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**MERCURY DILATOMETRY
IN PHYSICAL AGING STUDY OF a-Se**

Roman SVOBODA^{a1}, Pavla PUSTKOVÁ^b and Jiří MÁLEK^a

^aDepartment of Physical Chemistry,

^bDepartment of Inorganic Technology,

The University of Pardubice, CZ–532 10 Pardubice

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Volume relaxation of amorphous selenium (a-Se) was studied by mercury dilatometry. Two differently constructed dilatometers (different sensitivity of sample volume change and different values of characteristic time constants of the dilatometers) were used to study the influence of experimental setting on the relaxation measurements. Temperature of glass transition and thermal expansion coefficients in glassy and undercooled liquid state were determined from non-isothermal experiments. Four sets of isothermal experiments including temperature down-jump, up-jump and combined experiments were performed to study the volume relaxation. The Tool–Narayanaswamy–Moynihan model was applied to describe the relaxation behavior of a-Se. All four sets of isothermal experiments were described using one set of TNM parameters. The combined experiments were considered to be the most suitable for studying the structural relaxation because of the minimum of the information lost at the beginning of the experiment. The reaction of a-Se and mercury was found not to be influencing the results of volume relaxation measurements.

¹ To whom correspondence should be addressed.

Introduction

Physical aging is a very important process occurring in and below the glass transition region. The glass transition [1] is a widely studied phenomenon and can be shortly described as the process when the properties of the undercooled liquid during further cooling depart from the local equilibrium. The molecular mobility of the cooled system decreases so much that the cooling rate is too high for the liquid to continually follow it and the glass is formed. As the structure of the material turns back to the equilibrium represented by undercooled liquid its properties (volume, enthalpy ...) continually change — this process is called structural relaxation (or physical aging). The fictive temperature T_f can be used to describe the current state of the relaxing material. Evaluation of this quantity is suggested in Fig. 1.

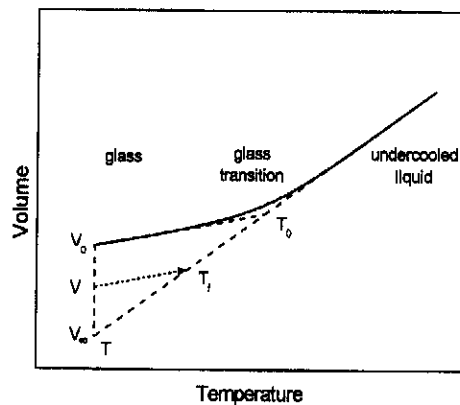


Fig. 1 Schematic depiction of changes in volume of amorphous material during relaxation at temperature T . Determination of the fictive temperature T_f is suggested

There are many ways how to describe this process. One of the common practices is that using the phenomenological Tool–Narayanaswamy–Moynihan model [2,3] characterized by the following equations

$$\frac{T_f - T}{T_0 - T} = \exp \left[- \left(\int_0^t \frac{dt}{\tau} \right)^\beta \right] \quad (1)$$

$$\tau = A \exp \left[\frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f} \right] \quad (2)$$

where T_f is the fictive temperature, T_0 and T are the initial and final relaxation temperatures (suggested in Fig. 1), τ is the relaxation time, t is time, T is temperature, R is the universal gas constant, x is the parameter of non-linearity, β is the parameter on non-exponentiality, A is the pre-exponential factor and h^* is the apparent activation energy of structural relaxation.

The method we selected to measure the volume relaxation response of the material is the mercury dilatometry [4]. Mercury dilatometry is a simple method used first and foremost for studying thermal properties and relaxation behaviour of polymers [5-8] — the first who used this method to study the structural relaxation was Kovacs [9]. The advantages of mercury dilatometry over several other methods commonly used to study relaxation behavior are discussed in this paper.

Amorphous selenium was chosen as a model example of chalcogenide glass. Relaxation and thermal properties of a-Se were studied by Echeverria *et al.* [10] or Bartos *et al.* [11]. Volume measurements on a-Se using mercury dilatometry were performed e.g. by Tammann and Kohlhaas [12], Hamada *et al.* [13] and recently by Slobodian *et al.* [14].

The main aim of this paper is to introduce advantages of the mercury dilatometry method beside measuring the volume relaxation and present the results obtained for amorphous selenium.

Experimental

Physical aging of a-Se was studied on two differently devised dilatometers to evaluate the influence of their construction on relaxation experiments. The dilatometers were labelled D50 and D70 where numbers correspond to their characteristic time constants (which will be discussed later).

