\circ C}$	$(4.2725 \cdot 10^{-6}T^2 - 4.665 \cdot 10^{-4}T + 2.1795 \cdot 10^{-1})x_E + n_{C,H_2O}^T$	measured by refractometer
n_S	1.525718	$1.52542 - 1.23 \cdot 10^{-6}T$	<i>a</i>
<i>a</i> - reference (Saini et al., 1994)			

Table 2. Deposited amount of the irreversible primary layer from the coffee extract on various surfaces at ambient temperature.

Surface	Extract Solid Content [wt%]	Deposited Mass [mg.m ⁻²]
Silica	13.3	1.2
Silica	1.33	1.1
Silica	0.034	1.1
Niobia	13.3	1.2
Alumina	13.3	0.7
PEG-3.5-PLL	13.3	0.4
Polystyrene	13.3	0.90

Table 3. Influence of pH on secondary deposition rates of concentrated coffee extract.

Temperature [°C]	pH	Deposition Rate [mg.m ⁻² .min ⁻¹]
25	4	0.006
	5	0.003
	6.5	0.003
65	4	1.6
	5	1.2
	6.5	0.3

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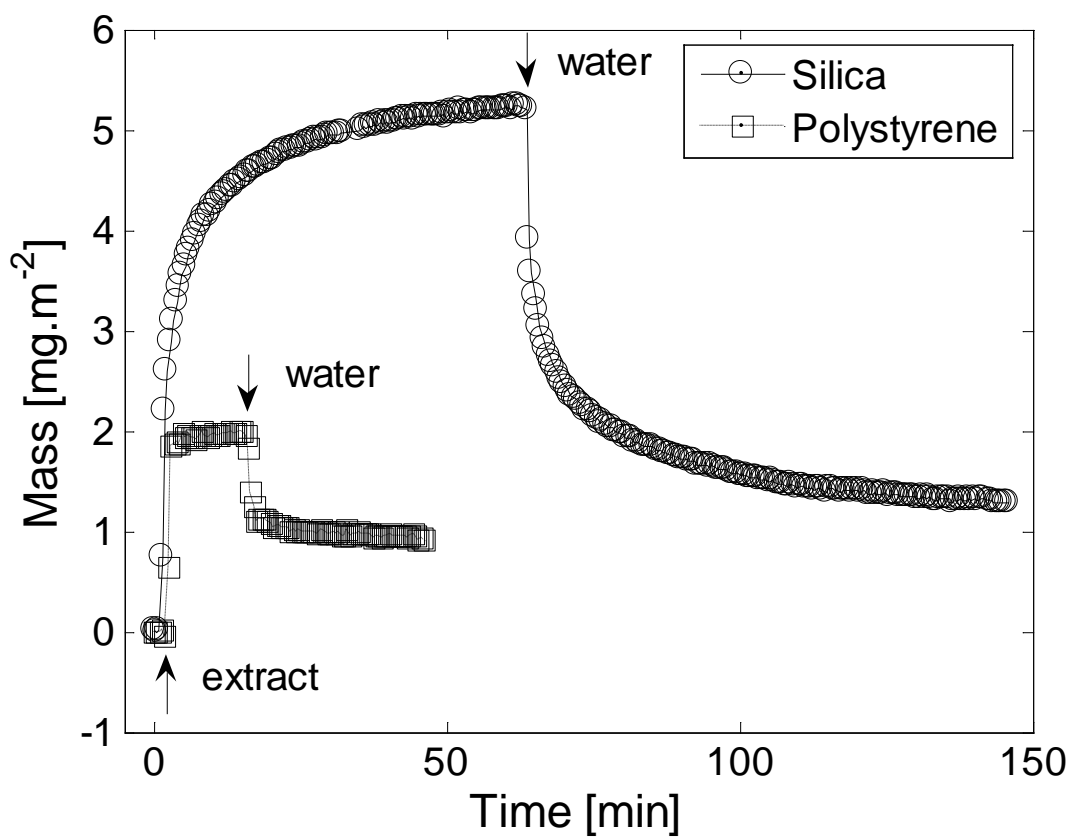


