The use of edible coatings in combination with antimicrobial

agents enhances the microbial stability of foods. In this study we

evaluated the potassium sorbate and sorbic acid permeability of an

edible methylcellulose (MC) - palmitic acid (PA) film with a MC:PA

ratio of 3:1.

Permeability cell measurements were used to evaluate the effect

of pH and water activity (a_w) on the film permeation rate by sorbic

acid and potassium sorbate. For films with a thickness of 55-66 μm,

potassium sorbate permeability increased from 2.3×10^{-10} to 2.0×10^{-8}

(mg/sec cm^2)/(cm)/(mg/mL) as a_w increased from 0.65 to 0.80. Films

were not stable at a_w levels above 0.80.

The permeability of the film to sorbic acid decreased from

3.3×10^{-8} to 9.1×10^{-10} (mg/sec cm^2)(cm)/(mg/mL) when pH in the

permeability cell was increased from 3 to 7. This permeability

decrease with pH could balance the loss of effectiveness of sorbates due to the lowering of the percentage of undissociated molecules at high pH.

Another characterization of the MC-PA film was the evaluation of the effect of relative humidity (RH) on its oxygen transmission rate (OTR). In general, the film was highly permeable to oxygen (OTR values at 24°C, 660 to 1400 mL O_2 (STP)/m^2 24h atm, average film thickness of 55 μm). Therefore, there is no risk to develop anaerobic conditions on food surfaces coated with the MC-PA film. There was no relative humidity effect on OTR in the 0-60% RH range; whereas, the OTR doubled when the RH was increased from 60 to 80%. These results agree well with the moisture uptake of the MC-PA film. Its moisture sorption isotherm shows a large moisture content increase at RH levels larger than 60%.

The application of methylcellulose-based films as moisture permeability barriers in simulated sundae ice cream cones showed that a MC-PA film practically stopped moisture transfer from the ice cream to the sugar cone. Sugar cone crispness was retained for a period longer than three months when stored coated at -10°F and +10°F. The crispness of commercial sundae ice cream cones is retained for periods much less than three months.

Permeability Properties of an Edible

Methylcellulose-Palmitic Acid Film

by

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INTRODUCTION

The production, storage, transport and handling of foods demand the maintenance of conditions under which food deterioration is minimized. Environmental conditions, to which foods are exposed and the type of packaging material used affect the product shelf-life. Edible coatings and films have been developed and tested to prolong the shelf-life of fresh, frozen and fabricated foods (Kester and Fennema, 1986).

The need to develop treatments that enhance surface resistance to microbial growth has led to the study of protein and polysaccharide-based coatings to be used in combination with antimicrobial agents to extend product shelf-life (Torres et al., 1985a; Vojdani and Torres, 1989a). These coatings have been developed to protect intermediate and high moisture foods. Intermediate moisture foods have been defined as those foods with water activity (a_w) from 0.60 to 0.85 (Quast and Teixeira, 1976), 0.65 to 0.90 (Karel, 1975), 0.70 to 0.85 (Cory, 1976) and 0.60 to 0.90 (Leistner, 1986). A major problem of intermediate moisture foods is the growth of yeast and molds which is controlled by the use of antimicrobial agents (Erickson, 1982).

The effectiveness of zein coatings as an edible diffusion barrier to enhance the microbial stability of foods has been confirmed through permeability cell experiments and extensive microbiological tests (Torres et al., 1985a,b). Recently completed studies of edible films of different polysaccharide-fatty acid ratios include potassium sorbate permeability through these films and the effect of temperature on the permeation process. Methylcellulose-palmitic acid (MC-PA) films are reported to be a good permeability barrier to the transfer of potassium sorbate (Vojdani and Torres, 1989b,c).

Lowering pH changes most antimicrobial agents from a dissociated to an undissociated form and water activity affects the hydration status of the film. Therefore, both factors could influence the permeability of the film to antimicrobial agents. Consequently, this research focused on the examination of the effect of pH and a_w on the preservative permeability of a film with a methylcellulose:palmitic acid ratio 3:1 (MC-PA film).

The oxygen permeability of films is an important consideration in food quality preservation. An oxygen impermeable coating could be used to prevent lipid oxidation problems. On the other hand, oxygen impermeable coatings could create anaerobic conditions and allow the growth of microorganisms not usually associated with the spoilage of a particular food. Therefore, the oxygen permeation rate of the MC-PA film under study needs to be determined.

Edible films made of hydroxypropyl methylcellulose (HPMC) and a lipid component have been shown to be effective in retarding

moisture transfer within heterogeneous food products (Kamper and Fennema, 1984a,b; 1985). However, few industrial applications have been reported in the literature. In this study we have shown that edible films could be used in sundae ice cream cones to extend the shelf-life of the product by retarding the loss of crispness of the sugar cone.

RESEARCH GOALS AND OBJECTIVES

The functional properties of edible films and coating are related to their resistance to solute, vapor and gas transport. The effects of two important parameters were of particular interest, pH and a_w. The oxygen permeability characteristics and the use of these films as moisture permeability barriers were also of interest. The specific objectives of this investigation were:

1) To evaluate the effect of a_w on potassium sorbate permeation rate through an edible methylcellulose-palmitic acid film (ratio 3:1).

2) To evaluate the effect of pH on sorbic acid permeation rate through an edible methylcellulose-palmitic acid film (ratio 3:1).

3) To determine the oxygen transmission rate of an edible methylcellulose-palmitic acid film (ratio 3:1) as a function of environmental relative humidity.

4) To test methylcellulose-based films as a moisture impermeable barrier in a simulated sundae ice cream cone.

LITERATURE REVIEW

Edible polysaccharide-lipid films

Edible packaging must have special properties because of its dual role as package and food component (Daniels, 1973). Edible bilayer films composed of a water soluble, carbohydrate layer (e.g. HPMC) and a lipid component are resistant to water vapor permeability. Films containing solids lipids, such as beeswax, paraffin, hydrogenated palm oil or stearic acid have water vapor permeability values of 0.2 g. mil. day^{-1}. mm Hg^{-1} or less which is a smaller value than that for low density polyethylene (Kamper and Fennema, 1984a).

Vojdani and Torres (1989a,b,c) have determined the potassium sorbate permeability of methylcellulose (MC) and hydroxypropyl methylcellulose-based films. Permeability values at 24°C were 5×10^{-7}, 9×10^{-9} and 12×10^{-9} (mg/cm^2 sec)(cm)/(mg/mL) for films containing beeswax, stearic acid and palmitic acid, respectively.

Films containing beeswax offer better permeability barrier properties to water vapor (Kamper and Fennema, 1984a) and to potassium sorbate (Vojdani and Torres, 1989c) than films containing fatty acids (Table 1). However, films containing beeswax are brittle and avoidance of cracks during film formation and subsequent handling would be difficult if not impossible (Kamper and Fennema, 1984a). It should be noted that brittleness problems were not observed in the studies done by Vojdani and Torres (1989c).

The major component of the edible films studied by Vojdani and

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Torres (1989a,b,c) is a cellulose ether. The film forming properties of the cellulose ether provide a structural matrix in which the lipid component is distributed. A flexible film structure is thus formed with good permeability barrier properties because of the lipid component.

Film preparation techniques

Four dispersion techniques are suggested for the preparation of cellulose ethers to form a film structure (Anonymous, 1986). They are, dispersion in hot water, dry blending, dispersion in non-solvent media and dispersion of surface-treated cellulose ether powders. The dispersion in hot water technique has been used to prepare films containing lipids following two different procedures, casting a lipid layer onto a dried water-soluble polysaccharide film (coating technique) and incorporating the lipid to the film-forming solution (emulsion technique) (Kamper and Fennema, 1984a; Vojdani and Torres, 1989a,b,c).

Coating technique

In the coating technique, the polysaccharide is dispersed in hot water (1/3 of the required volume, at least at 90°C). The agitation is continued until the particles are thoroughly wetted and evenly dispersed. The remainder of the water is then added as cold water or ice to lower the temperature of the dispersion. Once the dispersion reaches the temperature at which that particular polysaccharide becomes water-soluble, the powder begins to hydrate

and viscosity increases. Agitation is continued for at least 30 min
after the proper temperature is reached. The solution is then ready
to form a film (Fig. 1, Anonymous, 1987). The film forming solution
is spread with a thin layer chromatography (TLC) applicator onto
glass plates, dried in an oven at 90°C, cooled at room temperature
and the film is then removed from the plate. The lipid is melted
and applied onto the surface of the polysaccharide film (Kamper and
Fennema, 1984a).

Emulsion technique

In the emulsion technique, the lipid is added directly to the
film forming solution. If necessary, the solution is warmed to melt
lipids with high melting points. Water and ethanol are used as the
solvents. Air bubbles in the solution are removed by reducing the
pressure over the solution for 2 min. The TLC applicator is heated
to prevent solidification of the film components during application.
The film forming solution is then left for 4 min on the glass plates
to allow setting of the lipids. The coated plates are dried in an
oven at 90°C for 15 minutes. After drying, the plates are cooled
and the films are then peeled from the plates (Kamper and Fennema,
1984a; Vojdani and Torres 1989b).

The film forming solution to prepare films containing fatty
acids uses 9g polysaccharide, a variable amount of fatty acid, 1g
polyethylene glycol 400 (PEG), 100 mL distilled water and 200 mL 95%
ethanol. The polysaccharide is first hydrated in water at 90°C with
agitation. Ethanol is then added. The solution is thoroughly mixed

before adding PEG. After 5 min the fatty acid is added. The

mixture is heated until reaching 80-82°C, for a total preparation

time of 15 min. Addition of PEG aids in the removal of the dried

film from the glass surface and improves flexibility of the film

(Kamper and Fennema, 1984a). Reduction of the water:alcohol ratio

below 1:2 leads to grainy films, an indication of undissolved

polysaccharide (Kamper and Fennema, 1984a). Films prepared by the

emulsion technique are less permeable than films prepared by the

coating technique (Table 2, Kamper and Fennema, 1984a).

Surface microbial stability of foods

Edible coatings controlling preservative migration from surface

into food bulk could inhibit surface microbial growth which is often

the main cause of spoilage for many food products (Torres et al.,

1985a; Vojdani and Torres, 1989a,b,c).

Surface microbial stability can be improved by maintaining an

unequal preservative distribution, i.e., start with a higher

(initial) concentration of preservative(s) on the surface and use a

coating to maintain this concentration difference for as long as

possible. This approach requires the selection of a coating capable

of reducing preservative diffusion from surface into food bulk

(Torres et al., 1985a). Acceptance by the U.S. Food and Drug

Administration of this approach is predicted since the high

concentration of preservative is located just on the surface. The

overall concentration is maintained within legal limits by lowering

the concentration in the bulk, e.g., from 0.3% potassium sorbate to

0.1%. The amount corresponding to this reduction is the amount used on the surface. In addition, surface spraying of preservatives is a common industrial practice (Torres, 1987). Finally, preservative excess on the food surface could be washed out before food consumption (Vojdani and Torres, 1987a).

Torres (1987) noted that the antimicrobial effectiveness of the control of preservative concentration on food surfaces can be examined in terms of estimated values for food shelf-life extension. For example, when using a given coating/potassium sorbate spray combination (Table 3), it can be roughly estimated that the enhancement of surface microbial growth could be 3-12 weeks, 1-11 months or "indefinite". This effect on microbial stability should be compared with applying the preservative on the uncoated product.

Water activity (a_w)

Water activity is defined in the following manner (Fennema, 1985)

$$a_w = p / p^o$$

where a_w is water activity, p is the partial pressure of water above the sample, and p^o is the vapor pressure of pure water at the same temperature.

