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

Giulia L. Ferretti¹, João T. Cabral¹

¹ Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

Correspondence to: J. T. Cabral; e-mail: j.cabral@imperial.ac.uk; phone no.:
+44 (0)20 7594 5571

G. L. Ferretti: giulia.ferretti08@ic.ac.uk
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 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.

Keywords

Film formation, drying, kinetics, salt, aluminium chlorohydrate, glycerol, water sorption, glass formation, adhesion
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\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 the 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 ACH–glycerol–water solutions along the film formation pathway, i.e. during water evaporation. Subsequently, 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.

Materials and methods

ACH–glycerol–water ternary system

Aluminium chlorohydrate was obtained from Summit Research Labs Inc. under the form of a 50 wt% hydrated dialuminium chloride pentahydroxide 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.

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 altered between 200 and 400 minutes ensuring the sample reached its equilibrium composition prior to the following RH change. Once the 90% RH was reached, an identical desorption cycle initiated, enabling both sorption and desorption isotherms to be constructed.

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

Large-area films of 30μm initial thickness and 4 x 4 cm² surface area for gravimetric measurement and 23 cm x 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 5100/5200). 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.

Separate experiments on 200 µl droplets were carried out under the same environment to check for the effect of evaporative cooling on drying rates and are detailed in the supporting material section SM4.

*Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD)*

A TA Instruments Q2000 with Tzero aluminium pans and lids was employed for DSC measurements, under nitrogen environment, of viscous solutions and films. Samples were prepared by drying the solutions directly in the pan under prescribed humidity and temperature, and the final composition was determined gravimetrically. Glass transition temperatures, $T_g$, were determined at 10°C/min, unless stated otherwise. Powder X-ray diffraction was employed to ascertain glass formation of the films, as detailed in supporting material section SM5.

*Solution viscosity*

Viscosity measurements were carried out using a Brookfield DV-I Prime viscometer equipped with an UL adapter and attached to a LTC1 Grant temperature bath with temperature controller GD120 kept at 35°C to be representative of skin temperature.

*Probe tack measurements*

For probe tack measurements, a stainless steel cylinder of 1 mm diameter with bevelled edges was employed as a probe to manually interrogate large droplets (2 ml) of evaporating solution, at $24 \pm 1^\circ$C and 25% RH in the chamber, of different compositions ensuring that the bulk of the material was probed, rather than just the top surface layer. A qualitative liquid/tacky/solid outcome was recorded based on visual observation of the indentation left on the sample and deformation upon probe retraction. Measurements were carried every 20 min, over one week, and repeated at least five times for each composition.

*Visual observation of film morphology*

The effect of composition on large-area film morphology was observed by optical microscopy (Olympus BX 41M).

*Results and Discussion*

*Drying pathway*

We first consider theoretically how the ACH–glycerol–water solutions composition evolve along the film-formation pathway. Raoult and Dalton’s law (supporting material section SM1) confirms that drying, within the ambient pressure (1 atm) and temperatures 18–40°C used – a range relevant for practical applications of these systems – involved solely the (partial) loss of water. This was further validated by TGA and FTIR spectroscopy experiments (supporting material sections SM2 and SM3) where glycerol evaporation and ACH speciation due to water loss was only observed from 100°C onwards. An implication is that the ACH:glycerol mass ratio therefore remains constant during drying. The drying pathway can hence be represented by a straight line in the ternary composition diagram as depicted in Figure 1. Upon water loss, the final film composition depends on RH as detailed below.
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).

Drying kinetics

The mass loss of drying ACH–glycerol–water solutions was measured by DVS at 0% RH and 35°C. The results are shown in Figure 2 (a) which reports the normalised mass changes for various film compositions, with respect to the initial mass \( M_0 \). Two characteristic drying regimes can be identified. The initial regime corresponds to a ‘constant-rate’ period, in which \( \frac{d(M/M_0)}{dt} \approx \text{constant} \), during which most water evaporates with a well-defined rate dependent on composition at the given RH and temperature. A ‘falling-rate’ period ensues, during which compositional changes are smaller. The evolution of the drying rates with time is shown in Figure 2 (b) and the composition dependence of the constant drying rate in Figure 2 (c).

