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Diffusion of KCl in an amylose film

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Abstract

A method has been developed measuring the diffusion coefficient of KCl in amylose films. The films were soaked in potassium chloride solutions, then immersed in pure water and conductivity measured as a function of time. Different concentrations of the soaking solution were used and the measurements were made at several temperatures. The diffusion coefficient of KCl was found to be independent of the soaking solution KCl concentration, but found to increase with increasing temperature. The diffusion coefficient values were about one quarter of those found in water and varied from 4.8×10^{-10} to 11×10^{-10} $m^2\ s^{-1}$. The activation energy of diffusion was close to that found in water. Two values for the activation energy were obtained, 20.1 and 14 kJ mol^{-1}, indicating a change in the film structure at 45 °C. Amylose films swelled equally in KCl-solutions and water. The thickness of amylose films doubled and the increase in mass was 100–200% corresponding the decrease of amylose content from about 87 to 37%, when the conditions changed from normal humidity conditions to water.

Keywords: Amylose film; Diffusion; Swelling

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1. Introduction

Starch polysaccharides are based on 1–4 linked α-D-glucose chains, and amylose is the essentially linear starch polysaccharide. Amylose is known to produce good quality films, but reported applications are scarce (Langlois & Wagoner, 1967). Early and some recent studies have shown that under dry or moderate humidities amylose films are mechanically strong and exhibit good gas barrier properties. However, these properties are lost when the films are exposed to high humidity or plasticised with polyols such as glycerol (Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; Loudrin, Della Valle, & Colonna, 1995; Rankin, Wolff, Davis, & Rist, 1958; Wolff, Davis, Cluskey, Gundrum, & Rist, 1951). Furthermore, amylose films do not fragment or dissolve in water below 100 °C, and they have been observed to show resistance to gastric juices (Cairns, Sun, Morris, & Ring, 1995; Myllärinen, Buleon, Lahtinen, & Forssell, 2002; Parker & Ring, 2001).

In spite of their useful properties amylose films absorb water under aqueous conditions, leading to swelling and a more porous structure. This affects the functionality of the amylose films, especially to diffusion of molecules, as was noted during the development of amylose-based materials for controlled drug release (Milojevic et al., 1995). Leloup and co-workers (Leloup, Colonna, & Ring, 1990) examined the porosity of amylose gel networks by investigating gel accessibility to certain probe species, and by studying diffusion of bovine serum albumin within the gel. The amylose concentration in the gel was varied from 2 to 10%. The results demonstrated that accessibility depended on the hydrodynamic radius of the probe molecule, and that increases of the amylose concentration decreased significantly the accessibility of the gel to bovine serum albumin.

The importance of swelling has also been noted when developing drug delivery systems from cross-linked amylose maize starches (Moussa, Lenaerts, & Cartilier, 1998). The process of water transport into hydrophilic polymer matrices, and the corresponding changes in dimension that occur, have a major influence on the profile of drug release from these matrices. When swelling kinetics were studied the swelling capacity was observed to decrease with increasing NaCl concentration, but swelling profiles were found to be independent of pH in the range of 1.4–8.

This study describes an experimental technique for analysing the diffusion of electrolytes in a solid gel-like

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material immersed in water. The method has been applied to determine the diffusion coefficient of KCl in amylose films, with the main aim of obtaining a better understanding of the structure of amylose films and their transport properties under aqueous conditions.

2. Experimental

Film preparation: Amylose was purchased from Sigma Chemical Co. Ethanol from Primalco was used as complexing agent and water was ultrapure (18.2 MΩ). 10% amylose–water dispersions were prepared by mixing amylose with ethanol and water (ethanol to water ratio was about 20/80 vol/vol). The mixture was placed in a pressure cooker and temperature was raised to 130 °C with simultaneous stirring. The temperature was immediately decreased to 95 °C, and the mixture stirred for about 30 min in order to evaporate the alcohol. The hot solution was poured onto PTFE moulds, which were dried in a controlled environmental chamber at 70 or 80 °C and at relative humidity (RH) of 50%. The films were peeled off and placed in the chamber (RH 97%) for couple of days after which small round pieces with a diameter of 12 mm were removed with a cork bore. The thickness of the pieces was measured with a micrometer (Mitutoyo) at five points of the film. The thickness was measured immediately after cutting and then prior and after the diffusion experiment. The diameters of the samples were also measured. The film thickness values were confirmed by weighting the film samples. A density value of 1.2 g cm^{-3} was used for starch (Fish, 1957).

