Characterization of aggregates by the speed of sound waves and densitometry

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Abstract

Scattering methods like X-ray or neutron small-angle scattering and dynamic light scattering are standard methods for the characterization of amphiphilic aggregates like micelles, vesicles and gels. Rheological experiments show the formation of gels indicated by a strong increase of the viscosity. Precision measurements of the speed of sound waves (pulse method) can be used to follow the micellization process. This new technique utilizes the dependence of the speed of sound waves on the number of dissolved particles at fixed concentration. Experimental results show the formation of micelles in a triblock copolymer (P-85) solution in the concentration range from 0.5% to 30% (W/W). Precision densitometry uses the mechanical oscillator method based on the measurement of the eigenfrequency of a U-shaped glass tube. By introduction of a phase shifted excitation it is possible to measure the ratio between the damping force and the spring force of the system where the damping force is related to the viscosity of the fluid. With this instrument it is possible to detect the formation and the dissolution of the gel phase of P-85. The data from ultra-sound velocimetry and densitometry can be used together with scattering data to establish a phase diagram of the P-85 solution.

I) Introduction

Macromolecules form different kinds of aggregates in aqueous solution. This holds especially for amphiphiles with a hydrophilic and a hydrophobic part. Depending on the molecular structure of the amphiphiles, their concentration and the temperature, these aggregates may be micelles, vesicles, cubic phases, gels or lamellar stacks. Scattering methods like X-ray or neutron small-angle scattering /1/, dynamic and static light scattering /2/ are widely used to determine the structure of such aggregates. Rheological experiments show the formation of gels indicated by a strong increase of viscosity. Rheological experiments interact strongly with the sample and scattering experiments are rather time consuming and difficult to interpret, especially in the case of higher concentration.

Two new and complementary methods will be described in the following. The *speed of sound waves* depends slightly on the number of dissolved particles at fixed mass. Precision experiments using the pulse method can be used to follow micellization in a wide concentration range. *Densitometry* using the mechanical oscillator method is well established since about 2 decades /3,4/. A new modified version of this instrument allows the determination of the ratio between the damping force and the elastic force of the oscillator. This method can be used to monitor qualitatively the formation and dissociation of gels as will be shown.

II) The Sample

Triblock Copolymers of the type PEO/PPO/PEO (polyethylene oxide / polypropylene oxide / polyethylene oxide) exist in complex states of aggregation in aqueous solution depending on the relative block sizes. Monomers, micelles and larger aggregates coexist in relative proportions that depend on temperature and concentration. The presently used material (designated Pluronics P-85) has a monomeric molecular weight of 4600 ($PEO_{27}/PPO_{39}/PEO_{27}$) purified by Søren Hvidt (Roskilde, Denmark) to remove PEO/PPO dimers. This system has allready been studied by dynamic and static light scattering and oscillatory shear measurements /5/.

These experiments showed a transition from a mostly monomeric state at low temperatures to a micellar solution at about 20°C decreasing with concentration. This transition is difficult to measure with increasing concentration by means of scattering techniques due to increasing interparticle interaction. At concentrations higher than 25%

(W/W) and temperatures of about 35°C there is a sharp transition from the micellar phase to a solid-like glass-clear gel. At higher temperatures the gel "dissolves" again. The transitions to and from the gel state are accompanied by extreme changes in viscosity. It will be shown in the following that the formation of micelles can be followed in a wide concentration range by measurements of the speed of sound waves (pulses). The formation of the gel phase can be detected by densitometry with the advantage of negligible energy input into the sample (compared with oscillatory shear experiments).

