SURVEY OF ORGANIC MOLTEN SALT PHASES FOR GAS CHROMATO-GRAPHY

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SUMMARY

The organic molten salts tetra-*n*-hexylammonium benzoate, tetra-*n*-heptylammonium chloride, 1-methyl-3-ethylimidazolium chloride, ethylpyridinium bromide, tri-*n*-butylbenzylphosphonium chloride, tetra-*n*-butylammonium tetrafluoroborate, and sodium isovalerate are evaluated as stationary phases for gas chromatography. They all behave as stable isotropic liquids over a temperature range of at least 50°C, and in most cases, greater than 100°C. As a series these salts provide a range of liquid phases spanning temperatures from room temperature to *ca*. 290°C. The principal solute-retaining forces are orientation and proton donor interactions, the magnitude of which depends on the identity of the salt. The physical and chemical properties of the organic molten salts are compatible with their use in gas chromatography to separate a wide range of sample types including alcohols, halocarbon compounds, substituted benzene and naphthalene derivatives, and essential oils.

Calcium nitrate tetrahydrate is also evaluated as an example of a hydrated melt. Excessive retention of polar solutes and poor peak shape make its general use impractical.

INTRODUCTION

The majority of stationary phases employed in gas–liquid chromatography (GLC) are molecular liquids which retain solutes through dispersion, orientation, induction, and hydrogen bonding (complexation) interactions. Orientation, induction, and hydrogen bonding are examples of selective interactions which may be exploited to separate substances of similar volatility. Ionic liquids contain additional selective intermolecular forces due to the presence of charge-bearing groups. The forces between ions are strong, promote order in the liquid state, and are potentially useful for enhancing the separation of polar solutes. However, the general use of ionic liquids as stationary phases in gas chromatography (GC) is a virtually unexplored resource.

Ionic liquids can be divided into three categories: inorganic molten salts, organic molten salts, and inorganic hydrated melts. Inorganic molten salts and eutectic salt mixtures have beeen used to separate inorganic compounds, particularly metal

halides, by GC[1,2]. Their application to the separation of organic solutes, however, was less successful owing primarily to the low affinity of organic solutes for inorganic melts[3]. Organic molten salts should provide a better environment for partitioning with organic solutes. Their known physical and chemical properties, which include data on densities, viscosity, surface tension, dielectric properties, thermal stability, and miscibility with organic solvents, do not suggest any general incompatibility with their use as liquid phases in GC[4-6]. The earliest report of the use of organic molten salt phases in GC was that of Barker *et al.*[7], who separated a series of volatile organic compounds on columns containing manganese, cobalt, nickel, copper, or zinc stearates as liquid phases. These authors measured several thermodynamic properties of the salt but made few comments concerning their general use as liquid phases in GC. Gordon *et al.*[8] evaluated the stationary phase properties of tetra-*n*-pentylammonium bromide, tetra-*n*-pentylammonium picrate, and tetra-*n*-hexylammonium nitrate. These authors recorded retention data for 25 organic compounds on the above salts over the temperature range 103–113°C. Above 113°C tetra-*n*-pentylammonium bromide decomposed; the other salts were stable to at least 140°C. Because of the narrow temperature operating range and poor column efficiencies observed with these salts, the report by Gordon *et al.* seems to have received little attention. Sixteen years then passed until the next report of the use of an organic molten salt in gas chromatography. Pacholec *et al.*[9] used ethylammonium nitrate to separate a wide range of organic compounds. This salt had a usable temperature range from 20 to 120°C and retained solutes having large dipole or hydrogen bonding functional groups more strongly than Carbowax 20M. Columns showed usable efficiency but generally somewhat lower than columns prepared with conventional non-ionic liquid phases. The same group has recently proposed ethylpyridinium bromide for use as a selective liquid phase. This organic molten salt is the first such phase to exhibit acceptable column efficiency, acceptable peak symmetry for polar solutes, and excellent long term column thermal stability. It has a usable liquid range from 110–160°C and selectively retains solutes with dipolar and hydrogen bonding functional groups while hydrocarbons and other compounds of low polarity are only weakly retained.

The results obtained with ethylpyridinium bromide were sufficiently encouraging to warrant a search for other useful organic molten salt phases. In particular, salts with a wider liquid temperature range and greater thermal stability would be valuable. To this end a literature search was made to identify organic molten salts fulfilling the following criteria: a stable liquid temperature range exceeding 50°C, to provide a series of salts with overlapping liquid ranges from room temperature to *ca.* 300°C, and to include salts containing cations and anions of different size and characteristics to assess the importance of these parameters in controlling selectivity. This led to the selection of tetra-*n*-hexylammonium benzoate[11], tetra-*n*-heptylammonium chloride[12], tetra-*n*-butylammonium tetrafluoroborate[13], tri-*n*-butylbenzylphosphonium chloride[14], 1-methyl-3-ethylimidazolium chloride[15,16], and sodium isovalerate[17] for study. Their chromatographic properties are evaluated in this paper.

As well as the organic molten salts, an example of a hydrated melt is also evaluated in this paper. The hydrated melts are molten salts in which a cation (generally) has a filled or nearly filled coordination shell of water molecules[18]. The water is tightly bound in the inner coordination sphere of the cation, which forms part of the lattice structure of the melt, and thus provides considerable stability to the system.

Water vapor, for example, is not lost from the melt until temperatures well above the normal boiling point of water are reached. Recently Berezkin et al.[19,20] have used crystal hydrates maintained in dynamic equilibrium with steam-conditioned carrier gas to separate polar solutes. Separations reminiscent of those obtained using water as a stationary phase were found[2]. The requirement of a mobile phase containing water vapor of a fixed concentration presents certain experimental inconveniences which might be eliminated by using a hydrated melt.

EXPERIMENTAL

Tetra-*n*-hexylammonium benzoate and tetra-*n*-heptylammonium chloride were obtained from Eastman Kodak (Rochester, NY, U.S.A.). Calcium nitrate tetrahydrate, benzoyl chloride, tri-*n*-butylphosphine and tetra-*n*-butylammonium tetrafluoroborate were obtained from Aldrich (Milwaukee, WI, U.S.A.). Sodium isovalerate was obtained from ICN Pharmaceuticals (Plainview, NY, U.S.A.). 1-Methyl-3-ethylimidazolium chloride was a gift from Dr. J. S. Wilkes (Frank J. Seiler Research Laboratory, United States Air Force Academy, CO, U.S.A.). Tri-*n*-butylbenzylphosphonium chloride was synthesized as described elsewhere[14] and recrystallized to constant melting point (162–163°C) from diethyl ether–ethanol. Samples of essential oil of thyme and bergamot were obtained from Lorann Oils (Lansing, MI, U.S.A.). The sample of fuel oil No. 1 was obtained from Marathon Oil (Detroit, MI, U.S.A.). Other test compounds were available as Thetakits (Anspec, Ann Arbor, MI, U.S.A.) or were general laboratory chemicals from various sources.

Column packings containing from 3 to 20% (w/w) of organic molten salt on Chromosorb P or W (100–120 mesh) were prepared using the rotary evaporator technique. Solvents used for column preparation are given in Table I. The air-dried

TABLE I

COLUMN OPERATING CHARACTERISTICS FOR ORGANIC MOLTEN SALTS

Organic molten salt	Solvent for column coating	Minimum operating temperature (°C)	Maximum operating temperature (°C)	Average column efficiency (N m⁻¹)*
Tetra-*n*-hexylammonium benzoate	CH_2Cl_2	Liquid	110	400–500
Ethylammonium nitrate	CH_3OH	Liquid	120	1300–1500
Tetra-*n*-heptylammonium chloride	CH_2Cl_2	Liquid	130	1500–1800
1-Methyl-3-ethylimidazolium chloride	CH_2Cl_2	40	170	1700–1900
Ethylpyridinium bromide	CH_3OH	110	160	2000–2300
Tri-*n*-butylbenzylphosphonium chloride	CH_3OH	165	240	2300–2500
Tetra-*n*-butylammonium tetrafluoroborate	CH_2Cl_2	170	290	2500–3000
Sodium isovalerate	H_2O	188	280	–

* Approximate values for several columns at a 10% (w/w) loading on 100–120 mesh support measured at temperatures above 100°C.

packings were sieved before use and packed into glass columns of 1–3 m in length and 2 mm I.D. with the aid of vacuum suction and gentle vibration.

For GC a Varian 3700 or Hewlett-Packard 5880A gas chromatograph was used. Both instruments were fitted with heated on-column injectors, temperature programmer, and flame ionization detectors. Separation conditions are given in the legends to tables and figures.

RESULTS AND DISCUSSION

The liquid range for the organic molten salts is defined by the minimum and maximum column operating temperatures given in Table I. Several of the organic molten salts studied were liquids at room temperature. However, no attempt was made to study their chromatographic properties below 40°C. The minimum column operating temperature for tri-*n*-butylbenzylphosphonium chloride, (Fig. 1) and tetra-*n*-butylammonium tetrafluoroborate (Fig. 2) corresponds to the bulk melting point of the salts. No other phase changes were observed.

