Molten Quaternary Ammonium Salts as Stationary Liquid Phases for Gas–Liquid Partition Chromatography[1a]

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Molten tetra-*n*-pentylammonium picrate and bromide and tetra-*n*-hexylammonium nitrate (5% on Fluoropak) were investigated at 103–113°. Retention indices, *I*, are reported for 25 compounds on these and similar columns containing Apiezon L and Carbowax 1500. Retention dispersion diagrams were constructed for the polar stationary liquids employing measured retention indices for 1-substituted *n*-alkanes, RX, with X = $-CH{=}CH_2$, $-C{\equiv}CH$, OC_2H_5, Br, I, NH_2, $OCOCH_3$, CHO, $COCH_3$, CN, and OH. The general order of $\Delta I = I^{\text{polar liq}} - I^{\text{Apiezon}}$ values was similar for these liquid phases and for Emulphor-O, but many small and several large specific selectivity effects are superimposed. The range of ΔI values for the above functions is most extended for the molten picrate, the approximate order being picrate > bromide > nitrate ≥ Carbowax, Emulphor-O. The molten nitrate and bromide show pronounced selective retention of ROH and to a lesser extent of $RC{\equiv}CH$. The ΔI values were found to correlate reasonably well with the internal pressures of the RX, X ≠ OH, $-C{\equiv}CH$, I. An attempt was made to use the slopes of the ΔI *vs.* internal pressure relations to characterize the basic magnitude of the retention dispersion, and the deviations from these relations to characterize the specific selectivity effects semiquantitatively. The molten picrate shows a small but apparently genuine selectivity toward π-donor molecules. The physical behavior (HETP *ca.* 4–7 cm for alkanes, 0.3–0.7 cm for other compounds at linear velocities in the range 5–16 cm sec^{-1}) and chemical stability ($\text{picrate}^- > NO_3^- \gg Br^-$) of the fused salt columns are described. It is suggested that the fused picrate on a deactivated diatomaceous support will provide a column of practical value. Chemical transformations of RBr and RI on the molten nitrate and of RCl and RI on the molten bromide column were observed.

The great power of gas–liquid partition chromatography (glpc) in the separation and isolation of trace amounts of organic compounds from complex natural sources is well known. Using the retention index (*I*) system,[2a] which makes the retention data independent of operating and instrumental variables, Kováts[2a] and Wehrli and Kováts[2b] demonstrated that the difference in retention indices (ΔI) measured on a polar and a nonpolar stationary phase is a characteristic and predictable property of the identity and immediate environment of the functional groups present in the chromatographed molecule. This potentially makes of the method a sensitive tool for the elucidation of structure. The importance of such a structural tool, applicable to submicrogram quantites of the trace organic constituents of sea water[3] can be readily appreciated, and clear indications of its value in such investigations have been obtained in this laboratory.[3,4]

The spectrum of $\Delta I = I^{\text{polar liq}} - I^{\text{nonpolar liq}}$ values for various functional groups, X, derived from measurements of *I* for appropriate alkyl derivatives, RX, on a given polar stationary phase is termed the retention dispersion of the liquid.[5] Definite parallelism exists between the retention dispersion of commonly employed polar phases.[6] The availability of polar phases which generate substantially different dispersions, *i.e.*, with different, perhaps bizarre selectivity patterns, would thus enhance the diagnostic powers of the ΔI method.

It appeared to us that a family of polar liquid phases more different in character from those in common use could scarcely be found than that of the fused organic salts. Having at hand a collection of low-melting quaternary ammonium salts for which we have acquired some background knowledge of chemical stability and of liquid–liquid miscibility and chemical interactions with organic nonelectrolytes,[7] we considered it of interest to test certain of these as stationary liquid phases in glpc.

Results and Discussion

Retention Dispersion.—Table I summarizes the observed retention indices for a set of representative compounds on three molten quaternary ammonium salt columns as well as on Apiezon L (which served as the nonpolar phase in calculation of the tabulated $\Delta I = I^{\text{polar liq}} - I^{\text{Apiezon}}$ values), and on Carbowax 1500. The set of functional groups investigated was essentially that of Kováts[2] (whose results for Emulphor-O, a polyethylene glycol half-etherified with 1-octadecanol, are included in Table I for comparison), less the alkyl formate, but augmented by the $-C{\equiv}CH$, -I, and $-NH_2$ functions; $-OC_2H_5$ is substituted for $-OCH_3$.[8]

The retention dispersion of the five liquid phases is shown graphically in Figure 1. The impression is readily gained that this consists of a common basic order, whose scale expands and contracts, and which is varied by specific effects ranging in magnitude from small to rather large (*e.g.*, for OH). Sorting and giving a semiquantitative measure of these effects might ideally be best done with reference to a scale derived from some independent physical property of the set of compounds chromatographed. Wehrli and Kováts[2b] noted a correlation of $\Delta I^{\text{Emulphor-O}}_{130}$ with the dipole moments of the RX; this is reconstructed (with the inclusion of X = C_6H_5) in Figure 2A. The most useful parameter we have found for this purpose is the

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[1] (a) Contribution No. 1764 from the Woods Hole Oceanographic Institution. (b) Summer Fellow, 1965.