III) Speed of Sound Waves

A) Measuring Principle

The speed of sound wave (SSW) is a function of the adiabatic compressibility and the density of the fluid /6/. The compressibility of solutions is a function of the tempera-ture and of the solute properties. The speed of sound can be measured with high precision utilizing the pulse mode. The time required for a short pulse (170 ns) to run trough a well defined sample cell (total volume 2ml) is used to calculate the speed with an accuracy of ±1 m/s (DSA 48, Anton Paar K.G. Graz, Austria).
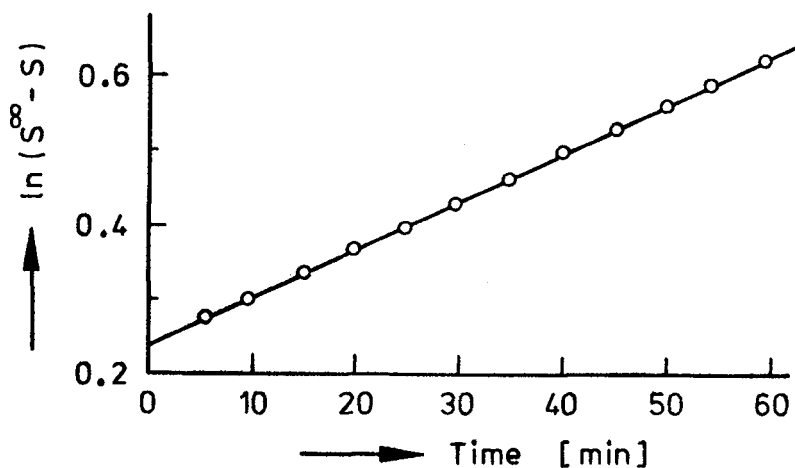

Fig. 1: Inversion of sucrose into glucose and fructose followed by SSW-experiments in a semi-logarithmic plot.

The speed of sound at low concentrations is linearly depending on the

amount of solute in the solution. In addition there is a further
dependence on the number of particles in the solution at fixed concen-
tration. So it is possible to follow the hydrolisis of sucrose into
glucose and fructose. This pseudo first order reaction leads to an
exponential decrease of the concentration of sucrose. In a logarithmic
plot the data points should fit a straight line. As shown in *Fig.1*,
this inversion can nicely be followed by *SSW* measurements.

   This increase of the speed of sound with increasing particle number
is the starting point for the micellization studies using *SSW* experi-
ments, as the number of particles is significantly reduced during
micellization. The dependence of the speed on the particle number is
very small. We therefore use the *specific speed* S_s of these waves:

$$S_s = \frac{(S_{solution} - S_{H_2O})}{S_{H_2O}}$$

   This specific speed S_s is the relative change of the speed in the
solution $S_{solution}$ compared to the speed in water S_{H2O}. The influence of the
temperature on the speed of sound waves in water is eliminated automa-
tically when the specific speed is introduced.

   We want to follow the formation of micelles with increasing tempera-
ture. First of all the specific speed will be reduced by the tempera-
ture dependence of the solution. In addition we expect an additional
reduction during micellization, as the number of particles in the
solution is reduced by this process. Changes can be best visualized by
taking the derivative of the interesting variable and, taking into
account the decrease, one can use the *negative first derivative of the
specific speed S'*:

$$S' = \frac{-d(S_s)}{dT}$$

B) Results

The dependence of S' on the temperature T for a sucrose solution (10% W/W) and a P-85 solution (5% W/W) is shown in *Fig.2*.
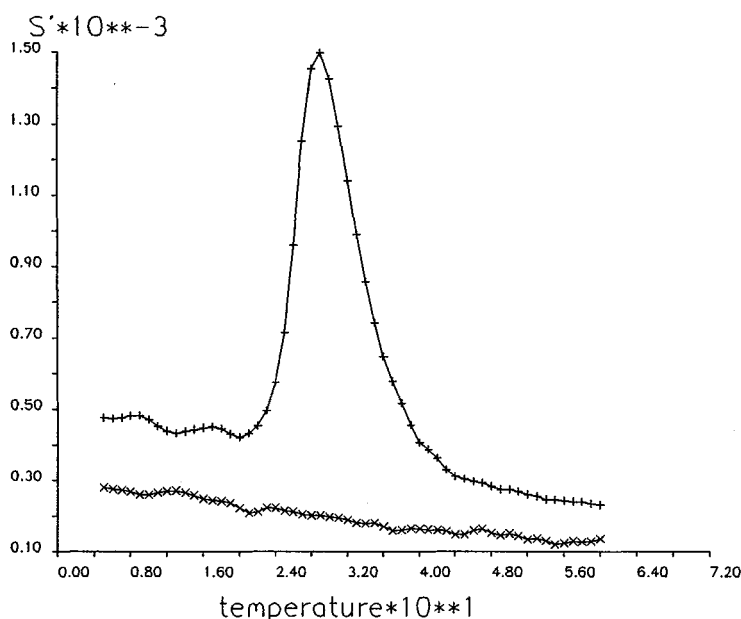

Fig. 2: Change of the specific speed of sound waves S' as a function of the temperature T for 10% sucrose (xxx) and 5% P-85 (+++).

