

KINETICS OF SUCROSE INVERSION IN MIXED SOLVENTS

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Abstract: Sucrose solvolysis was observed under the same conditions in water and in mixed solvents of aqueous ethanol and aqueous dimethyl sulfoxide. The reaction is a specifically acid catalyzed one and occurs as a pseudo first order reaction. Influence of the catalyst (sulfuric acid) concentration was observed and spontaneous and catalytic constants of reaction rate were calculated. The reaction was observed by a polarimetric method of examining the angle of polarized light plane rotation in the course of the reaction in an acid environment at 298K. The obtained experimental results were interpreted based on the Hughes-Ingold theory of the effect of ionizing power of a solvent onto the reaction in the solvent.

Key words: Sucrose solvolysis, mixed solvents, dimethyl sulfoxide

Introduction

The reaction of sucrose hydrolysis resulting in glucose and fructose is called sucrose inversion. That was at the same time also the first reaction studied from the kinetic point of view. Even back in 1850, Wilhelmy (Wilhelmy, 1850) noticed that the hydrogen ions catalyzed this reaction, the course of which could be easily observed from a change of optical angle of polarized light plane rotation in the course of the reaction in an acid environment. The solution of pure sucrose that turns the polarized light plane to the right changes the turning angle in time and after a certain period of time turns the polarized light plane to the left. Because of that „reversal“ of the turning angle caused by the origination of fructose that turns the polarized light plane to the left, the sucrose hydrolysis was called „sucrose inversion“. This reaction in the aqueous solution follows the rule of the second order reaction rate, while the rate depends on the concentration of sucrose and hydrogen ions (Ashrafi et al., 2011; Kwegyir Essel and Dufie Osel, 2014). Since the hydrogen ion is at the same time also a catalyst, that means that its concentration during the reaction does not change, so that one can consider this reaction as the pseudo first order reaction (Škundrić and Penavin, 1984; Škundrić et al., 1995; Škundrić et al., 2003).

This study represents a contribution to the experimental examination of kinetics of the sucrose inversion reaction in a non-aqueous environment (Laidler, 1965). The examination was conducted of the conditions of reaction rate depending on the change of the catalyst concentration at the appropriate temperature by measuring the change of angle of polarized light plane rotation of the sucrose solution for the same values of the catalyst concentration and the same temperature but in different mixed solvents, a mixture of proton-proton (water - ethanol) and proton-dipole proton solvent (water– dimethyl sulfoxide), in the course of which there occurs the change of dielectric constant of the reaction environment (Parker, 1969).

Sucrose, (C₁₂H₂₂O₁₁), in the aqueous solution is very slowly hydrolyzed to glucose, C₆H₁₂O₆, and fructose, C₆H₁₂O₆, in accordance with the stoichiometric equation:



The kinetics of this, practically irreversible reaction, is usually studied in the presence of a certain quantity of hydrogen ions that originate from adding a strong acid and there follows the rule of the second order rate:

$$v = k_2(H_3O^+) \cdot (S)$$

where the symbol S stands for sucrose.

Materials and methods

The following materials were used in the experimental study: sucrose (Merck Darmstadt, p.a.), sulfuric acid (p.a. Zorka Sabac), dimethyl sulfoxide (BDH Chemical Ltd. Poole, England) and ethanol (Budapest, Hungary).

The reaction temperature was 298K. The reaction was observed by the polarimetric method on the polarimeter (OPTECH Model PL 1), (Siddiqui, 2010).

The concentrations of sulfuric acid used as a catalyst in the experimental study were: 0.50, 1.00, 1.50 and 2.00 mol/dm³.

The quantitative composition of the mixed solvent was expressed in molar portions and amounted to 20% of the molar portion of ethanol and dimethyl sulfoxide (DMSO) in water.

The constant of the reaction rate of sucrose inversion was calculated based on the relation:

$$k = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

where α_0 represents the rotation angle of polarized light oscillation plane in the period $t=0$, and α_∞ is the value of the rotation angle for the system balance state, α_t is the rotation angle in the period t .

Results and discussion

The results of measurements are presented in tables as, for example, in tables 1, 2 and 3, and the constants of the sucrose inversion reaction rate were calculated graphically (from the coefficient of the obtained direction on the diagram).

