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Rheological properties of natural waters with regard to plankton thin layers. Part 1. A short review.

by

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2 tables
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Abstract

The science of Rheology is painted with a broad brush, and the structure of matter is reviewed from the scales of the electron to those of a manufactured or a biologically produced article. The development of theory and measurements of viscosity and other rheological properties is then reviewed, and it is shown that values have been derived without regard to the scales of most ocean processes. After introducing the scales of length, time and stress, we show how measurements and the young theory of non-compression rheology have developed over the last 25 years or so. Seawater viscosity is comprised of a Newtonian, perfectly dispersed component contributed by the water and salts, plus a non-Newtonian, less well dispersed component due to more or less lumpy organic exopolymeric substances derived mainly from phytoplankton. The rheological properties (excess viscosity) may be expressed as an empirical coefficient and 3 exponents: the first for abundance; the second for dependence of excess viscosity on shear rate, and the third for its dependence on length scale. We also show the conditions (generally speaking, high EPS abundance, low shear stress, small length scale), where excess viscosity is most often likely to be non-trivial relative to water viscosity.

KEYWORDS: rheology, viscosity, phytoplankton, exopolymeric substance, ecosystem, biogeochemistry.

1. Introduction

As a lad I filtered for DOC,
Now I leave whole for rheology
Am I older and wiser?
Perhaps also a miser?
Or just hoping to avoid contro’ versy?

Dave Carlson (1991)

At the 43rd Annual Colloquium of the Groupe Français de Rhéologie, François Chinesta (2009) was awarded the Maurice Couette Prize, and accordingly gave a lecture. This lecture takes the reader on a numerical walk across different scales of length, time and force that govern matter. Chinesta leads us from the scales of the electron and the atom, through those of polymer molecules, finally to the macroscopic [mm-dm] realm of fibres in a polymer melt being blow-moulded into a manufactured aircraft part. He teaches knowledge, debates and even outright contradictions that physicists accept or have provisionally resigned themselves to, about how best to model the static and dynamic structure of matter. He shows how both relativistic and quantum approaches are necessary at the scales respectively in large atoms and up to Brownian motion.

Exopolymeric substances (EPS) in the sea and lakes form not by injection moulding, but largely by assembly from RNA templates and subsequent intra- or extra-cellular self-assembly, and rheologists will understand this. My aim in citing Chinesta is to suggest that rheologists can in principle work in teams with aquatic scientists, teams that could combine rheological and ocean-science expertise to probe the role of macromolecules in modulating the hydrosphere: not only its viscoelasticity, but also both its deformation and the fluxes of all properties and substances within it.

As in industrial manufacture (Chinesta, 2009), astrophysics (Ogilvie, 2008) or rockslides (Iverson and Vallance, 2001), studying the behaviour of matter in biogeochemical processes in lake and marine ecosystems needs models and data at appropriate scales. Ocean and lake research needs critically to adapt rheologists’ experimental approaches, results and models to the scales of its own problems and, where gaps in knowledge thereby appear, investigate those gaps.

In natural waters, much of the microbial biomass is aggregated in “patches”, in space-time. Cohesive aggregates also lie at high stress. These include horizontal patches [cm-100s km, minutes-months], thin layers [cm-10 m vertically, 100s m?-10s km horizontally, hours-days] (Alldredge et al., 2002, and references therein), and polymerically aggregated marine snow [100s µm-dm, min?-

weeks?] and marine and lake organic aggregates [µm-100s µm] as well as transparent exopolymeric particles (TEP) [µm-100 µm] (Mari and Kiørboe, 1996).

This review will leave aside vital processes inside cells, in mineral particles, in sediments, and in the water-air interface. It will concentrate on the intercellular phase of the pelagos (including the glycocalyxes and boundary layers surrounding cells), life's substrate and support system, ecologically engineered by the biota and under Darwinian selection pressures (Jones et al., 1994; Jenkinson and Wyatt, 1995; Wyatt and Ribera d' Alcalà, 2006). Showing that viscosity in this phase is sometimes one or two orders of magnitude higher than that commonly supposed, I will briefly review existing data on viscosity and elasticity. I will also suggest to workers on ecosystem and biogeochemical processes the need to incorporate knowledge and models of deformation stress (force/area [$kg.m^{-1}.s^{-2}$]) and strain rate (deformation rate [s^{-1}]) at relevant, identified scales of length, time and deformation stress. Jenkinson (in press) has highlighted the need to incorporate rheological expertise in aquatic-ecosystem and biogeochemical research teams. The scales of deformation stress in the ocean, however, are generally orders of magnitude smaller than those encountered in most industrial or geological flows, so new measurement techniques at these scales are also required.

For the water-air film, the reader is referred to Ćosović (2005) for a review of the roles of organic matter in the water-surface film.

2. The rheology of natural waters

Rheology is the science of deformations and flows in matter, of the strains that result and of the stresses producing them. Mechanics, Physics, Chemistry and Biology provide the main bases for this interdisciplinary science, which is in turn an indispensable part of each one of them (GFR, 1990).

Flow may be divided into compressive flow, in which the volume of the material is functionally changed by the forces tending to deform it compressively, and non-compressive flow, in which the volume of the material remains functionally unchanged, but may deform without compression, such as by "simple" shearing, elongation, or pipe flow.

To provide a framework of scales in flow and rheology that I personally find more amenable to the mind's eye. Instead of the familiar framework of S.I. units of length [m], time [s] and mass [kg], I will use length [m], time [s] and pressure or stress [$kg.m^{-1}.s^{-2}$]. Of course, this is not a real change, just a rearrangement, because in considering mostly non-inertial flows, mass will be discussed little, but pressure and stress a lot.

2.1. Compressive flow in natural waters

Compressive flow means that the volume of a given mass of substance is changed by the flow. This volume per unit mass = $1/\rho$ where ρ is the density of seawater. How ρ varies as a function of hydrostatic pressure is published in hydrographic tables (UNESCO, 1987). This allows its elastic resistance to compression, the compression elastic modulus G'_k to be calculated (Copin-Montégut, 2002). This value is ~4 x 10^{13} Pa, varying by only about 2% within the oceanic range of temperatures and salinities (Jenkinson, 2008). Values of compression **viscosity** η_k, however, are of the same order as shear viscosity, around 10^{-3} Pa.s (Alemán et al., 2006). A characteristic time $t_k = \eta_k/G'_k$ is frequently used by rheologists to characterise materials in flow. For natural waters, t_k is of the order of 2.5 x 10^{-18} s (Jenkinson, 2008). Even if polymeric matter might increase compression viscosity and so t_k somewhat, time scales as short as this concerning plankton in deformation fields are never considered, yet.

Sound consists of compression waves, and variations in G'_k cause variations in the speed of sound and in its refraction. The phenomenon can be a help or a hindrance to whales and submarines in detecting their environment and in communicating (Tomkins & Jespers 2008). It seems unclear whether biological material significantly changes G'_k, but it does increase compression viscosity and is considered to refract, scatter and dissipate (absorb) acoustic energy in the sea (Richards, 1998; Richards et al., 2003; Rhodes, 2008). Bubbles trapped inside phytoplankton cells, in their extracellular secretions (EPS) or in both also change acoustic properties in the sea (Sandler et al., 1993).

Changes in compression rheology by phytoplankton and its EPS thus interfere with acoustic propagation and inversely can be detected acoustically, thus presenting important technological and economic opportunities. However, no direct relevance to current phytoplankton ecological models seems apparent, so compression rheology will not be further considered here.

2.2. Non-compressive flow in natural waters

2.2.1. Continua

In 1678, Robert Hooke developed his “*True Theory of Elasticity*”, while Issac Newton gave attention to liquids in the “*Principia*”, published in 1687. Hooke proposed that “the power of any spring is in the same proportion with the tension thereof”, i.e. *if you double the tension (force) you double the deformation*. Materials that behave thus have been termed perfect, or Hookean, solids.

For liquids, Newton proposed, “The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another”. This lack of slipperiness is what we now call “viscosity”. It is synonymous with “internal friction” and is a measure of “resistance to flow”. The stress (force per unit area) required to produce the motion is denoted by τ, and is proportional to the "velocity gradient" or "shear rate", i.e. *if you double the force you double the deformation rate*. Materials that behave thus have been termed perfect, or Newtonian, liquids.

For Hookean solids, the stress resisting deformation,

$$\tau = G'\gamma \qquad (1)$$

where G' is referred to as the "rigidity modulus" and γ is the strain (i.e. extension).

