Test Conditions. Heat coagulation times decrease with temperature. (See Figure 13.8.) On average, Q_{10} is about 3, apparent activation energy is about 150 kJ·mol^{-1} throughout most of the pH range, though Q_{10} tends to increase somewhat at higher pH. Among lots of milk Q_{10} may vary considerably (e.g., from 2–7).

At pH above 6.7, heat stability (of unconcentrated milk) tends to decrease considerably with available O_2. Hence, a larger headspace volume and rocking of sample tubes during heating may decrease coagulation time, for instance by a factor of 3 at a pH near 7. This must be caused by the increased rate of acid production.

Composition. The wide variability in heat stability among lots of milk must be caused by differences in composition. There is usually a large effect of season (coagulation time may vary by a factor of 4), presumably for the greater part caused by stage of lactation. The variation between individual cows also is considerable.

Part of the variability follows from factors involved in colloidal stability: Ca^{2+} activity, casein micelle size, phosphate content of micelles, and their voluminosity. Variation in protein composition appears to be too small to have much effect on heat stability. The most important component causing variation mostly is urea. Average coagulation time may be 14 min at 140°C for milk with 0.25 g of urea per kilogram of milk, and 26 min for 0.5 g·kg^{-1}; such variations are well within the normal range of urea contents. The action of urea is partly through its slight inhibition of acid formation. At higher temperature urea is converted partly into ammonium cyanate, and this compound can block ϵ-amino groups and affect thiol groups of the proteins. A watertight explanation has not been given. Urea content has no effect on coagulation near the minimum in the pH curve.

Concentration. The heat stability of concentrated milk is considerably less than that of milk. (See Figure 13.8.) Highly concentrated (skim) milk (e.g., > 40% s.n.f.) gives a firm gel on heating, even at temperatures near

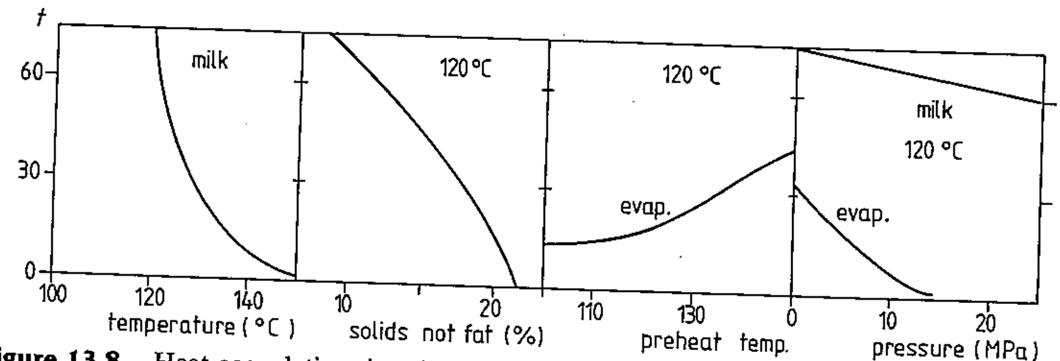

Figure 13.8. Heat coagulation time (t, minutes) of milk and evaporated milk as a function of test temperature, content of solids-not-fat of the milk, preheat temperature (duration, e.g., 4 min), and homogenization pressure. Approximate results from various sources.

100°C. There is little correlation between the heat stability of fresh milk and that of the concentrated milk prepared from it. Urea content, for instance, generally has no influence on the heat stability of concentrated milk. The coagulation mechanism is probably different, at least over much of the pH range. The difference in heat stability is especially striking at pH above 7; here, the stability of evaporated milk is very low (mostly < 1 min at 130°C), while most unconcentrated milk is very heat stable. (See Figure 13.7.) This implies that the decrease in pH during heating up to the coagulation point (which is considerable in unconcentrated milk) is insignificant in concentrated milk, which also points to a different coagulation mechanism. Conceivably, heat coagulation of concentrated milk at not too low pH is similar to age gelation. The concentration as such causes the pH to decrease and the pH optimum also shifts to a somewhat lower value; there is no minimum in coagulation time. Figure 13.8 gives the coagulation time at the pH optimum. Milk concentrated by ultrafiltration (rather than by evaporation) is much more heat stable than evaporated milk.

Preheating. For unconcentrated milk, preheating mainly causes a shift of the heat coagulation curve to lower pH values, and the stability at the pH optimum is hardly affected. But a very intensive preheat treatment (e.g., a few minutes at 150°C) causes heat stability to increase over the whole pH range, and the minimum in the curve disappears. Perhaps the second heat denaturation of β-lactoglobulin, which occurs near 140°C, is involved.

Concentrated (evaporated) milk hardly can be sterilized without preheating the milk before concentrating. The heat-stability maximum is shifted to lower pH values and becomes higher. (See Figure 13.8.) The pH of the milk before preheating also affects the heat stability of the evaporated milk, its optimum being, for instance, 6.45. The beneficial effect of preheating must be caused at least partly by reactions of the β-lactoglobulin; addition of this protein to the milk decreases the heat stability of evaporated milk, but this decrease can be eliminated largely by proper preheating.

Additives. Several additives (some of which are illegal) may enhance heat stability. NaOH or sometimes HCl is used to adjust the pH. Na_2HPO_4 also can be used for this purpose, and it usually gives an even better heat stability, presumably because it lowers Ca^{2+} activity.

Agents that interfere with free thiol groups can be beneficial. The effect of N-ethyl maleimide already has been discussed. Addition of 0.05% H_2O_2 to milk before evaporation considerably enhances the stability of the concentrated milk; higher additions become detrimental. Adding 0.5–1.0 mg Cu^{2+} per kilogram of milk, after preheating and before evaporation, usually gives a marked increase in heat stability of evaporated milk.

As will be clear from the discussion of composition above, addition of urea can increase the heat stability of (unconcentrated) milk. Several aldehydes in about 20 mM concentration have a similar effect. Those aldehydes that are effective are like urea in that they diminish the rate of acid production during heating.

Homogenization. This process is discussed in Section 14.4. Suffice it here to say that it causes a considerable transfer of milk protein, predominantly micellar casein, from the plasma to the newly formed fat globules. This phenomenon must be involved in the detrimental effect of homogenization on heat stability. Homogenization of skim milk makes no difference, and the heat stability of fat-containing products decreases with increasing fat content and increasing homogenization pressure, both of which go along with an increase in the amount of protein transferred. In the case of cream, this seems to be the main factor in determining heat stability. Examples are in Figure 14.10. It shows that higher homogenization temperatures, up to about 70°C, lead to a lower heat stability. Still higher temperatures or preheating of the cream drastically reduces coagulation time.

Homogenization has little effect on milk, but it renders concentrated milk far less heat stable. (See Figure 13.8.) The detrimental effect can be offset for a considerable part by preheating the milk before concentration. The effect of homogenization temperature seems to differ from that in cream.

Suggested Literature

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