Glass Transition and Reaction Rates: Nonenzymatic Browning in Glassy and Liquid Systems

Satu M. Lievonen,* Tommi J. Laaksonen, and Yrjö H. Roos

Department of Food Technology, P.O. Box 27 (Viikki B), FIN-00014 University of Helsinki, Helsinki, Finland

Effects of physical state and glass transition on nonenzymatic browning rate in water, glycerol, poly(vinylpyrrolidone) (PVP), and maltodextrin (MD) systems were studied. All systems had the same concentration of reactants, glucose and lysine, in the water phase. The systems, except water, had also comparable water activities (0.33). Sorption isotherms and glass transition temperatures (T_g) at various water contents for the freeze-dried PVP and MD systems were determined. Nonenzymatic browning rate was determined at several temperatures from optical density at 280 and 420 nm. The PVP and MD systems contained 12.9 and 8.2 g of H_2O/100 g dry matter and had T_g values of 67 and 62 °C at 33% relative humidity and 24 °C, respectively. The liquids exhibited significantly higher browning rates than the concentrated systems, especially below the T_g values. The browning rate was higher in the PVP than in the MD system, suggesting that a possible phase separation may affect nonenzymatic browning in foods.

Keywords: *Glass transition; nonenzymatic browning; physical state; reaction rate*

INTRODUCTION

The significance of glass transition on the stability of amorphous food materials has been intensively studied since the 1980s (Levine and Slade, 1986; Slade and Levine, 1988). The premise of these studies has been suggestions that the physical state of a food system has important implications in food processing and storage stability. There is a general agreement about the influence of glass transition on physical changes, such as collapse and crystallization (Roos et al., 1996), although the use of a single glass transition temperature has been criticized (Peleg, 1996, 1997). It has also been proposed that glass transition affects rates of diffusion-controlled chemical and enzymatic reactions through changes in molecular mobility, which is likely to be extremely slow below the glass transition because of the high viscosity of the matrix (Slade and Levine, 1991). However, experimental results have not confirmed that the glass transition, as such, results in a change in the reaction rates. For instance, in a study of aspartame degradation, the effect of the glass transition was found to be insignificant, although the reaction pathway was dependent on molecular mobility (Bell and Hageman, 1994). On the other hand, rotational mobility of a tempol probe increased 100-fold within the glass transition temperature range in an ESR study (Roozen et al., 1991). However, most studies have given evidence of the independent effects of glass transition on the reaction rates together with other factors, such as water content, water activity, temperature, and reactants concentration (Shimada et al., 1991; Karmas et al., 1992; Roos and Himberg, 1994; Buera and Karel, 1995; Bell, 1996).

Nonenzymatic browning is probably the most studied example of a possibly diffusion-controlled chemical reaction in connection with glass transition. It is a good model for studying the effects of the glass transition on reaction kinetics, because the reaction mechanism contains several condensation steps that require the diffusion and collision of reactants [e.g., Namiki (1988)]. Moreover, nonenzymatic browning is an important chemical reaction in foods, as it produces flavors and colors, but it may also decrease quality during processing and storage. Therefore, control of the reaction rate has been given much attention. Probably the first study relating glass transition temperature with nonenzymatic browning kinetics was published by Karmas et al. (1992). They found that even if the browning rate in different food models was strongly dependent on moisture and temperature, it was also affected by the glass transition. A corresponding conclusion was made by Roos and Himberg (1994), who studied nonenzymatic browning as a function of water content, water activity, and glass transition temperature at chilling temperatures. However, many studies have stressed that the effects of the physical changes of the matrix materials, such as crystallization and collapse, coinciding with the glass transition should also be taken into consideration (Karmas et al., 1992; Karmas and Karel, 1994; Buera and Karel, 1995).

It has been difficult to distinguish directly the effects of glass transition on the nonenzymatic browning rate from the effects of other factors, mainly temperature and moisture content. The glass transition temperature range in model systems is often controlled by changing the water content of the system. The problem is that water activity and a reactant concentration will be changed at the same time. Bell (1996) solved the problem by using PVP polymers with different molecular weights as matrix materials. The models had different glass transition temperatures, but the same water activities and moisture contents, and the effect of the physical state and water activity could be more clearly separated. The state of the system was observed

* Author to whom correspondence should be addressed (telephone +358 9 708 5206; fax +358 9 708 5212; e-mail satu.lievonen@helsinki.fi).

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to be a more rate-limiting factor than water activity. However, the most essential factor was the reactant concentration. A limitation of the study was that only one matrix material was studied, and generalizations of the results may not always apply to other systems. In the present study the nonenzymatic browning rate of four different matrix materials was followed to determine the effect of physical state and glass transition on the rate of nonenzymatic browning.

