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Approach to the design of model systems for food additive–food component interactions

B. L. Wedzicha, S. J. Goddard & Alam Zeb

Procter Department of Food Science, University of Leeds, Leeds, UK, LS2 9JT

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The rates of reactions between food additives and food components are affected by concentration, ionic strength, non-electrolytes, pH, surfactants and solute transport. All these variables must be considered in the design of model systems. The importance of the medium to the progress of test reactions is illustrated and critically appraised.

INTRODUCTION

Food chemists very often resort to simple chemical systems to mimic reactions which take place in foods. The general term 'model system' is applied somewhat indiscriminately and inspection of the literature shows that an appreciation of what should constitute such a model, in a given situation, varies considerably. Some of the most complicated questions arise when partially dehydrated or intermediate moisture foods are being considered. These are of particular interest because high chemical reactivity is often associated with them and the use of humectants to model such reactions is of considerable practical importance. In this paper we discuss some of the questions which need to be addressed to assist in the design of effective models for reactions in foods with particular reference to interactions between food preservatives and food components.

EFFECTS OF CONCENTRATION

The reactions of sulphur(IV) oxospecies, S(IV), i.e. SO_2, HSO_3 and SO_3^{2-}, in food dehydration offer much to illustrate the effects of concentration on the reactivity of ionic species. Consider first the following conversion of hydrogen sulphite to disulphite (metabisulphite) ion:

$$2\ HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$$

This equilibrium is rapidly established and its significance is that, at the pH of food, a high proportion of the S(IV) present in a sulphited food will be in the form of HSO_3^-, in equilibrium with $S_2O_5^{2-}$. The equilibrium constant, K, is given by

$$K = [S_2O_5^{2-}]/[HSO_3^-]^2$$

where, in aqueous solution, the concentration of water is omitted from the expression. A mathematical consequence of the above expression is that, as the concentration in the system is increased, e.g. by removing water as in dehydration, the position of equilibrium is displaced to the right. In addition, the value of K increases with ionic strength, thereby causing a greater bias for $S_2O_5^{2-}$ with concentration than is predicted from the law of mass action alone. If concentration is increased to such an extent that the concentration of water can no longer be neglected in the law of mass action expression, i.e. the water activity, a_w, is significantly reduced, one might expect extensive conversion of HSO_3^- to $S_2O_5^{2-}$. Indeed, $Na_2S_2O_5$ crystallises when solutions of $NaHSO_3$ are dehydrated. It has been established that sulphur(IV) oxospecies catalyse (probably though acid-base catalysis) the early stages of the Maillard reaction of glucose + glycine in the steps leading to formation of 3-deoxyosuloses (Wedzicha & Vakalis, 1988) but effectively inhibit browning by reacting with these intermediates to give a 3,4-dideoxy-4-sulpho osulose which is relatively unreactive towards browning. The interconversion of sulphur(IV) oxospecies is, then, expected to affect the kinetics of these early stages in the sulphite-inhibited Maillard reaction. It has been suggested (Wedzicha, 1987) that $S_2O_5^{2-}$ is a much better acid-base catalyst than any of the other S(IV) species and its potential formation in food and model systems is, therefore, of considerable interest, particularly when considering the high requirements for the additive in food dehydration.

The mathematical behaviour of the law of mass action expression applies to any equilibrium for which the equilibrium constant has units of $(\text{concentration})^{-1}$. Thus, we find that concentrations of ion pairs such as $Na^+SO_3^{2-}$ become significant in concentrated systems (Wedzicha & Goddard, 1991), reducing the activity of the sulphite ion and ability to act as a nucleophile or base catalyst; but perhaps the most important effect of concentration is on the extent of formation of hydroxy-

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sulphonate adducts between carbonyl components of food and HSO_3^-. At high concentrations, such adducts could be formed in sufficient yield to become kinetically significant and, in general, the distribution of S(IV) between free and reversibly bound forms will be altered, thereby changing the ability of S(IV) to catalyse the glucose-glycine reaction. The choice of concentration at which to study a model reaction is far from trivial and can have a significant effect on conclusions drawn from the model.