At temperatures below their melting points the salts can function as selective adsorbents. Compared with solutes retained above the melting point, column efficiency and peak symmetry is usually lower at temperatures below the melt (Fig. 3). Also, both column efficiency and peak symmetry usually decline continuously as temperatures further removed from the melting point are reached. The phase reten-
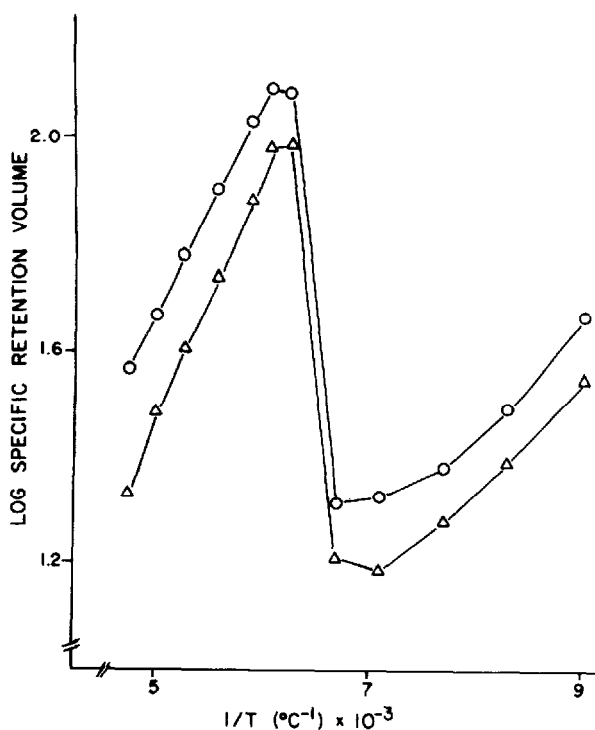

Fig. 1. Plot of specific retention volume as a function of the reciprocal of column temperature illustrating the phase change for tri-*n*-butylbenzylphosphonium chloride. Test solutes: ○, naphthalene; △, pentanol.
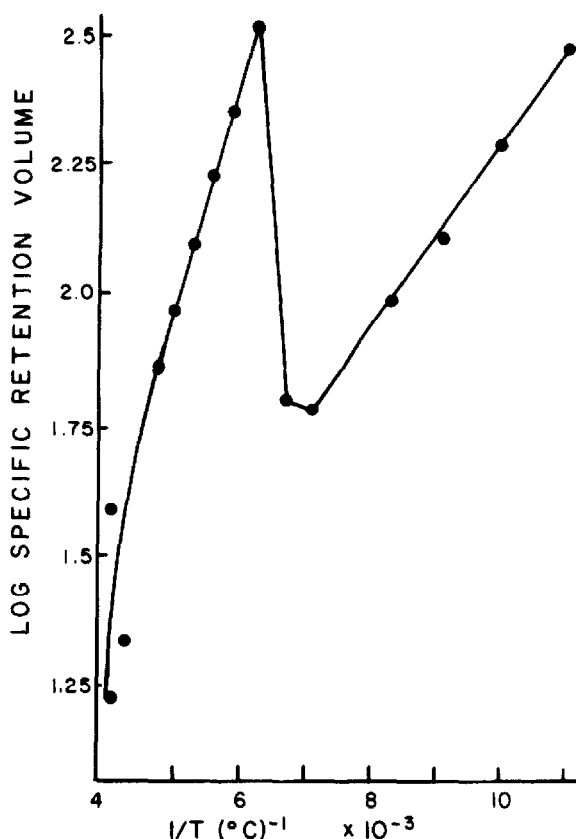
Fig. 2. Plot of specific retention volume as a function of the reciprocal of column temperature illustrating the phase change for tetra-*n*-butylammonium tetrafluoroborate. Test solute, nitrobenzene.

tion and selectivity can also vary dramatically above and below the melting point. This is illustrated in Fig. 4 for the separation of a mixture of substituted benzene derivatives recorded at different temperatures on tri-*n*-butylbenzylphosphonium chloride. In this case the elution order is unchanged and only the relative retention volumes are affected; in other cases the elution order may change as well[10].

The maximum column operating temperature was defined as the highest temperature the phase could be maintained at for 24 h without change in absolute retention and column performance parameters in a test chromatogram established before and after the conditioning period. Column bleed and not phase decomposition established this limit for the salts tested in Table I.

Values for average column efficiency are also given in Table I. These values are generally reasonable compared with those anticipated for conventional non-ionic liquid phases. Only tetra-*n*-hexylammonium benzoate yields columns of unacceptable efficiency. For the liquid organic molten salts in Table I, the column efficiency measured at 40°C may be only half that at 100°C. In general, the highest column efficiency was shown by salts with liquid ranges at high temperatures. For ethylpyridinium bromide, tri-*n*-butylbenzylphosphonium chloride, and tetra-*n*-butylammonium tetrafluoroborate the values for average column efficiency change little at temperatures
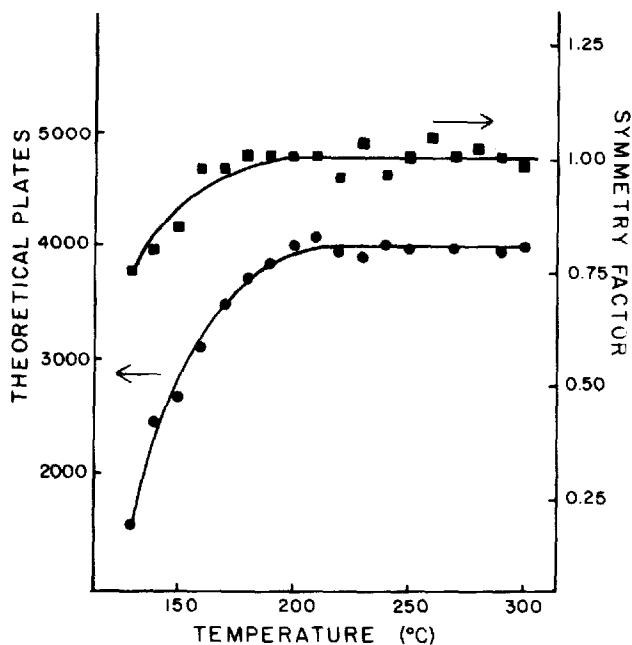
Fig. 3. The influence of column temperature on column efficiency and peak symmetry for nitrobenzene with tetra-*n*-butylammonium tetrafluoroborate as stationary phase.

greater than 10°C above the melting point. Presumably column efficiency is limited by viscosity considerations at low temperatures which become less important at higher temperatures.

McReynolds' constants for four of the organic molten salts are given in Table II. Values were determined at the highest column temperature compatible with reasonable retention for the test probes and the use of squalane as the non-polar reference stationary phase. The organic molten salts, although showing certain individual variations in their McReynolds' constants, show certain striking general trends. The principal intermolecular forces affecting retention are proton acceptor and orientation interactions. Proton donor interactions are weak or modest at best and dispersion interactions of small significance. The polarity of the molten salts, as measured by the sum of the first five McReynolds' constants (Σ_1^5), is not very remarkable compared with the values measured with non-ionic liquids. The selectivity of the organic molten salts is, however, different to that exhibited by non-ionic liquids. Of the non-ionic liquid phases commonly used in GLC, none provide such strong proton acceptor and orientation interactions (Y' and U') with such low dispersive and proton donor properties (X', Z' and S'). It must be admitted that the reliability of the McReynolds' system for characterizing polar phases can be questioned owing to the high probability of a mixed adsorption–partition retention mechanism for test probes and retention index markers[21]. However, it will be shown later, that the chromatographic properties of the organic molten salts are fully compatible with the above observations.