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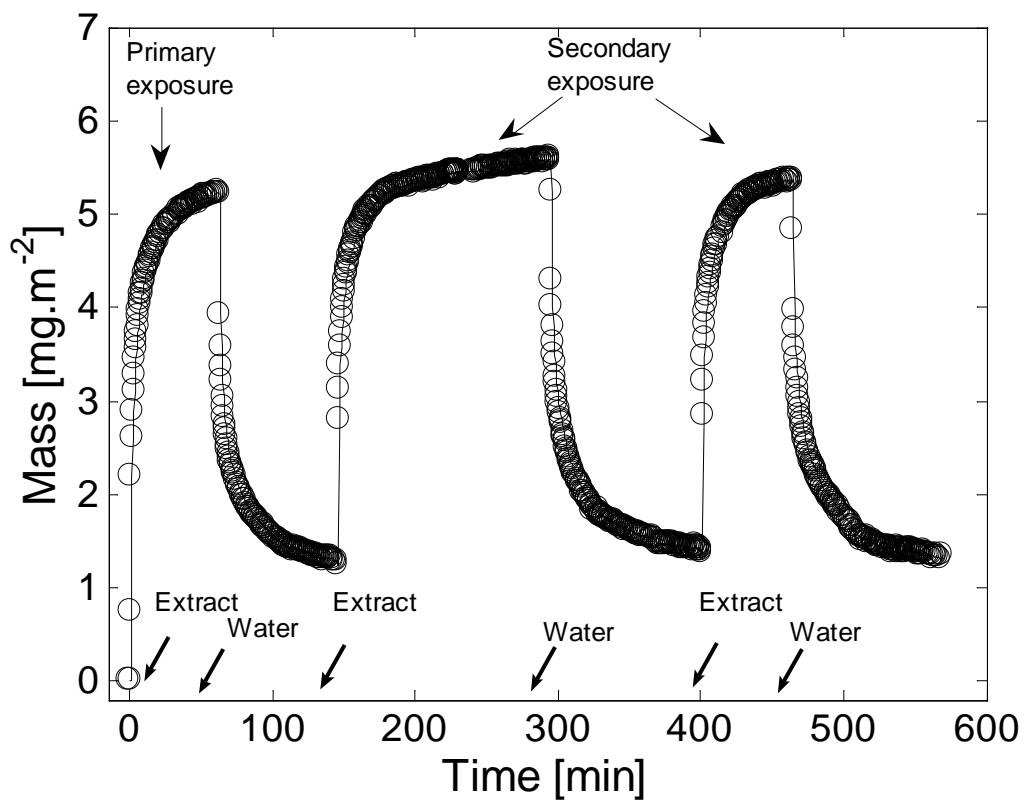


