Food Engineering Progress.
Vol. 1, No. 2, pp. 113~116 (1997)

글루코즈-라이신 마이얄반응에서의 엔탈피-엔트로피 보정관계

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Enthalpy-entropy Compensation for a Glucose-Lysine Maillard Reaction

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Abstract

To better understand compensation of the Maillard reaction associated with glucose-lysine solutions, enthalpy-entropy compensation was examined using the published data. Compensation was observed for the formation of Amadori compounds (monofructosyl lysine (MFL); difructosyl lysine (DFL)) and brown pigment (PG) in a glucose-lysine solution at different pH values (4, 5, 6, 7, and 8) at 90, 100, and 110°C. The data were analyzed using the transition state theory. Compensation existed with all isokinetic temperature (T_β) values being greater than the harmonic temperature (T_{hm}) values, indicating an enthalpy controlled reaction. These results imply that true compensation in Maillard browning reaction may occur at constant temperature as a function of pH. Two compensation relationships were developed. First, as pH increased with constant temperature, activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) values decreased. Second, as temperature increased at constant pH, $\Delta S^{\neq}$ increased. These responses may explain how $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are involved in changing the functionality of proteins as pH changes at constant tempeature and as temperatures change at constant pH, respectively. This compensation phenomena may be of considerable importance in the control of Maillard reactions in food processes.

Key words: enthalpy, entropy, Maillard reaction

Introduction

Chemical reactions play important roles in the quality of many food products. The Maillard browning reaction is one of the most important reactions in food and involves the formation of a protein-sugar complex. This reaction can produce both desirable and undesirable changes. In some foods, the reaction imparts the desired brown color associated with an acceptable appearance. The formation of the protein-sugar complex also reduces quality by reducing protein availability and leading to undesirable flavor development. Because there are positive and negative effects, it is important for the food technologist to understand the reaction and how it affects food quality.

Browning reactions are best studied by measuring the kinetics of the reaction under carefully controlled conditions. This helps quantify the factors that affect the reaction and may suggest a potential means for control.

Labuza (1980) reviewed the concepts of enthalpy-entropy compensation in food reactions. This effect, known as the isokinetic relationship, has been observed for a structurally related series of compounds undergoing a defined chemical reaction. This effect consists of enthalpy and entropy changes which compensate each other to produce minor changes in the free energy of the process. Enthalpy-entropy compensation has been observed in systems involving organic chemistry, protein/enzyme/water reactions, microbial death, and food deterioration. Labuza (1980) reported that prerequisites

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for applying the concept to food systems include data collected at a constant pH and aw (water activity) as a function of temperature, and data at a constant temperature as a function of pH or aw.

Research into the application of enthalpy-entropy compensation as it applies to other kinetic observations within food systems could prove beneficial by providing a better kinetic understanding leading to useful system design and control tools. Lumry and Erying (1954) suggested that compensation is a property of the proteins in the system and that such compensation is of major physiological importance in the stability of proteins. Also, enthalpy-entropy compensation analysis can lead to useful predictions of reaction rates and activation energies (E_a) from several conditions and could thus explain the change in Ea with a change in pH or aw without the need to postulate a change in mechanism (Labuza, 1980).

Though much research has been done on this phenomena with respect to small chemical molecules and protein denaturation, insufficient data is present to examine for compensation as it relates to occurrences common to food science. Therefore, in an effort to better understand compensation to Maillard reaction of glucose-lysine solutions, enthalpy-entropy compensation was examined.

Materials and Methods

Data of Kinetic Parameters

Using data from the work of Lee *et al.* (1984), the reaction rate constant (k) and E_a associated with the effects of temperature and pH on glucose-lysine solutions were estimated. They measured the extent of interaction by observing the change in the concentration of solutions over time, as a function of various pH values (4, 5, 6, 7, and 8) and temperature (90, 100, and 110°C). They reported on the kinetics of the formation of Amadori compounds (monofructosyl lysine (MFL); difructosyl lysine (DFL) and browning pigments (PG) with respect to temperature and pH.