For Newtonian liquids, on the other hand, the deformation stress,

$$\tau = \eta \frac{\gamma}{t} \qquad (2)$$

where $\frac{\gamma}{t}$ is change in strain per unit time, often abbreviated to $\dot{\gamma}$ (the dot means "per unit time"), and η is viscosity. Equation 2, expressed differently gives the classical definition of viscosity,

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad (3)$$

As we shall see later, many polymers and biological materials show behaviours combining Newtonian and Hookean components. Such behaviour is often termed "complex", and Rheology generally leaves aside Hookean solids and Newtonian liquids to deal only with the deformation of complex materials (Barnes et al., 1989)

The Industrial Revolution from the late 1700s to the mid 1900s, and the associated extraordinary rise in Engineering, was largely based on a conception of liquids (water, solvents) and solids (mostly metals) using the twin models of Hooke and Newton (and those of Avogadro and Charles for gas compression and adiabatics). Technology involving less noble, “soft” materials such as wood, foods, soil, cement, paints or sewage, did develop, but more slowly, as sound constitutive models of their mechanical behaviour had not yet developed. Slime and mucus were just disgusting “impurities”. In the 1930s, a group of physicists and chemists finally got together and founded the discipline of Rheology (Reiner, 1964) to produce constitutive models based on empirical measurement of deformation forces in materials considered as continua. The second half of the 1900s has seen the ascent of soft materials in technology, and this has certainly helped the subsequent rise of biotechnology.

2.2.2. Granular materials

Continuum models, however, were not very useful for dry powders and wet flocculated materials at scales <<10 times grain size. This lack of scale-related models may have been partly responsible for the homogeneity of most mid-twentieth-century industrial foods. It was only in the 1990s, helped by fractal theory, that grain-grain interactions affecting the flow, structuring and jamming of granular and lumpy materials largely started to be treated statistico-mechanically and geometrically as a branch of Rheology (e.g. Coussot, 2005; Clusel et al., 2009). The scale-related rheology of granular and lumpy materials is a vast and rapidly developing field. We will consider it only as it appears to affect the sea and HABs (sections 3.3 and 4).

3. Components of natural waters and their rheological properties

The largest component of the hydrosphere is water. In saline waters, low-molecular weight (MW) salts consist of up to ~40 (more typically ~35) parts per thousand (PPT). The oceans consist of a low-molecular weight (MW) solvent phase, with inclusions of organic and inorganic matter.

3.1. Water and its dissolved salt

Until recently, views have been that pure water showed a significant non-compressive elastic modulus, so far not measured, but only at time scales «10^{-12} s (Barnes et al., 1989). Based on the molecular-shell structure of water, however, Alemán et al. (2006) appear to suggest an absence of elasticity even at these picosecond scales.

Krümmel and Ruppin (1905) made the first measurements of the viscosity of seawater (relative to pure water) using an Ostwald viscometer (Fig. 1) over a range of temperature and salinity (Krümmel, 1907). The Ostwald viscometer method incorporates flow through a capillary tube (Wilke et al., 2000) at shear rates $\dot{\gamma}$ »100 s^{-1}, i.e. 2 to 7 orders of magnitude higher than general oceanic values (Jenkinson, 1986, 1993b). Another important scale in the Ostwald viscometer is the capillary diameter, usually of order 0.2 to 2 mm. Scales are discussed further below. Various workers, using similar methods have confirmed these values of viscosity closely. These have included Stanley and Batten (1969), and Miyake and Koizumi (1948). Seawater viscosity measured by these means is positively related to salinity and negatively to temperature. It barely doubles, however, from 0.80 mPa s at a temperature (*T*) and a salinity (*S*) of 30°C and 0.0 to 1.89 mPa s at 30°C and 36.1 (Miyake and Koizumi, 1948). These workers did not explicitly report any tendency for the flow to depart from the Newtonian model at the length, time and shear-rate scales of their measurements. That is seawater viscosity would not have noticeably varied from a function(T,S) remaining constant across the range of flow rates (implying shear rates) and capillary diameters. Although not stated explicitly, Miyake and Koizumi, however, did warn, “The most important source of error might be due to delicate change in the condition of the inner wall of the capillary but it was impossible to estimate its exact magnitude”. In hindsight, a principal suspect would be EPS, perhaps sticking to the wall. Indeed Wilke et al. (2000) warn of difficulties posed by contamination at the wall of capillary viscometers, particular when working with aqueous, rather than non-polar, media.

3.2. Mineral particles and gas bubbles

In very dense turbidity maxima found at intermediate salinities in certain estuaries, and also just above muddy bottoms, suspensions of mud and clay particles can occur, so dense that the particles exhibit "hindered settling", and the particles interact hydrologically so producing a viscoelastic "fluid mud" (Kineke et al., 1996; Faas, 2006; McAnally et al., 2007). In some cases the overlying fluid mud may grade into biological "fluff", by enrichment with, and finally replacement by microalgae, whose EPS adds further viscosity and elasticity (Jenkinson et al., 2007a). Bacteria also produce EPS in seawater, as they do in sewage, and so may add rheological properties without needing light, but further study is required.

3.3. Organisms and exopolymeric substances (EPS)

In this section, let us bear in mind that the time scale of deformation is the shorter of two times: firstly, 1/deformation rate; secondly, the duration of the deforming structure (Jenkinson and Wyatt, 1992).

There is a rapidly growing literature that may inspire thalassorheologists, on the rheological properties of intracellular cytoplasm (e.g. Lee et al., 2006). However, here we shall deal only with the *inter*-cellular environment of natural waters. If they are concentrated enough, however, by the volume fraction they occupy, living and non-living particles change the rheology at larger scales,

The combined volume fraction Φ of single-celled and multicellular organisms in the oceans is typically around 10^{-9} reaching ~10^{-6} in some dense algal blooms. Even extremely dense cultures of phytoplankton, in which the rheological properties have been determined, did not exceed 4×10^{-3} (in this case 569 cells mm^{-3} of *Amphidinium* sp. (Jenkinson, 1986). Appreciable (≥ 1%) increase in viscosity over that of the solvent viscosity does not occur at $\Phi < 0.1$ for suspensions of low aspect ratio (AR) particles (Giesekus, 1983) or <0.01 for those of high-AR fibres (Bennington et al., 1990). Thus, the concentrations of cells found in natural waters (except for fluid mud, etc) cannot possibly increase viscosity significantly by volume-fraction effects alone.

However, if the organisms secrete dissolved or colloidal polymers, or have glycocalyxes or long processes, thus increasing functional values of Φ in respect of flow, they may increase viscosity not only at the length scales of the individual plankters, but also at larger scales. Some EPS produced by algae disperse as dissolved or colloidal matter into the bulk phase “far” from the cells (Decho, 1990). Space filling by particles and aggregates, exemplified by Φ, is also length-scale dependent. An example of “loose” (*sensu* Decho) EPS is that secreted by *Karenia mikimotoi*, that acts allelopathically at the far field ($\leq 0.2 \times 10^{-3}$ m), modulated by fatty acids or glycoglycerolipids, probably associated with a polysaccharide matrix (Gentien et al., 2007). Rheological action by *K. mikimotoi* EPS has been detected at similar scales, trapping bubbles ($0.1\text{-}0.5 \times 10^{-3}$ m) (Jenkinson and Connors, 1980; Jenkinson, 1989), slowing or gelling flow between fish gills ($0.1\text{-}0.2 \times 10^{-3}$ m) (Jenkinson and Arzul, 1998), and increasing viscosity and elasticity in Couette flow with a measurement gap of 0.5×10^{-3} m (Jenkinson, 1993a). Tightly enveloping EPS makes up the glycocalyx or intracellular matrix (ICM) of, for example, bacteria (10^{-7} to 10^{-6} m) (Biddanda, 1986) and harmful raphidophytes including *Chattonella* (Yokote and Honjo, 1985) and *Heterosigma* (Yokote et al., 1985) ($\sim 10^{-5}$ m). At smaller scales, the diatom *Phaeodactylum* sticks to surfaces using adhesive nanofibres composed of modular (i.e. repeating) proteins (Dugdale et al., 2006) ($\sim 10^{-7}$ m). Also Yamasaki et al. (2009) showed that the harmful raphidophyte *Heterosigma* secretes megadalton-sized protein-polysaccharide complexes that adhere specifically to the cell surfaces of different competing phytoplankton species, thereby harming (or occasionally benefiting) them by allelopathy (scale of action $\sim 10^{-7}$ to 10^{-6} m). Yamasaki et al. (2009) further suggest that this allelopathy may be part of the control network within dense plankton ecosystems. Again in *Phaeodactylum*, Falciatore et al. (2000) showed that by cross-talk, the glycocalyx informs the cell interior about turbulence intensity. Cell-cell interactions, using similar cross-talk, control apoptosis and tissue development in flowering plants (Luu et al., 2000; Jones et al., 2006) and mammals (Geiger et al., 2001). At this range of scales (10^{-7} to 10^{-6} m), atomic force microscopy (AFM), a tool widely used by micro- and nano-rheologists, and increasingly by marine polymer chemists (Svetličić et al., 2006), will likely be useful to investigate cell-cell attraction, repulsion and adhesion forces in flow fields, not only in such allelopathic action, but also in processes such as flagellate grazing and mating (Schmid, 1993). AFM, and other rheological methods adapted to the scales of each problem, are thus becoming indispensable parts of quantitative study of how ecological and biogeochemical processes work in the ocean system.

