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VARIATION IN THE GAS CHROMATOGRAPHIC STATIONARY PHASE PROPERTIES OF TETRA-*n*-BUTYLAMMONIUM SALTS AS A FUNCTION OF THE ANION TYPE

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SUMMARY

The gas chromatographic stationary phase properties of fifteen tetra-*n*-butylammonium salts containing chloride, bromide, iodide, nitrate, nitrite, thiocyanate, perchlorate, hexafluorophosphate, tetrabutylborate, tetraphenylborate, picrate, tetrafluoroborate, 4-toluenesulfonate, methanesulfonate, and trifluoromethanesulfonate anions are described. For five of these salts the liquid temperature range exceed 100°C: 4-toluenesulfonate (55–200°C), tetrafluoroborate (162–290°C), trifluoromethanesulfonate (112–240°C), picrate (90–200°C), and methanesulfonate (79–180°C). The tetra-*n*-butylammonium salts exhibit unique solute selectivity, manifested in very weak dispersion and proton donor interactions, accompanied by strong orientation and proton acceptor interactions. For the anions picrate, tetrabutylborate, trifluoromethanesulfonate, 4-toluenesulfonate, nitrate, methanesulfonate, bromide, nitrite, and chloride dipole interactions are fairly constant and change little with the anion type (except for chloride), while the proton acceptor capability of the salts is a strong function of the anion type, increasing in the following order: picrate $\approx$ trifluoromethanesulfonate $<$ 4-toluenesulfonate $<$ nitrate $\approx$ methanesulfonate $<$ bromide $<$ nitrite $<$ chloride. The retention of organic solutes on tetra-*n*-butylammonium 4-toluenesulfonate, trifluoromethanesulfonate, methanesulfonate, picrate, and chloride salts occurs primarily by gas–liquid partition. Gas–liquid adsorption makes a small but significant contribution to the retention of hydrocarbons and to a lesser extent that of pyridine, but in general, does not contribute to the retention of polar solutes. The chromatographic characteristics of the tetra-*n*-butylammonium salts are illustrated by the separation of some essential oils.

INTRODUCTION

Organic molten salts are useful selective polar stationary phases for gas chromatography[1–7]. When coated onto diatomaceous supports or suface-modified glass open-tubular columns, they show acceptable chromatographic performance and selective retention of organic solutes by orientation and proton donor–acceptor interactions.

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Organic molten salts first attracted our attention for use as novel stationary phases for three primary reasons. Their synthesis is relatively straightforward and, as a wide range of ions with different properties exist, an equally wide variety of stationary phases with different characteristics are easily accessible. As the molten salts have a well-defined chemical structure, they are suitable for use as reference phases. Organic molten salts are unique among stationary phases in current use in that they contain charge-bearing groups. The coulombic forces present in these salts provide an additional interaction that is absent in covalent liquids and can be exploited to control selectivity.

In many aspects of their chemistry, the properties of the organic molten salts are poorly understood. Several reviews of organic molten salt chemistry exist[8–11], but much of the available material is not applicable to an understanding of their chromatographic properties. As a general model, it is assumed that in the melt the organic salts are comprised of ion pairs and free ions. The proportion of ion pairs to free ions is a function of the ion type and may also vary with temperature. Intermolecular interactions between ions and ion pairs can result in the formation of aggregates, containing several ion pairs and/or ions.

In this paper, we wish to discuss the influence of anion type on the chromatographic properties of a series of organic molten salts. Tetra-*n*-butylammonium salts were selected for study, because they are readily available commercially and melting point tables indicated that a reasonable number of low-temperature melts could be obtained among the different anions to be studied. Also, the large centrally symmetric tetra-*n*-butylammonium ion has a low charge–ion size ratio and, as it lacks hydrogen-bonding groups, it tends to form simple ion pairs rather than ion aggregates. This should simplify the interpretation of the chromatographic data in terms of the contributions made by the anion to thermal stability, selectivity, etc.

Only a few of the tetra-*n*-butylammonium salts evaluated here have been studied above their melting point before. Walden[12,13] made studies of the conductivity of the tetra-*n*-butylammonium picrate, iodide, and perchlorate salts. Decomposition of the iodide was observed at temperatures above 150–155°C while the picrate and perchlorate salts were stable to at least 200–220°C. Lampreia and Barreira[14,15] have made a detailed study of the density, viscosity, and conductivity of tetra-*n*-butylammonium picrate over the temperature range 89.5–193.5°C. Within this temperature range, the salt was thermodynamically stable. Likewise, Griffiths[16] determined the liquid densities of tetra-*n*-butylammonium bromide and iodide over the temperature range 123–146 and 149–169°C, respectively, without observing any decomposition of the salts. Lind *et al.*[17] determined the liquid densities, viscosities, and specific conductivities of tetra-*n*-butylammonium bromide (119–135°C), iodide (147–167°C), tetrafluoroborate (162–266°C), hexafluorophosphate (256–281°C), and tetraphenylborate (240–270°C) under an argon atmosphere. Lind *et al.* also proposed a model to fit the transport properties of the molten salts to their liquid structure, which may be of interest to chromatographers. The dipole moments of tetra-*n*-butylammonium bromide (12.2 D), picrate (15.3 D), chloroacetate (14.8 D), benzoate (12.1 D), and acetate (11.2 D) in benzene have been determined[18]. These values may be very different from those pertaining to the conditions in the melt but are illustrative of the dipolar character of organic salts.

