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SYNTHESIS AND GAS CHROMATOGRAPHIC STATIONARY PHASE PROPERTIES OF ALKYLAMMONIUM THIOCYANATES

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SUMMARY

Twenty-three alkylammonium thiocyanate salts were synthesized and characterized by spectroscopic techniques. Eleven of these salts were found to have useful stationary phase properties for gas chromatography. The characteristic stationary phase interactions for organic solutes were determined using a mixture of substituted benzene derivatives and the McReynolds' probe set as test solutes. McReynolds' constants are shown to be an unreliable measure of stationary phase selectivity due to the preponderance of the *n*-alkane retention index markers to be retained largely by gas–liquid phase adsorption while the polar probes are retained largely by gas–liquid phase partitioning. From qualitative evidence it is shown that dispersive forces are weak in solute–salt interactions, that they increase in importance with increasing size and number of alkyl groups attached to the cation, that the retention order of solutes with a significant dipole moment can be predicted by first ranking the solutes in terms of their dipole moments and then making allowances for volatility differences, and that the retention of proton donor solutes, such as alcohols, is most significantly influenced by the basicity of the cation.

INTRODUCTION

Liquid organic salts are novel, selective solvents with many potentially interesting chromatographic properties. The solubility of organic solutes in liquid organic salts is much greater than for liquid inorganic salts making them eminently more suitable and adaptable for the chromatography of organic compounds. The strength of polar interactions between organic solutes and liquid organic salts is enhanced by the presence of coulombic fields. The selectivity of such interactions is readily varied by changing the properties of the ions. Several studies have been performed using liquid organic salts as stationary phases for gas–liquid chromatography[1–9]. These studies demonstrate that a better understanding is emerging of the molecular properties of a salt which result in a large liquid–temperature range as well as demonstrating their utility for the separation of complex mixtures on both packed and

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open-tubular columns. It was recently shown that a number of alkylammonium nitrate and thiocyanate salts were liquid at room temperature and showed promise for use as mobile phases in liquid chromatography[10]. As one criteria for extending the useful liquid–temperature range of organic salts is to pursue the use of salts of lower than average melting points we have synthesized and evaluated the gas chromatographic properties of a series of alkylammonium thiocyanates. These results are presented in this paper. A second goal was to commence a systematic study of the influence of ion type on chromatographic selectivity. By varying the structure of the cation with a common anion, in this case the thiocyanate anion, we hoped to isolate the role played by the cation in governing relative retention. In a companion study[8], fifteen tetra-*n*-butylammonium salts with different anions were studied to determine the contribution made by the anion to chromatographic selectivity.

EXPERIMENTAL

All alkylamines, tetra-*n*-propylammonium hydroxide (20%, w/v), tetraethylammonium hydroxide (40%, w/v), and tetra-*n*-butylammonium nitrate were obtained from either Aldrich (Milwaukee, WI, U.S.A.) or Fluka (Hauppauge, NY, U.S.A.). The alkylamines were used as received, unless discolored, in which case they were distilled immediately before use. Ammonium thiocyanate and potassium thiocyanate were analytical reagent grade from J. T. Baker (Phillipsburg, NJ, U.S.A.). All solvents were HPLC grade from Burdick & Jackson (Muskegon, MI, U.S.A.).

The following general method was used to prepare all alkylammonium thiocyanates except for the quaternary ammonium salts. A slight excess of an aqueous solution of the alkylamine (70%, v/v) and an aqueous solution of ammonium thiocyanate (20–30%, w/v) were stirred vigorously at a gentle reflux (70–80°C). In some cases a portion of ethanol was added to the reaction mixture to prevent phase separation. The reaction was continued until the evolution of ammonia ceased; depending on the amine this required from 4 h to 2 days. Upon completion of the reaction, water was removed on a rotovapor, and the solid residue recrystallized to constant melting point from a mixed solvent such as ethyl acetate–ethanol. Room temperature liquid salts were extracted with toluene, the toluene phase discarded, and the salt dissolved in methylene chloride and treated with decolorizing charcoal. Methylene chloride was removed on the rotovapor and the salt freed of traces of solvent and volatile impurities by vacuum stripping (<0.2 Torr).

Tetra-*n*-ethylammonium and tetra-*n*-propylammonium thiocyanates were prepared from equal molar amounts of the aqueous tetraalkylammonium hydroxide and ammonium thiocyanate heated to reflux until the evolution of ammonia ceased (>48 h). Water was removed on the rotovapor and the solid residue recrystallized to constant melting point from ethyl acetate.

Tetra-*n*-butylammonium thiocyanate was prepared by stirring for 1 h at room temperature equal molar amounts of tetra-*n*-butylammonium nitrate and potassium thiocyanate dissolved in absolute ethanol. The volume of ethanol was reduced and the precipitate of potassium nitrate filtered off. The remaining ethanol was removed on the rotovapor and the solid residue recrystallized from ethyl acetate.

Yields of the alkylammonium thiocyanate salts generally exceeded 90% of the theoretical value. A list of all salts prepared, abbreviations used in the text, and experimental melting points are given in Table I.

Samples were prepared for infrared spectroscopy by depositing a thin film of the salt dissolved in a volatile solvent onto a sodium chloride plate and subsequently evaporating the solvent away with a stream of nitrogen. Spectra were recorded on a Nicolet 20DX Fourier transform–infrared spectrometer (Madison, WI, U.S.A.) at a resolution of 2 cm^{-1}.

^1H (300 MHz) and ^{13}C (75.5 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 or GN-300 (Fremont, CA, U.S.A.) spectrometer. Room temperature liquid salts were run neat using external calibration (deuteriochloroform). Solid salts were dissolved in methanol or acetonitrile and internal calibration was used (tetramethylsilane).

Fast atom bombardment (FAB) mass spectra were recorded using a Kratos MS 80-RAF mass spectrometer (Westwood, NJ, U.S.A.). The FAB source was operated at a voltage of 5.8 kV, tube current 30 μA, and argon gas as the primary particle. Positive ion mass spectra were recorded at an accelerating potential of 4 kV, scan-rate 30 s, mass range 50–1000 a.m.u., and a resolution of 1500. Room temperature liquid salts were run neat and solid salts in a glycerol matrix.

Decomposition temperatures for the salts were determined by sealing a small sample of the salt in a melting point capillary and slowly raising its temperature in a hot-block melting point apparatus until visible signs of discoloration or volatilization were observed. The maximum allowable column operating temperature was determined as the highest temperature that a column packing prepared with the salt could be maintained at 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.

