

EVAPORATION BLOCKER FOR CONE-PLATE RHEOMETRY OF VOLATILE SAMPLES

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ABSTRACT:

We report on the design and implementation of an evaporation blocker for cone-plate and plate-plate geometries. In addition to minimizing sample evaporation by trapping the saturated vapor inside a sample chamber, an important feature of the evaporation blocker is the suppression of solvent transport through condensation. Validation tests with DI-water, hydrogels, and colloidal suspensions demonstrate that the new accessory reduces solvent evaporation significantly more than commercially available environmental control chambers. Experiments were also performed to show that the evaporation blocker enables a variety of experiments on thermo-responsive complex fluids that were previously impossible, and provide new insight into the molecular organization of these materials. The evaporation blocker was specifically designed for an Anton Paar MCR rheometer, but the fundamental principles are widely applicable.

ZUSAMMENFASSUNG:

Wir berichten über das Design und den Einbau einer Verdampfungsbarriere für Kegel-Platte- und Platte-Platte-Geometrien. Eine wesentliche Eigenschaft zusätzlich zur Minimierung des Verdampfens der Probe durch Halten des übersättigten Dampfes innerhalb der Probenkammer ist die Unterdrückung des Lösungsmitteltransports durch Kondensation. Validierungstests mit DI-Wasser, Hydrogelen und kolloidalen Suspensionen zeigen, dass das neue Zubehör die Verdampfung des Lösungsmittels wesentlich mehr reduziert als kommerzielle Kontrollkammern für die Umgebung. Es wurden auch Experimente durchgeführt, um zu zeigen, dass die VerdampfungsbARRIERE eine Vielzahl von Experimenten an thermisch reagierenden komplexen Fluiden ermöglicht, die früher nicht durchführbar waren, und neue Erkenntnisse über die molekulare Organisation dieser Materialien liefert. Die VerdampfungsbARRIERE wurde speziell für ein Anton Paar MCR-Rheometer konstruiert, aber die Prinzipien sind in einem weiten Bereich anwendbar.

RÉSUMÉ:

Nous reportons la conception et l'implémentation d'un stoppeur d'évaporation pour des géométries plan-plan et cône-plan. En plus de minimiser l'évaporation de l'échantillon en emprisonnant la vapeur saturée à l'intérieur du compartiment de l'échantillon, une caractéristique importante du stoppeur d'évaporation est la suppression de transport de solvant causé par la condensation. Des tests de validation avec de l'eau dé-ionisée, des hydrogels, et des suspensions colloïdales, démontrent que ce nouvel accessoire réduit l'évaporation de solvant significativement mieux que les chambres de contrôle environnemental disponibles sur le marché. Des expériences ont également été réalisées afin de montrer que le stoppeur d'évaporation rend possible une variété d'expériences sur des fluides complexes thermo-sensibles qui étaient précédemment impossibles, et fournit un nouvel aperçu sur l'organisation moléculaire de ces matériaux. Le stoppeur d'évaporation a été spécifiquement conçu pour un rhéomètre Anton Paar MCR, mais ses principes fondamentaux sont largement applicables.

KEY WORDS: Evaporation, cone-plate rheometry, thermo-rheology, hydrogels, colloidal suspensions

1 INTRODUCTION

Complex fluids are encountered on a daily basis in a variety of products and materials: foods, biological fluids, personal care products, polymer solutions [1]. Measuring their rheological properties is an essential step towards understanding the behavior and structure of complex fluids, and subsequently tuning these properties for diverse applications.

