Phase behaviour and non-monotonic film drying kinetics of aluminium chlorohydrate–glycerol–water ternary solutions

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ABSTRACT

We study the drying and film formation of a model ternary system comprising an inorganic salt (aluminium chlorohydrate, ACH), a humectant (glycerol) and water. Employing viscometric, X-ray diffraction, calorimetric, dynamic vapour sorption, spectroscopic, gravimetric and adhesion measurements, we examine the roles of humectant concentration, temperature and relative humidity (RH) in the phase behaviour and kinetics of film formation. Equilibrium film compositions are found to be non-monotonic with glycerol content. Around 15:4 ACH:glycerol mass ratio, films exhibit enhanced, albeit slower, desiccation, with water content lower than that of binary ACH–water solutions. At higher glycerol content, drying is faster, yet the resulting films have higher water content and remain tackier. Water adsorption/desorption is shown to be fully reversible, and share a similar non-monotonic kinetic dependence on glycerol composition. These findings are rationalised in terms of the competitive binding of water and glycerol to ACH, the overall miscibility and glass formation within the ternary system. Our study is relevant to a range of salt formulations, employed in a variety of commercial applications, including lyoprotectants and personal care products.

1. Introduction

Hydroxyaluminum solutions, and specifically aluminium chlorohydrate (ACH), find a range of industrial applications including as coagulants in waste water treatments, catalyst support in pillared clays, geochemical modification reagents for soil [1,2]
and as the principal active ingredient in antiperspirant formulations [3,4]. Despite their importance, rigorous physical-chemical studies of such systems are lacking. This is partly due to the complexity associated to the many components and component types of commercial formulations [5] and to the ‘inorganic polymer’ structure of ACH comprising Al$\text{\textsubscript{13}}$ units, with a Keggin ion structure, which undergo complex transformations to form larger poly-aluminium complexes [4–6].

We consider a model system containing three key ingredients found in many antiperspirants: ACH, glycerol and water. In their practical use, antiperspirants are applied onto the skin surface and allowed to dry, and our aim is therefore to investigate the interplay between solution properties, film formation upon solvent loss and resulting film physical properties. Film formation from solution is regulated by temperature and relative humidity (RH), in addition to composition, thickness and surface properties, which in turn impact the rheological, mechanical and water transport properties throughout the drying pathway. Due to the importance of the drying stage in their practical utilization [7], we seek to dynamically probe the evolution of film properties as a function of time in addition to obtaining the final film equilibrium properties [8–10].

The hygroscopic nature of ACH and glycerol, in particular, is expected to underpin the RH-dependence of the solution drying kinetics during film formation and during the reverse process of film swelling when RH is increased. This behaviour is practically relevant since it dictates both functionality, hygienic, and sensorial characteristics of the mixture [11], although the simple system studied here may not be representative of the commercial applications involving other ingredients. The glass formation and water adsorption/desorption of the resulting ACH-rich films are also important from a fundamental perspective. Indeed, binary water–glycerol mixtures exhibit liquid–liquid and glass transitions [12] and eutectic behaviour [13] used in cryobiology [14], which we now seek to extend to a salt-containing ternary system.

The glass transition which occurs upon dehydration in saccharide–water or inorganic-salt–polyol–water systems is the mechanism behind anhydrobiosis [15,16], a reversible process allowing organisms such as seeds and certain crustaceans to survive dehydration and revive upon rehydration. These systems are thus exploited as lyoprotectants for the stable storage of biological materials, including borax–sucrose–polyol in [17] and magnesium chloride–calcium chloride–calcium nitrate–glycerol in [18]. Similarly, the glass transition behaviour of plasticised starch biopolymer systems and the competitive bonding between water, glycerol and starch has been extensively studied [9,19–21] and a recurring anti-plasticisation behaviour at small glycerol concentrations (<14 wt%) and low water activity (<23 wt%) is evident [19]. Under these conditions, glycerol preferentially binds to starch via hydrogen bonding in the place of water, altering the film’s mechanical properties (strength, elongation) [10], glass transition behaviour [22] and permeability [23], key variables in the fabrication of biodegradable packaging for food preservation.

