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Kinetics and equilibria of tea infusion—Part 12. Equilibrium and kinetic study of mineral ion extraction from black Assam Bukial and green Chun Mee teas

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The rates of infusion into distilled water of caffeine and of Cl^-, $H_2PO_4^-$, SO_4^{2-}, $C_2O_4^{2-}$, K^+ and Mg^{2+} ions have been measured at 80°C, using both black orthodox Bukial and green Chun Mee tea leafs in the size range 1.70–2.00 mm. The analytical techniques employed were HPLC and ion chromatography. The total moles of positive charge extracted per litre of infusion were several times as large as the moles of negative charge of all the anions analysed, pointing to large concentrations of organic anions including polyphenolates. The kinetic data were fitted to first order plots. From the resultant rate constants the diffusion coefficients of the various species within the tea leafs were calculated and compared with the corresponding diffusion coefficients in pure water at 80°C. The hindrance factors in the leafs were all of the order of 10^2.

INTRODUCTION

The mineral contents of tea leaf and the percentages extracted in aqueous infusions have been measured by several groups of workers, particularly in recent years (Saleh, 1982; Ramakrishna *et al.*, 1987; Ananthacumaraswamy *et al.*, 1990; Natesan & Ranganathan, 1990; Takeo, 1985; Takeo, 1992). For any given mineral species, the results span a wide range (Stagg & Millin, 1975) since they depend upon the country and area of origin, the mineral content of the soil, and the part and age of the tea plant analysed (Hasselo, 1965; Natesan & Ranganathan, 1990). Nevertheless, some general trends are well recognised: for example, the preponderance of potassium in tea leaf followed by calcium and magnesium and the low concentration of sodium. A similar picture applies to the percentages of the various species extracted under given conditions. These vary significantly in different publications but there is general agreement that aqueous infusions extract a high percentage of ions such as potassium and chloride but less than 10% of species like calcium and iron. Indeed, calcium ions (but not magnesium ions) are actually taken up by tea leaf when infusions are prepared in hard water (Anderson *et al.*, 1971). However, one aspect rarely investigated is the rate of mineral extraction and this forms the main subject of the present paper.

MATERIALS AND METHODS

Black orthodox Assam Bukial tea and green Chun Mee tea were sieved with a set of stainless steel Endecott sieves and the fractions 1.70–2.00 mm were selected. A fixed mass of tea (4.0 g) was added via a tea holder device (Spiro & Siddique, 1981) made of glass to 200 ml distilled water in a 250 ml conical flask held in a thermostatic water bath. The water had been prewarmed to 80°C and was kept at this temperature throughout, the infusion being stirred by means of a submersible magnetic stirrer. Samples (1 ml) of the infusion were removed at various times by means of a Sabre syringe fitted with a stainless steel needle whose tip was fitted with a Gilson filter (Anachem) to exclude leaves and particulates. The flask and contents were weighed before and after each run to correct concentrations for volumes lost through sampling and evaporation.

The samples taken for caffeine analysis were transferred to sample tubes containing 9 ml distilled water, thoroughly mixed, and analysed by reverse phase HPLC as described previously (Price & Spiro, 1985*a*). The system had been calibrated with aqueous solutions of caffeine of known concentrations.

Mineral ions were analysed by ion chromatography using a Dionex 2010i system as described earlier (Chen & Spiro, 1993). The samples were passed through

Sep-Pak C18 cartridges (Millipore) to remove organic components and then diluted by factors from 5 to 50 with water deionised by a Millipore RO6 + Q50 system. For anion analysis each diluted sample was first passed through an OnGuard-H filter (Dionex) and then through AG4A guard and AS4 separator columns using 0.75 mM $NaHCO_3$ + 2.2 mM Na_2CO_3 (M = mol dm^{-3}) eluent. For cation analysis a Minisart NML (Sartorius) filter preceded CG3 guard and CS3 separator columns using as eluent 27.5 mM HCl + 4.5 mM 2,3-diaminopropionic acid monohydrochloride. The filters had to be carefully rinsed beforehand. Calibration runs were carried out with standard solutions of salts of the various ions involved.

RESULTS AND DISCUSSION

The concentrations (c) of the various tea solubles rose rapidly at first and then asymptotically approached their equilibrium values (c_∞) at long times (t) of the order of 10^3s. As in previous papers in this series, the data points were fitted to the first order equations

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

where k_{obs} is the first order rate constant and a an empirical intercept. The uncertainty limits cited in the tables are the standard deviations of the means.

Caffeine extraction

The rates of caffeine extraction were measured first in order to compare them with those of the ionic constituents. The results are listed in Table 1. The equilibrium concentrations agree well with those obtained previously (Spiro *et al.*, 1992). The rate constants are somewhat higher, indicating a slow change in the leafs.