In general, complex fluids are multi-component systems, often in volatile solvents such as water, toluene, and propanol. For measuring samples that contain a high vapor pressure solvent in a rheometer, the Couette geometry has traditionally been selected, because the contact area between sample and air is relatively small, and because a layer of low-density immiscible fluid can be placed on top of the sample to prevent evaporation. However, a much larger sample volume (several ml) is required for a typical Couette geometry than for cone-plate and plate-plate geometries (typically 0.2 – 1 ml), which is disadvantageous for precious samples (e.g. biomaterials, lab-scale synthetic materials). Moreover, for highly viscous and elastic materials, sample loading in a Couette geometry is much more difficult and destructive than for a cone-plate geometry [2, 3]. Thus, rheological measurements in the latter geometry would often be preferred, if sample evaporation can be prevented.

Orafidiya minimized evaporation of oil-in-water emulsion samples in a cone-plate geometry by placing a layer of nonvolatile oil around the exposed outer surface of the samples in a cone-plate geometry [4]. The applicability of this method is limited, since difference in density or wetting properties between the nonvolatile liquid and sample can cause sample drainage and undesirable mass transport between the sample and the surrounding liquid layer. Even for poorly miscible liquids, sample properties can change significantly during long experiments, for example in the presence of surfactants in the sample. Finally, the layer of nonvolatile liquid generates stress at the edge of the sample, where the contribution to the measured torque signal is largest; for low-viscosity samples, this effect can be significant and thus affect measuring accuracy.

For measuring dynamic rheological properties, notably the storage modulus G' and loss

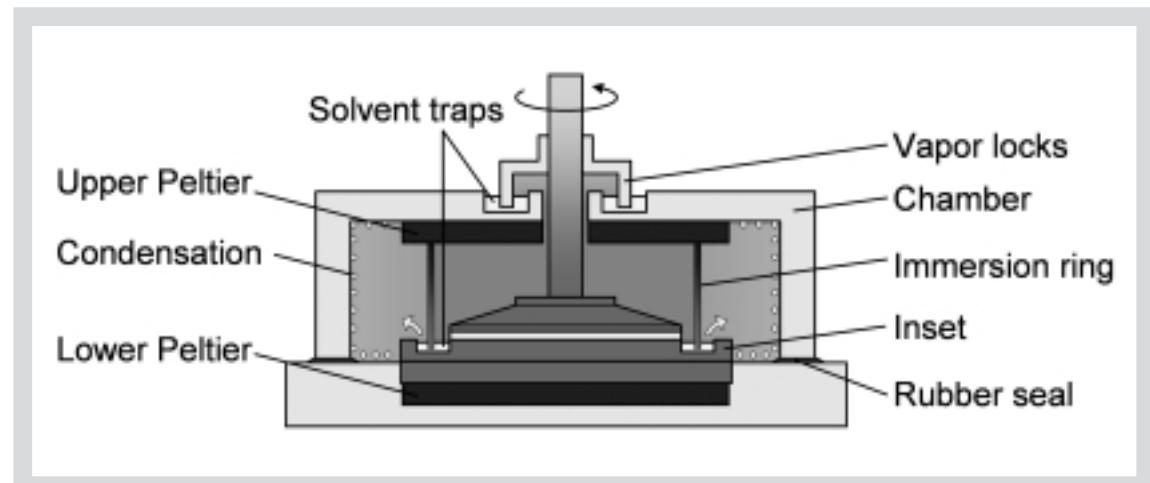
modulus G'' , oscillatory shear measurements are typically performed. During such experiments the required time for data sampling is inversely proportional to the frequency. It therefore takes a long time to take measurements at low frequencies: from tens of minutes up to hours. As a result, especially during oscillatory measurements, solvent evaporation is a major concern in cone-plate geometries. In particular at elevated temperatures the evaporation of most solvents, even water, becomes very relevant.

