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Kinetics of coffee infusion: a comparative study on the extraction kinetics of mineral ions and caffeine from several types of medium roasted coffees

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Abstract: A comparative study of the equilibrium concentrations, rates of infusion and intra-bean diffusion coefficients of caffeine, P (as $H_2PO_4^-$), K^+, Mg^{2+} and Mn^{2+} in Milli-Q-Water at 80 °C was carried out. Medium roasted coffees of particle size range 1.70–2.00 mm from six different countries—Special Kenya (Kenya), Santos (Brazil), Blue Mountain Java (Sumatra), Mocha (Ethiopia), Zimbabwe (Zimbabwe) and South African Grown (South Africa)—were used in the investigation. High-performance liquid chromatography was used for the analyses of caffeine, and inductively coupled plasma atomic emission spectrometry for the chosen elements. The equilibrium concentrations of all the species and the trend were found to be independent of the various coffee beans. The order of the rate of infusion was found to be $K^+ >$ caffeine $>$ P (as $H_2PO_4^-$) $> Mg^{2+} > Mn^{2+}$. Examination of the rate constants clearly indicated that P (as $H_2PO_4^-$), Mg^{2+} and Mn^{2+} cannot be used for identification of the coffee origin, but the values for caffeine and K^+ can be used. Diffusion coefficients of caffeine and mineral ions were calculated in two separate ways using rate constants and half-lives of infusion. These were then compared with known diffusion coefficients of the same species in water for determination of hindrance factors. The hindrance factor for caffeine was found to be much smaller than the corresponding factors recorded at 25.5 °C. In general the hindrance factors in the bean were all of the order of 10, with Mn^{2+} being the most hindered species. This is an indication that the infusion of the various species through the coffee bean is a hindered process. This is because of the association of caffeine and mineral ions with other coffee solubles and the physical restraint within the bean matrix.
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Keywords: coffee; caffeine; mineral ions; extraction kinetics; diffusion coefficient

INTRODUCTION

Coffee beans (Arabica and Robusta) contain a variety of different elements, of which potassium represents the largest proportion. In addition, other metallic elements found in reasonable quantity are magnesium and calcium, while the non-metallic elements are mainly phosphorus and sulphur. The other mineral ions exist in trace amounts. Numerous workers[1–4] have found that the mineral content of coffee beans depends upon the country of origin, a factor which is associated with the soil conditions. The other factor is the method of processing the green coffee, whether subjected to the wet or the dry method.[1,5,6] Clarke and Walker[7] have shown that soaking of coffee beans during the fermentation and washing stages causes potassium to diffuse out, resulting in a wide range of potassium contents in coffee beans. The mineral constituents in coffee beans are not lost during the roasting process, except for sulphur and phosphorus to a small degree.[1] It is also believed that minerals act as catalysts during roasting and during the various biochemical transformations in the plant. Arabica cannot be distinguished from Robusta by determination of mineral ions, as indicated by Kroplien's data.[8] However, recent work[9] has shown that the mineral content can be related to the origin of the green coffee and can be used as a tool for characterising coffee varieties.

A subject that has received very little attention until recently is the kinetics of extraction of mineral ions.[10] Even for caffeine there is no comparative study to determine whether the rate of extraction is dependent on the coffee species, the blend of coffee or the country of origin. This paper presents a comparative study of the extraction of caffeine and mineral ions from coffees from six different geographical regions. It was hoped that the kinetic and diffusion data could be used to distinguish the origin of each coffee bean or to shed

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some light on the differences or similarities of the beans.

EXPERIMENTAL

The coffee beans investigated were medium roasted Arabica or Robusta types, namely Kenyan Special, Sumatran Blue Mountain Java, Brazilian Santos, Ethiopian Mocha, Zimbabwean coffee and South African Grown (Colombo Coffee and Tea Co, Durban). A Glen Creston mill equipped with an agate mortar and pestle was used to grind the coffee beans, which were later sieved through a standard set of stainless steel Endecotts sieves using an Endecotts sieve shaker machine. The sieved fraction between 1.70 and 2.00 mm was selected for the study. All containers used were made of plastic, and the water was demineralised Milli-Q-Water (Milli-Pore). The cleaning process involved using Extran detergent (Merck), which is phosphate-free, then rinsing the apparatus with a 0.1 M HCl (BDH Aristar) solution. This precaution was necessary because of the determination of mineral ions.