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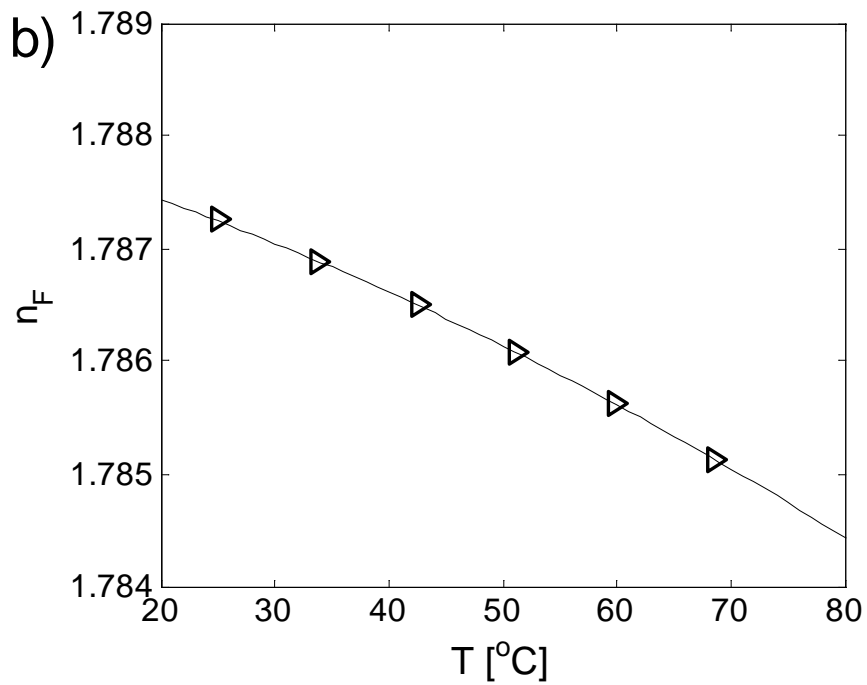
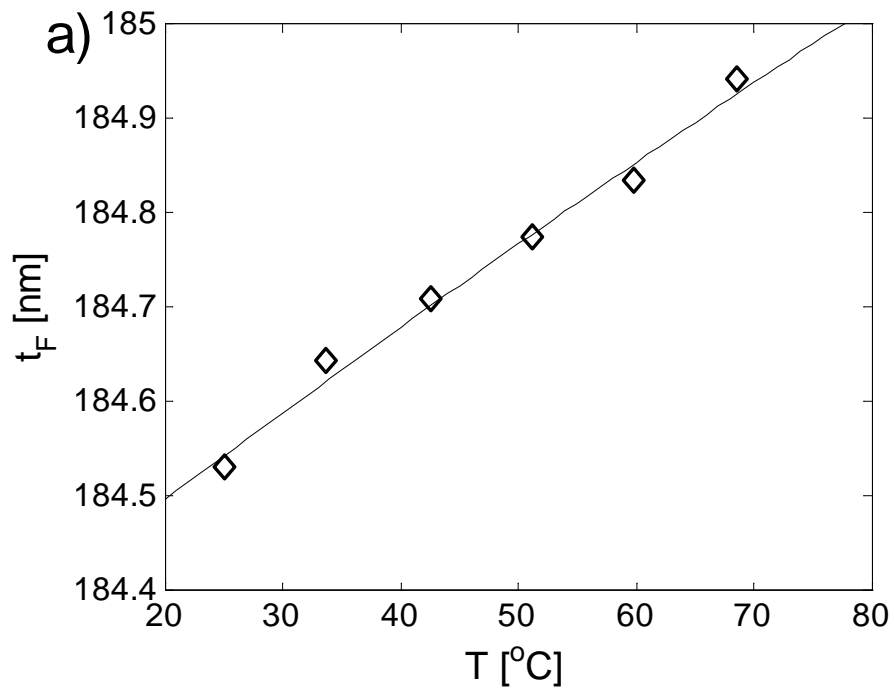