To minimize evaporation, the use of insulated sample chambers and vapor locks has been explored by rheometer manufacturers and academic researchers [5 – 7]. The design principle of these sample chambers has been to trap saturated solvent vapor and keep the temperature inside the sample chamber constant by minimizing heat transfer with the environment. Vapor locks play an important role in sealing the sample chamber; they are typically mounted on the shaft of the rotating measuring geometry and seal the chamber by being immersed into a solvent trap at the top of the chamber. As a result, the transport of solvent is limited to the inside of the sample chamber. Insulated chamber walls are used to prevent heat transfer to/from the environment and thus maintain a homogeneous temperature inside the chamber. However, even a small amount of thermal conductivity of the insulator will cause inhomogeneities in the temperature profiles inside the sample chamber, so called “cold spots”. Once such “cold spots” appear on the chamber wall, solvent continuously evaporates from the sample and condenses at the “cold spots”. Therefore, trapping saturated vapor inside the sample chamber is not sufficient to prevent sample evaporation. Controlling transport through condensation inside the chamber is equally important.

In this paper we report on the design and implementation of a new evaporation blocker for cone-plate and plate-plate geometries that minimizes sample evaporation. The underlying design concept is to minimize solvent transport through condensation by maximizing heat transfer rather than minimizing it. As a result, our device effectively minimizes solvent evaporation, especially when applied in combination with a more traditional vapor lock to seal the sample chamber.

Figure 1:
Schematic illustration of the evaporation blocking system.

Table 1:
Setup of the evaporation blocking system for water experiments.



| | Peltier hood | Vapor locks | Immersion ring | Solvent in the inset |
|---------------|--------------|-------------|----------------|----------------------|
| Setup A | Yes | Yes | No | Yes |
| Setup B | Yes | Yes | Yes | Yes |
| Setup C | Yes | Yes | No | No |
| No protection | No | No | No | No |

2 EVAPORATION BLOCKER DESIGN

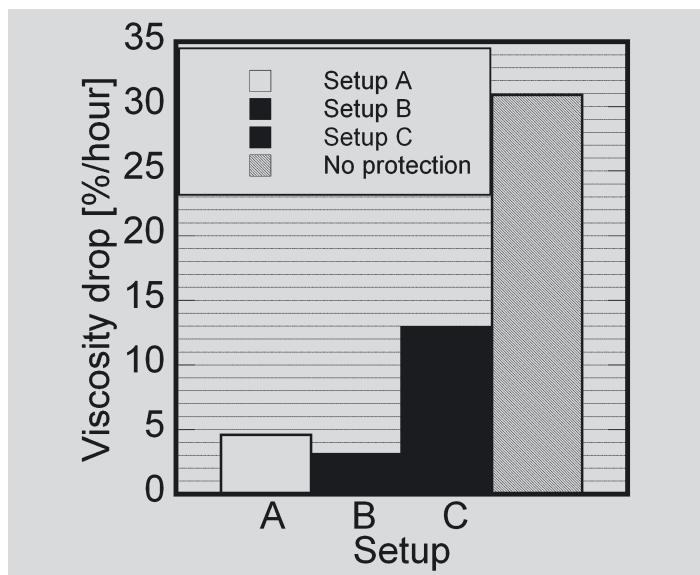
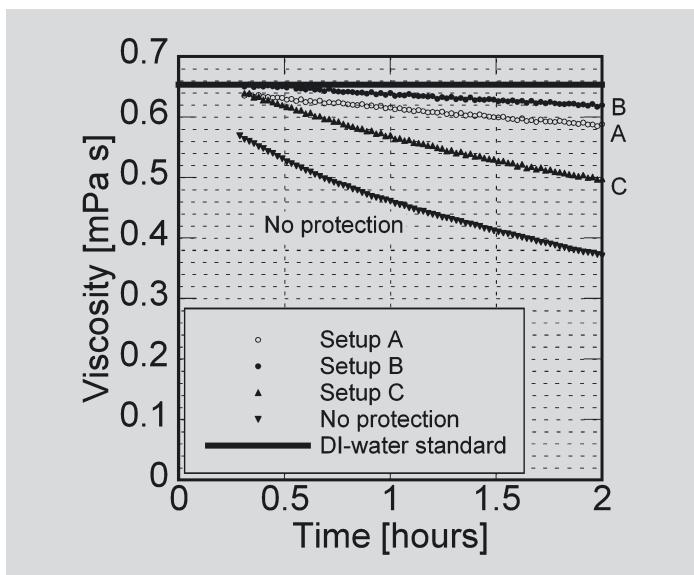
The accessory that we developed, was specifically designed for a commercially available rheometer (the MCR rheometer series from Anton Paar), but the fundamental principles are widely applicable. The device consists of a metal immersion ring (cuprum alloy; thickness ~ 0.5 mm, height ~ 13 mm, outer diameter 60 mm) and a plate inset (50 mm plate diameter) with liquid reservoir for a solvent trap (trap width 8.5 mm, depth 3.5 mm; see Figure 1). The accessory is mounted inside a commercial sample chamber (Peltier hood, Anton Paar), which is equipped with two Peltier temperature controllers at the top and bottom of the chamber. The immersion ring is mounted directly onto the upper Peltier element. To improve thermal contact, we applied petroleum grease to the contacting surfaces. The plate inset with the solvent trap is mounted onto the lower Peltier element. As a result, the liquid in the trap has the same temperature as the inset, which also forms the lower plate of the measuring geometry. When the sample chamber is closed and brought into measuring position, the immersion ring lowers into the solvent in the trap. The ring then provides a heat-conducting sample enclosure between the top and bottom Peltier controllers. This design ensures homogeneous temperature distributions and eliminates "cold spots" on the wall of the sample chamber where condensation could occur, which in turn would lead to solvent transport from the sample. Moreover, the solvent in the trap will help to maintain