Column packings containing from 3 to 20% (w/w) of the alkylammonium salts on Chromosorb W-AW (100–120 mesh) were prepared using the rotory evaporator technique and methanol as the slurry solvent. After coating the damp packing was dried in a fluidized-bed drier and then packed into glass columns 1–3.5 m × 2.0 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.

RESULTS AND DISCUSSION

The alkylammonium thiocyanate salts are easily prepared in high yield and high purity. Some salts require careful handling in the laboratory due to either photolytic instability or deliquescent behavior. Ethylammonium, dibutylammonium and the tetraalkylammonium thiocyanates are extremely deliquescent and should be handled in a dry box. Diethylammonium, triethylammonium, isobutylammonium, dibutylammonium, benzylammonium, and cyclohexylammonium thiocyanates gradually discolor, eventually becoming yellow, on standing in laboratory light. They should be stored in the dark.

As few of the alkylammonium thiocyanates were known compounds they were characterized by spectroscopic techniques. A copy of all spectral data is available elsewhere[16] and only the main characteristic features will be discussed here. A strong band in the infrared spectra between 2000–2300 cm^{-1} is characteristic of the thio-

TABLE I

SUMMARY OF THE PHYSICAL CHARACTERISTICS OF THE ALKYLAMMONIUM THIOCYANATE SALTS

Cation	*Abbreviations*	*Color*	*Experimental melting point (°C)*	*Literature melting point (°C)*	*Ref.*
Trimethylammonium	TMAT	White	195.5–196.5	–	–
Ethylammonium	EAT	White	45.5–47.5	–	–
Diethylammonium	DEAT	White	153.5–154.5	–	–
Triethylammonium	TEAT	White	50.5–51.5	–	–
Tetraethylammonium	QEAT	White	265	–	–
n-Propylammonium	PAT	White	69.5–70.5	–	–
Isopropylammonium	iPAT	White	81.5–82.5	85–86	11
Di-*n*-propylammonium	DPAT	Straw yellow	5.5	–	–
Tri-*n*-propylammonium	TPAT	White	140.5–141.5	–	–
Tetra-*n*-propylammonium	QPAT	Yellow	158.5–159.5	–	–
n-Butylammonium	BAT	Straw yellow	20.5	–	–
Isobutylammonium	iBAT	White	33	–	–
sec.-Butylammonium	sBAT	Straw yellow	22	–	–
tert.-Butylammonium	tBAT	White	121.5–122.5	–	–
Di-*n*-butylammonium	DBAT	White	45	*	11
Tri-*n*-butylammonium	TBAT	Amber	53	–	–
Tetra-*n*-butylammonium	QBAT	White	125.5–126.5	123	12
Triethanolammonium	TAAT	Yellow	37	–	–
Cyclohexylammonium	CHAT	White	93–94	93–94	11
Benzylammonium	BzAT	Pale yellow	99.5–100.5	99–100	11
				101	13
				102	14
Dibenzylammonium	DBzAT	White	158.5–159.5	158–159	11
				164–165	15
n-Octylammonium	nOAT	Amber	Gel	–	–
Tetramethylbutylammonium	tOAT	White	95.5–96.5	–	–

* b.p. given as 130–131°C at 0.2 mmHg.

cyanate anion. Proton and ^{13}C NMR chemical shifts are summarized in Tables II and III, respectively. The alkylammonium thiocyanate salts do not yield positive ion mass spectra under normal electron impact and chemical ionization conditions. By fast atom bombardment a series of cluster ions of the type $[(AB)_nAH_x]^+$ (A = cation; B = anion; n = 0–6; x = 0–2) characteristic of the salt are generated[17]. For most salts the base peak corresponds to the cation and the ion abundance of the cluster ions decreases appreciably as n increases.

TABLE II

^1H NMR DATA OF ALKYLAMMONIUM THIOCYANATE SALTS

Salt	*Chemical shift (ppm)*				
	NH	*CH*	*CH_2*	*CH_3*	*OH*
TMAT				3.5	
EAT	7.3		3.3	1.5	
TEAT	10.1		3.7	1.9	
QEAT			3.9	1.9	
TAAT	*		4.5, 4.0	1.6	5.3
PAT	8.0		3.4, 2.1	1.2	
iPAT	7.0	3.5		1.3	
DPAT	7.4		2.9, 1.6	0.9	
TPAT	6.6		3.0, 1.7	1.0	
QPAT			3.1, 2.3	1.6	
BAT	8.1		3.2, 1.5, 1.2	1.1	
iBAT	7.3		3.5	1.73	
sBAT	7.5	3.4	1.8	1.49, 1.03	
tBAT	7.9			2.1	
DBAT	7.4		3.7, 2.2, 1.7	0.8	
TBAT			3.2, 1.8, 1.5	1.0	
QBAT			2.5, 2.3, 2.1	1.7	
CHAT	7.5		3.6, 2.3, 1.8		
BzAT	**	8.1	4.7		
DBzAT	**	8.1	4.8		
nOAT	6.9		3.4, 2.1, 1.8	1.4	
tOAT	7.5		2.3, 2.1	1.7	

* OH proton is exchanging with NH proton so NH shift is not seen.

** NH peak may be obstructed by the aromatic protons.

The liquid temperature range and average chromatographic efficiency for all 23 alkylammonium thiocyanate salts are summarized in Table IV. Several general conclusions can be drawn from this data. First of all, there is generally a large disparity between the decomposition temperature measured in a sealed melting point capillary and the temperature tolerance established for the same salts when used as column packings. The decomposition temperature is usually much higher than the column temperature limit. The column temperature limit for all the low melting point salts in Table IV, except for triethanolammonium thiocyanate, is in the range 120–

TABLE III

^{13}C NMR DATA OF ALKYLAMMONIUM THIOCYANATE SALTS

Salt	*Chemical shift (ppm)*		
	SCN	*C–N*	*C–C*
TMAT	133.6	45.0	
EAT	133.1	36.7	13.2
DEAT	132.4	47.2	9.4
TEAT	133.5	47.1	9.1
QEAT	130.9	53.1	7.7
TAAT	133.7	56.4	56.1
PAT	133.3	42.5	21.3, 11.3
iPAT	133.4	45.7	20.2
DPAT	132.2	50.1	20.1, 11.6
TPAT	133.2	55.1	17.7, 11.1
QPAT	131.0	60.9	15.9, 10.8
BAT	133.2	40.8	29.6, 20.1, 13.9
iBAT	133.2	47.7	27.3, 19.9
sBAT	132.9	50.7	27.9, 18.1, 10.3
tBAT	133.4	53.9	1.8, 1.5
DBAT	133.2	48.4	28.5, 20.4, 13.8
TBAT	133.0	53.1	25.8, 20.3, 13.9
QBAT	130.9	59.2	24.2, 20.2, 13.7
CHAT	133.3	51.7	30.9, 25.1, 24.6
BzAT	133.8	44.1	133.2, 129.8, 129.4
DBzAT	131.9	51.7	129.7, 130.1, 130.4
nOAT	133.4	40.7	32.2, 29.5, 28.3, 27.0, 23.1, 14.3
tOAT	133.8	58.2	52.7, 31.7, 31.4, 27.3