MATERIALS AND METHODS

Preparation of Food Models. Four food models, liquids and concentrated systems, were designed. The main desired characteristics of the models were (a) the same concentrations of reactants, glucose and lysine, in the water phase (10% w/w, 1:1); (b) comparable glass transition temperatures of the concentrated systems; and (c) comparable water activities, except when the reactants were in water. The models included water, as an example of a completely free diffusional system, the more viscose glycerol, as well as amorphous concentrated poly(vinylpyrrolidone) (PVP) and maltodextrin (MD) systems. The PVP and MD systems were considered to represent diffusion-limited protein and carbohydrate matrixes, respectively. The composition of the systems was designed on the basis of literature (Eichner and Karel, 1972) and preexperiments. The 10% reactant concentration for the study was chosen for two reasons. First, an aim of the study was at keeping the reactant concentration constant and, second, during preexperiments the 10% concentration was found to be sufficient for producing a perceptible color in the food models designed.

The water and glycerol systems were prepared by dissolving the reactants, lysine (5.0% w/w) and glucose (5.0% w/w), first into water. For the glycerol system, the clear reactants/water solution was further dissolved into glycerol (1:10). Aliquots of 5 mL of the solutions were placed into glass ampules (5 mL), which were hermetically flame-sealed. The concentrated amorphous PVP (PVP-40) and MD (Maltrin M 100) systems were made by preparing solutions containing 20% total solids from the reactants, the matrix materials, and distilled water. The exact amounts of the reactants (10% w/w, 1:1, in the adsorbed water) were adjusted to the water content that the matrix materials obtained when equilibrated into $0.33a_w$. The 50 g solutions were frozen on Petri dishes (2 h at −20 °C and 24 h at −80 °C) and freeze-dried (48 h, $p < 0.1$ mbar) (Lyovac GT 2, Amsco Finn-Aqua GmbH, Germany). Before freeze-drying, the pH of all four liquid systems was measured (Beckman Φ31 pH meter, Beckman Instruments Inc., Fullerton, CA).

Sorption Isotherms. Sorption isotherms were determined gravimetrically for the concentrated PVP and MD systems. Samples of 1 g of the freeze-dried materials, prepared in the 20 mL glass vials, were further dehydrated by storing them in vacuum desiccators over P_2O_5 for 1 week, after which time the samples were considered anhydrous. The dehydrated triplicate samples were then kept at 24 °C over saturated salt solutions of LiCl, CH_3COOH, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl, and KCl having relative humidities (RH) of 11.5, 23.9, 33.0, 44.4, 53.8, 66.2, 76.4, and 85.8%, respectively (Greenspan, 1977; Labuza et al., 1985), until the sample weights leveled off, indicating the steady-state water contents. The samples were weighed at intervals during storage. The BET (Brunauer et al., 1938) and GAB (van den Berg and Bruin, 1981) sorption isotherm models were fitted into water sorption data using linear regression analysis, as described by Jouppila and Roos (1994a).

Differential Scanning Calorimetry (DSC). The glass transitions for the PVP and MD systems stored at various relative humidities were determined using DSC (Mettler TA4000 system with TC15 TA processor, DSC 30 measuring cell, and STAR^e Thermal Analysis System version 3.1 software; Mettler-Toledo AG, Switzerland). The instrument was calibrated using *n*-pentane (mp −129.7 °C; $\Delta H = 116.7$ J/g), *n*-hexane (mp −94.0 °C; $\Delta H = 151.8$ J/g), mercury (mp −38.8 °C; $\Delta H = 11.4$ J/g), distilled water (mp 0.0 °C; $\Delta H = 334.5$ J/g), gallium (mp 29.8 °C; $\Delta H = 80$ J/g), and indium (mp 156.6 °C; $\Delta H = 28.45$ J/g). The samples of ≈10 mg were sealed in aluminum DSC pans and scanned at 5 °C/min from at least 30 °C below the glass transition temperature range to at least 30 °C above the glass transition temperature range. An immediate rescan was run for each sample to eliminate relaxations and improve interpretation of the thermograms. The glass transition temperature was taken as the onset temperature of the glass transition temperature range. An average of three replicate samples was used as the glass transition. The glass transition values and corresponding water contents obtained from the sorption study were modeled using the Gordon−Taylor equation (Gordon and Taylor, 1952), as described by Jouppila and Roos (1994b).

