Thin Layer Chromatography with Electrospun Silica

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Abstract:

Thin layer chromatography (TLC) is a characterization method used throughout all disciplines of science to determine compound purity. This separation technique was studied in the hopes of making it more efficient by changing the morphology of the silica stationary phase using the electrospinning process. Silica was synthesized through a sol-gel reaction and was then electrospun into mats of nanofibers. These mats were then used as the stationary phase for the separation of a dye mixture of methylene blue, rhodamine B, and fluorescein. The electrospun plates supported some separation of the dyes comparable to the separation offered by the commercial silica plates. The results showed promise for electrospun silica as the stationary phase for TLC.

Introduction:

Chromatography is a separation technique in which a mixture is separated into its different, pure components. A mobile phase carries the components of the mixture through a stationary phase. The different components interact with the stationary and mobile phases based on their chemical compositions and thus move through the stationary phase to different extents and at different rates.[1]

Adsorption chromatography utilizes a solid stationary phase and a liquid or gaseous mobile phase. Solute is adsorbed on the surface of the solid particles of the stationary phase. The more strongly a solute is adsorbed, the slower it travels through the stationary phase.[2]

Thin layer chromatography (TLC) is a simple and inexpensive adsorption chromatography technique used to determine the quality of a synthesized compound or to determine the extent of progress of a chemical reaction. TLC plates are coated with a solid stationary phase, usually silica or alumina, to which the different chemical components of a mixture adsorb to different extents. The plates are placed in a solvent mixture, the mobile phase, to allow for the separation of the sample mixture.[3]

TLC can be made more efficient by changing the morphology and thickness of the silica on the plates, as evidenced by the use of different silica microstructures and thicknesses by Jim *et al*.[4] Their research investigated the separation behaviors of isotropic vertical posts, anisotropic chevron, and anisotropic blade-like films with thicknesses between 4.6 and 5.3 µm as stationary phase media for TLC. They found that the different microstructures performed similarly to the planar chromatography media and had the potential to expand the capabilities of TLC.

Silica can be made into fibers, changing the morphology into one that gives a greater surface area. Electrospinning is a process used to produce nanofibers that can be used for a number of synthetic and analytical processes. A charge is applied to a liquid droplet which acts against the surface tension of the liquid. As the charge increases, the solution elongates, forming a conical shape known as the Taylor cone. When the electrostatic force overcomes the surface tension a jet of the solution erupts from the Taylor cone. The discharged solution then undergoes a whipping process during which the solvent evaporates, leaving behind a charged fiber. The fibers form a non-woven mat on a grounded collecting plate.[5, 6]

TLC plates created using an electrospun polymer solution can make the separation more efficient by requiring shorter development times and smaller solvent amounts than TLC plates coated with standard silica stationary phase, as shown by Clark and Olesik.[7]

This research investigated the use of electrospun silica as a stationary phase to improve the efficiency of TLC plates.

Materials and Methods:

Silica, or silicon dioxide, was prepared through the hydrolysis of tetraethyl orthosilicate (TEOS) through a sol-gel reaction:

$$Si(OC_2H_5)_4 + 2\,H_2O \rightarrow SiO_2 + 4\,C_2H_5OH.$$

The silica was prepared following a procedure from Choi *et al*.[8] TEOS, ethanol, distilled water, and HCl

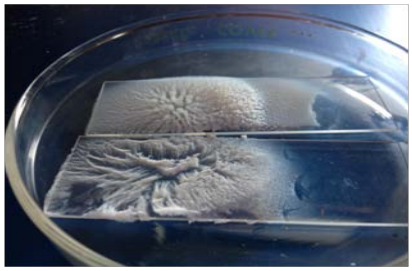

Figure 1. Silica nanofibers produced under the conditions of a 5 cm tip-to-collector distance, a 0.02 mL/hr flow rate, and an 11 kV voltage.

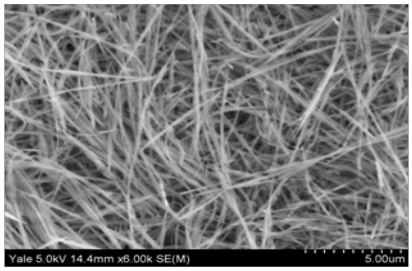

Figure 2. SEM image of non-woven mat of silica nanofibers.

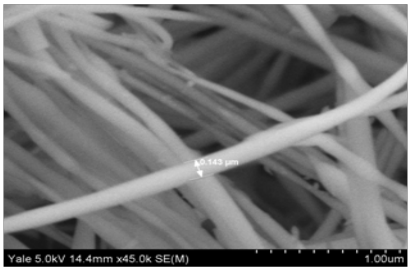

Figure3 SEM image of silica nanofiber with fiber diameter of 143nm.

were used in a molar ratio of 1:2:2:0.01 (TEOS:ethanol:water:HCl). The TEOS was mixed with the ethanol and then the water/HCl solution was added dropwise under vigorous stirring. The solution was heated at 30°C with stirring for 30 minutes and then cooled to room temperature.

Nanofibers were obtained through the electrospinning process using the synthesized silica. A high voltage supply provided electrostatic charge to create the fibers from the solution. The charged silica fibers were collected on a grounded collecting plate of aluminum foil, forming a non-woven fabric of fibers. Different conditions were used in order to optimize the electrospinning: voltages between 5 and 20 kV, tip-to-collector distances of 5 and 10 cm, and flow rates between 0.01 and 0.5 mL/hr.

