ELSEVIER

0308-8146(95)00236-7

Food Chemistry, Vol. 57, No. 2, pp. 295–298, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0308-8146/96 $15.00+.00

Kinetics and equilibria of tea infusion. Part 13. Further studies on tea scum: the effects of calcium carbonate, lemon juice and sugar

Michael Spiro, Yuen Ying Chong & Deogratius Jaganyi

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

(Received 4 August 1995; revised version received 24 October 1995; accepted 24 October 1995)

Experiments carried out on tea infusions with blown-over films of calcium carbonate ($CaCO_3$) have shown that it is the presence of calcium and bicarbonate ions in the water, and not the concomitantly produced $CaCO_3$, which mediates the formation of tea scum. Other experiments have refuted Lewin's (1993) theory that tea scum is mainly composed of epidermal waxes loosened from the tea leaves by hot water.

Addition of fresh lemon juice greatly decreased the amount of tea scum formed in temporary hard water. This effect was explained by the resulting drop in pH and by complexation of calcium ions by the citric acid contained in the juice. Addition of sucrose equivalent to two cubes of sugar per cup significantly reduced the mass of scum, far more than could be accounted for by the increase in solution viscosity. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The composition and the kinetics of formation of tea scum formed on the surface of black tea brewed in temporary hard water has been investigated in two previous papers (Spiro & Jaganyi, 1994*a*,*b*). The present paper presents further evidence on the mechanism of scum formation and reports how the amount of tea scum is affected by the addition of lemon juice and of sugar.

MATERIALS AND METHODS

The experiments were carried out in a similar way to those described previously (Spiro & Jaganyi, 1994*a*,*b*). In the standard procedure, one teabag of the same popular black tea blend (Typhoo) as used before was infused with stirring in 800 ml of water (either hard London mains water or synthetic water) at 80°C. After 5 min the teabag was withdrawn and any foam and surface film material removed with an aluminium scoop. Scum was then allowed to form at 80°C for 60 min before being collected with another scoop, dried and weighed. Some experiments were carried out with later batches of teabags. Almost all experiments were replicated and the mean values are reported. Uncertainty limits, where stated, are average deviations from the mean.

RESULTS AND DISCUSSION

Background data

The composition of the local London mains water used varied slightly during the course of the investigation. From analytical data supplied by Thames Water Utilities, the calcium content increased gradually from 98 to 114 mg litre^{-1} while the bicarbonate content was roughly constant at 230 mg litre^{-1}. The mean pH was 8.0–8.2.

The Typhoo teabags used previously and also in much of the present work generated an average of 9.7 mg of tea scum under the standard conditions. Drying the scum in a vacuum oven at room temperature instead of in an air oven at 80°C had no significant effect on the dry weight. Newer batches of teabags obtained in 1994 from major tea companies (Typhoo, PG Tips, Tetley) produced much smaller amounts of scum. There was little difference between these black tea products: the results of individual experiments at 80°C for 1 h ranged from 6.9 to 7.7 mg with an average of 7.4 mg. The amount of scum formed decreased rapidly with falling temperature. Standard infusions of new Typhoo teabags prepared at 80°C and rapidly cooled to 70°C produced only 2.6 ± 0.3 mg of scum after 1 h, equivalent to an activation energy of 107 kJ mol^{-1}.

Another batch of green Chun Mee tea, sieved to the range 250–850 μm, only formed 2.7 mg of scum, much less than the previous batch (Spiro & Jaganyi, 1994*b*).

Blank experiments with calcium carbonate and London mains water

Electron micrographs had shown that the tea scum contained islands of calcium carbonate ($CaCO_3$) (Spiro & Jaganyi, 1994*a*). This is not surprising since, in a blank experiment with 800 ml of mains tap water alone, $CaCO_3$ was observed to float on the surface. Its mass of 5.3 ± 0.8 mg after 1 h at 80°C was surprisingly large. The blank experiment was therefore repeated, but with the pH of the water first reduced from 8.2 to 6.83 by addition of some 7 ml of 0.1 M (mol dm^{-3}) HCl so as to correspond to the pH of tea infusions brewed in London mains water. The mass of $CaCO_3$ on the surface after 1 h at 80°C was now only 0.85 mg. This may be compared with the 1.4 mg of $CaCO_3$ associated with tea scum which, after 1 h at 80°C, had contained 6 wt% calcium, equivalent to 15 wt% $CaCO_3$ (Spiro & Jaganyi, 1994*a*). Thus the formation of organic tea scum had allowed a small increase in the simultaneous formation of $CaCO_3$.