Nonenzymatic Browning. For studying the rate of nonenzymatic browning, the PVP and MD systems were rehumidified to water activities of 0.33 at 24 °C. After freeze-drying, the sample materials on the Petri dishes were transferred into the vacuum desiccators at 33% RH for 24 h. The sample materials were then ground, and aliquots of ≈1 g were transferred into glass ampules, which were stored in the vacuum desiccators at 33% RH for another 24 h. Thereafter the ampules were flame-sealed. The samples of the four food models, water, glycerol, PVP, and MD, as the main reaction medium, were stored at 50, 60, 70, 80, 90, and 100 °C. Triplicate samples were removed at intervals after sufficient color formation. After heating, some samples were examined by microscope (Nikkon AFMB Labphot photomicrographic, Nippon Kogaku k.k., Japan). The extent of browning was determined spectrophotometrically (Perkin-Elmer Lambda 2 UV−vis spectrometer) from the optical density (OD) at 280 nm for colorless furfural compounds and at 420 nm for yellow and brown pigments (Whistler and Daniel, 1985). Samples with water and glycerol were diluted with ethanol/water (3:1) solution when necessary, and the PVP and MD samples were dissolved in water/ethanol (3:1) solution. Unheated samples were used as a blank. Rate constants, their 95% confidence limits, and coefficients of determinations (R^2) were calculated using linear regression analysis, as recommended by Labuza (1984). The statistical significance of different browning rates of the different food models at each temperature was tested using the general linear model in which optical density values were explained by constant, time, treatment, and interactions of time and treatment. If significant differences were found (F test, $p < 0.05$), pairwise comparisons were performed.

RESULTS AND DISCUSSION

Sorption Isotherms. The water contents of both the PVP and MD systems kept in the different RHs at 23−24 °C generally leveled off within a day. The exceptions were the PVP system when kept at 76.4% RH, which achieved the steady-state water content after 2 days, and both the PVP and MD systems kept at 85.8% RH, which did not seem to become steady during the experiment (Figure 1). These results agreed with the result of Jouppila and Roos (1997), who reported an equilibration of the water content of cornstarch in 24 h below 66.2% RH. On the other hand, materials in sorption measurements are often equilibrated over saturated salt solutions for considerably longer times than 2 days. For instance, Wolf et al. (1985) recommended an equilibration time of at least 14 days for real food materials. The difference in the equilibration times predominantly results from different methods used. As the absolute pressure in the sorption container is an important factor affecting the sorption kinetics, the samples achieve the steady-state water content more quickly in a vacuum than at atmospheric pressure (Wolf et al., 1985). Moreover, the control of a steady vapor pressure of water in nonevacuated containers is difficult.

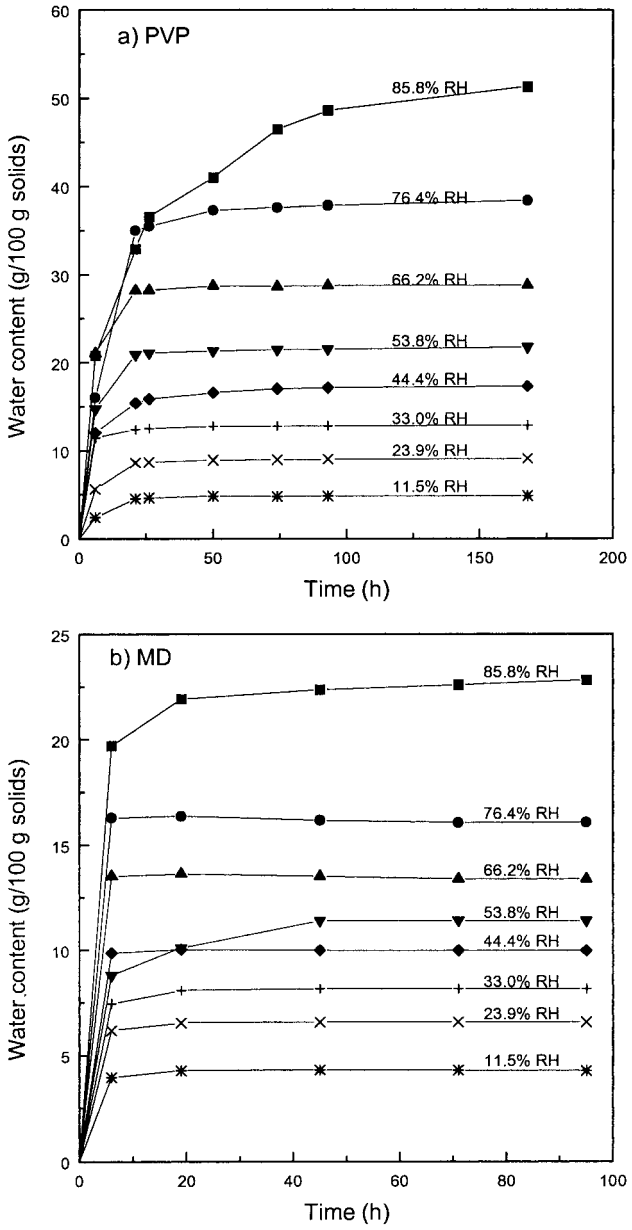

Figure 1. Water content of the (a) PVP and (b) MD systems stored at various RHs as a function of storage time.