EXPERIMENTAL

Tetra-*n*-butylammonium bromide, chloride, hexafluorophosphate, hydrogensulfate, iodide, methanesulfonate, nitrate, nitrite, perchlorate, tetrafluoroborate, thiocyanate, and 4-toluenesulfonate were obtained from Fluka (Hauppauge, NY, U.S.A.). Tetra-*n*-butylammonium tetrabutylborate and tetraphenylborate were obtained from Alfa Products (Danvers, MA, U.S.A.) and tetra-*n*-butylammonium picrate from RSA Corp. (Ardsley, NY, U.S.A.). All salts were recrystallized to constant melting point prior to use. Oil of bergamot and oil of rosemary were obtained from Lorann Oils (Lansing, MI, U.S.A.) and cold-pressed lemon oil from Sunkist Growers (Ontario, CA, 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 1 to 15% (w/w) of the tetra-*n*-butylammonium salts on Chromosorb W-AW (100–120 mesh) were prepared using the rotary evaporator technique. The Chromosorb support was sieved prior to coating with the organic salts, dissolved in methylene chloride. After coating, the damp packing was dried in a fluidized-bed drier and then packed into glass columns, 1–3.5 m in length 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 injectors, a temperature-programmable column oven, and flame-ionization detector was used. Separation conditions are given in the legends to tables and figures.

Decomposition temperatures for the salts were determined by sealing a small sample of the pure salt in a melting point capillary and slowly raising its temperature

TABLE I

COLUMN OPERATING CHARACTERISTICS FOR TETRA-*n*-BUTYLAMMONIUM SALTS

Tetra-n-butylammonium salt	*Melting point (°C)*	*Decomposition temperature* (°C)*	*Maximum operating temperature (°C)*	*Liquid temperature range (°C)*	*Average column efficiency (n/m)***
4-Toluenesulfonate	55	230 B	200	145	2000–2500
Tetrafluoroborate	162	320 D	290	128	2500–3000
Trifluoromethanesulfonate	112	270 B, D	240	128	1200–1700
Picrate	90	200 D	200	110	2500–3000
Methanesulfonate	79	220 B	180	101	2000–3000
Chloride	41	200 D	110	70	1500–2000
Nitrate	118	210 D	180	62	800–1300
Nitrite	81	180 B	110	29	500–1000
Tetraphenylborate	236	270 D	260	24	100–600
Hexafluorophosphate	247	270 D	260	13	500–1000
Perchlorate	208	220 D	220	12	1000–1500
Tetrabutylborate	109	170 D, B	–	–	2000–2500
Bromide	119	200 D	–	–	1000–1500
Iodide	146	230 D	–	–	500–1000
Thiocyanate	123	220 D	–	–	200–500

* B = vapor bubbles formed; D = discoloration (see Experimental section for details).

** Approximate values for a variety of test solutes on columns containing 10% (w/w) of salt.

in a hot-block melting point apparatus until visible signs of decomposition (D) or volatilization (B) were observed. The results of these experiments are summarized in Table I, together with the maximum column operating temperature.

RESULTS AND DISCUSSION

The column operating characteristics of the fifteen tetra-*n*-butylammonium salts are summarized in Table I. The minimum column operating temperature is given as the melting point of the salt and the maximum allowable column operating temperature as the highest temperature at which the column could be maintained for 24 h without change in retention or peak shape in a test chromatogram, obtained at a lower temperature before and after the conditioning period. The temperature difference between the melting point and the maximum allowable column operating temperature defines the liquid temperature range for the salts. The entries in Table I are organized by decreasing liquid temperature range and vary from the widest range of 145°C for tetra-*n*-butylammonium 4-toluenesulfonate to 12°C for tetra-*n*-butylammonium perchlorate. The tetra-*n*-butylammonium tetrabutylborate, bromide, iodide, and thiocyanate salts showed substantial column bleed at their melting points and are not acceptable stationary phases for chromatographic purposes. These same salts, when sealed in a melting point capillary, did not show any visible evidence of decomposition until temperatures well above their melting points were reached, Table I. The reason for their poor column thermal stability is not known at present but may be the result of catalytic decomposition induced by support impurities. The average column efficiency for a variety of test solutes on the molten salt phases is also summarized in Table I. The average column efficiency for individual salts is quite variable but the values obtained for the salts with the widest liquid temperature

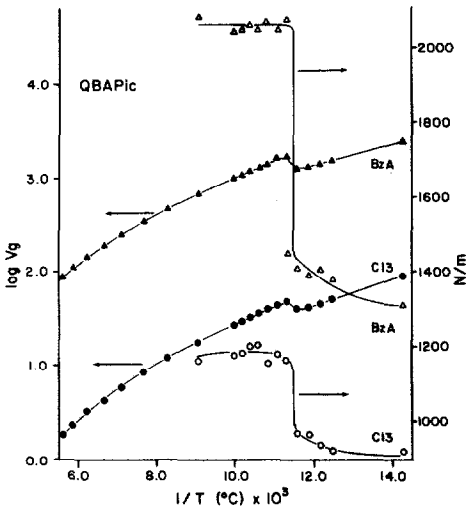


Fig. 1. Plot of log of the specific retention volume and column efficiency (plates per meter) as a function of column temperature for benzaldehyde (BzA) and *n*-tridecane (C13) on the stationary phase tetra-*n*-butylammonium picrate (QBAPic).

