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Influence of temperature, electrical conductivity, power and pH on ascorbic acid degradation kinetics during ohmic heating using stainless steel electrodes

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Abstract

Degradation kinetics of ascorbic acid was determined in pH 5.7 buffer solution using an isothermal batch ohmic heater with stainless steel electrodes. Variables included in this study were temperature (40, 60 and 80 °C); power (0, 100,150 and 300 W); and electrical conductivity (varied using 0.25%, 0.5% and 1.0% NaCl). Ascorbic acid concentration was detected by using a HPLC technique. The results indicate that ascorbic acid degradation can be described successfully by a first order model during both conventional and ohmic heating. The Arrhenius relation showed negative values for temperature coefficient (E_T) during most ohmic treatments, due to a combination of factors that may alter the reaction mechanism. In particular, it appears that at a given power level, higher electric field strengths are conducive to increased incidence of faradaic reactions. Increasing NaCl concentration appears to significantly influence reaction rates via its influence on dissolved oxygen, and through its participation in electrolytic reactions. Contrary to expectations, increasing temperature tended to significantly reduce reaction rate, likely due to decreased dissolved oxygen concentration at high temperature. The results indicate the importance of using inert electrodes in ohmic heating processes.

Keywords: Ohmic heating; Ascorbic acid; Degradation kinetics; Stainless steel electrodes

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1. Introduction

Electrical and electrothermal methods for processing food and biomaterials have attracted much recent attention in industry [1–5]. Methods include microwave and ohmic heating, and pulsed electric field processing. The latter two processes require contact between electrodes and the processed material. It is accordingly of interest to determine whether various bioactive components such as antioxidants degrade differently by such methods of processing. We focus in this study on ascorbic acid in a buffer medium at pH 5.7, which falls in the range of many low-acid foods that support the growth of pathogenic sporeforming bacteria.

Variation of the salt concentration, buffer pH, and applied electrical power during ohmic heating may alter the reaction kinetics of ascorbic acid. The pH level of the reaction environment is considered to be one of the most important factors that influence the degradation rate. It has been reported that the rate under anaerobic conditions reaches a maximum at pH 4.1, which is the pK_1 of ascorbic acid [6]. On the other hand [7], the degradation rate profile for uncatalyzed oxidation has an s-shaped curve that increases continuously through the pH corresponding to the dissociation level 4.1, and then flattens out above pH 6. Eison-Perchonok and Downes [8] reported that oxidation of ascorbic acid at pH 6.1 was dependent on the concentration of dissolved oxygen.

In addition, pH is an important factor in electrode corrosion and electrolytic reactions [9–11]. In particular, the anodic and cathodic half-reactions of electrolysis have strong pH dependence.

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Anodic half-reaction

$$2H_2O_{(l)} \leftrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e. \quad (1)$$

Cathodic half-reactions

$$2H^+_{(aq)} + 2e \leftrightarrow H_{2(g)}. \quad (2)$$

$$2H_2O_{(l)} + 2e \leftrightarrow H_2(g) + 2OH^-_{(aq)}. \quad (3)$$

Overall reaction

$$2H_2O_{(l)} + 2e \leftrightarrow 2H_{2(g)} + O_{2(g)}. \quad (4)$$

Our previous study [12] describes the influence of corrosion and electrolysis on the degradation of ascorbic acid at pH 3.5. Changing the pH of the environment may well yield different degradation kinetics, and provides the rationale for this investigation.

The specific objectives of this study were: (1) to determine the effect of ohmic heating, using stainless steel electrodes, on the degradation kinetics of ascorbic acid at pH 5.7 as compared with conventional heating; (2) to investigate the effects of environmental (temperature, field strength) and compositional (NaCl concentration) factors on the degradation rate; and (3) to compare the effects of buffer pH (3.5 and 5.7) on the degradation rate.

