Effect of viscosity on electrical conductivity in liquid foods

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Abstract

The electrical conductivities of foods affect their heating with ohmic heating and microwaves, and are required for electrical tomography studies. A range of model foods consisting of solutions of sodium carboxymethyl cellulose (NaCMC), NaCMC + sugars, concentrated skim milk, whey protein and viscous sugar solutions, with various amounts of electrolytes were prepared. The electrical conductivity was measured using a parallel plate sensor connected to an RCL meter using an a.c. voltage. The conductivity was found to increase with concentration, but was reduced by the effects of viscosity on ion mobility. The conductivity was closely related to bulk viscosity for sugar solutions following the modified Walden equation, but was unrelated to the viscosity of NaCMC solutions. Instead an "ion-diffusion" viscosity was defined and calculated from the electrical conductivity data, and this was found to relate well to the expected viscosity of the solution to which ions are exposed at a molecular scale.

Keywords

Liquid food, carboxymethyl cellulose, sugars, skim milk, whey protein, viscosity, electrical conductivity, ion mobility, salts

Introduction

Many liquid foods such as milk, yogurt, and honey are complex solutions and colloidal dispersions containing sugars, proteins, minerals, fat and other minor components in water. Knowledge of property contributions by each component in milk will provide a clear understanding of the liquids characteristics (Madoumier et al., 2015). In this study electrical conductivity is the main property of interest, especially in the way it relates to viscosity.

Sharifi & Young (2012, 2013) established a correlation between conductivity and the composition of concentrated milk solutions with up to 47% solids so that they could use the results for electrical tomography. They used multiple linear regression to relate the total solids content to temperature and electrical conductivity, but they did not consider the effect of viscosity.

St-Gelais et al. (1995) measured conductivity and viscosity of milk solutions as the pH was reduced in an attempt to monitor gelation. While their data show that both measurements changed, the changes appeared to be independent of each other. When the pH changed rapidly from 5.6 to 5.0, the viscosity increased about 100 times, while the conductivity only doubled. Henningsson et al. (2005) stated that proteins and lactose affected electrical conductivity of milk via viscosity, and that proteins, being charged, could contribute directly as a charge carrier.

A number of researchers have studied saccharide + electrolyte systems and have proposed modifications to Walden's rule. Stokes (1959) confirmed that for KCl + sucrose solutions conductivity was inversely proportional to viscosity raised to the power of 0.7. Miller et al. (2000) reported powers of 0.64 for NaCl in trehalose and 0.78 for glucose. Longinotti and

Corti (2002) gave similar results for $MgCl_2$, $CaCl_2$, NaCl and KCl in trehalose and sucrose. More data is given for these chlorides in sucrose by Mitra et al. (2010). Acquarone et al. (2007) used electrical conductivity with pH at different dilutions of honey to determine

Bordi and Cametti (1986) showed that the concentration (and hence the bulk viscosity) of carboxymethyl cellulose (NaCMC) has little effect on electrical conductivity when the concentration of added $BaCl_2$ was greater than about 3 mmol/L. Below that concentration they use Manning ion condensation concepts to explain the effect of NaCMC concentration.

This study was conducted to establish relationship for a range of food liquids at higher concentrations and hence higher viscosities. Model solutions were prepared using sugars, whey protein, milk powder, carboxymethyl cellulose and salts, and the electrical conductivity and viscosity of these was measured.

Theory

At low concentration the conductivity, σ, of a solution can be written as a sum for different ionic species

$$\sigma = \Sigma_i C_i \lambda_i \qquad (1)$$

where C_i is molar concentration of ion i, and λ_i is the ionic conductivity which in turn can be defined in terms of Faraday's number, F, ion charge, z_i, and ion mobility, u_i.

$$\lambda_i = F z_i u_i \qquad (2)$$

Ion mobility can be related to diffusion and hence to viscosity, η using the Walden equation.

$$u_i = \frac{e_0 z_i}{6\pi\eta r_i} \qquad (3)$$

Here e_0 is the charge of an electron and r_i is the Stokes' radius.