A plastic conical flask containing 200 ml of water equilibrated to 80 °C in a thermostatically controlled water bath was used in all the kinetic experiments. The lid of the flask had two holes, one for the thermometer and the second for the sampling tube made out of a thin plastic material. On the outside of the flask the sampling tube was attached to a 2 ml sabre syringe, while on the inside the end of the tube had a hollow plastic cone to which a Gilson filter (Anachem) was inserted so as to exclude coffee beans and particulates during sampling. It has been found[11] that simply dropping tea leaves into hot water tends to give irreproducible results. Because of this, 4 g of coffee beans were quickly added to the 200 ml of water via a long wide-spout glass funnel. The stopwatch and the immersible magnetic stirrer attached to the water bath were started as soon as the coffee was added.

Samples (1 ml) were withdrawn at 0.5 min intervals for the first 5 min, and the last equilibrium sample after 90 min. The samples taken were transferred into 20 ml plastic sample bottles containing 9 ml of water and mixed thoroughly. After each sampling, the sample tube was cleaned of any solution by attaching a clean syringe and injecting air through it and the filter. Corrections were made to the concentration of the solubles[12,13] for volume lost through sampling and evaporation by weighing the flask and the contents before and after each run.

Reverse phase high-pressure liquid chromatography (HPLC) was used for the analyses of caffeine. The instrument employed was a Thermo Separation Products fitted with a Spectra System UV 3000 (Scanning) detector which was set at 275 nm. The column used was a Waters Nova-Pak® C18 60 Å 4 μM which was calibrated with known concentrations of caffeine (Fluka). The mobile phase used was similar to that of Jaganyi and Price.[14] The peak integration was performed automatically by the PC1000 software which operated the HPLC. The mineral ions were analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The instrument was a Varian Liberty AXISO Turbo. The ICP-AES was calibrated against known concentrations of the various ions, and the instrument was set to accept calibration graphs with a correlation coefficient of 0.995 and over.

RESULTS AND DISCUSSION

The variation in caffeine and mineral ion concentration C with time t followed first-order behaviour according to the equation

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

which is predicted by the steady state theory of extraction.[15] Here C and C_∞ are the concentrations of the soluble components at any time t and at equilibrium, while k_{obs} and a represent the first-order rate constant and the intercept respectively. Plots of the ln function against time were indeed linear with small intercepts for all the coffees.

The mean rate constants obtained from the slopes of the graphs of eqn (1) and the half-life values $t_{1/2}$ of infusion determined from

$$t_{1/2} = (\ln 2 - a)/k_{\mathrm{obs}} \qquad (2)$$

are listed in Table 1. Each result is based on at least three independent experiments whose results were found to be reproducible. This is indicated by the standard deviations given in parentheses in Table 1. These were calculated using MINITAB statistical software.

Kinetic data

Statistical analysis (one-way analysis of variance) was performed on the equilibrium concentrations as well as the rate constants so as to determine which of the results were similar or significantly different. The analysis calculates *P*-factors at two levels: if the value is lower than 0.01, it means that there is a significant difference among the means; the opposite is true if the factor is greater than 0.05.

The analyses of the present results were based on individual 95% confidence intervals. The caffeine equilibrium concentrations fell into two groups: Kenya and Brazil with a *P*-factor of 0.28; and Sumatra, Zimbabwe, Ethiopia and South Africa with a *P*-factor of 0.31. Combining the two groups clearly indicated that there was a significant difference between them with a *P*-factor of zero. The concentrations of phosphorus and magnesium showed no significant difference, having *P*-factors of 0.08 and 0.04 respectively. The concentration of manganese from Ethiopian beans was very different from all the other beans investigated which had a *P*-factor of 0.21. The

Table 1. Mean kinetic data for the infusion of caffeine and mineral ions from different types of coffee beans (1.70–2.00 mm) into Milli-Q-Water at 80 °C

