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Kinetics of tea infusion: the effect of the manufacturing process on the rate of extraction of caffeine

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Abstract

The temperature effect on the rate of infusion of caffeine from South African black tea has been determined over a temperature range with the help of high performance liquid chromatography (HPLC). The activation energy was found to be 40.3 kJ mol^{-1} which is similar to the reports for other teas. The leaf size used was 1.40–2.00 mm. The rate constant at 80°C was determined to be 0.99 min^{-1} using a steady state model (Spiro and Jago, 1982). This value is slightly larger than the expected value for tea with similar particle size. Using the rate constants, diffusion coefficients of caffeine over a temperature range have been calculated. These have been compared with the corresponding values of caffeine in water at similar temperatures giving hindrance factors of 86 to 54 over the temperature range. These results indicate that the diffusion of caffeine through the leaf matrix is a greatly hindered process. A detailed comparison of kinetic and equilibrium data reported in the literature has been carried out between different teas manufactured through different processes. It is clear that the manufacturing method has a direct influence on the infusion of caffeine from the tea leaf. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

In recent years several studies have been published on the kinetics of infusion of solubles from loose tea leaves. The type of tea leaf used has mainly been from Kenya, India and Australia. The method of manufacturing of these teas is mainly crush, tear and curl (CTC), orthodox and green tea from China and Japan. The aim of this paper is to present rate constants and diffusion coefficients for the infusion of caffeine from South African black tea which is prepared by the Lawrie tea process (LTP). In addition, the activation energy and the temperature dependence of the hindrance factor for this tea were determined. Also of interest is the comparison of the rate constants of caffeine infusion from teas which have been subjected to different manufacturing processes. This is expected to shed light on the effect of the manufacturing method on the extraction process of tea solubles.

2. Materials and methods

The tea leaf used in this work was obtained from Richmond in Kwazulu Natal (South Africa). This was sieved into different sizes using a mechanical Endecott test sieve shaker. The fractional range selected for the experiment was 1.40–2.00 mm. For each kinetic run, 200 ml of distilled water was measured into a 250 ml conical flask. The flask, with the contents, was weighed before being transferred inside a thermostatic bath set at a particular temperature. The bath consisted of a thermostat (Thermomix 1441) which had variable temperature settings up to 150°C with an accuracy of ± 0.1°C. An independent thermometer reading 50–100°C with 0.1°C divisions was used to accurately measure the temperature of water in the conical flask. An immersion magnetic stirrer was incorporated into the water bath for stirring the mixture in the flask. The kinetic runs were carried out at five different temperatures ranging from 70 to 90°C.

When the set-up had equilibrated to the required temperature, exactly 4.0 g of tea leaves was added as quickly and uniformly as possible into the flask. This was achieved by using a simple wide-spout glass funnel, a modification of that used by Spiro and Siddique (1981). After the addition of tea leaves, 1 ml samples were withdrawn from the flask every 30 s for the first 3 min and then at longer time intervals. A total of 12 samples was withdrawn, the last equilibrium sample being after 60 min. The sampling was through a 1 ml

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syringe (Tuberculin Vernais) fitted with a 15 cm stainless steel needle having a Gilson filter (Anachem) at the tip to prevent withdrawal of any tea leaf. The 1 ml samples were transferred to vials containing 9 ml of distilled water.

High performance liquid chromatography (HPLC) was employed in the analysis of caffeine. The instrument used was a Waters 600E fitted with a reverse phase C_{18} Bondapak column, calibrated with known concentrations of caffeine (Fluka, HPLC grade). The detector (Waters 486) was set at 275 nm wavelength and the results recorded through a computerised recorder (Microsep M741). The mobile phase was made up of 10 vol% acetonitrile (BDH Hiper Solv™ for HPLC) and 90% vol. aqueous solution containing 0.5% w/v ammonium nitrate (UnivAR®), similar to that reported in the literature (Price and Spiro, 1985a; Jaganyi, 1993). To be able to calculate the diffusion coefficient of caffeine, the thickness of water-swollen leaves was measured with a micrometer, taking care not to squeeze the leaf which was free of veins.

3. Results

3.1. Rate constants

The concentrations obtained from HPLC analysis were corrected for volume lost due to sampling and evaporation (Spiro and Jago, 1982). A typical plot of concentration vs time yielded the curve shown in Fig. 1. The diagram shows an initial rapid increase in concentration tapering off towards the equilibrium concentration (c_∞).

