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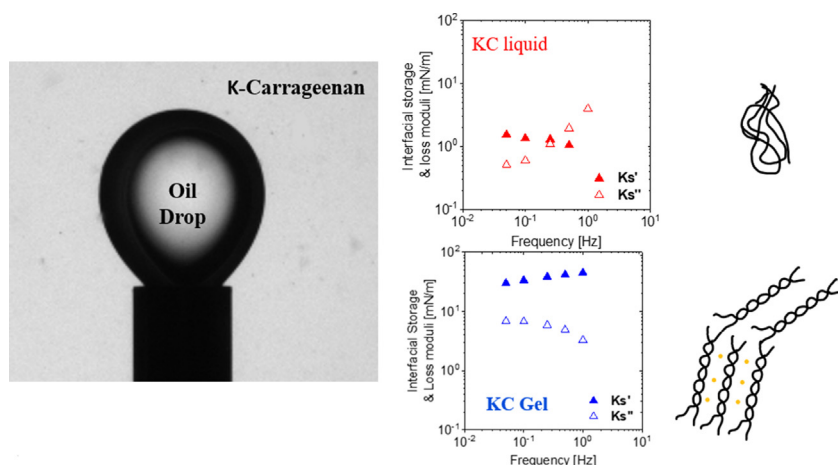
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## Interfacial viscoelastic moduli in a weak gel

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## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypothesis:** The measurement of interfacial viscoelastic moduli provides information on the ability of surface-active agents to texture the interface. However, the contribution of the bulk rheology cannot be ignored in particular when the continuous phase exhibits a gel-like behavior, even with low modulus.

**Experiments:** Between 2 and 6 g/L, κ-carrageenan aqueous solutions have no significant activities at interfaces. At low concentrations or high temperatures, they behave like Newtonian liquids. Upon heating or cooling, a reversible liquid/gel transition appears with a hysteresis where the rheological behavior can be easily modulated by adjusting κ-carrageenan concentration. The frequency dependence of bulk and interfacial viscoelastic moduli are determined using a conventional shear rheometer and a drop tensiometer with a polyisobutene oil, respectively.

**Findings:** The effect of concentration and temperature is analyzed and the frequency dependence of interfacial moduli is correlated with those of the bulk. In presence of a gelled κ-carrageenan solutions, an elastic behavior of the interface appears and strengthens as the elastic modulus of the suspended phase is

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high. It turns out that the oscillating pendant drop method could be a sensitive indicator of the presence of very weak gels, even hardly detected by a shear classical rheometry.

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## 1. Introduction

In emulsions and foams, all intra and intermolecular forces (Van der Waals, ionic, hydrogen...) contribute to the phase separation and the creation of an interface separating the two fluids. The minimization of this interface, favorable to the decrease of the global energy, is induced by a force, expressed per unit length, and called surface (air–liquid) or interfacial (liquid–liquid) tension [1].

The surface tension can provide an indication about the compatibility between the two phases. Indeed, high interfacial tension signifies a strong incompatibility between the liquids present and a less easy emulsification. This is usually overcome by using surface-active agents such as surfactants, which, by their amphiphilicity, lower the interfacial tension between the two liquids, promote mixing, and at the same time prevent coalescence through steric or electro-steric effects [2–4].

The accumulation of surface-active agents at the interface, their organization and their dynamics inevitably induce static moduli indicated by the diminution of the surface tension. In addition, it induces also dynamic moduli, called viscoelastic, when probed by oscillatory measurements for example. In the latter case, the interfacial rheology is concerned.

The measurement of surface tension [5] and dynamic interfacial rheology can be achieved through different techniques [6–9]. One of the most commonly used methods is the oscillating drop [10].

All these methods probe the interface itself in a quasi-static regime to limit bulk contribution [11,12] which is easily reached for low viscous fluid.

The determination of the interfacial tension is more critical for gels or yield stress fluids. This topic is only partially tackled in the literature and exclusively for strong gels and eventually for static measurements to determine the surface tension as reported in ref.[13,14]. The authors proposed a method to measure the surface tension of yield stress fluids of highly elastic modulus, of about one order of magnitude the value of the yield stress, using capillary bridges.

For dynamic measurements, Freer [15] reported that viscous forces cannot be neglected in dynamic pendant drop analysis. Yeung and Zhang [16] showed, by simulation, the shear resistance of the interface at high frequency when developing the interfacial films in a pendant drop method.

This study aims at evaluating the impact of an extremely low threshold or a weak gel on the interfacial rheology of an oil/water interface. For this purpose, a weak model gel, consisting in aqueous solution of  $\kappa$ -carrageenan (KC), is chosen for its reversible gelation with temperature.

$\kappa$ -carrageenan is an anionic polysaccharide extracted from edible red algae [17]. It has many industrial applications such as cosmetics, food, health and pharmaceuticals [18].  $\kappa$ -carrageenan is a sulfated polygalactan with an ester-sulfate content of between 15 and 40% and presents an average molar mass well over 100 kDa. It is formed by alternating units of D-galactose and 3,6-anhydro-galactose linked by  $\alpha$ -1,3 and  $\beta$ -1,4-glycosidic bonds. At high temperatures the KC chains are in a random coil conformation and the solutions are rather Newtonian liquids. By lowering the temperature below a critical temperature  $T_{gel}$ , the chains adopt a helix conformation. In the presence of salt, double helices can be formed and if the concentration is sufficient, they aggregate to form a 3D network conferring gel-like properties to the KC

solution. By heating above  $T_{sol} > T_{gel}$ , the helices regain the random coil conformation and highlights the existence of a fully reversible hysteresis [19]. The two critical temperatures depend closely on KC concentration and the ionic strength but also on the chemical nature of the salt, and justify the interest of this type of polysaccharide in various applications [20].