Type of coffee (country)	*Species*	C_∞ *(ppm)*	C_∞ *(mM)*	k_{obs} $(10^{-3} s^{-1})$	*Mean intercept a*	$t_{1/2}$ *(s)*
Special Kenya	Caffeine	269.8 (±21.5)	1.39	2.71 (±0.10)	0.11	215
(Kenya)	K^+	365.8 (±10.3)	9.36	3.50 (±0.09)	0.14	176
	P (as $H_2PO_4^-$)	25.1 (±3.8)	0.81	1.89 (±0.16)	0.14	293
	Mg^{2+}	28.6 (±0.9)	1.18	1.16 (±0.10)	0.14	477
	Mn^{2+}	0.39 (±0.02)	0.0071	0.98 (±0.08)	0.09	615
Santos	Caffeine	253.0 (±9.5)	1.30	3.59 (±0.14)	0.08	171
(Brazil)	K^+	318.2 (±13.7)	8.14	3.95 (±0.12)	0.11	135
	P (as $H_2PO_4^-$)	25.9 (±2.6)	0.84	2.42 (±0.18)	0.13	233
	Mg^{2+}	24.3 (±3.1)	1.00	1.55 (±0.14)	0.12	370
	Mn^{2+}	0.34 (±0.06)	0.0062	0.98 (±0.09)	0.16	544
Blue Mountain Java	Caffeine	292.2 (±16.4)	1.50	3.37 (±0.12)	0.11	173
(Sumatra)	K^+	376.0 (±17.8)	9.62	4.23 (±0.13)	0.06	150
	P (as $H_2PO_4^-$)	25.2 (±1.6)	0.81	2.13 (±0.15)	0.13	264
	Mg^{2+}	27.4 (±1.2)	1.13	1.25 (±0.12)	0.16	427
	Mn^{2+}	0.36 (±0.04)	0.0066	0.93 (±0.09)	0.20	530
Zimbabwe	Caffeine	295.7 (±12.9)	1.52	3.42 (±0.13)	0.14	162
(Zimbabwe)	K^+	190.6 (±10.5)	4.87	5.66 (±0.20)	0.25	78
	P (as $H_2PO_4^-$)	22.3 (±1.2)	0.72	2.23 (±0.21)	0.17	235
	Mg^{2+}	25.5 (±1.0)	1.05	1.24 (±0.09)	0.91	406
	Mn^{2+}	0.42 (±0.02)	0.0076	0.95 (±0.07)	0.13	593
Mocha	Caffeine	306.9 (±8.1)	1.58	2.72 (±0.12)	0.12	211
(Ethiopia)	K^+	345.4 (±12.9)	8.83	3.08 (±0.10)	0.13	183
	P (as $H_2PO_4^-$)	27.5 (±1.5)	0.89	1.96 (±0.19)	0.13	287
	Mg^{2+}	27.4 (±1.5)	1.13	1.34 (±0.12)	0.09	450
	Mn^{2+}	0.27 (±0.01)	0.0049	1.04 (±0.10)	0.14	532
South African Grown	Caffeine	287.6 (±9.2)	1.48	3.06 (±0.11)	0.13	184
(South Africa)	K^+	300.2 (±14.6)	7.68	4.48 (±0.15)	0.13	126
	P (as $H_2PO_4^-$)	22.6 (±0.4)	0.73	1.87 (±0.13)	0.16	285
	Mg^{2+}	23.5 (±2.4)	0.97	1.14 (±0.08)	0.16	468
	Mn^{2+}	0.38 (±0.03)	0.0069	0.75 (±0.05)	0.14	738

equilibrium concentrations which were found to be dependent on the origin of the coffee were those of potassium whose *P*-factor was zero.

Comparing the equilibrium concentrations shown in Table 1, the amount of potassium leached from the beans was highest, followed by caffeine. The values for phosphorus and magnesium were next with similar magnitude, while manganese was least. This trend was the same in all the coffees investigated, apart from the potassium concentration of the Zimbabwean coffee whose value (190.6 ppm) was less than that of caffeine. It was also 49% smaller than the highest equilibrium concentration of potassium. The difference between the potassium and the caffeine concentration of the South African Grown coffee was only 4% as compared with ~ 24% in all the other coffees, with the exception of Mocha with 11%. This difference in equilibrium concentration is also observed between the Special Kenya reported here and Kenyan A.[10] The reasons for this difference may be twofold. First is that the total potassium content in the coffees investigated was naturally very low. Second, and the most probable explanation as to the low level of potassium, is the handling of the green coffee, whether it underwent the wet or the dry process.[1,5,16]