This expression is an approximation of the original activity expression of Lewis, $a_w = f/f^o$, where f is the fugacity of the solvent (fugacity is the escaping tendency of a solvent from a

solution) and f° is the fugacity of the pure solvent. At low pressures the difference between f/f° and p/p° is negligible (less than 1%). Therefore, defining a_w in terms of p and p° is clearly justifiable (Fennema, 1985).

Water activity is also related to the equilibrium relative humidity (%) surrounding the product and to the mole fraction of solvent (water) as follows:

$$a_w = \%RH/100$$

$$a_w = n_1 /(n_1 + n_2)$$

where % RH is the percentage of relative humidity, n_1 is the moles of solvent and n_2 is the moles of solute. It is worth emphasizing that the water activity is an intrinsic property of the sample, whereas equilibrium relative humidity is a property of the atmosphere in equilibrium with the sample (Fennema, 1985).

Water activity and food stability are closely related. Most microorganisms grow best at relatively high a_w and, if a_w decreases, fewer genera of microorganisms are able to multiply. In general, molds are more tolerant of a decreased a_w than yeasts, and yeast are more tolerant than bacteria. Fennema (1985) presents the following water activity ranges for microbial growth: (0.95-1.0)- *Pseudomonas*, *Escherichia*, *Proteus*, *Shigella*, *Klebsiella*, *Bacillus*, *Clostridium perfringens* and some yeasts; (0.91-0.95)- *Salmonella*, *Vibrio parahaemolyticus*, *C. botulinum*, *Serratia*, *Lactobacillus*,

Pediococcus, some mold and yeasts (*Rhodotorula*, *Pichia*);
(0.87-0.91)- many yeasts (*Candida*, *Torulopsis*, *Hansenula*), and
Micrococcus; (0.87-0.80)- most molds (*mycotoxigenic penicillia*),
Staphylococcus aureus, most *Saccharomyces* (*baillii*) spp., and
Debaryomyces; (0.75-0.80)- most halophilic bacteria and
Mycotoxigenic aspergilli; (0.65-0.75)- xerophilic molds (*Aspergillus
chevalieri*, *A. candidus*, *Wallemia sebi*), and *Saccharomyces bisporus*;
(0.60-0.65)- osmophilic yeasts (*Saccharomyces rouxii*), few molds
(*Aspergillus echinulatus*, *Monascus bisporus*). Below 0.5, no
microbial proliferation is detected.

Permeability measurements

The permeability cell illustrated in Fig. 2, consisting of two
chambers separated by the film to be tested, can be used to
determine permeability constants. Under well-stirred conditions the
resistance to mass transfer for coatings with a low apparent
diffusion constant can be assumed to be due only to film properties.
The mechanical and magnetic stirrers reduce mass transfer resistance
at the interfaces. The side tubes are used to load the cell with a
highly concentrated solution, eliminate air bubbles, and adjust
levels to eliminate the influence of hydrostatic pressure on
permeability (Torres, 1987).

The use of large concentration differences and large reservoirs
facilitates the analysis of experimental data. Under these
experimental conditions, the permeability rate is constant and equal
to (Torres, 1987):

$$N = D A (c'_2 - c'_1)/x \qquad (1)$$

where:

N = flux of potassium sorbate

D = apparent diffusion constant

A = area of mass transfer

c'_i = concentration in the film which is in equilibrium with bulk solution concentration c'_i; the equilibrium is expressed as $c'_i = kc_i$

x = diffusion distance

Assuming constant k we obtain:

$$N = KA(c_2 - c_1)/x \qquad (2)$$

where $K = kD$. Using:

c_1 : concentration in upper reservoir at time zero = 0

c_2 : concentration in bottom reservoir at time zero = c = large

the permeability constant (K) will be:

$$K = \frac{N x}{A c} \qquad (3)$$

The K-sorbate permeability constant can be expressed using the
following units:

Permeability constant = (mg K-sorbate/sec cm^2)(cm)/(mg/mL)

After an initial lag time, the amount of preservative permeated
per unit area of film as a function of time shows a linear
relationship. The slope of this curve is the steady state rate of
preservative transferred through the film (Vojdani and Torres,
1989a).

Sorbates

Sorbates, the commonly used name for sorbic acid and its salts,
have been tested and used widely in the preservation of various food
products throughout the world. Sorbic acid, an α,γ-unsaturated
trans-trans, 2,4-hexadienoic monocarboxylic aliphatic acid and has
the molecular formula $CH_3CH=CH-CH=CH-COOH$. Sorbic acid salts,
especially the potassium salt are most frequently used due to their
high solubility in water. The low water solubility is a
disadvantage for sorbic acid. Solubility in water increases with pH
and temperature. In vegetable oil, the acid is more soluble than
the potassium salt (Table 4) (Sofos and Busta, 1981).

Sorbic acid and potassium sorbate are generally recognized as
safe (GRAS) for use in foods. No upper limits are imposed for foods
not under federal standards of identity. In regular cheese, the
maximum quantity may not exceed 0.3% by weight, calculated as

K-sorbate. The maximum is set at 0.2% in pasteurized cheese products (blended cheese, process cheese, cheese spread). In margarine the maximum is set at 0.1% (Chichester and Tanner, 1972).

Sorbic acids and its salts are effective preservatives at low concentration for the control of molds and yeasts in cheese products, baked goods, fruit juices, fresh fruits and vegetables, wines, soft drinks, pickles and sauerkraut and certain meat and fish products (Chichester and Tanner, 1972). Sorbates have also been shown to be effective against bacteria; however, its spectrum of activity is not as wide as that against yeast and molds (Sofos and Busta, 1981).

Sorbates can be used as direct additives, as a spray or a dip bath, and as a coating for wrapping material. Wrapping materials treated with sorbates have been used mainly to protect cheese products. Since mold contamination is a surface phenomenon, sorbic acid may be dusted onto the food surface, or protection may be afforded by sorbic-acid-impregnated wrappers (Chichester and Tanner, 1972).

The antimicrobial activity of sorbic acid in vacuum packaged beef and that of potassium sorbate in refrigerated wrapped raw beef, against *Pseudomonas spp.*, *Brochothrix thermosphacta*, *Lactobacillus spp.*, *enterobacteriace* and yeast has been tested using films of different oxygen permeability at different pH levels (Zamora and Zaritzky, 1987a,b). Low oxygen permeability films combined with sorbate treatments (27-1325 ppm sorbic acid) at pH < 6 retarded microbial growth (Zamora and Zaritzky, 1987a,b).

Potassium sorbate delays the growth of the spoilage bacteria, and *Salmonella*, *Staphylococcus aureus*, *Clostridium perfringens*, and *Clostridium botulinum* in cooked uncured sausage (Tompkin et al., 1981). Sorbate has been found effective in delaying *Clostridium botulinum* toxin production, especially in combination with low nitrite (40-80 ppm) levels. Its antimicrobial effect appears to be on spore germination as well as in outgrowth, but the mechanisms of action are not well understood (Sofos and Busta, 1981; Roberts et al., 1982). Moreover, Fletcher et al. (1988) reported that Clostridium botulinum type A toxin developed rapidly in the presence of sorbate in scallops in evacuated packages held at 27°C.

The antimicrobial effectiveness of sorbic acid and its potassium salt increases as the pH of the medium decreases. This has been attributed to the effect of pH on the amount of undissociated molecules present in solution (Freese and Levin, 1978; Sofos et al., 1980). The action of the undissociated acid is much greater than that of the dissociated one (Eklund, 1983). Food pH and acid pK_a values are needed to determine the percentage of undissociated sorbic acid. pK_a values depend upon water activity (Fig. 3; Pethybridge et al., 1983). Table 5 shows the percentage of undissociated sorbic acid in water at different pH levels, using a pK_a value of 4.76.

Permeability to gases

The ability to transmit liquids, gases, and vapors, a property called permeability, is an important factor in determining the

usefulness of packaging and coating materials. Excessive loss or gain of water, oxygen, or volatile organic compounds can cause deterioration of the packaged products (Lebovits, 1966). Gas and vapor exchange depends on the integrity of the packaging materials, including the seals and closures, and on the permeability of the packaging materials themselves (Karel, 1975).

Mass transport through polymeric materials, in contrast to mass transport through filter paper or other porous materials, occurs by a molecular mechanism called "activated diffusion" (Lebovits, 1966; Karel, 1975). This takes place in three steps. First, the permeate "dissolves" in the permeable membrane on the side of its higher concentration. Then, it diffuses through the membrane towards the side of the lower concentration, a process which depends on the formation of "holes" in the plastic network due to thermal agitation of the chain segments. Finally, the permeate becomes desorbed on the side of the lower concentration. In contrast to this, when permeating through porous materials, the permeating molecule does not change from undissolved to dissolved, and does not form transient "holes" in its passage (Lebovits, 1966).

Laws governing gas permeability

The gas transport in one direction (e.g. from the environment into the package) can be analyzed using the diffusion law: (Karel, 1975)

$$J = - DA (dc/dx) \qquad (4)$$

where J is the flux of gas in appropriate units (e.g., moles/sec); A is the area of film exposed and perpendicular to gas flux; D is the diffusion coefficient for the gas in the membrane; c is the concentration of gas in the membrane and x is the distance in the membrane measured in the direction of flux (usually approximated as the film thickness).

If D is assumed constant and steady-state conditions exist, then:

$$J = DA (c_1 - c_2)/ x \qquad (5)$$

However, c_1 and c_2 are difficult to measure within the membrane. If we apply Henry's law:

$$c = Sp \qquad (6)$$

where S is solubility and p is partial pressure of gas and combining equations (5) and (6), we obtain:

$$J = DSA (p_1 - p_2)/ x \qquad (7)$$

where the quantity DS is known as the permeability coefficient (B), which can be expressed as:

$$B = \frac{(amount\ of\ gas)(thickness)}{(area)(time)(pressure\ difference)}$$

The amount of gas is generally reported as the volume of gas permeating through the film at standard temperature and pressure (STP). In the case of heterogeneous materials, such as coated films, it is not valid to include the thickness of the film in the permeability coefficient equation. The results are then reported as gas transmission rate (GTR) and include film thickness, temperature and % of relative humidity conditions of the test.

Methods for measuring gas permeability

There are several methods for measuring gas permeability, the pressure increase method, the volume increase method and the concentration increase method. The first two are described in the standard ASTM method number D1434-82. The concentration increase method is described schematically in Fig. 4. The film is mounted between the low and high concentration sides (c_L and c_H) of the permeability cell and both sides are at the same total pressure ($\pi - \pi_H - \pi_L$). A partial pressure difference is maintained by filling one side with pure or highly concentrated test gas and maintaining on the other side an inert gas into which the test gas is diffusing. Experimentally, gas chromatography can be used to determine concentration increase of the test gas (O_2, CO_2, etc.). Modern instrumental methods allow continuous direct recording of oxygen permeation, e.g., use of oxygen electrodes or head space analyzers, directly connected to the low concentration side. The concentration increase of the test gas is measured as a function of time. When the concentration of the test gas in the high

concentration side remains much larger than the concentration in the low concentration side, it is possible to determine the permeability coefficient from the shape of the curve by the so called "time-lag" method. The slope of the linear steady state portion of the curve is multiplied by the membrane thickness and the product is divided by its area and by the partial pressure difference (Lebovits, 1966).

TABLE 1.   Water vapor transmission rate and
            potassium sorbate permeability of
            HPMC-beeswax and HPMC-fatty acid films.

FILM	WVTR[1] g/m² day	K-SORBATE PERMEABILITY[2] (mg/sec cm²)(cm)(mg/mL)
HPMC-beeswax	1.4	4.5×10^{-11}
HPMC-PA,SA	49.3	
HPMC-PA		2.0×10^{-8}

PA = palmitic acid, SA = stearic acid.

[1] (Kamper and Fennema, 1984a), T = 25°C, 85% RH,
WVTR = water vapor transmission rate.

