

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Received 00th January 20xx
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Evidence of Pressure Induced Intermolecular Proton Transfer *via* Mutarotation: The Case of Supercooled D-fructose

Adam Cecotka^{a,b}, Satya N. Tripathy^{a,b} and Marian Paluch^{a,b*}

^aInstitute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland.

^bSilesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland.

This paper describes a systematic investigation on the role of pressure in mutarotation kinetics of supercooled D-fructose using dielectric spectroscopy. The structural relaxation time acts as a suitable dynamical observable to monitor the mutarotation process that enables to construct the kinetic curves. The reaction kinetic shapes have been analyzed using Avrami model. At low temperature, sigmoidal kinetic curves are noted which correspond to high concentration of furanosidic forms. The magnitude of activation energy of the process significantly decreases with increasing pressure and comparable to the solvated systems at 100 MPa. A potential connection between cooperative motion and origin intermolecular proton transfer *via* mutarotation at elevated

pressure is also discussed. These experimental observations have fundamental significance on theoretical explanation of mechanism involving mutarotation in sugars.

Introduction

Carbohydrates (sugars) are time-honored organic compounds in nature with empirical formula $C_m(H_2O)_n$ and play an indispensable character in numerous fundamental bio-chemical reactions¹⁻⁵. It entails the ideal sources of energy for living organisms and conveys suitable potential applications in the field of material chemistry¹⁻⁵. Typically mono-sugars occur in four different cyclic-forms *i.e.*, α -pyranose, β -pyranose, α -furanose and β -furanose. Pyranoses are six-membered rings while furanoses form five-membered ones. The α and β tautomers differs from the position (up or down) of the hydroxyl group attached to the first carbon in the ring. One of the most striking features in the chemistry of sugar is the mutarotation which corresponds to the change of specific optical rotation of the solution in which the sugar is dissolved⁶. Dissolved crystalline forms (pyranoses) try to attain different ring configurations and average dipole moment (*i.e.*, optical density) of the system perturbs with time until thermodynamic equilibrium gets established¹⁻¹⁴. Consequently, the time evolution of specific optical rotation of the solution is witnessed. In the chain structure, there is a carbonyl group which is converted into the hydroxyl substituent when the ring is created. The carbon atom from the carbonyl group becomes chiral when the ring is closing and it is called an anomeric center. The mutarotation mechanism is related to the proton transfer (intra- as well as intermolecular) between the hydroxyl group attached to the anomeric carbon and the oxygen from the ring¹⁵⁻¹⁶.

Up to now, numerous experimental studies have been done essentially in solvated frameworks.¹⁻¹⁴ Yet the underlying mechanism of this phenomenon is still in debate. In the gas phase, mutarotation is determined by the direct proton exchange from anomeric hydroxyl group to the oxygen which is enclosed in the ring (intramolecular). On the contrary, the solvent molecules can assist the proton transfer in the liquid phase (intermolecular)¹⁵⁻¹⁶. In solvated systems, sugar concentration is typically very small

^aInstitute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland.

^bSilesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland.

*Author to whom correspondence should be addressed: marian.paluch@us.edu.pl

and sugar-solvent interactions dominate over sugar-sugar ones. At equilibrium, temperature, pressure and solvent (environment) determine the percentage of each tautomer. Again, the mechanism in pure saccharides in supercooled liquid state and in glassy state are unknown and warrant further experimental investigation. Very few studies report such an observation in supercooled state and discuss this fundamental issue. Descamps has pointed out the possible intermolecular proton transfer mechanism in the supercooled liquid state. They also revealed a coupling between structural relaxation and mutarotation in the glassy state of glucose¹⁷⁻¹⁹. Broido *et al.* studied the process in molten D-glucose and proposed that the proton jump in glucose can be assisted by other glucose molecules²⁰. Silva *et al.* estimated the activation energy ($E_a \approx 53$ kJ/mol) of D-Fructose in aqueous environment²¹. This lower value of the activation energy suggests intermolecular interactions and the proton transfers are assisted by the environment. Later Włodarczyk *et al.* found the activation energy in supercooled state is around $E_a \approx 107$ kJ/mol in D-fructose. This order of magnitude indicates that mutarotation mechanism in supercooled state is different from the solvated systems^{15-16, 22-24}. In perspective of the above, we anticipate that application of pressure could enhance the degree of cooperative motion in a supercooled state near glass transition and eventually translate a stronger sugar-sugar interaction which will support intermolecular proton transfer.