a saturated atmosphere. To provide a tight seal between the rotating shaft and the chamber, the standard method is used: a vapor lock connected to a shaft of the measuring geometry immerses into the solvent in a solvent trap at the top of the sample chamber [5 - 7].

3 EXPERIMENTS

3.1 VALIDATION TEST: DI-WATER

For validating the effectiveness of the evaporation blocker, we first investigated the impact of the accessory on viscosity measurements of DI-water. The advantage of using a pure solvent is that an observed drop of the measured viscosity is unambiguously caused by sample loss through evaporation because DI-water is pure liquid. Moreover, water is volatile and used as solvent in many complex fluids. The measurements were performed with a stress-controlled rheometer (MCR-300, Anton Paar), which was operated at a constant shear rate (500 s^{-1}), at constant temperature of 40°C , and with a cone-plate geometry (50 mm diameter, 1° angle, sample volume 0.6 ml). Trace amounts of surfactant (dish soap) were added to the solvent in the traps to minimize curvature of the meniscus and prevent contact between the solvent and the sample. Three experimental configurations were used to evaluate the effect of the individual elements of the system (see Table 1): the chamber itself (Peltier hood), the immersion ring, and the presence of solvent in the lower solvent trap.



The results of the measurements are shown in Figs. 2a and 2b. The viscosity data from the first 15 minutes were eliminated from the graph because they are affected by inertia of the measuring geometry during start-up; the rheometer was operated without inertia compensation in order to avoid stress overshoot during the test. The horizontal line represents the literature value for the viscosity of water at 40°C [8]. Ideally, the viscosity should be constant in the absence of sample loss. The observed gradual drop in viscosity must therefore come from changes in sample volume due to evaporation. The viscosity curve with Setup C (no immersion ring, no solvent in inset) dramatically dropped over two hours while with Setup A and B (solvent in inset) the measured viscosity did not change as much. After 2 hours with Setup A and C, a significant amount of condensation was observed on the inner surfaces of the Peltier hood. With Setup B, on the other hand, we did not observe significant condensation. These results indicate that the commercially available chamber and vapor lock are not sufficient to block solvent evaporation for DI-water, because of condensation at “cold spots” in the system. Comparison of the results for Setup A and Setup C also shows that the presence of solvent in the inset is already sufficient to significantly decreased evaporation: the water in the inset acts as sacrificial liquid and prevents sample evaporation.

