

The influence of non-aqueous solvents on lime and pickle swelling of goat skin

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Abstract

Swelling during leather manufacture is of great importance in controlling the quality of final leather. A more intensive fibre separation produces finished leather that is softer and more flexible, but also shows a decrease in hide substance and mechanical strength, whilst at the same time exhibiting an increased looseness. The amount of collagen degradation is dependent on the degree of swelling and occurs in a number of stages in the manufacture of leather. Conventionally, references to swelling are usually restricted to liming and pickling. Suggested mechanisms of swelling are charge effects, osmotic swelling and lyotropic swelling. In the case of the liming process, swelling is suppressed to a lesser degree by additives whereas in pickling, salt is added to suppress the swelling.

The swelling of skin in non-aqueous solvents and aqueous co-solvent system was investigated. Goat skin samples were limed and pickled in a series of alcohol (methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol and diacetone alcohol), acetone, dimethyl sulfoxide, urea and 1,4-dioxane to produce aqueous co-solvent systems of varying dielectric constants. The results confirmed that the degree of swelling in skins was suppressed, in both cases, as the concentration of the non-aqueous solvent increased. The solvent uptake of skin decreased from 500% (w/w) to 100% (w/w) in an ‘acidic’ non-aqueous solvent system, and was reduced from 400% (w/w) to 50% (w/w) in an ‘alkaline’ environment.

Key words: leather, solvent, non-aqueous, water, swelling

1. Introduction

A review of the literature of leather technology of the 20th Century reveals that a great deal of attention has been centred on the problem of swelling in collagen (Cassel and McKenna 1954; Herfeld and Schubert 1969; Highberger 1936; McLaughlin 1920; Stubbings and Theis 1950). The reason this subject has been considered so important is that in every phase of leather making a different state of swelling or plumping is encountered. It was found collagen degradation is impaired by the degree of swelling in different acid, acid/salt, alkaline, alkaline/salt systems (Ding and Zhang 2001). An elucidation of the process of swelling is essential to any real understanding and control of tanning processes.

The swelling phenomenon involves mass transfer of low molecular liquids and plays an important role in many technological processes of leather manufacture, processing and the quality of finished leather. Skin can be swollen by three mechanisms: osmotic swelling, lyotropic swelling and charge swelling (Covington 2009; Reich 2007; Guthrie-Strachan 2006). Osmotic swelling takes place when the ionic concentration between the inside and the outside of the pelt is not balanced (Figure 1a). Lyotropic swelling is caused by disruption to the collagen structures by compounds that can insert into the hydrogen bonding (Figure 1b). Charged swelling occurs by breaking salt links and creating charge in the collagen structure (Figure 1c) (Covington 2009; Reich 2007; Guthrie-Strachan 2006).

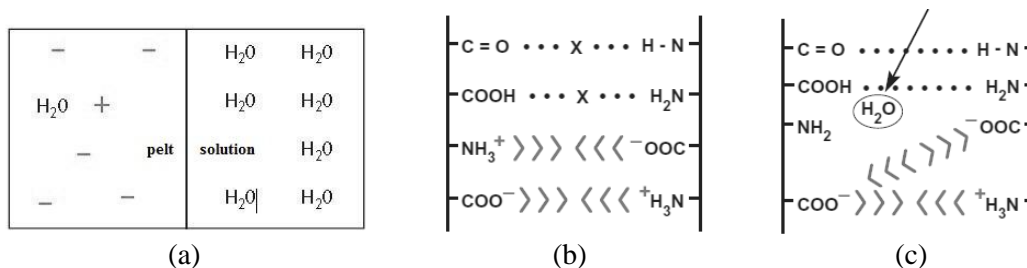


Figure 1: Swelling mechanisms (a) osmotic swelling; (b) lyotropic swelling; (c) charge swelling (Guthrie-Strachan 2006).

