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EVALUATION OF TETRAALKYLAMMONIUM TETRAFLUOROBORATE SALTS AS HIGH-TEMPERATURE STATIONARY PHASES FOR PACKED AND OPEN-TUBULAR COLUMN GAS CHROMATOGRAPHY

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SUMMARY

Four tetraalkylammonium tetrafluoroborate salts were evaluated as high-temperature polar stationary phases for packed and open-tubular column gas chromatography. Tetrapropylammonium and tetraoctylammonium tetrafluoroborates were found to have too limited a temperature operating range to be generally useful. Tetrahexylammonium and tetrabutylammonium tetrafluoroborates had liquid ranges from 90 to 230 and 162 to 285°C, respectively, and were studied in more detail. Both phases showed strong, selective dipole interactions these being slightly stronger for the tetrabutylammonium salt than for the tetrahexylammonium salt. The tetrabutylammonium tetrafluoroborate salt also provided higher column efficiencies, by about a factor of two, when used in packed-column gas chromatography. Retention of a wide range of organic solutes was found to occur by gas-liquid partition on the tetrafluoroborate salts.

Five surface roughening techniques were evaluated for the preparation of efficient, long-lived, open-tubular columns. Whisker-modified surfaces, alone or coated with a layer of microcrystalline sodium chloride, provided columns of acceptable efficiency (2000-2500 plates per meter) and greater durability than other column types. Barium carbonate-modified surfaces provided columns of the highest efficiency but of poor durability. Columns modified with a layer of Chromosorb R6470-1 were the least efficient and of poor durability. Examples of the separation of complex mixtures on packed and open-tubular columns, coated with tetraalkylammonium tetrafluoroborates, are given to illustrate their practical utility.

INTRODUCTION

In several recent studies, the feasibility of using organic molten salts as polar stationary phases in packed-column gas chromatography has been demonstrated¹⁻⁴. Efficient separations and stable liquid ranges from 50 to about 150°C above the melting point of the salts were obtained. Retention of solutes on the organic salt

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phases is characterized by weak dispersion and unusually strong orientation and proton donor-acceptor interactions. At the moment, the separation of high-molecular-weight solutes is limited by a paucity of salts with high temperature tolerance. The only known exception is tetra-*n*-butylammonium tetrafluoroborate which has a useable liquid range from 162 to 290°C⁴. The temperature tolerance for this salt was established by its vapor pressure without any indication of thermal instability. Thus, it seemed probable that the temperature tolerance could be extended by synthesizing higher-molecular-weight homologues of the tetra-*n*-butylammonium tetrafluoroborate salts. A lack of suitable starting materials limited this study to the preparation of tetra-*n*-alkylammonium salts, containing identical alkyl substituent groups, e.g., tetra-*n*-butylammonium or tetra-*n*-hexylammonium.

The preparation of open-tubular columns, coated with organic molten salts is desirable because of the greater intrinsic efficiency that these columns can provide. However, for successful column preparation the deposited layer of organic salt must melt to form a continuous homogeneous film, resistant to bead formation as the column temperature is varied. This condition is not met by smooth glass surfaces, and an increase in surface activity by whisker formation^{5,6} or deposition of an intermediate layer of microcrystalline sodium chloride⁷ is necessary to obtain reasonably efficient, long-lived columns. In the case of the whisker-walled columns, it was shown that an optimum phase loading for maximum column performance existed and that higher or lower loadings than the optimum value gave columns of lower efficiency⁶. The temperature tolerance, 240°C for columns coated with tetra-*n*-butylammonium tetrafluoroborate, was established by film instability. In this paper alternative methods of film stabilization are evaluated in an attempt to improve column performance and temperature tolerance.

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents used were of general laboratory grade in the highest purity available. Tetra-*n*-propylammonium tetrafluoroborate and tetra-*n*-hexylammonium iodide were obtained from Fluka (Hauppauge, NY, U.S.A.), tetra-*n*-hexylammonium tetrafluoroborate from Aldrich (Milwaukee, WI, U.S.A.), and tetra-*n*-octylammonium iodide and tetrafluoroboric acid (45%) from Alfa Products (Danvers, MA, U.S.A.). Brij-35 was obtained from Fisher Scientific (Livonia, MI, U.S.A.) and Chromosorb R6470-1 and Chromosorb-W-AW (100-120 mesh) from Anspec (Ann Arbor, MI, U.S.A.). Glass capillary columns of various lengths and 0.25 mm I.D. were drawn from soda-lime blanks (Kimble 46485, 6.55 O.D. × 2.0 mm I.D.) using a GDM-IB capillary column glass-drawing machine (Shimadzu, Columbia, MD, U.S.A.).

*Preparation of tetra-*n*-hexylammonium and tetra-*n*-octylammonium tetrafluoroborates*

Silver hydroxide was prepared by adding 10 ml of an aqueous solution of sodium hydroxide (0.8 g) to silver nitrate (3.4 g) in water (10 ml)^{8,9}. The brown precipitate was filtered off, washed with ice-water, and dried for 1 h at 130°C. To a suspension of silver hydroxide (2.5 g) in methanol (20 ml) was added tetrahexylammonium iodide (9.4 g). The mixture was shaken vigorously, allowed to settle, and

TABLE I

NMR CHEMICAL SHIFTS FOR THE TETRA-*n*-ALKYLAMMONIUM TETRAFLUOROBORATE SALTS

Cation	^{13}C			^1H		
	C-N	CH ₂	CH ₃	CH ₂ -N	CH ₂	CH ₃
Tetra- <i>n</i> -propylammonium	60.0	15.1	10.3	3.2	1.7	1.0
Tetra- <i>n</i> -butylammonium	57.7	23.0 18.8	12.8	3.2	1.6 1.4	1.0
Tetra- <i>n</i> -hexylammonium	58.6	31.0 25.8 22.3 21.8	13.7	3.2	1.7 1.3	0.9
Tetra- <i>n</i> -octylammonium	58.6	31.6 28.9 26.2 22.5 21.8	14.0	3.2	1.7 1.35 1.27	0.9

centrifuged. The supernatant was removed and added to a slight excess of tetrafluoroboric acid (1.8 g). The solid tetra-*n*-hexylammonium tetrafluoroborate was filtered off and recrystallized to constant melting point from methanol-water. Melting point, 89.5–91.5°C (lit. 91°C¹⁰, 94°C¹¹); IR, ν (BF₄⁻) 1039 cm⁻¹, and NMR, see Table I. Tetra-*n*-octylammonium tetrafluoroborate was prepared in manner analogous to tetra-*n*-hexylammonium tetrafluoroborate, using 11.9 g of tetra-*n*-octylammonium iodide and 9.6 g of silver hydroxide. The tetra-*n*-octylammonium tetrafluoroborate was recrystallized to constant melting point, 122.5–123.5°C, from methanol-water. IR, ν (BF₄⁻) 1048 cm⁻¹, and NMR, see Table I.