To quantify the performance of the various configurations, the change in viscosity per unit time was determined:

$$\text{viscosity drop [%/hour]} = -\frac{\eta|_{t=2} - \eta|_{t=0.25}}{(2 - 0.25)\eta_s} \cdot 100 \quad (1)$$

where η is the viscosity, subscript s denotes the standard viscosity (0.653 mPa·s at 40°C), and t is

time (in hours). The rate of viscosity decrease was 4.6, 3.1, and 13 % per hour for Setup A, B, and C, respectively. The evaporation rate decreased by a factor 3 due to the presence of solvent in the inset, and by a factor of 4 with both the immersion ring and solvent. These results show that the immersion ring and solvent in the solvent trap successfully minimize evaporative sample losses.

Although the pure solvent evaporation experiments provide useful insight into the mechanisms of evaporation and the effectiveness of the evaporation blocker, the effects of solvent evaporation on the rheology of complex fluids is much more dramatic for solutions and dispersions. In order to highlight the potential of the evaporation blocker, we investigated the rheology of two typical rheological samples: hydrogels and colloidal dispersions. The results of these studies are described in the next two sections.

3.2 APPLICATION TEST 1: HYDROGELS

As the first example of a practically relevant sample, we used block copolyptide (BCP) hydrogels. Since Deming et al. discovered a method to synthesize block copolyptides [9, 10], these materials have attracted a lot of attention due to their biocompatibility [11, 12], and the tunability of molecular structure, molecular weight, and amino acid composition of the individual blocks. It has been found that the rheological properties of the hydrogels can also be modified by mixing two different BCPs in solution [13]. Understanding the rheology of these hydrogels is essential for optimizing their mechanical properties to satisfy specific requirements of diverse applications, such as scaffolds for tissue engineering and drug delivery. In particular for applications as biomaterials, the temperature dependence of hydrogel rheology needs to be understood to benchmark their performance in *in vivo/in vitro* experiments.

Figure 2a (left):
Transient viscosity of DI water at 500 s⁻¹ and 40°C with different setups.

Figure 2b:
Rate of viscosity decrease for DI water at 40°C for different setups.

Table 2 (above):
Setup of the evaporation blocking system for hydrogel experiments

Table 3:
Setup of the evaporation blocking system for colloidal suspension experiments.

| | Hood | Vapor locks | Immersion ring | Solvent in the inset |
|---------|------|-------------|----------------|----------------------|
| Setup A | Yes | No | Yes | Yes |
| Setup B | No | No | No | No |
| Setup C | Yes | No | No | No |

| | Peltier hood | Vapor locks | Immersion ring | Solvent in the inset |
|---------|--------------|-------------|----------------|----------------------|
| Setup A | No | No | No | Yes |
| Setup B | Yes | Yes | No | No |
| Setup C | Yes | Yes | Yes | Yes |
| Setup D | Yes | Yes | No | Yes |

and to test the resistance of these materials against sterilization.

The rheology of BCP solutions is extremely sensitive to polypeptide concentration, which therefore must be kept constant during rheological experiments. For thermorheological studies of these materials, it is critical to minimize evaporation even at elevated temperatures. Since the block copolypeptides are synthesized only in small amounts, preservation of sample material is essential and measurement geometries that require a small amount of sample (i.e. cone-plate and plate-plate) are preferred.