[2] (a) E. Kováts, *Helv. Chim. Acta*, **41**, 1915 (1958); (b) A. Wehrli and E. Kováts, *ibid.*, **42**, 2709 (1959).

[3] M. Blumer, M. M. Mullin and D. W. Thomas, *Science*, **140**, 974 (1963); M. Blumer and D. W. Thomas, *ibid.*, **147**, 1148 (1965).

[4] M. Blumer, private communication.

[5] Reference 2. ΔI is essentially independent of the precise type of nonpolar (saturated hydrocarbon) phase.[2]

[6] See ref 2 and trade literature.

[7] J. E. Gordon, *J. Am. Chem. Soc.*, **87**, 4347 (1965).

[8] We have taken one liberty with the original[2] elaboration of the retention dispersion, namely in failing to maintain the supporting alkyl backbone at hexyl for each of the functional groups. Wehrli and Kováts[2b] showed that ΔI for RX becomes constant for all X with increasing R only at R ≃ pentyl–hexyl. Partly as a result of our wish to work at low temperatures we have employed some butyl compounds; the resulting difference in ΔI is not significant.

TABLE I

RETENTION INDEX DATA[a]

	Emulphor-O	Apiezon L	Pe_4N^+ picrate		$Hex_4N^+NO_3^-$		$Pe_4N^+Br^-$		Carbowax 1500	
	$\Delta I^{b,c}$	I	I	ΔI^c	I	ΔI^c	I	ΔI^c	I	ΔI^c
1-Butanol	358	606			1205	599	1398	792	1036	430
1-Butylamine		637	849	212	807	170				305[d]
1-Chlorobutane	125	652	782	130	774	122	810[e]	158	774	122
Butyl ethyl ether	85	672	742	70	725	53	717	45	746	74
Benzene	172	680	852	172	833	153	876	196	868	188
Valeronitrile	345	706	1120	414	1097	391	1157	451	1082	376
1-Bromobutane	141	728	882	154	871[f]	143	890	162	872	144
1-Pentanol	366	705	1076	371	1304	599			1128	423[g]
1-Butyl acetate	217	750	992	242	928	178	950	200	982	232
1-Octene	44	787	813	26	808	21	810	23	806	19
1-Octyne		790	905	115	935	145	965	175	929	139
1-Hexanol	367	814	1174	360						
1-Iodobutane		833	986	153	*h*		*i*		969	136
2-Heptanone	233	838	1152	314	1085	247	1096	258	1071	233
1-Chlorohexane	130	843	982	139			*j*		962	119
Heptaldehyde	219	861	1135	274	1102	241	1106	245	1077	216
p-Xylene	147	886	1040	154	1007	121	1032	146	1030	144
Anisole	270	908	1174	266	1149	241	1197	289	1180	272
1-Bromohexane	135	930	1074	144			1063	133		
Mesitylene		994	1129	135	1089	95				
1-Iodohexane		1032	1175	143						
1-Phenylbutane	157[k]	1053	1200	147	1170	117	1221	168	1171	118
Nitrobenzene	411	1059	1482	423	1496	437				
Durene		1133	1279	146	1225	92				
1-Butyl nitrite					741					
Butyraldehyde					797					
1-Butyl nitrate					1036					

[a] Temperature: Emulphor column, 130°; bromide column, 113°; all others, 103°. Salt freezing points: picrate, 74.4°; bromide, 101.3°; nitrate, 69.3°. [b] Reference 2. [c] $\Delta I = I^{\text{polar liq}} - I^{\text{Apiezon}}$. [d] C. Landault and G. Guiochon, *J. Chromatog.*, **13**, 327 (1964); 130°. [e] See text. [f] Additional peak at $I = 1029$. [g] Landault and Guiochon[d] gave 540. [h] Peaks at $I = 781, 884$, and 1033; see text. [i] Peak at $I = 880$ attributed to butyl bromide. [j] Peak at $I = 1051$ attributed to hexyl bromide. [k] Propylbenzene.

cohesive energy density (internal pressure), $\Delta E_v/V$ (ΔE_v = energy of vaporization, V = molar volume),[9] against which $\Delta I_{130}^{\text{Emulphor-O}}$ is plotted in Figure 2B.[10] Approximate inverse parallelism between the mutual RX–stationary liquid phase solubility and the square of the difference in $(\Delta E_v/V)^{1/2}$ for the two liquids would be expected[9] for nonassociated liquids. The enhanced immiscibility of unassociated with associated liquids generally requires separate consideration of the latter;[11] this is evident also in the ΔI data (Figures 1 and 2, following section).