Inspection of the results in Table 1 shows that the order of infusion is $K > \text{caffeine} > P$ (as $H_2PO_4^-$) $> Mg^{2+} > Mn^{2+}$. This trend was found to be true for all the coffees investigated. Since a kinetic study of caffeine infusion from Kenyan coffee has been reported in the literature, the rate constant obtained with the Special Kenyan beans will be examined. The k_{obs} of $2.71 \times 10^{-3}\,s^{-1}$ obtained here is comparable with the value of $2.67 \times 10^{-3}\,s^{-1}$ reported by Jaganyi *et al*[10] for Kenyan A. Spiro and Selwood[15] (1984) have reported a value of $9.0 \times 10^{-3}\,s^{-1}$ for particle size 0.85–1.18 mm at 84.1 °C. Since the rate of infusion varies inversely with the square of the particle radius[15,17] and ln k_{obs} is inversely related to temperature in the Arrhenius equation, the reported value is equivalent to a rate constant of $2.68 \times 10^{-3}\,s^{-1}$ using the present experimental conditions of particle size and temperature. The agreement with the results given in Table 1 is very good considering the fact that food products do vary from year to year.

The statistical analysis of rate constants for different species revealed that the rate constants of P (as $H_2PO_4^-$) were not significantly different ($P = 0.12$). In the case of Mg^{2+} the value for the Brazilian coffee was significantly different from the rest which had a *P*-factor of 0.21. The analysis also showed that the values for Mn^{2+} were similar for all the coffees ($P = 0.61$), with the exception of the South African Grown. Because of the similarities observed in the rate

Table 2. Effective diffusion coefficients and hindrance factors of caffeine and mineral ions for various types of coffee beans (1.70–2.00 mm) at 80 °C

Type of coffee	Species	D_{bean} (from k_{obs}) ($10^{-11} m^2 s^{-1}$)	D_{bean} (from $t_{1/2}$) ($10^{-11} m^2 s^{-1}$)	Mean D_{bean} ($10^{-11} m^2 s^{-1}$)	D_{aq} ($10^{-9} m^2 s^{-1}$)	HF
Special Kenya	Caffeine	19.3	12.2	15.8	2.2	14
(Arabica)	K^+	22.5	14.9	18.7	5.0	27
	P (as $H_2PO_4^-$)	13.5	8.9	11.2	2.6	23
	Mg^{2+}	8.3	5.5	6.9	2.0	29
	Mn^{2+}	7.0	4.3	5.7	2.1	37
Santos	Caffeine	25.6	15.3	20.5	2.2	11
(Arabica)	K^+	30.6	19.2	24.9	5.0	20
	P (as $H_2PO_4^-$)	17.3	11.2	14.3	2.6	18
	Mg^{2+}	11.1	7.1	9.1	2.0	22
	Mn^{2+}	7.0	4.8	5.9	2.1	36
Blue Mountain Java	Caffeine	24.0	15.1	19.6	2.2	11
(Arabica)	K^+	30.2	17.4	23.8	5.0	21
	P (as $H_2PO_4^-$)	15.2	9.9	12.6	2.6	21
	Mg^{2+}	8.9	6.1	7.5	2.0	27
	Mn^{2+}	6.6	4.9	5.8	2.1	36
Zimbabwe	Caffeine	24.4	16.2	20.3	2.2	11
(Med-Arabica)	K^+	40.4	33.5	37.0	5.0	20
	P (as $H_2PO_4^-$)	15.9	11.1	13.5	2.6	19
	Mg^{2+}	8.8	6.4	7.6	2.0	26
	Mn^{2+}	6.8	4.4	5.6	2.1	38
Mocha	Caffeine	19.4	12.4	15.9	2.2	14
(Robusta)	K^+	22.0	14.3	18.2	5.0	27
	P (as $H_2PO_4^-$)	14.0	9.1	11.6	2.6	22
	Mg^{2+}	9.6	5.8	7.7	2.0	26
	Mn^{2+}	7.4	4.9	6.2	2.1	34
South African Grown	Caffeine	21.8	14.2	18.0	2.2	12
(Arabica)	K^+	31.9	20.8	26.4	5.0	19
	P (as $H_2PO_4^-$)	13.3	9.2	11.3	2.6	23
	Mg^{2+}	8.1	5.6	6.9	2.0	29
	Mn^{2+}	5.3	3.5	4.4	2.1	48

constants of these three species, they cannot be used for identification of the coffee origin. However, the values of caffeine can be used for grouping the coffees. The statistical analysis for caffeine showed that the rate constants fell into three groups: Kenya and Ethiopia; Brazil, Sumatra and Zimbabwe; with South Africa lying in between. This grouping was confirmed by performing a cluster analysis of the rate constants and the half-life values. The rate constants of K^+ produced a *P*-factor of zero and showed no clustering, an indication that the individual values were significantly different. Therefore, even though the Brazilian, Sumatran and Zimbabwean coffee beans have been grouped together in the caffeine analysis, they can be differentiated by using the rate constants for K^+ which are different. This is also true for the Kenyan and Ethiopian coffees. It can be argued that the rate constants are likely to change from one year's crop to the next, but if one looks at the rate constant for caffeine from Kenyan coffee which has been studied for many years,[10,15] it is clear that the change is very small.

