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Transport of Sodium Chloride and Water in Romano Cheese Slices During Brining

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ABSTRACT

The transport of NaCl into cheese appears to occur by a mutual diffusion process; however, water appears to be lost by a combination of mutual diffusion and by osmosis, the osmotic effect being more pronounced as the surface area to volume ratio increases, due to the higher salt uptake. The salt molality (m NaCl) in cheese slices was proportional to the square root of the brining period ($\sqrt{t}$)*; a rate parameter, K* ($moles\ kg^{-1}$) $min^{-0\cdot5}$)*, was defined as the slope of the m NaCl*$\sqrt{t}$ *plots. The rate parameter, K, was linearly related to the surface area to volume ratio of the cheese slices by the equation:*

$$K = (SA/V + 1{\cdot}2)/34{\cdot}70$$

where; SA = surface area and V = volume of the cheese slice. The value of K was a function of brine concentration; $K = 0{\cdot}009$ *(% NaCl in brine) +* $0{\cdot}029$*. K increased with increasing temperature to an extent dependent on slice thickness.*

Cheese slices are useful models in certain cases, e.g. absorption of expensive species (enzymes, flavours, amino acids, peptides) and studies of the influence of cheese geometry on salt and water changes during brining.

INTRODUCTION

The water activity (A_w) of cheese, which is an important factor in regulating the growth of starter bacteria (Ruegg & Blanc, 1981), enzyme

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activity (Aker, 1969; Schwimmer, 1980) and hence cheese ripening (Marcos *et al.*, 1981), is determined principally by the concentration and distribution of salt-in-moisture throughout the cheese. Although most, if not all, British cheese varieties are salted by mixing dry salt with the curd at the end of manufacture, most other major varieties are salted by immersion in brine and/or by surface application of dry salt. In such cases, movement of NaCl into, and H_2O out of, the cheese are major events regulating cheese composition and ripening (Godinho & Fox, 1981*a*,*b*; 1982; Guinee & Fox, 1983*b*, 1984). However, in spite of its significance, little information is available on the principles of salt diffusion in cheese during brining.

The transport of NaCl and H_2O in Gouda (Geurts *et al.*, 1974*b*, 1980) and Romano (Guinee & Fox, 1983*a*, *b*) cheese curd has been studied. Geurts *et al.* (1974*b*) concluded that the penetration of salt into cheese and the outward migration of water could be described as an impeded mutual diffusion process (i.e. the region of salt uptake coincides exactly with the region of changed moisture content) for which the coefficient depends upon curd composition and environmental factors, e.g. temperature.

However, it is conceivable that other forces, such as water loss by osmosis, may be operative during cheese brining. Indeed, osmotic dehydration of fruit in concentrated sugar solutions has been studied extensively (Ponting *et al.*, 1966; Farkas & Lazar, 1969; Ponting, 1973; Magee *et al.*, 1983). This study was undertaken to observe the effects of certain conditions during brine salting on the transport of salt and water in Romano cheese slices.

MATERIALS AND METHODS

Cheese

Romano cheeses were obtained from a commercial batch manufactured at a local factory as described by Guinee & Fox (1983*a*) and held at 4 °C for 2 to 3 days, during which they were inverted regularly in the moulds to allow uniform distribution of moisture throughout. After removal of cheese from the moulds, four cylinders (7·0 cm diameter, 8 to 9 cm high) were taken from each wheel. These cylinders were cut into slices, 0·25 to 1·5 cm thick, using a Bizerba meat slicer.

Brine

Brines were prepared by dissolving the appropriate quantity of NaCl in distilled water. $CaCl_2$ was added to all brines to a final concentration of 0·5% (w/v) Ca; because of the relatively short brining times (maximum 4·5 h) and the high brine concentrations (normally ~20%, w/v), this concentration of Ca is sufficient to prevent swelling (Geurts *et al.*, 1972) which may otherwise mask rate processes like diffusion or osmosis. Brines were distributed in 20 litre stainless steel vats which were placed in thermostatically controlled water baths. During salting, brines were agitated using overhead stirrers. A freshly prepared brine was used for each experiment at a rate of 15 litres per 400 g of cheese.

Procedure

Slices were submerged individually in the brine solutions which were agitated and maintained at constant temperature throughout the experiment. A slice of cheese was removed from the brine at times ranging from 0 to 270 min, rinsed with water to remove adhering brine, dried on filter paper, grated and analyzed in duplicate for NaCl by the potentiometric method of Fox (1963) and moisture by the International Dairy Federation (1958) method.