Several experimental techniques have been employed to study mutarotation. These are polarimetry, Raman spectroscopy, IR spectroscopy, chromatography and most recently also dielectric spectroscopy^{1-2, 17-19 16-25}. The first method is very common and it is the suitable option for analyzing this phenomenon in diluted solutions while for pure or highly concentrated sugars other methods are convenient. In the present work, mutarotation has been investigated by means of dielectric spectroscopy. It is a powerful tool to examine dynamical properties of the glass-forming liquids at very wide range of frequencies, $f = 10^{-3}$ – 10^9 Hz at different thermodynamic conditions (P , T)²⁶. It monitors the structural relaxation process by assessing complex dielectric permittivity as a function of frequency. The structural relaxation process is associated with the cooperative motion of molecules in the system and depends on the viscosity of the system. During mutarotation, the dynamical observable *i.e.*, structural relaxation time changes reasonably with time and finally enables us to construct the kinetic curves of reaction. Examination of mutarotation process in supercooled liquid also differs

significantly from the solutions²²⁻²⁴. At the melting temperature, when the crystalline sample is melted, all four ring forms are formed and subsequently equilibrium is quickly achieved. Then the sample is quenched to the desired measurement temperature. As a result, the previous equilibrium gets disturbed and a new one has to be accomplished. The fundamental objective of the paper is to study the mutarotation process in D-fructose using dielectric spectroscopy at elevated pressure and finally to model the reaction kinetics. A special attention has been focused to understand and explain the nature of mechanism involving proton transfer and its possible connection to the molecular cooperative motion.

Experimental

High purity sample (99%) of D-fructose ($T_g = 292$ K) was received by Sigma-Aldrich. It was melted in 395 K for less than one minute to avoid caramelization. In the next step, the sample was quenched to the room temperature with a copper plate. Next, a capacitor with the test sample was placed in a pressure chamber. The isolated capacitor was ensured through a Teflon ring and separated from the liquid by Teflon membranes in a pressure chamber. After the sample installation, the material waited for 20 minutes for the conditions to stabilize. Pressure was controlled by a Nova Swiss tensometric meter with precision of 0.1 MPa. The temperature was measured with the help of a liquid flow from a thermostatic bath. All the high pressure measurements were carried out with the help of a Novo-Control GMBH Alpha dielectric spectrometer in the frequency range 10^{-2} to 10^6 Hz.

Results and discussion

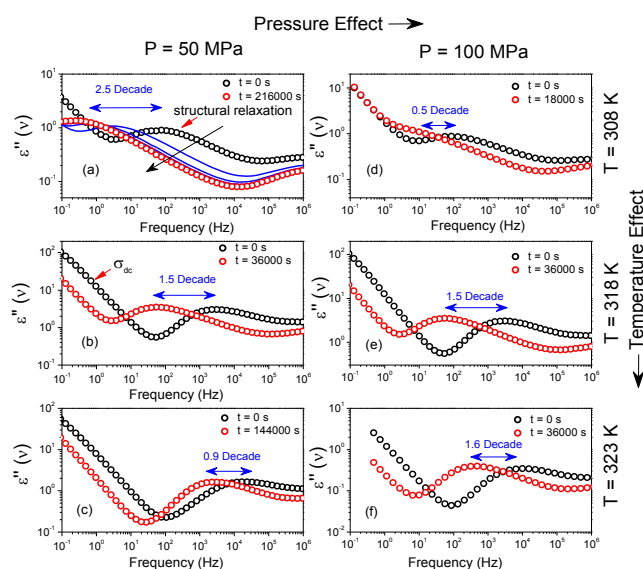


Figure 1. (Color online) Time evolution of the dielectric loss spectra of supercooled D-fructose at the several isotherms ($T = 308$ K, $T = 318$ K and $T = 323$ K) and at elevated pressure ($P = 50$ MPa and $P = 100$ MPa).

