NOTE

Density Gradient Columns Made of Water and Sodium Bromide Solutions with Isopropyl Alcohol as a Wetting Agent

INTRODUCTION

The purposes of this experimental note are to describe density gradient columns using sodium bromide with water and isopropyl alcohol and their utility in polymer science.

Density gradient columns made with organic solvents are used extensively in research and manufacture for the characterization of polymers.[1,2] The use of aqueous solutions of inorganic salts in density gradient columns has been described,[3,4] but there is a paucity of information on how to make these columns. This note describes the preparation of density gradient columns using aqueous solutions of sodium bromide and isopropyl alcohol. The latter has been added as a wetting agent for the organic polymers. These columns have found use in our laboratory for the characterization of polymers, such as polystyrenes, polystyrene blends, and polystyrene copolymers, that are dissolved, swelled, or degraded in organic solvent-based density columns.

EXPERIMENTAL

Column Preparation

Density gradient columns of 4800 mL volumes each, for the ranges $\rho = 1.12$ to 1.45 g/cc and $\rho = 0.94$ to 1.30 g/cc, have been prepared using water solutions of granular sodium bromide with isopropyl alcohol (IPA). IPA is preferred over ethanol as a wetting agent because IPA has lower volatility than ethanol. For each column, two separate, thoroughly mixed, solutions (high and low density, respectively) were combined by gravity feed in a modification of an earlier method.[1] Low-density solutions, prepared from IPA and distilled water, have density values of 0.83 to 0.89 g/cc, and high-density solutions, prepared from water, IPA, and NaBr, have density values of 1.32 to 1.49 g/cc.

The density gradient column of range 1.12 to 1.45 g/cc was prepared by combining a thoroughly mixed low-density solution of 1300 mL distilled water and 2200 mL IPA ($\rho = 0.89$ g/cc), contained in a 4000 mL one-nipple bottle, with a thoroughly mixed high-density solution of 1350 mL water, 100 mL IPA, and 1250 grams NaBr ($\rho = 1.49$ g/cc), contained in a two-nipple bottle.[5] Amber latex tubing[6] was used to connect the bottles.

The density gradient column of range 0.94 to 1.30 g/cc was prepared by combining a thoroughly mixed low-density solution of 530 mL water and 3250 mL IPA ($\rho = 0.83$ g/cc) with a thoroughly mixed high-density solution of 2100 mL water, 100 mL IPA, and 600 grams NaBr ($\rho = 1.32$ g/cc).

The 122 cm long, 4800 mL volume, columns[7] were filled by the gravity-feed method. Some density gradient columns are prepared with the most dense gradients at the top of the tube.[1] In our laboratory, the most dense gradients are at the bottoms of the tubes. Therefore, during preparations of our columns, the least dense solutions are fed continuously from the one-nipple bottle into and stirred with the most dense solutions contained in the two-nipple bottle before the mixture flows into the glass columns. The two-nipple bottle rests on a magnetic stirrer, and the rotation rate of the stirring bar is adjusted to produce a vortex of about 3 cm with no air bubbles. The columns are filled at a rate of approximately 20 mL/min. The solution from the two-nipple bottle is transferred to the glass column through amber latex tubing. Bubbles must be removed from the latex tubing before filling the column. The latex transfer tubing ends at the top of the 4800 mL column. The glass tube of an eye dropper is inserted into the end of the latex tubing to obtain a stream of liquid that is allowed to gently flow down the side of the vertically mounted column.

Calibrated glass floats of precisely known densities are introduced into the liquid and reside at heights in the column where their densities match that of the solution. Calibrated floats can be purchased[8] or made in the laboratory.[9,10] A series of floats of differing densities serve to calibrate a column. Floats can be gently placed into the liquid at the top of a finished column or placed in the basket at the bottom of the column prior to filling (*vide infra*). Columns are covered to minimize evaporation and prevent contamination.[11]

Maintenance and Use of Columns

The stability and longevity of density gradient columns is inversely related to the rate of diffusion of the miscible

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liquids. Disturbances, such as temperature fluctuations, vibrations, and shaking, will accelerate the diffusion process and shorten the lifetimes and usefulness of columns. Typically, density gradient columns are contained in water jackets maintained within 0.1°C of a specified temperature (e.g., 23°C) by a circulation pump and cooling system. We house our density gradient columns in an air jacket; the whole assembly is contained in a specially conditioned room maintained at 23°C and 50% relative humidity. We have observed that, if temperature changes are slow, density gradient columns can tolerate temperature variations of a few degrees and retain density gradients.