Material

Selenium pellets (5N purity) were inserted into a fused silica ampoule and sealed in a vacuum of 10^{-3} Pa. The batched ampoule was placed in a rocking furnace where it was annealed at 300 °C for 24 hours (selenium melting point is 221 °C [15]) The ampoule was then air quenched in vertical position to form glassy bulk at the bottom of ampoule. The applied cooling rate ($4.5\text{-}5\text{ K s}^{-1}$) was high enough to form the selenium glass but not as high as to make the glass fragile. This was quite important because fragile glass could not be screwed out of the ampoule without breaking. Nevertheless, only a relatively small piece of bulk glass was obtained from each ampoule. In the case of dilatometer D70 each ampoule was annealed twice before breaking to avoid creating gas bubbles in bulk, hence longer

compact pieces were obtained. As long selenium rods as possible were required for the measurements to lower the risk of gas bubbles interception on the sample edges during the filling of dilatometers with mercury. Total mass of selenium rods in dilatometer D50 was 14.1 g (11 pieces), and 26.2 g (6 pieces) in the case of dilatometer D70. Samples in D70 were in the form of cylindrical rods with diameter 6 mm – just as cut out from the ampoules. Samples for dilatometer D50 were prepared in the same form but then ground to have a square-shaped profile with diagonal of 6 mm. Later we found out that this grinding procedure roughly scratched the surface of the samples (increased reactivity with mercury) and was considered undesirable. The amorphous character of prepared samples was checked by X-ray diffraction.

Dilatometer Preparation

The dilatometers were prepared according to ASTM D 864 [4] – the dilatometer consists of the standard ground-joint, the capillary and the specimen tube. The dimensions of dilatometers depicted in Fig. 2 are following: for dilatometer D50 is $a = 620$ mm, $b = 140$ mm, $c_1 = 12.5$ mm, $c_2 = 10.5$ mm and the capillary diameter is 0.79 mm; for dilatometer D70 is $a = 740$ mm, $b = 210$ mm, $c_1 = 10.6$ mm, $c_2 = 8.2$ mm and the capillary diameter is 0.61 mm. Capillaries were carefully chosen to have a constant diameter along their whole length; precision of their diameter determination was ± 0.3 %. The angle between the capillary and the tube with specimen was approximately 80° to avoid blocking of the capillary by softening sample or by particles produced during the reaction of mercury and the specimen. The empty open dilatometers were cleaned properly with chromosulphuric acid, rinsed with redistilled water and dried at 100°C . This step was very important because the impurities in the capillary would have slowed down the mercury column movement and so would have influenced every measurement. The samples were inserted through the bottom of the specimen tube which was sealed afterwards. During this procedure it was important not to damage the samples by overheating. For this reason glass rod was inserted behind the samples to fill the space needed to avoid getting the samples damaged during sealing. In this way the specimen-mercury ratio was shifted in favour of the specimen which was important in order to get higher dilatometer sensitivity (see below). Clean dilatometers filled with sample and sealed were filled with mercury using special apparatus. The apparatus was similar to that used by Kovacs [16], the only difference being that the mercury was purified by filtration through microfilters not by distillation. The apparatus with inserted mercury was degassed for several hours at approximately 10 Pa and when mercury contained no visible bubbles it was poured into the dilatometer. The filled dilatometer was checked again, so that it contained no bubbles. Waste mercury was removed from the dilatometer by

heating it at 65 °C, which was 5 °C above the highest temperature planned for the experiments, and outpouring the overflowing mercury from the ground joint. A well filled dilatometer can be verified by turning it bottom up: no mercury should flow out. The final amounts of mercury in dilatometers D50 and D70 were 101.7 g and 62.1 g, respectively. The dilatometer capillary was provided with millimetre scale marking along its whole length.

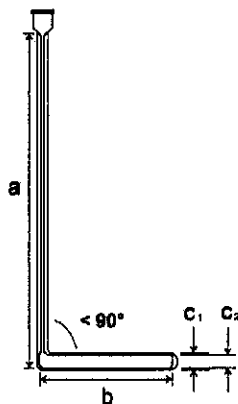


Fig. 2 Scheme of the mercury dilatometer (symbols are explained in text)

In order to determine the sample volume from the level of mercury in capillary, the dilatometer had to be calibrated at first. This was done by annealing the dilatometer at some reference temperature T_R high above T_g of the sample (to ensure that the sample is in equilibrium); $T_R = 56$ °C in the case of both our dilatometers. Reference mercury level h_R was taken at this reference temperature. Reference sample volume V_R at temperature T_R was calculated from the sample mass and temperature dependence of glassy selenium density taken from the literature [17]. Sample volume can be then determined [4] from the mercury column height

$$V = V_R + S\Delta h - V_{Hg}(\alpha_{Hg} - \alpha_{dil})\Delta T \quad (3)$$

where V is the sample volume at arbitrary time and temperature, V_R and V_{Hg} are the volumes of sample and mercury in dilatometer at reference temperature T_R , S corresponds to the cross-section area of the capillary, α_{Hg} and α_{dil} are the thermal expansion coefficients of mercury and glass the dilatometer is made of [18], Δh and ΔT are the differences between measured and reference values of mercury level and temperature, respectively.