Thus, it happens that it becomes possible to have a liquid or a weak gel at the same temperature depending on the thermal history and the composition of KC solution. In this way, we propose to highlight the effect of bulk rheology, especially in the case of very weak gel, on the behavior of interfacial viscoelastic moduli.

## 2. Materials and methods

### 2.1. Chemicals and solution preparation

A sulfated  $\kappa$ -carrageenan, extracted from seaweed, was supplied as a powder by Aldrich (batch #BCBX5072). It was used, without any supplementary modification or purification, to prepare aqueous solutions in pure MilliQ water (18 M $\Omega$ .cm).

Aqueous solutions were prepared at 2, 3, 4, 5 and 6 g/L of KC. The appropriate mass of  $\kappa$ -carrageenan powder was dissolved in water under stirring at 80 °C for 2 h. Then, the homogenous samples were stored in the fridge until the next day.

The oil phase was a polyisobutylene oil purchased under the trademark Indopol from INEOS Oligomers. The selected grade was L-6 (>99% pure, batch #10 PB0250).

Before any experiment, the samples were preheated at 60 °C during 15 min in a heating bath to bring them all to liquid state. Note that the aqueous  $\kappa$ -carrageenan solution was degassed 3 times using a vacuum desiccator in order to avoid air bubbles for all measurements.

For interfacial rheology experiments, the density of the oil (Indopol) and aqueous ( $\kappa$ -carrageenan solutions) must be known for each studied temperature. For that purpose, the density of Indopol as a function of the temperature of this study, extracted from the product brochure, is summarized in Table S1 (SM). In addition, the density of the  $\kappa$ -carrageenan solutions is measured at different temperatures using a Mettler Toledo densitometer (Mettler Toledo, France). Samples were first degassed for 10 min to remove any dissolved air then density was measured at the 4 temperatures (30 °C, 25 °C, 20 °C and 15 °C) for the concentrations of 0.05, 0.5, 1 and 5 g/L. Thus, the dependence of the density with the concentration was determined at each temperature and allowed to deduce the density of any other concentration.

### 2.2. Bulk and interfacial rheology

Bulk  $\kappa$ -carrageenan rheology was determined using a stress-controlled rheometer (DHR3; TA Instruments; Guyancourt, France). The lower limit of the torque was given as 0.5 nN/m in oscillatory mode and the sensitivity of about 0.05 nN/m. Consequently, the data were considered reliable only if the measured torque values were higher than or equal 50 nN/m. Before loading the sample, the coaxial cylinders (Couette) geometry (rotor radius = 14 mm; stator radius = 15 mm; immersed height = 42 mm) was preheated at 60 °C. Isothermal measurement was performed after maintaining the sample at a given temperature for at least 1000 s to reach a steady state in the sample before any rhe-

ological measurement. The frequency sweep was performed between 1 and 0.01 Hz at 10% strain which was in the linear regime for all samples and temperatures. Temperatures of 30, 25, 20, and 15 °C were selected in this study, unless specified. All measurements were repeated at least three times ensuring that the variability of the results is less than 5%.

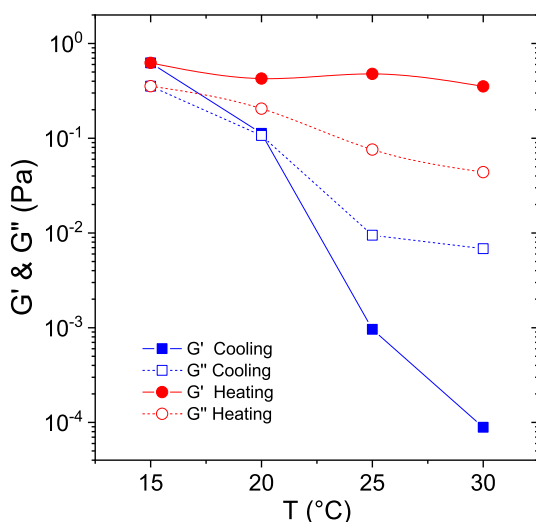
Interfacial tension (static) and interfacial viscoelastic dilatational moduli (dynamic) of KC/oil interface were investigated via a drop-profile tensiometer (TRACKER; Teclis; Civrieux-d'Azergues, France). For the experiments, a rising drop of indopol was put into contact with the aqueous  $\kappa$ -carrageenan solution filling the transparent cell. The temperatures were fixed to 30, 25, 20 and 15 °C and held up at least 10 min to get a thermal steady state. To avoid any evaporation of the sample, a layer of paraffin oil was deposited on the top of the aqueous solution. The frequency was varied between 0.05 and 1 Hz and the amplitude of oscillation was fixed at 10% of the initial drop volume chosen equal to 10  $\mu$ L. We have ensured that these conditions were in the linear domain of the interfacial viscoelastic moduli of the samples (see Fig. SM1 in SM). Five oscillations of volume were imposed followed by five blank cycles. This procedure was repeated until the steady state was reached. Then, the interfacial viscoelastic moduli were averaged on the last five oscillations. The viscoelastic moduli were extracted from the oscillations and the surface tension from the static part of the protocol. All measurements were repeated at least three times ensuring that the variability of the results was less than 10%. In particular, for static measurement, the determination of the surface tension was found accurate at  $\pm 0.5$  mN/m. Note that a thorough discussion about the reproducibility is given in the Discussion part.