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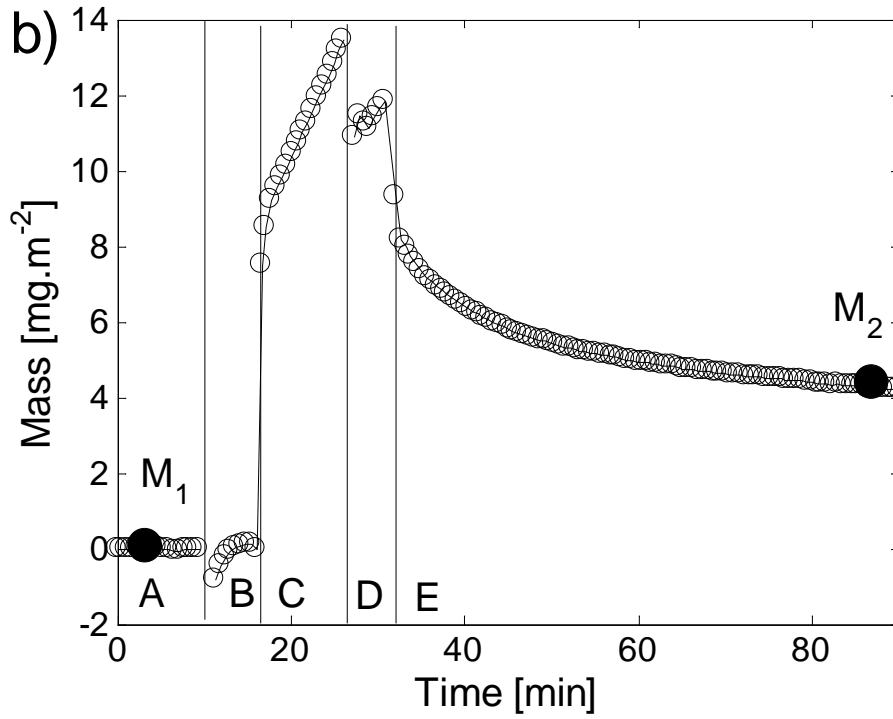
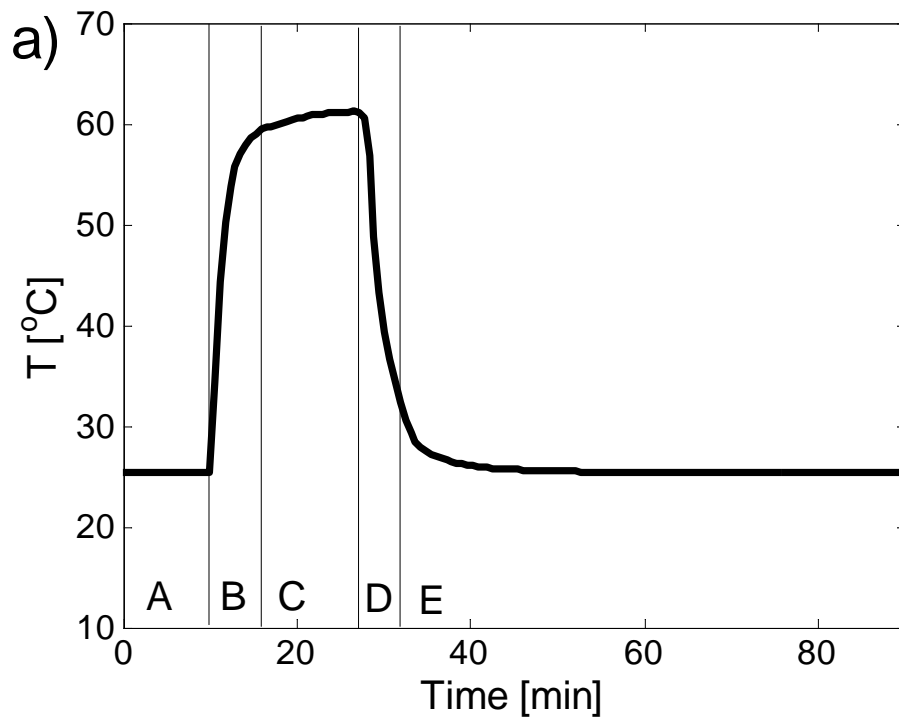


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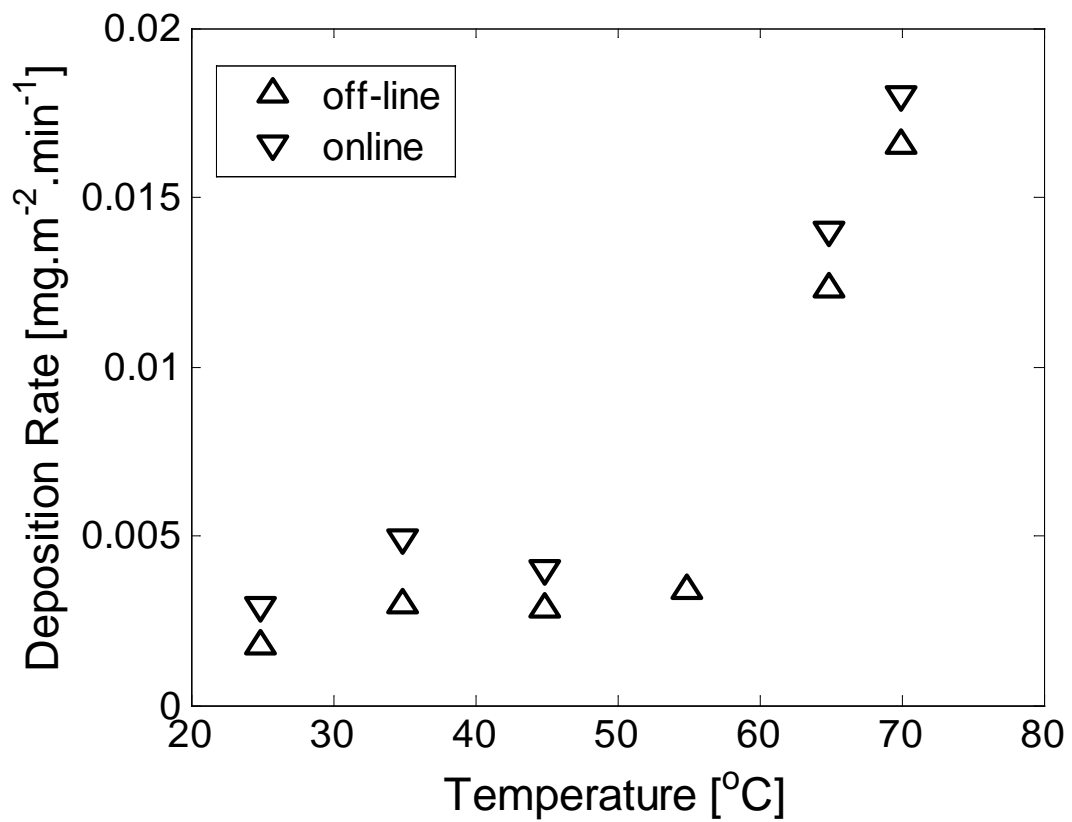