EFFECTS OF NON-ELECTROLYTES

It is normal practice to model chemical reactions in intermediate moisture systems with the aid of non-electrolytes acting as humectants, including glycerol, polyethylene glycols (PEG) or sugars. The many non-electrolytes present in foods are likely to affect the solvation of ionic species and thereby change their activities in solution. The possible magnitude of this effect is illustrated in Fig. 1 for the variation of the pK_a of HSO_3^- as ethanol, glycerol, PEG and sucrose are added (Wedzicha & Goddard, 1991). We see that it is possible to observe a change of pK_a by up to 2 units, but of particular interest is the fact that there exist considerable differences between the solutes, sucrose showing little effect. Whilst suggesting that one should apply pK_a values reported in the literature to foods with caution, we see that, in order to be able to model the behaviour of S(IV) during, say, a food dehydration operation, it is necessary to correctly model the non-electrolyte composition. There is no obvious relationship between the behaviours of the different non-electrolytes used to obtain the data in Fig. 1, and a_w does not represent the common independent variable for the x-axis of Fig. 1. It is likely that the observed behaviour is a combination of the effects of water content, the a_w, and specific interactions between the non-electrolyte and the ions in question.

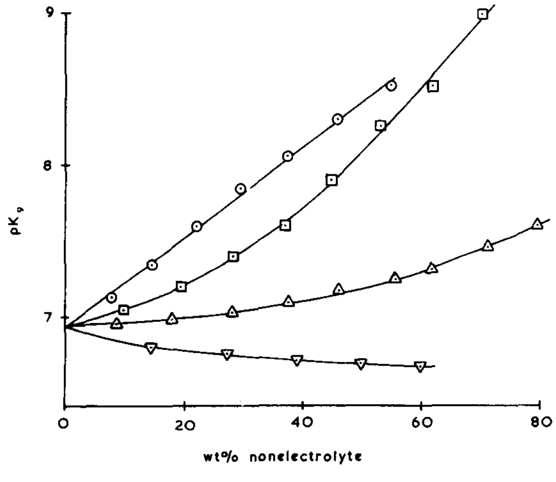

Fig. 1. Effect of concentration of non-electrolyte on the pK_a of a 50 mM solution of $NaHSO_3$ at 30°C: ○ ethanol; Δ glycerol; □ PEG-400; ∇ sucrose. Reproduced from Wedzicha & Goddard (1991).

Our belief in the need for an in-depth approach to the understanding of the behaviour of model systems is reinforced by considering again the HSO_3^-–$S_2O_5^{2-}$ equilibrium. The law of mass action predicts that a reduction of a_w should increase the extent of formation of $S_2O_5^-$, but the use of UV-visible and FTIR spectroscopy reveals (Wedzicha *et al.*, 1992) that the concentration of this product in fact decreases with non-electrolyte concentration. It is suggested that this is caused by an increase in ion-pairing, e.g. formation of $NaS_2O_5^-$, at reduced a_w, because the stabilities of such ion pairs are considerably enhanced by non-electrolytes. Similarly, the activities of other ions, e.g. SO_3^{2-}, are reduced through ion pairing and, as with the effect of non-electrolyte on pK_a value, there is no single variable which determines the extent of the association taking place. We see, therefore, that a successful model of interactions involving ionic species in foods requires a detailed description of the required composition of the system with respect to non-electrolyte.

SIGNIFICANCE OF pH

Arguably the most frequently made measurement of food composition is pH. Unfortunately this proves to be one of the most unreliable measurements whose significance is also difficult to interpret. In homogeneous systems the main problems arise from the fact that a liquid junction and asymmetry potential is set up at the measuring electrode and the magnitude of this is a complex function of the ionic composition of the medium or, more strictly, the difference in composition between the standard buffer and the unknown solution. For a given electrode, the addition of $NaNO_3$ to the solution whose pH is being measured gives rise (Wedzicha & Goddard, 1988) to a pH error which varies with ionic strength, I, to the extent of 0·15I pH units per mol litre^{-1}. The implication of this is that if one measures the pK_a of HSO_3^- at I = 0·08 and 2·3 M, the corresponding pH values at half neutralisation are 7·00 and 6·35, respectively, these values would normally be reported as the pK_a values. Correction for electrode response gives 7·16 and 6·81. If the pK_a in the more concentrated salt solution were used to calculate the ionic composition of the acid–salt mixture at a given pH, the use of the corrected value would result in a predicted salt:acid ratio which is nearly three times greater than that obtained using uncorrected data. Unfortunately, the pH measurement error depends on the anions and cations present, and a detailed analysis of measurements on complex mixtures of electrolytes has not yet been possible. We must also turn our attention to multiphase systems where one or more of the phases contains immobile acids and bases. Thus, for example, the pH of an insoluble protein gel cannot be measured, but application of the principles of the Donnan effect leads one to calculate that the pH of a surrounding aqueous phase will be lower than that of the protein, if the pH is below the isoelectric point of the protein. The value of the unknown pH is important to the design of the model system for interactions in the protein phase.

