MACROVOID DEFECT GROWTH DURING EVAPORATIVE CASTING OF POLYMERIC MEMBRANES

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Abstract

Macrovoid (MV) formation is a significant problem in evaporatively cast polymeric membranes. MVs are large, elongated or teardrop-shaped pores (~10–50 μm) that can impair membrane structural integrity. Although MVs have been extensively studied, there is no general agreement on the mechanisms governing MV growth. Recently, our research group has formulated the solutocapillary convection (SC) hypothesis, which contends that MV growth involves three principal forces: a Marangoni force generated by surface-tension gradients within the MV interface, a viscous drag force, and a gravitationally induced body force. Two sets of complementary experiments were conducted to test the SC hypothesis.

Ground-based videomicroscopy flow-visualization (VMFV) was utilized to measure the flow velocities at the MV-casting solution interface and deep within the casting solution. The measurements were performed with casting solutions containing 10 wt% cellulose acetate (CA), 30 wt% H_2O, 60 wt% acetone, and 200-ppm TiO_2 particles for flow visualization, and the surface tension was controlled by surfactant addition. Qualitatively, the experiments indicated that MV growth occurs in three distinct phases: (1) a very rapid initial growth period, (2) a much slower growth phase, and (3) absorption of selected MVs into the expanding demixed region. The presence of tracer particles inside the MVs suggests the presence of a convective flow, which transfers the particles from the bulk solution to the MV interior. Although the VMFV experiments did not establish any surfactant effect on the interfacial velocities, a statistically significant effect on the MV number density was observed.

In the second set of experiments, membranes were cast aboard a KC-135 aircraft under 0-g and 2-g conditions. Despite careful attention to the design and fabrication of the membrane casting apparatus (MCA), several problems were encountered, the most significant of which was the contamination of the casting solution by the activated carbon particles used for solvent absorption. Despite these difficulties, SEM analysis of uncontaminated membrane samples indicated that the MV morphology was strongly influenced by the solvent-nonsolvent ratio. However, dependence of MV size and number density on the magnitude of the buoyancy force could not be established since (in many cases) the MVs penetrated through the entire thickness of the cast membrane. Based upon the insights obtained from these experiments, a new MCA has been designed, which incorporates wider casting wells, deeper recesses for casting thicker membranes, and better isolation of the activated carbon. The new MCAs will be used in an upcoming KC-135 flight, and should enable complete quantitative evaluation of the SC hypothesis.

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1. Introduction

Polymeric membranes can be formed via evaporative (dry) casting whereby a single-phase polymer/ solvent/non-solvent (P/S/NS) solution is caused to phase-separate by evaporation of the volatile solvent. The resulting dispersed phase will ultimately become the membrane pores, whereas the continuous phase will become the solid polymer matrix of the membrane. Evaporative casting can produce macrovoids (MVs), large teardrop or finger-shaped pores (~ 10-50 μm) that are generally considered to be undesirable in separation applications (Figure 1). Under pressure, MVs lead to excessive compression of the porous sub-layer and possible failure of the permselective layer, thereby causing flux decline or a loss in permselectivity.[1] The methods used currently to avoid MV occurrence are largely based on trial-and-error approaches. A better fundamental understanding of MV initiation and growth would enable the development of more effective strategies for controlling their occurrence.

Although researchers have previously proposed a variety of mechanisms for MV formation, two main hypotheses are currently favored: one attributes MV growth solely to diffusion,[2,3] whereas the other states that solutocapillary convection at the MV interface contributes to growth.[4-7] Smolders *et al.*[2] and Reuvers[3] state that MVs initiate when stable (i.e., outside the binodal region of the P/S/NS ternary phase diagram) polymer solution is present directly ahead of a newly formed layer of polymer-poor nuclei near the top of a freshly demixed film. They explain that after MV initiation, growth occurs by diffusion of primarily solvent to the MV nuclei, and argue that MV growth occurs when "the diffusional flow of solvent from the polymer solution into the nuclei is larger than the flow of nonsolvent from the nuclei into the polymer solution."[3] In addition, they assert that interfacial processes do not affect MV formation. Because their growth mechanism does not involve body forces, buoyancy effects cannot be accommodated in predictions of MV size. Nonetheless, as MVs grow, their increased volume could result in larger buoyancy forces. Although this hypothesis (hereafter referred to as the *diffusive growth hypothesis*) was originally formulated for wet-cast membranes, the same logic should also apply to the dry-cast process.