In the first part of the paper we report the drying kinetics of A CH–glycerol–water solutions along the film formation pathway, i.e. during water evaporation. We study the evolution of the system across the phase diagram, employing a combination of viscometry, infrared spectroscopy (FTIR), calorimetry, X-ray diffraction (XRD) and adhesion measurements. We then consider the water uptake and loss of the resulting ACH-rich films, monitoring the composition changes at controlled RH and temperature with dynamic vapour sorption (DVS). The correlation between composition and physical properties provides insight into the different stages of film formation, and into the stoichiometric effects on drying kinetics and on equilibrium swelling/de-swelling of the model ACH-rich films.

2. Materials and methods

2.1. ACH–glycerol–water ternary system

Aluminium chlorohydrate was obtained from Summit Research Labs Inc. under the form of a 50 wt% hydrated dialuminium chloride pentahydrate aqueous solution. The ACH content (i.e. ‘dry mass’) was determined gravimetrically by desiccating the solution in a dry air chamber at 0% RH and 21 °C for the duration of a week. The ACH complex contains water molecules within its structure even post-drying. Glycerol of purity ≥99.5% was purchased from Sigma-Aldrich, and deionised water was obtained from a MilliQ source. The solutions were prepared by mass, homogenised and equilibrated overnight. Compositions are indicated by mass fraction throughout the paper. Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) were employed to confirm the drying pathway compositions and are detailed in the supporting material sections SM2 and SM3.

2.2. Dynamic Vapour Sorption (DVS)

DVS Advantage (Surface Measurements System UK Ltd) was used at 35 °C to measure water sorption/desorption of 10 µl initial volume samples (equivalent to films of 127 µm initial thickness) of different composition. The system was first programmed to dry the sample at 0% RH until its mass became constant and this value was taken to be the ‘dry’ mass reference. A sorption cycle was then initiated recording the mass change as a function of 20% RH step increase from 0% RH to 90% RH. The step duration was varied between 200 and 400 min ensuring the sample reached its equilibrium composition prior to the following RH change. Once 90% RH was reached, an identical desorption cycle initiated, enabling both sorption and desorption isotherms to be constructed.

2.3. Drying kinetics and rolling ball tack measurements on large-area films

Large-area films of 30 µm initial thickness and $4 \times 4$ cm$^2$ surface area for gravimetric measurement and 23 cm $\times$ 3 cm for rolling ball tack measurements were initially spread on a 100 µm-thick hydrophilic polyester substrate – a ‘transparency’ sheet (Lloyd Paton LPF/P) – using a model K101 (RK Print) control coater with Meyer’s bar #4. Blade casting by hand was found to yield equally consistent results and used for the work presented. Film drying was studied under a controlled environment set by a humidity- and temperature-controlled glove box (Coy Labs, equipped with PID-controlled heater and Electro-Tech Systems Inc. microprocessor controller series S100/S200). The air was static during experiments so as not to affect the evaporation rates. Temperature and RH sensors were placed in various locations of the chamber to ensure temperature and RH profiles remained homogenous spatially as well as temporally. Mass changes were monitored with a Sartorius type 1702 balance.