### 3. Results

#### 3.1. Bulk rheology

##### 3.1.1. Thermo-rheological behavior of $\kappa$ -carrageenan solutions

Fig. 1 shows  $G'$  and  $G''$ , the elastic and viscous moduli respectively at 0.01 Hz, after cooling or heating stage of  $\kappa$ -carrageenan solution at 6 g/L. At each temperature, to reach a steady state, the sample is maintained at least during 1000 s before to perform



**Fig. 1.** Viscoelastic moduli  $G'$  (●) and  $G''$  (○) at 0.01 Hz of  $\kappa$ -carrageenan solution at 6 g/L during cooling (blue) and heating (red) stage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the rheological measurement. As the temperature decreases, the two moduli follow a strong increase, whereas  $G'$  becomes higher than  $G''$  at 15 °C testifying for a sol–gel transition. The elastic modulus of the 6 g/L of KC solution taken at 0.01 Hz, increases from 0.0001 Pa at 30 °C to 0.39 Pa at 15 °C. However, it's important to mention that the moduli below 0.001 Pa are to be considered with caution even the measured torque is in the acceptable range of the device. In fact, other artefacts such as inertia may affect the measures. So, the data below 0.001 Pa are given as a guide for eyes.

When increasing the temperature,  $G'$  and  $G''$  both decrease but  $G'$  remains larger than  $G''$  revealing a hysteresis of the sol–gel transition of  $\kappa$ -carrageenan solution. If the temperature is increased further, a liquid state is obtained at higher temperature, namely up to 50 °C for this sample (not shown). Indeed, the chemical structure of  $\kappa$ -carrageenan is fundamental in determining the sol–gel transition. Polymer conformation and, consequently, self-aggregation changes with temperature. This molecular understanding is well documented [21,22] but is briefly mentioned here. Aqueous solutions containing  $\kappa$ -carrageenan at low concentrations and high temperatures are Newtonian liquids as the polysaccharide chains are under the form of loose coils. In presence of specific counterion, as the concentration rises and the temperature decreases, a coil to helix conformation transition occurs. Above a critical concentration  $C^*$ , interconnection of the double helices happens and a gel can be formed.

The transition temperatures during heating or cooling depend on the ionic strength, the nature of ions, and the concentration of polymer [17,18]. In the present study, the sulfated  $\kappa$ -carrageenan is used and thus the charges of the macromolecules are screened with potassium ions. The product is used as received without any further purification or adjustment of the ionic strength.

The interesting feature of this hysteresis is to obtain a liquid or a gel behavior for the same solution at the same temperature depending on the thermal history. Thus, it becomes possible to evaluate the effect of the bulk viscoelastic properties on the interfacial tension and the viscoelastic moduli of the oil/water interface independently of the surface activity of the polymer. It is worth mentioning that different heating and cooling cycles do not affect the reversibility of the hysteresis loop.

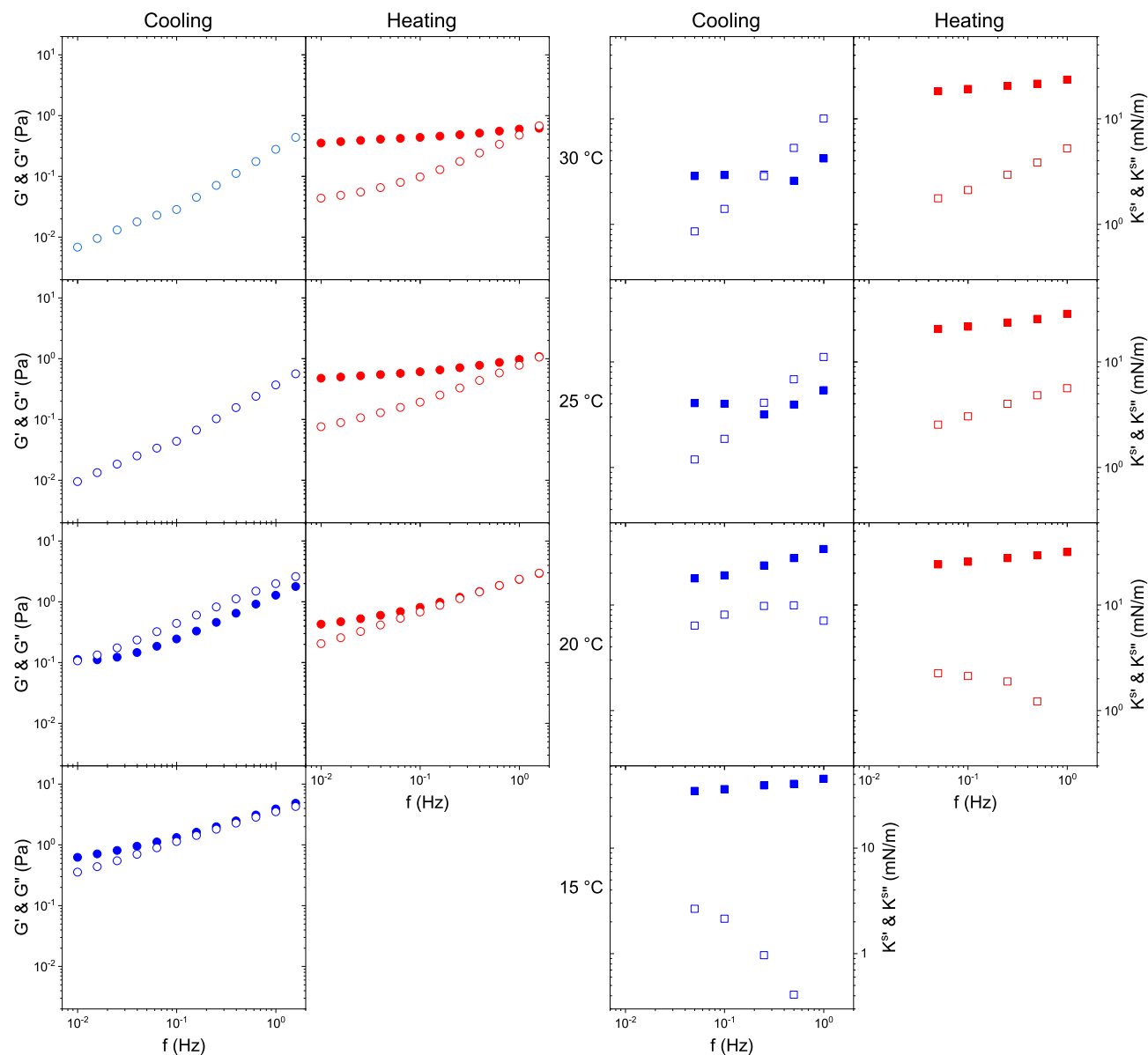
##### 3.1.2. Frequency dependence of the viscoelastic moduli of $\kappa$ -carrageenan solutions at various temperatures