The solution with sucrose shows a monotonically decreasing behaviour, i.e., there is only a slight change of the specific speed with temperature. The curve for the P-85 solution is quite different. It matches the sucrose curve only at low and high temperatures. Deviations from the temperature behavior of sucrose starting at about 20°C, show a clear maximum (highest micelle formation rate) at 29°C and vanish at about 45°C. This indicates that the formation of micelles essentially starts at 20°C and is finished at 45°C with a maximum in the formation rate at 29°C. We can also see from this figure that the magnitude of the effects depend on the chosen sample. We get a much higher signal for a 5% P-85 solution than for a 10% sucrose solution.

The influence of a varying concentration of P-85 is given in the *Figs. 3 and 4*. The signal has been divided by the concentration in order to scale the curves. From *Fig. 3* we can see that the maximum

formation rate of micelles is shifted from 26°C at 10% to 15°C at 30%.
We also see the nonlinearity of the effect for concentrations higher
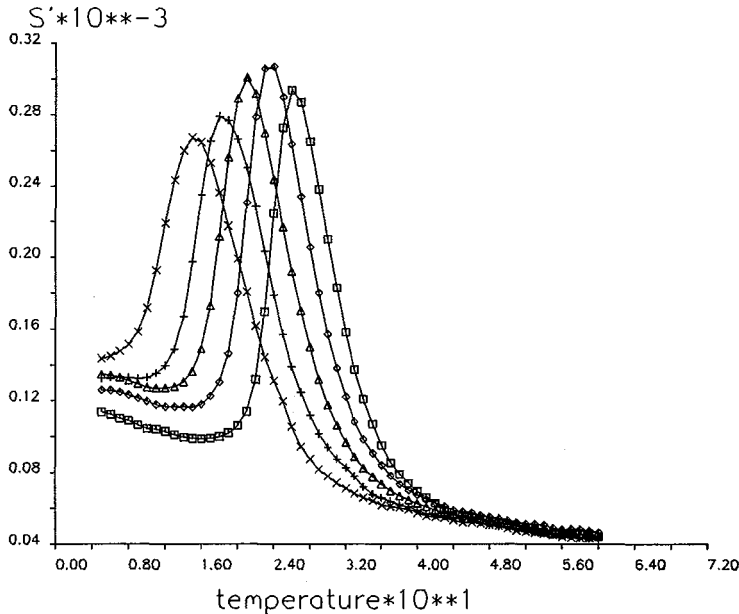than 20% P-85.

Fig. 3: Concentration dependence of the change of the specific
speed S' (signal divided by concentration for scaling). 10% □ □ □,
15% ◇ ◇ ◇, 20% △ △ △, 25% + + + and 30% x x x.

With decreasing concentration we have a constantly decreasing signal
with an increase of the relative error. The effect of micellization can
be measured nicely at concentrations as small as 0.5% (see *Fig. 4*). We
have performed experiments at even lower concentrations. There is still
a significant peak at the micellization temperature, but more sophisti-
cated data manipulations (smoothing) and repeated experiments would be
necessary at concentrations lower than 0.5%.

