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Kinetics and equilibria of tea infusion: Part 9. The rates and temperature coefficients of caffeine extraction from green Chun Mee and black Assam Bukial teas

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The rates of infusion of caffeine from green Chun Mee tea and from black orthodox Assam Bukial tea, using leaf of size 1·70–2·00 mm, were measured over a range of temperatures. The activation energies were found to be 62 and 40 kJ mol^{-1}, respectively. The diffusion coefficients of caffeine within the tea leaves, calculated from the first-order rate constants at 80°C, were respectively 96 and 132 times smaller than the diffusion coefficient of caffeine in water at 80°C. These results show that diffusion of caffeine through the leaf is a greatly hindered process.

INTRODUCTION

In previous papers in this series we have studied how the rate of extraction of caffeine from black tea leaf depends upon the leaf size and the manufacturing method (Price & Spiro, 1985*b*) and upon the composition of the aqueous extracting medium (Spiro & Price, 1987). The present paper compares the rates of caffeine extraction from large leafed black and green teas. For both teas the rate has been studied over a temperature range to provide data on the activation energy of caffeine infusion.

EXPERIMENTAL

The tea leafs investigated were green Chun Mee and black orthodox Assam Bukial FBOP. Both were sieved and the leaf fraction between 1·70 and 2·00 mm selected for study. The kinetic experiments were carried out with 200 cm^3 distilled and prewarmed water to which 4·0 g of tea leaf was added by means of a tea holder device (Spiro & Siddique, 1981). The mixture was stirred magnetically inside the thermostat bath. At least six samples of 1 cm^3 were removed at 30 s intervals with syringes fitted with stainless steel needles whose tips were protected by filter plugs to exclude leaf particles. An equilibrium sample was taken after 30–60 min and the equilibrium concentration corrected for evaporation and sampling (Spiro & Jago, 1982). All samples were diluted to 10 cm^3 in small standard flasks and analysed by hplc as described previously (Price & Spiro, 1985*a*). In the black tea experiments the hplc output was recorded on a Milton Roy CI4100 computing integrator. The columns were always calibrated with a series of solutions of known caffeine concentration.

The thicknesses of several water-swollen green and black tea leaves were measured with a micrometer, care being taken not to include any leaf veins or to squeeze the leaf.

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RESULTS

The variation of caffeine concentration, c, with time, t, was again found to follow first-order behaviour according to the equation

$$\ln\left(\frac{c_\infty}{c_\infty - c}\right) = k_{obs}\, t + a \qquad (1)$$

where c_∞ is the caffeine concentration at equilibrium. The mean c_∞ values for the green and black teas were 2·70 and 3·97 mmol dm^{-3}, respectively. The former was

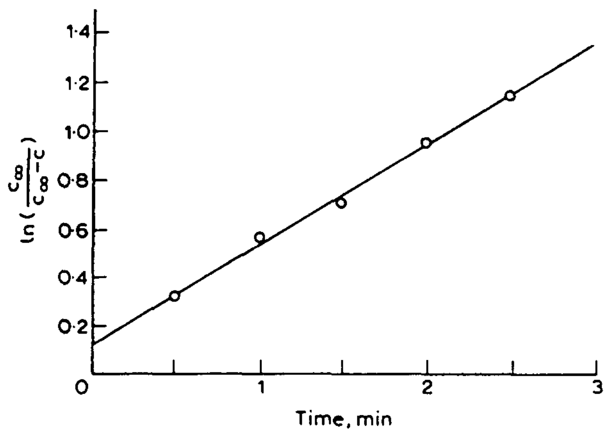

Fig. 1. Plot of ln $[c_\infty/(c_\infty - c)]$ versus t for the rate of extraction of caffeine from black Bukial FBOP leaf (1·70–2·00 mm) at 80°C.

essentially independent of temperature while the latter rose by 5% from 70°C to 90°C. Plots of the ln function against time were linear (as illustrated by Fig. 1) and yielded the rate constants k_{obs} and the intercepts a. The values obtained are summarised in Table 1. The uncertainties in k_{obs} are estimated as ± 3–4%. Three separate experiments with, respectively, 1, 3 and 4 g of green tea in 200 cm³ water yielded rate constants which agreed within these uncertainty limits while the intercepts agreed within ±0·05; neither parameter displayed any trend. The listed parameters were therefore independent of the (tea mass) : (water volume) ratio.