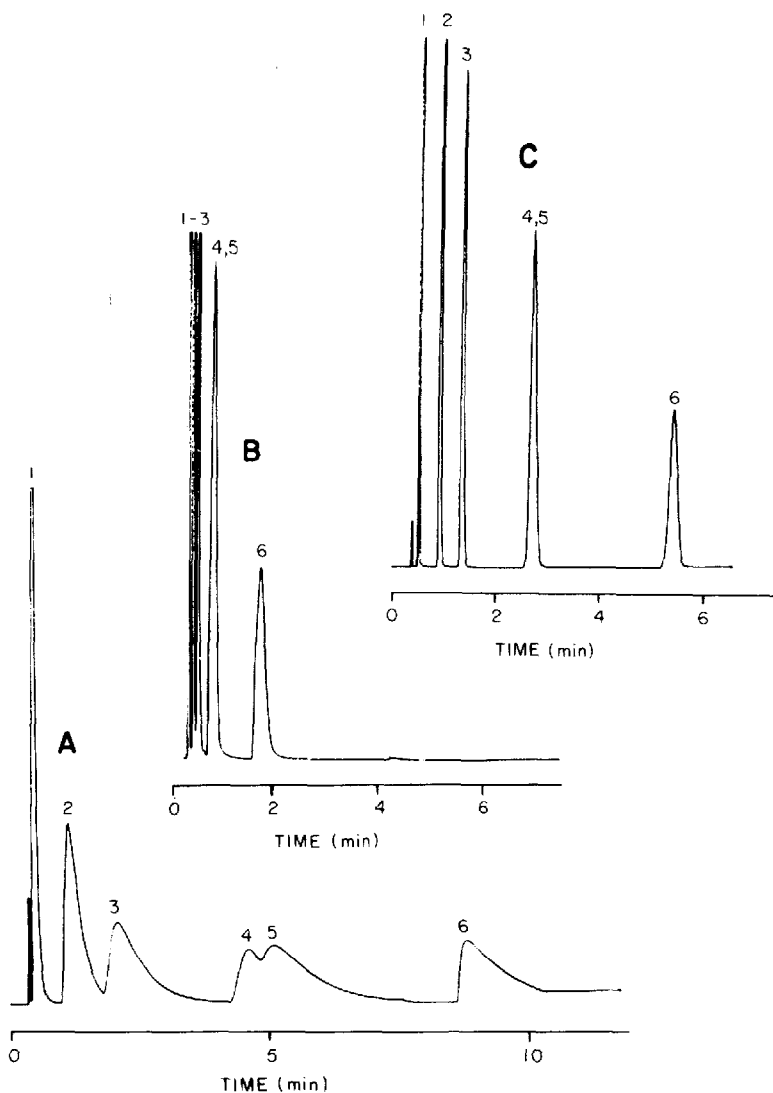There is no standard method for characterizing the selectivity of phases having

Fig. 4. Separation of a mixture of substituted benzene derivatives at (A) 60°C isothermal 2 min, then programmed at 5°C min^{-1}. (B) 120°C isothermal 2 min, then programmed at 5°C min^{-1} and (C) 165°C isothermal 2 min, then programmed at 5°C min^{-1}. All separations were carried out on a 2 m × 2 mm I.D. column of 10% (w/w) tri-*n*-butylbenzylphosphonium chloride on Chromosorb P (100–120 mesh). Elution order: 1 = benzene; 2 = chlorobenzene; 3 = bromobenzene; 4 = iodobenzene; 5 = benzaldehyde; 6 = nitrobenzene.

melting points higher than the maximum operating temperature of squalane. Although non-polar phases of greater thermal stability could be substituted for squalane[22–24], the test probes suggested by McReynolds are generally too volatile to provide accurate retention index values at temperatures much above 120°C. Alternative probes, such as benzene and naphthalene derivatives, have been proposed to eliminate this volatility problem[22,25,26]. Retention index values and retention index dif-

TABLE II

McREYNOLDS' CONSTANTS FOR THE ORGANIC MOLTEN SALTS*

Test probe	Symbol	EPBr	HABz	HACl	MEICl
Benzene	X'	—	154	161	87
Butanol	Y'	678	799	799	566
2-Pentanone	Z'	613	384	222	156
Nitropropane	U'	580	427	312	236
Pyridine	S'	485	330	326	273
2-Methyl-2-pentanol	H'	565	649	597	511
Iodobutane	J'	—	—	−42	−73
2-Octyne	K'	—	98	101	80
Dioxane	L'		236	237	187
cis-Hydrindane	M'	—	55	101	−179
Σ_1^5		—	2094	1820	1318
Temperature		120	100	120	55

* EPBr = ethylpyridinium bromide; HABz = tetra-*n*-hexylammonium benzoate; HACl = tetra-*n*-heptylammonium chloride; MEICl = 1-methyl-3-ethylimidazolium chloride.

ferences using OV-101 and Carbowax 20M as reference phases are given in Tables III and IV for a series of naphthalene derivatives on the high-melting organic molten salts. The difference in retention index values on the molten salts approaches or exceeds an order of magnitude the retention index difference between Carbowax 20M and OV-101. Selectivity differences exist between tri-*n*-butylbenzylphosphonium chloride and tetra-*n*-butylammonium tetrafluoroborate, the most obvious being the difference in proton acceptor ability, the retention of benzyl alcohol on the tetra-*n*-butylammonium tetrafluoroborate column was excessive, even at its maximum operating temperature. The general trends in selectivity are consistant with the McReynolds' constants data presented earlier for the lower-melting organic molten salts, although the two data sets cannot be compared directly owing to the differences in column temperature and structure of the probes. Proton acceptor and orientation

TABLE III

RETENTION INDEX VALUES FOR MOLTEN SALTS* AND REFERENCE PHASES AT 180°C

Test substances	OV-101	Carbowax 20M	TBATFB	TBBPCl
Naphthalene	1244	1236	2055	1924
1-Naphthalene methanol	1584	1838	—	—
1-Acetonaphthone	1575	1747	3001	2649
Nitronaphthalene	1601	1739	3034	2897
Isoquinoline	1311	1415	2475	2228
Chloronaphthalene	1407	1401	2424	2231
Bromonaphthalene	1485	1484	2575	2379
Iodonaphthalene	1612	1610	2723	2633
Cyanonaphthalene	1494	1649	2874	2646
1,4-Benzodioxan	1200	1256	2104	1955
Benzyl alcohol	981	1308	—	2611

* TBATFB = tetra-*n*-butylammonium tetrafluoroborate; TBBPCl = tri-*n*-butylbenzylphosphonium chloride.

TABLE IV

RETENTION INDEX DIFFERENCE VALUES CALCULATED FROM THE DATA IN TABLE III

Test substances	$\Delta I^{C20M}_{OV\text{-}101}$	$\Delta I^{TBATFB}_{OV\text{-}101}$	ΔI^{TBATFB}_{C20M}	$\Delta I^{TBBPCl}_{OV\text{-}101}$	ΔI^{TBBPCl}_{C20M}
Naphthalene	−8	811	819	680	688
1-Naphthalene methanol	254	−	−	−	−
1-Acetonaphthone	172	1426	1254	1074	902
Nitronaphthalene	138	1433	1294	1296	1158
Isoquinoline	104	1164	1060	917	813
Chloronaphthalene	−6	1017	1023	824	830
Bromonaphthalene	−1	1090	1091	894	895
Iodonaphthalene	−2	1111	1121	1021	1023
Cyanonaphthalene	155	1380	1225	1152	997
1,4-Benzodioxan	56	904	848	755	699
Benzyl alcohol	327	−	−	1630	1303

interactions are the important selective interactions for the organic molten salts in Table IV.

A very striking difference in absolute retention is shown by tetra-*n*-butylammonium tetrafluoroborate and tri-*n*-butylbenzylphosphonium chloride compared with Carbowax 20M and OV-101. This is reflected in the specific retention volume data in Table V. The retention of most probes on Carbowax 20M is less than on
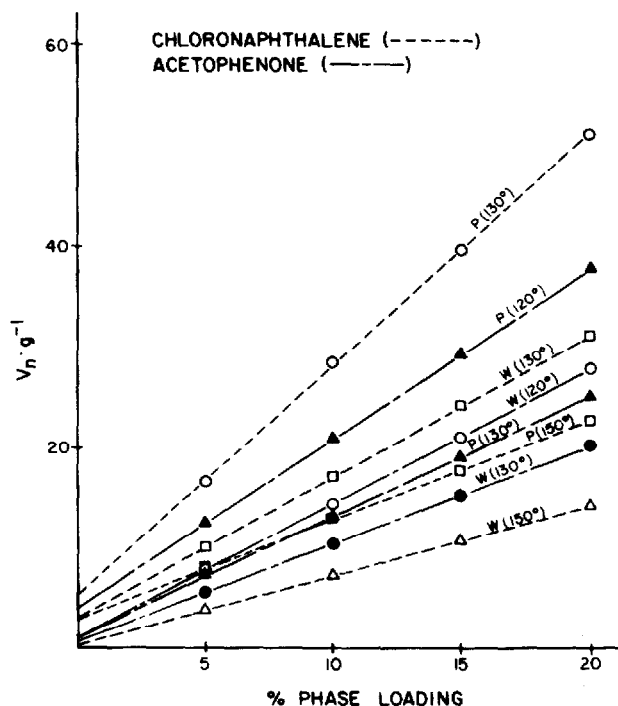

Fig. 5. Plot of net retention volume per gram of column packing (corrected to 25°C) against percent column loading of ethylpyridinium bromide. W and P refer to Chromosorb W and Chromosorb P respectively used as supports.

OV-101 and the polarity ranking of this phase, as measured by retention index differences, is due to a diminished retention of the hydrocarbon retention index markers rather than an enhanced retention of the polar probes[21]. This may apply, in part, to the organic molten salts as well but it is also clear from Tables IV and V that the selective interactions with the molten salts lead to an increase in retention.