Measurement Procedure

The structural relaxation experiments were performed using the previously described dilatometers D50 and D70 and two temperature-controlled water baths (Grant Instruments GR150 and GP200) with attached cooling device (Grant Instruments CG1). The baths were placed in hood to establish the surrounding temperature as constant as possible. As far as water was used as the thermostat liquid, the lowest temperature achieved during non-isothermal experiments at defined cooling rate was approximately 5 °C. Silicon oil could have been used instead of water but its higher viscosity would have caused temperature gradients within the bath — whether or not using the additional stirring unit. To avoid temperature oscillations and water vaporization during longer experiments water surface was covered (and this way reduced) with polypropylene balls. Baths were calibrated using independent thermocouples, accuracy of temperature calibration was ± 0.01 °C. Long-term temperature stability of baths over several days was ± 0.05 °C (this corresponds to 0.065 mm change of mercury column height for D70 that is noticeably lower compared with scale reading inaccuracy), short-term stability over several hours was ± 0.02 °C. This temperature stability was considered as not affecting relaxation measurements. Mercury level in capillary was read manually using magnifying glass (magnification 10 \times). The length scale resolution was approximately 0.1 mm which meant that dilatometer sensitivity in case of D50 was 14.67×10^{-6} cm³/cm³ of the sample and in case of D70 the sensitivity was 4.68×10^{-6} cm³/cm³.

Non-isothermal experiments performed on the dilatometers were realized applying cooling rates 0.2 and 0.5 °C min⁻¹. The dilatometers were retained at selected temperature at 60 °C for a short period of time to assure that the sample is in equilibrium and then they were cooled to 5 °C. The mercury level in capillary was read every 60 or 30 seconds during the experiment. In addition, temperature history had to be recorded independently because a slight delay of recorded versus programmed temperature was established. The cooling rate was verified this way too.

Structural relaxation was studied above all on the basis of isothermal experiments. The simplest relaxation experiments are the temperature down- and up-jumps. The first step during realization of these experiments was annealing at temperature T_0 for sufficiently long period of time to erase the previous thermal history of the sample and so ensure that the sample is in equilibrium state for temperature T_0 at the beginning of measurement. The dilatometer was then manually transferred to the second bath and annealed at temperature T ($T < T_0$ for down-jump and $T > T_0$ for up-jump). The transfer had to be as quick as possible to shorten the time needed for the sample to reach the thermal equilibrium in the second bath. Time zero for the relaxation experiment and the first readings were taken after certain period of time (dilatometer time constant t_i — will be explained later) just because of the distortion that would originate from the sample reaching

the thermal equilibrium. The readings were taken in logarithmic scale of time. Experiment was ended after the sample finished the relaxation process and reached the equilibrium represented by the undercooled liquid state – this was indicated by constant value of mercury level in capillary.

From among isothermal experiments the so-called combined experiments were found to be the most suitable for later analysis. This type of experiment provides extreme on the measured curve, which results from more complicated thermal history than in the case of simple down- and up-jumps. This experiment consists of down-jump from temperature T_0 , annealing at temperature T_B for certain period of time (annealing time t_B) followed by temperature up-jump to a temperature T ($T_B < T < T_0$). Time zero and first readings of mercury level were as in the case of the simple temperature jumps taken after the last temperature step (up-jump to T) after the time t_i needed for the sample to reach the thermal equilibrium.

Temperature in both annealing baths was recorded during all experiments to assure that no higher temperature fluctuations occurred and that the tempering fluid was stable enough not to influence the measurement. It is also important to mention that experiments on dilatometer D70 were made immediately after the dilatometer preparation while in the case of D50 the experiments were made after one year since the dilatometer preparation. This way the influence of the very mercury surrounding of the sample on the relaxation experiment could be determined.

Results and Discussion

Reaction of Se and Hg

Reaction of selenium and mercury produces HgSe compound [15]. We performed various experiments to investigate whether the extent and reaction rate are too high to significantly influence the relaxation experiments. The selenium sample was taken out of the dilatometer D50 after 3 years of continuing experiments to inspect a composition and morphology of a-Se sample. Thin layer of different color and fragile structure was observed on the surface of the samples. This layer was studied by scanning electron microscopy (Fig. 3) and it was confirmed that the layer is formed by HgSe. Thickness of the layer was variable, ranging from 5 to 100 μm . These values correspond to 0.15-3 % of original volume of a-Se sample inserted in the dilatometer. However, it has to be taken into account that this layer was accumulated during three years. Relaxation experiments are expressed in relative volume changes correlated to sample volume on the beginning of the experiment, so we only have to consider the influence of layer growing during every measurement which was negligible even during longest experiments. It appears that already very thin layer significantly slows down further reaction of

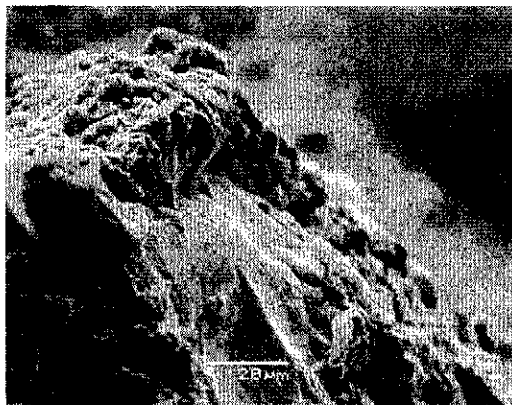


Fig. 3 HgSe layer on the SEM illustration. Flat areas correspond to raw a-Se fracture. Rough slivers and fragments represent the HgSe layer formed on the surface of the sample

a-Se and mercury. This conclusion was supported by results from an experiment when the reference a-Se samples were immersed in mercury and exposed to the same temperatures as the dilatometers during measurements. Percentual mass increase of these samples immersed for 22-280 days was approximately 0.15-0.33 %, the layer thickness was approximately 5 μm. This apparent slowdown of the HgSe mass increase confirms at least partial passivating properties of the formed layer. On the other hand, we found that higher temperatures largely support the reaction process. One reference sample was immersed in mercury for 18 days at 35 °C and 100 μm thick layer was formed. That is why the dilatometers had to be exposed to such temperatures for as short time as possible.