The physico-chemical behaviour of collagen combines with acid and base in the manner of an ordinary ampholyte, resulting as the swelling which occurs in environments of various reactions (Highberger 1936). These swelling mechanisms can operate simultaneously, in other words, it is not necessary to have single swelling mechanism in one time, *e.g.*, the predominant mechanisms operating in alkaline condition are charge swelling and lyotropic swelling (Covington 2009). The swelling curve has an upward trend at high value of pH and the suppression of swelling using neutral salt, such as sodium chloride is less marked, as indicated in Figure 2 (Covington 2009).

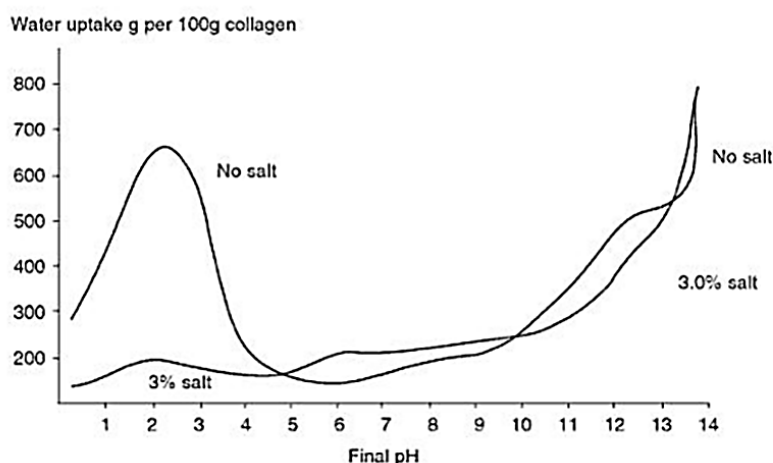


Figure 2: Collagen swelling curve as a function of pH (Covington 2009).

Bowes (1950) showed that lyotropic swelling associated with the present of hydroxyl ion at pH above 11.0 affects collagen swelling more than charge swelling. In addition, there is no decrease at high pH values corresponding to that occurring in acid solutions below pH 2.0. At pH 2.0, the reaction between carboxyl group and acid is complete. Swelling is maximised as the result of the maximum charge on collagen (Covington 2009).

Collagen swelling is not solely a pH-dependent reaction. The type of ions present in the solution is a factor that can manipulate the degree of collagen swelling during processes, *e.g.*, sodium ions produce more swelling than calcium ions in the liming process (Bowes and Kenten 1950; Mellon *et al.* 1960; Herfeld and Schubert 1969; McLaughlin 1920). Nucci and Vanderkooi (2009) elucidated the impact of salts on the equilibrium of hydrogen bonded water and showed a correspondence to the Hofmeister order for ions with the exception of ammonium salts. Meanwhile, Cheng *et al.* (2009) indicated that salt links and hydrogen bonds in the collagen molecular structure were cleaved by ion species during the swelling process in so-called “salting in”.

Co-solvent systems and non-aqueous solvents have been widely used in the pharmaceutical and biochemical fields to increase the solubility of drugs with poor solubility in aqueous environments, such as elixirs and syrups (Donzé *et al.* 1992; Kim *et al.* 2009; Miller 2009). Non-aqueous solvents can interact with collagen solely or as an additive to aqueous environment to form a co-solvent media via hydrogen bonding or/and hydrophobic interactions (Mok *et al.* 2008). The mechanism of co-solvent media is analogous to that of salt to protein and aqueous environment, *i.e.* salting in and its opposite effect, salting out of protein; meanwhile, hydrogen bonding and/or hydrophobic interactions between co-solvents. Collagen-solvent interactions can be investigated *via* the swelling of collagen and solvent-solvent interactions may be elucidated from physico-chemical properties of the co-solvent system, *e.g.*, excess molar volume (V^E), which is determined by density measurement and defined use the following equation:

$$V^E = V_m - \sum_{i=1}^2 V_i x_i$$

Where V_i is the molecular volume of non-aqueous solvent; x_i is the molar fraction of non-aqueous solvent; V_m is the molar volume of a co-solvent system (Zhang 2009).