[2] (Vojdani and Torres, 1989b), T = 24°C, 0.77 a_w

TABLE 2.   Comparison of the coating and emulsion techniques,
             HPMC-stearic, palmitic acid film.

TECHNIQUE USED	LIPID CONTENT mg/cm² film area	WVTR g H₂O/m² day
Coating	9.0	43.9
Emulsion	0.8	3.1

T = 25°C, 85 % RH
WVTR = water vapor transmission rate
(Kamper and Fennema, 1984a)

TABLE 3. Rough estimation of shelf-life extension achieved by the use of edible food coatings and potassium sorbate combinations.

PERMEABILITY VALUE (K) (mg/sec cm^2)(cm)/(mg/mL)		FILM THICKNESS mm	
		0.1	0.2
FILM	K	ESTIMATED[1] SHELF-LIFE	
Typical Foods (uncoated)	$\approx 10^{-6}$	"Few Days"	
Pure MC (24°C)	4.8×10^{-8}	3	12 weeks
MC-PA (45:20)			
24°C	4.9×10^{-9}	1	4 months
5°C	2.8×10^{-9}	2	11 months
HPMC-Beeswax	4.5×10^{-11}	"Indefinite"	

[1] Values calculated using Eq. 6 (Torres, 1987)

TABLE 4. Solubility of sorbic acid and potassium sorbate in water and vegetable oil (%)[1]

SOLVENT	pH	T°C	SORBIC ACID	POTASSIUM SORBATE
Water	3.1	25	0.16	58.2
water	4.4	25	0.22	
Water	5.9	25	1.02	
Water		100	4.00	64.0
Oil		20	1.00	0.01
Oil		100	10.00	0.19

[1]Sofos and Busta, (1981)

TABLE 5.   Effect of pH on sorbic acid dissociation
in water at 25°C[1]

pH	UNDISSOCIATED (%) ACID
7.00	0.6
6.00	6.0
5.80	7.0
5.00	37.0
4.75 (pK$_a$)	50.0
4.40	70.0
4.00	86.0
3.70	93.0
3.00	98.0

[1](Sofos and Busta,1981)
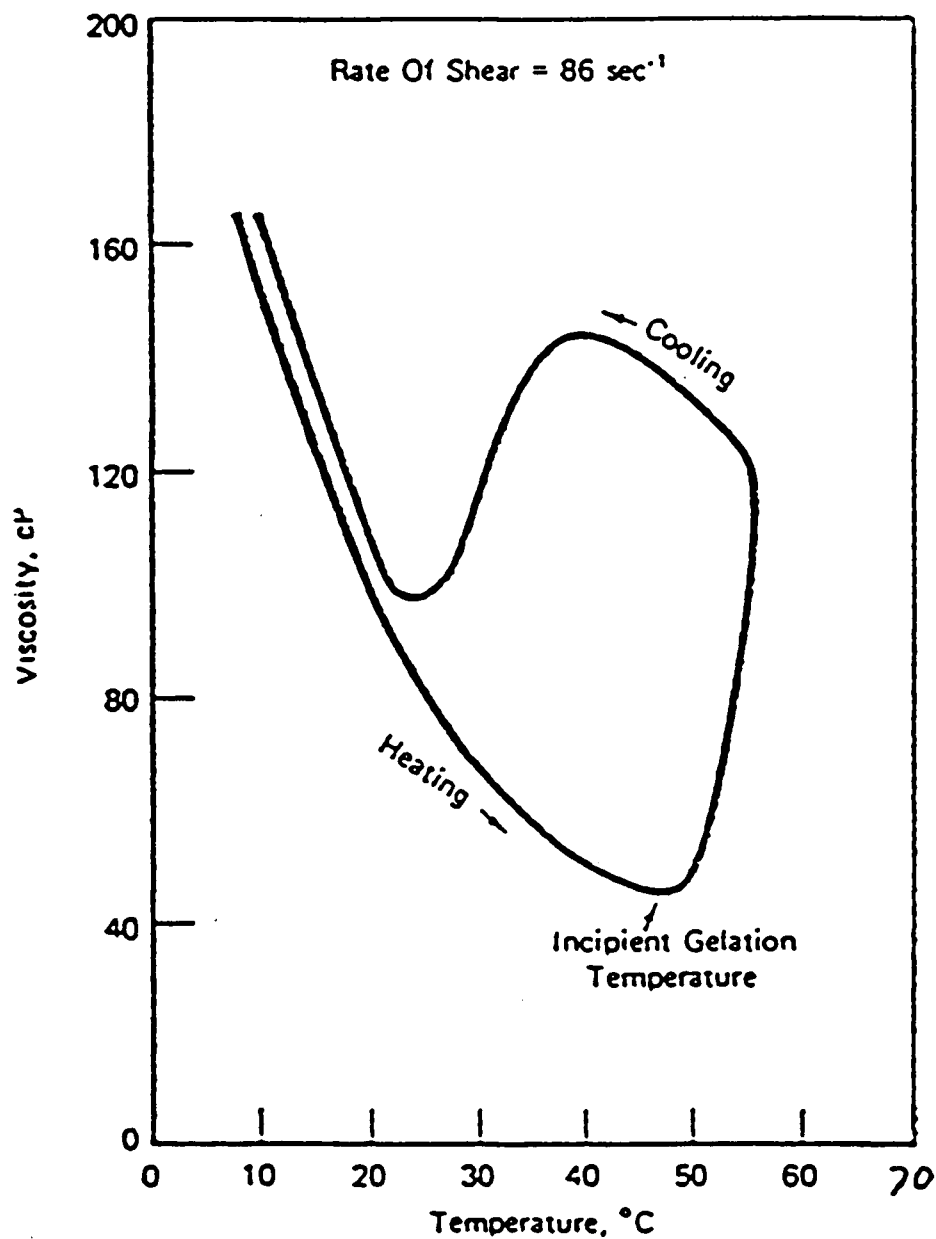
Fig. 1.   Thermal gelation of a 2% aqueous methylcellulose
           solution, with a viscosity of 100 cp at 20°C, heating
           rate 0.25 °C/min.   (Anonymous, 1987)

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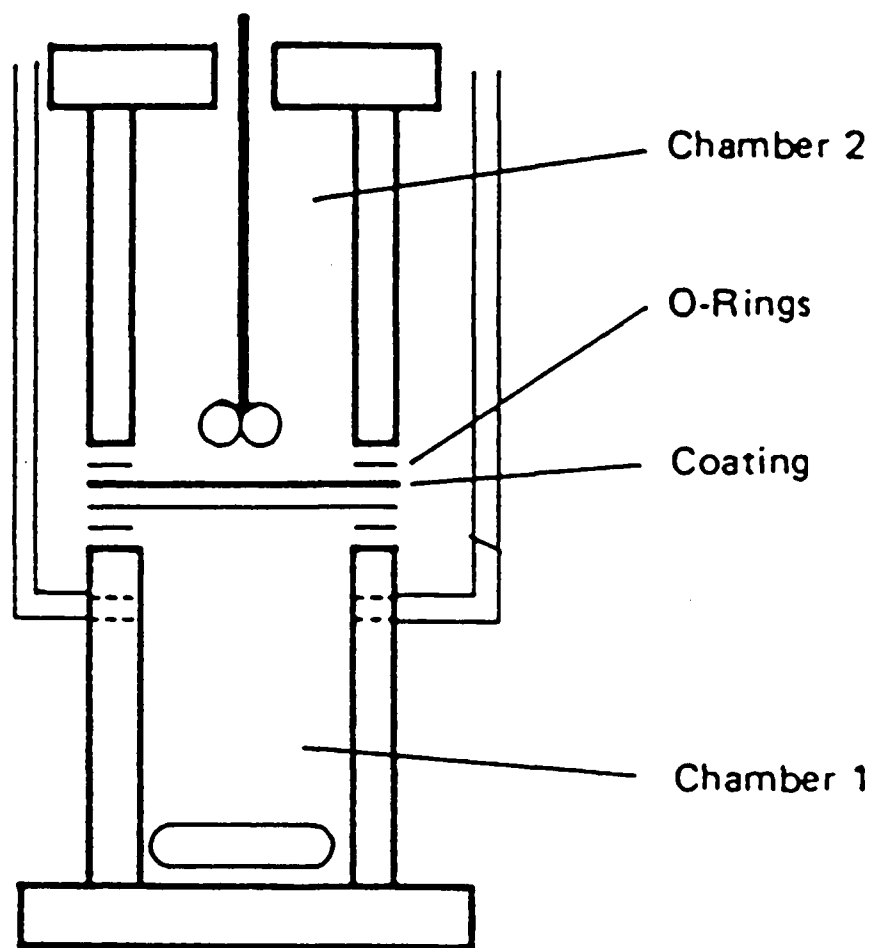
Fig. 2. Permeability cell used to determine film permeability constants (Torres, 1987).
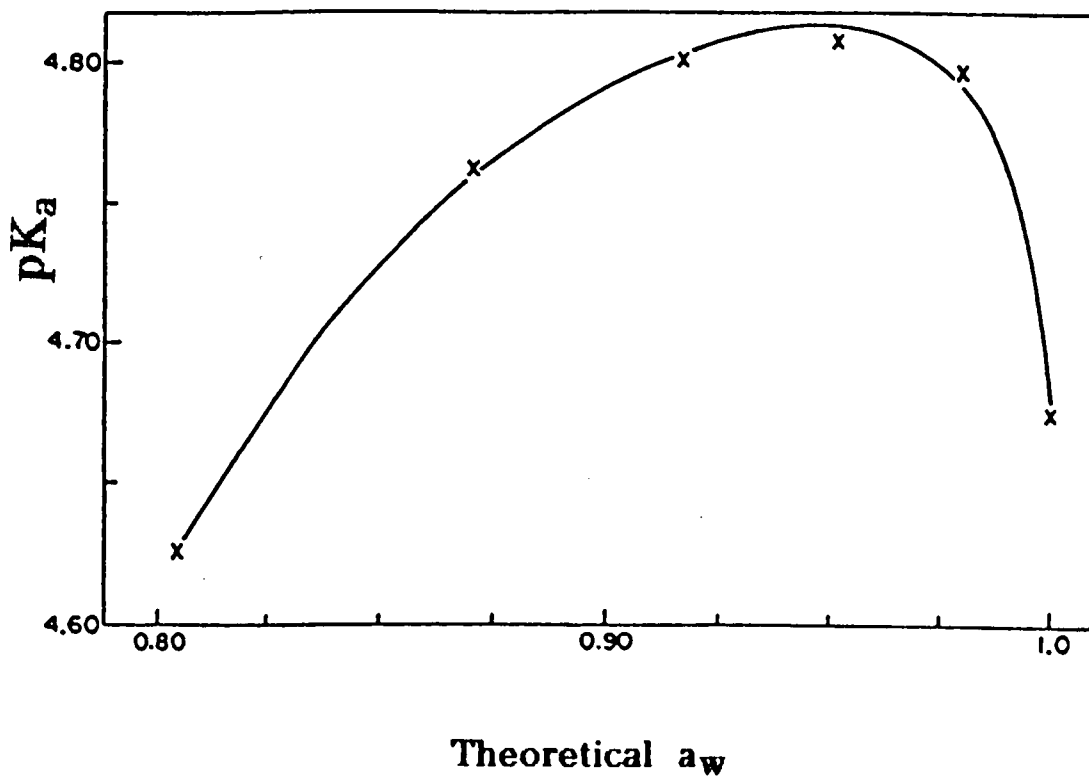
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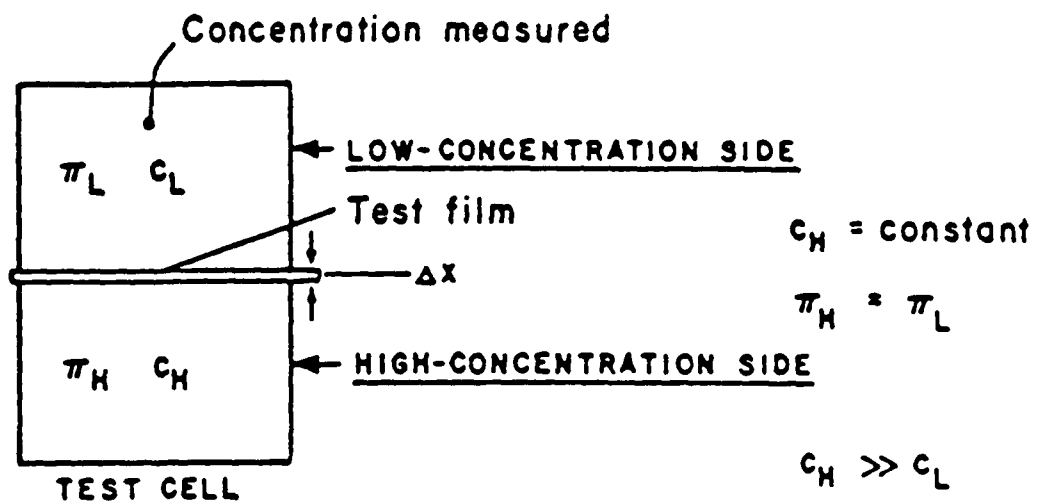
Fig. 4.   Schematic representation of the concentration-increase
method to determine the film permeability of gases.
(Karel, 1975)

