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# Kinetics and Equilibria of Tea Infusion: Part 7—The Effects of Salts and of pH on the Rate of Extraction of Caffeine from Kapchorua Pekoe Fannings

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## *ABSTRACT*

*The rates of extraction of caffeine from sieved Kapchorua PF (600–710 μm) have been measured at 80°C with a range of aqueous salt and buffer solutions of ionic strength 0·11 mol dm*$^{-3}$*. The first-order rate constants and the half-times of infusion showed no trend with pH when buffers from pH 3·0 to pH 8·3 were employed. The rate constants decreased on the addition of common salts like NaCl, KCl and* $CaCl_2$ *but increased in the presence of electrolytes such as* $Bu_4NCl$ *that contain large ions. The results cannot be interpreted by changes in osmotic pressure although Donnan effects may be involved. Close parallels were found between the rate constants and the solubilities of caffeine in electrolyte solutions at 25°C. In particular, the values of both properties rise appreciably in the presence of species containing aromatic or other organic rings with which caffeine molecules associate.*

## INTRODUCTION

The rate of extraction of caffeine from tea leaf is very dependent on the size and quality of the leaf, being greater the smaller the leaf and the more severe the manufacturing method (Price & Spiro, 1985*b*). We now investigate how the rate from a given sieved leaf is affected by the composition of the aqueous extracting medium. Buffer solutions ranging in pH from 3·0 to 8·3 (at 80°C)

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were employed, as well as several salt solutions. Some of the salts were chosen to mimic constituents of the buffers in order to separate ionic and pH effects. The concentrations of all solutions were adjusted to an ionic strength of 0·11 mol dm$^{-3}$, a value sufficiently large to swamp the endogenically produced ionic concentration yet sufficiently low for inter-ionic attraction theories to be applicable (Robinson & Stokes, 1959). The experiments were again carried out at 80°C.

## EXPERIMENTAL

All experiments were carried out with Kenyan Kapchorua Pekoe Fannings, a black tea manufactured by the CTC process, using only the sieved fraction 600–710 $\mu$m. Four grams of leaf were added with a tea holder device (Spiro & Siddique, 1981*a*) to 194·4 g solution (200 cm$^3$ at 80°C) in a stoppered conical flask in a thermostat bath at 80°C. Normally, six samples of 2 cm$^3$ were removed at approximately 15-s intervals, accurately timed, with Segma syringes fitted with stainless steel needles whose tips were protected by new glass wool filter plugs to exclude tea leaves. A further sample was taken after 30 min to obtain the equilibrium concentration. The flask was reweighed after the run so that corrections (of the order of 5%) could be made for evaporation and sampling (Spiro & Jago, 1982). The pH of samples taken from buffer solution infusions was adjusted to 4·8 before analysis and the caffeine content was determined by hplc as described previously (Price & Spiro, 1985*a*). The compositions of the buffer solutions have been specified in Table 1 of the paper by Spiro & Price (1987).

## RESULTS

Both the two-phase (Spiro & Siddique, 1981*b*) and steady-state (Spiro & Jago, 1982) theories predict that the infusion kinetics should follow the first-order equation:

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

where $c$ is the concentration of caffeine in the aqueous solution at time $t$ and $c_\infty$ its concentration at equilibrium. Plots of the ln function versus time did give straight lines but with small intercepts, $a$. Values of the rate constant $k_{\text{obs}}$ and of $a$ were obtained by least-squares computer fitting of the data. The half-times of the infusion, $t_{1/2}$, were then calculated from the equation:

