SYNERESIS OF CURD

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**H.J.M. van Dijk**

# SYNERESIS OF CURD

*Proefschrift*
*ter verkrijging van de graad van*
*doctor in de landbouwwetenschappen,*
*op gezag van de rector magnificus,*
*dr. C.C. Oosterlee,*
*hoogleraar in de veeteeltwetenschap,*
*in het openbaar te verdedigen*
*op woensdag 6 oktober 1982*
*des namiddags te vier uur in de aula*
*van de Landbouwhogeschool te Wageningen.*

STELLINGEN

1. De synerese van wrongel kan op bevredigende wijze in model worden gebracht. Uit dit model blijkt dat de endogene syneresedruk ongeveer 1 Pa is.
   Dit proefschrift.

2. De vlokking van paracaseïnemicellen en de permeabiliteit, synerese(druk) en reologische eigenschappen van wrongel hangen alle nauw samen.
   Dit proefschrift.

3. Indien uitvlokking van colloïdale deeltjes ongestoord (dus bij afwezigheid van stroming en sedimentatie) plaatsvindt, resulteert deze in de vorming van één netwerk door de gehele vloeistof.

4. De hypothese van Van den Tempel dat de inhomogeniteit van een netwerk van uitgevlokte colloïdale deeltjes wordt bepaald door de tijd die nog niet geaggregeerde deeltjes hebben om naar het centrum van grote aggregaten te diffunderen, is onjuist.
   M. v.d. Tempel, 1979. J. Colloid Interface Sci., 71:18-20.

5. De belangwekkende proeven van Schmidt c.s. over de stabiliteit van kunstmatige caseïnemicellen van variabele samenstelling zouden met vrucht uitgebreid kunnen worden met stremproeven, teneinde het inzicht in het stremproces en de struktuur van caseïnemicellen te vergroten.

6. Het model van Payens voor de stremming van melk is onjuist. Veel betere resultaten kunnen worden bereikt met een simulatiemodel waarbij de volgende informatie tevens in aanmerking wordt genomen:
   - de onderlinge positie van de κ-caseïnemoleculen op het miceloppervlak
   - de splitsing van deze moleculen in aselecte volgorde
   - de gevolgen van nog niet volledige splitsing voor de repulsie tussen micellen
   T.A.J. Payens, 1979. J. Dairy Res., 46:291-306.

7. De opvatting van Beltman dat synerese door diffusie bepaald wordt, is in zijn algemeenheid onjuist.
   H. Beltman, 1975. Proefschrift, Wageningen.

8. Het lactosegehalte van de (verdunde) wei geeft aanvankelijk geen juist beeld van het waseffekt van warm water dat aan de wei-wrongel is toegevoegd.

8. Het subsidie dat in het kader van het scheppen van werkgelegenheid aan bedrijven in het Oosten en Noorden van het land wordt verleend, schept althans bij zuivelbedrijven geen extra werkgelegenheid.

10. Enkele door het Zuivel-kwaliteitskontrolebureau gehanteerde methoden ter beoordeling van de kwaliteit van boter, te weten de bepaling van diacetylgehalte en de stevigheid, kunnen misleidende uitkomsten geven.

11. Voedingswaarde-etikettering heeft voor de consument het meeste nut indien deze zeer globaal is en slechts die voedingsstoffen worden vermeld waarvan een niet onaanzienlijk deel van de consumenten te veel of te weinig gebruikt. Bij de opgegeven gehalten en energie-inhoud moet vermeld worden of deze relatief hoog of laag zijn.

12. Wiskundige statistiek en simulatietechnieken kunnen uitstekend worden toegepast bij het bepalen van de speltaktiek in de rugbysport.

13. Ingevolge de Wet Gelijke Behandeling dient bij een advertentie voor 'kaasmeisjes' de toevoeging M/V te worden geplaatst.

**Proefschrift van H.J.M. van Dijk**
**The syneresis of curd**
**Wageningen, 6 oktober 1982**

*Aan mijn ouders*

WOORD VOORAF

Aan het tot stand komen van dit proefschrift, wat mogelijk is gemaakt door de financiële hulp van de Stichting J.Mesdagfonds te Leeuwarden, hebben velen een bijdrage geleverd. In het besef niet volledig te kunnen zijn, wil ik de volgende personen met name noemen.

In de eerste plaats prof. dr. ir. P. Walstra, die het initiatief heeft genomen tot dit onderzoek en die me erbij heeft begeleid. Aan de verslaglegging heeft hij in sterke mate bijgedragen.

Vervolgens prof. dr. ir. J. Schenk, die vooral met betrekking tot de wiskundige weergave adviezen heeft gegeven.

Een groot deel van de experimenten is uitgevoerd door de heer H. Stempher (permeabiliteit en synerese), mevrouw A.E.A. de Groot-Mostert (reologie) en ir. J.G. van de Grootevheen (experimenten betreffende Fig. 8.4). De heer D. Schoonderbeek verrichtte de metingen met de Kwantimet Image Analyzer, welke door de Stichting voor Bodemkartering te Wageningen ter beschikking was gesteld.

Belangrijke adviezen heb ik mogen ontvangen van o.m. prof. dr. A. Prins, prof. dr. ir. S. Bruin en medewerkers van de Sectie Proceskunde, dr. ir. T. van Vliet en dr. ir. Th. J. Geurts.

De symbolen- en literatuurlijst zijn opgesteld door mevrouw ir. T.H. van Oijen.

De benodigde apparatuur is grotendeel gemaakt door de medewerkers van de werkplaats van het Biotechnion.

Aan het vormgeven werkten o.a. mee, wat betreft het typewerk: mevrouw B.A. de Jong - van der Luijt, mevrouw G.H.J. Pellemans - Wunderink en mevrouw N.J.Walstra; correctie en advies verslaglegging: mevrouw ir. M.C. van der Haven; foto- en tekenwerk: de heren A. van Baaren, C. Rijpma en M. Schimmel.

Mijn huidige werkgever Melkunie Holland te Woerden ben ik erkentelijk voor de medewerking verleend bij het voltooien van dit proefschrift.

Mijn oprechte dank aan allen die aan dit proefschrift hebben meegewerkt, vooral aan degenen die betrokken waren bij het op schrift stellen van dit onderzoek. Bij het nemen van deze laatste hindernis heb ik van u buitengewoon veel hulp gekregen.

PERSOONLIJKE GEGEVENS

De auteur werd geboren op 6 april 1948 te Uden. Hij behaalde in 1971 het diploma van de Hogere Landbouw Technologische School te 's Hertogenbosch. In datzelfde jaar werd met de studie aan de Landbouwhogeschool in Wageningen begonnen. Het kandidaatsexamen Levensmiddelentechnologie werd afgelegd in januari 1976 en het doctoraalexamen in januari 1978. De ingenieursstudie omvatte naast het verzwaard hoofdvak Zuiveltechnologie en Melkkunde het hoofdvak Industriele Bedrijfskunde. Van november 1977 tot mei 1981 werkte de auteur als promotie-assistent op het laboratorium voor Zuivel en Levensmiddelennatuurkunde. Sinds mei 1981 is hij werkzaam bij Melkunie Holland te Woerden.

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

| | | |
|---|---|---|
| $a$ | constant in Eq. 6.12 | |
| $a_t$ | radius of a tube | (m) |
| $b$ | constant in Eq. 6.12 | |
| $B;B_{k,t}$ | permeability (coefficient) | ($m^2$) |
| $B(0)$ | permeability (coefficient) at the moment of the first reading of $h(t)$ | ($m^2$) |
| $B_e$ | permeability (coefficient) at the moment when the gel is pressurized or deformed | ($m^2$) |
| $B_0$ | permeability of the curd slab at the start of syneresis | ($m^2$) |
| $c$ | constant in trial functions for $P(t)$; $c = d(P_{k,t}/P_{k,0})/dt$ | |
| $d$ | diameter | |
| $d_{vs}$ | volume-surface average diameter | (m) |
| $d_t$ | tube diameter | (m) |
| $\frac{D^s}{Dt}$ | substantial time derivate operator | ($s^{-1}$) |
| $D$ | $B(1 - \varepsilon)^3 P'/\eta$ (see Eq. 6.1) | ($s^{-1}$) |
| $g$ | acceleration due to gravity | ($m^2 \cdot s^{-1}$) |
| $G'$ | storage modulus | ($N/m^2$) |
| $G''$ | loss modulus | ($N/m^2$) |
| $G_0$ | instantaneous shear modulus | ($N/m^2$) |
| $h$ | difference between the levels of the unwetted curd and the adjacent whey (Chapter 3) | (m) |
| $h_c$ | height below surface of the gel | (m) |
| $h_{k,t};h(k,t)$ | thickness of slice number $k$ at time $t$ (in the model) | (m) |
| $h(t)$ | level of the whey in the tube (Eq. 4.2) | (m) |
| $H$ | height of the slab | (m) |
| $H_0$ | height of the slab at $t = 0$ | (m) |
| $\Delta H$ | shrinkage of a slab | (m) |

| | | |
|---|---|---|
| $i;i_{k,t}$ | volume of concentrated milk/volume of original milk; $h_{k,t}/h_{k,0}$ | |
| $k$ | number of the slice in the slab (in the model) | |
| $K';K$ | dimensionless time variable ($K' = 2K$) | |
| $L;L_{k,t}$ | dimensionless thickness | |
| $m$ | number of slices in the slab (in the model) | |
| $n$ | number of experiments | |
| $p_f$ | protein concentration of the sample/ protein concentration of original milk | |
| PCM | paracasein micelles | |
| $P;P_{k,t}$ | syneresis pressure | (Pa) |
| $P_0$ | pressure of the curd at $t = 0$ | (Pa) |
| $P^s$ | endogenous pressure | (Pa) |
| $P^g$ | pressure on the whey caused by weight of the matrix | (Pa) |
| $P_b^g$ | $P^g$ at the bottom of the slab | |
| $P_t$ | pressure difference between lower and upper surface of the gel in the tube (Eq. 4.1) | (Pa) |
| $Q$ | constant defined in equation 7.1 depending on $P(i)$ | |
| $r$ | (surface of tubes)/(surface of vat) | |
| $Re$ | Reynolds number | |
| $str_k$ | liquid volume flux that flows from slice $k$ into slice $k - 1$ (in the model) | (m/s) |
| $S;S_{k,t}$ | dimensionless pressure $P_{k,t}/P_0$ | |
| $t$ | time | (s) |
| $t_e$ | time at which the pressure difference was applied to the column | (s) |
| $T$ | temperature | ($^oC$) |
| $v_x$ | local velocity of the whey in the $x$-direction | (m/s) |
| $\vec{v}^1$ | local velocity of the liquid (whey) | (m/s) |

| | | |
|---|---|---|
| $\vec{v}^s$ | local velocity of the solid (matrix) | (m/s) |
| $\omega$ | $\omega$-coordinate (transformation distance coordinate) | (m) |
| WPN | whey protein nitrogen | |
| $x$ | $x$-coordinate, distance from the interface of curd/whey | (m) |
| $z$ | $z$-coordinate | (m) |
| $\beta$ | dimensionless permeability ($B_{(k,t)}/B_0$) | |
| $\gamma$ | shear strain | |
| $\gamma_0$ | maximum shear strain | |
| $\Gamma$ | dlog$H$/dlog$t$ | |
| $\delta$ | phase shift or phase angle between stress and strain (tg $\delta = G''/G'$) | |
| $\delta_s$ | average thickness of the strands | (m) |
| $\varepsilon$ | porosity (void fraction) | |
| $\Delta$ | difference | |
| $\eta$ | viscosity | (Pa•s) |
| $\rho$ | density | ($kg/m^3$) |
| $\rho_1$ | density of the whey (which is assumed to be independent of the time and position) | ($kg/m^3$) |
| $\sigma$ | shear stress | ($N/m^2$) |
| $\sigma_0$ | maximum stress | ($N/m^2$) |
| $\omega$ | angular frequency | ($rad \cdot s^{-1}$) |
| $\nabla$ | Laplace-operator | |

Milk samples used:

| | |
|---|---|
| A | milk A; reconstituted from 12 g skim milk powder per 100 g water, used for acid curd and for some experiments with rennet curd |
| R | milk R; 10.5 g skim milk powder per 100 g water used for rennet curd |

# 1 INTRODUCTION

Though cheese is made in an overwhelming variety of types, the technique of cheesemaking is in principle the same. Cheesemaking starts by curdling (clotting) the milk. As to the curdling method a division can be made between curdling with the aid of rennet and curdling without rennet but only by acidification. As most cheese is made by renneting we will mainly discuss this method.

After renneting the curd (i.e. a gel) must be cut slowly and carefully into pieces. Now whey is expelled from the curd pieces; this is called syneresis. Syneresis of these curd pieces can occur without external manupulation, but is enhanced by stirring. Shrinkage can be further enhanced by more vigorous stirring, temperature rise or increase of acidity. Finally fairly solid curd particles are collected and drained. According to the type of cheese the following additional treatments can be performed: cheddaring, pressing, salting, ripening.

Thus an important aspect of the technique of cheesemaking is the removal of the greater part of the whey which makes up the bulk of the milk. This process must be controlled well as the final water content is an essential property of the cheese. In industrial practice the control of this process is empirical.

A question which is still not answered is how syneresis proceeds. On syneresis of curd much has been published, but most publications deal with the overall effect of some variables on syneresis or even on final moisture content (e.g. Walstra, 1979; v.d. Waarden, 1947; Cheeseman 1962; Stoll, 1966). The experiments can not easily be compared, mainly because the curd is cut and stirred in different ways and precisely these variables have a large effect. We have only little understanding of the process. Before we go into any detail we will first look at what happens during renneting.

About 80% of the protein in the milk is found in the casein micelles which are globular particles with a volume surface average diameter of ~ 100 nm (Schmidt, Walstra & Buchheim, 1973). The enzymes in the rennet remove the protective hairy layer (Walstra, 1979) of the micelles. The resulting paracasein micelles (PCM) are unstable and flocculate. PCM assemble into growing aggregates. As calculations of

Sutherland (1967) predict and as observed by Mulder, De Graaf & Walstra (1966) these aggregates have a very open structure, i.e. the volume fraction is about the same as the volume fraction of the original milk. Unless disturbance (e.g. by stirring or streaming) or appreciable sedimentation occurs, finally one large aggregate, (i.e. the entire matrix) is formed. The interstitial liquid is called whey. Electron micrographs of Knoop & Peters (1975) give a good picture of the matrix. The schematic drawing in Fig. 1.1. shows two strands.

A hypothetical mechanism is proposed. After the gel is formed, the PCM surfaces that are not in contact with each other have still many more reactive sites. Possibly the whole surface is reactive. By Brownian motion or deformation these surfaces may locally come close together and stick, thus causing a (higher) stress in the strands (see Fig. 4.7.). In order to get enough freedom for movement it might be necessary that at some other place they first have to break. The resulting endogenous pressure causes syneresis.

Another mechanism may be "fusing" of PCM, i.e. the contact area between any two PCM becomes larger. This is also visible in electron micrographs (Knoop & Peters, 1975). This is apparently a slow process. According to Darling (personal communication) an explanation for the latter phenomenon may be the rearrangement of colloidal calcium phosphate, which apparently keeps the subunits of individual (P)CM together. We presume this effect to be small, particularly at the beginning.

If the pH is lowered the PCM shrink (Walstra & Delsing, unpublished) thus causing syneresis. In our experiments the pH was kept

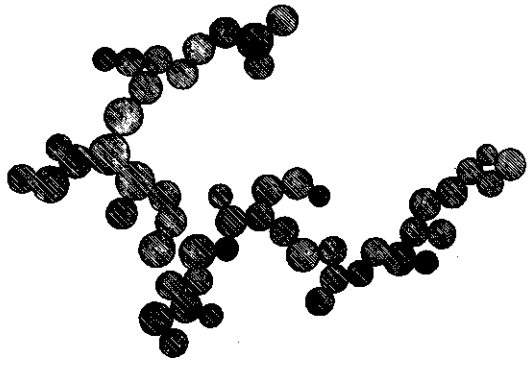


Fig. 1.1 Schematic drawing of two strands of paracasein micelles.

constant.

The stresses occurring on the strands of the matrix cause a tendency to shrink or synerize. The matrix does not comply momentarily because of the viscous drag on the outflowing liquid, or in other words, the limited permeability of the matrix. This implies that the whey in the matrix is under pressure. The whey also can be put under pressure by deformation of the curd. We thus must distinguish the latter external pressure from the endogenous syneresis pressure.

Syneresis is thus a function of the pressure and the resistance against flow through the matrix, expressed in the permeability. This flow and the resulting change in content of components should ideally be obtained from direct local measurements in the curd grains. This is practically impossible. In the absence of information from direct measurements of local properties and event, we must therefore rely on other sources, i.e. macroscopic experiments.

Permeability coefficients ($B$) as defined in the equation of Darcy (see Section 4.1) can be obtained from measurements on homogeneous pieces of curd which do not shrink during the experiments; casein concentration and other properties can be varied.

Syneresis pressure could not be measured in this way or any other. Evidence was found that this pressure is always very low (less than 10 Pa).

A mathematical model can be postulated, and depending on the assumptions made, syneresis rate can be predicted for various conditions. Comparison on the calculated results with the results on actual syneresis experiments may show whether a model is realistic. As permeability and endogenous pressure both depend on place and time, calculations are rather complicated. We have restricted ourselves to syneresis in one direction, as the calculations become unwieldy for the three dimensional case. Moreover, unequivocal experiments are much easier to perform.

Such an integrated theoretical and empirical approach can yield a better understanding of the process and the mechanism. Where appropriate, the results of this study are compared with those found in the literature and with practical experience.

Finally some experiments were carried out on acid milk gels,

produced by adding acid to milk at low temperature and then slowly warming it. This enables us to test the model for a gel of rather different properties.

## 2 MATERIALS AND METHODS

### 2.1. SKIM MILK POWDER

Skim milk powder was obtained by spray drying of one batch of low pasteurized skim milk. The dry matter content of this skim milk was 9.13% (m/m) (according to FIL/IDF 21:1962 standard). The dry matter content of the powder was 96.1% (m/m) (according to FIL/IDF 26/1964 standard).

For the experiment 10.5 g powder per 100 g of demineralized water was used. This resulted in a milk indicated as milk R with the same dry matter content as the original milk.

In the early stages of this study we dissolved the skim milk powder adding small quantities during about 1 hour at about 45 $^{o}$C; when all the powder was dissolved the reconstituted skim milk was kept for about 1 hour at 30 to 45 $^{o}$C. In the course of the study it appeared that the pretreatment of the reconstituted skim milk somewhat affected its renneting and curd properties (see Table 7.1). Therefore we soon standardized our pretreatment. After all the skim milk powder was dissolved, we kept the milk for 1 hour at 45 $^{o}$C. Then the milk was cooled to the desired temperature. However, the time until the milk was used varied between about 0.5 and 5 hours. This may, to a certain extent, explain the spread in some results, as it takes about 24 h at the temperatures used until equilibrium is reached, especially in the distribution of Calcium among the micelles and the serum (Snoeren, personal communication).

Undenaturated whey protein nitrogen (W.P.N.) in the original milk and the powder were determined (American Dry Milk Institute, 1971), Results were 6.7 mg W.P.N./g powder for the original milk and 6.3 mg W.P.N./g powder for the reconstituted skim milk.

For the experiments with acid gels, a different skim milk powder was used. For the reconstitution 12 g powder per 100 g water was used giving milk (indicated as milk A) with a higher total solids content (i.e. 10.2%) than the original milk.

## 2.2 RENNET

Commercial calf rennet (Coöp. Stremselfabriek Leeuwarden), strength 10 000 units was used and diluted 1:10 before use. 80% of the activity in the rennet originated from chymosin.

## 2.3 WHEY

Whey was prepared by renneting fresh skimmilk in a centrifuge tube at 30 °C and subsequent by separating the curd from the whey by centrifuging at 4000 g for 15-20 min.

The values for the viscosity at 30 °C were for the rennet and acid wheys 1.020 and 1.025 mPa•s, respectively.

## 2.4 THIMEROSAL

25-100 ppm Thimerosal, also named thiomersal ($C_2H_5.Hg.S.C_6H_4COO$ Na), was used as a preservative in milk and whey if the experiments lasted over 3 hours. It was checked whether the preservative affected the renneting or syneresis process in our experiments; no significant effects were found.

## 2.5 CONCENTRATED MILK

Concentrated milk was obtained by ultrafiltering reconstituted skim milk at room temperature. Molecular cut-off of the membrane was about 10 000 Daltons. A twofold concentration was reached.

## 2.6 TREATMENT OF THE GEL AND STARTING SYNERESIS

Rennet and acid gels stick to the surfaces of, for instance, glass and stainless steel with a low nickel content (Arentzen,1966; Hostettler, 1954). Hence, at these surfaces no syneresis will occur. This enables us to perform fairly simple experiments. However, the gels should be handled with care as they are easily disrupted from the wall surface before they are firm enough.

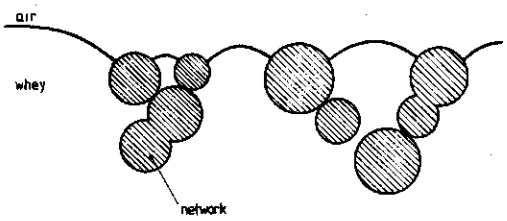



Fig. 2.1 Interface of curd/air with large contact angle of the whey.

The syneresis was started by wetting the upper, free surface of the gel. Until this moment no syneresis occurred. An explanation may be that the surface of the casein network that is in contact with air during renneting is not easily wettable; in other words, the contact angle, as measured in the whey would be > $90^{o}$ (see Fig. 2.1). The capillary pressure trying to force the whey inwards would then easily exceed the syneresis pressure. Of course, this does not hold for a freshly cut surface. A disadvantage of this method is a possible difference of the upper, free surface of the curd in contact with air and a surface formed by cutting, causing a different syneresis. However, the layer in which the difference resides must be extremely thin. Measuring syneresis at a freshly cut surface was expected to cause considerable practical problems in apparatus design and reproducibility. Care was taken that the moisture content of the air above the surface of the gel remained high until it was wetted. The wetting could not be done by simply pouring whey over the surface, because it caused local damage to the gel. Therefore, the surface was wetted first by gently spraying whey on it (followed by pouring).

## 2.7 STANDARD CONDITIONS FOR RENNET GELS

Unless mentioned otherwise milk R was prepared as described in Section 2.1 and used between 1 and 4 hours after preparation, 500 ppm rennet was added and the temperature during the whole experiment was kept at 30 $^{o}$C. No $CaCl_2$ was added. These will be called standard conditions.

## 2.8 STANDARD CONDITIONS FOR ACID GELS

Milk A was prepared as described in Section 2.1. 3 N HCl was used for acidification at 4 $^{o}$C to pH 4.3-4.8. The milk was then heated at a rate of 0.5 $^{o}$C per minute to 30 $^{o}$C, which caused a gel to form.