Analysis of Enthalpy-entropy Compensation

The transition state theory was utilized to investigate whether enthalpy-entropy compensation in Lee's experiments occurred. The linear relationship between enthalpy (Y-axis) and entropy (X-axis) implies the existence of a unique temperature called the isokinetic temperature (T_β). At this temperature, the rate k values for all reactions of the series have the same value. The slope of the plot of entropy ($\Delta S^{\neq}$) versus enthalpy ($\Delta H^{\neq}$) yields T_β. The activated thermodynamic parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$, free energy ($\Delta G^{\neq}$), and the harmonic mean of the temperatures (T_{hm}) (Labuza, 1980) for the reaction, were calculated from the the following kinetic relationships:

$$k^{\neq}=kNh/(RT) \tag{1}$$

$$\Delta G^{\neq}=H^{\neq}-T\Delta S^{\neq}=-RT\ln k^{\neq} \tag{2}$$

$$\Delta H^{\neq}=E_a-RT \tag{3}$$

$$\Delta S^{\neq}=(\Delta H^{\neq}-\Delta G^{\neq})/T \tag{4}$$

$$T_{hm}=n/\Sigma(1/T) \tag{5}$$

where,

h=Planks constant=6.6×10^{-27} erg · sec
N=Avogadro Number (6.02×10^{23} molecules/mole)
R=Universal gas constant=8.314 J/mole°K

Results and Discussion

The k and E_a values with respect to pH and temperature are shown in Table 1 for MPL, DFL and PG as reported by Lee *et al.* (1984). The reaction of the glucose-lysine solution was shown to have pseudo-first order kinetics under conditions of excess glucose.

From Table 1, the rate of browning increased with increasing pH and temperature (T_{hm}). In general, the rate or extent of browning increases with increasing pH and temperature during processing or storage of foods (Warmbier *et al.*, 1976). They also noted that the browning rate is significantly influenced by the moisture content and the concentration of reducing sugars and free amino groups from proteins which are the primary reactants.

Regressions for $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ for each of the pH conditions noted in Table 1 for the formation of MFL, DFL and PG were made at 90, 100 and 110°C. T values and the respective correlation coefficients (R^2) are shown on Figures 1 to 3.

For most data sets, correlation coefficients were

Table 1. Effect of pH and temperature on the dissociation constant and activation energy in browning reactions (Estimated from figures in Lee *et al.*, (1984))

Temperature	MFL[1]		DFL[2]		PG[3]	
°C (K) (Thm)	k (/min)	Ea (kJ/mol)	k (/min)	Ea (kJ/mol)	k (/min)	Ea (kJ/mol)
pH4						
90(363)	0.080	35.6	-	-	0.011	75.3
100(373)	0.163	35.6	-	-	0.051	75.3
110(383)	0.360	35.6	-	-	0.220	75.3
pH5						
90(363)	0.160	33.5	0.030	48.1	0.060	41.8
100(373)	0.290	33.5	0.065	48.1	0.130	41.8
110(383)	0.430	33.5	0.150	48.1	0.270	41.8
pH6						
90(363)	0.175	25.9	0.042	34.3	0.120	30.1
100(373)	0.300	25.9	0.085	34.3	0.180	30.1
110(383)	0.450	25.9	0.165	34.3	0.310	30.1
pH7						
90 (363)	0.190	23.8	0.075	26.4	0.180	21.3
100 (373)	0.320	23.8	0.120	26.4	0.220	21.3
110 (383)	0.470	23.8	0.175	26.4	0.340	21.3
pH8						
90(363)	0.200	23.0	-	-	0.250	12.6
100(373)	0.340	23.0	-	-	0.310	12.6
110(383)	0.500	23.0	-	-	0.400	12.6

[1] MFL is a monofructosyl lysine.
[2] DFL is a difructosyl lysine.
[3] PG is a browning pigments.

found to be at or near one. Krug *et al.* (1976) noted that, if experimental error is high, the harmonic temperature (T_{hm}) is approximately equal to T_β and true compensation does not exist. In all cases of this study, no T_β values are equal to T_{hm}. The compensation plots demonstrated similar trends for each product. All T_β for MFL, DFL, and PG are much higher than for the range suggested by Lumry and Rajender (1970). They reported that the existence of a similar pattern of compensation over a wide range of protein reactions in processes involving solutes. They suggested that this compensation is due to the participation of liquid water in the protein reactions. However, Labuza (1980) noted that

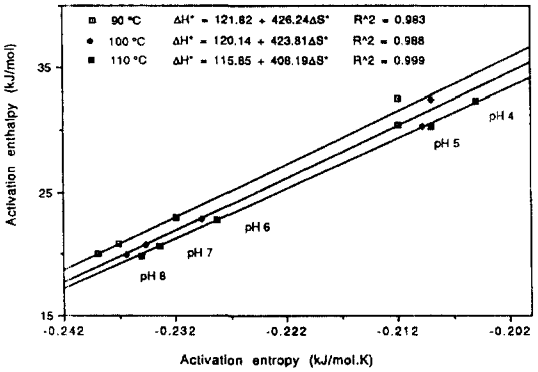

Fig. 1. Enthalpy and entropy compensation of monofructosyl lysine products (MFL). Temperatures given are T_{hm}.

