Journal of Chromatography, 324 (1985) 415–421
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 659

Note

Influence of phase loading on the performance of whisker-walled open tubular columns coated with organic molten salts

SUBHASH C. DHANESAR*, MYRA E. CODDENS and COLIN F. POOLE*
Department of Chemistry, Wayne State University, Detroit, MI 48202 (U.S.A.)
(Received February 18th, 1985)

The presence of strong coulombic forces in liquid salts with their concomitant ability to enhance chromatographic selectivity through the unusual strength of solute orientation and complexation interactions has provided the impetus for their study in gas chromatography (GC). The practical use of inorganic molten salts is limited by the low solubility of organic solutes in inorganic melts, the limited number of low temperature melts with low chemical reactivity, and the excessive retention of most polar solutes frequently accompanied by poor peak shape[1,2]. Fortunately, these properties are not generally found among organic molten salts which offer a greater variety of low melting salts and more favorable solubility characteristics for organic solutes. The chromatographic properties of ethylammonium nitrate[3], ethylpyridinium bromide[4,5], tri-*n*-butylbenzylphosphonium chloride[5], tetra-*n*-heptylammonium chloride[5], tetra-*n*-hexylammonium benzoate[5], 1-methyl-3-ethylimidazolium chloride[5] and tetra-*n*-butylammonium tetrafluoroborate[5] have been evaluated as packed column stationary phases. A single report describes the preparation of whisker-walled open tubular columns coated with the organic molten salt tetra-*n*-butylammonium tetrafluoroborate[6]. The purpose of this paper is to define more clearly the influence of phase loading and temperature on the chromatographic performance of whisker-walled open tubular columns coated with several different organic molten salts.

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were analytical or chromatographic grade in the highest purity available. Tetra-*n*-butylammonium tetrafluoroborate was obtained from Aldrich (Milwaukee, WI, U.S.A.) and 1-ethylpyridinium bromide and tetra-*n*-heptylammonium chloride from Eastman Kodak (Rochester, NY, U.S.A.). Tri-*n*-butylbenzylphosphonium chloride was synthesized as described previously[5]. Extra-fast setting epoxy glue (cat. No. K-8778-00) was obtained from Cole Parmer (Chicago, IL, U.S.A.). Soda-lime glass (Kimble 46485) capillary columns of various lengths and 0.25 mm I.D. were drawn from glass blanks, 6.5 mm O.D. and 2.0 mm I.D., with a Shimadzu GDM-1B glass drawing machine (Shimadzu, Columbia, MD, U.S.A.). A Varian 3700 gas chromatograph with capillary column

---

* Present address: Department of Chemistry, Pace University, Pleasantville, NY 10570, U.S.A.

0021-9673/85/$03.30

inlet splitter and flame ionization detector was used for column evaluation. Hydrogen was used as carrier gas, the split ratio was 30:1, and the injector and detector temperatures were 250°C. Other experimental conditions are given in the figure legends.

For column preparation, each soda-lime capillary column was filled with a solution of ammonium bifluoride (5%, w/v) in methanol and allowed to stand for 1 h. The columns were then emptied by nitrogen pressure at a velocity of *ca.* 2 cm/sec. Residual solvent was removed with nitrogen flow-rate of 8 ml/min overnight. Each column was sealed at both ends with a microtorch and placed in a temperature programmable oven. The oven temperature was raised from room temperature to 350°C at 10°C/min and held at the higher temperature for 3 h. The columns were then cooled to room temperature, the ends broken off, and the column flushed with 10 to 20 column volumes of methanol at *ca.* 2 cm/sec. Each column was then dried overnight with a nitrogen flow-rate of 8 ml/min. Surface roughening was completed by re-etching each column a second time following the sequence of operations just described.

Each etched column was filled by nitrogen pressure with a solution of the organic salt (4–30 mg/ml) in dichloromethane. Each column was allowed to stand for several hours to allow trapped gas to dissolve in the coating solution. By attaching a syringe to one end of the capillary and immersing the other into a smaller beaker of deionized water, a short (*ca.* 5 cm) water plug was sucked into the column. To seal the column end, epoxy glue was applied to the column with an applicator while using slight syringe suction to pull a small plug of epoxy glue into the column. The sealant requires about 5 min to harden. After which each column was immersed in a water bath and its unsealed end connected to a vacuum pump (*ca.* 0.2 Torr). Evacuation requires from one to two days depending on the column length.

