

RESEARCH ARTICLE | FEBRUARY 20 2024

A method for rheological measurements of air sensitive samples

Ben A. Russell   ; Klaas Wynne 

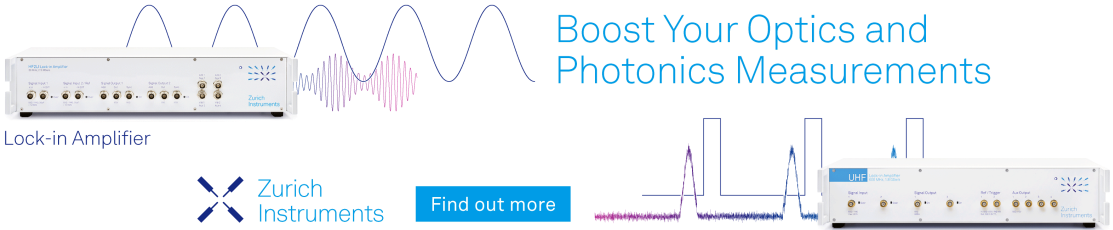


Rev. Sci. Instrum. 95, 025108 (2024)


<https://doi.org/10.1063/5.0169326>



Boost Your Optics and Photonics Measurements



Lock-in Amplifier

 [Find out more](#)

Boxcar Averager

A method for rheological measurements of air sensitive samples

Cite as: Rev. Sci. Instrum. 95, 025108 (2024); doi: 10.1063/5.0169326

Submitted: 25 July 2023 • Accepted: 21 January 2024 •

Published Online: 20 February 2024



View Online



Export Citation



CrossMark

Ben A. Russell^{a)}  and Klaas Wynne 

AFFILIATIONS

School of Chemistry, University of Glasgow, Glasgow, United Kingdom

^{a)} Author to whom correspondence should be addressed: Ben.Russell@glasgow.ac.uk

ABSTRACT

The rheology of air or moisture sensitive liquids, gels, and glasses requires complicated rheometer-in-glovebox laboratory setups. Here, we demonstrate the use of a heavier-than-air cover gas, sulfur hexafluoride, and the design of a cover gas container that can attach to the lower geometry plate of any rheometer to carry out rheology experiments on air-sensitive liquids and soft solids. Rheological measurements of air-reactive ionic liquid trimethylsulfonium bromide–AlCl₃, moisture sensitive titanium(IV) propoxide, and glycerin demonstrate the effectiveness of the cover-gas method for loading samples on acquiring correct temperature dependent viscosity data of the sample in the absence of reaction products.

© 2024 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0169326>

I.. INTRODUCTION

Rheology concerns the study of the flow and deformation behavior of materials in a fluid or solid state.¹ A typical quantitative measurement consists of applying a strain to a material and observing the resulting stress. The viscosity (or, more generally, the elastic modulus for a solid or very viscous fluid) can be found by taking the ratio of stress to strain rate.² Viscosity describes the internal friction between molecules of a given material as they are forced past one another and is, therefore, a function of a multitude of parameters, e.g., strain magnitude, temperature, and time. However, different pieces of information on the internal structure can be implied from the viscosity as a function of these parameters, making rheology a versatile tool with a wide range of application fields, including the development of construction³ and energy materials;³ quality control of food;⁵ development of pharmaceutical products;⁶ and development of advanced materials, such as polymers,⁷ metal–organic frameworks (MOFs),^{8,9} and nanomaterials.¹⁰

In general, rotational and capillary type rheometers are the two most widely used methods of rheometry for studying fluids and soft solids, each with their own merits. Capillary type rheometers employ the flow of a liquid inside a tube resulting from a difference in pressure between the inlet and outlet of a tube, driven by gravity or other mechanical means. Rotational rheometers in their most basic

form consist of two surfaces (plates or other geometry types), one motionless and the other driven by a high precision motor with a liquid or soft solid sample sandwiched between the two, as shown in Fig. 1. The viscosity of the liquid is then calculated from the force (stress) that the liquid imposes to an applied strain (displacement). The rotational type rheometers is advantageous in that it offers a wider variety of experiment types that can be carried out due to the different modes the motor can operate in and so more information on the rheological properties of a sample can be observed. The rotational technique also has the benefit of needing a much smaller sample volume in comparison with capillary methods, which can be critical when studying new materials that are expensive, scarce, or not easily produced.