Furthermore, apparently providing exceptions to the measurements of seawater viscosity mentioned above, there have been many anecdotal reports of slimy, viscous, elastic or syrupy water during algal blooms, (references in e.g. Jenkinson, 1986, 1993b; Jenkinson and Biddanda, 1995).

Hoyt and Soli (1965) and later Gasljevic et al. (2008) measured elasticity in algal polymers, and found that in highly turbulent bioreactors this elasticity reduces turbulent drag. To produce drag reduction by elastic effects the relaxation time of the polymer molecules T_z should be shorter than the time scales associated with shearing (de Gennes, 1990). It has been so far ignored in models of biorheological modification of ocean turbulence, on the grounds that the time scales of oceanic shearing (1 to 10^3 or 10^4 s) are probably $>>T_z$. While fish secrete elastic mucus that reduces turbulent drag near their skin and so increases their swimming speed and efficiency (Daniel, 1981; Parrish and Kroen, 1988), the shear rate in the boundary layer next to the fish can be several hundreds or thousands of s^{-1}, several orders of magnitude higher than general oceanic shear rates.

Jenkinson and Connors (1980) had speculated that bubbles found stationary, as if trapped, in a bloom of *Karenia mikimotoi* (as *Gyrodinium aureolum*) in Ireland might be a manifestation of rheological thickening by secreted mucus. By increasing viscosity, they suggested that the presence of such mucus could then make ventilation by fish more difficult, and thereby explain mass mortalities of fish and other organisms, notwithstanding that toxic effects and toxins were also found (Jones et al., 1982, Gentien and Arzul, 1990).

Carlson (1987) found viscosity, estimated by fluorescence depolarisation (FD), higher in water from sea-surface slicks than in non-slick water, although FD is not associated with explicit scales of $\dot{\gamma}$ or length (see below).

Later Jenkinson, working with rheometers equipped with Couette geometry (Fig 4), at low shear rates (0.002 to 0.97 s^{-1}) and with a measurement gap of 0.5 mm, found both algal cultures (Fig. 2) (Jenkinson, 1986, 1993a) and seawater (Fig.3) (Jenkinson, 1993b; Jenkinson and Biddanda, 1995) to show both elasticity and increased viscosity. The viscosity was found to correspond to the sum of two components, one η_W corresponding to values previously found, that likely corresponds to the aquatic phase, plus a variable excess viscosity η_E probably contributed principally by algal EPS, such that. The rheological properties of the cultures as well as seawater corresponded to a "solution" viscosity η_W on which was imposed an excess viscosity, η_E . Total viscosity,

$$\eta = \eta_W + \eta_E \qquad \text{[Pa.s]} \qquad (4)$$

As mentioned above, (section 3.1), η_W varies little in seawater. Broadly, η_E showed a negative relationship power-law relationship with shear rate $\dot{\gamma}$, so that

$$\eta_E = k.\ \dot{\gamma}^P \qquad [\mathrm{Pa.s}] \qquad (5)$$

where k is a coefficient related to EPS concentration and type.

P varied both between cultures and with $\dot{\gamma}$ (e.g. Figs 2, 3), probably reflecting the molecular structure of the phytoplankton-secreted expolymeric substances (EPS). In the case of the *Amphidinium* culture shown in Fig 2a, viscosity was double that of unthickened water at a shear rate of 3 s^{-1}, >10 times as high at 0.5 $s^{-1,}$ while in a culture of *Dunaliella salina* (84 cells.µL^{-1}) η_E was ~400 times as high as η_W at 0.01 s^{-1}.

Subsequent measurements of rheology were made (Jenkinson, 1993b) at $\dot{\gamma}$ values ranging from 0.002 to 1 s^{-1} on phytoplankton-poor Mediterranean seawater and on seawater from the North Sea during blooms of *Phaeocystis* and *Noctiluca*. Like in most of the previously measured algal cultures, the water was found to be shear-thinning with P between -1.1 and -1.5. η_E was also a positive function of chlorophyll concentration (Fig. 5). Note how at $\dot{\gamma}$ values < 0.004 to < 0.06 s^{-1}, mean values of η_E exceeded η_W, meaning that the total viscosity was doubled or more. The effect in the sea at length used for measurement, 0.5 mm, and at shear rates <0.004 s^{-1} in oligotrophic water or <0.06 s^{-1} in blooms, is thus *not trivial*, as some other published studies have indicated because they used measurements performed at undefined or inappropriate scales of length or shear rate.

Subsequently Jenkinson and Biddanda (1995) compared the rheological measurements with measured chlorophyll *a* content (*chla*), bacterial abundance and the volume fraction of organic aggregates in the North Sea study, with published values of plankton abundance and chla in the Mediterranean. In general, over length scales from cm to 1000s km, excess viscosity has been found proportional to chlorophyll concentration to the power 1.3 (Fig. 5), consistent with its origin as phytoplankton EPS. As the above rheological measurements reported by Jenkinson and Biddanda were all carried out in similar apparatus with the same measuring gap of 0.5 mm, their reported η_E-$\dot{\gamma}$ relationships are intercomparable.

Thus we can now develop (5) by adding an exponent for phytoplankton concentration, e.g.

$$\eta_E = k.chl^Q.\ \dot{\gamma}^P \qquad [\mathrm{Pa.s}] \qquad (6)$$

where Q is the phytoplankton concentration exponent.

The results from seawater and algal cultures led to attempts to improve the Jenkinson (1986, 1993b) model of rheological modification of Kolmogorov turbulence at oceanic scales of shear rates by adding new ideas of intermittence in both turbulence and rheological thickening. The idea was to then test this model, initially in the laboratory, by generating turbulence at different values of ε with and without phytoplankton, and by calibrating the effect by measuring the effect when phytoplankton was replaced by dissolved sugar (increasing viscosity by a factor of 10 at all $\dot{\gamma}$ values, the solution thus remaining Newtonian) (Jenkinson 2004a, 2004b). Disappointingly, no significant effect of changing the viscosity with sugar could be discerned on the turbulence characteristics. This may have been due to stable harmonic circulation cells forming in the apparatus (Soloman and Mezic, 2003). In any case the hypothesis that phytoplankton EPS would change characteristics in isotropic ocean turbulence could not be tested, the question remains open and more work is required.

. Seuront's team (Seuront et al., 2006, 2007; Kesaulya et al., 2008) took a grid of seawater samples only 5 cm apart in blooms of *Phaeocystis*, and found viscosity often varied strongly at this length scale, with values up to 4 times that in "clean" seawater. They found that viscosity was most often positively correlated with chla, but that at certain stages of bloom decline became negatively correlated. They suggested that this was because during bloom decline, flagellated cells in the colony left their own mucus to swim in the zones relatively free of it. The supported the conjecture of Jenkinson and Wyatt (1992) had meanwhile predicted that, while many organisms would be found associated with EPS, "...it may be [sometimes] to their advantage [e.g. grazing avoidance] to curdle the polymer into aggregates and live in the spaces cleared of them". For further review of the microbial ecosystem in pelagic aggregates, see "Meet me at the goo" a mini-review by LaFee, (2000) and Azam and Malfatti (2007). From the manufacturer's specifications of the viscometers used by Seuront et al. and Kesaulya et al. (Table 1) it can be deduced that shear rates were of the order 1 s^{-1} and length scales ~0.2 to 0.5 mm, within the range of shear rates and close to the length scale used by Jenkinson and Biddanda. The length scales between the samples, used for making correlations, however, were different, cm to dm in Seuront et al.'s work but m vertically to km to 1000s of km horizontally in Jenkinson and Biddanda.