In contrast, the Solutocapillary Convection (SC) hypothesis[4] contends that MV growth is governed by three principal forces: a Marangoni force generated by surface-tension gradients within the MV interface that facilitates MV growth; a viscous drag force that resists MV growth; and a gravitationally induced body force that can either resist or promote MV growth depending upon its orientation. The schematic shown in Figure 2 explains the SC hypothesis of MV growth in the dry-casting of the cellulose acetate (CA)/acetone/water system. Water has a much higher surface tension (72 dyne/cm) compared to acetone (23 dyne/cm), and our measurements indicate that in binary water/acetone mixtures the surface tension increases with increasing water fraction (Figure 3). Thus, rapid evaporation of acetone (solvent) from the gas-liquid interface causes the water (non-solvent) fraction to increase thereby generating a surface-tension gradient between the solvent-poor region near the interface, and the solvent-rich region in the bulk solution. Due to this surface-tension gradient, material along the MV/solution interface moves from the leading edge (low surface tension) to the trailing edge (high surface tension) of the MV. This process, known as solutal Marangoni (solutocapillary) convection, exerts a force on the growing MV that propels it away from the gas/liquid interface and into the underlying bulk solution. At the same time, continuity of velocities at the MV/casting solution interface causes convection cells inside the MV. The overall effect is to enhance the mass transfer of non-solvent into the growing MV. MV growth is also simultaneously opposed by a viscous drag force as well as the gravity-induced buoyant force.

In this study, we attempted to test the validity of the SC hypothesis using two different approaches in which the solutal-Marangoni and the body forces were systematically varied. In the first set of experiments, membranes were cast aboard a KC-135 aircraft that produced short durations of microgravity and 2-g conditions. The second set of experiments involved the use of videomicroscopy flow visualization (VMFV) to measure and compare the velocities at the MV-casting solution interface in solutions containing different surfactant concentrations.

We have previously reported the results of experiments in which membranes were cast in a microgravity environment aboard KC-135 aircraft.[5] A specially designed membrane casting apparatus (MCA) suitable for microgravity casting was utilized for this purpose. However, due to several unforeseen limitations of the MCA, the membrane thickness was highly non-uniform thereby precluding any meaningful statistical analysis of the data. Qualitative observations from that study suggested that: (1) MV formation is closely linked to the S:NS ratio in the casting solution and (2) at the lowest S:NS ratio buoyancy appeared to hinder MV growth. Based upon the insights obtained from that study, the MCA was modified using (1) wider wells to obtain larger samples, (2) a different triggering mechanism to minimize sloshing, and (3) finer-machined surfaces to prevent thickness non-uniformities.

VMFV provides a direct means of measuring the interfacial velocities. However, since the membrane formation process is relatively rapid (~1-2 min) and the films typically are thin (100-500 μm), adapting flow visualization to monitor membrane casting has generally proven difficult. Recently we reported that VMFV could provide important information regarding the phenomena occurring at the MV interface.[6] In this study, VMFV was further extended to determine the effect of a surfactant on the MV interfacial velocities. Velocities were measured at the edge of the MVs as well as in the casting solution relatively far from the MVs; in addition, MV number density data were also obtained.

2. Materials and Methods

Materials

CA with a molecular weight of 40,000 and an acetyl content of 39.8% was obtained from the Eastman Chemical Company and stored in vacuum at 80°C before use. ACS certified grade acetone obtained from Fisher was utilized in the as-received condition, and deionized water was used for making the casting solution. The surfactant employed was Triton X-100 (J. T. Baker Company). Triton X-100 (polyoxyethylene iso-octyl phenyl ether) is a nonionic surfactant with a critical micellar concentration (CMC) in water of approximately 6×10^{-3} mol/L.

Experiments aboard KC-135 aircraft

The NASA KC-135A aircraft flies in a series of parabolic maneuvers that give rise to short periods (20-25 s) of near-zero gravity in the cabin followed by a high-g pullout lasting approximately 90 s. Typical accelerations experienced during the low-g portion of flight are on the order of ±0.02 g.

The MCA works on a sliding block principle[7] as indicated in Figure 4. First, the casting solution is loaded into the chimneys directly over 150 μm-deep casting wells machined into a Delrin® sliding block. To initiate membrane formation, the sliding block is manually moved forward rapidly until each well is aligned directly under a chimney filled with activated carbon (suspended on a fine nylon mesh approximately 1 mm above the cast membrane). Solvent and nonsolvent then evaporate, causing phase

inversion. The MCA has six separate casting wells (1-cm diameter) and laser probes mounted on the two central wells enable solution demixing to be monitored.

A full factorial experimental design was used in these experiments in which three variables were studied: gravity induced buoyancy force (0-g or 2-g), solvent/nonsolvent mass ratio (2:1, 2.33:1, or 2.75:1), and surface tension (using surfactant-free and surfactant-containing solutions). In order to optimize use of the limited time of low-g available, 1-g membranes were cast on the ground in the MCA.

