Water activity and viscosity—relations with glass transition temperatures in model food systems

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Abstract

Both thermodynamic and kinetic parameters are important in food processing and stability. Thermodynamic parameters are represented by water activity and generally applied to high and medium moisture content materials, where molecules can freely diffuse, without restrictions. In contrast, kinetic properties mainly apply to intermediate and low moisture content foods, where diffusional mobility of reactants is more or less restricted and where water acts as a plasticizer of amorphous compounds. Kinetic properties can be represented by viscosity and related to the glass transition temperature (T_g) by the Williams–Landel–Ferry equation. Thus, in a food system passing from high to intermediate and low moisture content and/or from high to low temperature, the prevailing control mechanism will gradually change from thermodynamic to kinetic.

The relationship between the water activity, temperature and viscosity is presented for some model solutions.

Keywords: Food systems; Glass; Transition; Viscosity; Water activity

1. Introduction

The water content of foods can vary within large limits: high moisture foods have water contents in the range of 80 to 95%, with water activities (aw) close to 1; intermediate moisture foods have water contents ranging approximatively from 50 to 80%, with aw from 0.75 to 0.95; semi-dry and dry foods have lower water contents, down to a few percent, with aw as low as 0.30 to 0.05. For a long time, water activity has

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been regarded by food technologists as the most important parameter controlling the behaviour of intermediate and low moisture food during processing and storage, with particular emphasis on its effects on the rates of degradative reactions.

This view is now the subject of considerable criticism. More recent studies on the relationships between structure and properties in food [1] have stressed that under many common circumstances the thermodynamic activity of water is far less relevant to processing and storage than structure-related properties, which can restrict the mobility and diffusion of reactants.

Water activity and kinetic parameters differ in particular aspects, among which are the following: (1) Water activity is an appropriate measure only if equilibrium conditions are achieved, and generally applies to systems with medium or high water content and/or at high temperature, where diffusional motions are not restricted. (2) The aw is a property of water that is modified by the presence of solutes. (3) The reference point relevant to the shelf life of food is zero aw, corresponding to a virtually unlimited stability. (4) The measurement of aw is relatively easy, and it is widespread in research and industry.

In contrast, kinetic parameters refer mainly to non-equilibrium conditions, such as amorphous systems, supercooled systems and other metastable conditions. They generally apply to systems with medium or low water content and/or at low temperatures. They are a property of the solutes and are modified by water (plasticization effect).

The reference point for a virtually unlimited stability is the glassy state and the glass transition temperature T_g, below which translational motion of molecules is hindered and chemical reactions 'freeze' [2]. In real food systems, kinetic parameters are less easy to measure than aw, and only recently they have been regarded as key factors in food stability.

The kinetic properties of foods can be represented by many rheological relaxation parameters, such as storage, loss and complex moduli, but usually a simple (apparent) viscosity value is preferred. In real food, microviscosity, i.e. the viscosity of the liquid-soluble phase within the food, cannot be measured in most cases, typically in solid foods and in foods with insoluble components. For this reason, viscosity in real food is better evaluated by means of its relation with the glass transition temperature (T_g).

According to Ferry [3], in the temperature interval between T_g and approximately $T_g + 100°C$, the dependence of viscosity (and other relaxation properties) on temperature is described by the WLF (Williams–Landel–Ferry) equation, containing two universal constants C_1 and C_2 which have been extracted from data on numerous substances [4]. Glass transition temperatures can be measured on foods by thermal analysis, as DSC and TMA. The T_g of many food and food components with different water contents, can be found in the literature [1,4].

If the whole range of possible water contents is considered for a hypothetical food, a gradual change in the main controlling mechanism from thermodynamic to kinetic can be expected, when passing from high to low water content and/or from high to low temperature. This behaviour is well represented in the dynamics map proposed by Slade and Levine [1].