How length scale can effect flow is illustrated by a graph in Jenkinson et al. (2007a) drawn from data by Spinosa and Lotito (2003) on jamming (measured as yield stress) of sewage sludge in capillary tubes as a function of sludge concentration and tube diameter). The yield stress is roughly proportional to $1/(\text{tube diameter})^2$ (Fig.5). Like the sea (Mari and Kiørboe, 1996), except that it is much more concentrated and its major constitutive organisms are bacteria rather than algae and bacteria, sewage sludge (Liss et al., 1996) is a suspension of living cells secreting EPS that form organic aggregates of roughly fractal size distribution. Jenkinson and Wyatt (2008) proposed explicitly that rheological properties in the sea, and particularly in HABs, is likely to be a strong function of the length scale of the processes of interest, reflecting the size and shape distributions of the hard and soft particles present.

Equation (6) can now be "corrected" for length scale by a third exponent:

$$\eta_E = k.chl^Q.\ \dot{\gamma}^P\ .\ (L/M)^d \qquad \text{[Pa.s]} \qquad (7)$$

where L is the length-scale of interest, M is the length scale of measurement, and d is the length-scale exponent. For a perfectly dispersed substance, $d = 0$, but d will be negative for heterogeneous materials. This is further discussed in Jenkinson (submitted to this volume).

Jenkinson’s (1986, 1993b) model of biomodification by phytoplankton EPS of isotropic turbulence thus now needs matching between the length scale of rheometry (so far mostly 0.5 mm) and that of the scales acting on turbulent energy dissipation. (If complete matching is not possible, rheometry at a series of length scales could allow extrapolation of measured viscosity and elasticity to the length scale(s) of the process of interest.)

Flocculation (Squires and Yamazaki, 1995; Passow, 2000; Alldredge et al., 2002) as well as viscoelastic deformation and break-up (Alldredge et al., 1990; Jenkinson et al., 1991) of EPS (marine snow and marine organic aggregates) may extract further energy from flow (Abu-Orf and Örmeci, 2005). In oceans and lakes, more work is required in studying the energetics of how flocculation affect turbulence by both viscous and elastic effects, not just by producing turbulence-free zones within aggregates (Jenkinson and Wyatt, 1992) but also through small-scale transmission of the effects of viscous and elastic flocculation energetics to damp turbulence outside the flocs.

Table 1 compares rheological measurements so far made in bulk-phase seawater, benthic and intertidal algae-rich “fluff”, aggregates and algal cultures, with corresponding principle scales of length, shear rate (1/t) and stress.

Table 1

Following the speculation, mentioned above in section 3.3, by Jenkinson and Connors (1980) increased viscosity might kill fish in some HABs, a model of rheotoxicity, *Rheotox*, was form by Jenkinson (1989) on the effects of HABs and intertidal algae-rich fluff on flow through gi spaces, and hence ventilation by fish (Jenkinson and Arzul, 1998, 2002, Jenkinson et al., 200

2007b).

The hydrostatic pressure difference across the gills of fish during ventilation ranges from 5 Pa for a 26-g sole to 18.5 Pa for an 80-g fish (Claireaux *in* Jenkinson et al., 2007a). Opposing this hydrostatic pressure difference is an equal and opposite shear stress τ. When the water has negligible excess viscosity and aquatic viscosity η_W of 1.2 mPa.s, this gives a characteristic shear rate

$$\dot{\gamma} = \tau / \eta_W = H / \eta_W \qquad [\mathrm{s}^{-1}] \qquad (5)$$

where τ is shear stress and *H* is hydrostatic pressure difference. This gives $\dot{\gamma}$ values of 4,200 and 15,000 s^{-1} respectively for the 26-g and 80-g fishes. Table 1 shows that for all the investigations shown involving ichthyoviscometry, the maximum value of yield stress measured in both harmful algae cultures and fluff exceeded *H*, so that according to model, this excess thickening would have prevented ventilation in the worst cases, and the fish would have died of suffocation. The model, however, does not include any avoidance or other behavioural adaptation by the fishes.

4. Scales of interest

Table 2 suggests some length scales important to biodynamics in the oceans. From the viewpoint of isotropic turbulence, an obvious length scale to target for measurements of viscosity (and elasticity) is the Kolmogorov length *L*. To understand deformation of the water with its suspended particles at a range of length and time scales, current hot-wire and Doppler techniques are only a start. Any exchange between inertial energy and potential energy, as occurs in turbulent flow in both stratified and elastic fluids, decouples energy dissipation rate ε from shearing. Progress towards visualisation in space-time (3D+t), using particle tracking velocimetry (PTV) (Nimmo Smith, 2008), a technique that makes a series of particle positions rather than just pairs of positions as in particle image velocimetry (PIV), to measure particle tracks. PTV extends PIV (a Eulerian tool) to extract Lagrangian statistics as well, and to extend the data to a range of time scales rather than just one. The future results of such work will need to be input to existing models such as, perhaps, the General Ocean Turbulence Model (GOTM) (Burchard et al., 2008), refined as necessary to take it. In some combinations of cases and scales, but not in others, the rheology may be shown to be trivial. Such visualisation along with rheological measurements aided by rheological modelling may sometimes have to precede the turbulence modelling, as it is hard to make models incorporating what has not yet been seen or imagined.

From the viewpoint of thin-layer dynamics (Jenkinson, submitted to this volume) as well as the scales mentioned for processes in vertically mixed water, vertical length scales of layer thickness and step thickness, as well as the scales pertinent to organisms, should be targeted, both for PTV and for rheometry.

For allelopathic action by harmful algae that use megadalton protein-polysaccharide complexes for cell-cell recognition and adhesion (Yamasaki et al., 2009), the development, dynamics and strength of adhesion are important, as they are in similar mechanisms between the cells of higher organisms. Atomic force microscopy (AFM), a tool widely used by micro- and nano-rheologists, will be likely useful to investigate cell-cell attraction, repulsion and adhesion forces in flow fields, not only in such allelopathic action, but also in processes such as flagellate grazing and mating (Schmid, 1993). AFM and hanging-drop electrochemistry are already being used (Svetličić et al., 2006) to study the chemistry, mechanics and molecular dynamics of EPS.

4.1. Prospects for methodological improvement

As far as possible, measurements should be made at the scales of length, time and stress, as well as within a geometry, similar to those dominating the process(es) of interest. Sometimes, however, methods available within these scales may be difficult to implement or not be sensitive enough.

4.1.1. Capillary tubes, filters and nets

Capillary measurements are attractive because they are low-tech, low-cost. By using diameters down to about 0.2 mm, they can be sensitive even in water with relatively little thickening. They are suitable for measurements related to process taking place in similar geometries, such as, perhaps, flow through fish gills, or through man-made fine tubes. However, their form is far from the more compact geometries thought to be associated with turbulent eddies in completely mixed water, where Couette-type geometries might be more appropriate.

Capillaries so short that their length is comparable to their diameter could be of interest for measuring flows in compact geometries, but more study is required. Batteries of capillaries in parallel could be useful for eliminating the “noise” due to the stochastic arrival and orientation of aggregates at each capillary. If the capillaries in such a battery are made even shorter than their diameter, then the apparatus becomes a filter, sieve or net. Plankton workers know about the retention characteristics of both plankton nets (Smith et al., 1968) and filters (Nayar and Chou, 2003), and that gelatinous phyto- or zoo-plankton promote clogging. Clogging (apart from granular jamming) is not considered part of Rheology, however, and despite its obvious economic importance in many fields, little scientific research seems to have been done on it (Zhuravlev et al., 1984; Mikkelsen, 2001).

Commercial rheometers with Couette measurement systems, adjustable to either constant-shear-rate or constant-stress mode, continue to improve. They will continue to provide reference data for future research, particularly in complementing new types of rheometry developed for the scales of processes in natural waters

5. Conclusions and future perspectives

The viscosity of the bulk phase of seawater is contributed by two components: firstly an aquatic phase due to water and salts of small molecules; secondly, an excess polymeric phase, mainly or entirely organic.

The aquatic phase gives a viscosity precisely dependent on temperature and, to a smaller extent, salinity, but independent of shear rate, plankton content, and length scale at least down to nm scale. This phase shows no elastic modulus.

The excess phase is contributed by dissolved and colloidal polymers, mainly or totally organic, of which the rheologically active part is secreted by the biota, particularly phytoplankton. It depends on shear rate with which it shows a mainly negative power-law relationship, with high variance due to the differing nature of the polymers and thus phytoplankton present. It depends also on polymer concentration and thus shows a variable, but mainly positive power-law relationship with chlorophyll *a* concentration. Because these polymers are generally partly flocculated (lumpy), excess viscosity probably also shows high spatial and temporal intermittence, perhaps corresponding with the length scales of transparent exopolymeric particles (TEP), marine organic aggregates and marine snow. In addition, because of the way suspended lumpy materials interact when the suspension flows in geometries of different shapes and sizes, this viscosity depends on the characteristic length scale(s) and the geometry of the apparatus. It has been found to show a strong negative power-law relationship with length scale, and this may also be true for the length scale of the processes unenclosed by a wall but governed by viscosity. The relationships of excess viscosity with, respectively, shear rate, chlorophyll concentration, and length scale, can be considered multiplicative. The viscosities of the aquatic and polymeric phases are then additive to give the total viscosity of the seawater.