## 3 ENDOGENOUS SYNERESIS PRESSURE

As stated in Section 1, syneresis must be caused by an endogenous syneresis pressure. In principle the pressure could be measured by fixing the gel between two plates and measuring the force needed to keep the plates at constant distance. We concluded this to be not feasible, the main reason being the very low stress. However, two experiments working on different principles gave some idea of the stresses involved.

In one experiment (see Fig. 3.1.), curd was formed in a vat and cut carefully only in the vertical direction. The curd was not disturbed, and its surface kept dry. In this way blocks of curd were formed with a height of 2 cm and width of 1 cm. The upper surfaces of some of these blocks were wetted with whey while other remained dry. After 1 hour at 33 $^{o}$C the blocks with the wetted upper surface were shrunk, while others shrunk far less: the difference ($h$) between the levels of the unwetted curd and the adjacent whey was always below 1 mm. The stress pulling the upper surface down must be equal to the pressure exerted by the whey column $h$, amounting to $h\ \rho\ g$. Consequently, the syneresis pressure was in this situation < 10 Pa at 33$^{o}$ C. It should be noted that this is not the original situation as the volume has changed during the experiment.

In another experiment it was tried to measure the pressure exerted on the whey in the matrix. A small and sensitive pressure transducer would be needed, but we could not find one that was

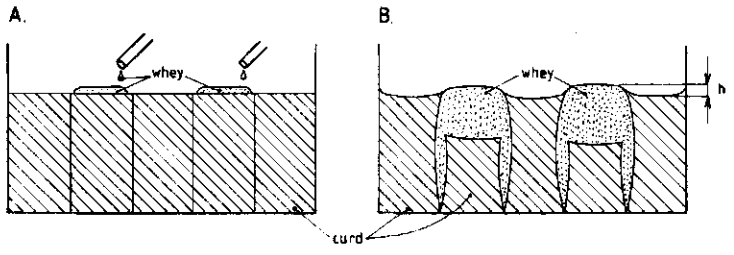



Fig. 3.1 Syneresis of blocks of curd. A: The curd in the vat has been cut in a number of blocks. The upper surface of some of these blocks are wetted. B: After 1 hour at 33$^{o}$ C the blocks with the wetted surface are shrunk far more than the other blocks ($h$ = vertical shrinkage of blocks with unwetted surface).

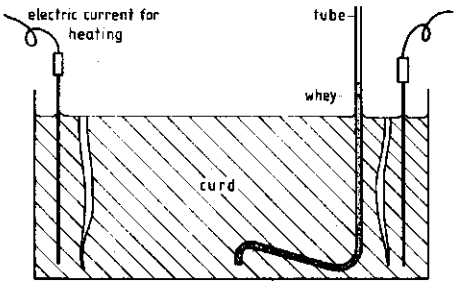



Fig. 3.2 Estimation of the endogenous syneresis pressure by recording the pressure exerted on the whey.

sensitive enough. Therefore, we tried an experiment as shown in Fig. 3.2. In a vat a glass tube was placed; the tube had a diameter of 0.5 mm and was filled with whey. Milk with rennet was added and after setting the curd was cut loose from the wall. At first the whey level was higher than the level of the curd because of capillary rise. The syneresis pressure now should further raise the whey level. Only if the curd was warmed as high as 40 $^{o}$C, the level in the tube did raise perceptibly, i.e. about 1 mm corresponding to 10 Pa. The actual syneresis pressure must have been higher as considerable transport of whey is needed for the measurement.

Another cause for syneresis could be the weight of the casein matrix. The lower parts of the network have to bear more or less the network above their level. This means that in curd at a level $h_c$ below the interface a pressure of $(\rho_{curd} - \rho_{whey})\ g\ h_c \approx 75\ h_c$ (in S.I. units) would exist. In Chapter 7 it will be concluded that the weight of the casein network plays a role in syneresis pressure.

Also from creep measurements (see Section 5.3) we concluded that endogenous syneresis pressure was probably lower than 10 Pa, maybe ~ 1 Pa at standard conditions (Section 2.8). Consequently, an order of magnitude can be given.

# 4 PERMEABILITY

## 4.1 INTRODUCTION

For the calculational model we are interested in the resistance a fluid meets when it flows in one direction through a fixed matrix. A measure for this is the permeability or permeability coefficient. It is the proportionality constant in the equation of Darcy (see e.g. Scheidegger (1960)):

$$v = -\frac{B}{\eta} \nabla P \tag{4.1}$$

in which:

$v$ = superficial velocity (i.e. volume flow rate/cross-sectional area)

$\eta$ = viscosity

$\nabla P$ = pressure gradient. In our case this is always in the same $x$-direction (i.e. parallel to the tube). So $\nabla P = dP_t/dx$. The pressure difference between the lower and the upper surface of the gel is called $P_t$ or $P_t(t)$ (see Fig. 4.2).

$B$ = permeability coefficient. It is a property of the matrix and its geometry and scale. The dimension is length squared. (Compare the laminar flow through a cylinder with radius $a_t$ where

$$v = -(a_t^2/8\eta)\, dP_t/dx.) \tag{4.1.a}$$

The equation is valid in a certain velocity domain (see Section 4.3.1).

## 4.2 MATERIALS AND METHODS

### *4.2.1 "Tube" method*

For measuring the permeability of the curd it is necessary that the curd does not shrink during the experiment. This was achieved by making the curd in tubes of 2.0 or 3.7 mm internal diameter and 25 cm length. Unless mentioned otherwise the 3.7 mm diameter tubes were used.

The tubes were cleaned thoroughly so that the curd would stick to

the wall and either placed in a holder whereby the tube was resting on a plexiglas base or sealed on lower side with laboratory film in which a pinhole was made. They then were slowly lowered in a vat filled with milk to which rennet had been added, thereby slowly filling the tubes (see Fig. 4.2). When the clot was firm enough the tubes were drawn out of the vat. The tube holders or the laboratory films were removed. The tubes were put in a rack in the whey. The whey then started flowing through the curd. The whey-level in the tubes was read at regular intervals with the aid of a cathetoscope. The whey-level in some tubes without a gel also was measured. The experiments were executed in 3- or 4-fold as about 10% of the curds became unstuck from the tubes.

*4.2.2 The "Torsionflux" method*

When measuring $B$, e.g. as described in the previous Section, the gel is being deformed, because of the pressure difference applied (see Section 4.3.2.1). The deformation of the gel (in the direction of the flow) affects the permeability of the curd. With the tube method we cannot measure the deformation. Moreover the deformation depends on the distance to the wall of the tube and on the rigidity of the gel.

The method described here was applied to measure the permeability as a direct function of deformation of the gel, if deformation was perpendicular to the direction of flow. The gel was made between a metal inner cylinder and a glass outer cylinder (see Fig. 4.1). One hour after adding rennet the inner cylinder was rotated over a certain angle and kept so for one hour. In this way the deformation is precisely known. Then the whey inlets were opened, about 5 mm of whey was placed on top of the curd and the walls of the cylinders were wetted. The whey-level was read at regular intervals with the aid of a cathetoscope.

*4.2.3 Calculation of permeability coefficient (B)*

Generally, for the purpose of permeability measurements, an apparatus is used which holds the pressure constant. In this way the equation of Darcy (eq. 4.1) simply can be used. But during our experiments (see Fig. 4.2) the pressure difference ($P$) between the ends of

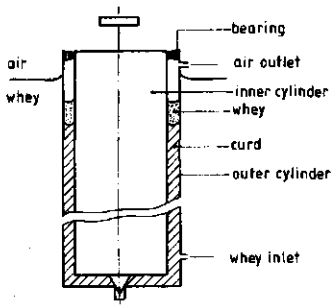



Fig. 4.1 Schematic representation of the "torsionflux" apparatus

the column changed depending on the velocity ($v(t) = dh(t)/dt$):

$$\frac{d}{dt}\frac{P_t(t)}{\rho g} = \frac{d\{h(\infty) - h(t)\}}{dt} = -v(t) \qquad (4.2)$$

with $\rho$ = density of the whey and $g$ = gravitational acceleration.

In this case the equation of Darcy (Eq. 4.1) can be written as:

$$\frac{dh(t)}{dt} = \frac{B}{\eta}\frac{P_t(t)}{H} \qquad (4.3)$$

$P(t)$ is caused by the difference $h(\infty) - h(t)$ in the level of the whey.

$$\frac{dh(t)}{dt} = \frac{B}{\eta}\frac{\rho g\{h(\infty) - h(t)\}}{H} \qquad (4.4)$$

Integration leads to:

$$h(t) = -\{h(\infty) - h(0)\} \exp\left(\frac{-B \rho g t}{\eta H}\right) + h(\infty) \qquad (4.5)$$

This can be rewritten as:

$$B = \frac{-\ln\left(\frac{h(\infty) - h(t)}{h(\infty) - h(0)}\right) \eta H}{\rho g t} \qquad (4.6)$$

A problem is that $B$ was not constant: it usually increased during the measurements. For sake of simplicity we assumed $B(t)$ to change linearly with time; subsequent measurements showed this to be true within the

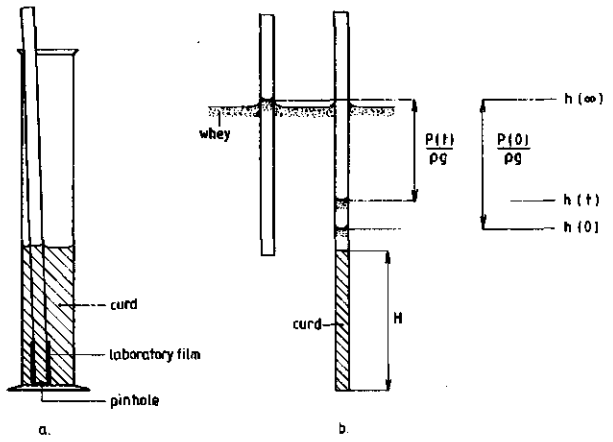



Fig. 4.2 Schematic representation of permeability measurement.
a. formation of curd in a tube
b. permeability measurement.

accuracy of the experiments. If $B(t)$ is changing linearly with time Eq. 4.3 turns to:

$$\frac{dh(t)}{dt} = \frac{B(0) + \frac{dB}{dt}\, t}{\eta}\, \frac{P_t(t)}{H} \tag{4.7}$$

in which $dB/dt$ is a constant. Following the same method as described above we obtain:

$$B(0) = \frac{-\ln\left(\frac{h(\infty) - h(t)}{h(\infty) - h(0)}\right) \eta\, H}{\rho\, g\, t} - \tfrac{1}{2}\frac{dB}{dt}\, t \tag{4.8}$$

Since $B(t)$ is linear with time $B(\frac{1}{2}t) = B(0) + \frac{1}{2}\frac{dB}{dt}\, t$, and at $B(\frac{1}{2}t)$ we find the same result as with Eq. 4.6. So Eq. 4.6 can still be used if the permeability coefficient $(B)$ is taken at the half time between the readings of $h(0)$ and $h(t)$.

Up till now we have tacitly assumed that the level of the whey outside the tube is constant. This need not be true. If the level is not constant, and the surface ratio of the tubes to the vat is $r$ then:

$$\frac{d}{dt}\frac{P(t)}{\rho\, g} = -(1 + r)v(t) \tag{4.9}$$

A possible small effect of different $v(t)$ in different tubes is neglected. We find in analogy to previous solutions:

$$h(t)-h(0) = \frac{P(0)}{\rho\, g(1+r)} \exp\left\{\frac{-\{B(0)t + \frac{1}{2}\frac{dB}{dt}t^2\}\,\rho\, g(1+r)}{\eta\, H}\right\} - 1 \qquad (4.10)$$

or rewritten:

$$B(0) = \frac{-\ln\{\frac{(1+r)\,\{h(\infty)-h(t)\}}{h(\infty)-h(0)}\}\,\eta\, H}{(1+r)\,\rho\, g\, t} - \frac{1}{2}\frac{dB}{dt}\,t \qquad (4.11)$$

In the experiments always $r < 0.01$. If the velocities in the various tubes during one experiment differed, $r$ was made as small as possible ($< 0.001$) and neglected.

To find $dB/dt$ a number of subsequent readings had to be made and from these $B$ at different times was calculated.

As mentioned already $dB/dt$ indeed was found to be not significantly dependent of time. In some experiments, especially with the torsionflux apparatus (see 4.2.2), the readings were less accurate. A better estimate of $B$ and $dB/dt$ can be made by second degree polynomial regression, provided $dB/dt$ is independent of time. We can use the rewritten Eq. 4.10 for analysis:

$$\ln\{h(\infty)-h(t)\}\,\frac{\eta\, H}{\rho\, g(1+r)} =$$

$$\ln\{h(\infty)-h(0)\}\,\frac{\eta\, H}{\rho\, g(1+r)} - B(0)t - \tfrac{1}{2}\frac{dB}{dt}\,t^2 \qquad (4.13)$$

where $B(0)$ and $\frac{1}{2}dB/dt$ are the regression coefficients.

Finally, it should be noted that $B(0)$ is the permeability of the gel at the moment that measurements started. Mostly, the pressure difference had to be applied 10 to 20 minutes earlier, for practical reasons. Consequently, $B_e$ i.e. $B$ at the moment that pressure difference was applied, can only be had from extrapolation.

*4.2.4. Calculation of the viscosity of the whey*

Because of the limited accuracy of the measurements, it was not necessary to determine the viscosity for every whey sample, except

when the temperature or the concentration were changed. According to Eilers (1945) the viscosity changes considerably with temperature and we used his results. Any concentration of the milk was done by ultrafiltration. By this method the whey is concentrated also.

The ensuing increase in viscosity was calculated with the aid of the experimental results of Peri (1976).

## 4.3 RESULTS

### *4.3.1 Validity of the equation of Darcy*

It should be checked whether the equation of Darcy is valid in the performed experiments. This is normally so if laminar flow occurs. The result shows however that the permeability changes with time. It should be proven however that at a given time $B$ is independent of liquid velocity. To characterize the flow, it is customary to introduce a "Reynolds number" ($Re$) as follows:

$$Re = v\ \rho\ d/\eta$$

where $d$ is a diameter associated with the porous medium. If porosity is low, $d$ could be the average hydraulic pore diameter of the strands. We always kept $v < 10^{-4}$ m•s$^{-1}$; $\rho \approx 10^{3}$ kg•m$^{-3}$ and $\eta \approx 1$ mPa•s. For $d <$ 1 mm we then find $Re < 10^{-1}$. Since always $d \ll 1$ mm, $Re \ll 1$. So laminar flow can be expected.

Moreover, measurements were performed at different $dP/dx$, by changing the column length and/or $P$, and different tube diameter ($d_t$). For practical reasons the measurements could only start 10-20 minutes after $t_e$ : the time at which the pressure difference was applied to the column. Fig. 4.3 shows that there is no significant difference between the extrapolated values $B_e$ at $t_e$.

### *4.3.2 Results with the tube method*

#### 4.3.2.1 Influence of deformation on permeability

As stated before, curd deforms during measurement as a result of

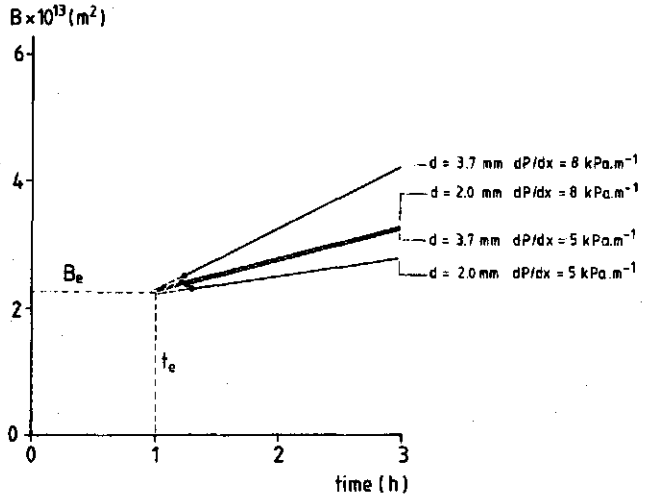



Fig. 4.3 Permeability as a function of time. Illustrating the time derivative depends on $d_t$ and $dP_t/dx$. At time $t_e$ the tubes were placed in the whey. The dots represent the calculated $B(0)$ values (see Eq. 4.10).

the applied pressure gradient ($dP_t/dx$). For instance, at 8 kPa•m$^{-1}$ it was visibly deformed. This deformation depended on the distance to the wall, on $dP/dx$, on tube diameter ($d_t$) and gel strength. The results in Table 4.1 show that larger $dP_t/dx$ and larger $d_t$, which gave larger deformations, resulted in a higher $dB/dt$. Eventually, the gel breaks. Incidentally, the gels always broke at a distance of about $\frac{1}{4}d_t$ from the wall; this is indeed the region where the deformation of the gel should be largest. Some results are also shown in Fig. 4.3.

Table 4.1 Influence of pressure gradient ($dP_t/dx$) and tube diameter ($d_t$) on $dB/dt$. Average values and range of three experiments.

| $d_t$ (mm) | $dP_t/dx$ (kPa•m$^{-1}$) | $dB/dt \times 10^{17}$ (m$^2$•s$^{-1}$) |
|---|---|---|
| 3.7 | 0 | 0.8[1)] |
| 3.7 | 5 | 1.4 (1.4 - 1.5) |
| 3.7 | 8 | 2.8 (2.6 - 2.8) |
| 3.7 | 20 | gel breaks |
| 2.0 | 0 | 0.8[1)] |
| 2.0 | 5 | 0.8 (0.6 - 0.8) |
| 2.0 | 8 | 1.4 (1.3 - 1.5) |

[1)] From Table 4.2 : $\{B_e(2h) - B_e(1h)\}/3600$

4.3.2.2 Change of permeability of undeformed curd with time

Gels in tubes were put under pressure for measurements at different time after rennet addition. From the flow in 4 - 12 tubes the average $B_e$ value and range and the average $dB/dt$ value and range were calculated (see Table 4.2 and Fig. 4.4). In Table 4.2 also $\Delta B_e/\Delta t = \{B_e(t_2) - B_e(t_1)\} / (t_2 - t_1)$ is given.

4.3.2.3 Influence of concentration

The influence of casein concentration was studied by ultrafiltering fresh skim milk. Concentration was expressed as i = volume of concentrated milk/volume of original milk. Naturally, we are interested more in the permeability of homogenous gels concentrated by syneresis, but such gels cannot be made homogenous and they will show syneresis on holding.

The length of the gel column was taken so that the flow of the whey was always between 0.1 and 0.3 $mm \cdot s^{-1}$. A constant clotting time of 0.25 was used. The results were fitted to power curves.

Table 4.2 Change of permeability with time. $dP_t/dx$ = 5 $kPa \cdot m^{-1}$. For explanation see text and Fig. 4.4 .
$n$ = number of experiments
$t$ = time after rennet addition

| $n$ | $t_a$ (h) | $B_e \times 10^{13}$ ($m^2$) | $\Delta B_e/\Delta t \times 10^{17}$ ($m^2 \cdot s^{-1}$) | $dB/dt \times 10^{17}$ ($m^2 \cdot s^{-1}$) |
|---|---|---|---|---|
| 8 | 0.5 | 1.5 (1.0 - 1.8) | 6.6 | 6.1 (4.2 - 7.0) |
| 4 | 0.67 | 1.9 (1.9 - 2.0) | 2.5 | 2.3 (2.2 - 2.8) |
| 8 | 1 | 2.2 (2.2 - 2.3) | 1.1 | 1.6 (1.2 - 1.9) |
| 4 | 1.5 | 2.4 (2.3 - 2.5) | 0.6 | 1.6 (1.5 - 2.5) |
| 12 | 2 | 2.5 (2.4 - 2.7) | 1.1 | 2.3 (1.5 - 3.0) |
| 4 | 3 | 2.9 (2.9 - 3.1) | 1.1 | 1.6 (1.5 - 1.8) |
| 8 | 4 | 3.3 (3.1 - 3.1) | 1.1 | 1.3 (1.1 - 1.7) |
| 8 | 24 | 11.1 (11.1 - 11.1) | | 1.3 (1.0 - 2.0) |

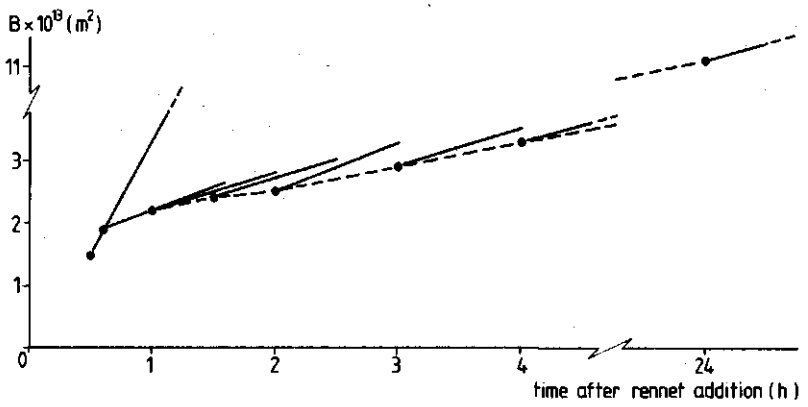



Fig. 4.4 Permeability as a function of time, of deformed curd during the experiment (solid line) and of undeformed curd (dashed line interconnecting calculated values of $B_e$).

We found:

$$dB_e/dt = 8 \times 10^{-18} - 2.2 \times 10^{17} (1 - i)^{2.4} \quad (m^2 \cdot s^{-1}) \qquad (4.14)$$

and:

$$B_e(i) = 2.3 \times 10^{-13} i^{2.6} \quad (m^2) \qquad (4.15)$$

with sample correlation coefficients ($r$) of 0.98 and 0.998, respectively. Integration and combination yields:

$$B_e(i, t) = \{8 \times 10^{-18} - 2.2 \times 10^{-17} (1 - i)^{2.4}\} t + 2.3 \times 10^{-13} i^{2.6} \quad (m^2) \qquad (4.16)$$

which relation was used in the model. Eqs. 4.14 and 4.15 are shown in Fig. 4.5. Note that $B_e(i, t)$ and $dB_e/dt$ for $i < 0.5$ were found by extrapolation. For $i = 0.5$ $dB_e/dt$ calculated from Eq. 4.14 has about twice the experimental value. This would only have a minor effect on the comparison of the calculated and the determined syneresis since only results for $\Delta H/H_0 < \sim 0.5$ were considered.

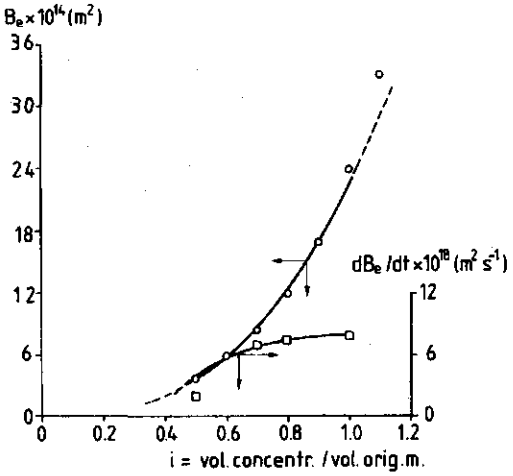



**Fig. 4.5 Permeability and its time derivate as a function of concentration of the milk before curdling.**

### 4.3.2.4 Influence of temperature during measurement

The gels were made and treated according to the standard method. One hour after rennet addition the temperature was changed. Results are given in Table 4.3. It shows that $dB/dt$ increases with increasing temperature.