Preparation of packed columns

Column packings, containing 3–15% (w/w) of tetraalkylammonium tetrafluoroborate salts on Chromosorb W-AW (100–120 mesh), were prepared using the rotary evaporator technique and methylene chloride as the slurry solvent. The air-dried packings were sieved before use and packed into glass columns, 1–3 m long and 2 mm I.D., with the aid of vacuum suction and gentle vibration. For column evaluation, a Varian 3700 gas chromatograph with heated on-column injector, temperature-programmable oven, and flame-ionization detector was used. Nitrogen was used as the carrier gas. Separation conditions are given in the legends to tables and figures.

Preparation of open tubular columns

Five methods were evaluated for the preparation of open tubular columns with tetra-*n*-butylammonium tetrafluoroborate as stationary phase.

(i) Whisker-walled columns. The experimental procedure has been described elsewhere^{5,6}. Briefly, the soda-lime columns were dynamically coated with a saturated solution of ammonium bifluoride in methanol, dried, sealed, and heated to 350°C for

3 h. Afterwards, the columns were cooled to room temperature, the ends broken off, and the columns rinsed with methanol and dried with a flow of nitrogen. The etching process was completed by repeating the above sequence of operations a second time prior to coating each column statically with a solution of tetra-*n*-butylammonium tetrafluoroborate (15 mg/ml) in methylene chloride.

(ii) Sodium chloride-roughened surfaces. The method used to deposit a layer of sodium chloride microcrystals on smooth or whisker-walled column surfaces is described elsewhere⁷. Briefly, a sodium chloride suspension was prepared by adding a saturated solution of sodium chloride in methanol to methylene chloride. The empty columns were then filled with the suspension, and, after a rest period, the suspension was removed at a constant velocity of 4 cm/s. Solvent residues were removed with a stream of nitrogen, and the columns were filled with a methylene chloride solution of tetra-*n*-butylammonium tetrafluoroborate (100 mg/ml), saturated with sodium chloride. After a rest period, the coating solution was removed at a constant velocity of 4 cm/s and residual solvent was evaporated with a stream of nitrogen.

(iii) Barium carbonate-roughened surfaces. Unetched capillary columns were cleaned by filling them with 10% (v/v) hydrochloric acid and allowed to stand for 20 min. The columns were then emptied and washed with distilled water until neutral to litmus. Afterwards, each column was dried by passing five column volumes of acetone through it at 3 cm/s, followed by flushing with nitrogen at 8 ml/min for about 2 h.

The barium hydroxide coating solution was prepared as follows. Distilled water was boiled for about 2 h to expel dissolved carbon dioxide. After it had cooled to room temperature, an excess of barium hydroxide was added, the suspension was sonicated for about 10 min, and undissolved solid was removed by filtration. To this solution was then added sufficient Brij-35 (a non-ionic wetting agent) to give a concentration of 0.1 mg/ml in the coating solution. The resulting solution was sonicated for a further 5 min to dissolve the Brij-35 and then allowed to stand for about 20 min prior to use.

Each acid-rinsed and dried capillary column was completely filled with the barium hydroxide coating solution and allowed to stand for about 10 min. A buffer volume of about 5 cm of air was introduced following the coating solution, which was then expelled from the column at a steady velocity of 3 cm/s by a regulated supply of carbon dioxide gas. When all the coating solution had left the column, the remaining carbon dioxide was removed by flushing nitrogen through the column for about 5 min. Water was removed from the column by heating it in a GC oven at 80°C for about 6 min with a nitrogen flow through the column. After cooling to room temperature without interrupting the nitrogen flow, the column was removed from the oven and rinsed with three column volumes of acetone, and then dried for 3 h with a nitrogen flow of about 8 ml/min. To produce a dense barium carbonate layer, required for coating with molten salts, the roughening procedure was repeated once more, following the sequence of operations just described.

The barium carbonate-modified columns were coated dynamically with a 10% (w/v) solution of tetra-*n*-butylammonium tetrafluoroborate in methylene chloride at a velocity of 3 cm/s. After the plug of coating solution had passed through the column, residual solvent was removed with a nitrogen flow of 8 ml/min for about 2 h.

(iv) Chromosorb R 6470-1-roughened surfaces. Whisker-walled columns, prepared as described in (i), were filled with a stable suspension of Chromosorb R6470-1 in iodomethane. After a rest period of 30 min, each column was emptied at a constant velocity of 5 cm/s, and then dried for several hours with a nitrogen flow of about 10 ml/min. Each column was then dynamically coated at a constant velocity of 3 cm/s with a chloroform suspension of Chromosorb R6470-1, containing 10% (w/v) of tetra-*n*-butylammonium tetrafluoroborate. Each column was then dried with a nitrogen flow of 8 ml/min for several hours.

Prior to testing, the first few coils at both ends of each column were discarded. Each column was then conditioned by temperature-programming from room temperature to 240°C at 5°C/min with a hydrogen carrier gas flow of about 1.0 ml/min. After 10 min at 240°C, the columns were ready for use. Each column was then evaluated for efficiency, thermal stability, and longevity using standard methods detailed elsewhere^{12,13}. Unless otherwise stated, test columns were 8–10 m long, and chloronaphthalene or bromonaphthalene were used as the probes for evaluation. A Varian 3700 gas chromatograph with capillary column 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 legends to tables and figures.