The excess, polymeric component also contributes measurable elasticity to the seawater, and this component, like viscosity, appears to depend on shear rate, phytoplankton content, length scale, as well as showing variations due to polymer variation and flocculation.

Rheological effects may modulate: the dynamics of thin layer formation and maintenance; sinking and rising of organic and other materials, associated with marine snow; dynamics of encounter in swimming plankton; adhesion processes, including lock-and-key recognition for feeding, allelopathy and fertilisation especially in protists; dynamics of microzones of nutrients, toxins and dissolved allelopathic substances. My conclusion (Jenkinson, 1986), “Rheological study of the sea is... required at ambient shear rates and length scales down to those of the smallest turbulent eddies”, is still true, as little has been done. With the aid of more recent micro- and nano-rheological models and measurement techniques, including for granular materials, the length scales of future rheological study should range from up in the turbulent regime down to the scales of molecules.

Because of the complexity and importance of hydrosphere rheology under combinations of scales and conditions, mixed teams of aquatic scientists and rheologists should be established to tackle these problems, to develop new rheological oceanographic techniques and ways of thinking, and to train young scientists and engineers (Jenkinson, in press).

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8. Figure legends

Figure 1. An Ostwald viscometer. Liquid is introduced into the filling tube (3) using a pipette, and sucked into tube (2). On the release of the suction, the time is measured for the meniscus to fall between marks M1 and M2. From Wilke et al. (2000). Permission sought.

Figure 2. Rheograms, log-log plots of excess viscosity η_E and elastic modulus G' vs shear rate $\dot{\gamma}$. a) *Amphidinium*? sp. (171 cells.µL^{-1}). η_E vs. $\dot{\gamma}$. Exponent P of η_E vs. $\dot{\gamma}$ is -0.08 for part A of curve, and -0.51 for part C. b) Upper curve - *Noctiluca scintillans* (12 cells.mL^{-1}) with *Dunaliella marina* (167 cells.µL^{-1}) η_E vs. $\dot{\gamma}$. P is -0.98 for part B of curve, and -0.96 for part D; Middle curve - As for upper curve but after filtration; Lower curve - G' vs $\dot{\gamma}$ for unfiltered culture. From Jenkinson (1986). Permission sought.

Figure 3 For 4 times of year in the Mediterranean, and for one cruise in the North Sea, relationship of arithmetic mean (all measurements) of η_E vs. $\dot{\gamma}$. For Mediterranean data, successive curves are offset by one decade, but the North Sea curve is not offset. The horzontal dashed line represents η_W for comparison.

Figure 4 Couette system on a *Contraves*/*Mettler* LOWSHEAR 30 rheometer. The cup is rotated either steadily (viscosity measurements only) or in sinusoidal oscillation, (for viscosity and elasticity) with test material in the cup. Force is transmitted through the test material to the lateral surface of the bob, which is measured by the apparatus as torque. (Manufacturers' documentation.)

Figure 5. Excess complex modulus (G^*_E) versus chlorophyll *a* concentration. Open squares - bulk-phase samples from North Sea cruise during blooms of *Phaeocystis* and *Noctiluca*; Filled squares - surface microlayer samples. The middle and lower dashed lines represent the respective regressions in equations (1) (all samples) and (2) (bulk-phase samples only). Large diamonds - log co-ordinates of arithmetic averages for fairly oligotrophic Mediterranean water (lower left) and the above-mentioned North Sea study (upper right). Dashed circle, estimated error zone (factor of 5) around Mediterranean co-ordinate. From Jenkinson and Biddanda (1995). Permission sought.

Figure 6. Effect of tube diameter and sludge suspension concentration on yield stress of sewage

sludge, measured using a Kasumeter. Drawn from data published by Spinosa and Lotito (2003). From Jenkinson et al. (2007a). Permission sought.

Table 1. Scales of rheometry

Material	Measurement method	Possible Length scale (mm)	Possible shear rate (s-1)	Excess thickening found	Notes	Reference
Carlson's papers						
Seawater at 20 cm depth (unfiltered)	Fluorescence depolorisation (FD)	?	?	Viscosity increase by ~ 0-1%		Carlson et al (1987)
Seawater at 20 cm depth (3 µm filtered)	FD	?	?	Viscosity increase by ~ 0-1%		Carlson et al (1987)
Seawater at 20 cm depth (0.2 µm filtered)	FD	?	?	Reference values (No change)		Carlson et al (1987)
Water from sea slicks (unfiltered)	FD	?	?	Viscosity increase by up to 6%		Carlson (1987)
Water from sea slicks (3 µm filtered)	FD	?	?	Viscosity increase by up to 2%		Carlson (1987)
Water from sea slicks (0.2 µm filtered)	FD	?	?	Reference values (No change)		Carlson (1987)
Special environments						
Cultures of 114 spp of phytoplankton and macroalgae	Falling ball & rolling ball	?	?	Increase by up to ~120%		Petkov and Bratkova (1996)
Hypersaline water in tropical saltings, W. Austalia. Overlying mats of cyanobacteria. Water noticeably slimy.	ASTM D445 method (capillary U tube)	O(0.1 – 0.5 mm) ?	?	Increase by up to 80%	A, B	Roux (1996)
Shallow (0.5 m) tropical solar saltfield, W. Australia	?	?	?	Increase by up to 6%		Coleman (1998)
Cultures of the diatom *Skeletonema costatum* from the northern Adriatic	Falling ball	?	?	Relative viscosity increased by up to 7% in some cultures, when formation of mucous aggregates could be seen by eye	C	Thornton et al (1999)
Jenkinson's papers						

Karenia mikimotoi bloom (2.7 million cells/L)	Bubbles 0.1 to 0.5 mm trapped in water column	0.1 to 0.5 mm	~30	Viscosity from 2 mPa.s (increase by 200%) at shear rate ~30 /s if bubbles were 0.1 mm to 200 mPa.s (200-fold increase) at shear rate ~ 3 /s if bubbles were 0.5 mm		Observations in Jenkinson & Connors (1980), Calculations in Jenkinson (1989)
Cultured phytoplankton	Contraves/Mettler LOWSHEAR 30	0.5 mm	0.017 - 129	Over 100-fold increase in viscosity at shear rate 0.017 /s, for *Dunaliella* culture (818 cells.mm^{-3})		Jenkinson (1986)
Culture of *Karenia mikimotoi* (4400 cells.mL^{-1})	Contraves/Mettler LOWSHEAR 30	0.5 mm	0.0021 - 8	Up to 40 fold increase in viscosity at 0.0021 s^{-1}. See Jenkinson (submitted to this volume) for more details		Jenkinson (1993a)
Filtrate of a plankton tow of *Noctiluca scintillans* left to stand for 3 - 5 days	Contraves/Mettler LOWSHEAR 30	0.5 mm	0.0021 - 8	Up to 100-fold increase at 0.0021 s^{-1}		Jenkinson (1993a)
Oligotrophic Mediterranean seawater	Contraves/Mettler LOWSHEAR 30	0.5 mm	0.0021 – 0.286	Mean: 200% increase at shear rate of 0.0021 s^{-1}		Jenkinson (1993b)
Blooms of *Phaeocystis* and *Noctiluca* in N. Sea	Contraves/Mettler LOWSHEAR 30	0.5 mm	0.0021 – 0.973	2800% increase at shear rate of 0.0072 s^{-1} and chl *a* conc of 26 μg.L^{-1}		Jenkinson (1993b), Jenkinson & Biddanda (1995)
Seawater from Adriatic in area where *mare sporco* occurred 1 month later	Mettler LOWSHEAR 40	0.5 mm	unpublished	unpublished	D	Jenkinson et al (1998)
Ichthyoviscometry						
Phytoplankton cultures	Fish gills (~80-g fish)	~0.003	15 000, giving shear stress in clean water of 23 Pa	Yield stress up to 60 Pa	E,F	Jenkinson & Arzul (1998)
Phytoplankton cultures	Fish gills (~80-g fish)	~0.003	as above	Yield stress up to 38 Pa	F,G	Jenkinson & Arzul (2002)