### 4.3.2.5 Influence of temperature during renneting

For these experiments skim milk A was used. One hour after rennet addition the tubes were placed in whey of 30 °C with $dP/dx$ = 4 kPa·m$^{-1}$. The results are shown in Table 4.5a. Permeability as measured one hour after rennet addition ($B_e$) increased with increasing renneting temperature. The influence on $dB/dt$ was less consistent. A probable cause is that only a few readings of $h(t)$ were done.

In another series of experiments skim milk R was used and the temperature during renneting was maintained during measurement. The results are shown in Table 4.5b. In these experiments $B_e$ and $dB/dt$ increased with increasing temperature.

Table 4.3 Influence of temperature during measurement on $dB/dt$

| Temperature (°C) | $dB/dt \times 10^{17}$ ($m^2 \cdot s^{-1}$) | | | |
|---|---|---|---|---|
| | $dP_t/dx$ : 0 | | 8 ($kPa \cdot m^{-1}$) | |
| 12 | < 0.05 | | < 0.05 | |
| 25 | 0.7 | (0.6 - 0.7) | 1.0 | (0.9 - 1.2) |
| 30 | 1.0 | (0.8 - 1.1) | 2.8 | (2.6 - 2.9) |
| 35 | 5.1 | (4.9 - 7.3) | 8 | (7 - 8) |

4.3.2.6 Influence of rennet concentration and type of skim milk

Two series of experiments were done. In the first series fresh skim milk was used and in the second the usual reconstituted skim milk. Results are shown in Table 4.4. From Table 4.1 and Fig. 4.4 values of $dB/dt$ and $B$ for 500 ppm rennet were taken.

The results show that initially $B$ increased and $dB/dt$ (during measurement, i.e. while there is deformation) decreased with increasing rennet concentration. After 2¼ hours, influence of rennet concentration was small, if existent. Fresh milk gave higher results for $B$ and $dB/dt$.

4.3.2.7 Influence of $CaCl_2$ addition

$CaCl_2$ was added in different concentrations and rennet was added in such a quantity that the same clotting time was achieved in all experiments. The results in Table 4.6a show that at $t_a$ = 1 h, $B_e$ does not depend on the applied Ca concentration and $dB/dt$ decreases with increasing Ca concentration. At $t_a$ = 2 h, $B_e$ and $dB/dt$ decreased with increasing concentration.

In another experiment only the $CaCl_2$ concentration was varied. The results in Table 4.6b show that $B$ was constant or slightly increased at $CaCl_2$ concentrations of 0 to 500 ppm and decreased at concentrations of 7400 to 22100 ppm. $dB/dt$ decreased with increasing concentrations.

Table 4.4 Effect of rennet concentration on $B_e$ and $dB/dx$. $dP_t/dx$ = 8 kPa·m$^{-1}$

a. Fresh skim milk

| Rennet concentration (ppm) | clotting time (s) | $B_e \times 10^{13}$ ($m^2$) | $dB/dt \times 10^{17}$ ($m^2 \cdot s^{-1}$) | $B_e \times 10^{13}$ ($m^2$) | $dB/dt \times 10^{17}$ ($m^2 \cdot s^{-1}$) |
|---|---|---|---|---|---|
| | | $t_a$ = 1.1 h | | $t_a$ = 3 h | |
| 600 | 600 | 4.0 (3.8 - 4.2) | 3.6 ( 3.4 - 3.6) | 4.9 (4.7 - 5.2) | 4.2 (4.0 - 5.1) |
| 500 | 720 | 3.5 (3.5 - 3.6)[3] | 4.0 ( 3.9 - 4.2)[3] | - | - |
| 200 | 1680 | 4.0 (3.8 - 4.1) | 6.4 ( 6.0 - 6.7) | 5.5 (5.4 - 5.7) | 4.4 (3.4 - 5.2) |
| 140 | 2400 | 4.3 (4.0 - 4.5) | 11.6 (10.1 - 14.8) | 5.4 (5.3 - 5.5) | 4.6 (4.3 - 4.7) |
| 100 | 3600 | 1.1 (0.6 - 1.6) | 48 (41 - 53 ) | 5.1 (4.8 - 5.2) | 5.0 (4.3 - 5.7) |

b. Reconstituted skim milk R

| | | $t_a$ = 2.25 h | | $t_a$ = 3.75 h | |
|---|---|---|---|---|---|
| 600 | 780 | 2.5 (2.3 - 2.6) | 3.0 ( 2.8 - 3.3) | 3.5 (3.1 - 3.8) | 3.5 (2.7 - 3.4) |
| 500 | 900 | 2.3[1] | 2.8[2] | 3.2[1] | - |
| 200 | 2280 | 2.5 (2.3 - 2.8) | 3.0 ( 2.4 - 4.0) | 3.5 (3.0 - 3.8) | 3.2 (3.0 - 3.5) |
| 140 | 3180 | 2.3 (2.0 - 2.6) | 3.1 ( 2.8 - 3.5) | 3.3 (3.0 - 3.6) | 3.2 (3.1 - 3.3) |
| 100 | 4500 | 2.2 (2.0 - 2.4) | 3.6 ( 3.1 - 3.7) | 3.8 (3.4 - 3.9) | 3.6 (3.2 - 5.7) |

[1] from Fig. 4.4
[2] from Table 4.1
[3] from experiment with temperature at 29.5 °C

Table 4.5 Influence of temperature during renneting.

a. $dP_t/dx$ = 4 kPa•m$^{-1}$.Skim milk A

| Temp. (°C) | $B_e \times 10^{13}$ ($m^2$) | $dB/dt \times 10^{17}$ [2] ($m^2 \cdot s^{-1}$) |
|---|---|---|
| 30.2 | 2.4 (2.1 - 2.5) | 2.6 (2.0 - 3.0) |
| 32.8 | 3.0 (3.0 - 3.1) | 3.6 (3.0 - 4.4) |
| 35.6 | 6.5 (6.1 - 6.8) | 3.4 (2.9 - 3.7) |

b. Temperature maintained during measurement. $dP_t/dx$ = 5 kPa•m$^{-1}$.Skim milk R

| | | |
|---|---|---|
| 27 | 1.7 (1.9 - 2.2) | 2 (1 - 2) |
| 30 | 2.2[1] | 1.6[1] |
| 33 | 3.0 (2.8 - 3.4) | 5 (4 - 7) |

[1] from Table 4.1
[2] less accurate as only a few readings of $h(t)$ were available

4.3.2.8 Influence of acidity on permeability

The pH of the gels was varied by adding HCl or NaOH. As in Section 4.3.2.5 skim milk A was used for the experiments shown in Table 4.7a and b.

The results in Table 4.7 show that $B_e$ at $t$ = 1 h decreased with increasing pH. The effect on $dB/dt$ will be discussed later.

4.3.2.9 Influence of fat content

The fat content of fresh milk was varied by taking whole milk (3.32% fat), separated milk (0.10%) and a mixture (1.96%).

The results in Table 4.8 show that $B$ decreased with increasing fat content. There was found no significant correlation between $dB/dt$ and fat content.

Table 4.6 Influence of $CaCl_2$ concentration on permeability.

a. At constant clotting time $dP_t/dx$ = 5 Pa·mm$^{-1}$

| $CaCl_2.2H_2O$ (ppm) | rennet (ppm) | $B_e \times 10^{13}$ ($m^2$) | $dB/dt \times 10^{17}$ ($m^2.s^{-1}$) |
|---|---|---|---|
| | | $t_a$ = 1 h | |
| 0 | 500 | 2.2 (2.1 - 2.3) | 1.6 (1.2 - 1.8) |
| 450 | 250 | 2.3 (2.2 - 2.5) | 1.2 (0.6 - 1.6) |
| 1600 | 125 | 2.1 (2.1 - 2.3) | 1.1 (1.1 - 1.2) |
| 3200 | 62.5 | 2.3 (2.3 - 2.3) | 1.0 (0.7 - 1.3) |
| | | $t_{a'}$ = 2 h | |
| 0 | 500 | 2.6 (2.4 - 2.7) | 1.8 (1.5 - 1.9) |
| 450 | 250 | 2.5 (2.3 - 2.7) | 1.4 (1.2 - 1.5) |
| 1600 | 125 | 2.3 (2.1 - 2.4) | 1.2 (1.1 - 1.3) |
| 3200 | 62.5 | 2.4 (2.1 - 2.5) | 1.0 (1.0 - 1.0) |
| b. At constant rennet concentration $dP_t/dx$ = 8 Pa·mm$^{-1}$. $t_a$ = 1 h | | | |
| 0 | 500 | 2.3 (2.1 - 2.4) | 2.7 (2.3 - 2.9) |
| 250 | 500 | 2.3 (2.2 - 2.4) | 2.5 (2.2 - 2.8) |
| 500 | 500 | 2.5 (2.3 - 2.5) | 2.4 (2.1 - 2.6) |
| 7400 | 500 | 2.4 (2.2 - 2.6) | 1.3 (1.0 - 1.7) |
| 14700 | 500 | 2.2 (2.0 - 2.4) | 0.8 (0.8 - 1.0) |
| 22100 | 500 | 2.0 (2.0 - 2.1) | 0.9 (0.7 - 1.1) |

4.3.2.10 Permeability of acid gels

Gels were made in tubes as described in Section 2.8. Permeability and storage modulus $G'$ were measured 20 hours after heating. The results are in Fig. 4.6. At pH 4.6 the permeability was also measured 2 hours after heating; it was higher (i.e. $1.9 \times 10^{-13}$ $m^2$) than after 20 h, this in contrast to the permeability of rennet gels, which increases with time. During measurement ($dP_t/dx$ = 5 kPa·m$^{-1}$), $B$ remained constant (i.e. $dB/dt$ was zero) in all cases.

Table 4.7 Influence of acidity on permeability

a. Milk R (12 g powder/100 g water). 250 ppm rennet. Temp.: 30.5 °C
Rennet added ∿1h after pH setting. Original pH : 6.5. $dP_t/dx$ = 8 kPa•m$^{-1}$)

| pH | Clotting time (min) | $B_e \times 10^{13}$ ($m^2$) | $dB/dt \times 10^{17}$ ($m^2 \cdot s^{-1}$) |
|---|---|---|---|
| 6.0 | 15 | 3.0 (2.9 - 3.1) | 1.0 (0.9 - 1.2)[2] |
| 6.3 | 25 | 2.0 (1.9 - 2.0) | 0.4 (0.3 - 0.7)[2] |
| 6.6 | 40 | 1.3 (1.3 - 1.3) | 1.3 (1.3 - 1.4)[2] |
| b. Standard conditions (see 2.7). Rennet addition ½ h after pH setting. Original pH : 6.65. $dP_t/dx$ = 5 kPa•m$^{-1}$. | | | |
| 6.55 | | 2.7 (2.5 - 2.7)[1] | 1.2 (1.0 - 1.6)[1] |
| 6.65 | | 2.2 (2.2 - 2.3)[1] | 1.6 (1.2 - 1.9)[1] |
| 6.75 | | 2.0 (2.0 - 2.3) | 2.2 (1.8 - 2.3) |
| c. Same milk and conditions; rennet added 3 h after pH adjustment. | | | |
| 6.55 | | 2.3 (2.3 - 2.4)[1] | 2.2 (1.8 - 2.6)[1] |
| 6.65 | | 2.2 (2.2 - 2.3)[1] | 1.6 (1.2 - 1.9)[1] |
| 6.75 | | 2.1 (2.1 - 2.3) | 2.4 (2.0 - 2.6) |

[1]) Results taken from Table 4.2
[2]) Less accurate as only a few readings of $h(t)$ are done

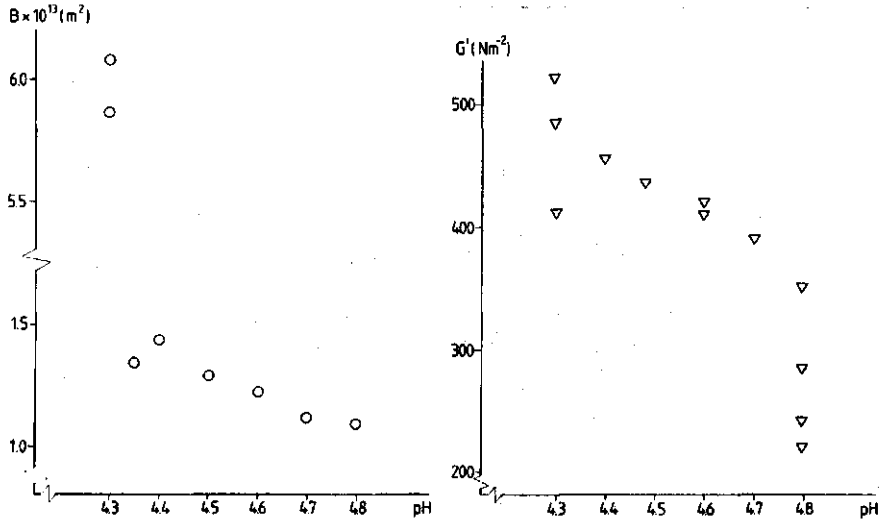



Fig. 4.6 Permeability ($B$) and storage modulus ($G'$) of acid gels as a function of pH.

Tabel 4.8 Influence of fat content on permeability. Fresh milk was used. $dP_t/dx$ = 5 kPa•m$^{-1}$. Experiments starting ½ h after rennet addition ($t_a$ = ½ h)

| Fat content (%) | $B_e \times 10^{13}$ (m$^2$) | $dB/dt \times 10^{17}$ (m$^2$•s$^{-1}$) |
|---|---|---|
| 0.10 | 5.2 (5.1 - 5.3) | 4.2 (4.1 - 4.5) |
| 1.96 | 4.8 (4.7 - 5.0) | 4.5 (4.4 - 4.9) |
| 3.82 | 4.5 (4.3 - 4.5) | 3.1 (2.6 - 3.2) |

*4.3.3 Influence of deformation, temperature and pH on permeability as measured with the torsionflux method*

Temperature during the experiment was varied between 28 and 33 °C. The results in Table 4.9 show that $B$ increased with increasing deformation and temperature. $B$ increased roughly exponentially with shear strain $\gamma$. At higher temperatures $B$ depended more on $\gamma$. Most gels broke if $\gamma$ = 1.05 (see Table 4.9). From Fig. 5.4 it can be deduced that gel will break if $\gamma \approx 1$ after 1 hour (standard conditions).

$dB/dt$ (during measurement) increased a little with increasing deformation and temperature.

The influence of acidity was studied by changing the pH by 0.1 unit. Permeability was increasing with decreasing pH and increasing shear strain ($\gamma$) (see Table 4.9).

## 4.4 DISCUSSION

The general results of the experiments are:

A) The permeability of the different gels varied between $\sim 10^{-13}$ and $10^{-12}$ m$^2$.

This result can be expected from electron micrographs (Knoop & Peters, 1975; Mulder, De Graaf & Walstra, 1966; Green, Turvey & Hobbs, 1981). They show an average thickness ($\delta$) of the strands of $\sim$ 250-500 nm. The matrix is not homogeneous. While $\varepsilon$ is on average about 0.93, there are regions with a high density of strands (local $\varepsilon$, say 0.8) which alternate with pores (where local $\varepsilon$ = 1). The pores

Table 4.9 Influence of deformation, temperature and pH on the permeability as measured with the torsionflux method. $dP_t/dx$ = 5 kPa·m$^{-1}$. Values of $B_e$ are in $10^{-13}$ m$^2$, values of $dB/dt$ in $10^{-17}$ m$^2$·s$^{-1}$; ranges between parenthesis. $n$ = number of experiments. Deformation started 1 hour after rennet addition, pressure was applied 1 h later ($t_e$ = 2 h).

| Rotation of inner-cylinder (degrees) | | 0 | 5 | 10 | 12.5 | 15 |
|---|---|---|---|---|---|---|
| Resulting shearing strain ($\gamma$) | | 0 | 0.35 | 0.7 | 0.88 | 1.05 |
| temperature (°C) | | | | | | |
| 28 | $n$ | 3 | 3 | 3 | 3 | |
| | $B_e$ | 1.9(1.4-2.0) | 1.8(1.5-2.1) | 2.1(1.9-2.3) | 2.4(2.1-2.7) | |
| | $dB/dt$ | 2(1-2) | 1(1-1) | 2(1-2) | 4(3-5) | |
| 30 | $n$ | 8 | 6 | 11 | 4 | 1 |
| | $B_e$ | 2.5(2.2-2.6) | 2.6(2.2-2.7) | 3.0(2.4-3.5) | 3.6(3.1-4.0) | 5.2 |
| | $dB/dt$ | 2(1-2) | 1(1-1) | 2(1-2) | 4(3-5) | 12 |
| 32 | $n$ | 1 | 1 | 1 | 1) | 1) |
| | $B_e$ | 4.4 | 5.0 | 5.5 | | |
| | $dB/dt$ | 6 | 5 | 7 | | |
| 33 | $n$ | 2 | 2 | 2 | 1 | 1) |
| | $B_e$ | 4.2(4.0-4.4) | 4.9(4.6-5.2) | 5.5(5.1-6.0) | 6.3 | |
| | $dB/dt$ | 6(4-8) | 6(4-7) | 7(5-8) | 15(11-20) | |
| pH | | | | | | |
| 6.55 | $n$ | 4 | 4 | 3 | 2 | |
| | $B_e$ | 3.3(3.2-3.4) | 3.4(3.1-3.6) | 4.0(3.6-4.5) | 5.0(4.6-5.4) | |
| | $dB/dt$ | 4(3-4) | 4(3-5) | 5(4-6) | 10(8-13) | |
| 6.65 (see T=30°C, above) | | | | | | |
| 6.75 | $n$ | 4 | 4 | 3 | 4 | |
| | $B_e$ | 2.6(2.2-3.0) | 2.8(2.2-3.2) | 2.9(2.6-3.2) | 3.4(2.9-4.0) | |
| | $dB/dt$ | 3(1-4) | 3(2-4) | 3(2-4) | 4(3-5) | |

1) gel breaks (also at 30°C and $\gamma$ = 1.05 the gel was broken in two experiments)

comprise roughly half the volume of the gel. Typical values for pore diameters are 5-10 μm. The effective volume fraction of the para-casein micelles (1-ε) is taken to be 0.07. In literature (e.g. Scheidegger, 1960) a number of equations are given which predict the permeability of model systems.

The equation of Iberall deals with a model of a random distribution of circular cylindrical fibres. According to this equation

$$B = \frac{3}{16} \frac{\varepsilon \delta^2}{1-\varepsilon} \frac{2 - \ln Re}{4 - \ln Re} \qquad (4.18)$$

in which the Reynolds number ($Re$) $\sim 10^{-5}$, we find $B \sim 10^{-13}$ m$^2$. The Kozeny-Carman theory represents the porous medium by an assemblage of channels of various cross-sections, but of definite length. According to the equation of Kozeny-Carman (Scheidegger, 1960)

$$B = \frac{\varepsilon^3 d_{vs}^2}{180\ (1-\varepsilon)^2} \qquad (4.19)$$

in which $d_{vs}$ = volume surface average diameter of the micelles ($d_{vs}$ = 104 nm according to Schmidt, Walstra & Buchheim, 1973), we would find $B = 1 \times 10^{-14}$ m$^2$. Since the (superficial) flow through a collection of pores is proportional to pore diameter squared, flow through the very small pores inside the dense regions of the matrix will be negligible as compared to the larger pores between dense regions. Hence, the regions with a high density of strands, as shown in the electron micrographs, may be considered impermeable. Assuming them to be spheres with a diameter of 10 μm, and effective ε to be 0.5 (see above), we find from Eq. 4.19 $B = 3 \times 10^{-13}$. Experimentally we found under standard conditions $B = 2 \times 10^{-13}$ and $4 \times 10^{-13}$ for gels of reconstituted and fresh skim milk respectively.

We will continue this discussion later when we deal with the influence of the porosity or concentration on the permeability coefficient.

B) $B$ changed with time

This leads to the conclusion that the strands in the network are rearranged or change in diameter, or both. The fact that $B$ is

increasing implies that the matrix becomes less homogeneous and/or that the diameter of the strands or the micelles is reduced. The latter indeed holds for casein micelles and rennet curd when the pH falls (unpublished results, Walstra & Delsing). Strands as a whole may be reduced in effective diameter when the strands become less frayed. This can be seen in electron micrographs (Knoop, 1975). A less homogeneous gel would result from rearrangement of strands. This can occur when strands are moved by Brownian motion or by deformation (slight vibrations, as occur in a building, might be enough) and are thus anabled to touch and form new crosslinks. Two examples are given in Fig. 4.7 and 4.8. As a result of the newly formed cross-links the strands will be under stress. And the matrix will either relax by shrinking (syneresis) or, especially when the gel is fixed, by breaking of bonds (micro-syneresis) (see Fig. 4.7). The broken strands which have more freedom to move may fuse again with other strands. The latter step certainly enhances permeability as the interface matrix-whey will decrease and most likely the pores will enlarge. Micro-syneresis may then continue until the strands are so rigid that these processes stop or macroscopic rupture occurs.

$dB/dt$ was constant with time under the applied circumstances (within the limit accuracy of the experiments) except for $dB_e/dt$ for a short while (i.e. within 1 hour) after rennet addition (standard conditions). An explanation for this linearity could not be given.

C) $B$ increased exponentially with deformation as measured with the torsionflux method and increased more at higher temperature.

The strands will break at a certain yield stress. Probably this implies that the yield stress varies among strands, and in such a way that the number of strands that break increase exponentially with the applied deformation. When a strand is broken the resulting free ends now have more freedom of movement, hence a greater probability to touch another strand, forming new crosslinks. This would result in wider pores, hence a higher permeability.

Note that the deformation in the tubes depends on $dP_t/dx$ and on the rigidity of the gel (see Section 7.3.3).

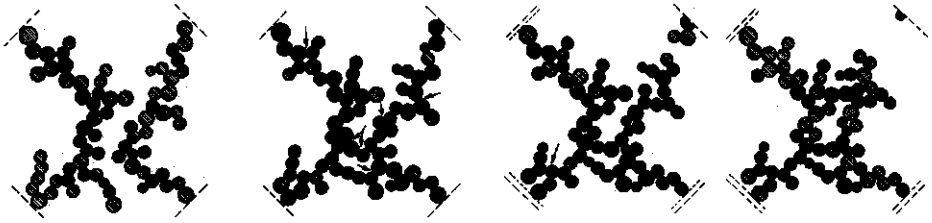


Fig. 4.7 Schematic drawings of two strands forming new crosslinks. This results here (in this particular example) in shrinkage of the network and the breaking of the strand. Arrows indicate new crosslinks.

D) The dependence of the permeability on concentration is poorly predictable from previously published models.