A combination of these two experiments was then carried out. A $CaCO_3$ film was again allowed to form on 800 ml of mains water at 80°C for 1 h. The surface film was then blown over onto a second beaker which contained 800 ml of acidified mains water at 80°C at pH 6.85. The second beaker was allowed to stand for 1 h at 80°C, after which 1.8 ± 0.2 mg of $CaCO_3$ were collected from the surface. Most of the $CaCO_3$ film formed in the first beaker had therefore dissolved on the acidified water in the second beaker, probably as a result of the following reactions:

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \qquad (1)$$

and

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$

The reaction in Eq. (2) is the process by which water acquires temporary hardness on flowing through limestone beds.

Effect of calcium carbonate on tea infusions

The following experiments were designed to test whether the presence of $CaCO_3$ on the surface was the crucial factor leading to tea scum. First, a tea infusion was prepared in distilled water at 80°C where no scum is known to form. Some 7 ml of 0.1 M NaOH were then added to raise the pH from 4.96 to 6.84, the same pH as that of a standard tea infusion in mains water. An hour earlier, 800 ml of mains water alone had been allowed to stand at 80°C, and its surface layer of $CaCO_3$ was then blown over on to the distilled water tea brew. After a further hour at 80°C, the white surface layer was scooped off and weighed. Its colour indicated the absence of polyphenolic compounds and its mass was 5.7 ± 1.3 mg (four experiments), similar to that for the $CaCO_3$ film on mains water alone. Thus the blown-over $CaCO_3$ had simply remained on the surface, neither dissolving because of the absence of CO_2 nor leading to the formation of organic tea scum.

In a second set of experiments, the surface layer of $CaCO_3$ from 800 ml of mains water stood at 80°C for 1 h, was blown over on to a standard tea infusion which had just been prepared in mains water at 80°C. The resulting tea solution, of pH 6.88, was then allowed to stand at 80°C for 1 h. Observation of the surface showed two distinct regions, one formed by the blown-over $CaCO_3$ layer with a thick matt and slightly oily appearance, while the other covered a larger area of 'clear' infusion on which the usual shiny-looking tea scum was being generated. The mass of scum scooped off the whole surface was 12.2 ± 0.8 mg (six experiments). This was several milligrams greater than the scum formed in standard experiments, as expected from the additional $CaCO_3$. However, chemical microanalysis of the scum scraped off the sintered glass crucible gave only 5.9_1% calcium, which made us suspect that some of the white carbonate may have been retained in the porous glass filter. Accordingly, the experiments were repeated with crucibles which had been thoroughly cleaned with HCl to remove all previous carbonate. When the scum had been collected, dried and weighed, the whole crucible was treated with 1 M HCl to dissolve all carbonate from the scum and filter. The acid and wash water were then collected and analysed for calcium by inductively coupled plasma atomic emission spectroscopy. The washed crucible was dried again and weighed. As a test, the same procedure was also applied to scum collected from a standard mains water tea infusion using a similar (new batch) Typhoo teabag. The results are summarized in Table 1.