The main question of this chapter was to confirm whether the relaxation response of the sample is really the same within the whole time of experimental examination. This was solved by performing the set of exactly the same experiments on dilatometer D70. Combined experiment ($T_0 = 39\text{ °C}$, $T_B = 9\text{ °C}$, $t_B = 1\text{ hour}$, $T = 32\text{ °C}$) was made immediately after dilatometer preparation and the measurement with the same thermal history was twice reproduced after four months of measuring. The relaxation function M_V as a function of time is shown in Fig. 4 for these experiments. The M_V function is defined as follows

$$M_V = \frac{V - V_\infty}{V_0 - V_\infty} \quad (4)$$

where V is the actual volume, V_0 is an initial volume and V_∞ stands for the equilibrium volume. As can be seen, all three curves are almost perfectly superimposed. The inserted figure shows the dependence of the volume of the sample on $\log t$. From here it can be seen that the absolute volume of the sample

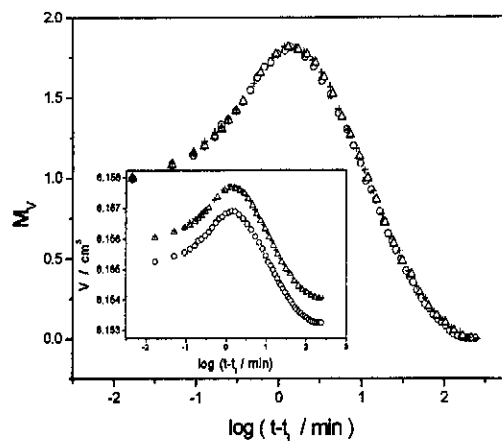


Fig.4 Combined temperature jump experiment ($T_0 = 39\text{ }^\circ\text{C}$, $T_B = 9\text{ }^\circ\text{C}$ for 1 hour, $T = 32\text{ }^\circ\text{C}$) for dilatometer D70 measured after different period of time elapsed from filling the dilatometer. Measurement immediately after filling (\circ), measurement after 4 months – 1st run (Δ) and 2nd ($+$). Absolute volumes measured during experiments are displayed in the inserted figure

is slightly changed by the proceeding reaction (layer of lower density is formed) but the shape of the curve remains the same. Furthermore, reproducibility of this method is quite high — the two measurements made just after each other excellently overlap. Because the analysis of relaxation experiments is made on the basis of the normalized relaxation response represented by the M_v function, a conclusion can be made that the reaction between selenium and mercury does not affect the final volume relaxation results.

The only practical problem was connected with continuing polluting of the capillary. The HgSe layer formed on the surface of the samples was not compact and produced tiny particles that caused problems with mercury level determination. However, this difficulty referred only to dilatometer D50 when the first experiments were performed two years after the dilatometer preparation.

To summarize, mercury dilatometry is an acceptable method for measuring volume relaxation of amorphous selenium (tested for relaxation experiments up to 12 days of annealing).

Influence of Dilatometer Construction on Relaxation Measurements

In this chapter we are going to introduce the main features and advantages of mercury dilatometry as well as the influence of the dilatometer construction on the relaxation measurements.

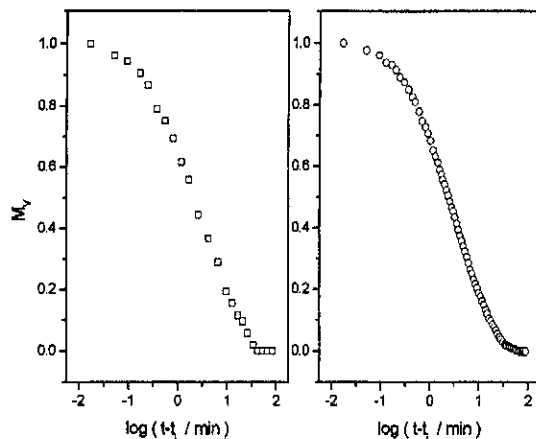


Fig. 5 Temperature down-jump experiment performed for both dilatometers $T_0 = 39\text{ }^\circ\text{C}$, $T = 34\text{ }^\circ\text{C}$: \circ – D70; \square – D50