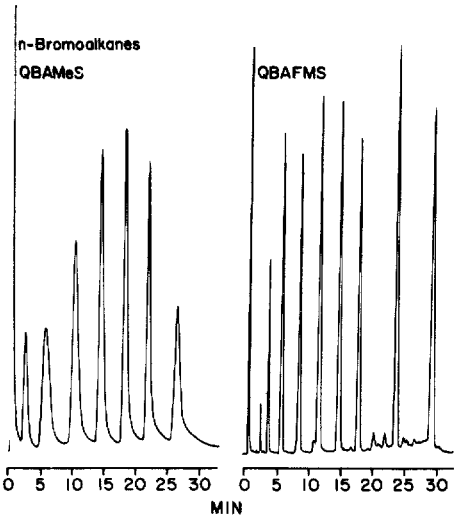


Fig. 2. Separation of a homologous series of *n*-bromoalkanes by gas–solid chromatography on tetra-*n*-butylammonium methanesulfonate (QBAMeS) (C_5–C_{11}) and by gas–liquid chromatography on tetra-*n*-butylammonium trifluoromethanesulfonate (QBAFMS) (C_8–C_{14}, C_{16}, C_{18}). Each column was 2 m × 2 mm I.D. and was packed with 10% (w/w) salt on Chromosorb W-AW (100–120 mesh). The QBAMeS column was held isothermally at 30°C for 5 min and then temperature programmed at 3°C/min to 80°C. The QBAFMS column was held isothermally at 115°C for 5 min and then temperature programmed at 3°C/min to 180°C. In both cases the carrier gas was nitrogen at a flow-rate of 30 ml/min.

ranges, and therefore the salts most useful for gas chromatography, were generally acceptable. In several cases there is no difference between the efficiency of the molten salt columns and similar ones prepared using standard liquid phases.

Plots of log V_g^0 *vs.* $1/T$ were made for the first seven salts listed in Table I. As a representative example the results for tetra-*n*-butylammonium picrate are shown in Fig. 1. In all cases, the only phase transition observed corresponded to the bulk melting point of the salt. At the melting point, a fairly large increase in efficiency was observed that may or may not be accompanied by a large change in retention of the test solutes, depending on the salt under investigation. The efficiency of all the tetra-*n*-butylammonium salts below their melting point was comparatively low, limiting the value of these salts for gas–solid chromatography. A representative example of the column performance of the tetra-*n*-butylammonium salts in the gas-solid mode is shown in Fig. 2 for the separation of a mixture of *n*-bromoalkanes on tetra-*n*-butylammonium methanesulfonate. For contrast, in the same figure, a similar mixture of *n*-bromoalkanes is separated above the melting point on tetra-*n*-butylammonium trifluoromethanesulfonate. The improved performance for the liquid salt is clearly discernible. It was also observed with the methanesulfonate salt that at temperatures above 120°C, within its liquid temperature range, the injection of *n*-bromoalkanes caused rapid column degradation. The methanesulfonate salt was the only salt of those studied that showed any evidence of on-column chemical reaction. Substances containing many different types of functional groups have been separated during these studies without noticeable change in peak shape or loss of injected mass on the column. Therefore, in general, undesirable solute-phase chemical reactions are not a significant problem.

TABLE II

McREYNOLDS CONSTANTS FOR SOME TETRA-*n*-BUTYLAMMONIUM SALTS AT 120°C

TBB = tetrabutylborate; Pic = picrate; FMS = trifluoromethanesulfonate; pTS = 4-toluenesulfonate; MeS = methanesulfonate; Br = bromide; Nat = nitrate; Cl = chloride; Nit = nitrite.

Test solute	*Symbol*	*Anion*								
		TBB	*Pic*	*FMS*	*pTS*	*MeS*	*Br*	*Nat*	*Cl*	*Nit*
Benzene	X′	223	323	352	335	342	308	414	370	403
Butanol	Y′	640*	518	670	844	940	1053	930	1198	1096
2-Pentanone	Z′	401	439	485	425	424	468	502	434	482
Nitropropane	U′	441	612	694	692	720	785	802	769	797
Pyridine	S′	359	534	598	575	594	669	693	632	679
2-Methyl-2-pentanol	H′	254	390	509	628	715	797	717	921	841
Iodobutane	J′	−9	286	285	205	201	230	445	101	721
2-Octyne	K′	102	147	167	190	183	207	185	194	215
Dioxane	L′	308	447	471	433	441	486	525	443	505
cis-Hydrindane	M′	87	173	168	190	180	206	211	192	204

* Broad tailing peak unreliable assigned.