The figures show that about 84% of the mass lost on HCl washing can be accounted for by $CaCO_3$. The remainder will have been due to smaller amounts of magnesium, manganese and other metal carbonates and hydroxides present in the tea scum (Spiro & Jaganyi, 1994*a*). However, the calcium content in the standard tea scum obtained by the present procedure was 8.9_9% ($0.665 \times 100/7.4$), a larger figure than the 6.0_6% reported

Table 1. Analysis of tea scums formed after 1 h at 80°C from London mains water infusions

Property	Standard tea experiment	Blown-over tea experiment
Total mass of scum (mg)	7.4	13.8
Mass of HCl-washed scum (mg)	5.4	5.3
Loss on HCl treatment (mg)	2.0	8.5
Calcium (as $CaCO_3$) in HCl wash (mg)	1.66	7.21
Elemental analysis of HCl-washed scum (wt%)		
C	41.26	48.81
H	3.03	3.47
N	0.51	0.68
Ca	<0.2	1.64
P	<0.3	<0.3

previously. It therefore seems likely that in the earlier work some of the white $CaCO_3$ had remained behind in the sintered disc when scum was collected for analysis. Comparison of the two scums analysed in Table 1 now leads to several important conclusions. First, the extra mass of $CaCO_3$ in the blown-over experiment is $7.2_1 - 1.6_6 = 5.5_1$ mg, just the amount expected to have been transferred from the first beaker. Although the mains water acidified by the tea solubles will have contained CO_2 (Eq. (1)), it would appear that the floating $CaCO_3$ had been protected from dissolution via Eq. (2) by the formation of the organic scum layer next to it. This protection seems to have been mutual, with the partial shelter from the air provided by the $CaCO_3$ layer accounting for the lower percentage of oxygen (by difference) in the blown-over scum. The latter still contained some calcium, which may have been due to acid not having penetrated all parts of this larger sample. Nevertheless, it is striking that the mass of organic scum produced was essentially the same in both experiments, despite the much greater amount of floating $CaCO_3$ present in one case. It is therefore the calcium and bicarbonate ions in the water, rather than the $CaCO_3$ produced, which mediate the formation of tea scum.

Presence of bicarbonate, calcium, manganese and phosphate ions

As shown in the previous work (Spiro & Jaganyi, 1994*b*), tea scum always formed in the presence of calcium (or magnesium) ions, bicarbonate ions and a fairly high pH. To disentangle the latter two factors, a tea infusion had been prepared in distilled water containing 2.7 mM $CaCl_2$ and a borate buffer to control the pH but without added bicarbonate. This produced only 1.3 mg of scum after 1 h at 80°C, indicating that bicarbonate ions were needed to form scum (Spiro & Jaganyi, 1994*b*). However, bathochromic spectral shifts in solutions of phenolic compounds containing boric acid (Jurd, 1956; Häusermann & Brandenberger, 1961) suggest the possibility of complexation of boric acid with tea polyphenols which could have vitiated the above conclusion. Such complexation between the boron atom in the reagent flavognost and the 1,2-dihydroxy group in theaflavins is even used for spectrophotometric analysis of the latter (Spiro & Price, 1986). The experiment was therefore repeated, using added NaOH alone to raise the pH of the tea infusion in distilled water before making it also 2.72 mM in $CaCl_2$. After 1 h at 80°C the pH was 6.53 and only 0.55 mg of scum had formed. This result confirms that bicarbonate ions are essential ingredients for tea scum formation. The small amount of scum formed in the absence of added bicarbonate may have resulted from the dissolution of carbon dioxide and its conversion to bicarbonate ions.

Tea was also infused in distilled water containing 2.72 mM $CaCl_2$ and 2.72 mM Na_2SO_4, a composition resembling permanent hard water. The resulting pH was 5.18, but even such an acidic solution would have produced about 1 mg of scum had bicarbonate ions been present, according to the equation (Spiro & Jaganyi, 1994*b*):

$$\log_{10}(w) = 0.714\text{pH} - 3.758 \qquad (3)$$

where w is mass of scum in mg h^{-1}. In fact, no scum at all was observed, again indicating the need for bicarbonate ions in scum formation.

The analysis of tea scum had shown it to contain, not only calcium, but also just under 1 wt% manganese (Spiro & Jaganyi, 1994*a*). A tea infusion was therefore prepared in distilled water containing 2.72 mM $MnCl_2$ and 5.44 mM $NaHCO_3$. The resulting pH was 6.09 and only 1.95 mg of scum was produced, less than half the amount expected at this pH according to Eq. (3). Thus magnesium (Spiro & Jaganyi, 1994*b*) and manganese bicarbonates are both able to produce tea scum but to a much smaller extent than the calcium salt.

