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Aqueous extraction of solubles from oranges: a kinetic study

Clark Chambers, Kim Exaudi-Larsen & William E. Price*

Department of Chemistry, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

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The kinetics of the aqueous extraction of solubles from oranges has been investigated as a function of temperature (50–88 °C). The data fit simple first-order kinetics and indicate rate constants of between $4.8\times10^{-4}\ s^{-1}$ and $2\times10^{-3}\ s^{-1}$. This is equivalent to a half-life for the process of between 22 min and 7 min. The temperature-dependence of the kinetics of extraction was found to be similar to that obtained for the extraction of other foodstuffs, including the extraction of solubles from black tea. An activation energy of 37 kJ mol^{-1} was obtained over the temperature range considered. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Extraction of soluble solids from food products has typically been achieved through the rupturing and squeezing of cells in the food and forcing out the cell contents via mechanical means such as pressing or reaming. There has been much interest recently in alternative approaches. For example, the use of counter-current extraction (CCE) techniques for the extraction of components from foodstuffs (Anonymous, 1986; McPherson, 1987), such as concentrates from seafood, juice from fruit, sugar from sugarbeet and oils from grape seeds (Anonymous, 1986), has been touted as a potential alternative. CCE (sometimes called counter-current diffusion extraction) is based on the diffusion of soluble material from within a cell structure under the driving force of a concentration gradient (McPherson, 1987). This is achieved by disruption of the cell structure making the cell walls permeable. This is readily done by the action of heat (Binkley & Wiley, 1978; Casimir, 1983), and consequently CCE is usually carried out at elevated temperatures.

The most common form of CCE is continuous counter-current extraction (Schwartzberg, 1980), and the type of equipment used within the food industry has been recently reviewed. In a typical CCE, a single screw rotates continuously (either in one direction or backwards and forwards; Gunasekaran *et al.*, 1989), and close contact is made between two streams, one containing the food pulp and the other heated water. The CSIRO (The Commonwealth of Australia Science and Industrial Research Organisation) has recently developed, in cooperation with an industrial partner, a single-screw CCE capable of very high extraction efficiencies (e.g. 92.6% for the extraction of apple juice). CCE has found much use in the fruit juice industry (Osterberg & Sorensen, 1981), including citrus fruit. It has distinct advantages because of the high extraction efficiencies possible and makes use of more of the fruit. This has led to a proliferation of orange juices which contain CCE-extracted solubles and are not pure 'squeezed orange juice' (Johnson, 1994; Patel, 1994). This has caused concern over the indiscriminate use of CCE for adulteration of citrus juices and the problem of detection and legislation of CCE-produced juices made from whole oranges, including the peel (Robards & Antolovich, 1995).

Against this background, we became interested in the technique. In particular, little quantitative work had been carried out on the kinetics of the aqueous extraction of solubles from citrus fruit, initially oranges. Consequently, we set out to investigate the effect of a number of experimental variables on the rate of extraction of components from sliced oranges into aqueous media. The components followed were total solubles as measured by peak absorbance. Previous studies (Spiro & Siddique, 1981*a*,*b*; Spiro *et al.*, 1990; Price & Spitzer, 1994) had shown the benefits of using basic quantitative physicochemical methods to model the equilibrium and kinetics of extraction of

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*To whom correspondence should be addressed.

components from a variety of foodstuffs including tea, coffee and ginger.

MATERIALS AND METHODS

Preparation of fruit samples

Navel oranges were obtained commercially and kept in cold storage until required. Orange samples were prepared for experiment by cutting whole oranges into slices (approximately one-eighth of an orange) leaving the skin and pith on. Each slice therefore had two cut surfaces.

