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Hydrolysis of sucrose by radiation grafted sulfonic acid membranes

Mohamed Mahmoud Nasef[a,*], Hamdani Saidi[a], Magdy Mohamed Senna[b]

[a] *Business and Advanced Technology Centre, Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia*
[b] *Department of Radiation Chemistry, National Center for Radiation, Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt*

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Abstract

The hydrolysis of sucrose to glucose and fructose by poly(tetrafluoroethylene-*co*-perfluorovinyl ether)-*graft*-polystyrene sulfonic acid (PFA-*g*-PSSA) membranes was investigated. The membranes were prepared by simultaneous radiation-induced grafting of styrene onto poly(tetrafluoroethylene-*co*-perfluorovinyl ether) (PFA) films using γ-radiation followed by sulfonation with chlorosulfonic mixture. The kinetics of the reaction was determined for various membranes in batch mode and the reaction rate constants were obtained in a temperature range of 40–70 °C. The catalytic activity of the membranes was found to be dependent on the reaction temperature and the concentration of the sulfonic acid groups in the membranes. The results of this work suggest that PFA-*g*-PSSA membranes have strong potential to replace liquid sulfuric acid and ion exchange resins in sugar hydrolysis processes.

Keywords: Hydrolysis of sucrose; Sufonic acid membranes; Radiation-induced grafting; Styrene; PFA films; Reaction kinetics

1. Introduction

Sucrose continues to constitute a significant part of the human diet and therefore, it is widely used in the food industry as such and as a precursor of invert sugar through its partial or total hydrolysis [1]. Other uses in the non-food industry, such as the use of sucrose as a starting material for the formation of high added value furanic derivatives (5-hydroxymethylfurfural) are also appealing [2,3]. Enzymes are the most used catalysts to hydrolyze sucrose and transform it into inverted sucrose on the industrial scale [4]. However, their use is restricted to the food industry with a conversion of sucrose below 95% because the formed glucose and fructose tend to inhibit the hydrolysis reaction [5]. To overcome this problem strongly acidic ion-exchange resins containing sulfonic acid groups are used and allowed a complete conversion of sucrose in the temperature range compatible with their stability, but with a relatively high level of impurities [6,7]. Conventional ion exchange resins composing of divinylbenzene crosslinked polystyrene (PS-DVB) network structure containing sulfonic acid groups, inhibit the access of reactants with sizes larger than the interstices of the polymer chains [8]. Unlikely, polystyrene–polypropylene fibrous ion exchange catalysts showed more effective catalytic activity towards sucrose hydrolysis due to the increase in their surface area together with the increase in the reactant molecular size accessibility [9].

Radiation-induced grafting using high energy radiation has been found to be powerful method to produce graft copolymers capable of hosting sulfonic groups and having more effective catalytic activity toward sucrose hydrolysis [10]. Aiba et al. [10] has prepared polystyrene sulfonic acid grafted microporous poly(tetrafluoroethylene) (PTFE) membranes by radiation induced grafting of styrene onto PTFE films with γ-rays followed by sulfonation and tested their catalytic activity for hydrolysis of dextrin. Mizota et al. [8] prepared sulfonic acid containing hollow fiber membrane by radiation-induced grafting of styrene sodium sulfonate onto polyethylene (PE) hollow fiber using electron beam fol-

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[*] Corresponding author. Tel.: +60 3 26914020; fax: +60 3 26911294.
E-mail address: mahmoudeithar@mailcity.com (M.M. Nasef).