Dilatometer sensitivity (the sensitivity of the volume change) is one of the most important parameters influencing each measurement. Higher sensitivity was also the greatest advantage of the D70 dilatometer. This is illustrated in Fig. 5 which shows the difference in similar measurements (simple down-jump from 39 to 34 $^\circ\text{C}$) between the dilatometers caused by the different dilatometer sensitivity. The curves are depicted separately to stress the difference in smoothness (otherwise the curves would overlap each other). The D70 curve is much smoother and ideal for further evaluation by fitting analysis. Higher sensitivity of D70 dilatometer allowed us to apply much finer time scale during the reading of the mercury level progression inside the capillary (much smaller shift of mercury level was distinguishable). Resulting dilatometer sensitivity can be influenced by many decisions made when constructing the dilatometer. Reduction of the capillary diameter is the best way to increase the dilatometer sensitivity but in reality, a limitation is tied to this accomplishment. The narrower the capillary is, the longer it must be to display the shift in the mercury level corresponding to the temperature change. Dilatometer with an exceedingly long capillary is very difficult to handle, apart from the fact that along such a lengthy capillary quite high temperature gradient would arise. Thus the difference in temperatures in various capillary parts would cause certain distortion in its response to the relaxation of the sample, thermal expansion of mercury in dependence on the mercury column length and position would have to be taken into account. The sensitivity of a dilatometer can be also increased by increasing the amount of the sample at the expense of the mercury amount (to keep the capillary length suitable). This step has, of course, its limitations, too. The first one is that the sample has to be fully surrounded by mercury which means that taking into account high interfacial tension of mercury there has to be sufficiently wide gap

between the sample and the wall of the specimen tube (which determines the minimum amount of mercury). The condition that the length and not width of samples is increased has to be fulfilled. Widening of the sample would avoid the first limitation but would cause significant increase of dilatometer time constant t_i (will be explained in the next paragraph). Heat conduction between the sample and the thermostat liquid is essential for magnitude of time t_i , hence lesser thickness of dilatometer tube containing specimen (constant c_2 in Fig. 2) and lesser thickness of the glass the tube is made of (term $|c_1 - c_2|$ in Fig. 2), is demanded. It seems that increasing the length (keeping the width constant) of the sample is the best solution of this problem. Slightly worse manipulation with the dilatometer and efficient stirring (to suppress any temperature gradient along the specimen tube) are the only drawbacks of this option. Moreover, the reaction of a-Se and mercury has to be borne in mind so the specimen should be composed of so few pieces as possible to decrease the surface of the sample exposed to the reaction.

Next to the dilatometer sensitivity belongs the time constant t_i among the most significant characteristics of the dilatometer. Dilatometer time constant t_i is the time the sample in dilatometer needs to reach thermal equilibrium after the instant change of temperature. Due to this lag were the first readings of mercury level taken after this time elapsed. Dilatometer time t_i is a real constant for the dilatometer, it is not affected by any of the experimental conditions and was the same for all the measurements performed with the same dilatometer. Various temperature up- and down-jumps were performed with each dilatometer to determine t_i . The readings were taken immediately after the transfer for about 2-3 minutes. Figure 6 shows an example of such measurements — the identical down-jumps ($T_0 = 39\text{ }^\circ\text{C}$, $T = 32\text{ }^\circ\text{C}$) for both dilatometers (reproduced for D70).

Volume of the sample was normalized to compare both data sets. The dashed line suggests determination of the time t_i as of the moment when the intense decrease slows down and becomes mild, caused only (or at least from the main part) by structural relaxation. The figure inserted in Fig. 6 depicts the whole experiment (made on D70) i.e. the complete response of the material after the transferring of the dilatometer into the bath maintained at temperature T . Triangles in this picture represent the establishing of thermal equilibrium while circles distinguish the very volume relaxation till achieving the equilibrium volume. The dilatometers were labelled using their time constants: $t_i = 50\text{ s}$ for D50 and $t_i = 70\text{ s}$ for D70. Another method of the determination of dilatometer time constant was inquired to confirm these eductions. Hamada *et al.* [14] described evaluation of t_i using dilatometer filled only with mercury alone. We repeated his procedure: in the case of D70 (filled only with mercury) was the thermal equilibrium achieved to 95 % within 50 s. The heat conductivity of mercury is higher than that of amorphous selenium so the equilibrium was attained earlier than in the case of real dilatometer. Therefore, the next step to confirm our evaluation of t_i was to directly find out how much time does the sample need to reach the thermal equilibrium.

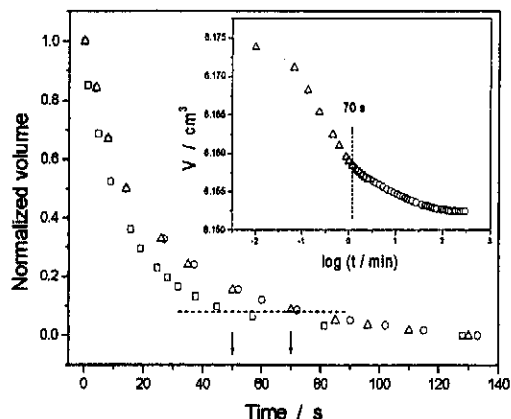


Fig. 6 Determination of time constant t_i for both dilatomers (Δ) and (\circ) – D70; \square – D50 from first five seconds of the simple temperature down-jump experiment ($T_0 = 39^\circ\text{C}$, $T = 32^\circ\text{C}$). Inserted figure shows the entire measurement till reaching structural equilibrium (see text)