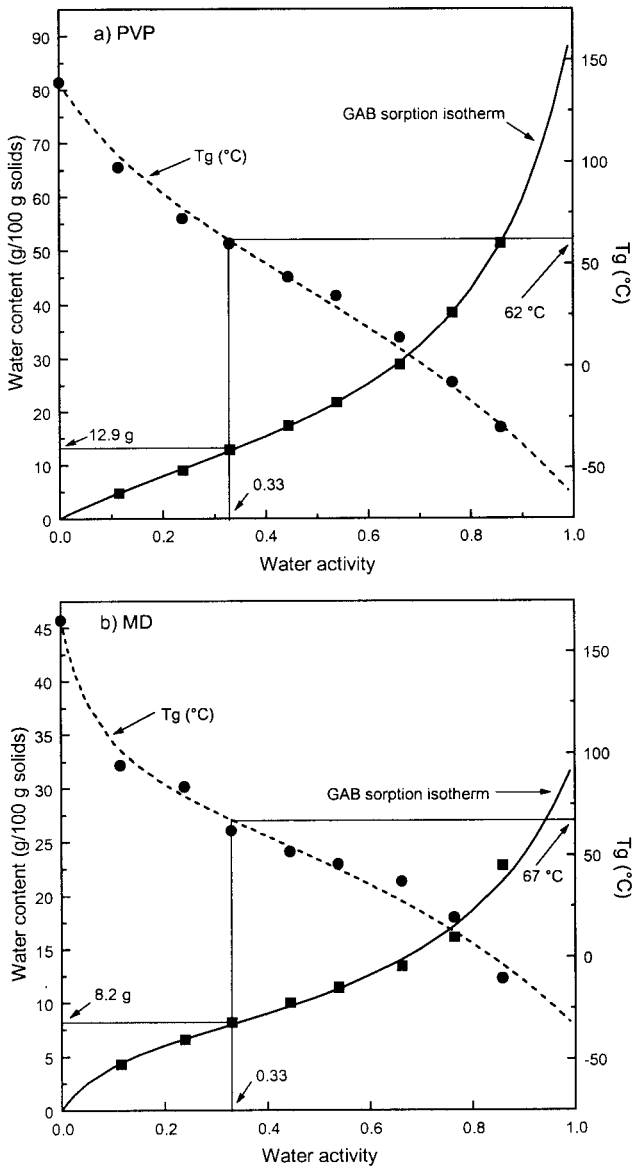

Figure 2. Relationship between water activity, glass transition temperature (T_g), and water content for the (a) PVP and (b) MD systems.

The PVP and MD systems showed sigmoid water sorption behavior typical of amorphous materials, and experimental data could be modeled using the BET and GAB sorption isotherm models. The GAB isotherm fitted well to the water sorption data of the systems over the whole water activity range ($0.11-0.85a_w$), whereas the BET isotherm fitted to the experimental data only between 0 and $0.4a_w$, as was expected on the basis of the literature (Labuza, 1968; van den Berg and Bruin, 1981; Roos, 1993). The BET monomolecular layer values of the PVP and MD systems were 12.9 and 6.2 g of H_2O/100 g of dry matter (dm), respectively. Corresponding GAB monomolecular layer values were 16.1 g of H_2O/100 g of dm for the PVP system and 7.2 g of H_2O/100 g of dm for the MD system. The same materials stored at 33% RH at 24 °C contained water 12.9 ± 0.04 and 8.2 ± 0.04 g/100 g of dm, respectively (Figure 2). These water contents were slightly higher than were found in other studies. Bell and Hageman (1995) reported a water content of pure PVP-K30 kept over 33% RH at 25 °C to be 11.1 ± 0.3 g of H_2O/100 g of dm. Addition of glucose and glycine into the PVP-K30 matrix, so that the concentration of the reactants was 1 molal, did not change water sorption, which was 11.4 g of H_2O/100 g of dm at the same conditions (Bell, 1996). Roos and Karel (1991) found that the water content of maltodextrin (Maltrin M100) kept at 33% RH at 25 °C was 5.4 g of H_2O/100 g of dm.

Glass Transitions. The glass transitions of anhydrous PVP and MD systems had onset temperatures (T_g) at 139 and 165 °C, respectively. The T_g decreased when water contents and water activities of the materials increased, being 60 °C for the PVP system and 62 °C for the MD system when kept over 33% RH at 24 °C. These temperatures agreed well with the literature, according to which the T_g values of the pure anhydrous PVP and MD materials were 139 and 160 °C, respectively (Roos and Karel, 1991; Buera et al., 1992). Furthermore, the corresponding values for the pure PVP and MD materials kept at 33% RH were reported to be 63 and 66 °C, respectively (Roos and Karel, 1991; Bell and Hageman, 1995). The addition of glucose and lysine was not found to affect the glass transition in the

present study, although the studies of Buera and Karel (1995) and Bell (1996) found lower glass transition temperatures of 55 and 46 °C, respectively, for the PVP−reactants systems. The differences may be due to inevitable variation in the determination of the glass transition and a slightly different composition of the models. The reactant concentration in the present study was approximately one-third of the concentrations Buera and Karel (1995) and Bell (1996) used in their studies.