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Nomenclature

C	concentration of sucrose at time t (mol l^{-1})
C_0	initial concentration of sucrose (mol l^{-1})
E	activation energy (kJ mol^{-1})
k	reaction rate constant (min^{-1})
k_0	Arrhenius constant (min^{-1})
R	gas constant (kJ mol^{-1} K^{-1})
T	reaction temperature (K)

lowed by chemical treatment to convert Na-form of the membrane to H-form. The catalytic activity of the obtained sulfonic acid membranes was tested for hydrolysis of methyl acetate and sucrose. Nevertheless, the use of radiation-induced grafting method to prepare various membranes for sucrose catalysis has not been well exploited as indicated by the scarce number of studies reported in literature. The objective of this study is to report on the reaction kinetics of the hydrolysis of sucrose using newly prepared radiation grafted poly(tetrafluoroethylene-*co*-perfluorovinyl ether)-*graft*-polystyrene sulfonic acid (PFA-*g*-PSSA) membranes.

2. Experimental

2.1. Preparation of sulfonic acid containing membranes

PFA-*g*-PSSA membranes were prepared using a three-step procedure. In the first step, the non-porous PFA film (Porghof) (120 μm thick) was exposed to elevated temperature (below its melting point) while clamped and stretched using a special steel fixture to allow the formation of porous structure. The obtained porous film has an average pore diameter of 0.24 μm and porosity of 47%. Secondly, the porous PFA film was grafted with styrene of known concentration in dichloromethane using the procedure reported in our previous study [11]. The grafting mixture was placed in tightly sealed glass ampoule and irradiated to a total dose of 20 kGy for 15 h using γ-rays from a ^{60}Co source under nitrogen atmosphere at room temperature. The grafted film was thoroughly washed with toluene several times and dried under vacuum. In the third step, the grafted PFA film was sulfonated using a chlorosulfonic acid/1,1,2,2-tetrachloroethane mixture (30/70, v/v) at a temperature of 90 °C for 5 h as described elsewhere [12]. The degree of grafting was calculated as the percent of weight increase in the grafted film with respect to the weight of the original PFA film. A degree of sulfonation close to 100% was achieved in all membranes and therefore, membranes properties are functions of the degree of grafting.

2.2. Hydrolysis of sucrose

The catalytic activity of the membranes containing sulfonic acid groups was tested for sucrose hydrolysis (inversion) in a batch process. The membrane of known degree of grafting was cut into small pieces (10 mm × 10 mm), soaked in 100 ml of sugar solution having a concentration of 0.58 mol l^{-1} hosted in a small glass reactor placed in thermostat controlled oil bath and equipped with condenser and a round-shaped Teflon blade stirrer. At prescribed time, samples (size 0.1 ml) were extracted and analyzed for concentration of sucrose, glucose and fructose. The size of sample is negligible with respect to the total volume of sucrose solution. Analyses were performed by HPLC using a Shimadzu LC-6A pump and a refractive index RID-6A detector, and controlled by a PC with a software package (ICS). The column used was a Ca-form ion-exchange resin (HPX 87C from Bio-Rad), thermostated at 80 °C. The mobile phase was deionized water (0.5 ml min^{-1}), and D-mannitol was used as external standard. The kinetic analysis was made based on the variation in the reaction temperature from 40 to 70 °C.

3. Results and discussion

The PFA-*g*-PSSA membrane used as catalyst for sucrose hydrolysis were prepared by radiation-induced grafting of styrene onto PFA film followed by sulfonation with chlorosulfonic acid according to the reaction scheme shown in Fig. 1. Styrene concentrations of 40, 50 and 60 vol.% in dichloromethane were used to obtain homogenous and uniform membranes having degrees of grafting of 28, 45 and 63%, respectively. A summary of the physico-chemical properties of PFA-*g*-PSSA membranes is given in Table 1.

The reaction of the hydrolysis of sucrose to glucose and fructose using sulfonic acid bearing cation exchange membranes proceeds according to Eq. (1)

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \qquad (1)$$

The reaction is irreversible and first order with respect to the concentration of sucrose (C) at time t and acid

$$\frac{dC}{dt} = -kC \qquad (2)$$

where k is the reaction rate constant.