RESULTS AND DISCUSSION

The molal concentration (m) of NaCl in cheese slices was linearly related to the square root of the brining time (Fig. 1) and may be expressed by the equation:

$$m\,\mathrm{NaCl} = K\sqrt{t} + c$$

where $m\,\mathrm{NaCl} = (\%\,\mathrm{NaCl})/(\%\,H_2O) \times 1000/58{\cdot}5$; $\sqrt{t}$ = square root of brining time (min); c = intercept of the $m\,\mathrm{NaCl}/\sqrt{t}$ plot on the m NaCl axis and K = a rate parameter (moles $\mathrm{kg}^{-1}\,\mathrm{min}^{-0{\cdot}5}$) for salt uptake.

The rate of salt uptake, and hence K, is a function of brine concentration, the pseudo-diffusion coefficient, D^* (Geurts *et al.*, 1974*b*, 1980; Guinee & Fox, 1983*a*; Guinee, 1985), slice thickness, brining time and water content of the cheese. However, during any one experiment all these variables were fixed, with the exception of that under investigation.

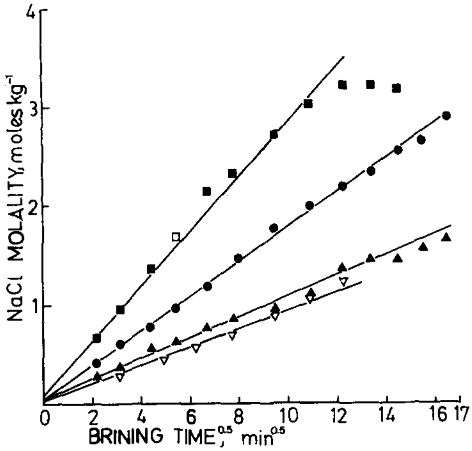

Fig. 1. Molality of NaCl in the 0·25(■), 0·5(●), 1·0(▲) and 1·5 cm (∇) thick cheese slices as a function of contact time with 19·4% NaCl brine at 21 °C.

Indeed, the initial moisture content and the pseudo-diffusion coefficient are intrinsic properties of a given cheese.

Transport of NaCl and water over time

The mass (g) of NaCl gained and water lost per 100 g of cheese brined in 19·4% NaCl, as a function of time for varying slice thickness, are shown in Fig. 2. For any slice thickness, the quantity of H_2O lost exceeded the quantity of NaCl absorbed. NaCl uptake was rapid initially (first 20 min) and thereafter the NaCl concentration increased more slowly as equilibrium was approached. In agreement with earlier work (Breene *et al.*, 1965; Gilles, 1976), the rate of salt absorption per 100 g of cheese increased as the slice thickness decreased. Such a trend was expected as the surface area available for absorption per unit volume of cheese increased with decreasing slice thickness; the surface area (SA) to volume (V) ratios for the 0·25, 0·5, 1·0 and 1·5 cm thick slices were 8·53, 4·53, 2·53 and 1·56 cm^{-1}, respectively. The data in Fig. 2 were transformed into m NaCl/$\sqrt{t}$ plots (Fig. 1) from which the rate parameter, K, was calculated. The value of K was linearly related to the ratio of surface area to volume of the cheese slices (Fig. 3), and may be expressed as:

$$K = [(SA/V) + 1{\cdot}2]/34{\cdot}70$$

where K = rate parameter (moles kg^{-1} $\mathrm{min}^{-0{\cdot}5}$); SA/V = surface area to

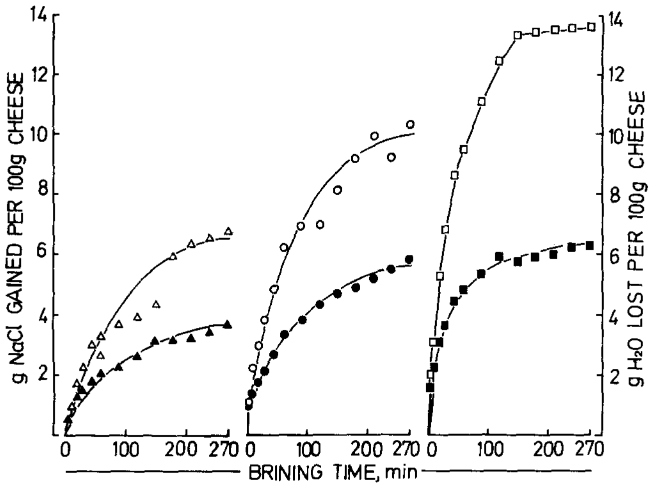

Fig. 2. Salt uptake (closed symbols) and water loss (open symbols) by the 0·25 (■,□), 0·5 (●, ○) and 1·0 (▲, △) cm thick cheese slices as a function of contact time with 19·4% NaCl brine at 21 °C.