For saccharide + electrolyte systems it has been found that as the viscosity increases $\lambda \propto 1/\eta^{\alpha}$ where the constant α has been determined to be in the range 0.64 to 0.78 for various sugars. Hence the modified Walden equation is written.

$$u_i = \frac{e_0 z_i}{6\pi \eta^{\alpha} r_i} \qquad (4)$$

But to be dimensionally correct it, the viscosity term should be written as $\eta_0 \left(\eta/\eta_0\right)^{\alpha}$ where η_0 is a reference viscosity in consistent units.

Longinotti and Corti (2002) concluded "*It is believed that the reason for the enhanced ion mobility in the aqueous sugar solutions is the existence of structural microheterogeneities in the fluid. The local environment around the ions would be richer in water and consequently the local viscosity will be lower than the bulk viscosity.*".

Hu et al. (2010) favoured a form with $\eta^{0.5}$ which they applied for using binary solutions with a water activity the same as the mixed solution. This approach, while valid, is problematic at very high concentrations where water activity is not well defined for all solutes.

For binary aqueous electrolyte solutions, as the salt concentration, C, increases the calculated conductivity decreases and is often described by Kohlrausch's Law

$$\sigma = C\,\Lambda_m = C\left(\Lambda_m^0 - K\,C^{0.5}\right) \tag{5}$$

where Λ_m and Λ_m^0 are the molar conductivity of the solution at concentration C and at infinite dilution respectively, and K is a constant. Conductivity data for binary aqueous solutions of NaCl and KCl are available from Shreiner and Pratt (2004) and Weast (1978). Using this form but with mass fraction, w, the conductivity of NaCl solution (in mS/cm) was fitted to be given by Equation (6).

$$\sigma = 1734\,w_{NaCl} - 1489\,w_{NaCl}^{1.5} + 0.0003 \tag{6}$$

van Rysselberghe and Nutting (1934) showed that adding NaCl and KCl conductivities on a molar basis was satisfactory if the component (binary) conductivities are calculated at the total salt concentration.

$$\Lambda_{m,mix} = \frac{\sum\left(C_i\,.\,\Lambda_{m,i}\left(\sum C_i\right)\right)}{\sum C_i} \tag{7}$$

Combining various equations in a more general form for a vector of concentrations in a mixed solution, C, we can write:

$$\sigma = \frac{f\left(C\right)}{\eta} \tag{8}$$

It is proposed to obtain data from dilute solutions with a low viscosity, η^o, to obtain estimates of $f\left(C\right)$ for each of the components in a solution and combine these using an equation of the form of (6). In food systems the exact composition is often unknown so it is intended to fit the data using equation (8) and obtain an effective concentration of all salts lumped together as single salt such as NaCl.

Then when conductivity is measured in a concentrated solution, the effective viscosity, which we refer to as “diffusion viscosity”, η_{diff}, can be determined.

$$\eta_{diff} = \frac{f\left(C\right)}{\sigma_{conc}} \tag{9}$$

Procedure

1. Obtain conductivities for commonly used salts, and the solution viscosity at the same temperature. Hence get an expression for $f\left(C\right)$ in equation (8) for each salt.
2. For mixed solutions with a common dry basis composition, obtain conductivities at low concentrations with low viscosities and hence obtain estimates of the effective salt concentration on a dry basis.
3. At higher concentrations, use the dry basis ion concentrations to calculate the salt concentrations, then calculate the expected conductivity of the solution.
4. Use the measured conductivity to calculate η_{diff}.
5. Compare η_{diff} with η_{bulk}. Relate η_{diff} to the components that are likely to affect ion transport, i.e., estimate the composition of the solution through which ions move at a molecular scale.