RESULTS AND DISCUSSION

The useable liquid range for the tetraalkylammonium tetrafluoroborate salts was taken to be the difference between the melting point and the maximum column operating temperature for the column. The maximum column temperature in these studies was established as the highest temperature at which the column could be maintained for 24 h without any change in retention or peak width of the components in a test chromatogram, recorded at a lower temperature before and after the conditioning period. The data obtained for the four tetrafluoroborate salts are summarized in Table II. Two of the salts, tetra-*n*-butylammonium and tetra-*n*-hexylammonium tetrafluoroborate show useful liquid ranges of 113 and 140°C respectively. Tetra-*n*-octylammonium tetrafluoroborate has a more restricted range of 50°C. In

TABLE II
COLUMN OPERATING CHARACTERISTICS OF TETRAALKYLAMMONIUM TETRAFLUOROBORATE SALTS

<i>Tetrafluoroborate salt</i>	<i>Abbreviation</i>	<i>Melting point (°C)</i>	<i>Maximum operating temperature (°C)</i>	<i>Liquid range (°C)</i>	<i>Average column efficiency* (n/m)</i>
Tetra- <i>n</i> -propylammonium	TPATFB	245–247	—	—	2500
Tetra- <i>n</i> -butylammonium	TBATFB	160–162	285	113	3000
Tetra- <i>n</i> -hexylammonium	THATFB	89.5–91.5	230	140	1200
Tetra- <i>n</i> -octylammonium	TOATFB	122.5–123.5	170	50	1300

* An average value for several probes on columns with a 10% (w/w) loading on Chromosorb W-AW (100–120 mesh).

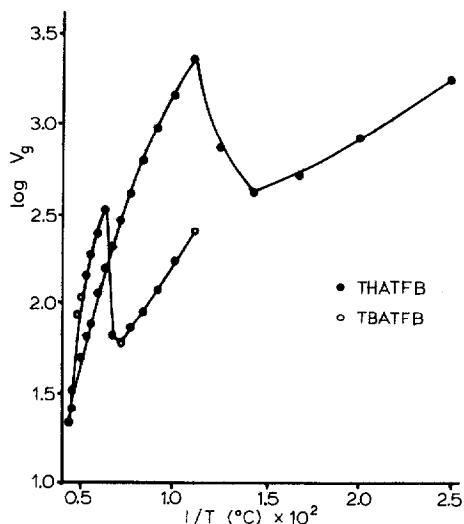


Fig. 1. Plot of the specific retention volume as a function of the reciprocal of column temperature, illustrating the phase change for tetra-*n*-butylammonium tetrafluoroborate (○) and tetra-*n*-hexylammonium tetrafluoroborate (●). The test substance was nitrobenzene.

the case of tetra-*n*-propylammonium tetrafluoroborate the melting point and the onset of column bleed or decomposition virtually coincide, making this salt useless as a liquid phase for gas chromatography. For the other salts, the maximum column temperature was established by the vapor pressure of the salt, and no evidence of decomposition was observed. For the salts studied, the vapor pressure is lowest for the tetra-*n*-butylammonium salt and then increases with increasing size of the tetra-alkylammonium cation. There is also a noticeable difference in the chromatographic efficiency of the tetra-*n*-butylammonium tetrafluoroborate salt and the two higher tetra-*n*-alkylammonium homologs. Columns prepared with tetra-*n*-butylammonium tetrafluoroborate are about twice as efficient as those prepared with the other two salts. However, efficiency of the tetra-*n*-hexylammonium and tetra-*n*-octylammonium tetrafluoroborate salts is sufficient for general chromatographic applications. The viscosities of tetra-*n*-butylammonium tetrafluoroborate and tetra-*n*-hexylammonium tetrafluoroborate over their common temperature range differ by about 25%¹⁰. This difference is probably too small to account for the results observed, particularly since the absolute value for the viscosity is fairly low. The only phase transitions observed for TBATFB and THATFB corresponded to the melting points of the salts (Fig. 1).

McReynolds constants for tetra-*n*-hexylammonium tetrafluoroborate (THATFB) are given in Table III. It shows that dispersive interactions are relatively weak, and the important selective interactions are orientation interactions with possibly some weak proton-acceptor capability. The capacity factor values for the probes on THATFB are small and, therefore, the phase constants should be considered approximate.

Several problems are inherent in the use of the McReynolds probes to determine stationary phase selectivity of the tetrafluoroborate salts. Not the least of them are the low retention of the probes at the temperature used for the determination, conventionally 100°C or 120°C, and the fact that several salts have melting points

TABLE III

McREYNOLDS CONSTANTS FOR TETRA-*n*-HEXYLAMMONIUM TETRAFLUOROBORATE DETERMINED AT 100°C

<i>Test solute</i>	<i>Retention index, I</i>	$\Delta I_{\text{squalane}}^{\text{THATFB}}$	<i>Capacity factor, k</i>	<i>Specific retention volume, V_g^o</i>
Benzene	869	216	0.79	17.1
<i>n</i> -Butanol	1063	493	3.00	64.8
2-Pentanone	972	345	1.48	32.0
1-Nitropropane	1174	522	4.93	106.5
Pyridine	1116	417	3.51	76.0
2-Methyl-2-pentanol	1073	383	2.72	58.8
1-Iodobutane	1016	198	1.93	41.7
2-Octyne	960	119	1.38	29.8
1,4-Dioxane	964	310	1.40	30.5
<i>cis</i> -Hydrindane	1083	77	2.90	62.5

higher than the maximum operating temperature of the non-polar reference phase, squalane. This precludes comparison of the properties of TBATFB and THATFB, which was considered desirable for these studies. As an alternative to the McReynolds method, a scheme was devised in which a series of substituted naphthalene derivatives is used as test probes and OV-101 as the non-polar reference phase. Either 180 or 200°C was used for the column temperature and retention index values, and retention index differences were determined in the usual way. To provide a reference point, equivalent data were determined for the moderately polar phase, Carbowax 20M. The results of these experiments are summarized in Tables IV and V. Although not all the McReynolds probes are represented in the naphthalene series, the more important interactions are evaluated. Again, the data support the view that the dominant selective interactions are due to dipole interactions and that other interactions, including dispersion, are relatively weak.