The Gordon−Taylor equation (Gordon and Taylor, 1952) was used to model the experimental data. The constant, k, for the Gordon−Taylor equation was found to be 3.1 ± 0.4 for the PVP system and 6.1 ± 0.5 for the MD system. The correlations between experimental data points and predicted values obtained with the Gordon−Taylor equation were 0.996 for the PVP system and 0.991 for the MD system. The predicted glass transition temperatures for the PVP and MD systems at 24 °C were 62 and 67 °C, respectively. It should be noted that these were the glass transition temperatures used in the present study. The effect of water activity on the glass transition and sorption behavior of the PVP and MD systems is shown in Figure 2.

Nonenzymatic Browning. The rates of the nonenzymatic browning reaction in all four materials increased with increasing temperature. The rate observed from increasing optical density at 280 nm was higher than at 420 nm. In the liquid systems a lag period was observed. This was followed by a linear increase in optical density. In the concentrated systems the linear region leveled at a plateau or decreased at the end of the reaction (Figure 3). In the determination of the reaction rate constants the linear region of the plots of optical density against storage time was used. The number of data points included varied from 8 to 18 depending on the length of the linear region. The average 95% confidence limit of the rate constants was ~±10% of the actual rate constant value. The coefficients of determination of the reaction rate constants were fairly high, varying from 0.716 to 0.999. As shown in Figures 4 and 5, the reaction rate in the water system decreased when 100 °C was approached, probably because of a change in temperature dependence and leveling of the rate constants. The reaction followed pseudo-zero-order kinetics, as often reported for nonenzymatic browning (Labuza and Basier, 1992; Villota and Hawkes, 1992), and the temperature dependence could be modeled using the Arrhenius equation. The activation energy of the reaction varied from 99 to 147 kJ/mol, typical of nonenzymatic browning reactions (Labuza and Basier, 1992). The activation energies, their 95% confidence limits, and coefficients of determination for the reaction, as observed from the optical density at 280 and 420 nm for all models, are given in Figure 4.

Nonlinearity of an Arrhenius plot and applicability of the WLF equation in a region above the glass transition have been assumed to occur in the vicinity of the glass transition in diffusion-controlled chemical reactions occurring in amorphous systems (Slade and Levine, 1991; Roos, 1995). Moreover, Karmas et al. (1992) were able to show that the temperature dependence of the nonenzymatic browning reaction in several amorphous food models changed in the vicinity of the glass transition. In some cases the WLF model has also been fitted to the data, as was reported by Nelson and

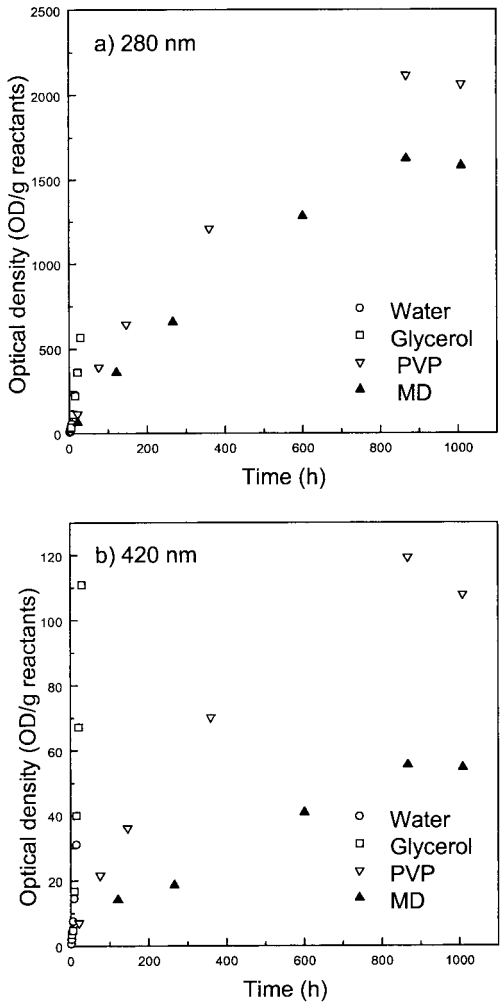

Figure 3. Optical density development of the food models at (a) 280 and (b) 420 nm vs storage time at 50 °C.