The bulk viscosities, η, of binary solutions of glucose, fructose and sucrose were obtained from Weast (1977) and equations were fitted in the form of Equation (10) recommended by Morison and Hartel (2007) to obtain constants.

$$\eta_i(T)=\eta_w(T)e^{\sum_i a_i \frac{w_i}{w_w}+b_i\left(\frac{w_i}{w_w}\right)^2} \quad (10)$$

Here *T* is the temperature, *w* is mass fraction, *a* and *b* are constants for a binary solution, subscript *i* refers to a single component *i* and subscript *w* refers to water. **ADD MORE RESULTS AND COEFFICIENTS.**

Materials and Methods

Skimmed milk solids purchased from a local supermarket (Alpine brand) was used to prepare milk solutions. A stick homogenizer was used to disperse the milk solids in milli-Q water in the preparation of milk solutions. The solutions were held at 45 °C for 40 minutes to enable hydration. Binary solutions of glucose, fructose and sucrose were prepared from food grade sugars. Sodium carboxymethyl cellulose (NaCMC) (Walocel C, DOW) solutions were prepared at concentrations up to 1% by mass of NaCMC. In addition various concentrations of KCl, NaCl and sucrose were added. Solutions of whey protein isolate (WPI) (Balance Sports Nutrition, New Zealand), with and without lactose and NaCl were also prepared. The set of solutions tested is given in Table 1.

Table 1. Aqueous solutions prepared

Main component	Mass fraction	Added component	Mass fraction
NaCMC	0 – 1%		
NaCMC	0 – 1%	NaCl	0.01%
NaCMC	0 – 1%	KCl	0.01%
NaCMC	0 – 1%	Sucrose KCl	30% 0.013%
WPI	1, 10, 20, 30%		
WPI	20%	NaCl	0.01%, 0.1%, 1%
WPI	20%	Lactose NaCl	20% 0, 0.01%, 1%
Fructose	0.01% - 55%		
Glucose	0.01% - 60%		
Sucrose	0.1% - 70%		
Skim milk reconstituted	1% - 45%		

The electrical conductivity of the solutions were measured using a Schott conductivity probe LF413T connected to a FLUKE PM6306 programmable RCL meter. The RCL meter was used because standard benchtop conductivity meters give insufficient precision at low conductivities. A custom-made sample holder was used to seal the conductivity probe in place and to provide similar experimental conditions. The container was immersed in a water bath with control of ±0.02 °C. The temperature was measured with a precision platinum thermometers with an accuracy of ±0.01 °C. The resistance at a frequency with zero or near zero phase angle was selected for the conductivity calculations. The cell was calibrated using standard KCl solutions with different mass fractions. When the temperature deviated from 20.0 °C the measured resistance were corrected to 20.0 °C using a measured temperature coefficient of 2% $°C^{-1}$.

For all solutions, a Haake Rotovisco RV20 with an NV cylinder set was used to measure the viscosities at 20.0 °C. The Haake viscometer was calibrated using a Cannon N1000 calibration oil to within ±1% over the rotational speed range of the viscometer. The apparent viscosities are given at a shear rate of 2700 s^{-1}.

Results and Discussion

The relationship between conductivity and viscosity with concentration for four different liquids is shown in Figure 1. Here there is a progression of behaviours. The conductivity of the NaCMC solution is linearly related to concentration and is hardly affected by the increasing viscosity. The conductivity increases due to the sodium counter-ions and also the residual NaCl normally present in NaCMC. The long NaCMC molecules form a tangled network which increases the bulk viscosity, but within which ions can freely move. The molecular mass of the NaCMC was unknown but it typically about 10^5 g/mol. At the other extreme is sucrose (and other sugars) which show a marked decline in conductivity as the viscosity rises. This has been well studied. The WPI solution is similar to NaCMC but there is a reduction in the slope of the conductivity curve. The whey proteins in WPI are β-lactoglobulin and α-lactalbumin, with molecular masses of 18400 and 14200 g/mol respectively, and are small enough to interact more with ions thus reducing their mobility. Skim milk concentrate contains about 50% lactose and 40% protein on a dry basis so the resulting conductivity shows behaviour intermediate between the WPI solution and sucrose solution. The near-constant conductivity above 25% solids is most likely caused by the coincidental opposite effects on increased ion concentration and increased viscosity. The conductivities of skim milk solutions were very similar to those obtained by Sharifi and Young (2012).