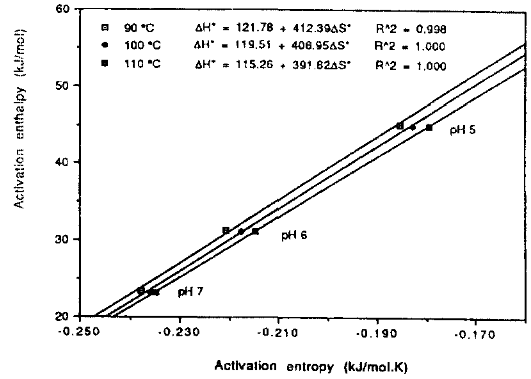

Fig. 2. Enthalpy and entropy compensation of difructosyl lysine products (DFL). Temperatures given are T_{hm}.

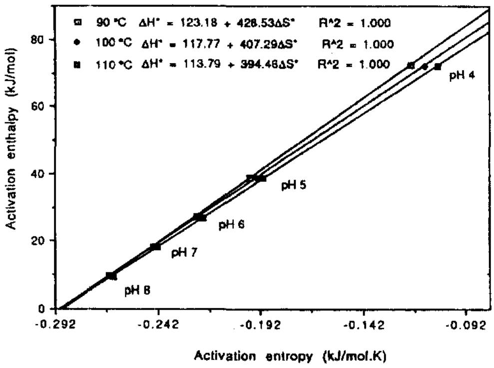

Fig. 3. Enthalpy and entropy compensation of browning pigment (PG). Temperatures given are Thm.

higher T_β values are found for higher test temperature It might be explained that a few ice-like clusters are possible in high temperatures.

Conclusions

From the Fig. 1 to 3, two points are evident. First, there is a relationship between pH of formation and enthalpy and entropy of activation. With increased pH, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values decreased. The same trend existed for ascorbic acid (Labuza, 1980). The effect of high pH on Maillard browning is significant (Whisler and Daniel, 1985). Under high pH conditions, the Maillard reaction is activated. The compensation plots could be attributed to help to yield a general mechanism, i.e. changing charges on the protein may lead to a change in the Maillard reaction. The meaning of lower $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values may be due to the breaking of fewer bonds during the dissociation, or the making of more bonds during formation, of the activated complex. With high pH levels, the bonds between protein (lysine) and sugar (glucose) are more easily formed, i.e. glycosylamine formation is more highly activated.

Second, as T_{hm} increased T_β decreased. According to Leffler (1955) when $T_\beta > T_{hm}$ the reaction is enthalpy controlled and when $T_\beta < T_{hm}$ the reaction is entropy controlled. By Leffler's definition, all reactions are enthalpy controlled. However, using a formula (as for T_β-T_{hm}), the relative effectiveness of enthalpy controlled may be listed as: 90°C> 100°C> 110°C. The order will be decreased the enthalpy controlled.

These two points may be considerable importance in understanding changes in functionality of protein and/or sugar as a function of pH and temperature, and may help control the Maillard reaction in food processes. For example, if reactions are enthalpy controlled and/or low $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values in a food system result, control of the Marllard reaction may be possible by altering the temperature and pH conditions.

Table 2. Isokinetic temperatures and correlation coefficients for compensation behavior in browning reactions

Temperature	MFL[1]		DFL[2]		PG[3]	
°C (K)	R^2	T	R^2	T_β	R^2	T_β
90(363)	0.983	426.24	0.998	412.39	1.000	428.53
100(373)	0.988	423.81	1.000	423.81	1.000	407.29
110(383)	0.999	408.19	1.000	408.19	1.000	394.46

[1] MFL is a monofructosyl lysine.
[2] DFL is a difructosyl lysine.
[3] PG is a browning pigments.

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