The model of Iberall predicts that $B \propto \varepsilon/(1-\varepsilon)$, while experimentally $B \propto (1/1 - \varepsilon)^{2.6}$ was found. The model rests on the assumption that the thickness of the strands is constant and that the volume fraction of the strands is so low that any mutual effects of the strands on the flow disturbance are negligible. Particularly the latter assumption does not hold in our case. The model of Kozeny-Carman with $d_{vs}$ = 0.1 µm gives better results. (E.g. for 2 x concentration the equation predicts $B_0$ ($i$ = 0.5)/$B_0$ ($i$ = 1) = 0.20, while experimentally 0.15 was found; nevertheless this model is usually considered to be restricted to systems with a porosity lower than 0.5. If we assume the curd to be a matrix of impermeable 'spheres' of about 10 µm diameter, as discussed in Section 4.4 A, these 'spheres' should increase in diameter or decrease in total volume while $\varepsilon$ decreases due to concentration, in

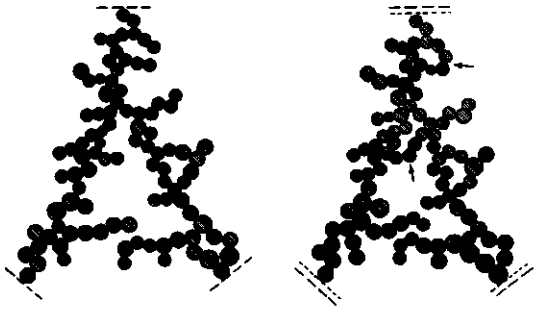


Fig. 4.8 Zipperlike crosslinking of two strands

order to fit the model to the experimental results. For instance if $i$ = 0.8 the diameter should increase to 11 μm or the spheres should comprise only 58% instead of 60% of the volume of the gel. Electron micrographs indeed show that the micelles in the curd made from 2 or 4 fold concentrated milk are packed in larger, more compact regions (Green, Turvey & Hobbs, 1981).

E) The permeability of the skim milk in the experiments described in Sections 4.3.2.6 and 4.3.2.9 was almost twice as high as the permeability of the reconstituted skim milk. An explanation could be that this is caused by the denaturation of the whey protein, although low heat powder was used or is caused by the slow equilibration of the reconstituted skim milk. The permeability might also depend on the seasonal variation in milk composition.

In the experiments some other factors were varied (composition, temperature). For most of these factors there is a correlation between clotting time, rate of syneresis, permeability and rheological properties. We will discuss these aspects and some aspects that are already mentioned in this section and in Section 7.3.3.

# 5 THE RHEOLOGICAL BEHAVIOUR OF CURD

## 5.1 INTRODUCTION

The viscoelastic properties of curd can give information about gel structure and changes therein. It may thus enhance understanding on what happens during syneresis and particularly on the effect of deformation on syneresis.

Tuszyński et al. (1968) studied by means of a torsiometer and a trombelastograph the rate of increase of the so-called average complex rigidity modulus of renneted skimmilk. This modulus is a measure of the elasticity or firmness of a gel. The principle of these two apparatus is the same. The gel is formed between two coaxial cylinders. The resistance of the gel against deformation is measured. They found, for instance, that in undiluted milk a fall in pH from 6.66 to 6.18 does not affect maximum firmness. For the same purpose Scott Blair (1957) used an apparatus described by Saunders (1953), which itself is a modification of a method proposed much earlier by Kinkel and Sauer (1925). Hereby the gel is made in an U-tube and deformed by constant air pressure on one surface of the sample. From the volumetric displacement of the other surface at a certain pressure the rigidity modulus (comparable to an instantaneous modulus) was calculated. The change of this modulus during setting was given as a function of time. Torado (1969) and Hossain (1976) used the trombelastograph. The influence of various factors on the rheological behavior of curd was studied. In contrast to the results of Tuszyński, Hossain found a small influence of pH on curd firmness, if the pH was varied from 6.70 to 6.51.

Further publications about rheological behavior of curd are by Douillard (1973), Burnett et al. (1963), Jacquet (1964), Marçais (1965), Frentz (1965) and Thomasow (1968).

The type of rheological parameter measured and its magnitude depend e.g. on time scale, extent of deformation and size and shape of the sample. Since different authors generally used different types of apparatus, yielding different rheological parameters, comparison of results is not easy. For the rheological characterization of the curd we defined moduli that can easily be used for further calculation

and are generally accepted by rheologists.

Two techniques were used. First, dynamic measurements which are especially suited to obtain the viscoelastic properties of the gel as a function of time after rennet addition and as a function of the time scale of deformation. Second, creep measurements were used to study the regime where irreversible breakdown of the gel structure occurred. Both techniques gave e.g. information of the relaxation behavior of the gels and the point at which irreversible change in the structure of the gel starts.

## 5.2 METHODS

### *5.2.1. Dynamic measurements with the "Den Otter" rheometer*

The rheometer was developed and described extensively by Duiser (1965) and Den Otter (1967). In brief, the apparatus consists of two coaxial cylinders. The inner one is suspended between a torsion wire and a strain wire and has a length of 15 cm and a radius of 3.75 mm. The outer cylinder has an inner radius of 4.5 mm. The gel is formed in the space between the cylinders. The whole apparatus is thermostated to within 0.1 $^{o}$C.

The torsion wire is connected to a drive shaft that brings the wire, and thus the inner cylinder, in harmonic oscillation. The frequency ($\omega$) can be varied between $2 \times 10^{-4}$ and 300 rad$\cdot$s$^{-1}$. The amplitude difference and the phase shift ($\delta$) can be measured. From these the storage and the loss moduli $G'$ and $G''$ can be calculated. The storage modulus ($G'$) is a measure for the energy stored during a periodic application of strain on the gel, and is thus a measure for the elasticity of the gel. The loss modulus ($G''$) is a measure for the energy dissipated. In formulae

$$G' = (\sigma_0/\gamma_0) \cos \delta$$
$$G'' = (\sigma_0/\gamma_0) \sin \delta$$

in which

$\sigma_0$ = maximum shear stress

$\gamma_0$ = maximum shear strain

A comprehensive discussion is given by Ferry (1970). Correct values for $G'$ and $G''$ are obtained in an easy way only if the viscoelastic deformation of the gel is linear, i.e. at constant frequency of the oscillation the deformation of the gel changes proportionally to the applied amplitude. For all curds linear behaviour appeared to exist if $\gamma < 0.03$.

*5.2.2 Creep measurements with the "Deer" rheometer*

With this rotational instrument constant stress can be applied by an air-bearing induction type electric motor. The moment can be varied between $5 \times 10^{-7}$ and $10^{-3}$ N•m. Angular displacement is determined by a non-contacting electronic sensor which measured the disctance between a circular ramp and the sensor. The sample was brought between two coaxial cylinders. The stress can range between 0.05 and 600 $N \cdot m^{-2}$.

*5.2.3 Results and discussion*

The influence of time after renneting on $G'$ and $G''$ is shown in Fig. 5.1. The moduli kept increasing for a long time (~ 3 h). Lower pH values and a higher rennet concentration gave an earlier increase in $G'$ and $G''$ (which agrees with the shorter clotting time) and also high rates. However, the final values of $G'$ only varied between 110 and 140 and for $G''$ between 34 and 43 $N \cdot m^{-2}$.

As discussed in Section 4.3.2.2, permeability also increased with time. Electron micrographs as published by Knoop & Peters (1975) showed a change in the appearance of the gel matrix. One hour after renneting the strands in the matrix were frayed. Three hours later they were more compact. Such a change may cause an increase in permeability and in moduli. The latter may also or even more increase by an increase of bonds between already attached micelles. As discussed in Section 4.4, strands may break. The resulting and already existing spoiled strands may fuse with other strings. This creates both thicker, i.e. firmer, strands and larger pores. Thus moduli and permeability increase.

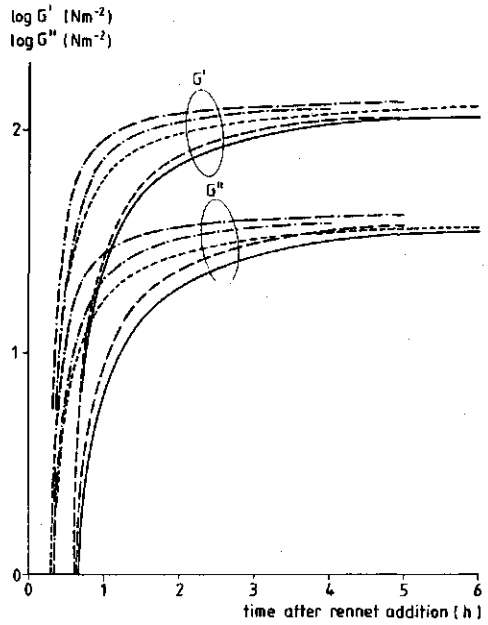



Fig. 5.1 Storage ($G'$) and loss ($G''$) modulus as a function of time after rennet addition. Standard conditions: $\omega$ = 1.0 rad·s$^{-1}$. Temperature 30 °C.

——————— pH = 6.65 rennet 250 ppm
— — — — — pH = 6.64 rennet 250 ppm
— . — . — pH = 6.55 rennet 250 ppm
— . — — — . pH = 6.45 rennet 250 ppm
— — — — — — pH = 6.65 rennet 500 ppm

Fig. 5.2 shows the moduli $G'$ and $G''$ as a function of angular frequency. The measurements were started after the moduli of the gel did not increase any more (e.g. 3-6 h). There was no significant difference in the dependence of the moduli or angular frequency if the pH was varied between 6.40 and 6.65 (see also Fig. 5.1). $G'$ and $G''$ increased with $\omega$, while $G''/G'$ (= tg $\delta$) decreased (see Fig. 5.2 ). It can be shown that $G''$ is due to the relaxation of bonds. An energy content of only a few kT per bond would then be sufficient to explain the magnitude of $G''$, while the energy dissipation caused by flow of the continuous liquid through the matrix (either around or through the strands) is very much lower (Van Vliet, to be published). For $\omega < 0.5$ rad·s$^{-1}$, when the gel is under stress for periods of $\pi/0.5$ s, the slope of $G'$ and the magnitude of tg $\delta$ increased as a function of $\omega$. Both phenomena indicate that the system has more the character of a fluid

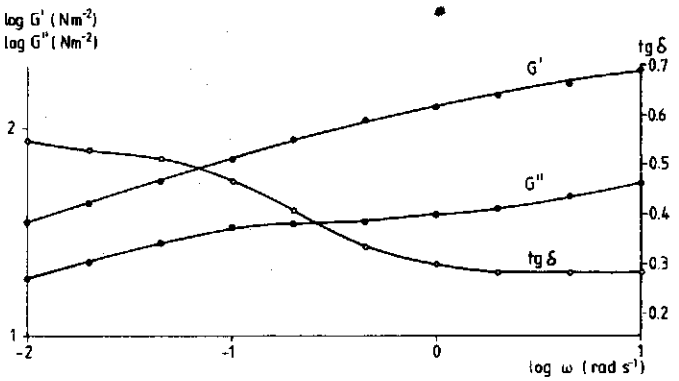



Fig. 5.2 $G'$, $G''$ and tg $\delta$ as a function of $\omega$ at 30 °C and ~ 16 h after rennet addition

when the time scale increases. This implies that a large part of the bonds spontaneously break and reform (relax) over time scales longer than seconds. It should be noted that this does not imply that whole strands in the network are broken. Many bonds in a strand can break, still leaving the strand as a whole intact. From the creep curves it can roughly be calculated (Ferry, 1970) that the relaxation time is, say, 10 - 50 s.

Fig. 5.3 shows the instantaneous shear modulus ($G_0$) as a function of the protein concentration factor ($p_f$ = protein concentration of the sample/protein concentration of original skim milk), for various times after rennet addition ($t_a$). For not too great values of $p_f$, $p_f \propto \frac{1}{i}$. The skim milk was concentrated by ultrafiltration as described in Section 2.5 Except for one measurement with a lower value for $G_0$ (probably caused by a longer clotting time) the results fit reasonably well to the equation:

$$G_0 = G_0(p_f = 1)p_f^{2.7} \qquad (5.1)$$

If an increase in concentration only would result in an increase in the number of strands of the same diameter, theory (see e.g. Van Vliet, 1978) would predict $G_0$ to be proportional to $p_f$. There are two possible explanations for the discrepancy in the literature. Firstly, the proportion of spoiled strands will decrease with increasing $p_f$.

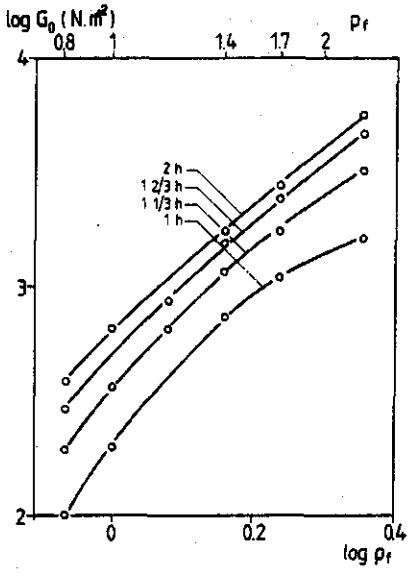



Fig. 5.3 Instantaneous shear modulus ($G_0$) as a function of protein concentration factor ($p_f$). Parameter is time after rennet addition ($t_a$)

Secondly, the distribution of the strength over the strands is wider at a lower $p_f$ (Van den Tempel, 1979). Both explanations are based on an only partly effective contribution of the casein to the network. A precise physical explanation for Eq. 5.1 cannot be given.

Fig. 5.4 gives the shear strain as a function of shear stress as determined from creep curves. The stress was applied 1 h after rennet addition. Parameter is the duration of the applied stress ($t_s$). The pH of the curd in Fig. 5.4 was 6.65. At the moment no real explanation can be given for the behavior shown in Fig. 5.4. It even is not known for sure whether the increase in Gibbs free energy of the network caused by deformation stems from a change in entropy (Flory, 1953) or in enthalpy (Lyklema et al., 1978) or both. The shape of the curves resembles that of an ideal entropic gel, although the linear region is much smaller. A possible, though speculative, explanation is that the increase stems from the same cause as the increase found for non-ideal entropic gels (Treolar, 1975) and/or from an increase in number of elastically effective strands by means of an entanglement which

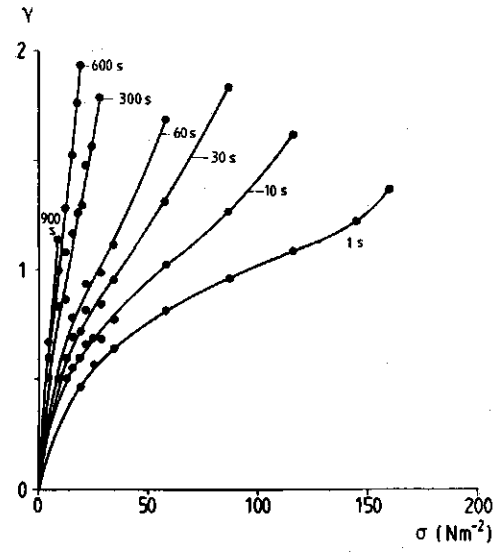



Fig. 5.4 Shear strain ($\gamma$) as a function of shear stress ($\sigma$). Parameter is the duration of the applied stress ($t_s$). The pH of the gel was 6.65.

starts to work at higher deformations (Ferry, 1970). Besides it is also possible that enthalpic effects like bending of strands start to play a more important part at higher deformations (Bailey et al., 1977).

At pH = 6.65 and $\gamma \approx 1.1$ the slopes of the curves increase. Probably the network structure gradually starts to break. The curves end where the gels break. Since for $t_s$ = 900 s at pH = 6.65 the breaking stress of the matrix was $\sim$ 10 Pa, we conclude that the syneresis pressure should be below that value.

At pH = 6.54 the curd was firmer. A smaller $\gamma(\sigma, t_s)$ for all values of $\sigma$ and $t_s$ was found. At pH = 6.54 the slope of the curves increased at $\gamma \approx 1.3$ and for $t_s$ = 900 s the breaking stress was 25 Pa. So we conclude that at pH = 6.54 syneresis pressure is lower than 25 Pa. From the creep curves also a relaxation time of $\sim$ 30 s could be calculated (Van Vliet, to be published).

# 6. THE MODEL

## 6.1 THE DIFFERENTIAL EQUATION

The model is based on an analytical description of the transport of whey inside the curd. For a preliminary description we start from a fixed cartesian coordinate system. Later on we will turn to another coordinate system that refers to the curd matrix as a reference system.

Thus we write a mass balance over a stationary volume element $\Delta x\ \Delta y\ \Delta z$ through which the whey is flowing:

$$\left\{\begin{matrix}\text{rate of whey}\\ \text{accumulation}\end{matrix}\right\} = \left\{\begin{matrix}\text{rate of whey}\\ \text{going in}\end{matrix}\right\} - \left\{\begin{matrix}\text{rate of whey}\\ \text{going out}\end{matrix}\right\} \qquad (6.1)$$

or (in formula)

$$\begin{aligned}\Delta x\ \Delta y\ \Delta z\ \frac{\partial(\varepsilon\ \rho_1)}{\partial t} = {} & \Delta y\ \Delta z\ \{(\varepsilon\ \rho_1\ v_x^1)|_x - (\varepsilon\ \rho_1\ v_x^1)|_{x\ +\ \Delta x}\} + \\ & + \Delta x\ \Delta z\ \{(\varepsilon\ \rho_1\ v_y^1)|_y - (\varepsilon\ \rho_1\ v_y^1)|_{y\ +\ \Delta y}\} + \\ & + \Delta x\ \Delta y\ \{(\varepsilon\ \rho_1\ v_z^1)|_z - (\varepsilon\ \rho_1\ v_z^1)|_{z\ +\ \Delta z}\} \qquad (6.2)\end{aligned}$$

where:

$t$ = time

$\varepsilon$ = porosity (i.e. volume fraction of whey)

$\rho_1$ = density of whey which is assumed to be independent of time and position

$v_x^1$ = local velocity of the whey in the $x$-direction (i.e. $\varepsilon\ \rho\ v^1$ = bulk mass flux per unit cross section)

$|x$ = at position $x$

We divide the equation by $(\Delta x\ \Delta y\ \Delta x)$ and take the limit as these dimensions approach zero.

$$\frac{\partial(\varepsilon\ \rho_1)}{\partial t} = -\frac{\partial(\varepsilon\ \rho_1\ v_x^1)}{\partial x} - \frac{\partial(\varepsilon\ \rho_1\ v_y^1)}{\partial y} - \frac{\partial(\varepsilon\ \rho_1\ v_z^1)}{\partial z} = -\nabla\cdot\{\varepsilon\ \rho_1\ \vec{v}^1\} \qquad (6.3)$$

This is the equation of continuity, which in this case describes the rate of change of whey content at a fixed point, resulting from the change in the mass velocity vector. We want to replace $v^1$ by the permeability coefficient ($B$) and syneresis pressure ($P$). Clearly this is possible if we first introduce the relative velocity $(\vec{v}^1 - \vec{v}^s)$ of the liquid with respect to the curd matrix. In the theory of binary diffusion the use of reference component centered velocities has been developed, where the velocity of one component is expressed as the velocity with respect to the second or reference component. The "Fickian" form of the mass balance in the reference component centered description is to be found in the literature. Van der Lijn gave a useful review in appendix A of his thesis (1976). Quoting Van der Lijn we start from his equation (A39) where we substitute our notation.

$$(1-\varepsilon)\ \rho_s \frac{D^s}{Dt}\left(\frac{\varepsilon\ \rho_1}{(1-\varepsilon)\rho_s}\right) = \frac{\partial \varepsilon}{\partial t}\rho_1 + \nabla\cdot\{\varepsilon\ \rho_1 \vec{v}^s\} \qquad (6.4)$$

in which

$\frac{D^s}{Dt} = \frac{\partial}{\partial t} + \vec{v}^s\cdot\nabla$ = the substantial derivative operator, describing changes with time at a point moving with the velocity $v^s$ of a local volume element of the solid matrix.

$\rho_s$ = the density of the solid phase

As the densities $\rho_s$ and $\rho_1$ are constant we divide both sides by $\rho_1$ and eliminate $\rho_s$.
By inserting the right hand part of Eq. 6.3 we obtain:

$$(1-\varepsilon)\ \frac{D^s}{Dt}\left(\frac{\varepsilon}{1-\varepsilon}\right) = -\nabla\cdot\{\varepsilon\vec{v}^1\} + \nabla\cdot\{\varepsilon\vec{v}^s\} = -\nabla\cdot\{\varepsilon(\vec{v}^1 - \vec{v}^s)\} \qquad (6.5)$$

For our experiments we used a one-dimensional system. So $\nabla$ may be written as $\frac{\partial}{\partial x}$. Introduction of the law of Darcy:

$$\varepsilon\ (\vec{v}^s - \vec{v}^1) = \frac{B}{\eta}\ \frac{dP}{dx}$$

and of

$$d\left(\frac{\varepsilon}{1-\varepsilon}\right) = d\left(\frac{1}{1-\varepsilon}\right)$$

then leads to

$$(1-\varepsilon)\,\frac{D^s}{Dt}\left(\frac{1}{1-\varepsilon}\right) = \frac{d}{dx}\left(\frac{B}{\eta}\,\frac{dP}{dx}\right) \qquad (6.6)$$

Here we leave our original stiff coordinate system and turn to a new system that is fixed to the shrinking solid phase of our mixture. Clearly the substantial time derivative in the old system equals the partial time derivative in the new system. Moreover we have to introduce a new local coordinate that must satisfy

$$d\omega = (1 - \varepsilon)\,dx$$

Introduction in Eq 6.6 yields

$$\frac{\partial}{\partial t}\left(\frac{1}{1-\varepsilon}\right) = \frac{\partial}{\partial \omega}\left\{\frac{B(1-\varepsilon)}{\eta}\,\frac{\partial P}{\partial \omega}\right\}$$

If $P$ were a unique function of the porosity $\varepsilon$ the pressure gradient in the new coordinate system, $dP/d\omega$ may be written as $dP/d\varepsilon.d\varepsilon/d\omega$, while also $(1-\varepsilon)d\varepsilon = (1-\varepsilon)^3\, d(1-\varepsilon)^{-1}$. Introduction in the equation gives

$$\frac{\partial}{\partial t}\left(\frac{1}{1-\varepsilon}\right) = \frac{\partial}{\partial \omega}\left\{\frac{B(1-\varepsilon)^3 P'}{\eta}\,\frac{\partial}{\partial \omega}\left(\frac{1}{1-\varepsilon}\right)\right\}$$

in which $P'$ is the first derivative of $P(\varepsilon)$.

Calling $B(1-\varepsilon)^3 P' \frac{1}{\eta} = D$ we obtain the "Fickian" form

$$\frac{\partial}{\partial t}\left(\frac{1}{1-\varepsilon}\right) = \frac{\partial}{\partial \omega}\left\{D\,\frac{\partial}{\partial \omega}\left(\frac{1}{1-\varepsilon}\right)\right\} \qquad (6.7)$$

The latter equation is the equivalent of Van der Lijns equation (A.46).