volume ratio of the cheese slices (cm^{-1}); 1·2 = intercept of the $(SA/V)/K$ plot on the y axis (the intercept was negative but became positive on rearranging the equation) and 34·70 = slope.

The magnitude of K increased as the SA/V ratio increased; the experimental (linearly regressed) values of K for 0·25, 0·5, 1·0 and 1·5 cm thick slices were 0·25, 0·165, 0·107 and 0·058 moles kg^{-1} min$^{-0·5}$, respectively. However, the predicted K values for the 0·25, 0·5 and 1·0 cm thick slices calculated from the experimental K value for the 1·5 cm thick slice (e.g. $Kp\ (0·5) = [(SA/V)(0·5)/(SA/V)(1·5)]K(1·5)$; where Kp is the predicted value and the subscripts 0·5 and 1·5 refer to slice thicknesses) were 0·40, 0·21 and 0·12 moles kg^{-1} min$^{-0·5}$, respectively (Fig. 3). Hence, the average quantity of salt absorbed per unit surface area of cheese slices, over the experimental brining period, decreased as the surface area to volume ratio of the cheese slices increased.

A plot of the natural logarithm of the grams of NaCl gained per 100 g of cheese per minute, over the linear region of salt uptake ($\sim$ 60 min) against the natural logarithm of brining interval, was linear (Fig. 4). It was considered inappropriate to take samples at brining times < 5 min because of possibly high errors that might be introduced by pockets of brine trapped in small crevices on the cheese surface and the absorption of 'initial' cheese

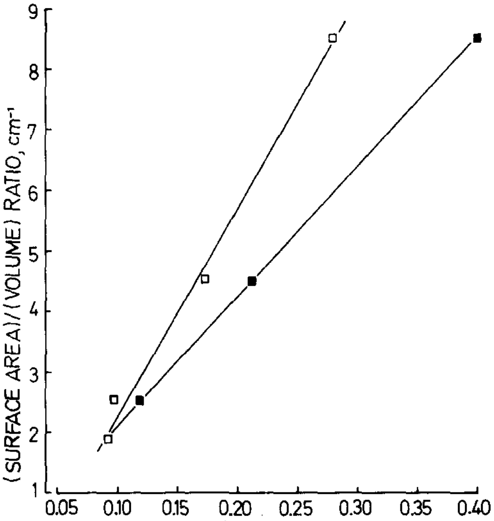

Fig. 3. Theoretical (■) and experimental (□), rate parameter, K, for salt uptake, as a function of the surface area: volume ratio of cheese slices.

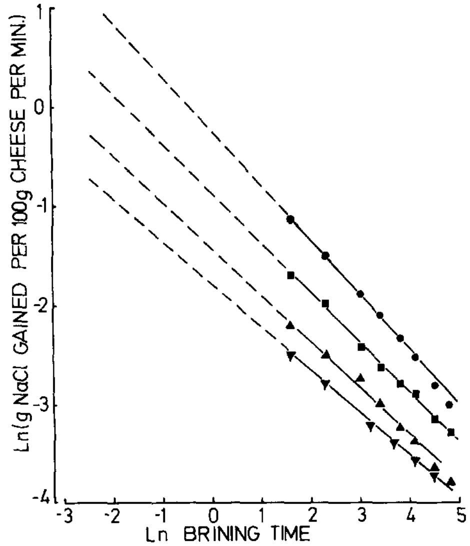

Fig. 4. Natural logarithm of grams of NaCl gained per 100 g of cheese per minute by the 0·25 (●), 0·5 (■), 1·0 (▲) and 1·5 (▼) cm thick cheese slices as a function of the natural logarithm of brining time; the experimental values (——) were extrapolated (----) to estimate values for salt uptake after very short brining intervals (< 5 min).

