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# OBSERVATIONS ON THE CRYSTALLIZATION OF GLUCOSE FROM AQUEOUS SOLUTION

*Danuta M. Napierała[1], Piotr Biskupski[2], Grażyna B. Plenzler[1]*

[1]Department of Physics, Agricultural University
ul. Wojska Polskiego 38/42, 60-637 Poznań
e-mail: dnapiera@woodcock.au.poznan.pl
[2]Faculty of Physics, A. Mickiewicz University
ul. Umultowska 85, 61-614 Poznań

Abstract. The kinetics of the spontaneous, irreversible processes of water evacuation from the glucose solution accompanying the crystallization of glucose have shown a susceptibility to the initial conditions and the significant role of the water on the formation of and on the patterns of sugar crystals. The crystallization of glucose of the same amount was controlled by a different solvent content. The study by polarized light microscopy has proved that the considerable slowing down of the process of glucose dehydration due to a 10 – fold greater water content results in different patterns of crystalline material obtained.

Keywords: glucose, crystallization, evaporation kinetic, polarization light microscopy

## INTRODUCTION

Many industrial processes and most natural phenomena occur in systems driven far from thermodynamic equilibrium. The majority of food products are non-equilibrium open systems in which nontrivial spatial structures and dynamics frequently arise and can influence such quantities as the transport of mass, transport of heat and the aggregation of particles. The acquaintance of all the mechanisms responsible for these phenomena at molecular level and the predicting of the self organization and dynamics on a larger length scale are the reason for the great interest shown in this subject [2-5,9]. Crystallization from solution is an important example of these kinds of phenomena. Little is understood about the interactions between molecules that lead to the formation of

solid crystal structures from solution. An increased understanding of the solution phase and of the interface phenomena will provide a background for the direct measurement of species leading to nucleation and growth. The studies on fundamental solvent – solute interactions, performed in systems with the use of probe molecules, detected solution phase self-assembly [8]. In our previous work we considered the changes of the thermodynamic parameter of intra-molecular interaction in glucose aqueous solution as a function of the glucose volume fraction in the system [6]. In this work we have focused on the effect of the water content on the behavior and molecular dynamics of glucose and its role in the formation of glucose crystal patterns during spontaneous air drying from the solution.

## MATERIALS AND METHODS

The experiments described were performed in aqueous glucose solutions of 1g glucose content. Anhydrous D-glucose, obtained from POCH S.A. – Gliwice was used without further purification. The solutions were prepared by weighing 1g of glucose powder, dissolved in doubly distilled water of 5 $cm^3$ or 50 $cm^3$ volume, heating to 60°C to ensure complete dissolution. The solutions (three replicates for each water content) prepared in weighing bottles of the 60 $cm^3$ maximum volume, and inner diameter 5.5 cm were placed in a temperature controlled chamber whose temperature was maintained at (295 ± 1) K. The probes were kept first for 24 h in closed vessels before removing the cover. After that they were exposed to evaporation in open vessels in the same thermostatic chamber. The drying kinetics were performed by recording the mass loss of the freshly cast solutions as a function of time until the mass of water has been changed, *i.e.* for up to 45 days. The progressive crystallization of glucose from the solutions, followed by water evaporation, was observed. The mass decrease was measured on a Gibertini E 50 S analytical balance with an accuracy of 0.01 mg. The air pressure and relative humidity were noted on each day of the experiment. The mean air pressure was 1025 hPa, which varied between 1005 and 1046 hPa, whereas the mean value of relative humidity in the chamber was (48 ± 5)%.

The patterns of crystallized glucose in polarized light were recorded on a JENAPOL polarization microscope made by Carl Zeiss Jena and the photos of the probes were obtained with a CCD, Olympus Camedia 2500 camera.