The casting solutions were prepared one day prior to the flight and stored in vials. Solutions to be cast on board the KC-135 were loaded in 1-cc syringes (Benton-Dickinson #309602) less than 1 hr before flight. Shortly after takeoff, the solutions were transferred to and sealed in the MCA (gravimetric measurements indicated that solvent-vapor leakage from the apparatus was insignificant when solutions were stored in syringes for fewer than 3 hr and in the MCA for less than 1 hr). In microgravity, the MCA was allowed to free-float in the aircraft cabin such that each nascent membrane experienced at least 25 s of zero gravity immediately after casting. All samples were dried for at least 2 hr prior to removal from the MCA. Scanning electron micrographs of the cross-sections of all membranes were obtained using a RJ Lee PSEM scanning electron microscope.

Videomicroscopy Flow Visualization

For the VMFV experiments, casting solutions containing 0, 31.4, 300, and 3000 ppm Triton-X surfactant were used. The solutions were stirred vigorously for several hours and taken off the stir plate 30 min prior to the experiments to allow entrained air bubbles to escape from the solution. A small amount of tracer particulates – 200 ppm of TiO_2 particles – was added to the casting solution to facilitate visualization of the microscopic flows. Although the individual TiO_2 particles were only a few nanometers in diameter, they typically formed aggregates, which were in some cases as large as 1 micron.

Figure 5 shows a schematic of the VMFV experimental arrangement. Using a syringe, the casting solution was injected into the space between two microscope slides separated by a Teflon shim until the solution reached a barrier (pin). The pin helped in isolating the casting solution from the air, and also provided a constant diffusion length of 1 cm between the solution/air interface and the leading edge of the microscope slides. Contact between the casting solution and the air was initiated by removing the pin. The preferential evaporation of acetone upon contact of the solution with air led to solution demixing and membrane formation. As shown in Figure 5, the casting solution had two interfaces with air – the front and the rear interface. Since evaporation from the rear interface could confound the experiment by affecting the bulk flows, a drop of acetone was inserted close to the rear interface – the vapor pressure generated by the drop significantly reduced evaporation from the rear interface.

The demixing front and the MVs were tracked using a video microscope. A CCD camera with a view window of 730×550 microns was attached to a video microscope, and recorded images at 1 s intervals. The PC software Scion Image[8] was used for the flow visualization analysis. Typically, tracer particles close to the MV interface were tracked over five frames to obtain the MV interfacial velocities. Wherever possible, two particles were tracked at the MV edge, and the average of the two velocities was used as the "raw" edge velocity. Similarly, four tracer particles far from the MV but at almost the same distance from the demixing front were chosen and tracked for five frames and the "raw" bulk velocity was obtained by averaging these four velocities. The leading edge of the MV was also tracked during the same time interval to obtain the MV velocity, which was then subtracted from the raw velocities to obtain the actual

edge and bulk velocities. Only those MVs whose size stayed relatively constant during the time interval were considered for the computation of the edge velocities. In this fashion, the artifacts associated with the growth/shrinkage of the MVs were minimized. The edge velocity ratio (EVR) was calculated by dividing the edge velocity by the bulk velocity. In addition to measuring the particle velocities, the number of the MVs seen in the viewing frame was also determined.

3. Results

Microgravity and 2-g experiments

The parabolic maneuvers of the KC-135 aircraft only produce relatively short intervals of 0-g and 2-g, and it was necessary that the entire casting solution demix within this interval. Light reflection measurements using the two laser probes confirmed that complete demixing did occur within 20 s. Although the membranes prepared in the new MCA were larger and more uniform in thickness compared with those of an earlier study, some problems were still encountered. In some instances, the nylon mesh holding the graphite particles tore and the particles dropped into the casting solution, affecting the membrane morphology. In other cases, the MCA had to be hand-held during the microgravity maneuver, and hence did not free-float. As a result, only a limited number of "good" membrane samples were available for analysis.

Since the buoyancy force opposes MV growth, one would expect the MVs formed in 0-g to penetrate deeper into the membrane (thickness direction) as compared to those formed in 2-g. In contrast, adding the surfactant should reduce MV penetration because of the smaller surface-tension gradient. However, the limited time interval of 25 s for demixing restricted the initial film thickness. Consequently, in most cases the MVs penetrated through the entire membrane thickness. Figures 6 and 7 show the influence of the surfactant (at 2-g) and the buoyancy force, respectively, on the MV size (average MV area) at two different S:NS ratios. These data do not indicate a statistically significant dependence of MV size on the surfactant concentration or the buoyancy force, most likely due to the penetration of the MVs through the entire thickness of the cast membrane.

