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Kevin Roger. Comment on the article Primary structure of gum arabic and its dynamics at oil/water interface by Isobe et al.: The primary structure of gum Arabic species is not two-dimensional. Carbohydrate Polymers, 2020, 253, pp.117234. 10.1016/j.carbpol.2020.117234 . hal-03077526

HAL Id: hal-03077526

<https://hal.science/hal-03077526>

Submitted on 17 Dec 2020

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To cite this version:

Roger, Kevin *Comment on the article Primary structure of gum arabic and its dynamics at oil/water interface by Isobe et al.: The primary structure of gum Arabic species is not two-dimensional.* (2021) Carbohydrate Polymers, 253. 117234. ISSN 0144-8617

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Comment on the article *Primary structure of gum arabic and its dynamics at oil/water interface* by Isobe et al.: The primary structure of gum Arabic species is not two-dimensional

Kevin Roger

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, Institut National Polytechnique de Toulouse, Université Paul Sabatier, Toulouse, France

Gum Arabic is a natural product harvested from acacia trees exudates in sub-Saharan countries. Since ancient times, this hydrocolloid has been used in a large diversity of applications, which has prompted a research effort to describe its composition, structure, and functional properties. Gum Arabic is described as a complex mixture of covalently linked protein and polysaccharides macromolecules with various size, hydrophobicity, and protein content. We have recently dedicated three articles to gum Arabic composition and structure in solution and at oil/water interfaces (Atgié, Chennevière, Masbernat, & Roger, 2019; Atgié, Garrigues, Chennevière, Masbernat, & Roger, 2019; Atgié, Masbernat, & Roger, 2019).

In the article *Primary structure of gum Arabic and its dynamics at oil/water interface*, Isobe et al. state that they evidence that the primary structure of gum Arabic was a disk-like star shaped nanoparticle. Their conclusion follows from two arguments:

- The collapse of their data (SAXS of a 0.5% gum Arabic aqueous solution) with the data reported by Sanchez et al. (2008) (1% aqueous solution of a gum Arabic fraction (F1), 50 mM NaCl).
- The assumption that the flat object models (Renard et al., 2014; Renard, Garnier, Lapp, Schmitt, & Sanchez, 2012; Sanchez et al., 2008) proposed by Renard, Sanchez and coworkers for different gum Arabic fractions are correct.

In a recent work (Atgié, Garrigues et al., 2019), we also obtained SAXS results comparable to the ones from Renard and Sanchez as shown in Fig. 1A. However, we challenged this structural view and rather proposed a multi-scale three-dimensional porous structure for polysaccharides hyperbranched polymers, attached by a protein chain. To examine this controversy, it is worth to first recall the arguments underlying Renard, Sanchez and co-workers models. In a series of three papers (Renard, Garnier, Lapp, Schmitt, & Sanchez, 2012, 2014; Sanchez et al., 2008), they performed microscopy (TEM) and scattering

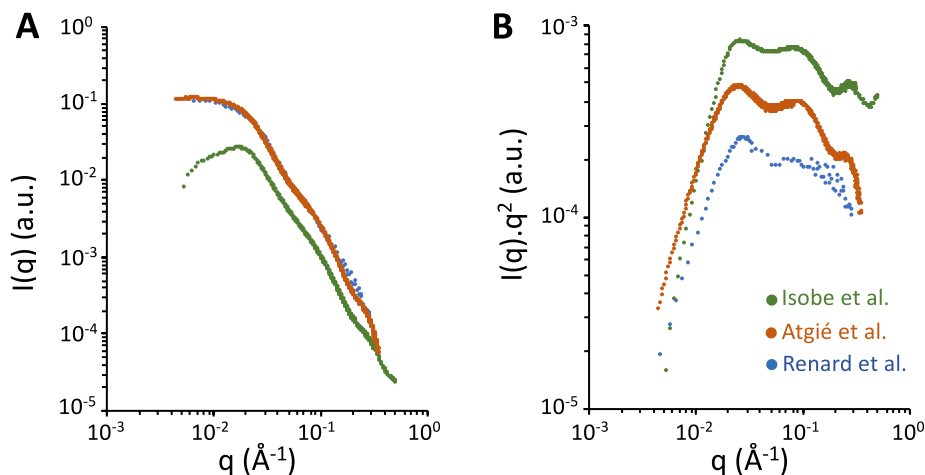
(SANS or SAXS) measurements on three gum Arabic fractions isolated via chromatographic separation. TEM evidences porous structures but since sample preparation requires water evaporation, it is not possible to conclude that the two-dimensional structures observed on the grid are also present in solution. TEM cannot thus be used in itself to assess the conformation in solution of gum Arabic species. Renard, Sanchez and co-workers have rather used these observations as an additional support for the models deduced from their scattering measurements. Indeed, while TEM provides pictures that do not represent the state in solution for such soft and surface-active objects, small-angle scattering methods provide an in situ and non-destructive characterization but in the reciprocal space. However, these techniques do not provide images but correlation distances between electron densities (SAXS) or neutron densities (SANS). The main argument underlying flat models for gum Arabic species is the following: at intermediate scattering wave vectors, the scattering intensity $I(q)$ follows a power law of the form $I(q) \propto q^\alpha$, with α between 2 and 2.2. Renard, Sanchez and coworkers state that a value of α equal to 2 indicates “the presence of an isolated population of disk-like particles or more generally of a two-dimensional particles (Sanchez et al., 2008)”. They added in later manuscripts “or of a fractal structure” (Renard et al., 2012, 2014), which would be a porous three-dimensional structure.