Our procedure has been to use the set of functional groups for which ΔI is available on each column (–CH=CH$_2$, OC$_2$H$_5$, Cl, Br, OAc, CHO, COCH$_3$, and CN, excluding only OH on the above grounds) to generate the rather smooth ΔI *vs.* $\Delta E_v/V$ curves of Figure 3; numerical intercomparison of the curves and the deviations of ΔI values observed for the various other functional groups then afford a semiquantitative basis for comparisons of dispersion and selectivity. In the plots of Figures 2B and 3 the $\Delta I = 0$ intercept corresponds chemically to X = alkyl.[2] The data were fitted to equations of the form

$$\Delta I = a(\Delta E_v/V - c) + b(\Delta E_v/V - c)^2 \qquad (1)$$

and it was possible to accommodate the data with c = 34 cal/ml, the known value of $\Delta E_v/V$ for propane (X = CH$_3$),[12] in accordance with this boundary condition. Values of a and b determined by the method of least squares are given in Table II.

TABLE II

CONSTANTS FROM EQUATION 1

Stationary phase	a	b
$(n\text{-}C_6H_{13})_4N^+NO_3^-$	1.39	0.044
$(n\text{-}C_5H_{11})_4N^+Br^-$	1.45	0.051
$(n\text{-}C_5H_{11})_4N^+$ picrate$^-$	2.01	0.044
Emulphor-O	3.68	0.0034

The fused salts have essentially the same b value, and the relative dispersion slopes can be measured by a. Tetra-*n*-hexylammonium nitrate, with the larger cation and correspondingly lower polarity[7] has the smallest slope. The curve for Emulphor-O has a distinctly different shape and though the dispersion is most similar qualitatively to $R_4N^+NO_3^-$ the coefficients are not comparable.

Turning next to the hydrogen-bonding functions, one can calculate ΔI for –C≡CH ($\Delta E_v/V$ = 66.7 cal/ml) on R_4N^+picrate$^-$ from eq 1 as 113 *vs.* 115 observed; *i.e.*, this groups falls on the curve and no special selectivity is indicated. This is in accord with the apparent absence of enhanced miscibility with proton donor type nonelectrolytes noted[7] for the molten picrate. By contrast, the observed ΔI values for

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[9] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, Inc., New York, N. Y., 1964, Chapters 7, 23.

[10] Owing to the paucity of data for higher molecular weight compounds, the $\Delta E_v/V$ scale used throughout this paper is for R = C$_2$H$_5$ at 20–25°. This scale is plotted at the right side of Figure 1. Requisite data were taken from (a) Landolt-Börnstein, "Physikalisch-Chemisch Tabellen," 5th ed, J. Springer, Berlin, 1923–1936; (b) D. E. Holcomb and C. L. Dorsey, Jr., *Ind. Eng. Chem.*, **41**, 2788 (1949); (c) T. E. Smith and R. F. Bonner, *ibid.*, **43**, 1169 (1951).

[11] Reference 9, pp 162, 254, 267.

[12] Reference 9, Appendix 1.

TABLE III

ESTIMATED SELECTIVITIES FOR SEVERAL FUNCTIONAL GROUPS

	Emulphor-O			R_4N^+ picrate$^-$			$R_4N^+NO_3^-$				$R_4N^+Br^-$			
	ΔI			ΔI			ΔI			$\Delta\Delta I_{NO_3^-} - \Delta\Delta I_{Pic^-}$	ΔI			$\Delta\Delta I_{Br^-} - \Delta\Delta I_{Pic^-}$
	Calcd	Obsd	$\Delta\Delta I^a$	Calcd	Obsd	$\Delta\Delta I^a$	Calcd	Obsd	$\Delta\Delta I^a$		Calcd	Obsd	$\Delta\Delta I^a$	
-C≡CH				113	115	2	93	145	52	50	102	175	73	71
OH	546	367	−179	1039	360	−679	952	599	−353	326	1076	791	−285	394
NH_2				260	212	−48	223	170	−53	−5				
I				228	143	−85								

[a] $\Delta I_{obsd} - \Delta I_{calcd}$.