It can be concluded from the above results, that *SSW* experiments can
be used to follow micellization. The resulting change in the specific
speed of the sound waves indicates and covers the temperature regime
where the micellization takes place. The maximum of this formation
curve can be used as a parameter for a mean micellization temperature.
The fact that it is really a micellization that takes place cannot be
found from such experiments. For this purpose it is still necessary to
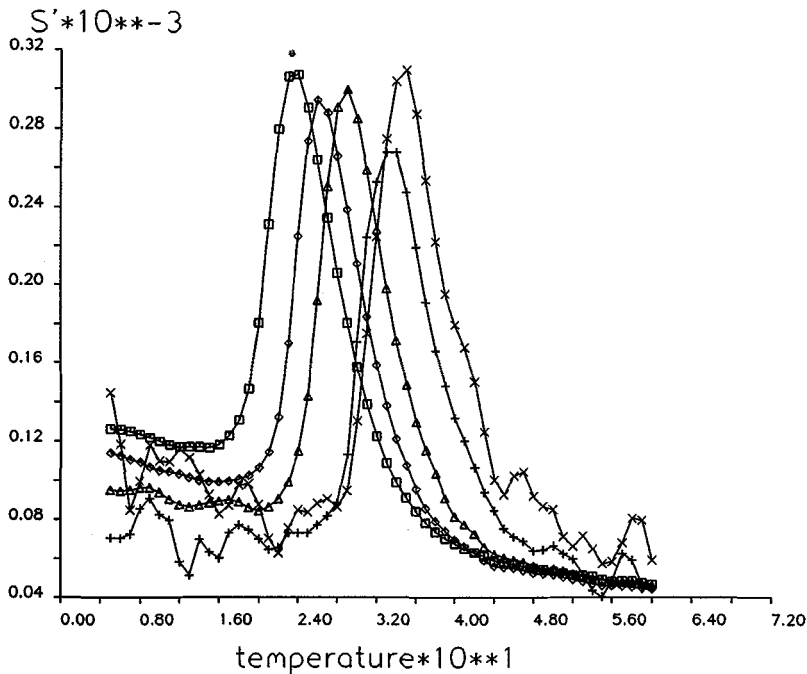perform some, much more time consuming, scattering experiments.

Fig. 4: Concentration dependence of the change of the specific speed S' (signal divided by concentration for scaling) towards low concentrations. 15% □ □ □, 10% ◇ ◇ ◇, 5% △ △ △, 1% + + + and 0.5% x x x.

IV) Densitometry

A) Measuring Principle

Precision densitometry uses the mechanical oscillator method /3,4/. This method is based on the measurement of the eigenfrequency of a U-shaped glass tube filled with the sample. In the standard setup (DMA 58, A. PAAR K.G., Graz, Aus-tria) the external force is of the same amplitude as the damping force but phase shifted by 180 degrees to maintain steady oscillation. Such a mechanically driven oscillation can be represented by the external force F_{ext} and the following three internal forces: the elastic *spring force* which is proportional to the dislocation x of the mass cx (c is the spring constant), the *damping force* (energy absorbing) which is proportional to the velocity x' of the mass bx' (b is the damping constant) and the *mass force* which is proportio-

nal to the acceleration mx'' of the mass m of the system /7/. The exter-
nal force F_{ext} must compensate the damping force, i.e., it must be equal
to $-bx'$. Such a system with synchronized external force will perform a
steady harmonic oscillation with a dislocation

$$x = a.\sin\omega t$$

with the circular frequency ω

$$\omega = \sqrt{\frac{c}{m}} = \frac{2\pi}{T}$$

and T being the oscillation period. The corresponding forces are:

> *spring force:*   *c.a.sin(ωt)*
> *damping force:*   *ω.b.a.cos(ωt)*
> *acceleration force:*   *-ω².m.a.sin(ωt)*
> *external force:*   *-ω.b.a.cos(ωt)*

This situation is visualized in *Fig. 5*. We call this operation mode,
where the external force is balancing the damping force, *in phase mode*.
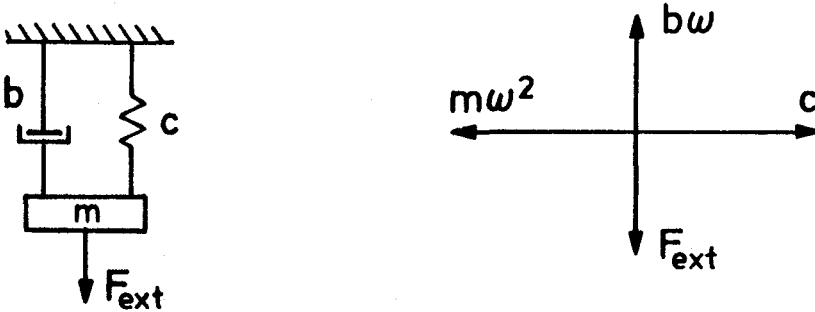

Fig. 5: Schematic representation of the forces in the *in phase mode*.

The density d of the fluid is related to the oscillation period T
simply by:

$$d = AT^2 - B$$

with the two calibration constants A and B taking into account the
specifications of the instrument. These calibration constants are
determined by two calibration experiments with the cell filled with air

and water, respectively.