130°C. This temperature limit is established by material loss from the column due to either volatilization or sublimation of the salts or as a consequence of thermal degradation. A similar temperature tolerance was found for TMAT, QEAT, TPAT, QPAT, and QBAT even though this temperature is below the melting point of these salts. This might tend to support a thermal degradation mechanism to explain the above results except that no new products were identified from several columns and similar behavior was not observed for samples sealed in melting point capillaries and heated to the same temperature. The effective maximum allowable operating temperature for the alkylammonium thiocyanate salts can be taken as 120–130°C although the fundamental reason for this limit remains obscure.

In general, the lower column operating temperature coincides with the melting point of the salt for the lower melting point salts in Table IV. In three cases, ethylammonium, dipropylammonium, and dibutylammonium thiocyanate, the column efficiency was very low in the region of the melting point and did not show acceptable column performance until higher temperatures were reached. For these salts the temperature at which acceptable column efficiency was obtained was used to define the lower column temperature limit.

The column efficiency varies substantially from salt to salt and also with the test probe used to make the measurements. The results given in Table IV were ob-

TABLE IV

COLUMN OPERATING CHARACTERISTICS FOR ALKYLAMMONIUM THIOCYANATES

Salt	*Lower temperature limit (°C)*	*Upper temperature limit (°C)*	*Decomposition temperature (°C)*	*Liquid range (°C)*	*Average efficiency (N/m)**
TMAT	–	140	196	–	300–1100
EAT	80	125	>240	45	1000–1400
DEAT	80	120	>200	–	800–1000
TEAT	50	120	195	70	700–1200
QEAT	–	180		–	100–300
PAT	70	130	>200	60	1000–1700
iPAT	85	115	185	30	1300–1600
DPAT	40	125	140	85	1100–1600
TPAT	–	120	>200	–	150–400
QPAT	–	123	210	–	≈100
BAT	30	130	120	100	1000–1900
sBAT	30	120	–	90	1000–1600
iBAT	30	120	130	90	1100–2000
tBAT	122	130	>270	8	≈200
DBAT	55	130	142	75	500–1500
TBAT	50	130	210	80	1000–1300
QBAT	–	125	220	–	200–500
TAAT	40	150	>200	110	1000–1600
CHAT	90	120	220	30	600–1100
BzAT	100	130	230	30	150–900
DBzAT	60	145	230	–	≈100
nOAT	40	130	–	90	1500–2500
tOAT	100	120	>200	20	750–1000

* Measured as the number of effective plates per meter for a variety of test probes of different structure on 2 m × 2 mm I.D. columns with a 10% (w/w) loading of stationary phase on Chromosorb W-AW (100–120 mesh).

tained using several substituted benzene derivatives and *n*-alkanes. The entry for column efficiency is given as the range of the observed values. All columns were prepared from the same batch of support to minimize variations from this source. A column prepared with a 10% (w/w) loading of ammonium thiocyanate produced 400–600 effective plates per meter. A value inferior to that obtained with most of the low melting point alkylammonium thiocyanate salts. A column prepared with a 10% (w/w) loading of squalane produced 1100–1900 effective plates per meter and can be considered as a bench mark figure to compare the efficiency of the alkylammonium thiocyanates to. From Table IV it can be seen that a number of the alkylammonium thiocyanates investigated show acceptable column performance characteristics. Using the data in Table IV as a guide the following salts were selected for further evaluation: triethylammonium thiocyanate (TEAT), triethanolammonium thiocyanate (TAAT), *n*-propylammonium thiocyanate (PAT), di-*n*-propylammonium thiocyanate (DPAT), *n*-butylammonium thiocyanate (BAT), *sec.*-butylammonium thiocyanate (sBAT), isobutylammonium thiocyanate (iBAT), di-*n*-butylammonium thiocyanate (DBAT), tri-*n*-butylammonium thiocyanate (TBAT), *n*-octylammonium thiocyanate (nOAT), and cyclohexylammonium thiocyanate (CHAT).

TABLE V

McREYNOLDS' CONSTANTS FOR SOME ALKYLAMMONIUM THIOCYANATE SALTS

Identification of probe numbers: X' = benzene; Y' = *n*-butanol; Z' = 2-pentanone; U' = 1-nitropropane; S' = pyridine; H' = 2-methyl-2-pentanol; K' = 2-octyne; L' = 1,4-dioxane; M' = *cis*-hydrindane.

Salt	*X'*	*Y'*	*Z'*	*U'*	*S'*	*H'*	*K'*	*L'*	*M'*
TEAT	405	773	519	756	*	568	120	585	63
PAT	572	1209	939	1025	1135	996	318	1104	262
DPAT	445	875	631	792	977	715	242	649	192
BAT	428	1070	805	875	*	882	247	909	215
iBAT	453	1086	830	898	*	887	262	939	232
sBAT	472	1106	870	912	1429	907	241	972	209
DBAT	343	711	485	617	*	567	162	477	130
TBAT	340	667	450	637	*	517	185	456	139
CHAT	378	694	491	603	668	520	182	469	112
TAAT	271	672	452	556	729	484	47	602	−62
nOAT	178	525	294	348	495	370	88	327	90

* Probe was not eluted with normal peak shape.