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

**TABLE 1**
Kinetic Data for Caffeine Infusion from Kapchorua PF into Different Aqueous Media of Ionic Strength 0·11 mol dm$^{-3}$ at 80°C

| *Solution* | *pH*[a] | $k_{obs}$ (*min*$^{-1}$) | *Intercept* | $t_{1/2}$ (*s*) |
|---|---|---|---|---|
| Water | 4·8 | 1·51 | −0·03 | 29 |
| NaCl | | 1·32 | 0·11 | 27 |
| KCl | | 1·30 | −0·04 | 34 |
| $CaCl_2$ | | 1·09 | 0·14 | 30 |
| $NaO_3SPh$ | | 1·58 | 0·08 | 23 |
| $Bu_4NCl$ | | 1·64 | −0·06 | 28 |
| Citrate buffer | 3·0 | 1·23 | 0·06 | 31 |
| Acetate buffer | 4·7 | 1·27 | 0·08 | 29 |
| Phosphate buffer | 6·8 | 1·35 | 0·05 | 29 |
| CHES buffer | 8·0 | 1·68 | 0·20 | 18 |
| Ethanolamine buffer | 8·0 | 1·77 | −0·13 | 28 |
| Borate buffer | 8·3 | 1·31 | 0·13 | 26 |

[a] Final pH of equilibrium tea infusion.

The results are summarised in Table 1. All kinetic data are the mean values of at least two independent runs. The uncertainties, taken as standard deviations of each mean, are ±0·08 min$^{-1}$ for $k_{obs}$, ±0·06 for $a$, and ±3 s for $t_{1/2}$.

## DISCUSSION

### Examination of the results

Inspection of Table 1 shows that addition of 0·11 mol dm$^{-3}$ NaCl or KCl depressed the rate constant by some 13%. A much bigger drop of 28% was brought about by 0·037 mol dm$^{-3}$ $CaCl_2$. Decreases of 11–17% were also produced by the citrate, acetate, phosphate and borate buffers. These span a pH range from 3·0 to 8·3 and there is therefore no evidence for a pH trend in $k_{obs}$. No pH effect should have arisen from any protonation of caffeine since it is a very weak base with a pK value around 0 (Wood, 1903). Rate constants that were higher by 5–9% than the value in distilled water were obtained with the two salts that contain a large cation ($Bu_4N^+$) and a large anion ($PhSO_3^-$), and they were higher by 11–17% with two of the buffers that likewise contain large species, CHES (2-[cyclohexylamino]ethanesulphonic acid) and ethanolamine ($HOCH_2CH_2NH_2$). The larger rise in $k_{obs}$ for these buffers is consistent with the fact that both their acid and their base forms are large so that these solutions contain 0·22 mol dm$^{-3}$ of large ions and molecules. However, the citrate buffer solution also contains large species but its rate constant falls into the 'normal' group.

The half-times, which take into account the intercepts as well as the rate constants, exhibit less variation. Attention may be drawn to the very low $t_{1/2}$ values obtained with sodium benzenesulphonate and with CHES buffer, the two solutions whose species are not only large but also contain six-membered rings.

## Infusion mechanism

Any interpretation of these salt effects must depend upon an understanding of the mechanism of caffeine extraction. It has been shown (Price & Spiro, 1985*b*) that the rate-determining process involves the hindered diffusion of caffeine through the leaf coupled with the absorption of water. The water content of black tea leaf is originally *ca.* 5% and rises to *ca.* 75% after aqueous infusion. The rate of solubles loss by the leaf and its rate of water uptake are known to be of similar magnitude (Long, 1979; D. R. Haisman and M. J. Izzard, private communication). Although the effect of water absorption was not specifically allowed for in the steady-state model of Spiro & Jago (1982), one can use the theory to calculate the *effective* diffusion coefficient, $D$, of caffeine in the leaf by the equation:

$$D = \tfrac{1}{2} k_{\mathrm{obs}} d^2/(1 + w/K'V) \tag{3}$$

where $2d$ is the thickness of a laminar leaf, $w$ the mass of the original leaf infusing in a volume, $V$, of solution and $K'$ the notional partition constant of caffeine between leaf and solution. The value of $D$ for large-leafed Betjan FBOP was found to be $1{\cdot}8 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ (Price & Spiro, 1985*b*), some 100 times smaller than the diffusion coefficient of caffeine in pure water at 80°C. To find the extent to which such a large decrease was caused by the concomitant uptake of water, an infusion experiment was carried out with pre-swelled leaf.