Figure 1 depicts the mutarotation process with reference to the time evolution of dielectric response at several isotherms (298 K to 323 K) and elevated pressure (*i.e.*, 50 MPa and 100 MPa) in supercooled D-fructose. The reaction was examined by assessing the changes in dynamical observable *i.e.*, structural relaxation time as a function of frequency. In **Figure 1(a)**, the experimental window ($T = 308$ K; $P = 50$ MPa) contain following features: (a) contribution of dc-conductivity at lower frequencies (below 100 Hz) explained by electrodynamic relation, $\epsilon''(\omega) = \frac{\sigma_{dc}}{\epsilon_0 \omega}$, (b) non-equilibrium state ($t = 0$ s) gets established due to quenching with maxima in dielectric spectra around $f_{max} = 100$ Hz (black circles) and the spectrum moves towards the low frequency side on increasing time (blue lines). Eventually a change in structural relaxation time *i.e.*, $\Delta f = 2.5$ decade is detected, (c) equilibrium state ($t = 216000$ s) with peak in dielectric spectra around $f_{max} = 1$ Hz (red circles). Analogous natures in dielectric spectra are also seen for other thermodynamic conditions (P, T). This indicates that the structural relaxation becomes slower during the whole mutarotation process. It is to be noted that with increasing temperature at $P = 50$ MPa, Δf magnitude decreases while Δf increases for $P = 100$ MPa. Additionally, pressure accelerates the reaction. The asymmetric power-law behavior of the loss spectra data at low and high frequencies, suggests that structural

relaxation and dc-conductivity contribution can be appropriately analyzed by the Havriliak-Negami (HN) relaxation function²⁷, which takes the mathematical form

$$\epsilon(\omega) = \epsilon' - i\epsilon'' = -i \left(\frac{\sigma_0}{\epsilon_0 \omega} \right)^N + \left[\frac{\Delta\epsilon}{(1 + (i\omega\tau)^a)^b} + \epsilon_\infty \right] \quad (1)$$

where $\Delta\epsilon$ is the relaxation strength, a and b are shape parameters. ϵ_∞ is permittivity when frequency goes to infinity, and τ is a parameter that describes the position of the peak. The characteristic frequency related to the frequency of maximum loss is given by

$$\omega_{max} = \frac{1}{\tau_{max}} = \tau^{-1} \left(\frac{\sin\left(\frac{a\pi}{2+2b}\right)}{\sin\left(\frac{ab\pi}{2+2b}\right)} \right)^{\frac{1}{a}} \quad (2)$$

Using HN fittings, we have obtained structural relaxation times as function of time for each temperature, $\tau_{max} = f(t)$. Therefore, we were able to construct kinetic curves for each studied isotherm. By plotting the relaxation time, which is defined as $\tau_{max} = \frac{1}{2\pi f_{max}}$ one can construct kinetic curves. To compare all the isotherms in one plot, degree of reaction has been used instead of relaxation time. Degree of reaction (α) is a measure of reaction progress. The kinetic curves obtained for different isotherms have the same asymptote at $\alpha = 1$, and thus the curves can be easily compared. The degree of reaction can be easily calculated by using the equation