2. Materials and methods

The present experiment was performed in a batch-isothermal ohmic heater with stainless steel electrodes as described in detail in the study by Assiry et al. [12]. The buffer solution was adjusted at pH 5.7±0.30 using double distilled water buffered with citric acid (0.04306%), and dibasic sodium phosphate (0.239%). The electrical conductivity of the buffer solution was varied using 0.25%, 0.5% and 1.0% sodium chloride. While the experimental setup and procedure were described by Assiry et al. [12], we present an abbreviated description herein. Samples were treated within a test chamber illustrated in Fig. 1, wherein the electrode geometry and configuration is illustrated. The jacket was used to circulate controlled temperature liquid. For conventional treatments, temperature control was accomplished entirely using the jacket, since no electric field was applied between the electrodes. For ohmic heating treatments, a 60 Hz. alternating electric field was applied across the electrodes, consequently the jacket fluid was used as a coolant for temperature control. In both cases, conventional or ohmic, the buffer was heated to a steady set-point temperature, and 1 ml of 8% L-ascorbic acid solution was injected into the sample chamber. At least five samples were withdrawn at various time intervals and their ascorbic acid concentrations determined using a HPLC technique. The variables and levels of study are summarized in Table 1. Then the pseudo-first order rate constant for degradation (k) was obtained by performing a linear regression on the $\ln(C_0/C)$ versus t data. The dependence of k on key variables (temperature, electric field strength and NaCl concentration) was determined. Finally, the results of the present study at pH 5.7 were compared with that obtained previously [12], at pH 3.5.

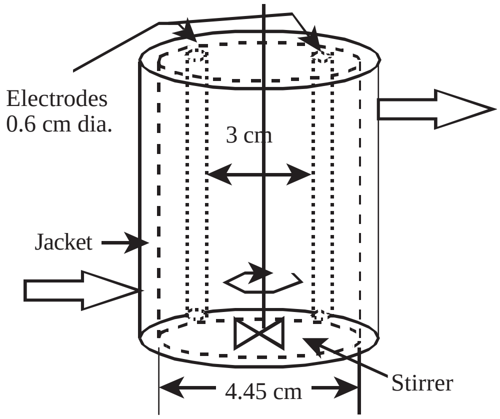

Fig. 1. Schematic diagram of experimental setup showing the configuration and shape of electrodes within the test chamber.

Table 1
Summary of investigated experimental variables

Power (W)	Temperature (°C)		
	40	60	80
	%NaCl		
0	0.25, 0.5, 1	0.25, 0.5, 1	0.25, 0.5, 1
100	0.25, 0.5, 1	0.25, 0.5, 1	0.25, 0.5, 1
150	0.25, 0.5, 1	0.25, 0.5, 1	0.25, 0.5, 1
300	–	–	0.25, 0.5, 1

All tests conducted in duplicate.

3. Results and discussion

3.1. Reaction rate order

Example results for the degradation of ascorbic acid are represented in Fig. 2. These data fitted the first order degradation rate model well, as did the degradation data for all experimental variables. The average data for treatments treated in the same manner are summarized in Table 2.

As in our previous study [12], it was observed that during ohmic treatments there was an increase of about 17% in the pH of the buffer solution, from the initial level 5.7. Generally, increasing the voltage and/or the NaCl concentration resulted in higher pH. This increase in the pH can be related to loss of buffering capacity due to metal-citrate complexation, as described by Assiry et al. [12]. Generally, however R^2 was still acceptable (average $R^2=0.93\pm0.04$), and first order model can be used to describe the degradation during ohmic heating.

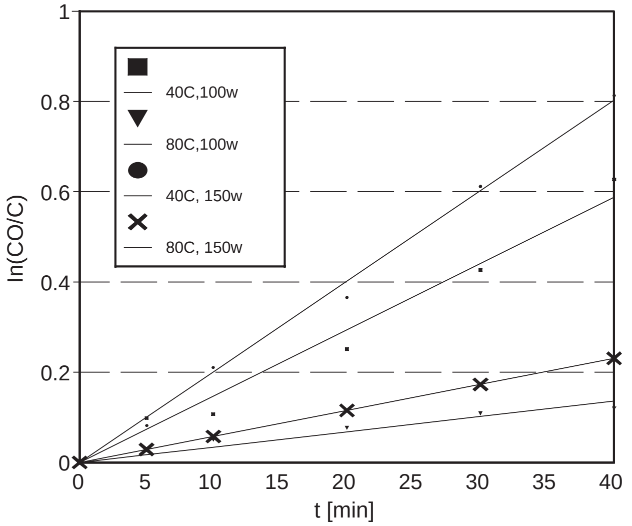

Fig. 2. Sample of actual data fitted by first order model at 80 °C and 1% NaCl.

