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SHORT COMMUNICATION

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Digitally controlled high-precision thermostat for X-ray investigations on lyotropic and thermotropic liquid crystals

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Abstract The construction of a special hot air generation system for X-ray diffraction investigations of lyotropic and thermotropic mesophases at different temperatures is described. The sample is positioned at the center of the X-ray diffractometer contained in a long cylindrical capillary, and resides at a small goniometer head used to adjust the precise position and inclination of the sample. It was decided to use air as the medium and initially the medium was intended to flow axially. A stream of air is blown from a small and high rectangular opening sideways toward the sample. The gas streaming out of the vessel has to pass through a vortex cell. The air leaving the vortex cell forms a core of whirling gas with constant temperature. A temperature sensor is mounted longitudinally above the sample and is positioned inside the same airflow core. The sensor provides the input signal for a microprocessor-based controller which regulates the power of the heating or cooling system in the inlet tube providing constant temperature in the gas core.

Key words X-ray diffraction – Lyotropic liquid crystals – Hot air generation system – Vortex cell

Introduction

Our previous work [1–17] particularly referred to polarized microscopy investigations of the phase of behaviour of binary and ternary systems. The main objective of these investigations was the determination of lyotropic mesophases, namely regions with hexagonal phases, lamellar phases, gel phases and lyotropic-cholesteric phases as well as lyotropic nematic phases. Furthermore, the influence of solvents such as ethylene + glycol, butylene + glycol and glycerol on the formation of mesophases of homologous K soaps in binary systems has been throughly studied. Theses investigations revealed isotropic phases, which could not be identified by means of polarized microscopy. Cubic phases as well as gel phases were conceivable. Consequently, X-ray diffraction (XRD) investigations were inevitable to reveal further information about structural details.

The intended structural investigations required the development of a digitally controlled high-precision sample thermostat capable of executing extended temperature/time programs and especially enabling the study of phase transitions in very small temperature ranges. Therefore highest demands had to be put on the sample temperature stabilization: $\Delta T < \pm 0.1$ K needed to be achieved including regulator deviation. The sample thermostat subsequently described has been integrated and used within a HZG 4 (Seifert, Germany) XRD measurement system.

Determination of the thermostat construction principle

The challenge arose to find a setup capable of keeping a sample contained in a long cylindrical capillary with the highest possible precision at a given temperature without limiting the access to the sample for XRD scattering or other electromagnetic structural measurements. Three basic principles are feasible: heating by thermal contact, heating by radiation and heating by convection [18].

Obviously the first principle, heating by direct contact, had to be rejected since insurmountable practical problems would arise in the case of rotating cylindrical samples subject to X-ray transmission diffraction. Initial experiments confirmed that the second principle, heating by radiation, also implied various problems that would limit the precision achievable.

For the remaining principle of convection, solutions are known which implement the use of a liquid or vaporous medium of controlled temperature to keep a sample at constant temperature by leading a steady flow of the medium along the sample. Comparable setups are described, for example, by Rudman [19] and by Kobayashi and Nakamura [20]. However, the use of liquids implies significant ramifications for the construction and limits the accessibility of sample. Generally certain types of windows have to be used that in connection with the liquid unavoidably introduce intolerable attenuation of the X-ray flux. Furthermore, also in case of gases as media, it is only possible to control the temperature of the medium precisely at one single point. Generally, a temperature gradient of about $\Delta T/\Delta x \approx 10^{-1}$ K/cm within such streaming media occurs introducing a further error for axially directed media flow since common samples have lengths of up to 5 cm.

Figure 1a shows such a setup: the sample mounted in sample holder is surrounded by a flowing medium (arrows) streaming from the bottom to the top of the sample. Even assuming a steady laminar flow along the sample axis as illustrated in Fig. 1 at the top left position, the influence of the temperature gradients mentioned is not negligible for the intended high-precision investigation. Consequently for the construction of a convection-based thermostat the manner in which the medium, in our case air, is directed at the sample is crucial. This will be described in detail in the next section.