An attempt to pre-swell Kapchorua leaf by placing it in an atmosphere saturated with water vapour at 80°C proved unsuccessful. The leaf absorbed only *ca.* 30% of its weight of water even after several days; it looked wet and shiny and produced a bitter pungent smell. It seems likely that, under these conditions, polyphenols in the leaf were polymerised further and altered the leaf composition. The swelling was therefore carried out in solution. Six grams of Kapchorua PF (600–710 $\mu$m) were infused in 200 cm$^3$ distilled water at 80°C for 30 min to reach equilibrium. After this the leaf was removed with a strainer, leaving 170 cm$^3$ of clear tea liquor. This liquor was then infused with 4·2 g of fresh Kapchorua leaf for 30 min at 80°C. During this period the leaves swelled with water but lost only a small fraction of their solubles content. The swollen leaf and equilibrium tea liquor were again separated with a strainer but this time the leaves were retained. They were quickly mixed with 200 cm$^3$ fresh distilled water at 80°C, and a kinetic run was carried out in the usual way by periodically sampling the stirred infusion. The ln function of eqn (1) yielded a linear plot against time. The intercept $a$ of 0·48 was exceptionally large, undoubtedly due to the presence of some equilibrium liquor from the swelling experiment that had been trapped between the wet leaves. The slope gave a rate constant of 3·45 min$^{-1}$, just over twice the normal value (Table 1). The effective diffusion coefficient of caffeine is therefore about twice as big in an extraction experiment begun with swollen leaf as in one begun with 'dry' leaf. Thus, while water uptake into 'dry' leaf does significantly decrease the effective intra-leaf diffusion coefficient of caffeine, its extremely low value must be largely attributed to the internal structure of the leaf (Harris & Ellis, 1981) and the way in which it hinders the diffusion process.

## Effect of electrolytes

We shall now consider a number of ways in which the infusion rate could be changed by the presence of ions in the extracting medium. Their most direct effect might be thought to be on the contributory process of water uptake into the leaf. Thus, most electrolytes increase the viscosity of water and this would reduce its flow rate. However, at 80°C the addition of 0·11 mol dm$^{-3}$ of salts such as NaCl or KCl will increase the viscosity by less than 2% (Stokes & Mills, 1965). Related to this property is the self-diffusion coefficient of water itself. Addition of 0·1 mol dm$^{-3}$ NaCl or KCl at 25°C increases it by approximately 1% while addition of 0·1 mol dm$^{-3}$ $MgCl_2$ or $BaCl_2$ decreases it by less than 2% (Anderson & Paterson, 1975; Tanaka, 1978; Harris *et al.*, 1978). These changes are always smaller at 25°C than at 10°C (Harris *et al.*, 1978) and so they are likely to be much smaller still at 80°C. It follows that the variation in neither solution viscosity nor water diffusion coefficient can account for the effect of electrolytes on the rate constants in Table 1. Nor can they be explained by the change in the diffusion coefficient of caffeine itself as this should decrease by only *ca.* 1% at 25°C in the presence of common electrolytes of ionic strength 0·11 mol dm$^{-3}$ (Tham & Gubbins, 1972). The changes in the caffeine diffusion coefficient and in the solution viscosity are, in fact, inversely related by the Stokes–Einstein equation.