The McReynolds constants for the nine liquid tetra-*n*-butylammonium salts at 120°C are summarized in Table II. The most noticeable general features of the tetra-*n*-butylammonium salts are the very weak dispersion and proton donor interactions, combined with strong orientation and proton acceptor capability. In this respect, the tetra-*n*-butylammonium salts are unique among the stationary phases currently used in gas–liquid chromatography.

The influence of anion type on the gas chromatographic selectivity of the tet-

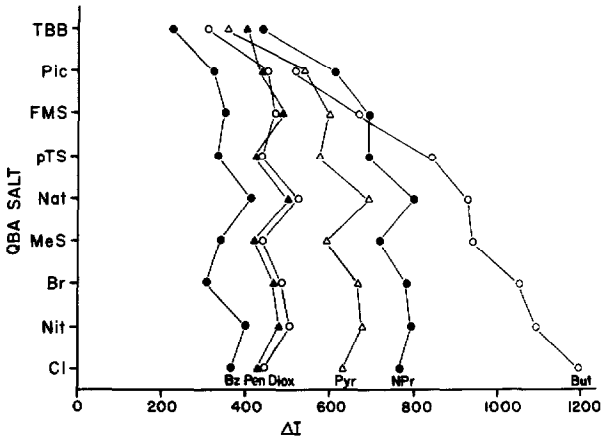


Fig. 3. Variation of retention index differences for six McReynolds probes on nine tetra-*n*-butylammonium salts. The anions are ordered by increasing proton acceptor capability. TBB = tetrabutylborate, Pic = picrate, FMS = trifluoromethanesulfonate, pTS = 4-toluenesulfonate, Nat = nitrate, MeS = methanesulfonate, Br = bromide. Nit = nitrite, and Cl = chloride. Test solutes: Bz = benzene, Pen = 2-pentanone, Diox = dioxane, Pyr = pyridine, NPr = 1-nitropropane, and But = 1-butanol.

TABLE III

SPECIFIC RETENTION VOLUMES FOR SOME TEST SOLUTES ON A SERIES OF TETRA-*n*-BUTYLAMMONIUM SALTS AT 120°C

TBB = tetrabutylborate; Pic = picrate; FMS = trifluoromethanesulfonate; pTS = 4-toluenesulfonate; MeS = methanesulfonate; Br = bromide; Nat = nitrate; Cl = chloride; Nit = nitrite.

Test solute	*Anion*								
	pTS	*FMS*	*Pic*	*MeS*	*Cl*	*Nat*	*Nit*	*TBB*	*Br*
Benzene	18.6	18.4	23.2	21.0	24.4	25.2	25.9	28.0	21.6
Toluene	30.7	30.5	41.5	32.8	37.1	39.6	37.8	52.0	36.7
Xylene	45.9	45.0	66.9	48.8	55.1	57.9	56.4	85.4	53.6
Ethylbenzene	46.8	45.5	63.9	49.3	55.5	58.3	56.9	87.3	54.0
Chlorobenzene	93.2	73.9	93.1	104.0	134.6	123.7	122.2	102.2	124.4
Bromobenzene	176.6	133.7	180.7	195.7	261.6	233.8	232.5	193.7	243.2
o-Dichlorobenzene	412.2	266.0	343.3	444.5	623.3	509.1	517.2	356.2	537.0
Iodobenzene	393.2	266.9	404.7	448.0	845.9	539.5	587.1	413.4	759.5
Benzaldehyde	822.3	403.6	528.1	592.0	1140.6	759.3	755.9	542.3	788.4
Acetophenone	801.2	734.0	1040.0	913.1	2342.6	1154.9	1093.4	1155.8	1082.2
Nitrobenzene	1419.4	986.8	1340.0	1633.9	3228.7	1968.1	1996.3	1269.7	2058.5
Aniline	2147.3	1168.5	1137.7	3349.4	5543.7	3148.9	4621.2	768.9	4017.6
Hexanol	534.4	193.7	158.6	896.1	3254.2	637.4	1325.4	2373.3*	1209.6

* Broad, tailing peak, unreliably assigned.

ra-*n*-butylammonium salts is illustrated in Fig. 3. The McReynolds constants for the first five probes and dioxane are ordered by increasing proton acceptor capability. Varying the anion has only a small effect on dispersive or proton donor interactions, even for relatively large lipophilic anions, such as tetrabutylborate and 4-toluenesulfonate. Changes in the anion type (if tetrabutylborate is ignored) do not cause large changes in the orientation interactions. These interactions are strong and of