TABLE IV

RETENTION INDICES FOR SUBSTITUTED NAPHTHALENE DERIVATIVES ON THE TEST PHASES AT 180°C

<i>Solute</i>	<i>Retention index</i>			
	<i>TBATFB</i>	<i>THATFB</i>	<i>Carbowax 20M</i>	<i>OV-101</i>
Naphthalene	2055	1763	1236	1244
Acetonaphthone	3001	2407	1747	1575
Nitronaphthalene	3034	2505	1739	1601
Isoquinoline	2475	1997	1415	1311
Iodonaphthalene	2723	2306	1610	1612
Benzodioxan	2104	1783	1256	1200
Cyanonaphthalene	2874	2384	1649	1494
Bromonaphthalene	2575	2153	1484	1485
Chloronaphthalene	2424	2022	1401	1407
Naphthalenemethanol	—	—	1838	1585

TABLE V
RETENTION INDEX DIFFERENCES, CALCULATED FROM THE DATA IN TABLE IV

<i>Solute</i>	$\Delta I_{OV-101}^{TBATFB}$	$\Delta I_{OV-101}^{THATFB}$	$\Delta I_{OV-101}^{Carbowax}$
Naphthalene	811	519	-8
Acetonaphthone	1426	832	254
Nitronaphthalene	1433	904	138
Isoquinoline	1164	686	104
Iodonaphthalene	1111	694	-2
Benzodioxan	904	583	56
Cyanonaphthalene	1380	890	155
Bromonaphthalene	1090	668	-1
Chloronaphthalene	1017	615	-6

Naphthalenemethanol, the probe included in the above series to measure proton-acceptor properties, was irreversibly retained by TBATFB and THATFB. This behavior of alcohols is quite general. Alcohols with short column residence times usually pass through the column without noticeable problems, at intermediate residence times peaks are usually broadened and the recovery of injected mass is incomplete, while for alcohols with long residence times no peaks can be observed. Primary alcohols are absorbed to a greater extent than secondary alcohols, which, in turn, are absorbed to a greater extent than tertiary alcohols. Phenols and amines with a hydrogen atom on the nitrogen are also strongly absorbed by the column. This effectively makes any discussion of the proton-acceptor power of the tetrafluoroborate salts meaningless; these salts should be considered unsuitable for the separation of proton-donor solutes. However, the nature of the strong interaction-reaction with proton-donor solutes remains ambiguous. Similar problems were not observed with any other group of chemical substances, including most of the common functional groups encountered in organic compounds.

An interesting feature of the data shown in Table V is that the retention index differences are frequently one order of magnitude larger for TBATFB and THATFB

TABLE VI
SPECIFIC RETENTION VOLUMES OF TEST SOLUTES ON TETRAALKYLAMMONIUM TETRAFLUOROBORATE AND REFERENCE PHASES, MEASURED AT 180°C

<i>Solute</i>	<i>Specific retention volume (cm³)</i>			
	<i>TBATFB</i>	<i>THATFB</i>	<i>Carbowax 20M</i>	<i>OV-101</i>
Naphthalene	80.6	72.6	7.8	56.9
Acetonaphthone	1280.2	827.3	79.3	219.6
Nitronaphthalene	1398.6	1198.6	76.8	241.3
Isoquinoline	287.7	174.6	18.5	76.2
Iodonaphthalene	558.9	564.3	45.6	252.9
Benzodioxan	92.0	74.5	8.2	47.3
Cyanonaphthalene	878.9	755.9	53.0	164.3
Bromonaphthalene	384.1	308.0	25.9	157.9
Chloronaphthalene	242.6	191.6	17.3	111.4

than for Carbowax 20M. Also, the retention index differences are smaller for THATFB and TBATFB. This observation is also supported by the specific retention volume data in Table VI. All solutes are retained longer by the tetrafluoroborate salts than by OV-101 and Carbowax 20M. For the polar solutes this would have been anticipated, but it was unexpected for naphthalene. Table VI also illustrates that the retention of the polar solutes is greater on OV-101 than on Carbowax 20M. If the selectivity of a phase is due to the strength of specific interactions increasing the affinity of the solute for the stationary phase, then an increase in retention due to these interactions would be expected. This is the case for the tetrafluoroborate salts. In the case of Carbowax 20M, its selectivity, as measured by its McReynolds constants, is probably accounted for by the diminished retention of the hydrocarbon retention index markers on Carbowax 20M and less by increasing retention of the probes themselves. Aue and Paramasigami¹⁴ have presented a detailed discussion of similar observations, made with several popular polar stationary phases.

The data in Tables IV–VI show that the principal differences in the chromatographic properties of TBATFB and THATFB are that dispersive interactions are slightly stronger for THATFB than for TBATFB while dipole interactions are slightly stronger for TBATFB than for THATFB.

Very little is known about the mechanism of retention of organic solutes by organic molten salt phases. Adsorption at the gas–liquid interface was the dominant retention mechanism for hydrocarbons and proton-donor solutes on N-ethylpyridinium bromide, whereas solutes containing large dipole moments were retained mainly by gas–liquid partition^{3,4}. Martin has shown that for a solute retained only by gas–liquid partition, a plot of the net retention volume per gram of packing for several phase loadings should be a straight line with a zero intercept when extrapolated to zero phase loading¹⁵. For retention by adsorption at the gas–liquid interface the change in retention with increasing phase loading should be small, theoretically zero if the surface area of the liquid phase per gram of packing remains unchanged with increasing phase loading. Also, extrapolation to zero phase loading should result in a positive y -intercept. The results of such an analysis for a variety of test solutes on TBATFB at 180°C (Fig. 2) and 230°C (Fig. 3) indicates that retention occurs primarily by partition. Statistical analysis of the data showed that only the hydrocarbons heneicosane and docosane at 180°C have y -intercepts greater than 3 S.D. from zero. This indicates a small contribution by adsorption at the gas–liquid interface (or gas–solid interface) for the retention of these probes. In all other cases, the y -intercept values were within 2 S.D. from zero, and generally less than 1 S.D.

The high temperature stability and wide liquid range for TBATFB makes it suitable for temperature-programmed separations of substances of low volatility such as the mixture of polycyclic aromatic hydrocarbons shown in Fig. 4. The separation of a polarity test mixture on THATFB is shown in Fig. 5. The elution order of the solutes is in keeping with the previous discussion. The substances eluted towards the end of the chromatogram are those with the largest dipole moments. The efficient separation of a homologous series of n -alkylbromides is shown in Fig. 6.