3.2. Effect of temperature

The relationships among temperature, power and reaction rate can be represented by Arrhenius plots in Figs. 3 and 4 at 0.5% and 1.0% NaCl respectively. During ohmic heating, the effect of power and temperature on the rate of ascorbic acid degradation appears to be interdependent and follow unexpected patterns. As the temperature increased from 40 to 80 °C, the reaction rate declined. By using the Arrhenius equation [$\ln(k)=\ln(k_0)-E_T/RT$], the temperature coefficient (E_T) and the frequency factor (k_0) were determined by a linear regression for each set of data and are expressed in Table 3. The values obtained for the temperature coefficient and frequency factor at 0.5% and 100 W indicate a shift in the reaction mechanism [13], in which no straight regression line was possible (low R^2). To understand some of these trends further, we consider the influence of a number of factors.

Table 2
Summary of the experimental results, at pH 5.7, and by using an ohmic heater with uncoated stainless steel electrodes

NaCl (%)	T (°C)	I (Amp)	V (Volt)	k (1/min)	R^2
0.25	79.77	0	0	0.0054	0.95
	80.64	3.43	28.63	0.00324	0.89
	80.06	4.26	34.63	0.00293	0.95
	80.74	6.04	49.09	0.01432	0.94
0.5	39.63	0	0	0.008560	0.96
	59.45	0	0	0.009630	0.98
	79.56	0	0	0.010214	0.98
	39.93	2.84	35.66	0.006930	0.93
	59.49	3.33	30.79	0.009840	0.95
	79.50	3.71	27.28	0.007720	0.90
	39.86	3.51	43.64	0.027149	0.98
	59.46	4.03	37.75	0.009020	0.93
	79.26	4.56	33.47	0.005400	0.95
	80.11	6.25	46.24	0.006120	0.93
1	40.25	0	0	0.005220	0.97
	60.11	0	0	0.006480	0.96
	80.43	0	0	0.007500	0.95
	40.35	3.69	27.88	0.016088	0.93
	60.54	4.31	23.97	0.011264	0.83
	80.31	4.87	21.64	0.005270	0.93
	40.38	4.68	33.61	0.018433	0.99
	60.43	5.25	29.33	0.005900	0.89
	80.65	6.13	25.6	0.004530	0.84
	80.75	8.82	34.44	0.002910	0.88

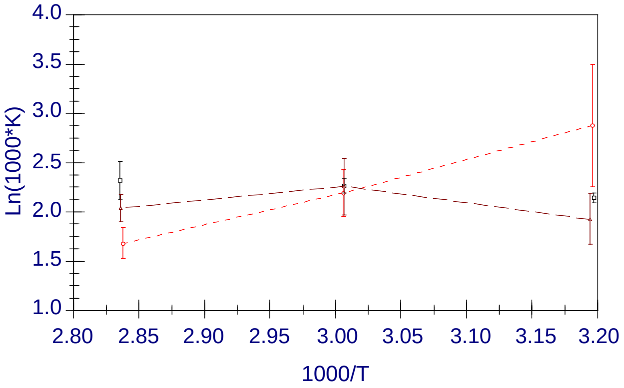

Fig. 3. Arrhenius relation at 0.5% NaCl, $P0$=conventional, $P1=100$ W, $P2=150$ W. Temperature (T) is in °K.

3.3. Effect of electrical conductivity

The electrical conductivity of the solution ranged from 6.2 mS/cm up to about 19 mS/cm depending on the temperature level and NaCl content of the buffer solution. Eq. (1) describes the significant dependence of the electrical conductivity on temperature and NaCl content ($R^2=0.95$ and $p<0.005$);

$$\sigma = -7.05 + 0.164T + 11.6[\mathrm{NaCl}]. \tag{5}$$

A plot (Fig. 5) of rate constant versus electrical conductivity at various power levels and salt concentrations shows the following basic trends. In general, the degradation rate decreases with increasing electrical conductivity (which is linearly related to temperature and salt content). Temperature normally tends to accelerate, rather than