The McReynolds' constants of the selected phases are summarized in Table V. Because of poor peak shapes and/or evidence of chemical reaction the values for pyridine and iodobutane were not calculated for all thiocyanate salts. Normal peak shape and complete recovery of injected mass was observed for the other probes. To depict general trends, the McReynolds' constants for benzene, 2-pentanone, 1-nitropropane, 1,4-dioxane and *n*-butanol as a function of the cation type are shown in Fig. 1. The trends that are observed are quite contrary to expectations with, for

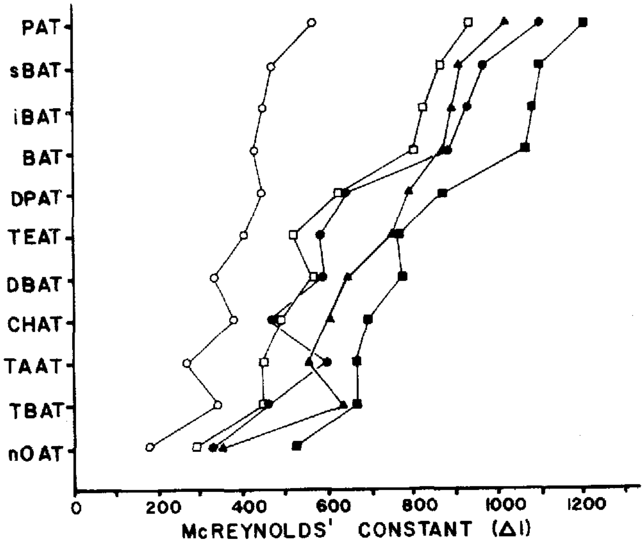

Fig. 1. Plot of selected McReynolds' constants for eleven alkylammonium thiocyanate salts. The cations are arranged in descending order of proton acceptor capability. Key to symbols: ○ = benzene; □ = 2-pentanone; ▲ = 1-nitropropane; ● = 1,4-dioxane; ■ = *n*-butanol.

example, the McReynolds' constant value for benzene being lower on *n*-octylammonium thiocyanate than for *n*-propylammonium thiocyanate. Similar trends are seen for the orientation and proton donor–acceptor interactions. The largest interactions are observed for the monoalkylammonium cations with the notable exception of *n*-octylammonium thiocyanate (this salt shows the lowest values for all probes). Likewise, there seems to be a general reduction in the values for all constants as the degree of alkyl substitution is increased. For example, the values for the McReynolds' constants decline in the order PAT > DPAT and BAT > DBAT > TBAT.

A fundamental assumption made in the calculation of McReynolds' constants is that the test probes and the *n*-alkanes used to determine the retention index values are retained solely by partition with the stationary phase. For polar phases this assumption may not be true. Adsorption at the gas–liquid interface may make a significant contribution to retention. This is most likely to occur when the polarity of the injected substance is very different from that of the stationary phase, for example, the retention of *n*-alkanes on polar stationary phases. These circumstances can lead to erroneous values for the McReynolds' constants due to a plurality of retention mechanisms in which the *n*-alkanes are retained largely by gas–liquid phase adsorption while the test probes are retained by partition.

To test for the above occurrence phase loading studies were made for triethanolammonium, *n*-octylammonium, *sec.*-butylammonium, and di-*n*-propylammonium thiocyanates using the procedure described by Martin[18]. If retention occurs entirely by partition then a plot of V_N/g (V_N is the net retention volume) of column packing (corrected to 20°C) as a function of the stationary phase loading should show an integral increase in retention with increasing phase loading and a zero intercept at zero phase loading. If gas–liquid phase adsorption occurs to a significant extent then a positive *y*-intercept at zero phase loading is observed, and if the dominant mechanism is gas–liquid phase adsorption, then the slope of the plot may be close to zero or even negative depending on how the surface area of the phase varies with increasing phase loading. It is assumed in these considerations that adsorption at the gas–solid (support) interface is negligible, that adsorption or partition with a structured liquid phase layer can be neglected at the high phase loading employed, and that the liquid phase shows good support coating characteristics. These assumptions are reasonable for a qualitative understanding of the retention mechanism which is adequate for these studies. Plots for the extreme cases, Fig. 2, exhibiting the highest degree of gas–liquid phase adsorption (TAAT) and a more general case, Fig. 3, for *n*-octylammonium thiocyanate, are shown here. Hydrocarbons and alcohols are retained mainly by gas–liquid phase adsorption while the other probes, benzodioxan, nitrobenzene, acetophenone, 2,6-dimethylaniline, 2,6-dimethylphenol and naphthalene are retained largely by partition with a small contribution from adsorption on triethanolammonium thiocyanate. On *n*-octylammonium thiocyanate all probes are retained largely by partition with adsorption being significant for the hydrocarbons, nitrobenzene, and benzodioxan. A summary of the statistical analysis of the data for all phases is given in Table VI. As a consequence of the different dominant retention mechanisms for the hydrocarbons and the polar probes the values for the McReynolds' constants should be considered to be unreliable. However, a useful qualitative picture of the relative importance of the different selective solute–stationary phase interactions for the various salts could be obtained from a comparison of the corrected retention volume data for suitably selected probes.

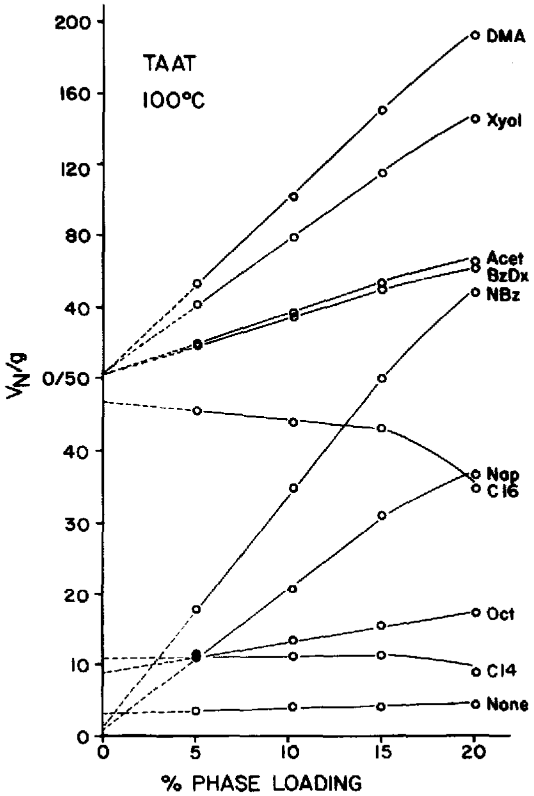

Fig. 2. Plot of V_N/g of packing (corrected to 20°C) as a function of the amount of triethanolammonium thiocyanate loading. Test solutes: None = nonanone; C14 = tetradecane; Oct = octanol; C16 = hexadecane; Nap = naphthalene; NBz = nitrobenzene; BzDx = benzodioxan; Acet = acetophenone; Xyol = 2,6-dimethylphenol; DMA = 2,6-dimethylaniline.