Videomicroscopy experiments

The viscosities of casting solutions with and without the 200-ppm TiO_2 tracer particulates were measured and found to be statistically identical. Thus, a change in the MV formation hydrodynamics associated with a difference in viscosities was not a concern for the VMFV experiments. Information regarding the effect of the surfactant on the casting solution surface tension would also be valuable; this becomes particularly important in view of the fact that the surface tension of the ternary solution cannot be predicted on an *a-priori* basis even though the CMC of Triton X-100 in water is known. However, this measurement is difficult because of high casting-solution viscosity and rapid acetone evaporation from the gas/solution interface. In addition, the surfactant concentration in the compositions utilized is diluted since water comprises only 30 wt% of the solution. Consequently, surfactant concentrations that differed by an order of magnitude (30, 300, and 3000 ppm in water) were selected for this study.

Figures 8 and 9 show the effect of surfactant concentration on the EVR and the MV density, respectively. Analysis of the EVR data via standard analysis of variance techniques indicated that there was no statistical difference among the four cases, *i.e.* 0, 31.4, 300, and 3000 ppm of Triton X-100. On the other hand, analysis of the MV density data indicated that there was a statistically significant difference among the groups. A multiple comparison procedure established that the number density of MVs with a casting solution containing 300-ppm surfactant was distinct from that for a surfactant-free casting solution.

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Observations during the experiments indicated that in most cases, the MVs grew "explosively" from the demixing front (within 2-3 s). Over time, tracer particles became visible inside the MVs. This is a particularly significant observation, since the presence of tracer particulate inside the MVs cannot be explained by diffusion, and thus suggests the presence of a convective flow that enables transfer of the particles from the bulk solution into the MVs.

4. Discussion

In a previous study,[6] a scaling analysis was conducted to compare the magnitudes of the buoyancy and viscous drag forces for a MV approximately 50 microns in diameter. This analysis indicated that the buoyancy force is much smaller than the viscous drag force. Additionally, while the viscous drag force is proportional to the MV radius, the buoyancy force is proportional to its third power, thus implying that in the initial growth phase, the buoyancy force would be negligibly small compared to the viscous drag force. However, the viscous drag force depends upon the velocity of the growing MV; whereas this force would be significant in the initial growth phase of the MV, it would diminish to zero in a fully grown MV. Therefore, the buoyancy force can indeed become significant in determining the final size and shape of the MV. However, for the buoyancy effect to be significant, the MV must be sufficiently large (~ 80-100 μm).

In the present experiments at the lowest S:NS ratios, MVs penetrated through the entire membrane thickness under 0-g as well as 2-g conditions. Hence, the effect of buoyancy or surface tension could not be validated. Our calculations indicate that such validation would require a much greater initial casting solution thickness (~ 500 μm).

Although the VMFV results indicated that the presence of surfactant did have a statistically significant effect on the MV density, the EVR was not significantly altered. This result appears to imply that the relationship between solutocapillary convection and MV growth is tenuous. However, several important factors must be considered in interpreting these results. First, the drag forces on the particulate aggregates (assumed negligible) might have been significant and second, not all of the "interfacial particles" were exactly at the MV/solution interface. Hence, these particles might not have accurately tracked the actual edge velocity. Furthermore, velocities were tracked only during the mature phase of the MV growth process in order to avoid the artifacts associated with MV rapid growth/shrinkage. At this point in the MV growth process, the concentration gradients might already have become too small to be of significance. Finally, the overall hydrodynamics in the VMFV arrangement are different from "usual" membrane casting conditions in that the former has a vertical face exposed to air and the demixing front moves horizontally.

Nonetheless, observations during the VMFV experiments yielded important information about MV growth via the observation of tracer particulate inside the MVs. Their presence cannot be explained either by diffusion or by the SC hypothesis, and strongly implies the presence of a convective flow that transports the particles from the bulk solution to the interior of the MVs. This occurrence suggests that multiple mechanisms may be associated with MV growth. This possibility is reinforced by the observation that although the surface tension gradient during the subject CA membrane casting is significant, MVs are also observed in systems where the surface tension difference between the solvent and non-solvent is not very large.[3] Hence, whereas solutocapillary convection may well facilitate MV growth in the CA/acetone/water system, this phenomenon may not generally represent the principal mechanism driving MV growth.

5. Future Work

While the KC-135 and VMFV experiments have provided new and intriguing data regarding the formation and growth of MVs, the results did not provide complete statistical evidence for the influence of solutocapillary convection on the MV growth process. Indeed, results from both the KC135 and VMFV experiments indicate that MV growth is a complex process and emphasize the need for additional studies that employ more sophisticated approaches. We have recently fabricated a new MCA based on a modified design. The new MCA incorporates solid carbon monoliths for absorbing volatile solvent (acetone). This approach should eliminate the problem of carbon particles falling into the casting solution. Also, the new MCA has a movable aluminum substrate that will enable controlled variation of the casting solution thickness and facilitate removal of the final membrane. Water-holding compartments facilitate a wet-casting option. The new MCA will be extensively tested on the ground (1-g) prior to future KC-135 flights to identify the set of parameters including casting solution concentration and initial film thickness that will provide partial MV penetration. These parameters will then be used to cast membranes aboard the KC-135 at 0-g, 1-g and 2-g. The use of multiple MCAs for the KC-135 casting experiments should enable us to obtain a much more extensive database that can provide complete quantitative evidence regarding the significance of SC convection on MV growth.