Sorbic Acid and Potassium Sorbate Permeability
of an Edible Methylcellulose-Palmitic Acid Film:
Water Activity and pH Effects

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ABSTRACT

Edible films and coatings may be used as vehicles for incorporating food additives such as antioxidants and antimicrobial agents onto food surfaces where deterioration by microbial growth or oxidation often begins. The potassium sorbate and sorbic acid permeability through an edible film composed of methylcellulose and palmitic acid (ratio 3:1) were evaluated as a function of water activity (a_w) and pH. For films with a thickness of 55-66 μm, potassium sorbate permeability increased from 2.3×10^{-10} to 2.0×10^{-8} (mg/sec cm^2)(cm)/(mg/mL) as a_w increased from 0.65 to 0.80. Films were not stable at a_w levels above 0.80. The permeability of the film to sorbic acid decreased from 3.3×10^{-8} to 9.1×10^{-10} (mg/sec cm^2)(cm)/(mg/mL) as pH increased from 3 to 7. At these pH values the percentage of undissociated acid was 97.5% and 0.4%, respectively.

INTRODUCTION

The quality and stability of foods are often affected by diffusion phenomena. In many foods, particularly in fabricated foods, the presence of concentration gradients gives rise to non-equilibrium states resulting in the movement of water and other solutes. This often leads to undesirable changes in texture, color and flavor, which become particularly important during long-term storage of foods (Guilbert et al., 1985).

Antimicrobial additives are increasingly used as one of the numerous "hurdles" employed in the preservation of foods (Giannakopoulos and Guilbert, 1986). Sorbic acid and its salts have been used in the preservation of poultry products (Robach and Ivey, 1978; Robach, 1979; Cunningham, 1979), intermediate moisture foods (Troller and Christian, 1978a,b; Torres and Karel, 1985), and meat products (Greer, 1982; Zamora and Zaritzki, 1987a,b). A pH reduction increases the availability of the most active form of sorbic acid and other lipophilic acids used as preservatives (Eklund, 1983). The concentration of undissociated acid can be calculated on the basis of acid pK_a and food pH. pK_a values depend upon water activity since dissociation is mediated by water to form a hydronium ions (Pethybridge et al., 1983).

The growth of microorganisms on food surfaces, plays an important role in the spoilage of meat, fruits and vegetables (Roth and Loncin, 1985). To cope with surface microbial problems, food processors use preservatives in surface treatments. A potassium

sorbate dip reduces the total number of viable bacteria at refrigeration and temperature abuse conditions (Robach and Ivey, 1978; Robach and Sofos, 1982; Lueck, 1984). However, the shelf-life extension achieved is limited. Reduction of the surface preservative concentration due to diffusion into the food bulk reduces the effectiveness of the surface treatment (Torres et al., 1985; Vojdani and Torres, 1989a,b,c). Therefore, it is important to predict and control the migration of these preservatives.

An edible film or coating may be used as a vehicle for incorporating food additives such as antioxidants and antimicrobial agents onto food surfaces where deterioration by microbial growth or oxidation often begins (Kester and Fennema, 1986). Vojdani and Torres (1989a,b,c) evaluated the permeability to potassium sorbate of several polysaccharide-based films alone and in combination with various lipids. A methylcellulose-palmitic acid (MC-PA) film (ratio 3:1) was reported as the most promising permeability barrier. The evaluated permeability constant (K) for a MC-PA film with an average thickness of 40 μm was 1.2×10^{-8} (mg/sec cm^2)(cm)/(mg/mL). Vojdani and Torres (1989a,b) also found an excellent agreement between experimental data and the Arrhenius activation energy model. This suggests that it should be relatively simple to conduct storage stability studies under changing storage temperature conditions for foods coated with such films. Further evaluation of the effectiveness of this film combined with antimicrobial agents to improve surface microbial stability are needed to facilitate its application by industrial users. This study focuses on the

permeability of an edible MC-PA film (ratio 3:1) as affected by a_w and pH. Lowering pH changes most antimicrobial agents from a dissociated to an undissociated form and water activity affects the hydration status of the film. Therefore, both factors could influence the permeability of the film to antimicrobial agents.

MATERIALS AND METHODS

Reagents

Methylcellulose (MC, Methocel A 15-LV, Premium) was donated by Dow Chemical Co. (Midland, MI). Palmitic acid (C_{16}, 99%) and polyethylene glycol 400 (PEG) were purchased from Sigma Chemical Co. (St. Louis, MO). Glycerol was purchased from J.T. Baker Chemical, Phillisbury, NJ. Potassium sorbate (K-sorbate) and sorbic acid were donated by Monsanto Co. (St. Louis, MI). Ethanol (95%, reagent) was purchased from the OSU Chemistry Store.

Film preparation

Methylcellulose-palmitic acid films (ratio 3:1) were prepared by the emulsion technique using glass plates and a thin layer chromatography (TLC) applicator (Kamper and Fennema, 1984a; Vojdani and Torres, 1989b). The TLC applicator was set at 0.125 cm which resulted in films with a thickness of 55-66 μm. Films were dried at 90-95°C for 15 minutes.

Permeability tests

A permeability cell similar to the one described by Torres

(1987) was used to determine the effects of water activity (a_w) and pH on the permeation process. Potassium sorbate was used to determine the effect of a_w and sorbic acid for the effect of pH. All tests were run at constant temperature (24°C).

Effect of a_w

The upper chamber of the permeability cell contained pure glycerol solutions at four different a_w levels (0.65, 0.70, 0.75 and 0.80). The lower chamber contained a 2.5% w/v potassium sorbate solution at the same a_w as the upper chamber. Samples (0.5 mL) were taken from the upper chamber and then diluted to 3 mL. Potassium sorbate concentration of the collected samples was determined spectrophotometrically at 257 nm (UV/VIS Spectrophotometer, Varian DMS 100, Victoria, Australia).

Effect of pH

Pure water-glycerol solutions were placed in the upper chamber. The lower chamber was filled with a 0.1% w/v sorbic acid solution at the same a_w and pH as the upper chamber. Undissociated sorbic acid concentrations at pH 3.0, 4.5, 5.0, 6.0 and 7.0 for 0.80 a_w glycerol-water solutions (pK_a = 4.6; Pethybridge, 1983) were calculated as 97.5, 55.6, 28.4, 3.8 and 0.4%, respectively. In this experiment, sorbic acid was used instead of potassium sorbate because the latter precipitated when pH was lowered. Sorbic acid is highly insoluble, therefore, the lower chamber concentration had to be reduced and the solution prepared as follows. A supersaturated

solution (at room temperature) was filtered using folded filter paper No. 588 (Schleicher and Schuell Inc., Keene, NH). The concentration of the filtrate was determined spectrophotometrically. Finally, the solution concentration was adjusted with pure aqueous glycerol to 0.1% w/v sorbic acid.

The wavelength for maximum absorbance (λ_{max}) used to determine sorbic acid concentration changed with pH from 253 to 264 nm. Calibration curves were prepared for each pH value at the corresponding λ_{max}.

Film thickness measurement

Film thickness was measured using a top mounted Best Test Indicator (EDP No. 45987, Brown and Sharp Mfg. Co., N. Kingston, RI). Measurements were made after running the permeability test to avoid mechanical damage to the film when determining its thickness. Reported thickness values are the average of at least 20 measurements taken over the film area exposed to the permeation process.

Determination of permeability constants

Permeability constants (K) were calculated as described by Torres (1987). The preservative amount permeated per unit area of film was plotted as a function of time. The slope of the linear portion of the curve was calculated and used in the following expression:

$$K = F\ell/c \qquad\qquad (8)$$

where K is the permeability constant; F is the slope of the curve expressed as amount of preservative per film area and unit time; ℓ is the film thickness and c is the initial preservative concentration in the lower chamber (25 mg/mL for K-sorbate and 1 mg/mL for sorbic acid).

RESULTS AND DISCUSSION

Effect of a_w

The amount of K-sorbate diffused per unit area as a function of time and a_w (0.65, 0.70, 0.75 and 0.80) for MC-PA films with thickness varying from 55 to 66 nm is shown in Fig. 5. Average values of triplicate runs could not be calculated because of the small variation in film thickness. At constant temperature, the K-sorbate permeation rate decreased significantly as a_w decreased (Fig. 5). At 0.80 a_w, the amount permeated in 2 h was 0.6 mg/cm^2; at 0.75 a_w, the amount permeated in 6 h was 0.5 mg/cm^2; at 0.70 a_w, the amount permeated in 15 h was 0.1 mg/cm^2; and at 0.65 a_w, the amount permeated in 26 h was 0.04 mg/cm^2, reflecting significantly lower permeation rates at lower a_w's. This agrees well with Guilbert et al. (1985) who noted that as a_w is lowered less solvent is available as a diffusion medium.

The evaluation of the permeability constant (K, (mg/sec cm^2)(cm)/(mg/mL)) using Eq. (8) yielded the following values: 2.0×10^{-8} at 0.80 a_w, 8.5×10^{-9} at 0.75 a_w, 6.6×10^{-10} at 0.70 a_w,

and 2.3×10^{-10} at 0.65 a_w. These results indicate that the hydration status of the films, which depends on the water activity of the food being coated, will affect the potassium sorbate permeation rate as noted earlier by Vojdani and Torres (1989a).

According to Crank (1976, Eq. 4.26) extrapolation of the steady state rate of potassium sorbate transfer through the film can be used to confirm the above results. For example, at 0.80 a_w for a film with a thickness of 66 μm the obtained intercept on the time axis was 6 min and the calculated value using Crank's equation was 5.86 min. This value, known as the lag period, increased as the a_w decreases; consequently, at 0.65 a_w for a film with a thickness of 63 μm, the observed lag phase was 8 h and the calculated lag period was 8.2 h.

In tests at low water activity, the time of exposure of the film to mechanical abuse in the permeability cell was excessively long. For example, at 0.65 a_w and after running the test for several hours, sometimes, the slope of the curve increased suddenly. Most likely, this increase in permeation rate reflected mechanical damage to the film.