It would be reasonable at this point to ask whether the organic molten salts should be classified as liquid phases or as liquid adsorbents. Their high retention for polar solutes would not be unusual for an adsorbent. However, to establish a retention mechanism for a solute on a liquid phase is a complex problem[27–30] as it is necessary to consider contributions to the retention volume arising from partition with the bulk liquid phase, partition with a structured liquid phase layer close to the support surface, adsorption at the gas–bulk liquid interface, adsorption at the gas–structured liquid interface, and adsorption at the gas–support interface. A general equation can be written to establish the importance of the above contributions to retention[29] but its solution for any particular solute requires a knowledge of phase
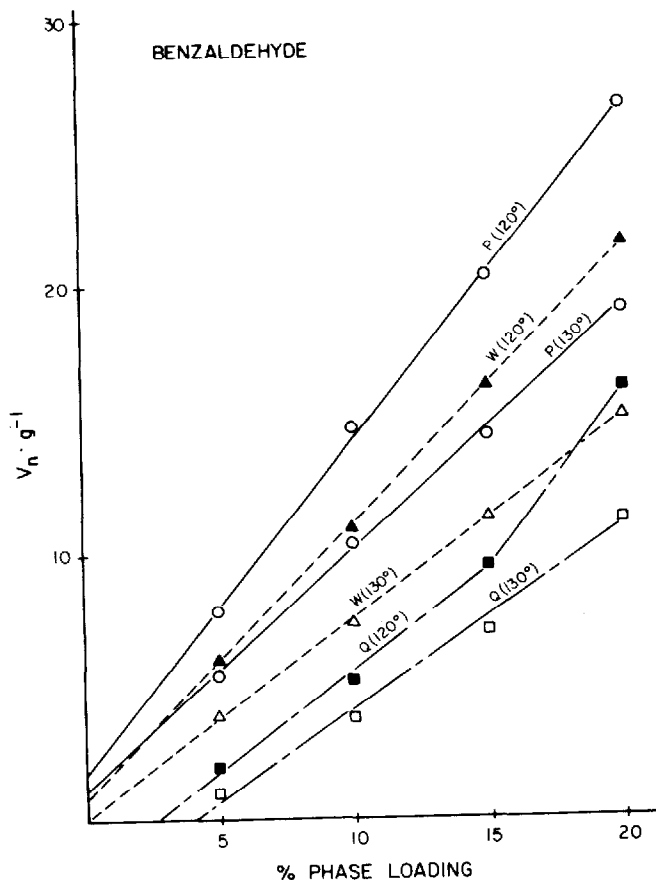

Fig. 6. Plot of net retention volume per gram of column packing (corrected to 25°C) against percent column loading of ethylpyridinium bromide. W, P, and Q refer to Chromosorb W, Chromosorb P, and Gas Chrom Q, respectively used as supports.

TABLE V

RETENTION OF TEST SUBSTANCES ON ORGANIC MOLTEN SALTS* AND REFERENCE PHASES

Test substances	OV-101	Specific retention volume		
		Carbowax 20M	TBATFB	TBBPCl
Naphthalene	39.3	4.8	37.1	75.2
1-Naphthalene methanol	157.5	78.9	—	—
1-Acetonaphthone	151.7	52.5	590.2	936.2
Nitronaphthalene	167.0	50.9	643.9	1560.4
Isoquinoline	52.6	12.2	132.5	218.5
Chloronaphthalene	73.0	11.4	111.7	218.5
Bromonaphthalene	109.1	17.1	176.8	368.8
Iodonaphthalene	174.7	30.1	257.3	887.9
Cyanonaphthalene	113.5	35.1	404.6	927.7
1,4-Benzodioxan	32.7	5.4	42.3	85.1
Benzyl alcohol	12.7	7.3	—	822.7

* TBATFB = tetra-n-butylammonium tetrafluoroborate; TBBPCl = tri-n-butylbenzylphosphonium chloride.

characteristics (volume of liquid phase, area of the gas–liquid interface, and the area of the liquid–support interface) for a minimum of five columns having different phase loadings as well as a complex iteration procedure to estimate a value for the thickness of the structured liquid phase layer. Such a complex procedure is beyond the scope of this paper. Instead, we have adopted a qualitative approach, similar to that described by Martin[30], using plots of the net retention volume per gram of column packing ($V_n \cdot g^{-1}$) as a function of the percentage liquid phase loading to estimate the importance of adsorption to the retention mechanism.

Some typical results for ethylpyridinium bromide on three supports (Chromosorb P, Chromosorb W and Gas Chrom Q) are given in Figs. 5–7. Figs. 5 and 6 indicate that partition does contribute to the retention of chloronaphthalene, acetophenone, and benzaldehyde. The positive intercept on the $V_n \cdot g^{-1}$ axis indicates that adsorption at the bulk liquid–structured liquid–support–gas interface must also contribute to their retention. Other factors are also involved in establishing the retention mechanism. Solute retention was always greater on Chromosorb P than for the same liquid phase loading on Chromosorb W. This would not be expected if the retention mechanism was dominated by partition with a bulk liquid phase. On the other hand, it does not necessarily indicate that adsorption at the support interface is affecting the retention mechanism, as assuming reasonable wetting of the support by the phase, the volume of the structured liquid phase would be expected to increase with increasing support surface area (the surface area of Chromosorb P being of the order of three to four times greater than for Chromosorb W). Both adsorption and partition with a structured liquid phase layer would be expected to be greater on Chromosorb P than for Chromosorb W.

Temperature can also be seen to affect the retention mechanism. At higher temperatures all solutes have a smaller $V_n \cdot g^{-1}$ intercept independent of the type of support. As the temperature is increased partition becomes more important and the

contribution from adsorption is diminished or completely absent in some cases.

A different conclusion can be reached from the data presented in Fig. 7 for the retention of nonanol and heptadecane. The change of retention volumes with increasing phase loading are generally small and in most cases negative. The above observations are in keeping with the properties expected of an adsorbent. It does not, however, indicate whether adsorption occurs at a liquid interface only, at the support surface only, or at both interfaces simultaneously. If it could be assumed that the salt wets the support surface reasonably well, then it would follow that at the high liquid phase loadings used in this study, adsorption at the gas–liquid interface makes an important contribution to the retention of alkanes and alcohols. In support of the above hypothesis, the maximum sample size which can be injected without producing peak distortion and inconsistency of retention volumes is significantly lower for alkanes and alcohols than for naphthalene, chloronaphthalene, acetophenone and benzaldehyde. Such behavior is not unusual for adsorbents, since adsorption isotherms generally have much shorter linear ranges than partition isotherms.

It is likely that the data presented in Figs. 6 and 7 for Gas Chrom Q as support are erroneous. Visual inspection of packings prepared with Gas Chrom Q indicated inefficient coating of the support. Significant amounts of packing remained firmly
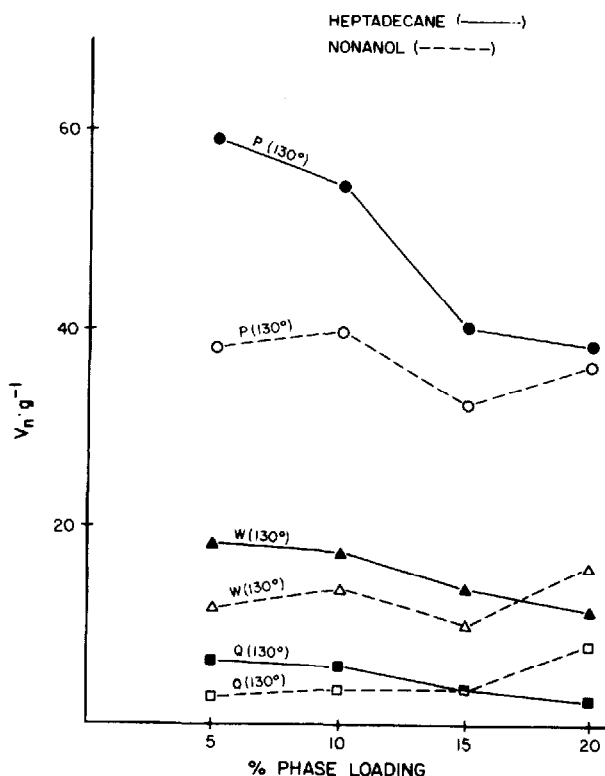