After coating, the first few coils of each column at either end were discarded. Each column was conditioned by temperature programming to the maximum allowable operating temperature for the salt (see Table I) at 5°C/min with a hydrogen carrier gas flow-rate of 1.0 ml/min. After about 10 min at the maximum allowable operating temperature the columns were ready for use.

TABLE I

COLUMN OPERATING TEMPERATURES FOR ORGANIC MOLTEN SALTS

Salt	*Melting point (°C)*	*Maximum column operating temperature (°C)*	
		Packed	*Capillary*
Tetra-*n*-heptylammonium chloride	−9	130	115
Ethylpyridinium bromide	110	160	150
Tri-*n*-butylbenzylphosphonium chloride	163	240	225
Tetra-*n*-butylammonium tetrafluoroborate	162	290	240

RESULTS AND DISCUSSION

None of the salts studied here produced stable columns when coated on lightly-etched glass surfaces. Success was achieved only when highly roughened whisker surfaces were used. Soda-lime, rather than borosilicate glass, was used in these studies as it enables whisker columns to be prepared at lower temperatures using a standard GC oven. The etching of borosilicate glass requires a temperature programmable oven with an upper temperature limit of at least 450°C[7,8]. Soda-lime glass is etched by hydrogen fluoride (generated by the pyrolysis of ammonium bifluoride) at a faster rate and lower temperature than borosilicate glass. A single etch of soda-lime glass at 350°C results in a sparsely whiskered surface unsuitable for coating with organic molten salts. At temperatures between 350–400°C the whiskers collapse and, therefore, to obtain a dense covering of whiskers each column was etched twice at 350°C.

The efficiency of whisker-walled open tubular columns coated with tetra-*n*-butylammonium tetrafluoroborate was found to vary with the phase loading and the column temperature used for evaluation, Fig. 1. A maximum in the column efficiency was observed at a phase loading of about 15 mg/ml. At any phase loading the column efficiency declined with increasing temperature. At any particular column temperature the highest efficiency was obtained with the 15 mg/ml phase loading. Similar results were observed for tri-*n*-butylbenzylphosphonium chloride.

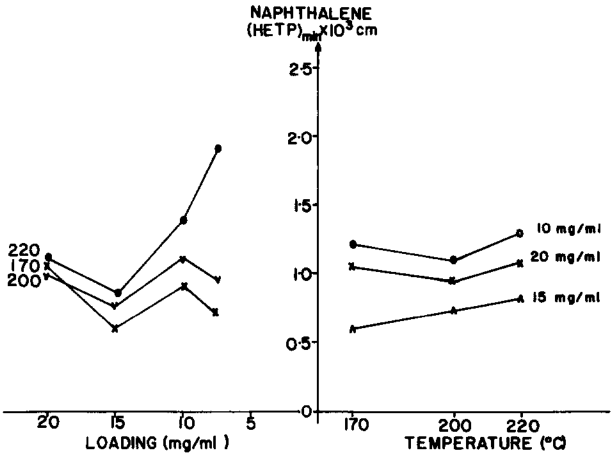


Fig. 1. The influence of phase loading of tetra-*n*-butylammonium tetrafluoroborate and temperature on column efficiency.

The coating efficiency and column efficiency as a function of phase loading for ethylpyridinium bromide and tetra-*n*-heptylammonium chloride are shown in Fig. 2. For both salts a maximum in column performance was observed at a phase loading of about 24 mg/ml.

The net retention volume of a series of test solutes as a function of phase loading for tetra-*n*-heptylammonium chloride is shown in Fig. 3. From packed column studies it is known that the retention of 2,5-dimethylphenol, 2,5-dimethylaniline and 1-octanol occurs by an adsorption mechanism while naphthalene is retained by a mixed adsorption/partition mechanism[9]. Most noticeable in Fig. 3 is that the retention volumes of the probes retained by adsorption are independent of the phase loading at levels exceeding about 20 mg/ml.