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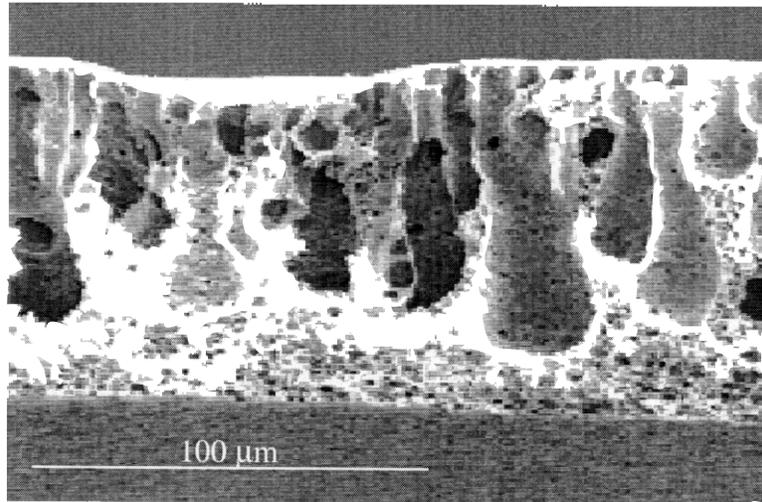
Figure 1. Cross-section of a membrane cast from a CA/acetone/water solution showing the presence of macrovoids.
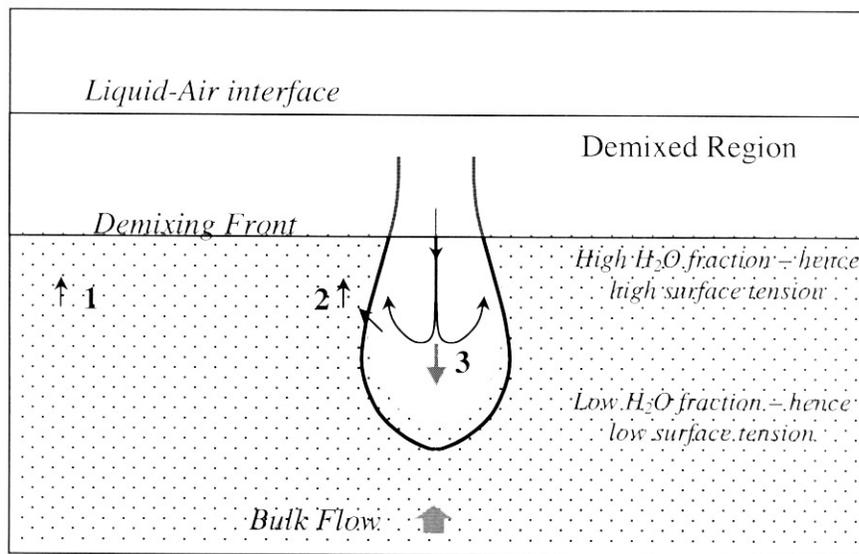
Figure 2. Schematic explaining the SC mechanism for MV growth. The surface-tension gradient induces an interfacial flow at the MV interface, which in turn induces a bulk flow in the surrounding solution. The velocities at points 1, 2, and 