Kinetics procedure

Kinetic experiments were carried out in a water-bath under controlled temperature conditions (50–88 °C), where the control using a Braun Thermomix ME controller was better than ±0.2 °C. A conical flask with a pre-weighed amount of water was thermostatted. A weighed amount of sliced orange was added at time $t = 0$. A range of volume of water:mass of orange ratios (2–10) were employed. The solution was gently stirred using a magnetic submersible stirrer (Kartell, Milan). The rate of stirring was sufficient to obtain good mixing for the water:fruit ratios used. It did cause some damage to the fruit pieces but this was minimal. Ten samples of approximately 1 ml were taken over a period of time using a syringe and needle. In addition, an equilibrium sample value was obtained. Samples were filtered through 0.45 μm filters (Bonnet, Sydney) and diluted by a factor of 10 with distilled water. These samples were then analysed by UV–vis spectrophotometry (Hitachi) at a wavelength of 263.4 nm. This wavelength was chosen as it was found to be the peak maximum for an aqueous solution of orange solubles. Each kinetic experiment was carried out under the same conditions at least three times, and those at a water:fruit ratio of 3:1, six times.

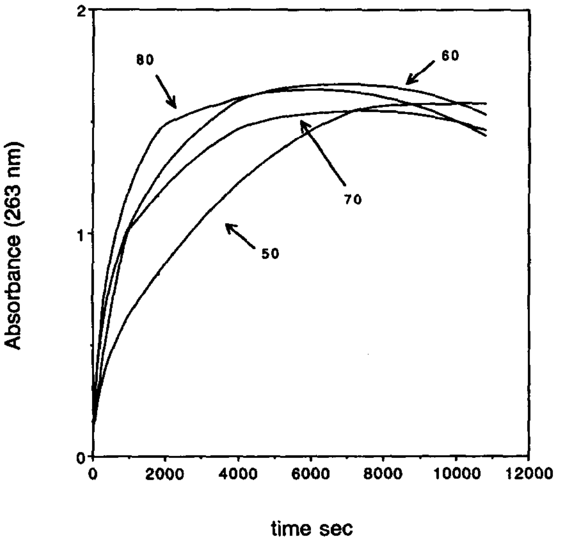

Fig. 1. Absorbance at 263 nm vs extraction time for aqueous solutions of orange pieces (3:1 volume:mass ratio) at different temperatures (as shown).

Corrections to the concentrations determined were made to account for sampling and evaporation as described previously (Spiro & Jago, 1982).

RESULTS AND DISCUSSION

Figure 1 shows typical plots of absorbance vs extraction time for a water:fruit ratio of 3:1 at various temperatures. One important feature to note is that, because of the heterogeneous nature of the product (oranges), the absolute value of the absorbances varies. However, it is clear from these plots that the extraction of solubles is quite rapid and is complete (within experimental error, ±1%) by 3 h for all temperatures investigated. Plots of this type were used to estimate the stable equilibrium absorbance for use in the kinetic analysis.

At long extraction times, particularly at higher temperatures (80 °C and above), it was noticed there was a slow decrease in the total absorbance after it had plateaued off, indicating some chemical degradation of some soluble components in the solution. This tended to occur between 2 and 3 h extraction time. This may be seen in some of the results in Fig. 1 and is illustrated also in Table 1 for the absorbance at 263 nm for an orange/water mixture as a function of time at 80 °C. These absorbances have been corrected for sampling and evaporation. In this example there is a decrease in the absorbance of 15% between the 1 h sample and the 3 h sample. There is clearly a slow chemical degradation reaction (or more than one) occurring.

In other work (W. Price, unpublished results), analysing the sugar content of the solution as a function of time, a similar degradation effect was found. In these present experiments it was hoped to use the individual sugars, glucose, fructose and sucrose, as components to study the aqueous extraction process. However, it was not possible to obtain reproducible kinetic sample concentrations or an equilibrium concentration for any of the three sugars at temperatures in the range 70–85 °C. This was thought to be due to degradation of the sugars in solution. This is quite surprising as it is believed that these carbohydrates are stable (Belitz & Grosch, 1987) in solution at low concentrations up to temperatures of 100 °C. This work on the stability of the sugars is continuing.