A rolling ball tack test was employed for continuous adhesion measurements during film drying. A ruler was laser printed on the substrate for distance measurements, onto which the sample was blade cast. The substrate was placed on a levelled surface and a 20 cm copper tube was inclined at a 6.6° angle, yielding measurements of sufficient sensitivity during the entire film drying period. Measurements were carried out with 8 mm-diameter glass spheres (Smith GS) approximately every 2 min until no adhesion was recorded. The composition of a film of identical initial wet thickness was recorded in parallel, gravimetrically, in the same humidity and temperature controlled glove box in order to correlate film tackiness and composition.
Drying and film formation pathway of ternary mixtures containing aluminium chlorohydrate (ACH), glycerol, and water which solely and partly evaporates during film formation. The ACH apex is defined in the materials and methods section, as ACH is itself a water-containing complex. The coloured arrows indicate pathways for solutions of initial mass fractions ACH:glycerol:water of 0.15:0.00:0.85 (pink), 0.15:0.02:0.83 (yellow), 0.15:0.04:0.81 (green), 0.15:0.06:0.79 (cyan), 0.15:0.08:0.77 (blue), 0.15:0.10:0.75 (mauve) and 0.15:0.15:0.70 (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 1. Drying and film formation pathway of ternary mixtures containing aluminium chlorohydrate (ACH), glycerol, and water which solely and partly evaporates during film formation.
were thus carried out. A temperature decrease of \( \approx 10 \, ^\circ \text{C} \) was found across all film compositions (supporting material Fig. S8). This is in line with the expected dry and wet bulb temperature difference for pure water at these conditions [24]. Since the transient cooling is similar for all compositions (as the initial water content > 70 wt%), it should not be responsible for the non-monotonic kinetics of the system.

DVS was employed for these measurements due to its precision, owing to the 0.1 \( \mu \text{g} \) sensitivity microbalance and RH and temperature control. Complementary experiments were, however, carried out for large-area drying films (approximately 4 \( \times \) 4 cm\(^2\) and 30 \( \mu \text{m} \) thick) recorded with a mass balance in the humidity and temperature-controlled chamber. Similar non-monotonic kinetics with glycerol content are observed (supporting material Fig. S9), albeit with larger uncertainty.

We next investigate the origin of the non-monotonic drying kinetics with respect to glycerol composition.

### 3.3. Glass transition

Upon drying, solutions of sufficiently high ACH content, within the red region defined in Fig. 3, solidify into a transparent glassy film. Glass formation was confirmed by XRD (supporting material Fig. S10), whose powder diffraction patterns indicate an amorphous structure. DSC provides further evidence for glass formation (supporting material section SM5). Points along the straight lines are liquid compositions for which the rheology was measured in the following section. Ternary ACH–glycerol–H\(_2\)O mixtures have (ACH:Glycerol) ratios of (15:2) yellow, (15:4) green, (15:6) cyan, (15:8) blue, (15:10) mauve and (15:15) purple lines. The dry film compositions are indicated with and assigned to a non-glassy (◇) or glassy state (○) at 18 \( ^\circ \text{C} \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

![Fig. 3. Glass transition temperature, \( T_g \) ranges for the ternary ACH–glycerol–water system measured by DSC. The figure results from a compilation of \( T_g \) data from thermograms including those presented in supporting material section SM5. Points along the straight lines are liquid compositions for which the rheology was measured in the following section. Ternary ACH–glycerol–H\(_2\)O mixtures have (ACH:Glycerol) ratios of (15:2) yellow, (15:4) green, (15:6) cyan, (15:8) blue, (15:10) mauve and (15:15) purple lines. The dry film compositions are indicated with and assigned to a non-glassy (◇) or glassy state (○) at 18 \( ^\circ \text{C} \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

### 3.4. Viscosity evolution

Viscosity measurements were carried out to investigate how the system approaches the glassy state on drying. An initial ACH mass fraction of 0.15 and several initial glycerol contents from 0 to 0.15 mass fractions were considered, as solid films do not form outside this range. Compositions along the drying pathway were individually prepared and their viscosity measured and plotted in Fig. 4. Binary ACH–water and glycerol–water solutions were also prepared and measured for comparison, as detailed in supporting material section SM6.

We note that the viscosity of all ACH ternary mixtures is higher than that of either binary mixture of identical respective solute mass fraction. The same applies to the viscosity of ACH–water with respect to glycerol–water at the same mass fraction (supporting material Fig. S11(a)). This is expected as ACH is charged and forms...
poly-aluminium complexes in aqueous solution, with increasing concentration [3–6].

