Kinetic study of mineral ion extraction from Kenyan Arabica coffee

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Abstract: The rate of infusion into distilled water of caffeine and of Mg, Mn, K and P have been measured. The coffee used was roasted Kenyan Arabica coffee, ground, and sieved to a size range of 1.70–2.00 mm. The analytical techniques employed were HPLC for the analysis of caffeine and ICP-AES for analysing mineral ions. The kinetic data have been interpreted in terms of a steady-state theory, and the rate constants of infusion have been calculated. The diffusion coefficients of the various species within the bean were calculated from the resultant rate constants. These values have been compared with the corresponding diffusion coefficients in pure water at 80°C and the hindrance factors in the bean have been determined.
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INTRODUCTION

Previous papers on the kinetics of coffee infusion have concentrated on the rate of extraction of caffeine.[1] The hindrance effect on caffeine infusion has also been investigated.[2,3] There have been no studies on the extraction kinetics of mineral ions. The present paper determines the rates of extraction of mineral ions and compares them with that of caffeine. This comparison, especially between caffeine and potassium, is likely to shed light on the infusion of the caffeine–potassium chlorogenate complex.

EXPERIMENTAL

The coffee used was Kenyan medium-roasted Arabica coffee beans commercially obtained. These were ground and sieved by means of an Endecott test sieves. Coffee particles of size 1.70–2.00 mm were chosen for this investigation. All the apparatus used was plastic except for the 100 ml burette which was used for the preparation of standard solutions. All the apparatus were cleaned with Extran detergent (Merck) which was washed off, then rinsed with 0.1 M HCl (BDH Aristrar) solution. Finally, the apparatus were rinsed with Milli-Q water (Millipore).

The kinetic experiments were carried out in a thermostatted waterbath using a Julabo thermostat circulator, with a temperature stability of ± 0.02°C. The bath was left to equilibrate to the desired temperature. Using a holder device,[4] a known amount of coffee (4 g) was added to 200 ml of Milli-Q water. The container used was a plastic conical flask with a screw top, which had two holes. One hole was used for the thermometer and the second opening accommodated a narrow plastic tube which reached down into the coffee infusion. The plastic tube was used to sample the coffee liquor by means of a plastic syringe without using a needle. The end of the tube in the flask had a U-shaped end. This was used to hold a Gilson filter (Anachem) to prevent the uptake of coffee particles. The filter was replaced after each experimental run. Before sampling, air in the syringe was used to flush the tube and the filter. The weight of the flask and its contents was determined before and after each experiment, for the purpose of correcting the concentrations due to volume lost through sampling.[5,6] The mixture was stirred by means of an immersible magnetic stirrer.

Samples were withdrawn at 30 s intervals for the first 3 min and then at 60 s up to 5 min. Afterwards, the time interval was lengthened, the equilibrium sample being taken after 90 min. The samples withdrawn were diluted ten times, with 9 ml of Milli-Q water. All the experiments were performed in duplicate and the average results recorded.

The analysis of the sample for caffeine was carried out using high-performance liquid chromatography (HPLC). The mobile phase and the procedure applied was similar to that of Spiro and co-workers.[7] The column used was a reverse-phase C_{18} Bondapak, while the instrument was Waters 600E. The detector (Waters 486) was set at a wavelength of 275 nm and the HPLC output was recorded on a Microsep M741 computing integrator. The column was calibrated with a series of caffeine standards.

Determination of mineral ions was by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The instrument make was Varian Liberty AC150 Turbo. Using the ICP-rapid scan programme, it was possible to determine the approximate concentrations of the various mineral ions in the bean. Twelve elements – Mg, Mn, P, K, Ba, Na, Cu, Ca, Zn, Fe, B and Sr – were chosen from the preliminary analysis of the rapid scan for kinetic runs. To monitor the kinetic runs, solutions of known concentration containing all the chosen elements were prepared and used as standards. Calibration graphs with a correlation coefficient of not less than 0.995 were generated and used in the analysis. Before the addition of coffee into the flask a sample of plain water was withdrawn and used as a blank.

RESULTS AND DISCUSSION

Plots of concentration (C) against time (t) for various solubles had a steep rise initially then tailed off towards an equilibrium concentration (C_∞). A typical graph is shown in Fig 1.

Using the steady-state theory,[1] the kinetic data were found to fit the first-order kinetic equation with small y-intercepts (a).