Figure 5. Comparison between deposition rates determined online and off-line for diluted extract (1.3 wt%) as a function of temperature.

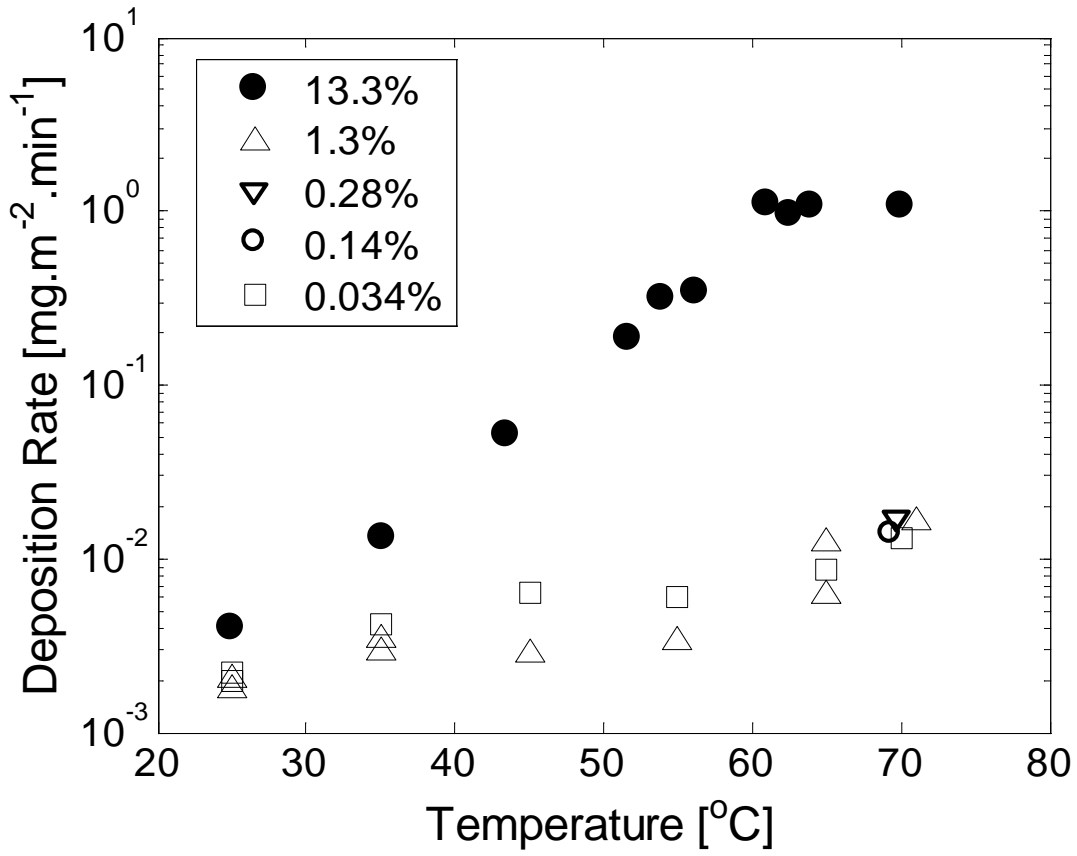


Figure 6. Deposition rates for the original extract as a function of temperature.