The driving force behind the uptake of water by the 'dry' leaf is the difference between the osmotic pressures of the internal and external solutions. Ion chromatography measurements (M. Spiro and A. J. Pierce, unpublished work) indicate that there are approximately 4 mmol electrolyte (mainly KF) in 4 g 'dry' Kapchorua tea leaf which, on immersion, swells to *ca.* 16 g. The solution in the swollen leaf may thus be treated as *ca.* 0·25 mol dm$^{-3}$ in KF and much more concentrated in the 'dry' leaf. The total solute concentration in the leaf will, of course, be higher still. The osmotic pressure of the internal leaf solution is therefore much greater than that of the external solution. The initial difference between these pressures will be significantly reduced if distilled water is replaced by a 0·11 mol dm$^{-3}$ salt solution. This argument qualitatively explains the decreases in $k_{obs}$ observed on adding NaCl, KCl and $CaCl_2$ but not the increases found on the addition of $NBu_4Cl$ and $PhSO_3Na$. Nor can these last two cases be justified by thermodynamic non-ideality. The osmotic pressure of a salt solution depends upon the concentration of the electrolyte, its charge type and its osmotic coefficient $\varphi$; for 0·1 mol kg$^{-1}$ solutions of the four uni-univalent salts the values of $\varphi$ are 0·932, 0·927 (Robinson & Stokes, 1959), 0·918 (Lindenbaum & Boyd, 1964) and 0·936 (Bonner & Rogers, 1960), respectively, at 25°C. The variation with temperature is small: for NaCl $\varphi$ falls from 0·932 at 25°C to 0·926 at 80°C (Robinson & Stokes, 1959). According to these figures the rate constant should be lowered to approximately the same extent for every 1:1 salt. Osmotic pressures by themselves, therefore, do not explain the kinetic results either.

Since $k_{obs}$ was increased by the presence of large ions which diffuse less readily than small ones through the solution/leaf interface, then effects of the Donnan type might be expected. One consequence would be the setting up of a potential difference across the interface. Its sign with $Bu_4NCl$, where the cation is bulky, will be the opposite to that with $PhSO_3Na$ where the anion is bulky. Since both electrolytes produced a rise in $k_{obs}$, and since, in any case, caffeine is an uncharged species, such potential differences cannot provide the answer. On the other hand, simple Donnan calculations (Price, 1985) show that, compared with extraction by pure water, less $K^+$ is transferred from leaf to solution when the extracting medium contains KCl while more $K^+$ is transferred when the extracting medium contains RCl, where $R^+$ is a large cation that does not penetrate the leaf. Now $Bu_4N^+$ (as $R^+$) will certainly penetrate the leaf in due course but it should do so more slowly than $K^+$ since its trace diffusion coefficient is much smaller (by a factor of 3·8 at 25°C; Robinson & Stokes, 1959). The equilibrium Donnan calculation ought therefore to give a reasonable indication of the relative ionic distributions part way through the infusion experiment. The sequence of net $K^+$ transfers so calculated is the same as that of the observed rate constants, namely:

$$k_{obs}(Bu_4NCl) > k_{obs}(\text{water}) > k_{obs}(KCl)$$

Although it is not clear why net $K^+$ transfers should parallel the rates of caffeine transfer, this calculation does suggest that Donnan effects may play a role in the extraction process.

The most promising insight into the kinetic results is obtained by considering the specific interactions of caffeine. Strong evidence for these comes from the solubility of caffeine in various electrolyte solutions. The main data from two independent investigations are listed in Tables 2 and 3: further data are due to be published (Pérez-Tejeda *et al.*, 1987). It can be seen that most ordinary salts such as NaCl and KCl depress the solubility of caffeine, with salting-out effects of the same magnitude as for other moderately large organic solutes (Harned & Owen, 1958). On the other hand, the solubility is considerably enhanced by the presence of species that form complexes with caffeine: acids which partly protonate the purine (Wood, 1903), $I^-$ and $SCN^-$ which may form donor–acceptor complexes, and particularly the ions $PhCOO^-$ and *o*—$HOC_6H_4COO^-$ that contain benzene rings. Confirmation of strong association between caffeine molecules and both benzoate and salicylate ions was obtained by Emery & Wright (1921) from freezing point measurements. In tea solutions themselves, two fractions of tea cream are complexes between caffeine and theaflavins or thearubigins (Rutter & Stainsby, 1975), both being species that possess aromatic and other rings. Finally, caffeine molecules even associate with each other in aqueous solution, a progressive process known as base-stacking (Bothe & Cammenga, 1983; Yanuka *et al.*, 1986). Ample evidence therefore exists for specific association between caffeine molecules and other species, especially ones that contain aromatic or other rings.