Spiro's steady state kinetic model (Spiro and Jago, 1982) which predicts first order behaviour was used to analyse the concentration data, which fitted an equation of the form:

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

where c_∞ is the concentration of caffeine at equilibrium and c is the concentration at any time t, k_{obs} is the observed first order rate constant and a is an intercept not predicted by the model. Fig. 2 shows one of the first order rate plots obtained. The results are based on an average of three independent experiments. The average kinetic data are summarised in Table 1.

3.2. Diffusion coefficient

It has been shown through coffee studies (Spiro and Selwood, 1984) that the rate-determining step in the infusion process is the diffusion of caffeine through coffee beans. Applying the coffee finding to tea, it can be concluded that the rate determining step is the infusion of caffeine through the swollen leaf. This cannot be proved experimentally due to the fact that the thickness of the leaf cannot be varied. Therefore, from the steady-state model (Spiro and Jago, 1982), the observed rate constant can be expressed as in Eq. (2) assuming that the infusion is dilute.

$$k_{\text{obs}} = 2D_{\text{leaf}}/d^2 \tag{2}$$

The effective internal diffusion coefficient of caffeine is denoted by D_{leaf} while the thickness of the swollen leaf is

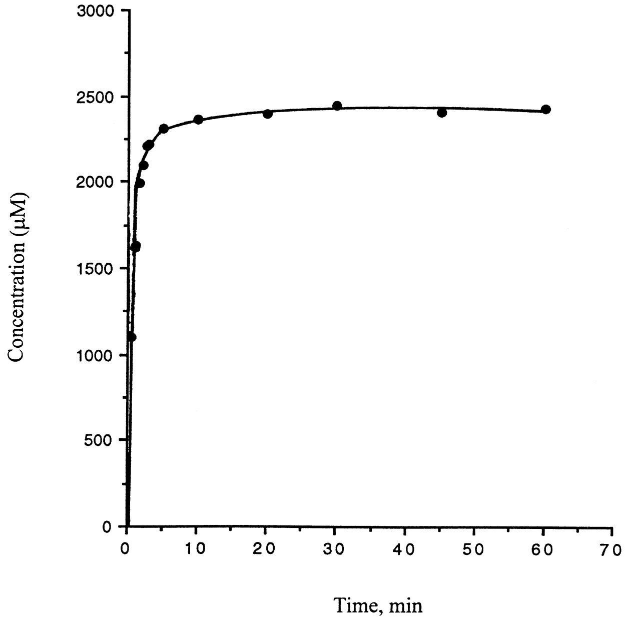

Fig. 1. A plot of caffeine concentration vs time for a South African black tea infusion.

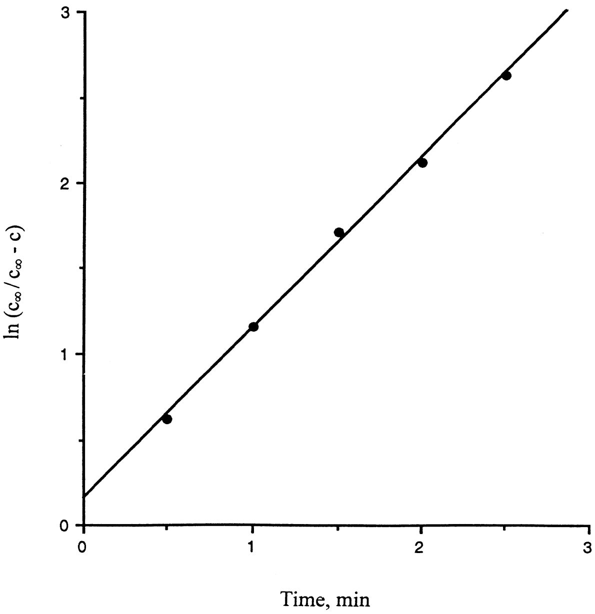

Fig. 2. Kinetic plot for the infusion of caffeine from South African black tea.

2d. An average of 10 tea leaves was used to determine the thickness of the leaf. The mean value and the standard deviation of the leaf thickness were found to be 0.129 ± 0.003 mm. The diffusion coefficients of caffeine within the tea leaf, D_{leaf}, for each temperature were calculated using Eq. (2). The results are tabulated in Table 2. To add meaning to these values, they were compared with diffusion coefficients of caffeine in aqueous solution, D_{aq}, at the same temperature. These D_{aq} values were obtained by fitting Price's data (Price et al., 1989) into a quadratic equation in temperature (T°C).

$$D_{\mathrm{aq}} = 0.5804 \times 10^{-9} + 1.3625 \times 10^{-12} T + 2.2129 \times 10^{-13} T^2 \tag{3}$$