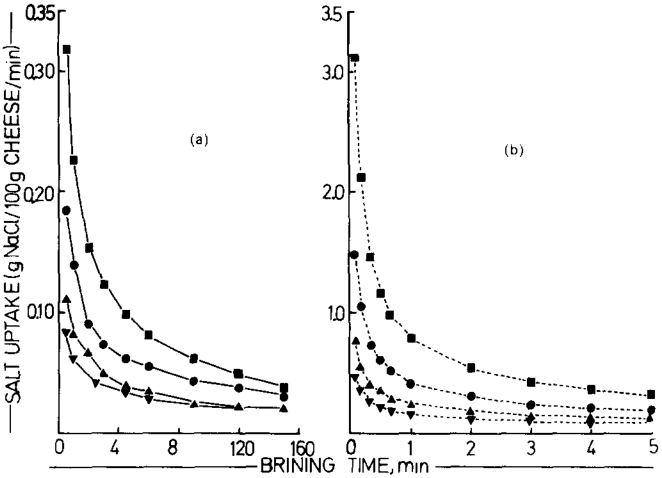

Fig. 5. Salt uptake (grams of NaCl per 100 g of cheese per minute) by the 0·25 (■), 0·5 (●), 1·0 (▲), 1·5 (▼) cm thick cheese slices as a function of brining time; a and b represent experimental and extrapolated plots, respectively.

moisture by the filter paper. Extrapolation of these plots (Fig. 4) permitted estimation of the rates of salt absorption by cheese slices of varying thickness, even after a few seconds in the brine (Fig. 5(a) and (b)). The rate of salt absorption decreased rapidly during the first minute of brining, possibly due to the reduction of the differences in the NaCl concentration between the cheese moisture and the brine as the concentration of NaCl in the cheese increased. The initial (first 2 min) rate of salt uptake per unit surface area increased with increasing surface area to volume ratio (Fig. 5(b)). Since the adsorption of NaCl to paracasein is very low, i.e. 0·21 to 0·43 mmoles NaCl/g paracasein (Geurts *et al.*, 1974 *a*), increased binding of NaCl molecules to the cheese surface at high surface area to volume ratios, which might otherwise be expected, does not appear to be a satisfactory explanation of the above effect. Geurts *et al.* (1980) found that, on brining Edam-type cheese, the quantity of NaCl absorbed per square centimetre of cheese surface was greater for an infinite, flat slab than for a sphere, and decreased further with increasing degree of curvature. Since the planar surface area, relative to total surface area, increased as the cheese surface area to volume ratio increased (Fig. 6), the high initial rates of salt absorption by the thin slices (high surface area to volume ratios) may be due to this. Figure 6 shows that plots of grams of NaCl absorbed per square centimetre of cheese surface and of

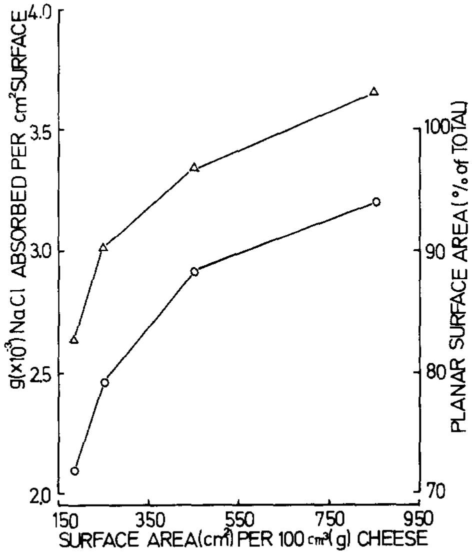

Fig. 6. Salt uptake, g × 10^{-3} NaCl per square centimetre of cheese surface (△), and planar surface area as a percentage of total surface area (○), as functions of the surface area: volume ratio per 100 cm^3 cheese slice.

the planar surface as a percentage of total surface area, both as a function of total surface area per 100 g (~100 cm^3) of cheese, were parallel.