To begin investigating the kinetics of the hydrolysis of sucrose, a PFA-*g*-PSSA membrane of 63% degree of grafting was used as a catalyst and the reaction was conducted at specified temperature and various time intervals. A sample of small volume is extracted from the reaction vessel and analyzed by HPLC for three components i.e. sucrose, glucose

Table 1
Summary of the properties of radiation grafted PFA-*g*-PSSA membranes

Degree of grafting (wt.%)	Water uptake (wt.%)	Ion exchange capacity (mmol/g)	Thickness of wet form (μm)
28	41	1.7	160
45	79	2.3	170
63	88	2.8	180

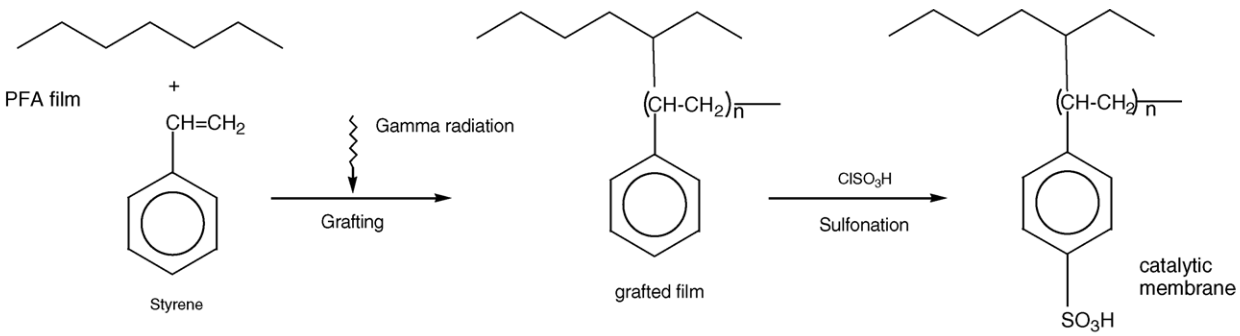

Fig. 1. A reaction scheme for preparation of PFA-*g*-PSSA membranes by radiation-induced grafting.

and fructose. The time courses for the hydrolysis of sucrose into glucose and fructose at 60 °C is shown in Fig. 2. As can be seen, the sucrose concentration decreases gradually with the increase in the reaction time. Inversely, the concentration of both glucose and fructose increases with the increase in the reaction time and the amount of such increase is equivalent to the decrease in the sucrose concentration. This is going along with the mass balance consideration. Therefore, it is the intention of the author to monitor the sucrose conversion into glucose and fructose in terms of variation of sucrose concentration at certain time (C) with respect to initial concentration (C_0).

The time courses for the hydrolysis of sucrose into glucose and fructose by 63% grafted PFA-*g*-PSSA membrane at temperatures ranging from 40 to 70 °C is shown in Fig. 3. The ratio C/C_0 was plotted against time to provide kinetic data that can best explain the effect of reaction variables on the overall conversion. At all temperatures, the C/C_0 ratio decreases steeply with the increase in time intervals until it reaches minimum values, which varies depending on the reaction temperature. For instance, the C/C_0 ratio decreases until it reach almost zero at 70 °C after 4 h, whereas the time is getting longer at lower temperature. This clearly shows that raising the reaction temperature causes a remarkable increase in the rate of the reaction coupled with lower diffusion resistance that helps achieving complete conversion rapidly. Hence, hydrolysis of sucrose with PFA-*g*-PSSA membrane is favored at high temperature.

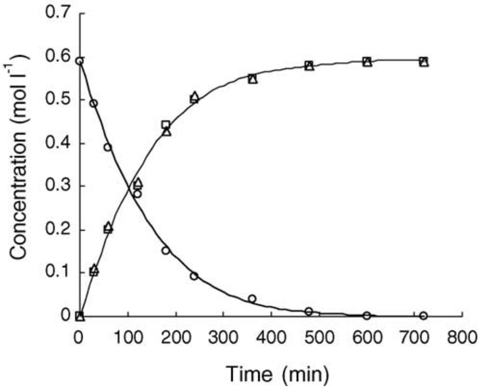

Fig. 2. Time courses for concentration of: (◯) sucrose, (☐) glucose and (△) fructose concentrations at 60 °C.