Diffusion measurement: Film pieces, which had been stored at a RH of 50% for several days, were immersed in aqueous KCl solutions of known concentration for at least 24 h before the diffusion experiment. The KCl concentrations used were 0.1, 0.2, 0.5, 1, 2, 3 and 4 mol dm^{-3}, and the soaking procedure was performed at room temperature.

Diffusion of KCl from the film was measured by monitoring the conductance of the water in which the KCl-containing amylose films were immersed. Diffusion experiments were performed at constant temperature over the range from 25 to 65 °C. Ultrapure water was weighed (650 g) in to the thermostated vessel and the temperature was allowed to equilibrate for 30 min. During the measurement the water was stirred vigorously with a magnetic stirrer. Five film-pieces were added to water and the conductance was measured over a time period of 30 min at 15 s intervals. For the conductance measurements a WTW LF323 conductivity meter with a standard conductivity cell WT-325 was used. The conductivity meter was connected to a computer via an AD converter and a QuickBasic program was written and used for data collection.

Calculation of diffusion coefficient: Typical results of the diffusion experiment are presented in Fig. 1, which shows the measured conductivity as a function of time. κ_0 represents the conductivity of KCl originating from the small amount of KCl solution on the surface of the film-pieces. κ_∞ represents the conductivity originating from both the surface KCl solution and KCl from inside the amylose film. A piece of an amylose film is a flat plate with a diameter 30 times, or more, of thickness. The KCl concentration in the piece of the film is initially uniform and the surface concentrations on both sides of the plate are equal. According to Crank (1975) the amount of KCl diffusing out from the amylose plate is given by Eq. (1).

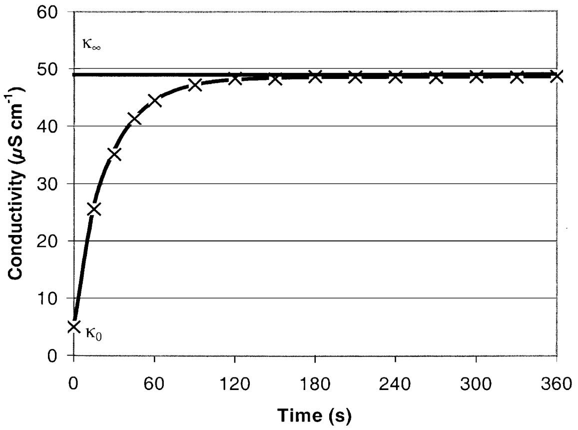

Fig. 1. Measured (×) and calculated (full line) conductivity of water in a diffusion experiment. κ_0 is the conductivity of water solution just after the beginning of diffusion experiment and κ_∞ is the conductivity of solution when all the KCl has diffused out from the plates.

$$\frac{n(t)}{n_{\mathrm{tot}}} = 1 - \sum_{i=0}^{\infty} \frac{8}{(2i+1)^2\pi^2} \exp\left\{ \frac{-D(2i+1)^2\pi^2 t}{L^2} \right\} \qquad (1)$$

where t is time, $n(t)$ is the amount of KCl diffused out from the plate at time t, n_{tot} is total amount of KCl inside the plate at the beginning of the experiment, D is the diffusion coefficient of KCl inside the plate, and L is thickness of the plate. The conductivity of the solution, κ, can be calculated from Eq. (2).

$$\kappa(t) = \kappa_0 + (\kappa_\infty - \kappa_0) \times \left[1 - \sum_{i=0}^{\infty} \frac{8}{(2i+1)^2\pi^2} \exp\left\{ -\frac{D(2i+1)^2\pi^2 t}{L^2} \right\} \right] \qquad (2)$$

Here $\kappa(t)$ is the conductivity of the solution at time t, κ_0 is the conductivity of the solution at the beginning of the diffusion experiment, and κ_∞ is the conductivity of the solution when all of the KCl has diffused out from the plates. When using Eq. (2) the conductivity and quantity of KCl (n) should be linearly related. This is true when the conductivity remains very low during the whole experiment, which was the case found in the present study. In practice the constants κ_0, κ_∞ and D are adjustable parameters, which can be fitted to the experimental data ($\kappa = f(t)$).