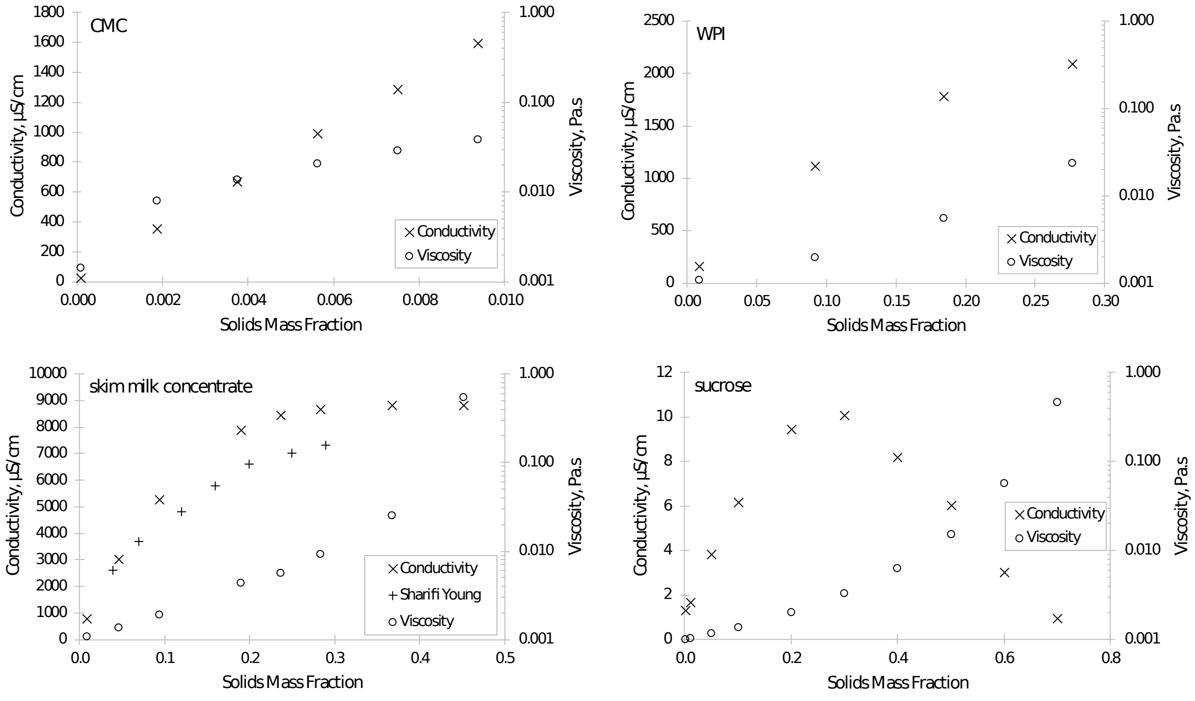

Figure 1. Electrical conductivity and viscosity of four different solutions: NaCMC, whey protein isolate, skim milk powder and sucrose. Conductivities for skim milk solutions from Sharifi and Young (2012) are included. Note the logarithmic scale for viscosity.

If the modified Walden Equation (4) is applied to NaCMC, a best fit is obtained using $\alpha = 0.03$, which effectively shows the insignificant contribution of bulk viscosity. It was concluded that Equation (4) is not suitable for NaCMC. As an alternative approach the "diffusion viscosity" was calculated using (9). First, using NaCMC as an example, the equivalent concentration of NaCl was fitted. Using an equivalent concentration of NaCl of 11.2% dry basis in NaCMC powder, the conductivity of the equivalent solution of NaCl, as plotted in Figure 2, was found to best match the conductivity of the NaCMC at low concentrations (where there was negligible viscosity effect).

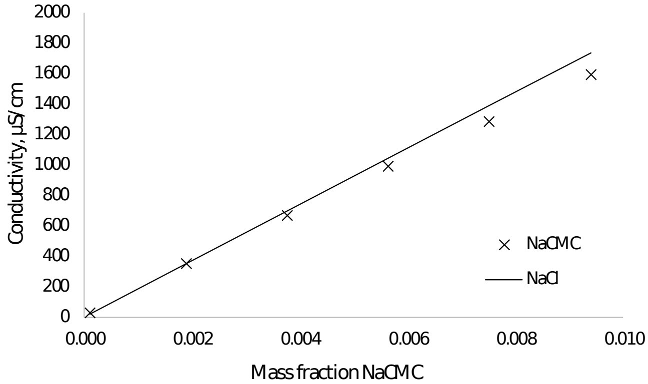

Figure 2. Conductivity of NaCMC solution and of an equivalent solution of NaCl fitted by eye as concentration tends to zero.