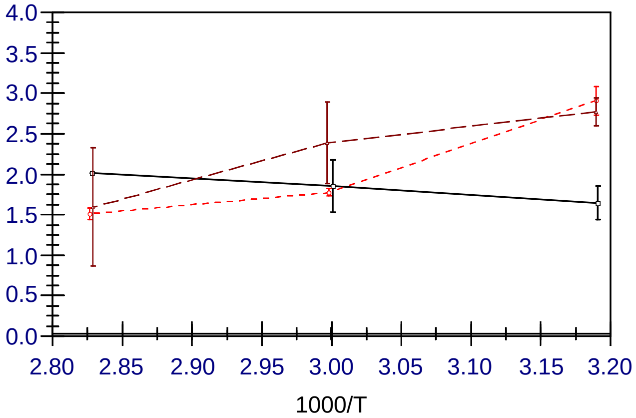

Fig. 4. Arrhenius relation at 1.0% NaCl, $P0$=conventional, $P1=100$ W, $P2=150$ W. Temperature (T) is in K.

Table 3
The frequency factor (k_0) and the temperature coefficient (E_T) of both conventional and ohmic heating for temperature range 40–80 °C, at pH 5.7 and using uncoated stainless steel electrodes

P (W)	NaCl (%)	k_0 (1/min)	E_T (KJ/mole)	R^2
0	0.5	3.972×10^{-2}	3.970	0.97
0	1.0	0.133×10^{-2}	8.446	0.99
100	0.5	2.180×10^{-2}	2.783	0.13
100	1.0	5.661×10^{-7}	−26.916	0.94
150	0.5	3.875×10^{-7}	−27.889	0.99
150	1.0	64.90×10^{-7}	−32.394	0.91

decelerate ascorbic acid degradation. Thus it would appear that the observed trends may be partially traceable to salt content.

3.4. Effect of electric field strength

A plot (Fig. 6) of reaction rate constant against electric field strength (applied voltage), yields some general trends and observations:

1. For the same power level, the reaction rate increases with decreasing temperature (with one exception; 100W, 0.5% NaCl, 40 °C).
2. For the same power level, the reaction rate increases with field strength (applied voltage).
3. Temperature and voltage are not independently controllable in this experiment. At a given power level and temperature, the field strength may be increased only if the electrical conductivity of the medium is decreased (thereby reducing current flow) to keep power constant. Electrical conductivity may be changed either by changing temperature or NaCl concentration.

From the above, it appears that electric field strength has an accelerating effect on reaction rate, which more than compensates for the effect of the reduced temperature needed to maintain the same power level. The effects of electric field strength may be further explained by considering faradaic reactions at the electrodes. Venkatesh et al. [14] and Lalvani et al. [15] reported that faradaic current increases with the amplitude of the applied voltage signal. Since the interfacial potential achieved across the electrode is proportional to the peak voltage amplitude, the faradaic current and thereby rates of faradaic reactions, increase with increasing voltage. At low NaCl concentration, molecular oxygen generated by electrolysis (Eq. (4)) can cause oxidation of ascorbic acid. However, at high NaCl concentration, the following anodic half-reaction (Eq. (6)) hinders oxygen generation (Eq. (1)) resulting in a lower degradation rate.

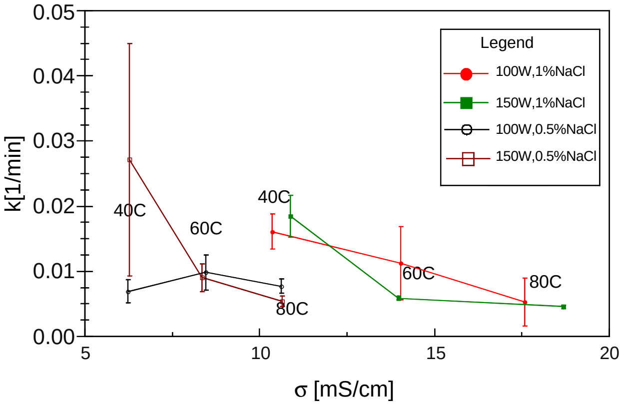

Fig. 5. Degradation rate constant (k) as influenced by electrical conductivity (σ), NaCl concentration and power.