The thermocouple was placed in the middle of the a-Se sample in dilatometer similar to D70 and the same temperature jumps as in the case of relaxation measurements were realized. Thermal equilibrium was achieved to 90 % within 70 s for all the measurements. All these results correspond to the earlier made conclusions. The set of experimental measurements represented by that depicted in Fig. 6 was thereto used to model the heat transfer to the sample. The temperature evolution of the sample in dilatometer follows the heat transfer equation:

$$\frac{dT}{dt} = c(T_{surr} - T) \quad (5)$$

where T is the average temperature of the sample, T_{surr} is the temperature in the annealing bath, t is time and c is the heat transfer coefficient. The parameter c was found to be $0.035 \pm 0.003 \text{ s}^{-1}$ based on the fit of down- and up-jump data.

Though the time t_i is determined to calibrate the dilatometer, it was still advantageous to have as low dilatometer time constant as possible. Higher value of this parameter was the main disadvantage of dilatometer D70. Generally, the dilatometer time constant is probably the biggest disadvantage of the method of mercury dilatometry. During measuring the relaxation experiments there is always lost some amount of information in dependence on the time constant of the used instrument. Even techniques as e.g. the differential scanning calorimetry (DSC) with very fast temperature change response and very small amounts of the measured material show certain loss of relaxation data due to the inability to heat or cool the samples sufficiently quickly. On the other hand, in case the of mercury

dilatometry this feature can be at least partially restrained by performing experiments with proper thermal history, which will be discussed below. Moreover, mercury dilatometry has a lot of advantages among which one of the most important is that a thermodynamic property proportionate to the fictive temperature is directly measured (compare to e.g. enthalpy in case of DSC measurements). The measurements by mercury dilatometry can be – with a proper dilatometer construction – very precise and insure a comfortable evaluation by various methods including those based on determination of the slope in the point of inflexion [19].

Non-Isothermal Experiments

Glass transition of amorphous selenium was measured according to the procedure described above. Glass transition was measured for samples in both dilatometers at cooling rates 0.2 and 0.5 $^{\circ}\text{C min}^{-1}$. Measurements for 0.2 $^{\circ}\text{C min}^{-1}$ and both dilatometers are shown in Fig. 7, normalized sample volume was used in order to

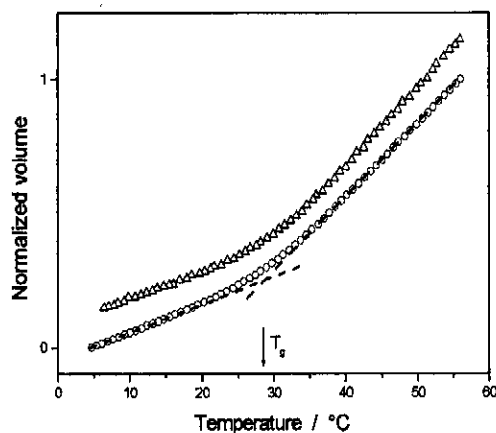


Fig. 7 Temperature dependence of volume for both dilatometers and cooling rate $q = 0.2$ $^{\circ}\text{C min}^{-1}$ with suggested evaluation of T_g ; \circ – D70; Δ – D50

compare both measurements. The temperature of glass transition was evaluated as the intersection of extrapolated slopes of the curve in the range of glass and undercooled liquid, as suggested by the dashed line. This evaluation is, in the case of mercury dilatometers, affected by the thermal lag between the thermostat liquid and the sample. This was taken into account using correction based on the values of applied cooling rate and time constant of the dilatometer. Temperature of glass transition differed in the range of 28 – 32 $^{\circ}\text{C}$ depending on the used dilatometer

(D50 or D70) and applied cooling rate (0.2 and 0.5 °C min⁻¹). Hamada *et al.* [13] performed the same experiment applying cooling rate 0.2 °C min⁻¹, they found $T_g = 32$ °C. Eisenberg and Tobolsky [20] report for the same cooling rate the value $T_g = 31.0 \pm 0.5$ °C. Dzhililov and Rzaev [21] (dilatometer filled with water) report $T_g = 30.3$ °C for amorphous selenium and cooling rate 0.2 °C min⁻¹. The slight variety in reported values can probably be caused by different dilatometer constructions: the same thickness of the sample would be needed to ensure the same heat conduction.