Benthic and intertidal microalgal "fluff"	Fish gills (~25-g fish)	~0.0025	4,200, giving shear stress of ~5 Pa	Yield stress up to 150 Pa	F	Jenkinson et al (2007a)
Phytoplankton cultures & seawater	Fish gills (~25-g fish)	~0.0025	as above	Yield stress up to 17 Pa	F,H	Jenkinson et al (2007b)
Seuront's papers						
Phaeocystis blooms (different stages)	ViscoLab 400 viscometer	O(0.2 – 0.5) ?	O(1)	Up to 350% increase at chl *a* conc of ~60 µg/L	I	Seuront *et al* (2006, 2007)
Phaeocystis blooms (different stages)	ViscoLab2000Pro viscometer		O(2) ?	Up to ~30% increase at chl *a* conc of ~18 µg/L	I	Kesaulya et al (2008)
Aggregates						
Marine organic aggregates	(Breakup in laboratory-generated turbulence)	3 to 22 (aggregate size)	1 to 10 ?	Yield stress ("strength") 1 to 10 mPa		Alldredge et al (1990)
Marine organic aggregates	"Leaning" Couette	~0.25 (measurement gap size)	~0.004 upwards	Yield stress 15 to 28 Pa	J	Jenkinson et al (1991)

A - The ASTM D445 method is at DOI: 10.1520/D0445-97

B - Increase in viscosity in laboratory cultures of cyanobacteria from a solar saltfield, was proportional to cell density.

C - Viscosity was correlated positively with Ca++ concentration (suggesting to the authors that that Ca++ promoted cross-linking between polysaccharide chains), and negatively with EDTA addtion, (suggesting that the EDTA chelated the divalent Ca++)

D - Unusual properties, with shear-thickening, and elastic modulus > viscous modulus

E - Species showing most rheological effect was *Karenia mikimotoi* (28,000/ml)

F - Length scale Is taken as width of gill passages in smallest dimension (Langille et al, 1983)

G - Species showing most rheological effect was *Karenia mikimotoi* (23,000/ml)

H - Species showing most rheological effect was *Chattonella antiqua* (19,500/ml and undetermined concentration)

I - Scales estimated from manufacturers' specification for instrument

J - Squashed somewhat between Couette system bob leaning against inner surface of cup (to maintain traction for measurement)

Table 2. Length scales in thin layers and algal blooms that may be relevant to modifications of molecular viscosity

Description of structure	**Dominant scale (m)**	**Orientation/shape**	**Reference**
Thickness of thin layer	0.5 to 5	Vertical	E, F
Distance between density steps	0.1 to 1	Vertical	E, F
Dissipation eddies in isotropic turbulence	0.005 to 0.035 (to 0.2)	Isotropic	N
Marine snow and organic aggregates	10^{-4} to 10^{0}	Isotropic	A, L, M
Prokaryote and eukaryote colonies	10^{-5} to 10^{-2}	Spherical to foliose to elongated	
TEP	10^{-6} to 20 x 10^{-6}	Isotropic	D
Microzones around prokaryote and eukaryote cells (For a secreted substance, the length scale of the microzone of a substance at a distance corresponding to a concentration of 0.1 that at the cell surface has 10 times the cell radius.)	10^{-5} to 10^{-3}	Follow shapes of cells, but generally more compact	B, C
Phytoplankton and bacterial cells (including any glycocalyx, processes, spines or mucous threads)	10^{-6} to 10^{-4}	Spherical to foliose to fibre-shaped	H, I
Thickness of glycocalyx (= pericellular matrix) in prokaryote and eukaryote cells	10^{-7} to 10^{-5}	Layer around cell	J,K
Perception zones of grazers on prokaryote and eukaryote cells (from nanoflagellates to fish larvae)	10^{-6} to 10^{-2}	Isotropic to shear-directed, or other shapes and orientations	C, G
Cell-cell recognition and adhesion	10^{-9} to 10^{-5}	Layer around cell or object	

References: A- Alldredge *et al* (2002); B – Mitchell *et al* (1985); C - Jenkinson and Wyatt (1992); D – Mari and Kiørboe (1996); E – GEOHAB (2008); F – Dekshenieks (2001); G – Lewis (2003); H – Lewis (1976); I – Sournia (1982); J- Yokote and Honjo (1985); K - Nijenhuis *et al* (2009); L – Kepkay (2000); M - Žutić and Svetličić (2006); N – Oakey (1982); Woods (1968).