The introduction of specimens into a column can cause mixing. Massive samples, such as polymer resin pellets, should be gently placed into the column liquid with forceps, rather than dropped into the liquid. Film and sheet samples should be cut into distinguishing shapes and sizes so that they can be easily identified. Shapes that can be used include: squares, circles, rectangles, triangles, diamonds, bow ties, and those same shapes with circular holes cut into them. Core borers #2, 3, or 4, can be used. A specimen size of about 1 cm long is large enough to be seen in the column liquid, yet small enough so that its center of gravity can be estimated to within 1 mm. It is imperative that samples not be touched with fingers because body oils on samples may affect density readings. A flat sample can be introduced into a column liquid with a long piece of wire that has a loop at one end. For the columns described in this NOTE, all samples should be prewetted with a water/IPA mixture; the surface tension of this solution will hold a film sample on the looped wire so that samples can be gently placed into the column liquid. It takes 2 to 4 h for a sample to reach an equilibrium position in a density gradient column.

Large numbers of test specimens can clog a density gradient column. Specimens can be removed, without disturbing the density gradient, by slowly pulling a basket through the liquid. In our laboratory, baskets, stored at the bottoms of columns, are tied to lines made of polyester.[12] The lines, which are always present, run the lengths of the columns, but only rarely interfere with density determinations by catching samples. Polyester, which is not wetted by water, is superior to cotton string or nylon lines, both of which allow salt solutions to wick out of the columns. Baskets were made in our machine shop of bronze tubing, wire, and foil. Thin, flexible, bronze foils were used to make "fingers" along the periphery of the basket in order to contact the inside of the glass tube and sweep all samples when cleaning the columns. Baskets are raised and lowered at a rate of about 0.5 cm/min. The rate can be controlled by connecting the polyester lines to a low-speed synchronous electric motor mounted on the steel table on which the columns are set.

DISCUSSION

The density of a solid can be used as a means of identification, as an indication of uniformity among samples, to determine the yield in the polymer extrusion process, and for following physical and chemical changes in a sample. Although the gradient method is both simple and elegant, it has not been fully utilized by some polymer scientists. The method can be used for materials in almost any form (e.g., sheet, fiber, film, powder, pellet, granules, etc.) and with samples too small for use with instruments based on liquid displacement (e.g., pycnometers).[13]

The principle of the method of density gradient columns was first noted by Galileo in 1612[14] and rediscovered by Linderstrøm–Lang[15–17] in 1937–1938. The growth of polymer research and the plastics industry, commencing in the 1940s, spurred the development of density gradient methods for characterizing of materials.[18] Although techniques may vary, preparation of columns involves, simply, the mixing of two miscible liquids that have density ranges in excess of the density range of investigation, in long cylindrical glass tubes. The densities of the liquids vary linearly from the top to bottom of the tube. A calibration curve of float density vs. float height in the column is drawn, and this curve is used to determine the densities of samples.[19] In our laboratory, metric tape measures are adhesively mounted to the outsides of the glass columns. The center of gravity of a float determines its height in the column for calibration purposes. New calibration curves must be obtained as columns age and after specimens have been "swept" from columns with the baskets.

The utility of density gradient columns for materials' characterization led to developments in the preparation of them: gravity fill[20–22] and mechanical pumping[23,24] methods are described in the literature. In addition, temperature gradient[10,25] techniques find use for certain applications. Density gradient columns, because of the ease and speed of the method, have largely supplanted the use of pycnometer methods[13,26,27] for determining polymer densities. Sodium bromide is the inorganic salt of choice because it has excellent water solubility, is economical, and its solutions have high densities.[28]

CONCLUSION

The characterization of polymers that are dissolved, swelled, or degraded by organic solvents can be done with water-based density gradient columns of sodium bromide, with isopropyl alcohol added as a wetting agent. Also, density gradient columns based on aqueous solutions of inorganic salts are more environmentally friendly than those made with silicone oils[27] or organic solvents.[1] With moderate use, water/NaBr/IPA columns can be expected to be stable for 1 year.

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