



Spin casting of dilute solutions: Vertical composition profile during hydrodynamic-evaporative film thinning



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HIGHLIGHTS

- Spin casting is analyzed as hydrodynamic-evaporative film thinning.
- As film is assumed an ideal mixture of volatile solvent and non-volatile solute.
- The analysis reveals the time evolution of the internal vertical composition profile.
- A characteristic Sherwood Number is introduced as fundamental process parameter.
- The results are also quantitatively relevant for spin casting non-ideal solutions.

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ABSTRACT

We analyze the vertical composition profile during hydrodynamic-evaporative film thinning (spin casting) of mixtures of non-volatile solutes and volatile solvents. We present a generic approach based on ideal solution behavior. Our analysis complements more detailed (but more system specific) studies that are available in the literature. The hydrodynamic-evaporative film thinning is described analytically based on the solvent properties. We find a universal film thinning behavior as a function of the rotation speed, viscosity and evaporation rate. The thinning process is uniquely characterized by its transition height i.e., the film thickness where hydrodynamics and evaporation contribute equally to film thinning. The theoretically predicted film thinning is in agreement with experimental results. The evolution of the internal film composition is calculated numerically. The numerical description is tractable and offers quantitative insights into the influence of the experimental conditions on the evolution of the internal composition. A characteristic Sherwood Number is introduced as a fundamental process parameter. It characterizes the vertical solution profile and serves as a well-defined and experimentally accessible criterion for the regimes of quantitative validity of our analysis. We also present new power laws, which link the process control parameters to the composition evolution, process duration, and final solute coverage. Because the analysis is generic and tractable, it also yields valuable insights for solutions behaving non-ideally.

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1. Introduction

Liquid on a spinning, planar, wettable substrate forms a thinning film of uniform thickness h (Emslie et al., 1958). With evaporation of volatile film components, nonvolatile components enrich continuously (Fig. 1). Eventually they exceed saturation and finally precipitate as a deposit. This “spin casting” process has been investigated since decades. Yet rather few studies (Meyerhofer, 1978; Bornside et al., 1987; Lawrence, 1988, 1990; Ohara et al., 1989; Bornside et al., 1989; Shimoji, 1989; Lawrence and Zhou, 1991; Reisfeld et al., 1991a, 1991b; Yonkoski and Soane, 1992;

Cregan and O'Brien, 2007; Temple-Boyer et al., 2010; Muench et al., 2011) focused on the evolution of the internal film composition during thinning. They applied different approximations such as “boundary layers” (Lawrence, 1988, 1990; Lawrence and Zhou, 1991) or “split mechanism models” (Yonkoski and Soane, 1992). There are purely numerical investigations (Ohara et al., 1989; Bornside et al., 1989; Shimoji, 1989). Most of them are a combination of numerical and analytical approaches. These studies reveal many facts but the general insight is somewhat limited because, typically, complicated nonlinear viscosity and diffusivity behaviors (Muench et al., 2011) are assumed. For instance (Lawrence, 1988; Yonkoski and Soane, 1992; Norman et al., 2005; Muench et al., 2011), there is even no agreement in the literature on the amount of final solute deposit as a function of the process parameters (initial concentration, speed, etc.). The limited general relevance of

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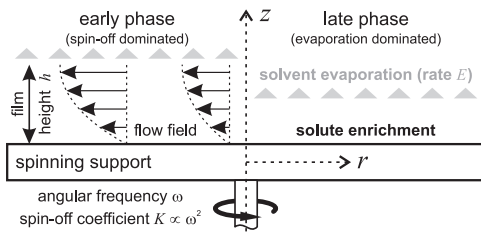


Fig. 1. Schematics of spin-casting with processes dominating early and late stages.

existing studies roots in their focus on polymeric solutions. These behave rather nonideally and case specific. Yet, increasingly spin casting is used for nucleation and growth studies (Riegler and Köhler, 2007; Berg et al., 2010) and for the deposition of structured (sub)monolayers (particle arrays, etc. Rabani et al., 2003; Bigioni et al., 2006; Hanrath et al., 2009; Heitsch et al., 2010; Klecha et al., 2010; Berg et al., 2010; Johnston-Peck et al., 2011; Marin et al., 2011; Brookshier et al., 1999). This means dilute solutions, which behave rather ideally during most of the spin cast process. Therefore we analyze here spin casting, assuming ideal solution behavior. We will show that this approach can also be used to quantitatively describe the spin casting of real, non-ideal solutions.