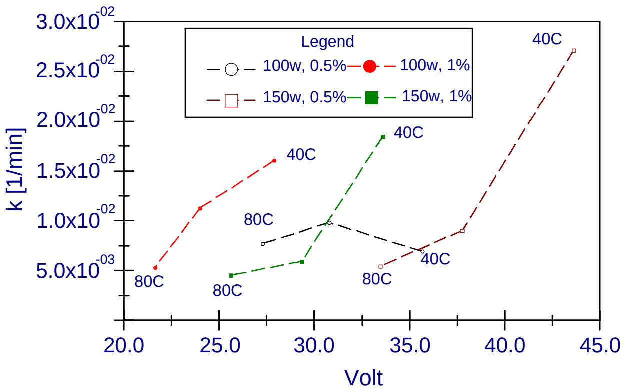

Fig. 6. Effect of applied voltage on the rate constant for degradation.

$$2Cl^-_{(aq)} \leftrightarrow Cl_{2(g)} + 2e. \tag{6}$$

Dissolved oxygen in the system apparently caused greater degradation at 40 °C, compared to 80 °C, where lesser amounts of dissolved oxygen exist with increasing temperature. It should be pointed out that the effect of voltage on the degradation rate at 0.5% and at 100 W was not significant. The reason for this effect was not clear.

3.5. Effect of salt concentration

In this section, discussion will be limited to the degradation rate at a constant value of temperature (80 °C). Fig. 7 illustrates the effect of conventional heating (P=0 W), and the applied electrical power on the degradation rate

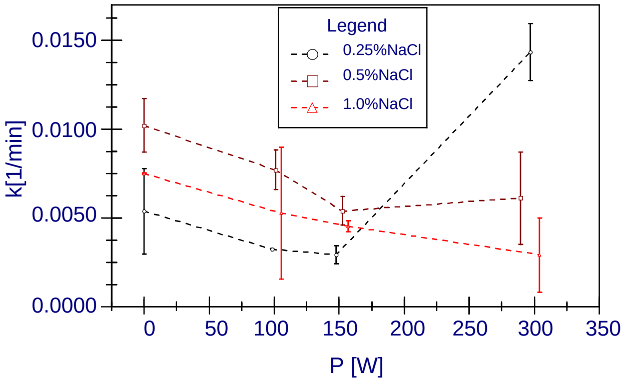

Fig. 7. Effect of power on the rate constant for degradation at constant temperature (80 °C).

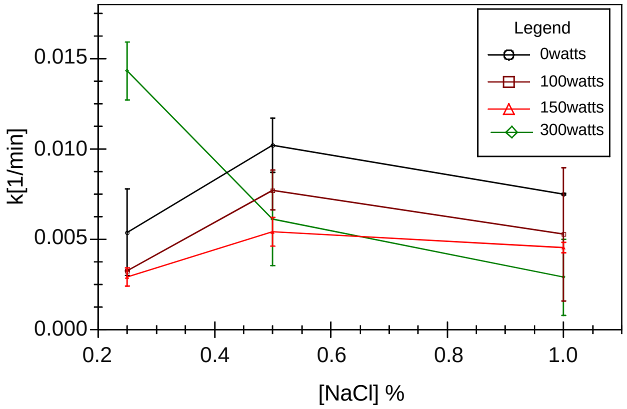

Fig. 8. Influence of NaCl concentration on the degradation constant during conventional and ohmic treatments at constant temperature (80 °C).