The values used to generate Eq. (3) were all adjusted so as to represent the intradiffusion value for caffeine at 0.05 mol kg^{-1}. This concentration corresponds to that of caffeine in a swollen black tea leaf (Spiro et al., 1992). Included in Table 2 are the corresponding hindrance factors (HF) calculated using Eq. (4)

$$\mathrm{HF} = D_{\mathrm{aq}}/D_{\mathrm{leaf}} \tag{4}$$

3.3. Activation energy

The activation energy E_a was calculated using the Arrhenius equation

$$\ln(k_{\mathrm{obs}}) = -E_a/RT + \ln A \tag{5}$$

where k_{obs}, R, T and A are the observed rate constant, gas constant, temperature (kelvin) and pre-exponential factor, respectively. A plot showing the temperature dependence of the infusion process was obtained by plotting $\ln(k_{\mathrm{obs}})$ against $1/T$. This produced a straight line as shown in Fig. 3, from which an activation energy of 40.3 ± 3 kJ mol^{-1} was derived. The activation energy of D_{leaf} will be the same as for k_{obs}, namely 40.3 kJ mol^{-1} since the rate constant is proportional to the diffusion coefficient. This value was compared with a corresponding activation energy of caffeine in water which was determined to be 9.6 kJ mol^{-1} from the plot of $\ln(D_{\mathrm{aq}})$ vs $1/T$ as depicted in Fig. 4.

Table 1
Kinetic and equilibrium data for caffeine infusion from South African black tea over a temperature range

Temperature (°C)	$k_{\mathrm{obs}}/10^{-2}$ s^{-1}	c_∞/ppm	a
70	0.98	2472	0.27
75	1.27	2596	0.21
80	1.65	2664	0.14
85	1.88	2659	0.12
90	2.23	2688	0.17

Table 2
Diffusion coefficient and hindrance factors for caffeine over a temperature range

Temperature (°C)	$D_{\mathrm{leaf}}/10^{-11}$ m^2 s^{-1}	$D_{\mathrm{aq}}/10^{-9}$ m^2 s^{-1}	HF
70	2.04	1.76	86
75	2.64	1.93	73
80	3.43	2.11	62
85	3.91	2.30	59
90	4.64	2.50	54

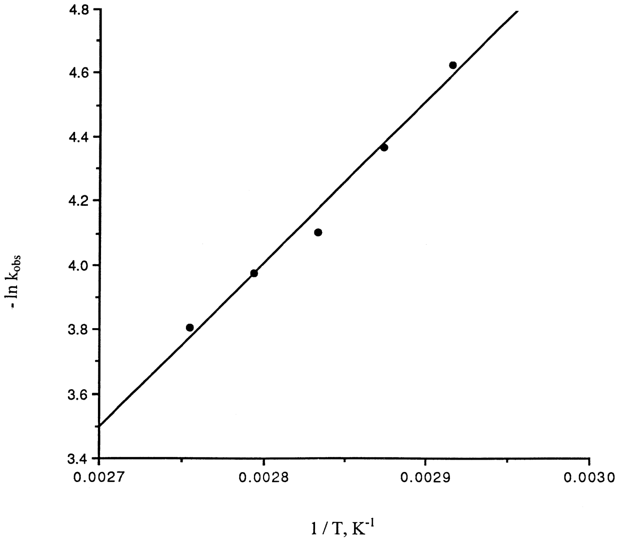

Fig. 3. Arrhenius plot for the extraction of caffeine from South African black tea.

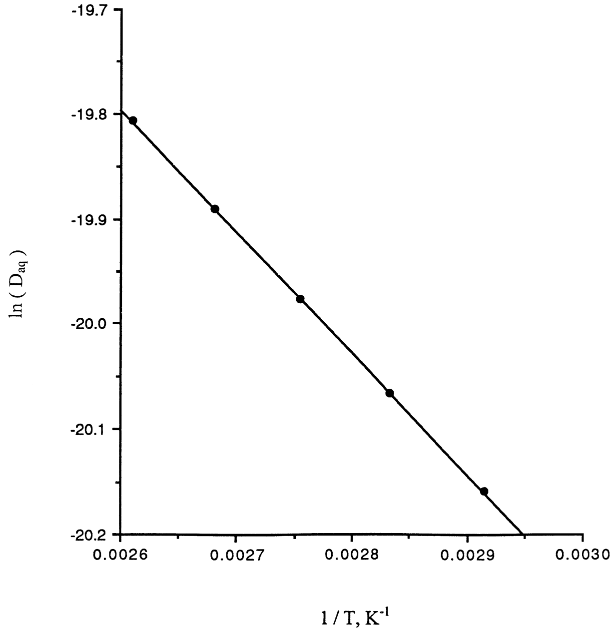

Fig. 4. Plot of ln D_{aq} vs $1/T$ for the diffusion of caffeine in water.