With the development of more exotic advanced materials, environmental considerations, such as humidity, air reactivity, and lighting conditions, are becoming more important when studying new materials in the laboratory setting. For example, MoltenFLEX, an energy company, have recently installed a high temperature rheometer in an inert glovebox at great complexity and cost to study the viscosity and density of molten salts at high temperatures that will be used as a fuel and coolant in a novel energy reactor.¹⁰ More generally, the measurement of viscosities of, for example, moisture-reactive ionic liquids can be difficult, requiring complicated setups as demonstrated by Okoturo and VanderNoot who used a heavily



FIG. 1. Diagram of a typical rotational rheometer setup. As the upper geometry must be lowered onto the lower geometry with a precisely controlled gap containing the sample, accessibility implies exposure to the surrounding air.

modified rolling-ball viscometer to allow viscosity measurements to be made outside of a glovebox.¹¹ Hembree *et al.* developed a Couette rotating cylinder rheometer solely for the purpose of measuring high temperature metallic glass-forming liquids in an inert atmosphere, again highlighting the difficulty and complexity of measuring the viscosity of air reactive samples.¹² Giacomini and Gilbert also highlighted the difficulty in measuring oxygen reactive samples in air using cone plate rheometers and offered suggestions to mitigate such problems; however, they are only applicable to their measuring system.¹³

Manufacturers of rheometer systems have made strides to supply accessories that alleviate environmental problems, such as relative humidity chambers, which can finely control the humidity of the air around the sample during measurement but are limited by the temperature ranges they can operate in and generally cannot remove all moisture from the sample chamber air. Moreover, these accessories are expensive and are not universally suitable for all apparatus setups. Air sensitivity is less catered for currently, with the typical solution being to situate your rheometer inside a sealed glovebox pumped with the inert gas of your choice. This, however, is costly and not always a viable option due to either the confined laboratory space or the heating/cooling elements of the rheometer requiring regular air to control temperature.

Here, we show that these problems can be overcome in a simple and cost-effective manner, by the development of a method of isolating the measuring geometries of a rotational rheometer and sample using a heavier-than-air gas, such as sulfur hexafluoride (SF_6). We demonstrate its use to study two moisture-from-air reactive molecular liquids, trimethylsulfonium bromide- AlCl_3 and titanium(IV) propoxide, and moisture-sensitive glycerin in a standard rotational rheometer with heating and cryogenic cooling capabilities.

II. METHODS, CONTAINER DESIGN, AND INITIAL TESTING

To hold the cover gas in place around the sample and measurement geometries, a plastic cup was designed to seal the surface of the bottom geometry through a ring-shaped graphite gasket (outer ring diameter 57 mm and inner ring diameter 42 mm) cut from a 1 mm Klinger graphite sheet, typically found in vehicle engine seals and other high temperature/pressure environments. Graphite was chosen due to its ability to withstand a large range of temperatures and the ease with which it can be cut and shaped from readily available sheets of material. The cover gas container described here (see Fig. 2) was specifically designed to fit the lower measuring plate (L-PP50) of an Anton Paar MCR 702e Multidrive type rheometer (with an oven heating and cryogenic cooling accessory attached) with an open top to allow the upper measuring geometry to contact the sample unrestricted. While the cup was designed to fit this particular setup, it would be trivial to alter the cup dimensions to fit other apparatuses. Figure 2 shows a graphical representation of the cup and its attachment to the rheometer, while a 3D computer aided design (CAD) design file is available in the supplementary material. Dimensions for the cup used in our experiments are shown in Fig. 3.