Fig. 7. Plot of net retention volume per gram of column packing (corrected to 25°C) against percent column loading of ethylpyridinium bromide. Support designations are given in Fig. 6.
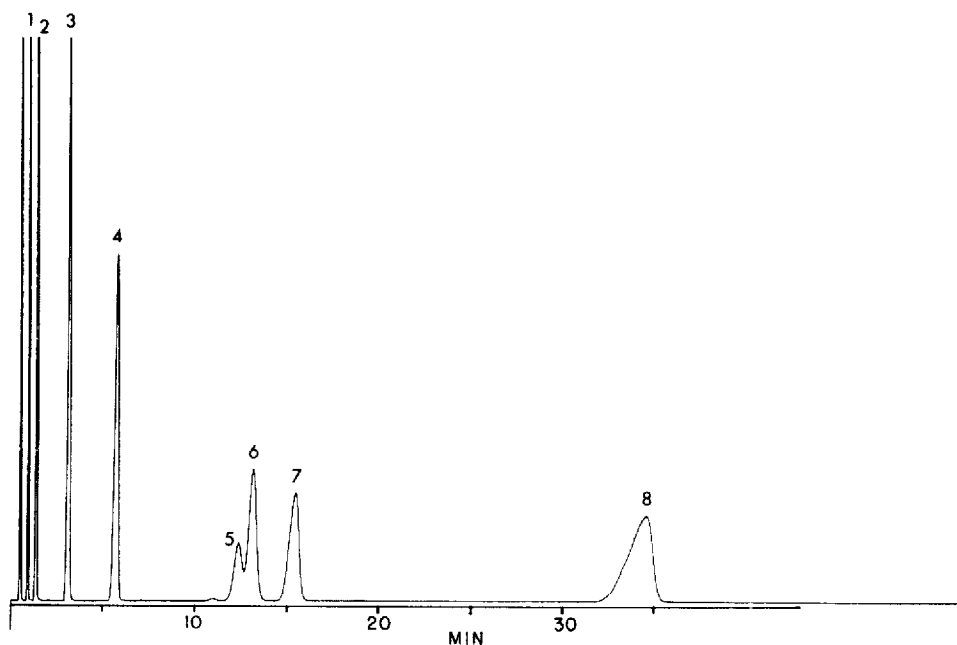
Fig. 8. Separation of substituted benzene derivatives on a 2 m × 2 mm I.D. column of 10% (w/w) tetra-n-heptylammonium chloride on Chromosorb P (100–120 mesh) at 120°C and nitrogen flow-rate 30 ml min^{-1}. Order of elution: 1 = benzene; 2 = toluene; 3 = chlorobenzene; 4 = bromobenzene; 5 = benzaldehyde; 6 = o-dichlorobenzene; 7 = iodobenzene; 8 = nitrobenzene.

attached to the coating vessel and that which was removed from the flask probably contained a lower loading of salt than indicated on the figure axes. These packings also produced very low column efficiencies. Silanized supports are not useful for preparing packings with organic molten salts.

The organic molten salts should find many uses as selective liquid phases in GLC. In the following section some of these applications will be illustrated as well as providing additional evidence to support the conclusions discussed above. Separations using ethylammonium nitrate[9] and ethylpyridinium bromide[10] are presented elsewhere. Sodium isovalerate had no useful chromatographic properties as an adsorbent or liquid phase. In all cases retention was very low and no significant selectivity to different functional groups was observed. Tetra-n-hexylammonium benzoate showed useful column selectivity but poor column efficiency. Its efficiency was felt to be too low for general chromatographic use.

Tetra-n-heptylammonium chloride

The general retention properties of tetra-n-heptylammonium chloride are illustrated in Fig. 8 for the separation of a mixture of substituted benzene derivatives. The trend in retention is clearly discernible with the least polar components of the mixture at the front of the chromatogram and components with large dipole moments at the end. Benzyl alcohol was too well retained to be eluted in a convenient analysis time. Fig. 9 shows the separation of an essential oil, in this case oil of bergamot,
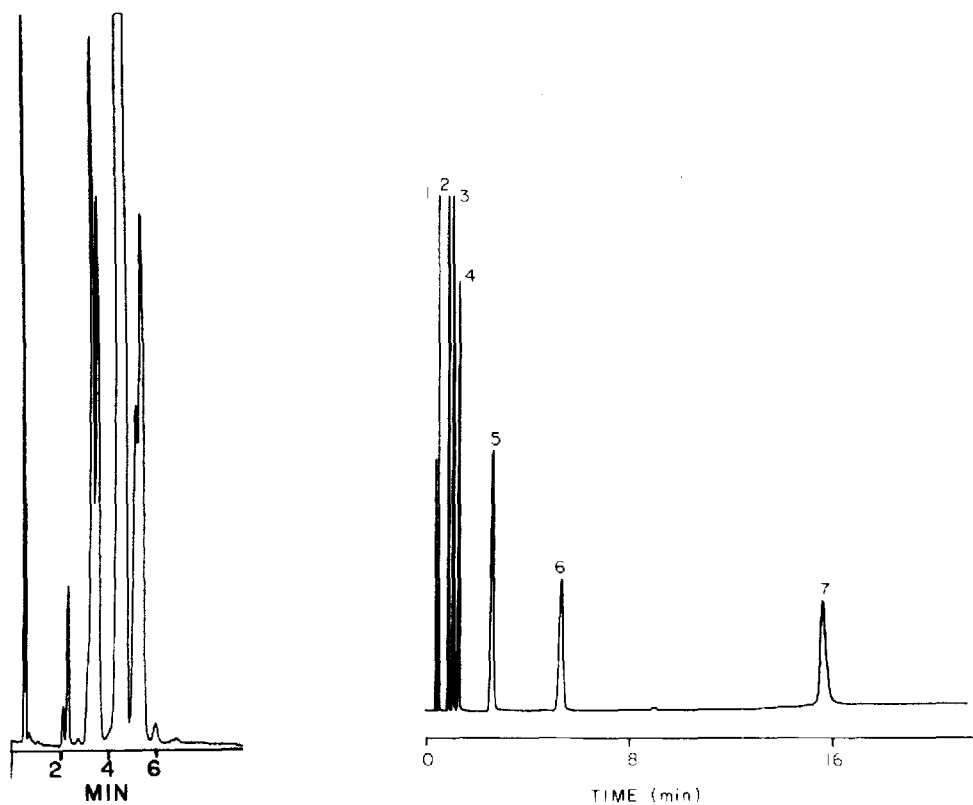
Fig. 9. Separation of oil of bergamot on the same column used in Fig. 8. Column temperature, 110°C; nitrogen flow-rate, 30 ml min⁻¹.

Fig. 10. Separation of substituted benzene derivatives on a 2 m × 2 mm I.D. column of 10% (w/w) tri-*n*-butylbenzylphosphonium chloride on Chromosorb P (100–120 mesh) and nitrogen flow-rate 30 ml min⁻¹. Isothermal for 2 min at 165°C and then temperature programmed at 5°C min⁻¹. Elution order: 1 = benzene; 2 = chlorobenzene; 3 = anisole; 4 = bromobenzene; 5 = benzaldehyde; 6 = nitrobenzene; 7 = benzyl alcohol.

under isothermal conditions. The principal components are well separated in a reasonable time.

Tri-n-butylbenzylphosphonium chloride

 The separation of substituted benzenes on tri-*n*-butylbenzylphosphonium chloride (Fig. 10) shows the same general trends as discussed for tetra-*n*-heptylammonium chloride except that the column efficiency is significantly improved and proton donor solutes such as benzyl alcohol can be eluted with good peak shape. Likewise in the polarity test mixture (Fig. 11), 5-nonanone, 1-octanol, 2,6-dimethylphenol and 2,6-dimethylaniline are eluted without peak tailing. Tri-*n*-butylbenzylphosphonium chloride provides excellent separations of alcohols as can be seen from Fig. 12, the separation of isomeric butanols, and Fig. 13, the separation of an homologous series of alcohols. In spite of the relatively high phase temperatures even the most volatile
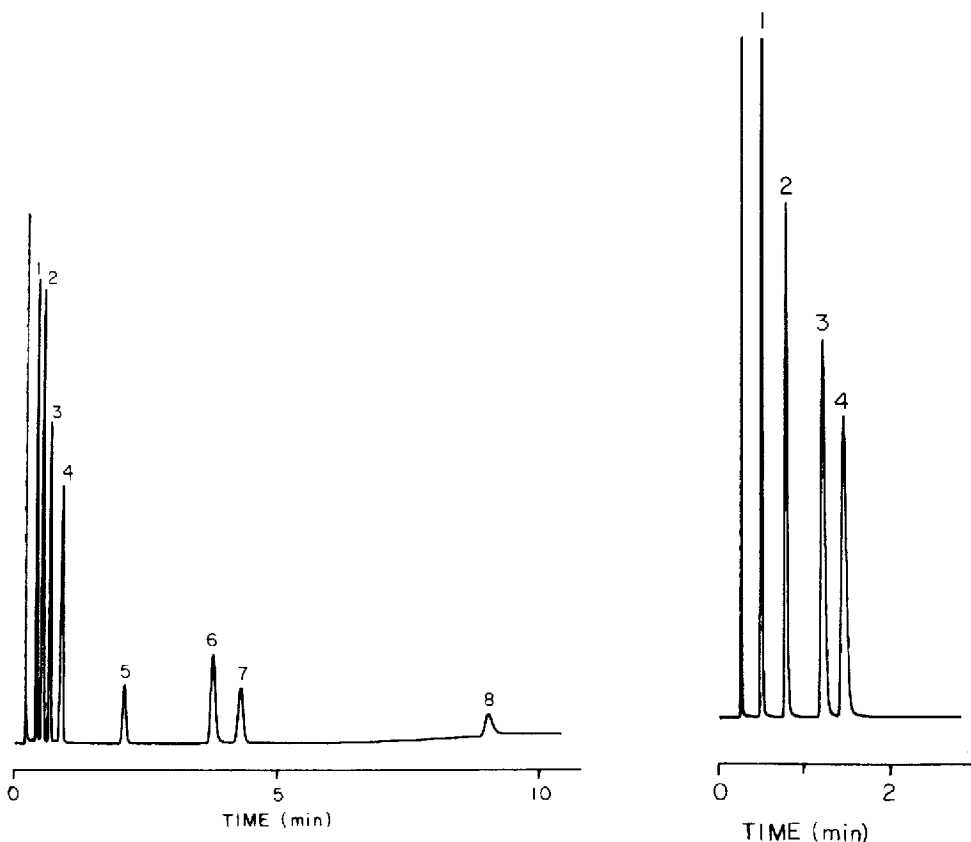
Fig. 11. Separation of polarity test probe mixture on the same column and conditions used in Fig. 10. Elution order: 1 = tridecane; 2 = 5-nonanone and tetradecane; 3 = pentadecane; 4 = hexadecane; 5 = naphthalene; 6 = 2,6-dimethylaniline; 7 = octanol; 8 = 2,6-dimethylphenol.