Boltzmann (1894) showed (see e.g.Crank (1975)) that for certain

boundary conditions, and provided $D$ is a function of $\varepsilon$ only, $\varepsilon$ may be expressed in terms of a single variable $w/2t^{\frac{1}{2}}$ and that Eq. (6.7) may therefore be reduced to an ordinary differential equation with one new variable $n$, where

$$n = \tfrac{1}{2}w/t^{\frac{1}{2}} \tag{6.8}$$

So that Eq. (6.7) becomes

$$-2n \frac{d}{dn} \frac{1}{1-\varepsilon} = \frac{d}{dn} \left( D \frac{d}{dn} \frac{1}{1-\varepsilon} \right) \tag{6.9}$$

It is only if the initial and boundary conditions can be expressed in terms of $n$ alone, and $t$ and $w$ are not involved separately, that the transformation (6.8) can be used. They can be used, for example, when syneresis of a thin slab occurs and the porosity at the deepest layer of the slab is still unchanged (i.e. during the penetration period).

If the transformation is allowed it also follows that $w^2 \propto t$ (for constant $\varepsilon$) and $\Delta H \propto t^{\frac{1}{2}}$; $\Delta H$ = shrinkage of a thin slab (see Fig. 6.1).

Some methods of solving Eq. (6.9) are given in the literature (Crank (1975), Phillip (1969)).

## 6.2 NUMERICAL SOLUTION

The approach described in section 6.1 is not satisfactory for several reasons: we had to postulate $P$ and $B$ as a unique function of $\varepsilon$. So the quantity $D$ introduced in equation (6.7) should be exclusively dependent on $\varepsilon$ to allow an analytical solution. Both assumptions are untenable. As we have seen in Section 4.3.2.3 $B$ changes with time, even if $\varepsilon$ remains constant. In Chapter 7 it will be shown that $P$ changes with time as well. Since it is very unlikely that $B.P'$ remains constant, this implies that $D$ is time dependent.

We now start the search for a numerical solution with a more general validity. In this section we report an explicite difference scheme. For that purpose we consider a thin slab of curd with initial thickness $H_0$ devided into $m$ thin slices of thickness $h_{k,0}$. The original thickness of the slices varies with the position, that of the $k^{th}$

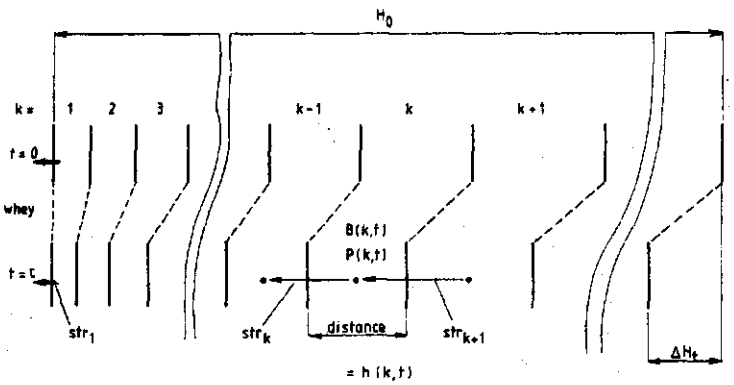



Fig. 6.1 Schematic drawing of a thin slab of thickness $H_0$ at $t = 0$ and of thickness $H_0 - \Delta H_t$ at $t = \tau$. The slab is divided in a number of slices that correspond with the mathematical grid. In the experiments the slab was in a horizontal position.

slice being 1.2 times that of the $(k\text{-}1)^{th}$. During the shrinkage the thickness $H$ of the slab (and consequently the thickness of at least some of the slices $k$) change with time ($t$) and with position in the slab ($k$; $1 \leqslant k \leqslant m$). We define

$$\text{relative remaining volume } (i) = \frac{\text{actual volume}}{\text{volume at } t=0} = \frac{h_{k,t}}{h_{k,0}} = \frac{1-\varepsilon_0}{1-\varepsilon_{k,t}}$$

In Section 4.3.2.3 $i$ was already defined in a different context as volume of concentrated milk/volume of original milk. Darcy's law for the flow of whey in the curd was given in Section 6.1. For the present calculation it is rewritten as

$$\Delta P = str_k \, \eta \, \Delta x/B$$

where $str_k$ is the liquid volume flux that flows from slice $k$ into slice $k$-1. Consequently we have $\Delta P = P_k - P_{k-1}$. For $(\Delta x/B)$ we introduce along the same lines $\frac{1}{2}\{(h_{k-1}/B_{k-1}) + (h_k/B_k)\}$, being an intermediate value between the slices $k$ and $k$-1. With these substitutions the formula of Darcy turns to

$$P_k - P_{k-1} = str_k \, \eta . \tfrac{1}{2} \left( \frac{h_k}{B_k} + \frac{h_{k-1}}{B_{k-1}} \right)$$

In our model of the shrinking process the shrinkage is exclusively caused by the loss of whey. So we may state

$$\Delta h_{k,t} = ( str_{k+1,t} - str_{k,t} ) \Delta t$$

Note that $\Delta h_{k,t}$ is negative. Substituting the formula of Darcy we obtain

$$\frac{\Delta h_{k,t}}{\Delta t} = \frac{P_{k+1,t} - P_{k,t}}{\eta} \left( \frac{h_{k+1,t}}{2B_{k+1,t}} + \frac{h_{k,t}}{2B_{k,t}} \right)^{-1} -$$

$$- \frac{P_{k,t} - P_{k-1,t}}{\eta} \left( \frac{h_{k,t}}{2B_{k,t}} + \frac{h_{k-1,t}}{2B_{k-1,t}} \right)^{-1}$$

In order to arrive at a more convenient calculation procedure we introduce dimensionless variables for the pressure $P$, the permeability $B$ and the thickness $h$:

$$S_{k,t} = P_{k,t} / P_0 \ , \ \beta = B_{k,t} / B_0 \text{ and } L_{k,t} = h_{k,t} / H_0 \ ,$$

where $P_0$, $B_0$ and $H_0$ are the values of pressure, permeability and total thickness of the curd slab at $t = 0$. Introduction of these reduced quantities in the equation yields

$$\Delta L_{k,t} = \Delta K' \{ (S_{k+1,t} - S_{k,t}) \left( \frac{L_{k+1,t}}{\beta_{k+1,t}} + \frac{L_{k,t}}{\beta_{k,t}} \right)^{-1} -$$

$$- (S_{k,t} - S_{k-1,t}) \left( \frac{L_{k,t}}{\beta_{k,t}} + \frac{L_{k-1,t}}{\beta_{k-1,t}} \right)^{-1} \} \qquad (6.10)$$

We have introduced in this formula the dimensionless time variable

$$\Delta K' = (2B_0 P_0 \Delta t)/(\eta H_0^2)$$

The value of $\Delta K'$ was increased for each time interval by a factor 1.005 to 1.05. During the calculation it was checked whether

$$\sum^{k} \Delta L_{k,t} + \frac{str_{1,t}\,\Delta t}{H_0}$$

being the difference between the shrinkage calculated by addition of the shrinkage of all the slices and the shrinkage calculated by the flow of whey out of the slab, which should be zero theoretically, was smaller than $10^{-9}$. If its absolute value was greater the time interval was lowered by 5%.
Finally $\Delta H_t/H_0$ was plotted versus $K$ where $\Delta H_t = - \sum^{tk} \Delta h_{k,t}$ and

$$K = \sum^{t} \Delta K' = \frac{B_0\, P_0\, t}{\eta\, H_0^2} \qquad (6.11)$$

A major problem in the application of difference schemes to highly non-linear partial differential equations is that it is often difficult to prove stability and convergence to a true solution. Here too there is no such proof.

However, in literature we find many succesful examples: e.g. Van der Lijn (1976), Kerkhof (1975), Schoeber (1976) and De Wit (1972).

Moreover, the numerical method was checked by comparing with the results of the analytical solution whenever possible. Results with an unequally spaced 15 compartments slab were accurate within 2%. Furthermore no substantial changes could be detected when the number of compartments or the time intervals were modified within limits. Therefore these solutions seem to be reliable.

## 6.3 PARAMETERS (DEPENDENCE OF PRESSURE ON RELATIVE SHRINKAGE AND TIME)

Equation (6.10) permits calculation of the change of thickness ($\Delta L_{k,t}$) at any position $k$ and at any time $t$ if the conditions at that time (i.e. $L_{k,t}$) are known for any $k$. To obtain numerical results, however, we still need values for the permeability ($\beta$) and the pressure ($S$). For the permeability the reader is referred to Section 4.3.2.3 where the behaviour of the permeability as a function of shrinkage and time is already discussed. In the present section we will restrict

ourselves to a discussion of the pressure. As is discussed in Chapter 3, the pressure exerted on the whey is caused by the endogenous stress in the strands ($P^s$) and by the weight of the matrix ($P^g$):

$$P = P^s + P^g$$

As the matrix shrinks the pressure on the whey diminishes, since at a certain degree of shrinkage (i.e. when $i = 1/3$), syneresis stops, so $P = 0$. If only endogenous syneresis occurs, $P = 0$ means that the tendency of the gel to swell exactly compensates the tendency to shrink. If only gravity acts, $P = 0$ means that the elastic force resulting from compression of the matrix compensates the weight of the matrix. If $P^g = 0$, also $P^s = 0$ but it is not known in which way $P^s$ and $P^g$ decrease with $i$. However, it must be assumed that as long as endogenous syneresis occurs (i.e. $P^s > 0$), also $P^g > 0$. This is because a matrix with an endogenous tendency to shrink ($P^s$) will also yield to any external force (such as $P^g$).

It may be so that $P^g = \Delta\rho \cdot g \cdot h_c$ is independent of $i$ and only becomes zero when $P^s$ does; however, it is more likely that $P^g$ will start to diminish at higher values of $i$.

It is very likely that $P^s_{k,t}$ will monotonously and rather smoothly decrease with increasing $i_{k,t}$. Therefore five trial functions were introduced, taking this into account. As a general form of our relation between $P^s_{k,t}$ and $i_{k,t}$ we adopt

$$P^s_{k,t} = P^s_0 \cdot \{a(i_{k,t} - 1/3)^2 + b(i_{k,t} - 1/3)\} \qquad (6.12)$$

with different values for $a$ and $b$. As $P^s_{k,t} = P^s_0$ for $i = 1$ we have $4a + 6b = 9$.

Four of our trial functions are now found by varying the starting value $d(P^s_{k,t}/P_0)/di$ at $i = 1$, that we call $c$. We see at once that $c = (4a + 3b)/3$. Solving $a$ and $b$ with respect to $c$ we find $b = 3 - c$ and $a = 3/2c - 9/4$.

Introducing $c = 3$, $8/3$, $7/3$ and 2 successively we find the four parabolic trial functions represented in Fig. 6.2. The fifth trial function of Fig. 6.2 is defined as:

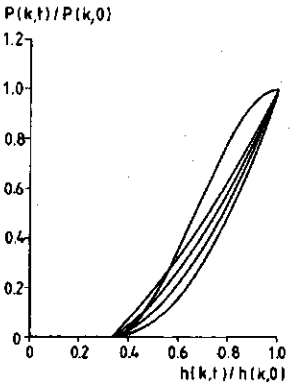



Fig. 6.2 Trial functions; S-shaped curve and (going upwards) $e$ = 3, 8/3, 7/3 and 2 (see text). Syneresis pressure as a function of porosity.

$$P^s_{k,t} = 27P^s_0\{(-i^3 + 2i^2 - i)/4\} + P^s_0 \qquad (6.13)$$

which leads to an S-shaped curve.

For sake of simplicity, we assumed the effect of gravity either to diminish linearly with $i$ or to be constant for $i > \frac{1}{2}$ and then to diminish linearly with $i$, $P^g$ becoming zero for $i = 1/3$. Other trial functions did not materially improve the fit between theory and results. $P^g_k$ depends, of course, also on the thickness of the layer above $k$. These considerations lead to the following formula for the pressure (on the whey):

$$P_{k,t} = P^s_{k,t} + P^g_b \frac{\left(\sum_1^k h_{k,0} - \frac{1}{2}h_{k,0}\right)}{H_0} 1.5(i_{k,t} - 1/3) \qquad (6.14)$$

in which:

$P^g_b$ = pressure caused by the weight of the slab at the bottom of the slab at $t = 0$.

$1.5(i_{k,t} - 1/3)$ denotes the fraction of the pressure that is left in case $P^g$ decreases linearly with $i$ in case $P^g$ decreases linearly with $i$.

As will be shown later $P^s$ and $P^g$ also depend on time when $i$ is kept constant. In Eq. 6.11 $P_0$ is substituted by $P^s_0$.

# 7 SYNERESIS OF THIN SLABS (testing the model experimentally)

## 7.1 INTRODUCTION

As mentioned earlier (Section 6.1) the mechanism of syneresis is easiest examined if the flow of the whey and the shrinking occur along the same axis (one-dimensional model). Moreover, the flow and shrinkage should not be disturbed by side effects. This can be achieved by using relatively thin slabs of curd, so that a region in the centre of the slab remains plan parallel (i.e. within the accuracy of measurement).

## 7.2 METHODS

When curd is formed in a vat and the curd keeps adhering to the walls it will not shrink by syneresis. Also at the curd-air interface the casein matrix will not shrink, because this surface is not easily wetted. Syneresis starts after the curd is cut or the surface is wetted (see Section 2.6). The latter was done in the experiments.

Drops falling on the curd surface and whey flooding the dry surface easily damage it. Therefore the first portion of whey (or water) was put onto the surface by means of a fine spray.

Two methods were employed for measuring the shrinkage of a slab:

### I "Shadow" method

The apparatus used is shown in Fig. 7.1. The triangular blade was slid down until it touched its shadow on the surface of the curd. The height was read off on a scale gauged in 0.1 mm. The first reading was done before the whey was poured onto the curd. By this method a number of vats, which were stored in a thermostated tank could be examined simultaneously. Every 5 to 10 minutes a vat was placed under the apparatus and the height was measured. After about 2 hours had relapsed longer intervals were taken. The radius of the slab was 9 cm. This method was especially used to follow the shrinkage of a slab for a long time, allowing the slab to shrink to equilibrium.

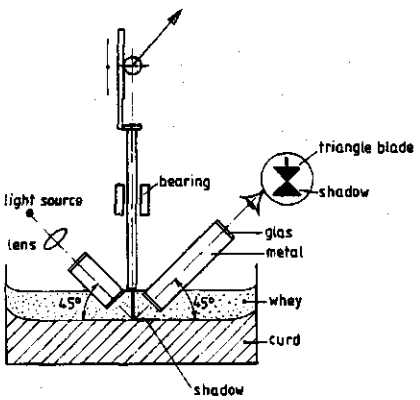



Fig. 7.1 Schematic drawing of the apparatus uded to measure the syneresis by the shadow method, with field of vision drawn in the circle. The radius of the slab was 9 cm.

## II "Microscope" method

A microscope with oblique illumination, employing a water-immersion objective was used in conjunction with a specially designed thermostated vat holding the slab of curd; see Fig. 7.2. At a fixed time the curd was wetted by first spraying and then flooding with whey. Syneresis then started. The microscope was focussed as soon as possible on one of a few corundum grains sprinkled on the surface of the curd and the focussing height was read on the scale of the micrometer knob of the microscope. The first reading could be made one or two minutes after starting the wetting. Every 30 seconds the microscope was focussed again and the (reduced) height of the slab was read off. After 10 and 20 minutes the time interval was doubled, and later on even longer time intervals were taken. The depth of focus was $\sim$1 μm and one unit on the microscope scale corresponded with 2 μm. The radius of the slab was 5 cm. This method was more accurate than the previous one in the semi-interval between 1 or 2 minutes and about 1 hour, though the absolute zero could not be determined.

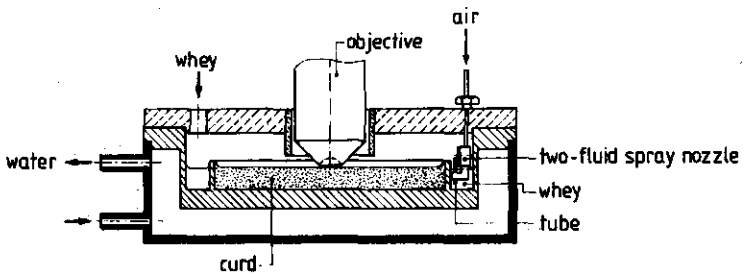



Fig. 7.2 Schematic drawing of the apparatus used to measure the syneresis by the microscope method. The radius of the slab was 5 cm.

## 7.3 RESULTS AND DISCUSSION

### *7.3.1 Testing the model*

The first experiments were done with slabs of various diameter and height, in order to find the influence of these variables on the shrinkage in the middle of the slab, where the syneresis was measured. The shadow method was used. As the slab stuck to the wall the height of the slab remained the same there and shrinkage was at maximum in the middle of the slab. We found that if the radius of the slab was ∿10 times the original height of the slab, the shrinkage in the middle of the slab remained uninfluenced by the size until equilibrium was reached. Then an area in the middle of the slab with a radius of 2 to 3 cm remained flat (difference in height less than 0.1 mm).

In Fig 7.3 double log plots of the results of the shadow method are given for slabs of different thickness under standard conditions (see Section 2.7). A curve was manually drawn through the experimental points resulting from 3 to 10 replicate experiments. The average deviation of the experimental points from the curve was 0.1 mm. The graphs show that initially the shrinkage of the slab was independent of its original thickness. The thinner the slab the sooner the curve deviated from those of thicker slabs. The deviation is expected to occur after the penetration period, i.e. as soon as the slabs also start to shrink significantly at the bottom.

After about one day the thickness of the slabs had decreased to about 1/3 (range 0.27 - 0.37) of the original value. The results of

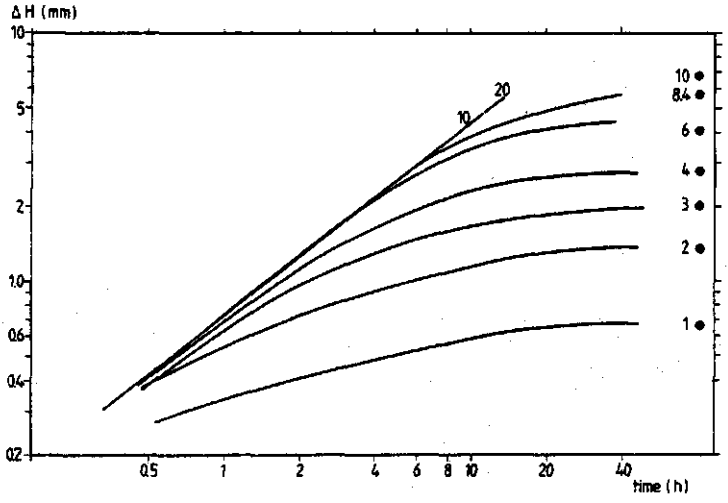



Fig. 7.3 Shrinkage ($\Delta H$) as a function of time (both on a log scale). Parameter is the original thickness of the slab (in mm). The dots (●) indicate 2/3 of original thickness. Numbers indicate original thickness of the slab itself.

the slabs of 10 and 20 mm were fitted to a straight line by regression analysis; here $\Gamma = d\log\Delta H / d\log t = 0.78$.

Fig. 7.4 shows double log plots from 4 experiments under standard conditions with the microscope method. The thickness of the slab was 5 mm. For the shrinkage of the slab during the first minute 0.04 to 0.08 mm was taken. In this way the results of this method agreed well with the results of the shadow method for 0.2 h < $t$ < 3 h where both methods were used.

For $t$ < 0.1 h, $\Gamma$ is not reliable. As will be reasoned later $\Gamma$ is expected to be $\sim$0.5 for small values of $t$. The results obtained with this method are not at variance with such a value.

Fig. 7.5 shows $\Delta H$ as a function of $t$ on a linear scale. Again the experiments were done at standard conditions and the microscope method was used. The thickness of the slabs was 5 mm except for one which was 10 mm.

Fig. 7.5 suggests that the shrinkage rate of the slabs tends to be very high as $t \to 0$.

Fig. 7.6 shows calculated results from the model (Chapter 6). Because $B$ and, as will be discussed further on, also $P$ depends on $t$

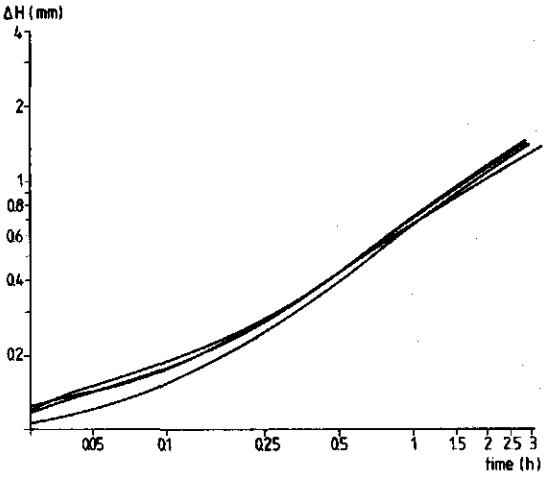



Fig. 7.4 Shrinkage of a slab as a function of time (both log scale). For the shrinkage during the first minute 0.05 mm was taken. Original thickness of the slab was 5 mm.

independently of $i$ and moreover $P$ is determined by the sum of $P^s$ and $P^g$, the graphs can only be used for one combination of the characteristic time $t/K = \eta\, H_0^2/(B_0\, P_0^s)$ and $P_b^g/P_0^s$.

For sake of clearness not these terms which were used in the calculation are noted in Fig. 7.6, but specific values of $\eta$, $B_0$ and $H_0$. $\eta$ and $B_0$ were taken as typical for the experiments at standard

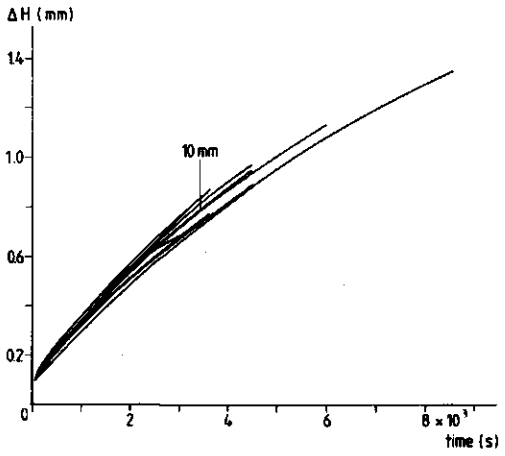



Fig. 7.5 Shrinkage of 11 slabs as a function of time. Original thickness of the slabs was 5 mm except for one slab which was 10 mm.