Figure 2: (a) Normalised gravimetric evolution of 10 µl film drying via DVS at 35°C ± 0.2°C and 0% RH for water and initial solution mass fractions ACH:glycerol:water 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). (b) Drying rate as a function of time calculated from the mass loss data. The transition from the constant-rate period to the falling rate period is marked on each curve. (c) Effect of initial glycerol concentration on the drying rate in the constant-rate period. A guide to the eye is provided, as well as the constant rate for pure water under identical drying conditions (horizontal dashed line).
The drying rate in the constant-rate period shows a clearly non-monotonic drying behaviour with glycerol composition, which is also observed during the falling rate period (supporting material section SM4, Figure S4). For reference, the kinetic data for a pure water film of same initial volume and drying conditions are included in Figure 2. As expected, the water droplet has a long constant-rate period and a relatively short falling-rate period. Interestingly, the water-drying kinetics fall within the range of the ternary systems of various glycerol content, as quantified (in the constant-rate period) by the dashed line in Figure 2(c). Pure water dries slower than 0–3 wt% and 7–10 wt% glycerol mixtures, but faster outside this range (at constant ACH 15 wt%). All ACH mixtures have pinned contact lines during drying (supporting material Figure S5) and thus the non-monotonic drying behaviour is not due to film geometry. By contrast, pure water films do exhibit receding contact lines under the same conditions, which explains why water evaporates slower than some of the compositions. Evidently, drying kinetics accelerate with increasing temperature and decreasing RH, as quantified for 10 µl pure water droplets in the supporting material Figure S6 and S7, for comparison with Figure 2.

Water evaporation in a DVS experiment is expected to reduce the temperature of the film due to evaporative cooling, which could in turn play a role in the drying kinetics. Should evaporative cooling depend on composition (e.g. glycerol content), this could contribute to the non-monotonic behaviour observed. Separate experiments monitoring the temperature of large droplets drying were carried out. A temperature decrease of ≈10 °C was found across all film compositions (supporting material Figure 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 µg sensitivity microbalance and RH and temperature control. Complementary experiments were, however, carried out for large-area drying films (approximately 4x4 cm² and 30 µm thick) recorded with a mass balance in the humidity and temperature-controlled chamber. Similar non-monotonic kinetics with glycerol content are observed (supporting material Figure S9), albeit with larger uncertainty.

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

Glass transition

Upon drying, solutions of sufficiently high ACH content, within the red region defined in Figure 3, solidify into a transparent glassy film. Glass formation was confirmed by XRD (supporting material Figure S10), whose powder diffraction patterns indicate an amorphous structure. DSC provides further evidence for glass formation and \( T_g \) estimation, with representative DSC scans shown in supporting material section SM5. As expected, water acts as a film plasticizer. [19-21, 23]
Figure 3: Tg ranges for the ternary ACH–glycerol–water system measured by DSC. The figure results from a compilation of Tg 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–H₂O 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°C.

A compilation of the DSC Tg data, summarised in Figure 3, enabled the determination of the liquid–glass boundary at ambient temperatures 18°C and 25°C. Films are glassy under ambient temperatures for a restricted range of ACH-rich compositions (ACH/glycerol > 15/8 and low water content). Further, small quantities of glycerol (ACH/glycerol ≥ 15/4) seem to have an anti-plasticising effect, raising the Tg higher than that of the ACH with an equivalent amount of water. A similar anti-plasticising effect of small amounts of glycerol has been observed in biopolymer systems [9, 20, 21]. This anti-plasticisation effect shares a similar non-monotonic dependence with glycerol composition as the film drying kinetics. It is not immediately obvious whether these effects are related, since glass formation should only impact the later stages of drying. We therefore consider next the film drying process in detail.

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 0–0.15 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 Figure 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 Figure 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 solidification approaches. The measured final solid compositions are also indicated in the graph and assigned the conventional glass formation viscosity of $10^{12}$ Pa.s [25]. The lines correspond to an empirical relationship 

$$\eta = \eta_{\text{water}} \left(1-\frac{\phi}{\phi_{\text{max}}} \right)^{2-\phi_{\text{max}}}$$

with $\eta$ the mixture’s viscosity, $\eta_{\text{water}}$ pure water viscosity, $\phi$ the ACH mass fraction, $\phi_{\text{max}}$ the maximum ACH mass fraction and $B$ an intrinsic viscosity ($\phi_{\text{max}}$ and $B$ are fitting parameters) [26] and serve as a guide to the eye.