The use of organic molten salts as stationary phases is relatively recent, and, therefore, there are few studies of the properties of open-tubular columns coated with these phases. Whisker surfaces were used to prepare open-tubular columns, coated with inorganic eutectic salt mixtures¹⁶ and organic molten salts^{5,6}. In addition, it has

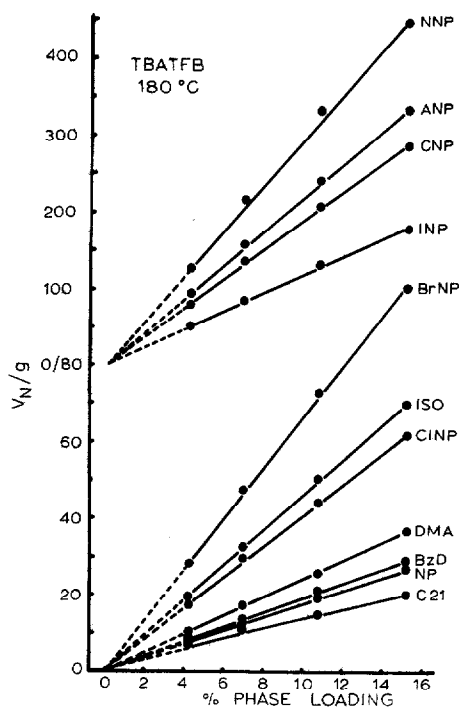
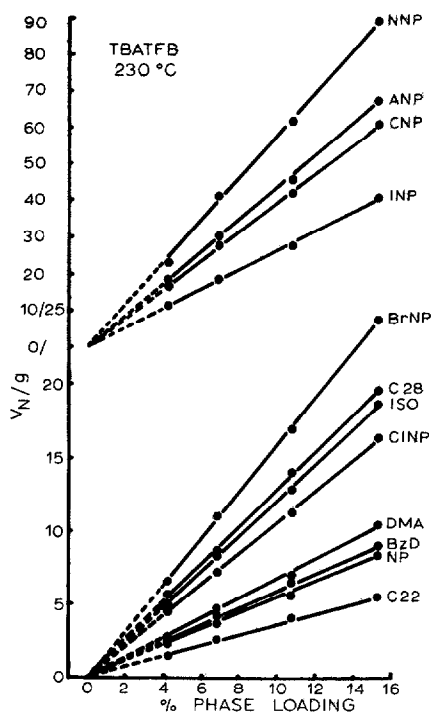


Fig. 2. Plot of the net retention volume (corrected to 25°C) per gram of column packing as a function of phase loading. The column temperature was 180°C and the stationary phase was tetra-*n*-butylammonium tetrafluoroborate. NNP = nitronaphthalene, ANP = acetonephthalene, CNP = cyanonaphthalene, INP = iodonaphthalene, BrNP = bromonaphthalene, ISO = isoquinoline, CINP = chloronaphthalene, DMA = 2,6-dimethylaniline, BzD = benzodioxan, NP = naphthalene, and C21 = *n*-heneicosane.

Fig. 3. Plot of the net retention volume (corrected to 25°C) per gram of column packing as a function of phase loading. The column temperature was 230°C and the stationary phase was tetra-*n*-butylammonium tetrafluoroborate. The identification of the test solutes is given in Fig. 2.

been shown that sodium chloride layers are an effective means of stabilizing organic molten salt films on smooth or whisker-modified surfaces⁷. As well as the above surface preparation procedures, we have investigated the use of barium carbonate and Chromosorb R6470-1 layers for the preparation of efficient and thermally stable open-tubular columns, coated with TBATFB.

Surface roughening can be achieved by chemical etching to produce a whisker-modified surface or by the deposition of an intermediate layer of inert particles¹³. Particle deposition methods evaluated in this study include deposition of sodium chloride⁷, barium carbonate^{17,18} and Chromosorb R6470-1¹⁹ on smooth or whisker-modified surfaces. The barium carbonate crystals formed as a result of the reaction of an aqueous barium hydroxide film on a smooth glass surface with carbon dioxide gave an even layer which lacked sufficient roughness to stabilize films of TBATFB. The columns prepared in this way deteriorate in a few hours when heated above the melting point of TBATFB. A double deposition of barium carbonate crystals gave a dense particle layer, milky white in appearance, that could be dynamically

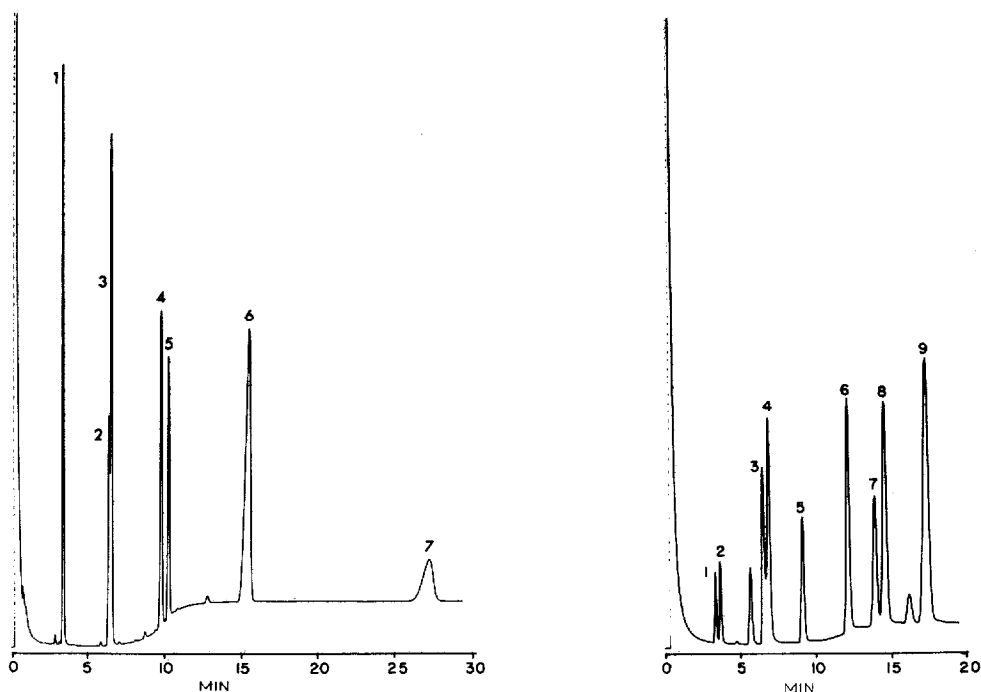


Fig. 4. Separation of a mixture of polycyclic aromatic hydrocarbons on a 2 m \times 2 mm I.D. column of 3% (w/w) TBATFB on Chromosorb W-AW (100–120 mesh). The column was temperature-programmed from 170 to 270°C at 10°C/min with a nitrogen carrier gas flow-rate of 30 ml/min. Peak identification: 1 = fluorene, 2 = phenanthrene, 3 = anthracene, 4 = fluoranthene, 5 = pyrene, 6 = benzo[*a*]anthracene and chrysene, and 7 = benzo[*b*]fluoranthene.