$$\alpha = \frac{\tau_{max} - \tau_i}{\tau_f - \tau_i} \quad (3)$$

Where τ_{max} the relaxation time is τ_i is the relaxation time of initial spectrum and τ_f is the relaxation time of the spectrum at the end of the reaction. Kinetic curves at elevated pressure for D-fructose for isotherms in the temperature range 298 K to 323 K are presented in **Figure 2**. The shapes can be suitably modeled by the Avrami equation²⁸⁻²⁹ with mathematical form

$$\alpha = 1 - \exp(-kt^n) \quad (4)$$

where rate constant k is the most important kinetic parameter which describes how fast the observed process is at a certain temperature and n is the Avrami parameter. This model satisfactorily agrees with the experimental data comparison to exponential law²⁸⁻²⁹ ($n = 1$).

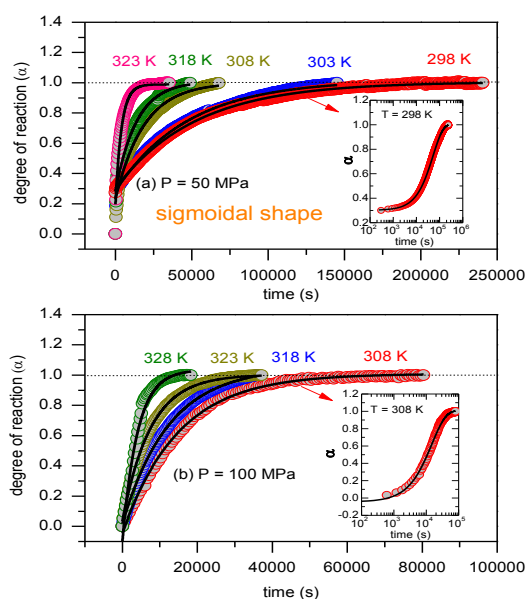


Figure 2. (Color online) Kinetic curves for D-fructose at (a) $P = 50$ MPa and (b) $P = 100$ MPa using structural relaxation time at several temperatures (inset- kinetic curves in log scale to demonstrate the sigmoidal curves at lowest temperature).

The kinetic curves have a sigmoidal shape at the lowest observed temperatures for elevated pressure. Such curves are characteristic for autocatalytic or subsequent reactions. In the case of saccharides, the sigmoidal shape of the curves is connected to the chemical complexity of the samples and represent the amount of furanoses in the sample. The appearance of sigmoidal shape is due to difference in activation energy between chain-furanose and chain-pyranose transformations. It is also to be noted that with increasing pressure, sigmoidal shapes become more prominent as shown in Figure. 2 (inset-log scale). An extensive study on the appearance of sigmoidal shapes at low temperature has been presented by Włodarczyk *et al.*^{15, 24}.

As the reaction is thermally activated, the activation energy of the phenomenon studied has been obtained from Arrhenius fits²⁸ ($\log(k)$ vs. $1/T$) for elevated pressure. In Figure.3 we have presented temperature dependences of rate constants in logarithms. Arrhenius fits were performed to describe data

$$\log(k) = \log k_0 - \frac{E_a}{2.303RT} \quad (5)$$

Where E_a is activation energy, T is absolute temperature, R denotes gas constant. It was found that activation energy