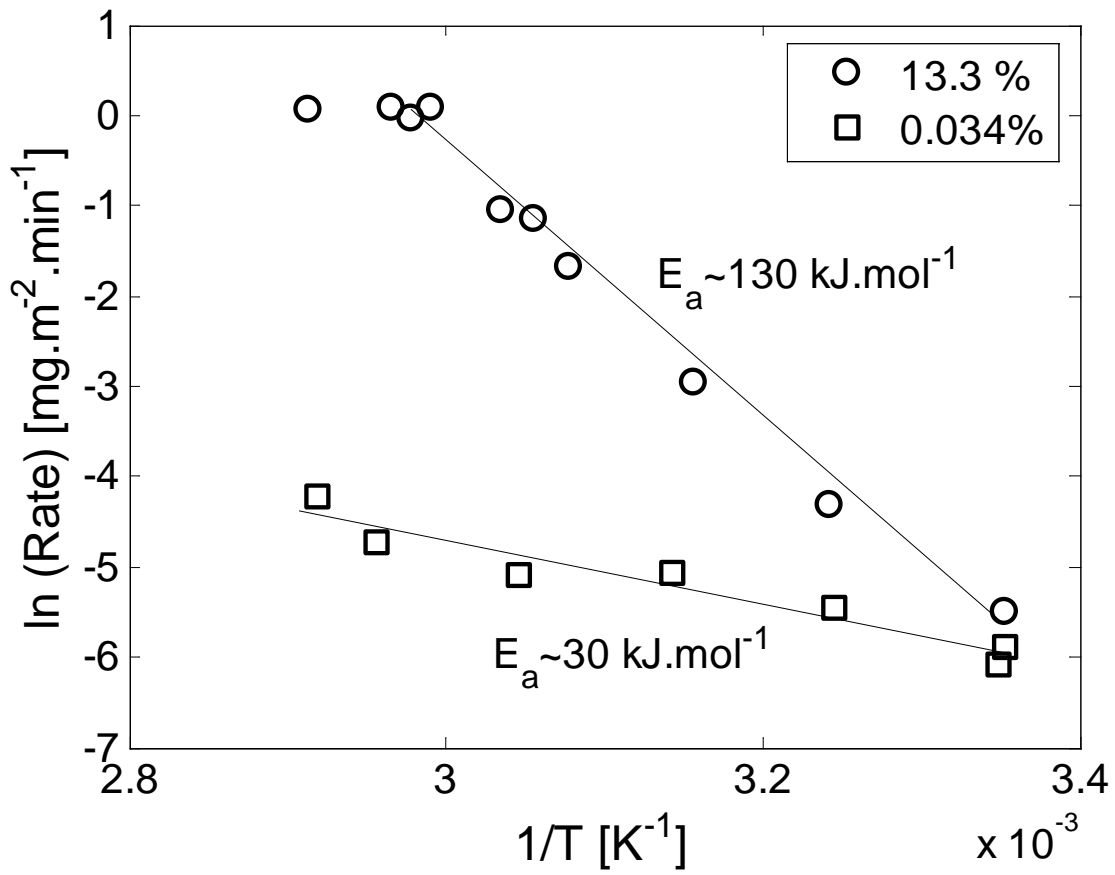


Figure 7. Arrhenius plot for the deposition rates.