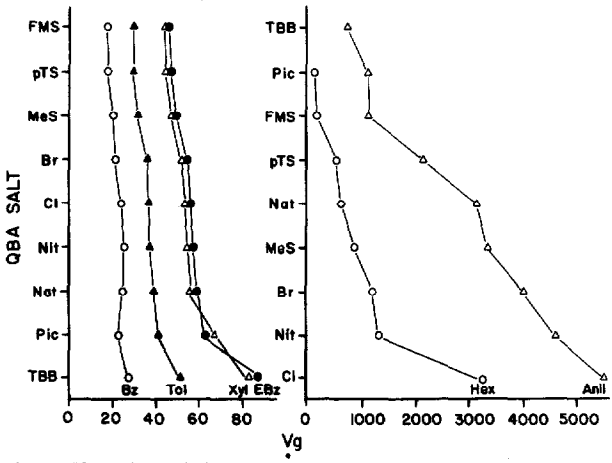


Fig. 4. Variation of the specific retention volume for dispersive and proton donor test solutes on nine tetra-*n*-butylammonium salts. The abbreviations used for the anions are identified in Fig. 3. Bz = benzene, Tol = toluene, EBz = ethylbenzene, Xyl = xylene, Hex = 1-hexanol, and Anil = aniline.

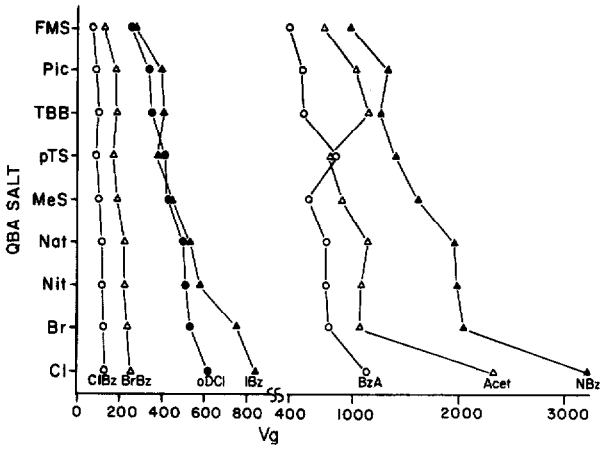


Fig. 5. Variation of the specific retention volume for dipolar test solutes on nine tetra-*n*-butylammonium salts. The anions are ordered by increasing strength of orientation interactions. ClBz = chlorobenzene, BrBz = bromobenzene, oDCl = *o*-dichlorobenzene, IBz = iodobenzene, BzA = benzaldehyde, Acet = acetophenone, and NBz = nitrobenzene. The abbreviations used for the anions are identified in Fig. 3.

similar magnitude for all salts. However, changing the anion type has a profound effect on the proton acceptor capability of the tetra-*n*-butylammonium salts.

To confirm the above observations, the specific retention volumes for a series of substituted benzene derivatives and hexanol were measured on the nine tetra-*n*-butylammonium salts, listed in Table II. The results are summarized in Table III. For interpretative purposes the specific retention volumes of the test solutes are ordered by increasing dispersion and proton acceptor interactions in Fig. 4 and by increasing orientation interactions in Fig. 5. The specific retention volumes change little for benzene, toluene, xylene, and ethylbenzene as a function of the anion type. However, the proton-donor solutes, hexanol and aniline, are retained much longer, in general, than the probes for dispersion and retention increases with changes in the anion type as indicated: picrate $\approx$ trifluoromethanesulfonate $<$ 4-toluenesulfonate $<$ nitrate $\approx$ methanesulfonate $<$ bromide $<$ nitrite $<$ chloride.

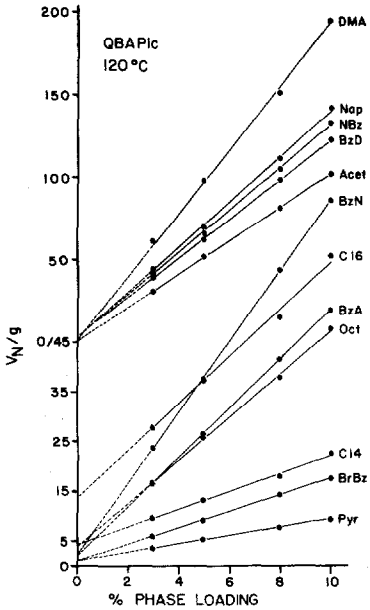
Intuitively, one might expect this order to reflect the increasing basicity of the anion, but unfortunately no independently derived scale of anion basicities in organic molten salts is available for comparison. For the probes used to measure orientation interactions, chlorobenzene (1.55 D), bromobenzene (1.55 D), *o*-dichlorobenzene (2.2 D), iodobenzene (1.36–1.43 D), benzaldehyde (2.96 D), acetophenone (3.1 D), and nitrobenzene (4.18 D), retention increases with increasing dipole moment if volatility differences are taken into consideration. Also, the change in retention for the individual probes is not a strong function of the anion type, except for the chloride anion, for which orientation interactions seem to be significantly stronger than for the other salts.