Values for the specific retention volumes of the McReynolds' probes and a series of substituted benzene derivatives on eleven alkylammonium thiocyanate salts are summarized in Tables VII and VIII, respectively. To aid evaluation, the data for the McReynolds' probes is organized in decreasing order of retention of butanol and benzene as a function of cation type in Fig. 4. A comparison between Fig. 1 (McReynolds constants as a function of cation type) and Fig. 4, essentially the same plot but this time of the specific retention volumes (V_g), illustrates that there is little similarity in the cation order. From Fig. 4 we see that the retention of the dispersive probes benzene, 2-octyne, and *cis*-hydrindane now increases with both the size and number of the alkyl substituents attached to the cation as would be expected. Note in particular the change in position of *n*-octylammonium thiocyanate on the two scales. The retention of the proton donor probes butanol and 2-methyl-2-pentanol do not vary very much with changes in the cation if the results for triethanolammonium thiocyanate are ignored. This is justified as alcohols are retained primarily by adsorption on triethanolammonium thiocyanate while partition is the dominant mechanism for the other salts. The data can be deconvoluted further if we consider reten-

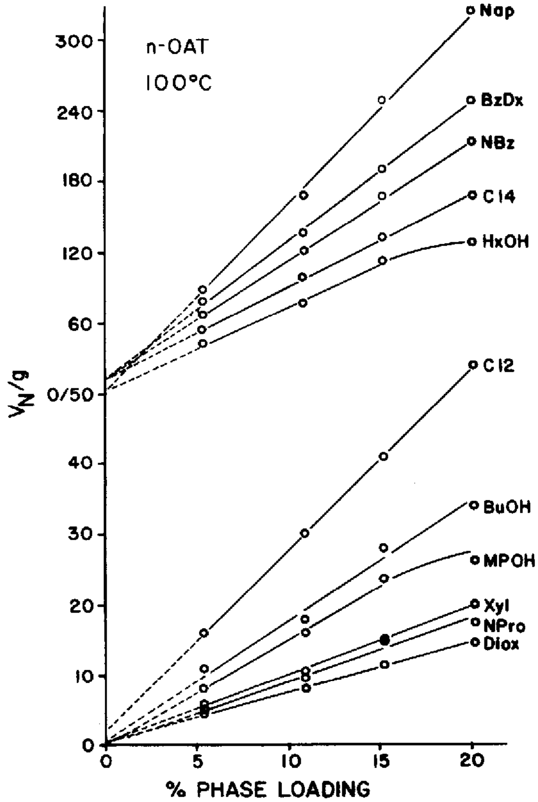

Fig. 3. Plot of V_N/g of packing (corrected to 20°C) as a function of the amount of *n*-octylammonium thiocyanate loading. Test solutes: Diox = dioxane; NPro = nitropropane; Xyl = xylene; MPOH = 2-methyl-2-pentanol; BuOH = butanol; C12 = dodecane; HxOH = hexanol; C14 = tetradecane; NBz = nitrobenzene; BzDx = benzodioxan; Nap = naphthalene.

tion of the test probes on a per mole of stationary phase basis. In Fig. 5, log V_N/mole corrected to 0°C is plotted as a function of carbon number and pK_a of some of the salts evaluated. For the homologous series *n*-butylammonium, di-*n*-butylammonium and tri-*n*-butylammonium thiocyanate there is a linear relationship between log V_N/mole and the number of carbon atoms attached to the cation. As the test probes hexanol, nitropropane, 2-methyl-2-pentanol and toluene represent a number of specific interactions this general trend must be due to a non-specific source, most probably, from an increase in dispersive interactions. On the same plot, Fig. 5, this time as a function of the pK_a values of the alkylammonium cations containing six carbon atoms a good correlation is seen between the retention of the proton donor solutes, hexanol and 2-methyl-2-pentanol, and the basicity of the cation. This is supported by the fact that there is no similar correlation observed for the retention of toluene and nitropropane which, lacking acidic protons, would not be expected to correlate with the basicity of the cation. It should be noted that to make di-*n*-butylammonium thiocyanate fit with the other salts the dispersive contribution to retention was calculated from the slopes of the lines on the left side of Fig. 5 and corrected to six

TABLE VI

STATISTICAL ANALYSIS OF DATA FOR PHASE LOADING STUDIES

All measurements were made at 100°C.

Probe	*Slope*	*Standard deviation*	*y-Intercept*	*Standard deviation*	*Correlation coefficient*
sec.-Butylammonium thiocyanate					
Xylene	0.30	0.06	1.31	1.01	0.957
Hexanol	5.53	0.26	6.73	4.16	0.998
Nonanone	2.82	0.67	4.17	0.93	0.999
Nitropropane	1.17	0.01	1.98	0.13	1.000
Dioxane	1.86	0.22	−1.92	3.42	0.987
Naphthalene	7.95	0.51	−10.05	7.06	0.992
Octanol	14.17	1.61	0.73	22.49	0.975
Acetophenone	17.28	0.65	16.04	9.03	0.997
Nitrobenzene	8.12	1.94	45.91	27.11	0.897
Benzodioxan	9.61	0.36	6.67	5.19	0.997
Decane	0.068	0.006	0.23	0.06	0.982
Undecane	0.11	0.01	0.34	0.12	0.971
Dodecane	0.14	0.02	0.82	0.18	0.956
Tetradecane	0.33	0.05	2.43	0.44	0.955
n-Octylammonium thiocyanate					
Butanol	1.60	0.15	1.82	2.10	0.983
Nitropropane	0.86	0.08	0.78	1.07	0.984
Dioxane	0.66	0.02	1.16	0.28	0.998
2-Methyl-2-pentanol	1.26	0.18	2.12	2.53	0.961
Naphthalene	16.22	0.53	−3.59	7.54	0.998
Nitrobenzene	9.90	0.18	13.20	2.54	0.999
Benzodioxan	11.50	0.28	13.23	4.08	0.999
Hexanol	6.02	0.71	11.04	9.99	0.973
Decane	0.40	0.21	4.00	2.96	0.645
Dodecane	2.52	0.02	2.48	0.28	1.000
Tetradecane	7.67	0.18	12.55	2.53	0.999
Di-n-propylammonium thiocyanate					
Xylene	0.88	0.03	−0.40	0.43	0.998
Butanol	2.10	0.06	0.16	0.83	0.998
Pentanone	0.76	0.02	−0.34	3.05	0.998
Nitropropane	1.91	0.06	−0.42	0.82	0.998
2-Methyl-2-pentanol	1.46	0.04	0.03	0.55	0.999
Dioxane	0.96	0.04	−0.12	0.53	0.997
Naphthalene	22.2	0.60	−7.95	8.27	0.999
Tetradecane	1.11	0.11	5.40	1.45	0.982
Hexadecane	2.78	0.35	19.13	4.85	0.968
Triethanolammonium thiocyanate					
Naphthalene	1.73	0.15	3.0	2.04	0.986
Octanol	0.41	0.02	9.2	0.28	0.995
Acetophenone	3.08	0.21	5.1	2.85	0.991
Nitrobenzene	2.97	0.15	3.8	2.07	0.995
Benzodioxan	2.93	0.14	4.0	1.97	0.995
Nonanone	0.06	0.01	3.2	0.18	0.920
2,6-Dimethylphenol	6.93	0.23	8.0	3.21	0.998
Dodecane*	y = 2.6	s = 0.34			
Tetradecane*	y = 10.8	s = 1.31			
Hexadecane*	y = 41.8	s = 4.80			

* Line is parallel with x-axis. Data treated as if four values for the same constant. Average value and standard deviation are given.