Frequency dependence of  $G'$  (elastic modulus) and  $G''$  (viscous modulus) of  $\kappa$ -carrageenan solution is studied as a function of concentration and temperature. Fig. 2 presents the isothermal frequency dependence of  $G'$  and  $G''$  at different temperatures after cooling or heating for 6 g/L of KC. The same data for the other concentrations of  $\kappa$ -carrageenan are given in Fig. 3 and Figs. SM3–SM5 in SM.

During cooling from 60 °C, it appears that at 30 °C,  $G'$  is almost undetectable while the  $G''$  versus the frequency exhibits a slope of  $0.99 \pm 0.00$  in a log–log scale, close to 1 as it was expected from a pure viscous liquid [23]. As a matter of fact, the solution behaves like a liquid at 30 °C.

Reducing the temperature to 25 °C, the  $G''$  increases slightly while its slope =  $0.92 \pm 0.001$  remains close to 1.  $G'$  becomes detectable but one order of magnitude lower than  $G''$ . The behavior of the  $\kappa$ -carrageenan solution remains liquid-like although the slope of  $G'$  has not reached 2 in the range of the explored frequencies indicating a large distribution of the relaxation time of these  $\kappa$ -carrageenan solutions [24].

At 20 °C,  $G'$  shows a remarkable increase and becomes almost equal to  $G''$  at lower frequencies. In addition,  $G'$  seems to tend towards a plateau of about 0.1 Pa. Both  $G'$  and  $G''$  present a power law dependence with the frequency with an exponent of about



**Fig. 2.** Isothermal frequency dependence of  $G'$  (●),  $G''$  (○),  $K^s$  (■) and  $K^{sn}$  (□) for 6 g/L of  $\kappa$ -carrageenan at different temperatures during cooling or heating, as indicated in the figure.

$0.62 \pm 0.007$  (i.e. a slope of  $0.62 \pm 0.007$  in a log–log scale). Clearly, the system undergoes a solid–gel behavior between 25 and 20 °C.

The gel behavior appears more pronounced when the temperature decreases to 15 °C. In fact, the two moduli increase with  $G'$  being superior for most of the frequency while the exponent of the power law decreases to  $0.430 \pm 0.008$ .

During the heating ramp, the gel behavior is more evident. At 20 °C, the elastic modulus continues to increase and surpasses  $G''$ , especially at low frequencies showing a plateau of about 0.7 Pa, which is a signature of a weak gel.

Reheating to 25 °C and 30 °C, this signature becomes clearer for almost the entire range of frequency, i.e. the  $G'$  plateau persists while  $G''$  slope increases slightly, in stark contrast with the cooling phase.

These results confirm and refine the previous finding obtained in the previous section. It points out that a liquid or a gel can be obtained at the same temperature based on the thermal history of the  $\kappa$ -carrageenan solutions.

Under heating,  $G'$  increases and becomes larger than  $G''$  with a well-marked plateau, even at 30 °C where the  $\kappa$ -carrageenan solution was a liquid after cooling from 60 °C. So, for the same temperature, 25 and 30 °C namely, the  $\kappa$ -carrageenan solution is a gel or a liquid-like depending if it is heated or cooled, respectively.

The samples containing 5 g/L of  $\kappa$ -carrageenan shows a similar behavior than 6 g/L except that the moduli are lower compared to 6 g/L (see Fig. SM5 in SM).

Different behaviors are encountered with lower concentrations of KC. At 4 g/L, the elastic modulus appears at 20 and 15 °C during cooling and then persists during heating (Fig. 4). However,  $G'$  remains mainly lower than  $G''$  even if the two moduli become close at 25 and 30 °C and at lower frequencies. Clearly  $G'$  appears tending towards a plateau at low frequencies whose value would likely be higher than  $G''$  and confirm the weak gel character of the 4 g/L KC solution.

At 2 g/L,  $G'$  is hardly detectable and  $G''$  presents a slope of about  $1.04 \pm 0.004$  versus frequency regardless of the temperature, even for heating or cooling (Figs. SM3 in SM). No sol–gel transition and