The viscosity of mixtures with high ACH/glycerol ratio increases monotonically and then rapidly at sufficiently high ACH content, as shown in Fig. 3. Ratios of ACH/glycerol reveal a 'skin' below which a liquid remains. The mixture's viscosity, \( \eta \), is given by \( \eta = \eta_{\text{water}} \left[ (1 - \phi) / \phi_{\text{max}} \right] - B \phi_{\text{max}} \), where \( \eta_{\text{water}} \) is the pure water viscosity, \( \phi \) the ACH mass fraction, \( \phi_{\text{max}} \) the maximum ACH mass fraction and B an intrinsic viscosity [26] and serve as a guide to the eye.

In order to assess the effect of glycerol concentration on viscosity, a relative viscosity \( \eta_{\text{rel}} = \eta / \eta_{\text{water}} \) was calculated and plotted as a function of the ACH volume fraction in supporting material section SM6, Fig. S11. Considering ACH to be 'particles' in a continuum of water–glycerol, one might expect the relative viscosities to fall onto a master curve, which should increase sharply approaching the maximum volume packing fraction of the ACH particles.

Indeed, we find that the relative viscosities collapse onto such master-curve, but only in the dilute region, for ACH volume fractions approximately below 0.2. Above such concentration, the curves diverge and glycerol increases the viscosity more than predicted from our simplistic ACH phase-volume model, especially at \( \text{ACH/glycerol} = 15/15 \), suggesting an attractive or binding interaction between the ACH and glycerol at these concentrations which could precede phase separation.

We next consider how the viscosity evolves throughout the drying process. Using the large-area film drying gravimetric data given in Fig. 9(a) and at each time point calculating a composition and, using the fits from Fig. 4, a viscosity, a plot of the viscosity as a function of drying time was constructed in supporting material Fig. S12. The slowest drying film composition, viz. \( \text{ACH/glycerol: water = 0.15/0.04/0.81} \) shows the earliest transition to very high viscosity. This drying pathway corresponds to the green line in Figs. 3 and 4, for which glass formation occurs at relatively higher water contents as mapped by the calorimetric \( T_g \) reported in Fig. 3.

3.5. Evolution of film tackiness upon drying

Drying films become qualitatively non-tacky (to finger touch) well before the glass transition composition is crossed. The rolling-ball tack method provides a means to probe viscous states between those than can be measured via the viscometer and the glassy state inferred from DSC. We therefore measured film adhesion using this method, as a function of temperature, RH and composition. Experiments were carried out at three fixed temperatures (20°C, 25°C and 35°C) and two RH (25% and 55%) – covering the practical application range of these systems – in order to obtain the boundary separating 'tacky' versus non-tacky compositions in Fig. 5(a). The method, raw data and analysis are detailed in supporting material section SM7. Briefly, a shorter rolling distance implies higher rolling friction which was interpreted as a more tacky film. Typical maximum rolling friction coefficients for this system range between 0.05 and 0.26 (supporting material section SM8). As water evaporates, rolling friction first increases, reaching a maximum before decreasing rapidly towards complete film drying. A non-tacky film was defined by the ball rolling off the film equivalent to a rolling friction coefficient \( \leq 0.01 \).

Fig. 5(a) shows that, for films of low humectant concentration (ACH/glycerol \( \geq 15/4 \)), the water content at the tacky/non-tacky boundary is unexpectedly high, corresponding to water concentrations where the film is expected, from Fig. 3, to be liquid. A possible explanation for this discrepancy is a difference between surface and bulk compositions and properties, discussed next.

Possible skin formation was investigated by comparing the tack of thin films to the tack of bulk samples using probe tack measurements described in the method section. In these latter measurements, the probe breaks through any skin that forms and therefore adhesion is only lost when the bulk has solidified.

Fig. 5(b) shows probe tack data on bulk samples which was compared to the rolling ball tack on thin films shown in Fig. 5(a). Regions of tacky versus non-tacky overall film compositions are indicated by blue and red shaded areas respectively. The two sets of results differ qualitatively. We can rationalise the differences recalling that directional drying of films often results in a non-uniform concentration profile in the direction normal to the substrate. A 'crust' or 'skin' is frequently observed during drying of solute–solvent films [25]. The data points indicated in Fig. 5(a) represent the overall film composition, rather than the surface composition at which the film loses its tackiness which we expect to be within the non-tacky region of Fig. 5(b), i.e. \( \geq 70\text{wt}\% \text{ ACH} \).