decreases reasonably with increasing pressure well within the experimental uncertainty. The magnitude of activation energy as follows: $P = 0.1$ MPa; $E_a = 107$ kJ/mol, $P = 50$ MPa; $E_a = 72$ kJ/mol and $P = 100$ MPa; $E_a = 53$ kJ/mol. The higher magnitude of activation energy at ambient pressure corresponds to intramolecular proton transfer whereas E_a at highest pressure correspond to the energy barrier for solvated D-fructose²¹. Therefore, we expect that at high pressure the mutarotation is assisted by fructose molecules *i.e.*, environment. Recently Włodarczyk *et al.* has performed DFT calculations²³ on L-sorbose (Expt. $E_a = 68$ kJ/mol) and found that for mechanism based on internal proton transfer, the activation energies of α -furanose, β -furanose, and β -pyranose of decay are estimated as 142.8, 168.1, and 170.3 kJ/mol, respectively. Activation energy of formation of α -pyranose is equal to 137.9 kJ/mol. The differences between experimental and theoretical results are significant. Performing calculation in L-sorbose with one water molecule, they found energies of decay of α -furanose and β -furanose in the presence of water are equal to 77.8, 92.3 kJ/mol, respectively. Energy of formation of α -pyranose is equal to 75.7 kJ/mol which is closest to the experimental one. They interpreted the result based on the possible presence of water that affect during the mutarotation process. In the recent studies by Decampas¹⁹, a crossover in the Arrhenius plot of ($\log(k)$ vs. $1/T$) near the glass transition temperature of D-glucose was observed. They explained the observation as an evidence of intermolecular mechanism *via* mutarotation in the glassy state and suggested possibility of proton transfer by the other sugar molecules from the surroundings. Therefore, we believe that role of pressure at low temperature (near glass transition, $T_g = 292$ K¹⁶) and environment has similar nature to facilitate the intermolecular proton-transfer instead of direct transfer.

After melting process, when the sample becomes liquid, the conversion of β -D-fructopyranose to other probable cyclic tautomer initiate. Three possible products are α -furanose, β -furanose and α -pyranose formed that leads to four sub-processes, *i.e.*, (i) stage-A: pyranose to pyranose, (ii) stage-B: pyranose to α -furanose (iii) stage-C: pyranose to β -furanose and (iv) stage-D: furanose to furanose conversions. All the conversion occurs simultaneously. Dielectric measurements provide information relating to changes of structural relaxation characteristic time during reaction. Perturbation in structural relaxation time is associated to change of viscosity²⁹. Anomeric transformation has a lower impact on viscosity change than ring conversion due to

similar magnitude of dipole moment²². For example, in D-glucose which is built of pyranosidic rings only there are mixtures α and β -pyranose in liquid sample, structural relaxation time does not change at all²². Though rod like configuration formed during ring conversion, nevertheless it is unstable from energy considerations. Kinetic curves obtained by structural time analysis can only be connected with the only pyranose-furanose transformation. Consequently stage-A and D are very much less plausible. Since we deal with classical particles in supercooled state, we have to use the Maxwell-Boltzmann distribution function²⁸. The distribution ratio of two states n_{pyranose} to n_{furanose} is given by the equation

$$\frac{n_{\text{pyranose}}}{n_{\text{furanose}}} = \exp\left(\frac{-\Delta E}{KT}\right) \quad (6)$$

According to the Boltzmann distribution, the population ratio depends on isotherm measurement. Now it is the thermal energy that decides the population strength. By comparison Gibb's free energy of isolated molecules, it may be concluded that pyranosidic form is usually more stable than furanosidic one. At higher temperature, furanose to pyranose conversion is preferred¹⁵. This leads to higher population of pyranose forms. On the contrary, we observe sigmoidal shape curves at low temperature, which is related to the higher concentration of furanose forms²⁴. In the present study, it is clear that at low temperature furanose population dominates whereas pyranose are ample at high temperature. On compression, the sigmoidal shape is more prominent at low temperature, which further influences the increase in furanose configurations. It is essential to note that size and dipole moment of molecules play a crucial role in mutarotation. The role of size of the molecule will be discussed in the latter section.