The quantity of salt absorbed per unit surface area decreased for all slices as the brining interval was extended and from ~ 2 min onwards, salt uptake was greatest when the cheese was salted as 1·5 cm thick slices (Table 1). However, the average salt uptake per 100 g of cheese at any time throughout the experimental brining period increased as the surface area

TABLE 1

Influence of Slice Thickness on Salt Uptake by Romano Cheese Slices Salted to 19·4% NaCl Brine at ~21 °C

Slice thickness (cm)	*Brining time(min)*											
	0·08	*0·5*	*1*	*5*	*10*	*20*	*30*	*45*	*60*	*90*	*120*	*150*
	g NaCl (× 10^{-3}) absorbed per cm^2 cheese slice surface per minute											
0·25	3·65	1·36	0·93	0·37	0·26	0·18	0·14	0·12	0·09	0·07	0·06	0·04
0·50	3·30	1·33	0·93	0·41	0·31	0·20	0·16	0·14	0·12	0·09	0·08	0·07
1·00	3·06	1·38	0·96	0·45	0·32	0·28	0·19	0·15	0·13	0·10	0·09	0·08
1·50	2·63	1·20	0·89	0·44	0·33	0·22	—	0·18	0·15	0·13	0·11	0·10

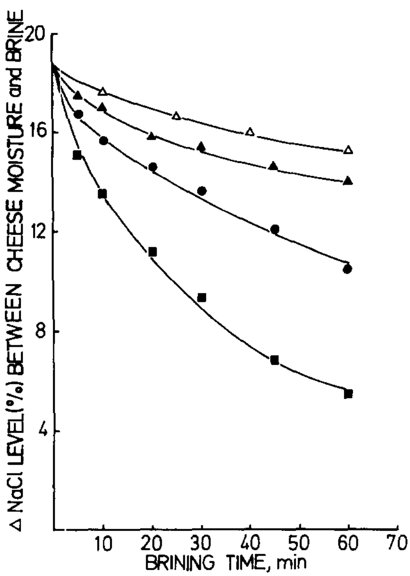

Fig. 7. Difference in salt concentration (grams of NaCl per 100 g of H_2O) between the cheese moisture and the brine as a function of brining time in the 0·25 (■), 0·5 (●), 1·0 (▲) and 1·5 (△) cm thick slices.

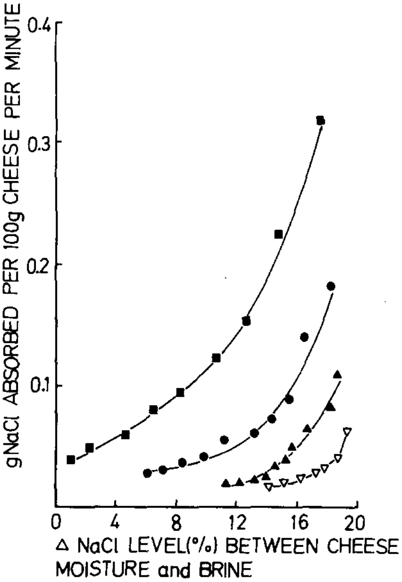

Fig. 8. Salt uptake (grams of NaCl per 100 g of cheese slice per minute) by the 0·25 (■), 0·5 (●), 1·0 (▲) and 1·5 (▽) cm thick slices as a function of the difference in the salt concentration between the cheese moisture and the brine.

to volume ratio increased, i.e. as the slice thickness decreased (Fig. 5(a)). This trend was expected because of the more rapid decrease in the difference (Δ) of the NaCl concentration between the cheese moisture and the brine as the slice thickness decreased (Fig. 7). Indeed, there was a sharp decrease in the quantity of salt absorbed per 100 g of cheese per minute as the difference between the NaCl concentration in the cheese moisture and in the brine decreased, especially when the difference was large (Fig. 8).

As for salt uptake, a plot of the natural logarithm of the grams of H_2O lost per 100 g of cheese per minute, over the first 45 min (linear region of water loss) against the natural logarithm of brining interval was linear (Fig. 9). The rates of water loss (Fig. 10) showed trends similar to salt uptake (Fig. 5). Using extrapolated data (Figs 5(b) and 10(b)), the rate of water loss during the first 2 to 4 min brining appeared to be less rapid than salt uptake, and decreased more slowly throughout the experimental brining period (Figs 5(a) and 10(a)). These trends were reflected in the