Retention in gas–liquid chromatography is the sum of several contributions, principal among which are gas–liquid partition, gas–liquid adsorption, gas–liquid partition with a structured liquid phase layer, gas–liquid adsorption at the structured liquid phase layer, and gas–solid adsorption at the support interface (for a detailed

TABLE IV

COEFFICIENTS FOR PLOTS OF V_N/g (Y) AGAINST PHASE LOADING (X) FOR SEVERAL TEST SOLUTES ON TETRA-*n*-BUTYLAMMONIUM SALTS AT 120°C

Anion	*Test solute*	*Slope*	*Standard deviation*	*Intercept*	*Standard deviation*	*Correlation coefficient*
4-Toluenesulfonate	Pyridine	0.932	0.066	0.635	0.467	0.9900
	Bromobenzene	2.005	0.098	0.357	0.691	0.9952
	Benzaldehyde	6.185	0.157	−0.904	1.104	0.9987
	Octanol	20.246	0.590	−1.297	4.152	0.9983
	Benzonitrile	9.967	0.223	−1.553	1.568	0.9990
	Acetophenone	9.889	0.177	−1.857	1.244	0.9994
	1,4-Benzodioxan	16.381	0.440	−0.729	3.097	0.9986
	Nitrobenzene	16.256	1.084	7.603	7.629	0.9911
	Naphthalene	12.117	0.259	−1.441	1.825	0.9991
	2,6-Dimethylaniline	29.690	0.828	−0.693	5.825	0.9984
	n-Hexadecane	4.325	0.082	3.316	0.574	0.9993
	n-Octadecane	11.345	0.119	8.017	0.840	0.9998
Methanesulfonate	Pyridine	0.994	0.057	0.479	0.400	0.9935
	Bromobenzene	2.098	0.035	0.226	0.244	0.9994
	Benzaldehyde	6.446	0.090	0.168	0.063	0.9996
	Octanol	26.646	0.254	7.827	1.785	0.9998
	Benzonitrile	10.401	0.136	0.174	0.954	0.9997
	Acetophenone	10.276	0.136	−0.916	0.955	0.9996
	1,4-Benzodioxan	16.951	0.225	−0.232	1.584	0.9996
	Nitrobenzene	17.953	0.244	0.506	1.717	0.9996
	Naphthalene	12.479	0.283	0.170	1.994	0.9990
	2,6-Dimethylaniline	34.641	0.332	−0.103	2.339	0.9998
	n-Hexadecane	3.930	0.075	5.533	0.528	0.9993
	n-Octadecane	9.920	0.110	16.019	0.772	0.9998
Trifluoromethane-sulfonate	Pyridine	0.848	0.045	0.761	0.316	0.9944
	Bromobenzene	1.483	0.041	0.357	0.288	0.9985
	Benzaldehyde	4.576	0.063	−0.201	0.441	0.9996
	Octanol	6.017	0.076	0.329	0.533	0.9997
	Benzonitrile	7.085	0.116	−0.615	0.818	0.9995
	Acetophenone	8.222	0.145	0.422	1.020	0.9994
	1,4-Benzodioxan	10.969	0.140	−0.879	0.987	0.9997
	Nitrobenzene	11.156	0.091	−0.037	0.638	0.9999
	Naphthalene	10.747	0.160	−0.731	1.123	0.9996
	2,6-Dimethylaniline	16.729	0.206	0.459	1.449	0.9997
	n-Hexadecane	3.539	0.068	1.307	0.475	0.9993
	n-Octadecane	8.807	0.181	3.218	1.276	0.9991
Picrate	Pyridine	0.854	0.019	1.011	0.131	0.9991
	Bromobenzene	1.719	0.023	0.604	0.162	0.9996
	Benzaldehyde	5.027	0.037	1.512	0.257	0.9999
	Octanol	4.368	0.091	3.742	0.641	0.9991
	Benzonitrile	7.219	0.046	1.860	0.322	0.9999
	Acetophenone	10.152	0.118	0.787	0.833	0.9997
	1,4-Benzodioxan	12.058	0.110	2.462	0.775	0.9998
	Nitrobenzene	13.076	0.273	1.771	1.923	0.9991
	Naphthalene	14.053	0.271	0.713	1.905	0.9993
	2,6-Dimethylaniline	18.967	0.612	3.168	4.308	0.9979
	n-Hexadecane	1.824	0.080	4.062	0.563	0.9962
	n-Octadecane	4.902	0.286	12.657	2.012	0.9932



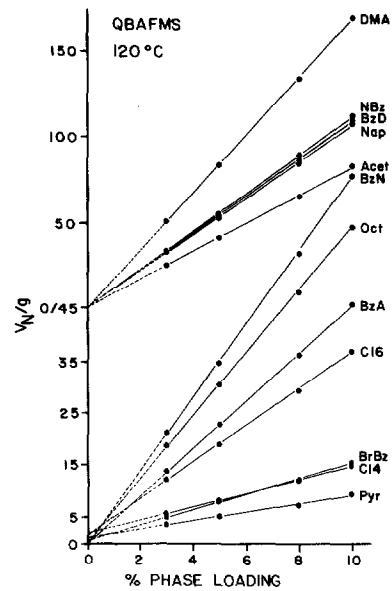


Fig. 6. Plot of V_N/g as a function of percent phase loading for a series of test solutes on tetra-*n*-butylammonium picrate (QBAPic). DMA = 2,6-dimethylaniline, Nap = naphthalene, NBz = nitrobenzene, BzD = 1,4-dibenzodioxan, Acet = acetophenone, BzN = benzonitrile, C16 = hexadecane, BzA = benzaldehyde, Oct = octanol, C14 = tetradecane, BrBz = bromobenzene, and Pyr = pyridine.