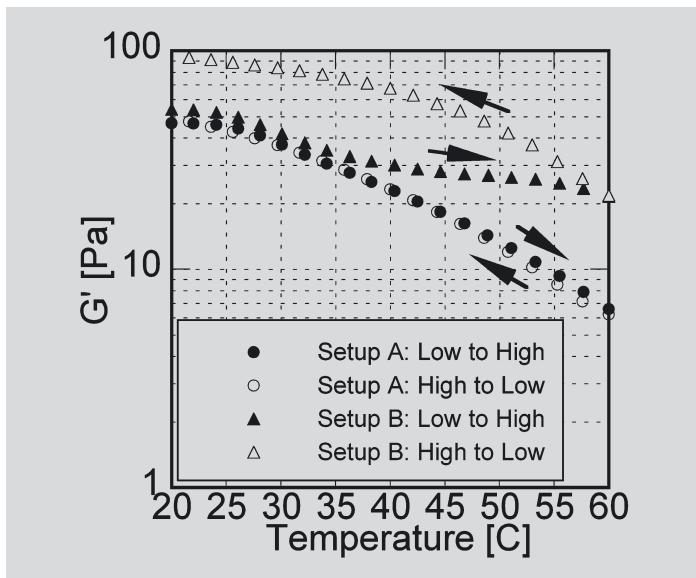
Recently, the authors have found that the BCPs possess strong temperature sensitivity and great thermo-reversibility in the presence of certain surfactants [14]. For this study, we used 1.06 wt% K170L30 hydrogel (diblock copolypeptide of 170 mers of L-Lysine (K) and 30 mers of L-Leucine (L)) with 0.55 wt% cetyltrimethylammonium bromide (CTAB) surfactant in DI-water. After preparation, the sample was rested overnight, and gently mixed and centrifuged (2 min at 2000 rpm) before sample loading.

As described in the previous section, rheological measurements were performed with a stress-controlled rheometer (MCR-300, Anton Paar) and cone-plate geometry (25 mm diameter, 2° angle, sample volume 0.14 ml). The storage modulus G' and loss modulus G'' , were measured in oscillatory shear experiments. First, a strain amplitude sweep experiment was carried out at 1 Hz for strain amplitudes from 0.1 to 100 % at 20°C to determine the linear viscoelastic regime. Successively, a frequency sweep was performed from 1 to 100 Hz at strain amplitude 50% and 20°C. In this measurement, a plateau of G' and G'' was observed over a wide frequency range. Finally, temperature sweep experiments were performed at strain amplitude 50% and frequency 10 Hz. The temperature sweep consisted

of two intervals, during which G' and G'' were monitored: in the first interval the temperature was increased from 20°C to 60°C (L-H) and during the second interval the sample was cooled down from 60 to 20°C (H-L). The sampling time for each data point was 30 seconds, which is sufficient to acquire accurate data at 10 Hz with Direct Strain Oscillation (DSO) [15]. The number of data points per interval was 20, so that the total measurement time for each interval was 10 minutes.

Two configurations were selected to evaluate the impact of our evaporation blocker, as listed in Table 2. The measurements were performed consecutively on the same sample with Setup A and Setup B with a brief 3 minute interval to adjust the setup: L-H (Setup A), H-L (Setup A), 3 minute interval, L-H (Setup B), H-L (Setup B). Since the measured torque in these measurements is relatively small, the vapor lock was not used to eliminate torque contributions due to solvent viscosity in the upper trap.

The results are shown in Fig. 3. Because the sample is an elastic gel, only the storage modulus G' is presented. With Setup A (immersion ring, hood and solvent in inset), the G' curve shows strong temperature sensitivity of the sample: G' decreased significantly (by a factor 10). Excellent thermo-reversibility was observed: the G' curves of the L-H and H-L intervals overlap nearly perfectly. However, with Setup B (no hood, no solvent and no immersion ring), the G' curve largely deviates from the one with Setup A and significant hysteresis was observed between the L-H and H-L intervals, which is attributed to solvent evaporation. Therefore characterization of the thermorheological properties of the sample cannot be performed with Setup B. Without the immersion ring (Setup C), a clear deviation from the curve with Setup A was also observed (data not shown here). These results suggest that the