TABLE VII

SPECIFIC RETENTION VOLUMES FOR McREYNOLDS' PROBES ON SOME ALKYLAMMONIUM THIOCYANATES

Identification of probe numbers: 1 = benzene; 2 = *n*-butanol; 3 = 2-pentanone; 4 = 1-nitropropane; 5 = pyridine; 6 = 2-methyl-2-pentanol; 8 = 2-octyne; 9 = 1,4-dioxane; 10 = *cis*-hydrindane.

Salt	*1*	*2*	*3*	*4*	*5*	*6*	*8*	*9*	*10*
TEAT	34.7	171.4	52.6	212.3	*	97.3	21.2	86.1	27.6
PAT	12.2	199.9	67.9	113.0	361.3	117.2	8.9	162.3	15.0
DPAT	30.5	195.7	70.0	173.5	544.2	138.2	28.3	98.3	50.3
BAT	17.7	246.9	86.7	132.1	*	167.7	17.7	160.4	32.9
iBAT	16.8	231.6	82.9	130.0	*	149.9	16.6	163.2	30.1
sBAT	13.4	222.5	80.3	117.6	2532.2	142.5	10.7	162.9	20.9
DBAT	32.8	227.7	78.3	189.4	*	177.2	41.1	86.9	89.4
TBAT	50.0	215.6	79.8	256.4	*	163.2	59.9	96.0	116.4
TAAT	3.8	37.5	10.6	25.8	116.4	20.4	3.0	36.2	4.4
nOAT	28.3	152.8	48.8	77.7	240.4	110.8	51.1	68.2	136.8
CHAT	14.4	190.6	63.5	92.8	688.1	133.8	19.6	118.3	31.6

* Probe was not eluted with normal peak shape.

carbon atoms. It would have been advantageous to have more experimental points in Fig. 5 but, unfortunately, those salts which might have been used to enhance the data presented were also those which showed unacceptable chromatographic performance. For example, results for the series PAT, DPAT, TPAT and QPAT, would have been useful to confirm the data observed for BAT, DBAT and TBAT (QBAT decomposes below its melting point) but both TPAT and QPAT are unstable at temperatures below their melting point.

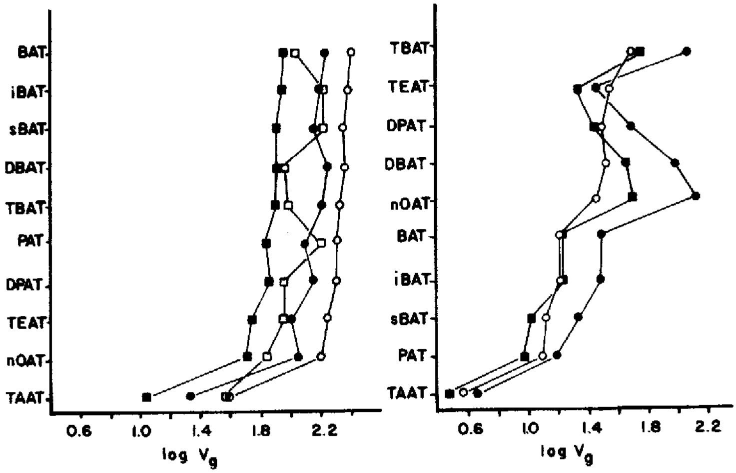

Fig. 4. Plot of log V_g on alkylammonium thiocyanate salts for McReynolds' probes. Salts are ordered by decreasing retention of *n*-butanol (left side, where ○ = *n*-butanol; ■ = 2-pentanone; ● = 2-methyl-2-pentanol; □ = 1,4-dioxane) and of benzene (right side, where ○ = benzene; ■ = 2-octyne; ● = *cis*-hydrindane).

TABLE VIII

SPECIFIC RETENTION VOLUMES FOR SUBSTITUTED BENZENES ON SOME ALKYLAMMONIUM THIOCYANATES

Identification of probe numbers: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = xylene; 5 = chlorobenzene; 6 = bromobenzene; 7 = iodobenzene; 8 = *o*-dichlorobenzene; 9 = nitrobenzene; 10 = acetophenone; 11 = benzaldehyde; 12 = hexanol; 13 = aniline.

Salt	*Probe number*												
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
TEAT	34.2	52.6	71.8	80.1	120.3	258.3	761.2	409.9	2141.6	1841.2	1044.0	413.0	*
PAT	12.7	18.1	25.1	24.7	38.5	78.2	201.5	141.2	1071.2	1622.5	*	563.1	*
DPAT	31.5	50.8	77.0	19.4	117.3	242.7	662.6	440.5	1828.4	1851.5	*	585.8	*
BAT	19.5	29.1	44.2	43.3	62.5	127.3	331.1	237.1	1241.3	1669.6	*	645.7	*
iBAT	17.2	26.6	48.4	39.7	58.2	116.5	292.5	215.5	1225.1	1624.3	*	631.4	*
sBAT	13.4	22.0	31.9	32.7	48.3	98.0	253.1	176.1	1146.6	1785.5	3400.3	561.2	361.8
DBAT	32.8	62.2	103.8	104.4	156.9	329.1	869.7	625.9	2240.2	2278.3	*	663.1	*
TBAT	50.7	85.4	137.8	137.8	219.5	449.4	1220.5	893.5	3212.3	2482.8	1332.1	719.4	*
TAAT	3.8	6.3	7.1	7.6	11.3	23.1	59.8	32.4	289.4	298.2	198.3	61.5	1208.8
nOAT	28.3	53.4	91.7	92.5	112.2	224.1	548.8	460.0	954.4	957.0	2947.9	951.1	1938.8
CHAT	14.4	23.7	38.8	39.0	57.5	123.2	340.0	320.4	1059.5	1510.4	*	533.4	*

* Peak was asymmetric and the recovery of mass injected onto the column was incomplete.