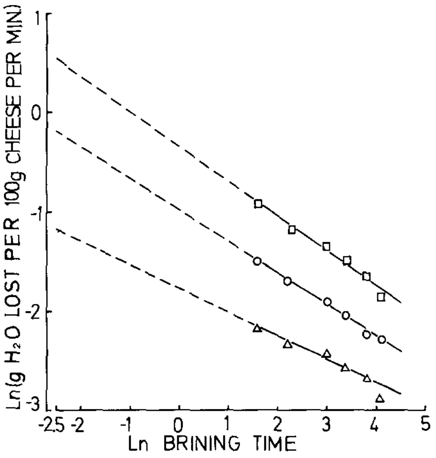

Fig. 9. Natural logarithm of the grams of H_2O lost per 100 g of cheese by the 0·25 (□), 0·5 (○) and 1·0 (△) cm thick cheese slices as a function of the natural logarithm of brining time; the experimental values (——) were intrapolated (----) to estimate values of moisture loss after very short brining intervals (5 min).

magnitude of the flux ratio, p (Fig. 11) which was < 1 during the first 2 to 5 min (depending on slice thickness) and > 1 for the remainder of the brining period. The very low flux ratios during the first minute of brining suggest that salt penetration is necessary to induce water loss. It is unlikely that swelling of the protein matrix would have occurred during this period because of the low salt-in-moisture level ($< 1{\cdot}5\%$) attained after such short brining times. The increasing flux ratio (p) observed with

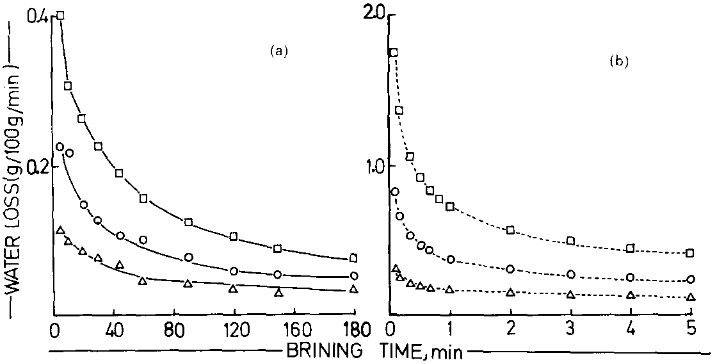

Fig. 10. Water loss (grams of H_2O lost per 100 g of cheese per minute) by the 0·25 (□), 0·5 (○) and 1·0 (△) cm thick cheese slices as a function of brining time; a and b represent experimental and extrapolated plots, respectively.

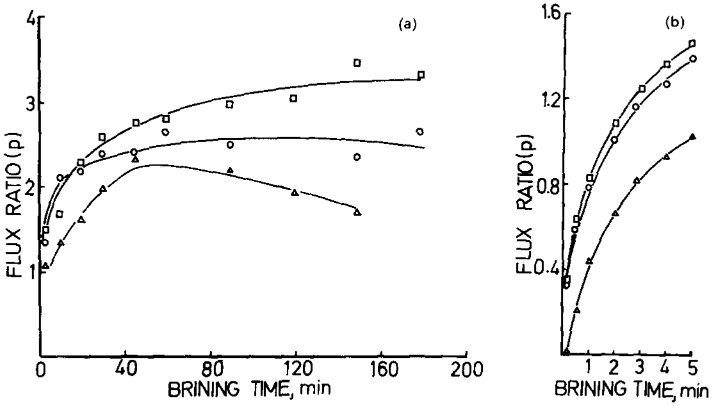

Fig. 11. Flux ratio (p) for the 0·25 (□), 0·5 (○) and 1·0 (△) cm thick slices as a function of brining time; b and a represent extrapolated and experimental plots, respectively.

all slice thicknesses over time as the salt and moisture levels increased and decreased, respectively, may be synonymous with the decrease in p from the interface to the centre observed during the unidimensional brining of Romano-type cheese wheels (Guinee & Fox, 1983*a*). Because the effective diffusion radius of NaCl molecules is larger than that of H_2O molecules, Geurts *et al.* (1974*b*) inferred that the diffusional flux for water should be 1·5 times greater than that for NaCl. A tentative explanation for the relatively high water loss ($p > 1·5$) after 5–10 min brining may be that water is lost by a combination of pseudo-diffusion and pseudo-osmosis. Indeed, the increasing flux ratio associated with increasing slice surface area to volume ratio lends support to this view. Although the osmotic effect occurs at any point where salt penetrated, it will be most pronounced where the NaCl concentration is highest, i.e. where the surface area to volume ratio is highest. Support for the view that loss of cheese moisture occurs via two processes is provided by plots of log percent cheese moisture as a function of time, which were biphasic (Fig. 12).