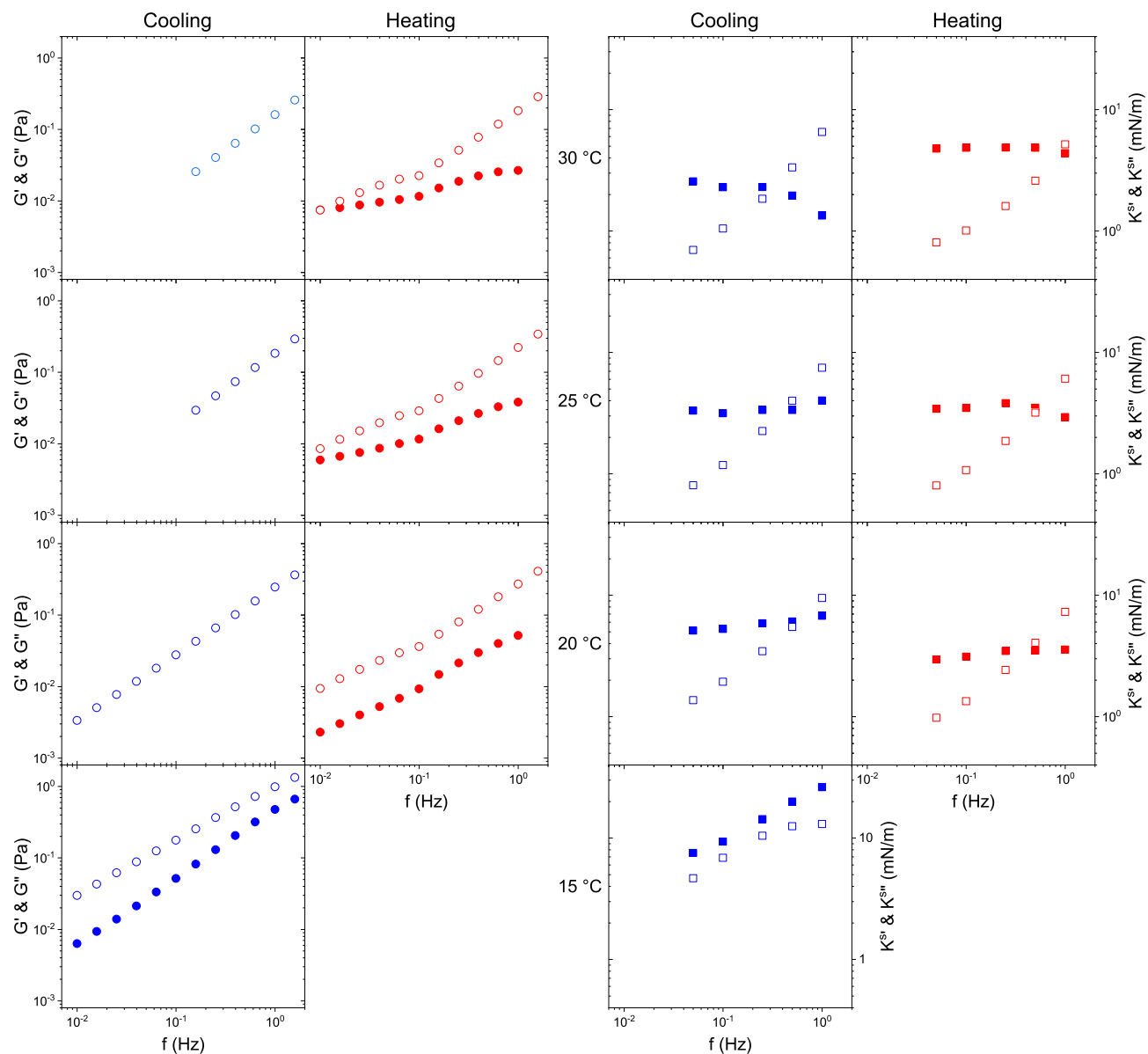


Fig. 3. Frequency dependence of  $G'$  (●),  $G''$  (○),  $K^s$  (■) and  $K^{sr}$  (□) for 4 g/L of  $\kappa$ -carrageenan at different temperatures during cooling or heating, as indicated in the figure.

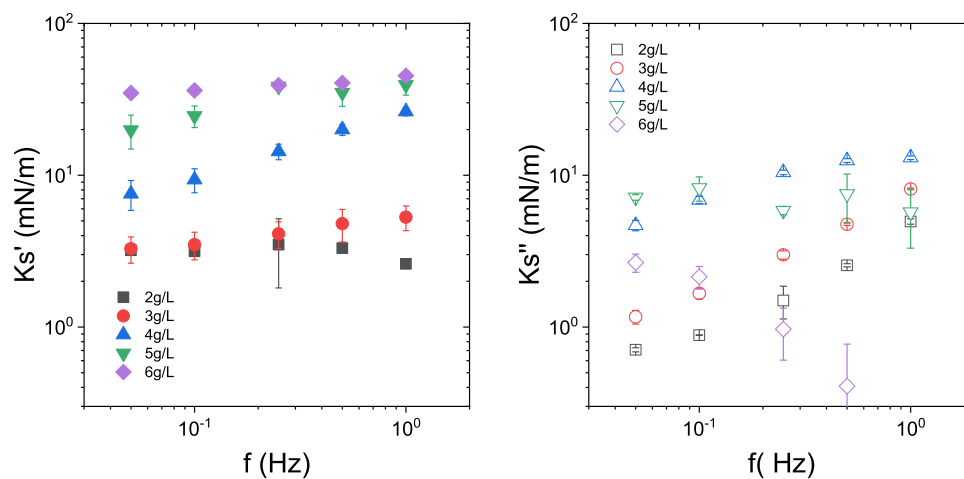


Fig. 4. Frequency dependence of  $Ks'$  and  $Ks''$  at 15 °C at different  $\kappa$ -carrageenan concentration as indicated in the figure.



no hysteresis of the rheological behavior are observed between 60 and 15 °C. Thus, for the same temperature, the same viscosity of the sample is measured either after cooling or heating. At 3 g/L, the rheological behavior is quasi-similar to that obtained at 2 g/L, except at 15 °C (Fig. SM4 in SM). For this latter temperature,  $G'$  increases significantly with the frequency but does not surpass  $G''$ . However, when heating the  $G'$  disappears rapidly.

As general trends, for lower  $\kappa$ -carrageenan concentrations (2 and 3 g/L), the liquid behavior dominates during cooling or heating stage. For 5 and 6 g/L of KC, the gel behavior appears at 20 °C during cooling and remains even after heating up to 30 °C. The 4 g/L shows an intermediate behavior (Fig. 3). It remains liquid during the whole cooling phase but changes to a gel-like behavior at 25 and 30 °C. Indeed, although  $G''$  remains higher than  $G'$  over the whole frequency window explored,  $G'$  clearly tends towards a plateau at low frequencies of the order of 0.01 Pa, denoting a very weak gel character.