Comparison of these data with the results in Table 1 reveals a good correlation between $k_{obs}$ values and caffeine solubilities. Both properties are depressed by common salts like NaCl, NaOAc, KCl and $CaCl_2$ and both are increased by $Bu_4N^+$ salts (Pérez-Tejeda *et al.*, 1987) and by the presence of species containing six-membered organic rings (such as $PhSO_3^-$ and CHES). Such parallels between rate constants and equilibrium properties are often encountered in chemistry in the form of linear free energy relationships that apply to both homogeneous (Chapman & Shorter, 1972) and interfacial processes (Spiro, 1984), and these have proved extremely helpful for predictive purposes. The discovery of such a correlation in the present work could prove equally useful in extraction kinetics.

It is more difficult to interpret these findings on a molecular basis. The dry leaf contains *ca.* 5 wt% water and 4 wt% caffeine so that most of the latter does not dissolve until the leaf swells with extracting solution. At that stage, however, the caffeine concentration is well below saturation, *ca.* 0·05 mol kg$^{-1}$. By a long extrapolation the equilibrium constant for successive self-associations can be estimated as around 1 kg mol$^{-1}$ at 80°C and so some 90% of caffeine in the swollen leaf will be in the monomeric

### TABLE 2

Solubilities of Caffeine in Aqueous Salt Solutions at 23·7°C (From the Data of Schryver, 1910)

| *Chloride salt* | *Concn.* (*mol dm*$^{-3}$) | *Caffeine soly.* (*mol dm*$^{-3}$) | *Sodium salt*[a] | *Concn.* (*mol dm*$^{-3}$) | *Caffeine soly.* (*mol dm*$^{-3}$) |
|---|---|---|---|---|---|
| Water | — | 0·098 5 | Chloride | 1 | 0·065 7 |
| Lithium | 1 | 0·110 2 | Bromide | 1 | 0·105 3 |
| Sodium | 1 | 0·065 7 | Iodide | 1 | 0·225 6 |
| Potassium | 1 | 0·068 0 | Sulphocyanide | 1 | 0·288 0 |
| Calcium | 0·5 | 0·084 6 | Sulphate | 0·5 | 0·049 4 |
|  |  |  | Acetate | 1 | 0·048 9 |
|  |  |  | Malonate | 0·5 | 0·042 3 |
|  |  |  | Citrate | 0·33 | 0·041 0 |
|  |  |  | Benzoate | 1 | 0·776 3 |
|  |  |  | Salicylate | 1 | 1·188 0 |

[a] Many of the salts were obtained by neutralising 2N NaOH solution with the acid using phenolphthalein as indicator. The salt concentrations in the original paper were all given as 1 Normal.

**TABLE 3**
Solubilities of Caffeine in Various Aqueous Electrolyte Solutions at 25°C (From the Data of Emery & Wright, 1921)

| *Electrolyte* | *Concn.*[a] *(mol dm$^{-3}$)* | *Caffeine soly.* *(mol dm$^{-3}$)* |
|---|---|---|
| Water | | 0·1066 |
| Potassium bromide | 1·0 | 0·1100 |
| Potassium bromide | 2·5 | 0·1048 |
| Sulphuric acid | 0·5 | 0·1728 |
| Citric acid | 0·33 | 0·3302 |
| Sodium benzoate | 0·1 | 0·1763 |
| Sodium benzoate | 1·0 | 0·7868 |
| Sodium salicylate | 0·1 | 0·2535 |
| Sodium salicylate | 1·0 | 1·144 |

[a] The concentrations in the original paper were given in normalities.

form. However, the extent of its association in the leaf with theaflavins and thearubigins is unknown. Diffusion into the leaf of a soluble species like $PhSO_3^-$ that complexes with caffeine may loosen its links with the larger polyphenols and so increase its effective diffusion coefficient. Alternatively, complexation of $PhSO_3^-$ (say) with caffeine at the leaf/solution interface will lower the concentration of *free* caffeine there and so increase the *free* caffeine concentration gradient through the leaf. This would speed up the intra-leaf diffusion. Further work is needed to differentiate between these possibilities.

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