   Here we are not further interested in the well known details of densitometry, but we have to discuss the modifications that allow the qualitative determination of the damping force (viscosity) with such a densitometer. Actually it can be shown that it is possible to measure the ratio between the damping force and the spring force utilizing a second experiment with a *phase shifted mode*. In this mode the external force F_{ext} is shifted by 45 degrees. The amplitude is increased so that the component in direction of the damping force remains constant (see *Fig. 6*).

   In this mode we observe a different frequency ω_p or period T_p. Combining the two corresponding differential equations we get

$$DR = \frac{b\omega_p}{c} = \frac{b}{cT_p} = (\frac{T}{T_p})^2 - 1$$

We see that the ratio *DR* between the damping force and the spring force is simply related to the oscillating periods.
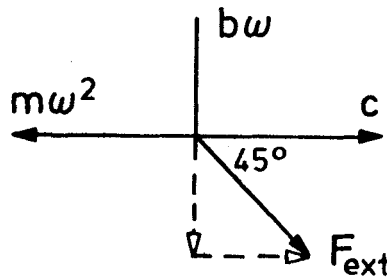

Fig. 6: Schematic representation of the forces in the *phase shifted mode*.

This function runs through a maximum at η^* (see *Fig. 7*) and goes to zero at high values of η, where the fluid is no longer streaming in the tube but acts like a stiff rod. The value η^* is about 100 mPa.s in the *basic mode (or fundamental mode, frequency ω_0)* of the oscillator. The maximum η^* can be shifted to about 600 mPa.s if the *first order mode oscillation (frequency ω_1)* of the tube is excited, but this does not change the situation essentially. This means that this technique is not suited to "measure" viscosity qualitatively in a wide range. We have to keep in mind these facts when we discuss the results from gelation data, where the viscosity increases in a sharp transition over many

orders of magnitude. The advantage of the densitometer method lies in
the facts that only a small amount of sample (~ 1 ml) is simply filled
in a well thermostated and closed glass tube and that only a negligible
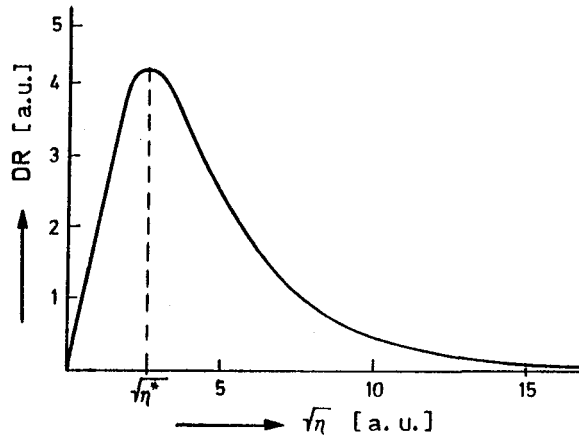energy input into the sample takes place (extremely low shear strain).

Fig. 7: Schematic representation of the dependence of the damping
ratio DR on the viscosity η. The maximum η^* is ~ 100 mPa.s in the
basic mode and ~ 600 mPa.s in the *first order mode*.

More difficult is the relation between this ratio (mostly depending
on the damping force with a quasi constant spring force) and the
viscosity η. There is a linear dependence for small values of $\sqrt{\eta}$.

B) Results

The P-85 solution is a fluid with low viscosity at low temperatures
and at low concentrations. At concentrations lower than 20% W/W there
is a weak temperature dependence up to 60°C as we can see from *Fig. 8*
for experiments using basic mode oscillation. The damping ratio (the
values for water have been subtracted) decreases slightly from 5°C up
to at least 60°C. Then follows a constant increase up to the maximum
measured temperature from 70 to 78°C. A gel phase with moderate visco-
sity exists in this high temperature regime and the transition is not
sharp. This behaviour is also found by oscillatory shear experiments.
At concentrations of 25% and more exists a gel phase with very high
viscosity and sharp boundaries in a certain temperature intervall
around 40°C. The width of this regime increases with concentration. If
we take for example a concentration of 25%, we see a slight increase of
the damping ratio (i.e. viscosity) between 20°C and 30°C. At 31°C the