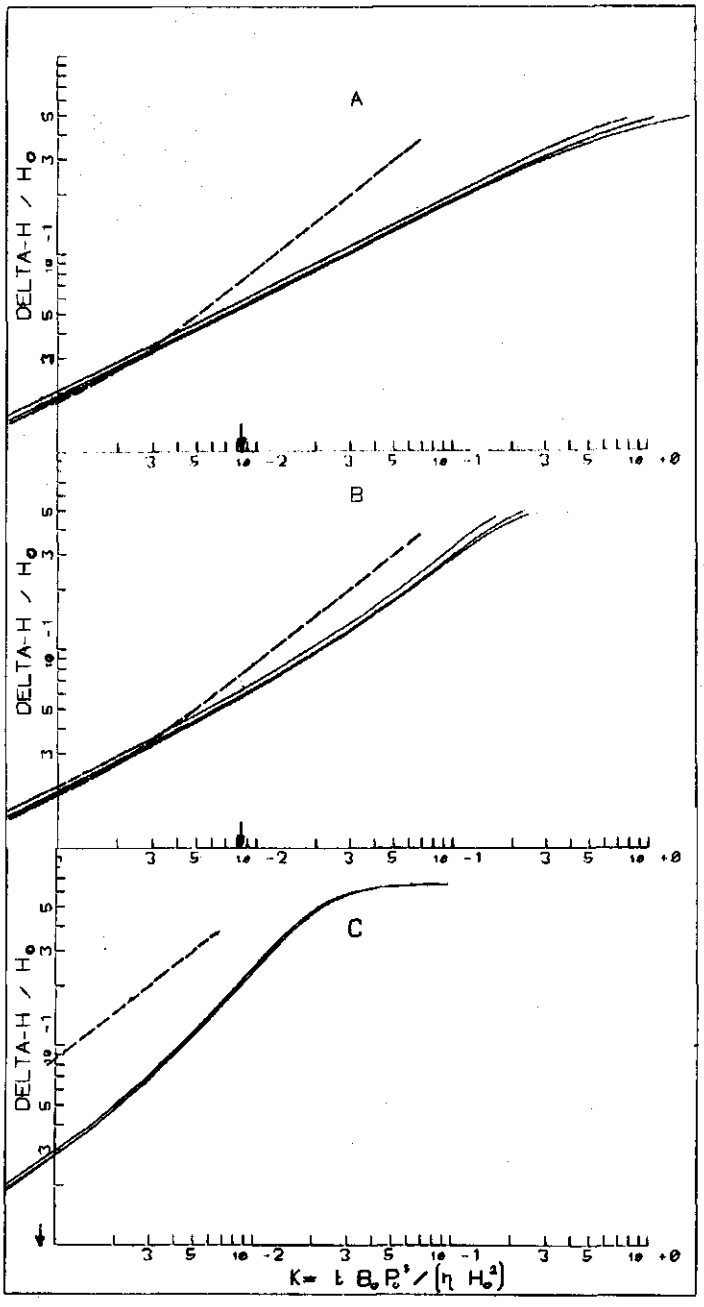
conditions. For $H_0$ 10 mm was taken, but calculations with other values gave analogous results. The other parameters were varied. Although the graphs are only correct for one combination of $t/K$ and $P_b^g/P_0^s$, they approximate calculations with other values of $t/K$ and $P_b^g/P_0^s$. Generally 10% deviation in the curve results from a 50% deviation of $t/K$ or a 10% deviation of $P_b^g/P_0^s$. On the $K$-axis $t$ = 1 h is indicated with an arrow. In all figures the experimental result with a slab of 10 mm thickness is indicated with a broken line.

The results of the calculation were only compared for $t > \sim 0.1$ h and $\Delta H/H_0 < \sim 1/3$. As stated before the value of $H$ cannot be determined accurately for $t < \sim 0.1$ h. The value of $H(t < 0.1$ h) that can be expected on theoretical grounds will be dealt with later. For $\Delta H/H_0 > \sim 1/3$ the model will be less accurate. The permeability for $i < 0.5$ is found by extrapolation. Moreover the permeability of a gel formed by renneting ultrafiltered milk may be somewhat different from that of a gel formed by syneresis at lower values of $i$ (if the permeabilities differ).

Though all five trial functions for $P_{k,t}^s = P_{k,t}^s(i)$ (see Fig. 6.2) were used in the calculations, only three are shown in the graphs of Fig. 7.6. For the top curves in each graph (except Fig. 7.6 G and H) the S-shaped curve was used, for the middle curves $c$ = 7/3 and for the lower curves $c$ = 3. The curves for $c$ = 2 and $c$ = 8/3 gave comparable results.

Fig. 7.6 shows the results of the calculations. The shape of the trial functions for $P_{k,t} = P_{k,t}(i)$ has only a small effect on the results. The difference is not only determined by the average value of $P_{k,t}^s(i)/P_0^s$. If $P_{k,t}^s(i)$ decreases more slowly with decreasing $i$, the gel near the interface curd/whey will shrink faster (see Fig. 7.8). Thus the permeability will also decrease more here. The shrinking of deeper layers will therefore be retarded.

Fig. 7.6 shows the results of calculations if $B$ and $P$ are independent of time (at constant $i$). As is to be expected from Eq. 6.9 $\Gamma$ = 0.5 (in this case) during the penetration period, i.e. the period where the total shrinkage of the slab is independent of the thickness of the slab because the shrinkage profile has not yet reached the deepest point of the slab.

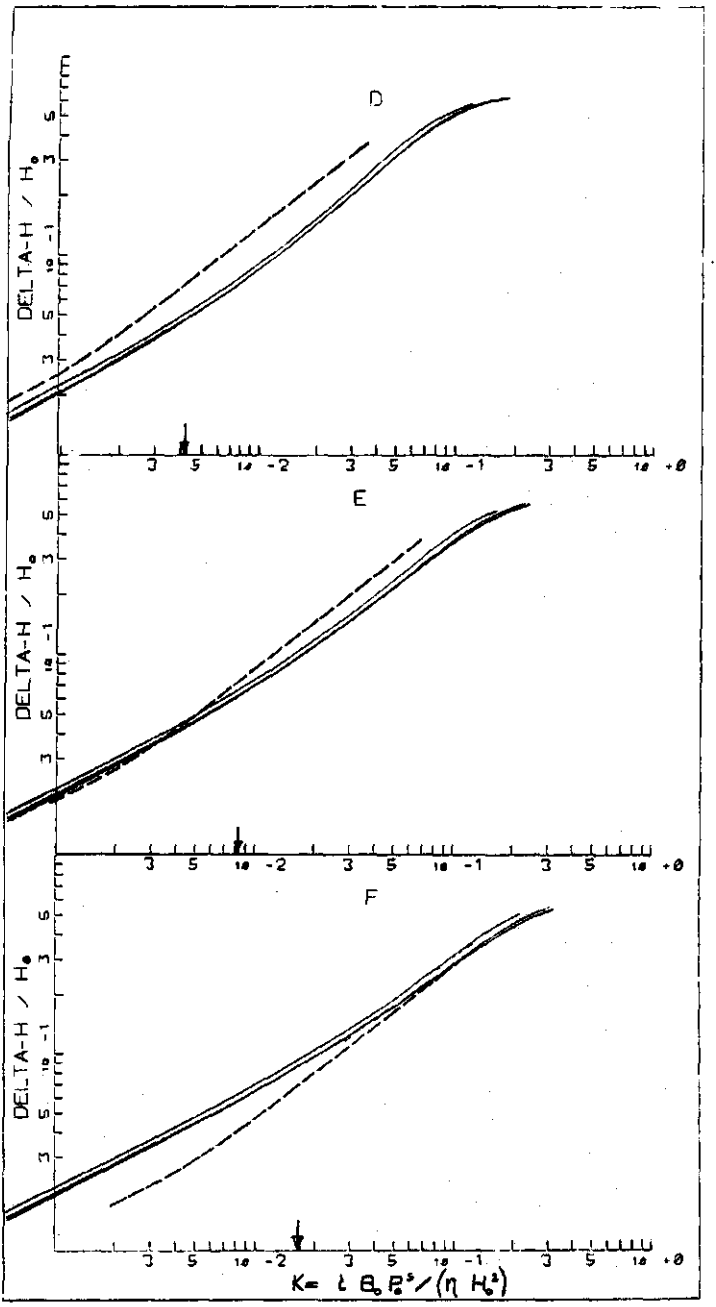



$B = B_0$ (constant with time)
$P_0^s$ = 1 Pa.
Trial functions:
$c$ = 3, 7/3 and S-shaped curve.
$P^g$ = 0.

$B = B(t)$ (see Eq. 4.16).
$P_0^s$ = 1 Pa.
Trial functions:
$c$ = 3, 7/3 and S-shaped curve.
$P^g$ = 0.

$B = B(t)$ (see Eq. 4.16).
$P_0^s$ = 0.1 Pa.
Trial functions:
$c$ = 3, 7/3 and S-shaped curve.
$P_b^g$ = 1 Pa.
Trial function:
$P_{k,t}^g(i) = 1.5(i_{k,t} - 1/3)$

Fig. 7.6 Experimental (---) and calculated (——) syneresis. $H_0$ = 10 mm $B_0$ = 0.23 μm$^2$. η = 1 mPa•s. The arrows indicate $t$ = 1 h.

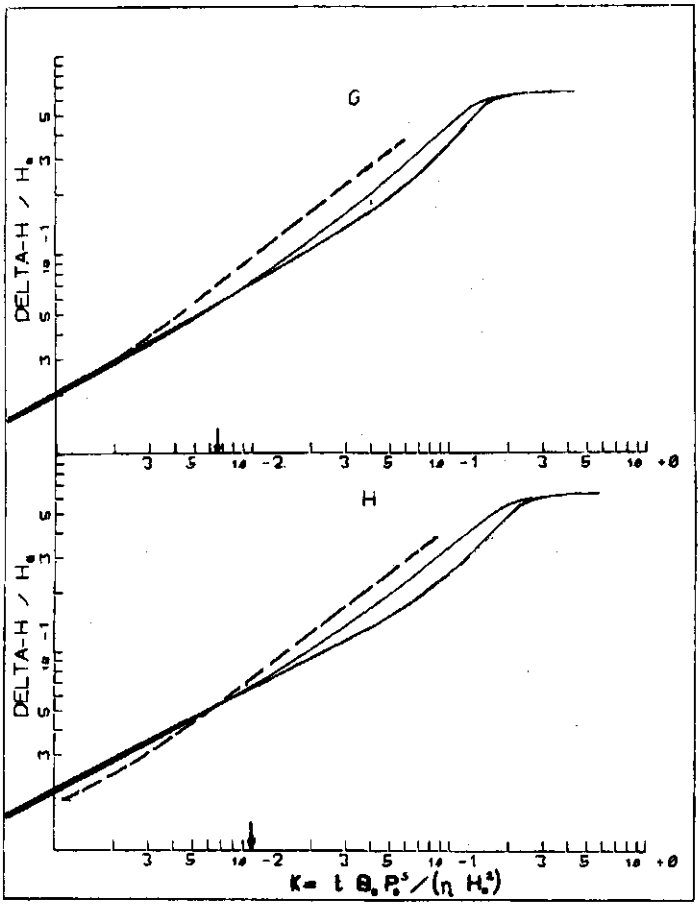



$P_0^s$ = 0.5 Pa.
Trial functions:
$c$ = 3, 7/3 and
S-shaped curve.
$P_b^g$ = 1 Pa
Trial function:
$P_{k,t}^g(i)$ =
$1.5(i_{k,t} - 1/3)$

$P_0^s$ = 1 Pa.
Trial functions:
$c$ = 3, 7/3 and
S-shaped curve.
$P_b^g$ = 1 Pa.
Trial function:
$P_{k,t}^g(i)$ =
$1.5(i_{k,t} - 1/3)$

$P_0^s$ = 2 Pa.
Trial functions:
$c$ = 3, 7/3 and
S-shaped curve.
$P_b^g$ = 1 Pa.
Trial function:
$P_{k,t}^g(i)$ =
$1.5(i_{k,t} - 1/3)$

Fig. 7.6 Continued. $B = B(t)$ (see Eq. 4.16)




$P_0^s$ 0.8 Pa.
Trial function:
$c$ = 3.
$P_b^g$ = 0.8 Pa.
Trial function:
$P_{k,t}^g(i) = P_{k,0}^g$
for $i > \frac{1}{2}$.
$P_{k,t}^g(i) =$
$6(i_{k,t} - 1/3)$
for $1/3 < i < \frac{1}{2}$.

$P_0^s$ = 1.2 Pa.
Trial function:
$c$ = 3.
$P_b^g$ = 0.8 Pa.
Trial function:
$P_{k,t}^g = P_{k,0}^g$
for $i > \frac{1}{2}$.
$P_{k,t}^g(i) =$
$6(i_{k,t} - 1/3)$
for $1/3 < i < \frac{1}{2}$.

Fig. 7.6 Continued. Upper full curve: $P^S$ independent of time at constant $i$. Lower curve: Eq. 7.4 used. $B = B(t)$ (see Eq. 4.16).

If $B$ increases with time at the rate given in Eq. 4.16, the results are as in Fig. 7.6 B. $\Gamma$ increases from 0.5 for $t < 0.01$ h to $\sim$0.8 for $K = 0.05$.

Up until here we have neglected any effect of gravity ($P^g = 0$). If only $P^g$ were active (i.e. $P^S = 0$), the initial $\Gamma$ would be 1; if $P^g$ were zero and only $P^S$ were active, initial $\Gamma$ would be 0.5 (see above). If both act, as is the normal case in our experiments, $\Gamma$ will

be in between. Figs. 7.6 C-F show results for finite values of $P_b^g$ and $P_0^s$; the curves can significantly improve and $P_0^s = P_b^g = 1$ Pa gives the best one. Here $P^g$ varies from 0 to $P_b^g$ from top to bottom; see Section 6.3. In these examples we assumed that $P_{k,t}^g = P_{k,0}^g(x)\ 1.5(i_{k,t} - 1/3)$, where $x$ is distance from the top of the slab; in other words $P^g(i)$ linearly decreases with $i$ until $i = 1/3$. In Figs. 7.6 G and H a different assumption was made, viz. $P_{k,t}^g = P_{k,0}^g$ for $i > \frac{1}{2}$ and $P_{k,t}^g = P_{k,0}^g(x)\ 6\ (i_{k,t} - 1/3)$ for $1/3 < i < \frac{1}{2}$. This assumption may be more realistic. However, no significant improvement of the fit is attained. The higher average $P$ may be offset by the more rapidly decreasing $B$ near the curd/whey interface.

Still $\Gamma = 0.5$ for $t \to 0$. This is to be expected since at the start shrinkage only occurs very near the surface of the slab and $P^g = 0$ at the surface. As $t$ increases $P^s$ decreases fastest near the surface, deeper layers of the slab come into play and $P^g$ becomes more important. Near the end of the penetration period (when $\Delta H/H_0 \simeq 0.1$) the profile of $P^s$ is roughly the same as the profile of $P^g$, either has about the same contribution to the syneresis, and $\Gamma$ will be about midway between 0.5 and 1.

It is also possible that $P$ depends on time independently of $i$. Approximate values of this function $P(t)$ can be obtained from the relation between $P_0^s$ and $d\Delta H/dt$. If the influence of $dB/dt$ and $dP/dt$ and of $P_b^g$ can be neglected we find the following relation, deduced from the numerical calculation as shown in Fig. 7.6 A:

$$\frac{\Delta H}{H_0} = Q\ K^{\frac{1}{2}}$$

Where $Q$ depends on the trial function $P^s(i)$ and varies between 0.58 and 0.62. Differentiation yields:

$$\frac{d(\Delta H/H_0)}{dt} = \frac{d(\Delta H/H_0)}{dK} \cdot \frac{dK}{dt} = \tfrac{1}{2} Q\ K^{-\frac{1}{2}}\ \frac{B_0\ P_0^s}{\eta\ H_0^2} \qquad (7.1)$$

Elimination of $H_0$ yields:

$$\frac{d\Delta H}{dt} = \tfrac{1}{2} Q\ \left(\frac{B_0\ P_0^s}{\eta\ t}\right)^{\frac{1}{2}} \qquad (7.2)$$

Or, rewritten:

$$P_0^S = \frac{\eta}{B_0} \frac{t}{} \left(\frac{d\Delta H/dt}{\frac{1}{2}Q}\right)^2 \qquad (7.3)$$

As long as $B$ and $P$ depend on $i$ only which is nearly true for small $t$, penetration theory may be applied for small $t$ (Section 6.1) and in that case $\Gamma = 0.5$. As seen in Fig. 7.6 this is indeed found, both in the experiments and from the numerical solutions, even up to $t = 500$ s.

We conclude therefore that Eq. 7.1 is indeed a useful approximation for the syneresis during the first 10 minutes. We did some experiments using the microscope method in which we varied the period between rennet addition and the start of the syneresis ($t_s$). As shown in Fig. 4.4 we also did this in the permeability experiments. The results of the calculation of $P_0^S$ from Eq. 7.3 are shown in part of Table 7.1 and Fig. 7.7. For the model the equation:

$$P^S = P^S(i)\ (0.25 - 0.25 \exp(-9.9 \times 10^{-4}\ t/s) +$$

$$+ \exp(-6.6 \times 10^{-5}\ t/s) \qquad (7.4)$$

was used for all values of $i$ (although it was only determined for $i = 1$). Results are shown in Fig. 6.7 G and H. The results fit poorer

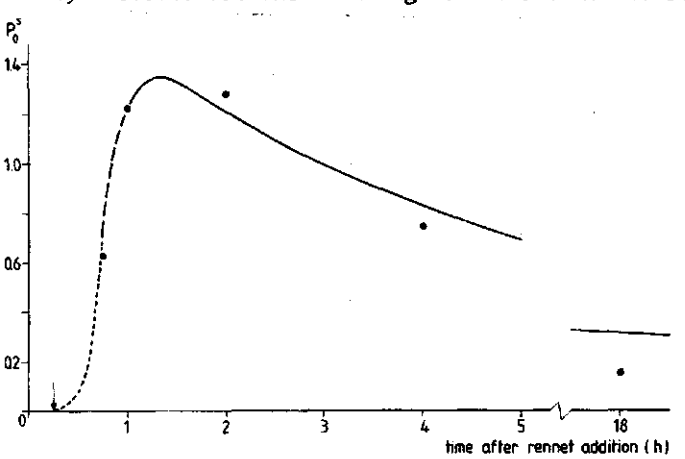



Fig. 7.7 $P_0^S$ as a function of time after renneting under standard conditions as calculated with Eq. 7.3, in which $Q = 0.6$ (——). Solid and broken (– – –) lines follow Eq. 7.4. The solid line was used in the model (see Fig. 7.6 G and H). (·····) is an assumed extrapolation. The arrow indicates the clotting point.

to the experimental results. It should, however, be taken into account that the stress in the strands either relaxes by syneresis or by micro-syneresis, while application of Eq. 7.4 implies, as it were, that relaxation occurs twice. Therefore it is not to be expected that Eq. 7.4 holds for $\dot{i} << 1$.

Of course it is possible to fit the results of the calculations with certain assumptions exactly to the experimental results. We could not (directly) determine $B(\dot{i},t)$ and $P(\dot{i},t)$ for all values of $\dot{i}$ and $t$. It is also possible that $B$ and $P$ depend on $d\dot{i}/dt$. Better results can for instance be obtained if $B$ or $P$ or both increase more strongly with time for $t \simeq \frac{1}{2}$ h. In addition to the total syneresis, shrinkage of the slab as a function of distance below the curd/whey interface ($x$) is of importance. We tried to measure it, but did not succeed. Nevertheless, model calculations may offer some interesting results. Fig. 7.8 is a typical example of such results. Here $P_0^s = P_0^g =$ 1 Pa combined with Eq. 7.4 was taken. $P^s$ has the largest effect for smaller values of $x$ while $P^g$ has the largest effect on the shrinkage at the bottom of the slab. This explains why the curves show a maximum. Such a phenomenon (stronger syneresis at the centre of a piece of curd than at some distance of the centre) will never occur in curd pieces floating in whey. It is a consequence of our experimental conditions, where the effect of gravity is comparitively large.

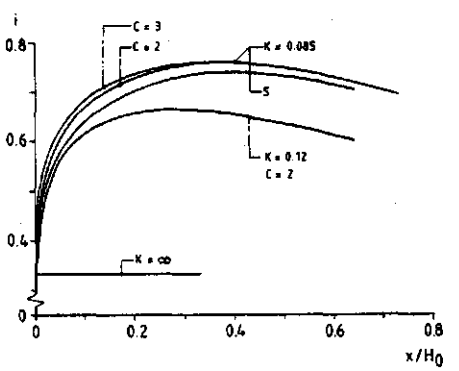



Fig. 7.8 Shrinkage profiles of a slab at different values of the dimensionless time ($K$) and different trial functions for $P^s(\dot{i})/P_0^s$. For $t/K = 4.35 \times 10^5$, $K = 0.085$ and 0.12 correspondends to $t = 10$ and 14 h respectively. $x/H_0$ is the relative distance below the curd/whey interface $c = d(P^s/P_0^s)/d\dot{i}$ at $\dot{i} = 1$. S means S-shaped trial function $P^s(\dot{i})/P_0^s$.

*7.3.2 Effect of some variables*

Syneresis rates were also determined as a function of some external variable (see Table 7.1).

A) Pretreatment of the milk

In the first series the milk powder was dissolved and stirred for 1 h at different temperatures. In the second series the milk was cooled at 4 °C after dissolving at 45 °C and stored until the next day. The milk was then heated for 1 h at different temperatures before rennet was added. In both series there was a significantly higher syneresis rate in the gels of the milks that had been heated to 45 °C as compared to 30 °C.

If the milk had been renneted the same day the higher temperature might speed up attaining equilibrium (especially of Calcium distribution between micelles and serum) in the milk after dissolving (Jenness & Patton, 1959; Walstra & Van der Haven, 1979; Snoeren, personal communication). If milk has been cold stored β-casein migrates to the micelles when the temperature is increased (Schmutz & Puhan, 1981). However at temperatures above 30 °C no further migration is found. The migration occurs within minutes (Van Hooydonk, personal communication). A better explanation for the effect of temperature is again that the distribution of Calcium among micelles and serum depends on temperature history.

B) Temperature and pH during the experiment (including renneting)

In accordance with general experience, the syneresis rate increased with increasing temperature (27 - 33 °C) and with decreasing pH. This was caused by increasing permeability and increasing syneresis pressure. At 27 °C $H$ was almost linear with $t$ above $t$ = 500 s. According to the model this would mean that $P^S \ll P^g$. When after renneting the temperature is lowered to 15 °C or below no syneresis occurs. So both $P^S$ and $P^g$ must be zero. The gel becomes firmer if it is cooled (Van Hooydonk, personal communication) and the static pressure caused by gravity is presumably counteracted by a yield stress of the gel.