A few efforts have been gained in the past to study mutarotation under elevated pressure by different research groups. In 1943, Sander *et al.*¹⁰ studied mutarotation in D-glucose solutions with pressure exerted up to $P = 7$ MPa. They found that pressure accelerates the reaction and activation volume decreases with increasing pressure. This change in activation volume was explained by assuming that the atoms of a glucose molecule enclose a relatively big amount of emptiness in the marrow of the closed ring. During activation the ring configuration will open into more or less rod-like ones that populate the previously unoccupied spaces. Later in 1979, Andersen *et al.*¹¹ performed high pressure experiments on D-glucose with maximum pressure on sample up to $P = 100$ MPa. The outcomes

of the experiment remained the same as witnessed by Sanders. Mathematically, pressure is connected at isothermal conditions with rate constant (k) by the equation¹⁰⁻¹¹

$$\frac{\partial \ln k}{\partial P} = -\Delta v \cdot (RT)^{-1} \quad (7)$$

where R is gas constant, T is the absolute temperature, P is the pressure, and Δv is activation volume. Pressure can speed up or slow down every reaction.

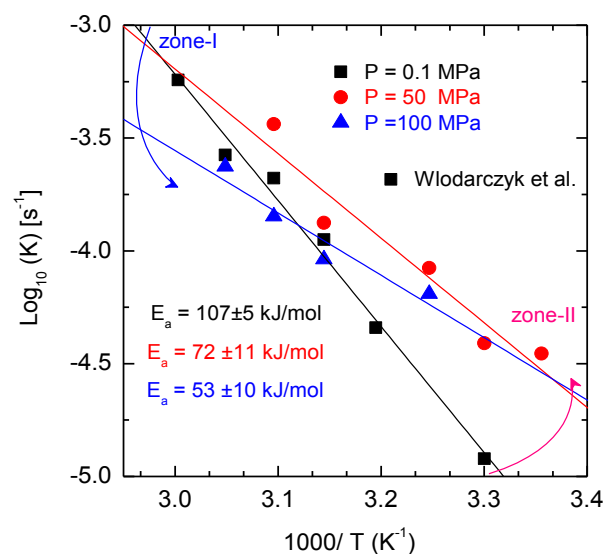


Figure 3. (Color online) Arrhenius plot: Temperature dependences of rate constants logarithmic for ambient and elevated pressure.

Until now, studies concerning mutarotation establish that the reaction kinetics depend on thermodynamic intensive parameter (temperature and pressure) and environment (solvent)^{15-16,22-24}. We recognize that the influence of pressure depends on the temperature of measurement and the environment in supercooled D-fructose. Taking into account Eq. (7), we notice that at high temperature (zone-I) on increasing pressure rate constant decreases (c.f. Figure 3 and 4). This is translated as a decrease in the activation volume and is consistent with earlier studies. However an altered scenario appears when the supercooled liquid

approaches glass transition temperature *i.e.*, activation volume increase with pressure at low temperature (zone-II). This is inconsistent with the previous reports in D-glucose solutions. Ultimately, a compressive analysis based on the effect of pressure on reaction kinetics is essential. However, we concur with the prior observation made by Sanders and Andersen *et al.* that pressure speeds up the reaction. Our finding implies that nature of rate constant at zone-I gets reversed to that of zone-II. It is well established that, the phenomenon of glass transition involves slowing down of cooperatively relaxing units from the order of picoseconds (10^{-12} s) in supercooled liquid state to the macroscopic times (≈ 100 s) in the glassy state²⁹. On approaching glass transition temperature the structural relaxation process emerges more cooperative. Therefore, it is expected that the degree of cooperative motion plays a vital role in nature of mutarotation mechanism observed at lower temperature (zone-II). On compression, one should anticipate a further amplification in degree of cooperative motion and eventually hold a stronger intermolecular interaction (sugar-sugar) in supercooled state. In solvated systems, sugar-solvent interaction is dominant with respect to sugar-sugar ones. Herein, we believe that in zone-II sugar-sugar interaction is much stronger on compression which expedites intermolecular proton transfer. Pressure acts as a promoter to accelerate the intermolecular proton transfer *i.e.*, pressure induced intermolecular proton transfer. From Arrhenius plot, we also found that at $P = 100$ MPa the activation energy of mutarotation process is equal to $E_a = 53$ kJ/mol which is nearly the same activation energy for D-fructose in solvated system. Hence the role of pressure and environment has similar nature of effect to the mutarotation process. At low temperature, we witnessed the sigmoid kinetic curves suggesting populated furanose structures whereas ample pyranose forms at high temperature. As a result the dimension of the ring configurations and the population of each tautomer tentatively are related to the opposite behavior in activation volume. As pointed out by Sander that unoccupied space enclosed by rings play a crucial role in decreasing the activation volume¹⁰⁻¹¹. Now it is clear that, for molecules having smaller size (five membered) will be associated with an increase in activation volume to carry out reaction at zone-II. Again a comparative yet inverse nature will show up for six membered pyranose. At low temperature, the structural relaxation time and reaction rate have comparable time scale, whereas at high temperature structural relaxation dominates over mutarotation. In conclusion, it is evident that when a system