Analysis of KCl content in film: The quantity of absorbed electrolyte in the amylose film can be calculated from the conductivity data. The equivalent conductivity of a strong electrolyte (Λ) is expressed as

$$\Lambda = \frac{\kappa}{c} \tag{3}$$

where κ is conductivity and c is the ionic concentration. The equivalent conductivity depends slightly on concentration

$$\Lambda = \Lambda_0\left[1 - a\left(\frac{c}{c^0}\right)^{\frac{1}{2}} + b\left(\frac{c}{c^0}\right)\right] \tag{4}$$

Λ_0 is the limiting equivalent conductivity at infinite dilution and a and b are electrolyte dependent constants. Eq. (4) is valid for strong electrolytes up to concentrations of 0.01 mol dm^{-3}. For aqueous KCl, when the temperature is in the range of 0–100 °C, the parameters a and b are in the range of 0.58–0.74 and 0.64–0.40, respectively (Parsons, 1959). At low concentrations ($<1.5 \times 10^{-3}$ mol dm^{-3}) the assumption $\Lambda \approx \Lambda_0$ can be made producing only few percent deviation from the correct value. Thus, if $V_{H_2}O$ is the volume of water in the diffusion vessel, the amount of KCl diffused from film-pieces can be approximated by Eq. (5).

$$n_{tot} = \frac{(\kappa_\infty - \kappa_0)V_{H_2O}}{\Lambda_0} \tag{5}$$

Furthermore, the initial KCl concentration in the amylose film (c_{film}) can be obtained from Eq. (6).

$$c_{film} = \frac{n_{tot}}{V_{film}} \tag{6}$$

Here V_{film} is the volume of the swollen amylose film. The equivalent conductivity depends strongly on temperature, and thus was taken into account when investigating the diffusion of KCl at different temperatures (Lobo, 1984; Lobo & Quaresma, 1981).

Temperature dependence of the diffusion coefficient: The diffusion coefficient depends on temperature and, in most cases, an Arrhenius relationship can be used to describe this dependence. The Arrhenius equation is expressed as

$$D = D_0 e^{-E_a R/T} \tag{7}$$

where D_0 is the pre-exponential factor, E_a is the activation energy of diffusion, R is gas constant, and T is temperature in degrees Kelvin. The activation energy of diffusion can be calculated from the log-linear plot

$$\ln D = \ln D_0 - \frac{E_a}{R}\frac{1}{T} \tag{8}$$

3. Results and discussion

Swelling of the film: In order to calculate the diffusion coefficient of KCl in the amylose film, the film thickness must be known. Thus swelling of the films under aqueous conditions was first examined.

Thickness and diameter of the films were approximately measured by using a micrometer. The films stored at RH 97% had the thickness of 170 ± 2 μm and the diameter of 12.0 ± 0.1 mm. When the films were treated in the salt solution the thickness increased to 370 ± 4 μm and the diameter increased to 13.5 ± 0.2 mm. The increase in thickness was about 115% and the diameter was about 13% larger. No significant differences were found in thickness when the films were treated in water or in salt solutions. The amylose content of the film stored at RH 50% was about 87% (based on the sorption data at 20 °C from Myllärinen, Partanen, Seppälä, & Forssell, 2002). The amylose content decreased with increasing RH and was about 75% at RH 97%. When the films were immersed in water they swelled even more and the amylose content was further decreased to ca. 37%. When the films were immersed in the KCl solution the amylose content decreased to 35–29% depending on the salt content. When considering the mass changes of the films, the mass increases in the films immersed in KCl were greater than for those immersed in water. The mass of water-swollen films was from 100 to 150% larger than the mass of films stored at RH 50%, whereas the mass of films treated in KCl solutions was from 100 to 200% larger. This result also indicated that the swelling in water is very similar to the swelling behaviour in KCl solutions.

Swelling studies of amylose films or gels have not been reported earlier, but swelling of modified amylose gels has been investigated. Moussa et al. (Moussa et al., 1998) reported that epichlorohydrin crosslinked high amylose corn starch gels in water showed about a 95% increase in thickness and about a 50% increase in diameter. Polyethylene glycol diglycidyl ether crosslinked amylose gel membranes in sodium phosphate buffer showed larger swelling. The increase in mass was from 200 to 550% (Yasunga, Matsumoto, & Kitamura, 2000).