EFFECTS OF SURFACTANTS

It has been known for some time that surfactant micelles can catalyse a wide range of chemical reactions, the greatest effects being seen for reactants which tend to associate strongly with micellar structures. Okun and Archer (1977) demonstrated that the *N*-nitrosation of secondary amines can be strongly catalysed by decyltrimethylammonium bromide micelles and that of hexylamine by lecithin and cell debris. The reaction of sorbic acid with thiols provided another useful test reaction and Table 1 shows the enhancement in rate when the reaction is carried out in the presence of various surfactants (Wedzicha & Zeb, 1990).

It is significant that the reactions are catalysed even when the thiols are ionically complex and will, therefore, tend not to partition into the hydrophobic interiors of micellar structures. The lack of an effect of SDS is probably the result of the negative charge on the micelles destabilising the transition state when thiolate anions add to the sorbic acid molecule (in position 5). Whilst cationic surfactants such as dodecyltrimethylammonium bromide might act as to stabilise such a transition state, this cannot be solely responsible for catalysis of the reaction because nonionic surfactants such as Tween 80 are also useful catalysts. The observation that lecithin and datem ester accelerate the reaction is interesting because these surfactants are insoluble in water and were used as dispersions in the reaction mixtures. Heterogeneous catalysis of the sorbic acid–thiol reaction appears to be possible.

Detailed kinetic studies reveal that the different thiols are found at different kinetically resolvable locations within the surfactant micelles, when they react with sorbic acid, and the behaviour of two thiols in a mixture is largely additive (Wedzicha *et al.*, 1991). Wedzicha and Zeb (1991) have identified that bovine serum albumin, BSA, behaves similarly to the micelle-forming surfactants. The possibility that the kinetic effect of BSA involves hydrophobic interactions between sorbic acid and the protein is evident from the fact that the reaction in the presence of BSA is inhibited by 3-hexenoic acid (Wedzicha & Picard, unpublished), hexenoic acid and SDS (Wedzicha & Campbell, unpublished).

Table 1. Maximum catalytic effect of surfactants on the reaction of thiols with sorbic acid.[a] **Extent of catalysis is expressed as relative initial rate, V_r = (initial rate in presence of surfactant)/(initial rate in absence of surfactant)**

Surfactant	Maximum V_r			
	Mercapto-ethanol	Mercapto-acetic acid	Cysteine	Glutathione
DoTAB[b]	10·1	15·5	4·6	2·7
SDS	1·1	2·4	1·8	0·9
Lecithin	5·3	6·5	3·9	2·2
Datem ester	5·4	5·5	3·4	1·5
Tween 80	6·7	7·3	3·2	2·8

[a] Reproduced from Wedzicha & Zeb (1990).
[b] DoTAB is dodecyltrimethylammonium bromide.

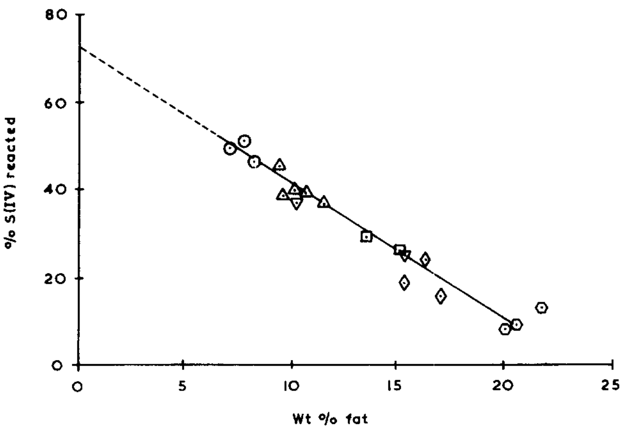

Fig. 2. Relationship between the fat content of different cuts of meat from various sources and the amount of S(IV) reacted when comminuted samples (5 g) were mixed with $Na_2S_2O_5$ (4·5 mg) at 15°C: ○ fillet steak; Δ pork steak; □ braising steak; ∇ shin beef; ◇ pork chop; ⬡ belly pork. Reproduced from Wedzicha & Mountfort (1991).