The non-aqueous solvents examined in the present work are listed in Table 1 according to their polarity. Excess molar volume of some co-solvent aqueous systems is illustrated in Figure 3. All systems show a negative value of V^E . A decrease in molar volume of polar liquid mixtures is due to formation of complexes *via* hydrogen bonding (Battino 1971). The volumetric behaviour of co-solvent systems can be used to provide information about non-aqueous solvent-water interactions and the influence of the non-aqueous solvents on the intermolecular structure of water.

The degree of collagen swelling taking place in the aqueous co-solvents systems in liming and pickling processes is investigated in this study, in which the aqueous co-solvents systems are homogenous mixtures of a non-aqueous solvent and water of different proportions (m/m).

Table 1: Physical parameters of water and non-aqueous solvents utilised in collagen swelling experiment (Weast *et al.* 1987).

Solvent	Density (g/cm ³)	Solubility in water at 25°C (g/100g)	Dipole moment	Dielectric constant
Polar protic				
Water	1.00	M*	1.85	80.18
Ethylene glycol	1.11	M	2.2	37.7
Methanol	0.79	M	1.7	33
Ethanol	0.79	M	1.69	24.55
2-propanol	0.79	M	1.56	20.18
1-propanol	0.80	M	1.68	20.1
Diacetone alcohol	0.94	M	2.72	15.45
Polar aprotic				
Dimethyl sulfoxide	1.10	M	3.96	47.24
Acetone	0.79	M	2.88	21.01
Urea	1.32	107.9	4.59	Nil
Non polar				
1,4-dioxane	1.03	M	0.45	2.3
*M in the water solubility column means solute is soluble in water in all proportions.				

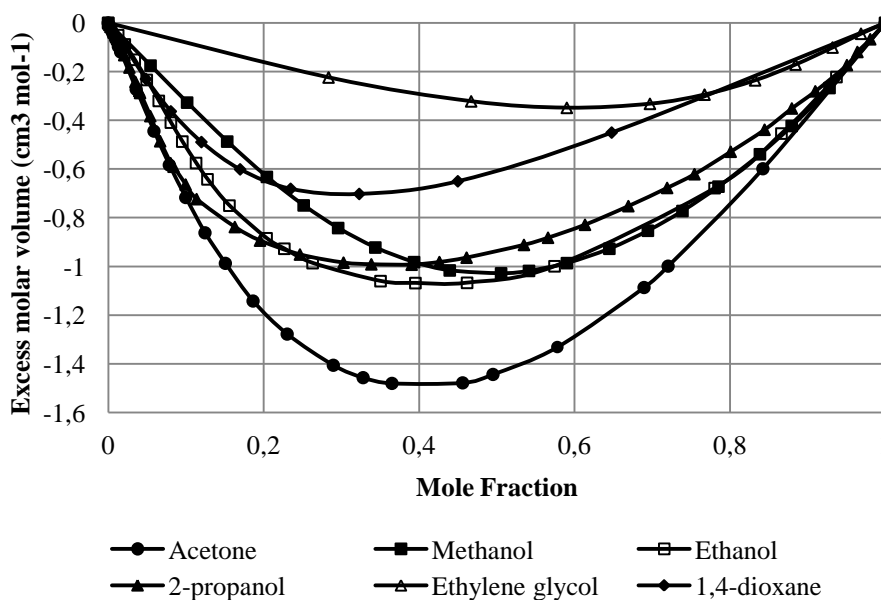


Figure 3: Excess molar volume of some co-solvent systems (Arce *et al.* 1993; Davis 1991; Grolier 1981; Koohyar *et al.* 2012; Miller *et al.* 2009; Muller and Rasmussen 1991).