Construction of the hot air generation system

The sample in the form of a capillary tube is positioned at the center of the X-ray diffractometer and resides at a small goniometer head used to adjust the precise (x, y) position and inclination of the sample. It was decided to use air as a medium, and initially the medium was intended to flow axially; however, this was not realized for the previously mentioned reason of unavoidable temperature gradients. The decisive improvement was to introduce an airflow directed sideward to the sample thereby avoiding any temperature gradient along the sample given an appropriate airflow speed and temperature distribution. The principle is depicted in Fig. 1b. A stream of air is blown from a small and high rectangular opening sideways toward the sample. In this way an air-flux distribution of the molecules of air in motion around the capillary tube is generated that creates a curled flow vector distribution within an air-flux core having a triangular shape behind the opening. The size of the base of the triangle is equivalent to the opening width and the length is approximately triple this length. The capillary has to be positioned inside the triangle and additionally applied rotation of the sample averages any remaining temperature gradient.

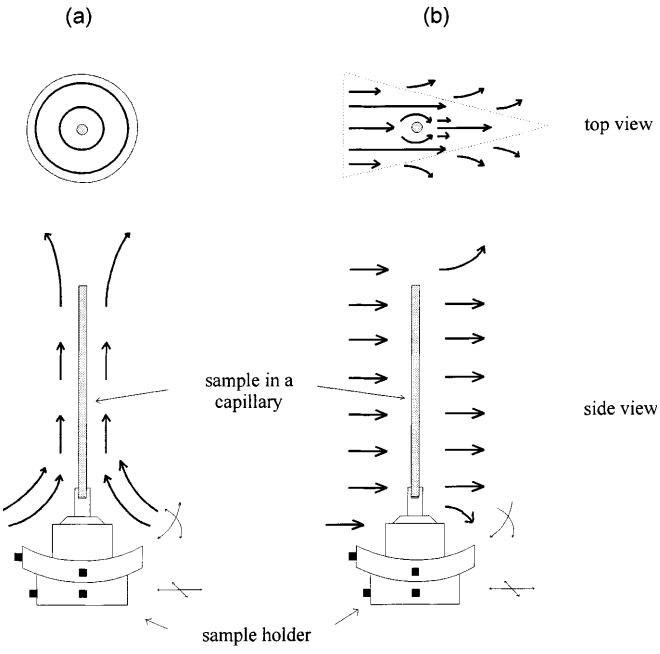

Fig. 1a, b Usable gas-flow modes to thermally regulate a capillary containing the sample. **a** axially directed gas flow, **b** sideward directed gas flow

With reference to Fig. 2 the function and actual construction of the thermostat's air generation and flow-forming unit developed by us shall be explained.

A vessel is positioned on one side of the capillary containing the sample to be tempered. Its walls consist of a highly thermally insulating material. The inlet tube contains a heating or cooling system suitable to change the temperature of the passing gas within the necessary range. In our case a heating and ventilation unit from a hot air fan (2 kW) was used.