Fig 1

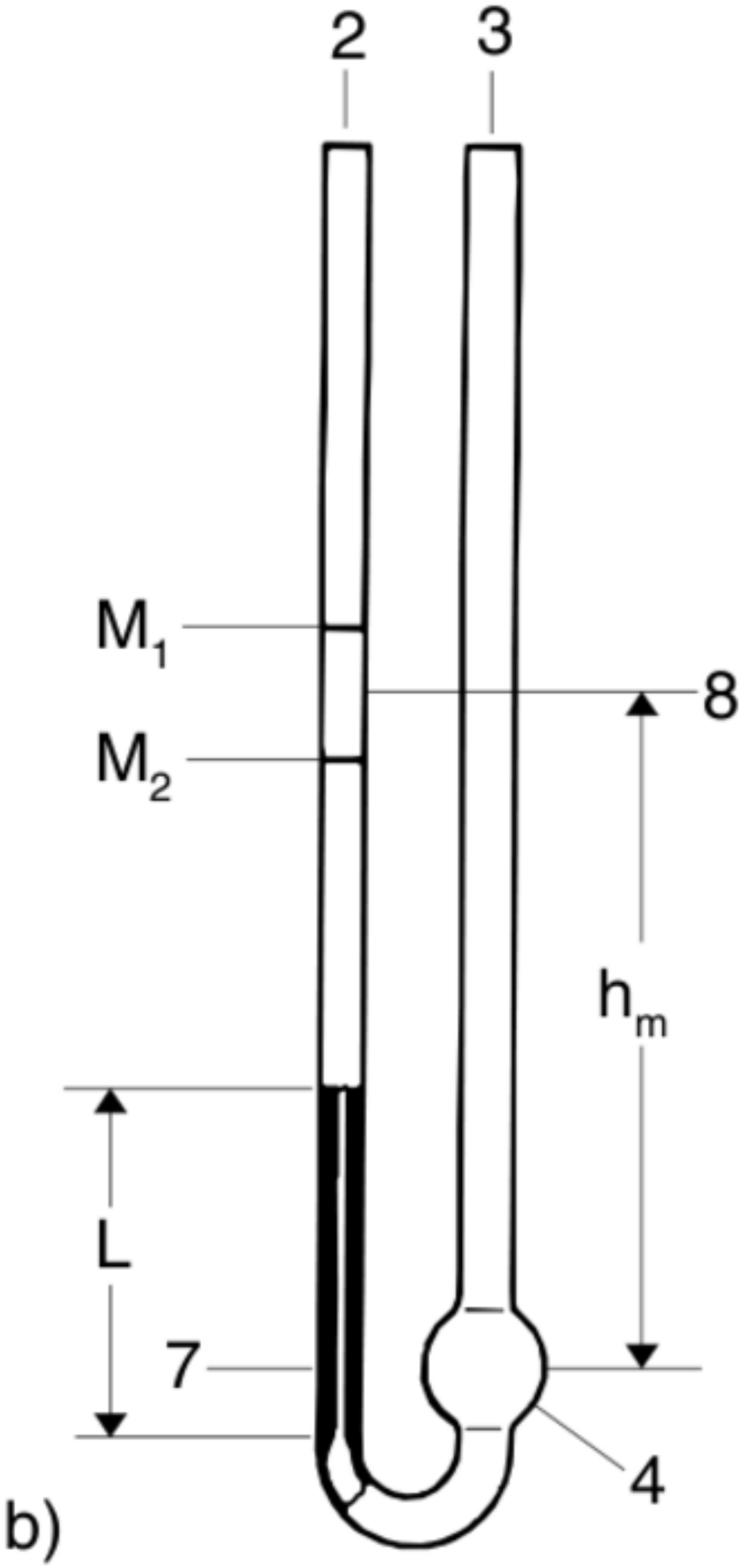

Fig 2

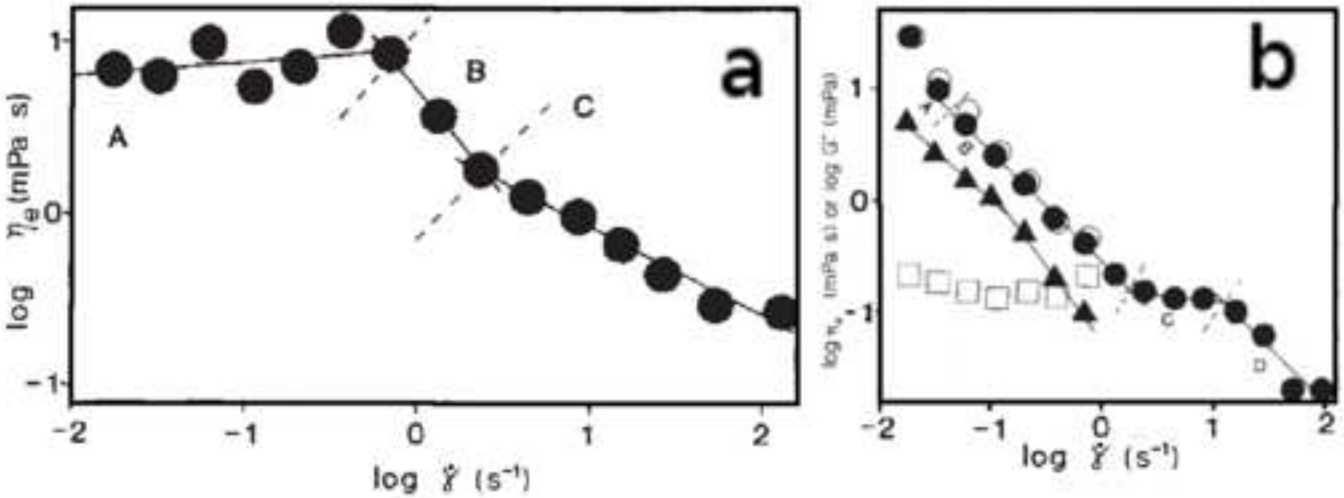
a
A
B
C
log η_e (mPa s)
1
0
−1
−2
−1
0
1
2
log $\dot{\gamma}$ (s⁻¹)
b
B
C
D
log η_e (mPa s) or log G' (mPa)
1
0
−1
−2
−1
0
1
2
log $\dot{\gamma}$ (s⁻¹)

Fig 3

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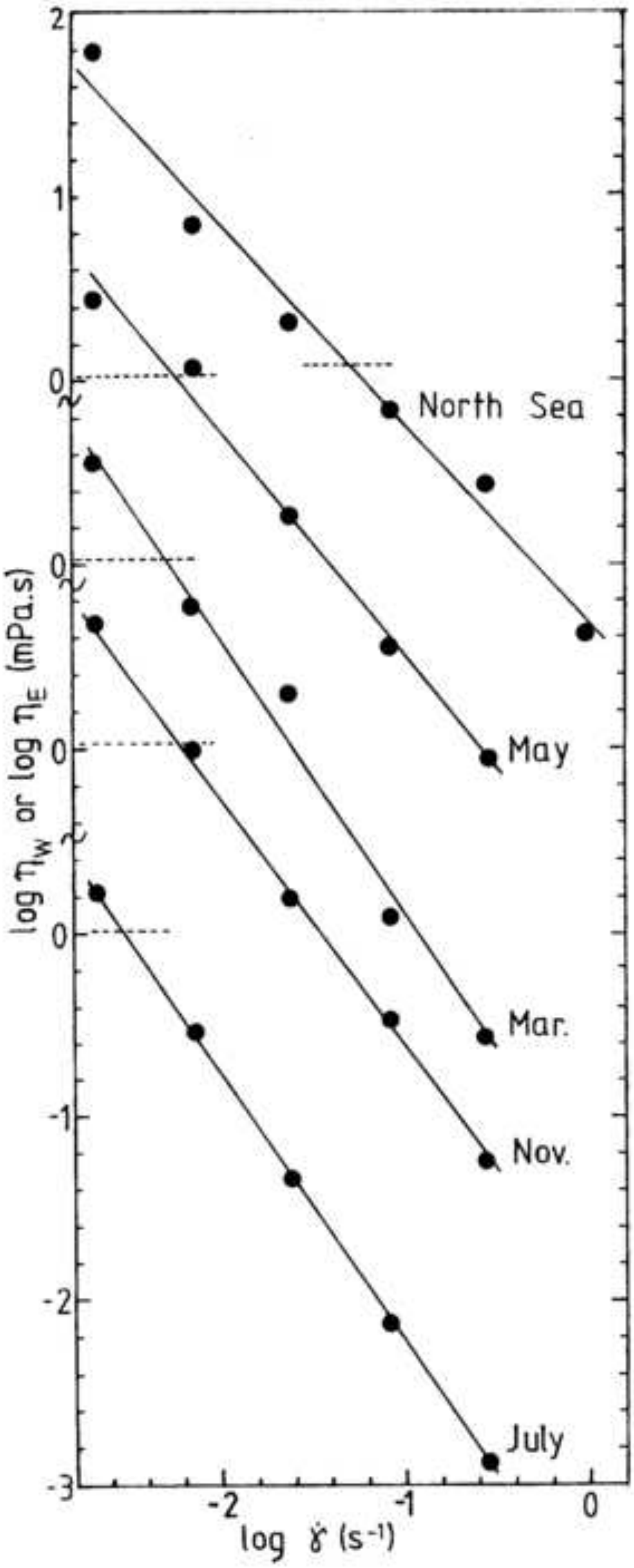

Fig 4

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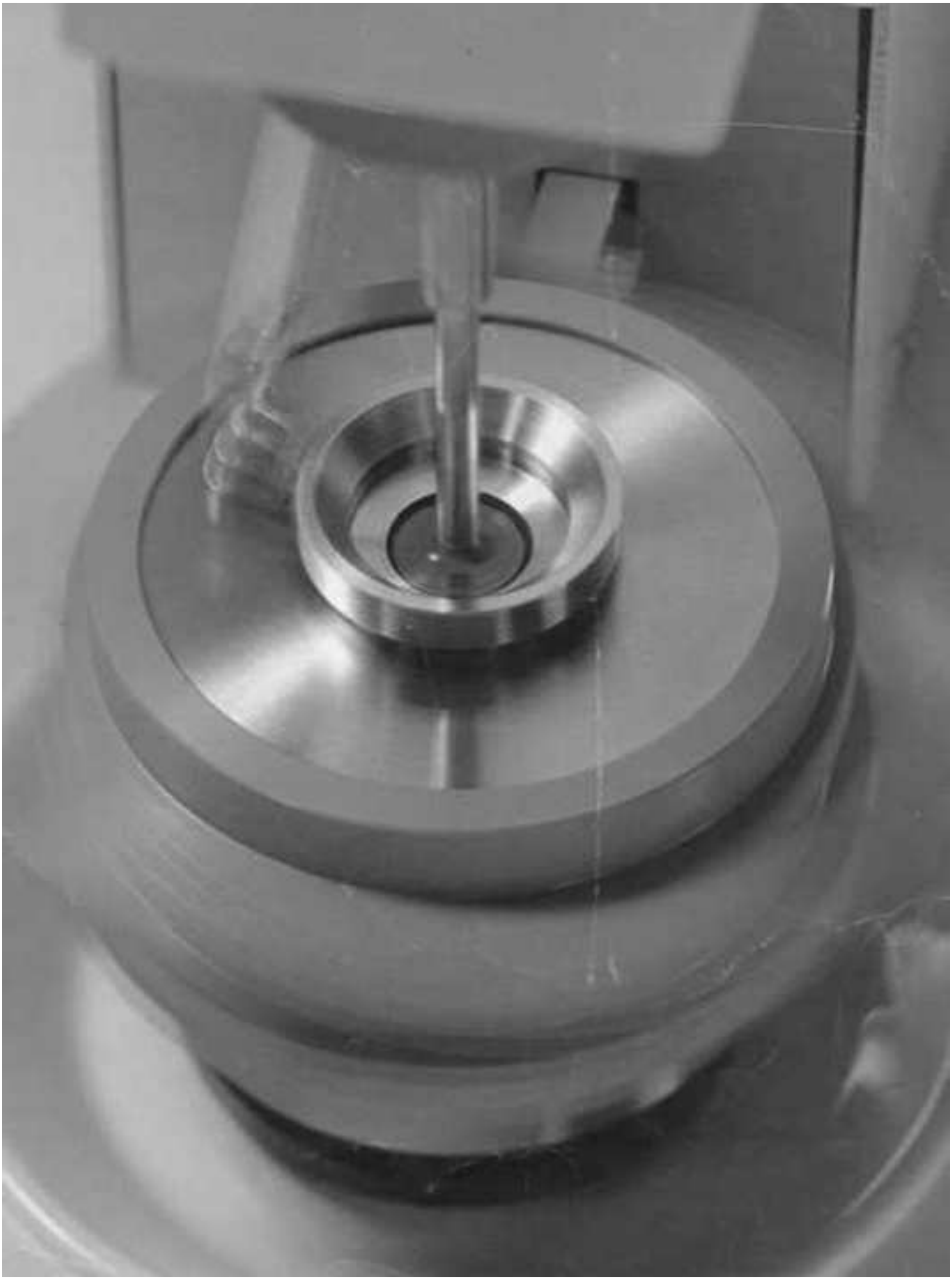