With this addition, the sentence is correct, however their experimental data actually lacked the precision of the SAXS curves we reported (Atgié, Garrigues, et al., 2019) and that Isobe et al. report in their article (Isobe et al., 2020). Indeed, while the curves reasonably overlay in a log-log scale of $I(q)$ vs. q , differences in precision are visible using the Kratky representation $I(q) \cdot q^2$ vs. q , as displayed in Fig. 1B. Note that this type of representation was used by Renard and Sanchez themselves but indeed evidence a rather noisy signal in their data at high q , most likely due to the use of SANS rather than SAXS based on our own experience. The interest of this representation for the present case is that flat objects would yield a horizontal profile in the intermediate q -range.

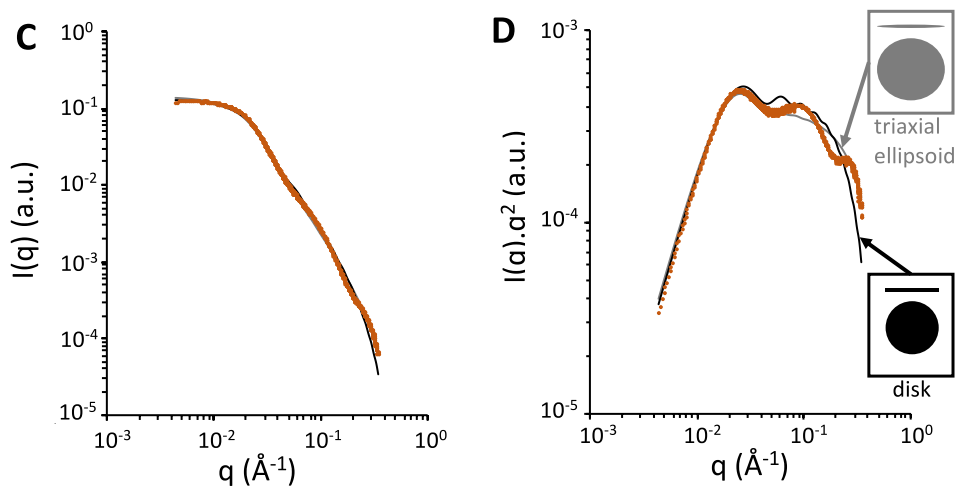
E-mail address: kevin.roger@toulouse-inp.fr.

<https://doi.org/10.1016/j.carbpol.2020.117234>

Data Comparison: log-log and Kratky plots



Flat structure modeling: log-log and Kratky plots



Strikingly, using this representation on both our data and Nori et al.'s data, rather evidences three well-defined bumps, at concentration-independent q -positions. This type of signature cannot be reproduced for a flat or semi-flat structure such as disks or tri-axial ellipsoids. Best fits of respectively a disk structure (black line) and tri-axial ellipsoid (grey line) using the SASView software are reported in Fig. 1C and D. Note that these values are comparable to the parameters used by Renard et al. notably for the disk model. Other examples are provided in our previous article (Atgié, Garrigues, et al., 2019), Figure SI5, for a different gum concentration. While both models seem to fit reasonably data in the log-log representation, they do not capture at all the profile signature evidenced in the Kratky representation. Since it is not possible to fit the SAXS curve of gum Arabic solutions with form factors of two-dimensional objects, the only conclusion is that the primary structure of gum Arabic hyperbranched polysaccharides is not a flat structure. The three well-defined bumps rather support three well-defined correlation length-scales, which can be rationalized within a multi-scale porous structure that is described in our article (Atgié, Garrigues, et al., 2019).

Interestingly, we demonstrated that this multi-scale structure was altered by adsorption of gum Arabic species to oil/water interfaces. We interpreted these structural changes to the combination of high surface coverages that force gum species into conformations promoting partial aggregation of polypeptide chains, locking the polysaccharides groups into less ordered structures. Isobe et al. have rather schematised a loosely covered interface, which may be consistent with the absence of a

Fig. 1. A and B: Data comparison of gum Arabic in aqueous solution measured by Isobe et al. (1 wt%, water) (Isobe et al., 2020), Atgié et al. (10 g/L, 20 mM NaCl in H₂O) (Atgié, Garrigues, et al., 2019) using SAXS, and the FI fraction of gum Arabic in aqueous solution measured by Renard et al. (1 w/w%, 50 mM NaCl in D₂O) using SANS (Sanchez et al., 2008). A reasonable overlap in log-log scaled is obtained between Atgié et al. data and Renard et al. data, the data by Isobe et al. slightly differs at low q due to non-screened ionic interactions yielding a correlation structure peak. In the Kratky representation $I(q) \cdot q^2$ vs. q , both Isobe and Atgié data display three bumps at the same q positions, the SANS data from Renard et al. not sufficiently resolved to visualize these. C and D: Modeling of Atgié et al. data using two flat structure models: a disk (thickness 1.3 nm, radius 9.4 nm) and a triaxial ellipsoid (radiuses: 0.6, 11 and 12 nm) as first suggested by Renard, Sanchez and co-workers (Renard et al., 2012, 2014; Sanchez et al., 2008). Both best fits performed using the SASView software fail to capture the three oscillations observed experimentally. Note that in all figures, the intensity is in arbitrary units and was rescaled to evidence similarities or differences in shape.

plateau value in their interfacial tension measurements, evidencing that the adsorption equilibrium has not yet been reached, contrarily to our own emulsion experiments. This rather questions the relevance of their interpretation to evaluate emulsion metastability, which we discussed in terms of packing density and network formation in two articles (Atgié, Chennevière, et al., 2019; Atgié, Masbarnat, et al., 2019).

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