Table 7.1 Effect of some external variables on syneresis rates of rennet gels. $H_0$ = original thickness. $n$ = number of experiments. $\Delta H/\Delta t = \{H(t = 3000) - H(t = 500)\}/25$ s. $B_0$ from tables in Chapter 4, from inter- or extrapolation, or from the most similar treatment (e.g. effect of pretreatment on $B_0$ was not determined). $P_0^s$ calculated with Eq. 7.3 ($Q = 0.6$).

| factor varied | $H_0$ (mm) | $n$ | 100 $d\Delta H/dt$ ($t$=500s) ($\frac{\mu m}{s}$) | $\Delta H/\Delta t$ ($\frac{\mu m}{s}$) | 100 $d\Delta H/dt$ ($t$=3000s) ($\frac{\mu m}{s}$) | $B_0/\eta$ ($\frac{\mu m^2}{Pa \cdot s}$) | $P_0^s$ (Pa) |
|---|---|---|---|---|---|---|---|
| pretreatment[1] | | | | | | | |
| same day: 1 h at 30°C | 5 | 2 | 13(12-14) | 12(11-12) | 11(11-11) | 220 | 0.4 |
| " " " " 45°C | 2 | 1 | 19 | 12 | 8 | 220 | 0.9 |
| " " " " " | 5 | 8 | 22(17-22) | 16(12-17) | 14(11-15) | 220 | 1.2 |
| " " " " " | 10 | 1 | 22 | 19 | 18 | 220 | 1.2 |
| day before: 0.5 h at 30°C | 5 | 5 | 20(17-22) | 18(17-20) | 15(14-16) | 220 | 1.0 |
| " " " " 45°C | 5 | 4 | 22(20-25) | 19(18-20) | 16(15-17) | 220 | 1.2 |
| " " " " 60°C | 5 | 3 | 23(20-27) | 18(17-19) | 15(11-17) | 220 | 1.3 |
| temperature[2] | | | | | | | |
| 27°C | 5 | 5 | 10(09-11) | 10(08-11) | 10(10-11) | 180 | 0.3 |
| " | 10 | 1 | 12 | 11 | 10 | 180 | 0.4 |
| 33°C | 5 | 4 | 31(29-32) | 24(22-25) | 19(18-20) | 280 | 1.9 |
| " | 10 | 4 | 32(29-34) | 27(26-30) | 24(32-26) | 280 | 2.0 |
| cooled to 5 or 15°C | 5 | 3 | ∿0 | ∿0 | ∿0 | 220 | ∿0 |
| pH[3] | | | | | | | |
| 6.55 | 5 | 3 | 28(26-29) | 21(20-22) | 16(15-17) | 270 | 1.6 |
| 6.75 | 5 | 3 | 20(18-23) | 16(12-18) | 15(13-16) | 200 | 1.1 |
| time after renneting | | | | | | | |
| 0.75 h | 5 | 5 | 15(12-17) | 16(14-18) | 16(14-16) | 200 | 0.6 |
| 2 h | 5 | 3 | 24(22-26) | 21(19-22) | 18(16-20) | 250 | 1.3 |
| 4 h | 5 | 5 | 21(18-24) | 13(12-15) | 12(10-14) | 330 | 0.7 |
| ∿18 h[4] | 5 | 2 | 13(13-13) | 10(09-10) | 8(07-08) | 1000 | 0.09 |
| ∿18 h[4] | 10 | 2 | 18(16-20) | 12(11-13) | 10(09-11) | 1000 | 0.2 |
| water instead of whey[5] | 5 | 1 | 24 | 18 | 15 | 220 | 1.5 |
| $CaCl_2$ addition | | | | | | | |
| 500 ppm $CaCl_2.2H_2O$ | 5 | 1 | 30 | 18 | 25 | 220 | 2.3 |
| 1600 " " " | 5 | 1 | 40 | 24 | 19 | 230 | 3.9 |
| 3200 " " | 5 | 1 | 45 | 28 | 21 | 230 | 4.9 |
| $CaCl_2$ (const. clott. t.)[6] | | | | | | | |
| 250 ppm $CaCl_2.2H_2O$ | 5 | 1 | 24 | 18 | 15 | 230 | 1.4 |
| 500 " " " | 5 | 1 | 29 | 22 | 22 | 250 | 1.9 |
| rennet concentration | | | | | | | |
| 200 ppm | 5 | 1 | 20 | 15 | 13 | 250 | 0.9 |
| 1000 " | 5 | 1 | 22 | 16 | 14 | 230 | 1.2 |
| acid gels (pH 4.6) | | | | | | | |
| time after preparation | | | | | | | |
| 0 h | 5 | 1 | 31 | 19 | 11 | | 2.8[7] |
| 1 h | 5 | 1 | 16 | 8 | 5 | 190 | 0.8 |
| 3 h | 5 | 1 | 9 | 4 | 3 | | 0.2[7] |
| ∿18 h | 5 | 1 | 4(2-5) | 4(2-6) | 1(0-1) | 120 | 0.07 |

1. Day on which the sample was prepared and time(min.) and temperature (°C) treatment after the powder was dissolved, or, in case the milk was prepared the day before, the milk was stored at ± 4°C and then heated at the indicated time (min.) and temperature (°C).
2. Renneting and syneresis at indicated temperature, except experiments at 5 and 15°C which were renneted at 30°C.
3. Original pH: 6.65. (pH: 0.1 unit lower or higher) $B_0$ from tables in Chapter 4, from inter- or extrapolation, or from the most similar treatment.
4. Time after renneting: 16 to 20 h. One of these experiments proceeded for 2-3 h. After 1 h the curves were linear.
5. Instead of whey water was used to moisten and flood the surface of a normal gel.
6. Rennet concentration adjusted to get the same clotting time (15 min.) as with 500 ppm rennet and no calcium addition.
7. Assuming $B_0/\eta = 190\ \mu m^2 \cdot Pa^{-1} \cdot s^{-1}$

C) Water instead of whey

If water was used on top of the slab instead of whey syneresis was not significantly different. It may be expected that dilution of whey also has little effect. There seems to be no appreciable osmotic effect on syneresis.

D) $CaCl_2$

Syneresis rate increased with increasing $CaCl_2$ addition (250-3200 ppm $CaCl_2.2H_2O$). Würster (1934) found a decrease in syneresis rate if more $CaCl_2$ was added. It must be noted that also the pH is decreased by adding $CaCl_2$. When the pH is adjusted $\Delta H_\infty/H_0$ decreases with increasing $CaCl_2$ addition (0-1500 ppm $CaCl_2.2H_2O$) (Cheeseman, 1966).

E) Acid gels

Qualitatively, the effect of the variation of the period between forming the gel and the onset of syneresis ($t_a$) had the same effect on acid and rennet gels. $B_0$, however slightly decreased with $t_a$ in acid gels, while it increased in rennet gels. These results suggest that the increase and decrease (relaxation) of $P^S$ occur faster in acid gels.

*7.3.3 The relation between clotting of the milk and permeability, syneresis (pressure) and rigidity of the curd*

In Chapters 4, 5 and 7 the influence of various factors on $B$, $P$, syneresis rate and rheological behaviour was determined. In the literature more information about this subject and about the influence on the enzymic and aggregation stage of renneting is found. We will discuss all the results in connection to each other. It should be noted that we speak of cross-linking when strands connect with one another, and that formation of bonds is meant to occur on a molecular scale between micelles. The trends observed are shown in Table 7.2. The curves are only meant to illustrate trends, and are thus very approximate; moreover the precise relationship may vary with other conditions.

When we compare the various results the following considerations

Table 7.2. Effect of some variables on clotting, permeability, syneresis (pressure) and rigidity of curd. Very systematic and only meant to illustrate trends; arrows indicate direction of change only; (....) indicates probable relation. *MP* = (caseino-) macropeptide. $dA/dt$ = aggregation rate (all κ-casein split). $B_e$ = permeability one hour after rennet addition. $dB/dt$(——) = rate of change of $B_e$ with time (no deformation). $dB/dt$(---) = rate of change of $B$ with time (with deformation). $P_o^s$ = initial syneresis pressure. $d\Delta H/dt$ = shrinkage rate at 500 s after start of syneresis $\Delta H_\infty/H_o$ = maximum syneresis. rig. = rigidity, measured with different instruments; (——) = rigidity after 1 h; = (---) = rigidity after 4 h. t = with torsion flux method.

| factor varied | range | clotting | | permeab. | | syneresis | | | rig. |
|---|---|---|---|---|---|---|---|---|---|
| | | $\frac{dMP}{dt}$ | $\frac{dA}{dt}$ | $B_e$ | $\frac{dB}{dt}$ | $P_o^s$ | $\frac{d\Delta H}{dt}$ | $\frac{\Delta H_\infty}{H_o}$ | |
| deformation (γ) | 0-1 | | | | t→ | | | | |
| temperature (°C) | 0-40 | 1,3,11 | 1,2,3 | | t→ | | | | 3,5,12 |
| pH | 6-7 | 1,2 | 1,15 | | t→ | | | | 5 |
| rennet conc. (°/oo) | 0-1 | | 7 | | | | | | 5 |
| $CaCl_2$ add. (%) | | | | | | | | | |
| a) const.rennet c. | 0-2 | | 2 | | | | | | 6 |
| b) const. clott. t. | 0-2 | | | | | | | | |
| c) cons. pH | 0-2 | 3,4,5,10 | 5,10 | | | | | 10 | 5 |
| $t_a$ (h) | ½-10 | | | | | | | | |
| protein conc. (%) | 3-7 | 3 | | | | | ? | 10 | |
| fat content (%) | 0-4 | | | | | | | 9 | 14 |
| acid gels | | | | | | | | | |
| time after preparation (h) | -1-20 | | | | | | | | 13 |

1. Foltmann, 1959; 2. Berridge, 1942; 3. Van Hooydonk, p.c.; 4. Green & Marschall, 1977; 5. Hossain, 1976; 6. Scott Blair & Burnett, 1957; 7. Walstra & Van der Haven, 1979; 8. Dalgleish, 1980; 9. Beeby, 1959; 10. Cheeseman, 1962; 11. Nitschmann & Bohren, 1955; 12. Torado & Alais, 1969; 13. Van Vliet, 1982; 14. Van Vliet & Dentener-Kikkert, 1982; 15. Kowalchyk & Olsen, 1977.

should be noted:

- The rate of the enzymic reaction does not affect the final properties of the paracasein micelles (PCM). But if the rate is varied and the measurements are started at a constant time after rennet addition this may have an affect on the results, since not all κ-casein may have been split. For the effect of the varied factor on the aggregation rate ($dA/dt$) it is assumed in Table 7.2 that this is done in an experiment in which all the κ-casein is split.
- The micelles aggregate since the enzymic splitting of the κ-casein causes a decreased repulsion between the micelles. Aggregation may be due to Van der Waals attraction or to specific bonds (e.g. electrostatic ones), or both. Little is known about these interactions between micelles. A low activation free energy for the aggregation of micelles (whether caused by weak repulsion or strong attraction) will both enhance the clotting reaction and the formation of new cross links between strands.
- It must be assumed that an activation free energy exists for the breaking of bonds and thus of strands (at least the bond free energy). In Chapter 5 it is already discussed that the relaxation time of the bonds is a few times 10 s. The variables mentioned may also affect this free energy. To which extent the variation in this activation free energy affects the observed effects is not clear. We assume the influence to be small for most variables. An exception may be the effect of $CaCl_2$ (see later on).
- If, because of a different composition or temperature more bonds exist between micelles, this does not imply that the clotting reaction or the formation of cross links in the matrix are enhanced also. But fewer strands will break under stress. Consequently, micro-syneresis is decreased and the gel will be firmer.
- An increase in the number of cross links results in a higher stress in the strands and a more rigid gel.
- The number of "spoiled" strands (i.e. strands only connected on one end with the matrix) decreases by cross-linking.

The relation between the varied and the measured factors can be explained as follows:

A) Deformation (by shear strain)

The effect of deformation is discussed in connection with the other variables and in Section 4.4. Generally, deformation causes an extra stress on part of the strands. Strands may break. In this way the stress in the strands causing the syneresis pressure may faster relax. Deformation as such will hardly affect the permeability. However, if some strands break the broken strands separate (as a result of the relaxation of the stress in the surrounding strands) and cross-linking of the broken strands may occur; this results in larger pores hence in an increased permeability.

B) pH and temperature

If the pH decreases or the temperature increases the activation free energy for contact between the micelles probably decreases. It is well established that the voluminosity of the micelles decreases with increasing temperature (see e.g. Walstra, 1979) or decreasing pH (Walstra & Delsing, unpublished); this may go along with increased Van der Waals attraction and decreased steric repulsion. A change in pH may influence the electrostatic interaction. Lower pH and higher temperature enhance the clotting reaction and, the formation of new cross links between strands in the network, and between "spoiled" strands in the network. Thus the permeability will increase faster. $B_e$ is also larger because of a shorter clotting time. An increased rate of cross-linking will result in an increased stress in the strands and a faster increase of the rigidity of the gel (Hossain, 1976). If strands break because of deformation, the increased stress and the lower free activation energy will locally result in wider pores (i.e. $B$ increases). A 0.2 units decrease in pH roughly gave a 50% increase in rate for all phenomena, while a 6 $^{o}$C increase in temperature gave a two - to five fold increase in all rates. This again points to a close relation between all phenomena.

The higher permeability and higher syneresis pressure cause a higher syneresis rate. The final volume ($\Delta H/H_0$) will decrease because of the lower voluminosity of the micelles (Walstra, 1979; Waltra & Delsing, unpublished).

The effect of temperature on the rigidity of the gel after 4 h

is not clear. Hossain (1976) found the same rigidity in gels renneted at 28 and at 31.6 °C after 2 h but at 28 °C the rigidity was still increasing. He and Torado & Alais (1969) found a decrease of the rigidity at temperatures above 30°C. If a gel formed by renneting at 30° C is subsequently cooled. it becomes more rigid (Van Hooydonk, personal communication). An explanation for the latter results may be that by cooling the voluminosity of the micelles increases (e.g. Walstra, 1979). It is not inconceivable that besides the temperature of measurement that of gel formation affects its rigidity.

As the syneresis rate is about zero if the gel is cooled to 5 or 15 °C we conclude that $P^s$ and $P^g$ are zero at these temperatures, unless $h_c$ is very large. $P^g$ will only act if the pressure caused by the weight of the matrix (which depends on $\Delta\rho\ g\ h_c$) surpasses the yield stress or if $P^s > 0$. With some simplification $P^g$ would either be zero or significantly larger than zero. If the temperature is increased $P^s$ will become positive at a certain temperature; so $P^g$ will also become significant, independently of $h_c$. Moreover the yield stress will decrease, so $P^g$ will become significant below a certain distance from the top of a gel ($h_c$), irrespective of $P^s$ (the critical $h_c$ will be smaller for a higher temperature). Table 7.1 shows that $d\Delta H/dt$ changes much less with time at 27 °C. As discussed before, this can be caused by $P^g$ being large compared to $P^s$. Calculation of $P_0^s$ indeed yielded a lower value (0.3 and 0.4) while $P_b^g$ was 0.4 and 0.8 for $H_0$ = 5 and 10 mm, respectively. At higher temperatures $P^s$ does increase while $P^g$ would remain constant, thus $\Gamma$ decreases.

The effect of acidity on $dB/dt$ (obtained by the tube method; see Table 4.7) deviates from the results in Table 4.9 (obtained by the torsionflux method). This can be explained by a higher rigidity of the gel resulting in less deformation in the tube at constant $dP_t/dx$ as the pH is decreased.

C) Rennet concentration

Increasing rennet concentration will result in an increasing enzymic reaction rate. The final result however will be the same if concentrations are not extreme. If the period between rennet addition and measurement is kept constant, rennet concentration may have some

effect, especially if the measurements start in an early stage of the formation of the matrix. In such an early stage, the gel is not yet completely formed and at that time the greatest changes occur.

D) $CaCl_2$ addition

Increasing the amount of $CaCl_2$ added increases the rate of coagulation of micelles. The increase in the rate of coagulation is only caused by a decrease of the pH. If the pH is kept constant the clotting time is constant too (Cheeseman, 1962) except for low Ca concentrations (< 10 *mM*) (e.g. Green & Marschall, 1977; Yamauchi & Yoneda, 1978).

Since the rate of coagulation increases at increasing $CaCl_2$ addition, one would expect that as a result of a lower activation free energy of the micelles for coagulation also the permeability would increase more (increasing $B_e$, $dB_e/dt$ and $dB/dt$). This is not so. The activation free energy appears only to be lowered by a decrease in pH. Apparently the extra Ca ions are only involved in the formation of extra bonds between molecules of already aggregated PCM. This results in stronger strands. Fewer strands will break if stress is exerted on them. This is in agreement with the experiments of Yamauchi & Yoneda (1978). The phosphorylated Calcium caseinate solutions coagulated almost as fast as native Calcium casein at Calcium concentrations above 20 *mM*. The yield of coagulated protein was the same for both caseins. Calcium content of the gel made of dephosphorylated casein was less than one fourth of that of native casein. Dephosphorylated casein gave a much softer gel than native casein. We conclude that both phosphate groups and Calcium are involved in the stronger bonds between the micelles. As a consequence of the decreased activation free energy, caused by pH reduction more cross links form, which results in a higher syneresis pressure. Also the rigidity increases as a result of $CaCl_2$ addition (Scott Blair, 1957; Hossain, 1976). This is probably not caused by an increased number of micelles being bound to others, but by an increased number of bonds between any two touching micelles.

E) Time after rennet addition

The greatest changes in the matrix occur shortly after the matrix

is formed, since many "spoiled" strands still will be available and more bonds between already aggregated micelles can still be formed. The strands become less frayed (so $B_e$ increases and $dB_e/dt$ decreases) and stronger (so $dB/dt$ decreases and the rigidity ($G'$) and ($G_0$) increases).

After a few hours $B$ and $G'$ still increase, though at a lower rate, and $P_0^S$ decreases. This can be explained as follows: There exists a distribution of yield stresses in the strands of the matrix. The weaker bonds between aggregated micelles cannot resist the contracting stress of the matrix. So they will break. The resulting "spoiled" strands will cross-link with other strands. This results in a less homogeneous matrix (increasing permeability), relaxation of the stress (decreasing $P_0^S$) and more rigid strands (increase in rigidity). This process will continue as long as there is a distribution of bond strengths between the aggregated micelles and as long as the overall stress is larger than the yield stress of the weakest bonds.

F) Protein concentration

Concentration of protein was achieved by ultrafiltration (see Chapter 2). A higher protein concentration will result in a higher rate of splitting (Van Hooydonk, personal communication). Just as in the case of rennet concentration, this will influence the other phenomena.

Van Hooydonk (personal communication) found an increase in the initial rate of change in rigidity (a measure for the aggregation rate) with concentration in the milks which were renneted normally, i.e. not all the κ-casein is split when aggregation starts. If all the κ-casein is split there is no indication that the activation free energy for the formation of bonds depends on the PCM concentration. Hence, the coagulation can be described by a bimolecular reaction according to Smoluchovski (Overbeek, 1952). Thus the aggregation rate is proportional to the PCM concentration squared. The influence of the enzymic reaction rate and of the aggregation rate on $B_0$, $P_0^S$, syneresis and rigidity, as a change in rennet concentration, appeared to be small. It is expected to be similar in this case. The effect of protein concentration on $B_0$ and $dB/dt$ is discussed in Chapter 4.

We did no experiments in syneresis with varying initial protein concentrations. Cheeseman (1962) found a decrease in $\Delta H_\infty/H_0$ if the concentration was increased. This is to be expected since the final concentration will to a lesser extent be influenced by the structure of the matrix (see effect of $t_a$). Green (1981) found that the basic structure of the matrix was laid down during the curd forming process and was not fundamentally altered later in cheesemaking. However, her results do not show whether there is an effect on $dH_\infty/H_0$. As is generally the case, the rigidity increases with increasing protein concentration (see Fig. 5.3). After 1 hour an S-shaped curve is obtained (see Table 7.2). This will be caused by a decreased rennet/casein ratio at higher casein concentrations, which results in a slower firming.

G) Fat content (unhomogenized)

If the fat content increases, the ratio of rennet to casein will slightly increase (at constant rennet addition to the milk). The permeability slightly decreases, probably due to a decrease in porosity. Also $dB_e/dt$ will decrease, as a smaller part of the solids can change in structure. $dB/dt$ decreases as the gel will be slightly weaker if part of the matrix is replaced by fat globules that are not part of the matrix.(The matrix will be less dense.) This will also cause a lower $P_0^s$. $P_0^g$ will lower as the density of the fat is lower than the density of the whey. A lower $P_0^s$ and $B_0$ will cause $dH/dt$ to be smaller initially. Later on $d\Delta H/dt$ will mainly be lower because of a lower $P_b^g$. $\Delta H_\infty/H_0$ will decrease since the fat globules are imcompressible.

H) Acid gels. Time after preparation

The syneresis of acid gels is basically similar to that of rennet gels. But there are differences. The experiments did not show a maximum in the rate of syneresis with time. This is probably caused by the nature of the experiments or by their limited number. $P_0^s$ will initially increase from zero to its maximum and subsequently decrease by relaxation. The maximum might already be reached during preparation. A possible explanation for the decrease of $B_0$ and $P_0$ may be that the micelles swell.

## 7.4 CONCLUSIONS

In this Chapter the shrinkage of slabs of curd was investigated. Both the shadow and the microscope method gave good results and were supplementary. The first series of experiments were done under standard conditions while only the thickness of the slab was varied. It was found that for $\Delta H/H_0 < \sim 1/3$ and $H_0 > 2$ mm $\Delta H$ was independent of $H_0$. The conclusion was that $\Gamma = 0.5$ for $t < \sim 10$ minutes. After $\sim 15$ - 30 minutes $\Gamma$ had increased to $\sim 0.78$ and it remained constant during a period depending on the thickness of the slab. After about one day the thickness of the slabs was 1/3 of the original value, irrespective of the original thickness.

A dynamic simulation model of the syneresis of a slab was developed. The model describes and interrelates, permeability, syneresis pressure and shrinkage as a function of time and position. In one version of the model it was assumed that the permeability increased with time and with concentration as determined experimentally; endogenous syneresis pressure ($P^S$) decreased with concentration only; maximum gravitational pressure ($P_b^g$) was constant; $P_0^S = P_b^g = 1$ Pa ($H_0 = 10$ mm). This model fitted the results fairly good. From the syneresis rate, the permeability coefficient and the viscosity, the initial syneresis pressure ($P_0^S$) can be derived. $P_0^S$ was found to be a function of time after renneting (thus independent of $t$). However, the application of such a relation into the model did not improve the fit to the experimental results.

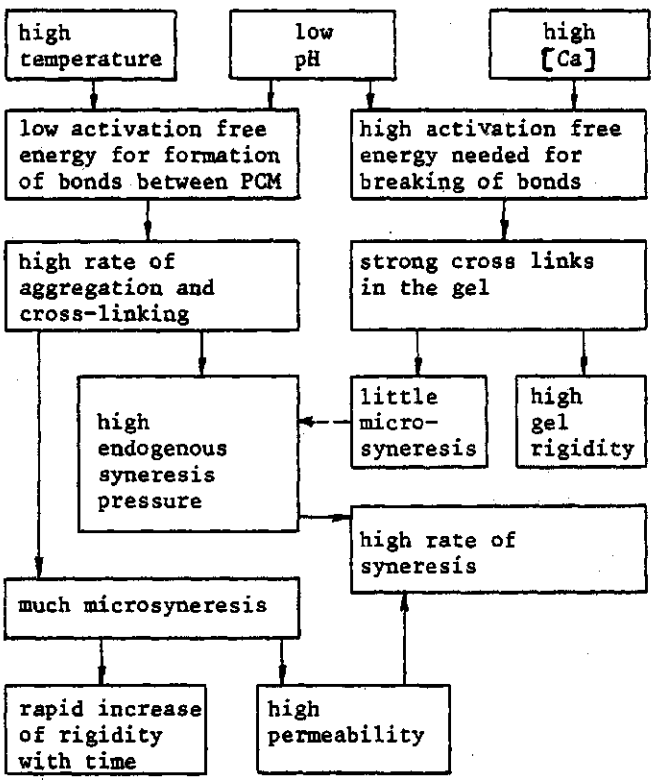
A perfect fit will probably be obtained if either $B$ or $P$ increases more strongly with time up to $t \simeq 0.5$ h. Our experimental evidence neither supports nor contradicts such behaviour; further experiments would be needed to settle the points.