approaches the glassy state, the intermolecular proton transfer is preferred instead of intramolecular.

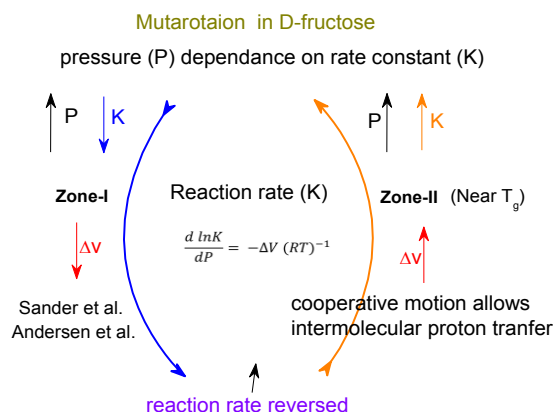


Figure 4. (Color online) Diagram represents the mechanism for pressure induced intermolecular proton transfer in mutarotation.

Conclusions

In summary, we performed measurements mutarotation kinetics of supercooled, D-fructose in the temperature range 298–323 K at elevated pressure using dielectric spectroscopy. The kinetic curves were constructed measuring structural relaxation time as a function of time. It was found that the kinetic curves have sigmoidal shape at a temperature near the glass transition temperature, which is related to the high concentration of furanosidic forms in the sugar at equilibrium. Our findings provide a suitable interpretation relating to pressure driven mutarotation involving the intermolecular proton transfer. The activation energy value decreases on compression and well correlated with the values for solvated systems at $P = 100$ Mpa. The potential connection between cooperative motion and mutarotation mechanism also presented. Therefore, the present study of mutarotation in supercooled D-fructose, has implications on theoretical elucidation and fundamental importance needs that to be addressed by further experimental investigation.

Acknowledgements

Authors thank Dr. Sebastian Pawlus and Dr. K. Kaminski (Institute of Physics, University of Silesia, Poland) for the fruitful suggestion on the manuscript. AC and MP are grateful for the

financial support from the Polish National Science Centre within the program OPUS3 (decision no. DEC-2012/05/B/ST3/02837). SNT is deeply grateful to the financial support of the project by the Polish National Science Centre on the basis of Decision No. DEC-2012/05 / B / ST4 / 00089.