Fig. 5. Separation of a mixture of naphthalene derivatives on a 2 m \times 2 mm I.D. column of 10% (w/w) THATFB on Chromosorb W-AW (100–120 mesh). The column was temperature-programmed from 140 to 200°C at 5°C/min with a nitrogen carrier gas flow-rate of 30 ml/min. Peak identification: 1 = naphthalene, 2 = benzodioxan, 3 = isoquinoline, 4 = chloronaphthalene, 5 = bromonaphthalene, 6 = idonaphthalene, 7 = cyanonaphthalene, 8 = acetophenone, and 9 = nitronaphthalene.

coated with a concentrated solution of TBATFB without disrupting the particle layer. All attempts to deposit a layer of Chromosorb R6470-1 on smooth glass surfaces were unsuccessful. Patchy, unstable layers were formed that could not be recoated with a suspension of Chromosorb R6470-1 or a solution of TBATFB without disrupting the Chromosorb R6470-1 layer and causing frequent column blockage. Stable layers of Chromosorb R6470-1 were prepared by deposition of Chromosorb R6470-1 from a suspension on a whisker-modified surface. These columns could then be dynamically coated with a suspension of Chromosorb R6470-1, containing TBATFB.

The chromatographic performance characteristics of the surface-modified open-tubular columns, coated with TBATFB, are summarized in Table VII. Van Deemter plots for the various column types are shown in Fig. 7. The lowest plate height values were found for columns prepared with a barium carbonate layer and a layer of sodium chloride, deposited on a whisker-modified surface. Further, these columns have shallow curves, permitting operation at high mobile phase velocities

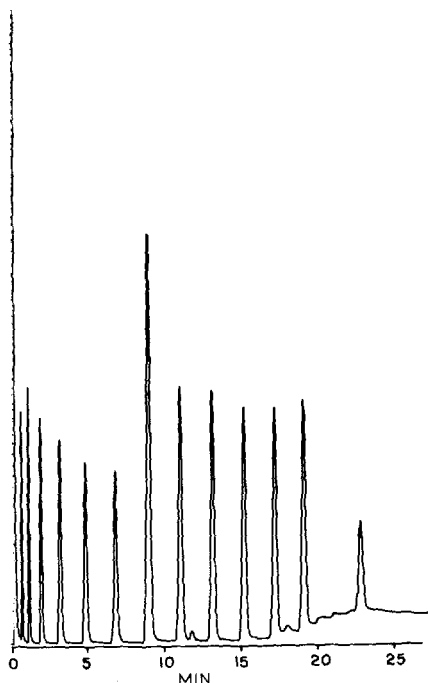


Fig. 6. Separation of a mixture of C_5 - C_{17} *n*-bromoalkanes on a $2\text{ m} \times 2\text{ mm}$ I.D. column of 10% (w/w) THATFB on Chromosorb W-AW (100-120 mesh). The column was held isothermally at 100°C for 1 min and then temperature-programmed from 100 to 200°C at $5^\circ\text{C}/\text{min}$ with a nitrogen carrier gas flow-rate of 30 ml/min.

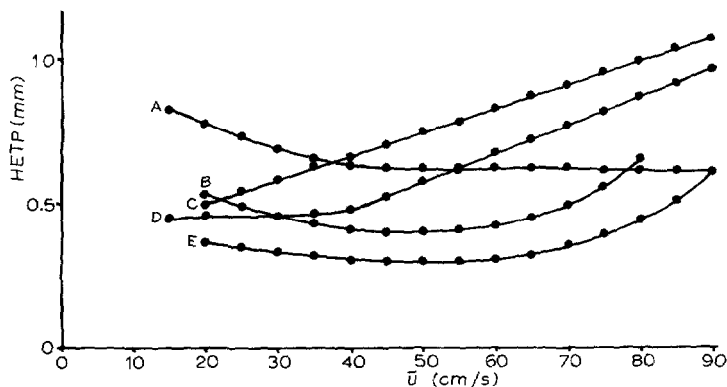


Fig. 7. Plot of plate height as a function of linear carrier gas velocity for open-tubular columns, coated with TBATFB and prepared by using different surface roughening procedures. A = unetched surface coated with a layer of sodium chloride, B = whisker surface with a layer of sodium chloride, C = whisker surface with a layer of Chromosorb R6470-1, D = whisker surface, and E = unetched surface coated with a layer of barium carbonate. All columns were approximately 10 m long and hydrogen was used as the carrier gas.

TABLE VII

PERFORMANCE CHARACTERISTICS AS A FUNCTION OF TEMPERATURE FOR OPEN-TUBULAR COLUMNS, COATED WITH TBATFB

H_{\min} = minimum plate height, h_{\min} = minimum effective plate height, U_{opt} = optimum linear carrier gas velocity; n/m = number of theoretical plates per meter, C.E. = coating efficiency, P.I. = performance index, and B_0 = column permeability constant ($\text{cm}^2 \cdot 10^{-6}$).

Column type	Column temperature ($^{\circ}\text{C}$)	H_{\min} (mm)	h_{\min} (mm)	U_{opt} (cm/s)	Capacity factor	n/m	C.E. (%)	P.I. (poise)	B_0
Whisker surface	170	0.60	0.65	27	56.5	2200	48	0.71	0.9
	200	0.75	0.78	30	18.5	1760	36	1.06	1.0
	215	0.84	0.80	30	12.3	1135	28	1.52	1.2
Whisker surface, coated with a layer of sodium chloride	170	0.40	0.41	50	58.0	2500	59	0.63	1.00
	200	0.59	0.65	55	19.8	1850	39	1.04	1.07
	215	0.59	0.68	50	13.8	1690	39	1.00	1.39
Smooth surface, coated with a layer of sodium chloride	170	0.52	0.54	55	57.8	1920	46	0.78	1.48
	200	0.65	0.70	65	24.2	1540	36	1.11	1.46
	215	1.10	1.30	85	13.9	990	21	1.99	1.62
Smooth surface, coated with a layer of barium carbonate	170	0.34	0.38	60	15.6	2960	67	0.30	1.47
	200	0.43	0.57	60	6.4	2310	50	0.54	1.47
	215	0.50	0.76	60	4.3	2000	41	0.77	1.47
Whisker surface, coated with a layer of Chromosorb R6470-1	170	0.70	2.40	40	10.5	1420	32	1.46	1.36
	200	1.00	9.50	55	4.8	950	21	3.27	1.50
	215	1.50	25.50	80	2.8	660	13	8.04	1.40

with little loss in efficiency. An opposite effect is seen for the whisker-walled and the whisker-walled Chromosorb R6470-1-modified columns. At high mobile-phase velocities, the efficiency of these columns declines markedly. In the case of the whisker-walled Chromosorb R6470-1 modified columns, the increase in plate height is virtually a linear function of the mobile phase velocity.