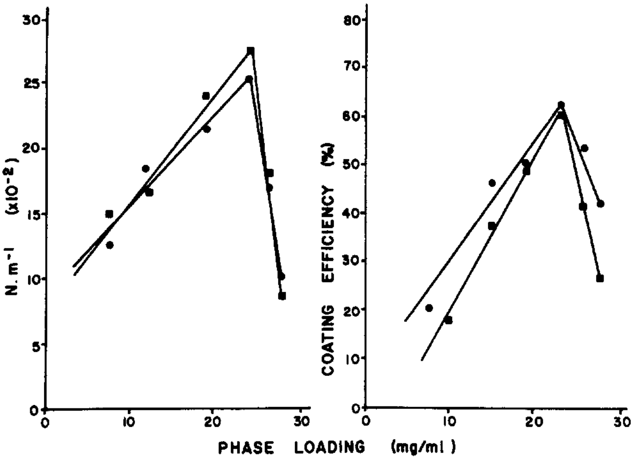


Fig. 2. The effect of phase loading on column performance (number of effective plates per meter) and coating efficiency. ■, Tetraheptylammonium chloride; ●, ethylpyridinium bromide.

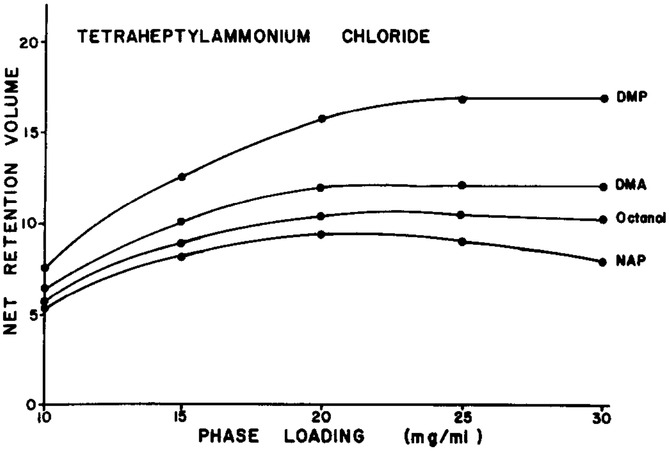
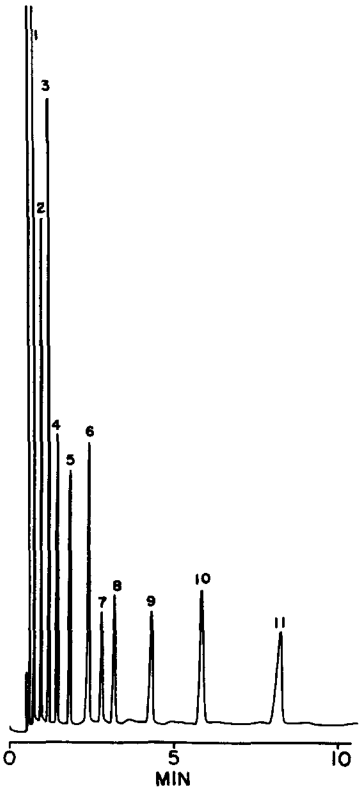


Fig. 3. The influence of phase loading on retention for 2,5-dimethylphenol (DMP), 2,5-dimethylaniline (DMA), octanol and naphthalene (NAP).

The above experimental observations can be rationalized if it is assumed that a minimum phase loading is required to form a homogeneous film. The highest column performance will be attained when the stationary phase is distributed as a thin, homogeneous film on the whisker surface. For the solid salts, the stationary phase is deposited as a layer which must melt to a continuous film when the column temperature is raised above the melting point of the salt.

The requirement of a minimum phase loading for film building is supported by the retention data in Fig. 3. If adsorption of the test solutes occurs essentially at the gas–liquid phase interface then retention should be independent of the phase loading once a homogeneous film is formed.