Influence of temperature on the rate parameter

Cheese slices, 0·5 and 1·5 cm thick, were brined in NaCl solutions (20 % NaCl) in the temperature range 4 to 26 °C. The values of K increased with increasing temperature (Table 2); the magnitude of the increases between 4 and 26 °C were 32 % and 61 % for slice thickness of 0·5 and 1·5 cm,

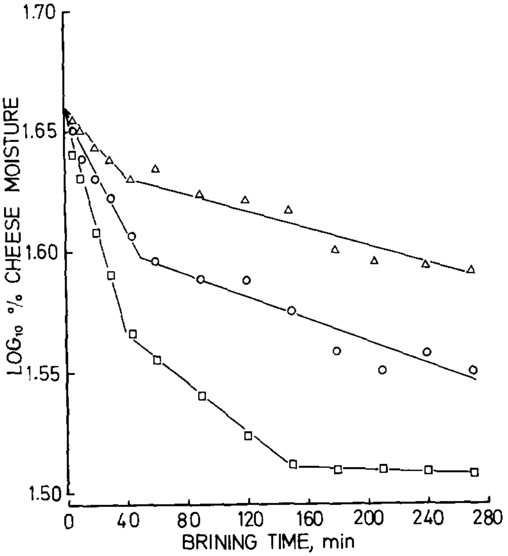

Fig. 12. Log_{10} of the moisture content of the 0·25 (□), 0·5 (○) and 1·0 (△) cm thick cheese slices as a function of brining time.

respectively. The increase in *K* with temperature was expected as NaCl and water transport processes are kinetic phenomena. Geurts *et al.* (1974 *b*) suggested that an increase in the pseudo-diffusion coefficient, *D**, associated with temperature was partly due to an increase in the effective pore width of the protein matrix as non-solvent water decreases with increasing temperature. The rate of increase of *K* would be expected to be approximately the same for both slice thicknesses because the rate

TABLE 2

Influence of Temperature on the Rate parameter, *K*, for Salt Uptake by Cheese Slices, 0·5 and 1·5 cm Thick

Temperature (°C)	*Slice thickness (cm)* *0·5*	 *1·5*
	K	
4·5	0·18	0·06
9·5	0·20	0·06
15	0·21	0·07
20	0·22	0·09
26	0·23	0·10

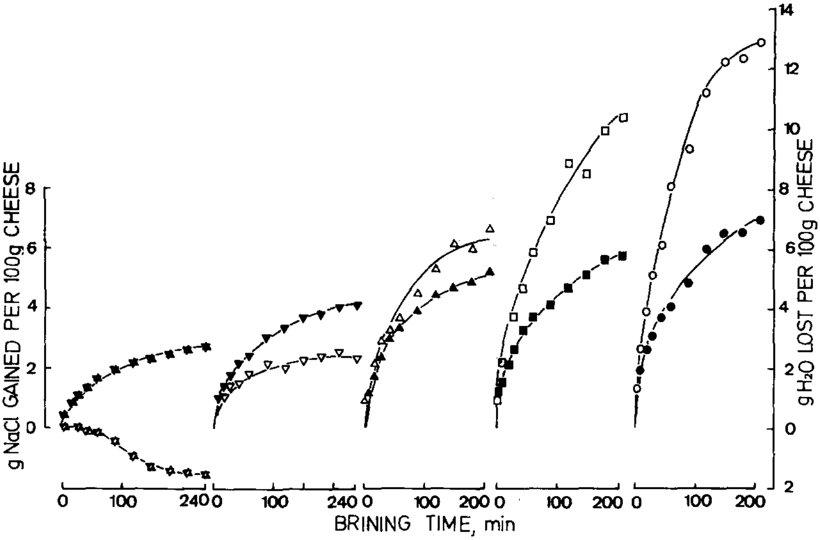

Fig. 13. Salt uptake (closed symbols) and moisture loss (open symbols) by 0·5 cm thick cheese slices brined in 6·5 (★, ☆), 10·7 (▼, ▽), 14·8 (▲, △), 18·9 (■, □) or 24·9 (●, ○) % NaCl brines at 20 °C.

parameter, *K*, is affected by the intrinsic properties of the cheese which were the same in both cases. No good explanation can be offered for the observed effect of slice thickness on the temperature dependence of *K*.