3 refer to the far-field, MV interface, and MV velocities, respectively. The EVR is calculated as $EVR=(v_2-v_3)/(v_1-v_3)$. The SC mechanism predicts that EVR would decrease if surfactants were added to the casting solution.
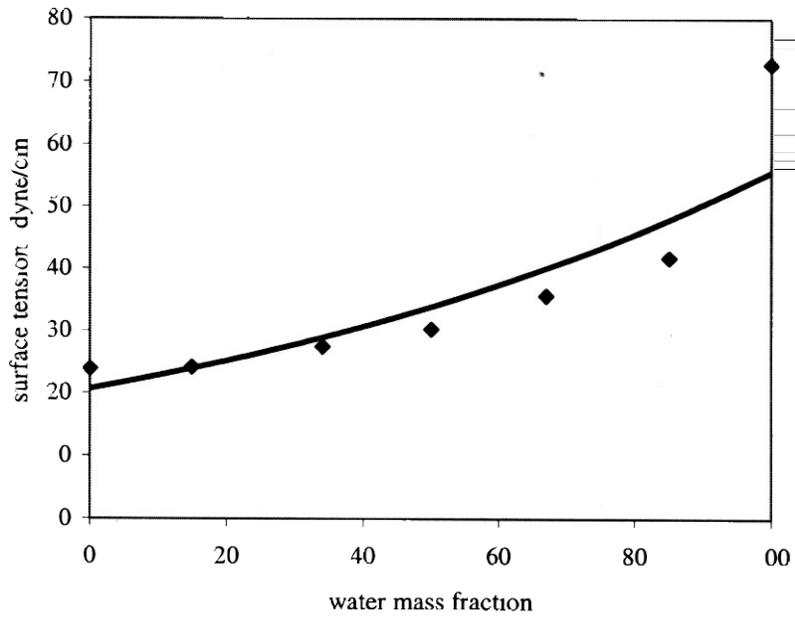
Figure 3. Variation in the surface tension of binary water/acetone solutions with increasing water mass fraction.
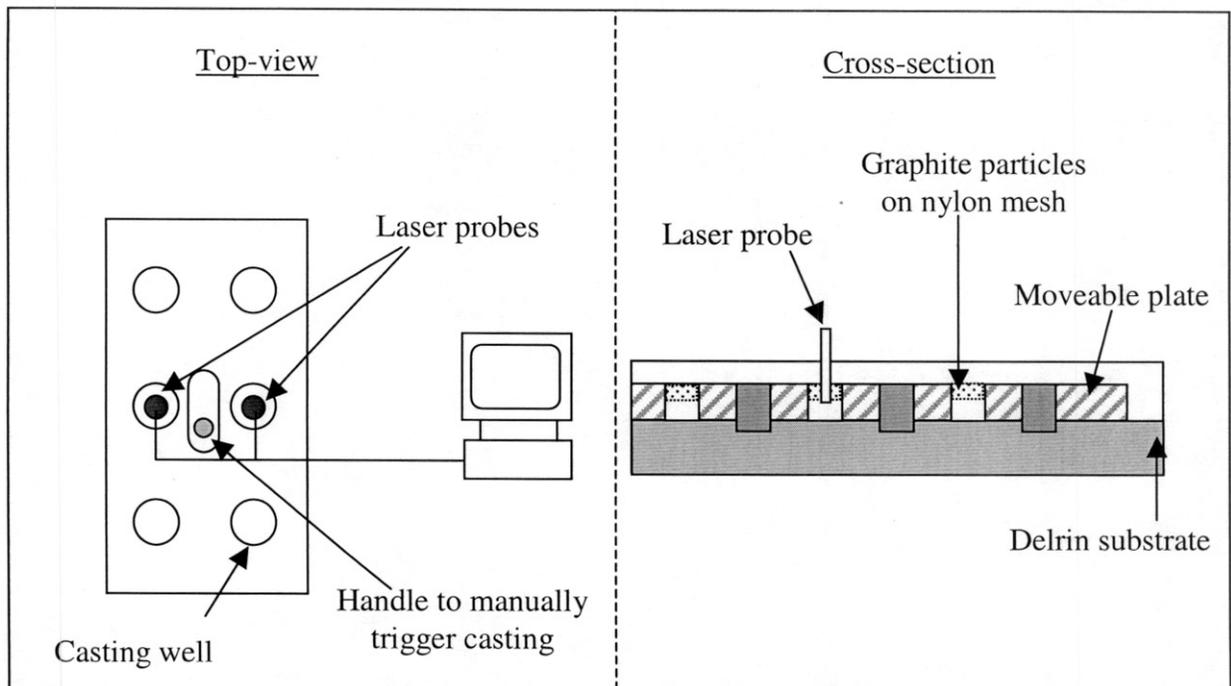
Figure 4. Schematic of the membrane casting apparatus (MCA).