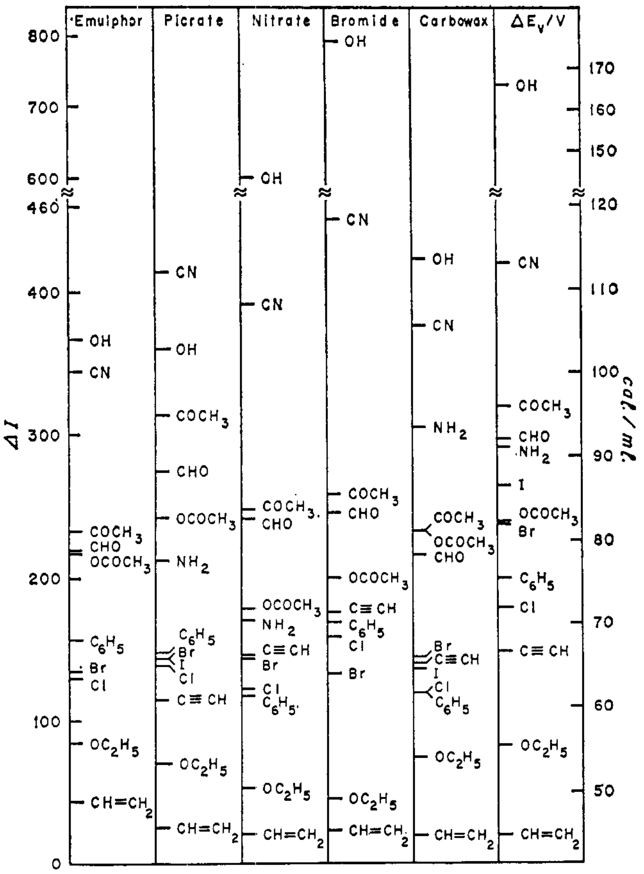

Figure 1.—Retention dispersion for five stationary liquid phases. Data for Emulphor-O is from ref 2. Description of the other materials is given in the text. $\Delta I = I^{\text{polar liquid}} - I^{\text{Apiezon L}}$.

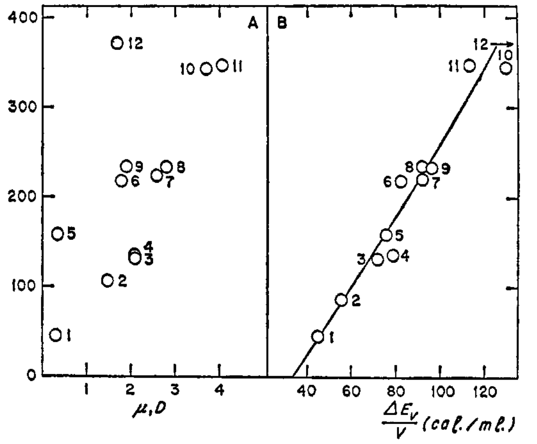

Figure 2.—A: $\Delta I_{130}^{\text{Emulyhor-O}}$ vs. dipole moment for alkyl derivatives RX; X = (1) -CH=CH$_2$, (2) OC$_2$H$_5$, (3) Cl, (4) Br, (5) C$_6$H$_5$, (6) OCOCH$_3$, (7) CHO, (8) OCHO, (9) COCH$_3$, (10) NO$_2$, (11) CN, and (12) OH; after ref 2. B: the same retention data plotted vs. the average cohesive energy density, $\Delta E_v/V$, in calories per milliliter for C_2H_5X.

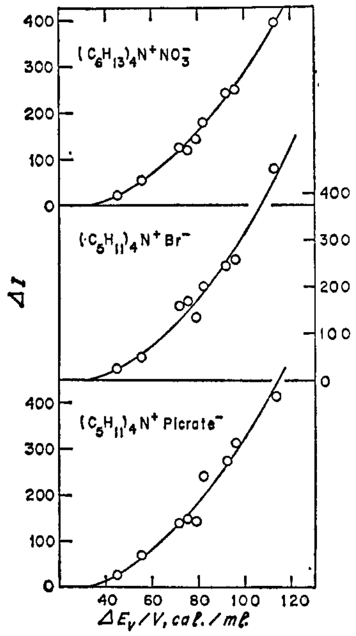

Figure 3.—ΔI vs. $\Delta E_v/V$ for three molten salt columns.