2. Materials and Methods

2.1 Preparation of wet salted goat skin samples

Twenty four circular skin pieces (45mm in diameter) were harvested from rehydrated wet salted goat skin. Skins were placed in a calcium hydroxide (4%) and sodium sulfide (4%) solution in a 250mL conical flask. Experimental solvents (20mL) were made up of water and a non-aqueous solvent at 20% (m/m) intervals from 0 to 100% of the non-aqueous solvent in duplicate, except urea. Urea solution is made up to 80% (m/m). The conical flasks were then sealed and agitated on a mixer for 20 hours for the liming process.

Sample and solvent preparation for pickling process was the same as the liming process, except sulfuric acid (1%) was used and samples were harvested from delimed goat skin and agitated in the prepared solution for 10 hours.

2.2 Determination of swelling of collagen

The swelling of collagen is measured based on mass of solvent loss relative to dry sample. It is determined according to ISO 4684:2005 determination of volatile matter: samples were dehydrated to constant weight in an oven at 100°C.

3. Results and discussions

Figure 4 illustrates the influence of collagen swelling in aqueous co-solvents in the liming process. The extent of this suppression increases as the amount of non-aqueous solvent increases. The effect of collagen swelling is suppressed in the co-solvent system. In Figure 4 and 5 (---) indicates the solvent content of a fully hydrated hide. Circumstances above (---) indicate for skin swelling, on the contrary, depletion and dehydration of the skin take place below (---).

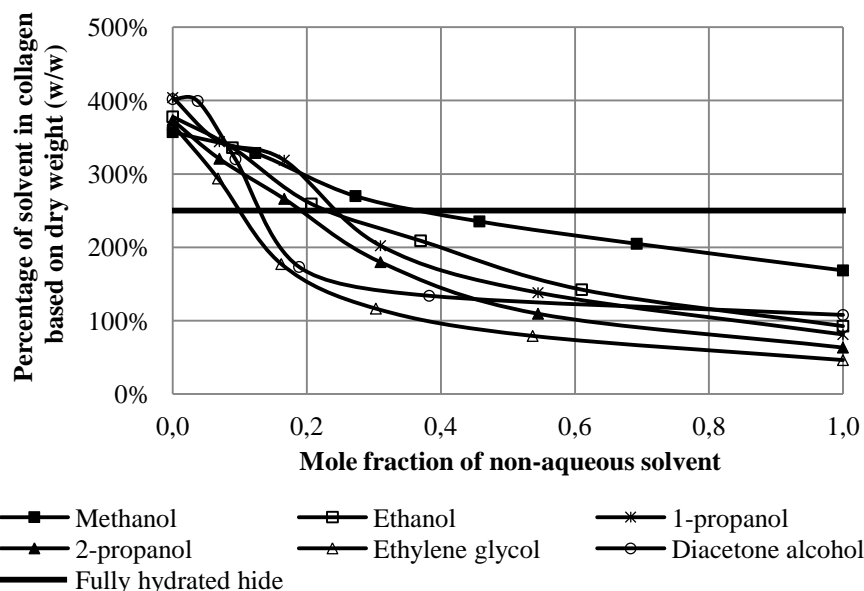


Figure 4a: Collagen swelling in alkaline (pH 12.8) environment resembling liming conditions, at different mole fractions of protic non-aqueous solvents in water.

The hydrogen bonding between water and the co-solvent reduces sites that are available to interact with protein. Solvent-solvent interactions are well demonstrated *via* V^E . The co-

solvent system of ethylene glycol is used as an example of how V^E of co-solvent system contributes the hydrogen bonding between solvent-solvent and corresponds to the swelling of collagen in present work. Zhang *et al.* (2009) reported that V^E went to a minimum at 0.4 mole fraction of ethylene glycol. This point indicates hydrogen bonding formation between ethylene glycol and water is maximised and it was reflected in the present work as close to the condition for minimum swelling.