Table 1. Dependence of rotation angle on time period in examining sucrose inversion reaction. Reaction temperature is 298 K, catalyst concentration (H_3O^+ -ions) is 2.0 mol/dm³.
Solvent-water

t/(s)	α_t (°)	$\ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$	k/10 ⁵ (s ⁻¹)
0	12.9	0	6.7642
600	12.2	0.0406	1.2217
1200	10.5	0.1466	1.5146
1800	8.7	0.2726	1.3595
2400	8.0	0.3263	1.4476
3000	6.7	0.4343	1.4882
3600	5.6	0.5358	$k_{\text{calc.}} = 12.8470$

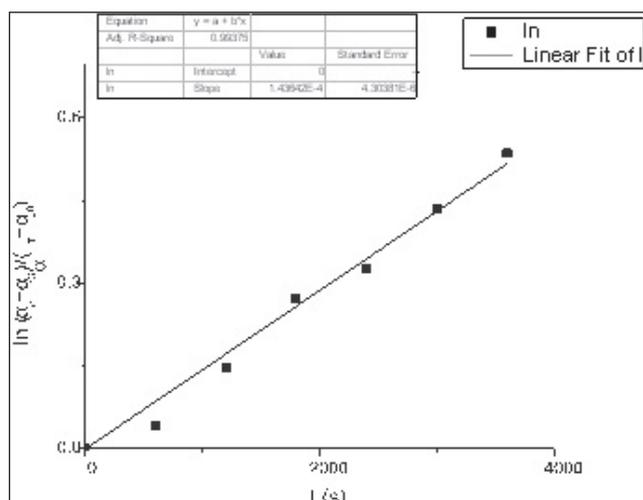


Figure 1. Dependence $\ln ((\alpha_0 - \alpha_\infty) / (\alpha_t - \alpha_\infty))$ on time t

$$k_{\text{calc.}} = 12,87 \cdot 10^{-5} \text{ s}^{-1}; k_{\text{graph.}} = 14,36 \cdot 10^{-5} \text{ s}^{-1}$$

Table 2. Dependence of rotation angle on time period in examining sucrose inversion reaction. Reaction temperature is 298 K, catalyst concentration (H_3O^+ -ions) is 2.0 mol/dm³. Solvent-aqueous ethanol

t/(s)	α_t (°)	$\ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$	k/10 ⁵ (s ⁻¹)
0	12.8	0	
600	11.9	0.0561	9.3482
1200	10.9	0.1223	10.1940
1800	9.7	0.2081	11.5610
2400	8.7	0.2857	11.9020
3000	7.8	0.3610	12.0330
3600	6.9	0.4425	12.2910
α_∞	-3.7		$k_{calc.} = 11.2220$

Table 3. Dependence of rotation angle on time period in examining sucrose inversion reaction. Reaction temperature is 298 K, catalyst concentration (H_3O^+ -ions) is 2.0 mol/dm³. Solvent-aqueous dimethyl sulfoxide

t/(s)	α_t (°)	$\ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$	k/10 ⁵ (s ⁻¹)
0	12.4	0	
600	11.0	0.0904	15.0640
1200	9.4	0.2048	17.0660
1800	8.3	0.2918	16.2110
2400	7.4	0.3691	15.3790
3000	6.3	0.4725	15.7490
3600	5.4	0.5658	15.7160
α_∞	-3.8		$k_{calc.} = 15.8640$

Table 4. Effect of hydrogen ions concentration on sucrose inversion kinetics

Solvents	c (mol dm ³)	$k_{calc.}/10^5$ (s ⁻¹)	$k_{graph.}/10^5$ (s ⁻¹)
WATER	0.5	1.6132	1.4252
	1.0	3.4085	4.0734
	1.5	6.7812	8.7067
	2.0	12.8470	14.3640
AQUEOUS ETHANOL, X=0.2	0.5	3.0991	4.2528
	1.0	5.3241	4.9199
	1.5	9.1288	7.4166
	2.0	11.2220	11.9550
AQUEOUS DMSO, X=0.2	0.5	6.7726	5.5824
	1.0	9.4324	9.0824
	1.5	13.8990	13.5600
	2.0	15.8640	15.7670

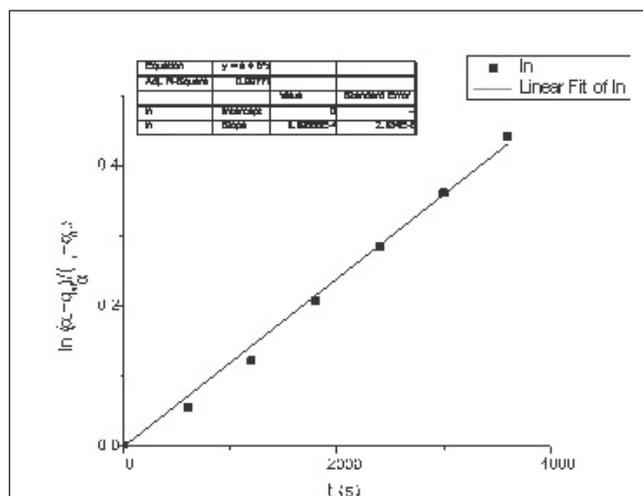


Figure 2. Dependence $\ln ((\alpha_0 - \alpha_\infty) / (\alpha_t - \alpha_\infty))$ on time t

$$k_{calc.} = 11,22 \cdot 10^{-5} \text{ s}^{-1}; k_{graph.} = 11,96 \cdot 10^{-5} \text{ s}^{-1}$$