Effect of pH

At constant a_w (0.80) and temperature (24°C), sorbic acid permeation rate decreased significantly when pH was increased. Fig. 6 shows the amount of sorbic acid in mg/cm^2 permeating as a function of time at pH 3.0, 4.5, 5.0, 6.0 and 7.0. Again, test replicates can not be reported as an average because of the small

differences in film thickness.

At pH 3.0, the amount permeated in 8 h was 0.16 mg/cm^2; at pH 4.5, the amount in 8 h was 0.07 mg/cm^2; at pH 5.0, the amount in 12 h was 0.07 mg/cm^2; at pH 6.0, the amount in 30 h was 0.06 mg/cm^2; and, at pH 7.0, the amount in 30 h was only 0.015 mg/cm^2. The values for the permeability constant at pH 3.0, 4.5, 5.0, 6.0 and 7.0 were 3.3×10^{-8}, 1.3×10^{-8}, 1.1×10^{-8}, 4.0×10^{-9} and 9.1×10^{-10} (mg/sec cm^2)(cm)/(mg/mL), respectively.

CONCLUSIONS

The permeability values reported in this study for MC-PA films (ratio 3:1) are consistent with those previously reported by our laboratory (Vojdani and Torres, 1989a,b,c). This film could be used to increase the surface microbial stability of foods with a_w and pH values in the 0.65-0.80 and 3-7 ranges, respectively.

Longer surface retention of sorbic acid is possible at higher pH's, lower a_w's and lower temperatures when using the MC-PA film selected in this study. It should be noted that the higher retention at higher pH will help balance the lowering of sorbic acid effectiveness as pH is increased (Eklund, 1983).

An approximation presented earlier by Torres (1987, Eq.6) can be used to estimate the relative effectiveness of the film/sorbate combination under various food conditions. For example, MC-PA films (ratio 3:1) with a thickness of 0.1 mm and 0.2 mm, on a food with pH 5.0, $a_w = 0.8$, and stored at 24°C would retain significant sorbate

surface concentrations for 14 and 54 days, respectively (K = 1.1×10^{-8} (mg/sec cm^2)(cm)/(mg/mL)). For products at pH 6.0 and 0.8 a_w, the same films will have a lower permeability constant (4.0×10^{-9} (mg/sec cm^2)(cm)/(mg/mL)) and the calculations would yield 37 and 147 days for 0.1 and 0.2 mm film thickness, respectively. Microbiological tests are needed to confirm these estimations (Torres, 1987).

Vojdani and Torres (1989b,c) suggests the possibility of using cellulose ether-based films to enhance the microbial stability of refrigerated meats. However, methylcellulose and hydroxypropyl methylcellulose films (data not reported) are unstable at a_w levels above 0.8. Practical film applications are thus limited to intermediate moisture food products.

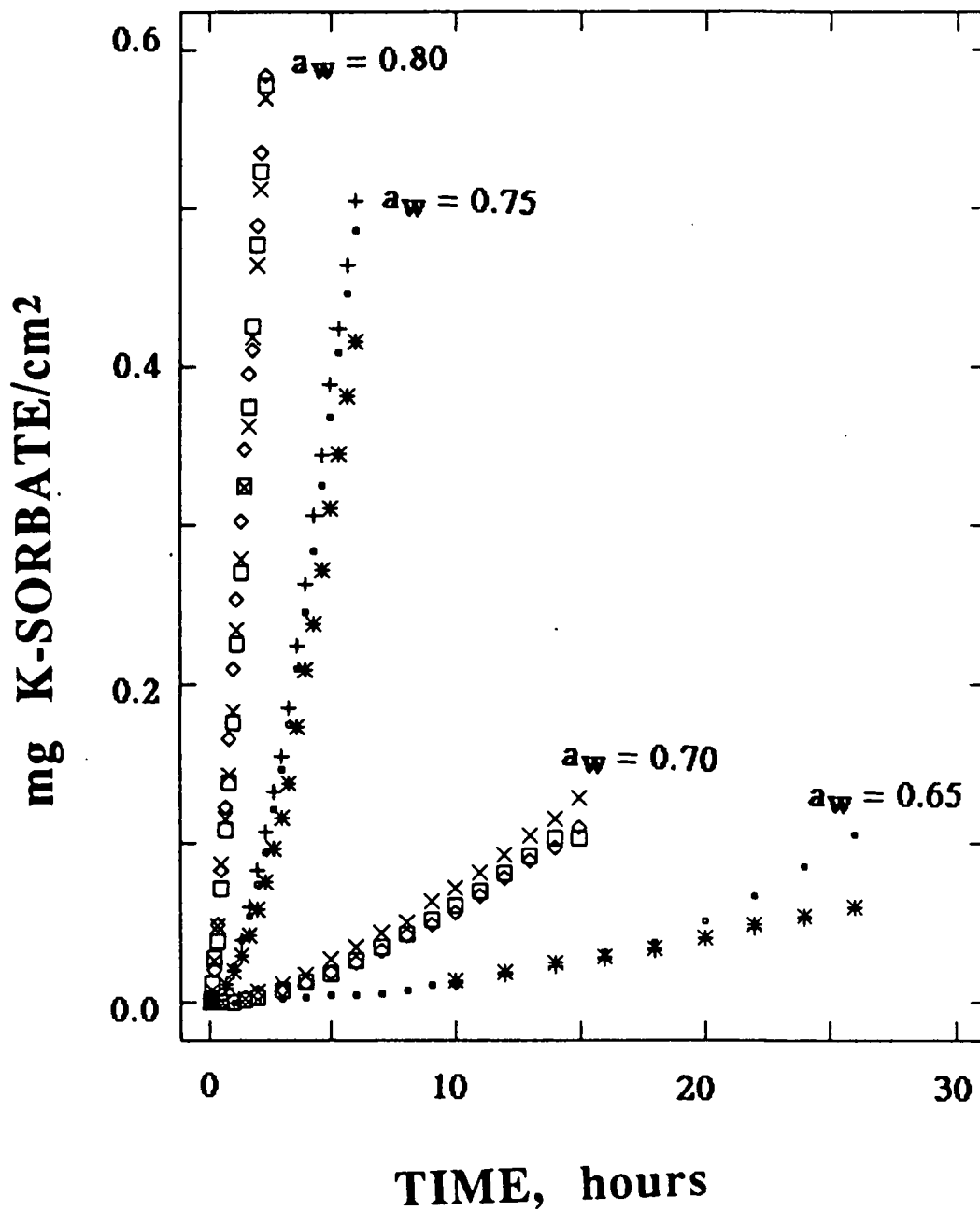Fig. 5.   Effect of water activity on the permeation
           rate of potassium sorbate through an edible
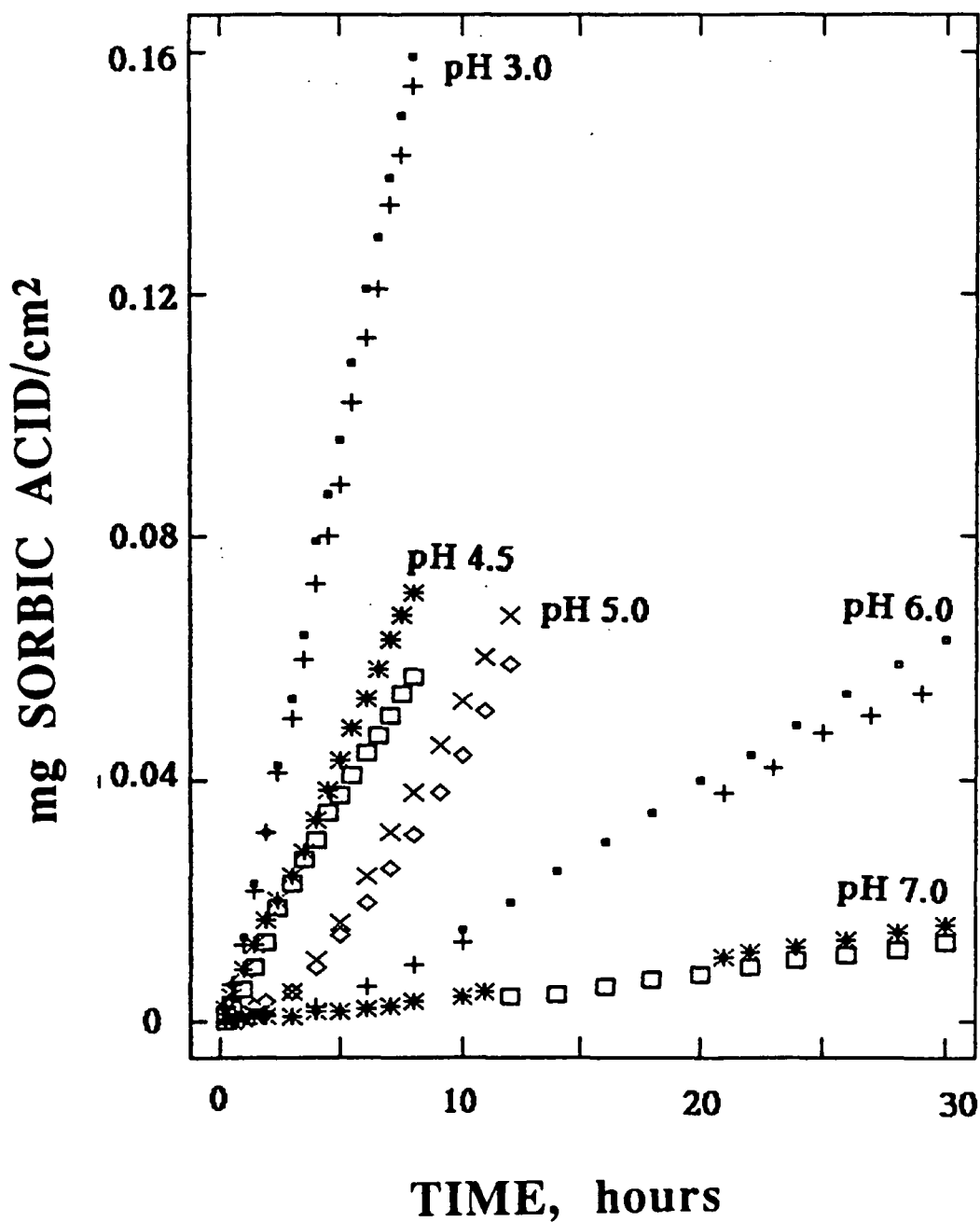   methylcellulose-palmitic acid film,
           ratio 3:1, 24°C.

Fig. 6. Effect of pH, at a_w 0.80, on the permeation rate of
sorbic acid through an edible methylcellulose-palmitic
acid film, ratio 3:1, 24°C.

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Oxygen Transmission Rate of an Edible
Methylcellulose-Palmitic Acid Film

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ABSTRACT

The oxygen permeability of an edible film (average thickness, 55 μm), composed of methylcellulose and palmitic acid (ratio 3:1), was evaluated at 24°C, atmospheric pressure, and at different percentages of relative humidity (RH). RH values in the 0-60% range had no significant effect on oxygen transmission rate (OTR); calculated OTR values ranged from 660 to 740 mL O_2 (STP)/m^2 24h atm. At 80% RH, the OTR doubled to 1,500 mL O_2 (STP)/m^2 24h atm). This effect correlated well with the moisture isotherm for the film which showed a low moisture content in the 0-60% RH range and a rapid increase at higher RH values.

INTRODUCTION

Oxygen permeability is a property of particular importance for the selection of food packaging materials. Many foods packaged in flexible films are sensitive to oxygen, and their shelf-life is determined largely by the oxygen permeability of the package (Davis and Burns, 1969; Kester and Fennema, 1986). Film composition, temperature and humidity affect the permeability to oxygen of films used for food packaging. Conditions of high relative humidity can increase the permeability of hydrophilic films, while hydrophobic materials are unaffected (Rigg, 1979).