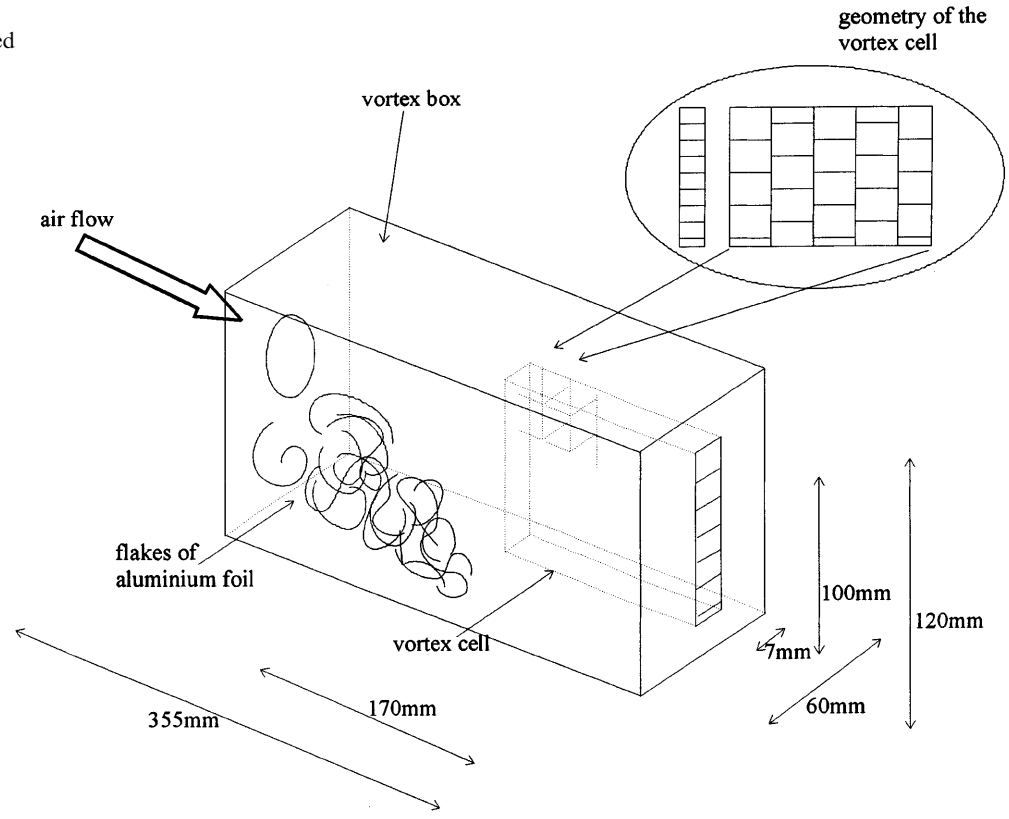

Fig. 2 Construction of the gas vessel including the vortex cell used to create a gas flow of homogeneous temperature around the sample during the X-ray diffraction measurements

After the gas has passed the heating unit it streams into the vessel containing flakes of aluminum foil as a thermally good conducting material. Thereby any remaining temperature inhomogeneities in the instreaming gas are averaged out. These kinds of inhomogeneities usually occur if electrical heating units with heated wires reaching very high temperatures are used. There is a rectangular gap at the side of the vessel directed toward the sample. In this gap a vortex cell is mounted with its main portion positioned inside the vessel. The vortex cell consists of numerous small, hollow metal-foil blocks arranged in a wriggled layout which mainly allows gas flow in an outward direction. The gas streaming out of the vessel has to pass through this vortex cell as can be seen in Fig. 2. Thereby a virtually total thermal homogenization of the gas stream in accomplished avoiding any temperature gradients. The side the vortex cell directed toward the sample may stick slightly outside the vessel to reach as close as possible to the sample. The width of the vortex cell is at least 3 times the diameter of the sample. The air leaving the vortex cell forms a core of whirling gas with constant temperature.

The temperature sensor is mounted longitudinally above the sample and is positioned inside the same airflow core. The sensor provides the input signal for a microprocessor-based controller which regulates the power of the heating or cooling system in the inlet tube, providing constant temperature in the gas core in front of the vortex cell and thereby inside the sample.

Generally, the thermostat is applicable over a temperature range of about $T = 220$–525 K.

Temperature measurement and digital control

For the temperature measurement the smallest available, laser-trimmed 100 Ω platinum (thin-film) chip sensor (series PC1.2005.1; M.K. Jumo Fulda, Germany) was used. The ceramic carrier of the resistors has a size of only $5 \cdot 2 \cdot 1.3$ mm^3, providing negligible thermal inertia.

The temperature regulator which was implemented in our experimental setup was a microprocessor-based digital controller PRS-96/51-2/13-31 (also Jumo). It features a 14-bit analog-to-digital converter (5 Hz sampling frequency) and a 13-bit digital-to-analog converter necessary for the targeted resolution and regulation precision. However, the most significant advantages are

– Different feedback modes can be stimulated. We used the PID mode.
– All control loop parameters are programmable and may be found by the controller itself in a self-optimizing autocalibration run.

– Nonlinearities of different temperature sensors are stored in an internal ROM and are fully compensated.
– The controller can communicate via a serial RS 232 port with a PC. All parameters may be changed and current values can be read out.
– The analog input amplifier allows the use of four-wire (Kelvin) wiring to suppress cable-resistant impact on the measurement.

The circuit schematic of the complete temperature control unit including watchdog circuits is summarized in Fig. 3. The temperature sensor, positioned directly above the sample, is connected to the input amplifier of the controller by four shielded wires. The normalized output signal of the controller ($I = 0 \ldots 20$ mA) provides the input for a phase control thyristor power modulator TYP020-110/1, 25, 230 (also Jumo) which influences the current in the heating unit. The back-to-back thyristor power modulator can operate at a maximum output current of $I_{max} = 25$ A and easily drives the 2-kW heating unit. However, after reaching an equilibrium state the average power consumption is significantly smaller. In addition to the temperature regulation itself, watchdog units for lower and upper limits of the heating fan motor current as well as internal fan temperature are used to provide secure unobserved operation necessary for long-term experiments.