According to Ferry [3], as the glass transition is approached, the temperature dependence of viscosity approaches the WLF model much more steeply than the familiar Arrhenius model, which applies at temperatures above $T_g + 100°C$. In this interval the temperature dependence of viscosity will be much stronger than that on aw. As a consequence, the critical range of water content at which the prevailing control mechanism first overlaps and subsequently changes from thermodynamic to kinetic, will also be temperature-dependent. Thus, a decrease in temperature could change an aw-controlled reaction into a diffusion-limited one, i.e. T_g controlled.

According to the specific case, both the aw and T_g approaches can help to define relationships among moisture, temperature and chemical reaction rates [4]. It must also be born in mind that diffusion in foods depends on many factors, among which are the relative molecular size of the diffusant(s) and the medium, the porosity of the matrix, and possible physical changes, e.g. collapse or crystallization. Simple T_g and/or aw relations should then be used with precautions.

The present work gives some experimental and theoretical examples of the relationships among water activity, concentration, temperature and viscosity in some model solutions.

2. Materials and methods

2.1. Viscosity data

Viscosity data at low concentrations were taken from the Handbook of Chemistry and Physics [5]; viscosities (η) at high concentrations were calculated from published or experimental glass transition temperatures (T_g) using the WLF equation with the universal constants ($C_1 = 17.44$; $C_2 = -51.6$) and setting the glass viscosity (ηg) at 10^{14} cP, according to Soesanto and Williams [6]:

$$\log(\eta/\eta g) = -17.44(T - Tg)/[51.6 + (T - Tg)]$$

The T_{gs} values of D-fructose, D-glucose, sucrose and maltose, were taken from Jouppila and Roos [7]. T_{gs} values for raffinose were obtained by DSC (Mettler, TA 4000) at a heating rate of 5°C min^{-1}, on a 15 μL sample, with an empty crucible as reference. The T_{gs} of freeze-dried solutions, equilibrated over saturated salt solutions at 11, 23, 33 and 43% relative humidity, were measured; those at RH 50% and 60% were extrapolated.

2.2. Water activity data

Literature data were used for D-glucose, D-fructose, sorbitol [8], and maltose [9]. The aw values of sucrose solutions were taken from Norrish [10] and adjusted for temperatures with a correction factor of -0.001 aw/°C. The aw values of sucrose solutions at sub-freezing temperatures were obtained from equilibrium freezing temperatures at the selected concentrations [11].

3. Results and discussion

In Figs. 1–4, the sequences of the physical properties relations for sucrose solutions are presented. Fig. 1 shows the sorption isotherm at 20°C, in the high concentration range. Fig. 2 shows the viscosities at 20°C in the whole range of concentrations. It can be observed that with 94% w/w sugar concentration, the system reaches 10^{14} cP at, or close to, the glassy state. In Fig. 3, obtained by combining the data of Figs. 1 and 2, viscosity is plotted against water activity. The curve has a quasi-linear slope. The linearity may reflect the approximately inverse relations between viscosity and water activity, with respect to molecular weight and mass concentration. Roos and Karel [12] reported on a quasi-linear relation between T_g and aw in the range 0.2–0.7 aw, for a large number of substances.