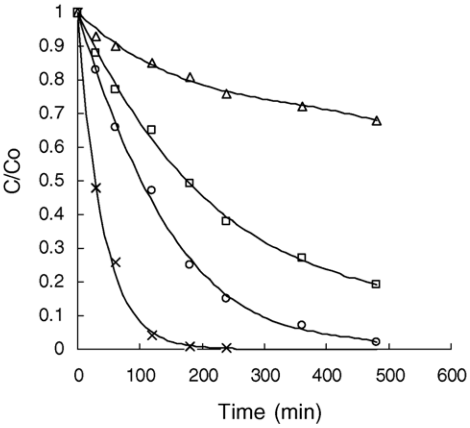

Fig. 3. Time courses for the hydrolysis of sucrose into glucose and fructose at various temperatures: (△) 40 °C, (☐) 50 °C, (◯) 60 °C, and (×) 70 °C.

The reaction rate constant (k) for the hydrolysis of sucrose at various temperatures was obtained from Eq. (2) using a standard integral method and can be expressed by:

$$kt = -\ln\left(\frac{C}{C_0}\right) \tag{3}$$

To obtain k graphically, $\ln(C/C_0)$ was plot against the reaction time at temperatures ranging from 40 to 70 °C as shown in Fig. 4. All reactions showed linear relationships and the rate constants obtained from the slops are in a good agreement with their respective values calculated from Eq. (3) as shown in Table 2. This kinetic data confirms that the reaction is first order.

Table 2
Comparison between the graphically obtained and the calculated reaction rate constants for hydrolysis of sucrose by PFA-*g*-PSSA membranes at various temperatures

Temperature (°C)	k obtained from the slops (Fig. 4)	k calculated from Eq. (3)
40	1.33	1.30
50	4.33	4.10
60	7.67	7.45
70	27.50	26.90

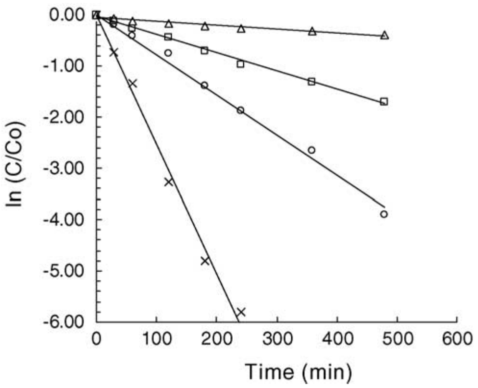

Fig. 4. Kinetics of hydrolysis of sucrose into glucose and fructose using PFA-*g*-PSSA membranes at various temperatures: (△) 40 °C, (□) 50 °C, (◯) 60 °C, and (×) 70 °C.

The activation energy (E) of the reaction was obtained using Arrhenius equation given below:

$$\ln k = \ln k_0 - \frac{E}{RT} \tag{4}$$

where k_0 is the Arrhenius constant. Fig. 5 shows Arrhenius plot for hydrolysis of sucrose into glucose and fructose using PFA-*g*-PSSA membrane (degree of grafting = 63%). The activation energy calculated from the slope is found to be 81.3 kJ mol^{-1}. This value is higher than that obtained upon hydrolysis of sucrose with commercial crosslinked ion exchange resins, which was reported to be 59 kJ mol^{-1} [8]. The lower activation energy is due to mass transfer limitation to the observed reaction rate. This agrees with the explanation of other authors and with the intermediated value compared to other results [7,8,13]. The membranes studied may have an intermediated level of effect of mass transfer. In their study, Mizota et al. [8] attributed the lower catalytic activity of the crosslinked ion exchange resin to the decrease in the accessibility of the sulfonic acid groups by sucrose molecules stemmed from the diffusional mass transfer resistance caused by presence of the crosslinked polymer network structure. However, the value of activation energy in this work is less than that for the hydrolysis of sucrose conducted by free acid (HCl) in a homogenous system [13] and also by sulfonic acid containing porous hollow fiber membrane prepared by radiation-induced grafting of styrene sodium sulfonated followed by conversion of Na-form to H-form [7], both of which equal 95 kJ mol^{-1}. This may be attributed to the reduction in water flux caused by the small average pore diameter of the membrane prepared in this study, which gives rise to the diffusional resistance and reduce the accessibility to the ionic sites.