Thermal expansion coefficients of glass α_g and undercooled liquid α_l were determined from the extrapolated slopes of the curve in the range of glass and undercooled liquid (Fig. 7) according to the equation

$$\alpha = \frac{1}{V} \left(\frac{dV}{dt} \right) \quad (6)$$

The values of α_g and α_l are for both dilatometers and both cooling rates summarized in Table I. The reliability of the evaluated values is relatively high, the correlation coefficient R of linear fitting was for both dilatometers higher than 0.999. As is also shown in Fig. 7, the scatter in experimental non-isothermal data is negligible — just a bit higher in the case of D50 due to the lower dilatometer sensitivity and polluted capillary. The value of α_l fully corresponds with literature [14,22] (in the case of Senapati and Varshneya [22] assuming the isotropic behavior and approximate validity of the relation $\alpha_{volume} = 3\alpha_{length}$). On the other hand, our value of α_g is lower than those reported in literature $\alpha_g \sim 1.3 \times 10^{-4}$ K⁻¹ [14,22,23] or $\alpha_g \sim 1.65 \times 10^{-4}$ K⁻¹ [12,21,24]. Determined value of $\Delta\alpha$ is most conformable with $\Delta\alpha = 2.8 \times 10^{-4}$ K⁻¹ reported by several authors [10,12].

Table I Determined values α_g , α_l , $\Delta\alpha$ obtained from non-isothermal experiments and $\Delta\alpha_{iso}$ obtained from isothermal experiments

Dilatometer	$\alpha_g \times 10^4, \text{K}^{-1}$	$\alpha_l \times 10^4, \text{K}^{-1}$	$\Delta\alpha \times 10^4, \text{K}^{-1}$	$\Delta\alpha_{iso} \times 10^4, \text{K}^{-1}$
D50	1.04 ± 0.05	3.50 ± 0.02	2.46 ± 0.07	2.60 ± 0.07
D70	0.98 ± 0.01	3.53 ± 0.01	2.55 ± 0.02	2.59 ± 0.06

Glass transition temperature had to be determined above all to suggest the proper temperature range for isothermal relaxation experiments. The annealing temperature T determines the time of relaxation, i.e. the time needed for sample to get in the equilibrium state. In our case ($T_g = 29$ °C at the cooling rate $q^- = 0.2$ °C min⁻¹) the best temperature range is approximately $T_g \pm 10$ °C.

Isothermal Experiments and TNM Fit

Four sets of isothermal experiments were performed on dilatometer D70 and the Tool–Narayanaswamy–Moynihan model was applied to describe the relaxation behavior of the amorphous selenium.

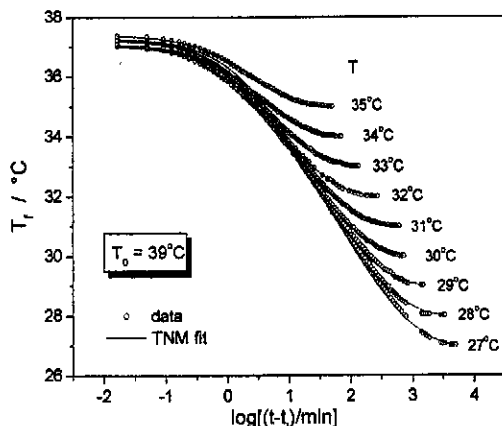


Fig. 8 Set of temperature down-jump experiments ($T_0 = 39^\circ\text{C}$, T marked in figure) performed on dilatometer D70. TNM model was applied using parameters listed in Table II

The most simple relaxation experiments are the temperature down-jumps (Fig. 8) when the sample relatively quickly attains the equilibrium at higher temperature T_0 and then is annealed at temperature T where the relaxation process proceeds. The main advantage of this type of experiment is the fast achieving of equilibrium at temperature T_0 (39°C). This simplifies this part of experiment — time of achieving the equilibrium has to be measured just once and it is sufficient then to double this time to be sure without further repeated measurements verifying that the sample is in equilibrium. However, this advantage is completely eclipsed by the disadvantage of the greater loss of information in the time t_i due to the fast relaxing sample. This loss of information depends on the temperature at which the sample is maintained before it is transferred to temperature T . The higher this temperature T_0 is, the less compact the structure of the sample is immediately after the transfer and the faster the relaxation process proceeds during the time t_i . This loss of information is represented by the difference between the temperature T_0 and the truly obtained value of T_f at the beginning of experiment.

This disadvantage is suppressed in the case of the temperature up-jump experiments (Fig. 9). During these experiments the relaxation immediately after the transfer to temperature T is much slower than in the previous case because the structure of the sample is from the annealing at lower temperature much more compact. Furthermore, the very measurement is quick. On the other hand, there is

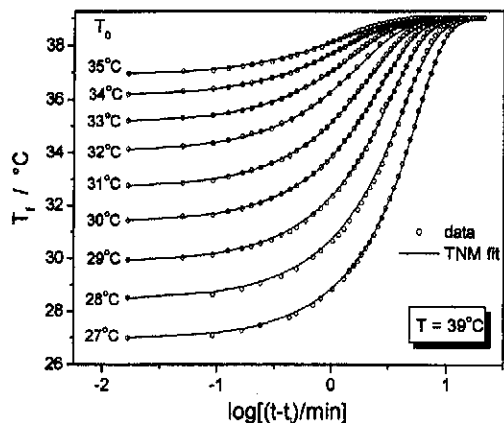


Fig. 9 Set of temperature up-jump experiments (T_0 marked in figure, $T = 39\text{ }^\circ\text{C}$) performed on dilatometer D70. TNM model was applied using parameters listed in Table II