at different NaCl concentrations. During conventional heating, it was evident that NaCl content influenced the degradation rate. Indeed, during conventional heating, the degradation rate at 1% NaCl was significantly less than that at 0.5% NaCl. In addition, the effect of NaCl concentration on the degradation rate seemed to have a tendency illustrated in Fig. 8. With one exception, the degradation rate increased, and then decreased as the NaCl concentration increased from 0.25% to 1%. It can be suspected that such a pattern might indicate that at least two factors were involved in the reaction process with opposing effects on the degradation rate of ascorbic acid. A possible reason for that pattern can be explained by considering, first the catalytic effect of the NaCl on ascorbic acid oxidation. It has been reported that increasing ionic strength of a solution has a possible catalytic impact on ascorbic acid oxidation [16,17]. Second, the dissolved oxygen in the buffer solution can promote the oxidation of ascorbic acid during heating. It is likely that the oxygen solubility decreases by increasing the NaCl concentration. For example, it has been reported that oxygen solubility decreases in the presence of sugar solution at constant temperature and affects the degradation rate of ascorbic acid [17]. Also, at higher temperature (80 °C), it is expected that the solubility of oxygen is small since the solubility of oxygen in pure water decreases with increasing temperature until it reaches zero at 100 °C. Ascorbic acid degradation at low NaCl appears to be due in part to the expected dissolved oxygen in the buffer solution, however at high NaCl, the degradation may have been due mainly to the catalytic effect of NaCl. In the case of high power (300 W) and low NaCl (0.25%) enhanced electrolysis and thereby more dissolved oxygen in the system can lead to a high degradation rate.

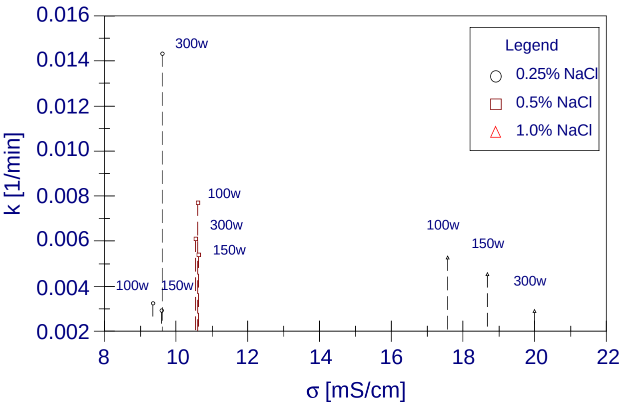

Fig. 9. Rate constant for degradation versus electrical conductivity (σ) as influenced by applied power and NaCl concentration at constant temperature (80 °C).

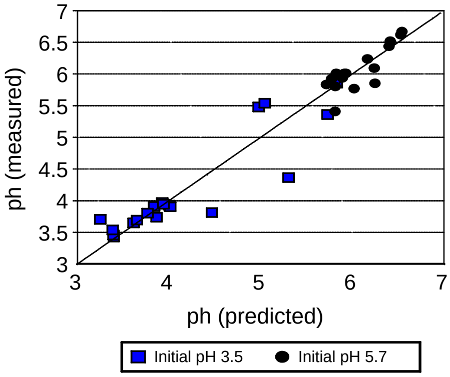

Fig. 10. The actual pH values versus the predicted values for both buffer systems (starting pH 3.5 and 5.7). Model: $\text{pH}=3.49-0.00566\ \sigma^2+2.99\ [\text{NaCl}]^2$.

Furthermore, a decreasing trend of the degradation rate can be observed in general, in Fig. 7, as the power increased except at 300 W and 0.25% NaCl, which shows a significantly higher degradation rate. At constant NaCl concentration, degradation rate decreased with increasing power, but no significant difference was noted between conventional and ohmic heating except at those conditions of high power and low NaCl concentration. This decreasing trend may be due to various effects, including slow rate of oxygen generation, and poor oxygen solubility in the system at higher NaCl concentrations.

Under the conditions of constant temperature and NaCl, electrical conductivity is expected to be constant. But results shown in Fig. 9, at 80 °C and 1% NaCl, indicated that as the power increased, a statistically significant (at 95% CI) increase (about 1 mS/cm) in the electrical conductivity was

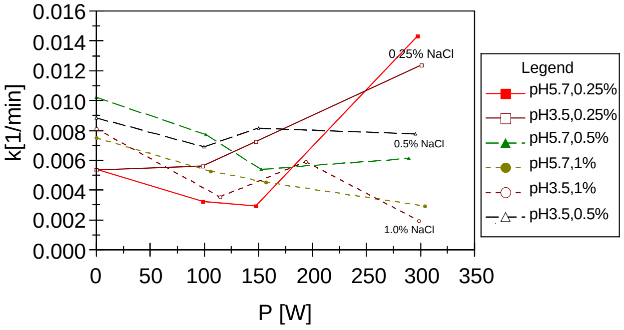

Fig. 11. The effect of power and NaCl concentration on the rate constant for degradation at pH 3.5 and pH 5.7, and at constant temperature (80 °C).