It is perhaps expedient to consider first the experiments investigating the effect of the water volume:fruit mass ratio on the extraction. Of particular interest is the effect of the ratio upon the equilibrium concentration in

Table 1. Kinetic data at long extraction times for a 3:1 water:fruit ratio at 80 °C

Time (min)	0.5	1	2	5	30	60	120	180
$A_{263\ \mathrm{nm}}$	0.180	0.245	0.396	0.652	1.389	1.662	1.614	1.445

the solution. It has been shown that it is possible to estimate the equilibrium constant for the extraction process from such data for extraction from other foodstuffs (Spiro & Siddique, 1981*a*). An equation based on a simple two-phase model of extraction has been proposed by Spiro and Siddique (1981*a*). This may be adapted for the present case as follows:

$$1/A_\infty = w/Vx_0 + 1/Kx_0 \qquad (1)$$

where A_∞ is the measured equilibrium absorbance in a particular experiment with weight w of fruit and volume V of water. K is the partition coefficient for the extraction, i.e. the equilibrium constant for the distribution of solubles between the spent fruit phase and the solution. This value assumes that there is no swelling of the fruit during the extraction and also that the loss of solubles from the fruit does not effect its mass or volume. x_0 is the initial concentration of solubles in the fruit (in this case in absorbance units). Independent preliminary experiments indicated that the amount of swelling was small, approximately 2% by mass.

A plot using this expression is shown in Fig. 2 for the data in Table 2 at 70 °C with volume:mass ratios varying between 2 and 10. Analysis of the current data indicates an equilibrium constant at 70 °C of $K = 1.1$ (± 0.4) assuming the fruit does not swell appreciably. This value is similar to those found for other extractions from foodstuffs such as tea (Spiro & Siddique, 1981*a*; Price, 1985) and is not unexpected given the predominantly aqueous nature of the fruit environment.

It was found that the absorbance kinetic data fitted simple first-order kinetics with equations of the form:

$$\ln[A_\infty/(A_\infty - A_t)] = kt + c \qquad (2)$$

where A_∞ and A_t are the measured absorbances at equilibrium and time t, k is a first-order rate constant and c is a constant (not predicted by the model). This form of extraction kinetics has been successfully applied to other foodstuffs by Spiro's group (Spiro *et al.*, 1990, 1992) and others. The fits were found to be extremely good in most cases ($r^2 > 0.99$) and the reproducibility between runs was reasonable considering the heterogeneous nature of the material. Table 2 summarizes the results averaged for each temperature.

If an Arrhenius plot is carried out to determine the temperature-dependence of the kinetics, an activation energy E_a of 37($\pm$3) kJ mol^{-1} is obtained over the temperature range considered. This is shown in Fig. 3. This E_a value is very similar to that obtained for the extraction of total solubles from black tea (Price & Spitzer, 1993) and for extraction of caffeine from an Assam black tea (Spiro *et al.*, 1992). The major barrier to loss of solubles from oranges is the rupturing of the cell structure. Even though there are cut surfaces on the orange slices, the structure of an orange with its many discrete cells means that this is a significant barrier to extraction. Hence, in these experiments and in CCE procedures, elevated temperatures were used (Binkley & Wiley, 1978), as mentioned in the Introduction. The plot shown in Fig. 3 is, however, definitely curved at the higher temperature end. This may be indicative of a change in the limiting step to extraction at these temperatures (80–88 °C). The temperature is sufficiently high to allow easy rupture of the orange cells and consequently the temperature-dependence in this region is less than at cooler temperatures.

It should be borne in mind that the analysis of equilibrium absorbances assumes that the effect of the slow degradation process highlighted above is very small. This also impinges on the kinetic analysis. However, the quality of the first-order plots, together with the Arrhenius plot, tend to suggest this is a reasonable assumption.

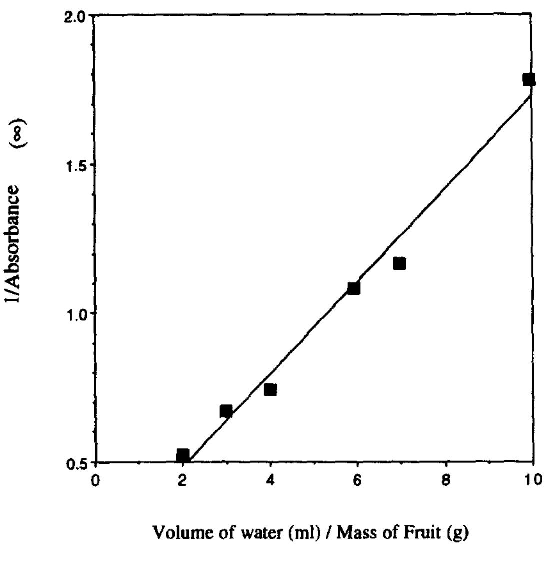

Fig. 2. Effect of water:fruit ratio on the equilibrium absorbance for extraction of solubles from oranges at 70 °C.