However, this is more like a plateau at low molar fraction in some of the co-solvent systems. It is explained as follows: as these non-aqueous solvents are first introduced into the aqueous environment there is a hydrophobic reaction between solvent-solvent; at this point, the suppression of collagen swelling is not favoured to operate. As shown in Figure 4a, the effect of suppressing increases as the length of carbon chain increases. It can be seen that the dielectric constant reduces as the carbon chain length of the alcohol increases, see Table 1. Less polarity of the non-aqueous solvent means less capability to insert into hydrogen bonds in collagen: therefore, swelling of collagen is suppressed to a greater extent.

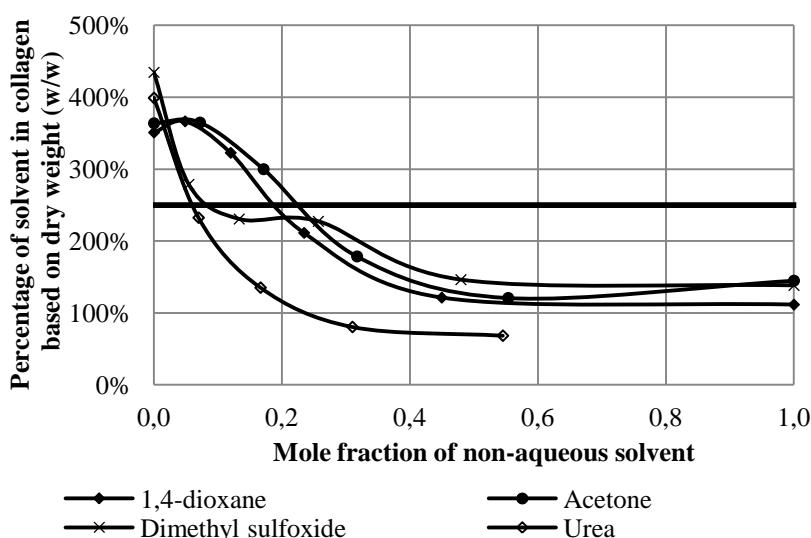


Figure 4b: Collagen swelling in an alkaline (pH 12.8) environment resembling liming conditions, at different mole fraction of aprotic non-aqueous solvents in water.

The suppression of collagen swelling in the co-solvent system operates similarly in the liming and pickling processes. However, Figure 5 (pickling) shows the degree of swelling suppression is less than it is in Figure 4 (liming).

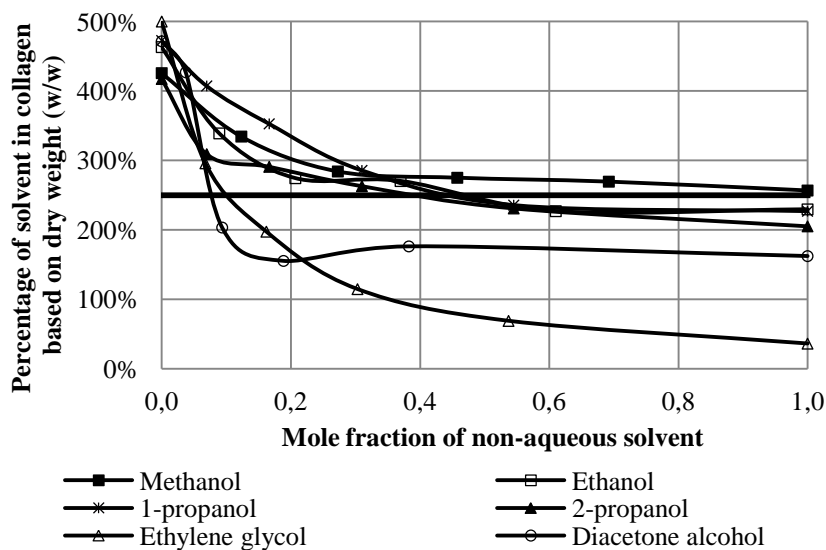


Figure 5a: Collagen swelling in an acidic (pH 2.5) environment resembling pickling, at different mole fraction of protic non-aqueous solvents in water.