Fig. 12. Separation of 1 = *tert.*-butanol; 2 = *sec.*-butanol; 3 = isobutanol; 4 = *n*-butanol isothermally at 165°C. Other conditions are the same as those given in Fig. 10.

of the alcohols is significantly retained, atesting to the strength of the proton donor interactions with this phase.

Tetra-*n*-butylammonium tetrafluoroborate

This phase shows high retention and good separation of the substituted naphthalene derivatives (Fig. 14). Those derivatives capable of strong orientation interactions being retained the longest. Fig. 15 illustrates an interesting feature of this phase. Neither octanol nor 2,6-dimethylphenol could be eluted from the column at any temperature. Subsequent studies have shown that tetra-*n*-butylammonium tetrafluoroborate retains alcohols, phenols, and alkylamines excessively, and in many cases, irreversibly. This may be associated with the proton-complexing power of the tetrafluoroborate anion, but in any case, this phase should be considered unsuitable for the analysis of solutes with strong proton donor properties. It is, however, an excellent phase for the separation of solutes with permanent dipoles. For example,
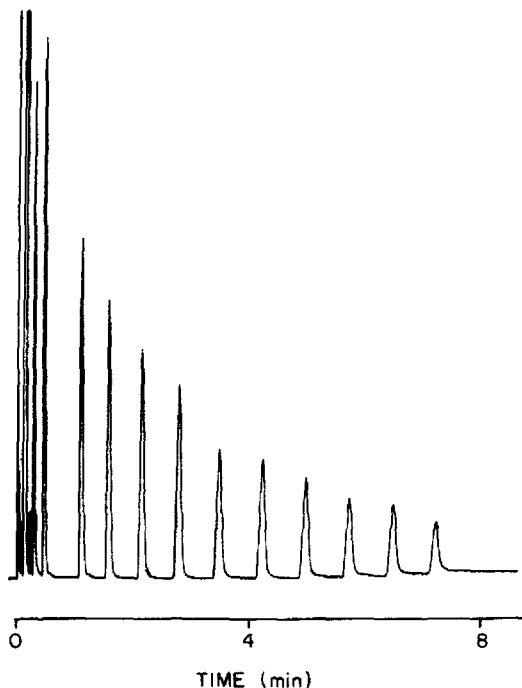
TIME (min)

Fig. 13. Separation of C_2–C_{13} *n*-alcohols, isothermally at 162°C for 3 min and then temperature programmed at 5°C min^{-1}. Other conditions are the same as those given in Fig. 10.

Fig. 16 shows a rapid separation of an homologous series of *n*-bromoalkanes and Fig. 17 the separation of Arochlor 1260.

1-Methyl-3-ethylimidazolium chloride

1-Methyl-3-ethylimidazolium chloride shows behavior typical of an adsorbent for a wide range of solutes (Fig. 18). It shows high selectivity for the separation of alkynes from alkenes. This is illustrated in Fig. 19 for the separation of decane (b.p. 174°C), decene (b.p. 181°C), and decyne (b.p. 174°C). At low column temperatures the salt shows high selectivity for alcohols (Fig. 20), but this is invariably accompanied by peak tailing. At higher temperatures this tailing disappears and alcohols are eluted with normal peak shape (Fig. 21). Tailing is observed for ketones in general on this phase (the small peak on the side of 5-nonanone in Fig. 21 is due to an impurity in the test mixture) and it is not recommended for their separation. Phenols and amines are generally too well retained to be eluted in a convenient analysis time. Good separations of essential oil extracts may be obtained on this salt as indicated in Fig. 22.

Calcium nitrate tetrahydrate

Calcium nitrate tetrahydrate was selected for study as an example of a hydrated melt. It had a usable liquid temperature range of *ca.* 40 to 180°C. The hydrated melt provides reasonable separations of hydrocarbons (Fig. 23) and useful selectivity for the separation of alkenes and alkynes (Fig. 24A). Substituted halobenzene derivatives
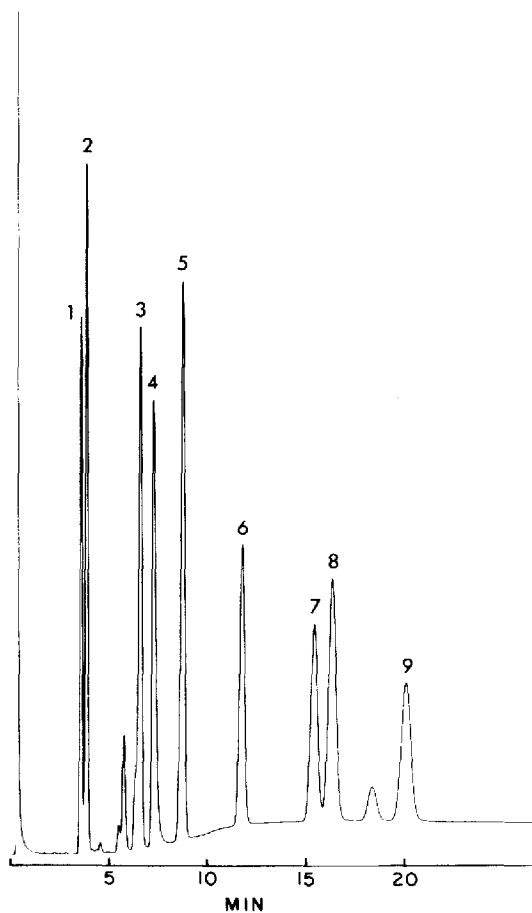
Fig. 14. Separation of substituted naphthalene derivatives on a 2 m × 2 mm I.D. column of 10% (w/w) tetra-*n*-butylammonium tetrafluoroborate on Chromosorb P (100–120 mesh) and nitrogen flow-rate 30 ml min^{-1}. The column was temperature programmed from 180 to 230°C at 5°C min^{-1} and then held at 230°C. Elution order: 1 = naphthalene; 2 = 1,4-benzodioxan; 3 = chloronaphthalene; 4 = isoquinoline; 5 = bromonaphthalene; 6 = iodonaphthalene; 7 = cyanonaphthalene; 8 = 1-acetonaphthone; 9 = nitronaphthalene.