Application of the Arrhenius equation

$$\frac{d \ln k_{obs}}{d(1/T)} = -\frac{E}{R} \qquad (2)$$

where R is the gas constant, allows calculation of the activation energy E over the range of temperatures T (in Kelvin). Figure 2 shows that the Arrhenius equation satisfactorily fits the change in the rate constant of extraction over a wide temperature range. Least squares plots of ln k_{obs} versus $1/T$ lead to an activation energy of 61·6 ± 2·7 kJ mol⁻¹ for the green tea and 40·0 ± 2·5 kJ mol⁻¹ for the black tea. It is rather surprising

Table 1. Kinetic data for caffeine infusion from the two teas over a temperature range

Tea	Temperature (°C)	k_{obs} (min⁻¹)	Intercept
Green	63	0·21	0·04
	68	0·27	0·05
	74	0·33	0·10
	78	0·48	0·03
	83	0·71	0·21
	88	0·87	0·10
	92	1·17	0·17
Black	70	0·29$_1$	0·12
	80	0·41$_4$	0·13
	90	0·63$_2$	0·24

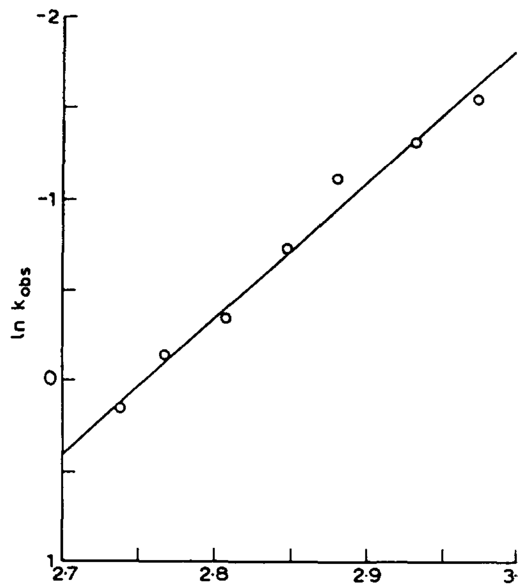

Fig. 2. Plot of ln k_{obs} versus $1/T$ for the extraction of caffeine from green Chun Mee tea.

that at around 80°C the rate constants for the two teas are so similar while the activation energies differ considerably. It would be interesting to see whether the same pattern is repeated for other green and black teas.

If the rate-determining step in the infusion process is the diffusion of caffeine through the swollen leaf, it follows from the steady-state model developed by Spiro and Jago (1982) that in dilute suspensions of leaf

$$k_{obs} = 2D_{leaf}/d^2 \qquad (3)$$

Here D_{leaf} is the effective internal diffusion coefficient of caffeine and $2d$ is the thickness of the swollen leaf regarded as a lamina. The means, and the standard deviations of the means, of $2d$ for the green and the black teas were found to be 0·137 ± 0·002 mm and 0·136 ± 0·002 mm, respectively. From the interpolated rate constant at 80°C for the green tea, 0·56 min⁻¹, and the above value for d, D_{leaf} for the green tea is found to be 2·2 × 10⁻¹¹ m² s⁻¹. Similarly, the diffusion coefficient of caffeine within the black leaf at 80°C is 1·6 × 10⁻¹¹ m² s⁻¹, very similar to the value of 1·8 × 10⁻¹¹ m² s⁻¹ reported for black orthodox Betjan FBOP tea (Price & Spiro, 1985*b*). These values may be compared with the experimental diffusion coefficient, D_{soln}, of caffeine in water at 80°C (Price *et al.*, 1989). This gradually decreases with increasing concentration but at 0·05 mol kg⁻¹, the lowest concentration measured and one which corresponds to the caffeine concentration in swollen black tea leaf, D_{soln} is 2·1 × 10⁻⁹ m² s⁻¹. Evidently caffeine diffuses much more slowly through swollen tea leaf than through water, with a hindrance factor at 80°C of 96 for the green tea and 132 for the black Bukial tea.

From the measured D_{soln} values of 0·05 mol kg⁻¹ caffeine at 65°C and 80°C (Price *et al.*, 1989), E may be calculated from eqn (2) to be 17·3 kJ mol⁻¹. Thus the activation energy for diffusion of caffeine in water is much lower than that for caffeine within tea leaves as would be expected from the fact that $D_{soln} << D_{leaf}$. Diffusion of caffeine through tea leaf is therefore a greatly hindered process, much more so than its diffusion through coffee beans (Spiro *et al.*, 1989).

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