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The temperature dependence of the rate of extraction of soluble constituents of black tea

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The temperature effect on the infusion of solubles from black tea leaf was examined by analysing the infusion characteristics of UV active solubles present in the tea leaf by spectrophotometric means. The results represent the first set of kinetic data for extraction of solubles from an Australian CTC tea (Nerada). From the experiments conducted, the activation energy for the infusion of solubles was determined to be 41 kJ mol^{-1}. This value is higher than previous ones in the literature. The results are discussed by comparing them with the temperature dependence for diffusion of species in aqueous solutions. The findings are consistent with the likely rate-determining step being the hindered diffusion of a soluble constituent through the leaf matrix.

INTRODUCTION

Tea is one of the most important food commodities in the world, and is made from the young leaves and leaf buds of the plant *Camellia sinensis*. The beverage prepared from the processed tea is made by infusing a quantity of leaf in boiling water. Elaborate ceremonies and customs have been established over the many thousands of years it has been consumed. Many of these pertain to the optimum conditions necessary for achieving perfection. It is thus surprising that little research had been carried out until the late 1970s on the rate of infusion of solubles from the tea leaf. This was remedied by the extensive studies by Spiro and co-workers.

Spiro introduced simple kinetic models (Spiro & Siddique, 1981*a,b*; Spiro & Jago, 1982) to explain the observed rates of extraction of individual constituents into aqueous solution. This type of model predicted simple pseudo first order kinetics which fitted the data extremely well. The steady state model (Spiro & Jago, 1982) shows that the overall observed rate constant may be broken up into three distinct parts reflecting the path taken by a constituent in the mass transfer process. These are:

(1) diffusion of the constituent through the leaf,
(2) partition across the leaf/water interface,
(3) diffusion through the Nernst layer.

A similar model was devised for the extraction of (approximately) spherical coffee grounds in aqueous solution (Spiro & Selwood, 1984). In the case of the coffee grounds, Spiro conclusively showed that the rate limiting step of the extraction process is the transport of the solubles through the particle to the surface (Spiro & Page, 1984; Spiro & Selwood, 1984). Although this has been shown to be the likely case for infusions of tea, it is difficult to prove this categorically because of the heterogeneous shape of a tea particle. If diffusion of the constituent through the leaf is rate-determining then the observed rate constant will depend on the thickness of the leaf. This is a parameter difficult to control or select accurately.

The objective of the current work is to investigate the temperature dependence of the extraction of soluble constituents from the tea leaf. This is done by simple spectrophotometric means. This enables the calculation of an activation energy for the extraction process. This value may be compared with existing literature values for the activation energies of specific constituents and also with the literature values for known diffusion processes. Comparison of these with the present results should shed light on the likely rate-determining step in the mechanism.

The work is also of relevance to the commercial extraction of tea solubles either for decaffeinated tea products or for 'instant' hot-water-soluble ones. The engineering design of extraction plants for tea products using aqueous media requires information of this kind.

MATERIALS AND METHODS

A small leaf Australian black tea, Nerada (Tea Estates of Australia Ltd, Innisfail, Queensland), was obtained

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commercially. It is manufactured using the modern cut-tear-curl (CTC) type technique. A large representative sample of the tea (2 kg) was sieved on a sieve shaker (Endecotts), with a standard set of sieves. The maximum fraction was the one that was retained on the 710 μm sieve but passed through the 850 μm sieve. This fraction was used for all the kinetic experiments.

Kinetic experiments were carried out at five temperatures from 25 to 65°C using a thermostatted water bath (Braun, Sydney). The bath temperatures, measured with a calibrated thermometer, are estimated to be constant to better than ±0·1°C and are accurate to better than ±0·5°C.

The procedure for the kinetic runs and sampling is similar to that described previously (Price & Spiro, 1985*b*). The tea (2·24 g) was added to 140 cm^3 of distilled water in a stoppered 250 ml conical flask equilibrated at the temperature of interest. Stirring of the mixture was achieved using a submersible stirrer and magnetic stirrer bar arrangement (Kartell, Italy). After addition, 1 ml samples were taken at intervals using a syringe and needle. Filters were used to ensure easy sampling and solid matter was excluded from the samples. Seven kinetic samples were taken as well as a sample when the reaction vessel had reached equilibrium. Preliminary experiments established the length of time necessary to achieve equilibrium for each temperature.

Corrections were made (for evaporation and sampling) to the concentration of the solubles of interest in the final equilibrium sample using methods detailed previously (Spiro & Jago, 1982; Price, 1985). The full correction term requires estimates of the partition of the solubles between the solution and the leaf. Partition coefficients for the solubles between the aqueous solution and the leaf matrix were not determined during this investigation. This leads to a small uncertainty in the equilibrium concentrations measured as is discussed later.