The coating efficiency and the effective plate height minimum as a function of temperature for the five column types is shown in Figs. 8 and 9, respectively. For all but the smooth-surface sodium chloride-modified layer, the coating efficiency declines linearly with increasing temperature over the temperature range investigated, 170–215 $^{\circ}\text{C}$. At all temperatures, the barium carbonate and sodium chloride whisker-modified surfaces show the best film forming and film stabilizing properties at their optimum phase loading. The poor film building properties of the Chromosorb R6470-1 whisker-modified surfaces is also clearly illustrated. The sodium chloride layer, deposited on a smooth glass surface, shows a large decline in film stabilizing properties between 200 and 215 $^{\circ}\text{C}$. A possible reason for this might be disruption of the surface

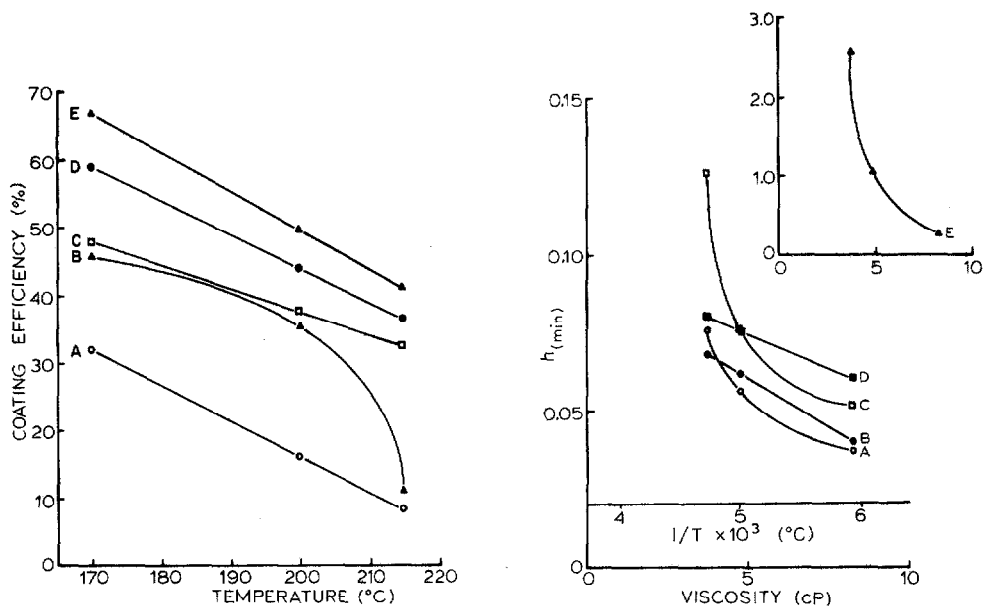


Fig. 8. Variation of coating efficiency with column temperature for open-tubular columns, coated with TBATFB and prepared by different surface roughening techniques. A = whisker surface with a layer of Chromosorb R6470-1, B = unetched surface with a layer of sodium chloride, C = whisker surface, D = whisker surface with a layer of sodium chloride, and E = unetched surface with a layer of barium carbonate.

Fig. 9. Variation of the minimum effective plate height with the reciprocal of the column temperature or stationary phase viscosity for open-tubular columns, prepared by different surface-roughening techniques. A = unetched surface with a layer of barium carbonate, B = whisker surface with a layer of sodium chloride, C = unetched surface with a layer of sodium chloride, D = whisker surface, and E = whisker surface with a layer of Chromosorb R6470-1. The stationary phase was TBATFB.

layer by dissolution of sodium chloride in the stationary phase film as the temperature is raised.

The general decline in film stabilizing properties with increasing column temperature for all five roughened surfaces suggests some common cause. The stability of a film on a surface, particularly as a function of temperature, depends on the degree of interaction between the liquid and the surface and the intrinsic viscosity of the liquid. Lind *et al.*¹⁰ have determined the viscosity of TBATFB over the temperature range 162–266°C. Values of 8.3, 4.0, 3.8, and 2.7 cP were obtained for TBATFB at 170, 200, 215, and 240°C, respectively. We surmise that the decline in viscosity with increasing temperature, resulting in destabilization of the film with subsequent redistribution to a less homogeneous film, is probably the cause of the result observed. Relaxation of the film to its original state occurs on lowering the column temperature, as observed by running test chromatograms at alternately higher and lower temperatures over several days. Within the temperature range 170–240°C the influence of temperature is primarily to induce changes in the local film homogeneity. Breakup of the film to cause droplet formation does not occur to a significant extent until temperatures exceeding 240°C are employed.

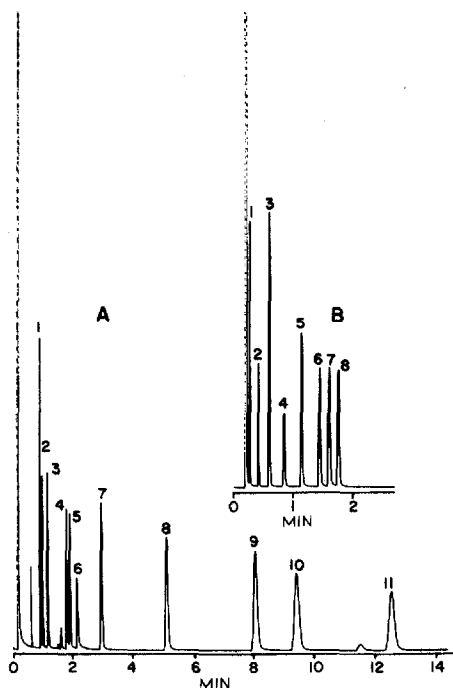


Fig. 10. Separations of a mixture of naphthalene derivatives (A) and benzene derivatives (B) on a 7.9 m \times 0.25 mm I.D. whisker-walled open-tubular column, statically coated with a 15 mg/ml solution of TBATFB in methylene chloride. The naphthalene derivatives were separated isothermally at 185°C with a hydrogen carrier gas flow-rate of 1.0 ml/min. Peak identification: 1 = naphthalene, 2 = benzodioxan, 3 = quinoline, 4 = chloronaphthalene, 5 = isoquinoline, 6 = bromonaphthalene, 7 = iodonaphthalene, 8 = cyanonaphthalene, 9 = acetonaphthone, 10 = naphthyl acetate, and 11 = nitronaphthalene. The benzene derivatives were separated isothermally at 165°C with a hydrogen carrier gas flow-rate of 1.0 ml/min. Peak identification: 1 = benzene, 2 = toluene, 3 = chlorobenzene, 4 = bromobenzene, 5 = cyanobenzene, 6 = iodobenzene, 7 = *o*-dichlorobenzene, and 8 = nitrobenzene.