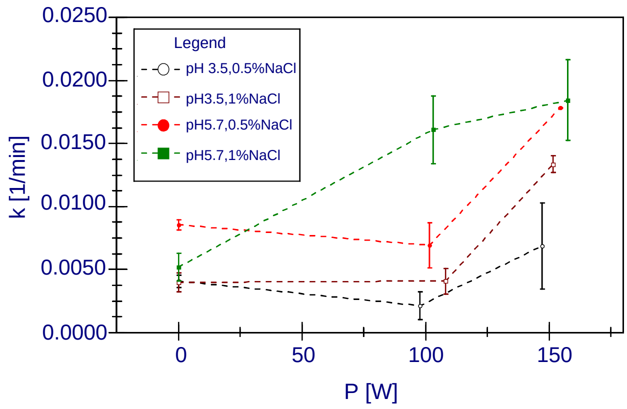

Fig. 12. The effect of power and NaCl concentration on the rate constant for degradation at pH 3.5 and pH 5.7 and at constant temperature (40 °C).

observed. This is an indication of the increase of ionic species in the system. The ionic species can be formed by electrode corrosion, and degradation of ascorbic acid as well as the buffer components [12].

3.6. Effect of pH

In light of the experimental results that have been obtained by Assiry et al. [12] (at pH 3.5) and the results of the present study (at pH 5.7), the following remarks may be made:

1. During ohmic heating treatments, the pH of the buffer solution, during some treatments, increased by as much as 70% when the starting pH was 3.5 and by as much as 17% when the starting pH was 5.7 as illustrated in Fig. 10. The reason for the change in pH has been attributed by Assiry et al. [12] to loss of buffering capacity due to metal-citrate complexation arising from electrode reactions. The lesser increase at pH 5.7 suggests that the rates of these reactions apparently decreased with increasing pH.
2. At high temperature (80 °C) no significant difference was observed between both buffer systems in terms of the degradation rate, as shown in Fig. 11. However, for both pH 3.5 and 5.7 buffers at 300 W, *k* significantly decreased by increasing NaCl concentration from 0.25 to 1%.
3. For both (pH 3.5 and 5.7) buffers at high temperature (80 °C), degradation rate under ohmic heating was not different from that under conventional except at 300 W and 0.25% NaCl, at which condition, degradation rate was significantly higher.
4. At low temperature (40 °C), as shown in Fig. 12, degradation rate at pH 5.7 was significantly higher than that at pH 3.5 during both conventional and ohmic heating. This enhanced degradation at pH 5.7 may be attributed to the increasing dissociation of ascorbic acid with increasing pH. The dissociated (anionic) form of ascorbic acid is more susceptible to degradation than the undissociated form.
5. In both buffer systems, the results indicate the importance of controlling faradaic reactions at the electrodes.

4. Conclusions

Ascorbic acid degradation in a pH 5.7 buffer system may be described by a first order model during conventional and ohmic heating treatments. The Arrhenius relation for ohmic heating treatments showed negative values for the temperature coefficient. At the same power level, degradation rate constants tended to increase with increasing field strength (applied voltage). This is consistent with known trends pertaining to the effect of field strength on faradaic reactions. Further, the combination of NaCl concentration and temperature (both of which influence dissolved oxygen concentration) cause decreased reaction rates at high temperature. Buffer capacity loss at pH 5.7 was significant but not as pronounced as at pH 3.5.

Symbols

σ	electrical conductivity (mS/cm)
CI	confidence interval
E_T	temperature coefficient (kJ/mole)
I	current (A)
k	rate constant for ascorbic acid degradation (min^{-1})
k_0	frequency factor (min^{-1})
k_c	ohmic heater (cell) constant=0.078 cm^{-1}
P	electrical power (W)
R	ideal gas law constant=8.3143 (kJ/mol.K)
R^2	coefficient of determination
T	temperature (°C)
V	Voltage (V)
[NaCl]	Sodium chloride concentration (g/100 ml)

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