The availability of oxygen has an influence on the type of microbial spoilage of a food product. This is largely determined by the packaging material used to protect it. Therefore, it is necessary to evaluate the permeability characteristics to oxygen of the packaging materials used. Several methods are used for testing the permeability of flexible films to gases and only permeability value ranges are given since unlike most analytical procedures no method of standardization is available (Karel et al., 1963; Davis and Huntington, 1977; Rigg, 1979).

Edible polysaccharide-fatty acid films have been developed to extend product shelf-life. Kamper and Fennema (1984a,b, 1985) evaluated the permeability characteristics of these films to the transfer of moisture and focused on practical applications of the films as moisture permeability barriers. Vojdani and Torres (1989b,c) evaluated the permeability properties of polysaccharide-

fatty acid films to the transfer of potassium sorbate, including the effect of temperature. These authors focused on the use of a coating/chemical preservative combination to improve the surface microbial stability of foods. Rico-Peña and Torres (1989) selected a methylcellulose-palmitic acid film formulation suggested by Vojdani and Torres (1989c) and evaluated the effect of a_w and pH on preservative permeation rate.

The industrial application of a coating/chemical preservative combination requires data on the transfer of gases through the coating. A low oxygen transmission rate could lead to the development of anaerobic conditions on the food surface. In this paper we report on the effect of a_w on the oxygen transmission rate of a methylcellulose-palmitic acid film (ratio 3:1).

MATERIALS AND METHODS

Reagents

Methyl cellulose (MC, Methocel A 15-LV, Premium) was donated by Dow Chemical Co. (Midland, MI). Palmitic acid (C16, 99%), polyethylene glycol 400 (PEG), potassium acetate, potassium carbonate, sodium bromide and ammonium chloride were purchased from Sigma Chemical Co. (St. Louis, MO). Potassium hydroxide, ammonium sulfate, potassium iodide, potassium nitrate, potassium chloride, sodium chloride, and potassium sulfate, all in analytical reagent quality, were purchased from VWR Scientific (Portland, OR). Ethanol (95%, reagent) was purchased from the OSU Chemical Store. Oxygen and nitrogen (pre-purified grade) gases were purchased locally

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(Industrial Welding Supply Inc., Corvallis, OR).

Film preparation

Methyl cellulose-palmitic acid films in a ratio of 3:1 were prepared by the emulsion technique described by Kamper and Fennema (1984a) and Vojdani and Torres (1989b,c) using glass plates and a thin layer chromatography (TLC) applicator. The TLC applicator was set at 1.25 mm which resulted in films with a thickness of 55-65μm. Films were dried at 90-95°C for 15 minutes.

Film thickness

The thickness of the films was measured using a top mounted Best Test Indicator (EDP No. 45987, Brown and Sharp Mfg. Co., N. Kingston, RI). Film thickness was measured after running the permeability test to avoid mechanical damage to the film when determining its thickness. Reported thickness values are the average of at least 20 measurements taken all over around the film area exposed to the permeation process.

Permeability tests

The oxygen permeation rate of the MC-PA film was determined at 24°C using a gas permeability cell (Fig. 7) similar to the one described by Davis and Huntington (1977). This cell operates on the concentration-increase principle developed by Landrock and Proctor (1952) and was custom built in Chile (Escuela Industrial, Valparaíso, Chile). The film was clamped between the two

compartments. Two neoprene O-rings and vacuum grease were used as sealing aids to prevent gas leaking. The test compartment (lower compartment, 566 mL) was flushed with nitrogen for 2 h and, simultaneously, the upper compartment was flushed with the test gas, oxygen. After 2 hours, gas flow from the supply cylinders was stopped. The inlet and outlet valves of the permeability cell were turned off in the mentioned order to ensure equal pressure (atmospheric pressure) in the two cell compartments as suggested by Davis and Huntington (1977).

Samples of gas (5 mL) were taken with a syringe from the test compartment. The increase in oxygen concentration was monitored using an oxygen head space analyzer (MOCON LC-700F, Minneapolis, MN). Five mL of nitrogen were added back to the lower cell compartment to replace the volume of gases removed during sampling and thus minimize changes in total pressure.

Relative humidity was controlled by passing each gas stream through a gas drying tower (0% RH). In the 20-80% RH range, the gases were passed first through a gas washing bottle containing distilled water to increase RH to 100%, followed by a second gas washing bottle containing a saturated salt solution corresponding to the required relative humidity condition, and finally through fiber glass to remove any saturated solution carry-over by the gas stream (Fig. 7). The saturated solutions used were potassium acetate (22% RH), potassium carbonate (43% RH), sodium bromide (57% RH) and ammonium chloride (79% RH) (Labuza, 1984).

Determination of oxygen transmission rate

Ideal gas behavior was assumed to correct oxygen concentration measurements because of the amount of oxygen lost during sampling and the 5 mL nitrogen added back to minimize pressure changes. Corrected O_2 data were plotted as a function of time. The slope of the linear portion of the curve was used to determine the amount of oxygen permeating per unit time at 24°C and at the prevailing atmospheric pressure. The value was then recalculated as the volume of oxygen permeating per unit time at standard pressure and temperature conditions, and used to calculate the oxygen transmission rate by the following equation:

$$\text{OTR} = \frac{\text{Volume } O_2 \text{ (STP)}}{\text{(film area)(time)(pressure difference)}}$$

OTR was expressed as mL O_2 (STP)/m^2 24h atm for a film with a given thickness at a given temperature and % RH.

Determination of film moisture isotherm

Triplicate samples of dehydrated MC-PA film were weighed and placed in tightly closed containers with a controlled RH environment and at 24°C (Labuza, 1984). Saturated salt solutions used to create the different %RH environments were potassium hydroxide (8% RH), potassium acetate (22% RH), potassium carbonate (43% RH), sodium bromide (57% RH), potassium iodide (69% RH), sodium chloride

(75% RH), ammonium chloride (79% RH), ammonium sulfate (81% RH), potassium chloride (84% RH), potassium nitrate (94% RH) and potassium sulfate (97% RH) (Labuza, 1984). After 7, 9 and 10 days, individual samples were withdrawn from the containers and the increase in moisture content determined by weight difference.

Statistical analysis

Statistical analysis of experimental data were done using Statgraphics (Version 3.0) on an IBM PS/2 model 30286.

RESULTS AND DISCUSSION

The amount of oxygen permeated as a function of time for a MC-PA film with a thickness of 55 μm at 0, 22, 43, 57 and 79% RH (24°C) is shown in Fig. 8. The calculated OTR values are shown in Table 6. RH values in the 0-60% range had no significant effect on oxygen transmission rate (OTR). Calculated OTR values ranged from 660 to 740 mL O_2 (STP)/m^2 24h atm. At 79% RH, the OTR doubled to 1,400 mL O_2 (STP)/m^2 24h atm). Statistical analysis showed this effect with a 95% confidence interval ($F_{calculated}$ = 812.8, $F_{tabulated}$ = 5.19; Devore and Peck, 1986). Further analysis of multiple comparisons of means showed that the mean of OTR obtained at 79% RH was different from the means of OTR values obtained for 0, 22, 43 and 57% RH and that the means of OTR evaluated in the 0-57% RH range were not different from each other. This observation is consistent with earlier studies. Rico-Peña and Torres (1989) noted that the

stability of MC-PA films is affected when exposed to environments with a_w's higher than 0.80. The moisture sorption isotherm (Fig. 9) indicates that the moisture content of the film changes significantly at % RH larger than 50-60%. Therefore, OTR values as a function of RH agree well with the moisture uptake of the film as affected by RH conditions.

CONCLUSIONS

The MC-PA film is highly permeable to oxygen when compared to data reported in the literature for various other films (Table 7). More studies on the permeability to oxygen of the MC-PA film are needed. It is particularly recommended to evaluate the effect of temperature on OTR and analyze such data using the Arrhenius relationship. The successful application of this model would allow the determination of OTR values at any temperature.

ACKNOWLEDGEMENTS

TABLE 6.   Oxygen transmission rate, MC-PA film, 24°C

% RH[1]	Thickness μm	OTR mL O_2 (STP)/m^2 24h atm
0	56	660
	52	700
22	55	710
	55	690
43	55	710
	55	720
57	55	740
		720
79	55	1,390
	55	1,400
	53	1,560

[1] Labuza, 1984

TABLE 7.   Effect of relative humidity on the oxygen transmission
rate (OTR) of commercial food packaging materials

FILM	% RH	THICKNESS (μm)	OTR mL (STP)/m^2 24h atm
Biaxially oriented polypropylene[1]	0	12-32	115-180
One side acrylic coated oriented polypropylene[1]	0	22-38	62
High opacity, oriented polypropylene[1]	0	31-44	62
Metalized coextruded biaxially oriented polypropylene[1]	0	18-36	77-155
Nitrocellulose cellophane[2]	53	20	210
	75	20	440
	100	20	2,740
Nitrocellulose coated cellophane[3]	0	20	0.87
	53	20	34.70
	92	20	726
Nitrocellulose coated cellophane[2]	0	20	13
	53	20	500

[1]Anonymous (1988), OTR at 23°C.
[2]Rigg (1979), OTR at 25°C.
[3]Davis (1964), OTR at 25°C.