Phosphate is another species of importance in drinking water supplies as some companies add it to reduce plumbosolvency. Tea itself contains about 1 mg soluble P per gram of leaf (Natesan & Ranganathan, 1990), and during the period of study the phosphorus content of mains water averaged about 0.7 mg litre^{-1}. The resulting tea scum had been found to contain <0.4 wt% P (Spiro & Jaganyi, 1994*a*). The effect of adding an extra 2 mg P litre^{-1} (in the form of KH_2PO_4) to a standard mains water tea infusion was therefore investigated. Its pH of 6.88 was unaffected but the amount of scum was reduced by 30%. This is an unexpected advantage of phosphate addition.

Is tea scum mainly epidermal wax?

Lewin (1993) has postulated that the major components of the surface scum on tea are epidermal waxy lipids removed from the tea leaves by boiling water. No microscopic or analytical data were presented to support this hypothesis which was, in fact, contradicted by evidence provided earlier, and elaborated later, by Spiro & Jaganyi (1993), (1994*a*). In particular, the wax hypothesis does not explain why no scum forms when tea leaf is infused with hot distilled water, or distilled water containing $CaCl_2$, or distilled water containing $NaHCO_3$, or soft water, but always forms in temporary hard water containing both calcium and bicarbonate ions.

If the insoluble waxy lipids were responsible for tea scum, then virtually none should form in solutions of completely soluble instant tea. However, experiments conducted with 1.4 g and 2.0 g of PG Tips instant tea dissolved in 800 ml of mains water at 80°C produced quite large amounts of scum: 13.0 and 12.7 mg, respectively, after 1 h at a pH of 6.74. Chemical microanalysis of scraped-off scum gave $38.9_4\%$ C, $3.2_5\%$ H, $0.6_0\%$ N, $6.0_5\%$ Ca, $0.6_8\%$ Mg, $0.2_4\%$ Mn and $0.2_1\%$ P. The percentages of the first four elements are similar to those reported for the scum analysed previously (Spiro & Jaganyi, 1994*a*), but the instant tea scum contained rather more magnesium and less manganese.

As a further test, the tea leaves were removed from a Typhoo teabag, washed with two lots of 10 ml of hexane to dissolve surface lipids, filtered, and dried at 60°C for 48 h. The dried leaf was placed inside a stainless steel mesh bag to simulate a teabag, and infused as usual. This gave 6.2 mg of scum at a pH of 6.76. A blank experiment carried out in the same way, but without the hexane treatment, yielded 6.7 mg of scum, pH 6.81. Removal of surface wax from the leaves therefore had little effect on the amount of scum. Moreover, Bianchi (1994) has recently observed that boiling water does not take off any of the wax components from tea leaf cuticle. Taken together, all this evidence conclusively refutes the wax hypothesis.

Addition of lemon juice

Various amounts of filtered juice from a fresh lemon were added to tea liquor in mains water after the infusion period. With 2 ml of lemon juice, the pH of the infusion fell to 5.66 and the amount of scum was only 1.0 mg h^{-1}. Addition of 10 ml of lemon juice reduced the pH to 3.54, turned the colour to the yellow–orange hue typical of lemon tea, and no scum at all was produced. The masses of scum (w) expected purely from the decreases in pH, as calculated from Eq. (3), are 1.9 and 0.1 mg h^{-1} for the addition of 2 and 10 ml of lemon juice, respectively. The still lower experimental values can be explained by complexation of calcium ions in the hard water by the citric acid present to the extent of 0.22 M in lemon juice (Coultate, 1989). The addition of 10 ml of juice will have therefore given an overall citric acid concentration of 2.7 mM. As shown previously (Spiro & Jaganyi, 1994*b*), the addition of just 1 mM citric acid to a tea infusion was enough to suppress scum formation completely. Although lemon juice also contains 1.8 mM calcium and 2.9 mM magnesium ions (Holland *et al.*, 1991), these small concentrations will have had little influence on the results.