Indeed, bulk probe tack measurements on droplets of ACH/glycerol \( \geq 15/4 \) reveal a 'skin' below which a liquid remains. The offset between the results of the two methods provides a useful comparison between bulk and thin-film behaviour.

Thin, large-area films with ACH-rich, glycerol poor compositions typically crack upon drying, while the inclusion of glycerol results in homogeneous films (microscope images provided in Fig. 5(a)). Ratios of ACH/glycerol \( \leq 15/4 \) generally result in crack-free films. At high glycerol concentrations (ratio of approximately ACH/glycerol \( \leq 15/15 \) phase separation was observed and the films were no longer smooth. A two phase system was equally observed for bulk samples of equivalent composition (ACH/glycerol = 15/15) and low water content (\( < 10\text{wt}\% \)) as shown at the bottom of Fig. 5(b)

In the large-area, ACH-rich films (with ACH/glycerol \( \geq 15/4 \)), increasing the temperature from 20 to 35°C results in skin formation at higher overall water content, as shown in Fig. 5(a). This is expected, as higher temperatures increase the evaporation rate which, in turn, favours skin formation. Models for skin formation of colloidal films typically predict the skin formation when the rate at which the film surface falls due to evaporation is greater than the rate of diffusion required to redistribute the particles in the
film [26,27]. The ratio of evaporation to diffusion, in a film of initial thickness \( H_0 \), is given by the dimensionless Péclet number \( \text{Pe} = \frac{E H_0}{D_0} \), where \( E \) is the flow velocity (i.e. of the film surface towards substrate) and \( D_0 \) is the diffusion coefficient. As a first approximation, we take the Stokes-Einstein relation \( D_0 = \frac{k_B T \eta}{6 \pi r g} \), assuming an \( \text{Al}_{13} \) chlorohydrate complex to be a spherical particle of radius \( R \approx 0.45 \) nm [3], and the viscosity \( \eta \) to be that of a binary glycerol–water mixture at temperature \( T \); \( k_B \) is the Boltzmann constant. Evaporation rates are estimated from the DVS and film drying data. Upon drying, \( \eta \) increases, we find qualitative agreement with \( \text{Pe} \ll 1 \) and the skin formation results recorded by the tack test, detailed in supporting material section SM6. This stage falls approximately at the transition between the constant and falling rate periods found in the kinetic data as presented in the supporting material section SM6.

Finally, we note that the calorimetric glassy region of Fig. 3, effectively overlaps with the solid-like non tacky region of Fig. 5(b), but the latter has an additional region for (initial) glycerol compositions above 4 wt% where drying rates are high, the viscosity increases abruptly and the films remain non-tacky, crack-free, yet above \( T_g \) at ambient conditions.

3.6. Equilibrium properties

We next consider the equilibrium between ACH–glycerol–water films and water vapour. Water sorption and desorption experiments were carried out by DVS to obtain equilibrium composition (viz. water content) as a function of RH. Fig. 6 shows a typical plot of mass change as a function of RH in (a) and resulting sorption and desorption isotherms in (b) which indicate the equilibrium sample mass at a given RH with reference to a dry basis. The equivalent (ternary) composition is then reported in (c). Measurements on ‘dry’ films, dried till equilibrium at 0% RH in situ via DVS, were carried out for a range of different formulations and the sorption and desorption isotherms are used to compute the equilibrium composition at 0% RH in Figs. 6 and 7.
drying kinetics, which could be a combined effect of the rapid the kinetic behaviour are related.

We next consider in detail whether the equilibrium behaviour and dependence with glycerol composition as the film drying kinetics.

The addition of small quantities of glycerol and rationalised in terms of plasticising effect has been reported for biopolymers upon addition of small amounts of glycerol [9,19–22] and rationalised in terms of the competition between glycerol and water for binding sites.