Anion extraction

The average retention times with the bicarbonate/carbonate eluent for F^-, Cl^-, $H_2PO_4^-$, SO_4^{2-} and $C_2O_4^{2-}$ ions were 1.23, 1.79, 5.27, 6.58 and 8.90 min, respectively. However, peaks due to formate and acetate ions appeared at almost the same retention times as fluoride, and a mixture of the three ions produced a fused peak at 1.25 min. Separation of the signals was made possible by substituting as eluent a 5 mM solution of sodium tetraborate, leading to retention times for F^-, CH_3COO^- and $HCOO^-$ of 1.97, 2.11 and 2.57 min, respectively. In this way it was shown that only some 15% of the previous 'fluoride' peaks in the tea infusions had been due to F^- ions.

Table 1. Kinetic and equilibrium data for caffeine extraction at 80°C

Tea	k_{obs} (10^{-3} s^{-1})	a	c_∞ (ppm)	c_∞ (mM)
Black	8.3 ± 0.3	0.20	809	4.17
Green	10.3 ± 0.3	0.36	516	2.66

Table 2. Kinetic and equilibrium data for anion extraction at 80°C

Tea	Ion	k_{obs} (10^{-3} s^{-1})	a	c_∞ (ppm)	c_∞ (mM)
Black	F^-			1.2	0.06
	Cl^-	16.6 ± 1.9	0.36	18.0	0.51
	$H_2PO_4^-$	10.9 ± 1.0	0.42	23.5[a]	0.76
	SO_4^{2-}	12.5 ± 2.2	0.40	29.0	0.30
	$C_2O_4^{2-}$	7.1 ± 1.6	0.20	130.1	1.48
Green	F^-			1.6	0.08
	Cl^-	23.0 ± 5.0	0.35	10.5	0.30
	$H_2PO_4^-$	8.0 ± 1.5	1.09	18.0[a]	0.58
	SO_4^{2-}	14.3	0.40	42.6	0.44
	$C_2O_4^{2-}$	6.3 ± 2.3	0.39	107.5	1.22

[a] As phosphorus

The anion results are summarised in Table 2. It may be noted that the major orthophosphate species in the tea brews will have been $H_2PO_4^-$, since the pH of the black and green tea infusions were 4.8 and 5.6, respectively. In the bicarbonate/carbonate eluent background, however, it will have been converted to HPO_4^{2-}.

Multiplication of the c_∞ figures in ppm by (200/4) x10^{-4} gives estimates of the wt% of the various species in the tea leaf, on the assumption that all the ions have been extracted. As mentioned in the Introduction, the degree of validity of this assumption varies with each species and also with the type of tea and the infusion conditions employed. As they stand, the results are quite comparable with literature data for leaf content and percentage extractability for fluoride (Singer *et al.*, 1967), chloride (Saleh, 1982) and phosphorus (Natesan & Ranganathan, 1990). The fact that similar results have been obtained for P in the form of $H_2PO_4^-$ ions in the present work and for total P in the literature, indicates that phosphorus in tea leaf is present largely in the orthophosphate form.

The first order rate constants and intercepts obtained for the anions are of similar magnitude to those for caffeine (Table 1). On average, there is little difference between the rate constants for the black tea and the green tea. The significance of the k_{obs} values is examined in more detail below.

Cation extraction

The average retention times for K^+, Mg^{2+} and Ca^{2+} ions were 3.08, 12.26 and 22.82 min, respectively. The rate and equilibrium data for potassium and magnesium are listed in Table 3, but the calcium results were not reproducible. The equilibrium concentrations of both K^+ and Mg^{2+} were greater in the infusions of the black tea than in those of the green tea, and their magnitudes are consistent with the range of values of leaf content and extractability reported in the literature (Stagg & Millin, 1975; Natesan & Ranganathan, 1990; Takeo,

Table 3. Kinetic and equilibrium data for cation extraction at 80°C

Tea	Ion	k_{obs} ($10^{-3}s^{-1}$)	a	c_∞ (ppm)	c_∞ (mM)
Black	K^+	7.0 ± 1.2	0.27	445	11.38
	Mg^{2+}	3.5 ± 0.9	0.14	38	1.56
Green	K^+	8.3 ± 0.6	0.45	315	8.06
	Mg^{2+}	4.9 ± 0.8	0.30	31	1.27

1985; Takeo, 1992). It is noteworthy that the number of millimoles of positive charge per litre represented by these two cations alone are 2.5 (green tea) –3.0 (black tea) times as large as the number of millimoles of negative charge per litre represented by all the anions analysed. This charge imbalance in the infusions must be made up by various organic anions including the formate and acetate ions detected by ion chromatography and by partially ionised polyphenolics.