2. Hydrodynamic-evaporative film thinning

The thinning of a Newtonian, volatile liquid film of thickness h on a rotating support is described by Meyerhofer (1978) (lubrication approximation, no slip at the liquid/substrate interface, free liquid surface):

$$dh/dt = -2Kh^3 - E, \quad (1)$$

with $K = \omega^2/(3\nu)$, ω = rotational speed, ν = kinematic viscosity and E = evaporation rate. The fundamental form of Eq. (1),

$$d\xi/d\tau = -\xi^3 - 1, \quad (2)$$

is obtained by rescaling $\xi = h/h_{tr}$ and $\tau = t/t_{sc}^*$ i.e., by the system inherent “natural” scales (see Cregan and O'Brien, 2007):

$$h_{tr} = (E/2K)^{1/3}, \quad (3)$$

$$t_{sc}^* = (2E^2K)^{-1/3}, \quad (4)$$

h_{tr} is the “transition height” where evaporative and hydrodynamic thinning are equal. t_{sc}^* is the “reduced process duration” (Eq. (6)).

We assume that the rotational speed is not changed during the process ($\omega = \text{const.}$). We assume further that the originally deposited amount of liquid is much larger than what is necessary to cover the entire substrate surface with a film of uniform thicknesses of less than 100 μm (=the range of film thicknesses in the focus of our analysis). We disregard the peripheral/edge behavior and analyze only the properties of the main film area. Typical widths of the substrate are a few cm so that peripheral effects are confined to a relatively small region of the total film area. Due to the rather large amount of liquid deposited initially and because of the limited sample size the loss of liquid in the early stages of the spin cast process is dominated by lateral spin-off. After a short transient regime hydrodynamics will rapidly form a film of uniform thickness independent from the shape of the initially deposited liquid (Emslie et al., 1958). As soon as the liquid has been planarized into a thin film of less than typically 100 μm gravity and surface tension contributions can be neglected (Emslie et al., 1958; Kitamura et al., 2002). Accordingly for thicknesses less

than typically 100 μm the thinning of a (volatile) liquid film can be described by Eq. (1) with hydrodynamic (viscous) and evaporative contributions originating from E and K only and assuming a film of uniform thickness.

Evaporation takes place from the film surface into the surrounding vapor phase. Therefore, assuming otherwise constant parameters, the evaporation rate E is independent from the film thickness as long as the film is not too thin. For films of only a few nm thickness and less the energetic conditions at the surface depend on film thickness (disjoining pressure) and thus the evaporation rate may depend on the thickness. The evaporation rate E is specific for the instrumental setup (sample chamber geometry). It depends on the environmental conditions (temperature, vapor pressure) and also on the liquid composition (solute concentration). Because of convection it also will depend on the rotation speed (Birnie and Manley, 1997).

Here we analyze an individual spin cast process while keeping the temperature, the vapor pressure, and the speed constant. We also limit our hydrodynamic-evaporative film thinning analysis to film thicknesses of more than a few nm. Therefore only the thickness-dependent impact on the evaporation rate from the thickness-dependent compositional changes has to be taken into account.

In the early stages of the spin cast process the liquid composition (solvent concentration) does not change because the loss of liquid in this stage is dominated by spin off. A (selective) evaporation of the volatile liquid components, which would change the composition of the liquid can be neglected in this thickness regime. The composition of the film starts to change when the film thickness reaches the transition height h_{tr} (Eq. (3)) at the transition time t_{tr} when (per definition) evaporative losses start to become an important contribution to film thinning. For typical process parameters (3000 rpm) and for typical solvents (toluene) the transition height is only a few μm .

In the evaporation-dominated film thinning regime at thicknesses below the transition height the liquid composition will change (this change is the main topic of this report, see Section 6). Thus the evaporation rate will also change in this thickness range. However, we assume an initially low concentration of the non-volatile solute. Therefore even a pronounced relative increase of the solute concentration, which will occur for film thinning below h_{tr} still can keep its absolute concentration at moderate levels. For instance, an initial solute concentration of 1% will increase to about 10% at film thicknesses of typically 100 nm (=about 10% of a typical transition height). One may argue that this estimation considering only the overall volume loss of solvent is wrong because the increase may be higher at the film surface from which solvent evaporation occurs. However, as will be shown in Section 6, the solute distribution within the thin film is vertically rather uniform for many solute/solvent combinations, because of a vertically efficient diffusive dilution (of which the Sherwood number at h_{tr} is a measure, see below).

The approximation becomes poor for large polymeric molecules with low diffusivity or liquids with high viscosity. In any case, as long as the solute concentration increase is only moderate, K also will hardly change because the (composition-dependent) liquid viscosity, η , also hardly changes. Hence, for the range of film thinning in the focus of our study here it is reasonable for many solvent/solute combinations and concentrations (see the discussion on several real cases at the end of this report) to assume that E and K are constants in Eq. (1).

The inverse of Eq. (2) can be integrated²:

$$\tau(\xi) = \frac{\sqrt{3}}{6} \left\{ \pi + 2 \arctan \frac{1-2\xi}{\sqrt{3}} + \frac{1}{\sqrt{3}} \log \frac{1-\xi+\xi^2}{(1+\xi)^2} \right\}. \quad (5)$$

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