There is now sufficient evidence to be able to suggest that any attempt to model reactions in foods should involve preliminary experiments to check for any effect of surfactant. This might be particularly relevant to the modelling of small molecule–protein interactions as in, for example, enzyme inhibition studies.

TRANSPORT BEHAVIOUR

It could be said that, no matter how good a chemical model of a reaction might be, there is no point in studying its kinetics if, in a real food situation, the rate of reaction is limited by the rate of solute transport. This is sometimes difficult to identify in practice, but relocation of solutes is known to take place, e.g. in food dehydration, and could represent the rate determining step for the reactions of S(IV) in the process of fruit and vegetable dehydration (Wedzicha, 1987).

Whilst trying to explain the different reactivities of comminuted samples of different cuts of meat (beef and pork) towards sulphur dioxide (Wedzicha & Mountfort, 1991), it is found that the most significant correlation exists between the fat content and the amount of additive which has undergone reaction, as illustrated in Fig. 2. An interpretation of these data is that fat with a low melting point is released during comminution when it smears over the particles of meat, providing a barrier around the protein fibres. The ability of fat to impede transport of S(IV) in meat products was confirmed by staining fibres of defatted minced pork with malachite green before adding back the fat. This dye is bleached by S(IV), but the extent to which colour was lost on treatment of the sample with the additive depended linearly on the amount of fat present.

CONCLUSION

We have presented here a diverse set of examples to show the need for a critical approach to model system design. Despite the range of problems encountered, the solutions are embodied in a relatively small number of principles concerned with solute–solute and solute–solvent interactions. Extension of these ideas to solute–solid interactions seems appropriate. The problem lies with identifying the kinetically significant components of the foods in question, but it should be evident that these need not feature in the stoichiometric equation for the reaction of interest.

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REFERENCES

Okun, J. D. & Archer, M. C. (1977). Kinetics of nitrosamine formation in the presence of micelle-forming surfactants. *J. Natl Cancer Inst.*, **58**, 409–11.

Wedzicha, B. L. (1987). Chemistry of sulphur dioxide in vegetable dehydration. *Int. J. Food Sci. Technol.*, **22**, 433–50.

Wedzicha, B. L. & Goddard, S. J. (1988). The dissociation constant of hydrogen sulphite ion at high ionic strength. *Food Chem.*, **30**, 67–71.

Wedzicha, B. L. & Goddard, S. J. (1991). The state of sulphur dioxide at high concentration and low water activity. *Food Chem.*, **40**, 119–36.

Wedzicha, B. L. & Mountfort, K. A. (1991). Reactivity of sulphur dioxide in comminuted meat. *Food Chem.*, **39**, 281–97.

Wedzicha, B. L. & Vakalis, N. (1988). Kinetics of the sulphite-inhibited Maillard reaction: The effect of sulphite ion. *Food Chem.*, **27**, 259–71.

Wedzicha, B. L. & Zeb, A. (1990). Catalysis of the reaction between sorbic acid and thiols by surfactants. *Int. J. Food Sci. Technol.*, **25**, 167–79.

Wedzicha, B. L. & Zeb, A. (1991). Catalysis of the sorbic acid–thiol reaction by bovine serum albumin. *Int. J. Food Sci. Technol.*, **26**, 381–4.

Wedzicha, B. L., Zeb, A. & Ahmed, S. (1991). Reactivity of food preservatives in dispersed systems. In *Food Polymers, Gels and Colloids*, ed. E. Dickinson. Royal Society of Chemistry, pp. 180–93.

Wedzicha, B. L., Bellion, I. & Goddard, S. J. (1992). Infrared and ultraviolet spectra of sulphur(IV) oxospecies in water–non-electrolyte mixtures. *Food Chem.*, **44**, 165–71.