Fig. 7. Plot of V_N/g as a function of percent phase loading for a series of test solutes on tetra-*n*-butylammonium trifluoromethanesulfonate (QBAFMS). The abbreviations are identified in Fig. 6.

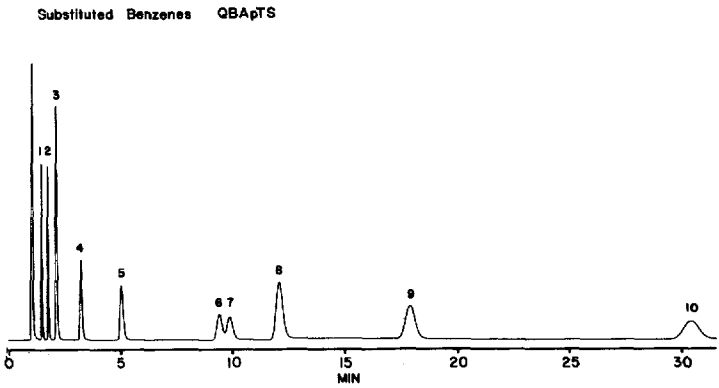


Fig. 8. Separation of a mixture of substituted benzene derivatives on a 3.5 m × 2 mm I.D. column of 10% (w/w) tetra-*n*-butylammonium 4-toluenesulfonate (QBApTS) on Chromosorb W-AW (100–120 mesh) at 140°C with a nitrogen carrier gas flow-rate of 15.0 ml/min. Peak assignments: 1 = benzene, 2 = toluene, 3 = ethylbenzene, 4 = chlorobenzene, 5 = bromobenzene, 6 = iodobenzene, 7 = *o*-dichlorobenzene, 8 = benzaldehyde, 9 = acetophenone, and 10 = nitrobenzene.

review see refs. 19 and 20). To determine the absolute contribution of the various partition and adsorption mechanisms to retention is a very difficult task. The stationary phase characteristics (volume of liquid phase, surface area of the liquid phase, and surface area of the support) must be determined for a minimum of five column packings with different phase loadings as well as an estimate of the thickness of the structured liquid phase layer, obtained by a combination of intuition and iteration[20]. A less demanding approach, and the one adopted here, was first proposed by Martin[21]. Martin showed that the relative contribution of adsorption and partition to the retention mechanism can be discerned from a plot of the net retention volume per gram of packing (V_N/g), corrected to 20°C, as a function of the percent stationary phase loading. A plot of V_N/g against phase loading for a partition mechanism should be a straight line, which, when extrapolated to zero phase loading, passes through the origin. Likewise, for an adsorption mechanism, a similar plot should show little change in retention as a function of phase loading and a postive *y*-intercept when extrapolated to zero phase loading. This treatment cannot distinguish between partition or adsorption occurring at the various interfaces, but to a first approximation, if the liquid phase shows good support wetting and deactivating characteristics and if measurements are made at fairly high stationary phase loadings, then it can be assumed that the dominant contributions to retention are gas–liquid partition and gas–liquid adsorption. The results obtained by applying the above methods to the tetra-*n*-butylammonium 4-toluenesulfonate, trifluoromethanesulfonate, methanesul-

