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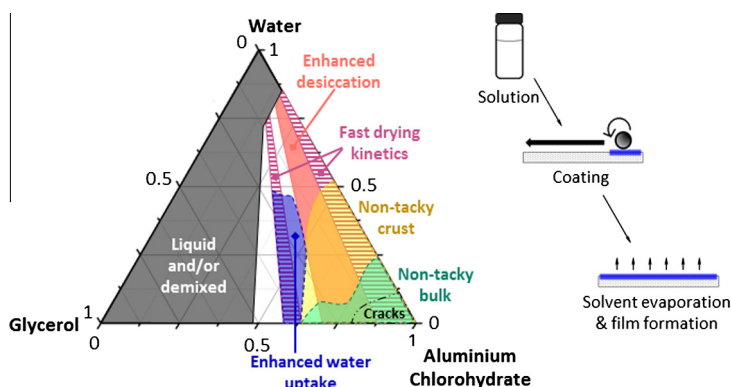
Phase behaviour and non-monotonic film drying kinetics of aluminium chlorohydrate–glycerol–water ternary solutions



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GRAPHICAL ABSTRACT



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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.

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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]

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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_3 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 ($\lesssim 14$ 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. 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 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 $\geq 99.5\%$ 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 μ l initial volume samples (equivalent to films of 127 μ m 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 μ m initial thickness and 4×4 cm² surface area for gravimetric measurement and 23 cm \times 3 cm for rolling ball tack measurements were initially spread on a 100 μ m-thick hydrophilic polyester substrate – a ‘transparency’ sheet (Lloyd Paton LPP/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.

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