An attempt was made to determine the flow yield stress of  $\kappa$ -carrageenan solutions through steady state flows. However, it was not possible to determine this value reliably due to the sensitivity limit of our rheometer and suggest that the yield stress would be lower than 1 mPa.

Note also that the data demonstrate the absence of strong moduli. Indeed, in the latter case, the elastic modulus  $G'$  would be one order of magnitude higher than  $G''$ . More particularly, the elastic modulus would remain constant with the frequency and the phase-shift angle very low. This configuration is never obtained in the present study since we deal with weak gels.

### 3.2. Interfacial phenomenon

#### 3.2.1. Static interfacial tension

The interfacial tension of indopol/water interface is given in Fig. SM2 for all  $\kappa$ -carrageenan concentrations and temperatures. The interfacial tension is quasi-independent of  $\kappa$ -carrageenan concentration and temperature. It varies only between 14 and 16.5 mN/m which is slightly lower than indopol/water net interface, found between 17 and 18 mN/m. This result confirms that  $\kappa$ -carrageenan has no interfacial activity and only slightly modifies the water/indopol interfacial tension, see discussion for more details.

#### 3.2.2. Interfacial rheology

Fig. 2 shows the frequency dependence of the interfacial dilatational viscoelastic moduli,  $K^S$  (elastic) and  $K^{S''}$  (viscous), for  $\kappa$ -carrageenan solution at 6 g/L between 30 and 15 °C during a cooling and heating cycle.

At 30 °C after cooling, the value of  $K^S$  is low and constant of about 3.64 mN/m. It is higher than that measured for Indopol/water net interface which is about 0.46 mN/m. Meanwhile,  $K^{S''}$  shows a power law dependence versus frequency.

The same trend is observed at 25 °C with slightly higher value of  $K^S$  of about 4.68 mN/m. At 20 °C, both moduli increase. However,  $K^S$  increases remarkably with frequency between 11.92 and 22 mN/m and surpasses  $K^{S''}$  (3.5–12.7 mN/m) on the entire frequency range. At 15 °C, a different behavior can be emphasized notably for the frequency behavior of  $K^{S''}$ . The gap between  $K^S$  and  $K^{S''}$  widens as the former reaches 30–45 mN/m, whereas the latter exhibits a negative trend with the frequency.

On reheating,  $K^S$  remains higher than  $K^{S''}$  for all the frequencies and temperatures. In addition, both moduli increase with the frequency. At 20 and 25 °C, there is almost no significant difference between the frequency dependence of the moduli. At 30 °C, the changes of  $K^{S''}$  are not significant whereas  $K^S$  shows a lower value but with the same frequency dependence trend at lower reheating temperatures.

The comparison between heating and cooling shows an important difference between  $K^S$  and  $K^{S''}$  for the same temperature depending on the thermal history of the sample, as it was observed for the viscoelastic moduli of the bulk.

Similar trends of the interfacial viscoelastic moduli are observed for the other concentrations (see Figs. SM3 to SM5 in SM).

The evolution of the interfacial viscoelastic moduli with the frequency during cooling and heating for a  $\kappa$ -carrageenan concentration of 6 g/L is similar to that observed with 5 g/L (Fig. SM5 in SM). In short, during cooling at 30 and 25 °C,  $K^S$  does not vary significantly with the frequency while  $K^{S''}$  increases with the frequency. At 20 °C and, mostly at 15 °C, no crossover between  $K^S$  and  $K^{S''}$  occurs. More interestingly,  $K^{S''}$  decreases with the frequency at 15 °C. On the heating part,  $K^S$  remains larger than  $K^{S''}$  for all the frequencies and temperatures. At 15 and 20 °C, the frequency behavior of the interfacial moduli are similar during heating and cooling. However, they display different frequency dependence at higher temperatures.

At 4 g/L, a great change in the absolute value and the frequency dependence of  $K^S$  happens (Fig. 3). Under cooling and heating, the moduli follow the same frequency dependence. In fact,  $K^S$  remains constant with the frequency while  $K^{S''}$  increases with the frequency. The cross-over between the two curves is affected by both the temperature and the  $\kappa$ -carrageenan concentration. A slightly different behavior can be seen at 4 g/L of  $\kappa$ -carrageenan at 15 °C. Similar behavior are reported for the  $\kappa$ -carrageenan concentrations lower than or equal to 4 g/L, see Figs. SM3 and SM4 in SM.

To summarize, the transition temperature where  $K^S$  surpasses  $K^{S''}$  increases with the concentration. Moreover, the modulus  $K^S$ , is higher for the higher concentrations as it can be seen particularly at 15 °C. Indeed, a great change in the absolute value and the frequency dependence of  $K^S$  happens at 4 g/L. In parallel,  $K^{S''}$  shows a maximum versus the frequency. If the concentration continues to increase,  $K^S$  reaches a higher plateau and remains almost independent of the frequency whereas  $K^{S''}$  drops with the frequency.

## 4. Discussion

First, it appears interesting to discuss the accuracy and reproducibility of the data. Fig. 4 displays the overall data obtained for different concentrations at 15 °C. The figure includes the different repetitions for each sample through the error bars. In spite of the difference between the values for the same system, the difference is significant when the conditions are varied (different concentrations of  $\kappa$ -carrageenan). This highlights that the difference between the data obtained for each concentrations and temperatures are significant. This also emphasizes that the difference are not due to low signal to noise ratio.

Regarding the interfacial dilatational viscoelastic moduli,  $K^S$  and  $K^{S''}$  vary with the concentration and temperature. Specifically,  $K^S$  increases and becomes higher than  $K^{S''}$  over the entire range of frequencies when the solution goes through a sol–gel transition, either by increasing concentration or by a thermal history.  $K^{S''}$  also increases with the concentration and temperature in the liquid state but it goes through an increase to a decrease with the frequency when the  $\kappa$ -carrageenan solution becomes a gel.