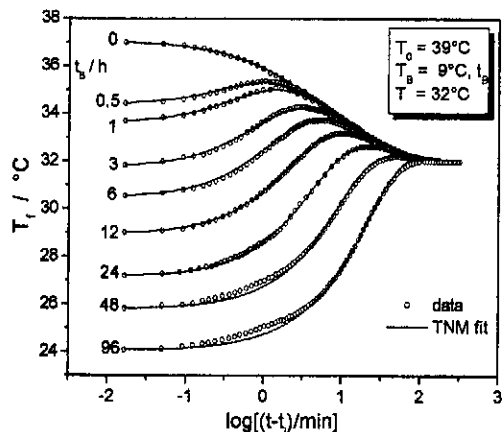


Fig. 10 Set of combined experiments ($T_0 = 39\text{ }^\circ\text{C}$, $T_B = 9\text{ }^\circ\text{C}$ for 1 hour, $T = 32\text{ }^\circ\text{C}$) performed on dilatometer D70. TNM model was applied using parameters listed in Table II

a certain uneasiness in determining whether the sample had already attained the equilibrium when annealed at temperature T_0 , especially in the case of the lowest temperatures.

Most of the problems of both these types of experiment were solved by performing the combined experiments (Figs 10 and 11). Duration of the measurement itself, i.e. the time when the mercury level was read could be chosen by the choice of the annealing temperature T . It was chosen to be $32\text{ }^\circ\text{C}$ so the final part of the experiment, the measurement itself, lasted about 4 hours. This was the best compromise between the length of an experiment and the magnitude of the volume

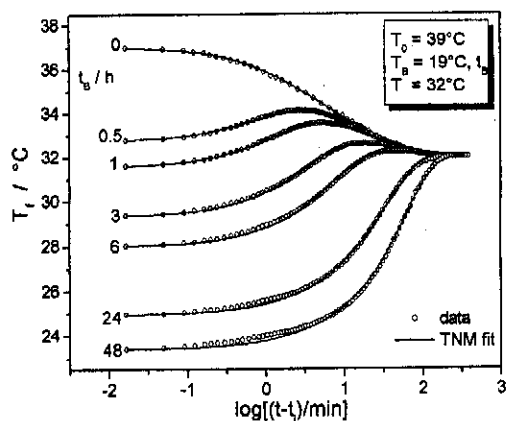


Fig. 11 Set of combined experiments ($T_0 = 39\text{ °C}$, $T_B = 19\text{ °C}$ for 1 hour, $T = 32\text{ °C}$) performed on dilatometer D70. TNM model was applied using parameters listed in Table II

change during this part of experiment (determines the effective resolution). The advantage of the high temperature T_0 remained as well as the merit of the highly compact structure and, therefore, the slow relaxation during the time t_i . In the case of the combined experiments the compact structure results from the fact that temperature T_B (9 °C and 19 °C) is far below the temperatures at which the equilibrium is normally attainable. That is because at T_B the equilibrium does not have to be attained contrariwise by choice of time t_B ratio of relaxation can be selected. Furthermore, this thermal history provides extremes on measured curves which were most suitable for the numerical evaluation of structural relaxation. This was probably the greatest advantage of the combined experiments. The TNM fit of the curves with extreme had to be much more accurate and the range of the TNM parameters could have been more reliably determined. All curves presented in Figs 8-11 were fitted using the same set of TNM parameters listed in Table II.

Table II Values of the TNM parameters obtained from fitting the down-jump, up-jump and combined experiment curves presented in Figs 8-11

Dilatometer	x	β	Δh^* , kJ kmol ⁻¹	$\ln(A/s)$
D70	0.42 ± 0.05	0.58 ± 0.05	356 ± 2	-133 ± 0.5

Conclusion

Mercury dilatometry was used to study the relaxation behavior of the amorphous selenium. The influence of the reaction between amorphous selenium and mercury on relaxation experiments was examined. It was confirmed that this reaction is

very slow in comparison with the physical aging experiments so that no single experiment is significantly influenced. The absolute sample volume slightly changes over the long period of time but the shape of a reproduced measurement remains right the same so the further evaluation is not affected by Hg-Se reaction at all. Furthermore, most advantages and disadvantages of the method of mercury dilatometry are discussed. Two dilatometers with different parameters were prepared to consider the influence of dissimilar construction on relaxation measurements. Dilatometer sensitivity and dilatometer time constant t_p , the main two characteristics dependent on the dilatometer construction, are discussed. The mercury dilatometry is from these points of view considered to be an acceptable method for measuring the volume relaxation of amorphous selenium.

From non-isothermal measurements the values of T_g , α_g and α_l were determined and the best temperature range for relaxation experiments was suggested. The values of T_g , α_g and α_l are in a good agreement with published results. Four sets of isothermal experiments including temperature down-jump, up-jump and combined experiments were performed to study the volume relaxation. One set of parameters of the applied Tool–Narayanaswamy–Moynihan model was used to describe all experimental data. Advantages of the combined relaxation experiment over the simple temperature jump experiments are suggested.

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