The fibers were collected on glass slides and silicon wafers. The coated glass slides were used as the TLC plates while the silicon wafers were used for SEM analysis.

The ability of the fibers to act as a stationary phase for TLC was tested. A dye mixture of methylene blue, rhodamine B, and fluorescein was run on the electrospun silica glass slides with a mobile phase of 3:2:1 volume ratio acetone: n-propanol: water. The same dye mixture was run on commercial TLC plates for comparison. The R_f values were calculated for both the electrospun plates and the commercial plates to analyze and compare the different separation media.

Results and Discussion:

Silica was prepared through the sol-gel process from TEOS and was successfully electrospun into fibers under the conditions of a 5 cm tip-to-collector distance, a 0.02 mL/hr flow rate, and an 11 kV voltage. Figure 1 shows the obtained fibers which formed a non-uniform, raised mat on the glass slides. Figure 2 shows the nanofibers viewed under a Hitachi SU-70 SEM. The SEM image shows the non-woven mat of the silica fibers. Figure 3 shows a close-up of one of the fibers from the mat with a fiber diameter of 143 nm. This image characterizes the fibers as being in the nano range. While fibers were obtained a number of times, the necessary conditions and physical appearance of the fibers were different for each set of fibers. Different conditions for the electrospinning process were studied in order to find an optimal set that consistently produced silica fiber mats.

Varying humidity in the lab made this difficult as the synthesis and the electrospinning of the silica were affected by the different humidity levels from day to day. Moisture in the air contributed to a quicker and more thorough hydrolysis of the TEOS resulting in a thicker solution. Thus, depending on the humidity level, the different silica solutions spun at different points in their aging process. The humidity also affected the electrospinning of the silica. In order to obtain fibers the solvent, ethanol, had to evaporate during the whipping process.

Increased humidity slowed this evaporation and decreased the formation of fibers. The electrospinning process was conducted on the silica solution on various days to find the point in the aging process of the solution in which the silica would spin. Success in the electrospinning of the silica usually occurred after the solution was allowed to age for a number of days. This aging time allowed for additional hydrolysis of the TEOS, forming a thicker solution of silica.

The electrospun TLC plates were studied using the dye mixture, and the plates supported some separation of the dyes. The methylene blue and rhodamine B dyes were separated and apparent on the electrospun plates. The fluorescein, however, was never visible on the plates which could be due to the nearly translucent background in combination with the light yellow color of the dye. The dye mixture was also run on a commercial plate in order to compare the separation between plates. Figure 4 shows the commercial and electrospun plates while Table 1 gives the R_f values for the plates shown.

		Commercial Plate	Electrospun Plate
Solvent front distance		2.00 cm	2.00 cm
Time of separation		3 min	10 min
R_f values	Methylene Blue	0.15	0.38
	Rhodamine B	0.550	0.550
	Fluorescein	0.975	-------

Table 1. TLC data for dye mixture on commercial plate and electrospun plate.

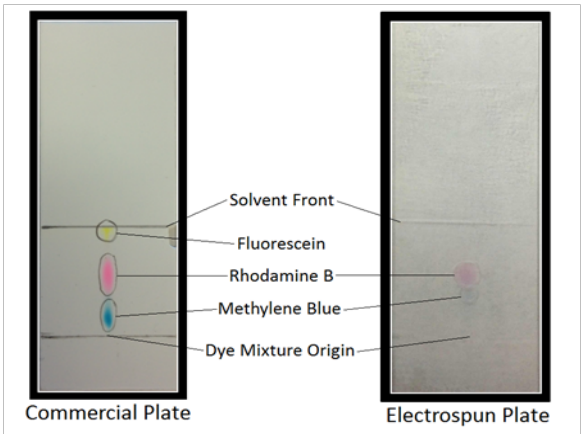

Figure 4. TLC with dye mixture on commercial plate and electrospun plate

The solvent front traveled the same distance on each of the two plates but the separations required different amounts of time. The separation on the electrospun plate was most likely slower because of the non-uniformity of the plate, whereas the commercial plate was made up of a coating of homogeneous silica powder. The electrospun plates also had inconsistent thicknesses of silica with the centers of the plates having a thicker layer than the edges, resulting in the slow and incomplete separations.

Conclusion:

Silica was synthesized through the sol-gel process of hydrolysis and condensation of TEOS. Silica nanofibers were then electrospun and used as the stationary phase for thin layer chromatography. The separations of the dye mixture on the electrospun plates showed promise and under further investigation might give more consistent results.

Inconsistent results suggest the variables of temperature and humidity had an effect on the synthesis of the silica and the electrospinning process.

Continued research on finding the optimal conditions of electrospinning will be investigated in order to consistently produce electrospun plates. Once this is achieved, additional dye mixtures will be run on the electrospun plates to see if they support separation.

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Biography:

Abigail Freyer is currently a senior at the University of New Haven majoring in Chemistry and Forensic Science. She hopes to attend medical school in the pursuit of becoming a surgeon. This was Abby's first experience with scientific research, and she appreciates the lessons she learned both in and out of the laboratory.

In her spare time, Abby manages the UNH NCAA softball team and actively participates in a number of clubs and organizations on and off campus.