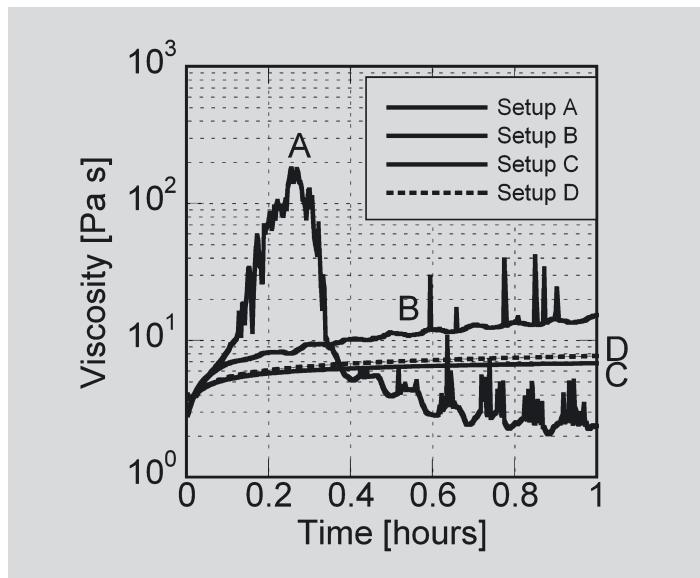
commercial Peltier hood is not sufficient to block solvent evaporation and prove the effectiveness of the evaporation blocker accessory for measurements of thermorheological properties of hydrogels.

3.3 APPLICATION TEST 2: COLLOIDAL SUSPENSIONS

As a second practical example of a complex fluid, we chose concentrated colloidal suspensions. The sample contained 71 wt% of solids and a small amount of dispersant in DI water. The solids were commercially available precipitated calcium carbonate (PCC) particles (average size of $0.4\text{ }\mu\text{m}$, aspect ratio $3 \sim 4$, density $\sim 2.71\text{ g/ml}$; Opacarb[®], Specialty Minerals Inc). These particles are widely used in the paper-coating industry. Understanding the rheology of PCC suspensions is crucial for optimizing industrial coating processes. Because of the high solids volume fraction (small fraction of solvent), the rheological properties of the suspensions are very sensitive to solvent evaporation.

Samples were prepared and mixed in 150 ml quantities. Samples for rheological measurements were transferred to a 2.0 ml vial after the bulk sample was stirred for 10 minutes at 1500 rpm. Before starting rheological measurements, the small sample vial was sonicated for one minute and mixed with a vortex mixer. The cone-plate geometry used for the experiments was the same as for the validation experiments with DI water (Section 3.1). We selected four sample chamber configurations to systematically study the impact of the evaporation blocker elements, as listed in Table 3.

Steady-shear viscosity measurements were performed at a constant shear rate, 1 s^{-1} , for 1 hour at room temperature, 23.5°C . The results are shown in Fig. 4. Several minutes into the measurement with Setup A (no Peltier hood), the viscosity dramatically increased and



the viscosity curve became very noisy. After about 15 minutes, the signal dropped dramatically. These results coincided with visual observations that a solid membrane formed at the interface of the sample, peeled off, started rotating in the gap between cone and plate, and eventually dropped into the solvent trap of the inset. Consequently, it was impossible to perform reliable rheological measurements with Setup A. With Setup B (hood and vapor lock, but no solvent in inset), the dramatic increase and noise that were observed with Setup A disappeared. However, the viscosity curve still increased significantly with time and contained noisy peaks. These results suggest that the combination of hood and vapor lock reduced the evaporation of solvent, but is insufficient to successfully perform measurements over long periods of time.

With solvent in the inset (Setup C and D), the viscosity initially went up, but then asymptotically reached a plateau. This suggests that the immersion ring and solvent in the solvent trap of the inset effectively prevented solvent evaporation even in long measurements. An initial increase in viscosity was observed for all measurements; this effect is not due to rheometer inertia (viscosity is 1000x larger than pure water), but most likely the result of structural rearrangements of the particles in the sample and thus a true material property. The origin of this effect was beyond the scope of the current research. No significant difference was observed between the curves with the immersion ring (Setup C) and without immersion ring (Setup D), which is reasonable because the measurements were performed at a room temperature so that condensation effects should be negligible. The slight improvement with the immersion ring is most likely the result of a decrease in volume of the sample compartment.