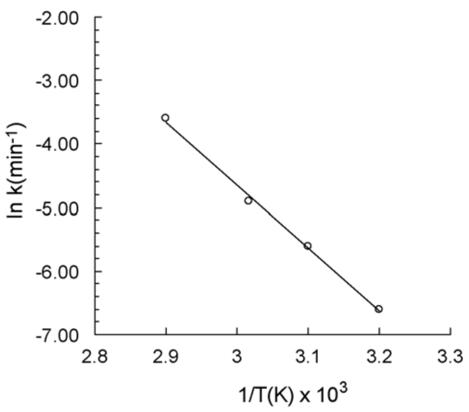

Fig. 5. Arrhinus plot for hydrolysis of sucrose into glucose and fructose using PFA-*g*-PSSA membrane.

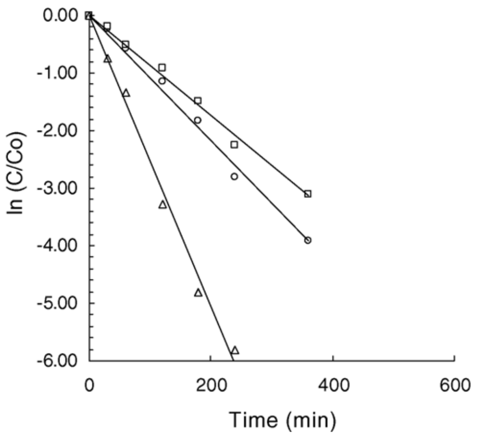

Fig. 6. The relationship between C/C_0 ratio and the reaction time for PFA-*g*-PSSA membranes having various degrees of grafting: (□) 28%, (◯) 45%, and (△) 63% at a temperature of 70 °C.

The effect of variation of the degree of grafting in sulfonic acid membranes on kinetics of the hydrolysis of sucrose was studied and the data obtained at a temperature of 70 °C is shown in Fig. 6. The rate constant of the reaction calculated from the slopes was found to rise with the increase in the degree of grafting. It increased from 7.5×10^{-3} to 27.5×10^{-3} with the increase in the degree of grafting from 28 to 63%. This behavior can be explained based on the fact that, the increase in the degree of grafting leads to an increase in the number sulfonic acid groups incorporated in the membranes. Consequently, the number of fixed sulfonic acid groups increases in the micropores providing more accessible sites to the chemical reaction i.e. the catalytic activity of the membranes increases with the increase in the degree of grafting. This is enhanced by improving the hydrophilicity of the membranes and increasing polymer chains mobility leading to a reduction in the diffusional resistance to sucrose molecules and allowing more accessibility to the ionic sites.

4. Conclusion

Kinetic investigations of the hydrolysis of sucrose catalyzed by PFA-*g*-PSSA membranes prepared by radiation-induced grafting of styrene followed by sulfonation reaction showed that the reaction is favored as the reaction temperature increases because of higher reaction rate constants. The catalytic activity of the sulfonic acid membranes is found to be higher than that of commercial catalytic crosslinked ion exchange resins. The increase in the degree of grafting i.e. concentration of fixed sulfonic groups was found to enhance the catalytic activity of these membranes. This work demonstrates the potential of radiation-induced grafting method in preparing catalytic membranes and such potential can be harnessed to prepare various shapes of sulfonic acid catalysts (beads, fiber or non-woven fabric) as radiation is capable of initiation grafting in polymer having different forms.

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