Since the interface rheology can be influenced by adsorption of surface-active agent at the liquid/liquid interface [25,26], the surface-activity of  $\kappa$ -carrageenan need to be discussed in details.

Firstly, in our knowledge, no article from the literature claims a possible interfacial activity of  $\kappa$ -carrageenan. On the other hand, the available data in the literature dealing with the surface and interfacial tension at liquid/liquid interfaces in the presence of  $\kappa$ -carrageenan confirm that this polysaccharide is not a surface-active molecule [23,24]. As an example, Huang et al. [27] used

the Du Nouy ring method to characterize O/W surface tension of about 14 polysaccharides. They concluded unambiguously that  $\kappa$ -carrageenan has no surface activity at O/W interfaces. Nakajima et al. [28] reported similar findings using the pendant drop method for the water/air surface.

Secondly, our measurements with  $\kappa$ -carrageenan confirm the previous finding since the O/W interfacial tension remains almost unchanged regardless of concentration and temperature, as showed in SI. The interfacial tension is found close but slightly lower than the Indopol/water net interface, of about 16 mN/m even the solution of  $\kappa$ -carrageenan is a gel or a liquid. In particular, the data are not ordered while the interfacial tension is expected to decrease regularly with  $\kappa$ -carrageenan concentration in the case of an eventual adsorption of  $\kappa$ -carrageenan at the liquid/liquid interface.

Finally, it is interesting to notice that our measurements reveal a slightly lower interfacial tension in presence of  $\kappa$ -carrageenan compared to the indopol/water pure interface. Two explanations are possible. The most plausible in our opinion would be the consequence of an averaging effect of the dielectric constant of the solution. Actually, when  $\kappa$ -carrageenan is added to the water, it modifies the dielectric susceptibility of the mixture (water +  $\kappa$ -carrageenan, compared to pure water) which impacts the Hamaker constant that is related to energy of cohesion arising from dispersion forces [29,30]. So, the interfacial tension is affected by the dielectric constant of the two media. This aspect is clearly visible when ethanol is added to water which leads to a significant drop of the water surface tension even at very low ethanol amounts [31] and we know that ethanol is not a surface-active molecule. The same reason induces the increase of the surface tension of water when adding salts [32]. Thus, we believe that the slight reduction of the interfacial tension in our case can be reasonably attributed to the change of the dielectric susceptibility of the water in the presence of the  $\kappa$ -carrageenan. Nevertheless, the second hypothesis could be a concentration gradient at the interface taking the form of depletion or concentration excess of polymer at the molecular scale. This phenomenon is mainly induced by surface segregation effect as it was reported for a film of a normal (hydrogenated) polystyrene film when blended with deuterated [33]. To prove this assumption, molecular scale measurement, like neutron scattering are necessary, which is out of the scope of this paper.

So, the changes in the interfacial viscoelastic moduli with the frequency, concentration and the temperature cannot be attributed to an evident surface activity of  $\kappa$ -carrageenan. Furthermore, at similar temperature and constant  $\kappa$ -carrageenan content, different interfacial activity in terms of elasticity are recorded while, if real, the adsorption of  $\kappa$ -carrageenan must remain similar. Consequently, the variation of observed interfacial elasticity is due to the sol–gel hysteresis behavior of the continuous phase since the aqueous solution of  $\kappa$ -carrageenan can be at gel state or liquid at the same temperature and concentration depending on the thermal history of the sample. Thus, we believe that it is not the  $\kappa$ -carrageenan interfacial layer but the viscoelasticity of the continuous phase which affects the recorded interfacial signal.

The bulk rheology reflects the thermal sensitivity of  $\kappa$ -carrageenan solutions. At low temperature, the change from coil to helix conformation explains the increase in the elastic part of the complex modulus. The plateau of  $G'$  at low frequencies denotes a gel behavior of the solution at higher concentrations (6 and 5 g/L of KC) and lower temperatures (15 °C and in certain cases 20 °C).

Comparing the behavior of  $K^{S'}$  and  $K^{S''}$  from one hand, and  $G'$  and  $G''$  on the other hand, one can see the evidence of the bulk rheology contribution on the interfacial viscoelastic moduli. The difference between the sol–gel mechanism in bulk becomes observable at 15 °C and is impacted by the  $\kappa$ -carrageenan concentration. For this purpose, we focus on the evolution of  $K^{S'}$  and  $K^{S''}$  as

a function of frequency at 15 °C for the different concentrations. The results are presented in Fig. 4.

The frequency dependence of both moduli depends on the concentration of  $\kappa$ -carrageenan and the sol or gel behavior of the continuous phase. However, the effect is more singular on  $K^{S''}$ .

On the one hand,  $K^{S'}$  increases with concentration and with frequency except for 2 g/L. The freezing behavior of the continuous phase seems to affect only the value of the modulus. The two highest values are recorded when the  $\kappa$ -carrageenan solutions form a gel at 5 and 6 g/L.

On the other hand, a different behavior can be highlighted with the modulus  $K^{S''}$ . At 2 and 3 g/L, the solutions show an unambiguous liquid behavior. The viscous interfacial modulus increases with frequency. At 4 g/L, an intermediate state between liquid and gel has been evoked. Conversely, at 5 and 6 g/L when the continuous phase is a weak gel, a totally different evolution is highlighted. In this concentration range, a decrease of  $K^{S''}$  with the frequency occurs. This appears as a clear signature of the weak gel of the continuous phase surrounding the indopol drop.