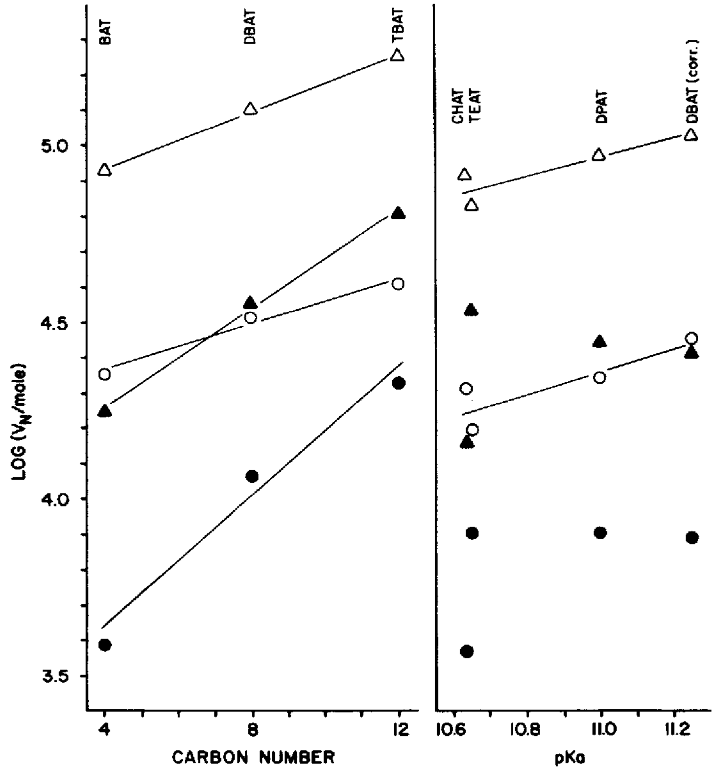

Fig. 5. Plot of log V_N/mole as a function of carbon number (left side) and pK_a of cations containing six carbon atoms (right side). The dispersive contribution to retention on DBAT was corrected to six carbon atoms as discussed in the text. Key to symbols: △ = hexanol; ▲ = nitropropane; ○ = 2-methyl-2-pentanol; ● = toluene.

The variation of the specific retention volumes of the substituted benzene derivatives as a function of cation type is shown in Fig. 6. The probes can be divided into two groups; those with significant dipole moments and those which show essentially dispersive interactions only. Dispersive interactions are weaker than the orientation interactions and generally increase in magnitude with increasing size and number of alkyl substituents as discussed previously. The orientation interactions show a general increase with increasing cation size. For example, the retention of the polar probes on matched columns of *n*-propylammonium thiocyanate and di-*n*-propylammonium thiocyanate is approximately doubled, Fig. 7. A similar trend is seen in Fig. 8 for the series, *n*-butylammonium, di-*n*-butylammonium, and tri-*n*-butylammonium thiocyanates except that in this case the change in retention between di-*n*-butylammonium thiocyanate and tri-*n*-butylammonium thiocyanate is less marked. In general, one would anticipate that the retention of the probes with significant dipoles would follow the same trend of increasing dipole moments for the salts. Dipole moments for the thiocyanate salts are not available, but for other systems, there is generally a fairly large change in dipole moment in going from a monoalkyl to the homologous dialkylammonium cation and a much smaller change in going from the

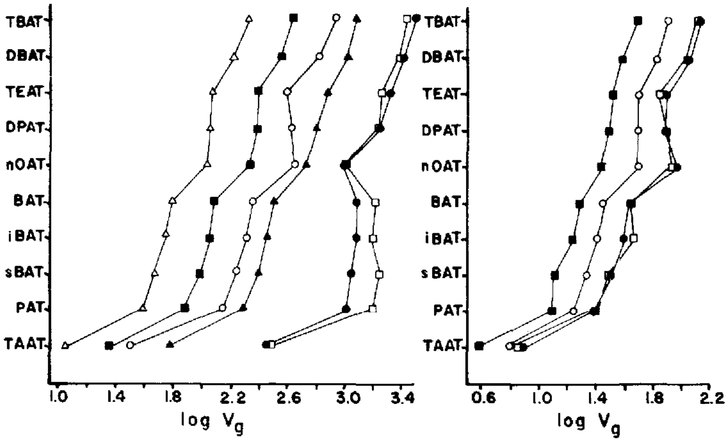

Fig. 6. Plot of log V_g on alkylammonium thiocyanate salts for substituted benzene derivatives. Salts are ordered by decreasing retention of chlorobenzene (left side, where △ = chlorobenzene; ■ = bromobenzene; ○ = *o*-dichlorobenzene; ▲ = iodobenzene; □ = acetophenone; ● = nitrobenzene) and of benzene (right side, where ■ = benzene; ○ = toluene; □ = ethylbenzene; ● = *p*-xylene).

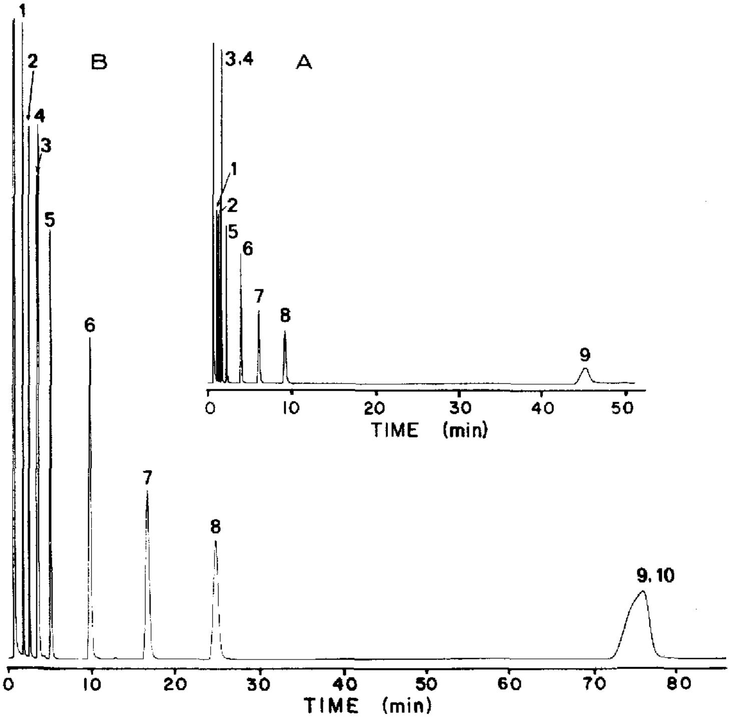

Fig. 7. Separation of substituted benzene derivatives on matched columns of (A) *n*-propylammonium thiocyanate and (B) di-*n*-propylammonium thiocyanate. Each column was 3 m × 2.2 mm I.D. packed with 10% (w/w) alkylammonium salt on Chromosorb W-AW (100–120 mesh) with a nitrogen carrier gas flow-rate of 20 ml/min and column temperature 100°C. Test solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-xylene; 5 = chlorobenzene; 6 = bromobenzene; 7 = *o*-dichlorobenzene; 8 = iodobenzene; 9 = nitrobenzene; 10 = acetophenone.