References

- (1) D. E. Levy and P. Fugedi, *CRC, Boca Raton*, 2006, 349–381;
- (2) J. F. Rabbit, *Essentials of Carbohydrate Chemistry. Springer-Verlag, New York*, 1998.
- (3) K. Kaminski, E. Kaminska, P. Wlodarczyk, S. Pawlus, D. Kimla, A. Kasprzycka, M. Paluch, J. Ziolo, W. Szeja, and K. L. Ngai, *Dielectric Studies on Mobility of the Glycosidic Linkage in Seven Disaccharides*, *J. Phys. Chem. B*, 2008 **112**, 12816-12823.
- (4) K. Kaminski, E. Kaminska, K. L. Ngai, M. Paluch, P. Wlodarczyk, A. Kasprzycka and W. Szeja, *J. Phys. Chem. B*, 2009, **113**, 10088-10096.
- (5) V. Molinero and W. A. Goddard, *Phys. Rev. Lett.*, 2005, **95**, 045701.
- (6) A. P. Dubrunfaut *C. R. Acad. Sci.* 1846, **23**, 38.
- (7) R. Lefort, V. Caron, J.-F. Willart and M. Descamps, *Solid State Commun.*, 2006, **140**, 329-334.
- (8) N. Le Barc'H, J. M. Grossel, P. Looten and M. Mathlouthi, *Food Chem.*, 2001, **74**, 119-124.
- (9) R. Behrends and U. Kaatze, *Biophys. Chem.*, 2004, **111**, 89-94.
- (10) B. Andersen and F. Gronlund, *Acta Chem. Scand.*, 1979, **A33**, 275-280.
- (11) F. V. Sander, *J. Biol. Chem.*, 1943, **148**, 311-319.
- (12) I. Alkorta and P. L. Popelier, *Carbohydr. Res.*, 2011, **346**, 2933-2939.
- (13) A. E. Flood, M. R. Johns, and E. T. White, *Carbohydr. Res.* 1996, **288**, 45-56.
- (14) C. S. Hudson, *J. Am. Chem. Soc.*, 1910, **32**, 889-894.
- (15) P., Wlodarczyk, A. Cecotka, K. Adrjanowicz, K. Kaminski, and M. Paluch, *J. Phys.: Condens. Matter.*, 2013, **25**, 375101.
- (16) P. Wlodarczyk, K. Kaminski, M. Paluch, and J. Ziolo *J. Phys. Chem. B*, 2009, **113**, 4379.
- (17) R. Lefort, V. Caron, J.-F. Willart, and M. Descamps, *Solid State Commun.*, 2006, **140**, 329-334.
- (18) N. Dujardin, J. F. Willart, E. Dudognon, A. Hedoux, Y. Guinet, L. Paccou, B. Chazallon, and M. Descamps, *Solid State Commun.*, 2008, **148**, 78-82.
- (19) N. Dujardin, E. Dudognon, J.-F. Willart, A. Hedoux, Y. Guinet, L. Paccou, and M. Descamps, *J. Phys. Chem. B*, 2011, **115**, 1698-1705.
- (20) A. Broide, Y. Houminer, and S. Patai, *J. Chem. Soc. B*, 1966, **5**, 411-414.
- (21) A. M. Silva, E. C. da Silva, and C. O. da Silva, *Carbohydr. Res.* 2006, **341**, 1029-1040.
- (22) P. Wlodarczyk, K. Kaminski, S. Haracz, M. Dulski, M. Paluch, J. Ziolo and M. Wygledowska-Kania *J. Chem. Phys.* 2010, **132**, 195104
- (23) P. Wlodarczyk, M. Paluch, A. Grzybowski, K. Kaminski, A. Cecotka, J. Ziolo, and J. Markowski, *J. Chem. Phys.* 2012, **137**, 124504.
- (24) P. Wlodarczyk, K. Kaminski, M. Dulski, S. Haracz M. Paluch, J. Ziolo, *Journal of Non Crystalline Solids*, 2010, **356**, 738-742.
- (25) Y. Wang, P. Wlodarczyk, A. Sokolov, and M. Paluch, 2013, *J. Phys. Chem. B*, **117**, 1475-1479.
- (26) A. Rivera, A. Brodin, A. Pugachev and E. A. Rössler, 2007, *J. Chem. Phys.* **126**, 114503.
- (27) S. Havriliak, S. Negami, 1967, *Polymer*, **8**, 161-210.
- (28) P. Atkins, J. de Paula, *Physical Chemistry*, 7th ed., Oxford University Press., 2002.
- (29) F. Kremer, A. Schönhal, *Broadband Dielectric Spectroscopy*, Springer, 2002.