Fig. 4 shows the aw/viscosity relationships from −30 to 60°C. These plots were obtained from viscosity/concentration data at different temperatures taken from the literature and substituting the concentration value with the corresponding water activity value, adjusted for temperature as previously described (see Section 2). The data on the high viscosity side of the figure were calculated by the WLF equation and glass transition temperatures, as described above. Fig. 4 shows the possibility of a dramatic change in the control mechanism as a consequence of a temperature change in systems with equal water activities. If a limiting viscosity of 10^8 cP is set for a hypothetical reaction, it will correspond to aw values of 0.14, 0.57 and 0.64 respectively at 60, 40 and 0°C. At sub-freezing temperatures, the aw/viscosity relations
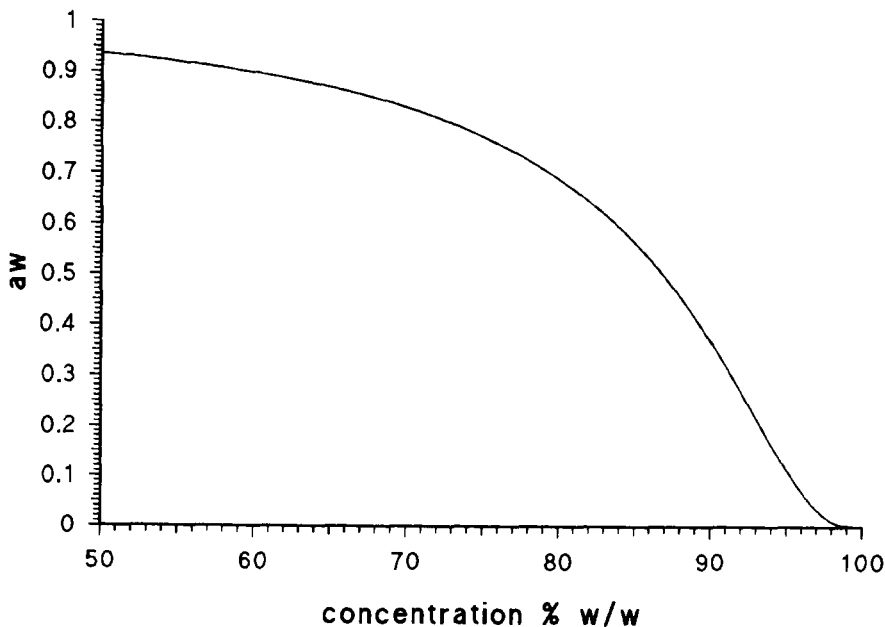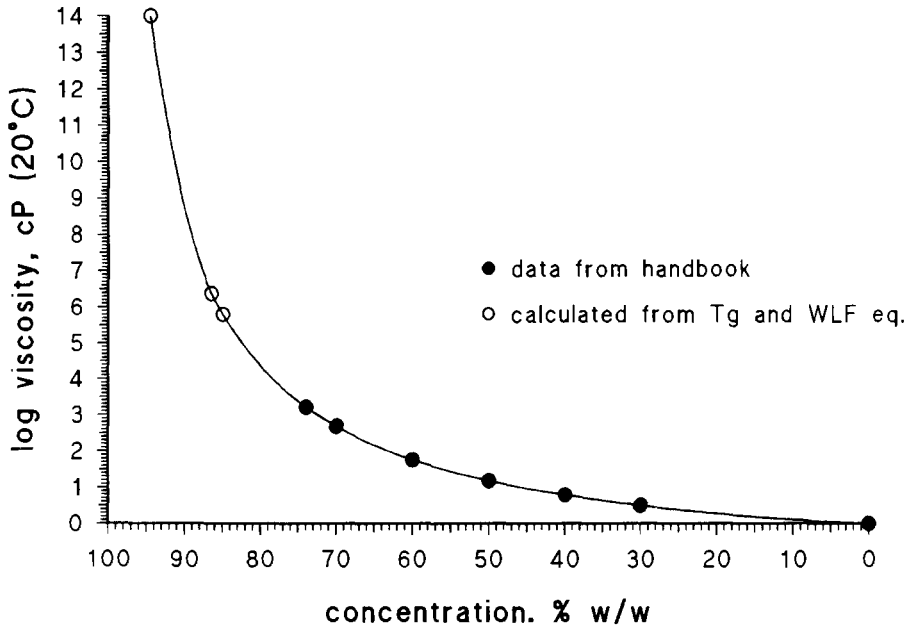

Fig. 1. Sorption isotherm of sucrose.