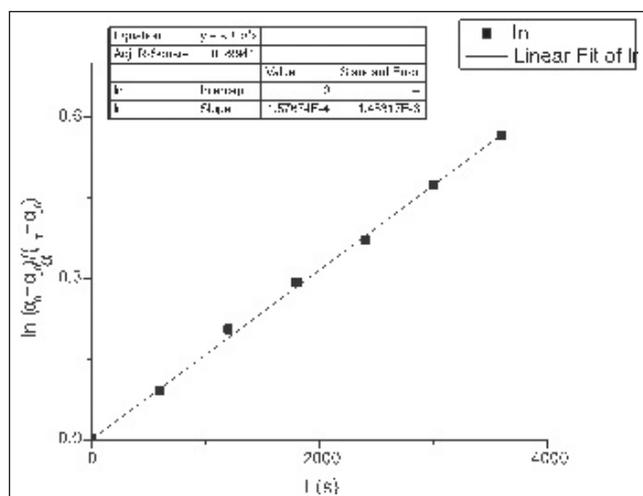


Figure 3. Dependence $\ln ((\alpha_0 - \alpha_\infty) / (\alpha_t - \alpha_\infty))$ on time t

$$k_{calc.} = 15,86 \cdot 10^{-5} \text{ s}^{-1}; k_{graph.} = 15,77 \cdot 10^{-5} \text{ s}^{-1}$$

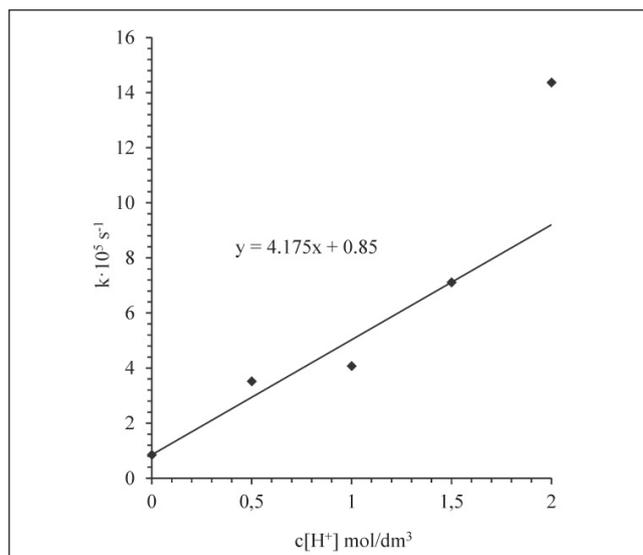


Figure 4. Dependence of sucrose inversion reaction rate constant on catalyst concentration at 298 K in water

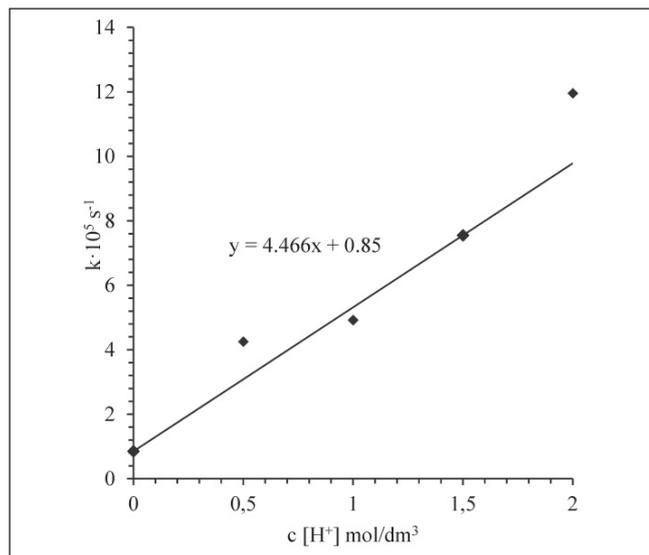


Figure 4. Dependence of sucrose inversion reaction rate constant on catalyst concentration at 298 K in water