Then using equation (9) the diffusion viscosity was calculated and shown in Figure 3. The first points corresponded to a low conductivity with corresponding large experimental error. The viscosity "experienced" by the conducting ions is shown to be very similar to that of water. Figure 3 shows two different sets of results obtained two months apart, indicating low experimental uncertainty.

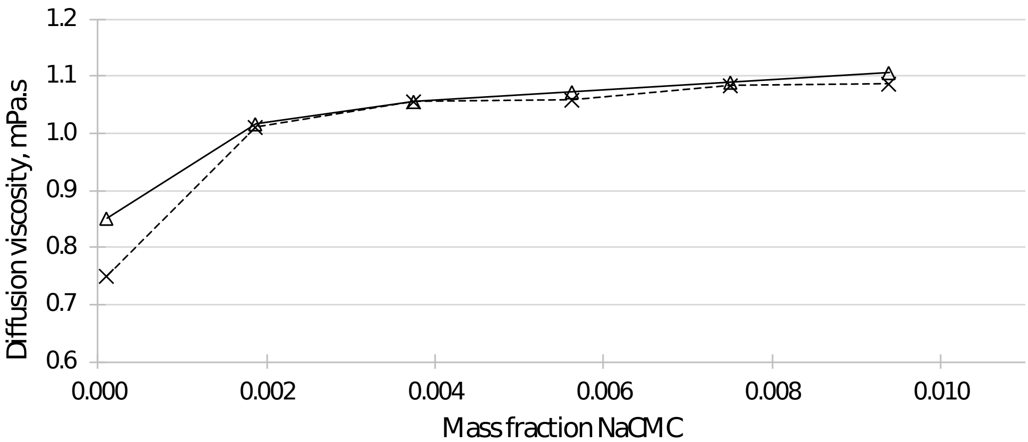

Figure 3. The calculated diffusion viscosity of NaCMC solutions from two different runs

Figure 4 shows the result of similar calculations for other mixtures. For comparison, the results for sucrose are included in each graph. The graphs show good consistency between similar solutions, but quite different results for different solutions. The diffusion of ions through NaCMC solutions, with and without salts, seems only slightly affected by mass fraction even though, as seen in Figure 1, the bulk viscosity increases significantly. Here the mass fractions are very low because higher concentrations are difficult to achieve. The diffusion viscosities for WPI and skim milk are higher than for sucrose at similar concentrations, showing greater resistance to ion flow. This is contrary to expectations as WPI and milk solutions have a lower bulk viscosity than sucrose at the same concentration. It is likely that there is significant interaction between ions and the protein which will at a negative charge in water. The different sugars show similar behaviour.