In order to elucidate the swelling of amylose in more detail the water and salt contents of the amylose film equilibrated in different salt solutions at 25 °C were calculated based on the mass changes of the film. The water content depended slightly on salt concentration, changing from 50 to 60% (Fig. 2). A maximum value was

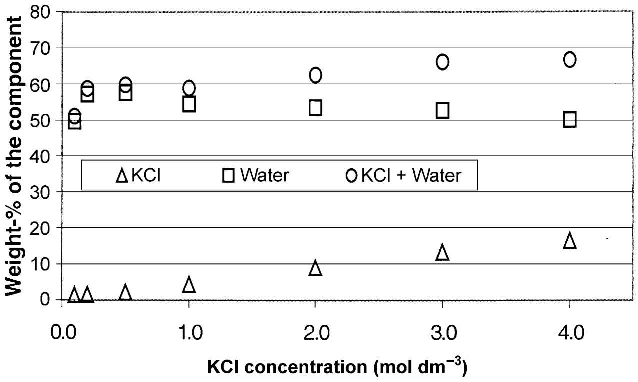

Fig. 2. The dependence of the composition of the film on the KCl concentration of the soaking solution at 25 °C.

observed at about 0.5 mol dm^{-3}. Salt content of the film increased with increasing salt concentration of the soaking solution. If swelling is assumed to depend directly on water content the results indicate that swelling of the film did not depend much on the salt concentration of the solution, which is in agreement with the dimensional studies. In spite of the high quantity of salt that the amylose film had absorbed when immersed in high salt concentration, the films appeared translucent and unbroken, and no salt precipitate was visually observed on the surface of the film.

The total KCl concentration in the wet amylose film was calculated based on the KCl content and the volume of the wet film, and was observed to depend linearly on the KCl concentration of the soaking solution (Fig. 3). By assuming that the salt concentration of the water inside the amylose film has the same concentration as that of the soaking solution the concentration of KCl inside the film, based on wet film volume, should be only about 66% of that in the soaking solution. Because the observed concentration was higher (87 ± 3%), it indicated that the amylose structure may solvate some salt. The excess salt content, which was left after assuming that water inside the film contains as much electrolyte as the soaking solution, was divided by the volume of the dry starch. This produced a parameter, which described the KCl concentration of the amylose matrix, the dependence of which on KCl soaking solution concentration is shown in Fig. 4. The degree of solvation increased with increasing salt concentration and finally reached a plateau at 3 mol dm^{-3}.

The solvation ability of amylose is most likely linked with the functionality of the hydroxyl groups present in the polymer, and that is why the mole ratio of OH/KCl in the amylose matrix was calculated. The ratio was found to depend greatly on the soaking solutions salt concentration and observed to decrease with increasing salt concentration, levelling out at about three moles of OH-groups per one mole of KCl. This means that one molecule of KCl is bound by three OH-groups. The result obtained is plausible because in the amylose structure there are three free OH-groups per every glucose unit (Fig. 5). Also, the result is of same order of magnitude as the hydratation number of KCl in water (0.6–7) (Robinson & Stokes, 1959).

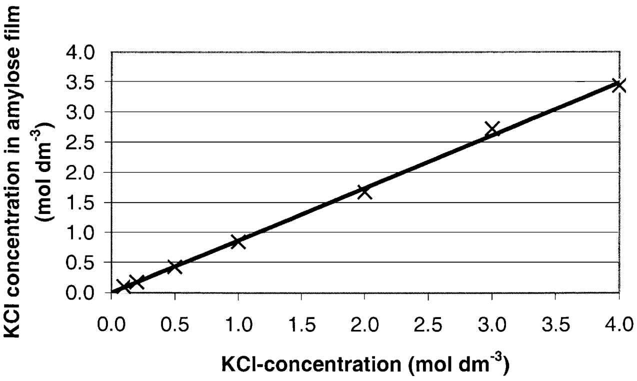

Fig. 3. The dependence of the KCl concentration of wet amylose film on the KCl concentration of the soaking solution.

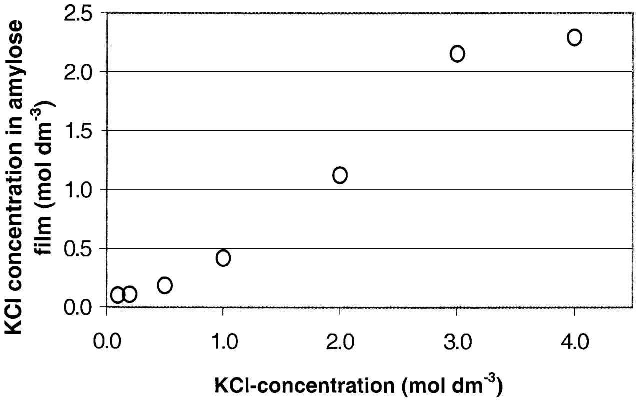

Fig. 4. The amount of KCl solvated by the amylose film at different KCl concentrations of the soaking solution.