The durability of the columns was found to depend on the surface preparation procedure. Columns prepared with a barium carbonate layer, although the most efficient, deteriorate in use relatively rapidly. Noticeable changes in performance can be seen after about 48 h. Precautions were taken to exclude from the chromatographic system moisture which might promote reaction between the barium carbonate layer and the molten salt. The reason for the short lifetime of the barium carbonate-modified columns is unknown but effectively limits their usefulness. The most stable columns are the whisker-modified and the whisker-surface sodium chloride-modified columns. Columns of both kinds have been in use for several months without significant change in properties, provided that the upper temperature limit of 240°C is not exceeded. The whisker-surface Chromosorb R6470-1-modified columns are reasonably stable, but their low column performance limits their practical use.

Fig. 10 illustrates the separation of a polarity test mixture on a whisker-modified surface coated with TBATFB. Fig. 11 compares the separation of chlordane, a chlorinated pesticide, on a whisker-modified surface, and on a whisker-modified sur-

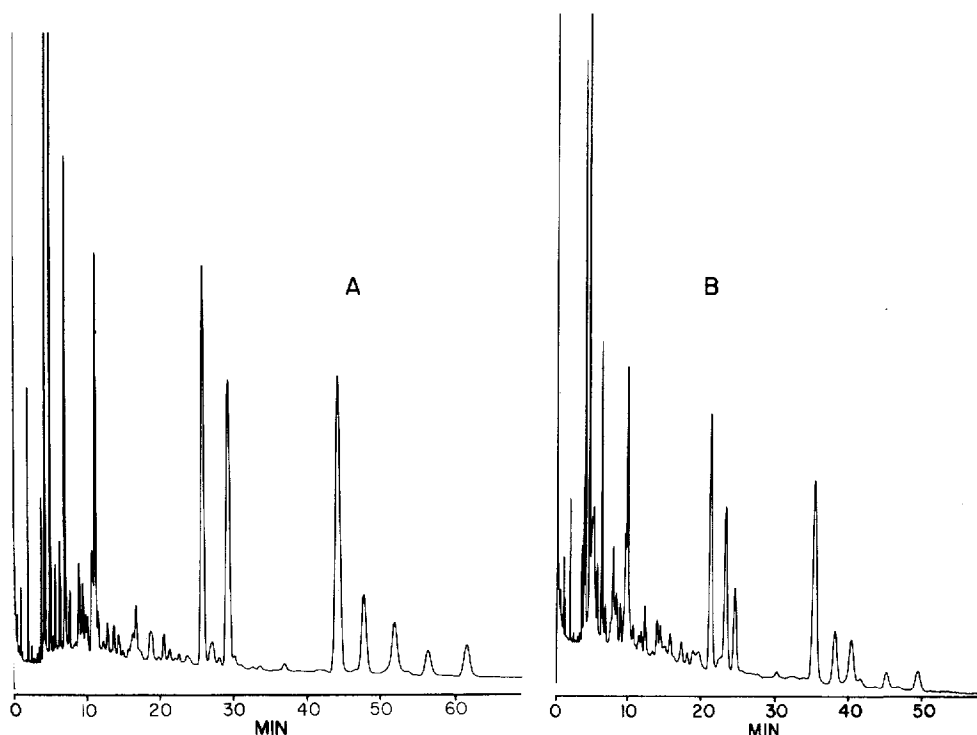


Fig. 11. Separation of chlordane on (A) a whisker-walled column, statically coated with 15 mg/ml solution of TBATFB in methylene chloride, and (B) a whisker surface with a layer of sodium chloride, dynamically coated with a solution containing 100 mg/ml of TBATFB in methylene chloride previously saturated with sodium chloride. For (A), a column 7.9 m \times 0.25 mm I.D., isothermally at 170°C, and hydrogen carrier gas flow-rate of 2.0 ml/min, was used. For (B) a column 8.1 m \times 0.25 mm I.D., isothermally at 180°C, and hydrogen carrier gas flow-rate of 1.5 ml/min was used.

face, coated with a layer of sodium chloride. The sodium chloride layer improves the efficiency of the column but does not change its operating temperature range.

CONCLUSIONS

Tetra-*n*-butylammonium and tetra-*n*-hexylammonium tetrafluoroborates are useful polar stationary phases for gas chromatography. The two salts provide overlapping temperature operating ranges from 90 to 230°C for THATFB and from 162 to 285°C for TBATFB. Retention occurs primarily by a partition mechanism, with orientation interactions dominating the selectivity of solute-phase interactions. Proton-donor solutes such as alcohols, phenols, and primary amines, do not show normal chromatographic behavior on the tetrafluoroborate salts, which are not suitable phases for their analysis.

Five surface modification techniques were investigated for the preparation of open-tubular columns, coated with TBATFB. Barium carbonate layers provide columns of the highest efficiency but showed poor durability and are not suitable for routine use. Whisker-surface Chromosorb R6470-1-modified columns showed poor

performance characteristics and, again, are not advised for routine use. The most durable and efficient columns were prepared using whisker-modified surfaces with or without a layer of sodium chloride. The effect of the addition of the sodium chloride layer is to increase the film homogeneity of TBATFB, leading to a small increase in column performance. It does not influence the operating temperature range for the columns. Columns prepared by deposition of sodium chloride on a smooth glass surface are easy to prepare and reasonably efficient in the temperature range 170–215°C. At higher temperatures, the film stabilizing properties of the sodium chloride layer shows a significant decline compared to the whisker surface and whisker-surface sodium chloride modified columns. To obtain open-tubular columns of greater efficiency and film stability than those described here, it will be necessary to identify new organic molten salt phases with a temperature stability and liquid range equivalent to TBATFB but possessing better film-forming properties at high temperatures.

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