are also eluted from the column (Fig. 24B), but some peak tailing is visible in this separation. Compounds more polar than the halobenzenes, for example certain of the McReynolds' test probes or the polarity test mixture used in Fig. 21 are either not eluted at the maximum operating temperature for the hydrated melt or are eluted with long retention times and unacceptable peak shapes. The retention of solutes with large dipole moments or hydrogen bonding functional groups was very large compared with hydrocarbons with similar boiling points. Their poor peak shape made further investigation of the retention mechanism of polar solutes pointless, although one could speculate that strong interactions with the coulombic field of the ions or displacement of water from the coordination sphere by the solute and co-ordination to the cation might be invoked to explain this behavior. Retention of
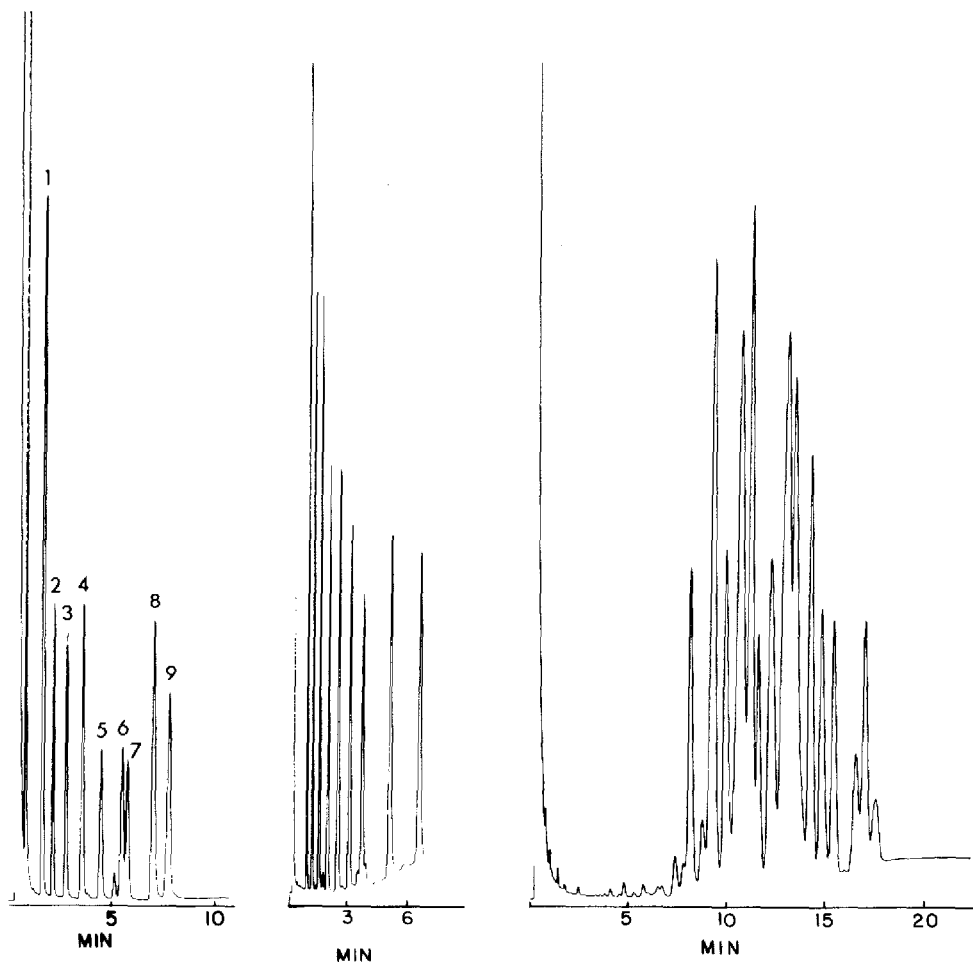
Fig. 15. Separation of polarity test mixture on the same column used in Fig. 14, temperature programmed 160°C to 260°C at 5°C min⁻¹, and nitrogen flow-rate 30 ml min⁻¹. Elution order: 1 = 5-nonanone; 2 = heptadecane; 3 = octadecane; 4 = nonadecane; 5 = eicosane; 6 = heneicosane; 7 = naphthalene; 8 = 2,6-dimethylaniline; 9 = tricosane.

Fig. 16. Separation of C_8–C_{14}, C_{16}, and C_{18} *n*-bromoalkanes on the same column used in Fig. 14. Temperature programmed from 170 to 230°C at 10°C min⁻¹.

Fig. 17. Separation of Arochlor 1260 on a 2 m × 2 mm I.D. column of 3% (w/w) tetra-*n*-butylammonium tetrafluoroborate on Chromosorb P (100–120 mesh), temperature programmed 170°C to 240°C at 4°C min⁻¹, and nitrogen flow-rate 30 ml min⁻¹.

hydrocarbons on the calcium nitrate tetrahydrate column occurs predominantly by adsorption (Fig. 25). Retention of hydrocarbons on the coated support is less than that observed with the uncoated support and it must be considered that the hydrated melt may simply act to diminish the adsorptive activity of the support and may not contribute to the retention process directly.
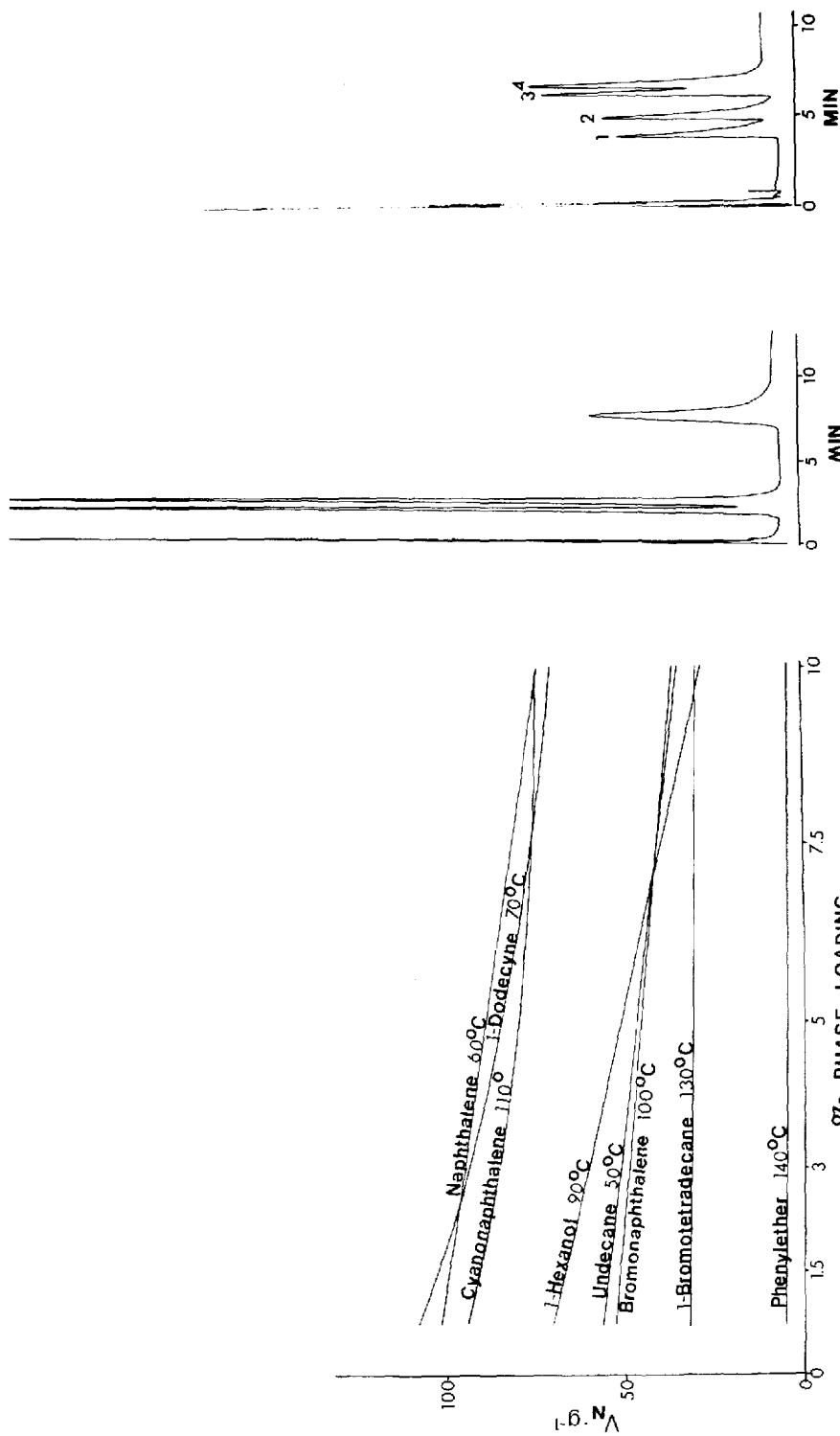
Fig. 18. Retention behavior of a series of solutes on 1-methyl-3-ethylimidazolium chloride at different phase loadings.

Fig. 19. Separation of decane, decene, and decyne on a 0.5 m × 2 mm I.D. column of 5% (w/w) 1-methyl-3-ethylimidazolium chloride on Chromosorb P (100–120 mesh) at 40°C with a nitrogen flow-rate of 30 ml min⁻¹.