-C≡CH on molten nitrate and bromide exceed the calculated values; *i.e.*, these liquids select RC≡CH, by 52 and 73 ΔI units, respectively. Again this accords with the order of miscibility of the fused nitrate and bromide with hydrogen-bonding proton donors,[7] and with the spectroscopically well-documented formation of -C≡CH···Br$^-$ hydrogen bridges.[13] This approach is extended to ROH ($\Delta E_v/V$ = 166 cal/ml) in Table III, which also summarizes the -C≡CH results.

In the case of ROH, no definite physical significance can be attached to any single $\Delta\Delta I = \Delta I_{obsd} - \Delta I_{calcd}$; ROH is "rejected" (as a negative $\Delta\Delta I$ might be described) by all of the stationary phases, with respect to prediction from $\Delta E_v/V$, corresponding to the special extra immiscibility proceeding from its self-association mentioned above.[11] One can, however, compare the $\Delta\Delta I$ values of the liquids with one another. The molten picrate rejects ROH the most strongly of the salts; if we agree again to take the picrate as a norm, we can evaluate the selectivity for ROH of molten nitrate and bromide relative to the picrate ($\Delta\Delta I_{X^-} - \Delta\Delta I_{Pic^-}$) as +326 and +394 ΔI units (Table III), respectively. This agrees well with the critical solution temperature behavior of the molten salt–polar, highly associated liquid systems previously studied,[7] where the miscibility order is Pic$^-$ ≪ NO$_3^-$ < Br$^-$. The existence of strong -OH···Br$^-$R$_4$N$^+$ hydrogen bridging was substantiated spectroscopically.[7] All of the solubility information

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[13] A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233 (1963).

now available suggests that NO_3^- in the fused salt is also a good hydrogen-bridging proton acceptor. On the other hand, Table III reveals that amines, RNH_2, give ΔI values much smaller in magnitude than ROH, and that these are substantially the same for molten picrate and nitrate. The last entry in Table III shows that RI is rejected by molten picrate according to the ΔI–$\Delta E_v/V$ correlation. Inspection of Figure 3 reveals that RBr consistently shows negative deviations from the correlation, although the magnitude is not so great. The behavior of RI thus most likely signals breakdown of the ΔI–$\Delta E_v/V$ correlation for this type of function.

Finally, we were interested to inquire whether any evidence for electron donor–acceptor interaction of molten quaternary picrate with π donors could be found. No special selectivity for the function C_6H_5 is apparent in Figure 3. Going one step further, comparative data for five substituted benzenes, taken relative to benzene itself, were assembled in Table IV for the five liquid phases. If one reasons that selectivity of this sort should show up as abnormally large ΔI values for the electron-donating methyl and methoxyl substituents, and small for electron-withdrawing nitro, it is clear that any such effect in the case of liquid tetrapentylammonium picrate is small.

TABLE IV

VALUES OF $\Delta I - \Delta I_{C_6H_6}$[a] FOR FIVE SUBSTITUTED BENZENES ON VARIOUS STATIONARY PHASES

Compd	Stationary phase: Emulphor-O[b]	R_4N^+ picrate$^-$	$R_4N^+NO_3^-$	$R_4N^+Br^-$	Carbowax 1500
p-Xylene	−25	−18	−32	−50	−44
Mesitylene		−37	−58		
Durene		−26	−61		
Anisole	98	94	88	93	84
Nitrobenzene	239	251	284		

[a] Temperature 103° except Emulphor-O, 130°; bromide, 113°. [b] Reference 2.

Comparison with the closely related molten nitrate, however, shows that the observed differences for the two liquid phases are in each case in the predicted direction, and the values of these picrate–nitrate differences are compared with the reported formation constants for complexes of the donors with related π acceptors in Table V. Electron-withdrawing substituents are known to destabilize the complexes formed by π donors; no electron donor–acceptor complex of nitrobenzene with π acceptors is apparently known.[14] The good correlation of $(\Delta I_{\text{picrate}} - \Delta I_{\text{nitrate}})$ with the formation constants for the substituted benzenes *vs.* each of three π acceptors seen in Table V suggests that the molten picrate indeed possesses weak π acceptor properties despite the negative charge carried by picrate ion.[7]

Column Behavior.—The background signals due to decomposition products from the molten salt columns fall in the order picrate$^-$ < NO_3^- ≪ Br^-. This is precisely the known order of thermal stabilities of these liquids.[15] Both the picrate and nitrate columns could be used at the highest sensitivity of the instrument. The picrate column gave a background very similar to that observed with the standard liquid phases, while that of the bromide column was a factor of *ca.* 100 greater.