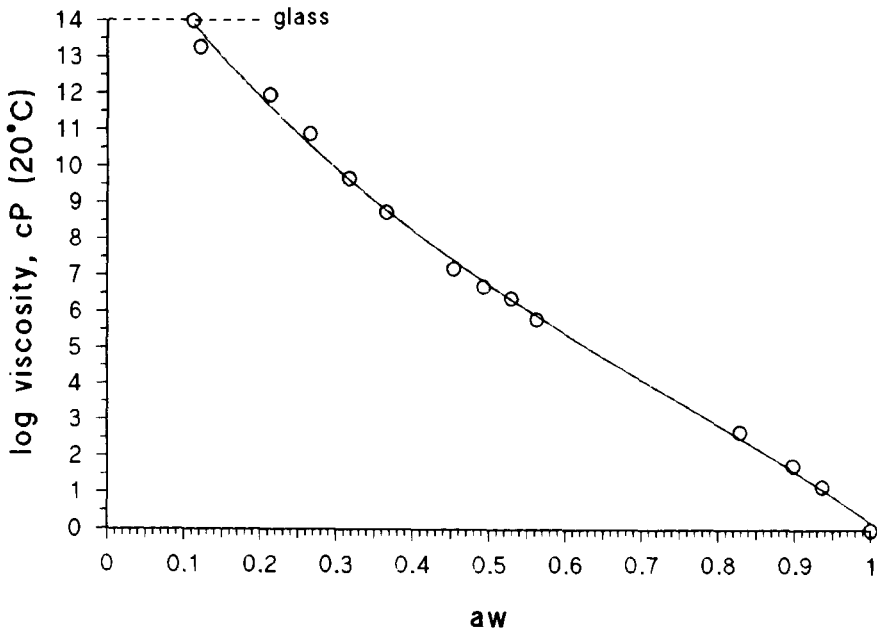Fig. 2. Viscosity of sucrose solutions.

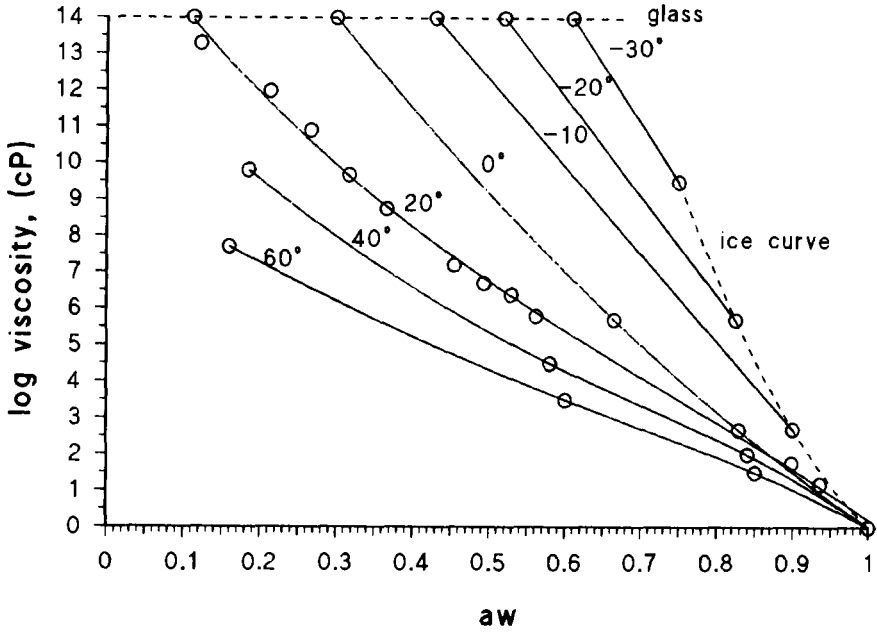Fig. 3. Viscosity versus water activity of sucrose solutions.