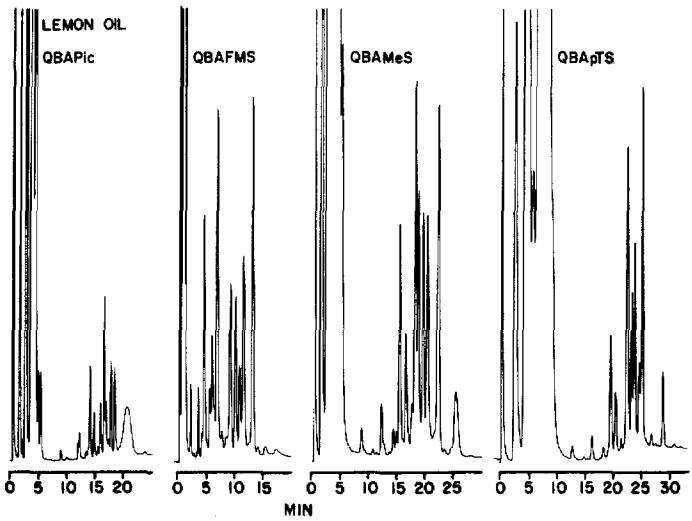


Fig. 9. Separation of cold-pressed lemon oil on four 2 m × 2 mm I.D. columns, coated with 10% (w/w) of tetra-*n*-butylammonium picrate (QBAPic), trifluoromethanesulfonate (QBFMS), 4-toluenesulfonate (QBApTS), or methanesulfonate (QBAMeS) on Chromosorb W-AW (100–120 mesh). The QBAPic column was temperature programmed from 90 to 150°C at 3°C/min with a nitrogen carrier gas flow-rate of 20 ml/min. The QBAFMS column was held isothermally at 115°C for 5 min and then temperature-programmed at 2°C/min to 140°C with a nitrogen carrier gas flow-rate of 30 ml/min. The QBAMeS column was held isothermally at 75°C for 5 min and then temperature programmed at 4°C/min to 120°C with a nitrogen carrier gas flow-rate of 30 ml/min. The QBApTS column was held isothermally at 60°C for 5 min and then temperature programmed at 4°C/min to 150°C with a nitrogen carrier gas flow-rate of 30 ml/min.

Fig. 10. Separation of oils of bergamot and rosemary on a 2 m × 2 mm I.D. column of 10% (w/w) tetra-*n*-butylammonium picrate (QBAPic) on Chromosorb W-AW (100–120 mesh) with a nitrogen carrier gas flow-rate of 20 ml/min. The column was temperature programmed from 90 to 150°C at 3°C/min for oil of bergamot and 5°C/min for oil of rosemary.

fonate, picrate, and chloride salts are summarized in Table IV. The retention mechanism is dominated by gas–liquid partition with only a small, or in many cases unmeasurable contribution from gas–liquid adsorption. Gas–liquid adsorption is most significant for the picrate (Fig. 6) and methanesulfonate salts. It makes a larger contribution to the retention of hydrocarbons than solutes containing a polar functional group. Alternatively, more typical of the general trends observed are the results shown for trifluoromethanesulfonate, Fig. 7. The intercept values are all within 3 standard deviations from zero and in most cases less than 1 standard deviation from zero.

In conclusion, the general chromatographic properties of the organic salts will be illustrated by a few typical chromatograms. Fig. 8 shows a separation of a mixture of substituted benzene derivatives on tetra-*n*-butylammonium 4-toluenesulfonate. The separation order is in accord with the previous discussion and illustrates the selectivity obtainable with these salts. If a proton-donor solute, such as benzyl alcohol was added to the mixture, it would be eluted much later than nitrobenzene. Fig. 9 illustrates the separation of cold-pressed lemon oil on four different salts; tetra-*n*-butylammonium 4-toluenesulfonate, trifluoromethanesulfonate, methanesulfonate, and picrate. Fig. 10 illustrates the separation of oil of rosemary and oil of bergamot on tetra-*n*-butylammonium picrate. The tetra-*n*-butylammonium salts are well suited to the separation of these complex polar mixtures.

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REFERENCES

1 J. E. Gordon, J. E. Selwyn and R. L. Thorpe, *J. Org. Chem.*, 31 (1966) 1925.
2 F. Pacholec, H. T. Butler and C. F. Poole, *Anal. Chem.*, 54 (1982) 1938.
3 F. Pacholec and C. F. Poole, *Chromatographia*, 17 (1983) 370.
4 C. F. Poole, H. T. Butler, M. E. Coddens, S. C. Dhanesar and F. Pacholec, *J. Chromatogr.*, 289 (1984) 299.
5 S. C. Dhanesar and C. F. Poole, *Anal. Chem.*, 56 (1984) 2509.
6 S. C. Dhanesar, M. E. Coddens and C. F. Poole, *J. Chromatogr.*, 324 (1985) 415.
7 S. C. Dhanesar, M. E. Coddens and C. F. Poole, *J. Chromatogr. Sci.*, 23 (1985) 320.
8 V. C. Reinsborough, *Rev. Pure Appl. Chem.*, 18 (1968) 281.
9 J. E. Gordon, in R. E. Denney (Editor), *Techniques and Methods of Organic and Organometallic Chemistry*, Vol. 1, Marcel Dekker, New York, 1969, p. 51.
10 J. E. Lind, *Adv. Molten Salt Chem.*, 2 (1973) 1.
11 C. L. Hussey, *Adv. Molten Salt Chem.*, 5 (1983) 185.
12 P. Walden, H. Ulrich and E. J. Birr, *Z. Phys. Chem. (Leipzig)*, 130 (1927) 495.
13 P. Walden and E. J. Birr, *Z. Phys. Chem. (Leipzig)*, 160 (1932) 57.
14 M. L. Lampreia and F. Barreira, *Electrochim. Acta*, 21 (1976) 485.
15 M. L. Lampreia and F. Barreira, *Electrochim. Acta*, 21 (1976) 491.
16 T. R. Griffiths, *J. Chem. Eng. Data*, 8 (1963) 568.
17 J. E. Lind, H. A. A. Abdel-Rehim and S. W. Rudich, *J. Phys. Chem.*, 70 (1966) 3610.
18 V. I. Minkin, O. A. Osipov and Y. A. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, 1970, p. 255.
19 C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984, p. 63.
20 R. N. Nikolov, *J. Chromatogr.*, 241 (1982) 237.
21 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.