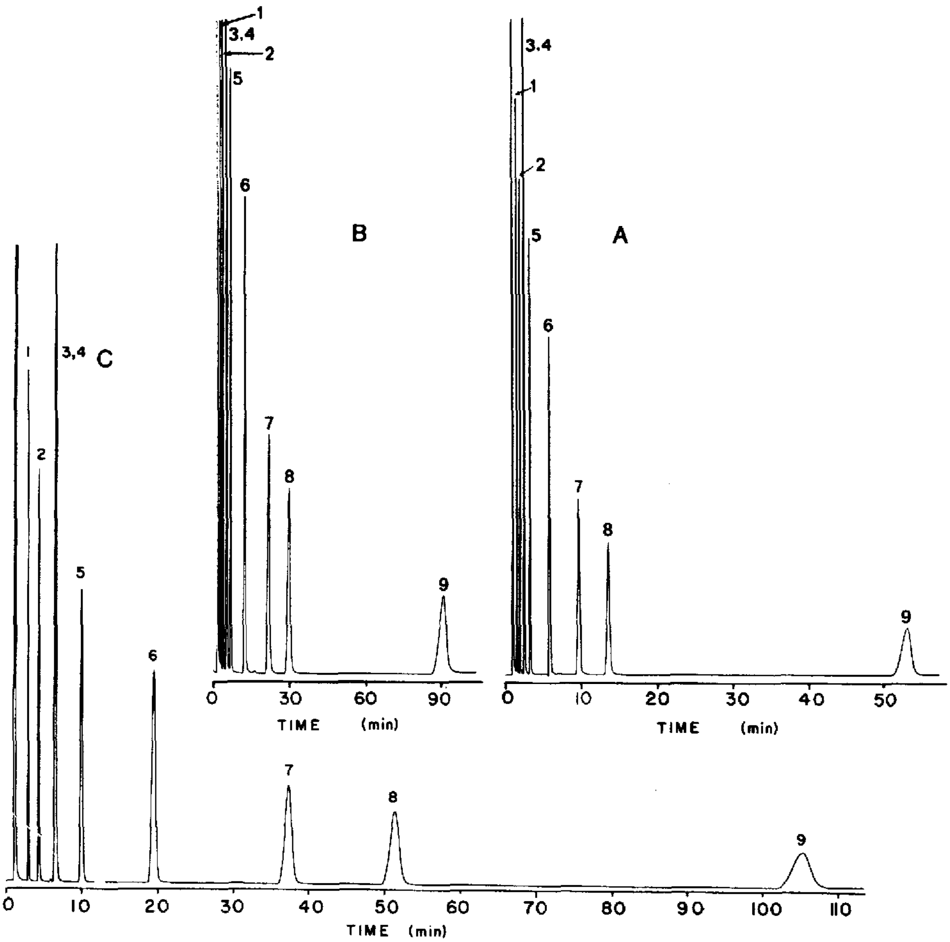

Fig. 8. Separation of substituted benzene derivatives on matched columns of (A) *n*-butylammonium thiocyanate, (B) di-*n*-butylammonium thiocyanate, and (C) tri-*n*-butylammonium thiocyanate. Column operating conditions and the identification of test solutes are given in Fig. 7.

dialkyl cation to the homologous trialkylammonium cation[19,20]. This fits the above picture although it must be pointed out that the total number of dipole moment measurements for all but the quaternary ammonium salts are very few. The selectivity of the alkylammonium salts is not significantly influenced by isomeric variations in the alkyl chain attached to the cation. There is little change in retention for all probes on *n*-butylammonium, isobutylammonium, and *sec.*-butylammonium thiocyanates, Fig. 9.

In conclusion, these studies have shown that a number of alkylammonium thiocyanate salts show acceptable chromatographic properties. The most profound limitation on their general use is their limited temperature operating range. At the upper end this is established by the onset of column bleed or thermal degradation at temperatures in the region of 120–130°C. Different factors effecting the retention of

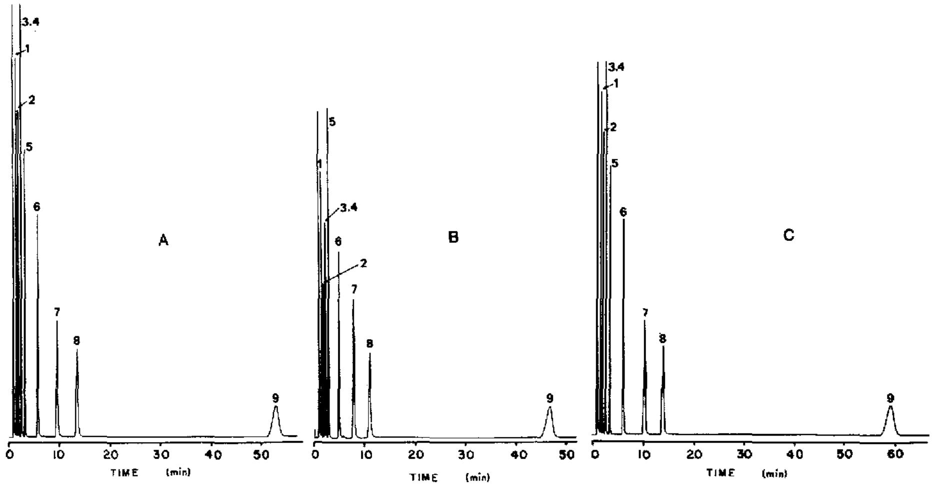

Fig. 9. Separation of substituted benzene derivatives on matched columns of (A) *n*-butylammonium thiocyanate, (B) *sec*.-butylammonium thiocyanate, and (C) iso-butylammonium thiocyanate. Column operating conditions and the identification of test solutes are given in Fig. 7.

organic solutes by the alkylammonium thiocyanate salts were discussed. In most cases solute–stationary phase partitioning was the dominant retention mechanism except for the alkanes, for which, gas–liquid phase adsorption frequently played an important role in controlling retention. In general, dispersive interactions are relatively weak but increase with the size and number of alkyl groups attached to the cation. The order of retention of solutes with significant dipole moments follows the order predicted by ranking the solutes first by dipole moment and then making allowances for differences in volatility. The retention of proton donor solutes such as alcohols is influenced most significantly by the basicity of the alkylammonium cation.

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