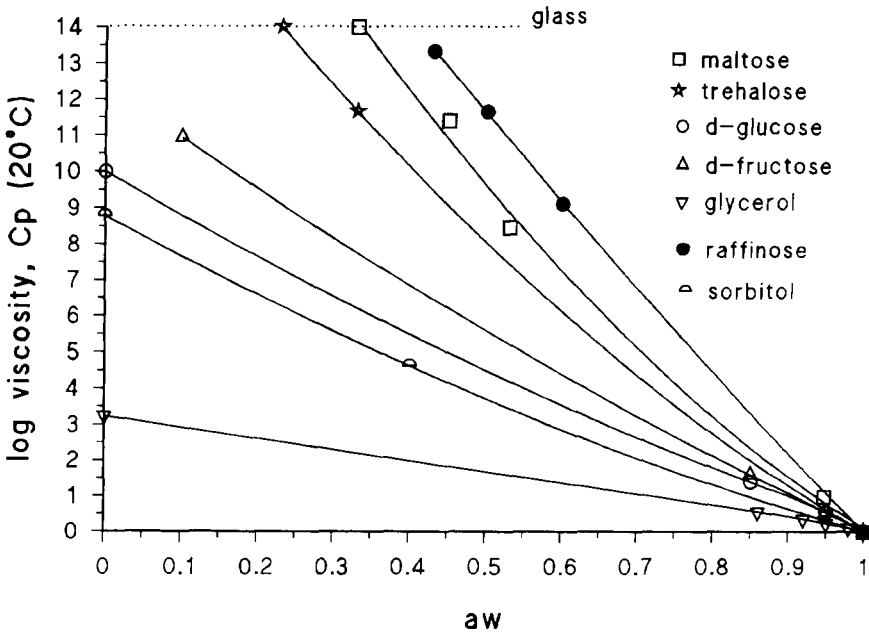Fig. 4. Viscosity versus water activity of sucrose solutions at different temperatures.

Fig. 5. Viscosity versus water activity of model solutions.

meet the ice freezing curve. The very high viscosities at temperatures below 0°C, more than the Arrhenius effect on reaction kinetics, can account for the greatly enhanced stability of frozen systems and foods.

Fig. 5 shows the estimated aw/viscosity plots of some model solutions. From Fig. 5, it can be inferred that at equal water activity, a system will be under thermodynamic or kinetic control, depending on the solute.

It should be stressed that in the figures presented here, WLF calculations are based on universal constants, which are not necessarily applicable, and on the assumed value of viscosity at T_g, also questionable [13]. Under these circumstances, it appears that the differences in $\log \eta$, among different substances with the same water activity, can be of many orders of magnitude, also within homogeneous classes of solutes, e.g. sugars. It is also quite evident that the aw/$\log \eta$ relationships are extremely sensitive to temperature.

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References

[1] L. Slade and H. Levine, Crit. Rev. Food Sci. Nutr., 30 (1991) 115.
[2] C.A. Angell, R.D. Bressel, J.L. Green, H. Kanno, M. Oguni and E.J. Share, J. Food Eng., 22 (1994) 115.
[3] J.D. Ferry, Viscoelastic Properties of Polymers, 3rd edn., John Wiley, New York, 1980.
[4] M.L. Williams, R.F. Landel and J.D. Ferry, J. Am. Chem. Soc., 77 (1955) 3701.
[5] Handbook of Chemistry and Physics, R.C. Weast and M.J. Astle (Eds.), CRC Press Inc., Florida, 1981.
[6] T. Soesanto and C. Williams, J. Phys. Chem., 85 (1981) 3338.
[7] K. Jouppila and Y. Roos, Proceedings ISOPOW V Symposium, Peniscola, Spain, 1992, p. 4. K.A. Nelson and T.P. Labuza, J. Food Eng., 22 (1994) 271.
[8] E. Sloan and T.P. Labuza, J. Food Sci., 41 (1976) 532.
[9] Y. Roos and M. Karel, Biotechnol. Prog., 7 (1991) 49.
[10] R.S. Norrish, J. Food Technol., 1 (1966) 25.
[11] F.E. Young and F.T. Jones, J. Phys. Chem., (1949) 1334.
[12] Y. Roos and M. Karel, J. Food Sci., 56 (1991) 38.
[13] M. Peleg, Crit. Rev. Food Sci. Nutr., 32 (1992) 59.