Fig. 20. Separation of 1 = *tert.*-butanol; 2 = *sec.*-butanol; 3 = isobutanol; 4 = *n*-butanol on a 2 m × 2 mm I.D. column of 5% (w/w) 1-methyl-3-ethylimidazolium chloride on Chromosorb P (100–120 mesh), temperature programmed from 55 to 95°C at 5°C min⁻¹ and nitrogen flow-rate of 30 ml min⁻¹.
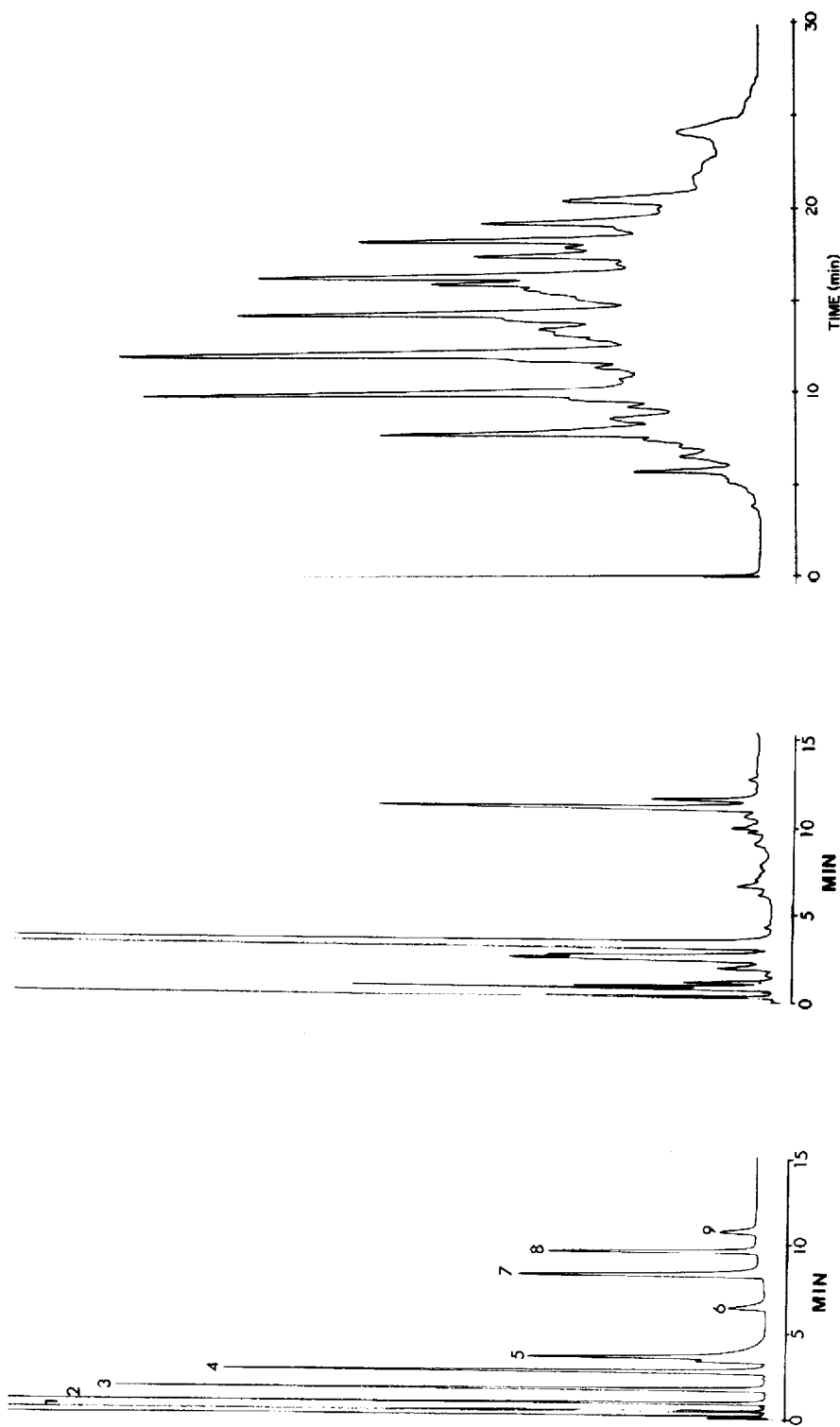
Fig. 21. Separation of 1 = nonane; 2 = decane; 3 = undecane; 4 = dodecane; 5 = 5-nonanone; 6 = 2,6-dimethylaniline; 7 = 1-octanol; 8 = naphthalene; 9 = 2,6-dimethylphenol on the same column used in Fig. 20. Temperature programmed from 70°C to 160°C at 10°C min^{-1} and then held isothermally at 160°C, nitrogen flow-rate 30 ml min^{-1}.

Fig. 22. Separation of oil of thyme on a 1.0 m × 2.0 mm I.D. column of 10% (w/w) 1-methyl-3-ethylimidazolium chloride on Chromosorb W (100-120 mesh), temperature programmed 55 to 165°C at 10°C min^{-1}, and nitrogen flow-rate 35 ml min^{-1}.

Fig. 23. Separation of fuel oil number 1 on a 0.5 m × 2 mm I.D. column of 10% (w/w) calcium nitrate tetrahydrate on Chromosorb P (100-120 mesh), temperature programmed from 40°C to 135°C at 5°C min^{-1}, and nitrogen flow-rate 30 ml min^{-1}.
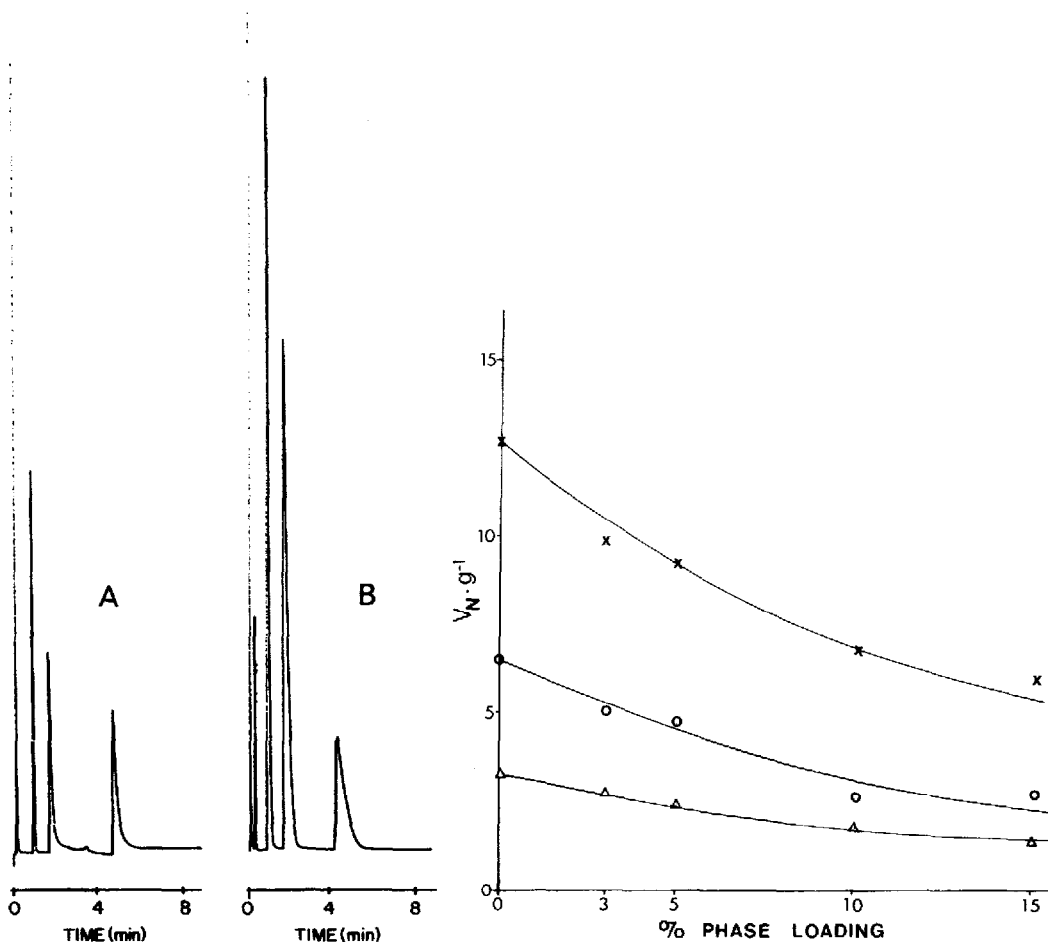
Fig. 24. (A) Separation of decane, decene, and decyne. Same column as in Fig. 23, temperature pro-grammed from 70 to 100°C at 5°C min^{-1}, and nitrogen flow-rate 30 ml min^{-1}. (B) Separation of benzene, chlorobenzene, bromobenzene, and iodobenzene on a 0.5 m × 2 mm I.D. column of 15% (w/w) calcium nitrate tetrahydrate on Chromosorb P (100–120 mesh), column temperature 40°C, and nitrogen flow-rate 30 ml min^{-1}.

Fig. 25. Retention of (×) dodecane, (○) undecane, and (△) decane at different phase loadings of calcium nitrate tetrahydrate on Chromosorb P (100–120 mesh). Column temperature, 100°C.

CONCLUSIONS

   The organic molten salts are a new and useful series of liquid phases for GC. Phases with high temperature liquid ranges provide column efficiencies equivalent to those expected for non-ionic liquids. The selective retention of polar solutes is gov-erned by the strength of orientation and proton donor interactions. Retention of solutes may not depend solely on partition and, at least in some cases, adsorption may contribute to or dominate the retention mechanism.

ACKNOWLEDGEMENTS

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