To confirm these trends, data at other temperatures can be used. Samples at 4, 3 and 2 g/L are representative of a liquid state of the continuous phase. For all samples, without exception,  $K^{S'}$  and  $K^{S''}$  increase with frequency. Moreover, a similar evolution is encountered at 30, 25 and 20 °C for 5 and 6 g/L under cooling since the aqueous phase is in the liquid state at these high temperatures. It thus appears that the thermal history of the sample affects the response of the interfacial viscoelastic moduli measurements.

This work suggests that the measurement of an apparent signature of interfacial viscoelastic properties, especially with the pendant oscillating drop, does not necessarily mean the consequence of an interfacial adsorption/desorption activity of a molecule or macromolecule at the interface. In fact, the principle of measuring the viscoelasticity of the Tracker is based on the instantaneous determination of the contact angle between the needle and the drop during expansion/compression. Then, through the Laplace equation, a viscoelastic modulus of the interface is determined. Currently, in the case of a volume phase of very low viscosity, the procedure is considered valid if the Bond number is very low.

In the case of viscoelastic mediums, the dynamic behavior of the drop oscillations is due to a subtle equilibrium between the stress and strain tensors of the continuous media, in the drop and the surrounding liquid, and if appropriate, of the interface. The latter is quite simple in the absence of surface-active species and only reflects the effect of interfacial tension. For surfactant-based films, the surface stress tensor is most likely solely an isotropic stress [10]. Thus, the extraction of the dilatational viscoelastic moduli from the drop shape oscillations, using Laplace equation, could be applied without too much error.

For strong gels, the presence of extra or deviatoric stresses does not allow to overcome their influence, as it was reported for gel-like protein layers on air/water interface in the Langmuir-Blodgett experiment present [34], or even with a very viscous oscillating drop [16].

The rigorous consideration of the stress tensors of the two liquids is essential to extract unambiguously the rheological properties of the interface. While this has already been addressed for static tests [35–37] the consideration of the rheology of the medium surrounding the oscillating drop has not yet been described.

To summarize, we show that the viscoelastic properties at the interface can be correlated to the bulk rheology derived from the sol–gel mechanism. We discuss the relationship between the elastic and viscous evolution with the frequency for various  $\kappa$ -carrageenan concentrations and temperatures taking into account the liquid or gel behavior of the continuous phase. However, the complete consideration of the rheology of the surrounding medium in the determination of the viscoelastic dilatational



properties of an interface will require a more complete and probably more complex modeling and numerical simulations in order to quantitatively separate the contribution of the volume and the interface.

## 5. Conclusion

In this study, the impact of an extremely weak gel on the interfacial rheology of an oil/water interface is addressed. In the case of a solution with no interfacial activity, we have shown that interfacial viscoelasticity measurements still display rheological signatures that would suggest, incorrectly, the presence of an elastic interface. Indeed, the viscoelastic signature of the interface seems to be clearly correlated with the rheology of the volume. The reported results provide useful guidelines for efficiently estimating interfacial viscoelastic properties at liquid/liquid interfaces in the presence of a weak gel.

A weak model gel, based on aqueous solution of  $\kappa$ -carrageenan (KC), is selected thanks to its reversible gelation with temperature and its non-interfacial activity. It can go through a sol–gel or gel–sol transition under cooling or heating, respectively. At low  $\kappa$ -carrageenan concentrations (2–4 g/L) or high temperatures (25–30 °C), the  $\kappa$ -carrageenan solutions behave like Newtonian fluids as the polysaccharide chains are under the form of loose coils. At lower temperatures (15–20 °C), they go through a liquid–gel transition for sufficiently high  $\kappa$ -carrageenan contents (mainly 5 and 6 g/L and in certain cases 4 g/L) since coils are joined into double-helices which produce the aggregation into the firm 3D network of a hydrogel if the concentration is above  $C^*$ . The two transitions happen at different temperatures depending on  $\kappa$ -carrageenan concentration revealing an interesting hysteresis feature. A liquid or a weak gel can be reached at the same temperature depending on the thermal history.

The interfacial viscoelastic moduli are probed by indopol drop volume oscillations in aqueous solutions containing  $\kappa$ -carrageenan at various concentrations and temperatures. On the one hand,  $K^s$  increases with frequency regardless of the liquid or gel behavior of the continuous phase. The presence of the gel affects only the value of the modulus which is enhanced as the strength of the gel increases. On the other hand, a more singular behavior is emphasized with the viscous modulus  $K^{sv}$ . When the continuous phase is liquid,  $K^{sv}$  increases with frequency. In the presence of an intermediate state between liquid and gel ( $\kappa$ -carrageenan 4 g/L)  $K^{sv}$  does not vary with the frequency. In the presence of a weak gel in the continuous phase (5 and 6 g/L) a diminution of  $K^{sv}$  with the frequency occurs. This appears as a clear signature of the weak gel of the continuous phase surrounding the indopol drop.

While previous works have addressed the effect of a viscous phase on the interfacial properties measured with an oscillating pendant drop experiment [15,16], only few works have reported on the impact of a gel rheology on this type of measurements. To our knowledge, the effect has only been reported for highly elastic gels [13,14]. In the case of weak gels, which do not even resist their weight if they are tilted, the question remains: how to extract the contribution of the bulk rheology from that of the interface? Modification or numerical simulations are still needed to properly account for the complex rheology of the bulk on the interface response during viscoelastic measurements by an oscillating pendant drop method.

## CRediT authorship contribution statement

**Ahmad Jaber:** Writing – Editing & Review, Visualization, Methodology, Investigation. **Thibault Roques-Carmes:** Writing – Editing & Review, Supervision, Conceptualization, Project

administration. **Philippe Marchal:** Validation, Supervision. **Tayssir Hamieh:** Project administration. **Lazhar Benyahia:** Writing – original draft, Writing – Editing & Review, Visualization, Methodology, Conceptualization, Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2022.04.047>.

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