## RESULTS AND DISCUSSION

The drying kinetics of glucose from the aqueous solutions with an initial specific volume 5 and 50 $cm^3 g_{glu}^{-1}$ are presented in figure 1. The final product of the process observed was 1g of crystallized monosaccharide on the bottom of the weighing vessel in both systems; however the process time-course was modified by the different amounts of water. The glucose molar fraction in solution, $X_g$, *i.e.* the ratio of glucose moles per total glucose and water moles, in both solutions analyzed, exposed on spontaneous, isothermal surface drying, was 0.02 and 0.002, respectively. As a result of water evacuation the initial glucose molar fraction increased to the limit value $X_g^S$ in the saturation state, 0.045 [7]. This was achieved after 2 days of drying in a glucose solution of 5 $cm^3$ volume and after 22 days of drying in a solution of 50 $cm^3$ volume.

When the saturation state in the solution is reached, crystallization of glucose begins. There are two competitive processes, which control the quasi-equilibrium state in the solution holding the glucose concentration constant in the liquid. The first is the process of water evacuation from the surface and the second is nucleation and the growth of glucose crystals, which effect an escape of solute molecules. The fraction of glucose molecules in the saturated solution remains constant, but the quantity of the liquid phase continuously decreases on account of the crystallization of the glucose. The first nucleation of glucose crystals causes a non-uniform pressure field within the liquid and this pressure gradient causes redistribution of the water within the crystals by capillary migration. The rate of evaporation in this drying period considerably decreases [10]. The mean rate of water mass loss in glucose solutions and in pure solvents of the same volume, stored in the same experimental conditions, is presented in table 1.

The influence of air pressure and humidity changes on the evaporation rate was checked by simultaneously evaporating a glucose solution and pure water of the same volume. In the first 24 hours of drying, after removing the cover, water evaporation in all the probes was the most pronounced. On account of the higher heat capacity, the rate of water loss in the glucose solution and in the pure solvent of 50 $cm^3$ was higher as compare with those of 5 $cm^3$ volume. Evaporation is a drying endothermic process which occurs on the surface of the liquid. The flux of water mass, leaving the system per unit area of liquid surface, $\Delta J_e$, is given as the difference between the evaporation rate, $J_{evap}$ and the condensation rate, $J_{cond}$ per unit area. The net evaporation flux, derived from the kinetic theory of gases, is given in the Hertz-Knudsen-Langmuir equation [11,12]:

$$\Delta J_e = J_{evap} - J_{cond} = \frac{\alpha_e p_e - \alpha_c p}{\sqrt{2\pi MRT}} \tag{1}$$

where: $\alpha_e$ and $\alpha_c$ – are the fractions of water molecules leaving and striking the surface, respectively (without dimension), $p_e$ is the equilibrium partial vapor pressure of the liquid, $p$ – is the actual vapor pressure near the surface, $M$ – the molecular weight of the vapor, $R$ – the ideal gas constant, $T$ – the temperature.

**Table 1.** Water evaporation rate [g (m$^2$ min)$^{-1}$] in a glucose solution of specific volume 5 and 50 cm$^3$ $g_{glu}^{-1}$, pure water of 5 and 50 cm$^3$ volume, stored under the same experimental conditions

| Drying period (days) | Glucose solution, 5 cm$^3$ $g_{glu}^{-1}$ | Water, 5 cm$^3$ | Glucose solution 50 cm$^3$ $g_{glu}^{-1}$ | Water, 50 cm$^3$ |
|---|---|---|---|---|
| 1 (1.5 h) | 0.625 | 0.508 | 0.870 | 0.778 |
| 1 (3.0 h) | 0.548 | 0.502 | 0.706 | 0.767 |
| 2 | 0.341 | 0.448 | 0.451 | 0.502 |
| 3 | 0.313 | 0.358 | 0.536 | 0.540 |
| 7 | 0.009 | | 0.711 | 0.654 |
| 10 | 0.006 | | 0.676 | 0.619 |
| 20 | 0.0004 | | 0.762 | 0.760 |
| 24 | 0.0003 | | 0.306 | 0.280 |

We calculated the net evaporation flux, $\Delta J_e$ and according to the relation (1) we estimated the values of $\alpha_e$ and $\alpha_c$ in both glucose solutions, taking into account the mean, 50% relative humidity. Some of these results are presented in table 2. Two conclusions can be drawn. Firstly, the very small values of $\alpha_e$ and $\alpha_c$ and, secondly, the net evaporation flux which can change dramatically with an insignificant change in one of the parameters.