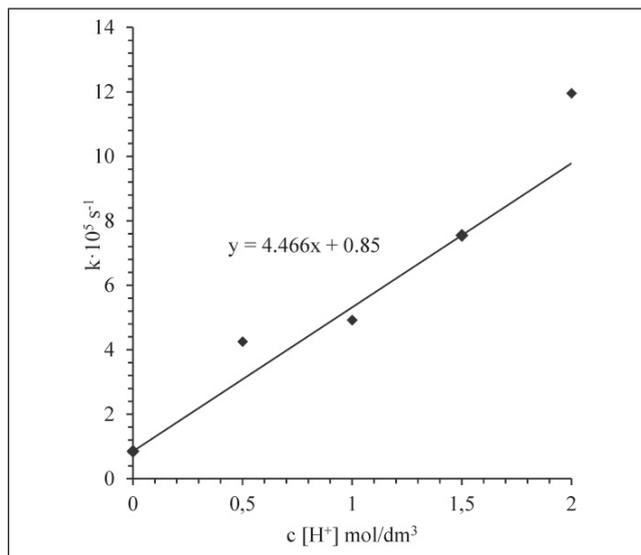


Figure 5. Dependence of sucrose inversion reaction rate constant on catalyst concentration at 298 K in aqueous ethanol

The sucrose inversion reaction rate constant in water as a solvent and in mixed solvents of aqueous ethanol and aqueous dimethyl sulfoxide increases with the growth of the concentration of sulfuric acid as a catalyst.

According to the theory of the overall acid-base catalysis (Laidler, 1965), the rate constant of this reaction is a summary size composed of the rate constant of the spontaneous reaction, which is the rate constant of the first order reaction, and the rate constant of the catalyzed reaction, which is the rate constant of the second order reaction, while the mathematical relation merging these two sizes is:

$$k = k_0 + k_{cat} \cdot [H_3O^+]$$

k_0 is the constant of the catalysis of the solvent itself (spontaneous rate constant), k_{cat} is the catalysis constant, where the catalytic effect depends only on the concentration of hydrogen-ion and that type of catalysis is called specific acid catalysis.

Figure 4, 5 and 6 present dependence of the experimentally obtained rate constants in function on the concentration of catalysts for the examined solvents, water, aqueous ethanol and aqueous dimethyl

Table 5. Spontaneous and catalytic rate constants for the sucrose inversion reaction in water and mixed solvents at 298 K and dielectric constants of the solvent

Solvents	c (mol dm ³)	k _{cal.} /10 ⁵ (s ⁻¹)	k _{graph.} /10 ⁵ (s ⁻¹)
WATER	0.5	1.6132	1.4252
	1.0	3.4085	4.0734
	1.5	6.7812	8.7067
	2.0	12.8470	14.3640
AQUEOUS ETHANOL, X=0.2	0.5	3.0991	4.2528
	1.0	5.3241	4.9199
	1.5	9.1288	7.4166
	2.0	11.2220	11.9550
AQUEOUS DMSO, X=0.2	0.5	6.7726	5.5824
	1.0	9.4324	9.0824
	1.5	13.8990	13.5600
	2.0	15.8640	15.7670

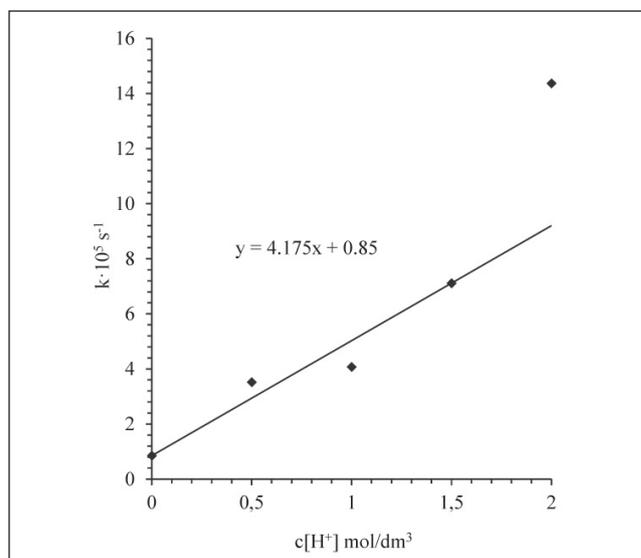


Figure 6. Dependence of sucrose inversion reaction rate constant on catalyst concentration at 298 K in aqueous DMSO

sulfoxide. The sizes k_0 and k_{cat} were determined from those diagrams for the used concentrations of catalysts for the sucrose inversion reaction (k_0 on the diagram represents a section on the ordinate, while k_{cat} is determined based on the coefficient of the course of the obtained direction. Data are to be found in table 5.