Upon further addition of glycerol, the film equilibrium composition becomes significantly richer in water. A possible explanation for this is that upon saturation of binding sites on the ACH with glycerol, the content of unbound glycerol in the film increases; in turn, the hygroscopic nature of glycerol causes an increase in water content within the film.

At even higher glycerol concentration (approximately ACH/glycerol ≤ 15/15), phase separation occurs, as evidenced earlier in Fig. 5(b), which apparently suppresses the hygroscopic nature of the glycerol resulting in a surprisingly low equilibrium water content in the film. Demixing has also been observed in starch–glycerol–water mixtures [22]. Phase separation, or the changes in the interaction between ACH and glycerol that precede it, may also explain the deviations from the relative viscosity versus phase volume master curve in supporting material Fig. S11(c).

These thermodynamic results share a similar non-monotonic dependence with glycerol composition as the film drying kinetics. We next consider in detail whether the equilibrium behaviour and the kinetic behaviour are related.

The addition of small glycerol quantities to ACH slows down drying kinetics, which could be a combined effect of the rapid increase in viscosity with ACH content for initial glycerol concentrations around 4 wt% (supporting material Fig. S12), crust formation and the anti-plasticisation behaviour of glycerol observed by calorimetry at the later drying stages. This viscosity increase and anti-plasticisation effect may share the same underlying cause as the enhanced drying, namely the binding between ACH and glycerol which increases the effective size of the ACH particles.

Upon further addition of glycerol (>7% initial), the drying rates increase, while the final equilibrium water content in the film is higher, likely due to glycerol plasticisation of the film and reduction of the phase volume of ACH. Thus both the kinetics and the equilibrium properties can be rationalised by the presence of unbound glycerol.

Eventually, above ≈12% initial glycerol content (or ≈45% final), drying is comparatively slow. This may be explained by the unexpectedly high relative viscosity shown in Fig. S11(c). The high viscosity may be explained by an attractive interaction between the ACH and the glycerol which manifests itself in the equilibrium behaviour. These attractive interactions must be of a different nature to those that dominate at low glycerol content, and are possibly driven by dispersion forces as we note that the refractive index of ACH and glycerol are both higher than that of water.

4. Conclusions

The phase behaviour, drying kinetics and film formation of AC H–glycerol–water exhibit a non-monotonic dependence on glycerol composition elucidated by a range of complementary experimental techniques. The ternary diagrams shown in Fig. 8 summarises the different stages of film formation, kinetics, resulting film composition and (qualitative) rheo-mechanical properties. The classification of the various regions of the diagram is detailed in supporting material section SM10. Films of ACH solution with zero or low glycerol content form a ‘skin’ upon drying which renders them transiently ‘tack-free’ regardless of their high water content. This phenomenon is temperature dependent. The addition of small glycerol quantities was observed to have an anti-plasticising effect, raising Tg and enhancing desiccation of the final dried film compared to the equivalent binary ACH–water mixture. Competitive binding for ACH sites between water and glycerol at low RH likely underpins this behaviour. Mixtures with larger glycerol-to-ACH ratio, whose mobility can be understood as due to a higher content of (hygroscopic) unbound glycerol, exhibit enhanced water uptake and fast kinetics of water sorption/desorption. For high glycerol concentrations and low water contents, an unexpectedly high viscosity suggests attractive interactions between glycerol and ACH which result in phase separation for
ACH/glycerol ≤ 15/15. This increase in viscosity and underlying phase behaviour explains the slow kinetics and small water uptake for this glycerol rich, water poor concentration region.

Understanding the role of water loss or uptake in the physical properties of organic and inorganic films (e.g., mechanical strength, permeability, viscous flow) is essential for a range of applications including biodegradable polymers used in packaging, with environmental implications for petroleum-derived plastics [9,10,19–23], in the sector of edible films for food preservation [28,29], in the clothing [30,31], automotive [32] and personal care industries and more recently in ion exchange membranes for fuel cells [8]. Our approach of simultaneous, complementary metrology and phase mapping can evidently be applied to a wide variety of contexts.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.07.064.

References