Samples were diluted (usually 1–10 or more) with distilled water and analysed with a UV-vis spectrophotometer (Shimadzu, Japan). This procedure was carried out immediately after the sample was taken and the average time between sampling and obtaining a spectrum of the diluted sample was less than 5 min. No signs of tea creaming were observed using this method, even for the lowest temperatures. The peak absorbance at 271 nm was taken to be a characteristic useful in describing the infusion kinetics. Preliminary experiments showed that, at the concentrations used, these UV-active constituents gave linear Beer–Lambert plots. In addition, variation in the wavelength of the peak maximum absorbance between samples was found to be small (less than 2 nm). Comparison of the spectra for the equilibrium samples at each temperature showed that there was very little discernible difference between them. Thus, although it is possible that the ratios of different absorbing species will vary at different temperatures, this was not obvious from the spectra.

RESULTS AND DISCUSSION

The concentration data for each temperature were analysed using Spiro's steady state kinetic model which predicts first order observed rate behaviour. This model has proved very successful for analysing extraction behaviour from foodstuffs. The concentration data fit an equation of the form:

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

where c_∞ is the measure of concentration at equilibrium and c is its value at any time t, k_{obs} is the observed first order rate constant and a is an intercept that is typically small but is not predicted by the model (Price, 1985). The present data fitted the Spiro model extremely well despite the fact that the measure of concentration they represent is an average of a wide range of constituents in the leaf. A typical first order rate plot is shown in Fig. 1. Table 1 shows the mean rate constant obtained at each temperature together with a measure of the uncertainty. Each result is based on at least three independent experiments. In addition the mean intercept, a, for each temperature is given together with an estimate of the uncertainty. The equilibrium concentrations were corrected for evaporation and sampling using equation (28) of the steady state model (Spiro & Jago, 1982). Partition coefficients for the ratio of the solubles concentration in the solution to that left in the leaf at equilibrium were not calculated in the present work. Thus the term in eqn (28) (Spiro & Jago, 1982) which involves this is ignored. For the conditions prevailing in the present experiments the resultant error in the value of ln $(c_\infty/c_\infty - c)$ is less than ±2% using literature values for the partition coefficients for specific constituents from black teas (Spiro & Siddique, 1981*a*; Price & Spiro, 1985*a*).

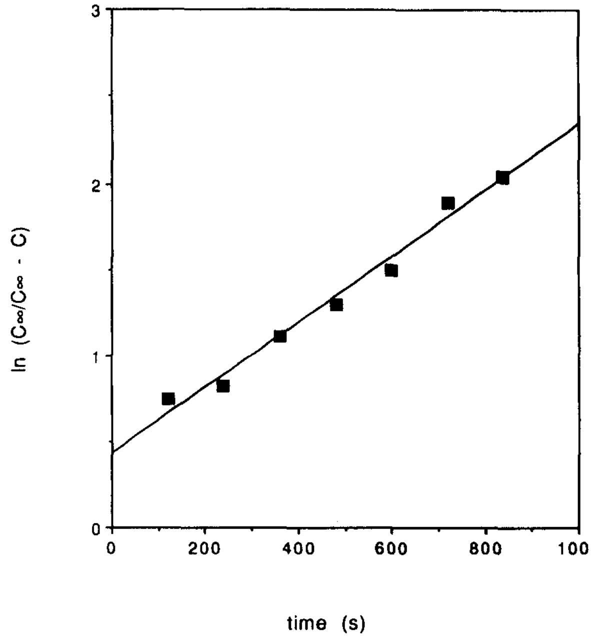

Fig. 1. First order rate plot for infusion of solubles from Nerada tea at 45°C.

Table 1. Kinetic data for the infusion of soluble constituents from Nerada tea leaf

Temperature (°C)	Mean k_{obs} ($\times 10^{-3}$ s^{-1})	Mean intercept *a*
25	1·041 (±0·001)	0·24 (±0·02)
35	1·80 (±0·80)	0·36 (±0·15)
45	2·70 (±0·33)	0·47 (±0·13)
55	5·19 (±0·14)	0·21 (±0·01)
65	6·26 (±0·18)	0·23 (±0·05)

Data in parentheses represent the standard deviations of the mean values.

These present data represent the first set of kinetic information for the extraction of solubles from an Australian black tea. From the mean rate constant data an Arrhenius plot showing the temperature dependence of the infusion process may be derived. This is shown in Fig. 2. A good line is obtained from which an activation energy of 41 (±3) kJ mol^{-1} is derived as shown from the equation below:

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

The only literature values (Spiro & Siddique, 1981*b*) are for the extraction of individual constituents, theaflavins and thearubigens (both 4 ± 4 kJ mol^{-1}) and for caffeine (1 ± 4 kJ mol^{-1}). The large difference between these values and the present ones may be ascribed to three reasons. First, the temperatures investigated by Spiro and Siddique were substantially higher than those reported here. It is not unreasonable to believe that the activation energy for the extraction process might be a function of temperature and decrease at elevated temperatures. However, it should be noted that in the present case a good linear fit was obtained over a wide temperature range. Second, the previous literature values were obtained from experiments at only two temperatures (79·5°C and 94°C). This practice is likely to lead to substantial errors. It must be remembered that the literature values are for individual components of black tea whereas the present work follows some average of the infusion process. It is hoped that the method adopted here has produced a predicted temperature dependence of the infusion characteristics that are representative for a small leaf (CTC manufacture) black tea. Support for this hypothesis comes from recent work by Spiro's group (Spiro, personal communication, 14 October 1991). For a black Assam Bukial tea they obtained an activation energy for the infusion of caffeine into aqueous solution of 40 kJ mol^{-1}, in excellent agreement with the present work. Spiro's value was obtained over a temperature range of 70–90°C. It is interesting that a similar activation energy was obtained for extraction of solubles over a very wide temperature range.