The maximum allowable operating temperature of the organic molten salts is lower on whisker surfaces than found for packed columns (Table I). In all cases the upper temperature limit for whisker columns is established by phase transport and not by volatility. At phase loadings in excess of the optimum value transport of some of the phase from the column occurs at the column conditioning temperature. This can be observed by hanging a vial below the free end of the column during column conditioning. It can also be seen from Figs. 2 and 3 that at higher phase loadings than the optimum value a heavily-loaded column will not naturally adjust itself to the optimum phase loading on conditioning but will rather revert to some value less than the optimum loading. A comparison of the retention of naphthalene with that of the adsorbed probes in Fig. 3 confirms this. As naphthalene is retained by a mixed adsorption/partition mechanism its retention as a function of phase loading depends partly on the liquid phase volume while those probes retained entirely by adsorption are affected only by changes in the surface area of the liquid phase. At high phase



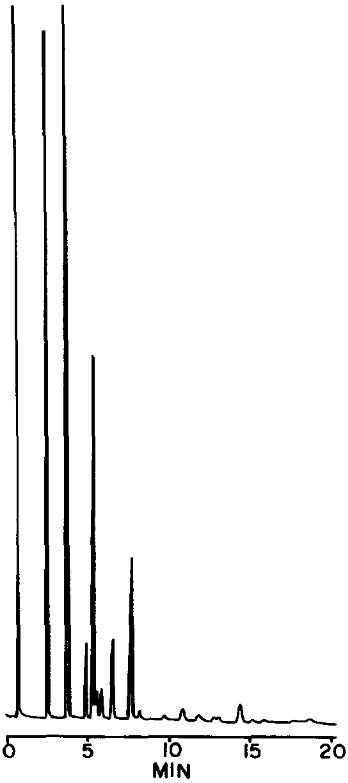
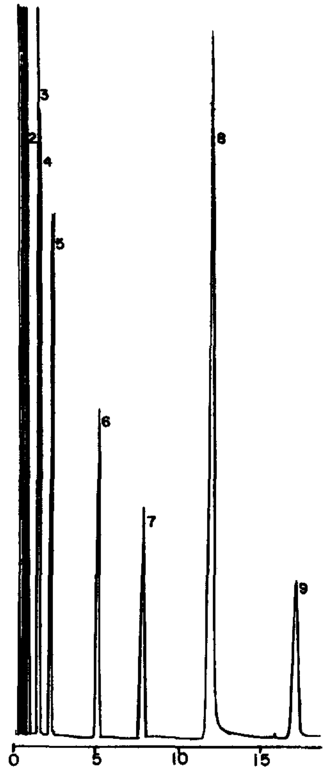


Fig. 4. Separation of a polarity test mixture on a 7.5 m × 0.25 mm I.D. whisker-walled capillary column coated with tri-*n*-butylbenzylphosphonium chloride at a phase loading of 15 mg/ml. The column temperature was 165°C and the hydrogen carrier gas flow-rate 1.5 ml/min. Peak identification: 1 = nonanone; 2 = hexadecane; 3 = heptadecane; 4 = octadecane; 5 = nonadecane; 6 = eicosane; 7 = naphthalene; 8 = heneicosane; 9 = 2,6-dimethylaniline; 10 = tricosane; 11 = 2,6-dimethylphenol.

Fig. 5. Separation of Aroclor 1221 on the same column described in Fig. 4. The column temperature was 200°C.

loadings the retention of the adsorbed probes is fairly constant while that of naphthalene shows a decline.

The performance of all columns is influenced by column temperature. At temperatures closer to the upper temperature limit it is lower than at temperatures just above the melting point. This effect is most noticeable for tetra-*n*-butylammonium tetrafluoroborate. We surmise that this is probably related to changes in the viscosity of the molten salts. According to Lind *et al.*[10], the viscosity of tetra-*n*-butylammonium tetrafluoroborate as a function of temperature changes in an exponential-like manner from a value of 8.3 cP at 170°C to 2.7 cP at 240°C. At elevated temperatures, therefore, the efficiency of tetra-*n*-butylammonium tetrafluoroborate columns is controlled by the ability of the film to resist motion leading to increasing film inhomogeneity. Viscosity data for the other organic molten salts is not available but similar influencing factors are probably operating.