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

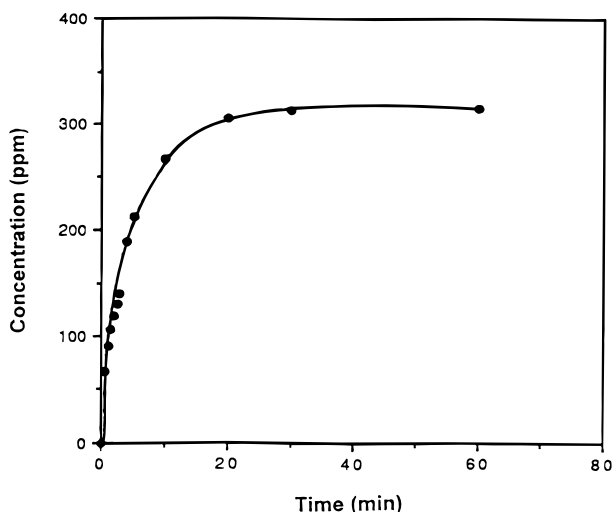The first-order rate constant is denoted by k_{obs} (Table 1).

Figure 1. Plot of concentration vs time for the extraction of potassium from coffee (1.70–2.00 mm) at 80°C.
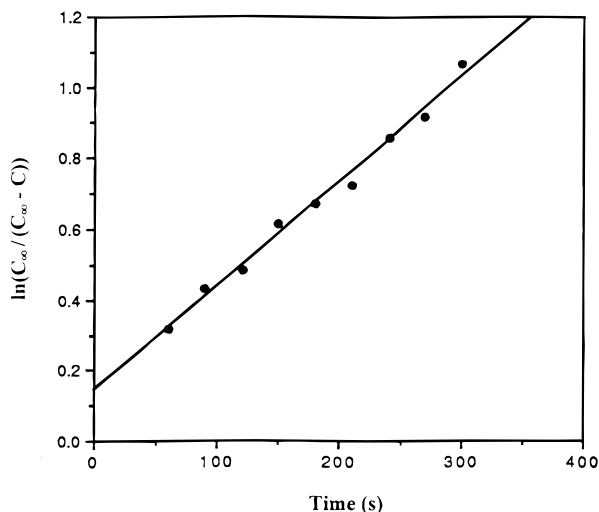

Figure 2. Plot of $\ln(C_\infty/(C_\infty - C))$ vs time for the rate of extraction of caffeine from coffee (1.70–2.00 mm) at 80°C.

Rate constants

Inspection of the rate constant results summarised in Table 1 shows that the first-order rate constants differ for different species except for the double charged ions Mn^{2+} and Mg^{2+} with similar magnitude. The intercept value for all the species are comparable. The caffeine average retention time was 4.93 min. The caffeine analyses were carried out for comparative purposes with the ionic species. The rate constant obtained for caffeine at 80°C is $2.67 \times 10^{-3}\,s^{-1}$ for 1.70–2.00 mm particles. Spiro and Selwood's[1] value was $9.0 \times 10^{-3}\,s^{-1}$ for 0.85–1.18 mm particles at 84.1°C. Interpolating their value to 80°C gives $7.94 \times 10^{-3}\,s^{-1}$. The radius of Spiro's bean particles was 507.5 μm while in the present work it is 925 μm. Substituting these values into eqn (2), Spiro's value of $7.94 \times 10^{-3}\,s^{-1}$ can be corrected to our average particle size: $7.94 \times 10^{-3}\,s^{-1} \times (507.5/925)^2 = 2.39 \times 10^{-3}\,s^{-1}$. This value is only about 10% smaller than our value. For different coffee supplies, these results agree very well.

Out of the 12 elements chosen for kinetic study, only four (Mg, Mn, K and P) fitted the Spiro model. A typical first-order plot is shown in Fig 2. Since the pH of coffee infusion was 4.5, the major orthophosphate ion which has been analysed as phosphorus will have been $H_2PO_4^-$.