Fig 5

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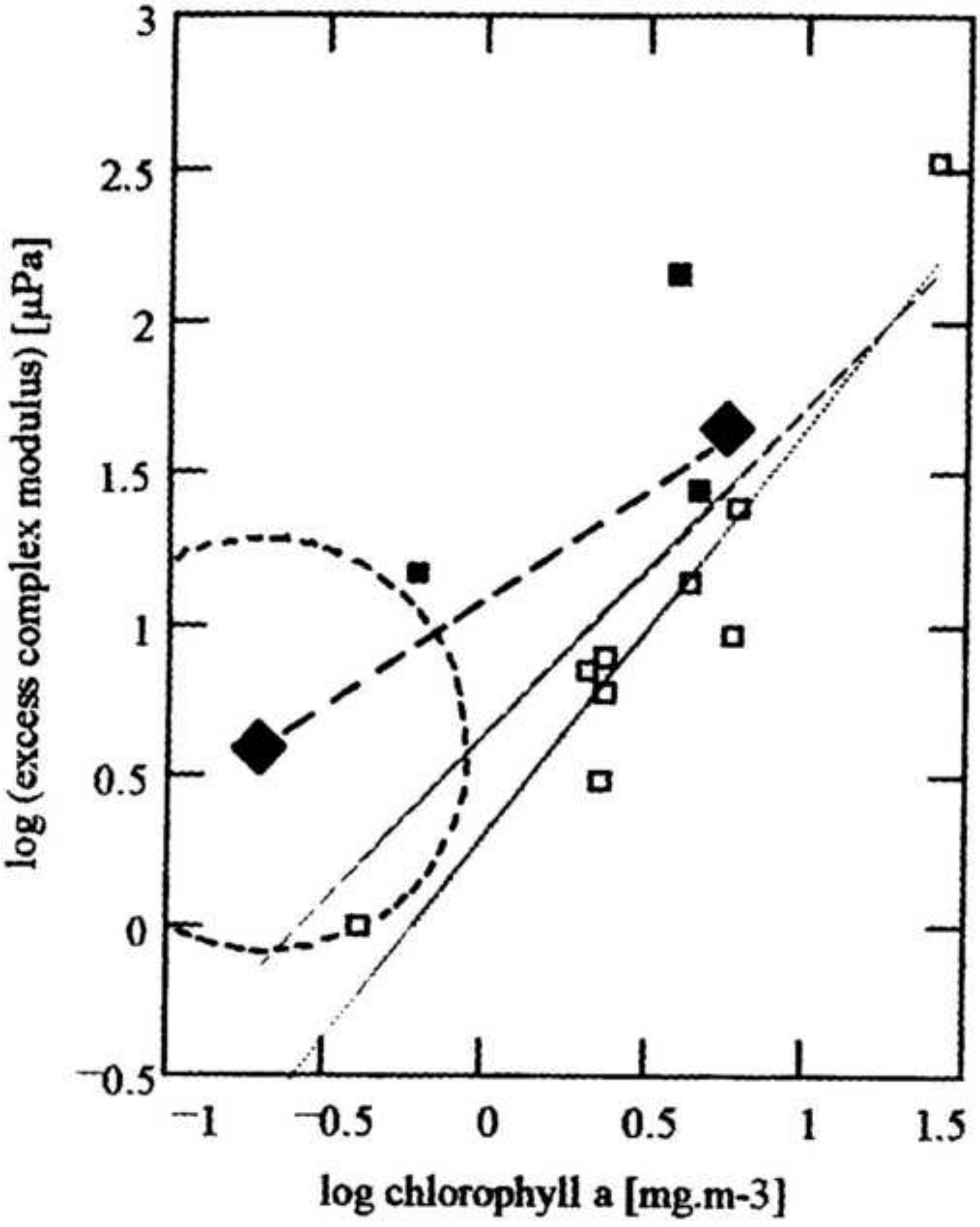
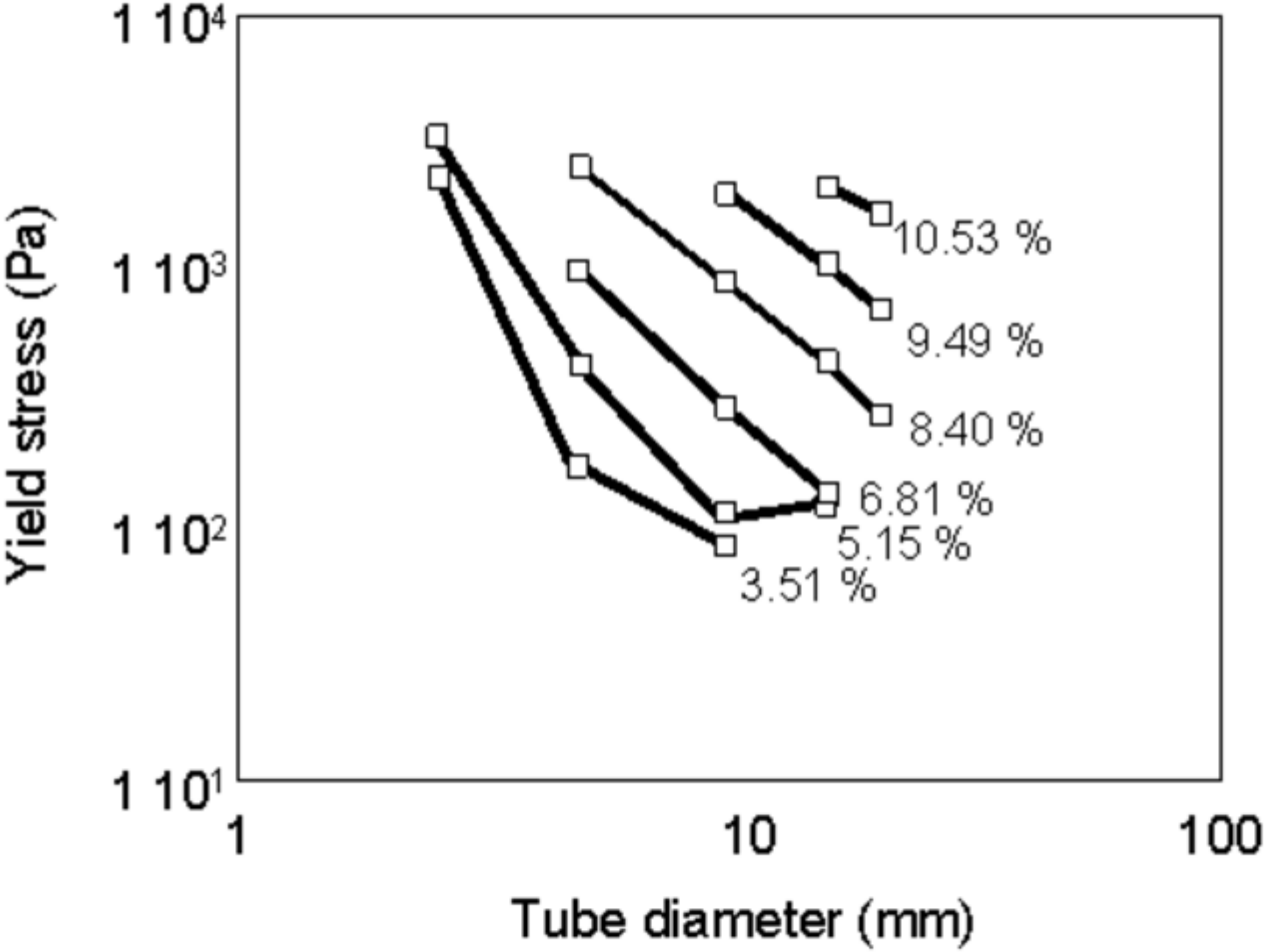


Fig 6


1 10⁴
1 10³
1 10²
1 10¹
1
10
100
Yield stress (Pa)
Tube diameter (mm)
10.53 %
9.49 %
8.40 %
6.81 %
5.15 %
3.51 %