TABLE V

RETENTION INDICES OF SUBSTITUTED BENZENES ON MOLTEN PICRATE RELATIVE TO MOLTEN NITRATE, COMPARED WITH FORMATION CONSTANTS FOR CHARGE-TRANSFER COMPLEXES IN SOLUTION

Compd	$(\Delta I_{ArX} - \Delta I_{ArH})_{\text{picrate}} - (\Delta I_{ArX} - \Delta I_{ArH})_{\text{nitrate}}$	Acceptor: TCNE[a]	Chloranil[b]	TNB–$CHCl_3$[c]	TNB–CCl_4[d]
		K_f[e]			
Nitrobenzene	−33	...	...	...	...
Benzene	0	31.1	5.2	0.82	2.4
Anisole	6	68.7			
p-Xylene	14	119	27[f]	2.08	9.0[f]
Mesitylene	21	269	55	2.67	
Durene	35	843	96		24.4

[a] Tetracyanoethylene in methylene chloride at 22°; ref 14, p 129. [b] In cyclohexane at 20°; ref 14, p 120. [c] 1,3,5-Trinitrobenzene at 25°; ref 14, p 122. [d] 1,3,5-Trinitrobenzene at 20°; ref 14, p 121. [e] Mole fraction units. [f] For *m*-xylene.

Some measurements of column efficiency are given in Table VI. These are very similar in form to those observed by Kirkland[16] for 10% Carbowax 400 on Fuoropak-80, showing no minimum in hetp (height equivalent to theoretical plate) in the range of gas velocities studied. The columns are seen to be poorly efficient. Use of the fluorocarbon support was dictated by the wish to supress all possibility of chemical interaction with the rather reactive liquid salt phases and to assure elimination of contributions of sample-support interaction to the ΔI values (see below); the poor column efficiencies were essentially no handicap in the chromatography of pure compounds in the present work. On the molten nitrate column undecane and anisole have nearly equal retention times; yet the efficiency is about a factor of ten greater when measured by the latter. This result is confirmed for dodecane *vs.* anisole on fused tetrapentylammonium picrate. As efficiency is liquid diffusion limited[16,17] under the conditions employed, these differences might be attributed to differences in molar volume of the solutes. However, the ~10-fold decrease in efficiency for decane and dodecane (molar volumes 195 and 227 ml/mole) seems difficult to reconcile on this basis alone with the trend established by anisole and 2-heptanone (109 and 139 ml/mole), and it seems likely that the performance with saturated hydrocarbons is different in kind from compounds containing a polar or unsaturated group and possessing greater miscibility with the fused salts. The saturated hydrocarbon peaks were slightly asymmetric (tailing sense) on each of the fused salt columns in contrast to the other compounds chromatographed, excepting only the amine which tailed very badly.

We were interested to find whether the fused salts as highly polar (at least in the microscopic sense[7]) liquids would be advantageous in the chromatography of polar, associated solutes by virtue of deactivation of surface adsorption sites on diatomaceous solid supports. Tailing of alcohol and amine peaks proved,

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(14) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961, Chapter 9. *m*-Dinitrobenzene is known not to form charge-transfer complexes with picric acid [S. D. Ross and I. Kuntz, *J. Am. Chem. Soc.*, **76**, 74 (1954)].

(15) J. E. Gordon, *J. Org. Chem.*, **30**, 2760 (1965).

(16) J. J. Kirkland, *Anal. Chem.*, **35**, 2003 (1963).

(17) S. Dal Nogare and R. S. Juvet, Jr., "Gas-Liquid Chromatography," Interscience Publishers, Inc., New York, N. Y., 1962, pp 93–94.

TABLE VI

COLUMN EFFICIENCY DATA[a] AT 103°

Stationary phase and sample	Height equivalent per theoretical plate, $\bar{H}$ cm(), and linear gas velocity (cm/sec), $\bar{u}$											
	$\bar{u}$	$\bar{H}$	$\bar{u}$	$\bar{H}$	$\bar{u}$	$\bar{H}$	$\bar{u}$	$\bar{H}$	$\bar{u}$	$\bar{H}$	$\bar{u}$	$\bar{H}$
Apiezon L												
Decane	5.34	0.68	7.05	0.78	8.91	0.94	12.04	1.1	14.9	1.3	23.0	1.4
Anisole	5.82	0.34	7.57	0.39	9.33	0.54	12.40	0.53	14.9	0.57		
R_4N^+ picrate$^-$												
Decane			7.20	4.2	8.62	4.7	12.5	5.9	14.8	5.9		
Dodecane	5.29	4.2	7.25	4.5	8.95	5.2	12.23	5.8	15.1	6.9		
Anisole	5.22	0.26	7.22	0.33	9.65	0.34	12.25	0.43	14.9	0.59		
2-Heptanone	5.27	0.35	7.21	0.42	8.68	0.71	12.2	0.74	15.0	0.60		
$R_4N^+NO_3^-$												
Undecane	5.27	4.2	7.84	5.4			12.18	7.0			16.12	6.9
Anisole	5.20	0.30	7.75	0.38			12.1	0.57			16.05	0.73