HUMIDITY CONTROL TOWERS

From O2 cylinder

O2 flux

GAS PERMEABILITY CELL

Glass fiber

From N2 cylinder

N2 flux

Distilled water

Saturated salt solution

Clamping device

Upper compartment

Inlet valves

Outlet valves

Film

Bottom compartment

To back pressure bottle
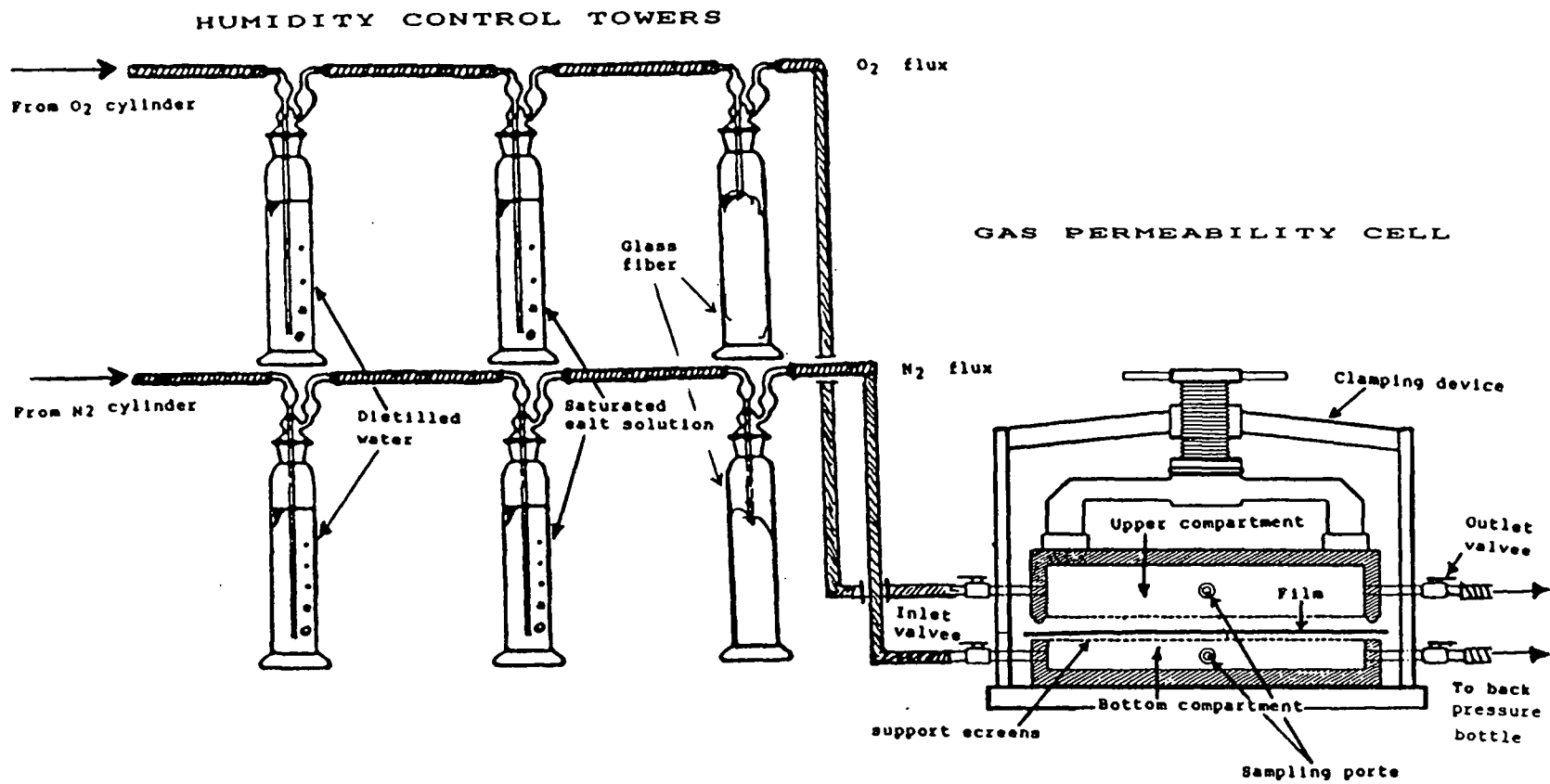
support screens

Sampling ports

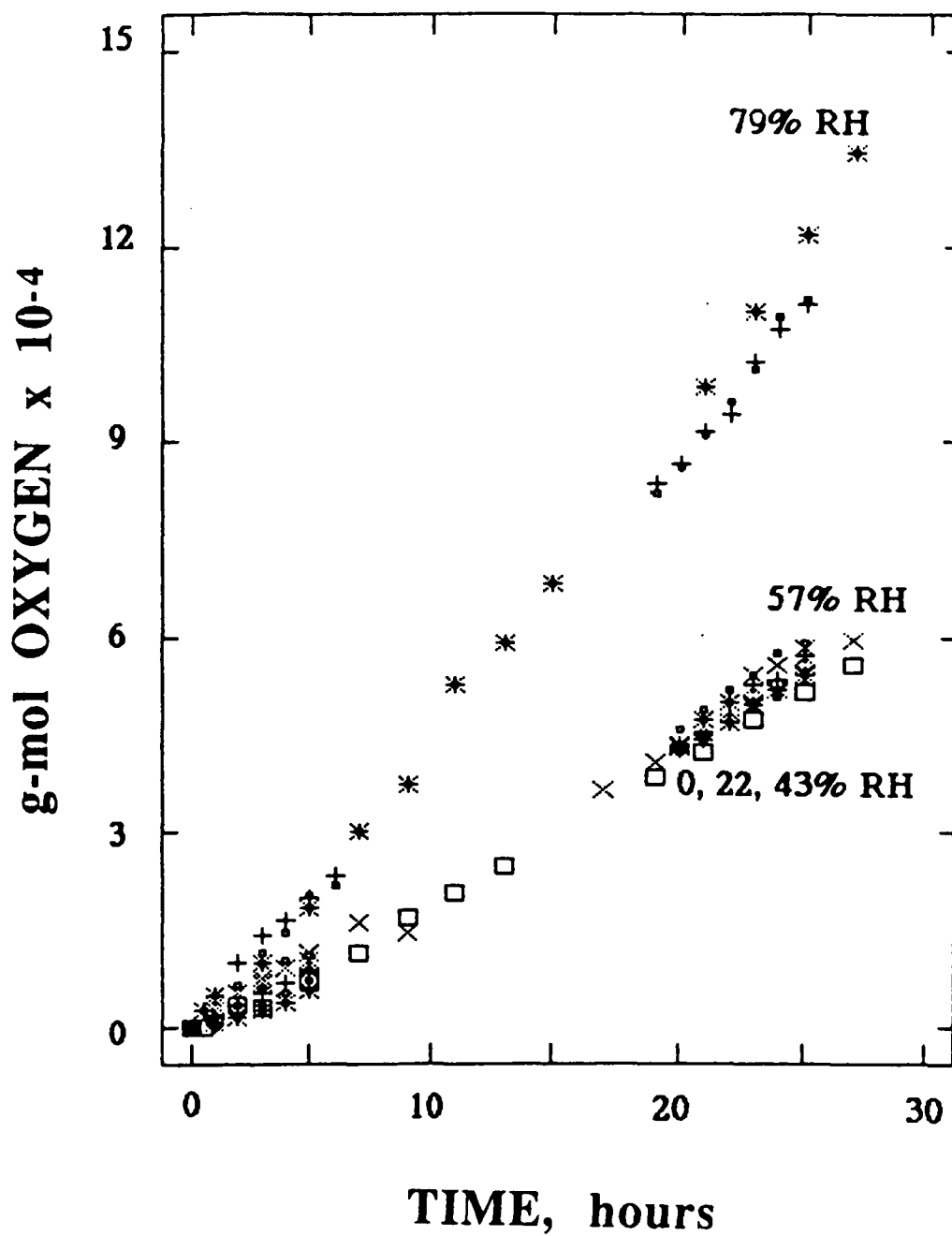Fig. 7.   Schematic representation of the oxygen permeability cell and related equipment

Fig. 8.   Effect of relative humidity on the oxygen
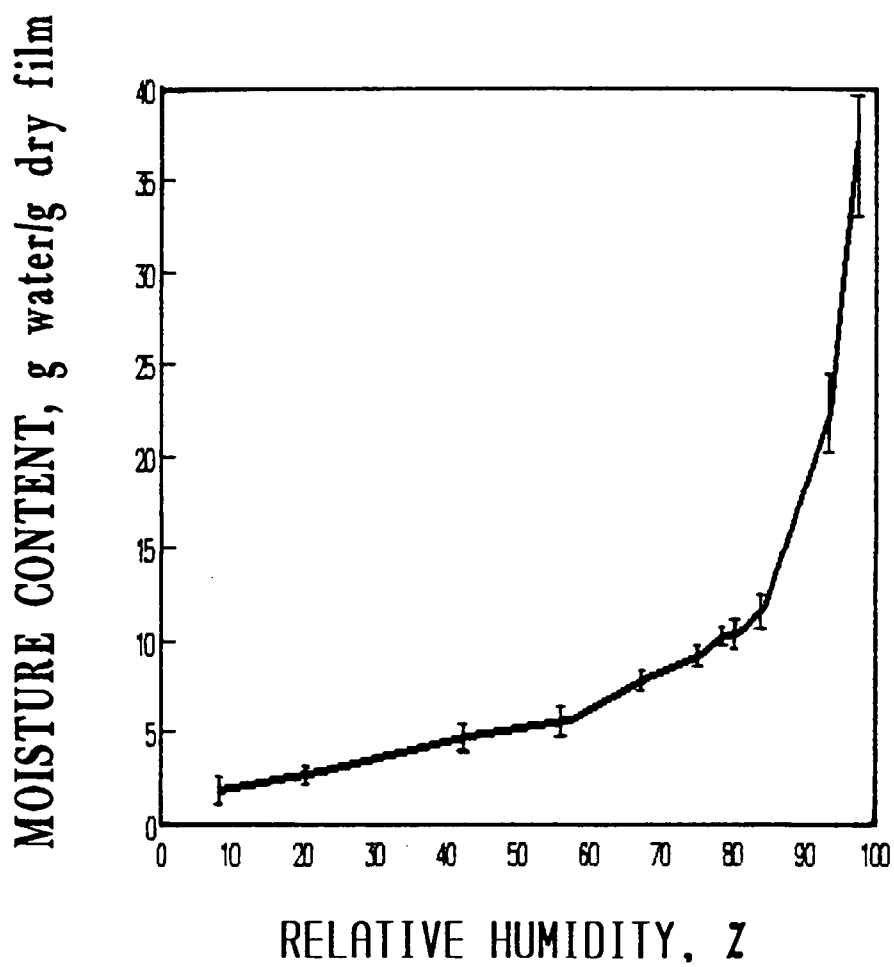permeability of an edible methylcellulose-palmitic
acid film, ratio 3:1, 24°C.

Fig. 9.   Moisture sorption isotherm of a methylcellulose-
palmitic acid film, ratio 3:1, 24°C.

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Edible Methylcellulose-based Films as
Moisture Impermeable Barriers in Sundae Ice Cream Cones

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ABSTRACT

An edible bilayer film composed of methylcellulose and palmitic acid in a 3:1 ratio and a pure methylcellulose film were tested as moisture impermeable barriers in a simulated sundae ice cream cone. Circular pieces of film were situated between the sugar cone and the chocolate layer of the samples. Sugar cones of samples containing methylcellulose-palmitic acid films showed no detectable moisture increase for 12 weeks storage at -10°F and for 4 weeks at +10°F and only negligible increments after these periods; the moisture increase was larger in samples containing pure methylcellulose films. Films retarded the moisture transfer from the ice cream to the sugar cone keeping its crispness for a period longer than three months which is the commercial shelf-life of the uncoated product.

INTRODUCTION

The dominant mechanism for moisture transfer in foods is the vapor pressure gradient between the food product and its environment, and between the internal components of foods. The transfer of moisture between a food product and its environment is controlled by moisture impermeable packaging materials. The control of moisture migration within heterogeneous foods can be achieved by eliminating or reducing the vapor pressure (water activity) gradient between food components, or by separating those food components with different water activities by an edible moisture-impermeable barrier (Kamper and Fennema, 1985).

Edible polysaccharide-fatty acid films have been studied by Kamper and Fennema (1984a,b; 1985) as moisture impermeable barriers and by Vojdani and Torres (1989b) as highly impermeable barriers to the diffusion of chemical preservatives. This report presents the use of a methyl cellulose (MC)-palmitic acid (PA) film (MC:PA ratio of 3:1) as a moisture impermeable barrier in a sundae ice cream cone (Drumstick Co., Columbus, OH). Moisture transfer was followed by monitoring weight gain of sugar cone samples stored under various temperature conditions and including temperature abuse.

MATERIALS AND METHODS

Materials

The materials used to prepare the films were methylcellulose (Methocel A 15-LV, Premium, Dow Chemical Co., Midland, MI), palmitic

acid (C_{16}, 99% purity, Sigma Chemical Co., St. Louis, MO),

polyethylene glycol (Sigma Chemical Co., St. Louis, MO), ethyl

alcohol (95%, reagent, OSU Chemical Stores) and distilled water.

Chocolate and sugar cones were supplied by Drumstick Co. and vanilla

ice cream was obtained from a local grocery store.

Film preparation

Methylcellulose-palmitic acid (MC-PA) and methylcellulose with

no palmitic acid (MC) films were prepared using glass plates and a

thin layer chromatography (TLC) applicator as previously described

(Kamper and Fennema, 1984a; Vojdani and Torres 1989b). The TLC

applicator was set at 1.25 mm which resulted in films with a

thickness of 55-65 μm. Films were dried at 90-95°C for 15 minutes.

Sundae ice cream cone simulation

Films were cut into disks to cover preweighed, flat, circular

sugar cone samples placed inside the cap of 150 mL plastic

containers (container-1, Fig. 10). Chocolate was melted at 125°F,

weighed over the film disks and quickly spread to give a thickness

of approximately 1 mm which is similar to the thickness of the

chocolate layer found in commercial products. The area of the film

was larger than the area of the sugar cone to prevent chocolate from

sticking to the sugar cone. 50 mL plastic containers (container-2,

Fig. 10) were filled with ice cream and immediately placed over the

chocolate layer. A chocolate seal was made around container-2 to

insure that moisture transfer from the ice cream to the sugar cone

samples was only through the chocolate layer and the film. An empty 150 mL container was placed over the 50 mL container and carefully closed with the cap holding the sugar cone sample. Immediately after preparation, samples were kept for 2 h at -35°F and then stored as described below.