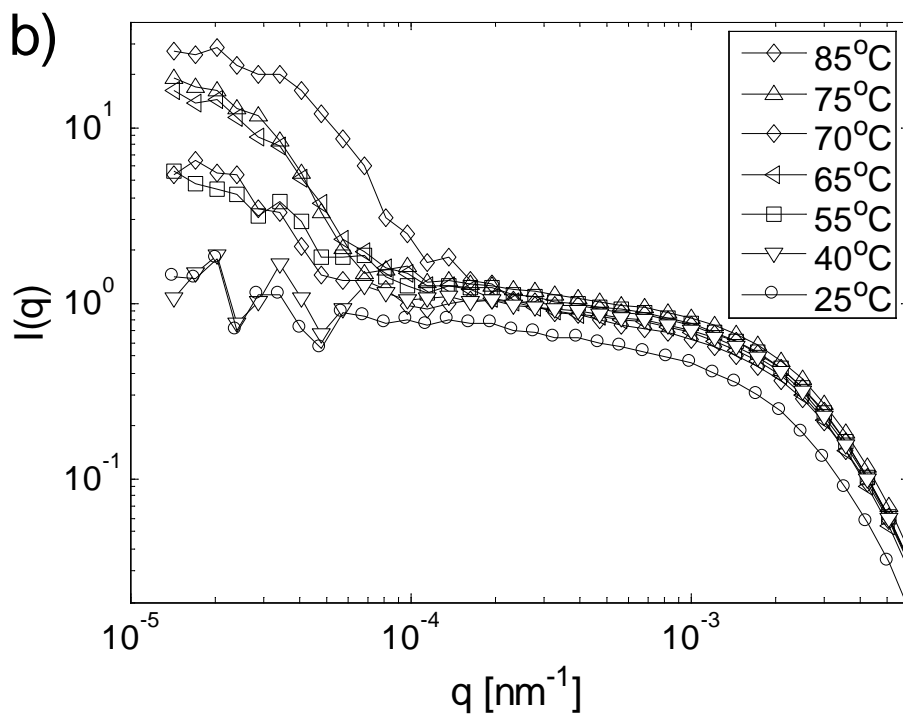
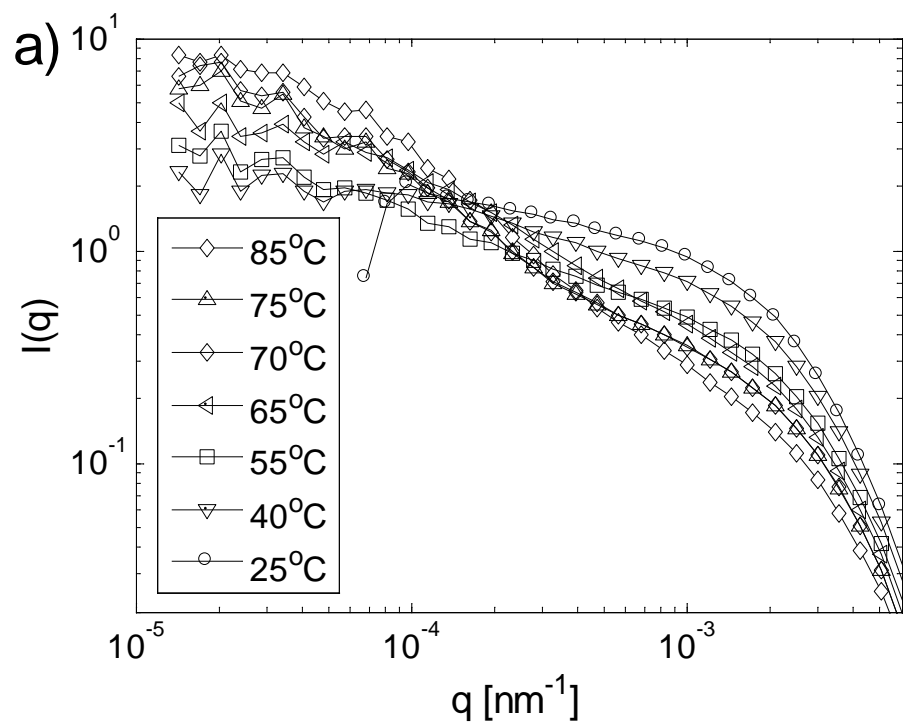