gel is formed. It has such a high viscosity ($\eta \gg \eta^*$) that the damping ratio is smaller than the one for water (negative values). The stiff gel is dissolved again between 50°C and 52°C. The regime of the stiff gel is much wider for the 30% solution, where it starts at 23°C and ends above 61°C. The anomaleous behavior of the 30% solution at temperatures higher than 65°C is not yet studied in detail.
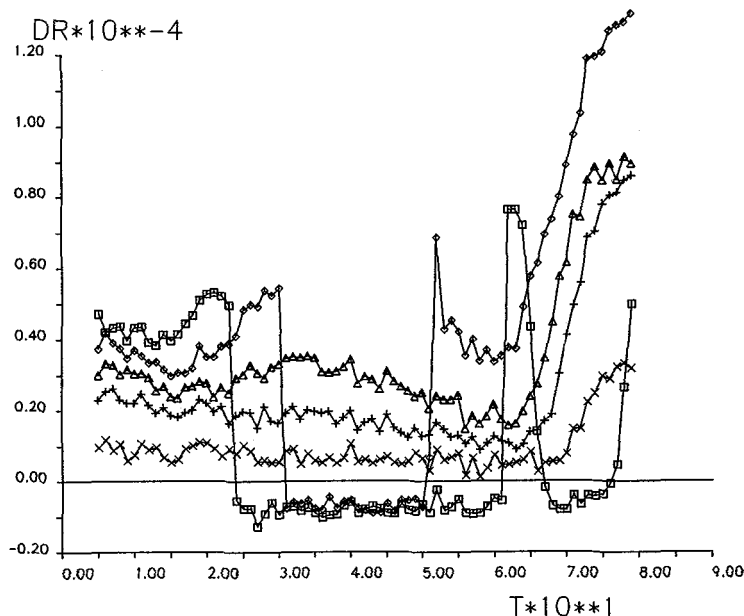

Fig. 8: *Basic mode oscillation:* Dependence of the damping ratio *DR* on the temperature *T* for 5 different concentrations: 5% x x x, 15% + + +, 20% △ △ △, 25% ◇ ◇ ◇ and 30% □ □ □.

If we use the first order mode of oscillation, we have to expect a higher damping ratio due to its linear dependence on the frequency ω ($\omega_1 \sim 6\omega_0$) and a wider range of measurable ratios as η^* increases. So it is possible to measure higher damping ratios at the sharp phase boundaries of the stiff gel (see *Fig. 9*).

Densitometry has proved to be a new and complementary method to follow qualitatively changes in the viscosity of a fluid with minimum energy input into the sample and small volume. Excellent temperature control is guaranteed. Formation and dissolution of gels in P-85 solutions can nicely be detected. Calibration techniques may allow quantitative experiments in the future.
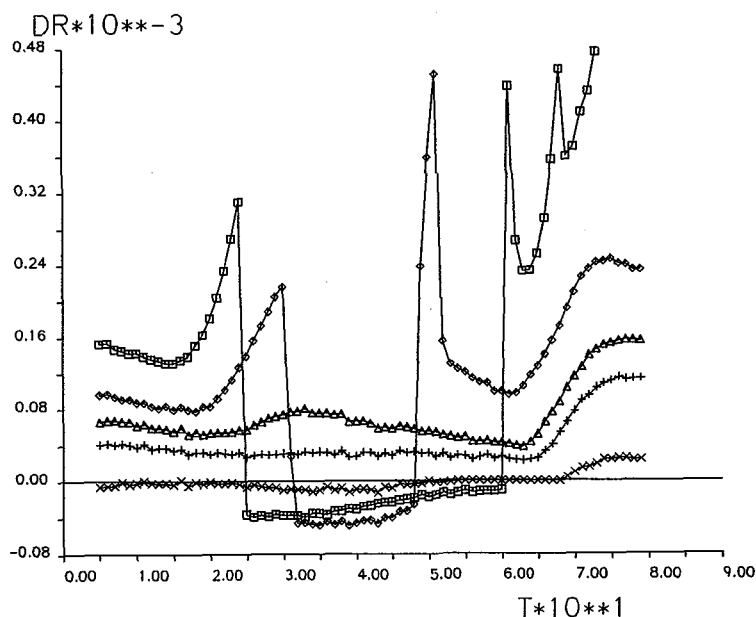
Fig. 9: *First order mode oscillation:* Dependence of the damping ratio *DR* on the temperature *T* for the same 5 different concentrations as in *Fig. 8:* 5% x x x, 15% + + +, 20% △ △ △, 25% ◇ ◇ ◇ and 30% □ □ □.

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