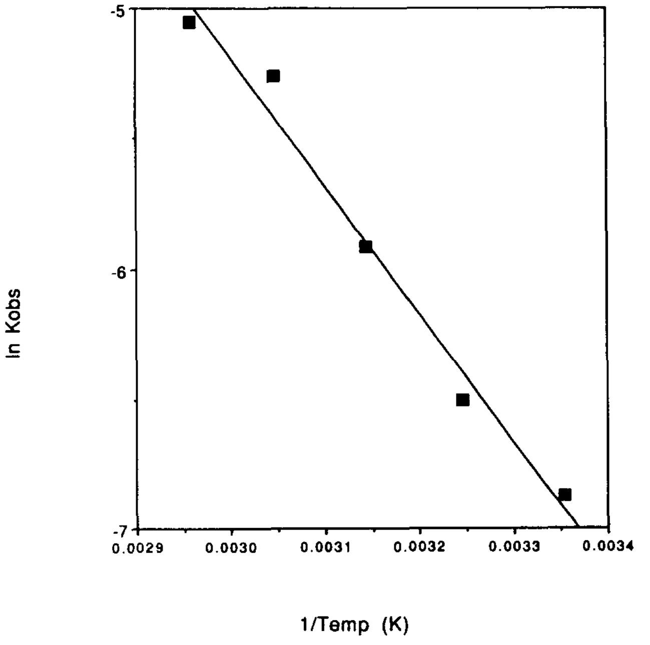

Fig. 2. Arrhenius plot for infusion of solubles from Nerada tea leaf.

This activation energy for the extraction process may be compared with other solution activation processes. If the controlling step of the infusion is diffusion of the constituents through the leaf matrix to the surface then it might be expected that the activation energy for extraction of a constituent would be similar in magnitude to activation processes for diffusion of species through solution. Easteal and co-workers (Easteal *et al.*, 1989) measured the self-diffusion of water at elevated temperatures and calculated an activation energy of 14–20 kJ mol^{-1} depending on the temperature. Price *et al.* (1989) determined the temperature dependence of the diffusion of caffeine through aqueous solutions. Over the temperature range considered, an activation energy for diffusion of nearly 18 kJ mol^{-1} was obtained. Caffeine is a major component of tea solubles, representing as much as 5% by dry weight of tea leaf. It has a peak absorbance at 273 nm (log ϵ_{max} = 3·99). In an ancillary experiment it was found that the contribution that caffeine makes to the total absorbance (at equilibrium) is more than 50% within the temperature range considered. This was done by extracting the caffeine from an equilibrated tea solution using chloroform. The measured values for the activation energy for the extraction process of around 40 kJ mol^{-1} are approximately twice that for the diffusion processes.

The values for activation energies for the extraction of tea solubles are very similar to that obtained for the temperature dependence of the extraction of caffeine from roast coffee grounds (Spiro & Selwood, 1984). These workers calculated an activation energy of 32 kJ mol^{-1} in this case. It is clear that, in both tea and coffee infusion, if the rate-determining step is diffusion of solubles through the matrix of the leaf/bean (for all temperatures) then additional factors hinder the extraction. This may be interpreted as a lowering of the diffusion coefficient inside the leaf matrix for a particular soluble compared with its value under the same conditions in aqueous solution. For caffeine infusing from coffee grounds, a number of possible reasons were put forward to explain this (Spiro & Selwood, 1984; Spiro *et al.* 1989). Similarly, for the case of fusion of solubles from black tea leaf, a number of likely factors contribute to the reduction of the diffusion of solubles through the leaf matrix. First, it is known that the rate of ingress of water into a tea leaf is the same order of magnitude (M. Izzard, personal communication) as the rate of infusion of tea solubles (contrary to the assumptions of the model). This counter-current flow will retard the outward diffusion of the tea solubles. Second, it is likely that physical restraints within the leaf matrix will lead to there being a tortuous path for diffusion of solubles. Again this would decrease the rate of infusion of tea solubles. For specific constituents it is also possible that there may be effects either of association with other solubles or with the internal surface of the leaf matrix. For example, caffeine is known to self-associate in aqueous solution, which has a direct influence on its diffusional behaviour (Price, 1989; Price *et al.*, 1989). It would be interesting to test these hypotheses using similar experiments to that used for coffee grounds (Spiro *et al.*, 1989).

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