SF_6 is a heavier-than-air colorless non-flammable non-toxic hypervalent gas with an octahedral geometry. At a density of 6.170 g/l, the gas is around five times heavier than air at 1.225 g/l, allowing it to settle in sealed bottom vessels (as such, it is critical to either work in an open ventilated area or monitor the oxygen levels at low heights to avoid accidental asphyxia while working with SF_6).¹⁴ In addition, SF_6 is virtually inert, driven largely by the fluoride atoms sterically hindering the sulfur atom at the core of the molecule, making it an ideal cover gas for use in separating reactive materials from air during rheometry measurements. It must, however, be noted that SF_6 is an extremely powerful greenhouse gas, trapping heat in the atmosphere with a radiative efficiency $\sim 23\,500\times$ higher per molecule than carbon dioxide. Therefore, actions to recover the gas after use must

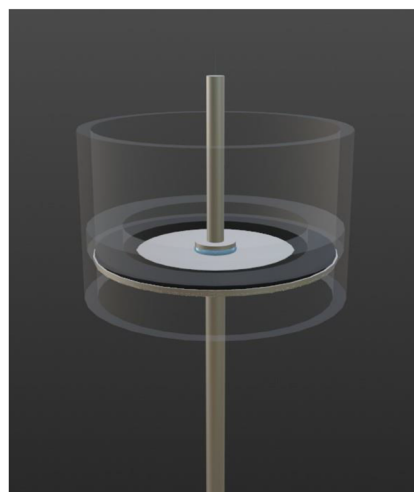


FIG. 2. Cover gas cup for carrying out rheometry isolated from the environmental air. Computer rendering of the cover gas cup (transparent) with a connecting gasket (black ring) sealed to the lower plate geometry.

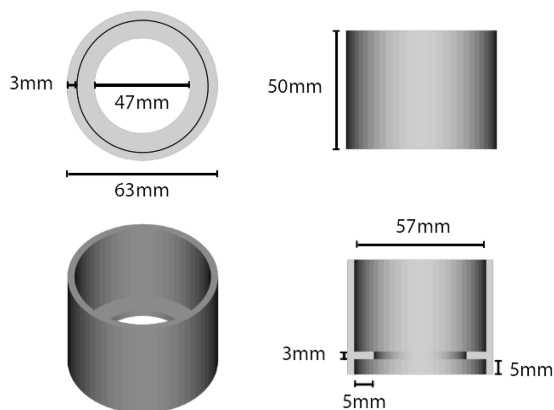


FIG. 3. Schematic diagram of the cover gas cup with dimensions specific to the PP50 lower geometry of the Anton Paar MCR702e rheometer.

be taken, despite the relatively small volume used for each experiment. An alternative to SF_6 that is not damaging to the environment is xenon, which is somewhat more likely to disperse from the cup due to its slightly lower density of 5.894 g/l.

Before testing the cover gas cup *in situ*, initial water and gas tightness tests were carried out. The watertightness test was carried out to account for the rare event of the rheometer being overloaded with a liquid sample. The watertightness test consisted of setting up the lower plate geometry with the cover gas cup attached outside the rheometer and filling it with water. A standard high vacuum silicon-based grease was applied to the contact area between the cup gasket and the lower geometry plate to ensure complete union between the two parts. The water was then left in the cup for 48 h, and the volume before and after was found to be unchanged.

The gastight seal was more difficult to determine due to the colorless nature of SF_6 . To track the volume of the gas, a small boat made from aluminum foil was floated on the SF_6 gas, and the height of the foil was noted. The cup was filled with the gas using a 7 mm diameter tube connected to a regulated SF_6 cannister, making sure the tube was at the bottom of the cup and filled at as low a gas flow as possible. Over a 48 h period, no change to the gas volume was observed. Prior to measuring with the cup under cover gas conditions, lowering of the upper geometry into the cup while situated in the rheometer was tested to make sure the geometry's movement did not displace the gas. This was carried out again using an aluminum foil boat to test the initial gas volume within the cup. The foil boat was then removed, while the upper geometry (PP10, diameter 10 mm) was lowered into a measuring position at a speed of 13 mm/s and placed back to measure the remaining cover gas volume. It was seen that the boat position had moved down slightly but negligibly with respect to the sample coverage. All further experiments were conducted using an Anton-Paar MCR702e with a rail mounted clam shell oven that splits down the middle and detaches from around the sample environment, rated from -160 to 550 °C, attached and fed with a liquid nitrogen boil-off gas. L-PP50 and PP10 geometries were used throughout with a measuring gap of 1.00 mm using the viscoelastic movement configuration. The temperature ramp used throughout was 2 °C/min. Rotational