Diffusion coefficients and hindrance factors

In deriving the kinetic theory using the steady-state theory of extraction,[1] the observed rate constant has been shown to be made up of three terms. Out of these the diffusion through the bean particle is the

Species	k_{obs} ($10^{-4}\,s^{-1}$)	Intercept	C_∞ (ppm)	C_∞ (mM)
Caffeine	26.7 (±1.0)	0.15	262.6	1.35
K^+	44.2 (±1.4)	0.24	195.4	5.35
Mn^{2+}	6.22 (±0.6)	0.08	0.8	0.014
Mg^{2+}	9.81 (±0.9)	0.12	25.6	1.05
P as ($H_2PO_4^-$)	15.3 (±1.5)	0.10	18.9	0.61

Table 1. Rate constants ($\pm$ SD) and equilibrium data for the infusion of caffeine and mineral ions at 80°C

rate-determining step. As a result, k_{obs} from eqn (1) can be expressed as shown in eqn (2).

$$k_{obs} = \frac{12D_{bean}}{r^2} \qquad (2)$$

where r is the radius of the bean particles assumed to be of uniform spheres, and D_{bean} is the diffusion coefficient of the various species in the coffee beans. Using eqn (2), the diffusion coefficient of caffeine and of the various mineral ions were calculated. These results are listed in Table 2. The radius of the particle was taken to be 925 μm. This value was obtained by taking the average radius of 1.70 mm and 2.00 mm, being the range of the bean particle size used.

For these values to have any meaning, they need to be compared with their diffusion coefficient, in aqueous media at the same temperature, D_{aq}. The aqueous data available at 80°C in the literature are of caffeine[8] and for K^+, Mg^{2+} and P as ($H_2PO_4^-$) the values are tabulated in Table 4 of Ref 9.

To determine the limiting tracer diffusion coefficient for Mn^{2+} the Nernst equation was used:

$$D_{aq} = RT\lambda^\circ / |z| F^2 \qquad (3)$$

where F is the Faraday constant, R the gas constant, z represents the ionic charge number, T is the temperature in Kelvins (in this case, 353.1 K) and λ° is the limiting equivalent conductance. The limiting equivalent conductance for Mn^{2+} is only available at 25°C.[10] As a result, the Walden rule given by eqn (4) was used to estimate the λ° value for the ion.

$$\lambda^\circ \eta = \text{constant} \qquad (4)$$

where η is the viscosity of water.[11] The limiting tracer diffusion coefficients for the various species in aqueous media are tabulated in Table 2.

To be able to compare how hindered the different species are during infusion inside the bean particles, the hindrance factors, HF, were calculated using eqn (5):

$$HF = D_{aq}/D_{bean} \qquad (5)$$

Inspection of Table 2 shows that the largest hindrance factor is four times bigger than the smallest. The results indicate that the neutral caffeine

Table 2. Diffusion coefficient and hindrance factors for caffeine and mineral ions at 80°C

Species	D_{bean} ($10^{-11} m^2 s^{-1}$)	D_{aq} ($10^{-9} m^2 s^{-1}$)	HF
Caffeine	19.0	2.2	12
K^+	31.5	5.0	16
Mn^{2+}	4.4	2.1	48
Mg^{2+}	7.0	2.0	29
P as ($H_2PO_4^-$)	10.9	2.6	24

migrates out of the bean much faster than the ionic species, an indication that the charged species are held back through some kind of bonding within the bean matrix. Looking at caffeine, Mn^{2+} and Mg^{2+}, their hydrodynamic radii in water are almost the same since their D_{aq} values are very similar. However, their HF are quite different, with that of Mn^{2+} being four times and twice as large as that for caffeine and Mg^{2+}, respectively. The difference in HF between Mn^{2+} and Mg^{2+} is most likely due to the nature and strength of bonding in forming complexes with the polyphenols or other constituents within the bean matrix. Manganese being a transition metal will tend to form mainly strong covalent bonds with the ligands. As a result it is more hindered compared with magnesium, which is likely to be attached by coulombic attraction.

Comparing our mineral ion results with those obtained in Ref 9 for extraction from black and green tea, the diffusion coefficients for the three ions K^+, Mg^{2+} and $H_2PO_4^-$ from coffee are 3.5 to 16 times bigger in magnitude compared to the corresponding ions in tea while the opposite is true for the hindrance factors. It can therefore be concluded that the diffusion of mineral ions as well as caffeine through tea leaf is a much more hindered process than its diffusion through coffee bean.

Spiro and co-workers[2] have found that the inward flow of water into the bean, the swelling of the bean, the delay involved in the dissolution of caffeine inside the bean and association of caffeine with other compounds contributes only 43% of the hindrance factor. The association of caffeine with itself has been shown not to be the reason for the slow infusion rate of caffeine from the coffee bean.[3] However, its complexation with other coffee solubles is believed to play a significant role. It therefore means that the slow diffusion of caffeine and mineral ions is mainly due to the physical restraint inside the endosperm.[2,12] This restraint causes the species to follow a tortuous passage within the bean particle during infusion.

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