The kinetics of the increase of the glucose molar fraction during the surface drying of glucose solutions have been shown in figure 2. One can estimate the kinetic of glucose drying as the superposition of two processes. We assumed the sigmoidal character of the glucose fraction changes in these processes as described by Boltzmann's sigmoidal function [1]:

$$y = \frac{A_1 - A_2}{1 + e^{(x - x_0/\Delta x)}} + A_2 \tag{2}$$

where: $A_1$ and $A_2$ are the upper and lower limits of the sigmoid, $x_0$ is the center of the sigmoid and $\Delta x$ is related to the slope of the tangent line at the center of the sigmoid.

**Fig. 1.** Kinetic curves of the air drying and evaporation processes: a) glucose solution of specific volume 5 $cm^3$ $g_{glu}^{-1}$ and of pure water of the same volume, b) glucose solution of specific volume 50 $cm^3$ $g_{glu}^{-1}$ and of pure solvent of 50 $cm^3$ volume, stored in weighted vessels under the same experimental conditions: $m_0$ – initial water mass, $m$ – actual water mass in the system

**Table 2.** The net evaporation flux, $\Delta J_e$ [mol (m$^2$ s)$^{-1}$], fractions of water molecules leaving the surface, $\alpha_e$, in the first period of air drying glucose solution of specific volume 5 and 50 cm$^3$ $g_{glu}^{-1}$

| Glucose specific volume in solution cm$^3$ $g_{glu}^{-1}$ | Drying period (days) | Net evaporation flux, $\Delta J_e$ [mol (m$^2$ s)$^{-1}$ ]$\cdot 10^{-3}$ | Fraction of evaporating water molecules $\alpha_e$, $\cdot 10^{-6}$ |
|---|---|---|---|
| | 1 | 0.41 | 5.13 |
| 5 | 2 | 0.32 | 3.98 |
| | 3 | 0.29 | 3.65 |
| | 1 | 0.42 | 5.29 |
| 50 | 2 | 0.42 | 5.27 |
| | 3 | 0.50 | 6.26 |

**Fig. 2.** Time-course of the glucose molar fraction (without dimension) increase during the air drying of glucose solutions of 5 cm$^3$ $g_{glu}^{-1}$ (a) and 50 cm$^3$ $g_{glu}^{-1}$ (b)

The first sigmoid described an increase in the glucose fraction caused by surface water evaporation; the second can be attributed to an increase in the monosaccharide fraction accompanying glucose crystallization and water capillary migration. In this manner, we obtained the values of sigmoidal parameters presented in table 3.

**Table 3.** The values of parameters of two Boltzmann sigmoidal functions, used in the description of glucose crystallization from aqueous solutions of specific volume 5 and 50 $cm^3\ g_{glu}^{-1}$

| Glucose solution, specific volume, $cm^3\ g_{glu}^{-1}$ | First sigmoidal function parameters | Second sigmoidal function parameters |
|---|---|---|
| 5 | $X_{g\infty} = 0.31 \pm 0.01$<br>$\Delta t_1 = 0.57 \pm 0.03$, (day)<br>$t_{1/2} = 3.64 \pm 0.03$, (day) | $X_{g\infty} = 0.22 \pm 0.01$<br>$\Delta t_2 = 4.22 \pm 0.18$, (day)<br>$t_{1/2} = 9.6 \pm 0.4$, (day) |
| 50 | $X_{g\infty} = 0.27 \pm 0.08$<br>$\Delta t_1 = 11.7 \pm 0.5$, (day)<br>$t_{1/2} = 59 \pm 3$, (day) | $X_{g\infty} = 0.44 \pm 0.01$<br>$\Delta t_2 = 0.74 \pm 0.01$, (day)<br>$t_{1/2} = 22.5 \pm 0.1$, (day) |

where: $X_{g\infty}$ - is the value of upper limit of sigmoid, $t_{1/2}$ – half time, is the center of the sigmoid, $\Delta t_1$ and $\Delta t_2$ are related to the slope of sigmoids in flex point. The lower limit of sigmoids was fixed as 0 in both cases.