measurements were taken with a shear rate of 0.3/s. The relative humidity of the lab was 18.6%–19.8% during all experiments. Titanium(IV) propoxide, glycerin, AlCl_3 , and trimethylsulfonium bromide were purchased from Sigma-Aldrich and stored under dry air conditions in a glovebox until use. Trimethylsulfonium bromide- AlCl_3 was prepared following the method of Okoturo and VanderNoot.¹¹

III.. EXPERIMENTAL RESULTS

Titanium(IV) propoxide is a molecular liquid that has recently been studied by us¹⁵ that does not undergo crystallization on supercooling but readily reacts with moisture in air, so it was chosen to test the cup and cover gas method under real-world conditions. The structure of titanium(IV) propoxide consists of three central titanium atom cores linked together by X–O–X type alkoxide bridges and terminal alkoxide ligands, which can easily exchange with other alkoxide ligands. In the presence of water, titanium(IV) propoxide readily hydrolyzes producing polymeric oxo-bridged species and, ultimately, titanium dioxide (TiO_2). This can be readily observed as a thin white film on the surface of the liquid (see Fig. 4). This reaction can take place within minutes in a suitably humid environment, and shorter alkoxide chain titanium alkoxides have been observed to react on the seconds timescale, making accurate rheometry measurements of the liquids impossible in open air (see Fig. 5).

To show the effect of measuring under open air conditions, titanium(IV) propoxide was loaded as rapidly as possible onto the rheometer lower geometry using a 1 ml pipette, bringing the upper geometry into contact with the sample. The oven was then closed, and the temperature controlled from that point onward by the oven that blows a constant supply of dry nitrogen boil-off into the chamber. The viscosity was then measured in rotational mode while lowering the temperature until the liquid titanium(IV) propoxide vitrified at *circa* -97 °C. The experiment was then repeated with the sample loaded in the same manner under cover gas conditions as described in Sec. II. The cup was then lifted from the lower rheometer plate to close the oven shut. The difference in viscosity as a function of temperature can be seen in Fig. 5. The air loaded sample



FIG. 4. Reaction of titanium(IV) propoxide liquid with moisture from the air. On the left: titanium(IV) propoxide under dry air conditions; on the right: a droplet of titanium(IV) propoxide after 5 min of exposure to natural air, both contained in a 17 mm diameter glass crucible. Note that the humid air exposed sample has turned to chalky white, indicating the formation of TiO_2 and loss of the original liquid structure.

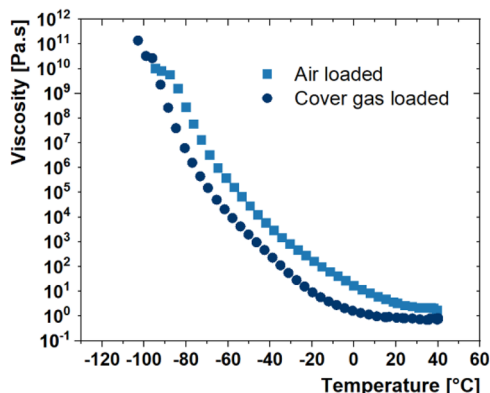


FIG. 5. Titanium(IV) propoxide viscosity as a function of temperature. The viscosity measurement results for a sample loaded in air are shown with square data points, while those loaded under the cover gas are shown with circular data points.

can be seen to have overall a much higher viscosity at all temperatures due to the presence of titanium oxide crystals forming as the liquid reacts with water from the atmosphere. The viscosity is also noticeably greater at high temperatures due to the formation of oxo-bridged polymers, which consequently leads to shear-rate dependent non-Newtonian effects and the breakdown of the double glass transition effect reported previously.¹⁵

The same experiment was also carried out with trimethylsulfonium bromide- AlCl_3 , an air/moisture sensitive ionic liquid with known temperature dependent viscosity values previously measured under inert air conditions by Okoturo and VanderNoot.¹¹ The viscosity values of the sample loaded under cover gas conditions compared well with the reference values, as shown in Fig. 6, whereas the viscosity of the sample loaded under normal air conditions can be seen to increase rapidly upon cooling, clearly suggesting that a new product has been formed through air/moisture interaction.