Diffusion coefficient and temperature: Diffusion coefficient of KCl in the amylose film were measured at temperatures from 25 to 65 °C, and for soaking solution concentrations varying from 0.1 to 4 mol dm^{-3}. The results showed that the diffusion coefficient did not depend on the KCl load of the film except at very low salt concentrations, which may originate from experimental errors (Fig. 6). At 25 °C the diffusion coefficient of KCl was observed to be $4.8 \pm 0.3 \times 10^{-10}$ m^2 s^{-1}, which is about one fourth of that in water (1.9×10^{-9} m^2 s^{-1}) (Robinson & Stokes, 1959). With increasing temperature the deviation of KCl diffusion coefficient from that in water was slightly decreased.

Only a few studies of electrolyte diffusion in starches have been reported. Powell (1971) has found the diffusion coefficient of ferrocyanide ion in a starch gel to be $4.7 \pm 0.1 \times 10^{-10}$ m^2 s^{-1}. Odake (2000) studied diffusion of NaCl in corn starch gels and found an increase in diffusion coefficient with increasing water content of the gel from 75 to 90% (dry basis). The values detected for the diffusion coefficient of NaCl were close to that in water (1.6×10^{-9} m^2 s^{-1}) (Robinson & Stokes, 1959). This is somewhat different to our observation that the diffusion coefficient of KCl is about 25% of that in water. The result

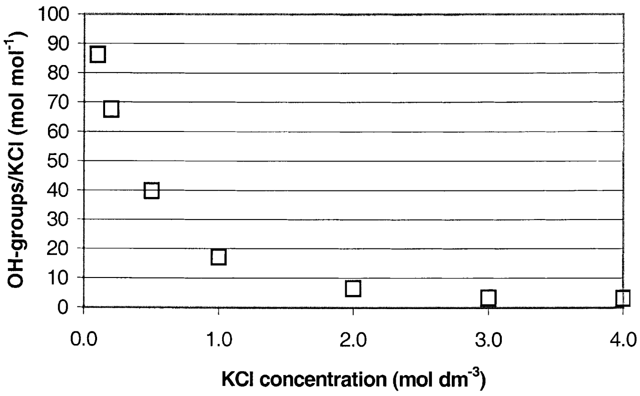

Fig. 5. The amount of OH-groups per the excess amount of KCl in the amylose film.

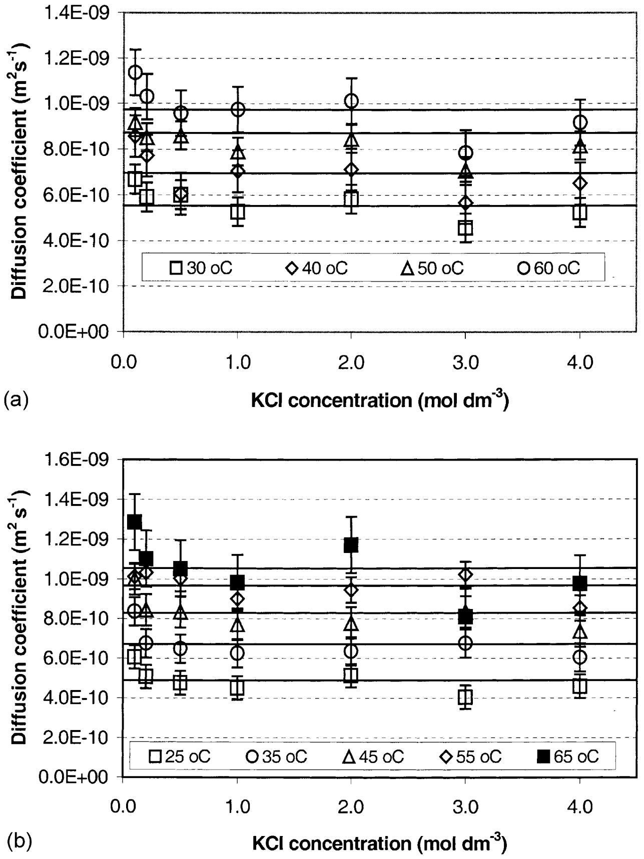

Fig. 6. Dependence of diffusion coefficient of potassium chloride on the soaking solutions concentration (a) at temperatures of 25, 35, 45, 55, and 65 °C and (b) at temperatures of 30, 40, 50, and 60 °C. Error bars are drawn at 95% confidence level.