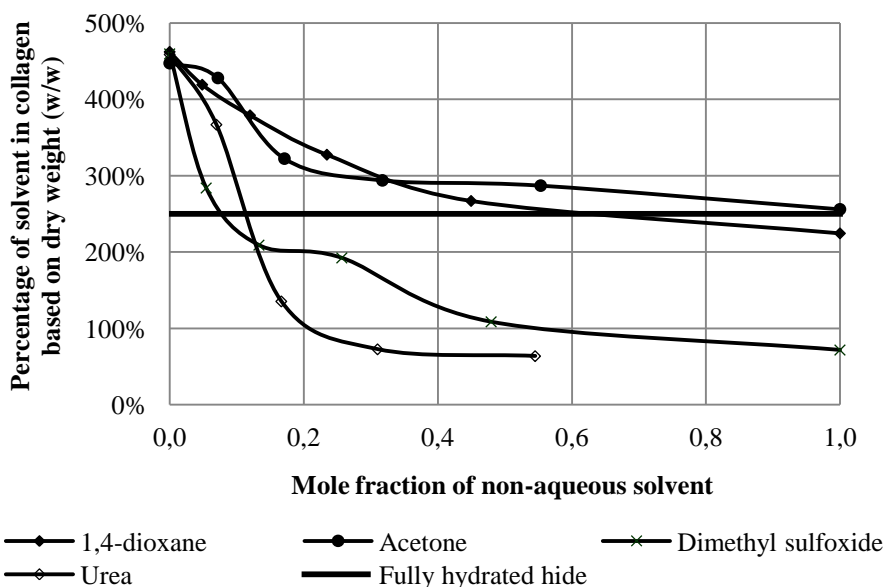


Figure 5b: Collagen swelling in an acidic (pH 2.5) environment resembling pickling conditions, at different mole fraction of aprotic non-aqueous solvents in water.

The results can generally be summarised as follows:

1. Collagen swelling is suppressed in almost all of the co-solvent systems and non-aqueous solvent in the present work. The extent of this effect depends on the capability to form hydrogen bonding and hydrophobic interactions between non-aqueous solvent and water.
2. Depleting and dehydration of processed collagen is observed in all non-aqueous solvents and large mole fraction of non-aqueous solvent in the co-solvent system.
3. The relative effects of the non-aqueous solvents on liming and pickling are not the same, reflecting the difference in swelling mechanisms. The impact of the co-solvent is greater on the lyotropic mechanism than on the charge separation mechanism.
4. Aprotic solvents can have a more powerful effect on suppressing swelling than protic solvents, in both liming and pickling. This indicates a contribution to disrupting the role of

water in the swelling process. The stronger influence of aprotic solvents on the swelling reflects the role of hydrogen bonding in the overall mechanism: lyotropic swelling can result, but also limited by the lyotropic agent causing it.

4. Conclusion

Swelling can be a damaging effect in conventional leather processing, so the use of additional components in the solvent medium may be a useful addition to the technology of the steps at risk. For example, this work offers an alternative to neutral electrolyte in pickling and there is the consequent powerfully positive effect on the efficiency of chrome tanning (Covington, 2009). It also prevents the usage of salt in the pickling process and provides facilitation for tannery effluent treatment.

The ability to modify the properties of the solvent during the preliminary steps towards the production of leather or other collagenic biomaterials may also be a way to modify the collagen itself. For example, the opening up processes traditionally use extreme chemical conditions, which might be substituted by more specific enzyme based reactions requiring more moderate conditions.

The understanding of the mechanism of solvent manipulation on collagen structure provides a potential alternative to water usage and the reduction and substitution of water in leather manufacture, an important investigation for a future strict water environment standards and global water crisis.

5. Acknowledge

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