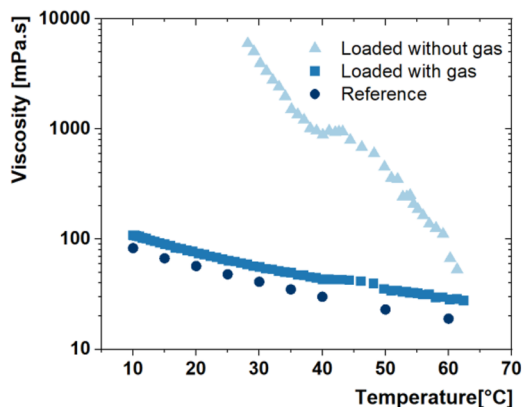


FIG. 6. Trimethylsulfonium bromide- AlCl_3 viscosity as a function of temperature. The viscosity measurement results for a sample loaded in air are shown with triangular data points, while those loaded under the cover gas are shown with square data points. The reference data taken from experiments carried out under an inert atmosphere are shown with circular data points.¹¹

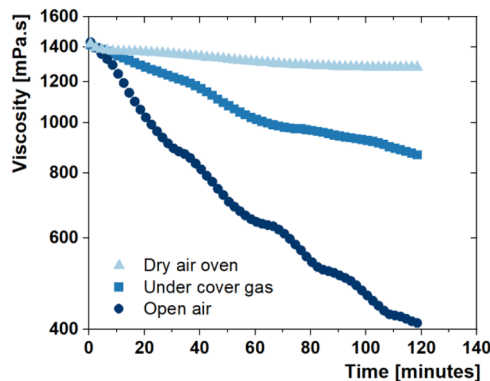


FIG. 7. Glycerin viscosity as a function of measurement time. The viscosity measurement results for a sample measured in air are shown with circular data points, those measured under the cover gas are shown with square data points, and those loaded under the cover gas and measured in the dry air oven are shown with triangular data points. Note that the room temperature fluctuates between 19.5 and 20.5 °C over the course of the measurement, resulting in the wiggles in the air and cover gas datasets.

To understand the ability of the cover gas method to measure rheological properties at room temperature without a closed-environment oven, we carried out a constant shear experiment of glycerin under different conditions. Glycerin is known to slowly absorb moisture from the air, resulting in a decrease in viscosity as the water impurity increases. Therefore, it makes for an ideal reference material for testing how much air interacts with a sample under open cup cover gas conditions. The shear rate was kept constant at 10 s^{-1} throughout all measurements for 2 h.

As shown in Fig. 7, the viscosity of glycerin under cover gas conditions decreases at a slower rate than that of glycerin in open air, showing that, while the cover gas has some effect in forming a moisture barrier, some air must be interacting with the sample over the course of the 2 h measurement. By comparison, the viscosity of glycerin in the dry air oven does not change significantly, decreasing from 1420 to 1280 mPa s due to a 2 °C increase in oven temperature over the duration of the measurement. Note that the room temperature fluctuates slightly between 19.5 and 20.5 °C over the course of the measurement, resulting in the wiggles in the air and cover gas datasets. We surmise that the rotation of the motor drive shaft pulls some air down and into contact with the sample.

IV. CONCLUSION

The cover gas method of carrying out rheological measurements on air sensitive liquids proved to be a success and allowed for the determination of the correct rheological properties of air/moisture sensitive trimethylsulfonium bromide- AlCl_3 and titanium(IV) propoxide liquids uncontaminated by hydrolysis products. This method is relatively simple to set up with minimal skill needed in construction or design in comparison with designing and building an airtight glovebox for an individual rheometer. While SF_6 was deemed to be the most suitable, other inert heavier-than-air gases, such as krypton or xenon, may also be used. Measurements at temperatures higher than the plastic's melting point are an obvious

concern but could easily be rectified by manufacturing the cup from aluminum or stainless-steel materials. With access to an inexpensive 3D printer or other means of rapid production, it could be relatively trivial to prototype several different dimensions of cup to fit around the individual's rheometer setup, making the cover gas method an efficient method for undertaking rheological measurements of air sensitive materials, and no doubt, it could be applied to other scientific methods.