is perhaps not surprising because in our case we have used amylose films and Odake used high water content gels. Ozdemir and Floros (2001) have studied the diffusion in protein films. They found that the diffusion coefficient of potassium sorbate in whey protein films at 25 °C was dependent on concentration. The diffusion coefficient of potassium sorbate increased with increasing initial potassium sorbate concentration, but the potassium sorbate was added to the whey protein film prior casting. The reported values of diffusion coefficient were in same order of magnitude than obtained in this study. Instead, for the diffusion coefficient of sorbic acid at 20 °C in a wheat gluten film a decade lower value (7.5×10^{-12} m^2 s^{-1}) has been reported (Redl, Gontrad, & Guilbert, 1996).

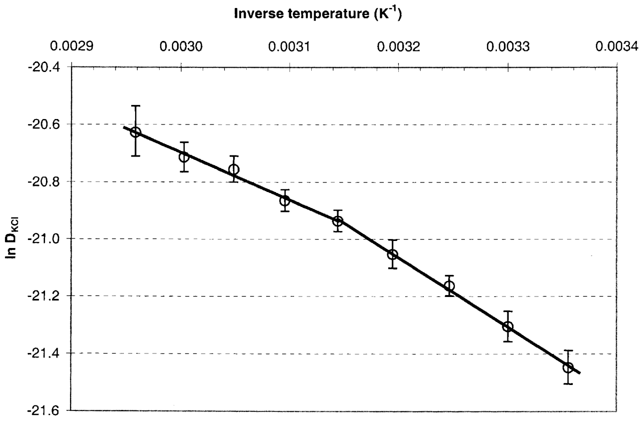

Fig. 7. Temperature dependence of the diffusion coefficient of KCl in amylose film. Error bars are at 95% confidence level.

Some studies concerning diffusion of larger molecules in amylose gels have been conducted. Increase in swelling was reported to increase the diffusion of fluorescein and fluorescein–dextran conjugate in amylose gel films (Yasunaga et al., 2000). Furthermore, the diffusion coefficient was found to be dependent on the amylose content of the gel. Leloup et al. (Leloup et al., 1990) found the diffusion coefficient of bovine serum albumin in amylose gel decreased with increasing amylose content of gel for amylose contents from 2 to 10%. The reported values were about half of that in water at 25 °C.

Table 1
Average values of the diffusion coefficient and their 95% confidence level at different temperatures

t, °C	25	30	35	40	45	50	55	60	65
$10^{10} \times D$, m^2 s^{-1}	4.8	5.6	6.4	7.2	8.1	8.7	9.7	10.1	11.0
$10^{10} \times \Delta D$, m^2 s^{-1}	0.3	0.3	0.2	0.4	0.3	0.3	0.4	0.5	1.0

Diffusion of KCl was virtually independent of KCl concentration but depended on temperature, increasing with increasing temperature (Fig. 6). The average values of the diffusion coefficients at different temperatures are listed in Table 1. When the Arrhenius equation was applied two linear regions were observed (Fig. 7). The activation energies were 20.1 ± 1.5 and 14 ± 3 kJ mol^{-1} over the temperature ranges from 25 to 45 °C and from 45 to 65 °C, respectively. The value of activation energy of diffusion of KCl in water is about 17 kJ mol^{-1} (calculated from the data of Robinson & Stokes, 1959), which lies between the two values obtained in the present study. Very similar values for activation energies of different diffusates in starch gels and granules have been obtained previously (Fish, 1957; Karathanos, Vagenas, & Sarvacos, 1991; Powell, 1971; Yasunaga et al., 2000). For example, the activation energy for ferrocyanide ion diffusion in starch gels was found to be 20.5 kJ mol^{-1} in the temperature range from 19.6 to 35.8 °C (Powell, 1971).

The presence of the two activation energies may be explained by a structural change occurring at 45 °C, at which temperature the amylose structure became more porous facilitating the diffusion. Another possible explanation is the increased molecular mobility of the polymer network due to increased temperature.

4. Conclusions

The method used in this work was suitable for the measurement of the diffusion coefficient of KCl in amylose films provided that the films were thick enough (> 200 μm). The diffusion coefficient of KCl was found to be about one fourth of that in water, and was independent of the soaking solution KCl concentration. The temperature dependence of the diffusion coefficient of KCl in the amylose film was Arrhenian in character with activation energy of about the same as that in water. The slight decrease of the activation energy at 45 °C indicated that a structural change might have occurred in the film.

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