It is obviously desirable to synchronize the thermostat control with the XRD system control in order to run arbitrary temperature/time programs, potentially over several days. As mentioned before, the temperature controller can communicate with a second computer via a serial RS 232 port [22]. Normally this would be the same computer that controls the XRD system; however, one has to ensure stable operation of both programs, the one used for controlling the XRD goniometer and receiving the X-ray diffraction signals as well as the one used to write and read data to and from the controller.

However, software communicating with external devices can be sensitive to timing problems and may fail under multitasking operating systems if designed to operate as a single task. This was the case for APX63, the program we had to use for the goniometer control. Therefore the temperature controller was programmed manually in temperature/time steps synchronized with the time of the APX63 file generation; however, some overlap time had to be taken into account since both systems ran independently after the start. To verify that both systems maintained their timing, the actual temperature of the sample was also measured via a second analog output of the temperature controller providing a normalized voltage ($U = 0 \ldots 10$ V) proportional to the regulated temperature. This voltage was converted by a 4.5 digit DVM (Voltcraft M-4650CR, Conrad, Germany) which also provides digital data read-out via a serial port. These values were recorded and stored in intervals of some $\Delta t = 10$ s by a small self-written program run on the computer that also controlled the XRD system. Though this analog detour of the signal might not be optimal, it was possible to run the XRD control software parallel to the temperature-measuring program, most likely since the latter only rarely required CPU load. Therewith it could be verified that XRD data had been recorded at the expected temperature. It

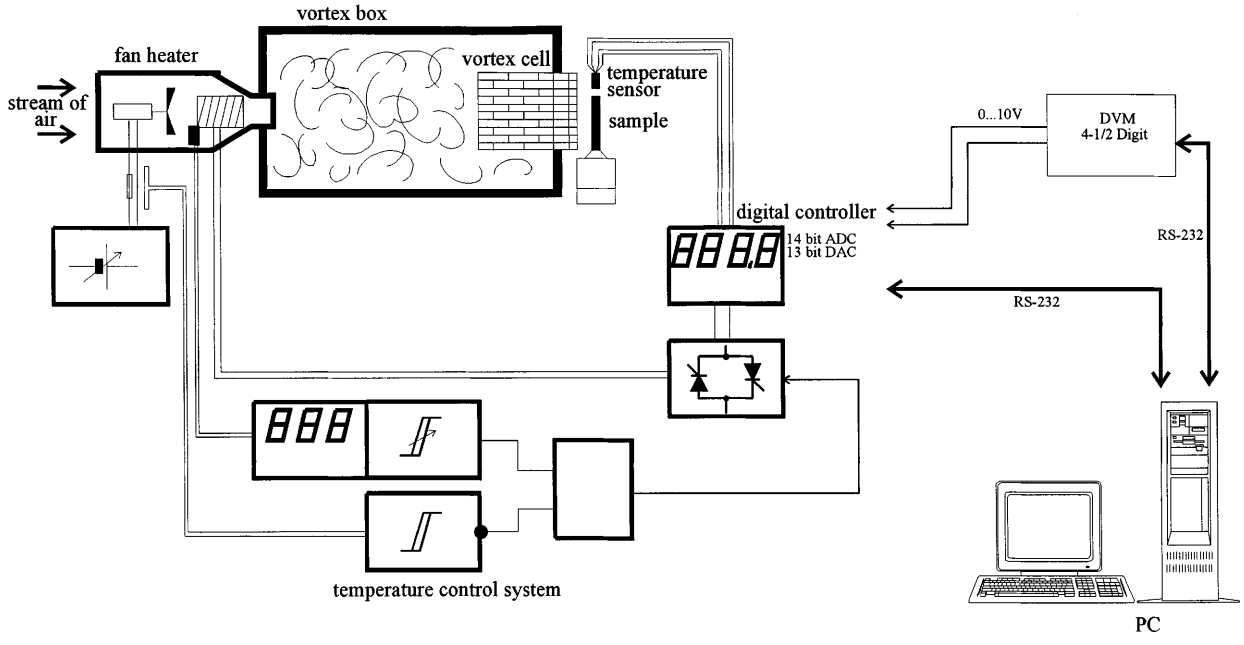

Fig. 3 Schematic of the complete temperature control unit including watchdog circuits