In this Chapter we also investigated the effect of the composition and temperature on the syneresis rate. Syneresis rate increased with increasing temperature during reconstitution of the skim milk, increasing temperature during the experiment, decreasing pH and increasing Calcium addition. Rennet concentration did not affect the syneresis. As discussed in Section 2.1 pretreatment of the milk has a larger effect on syneresis.

Finally the relations between clotting, permeability, syneresis and rigidity were discussed. The main conclusions are (under the conditions of these experiments):

- Temperature and pH affect the free activation energy; probably via effects on steric repulsion and electrostatic attraction. This affects the rates of all phenomena.
- Addition of Calcium (> ∿20 mM) only affects the strength of bonds between already aggregated micelles.
- After a gel has formed, formation of cross links still goes on. This results in a stress in the strands, which causes a tendency of the matrix to shrink. If the matrix is fixed, the strands will break at weak spots thus causing the stress to relax.
- The permeability increases with time. Initially this is mainly caused by the strands becoming less frayed, later on by breaking of strands.

Table 7.3 Tentative relation between physico-chemical parameters and curd properties.



A tentative explanation of the effect of temperature, pH and addition of Calcium is given in Table 7.3.

If we compare these results with the findings in pratical cheesemaking we see that the same relations are found between the composition and temperature and syneresis. However, whey expulsion happens much faster in practical cheesemaking. In the next Chapter it will be shown that external pressure can increase the syneresis rate by orders of magnitude.

# 8 SYNERESIS AS INFLUENCED BY EXTERNAL PRESSURE OR DEFORMATION

## 8.1 INTRODUCTION

In the experiments mentioned in Chapter 7 the curd was not deformed. It was our intention to test the model also under circumstances where the curd is deformed by external pressure. In the model the flow of whey occurs only in one direction in a cartesian coordinate system. This geometry can be approximated in a cylinder of curd, where pressure is applied on the flat sides and the transport of whey occurs only through the curved surface. Moreover the diameter of the cylinder should not be so large that the shrinkage in tangential direction can be neglected.

When a pressure is exerted on the two flat surfaces of the cylinder, the strands are compressed in the axial direction and elongated in radial and tangential direction. The matrix under stress will tend to shrink momentarily but cannot do this because of the viscous resistance of the outflowing whey. This situation is comparable to syneresis without external pressure; the difference is that the pressure is higher. External pressure may in principle affect the permeability but we cannot find considerations to support the view that such a change would be significant. The height of the cylinder as a function of time can be predicted in principle from the results of creep measurements by which means any syneresis in the axial direction could be predicted; axial syneresis can occur if the flat surfaces are not made impermeable to whey. Moreover extra cross links can in principle be formed in the axial direction. However calculation of the height of the slab in the absence of syneresis proved to be of little use because the measurements of the volume of the slab were insufficiently accurate and because the deformation mostly occurred outside the linear visco-elastic region.

## 8.2 METHODS

It turned out to be impossible to perform experiments with a cylinder of a height much larger than the diameter, because of

buckling. Ultimately we have chosen for flat cylindrical slabs with a diameter of 9 or 14 cm and a height of 5,10 or 15 mm. Milk was renneted in a bottomless mould which was placed in a thermostated vat (see Fig. 8.1). In the vat whey was poured around the mould. 50 Minutes after rennet addition the curd was cut free from the inner wall of the mould and moistened by spraying whey on the upper surface to the slab. The mould was removed and the slab cut free from the bottom. More whey was added. The wheight of the plate was counterbalanced by means of a counter weight and a pulley, to assure the pressure exerted by the plate itself being zero. Pressure on the curd slab is introduced by placing weights on the scale at the top (see Fig. 8.1). The height of the slab was recorded with a displacement transducer and its cross section was determined from photographs of the bottom of the slabs by means of a Quantimet image analyser. In this way the volume of the slab was calculated as a function of time, giving the syneresis.

One hour after rennet addition a weight was placed on the scale. Two series of experiments were done. In the first series pressure was

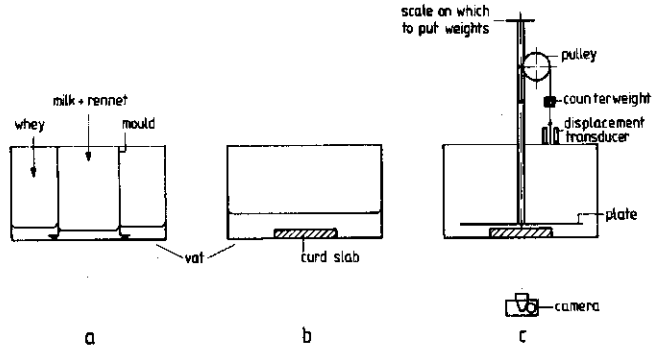



Fig. 8.1 Schematic representation of the apparatus for applying pressure on a slab of curd.

a. Milk provided with rennet is brought into a mould in a thermostated vat. Whey is added to the vat.

b. When the curd has formed it is cut free from the walls of the mould. The mould is removed and the slab is cut loose from the bottom of the vat. The bottom is cleaned.

c. A horizontal plate is brought into contact with the curd slab and the first photograph is taken. Weights can be placed on the upper plate.

applied for one minute, followed by 5 minutes without pressure. In the second series the weight was placed and removed from the scale each time for 5 and 10 s, respectively. This was done 12 times (i.e. during 3 minutes) whereupon no pressure was exerted for 3 minutes. The total time, during which the slab was under pressure thus was the same as in the first series. After 6 minutes the following scheme was used for both series: 10; 0; 50; 0; 100 g, each time for 1 minute (see Fig. 8.2).

## 8.3 RESULTS AND DISCUSSION

A typical result is given in Fig. 8.2. The curves giving the height of the slab as the result of the putting in and removing of weights, have a shape analogous to creep curves. The curd is a visco-elastic system. At the moment of applying the pressure elastic deformation occurs; after that the deformation is a result of retarded elasticity and viscous deformation.

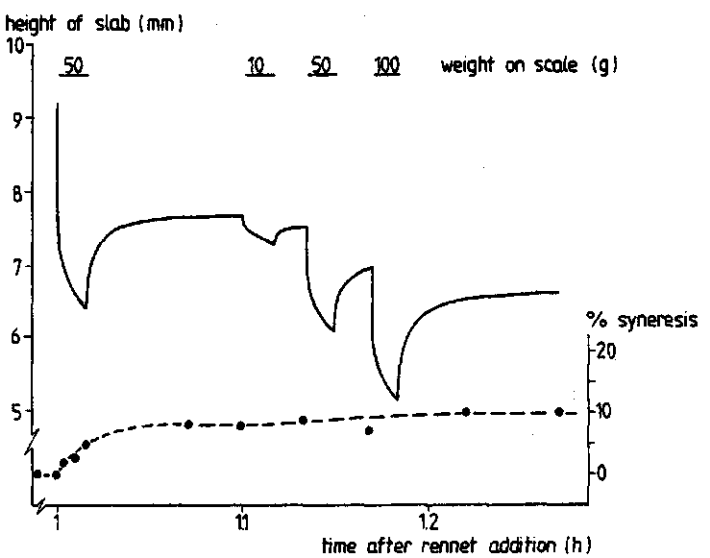



Fig. 8.2 Height of the slab ($H$, full curve) and % syneresis (bottom line) or relative volume reduction as a function of time. Example of an experiment of the first series (50 g for 1 minute. Further explanation in the text). Original cross section of the slab 153 $cm^2$. Original height 10 mm. At $t$ = 0 the pressure was 30 Pa.

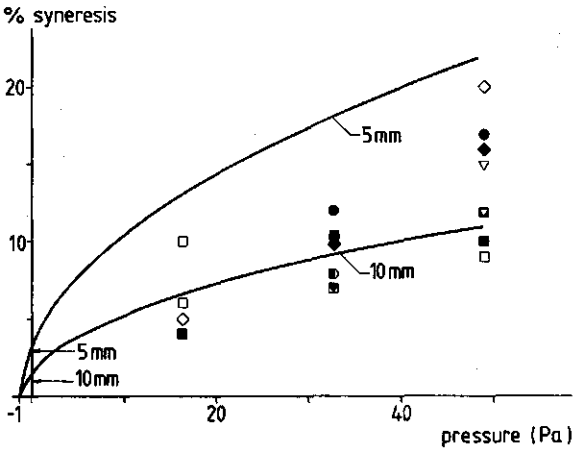



Fig. 8.3 Syneresis during the first 5 minutes of the experiments (see Fig. 8.2) as a function of pressure at $t = 0$. Without pressure the relative volume reduction was estimated at 0 - 4%. The curves indicate the function: % syneresis = 0.58 $K^{\frac{1}{2}}$; where $K$ is for total pressure (external and endogenous)

□ ◇ ▽ ○ = wheight on scale for 1 minute continuously.
■ ◆ ▼ ● = wheight on scale for 1 minute intermittant.
▽ ▼ = height of the slab: 5 mm, cross section 153 $cm^2$
□ ■ = height of the slab: 10 mm, cross section 153 $cm^2$
◇ ◆ = height of the slab: 15 mm, cross section 153 $cm^2$
○ ● = height of the slab: 10 mm, cross section 62 $cm^2$
⟵ = arrows indicating % syneresis after 5 minutes of a slab without external pressure (see Chapter 7)

From Fig. 8.2 it also appears that extra pressure enhanced syneresis. Without pressure the volume reduction after 5 minutes of a slab of 1 cm thickness was estimated at 0 - 4%. While an external pressure of about 30 Pa resulted in about 10% syneresis. The extra syneresis occurs as long as pressure is exerted on the slab, and for a short time afterwards. The latter is imaginable if one considers that after the weight is removed the stress in the matrix does not momentarily relax. In a number of experiments the pressure, the height and the surface of the slab were varied. The results are given in Fig. 8.3.

The syneresis is shown in Fig. 8.3 as a function of the pressure at the moment the weight is placed on the scale. Directly afterwards the slab is deformed and therefore the cross section area is enlarged

which implies that the effective pressure is somewhat lower.

The results of the measurements with the apparatus were found to be not very reproducible. Hence, the results are only approximate and it cannot be concluded that the introduced variations in height and diameter of the slab as well as the time scheme by which the pressure was exerted on the slab affected the syneresis rate. But the increase in syneresis rate with increasing pressure is unmistakable.

In Fig. 8.3 also Eq. 7.1 is shown for two values of $H_0$, i.e. 5 and 10 mm. Other parameters were $B_0 = 2.3 \times 10^{-13}$ m$^2$, $t = 300$ s, $\eta = 1$ mPa·s. For $P_0$ the external pressure + 1 Pa for endogenous pressure was taken. It is seen that the curves fit the results obtained from the experiments both with and without external pressure within an order of magnitude.

The results of these experiments show the same trend as the results given by Van Dijk et al.(1979) (see Fig. 8.4). Here also the pressure had a great effect on the syneresis. The first point in Fig. 8.4 (lowest pressure)pertains to curd grains in whey kept stirring for 2 h; the pressure here is roughly calculated from Bernoulli's equation from the velocity gradients in the whey. The second point pertains to curd merely pressed by its own weight under the whey; hence, this pressure is also somewhat uncertain. If the

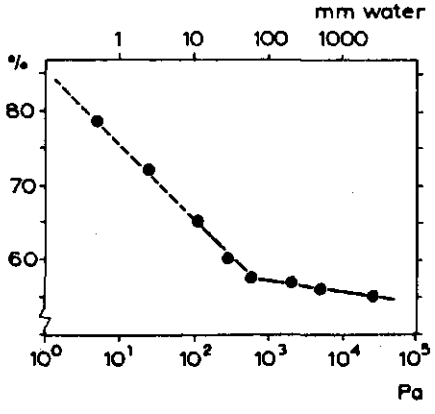



Fig. 8.4 Water content (%) of curd from whole milk after 1 h stirring and 1 h pressing under the whey at various pressures; temperature and pH were kept constant.

same curd had been left undisturbed for 2 h, and had been subject only to its own syneresis pressure of some 1 Pa, its water content would only have been lowered from its original 87% to some 85% according to measurements on thin slabs of curd. Finally it should be noted that Fig. 8.4 may not be taken as representative of actual cheesemaking practice, because experimental conditions were substantially different.

From the results of the experiments it can be concluded that in practical cheesemaking external pressure on the curd grains is very important. Such pressure is exerted in practical cheesemaking by stirring, draining and pressing.

SUMMARY

H.J.M. van Dijk, Syneresis of curd

This study deals with the syneresis of curd. Rennet gels are primarily considered; some comparisons with acid milk gels are given.

After curdling the milk, the curd tends to shrink; in other words, the network of aggregated paracasein micelles (PCM) will be under stress. If the curd is cut or - as was the case in our expirements - a curd surface is wetted, syneresis starts. The rate at which the whey is expelled depends on the pressure gradient in the whey and on the permeability of the network.

In Chapter 2 the materials and methods generally used are described. Unless mentioned otherwise, standard conditions were used in the experiments. By standard conditions is meant: reconstituted skim milk with the same dry matter content as the original milk, to which 500 ppm rennet was added; the temperature during the whole experiment was kept at 30 $^{o}$C; no $CaCl_2$ was added.

The endogenous syneresis pressure ($P^s$) appeared to be very low, about 1 Pa. In Chapter 3 two methods are described which give an order of magnitude of the stresses involved. Moreover, the weight of the network can cause an additional pressure. The maximum pressure caused by the weight ($P^g$) at a level $h_c$ below the interface is $(\rho_{curd} - \rho_{whey})\ g\ h_c \simeq 75 h_c$ Pa ($h_c$ in m).

The permeability measurements are described in Chapter 4. Two methods were used; in both, the flow of whey through a vertical column of curd was measured as a function of head pressure. A problem is that the curd is deformed during the experiment. In the "tube" method, deformation is a function of the pressure gradient ($dP_t/dx$), the diameter of the tube holding the curd ($d_t$), and the rigidity of the gel. In the second method the "torsionflux" method, the deformation was adjustable. The tube method led to the following results:

- The permeability is of the order of $10^{-13}$ m$^2$.
- Permeability increases with time, which is ascribed to "microsyneresis", i.e. syneresis at local sites in the gel. The rate of increase is approximately constant.

- The increase in permeability ($dB/dt$) is higher for a higher pressure gradient or a wider tube; both lead to larger deformation of the curd.
- The change of the permeability with time in the absence of deformation ($dB_e/dt$) was obtained by applying the head pressure at different times after addition of rennet. Shortly after clotting permeability increases fastest. Between 1 and 24 h $dB_e/dt$ was constant.
- The permeability of curd made from ultrafiltered skim milk ($B(i)$) and its change with time ($dB(i)/dt$) were determined. This yielded the permeability as a function of concentration and time ($B(i,t)$).
- The permeability also depends on temperature, $CaCl_2$ concentration, acidity, fat content and type of skim milk.
- In acid milk geld permeability was of the same order of magnitude, but it hardly changed with time.

The rheological behaviour of curd is discussed in Chapter 5. The dynamic measurments with the "Den Otter" rheometer show that the moduli $G'$ and $G''$ kept increasing for a long time ($\sim$3 h) after rennet addition. From the dependence of $G'$ and $G''$ on the angular frequency it was deduced that $G''$ is due to the relaxation of bonds and that the relaxation time is a few times 10 s.

The instantaneous shear modulus ($G_0$) was determined as a function of protein concentration. The obtained relation can be explained in terms of an only partly effective contribution of the casein to the network; this contribution being relatively smaller at lower concentrations. Also from the creep measurements it was concluded that the endogenous syneresis pressure was less than 10 Pa.

If both permeability and pressure are known for all values of concentration (or relative remaining volume ($i$)) and time ($t$), the syneresis can in principle be calculated. This is in the model described in Chapter 6, in which the equation of Darcy is combined with the equation of continuity. A numerical procedure is developed, for a one dimensional case; the syneresis of a thin slab.

The pressure in the whey is the sum of the endogenous syneresis pressure ($P^s$) and the pressure caused by the weight of the network ($P^g$). For $P^s(i)$ and $P^g(i)$ some trial functions were considered.

In Chapter 7 the syneresis of slabs is studied. The results of the experiments show that initially $\Gamma = d\log\Delta H/d\log t$ is about 0.5. For $t > 0.5$ h $\Gamma$ increases to $\sim$0.78. $\Gamma$ is independent of the original thickness of the slab ($H_0$) during a certain period (penetration period). The length of this period depends on $H_0$.

After one day $H$ did not change any more and $H_\infty/H_0$ was about one third. The best fit between model calculations and experimental results was obtained if it was assumed that:

- the permeability increases with time ($t$) and decreases with $i$, as was found in the experiments,
- endogenous syneresis pressure ($P^s$) decreases only with shrinkage,
- maximum gravitational pressure ($P_b^g$) is constant,
- $P_0^s = P_b^g = 1$ Pa ($H_0 = 10$ mm).

$P_0^s$ was found to be a function of time after renneting, at first increasing, then (after 1 - 2 h) decreasing. However, the introduction of such a relation in the model did not improve the fit to the experimental results. After all, the pressure cannot relax twice, both by shrinkage and by "ageing".

The effects of several parameters (pH, temperature, Ca concentration, etc.) on milk clotting, gel permeability, syneresis and curd rigidity are interrelated. A survey is given in Table 7.2 and a tentative explanation is summarized in Table 7.3.

In Chapter 8 it is shown that external pressure has a dramatic effect on the syneresis rate. Extrapolation to zero external pressure yields, again, an endogenous syneresis pressure of about 1 Pa.

SAMENVATTING

H.J.M. van Dijk, Syneresis of curd

Deze studie behandelt de synerese van gestremde melk. Onder synerese wordt verstaan: het samentrekken van een gel onder het uitdrijven van vocht. Synerese treedt met name op bij melkgelen. Bij de kaasbereiding wordt dit proces bovendien bewust bevorderd. Hierdoor worden de eiwitten en het melkvet van het grootste deel van het vocht gescheiden. Door dit proces te laten samengaan met een beheerste verzuring door melkzuurbacteriën wordt een smakelijk produkt verkregen, dat bovendien veel langer houdbaar is dan melk.

Het gel wordt in het algemeen verkregen door aan de melk stremsel toe te voegen en soms door de hiervoor genoemde beheerste verzuring. Bij beide methoden gaan de caseïnemicellen ("kaasbolletjes" met een diameter van ongeveer één tienduizendste millimeter), die in de melk zweven, aan elkaar kleven. Hierdoor worden vlokjes gevormd die vervolgens ook weer aan elkaar kleven. Tenslotte wordt één groot, ijl netwerk gevormd; de ruimten daartussen zijn opgevuld met wei. Door in de gestremde melk te snijden of het oppervlak te bevochtigen kan ze zich gaan samentrekken tot wrongel. Daarbij wordt wei uitgedreven.

Waardoor dit gebeurt, in welke mate en wat het effect is van veranderingen in samenstelling en temperatuur, alsmede de verklaring daarvan, waren de voornaamste vragen die we in dit onderzoek aan de orde stelden.

Het netwerk heeft de neiging om samen te krimpen en om in te zakken; het eerste gebeurt spontaan (endogene synerese), het tweede onder invloed van zwaartekracht. Deze processen worden echter vertraagd doordat wei uit het netwerk moet stromen om het netwerk te laten krimpen. Hierdoor komt de wei in het gel onder druk te staan. Indien deze syneresedruk en de doorstroombaarheid bekend zijn kan het verloop van de synerese berekend worden (Hoofdstuk 6). De syneresedruk bleek overigens te klein te zijn om ze met een instrument te kunnen meten, maar ze kon wel indirekt bij benadering bepaald worden. In hoofdstuk 3 worden twee experimenten beschreven waaruit deze druk indirekt valt te bepalen. De conclusie luidt dat de syneresedruk van

de orde van grootte is van 1 Pa (overeenkomende met 0.1 mm waterkolom). Onafhankelijk hiervan volgt dit ook uit de reologische metingen (Hoofdstuk 5) en uit de experimenten beschreven in Hoofdstuk 8.

De syneresedruk en de doorstroombaarheid bleken behalve van de samenstelling van de melk, de temperatuur en de mate waarin de synerese al had plaats gevonden ook afhankelijk te zijn van de tijd, die verlopen was na het toevoegen van stremsel. De doorstroombaarheid werd steeds groter; de syneresedruk nam aanvankelijk toe maar later weer af.

Om het aantal factoren dat invloed heeft op de synerese te verkleinen, werd gewerkt met een ééndimensionaal model, bestaande uit horizontale dunne plakken wrongel. Dit is ook de eenvoudigste manier om de uitkomsten van het wiskundig model van het syneresepproces, dat wij opstelden, te vergelijken met de resultaten van proeven. Verder kon op deze manier een praktisch probleem worden opgelost. De plak begon namelijk pas te synereren nadat ze bevochtigd was. Zo kon op een eenvoudige manier een experiment gestart worden.

De uitkomsten van de modelberekeningen komen het beste overeen met de uitkomsten van de experimenten als hierin het volgende wordt aangenomen:

- De doorstroombaarheid is een functie van de indikking en de tijd (zie vergelijking 4.16).
- De aanvankelijke endogene syneresedruk ($P_0^s$) is gelijk aan 1 Pa.
- De druk veroorzaakt door het gewicht van de wrongel ($P_b^g$) is gelijk aan 75 × de afstand (in meters) tot het oppervlak van de wrongel.

$P^s$ en $P^g$ nemen af naarmate de synerese voortschrijdt, maar de wijze waarop dat precies gebeurt, heeft, bij de door ons geprobeerde functies, slechts een geringe invloed op het resultaat. De endogene syneresedruk van nog niet gesynereerde wrongel verandert met de tijd na het toevoegen van het stremsel. Zodra synerese optreedt en daarmee indikking, zal deze relatie met de tijd echter geheel anders zijn: de druk kan immers niet twee maal relaxeren, door indikking èn door veroudering. De beste overeenkomst tussen modelberekeningen en experimenten werd gevonden door de invloed van tijd als zodanig te verwaarlozen.

De invloed van enkele parameters (pH, temperatuur Ca concentra-

tie, enz.) op de stremming van melk de doorstroombaarheid van het gel, synerese en de stevigheid en hun onderlinge correlaties worden gegeven in Tabel 7.2 en een voorlopige verklaring wordt gegeven in Tabel 7.3.

Uit de experimenten in Hoofdstuk 8 blijkt dat bij de praktische kaasmakerij de opgelegde druk door roeren, draineren en persen van overheersende invloed is op de synerese van wrongel.

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