Diversified glucose specific volume in solutions influences the patterns of crystallized sugar. Characteristic pictures of vessels with probes of 1g glucose crystallized from 5 and 50 $cm^3$ solutions are shown in figure 3. All the probes starting with a 5 $cm^3$ volume have shown a significant, 70% reduction in crystal area. A considerable central part of the bottom of the vessel was empty, without any crystal trace. Crystals grew around the edge of the bottom in thick layers. As a result of rapid water evacuation, the binary system exhibited highly dynamic behavior as if it were a microheterogenous system. In contradistinction, in those probes in which the glucose crystallization process was moderated by 10 times enlargement water volume, glucose crystals formed on the whole accessible surface of the bottom of the vessel, as shown in figure 3b. The slow aggregation of the glucose molecules and the slow hydration of the aggregates following the process of crystallization and dehydration of the glucose crystals from the saturated state, lead to a higher molecular ordering in the system. It is known, that, the lower the growth rate, the higher the morphological importance in the growth form of the crystal. We observed the effect of glucose crystallization by polarized light microscopy, which confirmed our earlier observations. Some different glucose crystal patterns - viewed in polarized light, after 45 days of drying, – are presented in figure 4.

**Fig. 3.** Patterns of the surface crystallization of 1g glucose from 5 $cm^3$ (a) and from 50 $cm^3$ of aqueous solution

**Fig. 4.** Polarized light micrograph of glucose: glucose powder before crystallization (~ 0.2-0.3 mm in size) (a), patterns of glucose crystals after surface air drying the aqueous glucose solution of initial specific volume 5 (b), and 50 $cm^3\ g_{glu}^{-1}$ (c, d)

## CONCLUSIONS

1. The pattern of the same amount of glucose crystallized from aqueous solution during air drying depends on the volumetric fraction of water in the system; this proves the role of water hydration on the form of the crystal's structure.

2. The moderation of glucose crystallization due to the greater volumetric fraction of water results in a more complicated and more expanded crystal structure as viewed in polarized light. In the case of the lower volumetric water fraction in the glucose solution, a significant reduction - of about 70%- in surface crystals was observed in relation to the free surface of the solution. The decrease of the surface of crystallized glucose by building up in layers around the bottom of the vessel points to higher energy loss during the endothermic crystallization process. The experiment illustrates the great sensitivity to the initial conditions of the process, on the formation of glucose crystals.

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# BADANIA KINETYKI EWAKUACJI WODY W PROCESIE KRYSTALIZACJI GLUKOZY

*Danuta M. Napierała*[1], *Piotr Biskupski*[2], *Grażyna B. Plenzler*[1]

[1]Katedra Fizyki, Akademia Rolnicza, ul. Wojska Polskiego 38/42, 60-637 Poznań
e-mail: dnapiera@woodcock.au.poznan.pl
[2]Instytut Fizyki, Uniwersytet im. A. Mickiewicza, ul. Umultowska 85, 61-614 Poznań

Streszczenie. Kinetyka samorzutnie przebiegającego procesu ewakuacji wody z roztworu glukozy w kontrolowanych termicznie warunkach, prowadząca do skrystalizowania cukru, wykazuje charakterystyczną dla dynamiki chaosu, czułość na warunki początkowe. Przebieg krystalizacji jednakowej ilości glukozy, spowalniany zwielokrotnionym udziałem objętościowym wody w roztworze, wskazuje na istotną rolę hydratacji molekuł cukru w formowaniu jego struktury krystalicznej. Zróżnicowany obraz skrystalizowanej glukozy z roztworów o objętości właściwej 5 i 50 $cm^3 g_{glu}^{-1}$ ujawnia, poprzedzający krystalizację, sposób dochodzenia układu do stanu nasycenia. Efekt rozbudowanej struktury uporządkowanej w spowolnionym procesie krystalizacji glukozy był szczególnie widoczny w obrazach, uzyskanych w świetle spolaryzowanym.

Słowa kluczowe: glukoza, krystalizacja, kinetyka parowania, mikroskopia optyczna