[a] 5% liquid phase on Fluoropak in 1/8 in. × 5 ft Pyrex columns. [b] 0.01 µl in 1 µl of carbon disulfide.

however, to be more pronounced on a 20% tetra-*n*-pentylammonium picrate on Chromosorb P column than on the analogous column prepared with Carbowax 1500 as liquid phase.

The utility of the salts containing reactive anions, such as the molten nitrate and bromide of the present study, is somewhat limited by intrusion of chemical transformations of the solute. As discussed below, these reactions interfere with only a very few classes of sample. In practical use, fused salt columns employing diatomaceous supports would probably be investigated in order to obtain satisfactory efficiency. In this event the possibility of reactions of the salt with or catalyzed by the support should be borne in mind.

In summary, it appears likely that the molten picrate on a deactivated diatomaceous support would constitute a practically useful polar column up to at least 140°[15] and probably to considerably higher temperatures.[18]

TABLE VII

COMPARISON OF VARIOUS RETENTION INDICES FOR APIEZON L ON THREE SOLID SUPPORTS

	Support				
	Fluoropak	Celite[a]		Chromosorb P	
Compd	I^{F}	I^{Cel}	$I^{Cel} - I^{F}$	I^{Csb}	$I^{Csb} - I^{F}$
1-Octene	787	785	−2	787	0
1-Chlorobutane	652	648	−4	645	−7
1-Chlorohexane	843	848	5	848	5
1-Bromohexane	930	945	15		
1-Bromobutane	728	738	10	737	9
p-Xylene	886	894[b]	8[b]		
Benzene	680	681	1	682	2
1-Butyl acetate	750	756	6	784	34
Heptaldehyde	861	866[b]	5[b]		
2-Heptanone	838	842	4	899–988[c]	61–150[c]
Anisole	908	921[b]	13[b]	926	18
Valeronitrile	706	720	14	807	101
1-Butanol	606	616	10	743–871[d]	137–265[d]
1-Pentanol	705	722[b]	17[b]		
1-Hexanol	814	822[b]	8[b]		
Nitrobenzene	1057	1066[b]	7[b]		

[a] Data from ref 2. [b] Extrapolation to 100° involves some uncertainty. [c] Sample size: 0.16–0.0002 µl. [d] Sample size: 0.04–0.00005 µl.

Influence of the Support on Retention Indices.—Our measured retention indices for a variety of compounds using Apiezon L as stationary liquid phase supported on (a) Fluoropak and (b) Chromosorb P in comparison with the original values of Kováts[2] on Celite provide a measure of the sensitivity of the retention index to adsorption effects involving the solid support. On Chromosorb P the pronounced tailing of polar compound peaks and the strong dependence of *I* upon sample size signify strong adsorption effects; on Fluoropak these indications were absent.[19] This behavior of both supports is well documented.[20] The Celite support and heavy (40%) loading employed by Kováts[2] would be expected to have kept solid-support contributions to his original *I* and ΔI listings relatively small; the data of Table VII for the three supports provides an experimental test. The values on Celite support, while quite comparable with those on the fluorocarbon, are indeed generally slightly larger. The compounds are arranged in order of increasing $\Delta I_{130}^{\text{Emulphor-O}}$. The values for the hydrocarbons (xylene possibly excepted) are identical within experimental error. There is a general trend toward increasing discrepancy between the supports with increasing polarity of the substance chromatographed, the major exceptions being the alkyl bromides.

Chemical Reactions.—Three solute–fused salt combinations within the set of materials chosen for this work could be anticipated to result potentially in chemical reactions in the chromatographic column: (1) oxidizable substrates (ROH, RCHO) and (2) halides (RX) with the molten nitrate,[21] and (3) halogen exchange, $RX_1 + X_2^- = RX_2 + X_1^-$, of alkyl halides on the bromide column.[15] No evidence of reactions of the first sort was encountered. 1-Butanol and butyraldehyde gave distinctly different, single peaks on the fused nitrate column, both with retention times widely different from that determined for butyric acid, and both giving retention indices consistent with those obtained on the other liquid phases. In the second case, butyl chloride was apparently stable to the molten nitrate while butyl iodide reacted completely with the salt, and the bromide gave an intermediate result. Three peaks were observed on injection of butyl iodide, two of which (*ca.* 10% of total, $I = 781$ and 884) cannot be identified as butyl iodide because of the negative or

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(18) P. Walden and E. J. Birr, *Z. Physik. Chem.*, **160**, 45 (1932).

