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Separations on Water-Ice

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Final Report, July, 1998

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FINAL REPORT

A. Normal Phase Columnar Chromatography

We have successfully performed normal phase chromatography on a stationary phase of water-ice. Presently, these experiments use a classical columnar gravity flow chromatography format. Using mobile phases of ethylacetate and hexane isooratically or in a gradient program, we have separated a number of synthetic and naturally occurring samples on a ice column maintained at -15 to -20°C. Video images of the separation of samples such as spinach extract, grape juice, mixtures of synthetic dyes etc., have been recorded. This type of separation requires microparticulate ice, not a solid column. A column of water frozen into ice has little or no permeability. Of the approaches that have been attempted thus far to make microparticulate ice, the most successful has been to grind "crushed ice" (as typically produced by a machine) with "dry ice" (as in solid CO₂) to form a slurry in the packing solvent (e.g. ethyl acetate) and gravity pack a 2.5 cm i.d., coolant-jacketed column. The separations we have achieved exhibit efficiencies typical of traditional columnar chromatography. Even as such, the pedagogic value of this is enormous. The copy of a relevant publication is attached as Appendix I. Other methods of slurry packing for a higher efficiency column have been developed.

B. Electrophoresis in a Planar Format

Work has been also conducted on electrophoretic separations on ice. Thus far, we have concentrated on planar, slab type separations. Techniques have been devised on the reproducible formation of an ice sheet, doped with desired substances or in virgin form, on a thermoelectrically cooled glass sheet. Devising a reproducible and uniform ice surface and maintaining reproducible electrode contact with such a surface is a nontrivial

task that we have succeeded in perfecting. There are several aspects to conducting electrophoresis on ice that are nonintuitive. Because of the high resistivity of the matrix, very high field strengths (several kV/cm) can be attained without dielectric breakdown. Indeed, the limiting factor appears to be the glass substrate on which we presently form our ice. These field strengths are so high that were it not for the fact that the absolute humidity on the top of the ice is quite low (we operate at surface temperatures of $\leq -10^{\circ}\text{C}$), dielectric breakdown of the surrounding air would have occurred. In addition, there appears to be a minimum threshold of applied field strength (around 1 kV/cm) below which no migration of species are observed. Above this field strength, however, things are readily and rapidly separated. Off the shelf detection methods are not readily applicable in such a system. We have therefore limited our experiments to dyes with visible absorption or compounds that are readily fluorescent under UV illumination,. We have observed very rapid separation (<1 min.) of constituents in samples such as black water soluble ink with confirmation of separation obtained by fraction collection. Current-voltage relationships of doped ice are not straightforward. The accompanying i-V plots for LiF (which is incorporated into the ice lattice) shows that 93 mM LiF-ice is substantially less conductive than 11 mM LiF-ice. Doped ice shows different separation abilities and apparently sharper separated zones.

C. Zone Melting type separations on a solid column of Ice.

In this mode, a high pressure pump pumps an aqueous solution on to a solid ice column up until a certain pressure (ca. 1000-2000 psi) is reached. The pressure causes the ice to melt at the top of the bed and the accompanying volume change reduces the pressure. The process is repeated, resulting in migration of liquid water through the ice column. We have observed large differences in retention time of ionic and nonionic solutes but mixtures do not separate - they appear at an intermediate retention time. Attempts are being made to better understand this phenomenon.

Other tasks accomplished

- (a) Microparticulate ice of smaller particle size have been made for higher efficiency separations. An water - organic solvent (m.p. below -20°C) was emulsified by high energy ultrasonication. The emulsion was frozen to make spherical microparticulate ice slurry that can be readily packed. One type of separation where efficiency increases with decreasing temperature is chiral separations involving cyclodextrins. Attempts have been made to dope the emulsion with β -cyclodextrin and attempt separation of commercially important chiral drugs such as Inderal.
- (b) A video microscopy CCD imaging system, was perfected to image the planar ice surface in a reflectance mode to quantitate separations being obtained.
- (c) Electrophoretic separations on doped planar ice surfaces were carried out to characterize separation efficiency quantitatively.
- (d) Short capillary column electrophoretic separations were examined, using transparent capillaries of short length (≤ 10 cm), initially investigating separation of analytes that can be measured by reflectance spectroscopy. The results were not promising, more detector development is needed.

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