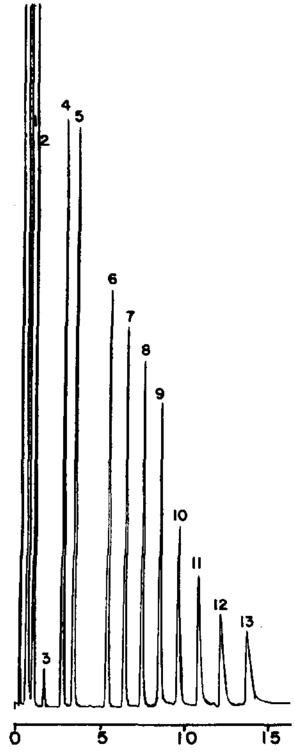


Fig. 6. Separation of a mixture of substituted benzene derivatives on a 10.5 m × 0.25 mm I.D.- whisker-walled capillary column coated with ethylpyridinium bromide at a phase loading of 24 mg/ml. The column temperature was 80°C and the hydrogen carrier gas flow-rate 1.3 ml/min. Peak identification: 1 = benzene; 2 = toluene; 3 = *p*-xylene; 4 = chlorobenzene; 5 = bromobenzene; 6 = benzaldehyde; 7 = *o*-dichlorobenzene; 8 = iodobenzene; 9 = nitrobenzene.

Fig. 7. Separation of a homologous series of C_1–C_5 and C_7–C_{14} *n*-alcohols on a 9.3 m × 0.25 mm I.D. whisker-walled capillary column coated with ethylpyridinium bromide at a phase loading of 24 mg/ml. The column was held isothermally for 1.0 min at 60°C and then temperature programmed at 4°C/min to 120°C. The hydrogen carrier gas flow-rate was 1.7 ml/min.

Reasonably efficient (1500–2500 plates/m) long-lived open tubular columns can be readily prepared with organic molten salt phases on whisker surfaces. For these columns, an optimum phase loading exists corresponding to the minimum concentration of coating solution required to give a complete and homogeneous film upon melting. As heavier loaded films than the optimum value are unstable film thickness cannot be manipulated to control retention. At the optimum phase loading column performance is acceptable as demonstrated by the separation of a polarity test mixture, Fig. 4, and Aroclor 1221, Fig. 5, on columns coated with tri-*n*-butylbenzylphosphonium chloride. Some molten salts can be used as selective adsorbents at temperatures below their melting points as shown in Fig. 6 for the separation of a mixture of substituted benzenes and Fig. 7 for the separation of a homologous series of alcohols on ethylpyridinium bromide. Not all phases exhibit useful adsorbent properties, for example, tetra-*n*-butylammonium tetrafluoroborate shows virtually no retention of organic compounds at temperatures below its melting point.

ACKNOWLEDGEMENTS

This research was made possible by funds from Eli Lilly and Company.

REFERENCES

1 W. A. Hanneman, C. F. Spencer and J. F. Johnson, *Anal. Chem.*, 32 (1960) 1386.
2 H. J. K. Koser, H. H. Oelert and J. Stremmler, *J. Chromatogr.*, 285 (1984) 289
3 F. Pacholec, H. T. Butler and C. F. Poole, *Anal. Chem.*, 54 (1982) 1938.
4 F. Pacholec and C. F. Poole, *Chromatographia*, 17 (1983) 370.
5 C. F. Poole, H. T. Butler, M. E. Coddens, S. C. Dhanesar and F. Pacholec, *J. Chromatogr.*, 289 (1984) 299.
6 S. C. Dhanesar and C. F. Poole, *Anal. Chem.*, 56 (1984) 2509.
7 F. L. Onuska, M. E. Comba, T. Bistricki and R. J. Wilkinson, *J. Chromatogr.*, 142 (1977) 117.
8 C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984.
9 M. E. Coddens and C. F. Poole, unpublished data.
10 J. E. Lind, H. A. A. Abdel-Rehim and S. W. Rudich, *J. Phys. Chem.*, 70 (1966) 3610.