Storage conditions

Samples containing methyl cellulose-palmitic acid films were stored at -10°F and at +10°F. Samples containing pure methyl cellulose films were stored at +10°F. To simulate temperature abuse during handling and distribution of the product, MC-PA samples stored at -10°F were transferred one day every week to a room at +10°F.

Moisture determination

The weight increase of the sugar cone due to moisture transfer from the ice cream was first measured every week and then every two weeks during a period of over three months.

<center>RESULTS AND DISCUSSION</center>

Sundae ice cream cones produced commercially have a shelf-life of about 3 months when the cone loses its crispiness and becomes soggy (Wyman, 1989). Moisture transfer from the ice cream to the cone is accelerated when the product is temperature abused. As shown in Fig. 11, the use of methylcellulose films with and without

fatty acids placed between the chocolate layer and the cone reduces the uptake of moisture dramatically. At the end of the study the crispness of the sugar cones was maintained with no indication of sogginess.

Samples containing the MC-PA films and stored at -10°F (with one day per week at +10°F) showed no detectable moisture content increase during the 12 week storage test whereas those stored at +10°F showed detectable but very small increments in moisture content after 4 weeks storage. As expected, samples containing the pure MC films with no added fatty acids showed significantly larger weight gains as compared to the samples containing MC-PA films (Fig. 11).

One experimental difficulty during these tests involved achieving perfect separation of the sugar cone sample from the film, chocolate layer and ice cream and its transfer to weighing dishes without sample losses. This step was important to measure accurately the small weight gain of the sugar cone samples. Another experimental difficulty relates to the poor stability of the films at water activities above 0.8 (Rico-Peña and Torres, 1989); therefore, when applied to the tested product, the chocolate layer must completely cover the film, otherwise direct contact with the ice cream destroys the film at that location.

CONCLUSIONS

Results have shown that methyl cellulose-palmitic acid films

constitute a good moisture-impermeable barrier to retard moisture transfer from the ice cream to the sugar cone, thus maintaining the crispness of the cone for a period longer than three months and extending the shelf-life of the sundae ice cream cones.

Finally, it is strongly suggested to evaluate the sensory properties of the product containing the film and predict its consumer acceptability.
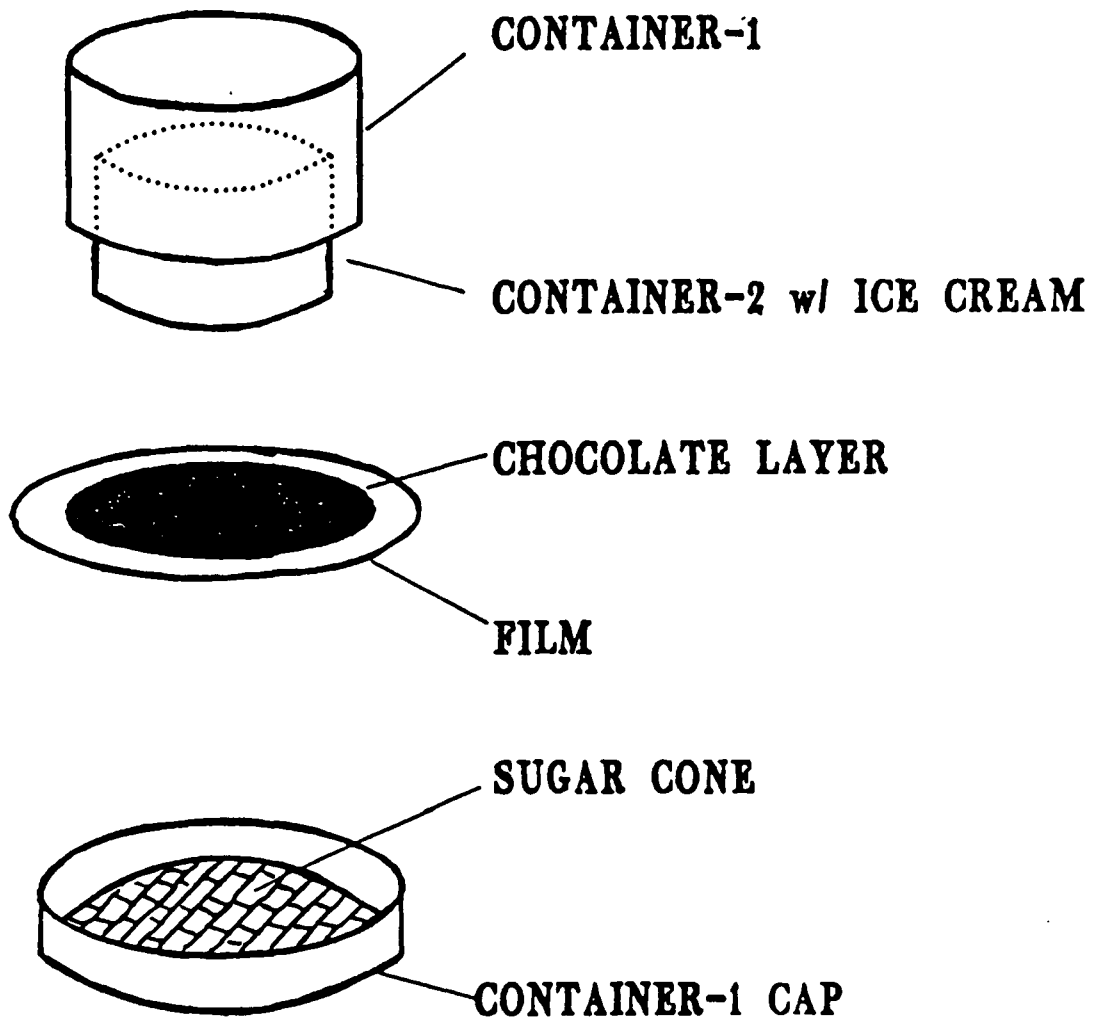
ACKNOWLEDGEMENTS

Fig. 10. Schematic diagram of the containers used to simulate a
sundae ice cream cone to test methylcellulose-based films
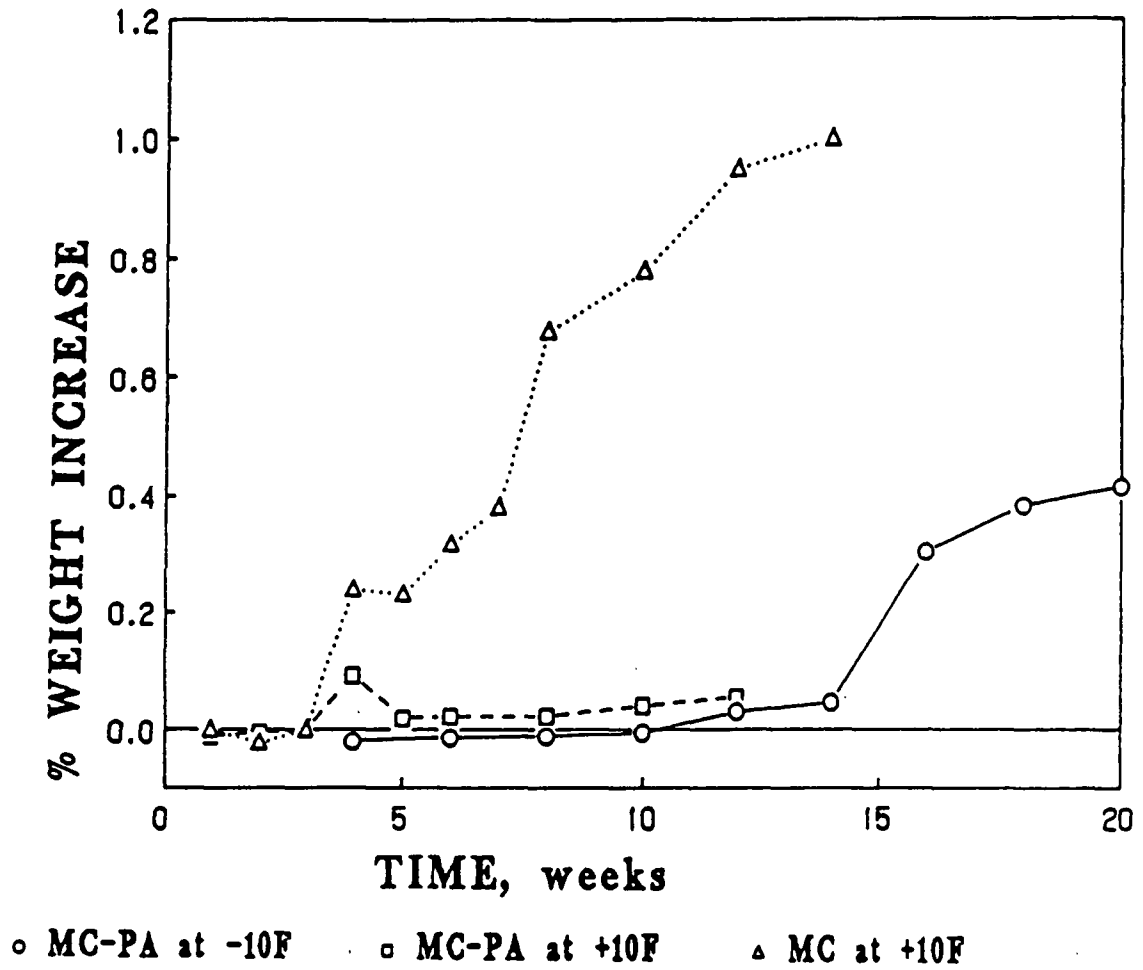as moisture impermeable barrier

Fig. 11. Moisture uptake of ice cream cone samples protected with methylcellulose based films

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SUMMARY AND CONCLUSIONS

The evaluation of the permeability properties of an edible MC-PA film to the transfer of solutes (sorbates), gases (oxygen) and moisture have confirmed the potential of methylcellulose-based films to increase the shelf-life of various foods.

First, MC-PA films can be combined with antimicrobial agents to improve the surface microbial stability of foods. Since MC-PA films are not stable at a_w's higher than 0.80, practical applications will be limited to intermediate food products (IMF). A mayor problem of IMF's is the surface growth of yeast and molds. Furthermore, sorbates are particularly effective fungistatic agents. Future studies should evaluate the effectiveness of the film/sorbate combination in IMF model systems challenged with yeasts and molds.

A great concern of food processors is the microbial surface problems of fresh meats; unfortunately, their high moisture content requires films resistant to a_w's higher than 0.8. Therefore, it will be necessary to continue research on film formulations. Chitosan films are resistant at a_w 1.0, and have been evaluated by Vojdani and Torres (1989b); however, there is no FDA approval for chitosan use in the U.S. as a food ingredient.

A more complete characterization of the properties of the film to the transfer of oxygen and other gases is still needed, particularly the effect of temperature on the film OTR. The successful application of the Arrhenius activation model to OTR data would facilitate the evaluation of the effect on product shelf-life

of the different temperature environments to which foods are exposed during production, transportation and handling.

The simulation of a practical application of methylcellulose-based films, as moisture permeability barriers, confirmed previous studies by Kamper and Fennema (1984a,b, 1985). In simulated sundae ice cream cones, these films were an excellent moisture permeability barrier.

Finally, there is a need to evaluate the effect of methylcellulose-based films on the sensory properties of coated foods. The effect is expected to be minor because of the relatively tasteless and odorless characteristics of these films and the small thickness required for effectiveness.

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