Figure 3 (left): Gel strength of block copoly peptide hydrogel during temperature sweep.

Figure 4: Transient viscosity of colloidal aqueous suspensions of precipitated calcium carbonate at 1 s^{-1} in different sample chamber configurations (see Table 3).

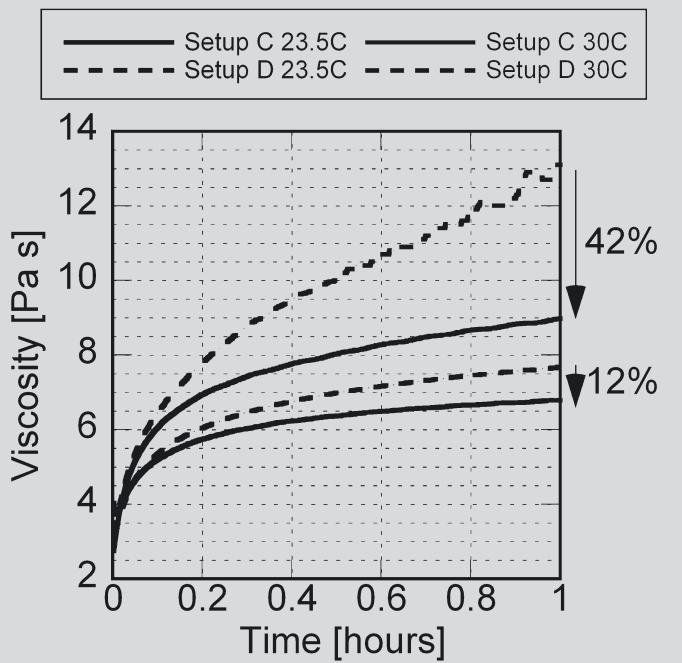


Figure 5:
Transient viscosity of colloidal aqueous suspensions of precipitated calcium carbonate at 1 s⁻¹ and different temperatures (Setup C and D).

To evaluate the effect of the immersion ring on sample evaporation, the experiments were repeated at a slightly elevated temperature, 30°C, only for the best performing configurations (Setup C and D). The results are shown in Fig. 5. After 1 hour, the measured viscosities without the immersion ring (Setup C) at room temperature, 23.5°C, and at 30°C were, respectively, 12 and 46% higher than with the immersion ring (Setup D). This suggests that the immersion ring dramatically prevents solvent evaporation even at temperatures that are only slightly higher than the ambient temperature. At higher temperatures, the effect of the immersion ring is expected to be even more dramatic.

4 CONCLUSION

We introduced a new rheometer accessory (evaporation blocker), which consists of an insulated sample chamber with temperature control elements (Peltier hood), vapor locks, immersion ring, and lower-plate inset with solvent trap. Through validation experiments with DI-water, we showed that this new accessory dramatically improves thermorheological measurements by minimizing solvent transport through evaporation and condensation.

The effectiveness of the individual parts of the system was investigated by using various combinations of the accessory parts. It was found that the biggest improvement in rheometer performance can be achieved by installing both the immersion ring and the solvent trap in the bottom plate to complement commonly used insulated chambers and vapor locks. We showed that

the complete evaporation blocker set-up works very well for different cone diameters, 25 and 50 mm, and different complex fluids.

The accessory enabled experiments on concentrated colloidal suspensions and temperature-sensitive hydrogels that were impossible with commercially available evaporation protection (insulated chamber with Peltier elements and vapor lock). The new tool will be instrumental in providing new insight into the molecular organization of thermosensitive materials.

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