Table 3
Kinetic and equilibrium data for caffeine infusion from different teas manufactured by different processes

Tea type	Process	k_{obs}/min^{-1} at 80°C	c_∞ (mM)	E_a/kJ mol^{-1}
Nevada	CTC	ca. 0.34	—	39.0
KPF[a]	CTC	ca. 0.62	3.08	—
ABFBOP[b]	Orthodox	ca. 0.48	3.97	40.0
Chun Mee	Green	ca. 0.63	2.70	61.6
Uji Tsuyu	Green	ca. 1.03	—	59.0
South African	LTP	0.99	2.66	40.3

[a] KPF = Kapchorua Pekoe Fannings (Price and Spiro, 1995b).

[b] ABFBOP = Assam Bukial Flowery Broken Orange Pekoe (Spiro et al., 1992; Spiro and Lam, 1995).

4. Discussion

The rate constant obtained in this work of $1.65\times10^{-2}\,s^{-1}$ at 80°C is equal to $0.99\,min^{-1}$. The expected value for CTC Kapchorua Pekoe Fannings (Price and Spiro, 1985b) from Kenya for a similar leaf size would be ca. $0.62\,min^{-1}$ and an average of ca. $0.48\,min^{-1}$ (Spiro and Lam, 1995; Spiro et al., 1992) for the Orthodox Assam Bukial FBOP. Looking at the data for green tea, the corresponding value for Chinese Chun Mee tea (Spiro et al., 1992) should be ca. $0.63\,min^{-1}$. The value cannot be compared with that for the Australian Nevada tea (Price and Spitzer, 1993) because their rate constant was for a mixture of tea solubles, not only caffeine. Regarding the Japanese Sen Cha Uji Tsuyu (Price and Spitzer, 1994), the expected rate constant is ca. $1.03\,min^{-1}$ for tea leaf of similar particle size. This value agrees well with that obtained in the current work. Kinetic and equilibrium data of the various teas discussed are compared in Table 3. The above comparisons indicate that caffeine infuses faster from South African tea as compared with all the other black teas. This is also true in the case of Chun Mee but, with regard to Uji Tsuyu, the values are very similar while their activation energies are quite different. This pattern is similar to that found by Spiro et al. (1992).

Comparing the activation energies, a pattern seems to emerge. All the black teas, irrespective of the manufacturing process, have a similar value for the activation energy which is approximately $40\,kJ\ mol^{-1}$ while the value for green teas is approximately $60\,kJ\ mol^{-1}$. These values are respectively four and six times larger, as compared to that of diffusion of caffeine in water. This shows, as expected, that the diffusion of caffeine through swollen tea leaf is a hindered process.

The rate of extraction clearly indicates that the manufacturing process does influence the infusion of caffeine from the tea leaf. The activation energy separates the teas into two groups, the green and the black teas whose processes of manufacturing are different. It can be argued that the difference observed is due to the differences in the 'leaf' matrix since the teas compared are from different geographical regions. It would be interesting to subject a particular type of tea leaf to different manufacturing process and then repeat the investigation.

The determined D_{leaf} values are smaller by factors of 50–90 in comparison with the corresponding D_{aq} values. These low values are an indication that the diffusion process of caffeine within the leaf is greatly hindered. The temperature dependence of the diffusion coefficient of caffeine within the tea leaf is tabulated in Table 2. The value of D_{leaf} doubles in magnitude from 70 to 90°C while the hindrance factor decreases by 37%. This effect can be explained by looking at the factors which cause a slower diffusion of caffeine through the tea leaf. These have been listed for the coffee bean (Spiro et al., 1989; Spiro and Chong, 1997). The delay involved in the dissolution of caffeine inside the leaf, as the hot water reaches it, will decrease with increase in temperature. Moreover, the higher the temperature of water, the faster is its penetration ability. A high temperature is likely to cause dissociation of caffeine complexes with other solubles which might have associated to form bulky and slow-moving entities. The adsorption of caffeine on the leaf matrix is also likely to decrease with increase in temperature. A combination of all these factors together is reflected in the increasing diffusion coefficient and the decreasing hindrance factor as the temperature increases.

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