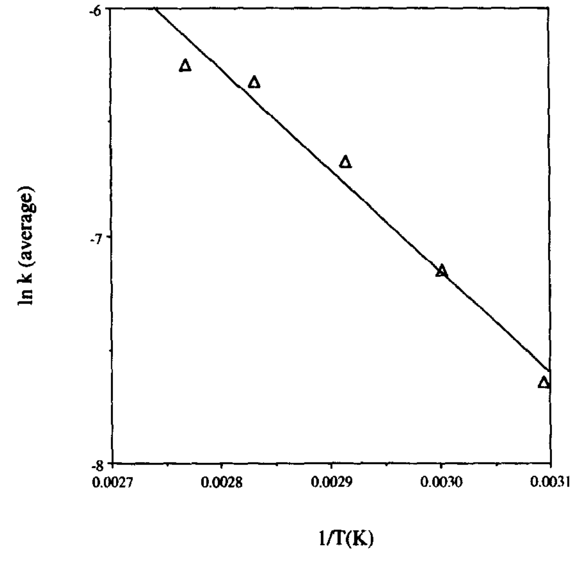

Fig. 3. Temperature-dependence of extraction of solubles from oranges from 50 °C to 88 °C.

Table 2. Summary of kinetic results for extraction of solubles from oranges at temperatures ranging from 50 °C to 88 °C

Temperature (°C)	Mean ratio (water:fruit)	Rate constant (s^{-1})		Corrected A_∞		Mean intercept	Mean $t_{1/2}$ (s)
		Mean	SD	Mean	SD		
50.00	3.00	4.81E-04	4.8E-05	1.58	0.26	0.09	1454
60.00	3.00	7.82E-04	1.0E-04	1.67	0.10	0.18	899
70.00	1.99	1.00E-03	1.5E-04	1.90	0.05	0.12	697
70.00	2.99	1.27E-03	5.1E-04	1.49	0.33	0.13	600
70.00	4.01	8.71E-04	2.0E-04	1.35	0.10	0.14	817
70.00	5.92	9.29E-04	1.4E-04	0.92	0.12	0.21	754
70.00	6.96	1.27E-03	7.4E-05	0.86	0.04	0.07	546
70.00	9.94	1.17E-03	4.4E-04	0.56	0.01	0.18	638
80.00	3.00	1.80E-03	3.7E-04	1.46	0.18	0.09	396
88.00	3.00	1.93E-03	5.6E-04	1.39	0.18	0.14	389

SD, standard deviation of the mean.

Most experiments were carried out using a water:fruit ratio of 3:1. This is typical (Gunasekaran *et al.*, 1989) of amounts used in CCE where temperatures of 75–95 °C and fruit residence times of 60–90 min are employed. Our present results suggest that such residence times must indicate poor bulk scale mixing of the aqueous and fruit phases as the half-life of the extraction in this temperature range is 6–8 min. In addition, in view of the observation of changes in composition of the solution with prolonged exposure to elevated temperatures, it is possible that the quality of the final juice produced would be in question.

CONCLUSIONS

The results presented represent the first aqueous extraction kinetics data for oranges. The temperature-dependence of the kinetics is similar to that for solubles extracted from black teas. Under the conditions normally used in CCE, it is expected that, under good mixing conditions, presumed to be present using the single-screw diffuser, the half-life for the extraction of solubles is about 7 min (for 80 °C). This would indicate that residence times typically used in CCE of 60–90 min are likely to be excessive. In addition, it was found that extended exposure of the solution to high temperatures caused chemical changes, including degradation reactions of the sugars present. This is likely to have a detrimental effect on the quality of the product.

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