Diffusion coefficients and hindrance factors

The diffusion coefficient was calculated in two different ways. The first calculation made use of the steady state theory equation

$$k_{obs} = 12D_{bean}/r^2 \tag{3}$$

where r and D_{bean} are the radius of the bean particle and the diffusion coefficient of the species within the bean respectively. The second value was calculated from the half-life values shown in Table 1 by applying the following equation,[18] which is a solution of Fick's second law of diffusion:[19]

$$1/t_{1/2} = 32.7D_{bean}/r^2 \tag{4}$$

The values obtained from Fick's law were lower than those obtained using the steady state equation. An average value Mean D_{bean} was used in calculating the hindrance factor HF from the equation

$$\mathrm{HF} = D_{aq}/D_{bean} \tag{5}$$

where D_{aq} is the diffusion coefficient of the species in aqueous medium. Price *et al*[20] have determined the aqueous value for caffeine at 80 °C. Spiro and Lam[21] have listed in their Table 4 the values for K^+, Mg^{2+} and P (as $H_2PO_4^-$) assuming that the major orthophosphate ion analysed as phosphorus was $H_2PO_4^-$, since the average pH of the coffee liquor was 4.5. To determine the limiting tracer diffusion coefficient for

Mn^{2+} at 80 °C, the Nernst equation

$$D_{aq} = RT\lambda^{o}/|Z|F^{2} \qquad (6)$$

was used. The symbols R, T, λ^{o}, Z and F in eqn (6) represent gas constant, temperature in kelvin, limiting equivalent conductance, ionic charge number and Faraday constant respectively. Since the limiting equivalent conductance for Mn^{2+} is only available at 25 °C,[22] the Walden rule

$$\lambda^{o}\eta = \text{constant} \qquad (7)$$

was used to determine the value of λ^{o} for Mn^{2+}. The values for viscosity (η) of water were taken from Ref 23. The diffusion coefficients and the resulting hindrance factors HF are listed in Table 2.

As regards the HF values, Table 2 shows that Mn^{2+} is the most hindered species in all the coffees. Its diffusion coefficient is approximately three to four times smaller than that of caffeine, which is the least hindered of the species investigated. The hydrodynamic radii in water for Mn^{2+}, Mg^{2+} and caffeine are very similar as indicated by their D_{aq} values, but their HF values are very different. The value of Mg^{2+} is approximately half-way between the other two. Even though some of the HF values for a particular species differ for different coffees, their magnitudes remain very similar.

When the results in Tables 1 and 2 are considered together, it is clear that the diffusion of caffeine and mineral ions within the coffee bean particle is a hindered process. The comparison of the HF values for caffeine, Mg^{2+} and Mn^{2+} clearly indicates that one of the causes of slower diffusion is the association between the species and insoluble components of the bean. Manganese, being a transition metal, has the ability to form more complexes than magnesium ion. Another explanation for the hindrance process is complex formation between the dissolved species and other solubles to create a more bulky and slower-moving entity. One of the compounds suspected to fall into this group is the caffeine–potassium chlorogenate molecular complex[15,18,24,25] which has been isolated as a 1:1 complex between caffeine and potassium chlorogenate. Spiro and Chong[26] have demonstrated that the slow infusion of caffeine is not due to its self-association as was originally suspected. The equilibrium concentration in Table 1 shows that the ratio of caffeine to potassium is mostly 1:6. This big difference may be an indication that potassium does not only exist as a caffeine–potassium chlorogenate complex in the coffee bean, a fact that can only be proven by determining the total amounts of the three species in the bean. Since aqueous K^{+} ions rarely associate with other species and potassium salts in water are completely dissociated, it can be concluded that in whatever form potassium exists in the bean, during infusion it ionises and the free potassium anion diffuses out of the bean as a single species much faster than the organic or the inorganic counterparts. This idea is clearly supported by the differences in rate constant and hindrance factor between potassium and caffeine. In addition to the above explanation, one factor which is believed to be the main cause of slow diffusion for all the species is the physical restraint within the bean matrix. This forces the solubles to follow a diffusion path which is tortuous in nature.

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