Labuza (1994), who fitted the WLF model to the data of Karmas et al. (1992). In the present study the WLF equation was not found to fit to the data. There were no perceptible breaks or step changes over the glass transition temperature range in the Arrhenius plots, except for a jump between 50 and 60 °C in the Arrhenius plots of the MD system (Figure 4). However, it should be noted that there was only one temperature (50 °C) well below the glass transition of the systems. A larger temperature range below and above the T_g could have revealed a better estimation of the temperature dependence of the reaction below glass transition.

The food models were divided into three groups on the basis of the reaction rates (Figure 5). The liquid water and glycerol systems exhibited significantly ($p < 0.05$) more rapid browning than the concentrated PVP and MD systems almost over the whole temperature range. Exceptions were the highest temperatures, 90 and 100 °C, followed at 280 nm, where the reaction rate of the PVP system reached that of the glycerol system and the reaction rate of the water system seemed to decrease. The similarity of the observed browning rates in the water and glycerol systems indicated that although there was a difference in the viscosities of the systems, it did not significantly affect the mobility of the reactants. There was also a possibility that in the water system the diffusion of the solvated glucose and lysine molecules occurred as clusters with surrounding water molecules, thereby reducing their mobility. The

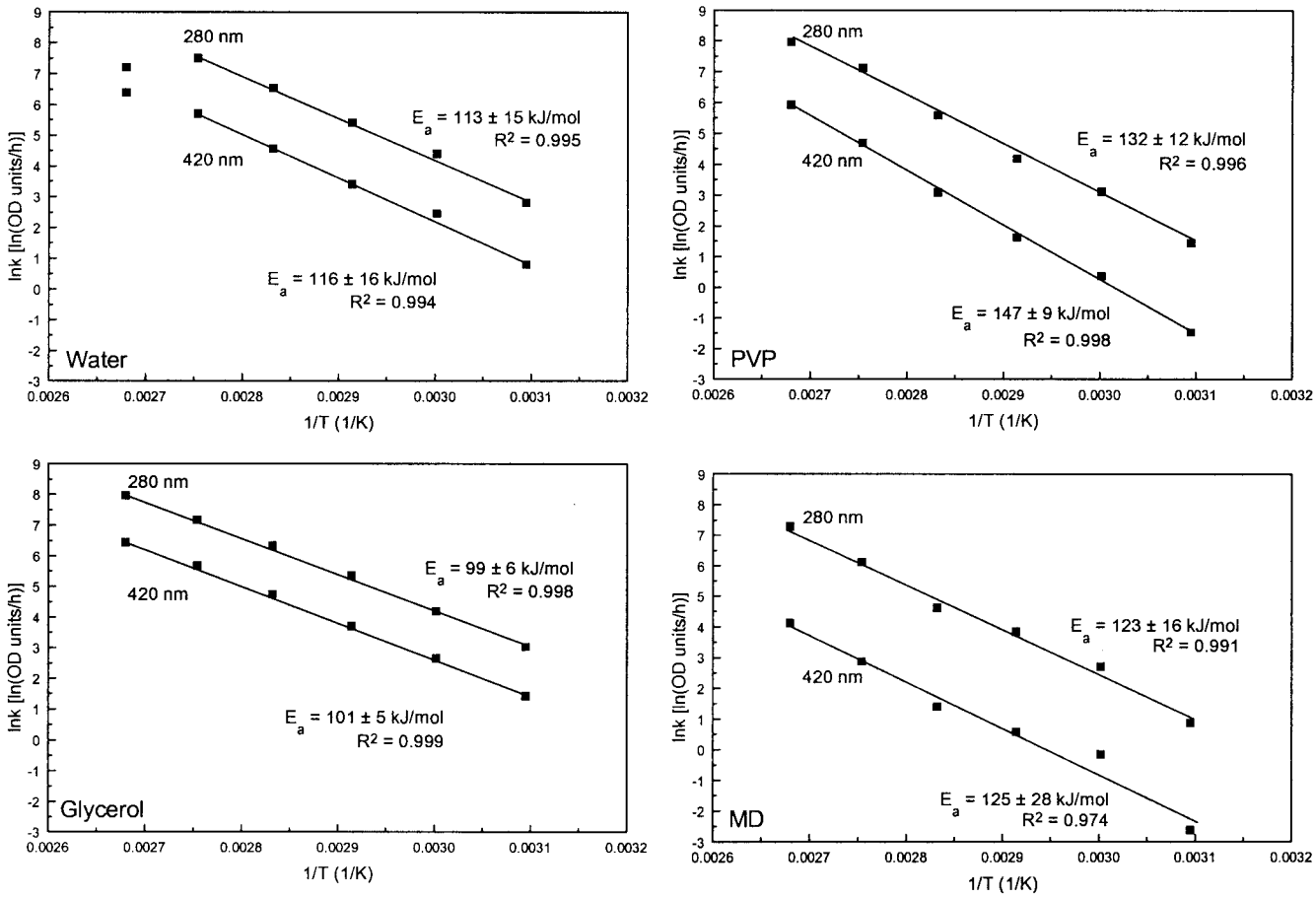

Figure 4. Arrhenius plots of the water, glycerol, PVP, and MD systems. The activation energies (E_a) with their 95% confidence limits and coefficients of determination (R^2) of the browning reaction as determined from OD at 280 and 420 nm are also shown.