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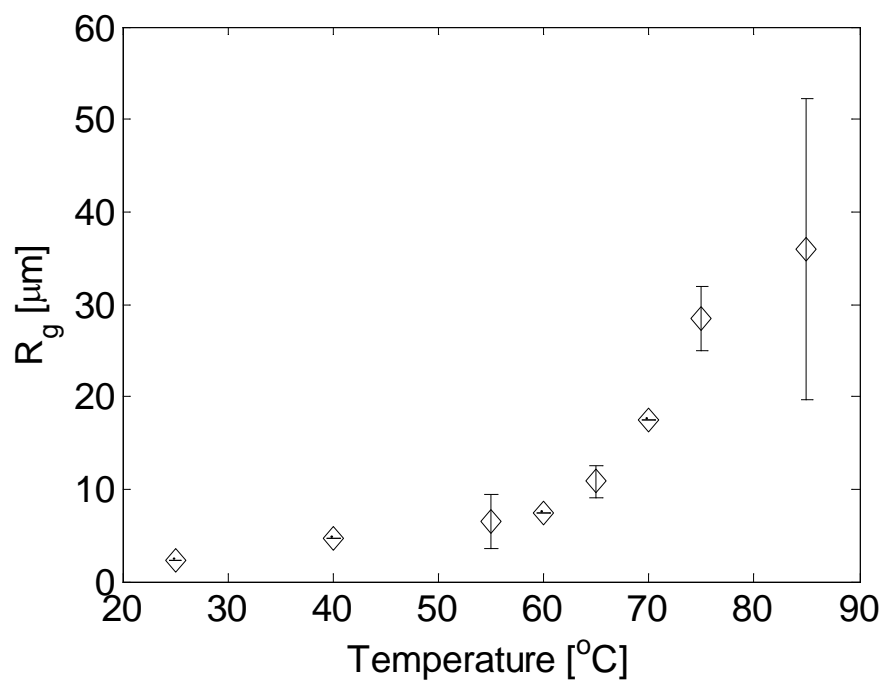


Figure 9. Radius of gyration measured by SLS for the 200 times diluted extract as a function of the aggregation temperatures. Error bars represent confidence intervals for radii of gyration estimated from data in Figure 8a.

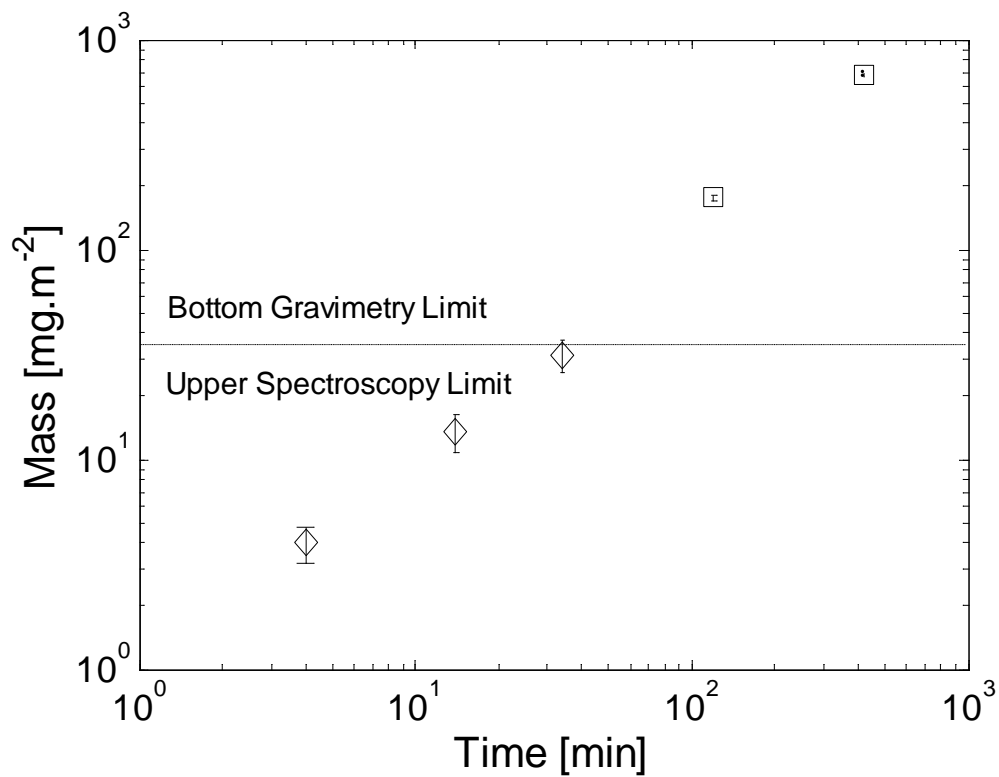


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