In order to assess the effect of glycerol concentration on viscosity, a relative viscosity $\eta_{\text{rel}} \equiv \eta / \eta(\text{water}:\text{glycerol})$ was calculated and plotted as a function of the ACH volume fraction in supporting material section SM6, Figure 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 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 Figure S9 (a and at each time point calculating a composition and, using the fits from Figure 4, a viscosity, a plot of the viscosity as a function of drying time was constructed in supporting material Figure S12. The slowest drying film composition, viz. 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 on Figures 3 and 4, for
which glass formation occurs at relatively higher water contents as mapped by the calorimetric \( T_g \) reported in Figure 3.

**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 that 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 Figure 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 \( \leq 0.01 \).

Figure 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 Figure 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.

![Figure 5](image-url)  
*Figure 5: Isothermal tack diagrams showing the transition between a tacky to non-tacky state during drying. (a) Rolling ball tack measurements on 30 µm films and (b) probe tack tests on bulk systems, carried out to decouple crust effects during film formation. All measurements carried out within a controlled temperature (± 2°C) and RH environment (± 5%).*
Figure 5 (b) shows probe tack data on bulk samples which was compared to the rolling ball tack on thin films shown in Figure 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 Figure 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 Figure 5 (b), i.e. $\gtrsim 70$ wt% 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 Figure 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 ($< 10$ wt%) as shown at the bottom of Figure 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 Figure 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 $\text{Pe} = \frac{EH_0}{D_0}$, 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 $D_0 = \frac{k_BT}{6\pi\eta R}$, assuming an 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 $\text{Pe} \leq 1$ and the skin formation results recorded by the tack test, detailed in supporting material section SM9. 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 Figure 3, effectively overlaps with the solid-like non tacky region of Figure 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.

**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. Figure 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 coincided exactly in all cases, establishing the reversibility of the sorption/desorption process and the equilibrium nature of the measured compositions.

![Graphs and diagrams]

Figure 6: (a) Dynamic water vapour sorption cycle for an aqueous mixture of initial (15:4:81) component ratios, with (ACH:glycerol:water) respectively, in steps of 20% RH until full equilibration; (b) resulting sorption and desorption isotherm and (c) corresponding ternary composition at 35.0±0.2 °C. The asymptotic values in Figure 2 (a) are used to compute the equilibrium composition at 0% RH in Figures 6 and 7.

All the equilibrium compositions for a given RH were mapped on a ternary diagram in Figure 7. Surprisingly the composition that showed the slowest loss of water, viz. ACH:glycerol:water = 0.15:0.04:0.81, shows the greatest loss of water at equilibrium. We therefore consider in greater depth the effect of glycerol on the system's thermodynamics.

Starting from ACH-rich and glycerol-poor mixtures, the addition of small quantities of glycerol (ACH/glycerol ≥15/4) actually promotes drying at low RH, resulting in lower water content than that of equivalent binary ACH–water mixtures. Consequently some compositions in Figure 7 have apparently negative water content which in reality simply have lower water content than the dried ACH–water binary mixture which was used to define the ACH apex of the diagram. This enhanced drying corroborates the anti-plasticising effects observed in the calorimetry (a slight $T_g$ increase) at the same levels of glycerol. This anti-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 Figure 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 Figure S11 (c).

![Equilibrium composition for films of varying ACH-to-glycerol ratio as a function of relative humidity, obtained by DVS. Both sorption and desorption equilibrium compositions are indicated on the ternary diagram (and agree closely). Apparent 'negative' water contents correspond to dehydrated ACH (discussed in text).](image)

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 Figure S12), crust formation and the anti-plasticisation behaviour of glycerol observed by calorimetry at the later drying stages. This viscosity increase and this 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 relatively slow. This may be explained by the unexpectedly high relative viscosity shown in Figure 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.

**Conclusions**

The phase behaviour, drying kinetics and film formation of ACH–glycerol–water exhibit a non-monotonic dependence on glycerol composition elucidated by a range of complementary experimental techniques. The ternary diagrams shown in Figure 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 $T_g$ 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) unbounded 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 $\leq$ 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.

![Ternary diagram summarising the phase behaviour, kinetic properties and physical properties of the ACH–glycerol–water system at 25°C, along the drying and film formation pathway.](image)

*Figure 8: Ternary diagram summarising the phase behaviour, kinetic properties and physical properties of the ACH–glycerol–water system at 25°C, along the drying and film formation pathway.*
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