pH values of the water and glycerol systems were 9.8 and 9.6 at 24 °C, respectively, which is optimal for nonenzymatic browning (Labuza and Baisier, 1992). Because of the scale in Figure 5, it seemed that the reaction rates in all four systems approached each other at the lowest temperature studied. However, when ratios of the rate constants for the reaction in the concentrated PVP and MD systems over the rate constant in the water system were compared (Figure 6), the ratio of the rate constants approached zero, as the materials became glassy. The ratios increased above the glass transition temperature range. The increase in the ratios was assumed to be at least partly a result of increasing molecular mobility and diffusion above the glass transition.

There was a statistically significant ($p < 0.05$) difference between the browning rates in the PVP and MD systems over the whole temperature range. The browning rates were low, and the difference was small at the lower temperatures. However, browning proceeded slowly also below the glass transition in both the PVP and MD systems. Similar results have been reported in several other studies, and it has been assumed that there are additional factors which influence the temperature dependence of the reaction (Karmas et al., 1992; Roos and Himberg, 1994; Buera and Karel, 1995; Bell, 1996). The reaction rates of the PVP and MD systems were notably higher above the glass transition temperature range. The browning rate in the PVP system increased rapidly above 70 °C, whereas the browning rate in the MD system increased significantly above 80 °C. However, the rapid increase in the browning rates did not occur immediately after the glass transition temperature of the systems but rather after the glass transition temperature range. The difference in the reaction rates was maintained at the higher temperatures, and it could be noted from optical density at both 280 and 420 nm (Figure 7). As the concentrations of the reactants were the same in the water phase in both systems, the difference was considered to result partly from a phase separation of the water−reactant phase in the PVP system. The models were studied using microscopy, and light and brown spots as separated areas could be observed in the PVP system, whereas the MD system exhibited a homogeneous color. According to the reaction rate results of this study, nonenzymatic browning may occur with different rates in foods based on proteins and carbohydrates, especially if the materials are kept above the glass transition temperature range.

The measured pH of the water solution containing 20% (w/w) PVP and the reactants was 7.3 at 25 °C, and the pH of the corresponding solution of MD and the reactants was 9.2 at 25 °C. There was a possibility that the difference of ~2 pH units between the PVP and MD solutions favored nonenzymatic browning in the MD system. However, the measured reaction rates suggested an opposite trend. If separate PVP and water−reactant phases were formed in the PVP system, it is possible that the pH of the water−reactant phase within the PVP matrix rose closer to the pH of the liquid water system (pH 9.8). On the other hand, it is also possible that the pH of the more homogeneous MD system decreased during the preparation of the samples, be-