(19) The sample size dependences for 1-butanol and 2-heptanone on Chromosorb P are included in Table VII. A 50-fold variation in sample size of 2-heptanone on Fluoropak produced an average deviation in *I* of <0.06% ($I = 838.5 \pm 0.5$).

(20) Reference 17, pp 41–42, 142 ff.

(21) J. E. Gordon, *J. Am. Chem. Soc.*, **87**, 1499 (1965).

impossibly small ΔI values to which such an assignment would lead. The major peak corresponded in retention index (1033) to 1-butyl nitrate (1036), and its identity was confirmed by trapping the effluent material from this peak and rechromatographing on another column (R_4N^+ picrate$^-$–Fluoropak). One peak was observed, which displayed a retention time (164 sec) identical with that of pure 1-butyl nitrate, 163 sec (butyl iodide has a retention time of 107 sec under these conditions). The retention indices of the minor peaks are not near that of 1-butyl nitrite, and one approximates only very poorly that of butyraldehyde (Table I).

The case of incomplete conversion of substrate, *i.e.*, of reaction half-life not short relative to the retention time of the reactant, is more complex, giving a situation in which the product signal would be expected to extend over the entire region between the retention times of pure product and reactant. Two effects tend to sharpen the product signal, however. The rate law for a pseudo-first-order reaction in the liquid phase, and the fact that the pressure drop along the column results in increase of carrier gas velocity from inlet to outlet, both cause the major fraction of the reaction to occur in the earlier part of the column, leading to the prediction of an observable peak for the reaction product. The product, if it has a longer retention time than the reactant, should appear somewhat earlier than that for injection of pure product, and trail to the substrate peak; a product of shorter retention time should give a similar chromatogram of the opposite symmetry. Results for 1-bromobutane chromatographed on the fused nitrate column were precisely of this type, giving a broadened peak at $I = 1029$ (*vs.* 1036 for 1-butyl nitrate) incompletely resolved from the main butyl bromide peak at $I = 871$. The double peak was trapped and rechromatographed as above, giving two peaks identical in retention times with those of 1-bromobutane and 1-butyl nitrate.

Similarly, 1-chlorobutane on molten quaternary bromide gave two rather sharp, though incompletely resolved, peaks assigned to 1-chlorobutane ($I = 810$) and 1-bromobutane ($I = 874$). 1-Iodobutane on the bromide column gave one peak with retention index near that of 1-bromobutane; rechromatography on a second column confirmed the identity of 1-bromobutane as major constituent, and also the presence of a smaller amount of unreacted 1-iodobutane. 1-Chlorohexane was >70% converted to the bromo compound, and one peak was observed (Table I). Trapping and rechromatographing the latter on molten picrate gave two peaks identical in retention time with hexyl bromide and hexyl chloride (202 *vs.* 201 sec and 117 *vs.* 118 sec).

Two other factors can conceivably sharpen an incompletely formed product peak—rate acceleration at the head of the column due to superheating of the gas stream by the injection port heating system, and accumulation of catalytic materials at the head of the column. We could find little effect of preheater temperature on our reacting systems. Previous work[21] suggests that nitrite may catalyze the RX–molten nitrate reaction; however, we found no effect on the 1-bromobutane chromatogram on reversing the column, head for tail. On the other hand, reversal of the bromide column caused further collapse of the resolution of 1-chloro- and 1-bromobutane peaks in the 1-chlorobutane chromatogram. In this case R_3NH^+-Br^-, a known decomposition product of the quaternary bromide, which might be expected in higher concentration at the somewhat superheated column head, could conceivably serve as an acid catalyst, hydrogen bonding to departing chloride ion: $Br^- \cdots CH_2R \cdots Cl^-—HNR_3^+$.

Experimental Section

The salt samples employed were those previously described.[7] Pyrex, $^1/_8$ in. × 5 ft columns were packed with 5% of the liquid phase, supported on Fluoropak. Retention times were measured employing a Wilkens Hi-Fi 600-D chromatograph equipped with hydrogen-flame detector. The column temperature was controlled to ±1°. Injection port temperature was *ca.* 150°. In each case the sample size was 0.002 μl; on all columns except the quaternary ammonium bromide, where neat samples were employed, samples were introduced as 1% solutions in carbon disulfide. Column efficiency was computed by the first method of James and Martin.[22]

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[22] A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).