Use of the Du Noüy Ring with a Rotational Rheometer to Measure Interfacial Rheological Properties

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ABSTRACT

The Du Noüy ring measuring system has been used to perform dynamic surface shear measurements for many years, as Warburton describes[1]. But until recently, it could only be used with specialised interfacial rheometers, as conventional rheometers did not have the required sensitivity. But in 2005 TA Instruments launched the AR-G2, with a low friction magnetic bearing, that has a comparable low torque performance to existing interfacial rheometers, combined with a low inertia. Here we show that the AR-G2 can be used with a Du Noüy ring measuring system to determine the time dependent interfacial dynamic properties of lysozyme and other proteins.

INTRODUCTION

Several ways of measuring surface and interfacial shear viscosity have been developed. These are summarised by Edwards[2]. In principle, most of them could be adapted for use with conventional rheometers to measure dynamic shear properties. In practice, rotational rheometers were too high in inertia and lacked the sensitivity to allow it.

Specialised interfacial rheometers have therefore been developed, with high sensitivity and low inertia. These are usually used in oscillating torsional mode with a Du Noüy ring measuring system, and the design described by Warburton[1] has been successfully commericialised. Much excellent rheology has been performed on instruments of this type, including work by Warburton[3], Graham and Phillips[4], and Buhaenko et al.[5]. But, useful though they have proved to be, specialised interfacial rheometers cannot readily be adapted to measure bulk rheological properties. In many laboratories both types of measurement are required, necessitating the purchase of two separate instruments. Moreover, the sensitivity is produced by using motors capable of operating only over relatively narrow torque ranges, of perhaps three orders of magnitude. This is not always adequate. For example, the interfacial dynamic moduli of protein solutions may change by six or more orders of magnitude as the protein migrates to the surface. To monitor this fully, the torque range of the instrument must be correspondingly broad, whatever the measuring system used. TA Instruments' AR-G2 rotational rheometer has a torque range of almost nine orders of magnitude, and a sensitivity comparable to that of specialised interfacial rheometers. Here we use the example of lysozyme, a globular protein that disrupts the polysaccharide components of bacterial cell walls, to show that the rheometer can be used to perform dynamic measurements over and beyond the range of specialised instruments.

THE AR-G2

Description

The principles and operation of the AR-G2 have been described in detail elsewhere by Costello et al.[6]. That description will not be repeated here, but the necessary sensitivity was achieved by using a magnetically levitated bearing, rather than the traditional air bearing. A magnetic bearing is lower in friction and smoother in operation than an air bearing, and a minimum torque of the order of nanonewton metres can be realised. It is also critical that the moment of inertia of the instrument should not be too high: for the AR-G2 this is about 18.5 mg m^2.

The Du Noüy ring is a thin Pt/Ir wire ring that is positioned in the plane of the interface, as in Fig 1. The sample is contained in a circular dish, and the ring is oscillated at fixed low amplitude about its circular axis. The torque required to achieve this amplitude, and the phase lag between the torque and displacement are monitored.

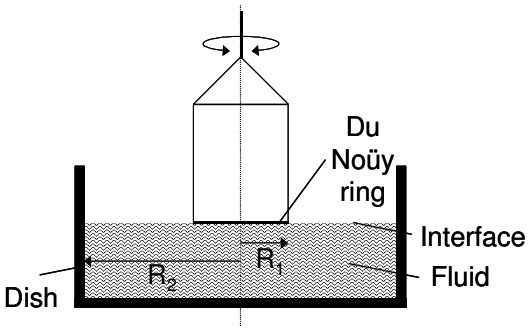

Figure 1. Schematic of the Du Noüy ring measuring system. The ring is positioned in the plane of the interface.

Theory

If the, usually negligible, contributions from the sample inertia and instrument compliance are ignored, then:

$$M^* / \phi^* = (G_i' + jG_i'') / F_{ms} - I\omega^2 \qquad (1)$$

where M^* is the complex torque, ϕ^* is the complex displacement, F_{ms} is the measuring system factor, I is the instrument moment of inertia, ω is the angular frequency, G_i' and G_i'' are the interfacial storage and loss modulus respectively, and $j = (-1)^{0.5}$. Since G_i' and G_i'' are usually low, for meaningful measurements to be made, both the torque and inertia must also be low.

The Du Noüy ring can be treated as a two-dimensional analogue of the concentric cylinder system, and F_{ms} is given by Eq. 2.

$$F_{ms} = (R_d^2 - R_r^2)/4\pi R_d^2 R_r^2 \qquad (2)$$

where R_d and R_r are the radius of the dish and ring respectively.

EXPERIMENTAL DETAILS

The sample used in this work was lysozyme. The protein solution was made up to 0.35 μmol dm^{-3} solution in phosphate buffer at pH 7.2. About 15 cm^3 of this solution were placed in the glass dish, and the Du Noüy ring was lowered into the surface. Purified decane was then gently pipetted onto the surface of the lysozyme solution, to form a layer of about 2 mm thickness.

The oscillatory procedure was conducted at a frequency of 0.05 Hz, at a strain of 2%, at 23ºC. Data are presented in Fig. 2. The increase in the storage and loss moduli over time can clearly be seen.

Studies on the use of the Du Noüy ring measuring system are continuing in our laboratories and elsewhere. In particular, promising comparisons have begun with the oscillating needle technique pioneered by Fuller[7]. The results of these studies will be published in due course. But we can say here that the sensitivity of the AR-G2, combined with its low inertia, make it the first commercially available rotational rheometer that can be used for the measurement of both bulk and interfacial rheological properties.

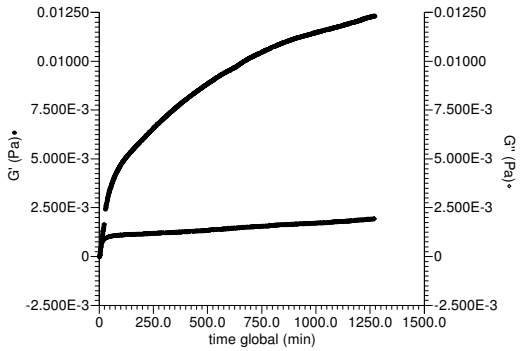

Figure 2. Interfacial storage and loss moduli, $G_i' + G_i''$, for 0.35μmol dm^{-3} solution of lysozyme protein

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