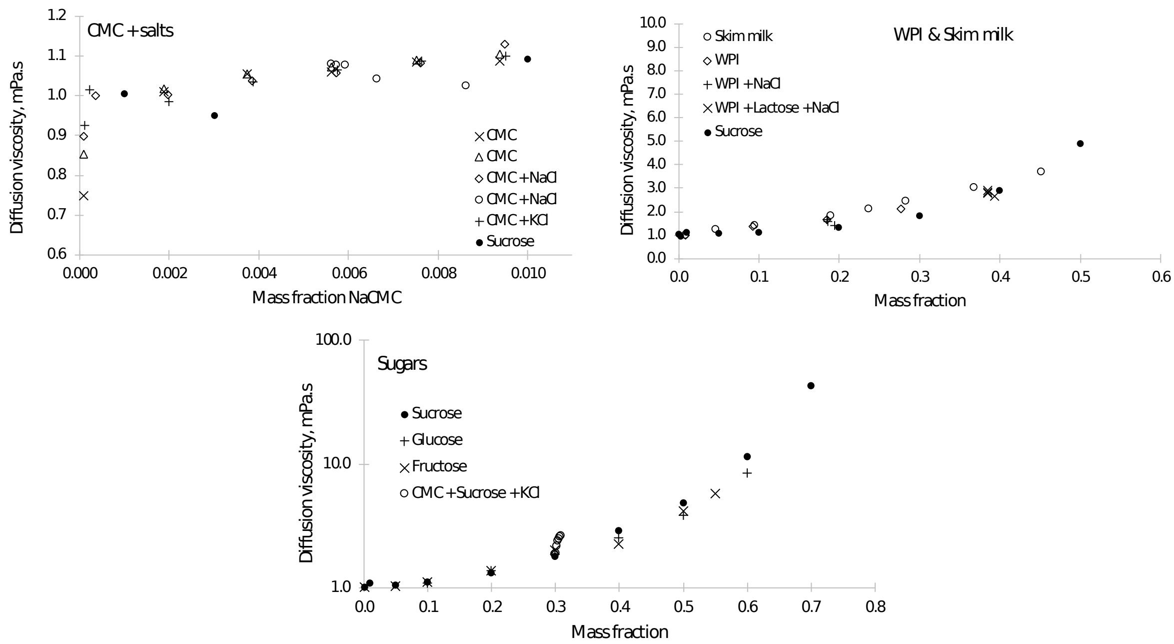

Figure 4. Calculated diffusion viscosity for different solutions. For comparison, results for sucrose are shown on all graphs. Note the log scale for sugars.

The ratio of the diffusion viscosity to the bulk viscosity was calculated and is shown in Figure 5. The relationship for sugars, WPI and skim milk is surprisingly linear with concentration, but there is no obvious reason for this.

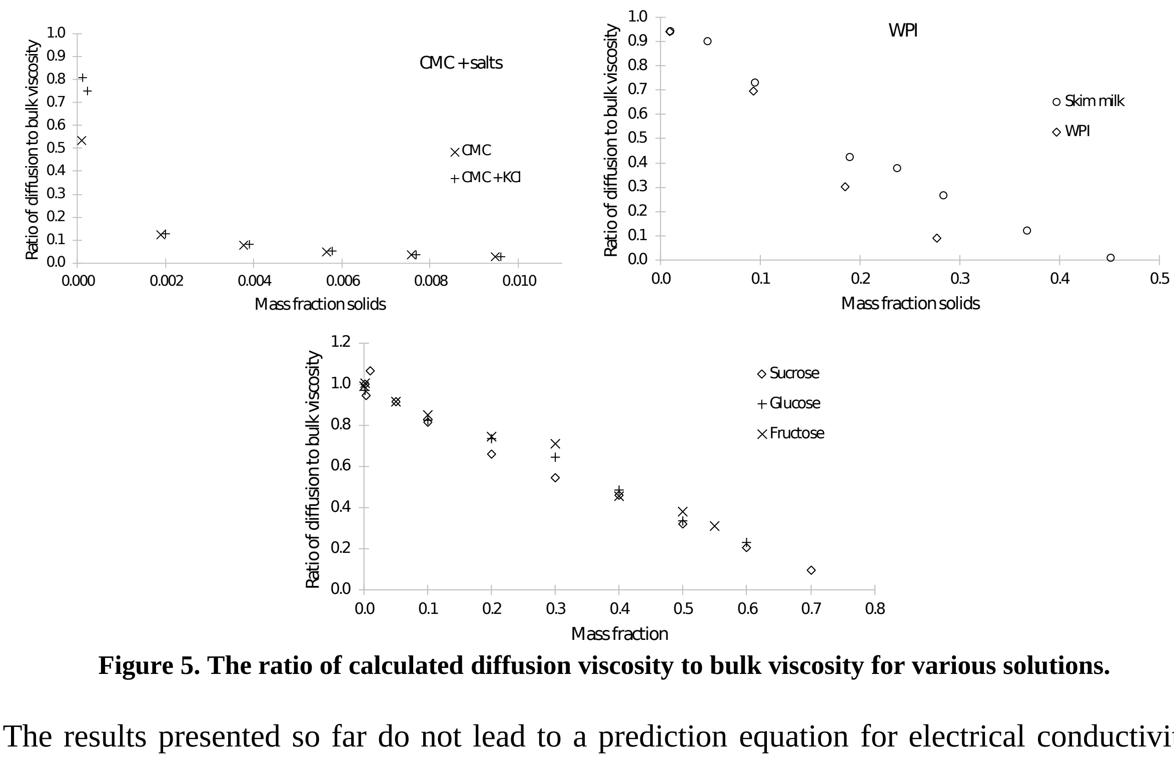

Figure 5. The ratio of calculated diffusion viscosity to bulk viscosity for various solutions.