The mean rate constants and intercepts for K^+ and Mg^{2+} were somewhat larger in the green tea experiments than in those with the black tea. On average, the cations infused more slowly than did the anions. This is discussed further in the next section.

Diffusion coefficients

It is generally accepted that the rate-determining step in tea infusion is the diffusion of the soluble constituents through the tea leaf. By applying the steady-state theory of extraction (Spiro & Jago, 1982) it can then be shown that the effective internal diffusion coefficients are given by the equation

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

where $2d$ is the thickness of the water-swollen leaf treated as a lamina. The mean values of $2d$ found in the present work were 0.15 and 0.14 mm for the black and green tea leafs, respectively. The diffusion coefficients of the various species calculated in this way are listed in Table 4.

Table 4. Calculated diffusion coefficients and hindrance factors at 80°C

Tea	Species	D_{leaf} (10^{-11} m^2 s^{-1})	D_{aq} (10^{-9}m^{2}s^{-1})	HF
Black	Caffeine	2.3	2.1	90
	Cl^-	4.7	5.4	116
	$H_2PO_4^-$	3.1	2.6	83
	SO_4^{2-}	3.5	3.2	91
	$C_2O_4^{2-}$	2.0	2.9	147
	K^+	2.0	5.0	255
	Mg^{2+}	1.0	2.0	202
Green	Caffeine	2.5	2.1	83
	Cl^-	5.6	5.4	96
	$H_2PO_4^-$	2.0	2.6	130
	SO_4^{2-}	3.5	3.2	91
	$C_2O_4^{2-}$	1.5	2.9	199
	K^+	2.0	5.0	248
	Mg^{2+}	1.2	2.0	165

To understand the significance of these figures they need to be compared with the diffusion coefficients of the same species at the same temperature but in aqueous solution, D_{aq}. This property has been directly measured only for caffeine (Price *et al.*, 1989). For the ions it can be calculated from known limiting equivalent conductances, $\lambda°$. Values of $\lambda°$ over the temperature range 0–100°C have been tabulated for Cl^-, SO_4^{2-}, K^+ and Mg^{2+} (Robinson & Stokes, 1959) while limiting conductances at 25°C only are available for $H_2PO_4^-$ (Selvaratnam & Spiro, 1965) and $C_2O_4{}^{2-}$ (Robinson & Stokes, 1959). For the latter two ions, values at 80°C were estimated from the simple Walden rule

$$\lambda°\eta = \text{constant} \qquad (3)$$

where η is the solvent viscosity (Robinson & Stokes, 1959). For the first four ions, plots $\lambda°\eta$ against temperature θ from 0 to 100°C gave gentle curves of various shapes which could be well fitted by quadratics in θ. Interpolation at $\theta = 80°C$ yielded the desired values of $\lambda°$. The corresponding limiting tracer diffusion coefficients were then calculated from the Nernst equation

$$D_{aq} = RT\lambda°/zF^2 \qquad (4)$$

where R is the gas constant, F the Faraday constant, $T = 353.1$ K and z is the ionic charge number. These D_{aq} values are presented in Table 4 and can be seen to be much larger than the experimental values of D_{leaf}. The last column in the table lists the corresponding hindrance factors HF given by

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

These were evaluated before rounding off the various diffusion coefficients to two significant figures.

Inspection of the HF column shows that the largest and smallest values differ by a factor of only 3. Cations migrate out more slowly than anions or the neutral caffeine molecule. Comparison between K^+ and Cl^- ions is particularly relevant since the hydrated ions possess similar radii, as shown by their similar D_{aq} values. The effective hydrodynamic radii of the hydrated Mg^{2+} ion and the caffeine molecule are also almost identical in water although HF for magnesium is twice as large as for caffeine. This suggests that cations may be held back by attraction to negative charges within the leaf matrix, perhaps by complexation with polyphenolic constituents.

Anion charge number seems to have little effect: the $H_2PO_4^-$ and SO_4^{2-} ions possess similar bare dimensions as well as similar hydrated ones but differ in charge, yet their average HF values are quite comparable. Overall it is striking that the HF values for species with charge numbers ranging from −2 through zero to +2 are all of the order of 10^2. Since the water uptake by the tea leaf accounts for a hindrance factor for caffeine of only just over 2 (Spiro & Price, 1987), it follows that the slow diffusion of all these solubles must be attributed mainly to their tortuous passage through the internal structure of the leaf. This is supported by the fact that extraction rates are greater with the more physically damaged CTC leaf than with orthodox black tea leaf (Price & Spiro, 1985*b*).

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