SUPPLEMENTARY MATERIAL

A .stl file of the cover gas cup used in the manuscript can be found in the supplementary material online.

ACKNOWLEDGMENTS

K.W. acknowledges the funding by a grant from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 832703) and the Engineering and Physical Sciences Research Council (EPSRC) for support through Grant No. EP/N007417/1.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ben A. Russell: Conceptualization (equal); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Project administration (supporting); Validation (lead); Writing – original draft (lead); Writing – review & editing (equal). **Klaas Wynne:** Conceptualization (equal); Funding acquisition (lead); Project administration (lead); Resources (lead); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are openly available in the Enlighten Research Data Repository at <https://doi.org/10.5525/gla.researchdata.1589>.

REFERENCES

- ¹T. Mezger, *Rheology Handbook* (Vincentz Network, 2020).
- ²M. A. Meyers and K. K. Chawla, *Mechanical Behavior of Materials*, 2nd ed. (Cambridge University Press, 2008).
- ³A. Yahia, S. Mantellato, and R. J. Flatt, *Science and Technology of Concrete Admixtures* (Elsevier, 2016), pp. 97–127.
- ⁴A. Madian, M. Leturia, C. Ablitzer, P. Matheron, G. Bernard-Granger, and K. Saleh, "Impact of fine particles on the rheological properties of uranium dioxide powders," *Nucl. Eng. Technol.* **52**(8), 1714–1723 (2020).
- ⁵Q. Zhong and C. R. Daubert, *Handbook of Farm Dairy and Food Machinery Engineering*, 2nd ed. (Academic Press, San Diego, 2013).
- ⁶J. Aho, S. Hvidt, and S. Baldursdottir, in *Analytical Techniques in the Pharmaceutical Sciences*, edited by A. Müllertz, Y. Perrie, and T. Rades (Springer, New York, 2016), pp. 719–750.
- ⁷S. Wu and Q. Chen, "Advances and new opportunities in the rheology of physically and chemically reversible polymers," *Macromolecules* **55**(3), 697–714 (2022).
- ⁸F. Lorignon, A. Gossard, M. Carboni, and D. Meyer, "Microstructural and rheological investigation of upcycled metal-organic frameworks stabilized Pickering emulsions," *J. Colloid Interface Sci.* **586**, 305–314 (2021).
- ⁹H. Sahabudeen, Q. Zhang, Y. Liu, M. Heuchel, and R. Machatschek, "Mechanistic insights into the deformation and degradation of a 2D metal organic framework," *npj 2D Mater. Appl.* **7**(1), 25 (2023).
- ¹⁰A British DebutAnton Paar, 2023.
- ¹¹O. O. Okoturo and T. J. VanderNoot, "Temperature dependence of viscosity for room temperature ionic liquids," *J. Electroanal. Chem.* **568**, 167–181 (2004).
- ¹²W. Hembree, B. Bochtler, and R. Busch, "High-temperature rotating cylinder rheometer for studying metallic glass forming liquids," *Rev. Sci. Instrum.* **89**, 113904 (2018).
- ¹³A. J. Giacomini and P. H. Gilbert, "Degradation in cone-plate rheometry," *Rev. Sci. Instrum.* **89**(12), 124101 (2018).
- ¹⁴T. Nakajima, B. Zemva, and A. Tressaud, *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*, 1st ed. (Elsevier, 2000).
- ¹⁵B. A. Russell, M. González-Jiménez, N. V. Tukachev, L.-A. Hayes, T. Chowdhury, U. Javornik, G. Mali, M. Tassieri, J. H. Farnaby, H. M. Senn, and K. Wynne, "A second glass transition observed in single-component homogeneous liquids due to intramolecular vitrification," *J. Am. Chem. Soc.* **145**(48), 26061–26067 (2023).