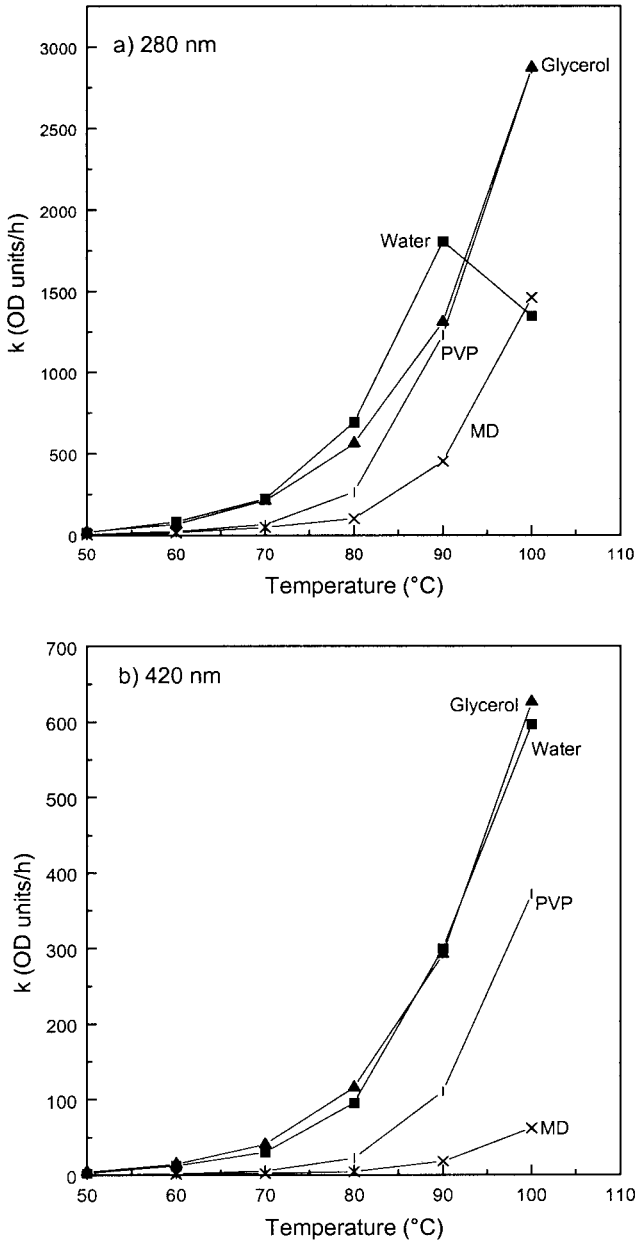

Figure 5. Rate constants of nonenzymatic browning for the water, glycerol, PVP, and MD systems as observed from increasing optical density at 280 and 420 nm.

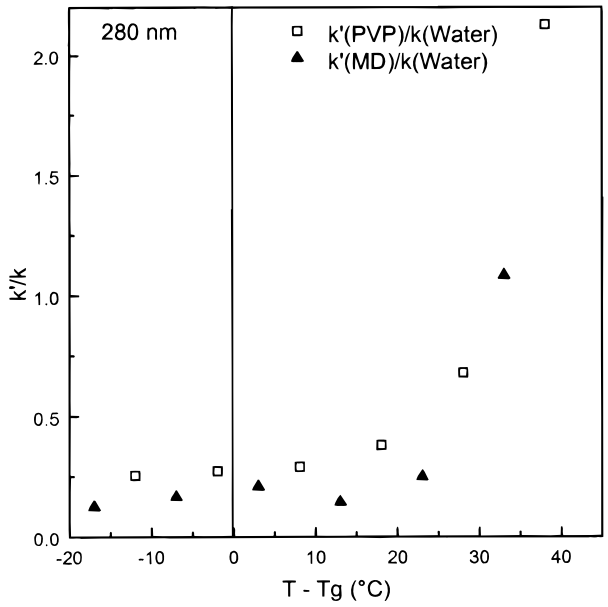

Figure 6. Effect of temperature difference ($T - T_g$) on the ratio of the rate constants in the PVP and MD systems (k') and the rate constant of the water system (k) at 280 nm.

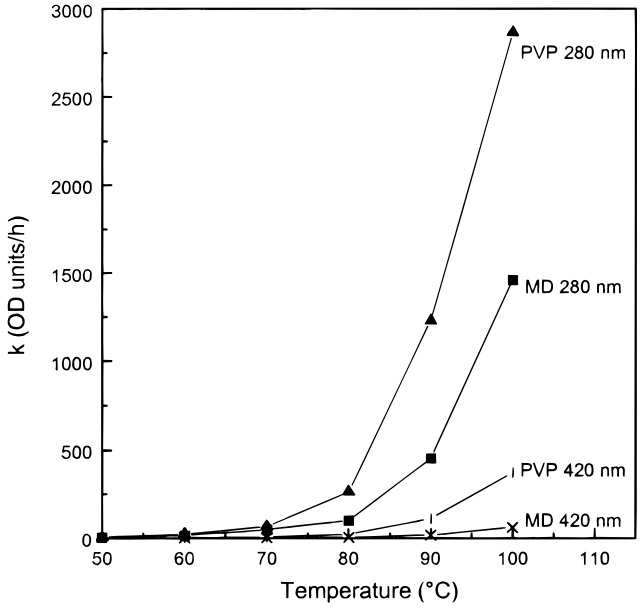

Figure 7. Rate constants for the PVP and MD systems at 280 and 420 nm as a function of temperature.

cause it has been stated that generally the pH in concentrated systems is lower than the pH of original hydrated systems (Bell and Labuza, 1992, 1994). In conclusion, the difference in pH of the initial PVP and MD solutions and a possible difference in the pH of the concentrated PVP and MD systems were probably not the significant factors to explain the difference in the reaction rates of the concentrated PVP and MD systems.

According to the present study, the decreased reaction rates in concentrated systems, especially at the lower temperatures and over the glass transition range, in comparison with the liquid systems, suggested that nonenzymatic browning was controlled by diffusion of the reactants. The significant increase in the reaction rates in the PVP and MD systems above the glass transition temperature range gave further evidence of the effects of glass transition on the rate of nonenzymatic browning. There was also a possibility that reaction rates in the PVP and MD systems differed as a result of phase separation, which may affect nonenzymatic browning rates in foods and other systems. The results of this study have potential applications in food processing and storage when time−temperature−moisture combinations are optimized to prevent deleterious changes or to allow formation of desired properties, such as color and flavor, provided by the Maillard nonenzymatic browning reaction. However, more studies are needed with systems having a high reactivity over the temperature range analyzed but suffering a glass transition within this temperature range.

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