The obtained data enable calculation of the rate constant of this reaction according to the equations in the general form in the examined solvents.

Since there is a change of the concentration of the catalyst of sulfuric acid, which is an electrolyte and dissociates in the reaction environment, it is acceptable also to apply Brensted-Bjerrum equation (where it was proved that the reaction rate constant depended on the ionic strength (μ) as well. The following relations were obtained for different solvents:

Solvent:

$$\text{Water: } X_{\text{H}_2\text{O}} = 1,00 = 3,30 \text{ s}^{-1}$$

Aqueous ethanol:

$$X_{\text{EtOH}} = 0,20 = 3,30 \text{ s}^{-1}$$

Aqueous dimethyl sulfoxide:

$$X_{\text{DMSO}} = 0,20 = 2,98 \text{ s}^{-1}$$

The rate constants were calculated based on the Bronsted Bjerrum relation, they are within the experimental error for the same ionic strength and are practically equal for all examined solvents.

The results proved that notwithstanding the fact that the value of dielectric constant falls from water to the solvent representing a mixture of water and ethanol, that the spontaneous rate constant of this reaction, as well as the catalytic constant, remained the same both for water and aqueous ethanol as solvents, and that both k_0 and k_{cat} are almost twice bigger in the aqueous dimethyl sulfoxide. The dielectric constant of the aqueous dimethyl sulfoxide is in between the values of dielectric constants of water and aqueous alcohol as solvents, amounts to 73, while the dielectric constants of water and aqueous ethanol $X_{\text{EtOH}}=0,20$ are 80 and 55, respectively. That information indicates the importance of the interaction between the solvent and the substrate.

Ethanol is a protic solvent, just like water. The characteristic of protic solvents is that, inter alia, they are also donors of hydrogen bonds and the interaction of the protons from water with the water molecules was realized by the hydrogen bonds with an equal force in the solvent that represents pure water and aqueous ethanol that in the examined area contained a high percentage of water (Huges and Ingold, 1935). The same effect, building of hydrogen bridges in water and aqueous ethanol with the proton of the acid that is a catalyst, explains the fact that the catalytic constants are equal.

The role of the dipolar aprotic solvent proved to have a different effect on the reaction rate. Dimethyl sulfoxide is not a donor of hydrogen bonds, which means that the solvation of the reactant can be realized only by the interaction of ion-dipole or dipole-dipole attraction (Penavin et al., 2004). It is obvious that a strong bondage of protons either from water or from acid as catalysts with the molecules of water or alcohol through hydrogen bridges decreases the activity of that ion that participates in the reaction, and therefore the inversion reaction rate is smaller and the same in the protic solvents.

It is obvious that in the aqueous dimethyl sulfoxide the dissociation of water is strengthened, the activity of hydrogen ion is bigger because it is more poorly solvatized and therefore "more active" in this reaction, which is manifested by a higher value of the spontaneous reaction rate constant, and the same interpretation refers to the catalyst proton, which is a reason for the catalytic constant to be much bigger than it was in two protic solvents.

The mixtures of protic and dipolar aprotic solvents are very interesting as the reaction environment. Authors Tommila and Murto, (1963) are of the opinion that in the mixtures of protic solvent with dimethyl sulfoxide in the area where the content of the protic component is high, the increase of the reaction rate is a consequence of the preferred solvation of the transition state with the mixed solvent compared with the pure protic solvent.

Conclusion

- Sucrose inversion is a pseudo first order reaction in water and mixed solvents, which were mixtures of water and alcohol and water and dimethyl sulfoxide (DMSO) at 298 K.
- Sucrose inversion rate depends on the concentration of sulfuric acid as a catalyst.
- Sucrose solvolysis rate constant is a summary size, composed of the contribution of rate constant of a non-catalyzed reaction and rate constant of a catalyzed reaction.
- Spontaneous sucrose solvolysis rate constant is a rate constant of the first order.
- Catalytic constant of this reaction is the rate constant of the second order reaction.
- The general form was determined of the relation for calculating the sucrose inversion rate constant in the presence of sulfuric acid as an acid catalyst for water, aqueous ethanol and aqueous dimethyl sulfoxide.
- The rate constant of the spontaneous sucrose solvolysis and catalytic constant in water and aqueous alcohol with the composition of $X_{\text{Etanol}} = 0.20$ are equal, while spontaneous and catalytic rate constant of solvolysis in the aqueous dimethyl sulfoxide with the composition of $X_{\text{DMSO}} = 0.20$ is almost twice bigger.
- The obtained kinetic data were interpreted based on the Hughes-Ingold theory.

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Recived: 30.3.2017.

Accepted: 10.6.2017.