Addition of sugar

To a standard infusion at 80°C, 25.7 g of sucrose (BDH AnalaR) were added and the solution stirred for 30 s to dissolve the solid. This amount of sugar is equivalent to two cubes per cup of 170 ml or 3.11 wt%. The pH of the infusion was then 6.77 and 7.5 mg of scum formed in 1 h, 18% less than in a standard sugar-free experiment.

Interpolation of Hosking's data (Hosking, 1900) shows that the viscosity of an aqueous 3.11 wt% sucrose solution at 80°C is 5.8% higher than that of water at the same temperature. The viscosity of the medium (η) inversely affects the diffusion coefficient (D) of any large solute species (radius r) according to the Stokes–Einstein equation (Tyrrell & Harris, 1984):

$$D = kT/6\pi\eta r \qquad (4)$$

where k is the Boltzmann constant and T the absolute temperature. Thus one would have expected a decrease in the mass of scum of about 5.8% if the rate-determining step had been the diffusion of some critical component through the solution towards the surface. That the actual decrease in scum mass was several times greater confirms the previous conclusion (Spiro & Jaganyi, 1994*b*) that the process of scum formation is not controlled by mass transport. The large effect observed may well be due to partial complexation of calcium ions in the solution by the sucrose molecules (Briggs *et al.*, 1981).

ACKNOWLEDGEMENTS

We thank Anglian Water Services Ltd for a Research Bursary awarded to Y. Y. C., Dexter Nonwovens for a Research Bursary awarded to D. J., Premier Brands for supplying the Typhoo tea, and Dr B. Croll, Mr J. Murrer, Dr M. N. Clifford, Dr T. M. Hardman and Dr H. F. Jones for useful discussion.

REFERENCES

Bianchi, G. (1994). Tea cream or tea scum? *Chem. Br.*, **30**, 638.

Briggs, J., Finch, P., Matulewicz, M. C. & Weigel, H. (1981). Complexes of copper(II), calcium and other metal ions with carbohydrates: thin-layer ligand-exchange chromatography and determination of relative stabilities of complexes. *Carbohydr. Res.*, **97**, 181–188.

Coultate, T. P. (1989). *Food: The Chemistry of its Components*, 2nd edn. Royal Society of Chemistry, London, p. 168.

Häusermann, M. & Brandenberger, H. (1961). Plant phenols. IV. Spectrophotometric methods for determination of chlorogenic acids and their application to plant extracts. *Z. Lebensm. Unters. Forsch.*, **115**, 516–527.

Holland, B., Welch, A. A., Unwin, I. D., Buss, D. H., Paul, A. A. & Southgate, D. A. T. (1991). *McCance and Widdowson's The Composition of Foods*, 5th edn. Royal Society of Chemistry, Cambridge, pp. 76, 352.

Hosking, R. (1900). Viscosity of solutions. *Philos. Mag.*, **49**, 274–286.

Jurd, L. (1956). A spectrophotometric method for the detection of *o*-dihydroxy groups in flavonoid compounds. *Arch. Biochem. Biophys.*, **63**, 376–381.

Lewin, R. A. (1993). Waxy tea. *Nature*, **366**, 637.

Natesan, S. & Ranganathan, V. (1990). Content of various elements in different parts of the tea plant and in infusions of black tea from southern India. *J. Sci. Food Agric.*, **51**, 125–139.

Spiro, M. & Jaganyi, D. (1993). What causes scum on tea? *Nature*, **364**, 581.

Spiro, M. & Jaganyi, D. (1994*a*). Kinetics and equilibria of tea infusion. Part 10. The composition and structure of tea scum. *Food Chem.*, **49**, 351–357.

Spiro, M. & Jaganyi, D. (1994*b*). Kinetics and equilibria of tea infusion. Part 11. The kinetics of the formation of tea scum. *Food Chem.*, **49**, 359–365.

Spiro, M. & Price, W. E. (1986). Determination of theaflavins in tea solutions using the flavognost complexation method. *Analyst*, **111**, 331–333.

Tyrrell, H. J. V. & Harris, K. R. (1984). *Diffusion in Liquids*. Butterworths, London, p. 259.