Effect of brine concentration

Cheese slices (0·5 cm thick) were brined at 20 °C in NaCl solutions (containing 0·5 % Ca, w/v) ranging from 6·5 to 24·9 %, w/w. The water loss and salt gain for the different brining solutions are shown in Fig. 13. At the end of the brining period (210–240 min), the ratio of water lost to NaCl gained per 100 g of cheese decreased in the order of 2·2, 1·8, 1·31 and 0·63 and −0·15 for the 24·9, 18·9, 14·8 and 10·7 and 6·5 % brines, respectively. As previously mentioned, for normal brine concentrations (20 %) the water lost usually exceeds the NaCl gained because of the greater impedance of the movement of Na^+ and Cl^- ions than on H_2O molecules by the structure of the cheese matrix (Geurts *et al.*, 1974*b*) and the loss of water by osmosis which increases over time as the salt-in-moisture level of the cheese increased. However, at the lowest brine concentration (6·5 %), the moisture content increased above its initial level which was attributed to a salting-in-effect on the protein matrix; the

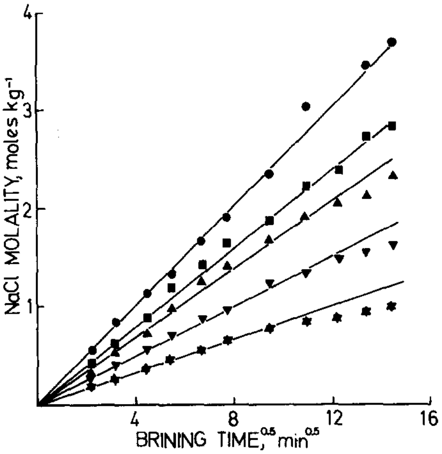

Fig. 14. Molality of NaCl in the 0·25 cm thick cheese slices brined in 6·5 (★), 10·7 (▼), 14·8 (▲), 18·9 (■) and 24·9 (●)% NaCl brines at 20°C.

increased protein solubility is responsible for the swelling and the smooth, uniform, soft surface observed in cheese pieces salted in dilute brines (Geurts *et al.*, 1972). K values were determined from the slopes of plots of salt molality as a function of the square root of contact time (Fig. 14). The relationship between K and brine concentration was linear; $K = 0{\cdot}009$ (% NaCl in brine) $+ 0{\cdot}029$; ($r = 0{\cdot}95$). This indicates that K is not a true rate constant, as is the pseudo-diffusion coefficient, D^*, which is essentially independent of brine concentration (Geurts *et al.*, 1974*b*; Guinee & Fox, 1983*a*). However, the relative magnitude of the rate parameter, K, is a good index of the rate of salt and water transport and the factors affecting it.

As far as can be ascertained, slices have not been used previously in studies of the movement of NaCl and H_2O (or indeed other molecular or ionic species) in cheese, although slices have been used in studies of the dehydration of fruit in sugar solutions (Ponting *et al.*, 1966; Farkas & Lazar, 1969; Ponting, 1973; Magee *et al.*, 1983). Obviously, cheese slices are of limited or no value for studies on certain aspects of salting, e.g. the determination of the diffusion coefficient and factors affecting it, but the results of the present study show that they may be very useful models in certain cases. Obvious advantages of slices over whole cheeses are the small sample size—and consequently brine volumes—reduced brining times and elimination of compositional and structural differences between cheeses which may influence salt and moisture movements

(Guinee, 1985). The smaller sample size may be particularly useful in studies of the absorption and diffusion of expensive molecules, e.g. enzymes, flavour compounds and certain sugars; such information is necessary in view of the increasing interest in the acceleration of cheese ripening via added enzymes. To minimize losses of expensive enzymes in whey (which may also render the whey less useful or unsuitable as a food additive), their addition in micro-encapsulated form is being investigated (Law, 1984). Inward diffusion of enzymes excreted by surface microflora or flavour components, e.g. fatty acids, peptides and amino acids, arising from the action of these micro-organisms or their enzymes, plays a major role in the ripening of many cheese varieties, especially Camembert, Brie, Tilsit, Limburger, etc. The infusion of cheese with flavour compounds may also be of interest. Furthermore, the results obtained with cheese slices can be extrapolated with some degree of confidence to investigations of the influence of cheese geometry and size on salt and water changes in cheese during brining.

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