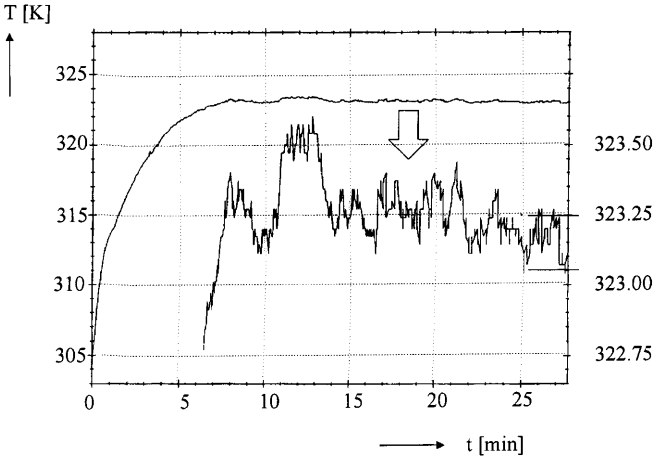

Fig. 4 Actual temperature of the sample as a function of time for a set value of $T = 323$ K

should be noted that different XRD systems control programs may act differently depending on their programming, data I/O organization and on the operating system used.

Calibration, control characteristics and modifications on the XRD control unit

Although the temperature sensors used provided relatively small tolerances, the remaining errors would be insufficient for the targeted precision [23]. Therefore the sensors were calibrated in the temperature range between $T = 293$ and 363 K using a water bath and a mercury reference thermometer with $|\Delta T| < 0.1$ K in the considered range.

The correct choice of the controller parameters (especially in PID mode) determines the speed and accuracy with which the set temperature is approached and maintained as already discussed. The quality of the temperature stabilization achieved can be seen in Fig. 4. It shows the actual temperature as a function of time for a set value of $T = 323$ K. After $t \approx 7$ min the target value of $T = 323$ K is reached within $|\Delta T| < 0.4$ K. After $t \approx 25$ min the remaining offset stabilizes at $|\Delta T| < 0.1$ K and the XRD measurements may be started.

References

1. Dörfler H-D (1992) Tenside Surf Det 29:352
2. Bartusch G, Dörfler H-D, Hoffmann H (1992) Prog Colloid Polym Sci 89:307
3. Dörfler H-D, Senst A (1993) Colloid Polym Sci 271:173
4. Dörfler H-D, Knape M (1993) Tenside Surf Det 30:196
5. Dörfler H-D, Knape M (1993) Tenside Surf Det 30:359
6. Dörfler H-D (1993) Prog Colloid Polym Sci 93:59
7. Dörfler H-D (1994) Z Phys Chem 187:135
8. Dörfler H-D (1994) Fat Sci Technol 96:346
9. Dörfler H-D (1994) Fat Sci Technol 96:371
10. Dörfler H-D (1995) Mol Cryst Liq Cryst 258:73
11. Dörfler H-D, Friedrich G, Swaboda C (1995) Tenside Surf Det 32:244
12. Friedrich G, Dörfler H-D (1995) Tenside Surf Det 32:252
13. Dörfler H-D, Swaboda C, Jacobi R, Beger J (1997) Tenside Surf Det 34:112
14. Dörfler H-D, Swaboda C, (1997) Tenside Surf Det 34:186
15. Dörfler H-D, Hintze H (1997) Tenside Surf Det 34:342
16. Dörfler H-D, Swaboda C (1998) Tenside Surf Det 35:18
17. Dörfler H-D, Swaboda C (1998) Tenside Surf Det 35:126
18. Hieke A (1995) Thesis. TU Dresden
19. Rudman R (1977) Int Lab 9/10:21
20. Kobayashi H, Nakamura N (1993) Cryst Res Technol 28:717
21. Juchheim GmbH (Fulda 1990) Elektronische Regler
22. Juchheim GmbH (Fulda 1990) DICON PRS Schnittstellenbeschreibung
23. Juchheim GmbH (Fulda 1990) DICON PRS 96 Handbuch