The results presented so far do not lead to a prediction equation for electrical conductivity. While the modified Walden's rule can be applied for pure sugar solutions and the effect of bulk viscosity can probably be ignored in solutions of long chain polymers such as NaCMC, the conductivities of other solutions cannot be predicted *a priori*.

For a specific type of liquid it is recommended that the procedure outlined above be used to correlate conductivity with solids content.

Conclusions

The application of the modified Walden equation to liquid foods other than sugars was unsuccessful. Experimental results showed that, in general, electrical conductivity was not well correlated with bulk viscosity. Instead it was found that a diffusion viscosity could be determined from conductivity data. Conducting ions were able to pass through NaCMC solutions with little extra resistance. It seems likely that electrical conductivities will be unaffected when the bulk viscosity is caused by entanglement of long polymer chains.

In liquids such as concentrated sugar solutions and honey in which the viscosity is dominated by small molecules, the electrical conductivity is strongly affected by viscosity.

In milk and whey protein solutions there is some evidence of interaction between ions and the charged proteins which slows the movement of ions and hence results in a higher than expected diffusion viscosity. A more complete model including the ion/protein interaction could account for the observed change. Experiments in which protein charge is changed by altering the pH should allow this effect to be quantified.

References

Acquarone, C., Buera, P., Elizalde, B. (2007) Pattern of pH and electrical conductivity upon honey dilution as a complementary tool for discriminating geographical origin of honeys, *Food Chemistry* 101 (2007) 695–703

Bordi, F. and Cametti, C. (1986) Equivalent conductivity of carboxymethylcellulose aqueous solutions with divalent counterions, J Phys Chem 90, 3034-3038.

Henningsson, M., Ostergren, K., Petr Dejmek, 2005, The electrical conductivity of milk – the effect of dilution and temperature, *International Journal of Food Properties*, 8, 15-22.

Madoumier, M., Azzaro-Pantel, C., Tanguy, G., Gesan-Guiziou, G., 2015, Modelling the properties of liquid foods for use of process flowsheeting simulators: application to milk concentration, *Journal of Food Engineering*, 164, 70-89.

Miller, D.P., Conrad, P.B., Fucito, S., Corti, H.R., de Pablo, J.J. (2000), Electrical conductivity of supercooled aqueous mixtures of trehalose with sodium chloride, *J. Physics and Chemistry B*, 104, 10419-10425

Morison, K.R.; Hartel, R.W. (2007), Evaporation and freeze drying in Heldman, D.R.; Lund, D.B. "*Handbook of Food Engineering*", 2nd ed., CRC Press: Boca Raton, FL, 495–552.

Shreiner and Pratt (2004)

Sharifi, M., Young, B., 2012, Milk total solids and fat content soft sensing via electrical resistance tomography and temperature measurement, *Food and Bioproducts Processing*, 90, 659-666

Sharifi, M., Young, B., 2013, Towards an online milk concentration sensor using ERT: Correlation of conductivity, temperature and composition, *Journal of Food Engineering*, 116, 86-96.

St-Gelais, D., Champagne, C. P., Erepmoc, F., Audet, P., 1995, The use of electrical conductivity to follow acidification of dairy blends, *International Dairy Journal*, 5, 427-438.

Stokes, R. H. (1959) Mobilities of ions and uncharged molecules in relation to viscosity – a classical viewpoint, in *The Structure of Electrolytic Solutions*; Hamer, W. J., Ed.; Wiley: New York, Chapter 20, p 298.

Weast, R.C. (ed) (1977), *CRC Handbook of Chemistry and Physics*, 58th ed. CRC Press, Florida.

Van Rysselberghe P, Nutting L. (1934) The conductivity of concentrated mixtures of alkali chlorides *Journal of the American Chemical Society*. 56: 1435-1437