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Note

Pluronics as liquid phases for capillary gas–liquid chromatography

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A large number of liquid phases have been recommended and, in the interests of communication between laboratories and the reproduction of published work by other workers, it is desirable to limit them to a reasonable number of widely used phases. Furthermore, products with low purity and ill-defined molecular structures should be eliminated.

The introduction of new phases is justified in only two instances: either the new material, owing to its particular molecular structure, is able to fill a gap between existing phases, or it is able to replace an existing phase because of superior characteristics. The Pluronic materials (Fluka, Buchs, Switzerland) belong to the second category. They have occasionally been used as liquid phases in the early years of gas–liquid chromatography (GLC)[1,2], but did not become popular. The introduction of glass capillary columns has led to a further evaluation of known liquid phases and a search for superior products. In our work we re-examined the Pluronics and as a result they have now replaced certain well known phases that we had used for many years.

PLURONIC MATERIALS

Emkalyx-Pluronics (Pluronics) are widely used as detergents. Compared with similar chemicals they are exceptionally pure and structurally well defined. According to information from the original producer, Wyandotte Chemical Corp., Pluronics are made by condensing propylene oxide with propylene glycol. The resulting chain is then extended on both sides by the addition of controlled amounts of ethylene oxide, yielding polar endgroups on a hydrophobic central chain.

The different types available vary in two respects: the length of the polypropylene glycol chain, and the amount of polyethylene glycol added. The molecular weight varies between 1000 and 14,000.

The polarity of the materials increases with increasing percentage of polyethylene glycol. The viscosity increases with molecular weight and the percentage of polyethylene glycol (the materials are generally solids at room temperature if the polyethylene glycol content exceeds 50% of the polymer).

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Polarity range

The polarity of a Pluronic containing 90% of polypropylene glycol is similar to that of Ucon LB 550, whereas that of a Pluronic containing 80% of polyethylene glycol is similar to that of Carbowaxes.

Pluronic L 61

Pluronic L 61 (Pl. 61) contains 90% of polypropylene glycol and has an average molecular weight of 2000. It has chromatographic characteristics almost identical with those of Ucon LB but has several advantages. On a glass surface covered with barium carbonate[3] it shows less bleeding. Its upper temperature limit is about 30° higher; there were no signs of deterioration (higher bleeding, increased adsorption and reduced retention) after heating at 200° for several days. Hence barium carbonate pre-treated columns with Pl. 61 can be used up to a maximum temperature of 220° in programmed runs.

In addition, Pl. 61 also possesses the outstanding low-temperature characteristics of Ucon LB. Its low viscosity at 25° (Brookfield viscosity 285 cP) and its freezing point of −29° lead to a high column efficiency at sub-ambient temperatures with a relatively high retention for a given film thickness.

Pluronic L 64

Pl. 64, a liquid containing 40% of polyethylene glycol and with a molecular weight of *ca.* 2900 has similar chromatographic properties to Ucon HB 5100 and Emulphor ON 870. The reasons for replacing these two phases with Pl. 64 are the same as those mentioned above. The bleeding is very low (again on catalytically inactive surfaces such as barium carbonate), probably owing to its high purity. The upper temperature limit is increased: on neutral or basic supports such as barium carbonate the columns withstand temperatures of 240–250° for several days (depending on the film thickness). On very acidic supports (columns that give no peak for 2,6-dimethylaniline) this limit is decreased (as for all polyglycols) to about 220°, but for short time periods the temperature limit is again about 240°.

The maximum film thickness that is stable on barium carbonate columns is about 0.8 μm; thicker films occasionally form droplets.

Pluronic F 68

Pl. 68 is a solid containing 80% of polyethylene glycol and a molecular weight of 8350. The melting point is 52°. The polarity of Pl. 68 lies between that of Ucon HB or Emulphor and that of Carbowax 20,000, and is closest to that of Ucon H 90,000.

The lower temperature limit is near the melting point of the phase; Pl. 68 behaves very reasonably above 60°. The upper temperature limit was found to be between 250° and 260° for long-term use (barium carbonate surface). This limit is probably due to degradation of the phase. Therefore, it is of no use coating columns with materials of higher molecular weight, with higher low-temperature limits, higher viscosity and no increased thermal stability.

COATING PROCEDURE

As described elsewhere[3] we use columns (Pyrex or soft glass) pre-treated with

concentrated barium hydroxide solution. Deactivation, although not essential, gives some improvement regarding adsorption of polar materials, mainly for Pl. 61 and less for Pl. 64 and 68. We apply a 0.1% solution of Carbowax 1.000 and heat the column after drying it at 280° for 10 min.

The Pluronics can be coated dynamically using methylene chloride solutions of the phases of concentration between 10 and 50% (depending on the film thickness desired), followed by a plug of mercury. For unknown reasons, the mercury plug behind Pl. 64 solutions on neutral or acidic surfaces may cause problems as it acquires a black tail, which is deposited in the column after some time. In this instance we prefer dynamic coating without mercury, using about 50% less concentrated solutions.

A film of 0.1 μm of Pl. 64 is obtained by using about a 15% solution with a mercury plug; 40% solutions without mercury yield films of Pl. 64 of thickness about 0.65 μm. Dynamic coating using Pl. 64 without solvent with mercury at 120–160° yields films more than 1 μm thick, which are too thick to be stable. Columns with the coatings described should show practically no tailing for 1-octanol (depending on the film thickness and deactivation used). On all glycol phases, especially with the polarity of Pl. 61, aldehyde peaks are very sensitive to acid–base effects; on neutral or basic columns they tail or disappear completely. The separation efficiencies are the same as for all columns of similar type. Columns of length 20 m and I.D. 0.3 mm should attain a separation number (TZ, according to Kaiser) of 30–35 when measured with the C_{13} and C_{14} *n*-alkanes.

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