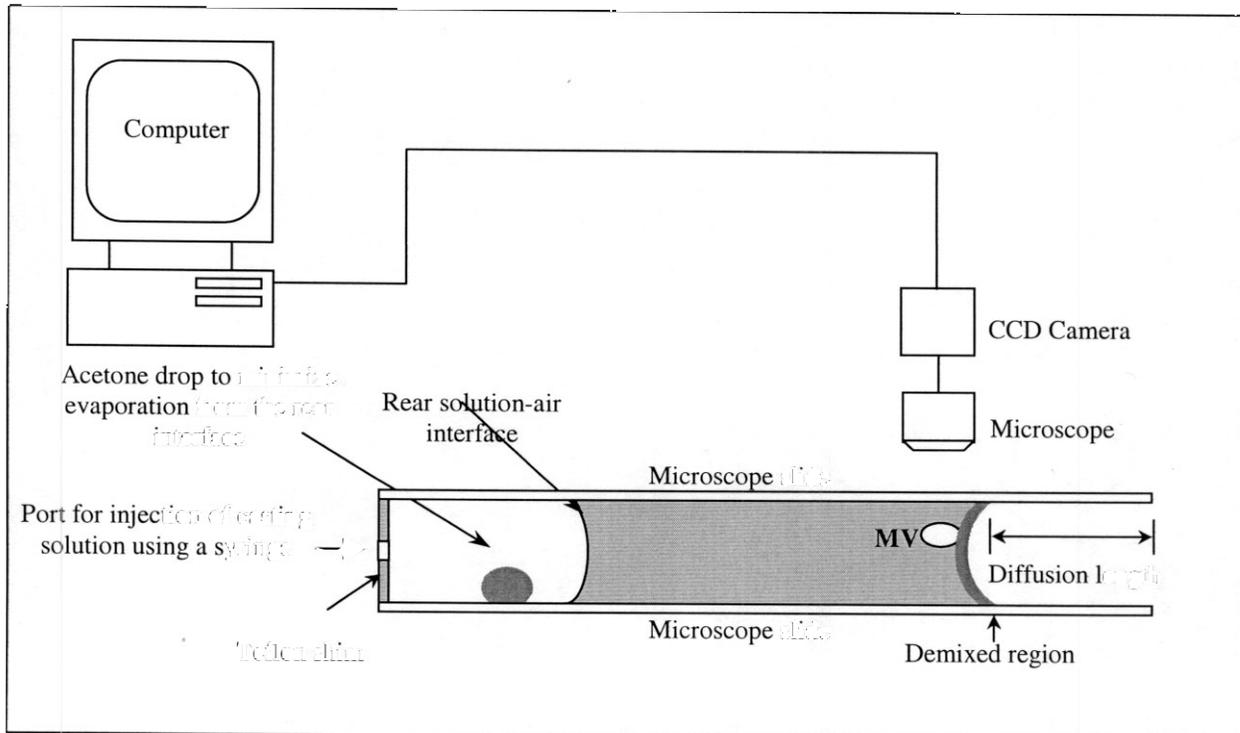
Figure 5. Schematic of the videomicroscopy set-up. The casting solution is inserted between two microscope slides that are separated by Teflon shims. The small "bulb" at the left of the demixing front is a macrovoid.
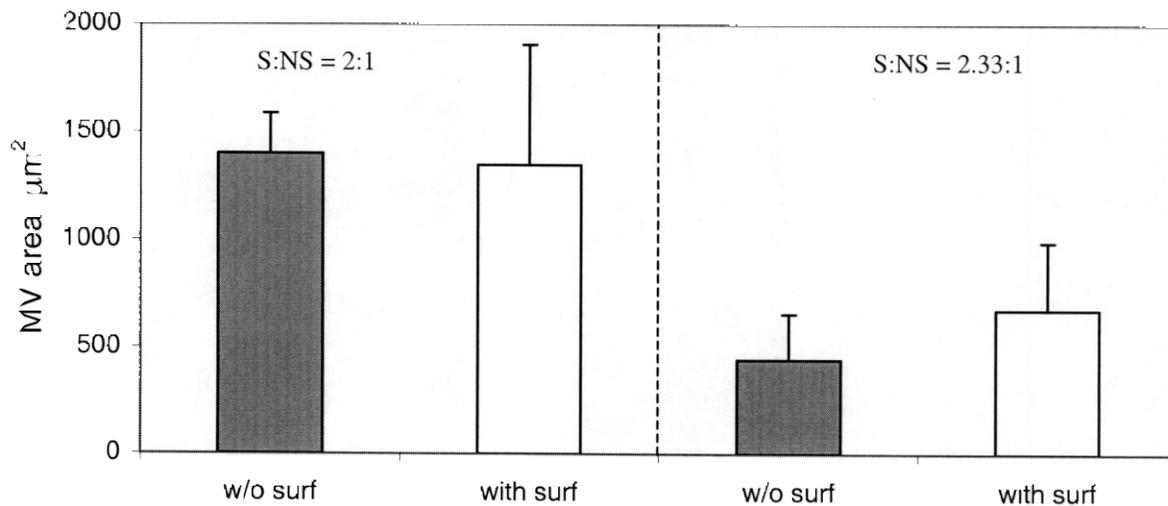
Figure 6. Influence of surfactant on the MV size at different S:NS ratios under 2-g conditions. Overall, the MV size decreases with the S:NS ratio but the surfactant does not appear to affect MV size.
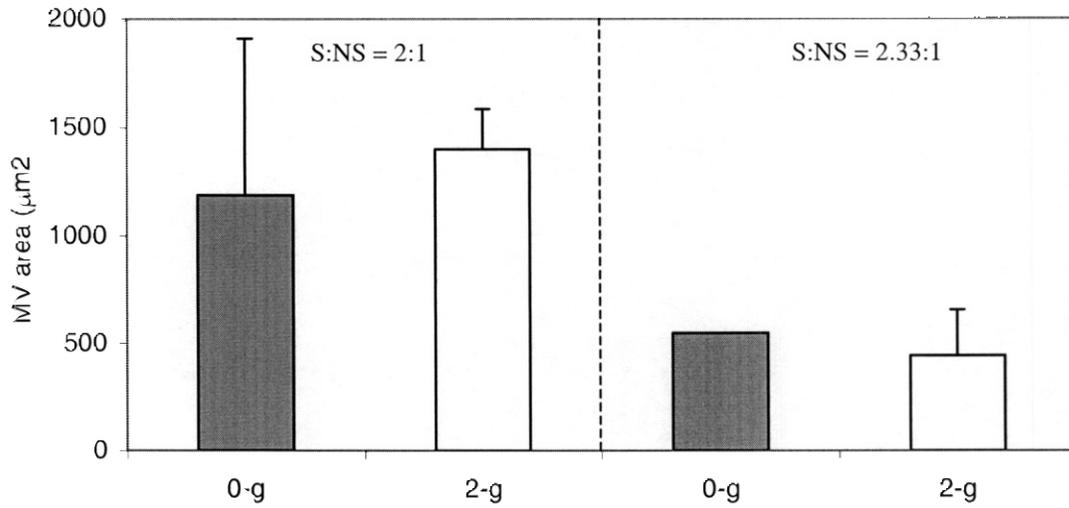
Figure 7. Influence of buoyancy on the MV size for two different S:NS ratios. Buoyancy does not appear to affect MV size.
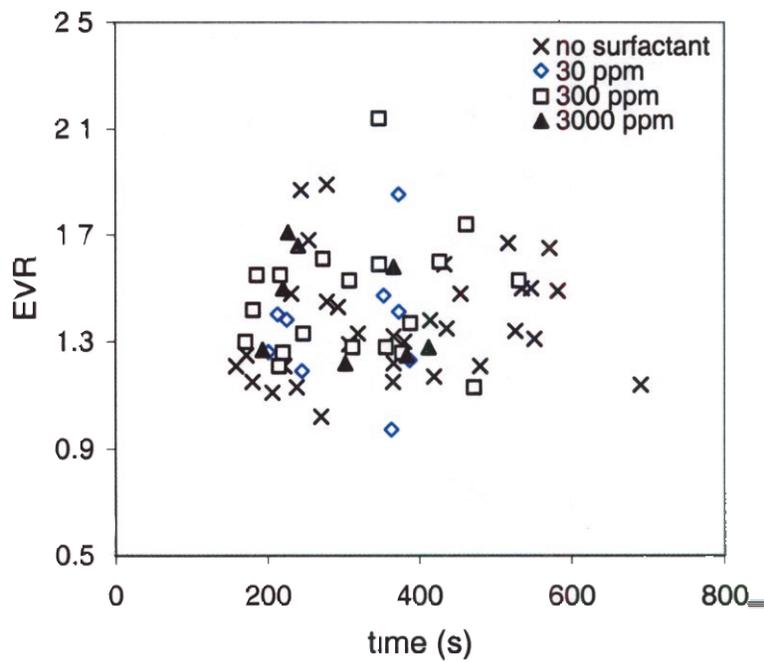
Figure 8. Influence of surfactant concentration on the EVR. No systematic trends were observed.
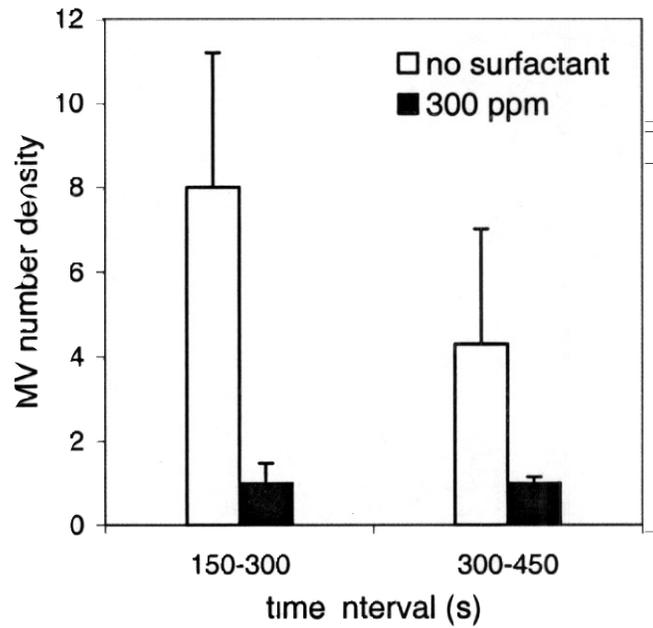
Figure 9. Influence of surfactant concentration on the MV number density, defined as the number of MVs viewed in a single frame.